# ETHYL LACTATE PRODUCTION BY HYBRID PROCESSES: DETERMINATION OF PHASE DIAGRAMS AND EVALUATION OF PERFORMANCE OF ORGANOPHILIC PERVAPORATION MEMBRANES

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# ABSTRACT

## ETHYL LACTATE PRODUCTION BY HYBRID PROCESSES: DETERMINATION OF PHASE DIAGRAMS AND EVALUATION OF PERFORMANCE OF ORGANOPHILIC PERVAPORATION MEMBRANES

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Ethyl lactate is a promising, and environmentally benign chemical, which requires efficient separation techniques to overcome the equilibrium limitations in its production. Pervaporation based hybrid systems are successful in these type of equilibrium limited reactions, where product and/or by-product are removed from reaction medium by pervaporation unit(s) so as to drive reaction to completion.

For the production of ethyl lactate four possible semi-batch hybrid systems were previously proposed. However, in order to select the suitable hybrid system within the proposed layouts phase equilibrium and reaction kinetics of the system must be well defined in addition to the performance data of the pervaporation membranes. Therefore, vapor pressure curve of ethyl lactate, VLE curves of ethanol-ethyl lactate and ethyl lactate-water were determined and performances of commercial hydrophobic membranes were investigated experimentally for the separation of ethanol-ethyl lactate mixtures.

As a result of vapor pressure and VLE experiments, azeotrope was observed at 71wt% of water for ethyl lactate-water binary mixture at 80mmHg pressure. Furthermore, dependence of vapor composition on pressure was found to be slight for ethanol-ethyl lactate mixtures.

Two commercial hydrophobic membranes, and an organoselective one were used in the separation of ethyl lactate-ethanol mixtures. It is found that hydrophobic membranes have sufficient fluxes and reasonable selectivities. Moreover, it is observed that as temperature increase flux increases and selectivity decreases. Finally, it is concluded that it would be possible to produce ethyl lactate by using the previously proposed integrated PV-esterification reactor systems.

**Keywords:** Hybrid systems, Pervaporation-Esterification Coupling, Ethyl lactate-Ethanol Separation, Pervaporation, Commercial Membranes

# ÖZ

# HİBRİD PROSESLERLE ETİL LAKTAT ÜRETİMİ: FAZ DİYAGRAMLARININ ELDESİ VE ORGANOFİLİK PERVAPORASYON MEMBRANLARININ PERFORMANSLARININ DEĞERLENDİRİLMESİ

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Etil laktat, çevreye zararlı olmayan, ancak üretimi için etkili ve ucuz yöntem geliştirilmesi gerekli olan bir çözücüdür. Pervaporasyon içeren hibrid sistemler, etil laktat gibi esterlerin üretiminde dönüşümü artırmak için kullanılan başarılı yöntemlerden biridir. Bu yöntemde, reaktör ortamından suyu ve/veya etil laktat'ı ayırarak, reaksiyon ürünler tarafına kaydırılmakta böylece dönüşüm artırılmaktadır.

Etil laktat üretimi için dört adet pervaporasyon içeren hibrid sistemi daha önceki çalışmada geliştirilmiştir. Ancak, önerilen bu sistemler arasında en uygun olanına karar verebilmek için reaksiyon karışımlarını içeren sıvı-buhar faz diyagramlarına, reaksiyon kinetik bilgisine, ve pervaporasyon membranlarının performanslarının değerlendirilmesine ihtiyaç vardır. Dolayısıyla, bu çalışmada öncelikle etanol-etil laktat ve etil laktat-su karışımlarının sıvı-buhar faz diyagramları bulunmuş ve daha sonra hidrophobik pervaporasyon membranlarının etil laktat-etanol karışımlarını ayırmadaki performansları araştırılmıştır.

Etil laktat-su karışımında, 80 mmHg basınç altında, %71 ağırlıkça su konsantrasyonunda azeotrop bulunmuştur. Bununla beraber etanol-etil laktat karışımlarında, basıncın buhar kompozisyonuna olan etkisinin az olduğu gözlemlenmiştir.

Etil laktat-etanol karışımlarının ayırılmasında iki adet hidrofobik ve bir adet organik seçici, ticari membranlar kullanılmıştır. Hidrofobik membranların, yeterli akı ve seçicilik değerlerine sahip olduğu gözlenmiştir. Bununla birlikte sıcaklık arttırıldığında, akının arttığı, seçiciliğin ise düştüğü gözlenmiştir. Son olarak etil laktat'ın pervaporasyon içeren hibrid sistemler ile üretiminin mümkün olabileceği sonucuna varılmıştır.

**Anahtar Kelimeler:** Hibrid Sistemler, Pervaporasyon-Esterifikasyon Entegrasyonu, Etil laktat-Etanol ayırımı, Pervaporasyon, Ticari Membranlar

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| | | | |
|---|---|---|---|
| A.acid | Acetic acid | $P_i^0$ | Saturation pressure of component “i” (bar) |
| $A_{12}$, $A_{21}$ | Van laar activity coefficient constants | PDMS | Polydimethylsiloxane |
| CAP | Cellulose acetate propionate | PEI | Polyetherimide |
| cP | Centipoise | PF | Polyfluourine |
| DES | Desorption | PPy | Polypyrole |
| DL | Diffusion in the liquid phase | PTFE | Polytetrafluoroethylene |
| DMC | Dimethylcarbonate | PV | Pervaporation |
| DV | Diffusion in the vapor phase | PVA | Polyvinylalcohol |
| E.Ac | Ethyl acetate | | Total mass flux (=g/m$^2$/min) |
| ETBE | Ethyltertbutylether | $J_i$ | Mass flux of species “i” (=g/m$^2$/min) |
| EtOH | Ethanol | R | Gas constant (=8.314 J/mol K) |
| EV | Evaporation | $R_0$ | Initial molar ratio of acid to alcohol |
| IPA | Isopropyl alcohol | S | Membrane area |
| LA | Lactic acid | T | Temperature (K or $^0$C) |
| LLA | Lactolyl lactic acid | V | Reacting mixture volume |
| M | Membrane | VLE | Vapour-liquid equilibrium |
| MeOH | Methanol | VOC | Volatile organic contaminant |
| MTBE | Methyltertbutylether | wt | Weight |
| n-butyl Ac. | n-butyl acetate | $x_{i(j)}$ | Weight fraction of species “i (j)” in the feed |
| $P^0$ | Saturation pressure (bar) | $y_{i(j)}$ | Weight fraction of species “i (j)” in the permeate |

Greek letters

| | |
|---|---|
| $\alpha_{i/j}$ | Selectivity of species "i" wrt species "j" |
| $\delta$ | Solubility parameter [=(MJ m$^{-3}$)$^{½}$] |
| $\gamma_i$ | Activity coefficient of species "i" |

Symbols

| | |
|---|---|
| $\overline{\Delta}H^{vap}$ | Heat of vaporization (kJ/mol) |

Subscripts

| | |
|---|---|
| A | Ethanol |
| l | Liquid |
| D | Dispersion |
| E | Ethyl lactate |
| H | Hydrogen bonding |
| P | Polarity |
| S | Sorption |
| t | Total |
| W | Water |

# CHAPTER 1

# INTRODUCTION

Each year, more than 3.8 million tons of toxic solvents are used as cleaners, degreasers and product ingredients in textile and electronics manufacturing, adhesives, paints, printing, de-inking and other industries in the United States only (Argonne National Lab., ANL). There are many effects of these toxic chemicals on the environment throughout their life cycles. One of these effects is global warming, or the greenhouse effect, the scientists estimate that increasing concentrations of greenhouse gases are likely to accelerate the rate of climate change in the future, which will lead to the drastic changes in the life cycles of living organisms in the world. Another example is the problem of acid rain. "Acid rain" is a broad term used to describe several ways that acids fall out of the atmosphere, a more precise term is acid deposition. The growing and essential awareness of such environmental problems lead to the manufacturers and the scientist to develop green technologies, either by changing the process materials that are directly or inherently toxic, or the production scheme in a way to reach to the concept of sustainable development (Reinert, K.H., 2001).

Unlike other solvents, which may damage the ozone layer or pollute groundwater, lactate esters are excellent solvents, which are non-toxic and biodegradable, because they are made from renewable carbohydrate. In general, lactate esters are used to meet the high quality demands of semiconductor industry as a safe solvent in photo resist and in edge beat removal formulations, useful for removal of pitch, wax polishing materials and protective films from the optical parts (Cargill Dow LLC, 2001). Lactate esters are used in the formulations of non-flammable and mild odor solvent cleaners (Suchy, M. *et al.* 1991), and in the preparation of herbicidal formulations (Weltman, H.J. and Phillips**,** T.L., 1995). Many toxic solvents used as cleaners, degreasers and product ingredients in textile and electronics manufacturing, adhesives, paints, printing, de-inking and other industries, can be replaced by lactate esters provided that the low-cost-production technologies are developed.

## 1.1 Industrially Important Properties of Ethyl lactate and Its Uses

Ethyl lactate, a hydroxyl ester, whose molecular formula is $CH_3CHOHCOOC_2H_5$, could replace a range of halogenated and toxic solvents, including ozone-depleting chlorofluorocarbons, carcinogenic methylene chloride, and toxic ethylene glycol ethers and chloroform. According to industry estimates, solvents and blends made with ethyl lactate can replace conventional solvents in more than 80 percent of these applications (Argonne National Lab., ANL). Ethyl lactate is also a versatile "building block" of a variety of chemical products such as degradable plastic polymers, three-carbon oxygenated chemicals, and derivatives of specialty products.

In fact, ethyl lactate is so benign that the U.S. Food and Drug Administration approved its use in food products long ago (Argonne National Lab., ANL). It has a good temperature performance range (boiling point: $154^0$C, melting point: $-40^0$C), is compatible with both aqueous and organic systems. Some of the properties of ethyl lactate are given at Table 1.1. Because of these properties ethyl lactate removes contaminants with >99.9% efficiency in electronics cleaning applications. In paint stripping applications it is advantageous due to its low toxicity and volatility, water solubility and compatibility with many substrates. In coatings and ink formulation applications it has the advantage of solubility in many resins including acrylic, poly (ethyl/methyl methacrylate), bisphenol A epoxy, haxamethoxy melamine, nitrocellulose, polyesters, and phenol resol resins (Cargill Dow LLC, 2001).

While ethyl lactate-based solvents have been used for many years in the high-grade electronics industry, their production cost has prohibited them from competing economically in the manufacturing sector with lower-priced petrochemical solvents. Ethyl lactate normally sells for $1.50 to $2.00 per pound, compared to between 90 cents and $1.50 per pound for conventional chemical solvents (Argonne National Lab., ANL). The lactate esters produced using non-conventional process may become economically viable alternatives to many chemical products ordinarily derived from petroleum. In the preceding section the production of ethyl lactate by conventional esterification techniques and the potential benefits of the proposed novel process are outlined.

**Table 1.1:** Important properties of Ethyl lactate for industrial applications

| | | Reference | | | Reference |
|---|---|---|---|---|---|
| Boiling Point ($^0$C) | 154 | Cargill Dow LLC, 2001 | Flash point ($^0$C) | 59 | Cargill Dow LLC, 2001 |
| Hansen Dispersion ($\delta_D$) | 15 | Cargill Dow LLC, 2001 | Viscosity (cP) | 195 | Snell, F.D. and Snell, C.T., 1962 |
| Hansen Polarity ($\delta_P$) | 7.6 | Cargill Dow LLC, 2001 | Refractive Index (at 20$^0$C) | 1.4125 | Snell, F.D. and Snell, C.T., 1962 |
| Hansen Hydrogen Bonding ($\delta_H$) | 12.5 | Cargill Dow LLC, 2001 | Solubility in water | Miscible | Snell, F.D. and Snell, C.T., 1962 |
| Surface Tension (dyne/cm) | 30 | Cargill Dow LLC, 2001 | Solubility in alcohols | Miscible | Snell, F.D. and Snell, C.T., 1962 |
| Density (g/cm$^3$) | 1.03 | Cargill Dow LLC, 2001 | Solubility in ketones, esters, and hydrocarbon oils | Miscible | Snell, F.D. and Snell, C.T., 1962 |

## 1.2 Production of Ethyl Lactate by Conventional Esterification Process and The Benefits of Proposed Novel Process

The process of the conversion of an acid into its alkyl salts is usually termed esterification, and is the common method by means of which esters are prepared. The reaction in most cases is so slow that the presence of a catalyst is essential. The process is then termed catalytic esterification as contrasted with direct esterification (Thorpe J.F. and Whiteley, M.A., 1956).

Ethyl lactate is produced by esterification of lactic acid via ethanol. Lactic acid (LA) decomposes easily at higher temperatures and has no boiling point. On the other hand, commercially available lactic acid has about 10-wt% water and further purification results with reversible polymerization to lactolyl lactic acid (LLA), i.e. self-esterification of lactic acid (reaction 2) (Ayturk, E., 2001). Lactic acid esterification with any alcohol can be represented as;

$$\mathrm{LA}+\mathrm{ROH}\Leftrightarrow\mathrm{Ester}+\mathrm{H_2O} \qquad \textbf{(1)}$$

$$\mathrm{LA}+\mathrm{LLA}_{x-1}\Leftrightarrow\mathrm{LLA}_x+\mathrm{H_2O} \qquad \textbf{(2)}$$

Esterification reactions, in general, are equilibrium limited and complete conversion never takes place if equal amounts of acid and alcohol are brought together, instead reaction proceeds until equilibrium is achieved (Thorpe J.F. and Whiteley, M.A., 1956). In the production of ethyl lactate, the presence of initial water, and its further formation as a by-product, limits the reaction to only about 60-

percent completion. One of the ways to enhance conversion is to use of one of the reactants, which is commonly alcohol, in excess amounts. As the alcohol to acid ratio increases both reaction rate, and equilibrium conversion increases and approaches to complete conversion. However it is well known that volatile alcohols form azeotropes with water and esters (Othmer, K. and Kroschwitz, J.I., 1991), and azeotrope has to be broken down by further solvent-distillation to remove water and obtain the ester. High temperature esterification, on the other hand has numerous problems. At high temperature, alcohols due to their high vapor pressure would form a vapor phase composed of mainly alcohol and the other low boiling compounds, whereas low-boiling compounds such as acids would remain in the liquid phase. Therefore, in order to achieve higher conversions large molar excesses of alcohol have to be used, vaporized, and re-condensed, all of which leads to increased costs and energy use. Furthermore, decomposition temperatures of reactants and/or products limit the esterification temperature.

There is also a growing interest to produce organic based products by using bioprocesses, such as fermentation. On the other hand, ethanol or lactic acid derived from fermentation broth suffers from purity. Fermentation-derived acids are always accompanied by some residual impurities such as simple sugars, carbohydrates, proteins, amino acids, and other organic and inorganic compounds. When conventional esterification techniques are used, these impurities may form large amounts of thermal- and acid-catalyzed breakdown contaminants. Under acidic conditions and high temperatures the residual carbohydrates produce aldehydes, which interfere with subsequent chemical conversion or polymerization reactions, and make colored residues or tars or Mallard reaction byproducts. Therefore in addition to the low conversion the presence of other impurities requires added separation task to purify the final product.

As an alternative to conventional methods, combination of a separation unit with reactor eliminates the above-mentioned drawbacks and provides a low-cost route to produce pure esters (Lipnizki, F., *et al.*, 1999). In the integrated system separation unit removes product and/or by-product from reaction medium, so as to increase conversion by driving reaction to product's side according to Le Chatelier's principle. In the selection of the type of the separation unit(s), several parameters have to be considered, such as mixture characteristics, production capacity and environmental concerns, all of which count for the unit cost. Between the several alternatives such as distillation, adsorption and extraction; membranes are selected for the separation unit; because in adsorption and extraction there is an additional cost of a third solvent and there is a high-energy cost together with the cost of azeotropic separation in distillation. Membrane separations, particularly pervaporation offer high selectivity for water, ability to overcome vapor-liquid equilibrium (VLE) selectivity, lowering of reaction temperatures, and handle the capacity requirements easily due to its flexible, compact and modular design (Feng, X. and Huang, R.Y.M., 1997). Furthermore, pervaporation is also suited for bioproduction processes, since mild conditions are sufficient for the separation, which is achieved by physical means. With these advantages, there is a little possibility of occurring of thermal stress or chemical alteration of the components of reaction mixture (Howell, J.A. *et al.*, 1993).

## *1.3 Pervaporation Based Hybrid Systems*

Pervaporation is a promising technology, especially useful in applications such as the dehydration and removal/recovery of organic compounds from aqueous or organic mixtures. Pervaporation is based on selective vaporization of liquid feed mixture through a membrane by means of a chemical activity gradient created between liquid feed and vapor downstream sides. Currently, about one hundred pervaporation units are operating worldwide, most of the dehydrating solvents, such as ethanol and isopropanol. Now that pervaporation has been proven in these end-of-pipe applications attention is turning to separations closer to chemical reaction step-more critical to production and promising much greater benefits. Over the next few years, pervaporation will be used increasingly to enhance reactor performance, either by purifying feeds or separating reaction products (Wynn, N., 2002).

The combination of pervaporation with the equilibrium limited esterification reactions offers many advantages, such as lower reagent consumption, higher reaction rates, and no requirement of further product purification. Because of these advantages integration of pervaporation into the conventional esterification reactions has been attracted much attention in the literature, a detailed survey given in the next chapter. Generally, two types of process can be adopted for the realization of the hybrid system. Pervaporation unit can either be integrated as an external process unit or directly inside to the reactor unit. The latter layout is often referred to as ‘membrane reactor’ in the literature. Catalytic membrane reactors, on the other hand, are equipped with a membrane, which has both catalytic activity and membrane selectivity. An extensive review on the types of pervaporation based hybrid systems could be found in the previous study of our group (Korkut, S., 2001).

## 1.4 Proposed Hybrid Systems

For the production of ethyl lactate four possible pervaporation based hybrid systems were previously developed (Korkut, S., 2001). These hybrid semi-batch systems are shown in figure 1.1. In the first layout; reaction mixture composed of acid, ester, water, and alcohol is sent directly to the pervaporation unit equipped with a hydrophilic membrane, where the removal of water is aimed. Since reaction mixture is acidic, an acid stable membrane is essential in this layout. In pervaporation unit, water selectively permeates through the membrane; and the retentate having lower water content is recycled back to the reactor. As pervaporation unit removes by-product water from the reactor, equilibrium reaction is shifted to the product's side. The concentration in the reactor changes as the reaction proceeds; hence the concentration of the pervaporation feed mixture changes, and so does the membrane performance. If water content is very low or water does not exist in the reaction mixture initially, higher reaction rate must be possessed according to the reaction kinetics, where membrane selectivity towards water is the highest. If the water concentration increases within the reactor; the decrease in pervaporation selectivity must be expected. At some point, the pervaporation unit reaches the pseudo-equilibrium, and the flux and selectivity at this stage would determine the overall efficiency of the layout (Korkut, S., 2001).

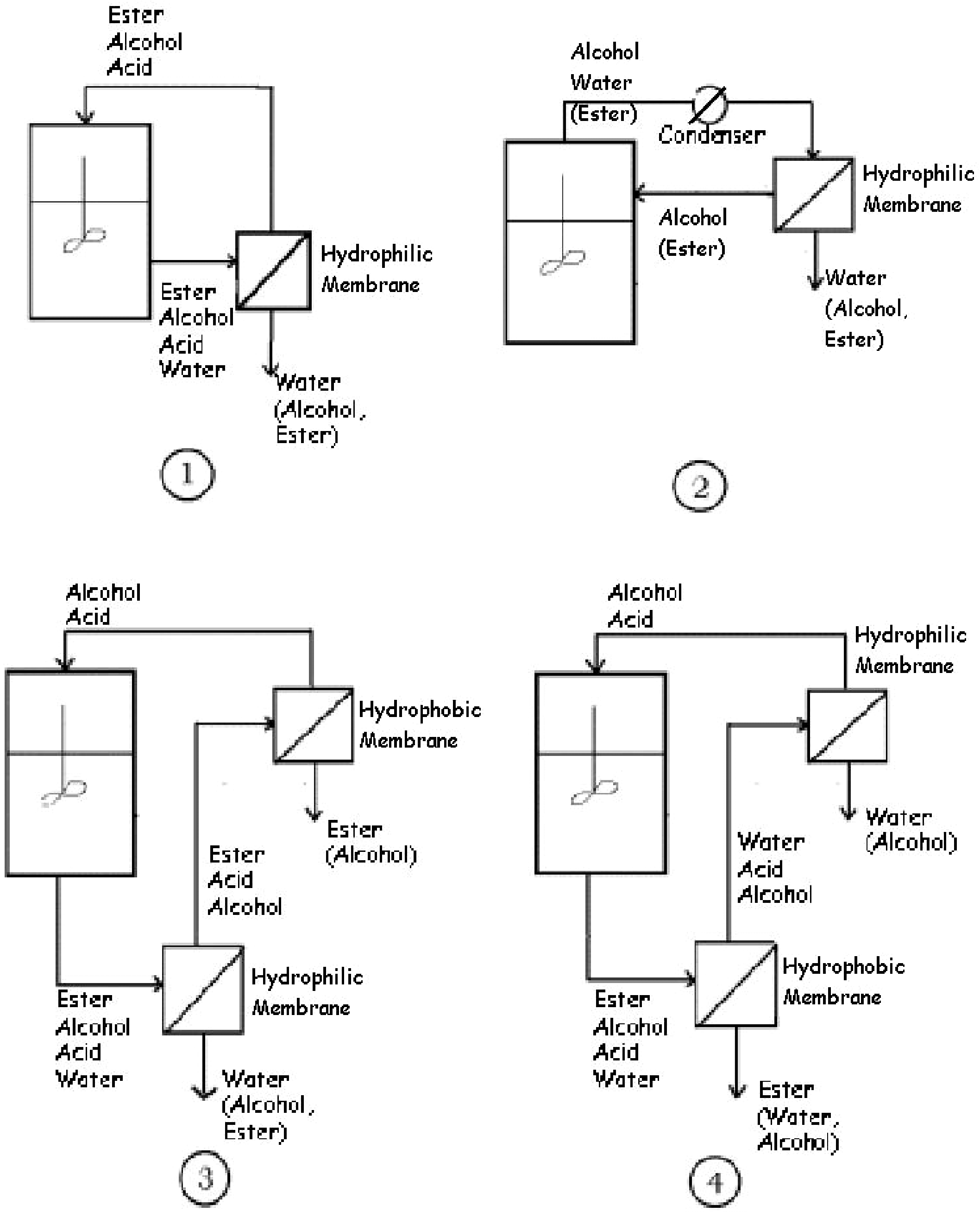

**Figure 1.1** Proposed hybrid systems for the production of ethyl lactate

In the second layout we proposed, vapor phase of the reaction mixture containing mostly more volatile components ethanol and water, is sent to the pervaporation unit after condensation. In this way the membrane will face mostly ethanol and water; therefore the adverse effects the other components, especially lactic acid in the reaction mixture would be reduced. Phase equilibrium data would determine the characteristics of feed mixture of pervaporation unit. In this hybrid layout a distillation column may be put in front of the pervaporation unit so as to separate ethanol and water; in that case pervaporation may serve so as to break the azeotrope and a final polishing step. As a second option a vapor permeation unit may be placed to the reactor exit, therefore instead of condensing the mixture and sending to the pervaporation unit, only one vapor permeation unit is used. This selection depends on the performance of vapor permeation and pervaporation units, however it was reported by Tanaka et al. (Tanaka, K. *et al*, 2002) that the performances of vapor permeation and pervaporation units were similar for ethanol water mixtures.

The third and the fourth hybrid systems may contain two pervaporation units, one with a hydrophilic membrane and the other with a hydrophobic membrane. Although these systems are composed of the same units, the resultant process efficiencies would not be the same because of the sequence of the membranes. If the organic composition is low hydrophobic membrane will show higher selectivity towards ethyl lactate, which is the case when the rate of the reaction is slow, or if an excess amount of the reactant, which is usually alcohol, is used. On the other hand, if the reaction precedes so fast that the final concentration is mostly composed of ethyl lactate and water the performance of the hydrophobic membrane placed just behind the reactor would be poor. In that case placing the hydrophilic membrane first will decrease the composition of the organics by removing water; hence the next pervaporation unit equipped with hydrophobic membrane would have better performance. The performance of hydrophobic membrane would be very important in the determination of the efficiency of these layouts. The discussions above were related to the semi-batch operation of the reactor and the pervaporation unit (Korkut, S., 2001).

Therefore, in the selection of the suitable hybrid layout phase equilibrium and reaction kinetics of the system must be well defined in addition to the performance data of the pervaporation membranes. Pervaporation performance of a commercial hydrophilic membrane, namely PERVAP©2201 was evaluated in the previous study (Korkut, S., 2001). Pervaporative separation of ethanol-water, ethyl lactate-water, and ethanol-ethyl lactate-water systems were carried out, and the relationship between feed concentration and pervaporation performance were investigated. It was concluded that vapor-liquid equilibrium data is necessary for better evaluation of the pervaporation efficiency. It was also reported that pervaporation performance of ternary systems is affected by ternary interactions, such as coupling effects. These interactions resulted in lower separation factors and higher permeation rates for ternary system when compared to binary systems. It was concluded that, hydrophilic PERVAP©2201 membrane is suitable for the production of ethyl lactate by hybrid processes, however, to evaluate feasibility of hybrid layouts and to compare them with each other, hydrophilic membrane performance data is not enough; performance data for hydrophobic pervaporation membranes (especially for third and four layouts) are also required.

Accordingly, in the first part of this study vapor pressure of ethyl lactate, vapor-liquid equilibrium of ethyl lactate-water, and ethyl lactate-ethanol system, which do not exist in the open literature, were determined experimentally. In the second part, pervaporation performances of commercially available hydrophobic and organoselective membranes were determined for ethanol-ethyl lactate mixtures

# CHAPTER 2

# LITERATURE SURVEY

## 2.1 *Vapor-Liquid Equilibrium*

Only very limited data for vapor pressure of ethyl lactate could be found from data sheets where only a few saturation pressures and temperatures were reported, as shown in Table 2.1. In open literature, there is not any vapor-liquid diagram of ethyl lactate containing mixtures.

**Table 2.1:** Ethyl lactate boiling point data.

| Pressure | Temperature | Reference |
|---|---|---|
| 5 mmHg | $30^0$C | Snell, F.D. and Snell, C.T., 1962 |
| 760mmHg | $154^0$C | Cargill Dow LLC, 2001 |

### 2.1.1. *Vapor Pressure and Boiling Point of Pure Components*

For the characterization of vapor-liquid equilibrium of pure substances, it is necessary to measure the pressures of the saturated vapors at given temperatures or the boiling points at given pressures and suitably to correlate the measured data.

There are several experimental methods of measuring the vapor pressure as a function of temperature, which can be used to determine heat of vaporization of pure substance (Hala, E., 1967). Heat of vaporization is found by using Clasius-Clapeyron equation in the form of Eqn. 2.1, where pressure is considered to be low enough to assume the vapor phase to be ideal and vapor volume is much larger so that volume of liquid is neglected. Assuming heat of vaporization is constant over the temperature range studied, the slope of the lnP versus 1/T line gives the heat of vaporization of the substance.

$$\frac{d(\ln P^{\circ})}{d(1/T)} = -\frac{\overline{\Delta H}^{vap}}{R} \qquad \text{Eqn. 2.1}$$

When lactic acid is considered, it is an organic hydroxy acid; which consists of a hydroxyl group in addition to the carboxyl group in its structure. The presence of hydroxyl group imposes some features to lactic acid and its derivatives in terms of the physical properties, such as vapor pressure, heat of vaporization, boiling point, etc. For instance, if the properties of hydroxy esters are compared to the esters, which do not have any hydroxyl group in their structures, hydroxy esters exhibit lower vapor pressures at the same temperature. This behavior is due to the hydrogen bonding forces, which keep the molecules together, associated with the hydroxyl group in their structure. Similarly, it can be deduced that hydroxyl esters have higher boiling point and heat of vaporization compared to esters without a hydroxyl group. In literature, although there are no VLE data for esters of lactic acid, data reported by

Steele, W.V. *et al.* (Steele W.V. *et al.*, 1996) for acetic acid, hydroxy-methyl ester allows making a relative comparison for heat of vaporization values of hydroxy esters, as shown in Table 2.2.

The similar discussion could be made in terms of Antoine equation, which is another way of expressing vapor pressure data of pure substances. Eqn.2.2 shows Antoine equation, where P denotes the vapor pressure in bars or mmHg, and T is the temperature in Kelvin, or Celsius.

$$\log_{10}(P) = A - (B / (T + C)) \qquad \text{Eqn. 2.2}$$

Table 2.3 shows the Antoine constants of the same esters shown in Table 2.2. The addition of hydroxyl group to the ester results in increase in constant B, which in a way represents heat of vaporization. Therefore, when the chemical structures are compared, it is expected to observe similar effect of a hydroxyl group on ethyl propionate as shown by Tables 2.2 and 2.3; moreover for the heat of vaporization of propionic acid, 2-hydroxy, ethyl ester, i.e. ethyl lactate, a closer value to acetic acid, hydroxy-, methyl ester is expected.

**Table 2.2:** Heat of vaporization of some esters

| *Name* | *Chemical formula* | *Boiling Point ($^0C$)* | *Heat of Vaporization (kj/mol)* | *Reference* |
|---|---|---|---|---|
| Acetic acid, methyl ester | $C_3H_6O_2$ | 57 | 30.32 | Majer, V. and Svoboda, V. (1985) |
| Acetic acid, hydroxy-, methyl ester | $C_3H_6O_3$ | 151 | 52.5 | Steele, W.V. *et al.* (1996) |
| Propionic acid, ethyl ester | $C_5H_{10}O_2$ | 99 | 33.88 | Majer, V. and Svoboda, V. (1985) |

**Table 2.3:** Antoine equation constants of some esters

| *Name* | *A* | *B* | *C* | *Reference* | *Applicable Temperature range* |
|---|---|---|---|---|---|
| Acetic acid, methyl ester | 4.2036 | 1164.426 | -52.690 | Polak, J. and Mertl, L. (1965) | 275-329K |
| Acetic acid, hydroxy-, methyl ester | 4.9964 | 1942.427 | -35.915 | Stull, D.R. (1947) | 283-425K |
| Propionic acid, ethyl ester | 4.1453 | 1274.735 | -64.218 | Polak, J. and Mertl, L. (1965) | 307-371K |

$\log_{10}(P) = A - (B / (T + C))$, P (bar), T(K)

### *2.1.2. Measurement Methodologies of Vapor-Liquid Equilibrium Determination for Multicomponent Mixtures*

There are large numbers of industrially important binary and multi component systems whose equilibrium relations can not be predicted from purely theoretical considerations and which must be obtained by a direct experimental determination (Reichl, A. *et al.*, 1998). The direct experimental determination of vapor-liquid equilibrium means that liquid and vapor, which are in true equilibrium at that specific pressure and temperature, are separated and concentrations of each phase is determined analytically. The determination of VLE data can be carried out either at constant temperature or at constant pressure. On the other hand, the design and construction of the equilibrium stills can be a source of various errors, which need not have the same importance in all systems, since the errors, which arise, are also dependent on the nature of the system measured (relative volatility, heat of vaporization, etc.) (Hala, E., 1967). The most widely used method for the experimental determination of VLE equilibrium data is circulation method although several alternatives such as static and flow-through methods exist. In static method vapor and liquid comes to an equilibrium by static means, i.e. there is not circulation of phases; on the other hand, in the flow method constant composition liquid or vapor streams are brought together to establish equilibrium. An extensive overview on these methods could be found in (Hala, E., *et al.*, 1967).

Gillespie type of still is one of the circulation stills, through which both vapor and liquid circulate. The realization of vapor-liquid circulation, which depends on the design and the operation of the still, is very important in terms of equilibrium. Rose and Williams (Rose, A. and Williams, E.T., 1955) reported that some precautions should be taken during the operation of Gillespie still due to under heating and overheating problems, for example when the Cottrell tube is unlagged, partial condensation of the binary mixture might occur; whereas when it is heated incorrect boiling points might be obtained. Similarly, when the liquid trap is unlagged, the vapor above the liquid might condense and enrich the liquid sample, when it is heated total vaporization of some of the liquid droplets on the walls of the trap resulted in a lowering of the vapor concentration. Therefore, to obtain accurate results Cottrell tube, entrainment separator, and liquid trap should be kept in an adiabatic condition. If the still is to be operated under vacuum Rose and Williams (Rose, A. and Williams, E.T., 1955) suggested the use of a Cottrell tube with a larger diameter, because the extra volume occupied by the vapor under vacuum might cause poor liquid circulation in the same manner as an excessive heat input did in the atmospheric pressure runs.

### 2.1.3. Vapor-Liquid Equilibrium of Reactive Systems

Although there are many non-reactive systems whose vapor-liquid equilibrium data could be found in data banks, there is only a little information about vapor-liquid equilibrium data of the systems, which are reactive, thermally unstable, or tending towards polymerization, furthermore there is no standard experimental equipment to be applied, since reaction takes place within the equipment in an uncontrolled way (Reichl, A., *et al.*, 1998). Table 2.4 shows the experimental work on reactive VLE found in literature. Three type of experimental methods could be distinguished as, static cells, circulation stills, and flow-through stills, which were explained in the previous section. In order to choose applicable method between these methods, several things should be considered, such as, chemical reaction rate constant(s), phase equilibrium time, mean residence time of reacting phase(s) in the apparatus, and the target compositions for the VLE measurement (Alsmeyer, F. *et al.*, 2002).

One of the possible approaches to VLE of reactive systems is to determine concentrations of each component in the mixture at some time intervals, during the reaction afterwards, a model is fitted to the values that obtained experimentally; finally VLE of the reactive components is obtained by extrapolating the curve to t=0 (no reaction). However, with this method to get satisfactory results, the reaction must not progress too fast, as reported by Winkler and Arlt (Winkler, B. and Arlt, W., 1997). Besides that, the activity coefficient models most commonly used like NRTL, Wilson, or UNIQUAC have not been designed for a multivariant regression (Reichl, A., *et al.*, 1998). Static or circulation cells might be used in this method.

Another method for the experimental determination of vapor-liquid equilibrium in reactive systems is the use of a non-recycle flow still as reported by Reichl *et al.* (Reichl, A., *et al.*, 1998). In this method the components pass the equipment only once, and the intensive mixing provides a large specific interfacial area, which is repeatedly renewed. The physical phase equilibrium is established very fast by use of this method. Due to short, well-defined residence times it is possible to get minimum amount of product formation, hence extrapolation to t=0 is not necessary in most cases. The disadvantages of this method are, first through the equipment presence of temperature gradients may severely affect the VLE data and second, if the residence times in the still is not sufficient, true VLE can never be reached.

In this study VLE of ethyl lactate-water mixture is evaluated at low pressure so as to neglect existence of the reaction products due to low conversion. In other words pseudo-steady state approach is followed, reaction is considered to be so slow to affect VLE

**Table 2.4:** Experimental reactive VLE studies (extracted from F. Alsmeyer *et al.*)

| *Reference* | *System* | *Static cell* | *Circulation still* | *Flow-through still* |
|---|---|---|---|---|
| Siddiqi, M.A. et al. (1997) | $SO_2$-water | √ | | |
| Heintz, A. and Verevkin, S. P. (2001) | MeOH-methyl styrene-methyl cumyl ether | √ | | |
| Arlt, W. (1999) | MeOH-Acetic acid/ MeOH-Propionic acid | √ | | |
| Hirata, M. et al. (1967) | acetic acid–MeOH–water–methyl acetate | | √ | |
| Kang, Y.W. et al. (1992) | Acetic acid- MeAc-MeOH- water | | √ | |
| Wang, L.and Zhao, S. (1994) | Methyl acetate–methanol–water–acetic acid | | √ | |
| Lee, L.S. and Kuo, M. (1996) | Acetic acid–isopropanol–isopropyl acetate–water | | √ | |
| Lee, L.S. and Lin, S.J. (1999) | Isoamyl alcohol-acetic acid | | √ | |
| Carvoli, G. and Delogu, P. (1986) | Acetic acid–ethylene glycol monoethyl ether acetate–ethylene glycol monoethyl ether–water | | √ | |
| Albert, M. et al. (1999) | Formaldehyde-water | | | √ |
| Hasse, H. and Maurer G. (1991) | Formaldehyde- water-MeOH | | | √ |
| Reichl, A., et al. (1998) | Methyl formate-water/ EtOH-acetic acid / EtAc.-water/ 2-Methyl-2-butene-MeOH/ MeOH – tert-amyl methyl ether/ 2-Methyl-2-butene-tert-amyl methyl ether | | | √ |

## *2.2 Pervaporation: Theory and Applications*

Pervaporation is a membrane process, which makes the separation of liquid by partly vaporizing it through a nonporous permselective membrane. It is a complex process in which both mass and heat transfer occurs. The chemical potential gradient across the membrane is the driving force for the mass transport. The heat needed for a phase change comes from the feed solution, which leads to a temperature gradient in the direction of permeate flow. The magnitude of the temperature drop depends on the permeation flux, latent heat of permeate, and the heat transfer coefficient in the boundary layer. Generally, there are three different layouts for pervaporation processes (Lipnizki, F., *et al.*, 1999):

1. Vacuum pervaporation
2. Thermopervaporation, and
3. Sweep gas pervaporation

In vacuum pervaporation (Fig. 2.1(1)), the driving force is realized by applying vacuum on the permeate side of the membrane. Hence, the partial pressure of evaporated permeate is lowered and a pressure gradient across the membrane is maintained using a vacuum pump. In thermopervaporation (Fig. 2.1(2)), the partial pressure difference between feed and permeate side is created by a temperature gradient across the membrane. The feed temperature has therefore to be increased significantly over the permeate temperature. Similar to vacuum pervaporation the vapor pressure difference, as a result of temperature gradient between permeate and feed side is the driving force for the separation. This system may be supplied by a condenser and feed side heat exchangers parallel to the membrane surface. Thirdly, sweep gas pervaporation in Fig. 2.1(3) can be applied, where the separation is driven by an inert sweep gas (normally air or steam) on the permeate side. As this gas can be heated there is an opportunity to supply the evaporation enthalpy on the permeate side. A condenser removes the permeate from the sweep gas (Lipnizki, F., *et al.*, 1999).

Generally vacuum pervaporation, which is customarily referred to as the standard pervaporation, is the most widely utilized mode of operation, while sweep gas pervaporation is normally of interest if the permeate can be discharged without condensation (Feng, X. and Huang, R.Y.M, 1997).

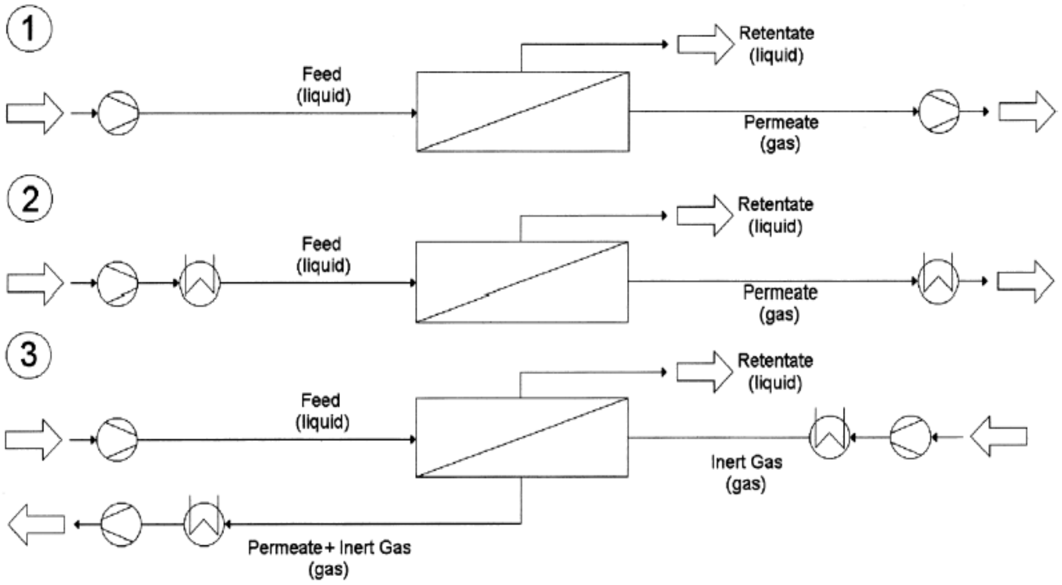

**Fig. 2.1** Process schematics for three different pervaporation units (Adapted from Lipnizki, F., *et al.*, 1999)

The applications of pervaporation are versatile (Scott, K., 1997), depending on the membrane type, which can be hydrophilic, hydrophobic or organoselective. Pervaporation can be used with (i) hydrophilic membranes in the dehydration of organic solvents such as:

-Alcohols: ethanol, methanol, butanol, IPA, allyalcohol, etc.

-Ketones: acetone, MEK, MIBK, etc.

-Esters: ethyl, butyl, propyl, acetates, etc.

-Others: THF, dioxane, MTBE, glycol ether, acetonitrile, etc.

-Acetic acid

-Organic amines, pyridine

Or, with (ii) hydrophobic membranes in the removal of organic compounds from aqueous solutions such as:

-VOC's from wastewater

-Removal of acids: acetic acid, formic acid

-Recovery of aromatic compounds: apple and fruit juice aroma compounds, coconut fragrance aroma compound

-Recovery of essential oils

-Wine and beer dealcoholization,

Or with (iii) organoselective membranes in the separation of organic/organic mixtures such as:

-Polar/nonpolar: methanol/toluene, ethanol/hexane,

-Aromatics/aliphatics: cyclohexane / benzene, hexane/toluene,

-Saturated/unsaturated: butane/butene,

-Isomers: x-ylenes, styrene, ethyl benzene

-Alcohols/ethers: ethanol/ETBE, methanol/MTBE

Pervaporation is attractive for separations in biotechnology due to its several features such as i) low operating temperatures, ii) low pressure, iii) high cross-flow velocities are not needed and iv) additional chemicals are not required. In this area, pervaporation could be used to

-Direct bioproduct recovery: in order to prevent inhibition effect of ethanol, butanol, isopropanol, acetone, 2-3 butanediol, glycol and acetic acid in fermentation broths

-Volatile by-product removal

-Concentration of sensitive bioproducts: generally high molecular species, eg. Amino acids, enzymes

-Dehydration of low molecular organics

-Extraction of aromas from fermentation reactors: Pervaporation offers advantages such as, recovered products are not contaminated so that extensive additional purification is not required, biological activity is not diminished, and product quality is not deteriorated (Belafi-Bako, K., *et al.*, 2000).

### 2.2.1. *Performance Criteria for Pervaporation*

Three issues are important in the evaluation of the performance of pervaporation units. These are (i) membrane productivity, (ii) membrane selectivity, and (iii) membrane stability (Feng, X., and Huang, R.Y.M, 1997). Membrane productivity is a measure of quantity of a component that permeates through a specific area of a membrane surface in a given unit of time. Membrane productivity is frequently characterized by permeation flux, *J*, which depends on both the intrinsic properties and the effective thickness of a membrane.

$$J = \frac{\text{Permeate flowrate}}{\text{Membrane Area}}\left[\frac{\text{(g/min)}}{(\text{m}^2)}\right] \text{.......................................Eqn.2.3}$$

Membrane selectivity is the affinity of the membrane to the desired component in permeate; it is defined by a separation factor, $\alpha_{ij}$, which is the ratio of the compositions of components *i* and *j* in the permeate relative to the composition ratio of these components in the retentate. When separation factor is unity there is no separation, when it approaches to infinity, membrane is perfectly semi permeable. Separation factor is given by equation. 2.4,

$$\alpha_{ij} = \frac{y_i / x_i}{y_j / x_j} \text{.............................................................Eqn.2.4}$$

Membrane stability is the ability of a membrane to maintain both the permeability and the selectivity under specific system conditions for an extended period of time. When considering polymeric membranes for the separation of anhydrous organic mixtures, the membrane stability is of prime importance.

### *2.2.2. Transport Through Pervaporation Membranes*

Nonporous membranes, used in pervaporation, perform separations on a molecular level based on the chemical nature and morphology of the polymeric membrane and the extent of interaction between the polymer and the permeants (Mulder, M., 1997). Pervaporation membranes are nonporous, preferably with anisotropic morphology, an asymmetric structure possessing a dense top layer and an open porous sublayer. The sublayer should have an open substructure to minimize resistance to vapor transport and to avoid capillary condensation and a high surface porosity with a narrow pore size distribution. The membrane should not swell too much with the feed mixture, otherwise selectivity will decrease drastically; on the other hand low sorption or swelling would result in a very low flux.

There are principally two approaches in describing mass transport in nonporous membranes: (i) the solution-diffusion model and (ii) the pore flow model. For pervaporative transport, the solution-diffusion model is accepted by majority of membrane researchers (Ten, P.K. and Field, R.W., 2000). According to this mechanism, pervaporation process consists mainly of the following three steps together with the phase change from liquid to vapor:

Step1: Migration of components through the boundary layer from the bulk to the interface on the feed side of the membrane (liquid)

Step 2: Sorption into and diffusion of components through the membrane (liquid and vapor).

Step 3: Desorption of the components into the permeate side (vapor).

The sorption of the component *i* into the membrane polymer on the feed side is related to component's total energy requirement to dissolve into the polymer. Generally, the component in the feed mixture with the lowest energy requirement is preferentially sorbed into the membrane polymer. The diffusion behavior however depends on the feed components, membrane polymer and process parameters. Across the membrane, diffusion will follow the gradient of the chemical potential, the driving force of pervaporation, can be described by Fick's law (Lipnizki, F., *et al.*, 1999).

One important consideration that should always be kept in mind is the phase transition from liquid to vapor within the membrane, since this phase transition brings its own selectivity to the overall selectivity attained by the system. According to the solution-diffusion model the separation selectivity of pervaporation process is expressed by eqn. 2.5, where $\alpha^{S}$ is sorption selectivity, $\alpha^{DL}$ is diffusional selectivity among liquid molecules, $\alpha^{EV}$ is evaporation selectivity, $\alpha^{DV}$ is the diffusional selectivity among vaporized molecules, and $\alpha^{DES}$ is the desorption selectivity.

$$\alpha^{PV} = \alpha^{S}\alpha^{DL}\alpha^{EV}\alpha^{DV}\alpha^{DES} \quad \text{...Eqn. 2.5}$$

If the properties of the membrane (sorption, diffusion and desorption) are collected in a single parameter $\alpha^M$, the selectivity becomes the product of $\alpha^M$ and $\alpha^{EV}$, which is the thermodynamic property of the penetrating mixture (Kujawski, W. 1996).

$$\alpha^{PV} = \alpha^M \alpha^{EV} \quad \text{Eqn. 2.6}$$

In the case of hydrophilic pervaporation of binary mixture composed of water and a more volatile compound with hydrophilic membranes, the phase transition step substantially decreases the overall separation, since more volatile compound is enriched by VLE but the membrane selectively removes water, which is the less volatile component. On the other hand, in pervaporation of binary mixtures containing water and a less volatile substance the more volatile component, water, is the same as the selectively removed component. For this case evaporation selectivity contributes to the pervaporation selectivity, however the challenging question arises, is it feasible to use pervaporation if the membrane selectivity contributes little to the evaporation selectivity. For these type of mixtures, therefore the first step before the process development should be comparison of the vapor-liquid equilibrium curve of the mixture to be separated with the data of permeate concentration (vapor-y) versus feed concentration (liquid-x) data.

### *2.2.3. Characteristics of Pervaporation Membranes*

Depending on the application area three types of pervaporation can be applied, which are, (1) hydrophilic pervaporation, (2) hydrophobic pervaporation, and (3) organoselective pervaporation.

In hydrophilic pervaporation the target compound water is separated from an aqueous-organic mixture by being preferentially permeated through the membrane. Pervaporation membranes could be made from polymers, inorganic materials, or polymer/inorganic composites. The polymeric membranes fail to resist harsh operation conditions, such as highly acidic media or high temperature; whereas inorganic materials have better capability but disadvantage of inflexibility. Besides, inorganic materials generally have molecular level defects, which results in selectivity loss. Inorganic hydrophilic materials are typically having high alumina to silica content, such as zeolites (Dhaval, S.S., 2001). The hydrophilic composites are mostly zeolite filled polymers, such as zeolite (NaX, CaX, NaA, KA, etc.) filled polyvinyl alcohol PVA membranes.

Polymeric hydrophilic membranes are generally made from glassy polymers (Huang, R.Y.M. and Yeom, C.K., 1991). There are three types of glassy polymers; crystalline, semi-crystalline and amorphous. The presence of crystallites affects many properties of the polymer including solubility and diffusivity in the membrane, for example highly crystalline polymers show high selectivity with lower permeability. In pervaporation, membranes made of semi-crystalline polymers generally show good flux and selectivity values, most commercial hydrophilic membranes are made of polyvinyl alcohol (PVA), more or less cross-linked. The other materials, that can be used for hydrophilic membranes are, polyvinyl alcohol/polyacrylonitrile (PVA/PAN), cellulose acetate (CA), polyethylene (PE), polyvinyl acetate (PVAc), nylon-6, polyophenyleneoxide (PPO), polyetherimide (PEI), 4,4-Oxydiphenylene Pyromellitimide (POPMI), Caesium Polyacrylate (Huang, R.Y.M. and Yeom, C.K., 1991; Dhaval, S.S., 2001, Lipnizki, F., *et al.*, 1999).

In hydrophobic pervaporation organic compounds are separated from aqueous-organic mixtures. Polymeric organophilic membranes are made from elastomers. Elastomers, which do not have polar groups in their structure; absorb organics and do not interact with water. The main chain consists of bonds like C-C, Si-O or C-O. The common polymeric membrane materials are, polydimethylsiloxane (PDMS), polyether-block-polymide (PEBA), polytetrafluoro-ethylene (PTFE), polybutadiene (PB), and polypropylene (PP) (Lipnizki, F., *et al.*, 1999). The two inorganic materials used as organophilic membranes are silicalite and ZSM-5.

In organic-organic separations, commonly encountered in petroleum, oil refining and petrochemical industries, organoselective membranes are used. Organoselective membranes are specially designed to remove one of the organic compounds; hence they require novel polymeric/inorganic materials. Some of the examples of membrane materials are, polydimethylsiloxane (PDMS), polyether-block-polymide (PEBA), polyacrylonitrile/polyacrylonitrile (PVA/PAN), polyetherimide (PEI) (Lipnizki, F., *et al.*, 1999). In the market there are alcohol selective membranes for the extraction of alcohols from mixtures, such as PERVAP©2256 from Sulzer.

In literature, there are many studies, in which pervaporation performances of different pervaporation membranes with various feed mixtures were investigated. The attempt here would be to list the pervaporation characteristics of the membranes subjected to alcohol/water/ester mixtures, so that in the further discussions a comparison with the experimental data could be made. Moreover, there are only a few concentration dependent pervaporation data of alcohol-ester binary mixtures existing in the literature; where hydrophilic, hydrophobic or organoselective membranes are used. Similarly, there is only a few concentration dependent hydrophobic pervaporation data of water-ester mixtures. Table 2.5 shows the overall flux and selectivity values for the performances of different membranes subjected to ester/alcohol/acid/water mixtures.

In the study of Molina *et al.* (Molina, J.M., *et al.*, 2002), ethanol-water mixtures are separated at different feed temperatures with PERVAP1060 and CMG-OM-010 membranes. The flux and separation factors were found to increase with increasing temperature. Temperature versus flux was observed to have an exponential behavior whereas the separation factor trend was logarithmic.

In the study of Jafar *et al.* (Jafar, J.J., *et al.*, 2002) zeolite NaA membranes were used to separate ethanol water mixtures at different temperatures for different feed water concentrations. Zeolite membrane showed quite high selectivity even for 10-wt% water feed concentration. It was observed that, as feed water content is increased flux values increase in a logarithmic way, and separation factor decreased almost linearly.

Liu *et al.* (Liu, Q., *et al.*, 2001) studied the separation of water/acetic acid and water/acetic acid/n-butanol/butyl acetate mixtures by PVA membranes at several temperatures. Parametric calculations were made with the results of pervaporation experiments, for water/acetic acid mixture partial fluxes of water and acetic acid followed a linear trend at the temperatures studied, whereas for the quaternary mixture an exponential function was found to fit to the partial flux values.

In the study of Won *et al.* (Won, W., *et al.*, 2002) separation of dimethylcarbonate (DMC)/methanol/water mixtures were carried out using chitosan membranes. In the separation of water from DMC/water mixtures, it was found that an increase in temperature leads to a decrease in the permeation flux, as the opposite is generally observed. This behavior was attributed to the poor miscibility of water with DMC, as temperature increased the solubility of water in DMC increases as a result at a given concentration the activity of water in the homogenous DMC/water solution decreases since more water can be dissolved by DMC. In other words, the forces that trap water in the solution become stronger, which results in less water being sorbed into the membrane matrix, thereby slowing down the diffusion rate of water because of the reduced driving force across the membrane and also the degree of swelling. Since degree of swelling is decreased, membrane shows a stronger resistance to diffusion of both components, hence fluxes decrease. In the separation of methanol from DMC chitosan membrane was found to be able to break azeotrope occurring at 65wt% methanol. For the ternary mixture the chitosan membrane was able to remove water and methanol from DMC, and the enrichment of water was much more significant than methanol.

**Table 2.5:** Pervaporation performances of different membranes for ester/alcohol/acid/water mixtures

| Water (wt%) | A.acid (wt%) | E. Ac .(wt%) | EtOH (wt%) | Temp ($^0$C) | Mem. | Flux (g/m$^2$min) | $\alpha_{W/A}$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| 37 | 13 | 37 | 13 | 60 | PEI | 0.628 | 18.9 | Zhu, Y. *et al.*, 1996 |
| 21 | 5 | 32 | 42 | 70 | GFT1005 | 3.204 | 116 | Krupiczka, R., *et al.*, 1999 |
| 10 | - | - | 90 | 50 | ZeoliteNaA | 2.5 | 1000 | Jafar, J.J., *et al.*, 2002 |
| | | | | | | | $\alpha_{W/Acid}$ | |
| 10 | 90 | - | - | 80 | PVA/PAA blend | 6.333 | 6.7 | Zhu, Y. *et al.*, 1998 |
| 10 | 90 | - | - | 80 | Crosslinked PVA | 5.867 | 9.9 | Zhu, Y. *et al.*, 1998 |
| | | | | | | | $\alpha_{A/W}$ | |
| 85 | - | - | 15 | 40 | PERVAP 1060 | 12 | 3 | Molina, J.M. *et al.*, 2002 |
| 85 | - | - | 15 | 40 | CMG-OM-010 | 10 | 6.3 | Molina, J.M. *et al.*, 2002 |
| | | | | | | | $\alpha_{Acid(Ester)/W}$ | |
| 94 | - | 6 | - | 30 | PDMS | 23.3 | 1103 | Nguyen, Q.T., *et al.*, 2000 |
| 15 | 85 | - | - | 60 | GFT1005 | 8.33 | 183 | Domingues, L., *et al.*, 1999 |
| Water (wt%) | A.acid (wt%) | n-butyl Ac. | EtOH (wt%) | | | | | |
| 10 | - | 90 | - | 70 | Crosslinked PVA | 2.567 | 441 | Zhu, Y., *et al.*, 1998 |
| | | DMC | MeOH | | | | $\alpha_{Alcohol/\ Ester}$ | |
| - | - | 46 | 54 | 50 | Crosslinked chitosan | 5.00 | 12 | Won, W., *et al.*, 2002 |
| - | - | 40 | 60 | 50 | GFT No. 270 | 31.7 | 33 | Nickel, A., *et al.*, 1994 |
| - | - | 32.1 | 67.9 | 70 | PVA | 1.67 | 19 | Pasternak, M., *et al.*, 1989 |

Gonzalez and Uribe (Gonzalez, B.G. and Uribe, I.O., 2001) have studied the mathematical modeling of the pervaporative separation of methanol-methyltertbutyl ether mixtures with organoselective PERVAP©2256 membranes. The selectivity values obtained by pervaporation were found to be much higher than vapor liquid equilibrium curve at the pervaporation feed temperature. As temperature of feed mixture was increased permeation flux of methanol increased slightly greater than that of MTBE, the temperature dependence of permeation flux found to follow an exponential fashion. It was found that both methanol and MTBE permeation rates decrease as the downstream pressure is increased (i.e., downstream activity is increased), although the methanol rate decreased more rapidly as a percentage of the initial value. In so far as it does not exceed a limit beyond which the swollen membrane is physically modified, the upstream pressure has no significant influence on the characteristics of the permselective barrier, in consistency with the solution-diffusion mechanism and not a microcapillary viscous flow. The preconditioning stage, where the membranes were put in a sample solution before the experiments, were found to effect the overall flux similar to the effect of feed composition.

In the study of Luo *et al.* (Luo, G.S., *et al.*, 1999) PVA-Cellulose acetate propionate (CAP) membranes, selective to ethanol, were prepared and used in the separation of ETBE/ethanol mixtures. The minimum values of ethanol concentration in the permeate and in the sorption solution were obtained near the azeotropic point. The pervaporation curve, the vapor-liquid equilibrium curve and the polymer-liquid mixture equilibrium curve showed the same tendency with a change of ethanol concentration in feed, and the selectivity of pervaporation was considerably higher than that of distillation. With temperature increase flux increased but selectivity decreased. The performance of PVA/CAP membrane found to be better than that of pure CAP membrane.

The removal of methanol from organic solvents was studied by Zhou *et al.* (Zhou, M., *et al.*, 1996). It was emphasized that in contrast to hydrophilic membranes the choice of organic/organic separation membranes is not distinct but depends on the mixtures to be treated. Ppy-PF membranes were tested continuously and a membrane leakage of was reported after 6 day-separation of methanol/toluene mixtures. The membranes were selective to methanol over IPA, toluene and acetonitrile, however when the methanol content in the feed was 90 wt% in methanol-acetonitrile mixture the pervaporate possessed exactly the same composition as the feed mixture. This characteristics concentration was termed as "permazeotropic concentration" as an analogy to the distillation azeotrope. Temperature effect on the selectivity found to be very small for acetonitrile-methanol mixtures although the flux doubles by changing the temperature from 30 to 63.$^0$C.

In the study of Kujawski and Roszak (Kujawski, W. and Roszak, R., 2002) different hydrophobic membranes, namely PERVAP©1060, PERVAP©1070, and PEBAX-4033 were used to separate binary and ternary water-organic mixtures. It was observed that by increasing temperature the selectivity does not change significantly but permeate flux increases. They have pointed out that any assumed degree of organic removal might be obtained simply by increasing the separation time, process temperature, or by decreasing the volume to separation area ratio (V/S). The fastest separation was obtained with PERVAP©1060 membrane, but the degree of removal of MTBE from water was lower than that of water-ester mixtures, which is due to the fact that MTBE is quite polar solvent and possesses relatively high solubility in water. In ternary water-methanol-MTBE mixtures MTBE, as the most hydrophobic component of investigated mixture was transported preferentially, however, both the selectivities and permeate fluxes of organic components were much smaller when compared to binary mixtures, which indicates ternary interactions. Between the membranes investigated PERVAP©1060 showed the best efficiency in the removal of organics from water, although PERVAP©1070 membrane was the most selective one, much lower efficiencies found for PEBAX-4033 membrane were caused by the fact that the selective layer of PEBAX-4033 membrane contained both the hydrophobic and hydrophilic blocks.

### 2.2.4. Pervaporation-Esterification Hybrid Systems

Integration of pervaporation into the conventional esterification reactions has been attracted much attention in the literature, due to numerous advantages of pervaporation integration; such as lower reagent consumption, higher yield, and no requirement of further product purification. The limitation in the use of membrane reactors in esterification reactions is the instability of polymeric membranes used with acidic medium.

An alternative approach to obtain better performance in membrane reactors is the development of inorganic or polymeric/inorganic composite membranes. Zhu *et al.* (Zhu, Y., *et al.*, 1996) studied the esterification of acetic acid with ethanol with a continuous flow pervaporation reactor utilizing a polymeric/ceramic composite membrane. Zhu and Chen (Zhu, Y., and Chen, H., 1998) carried out n-butyl alcohol-acetic acid esterification by using a membrane reactor having a composite catalytic membrane composed of a cross linked PVA dense active layer coated on a porous ceramic plate. The result of pervaporation experiments with ethanol-water mixtures at several temperatures showed that flux increase, however selectivity decrease with increasing temperature. The same trend observed in pervaporation experiments with water/acetic acid and water/n-butyl acetate mixtures. In the catalytic membrane reactor the permeation fluxes of acid, alcohol, and ester were found to be very small, $J_{water}>J_{acid}>J_{alcohol}>J_{acetate}$, whereas the separation selectivies were very high, $\alpha_{water-acetate}>\alpha_{water-alcohol}>\alpha_{water-acid}$. The separation selectivity of n-butyl acetate was the best and the acid was the lowest, which were attributed to their polarities and molecular sizes. Based on the experimental results, a theoretical model was established for a pervaporation membrane reactor. They reported a decrease in performance of the membranes after continuous experimentation over the two-week period; the failure was detected by a minor decrease in the separation factor and an increase in permeance. Some of the pervaporation data for ethanol/water separation reported in the literature were included in their paper. Tanaka *et al.* (Tanaka, K., *et al.,* 2001) investigated same reaction using zeolite T membranes. It was reported that the conversion exceeded the equilibrium limit and reached to almost 100% for the initial molar ratios of alcohol to acetic acid 1.5 and 2, however long term stability of zeolite T membranes to acid solutions should be improved for realization of the process.

Gao and his coworkers have used zeolite fillers to enhance the performance of hydrophilic pervaporation membranes (Gao, Z., *et al.*, 1996). Zeolite facilitates the permeating of smaller molecules but hinders that of larger molecules. In their study; acetic acid/ethanol esterification was carried out with the composite zeolite membranes. The reaction conversion was reached to 95% in decreasing order time intervals for the membranes PVA, PVA+KA, and PVA+CaA, respectively under $70^0$C. The results indicated that the pervaporation through zeolite filled hydrophilic membranes could be used to enhance the conversion in esterification reactions.

The esterification of acetic acid with n-butanol in a membrane reactor equipped with PVA/ceramic composite membrane was studied by Liu and Chen (Liu, Q.L., and Chen, H.F., 2002). The operating parameters for the pervaporation-coupled esterification: process temperature (T), initial molar ratio of acetic acid to n-butanol ($R_0$), ratio of the membrane area to the reacting mixture volume (S/V), and the catalyst content were changed to investigate the relative effects of these parameters on conversion. Since reaction rate constants for the esterification increase with the increase of the temperature, water production rate was higher at high temperatures. The permeation flux also varied with the temperature and increased with the increase of temperature. The water content in the reacting mixture during the process had maximum amplitude and increased at the beginning. This may due to the fact that water production rate was higher than the rate of water removal by pervaporation at the earlier stage during the process and was reverse when water content reached the maximum value. The maximum point shifted to the up as temperature increased, which means that the acceleration for water production rate has higher value at higher temperatures. The effect of $R_0$ was in terms of reaction kinetics, as $R_0$ increased the water content in the reactor decreased. S/V, on the other hand have an influence on the pervaporation kinetics, i.e. the water extraction rate. As S/V was increased water content in the reactor decreased as a result of high water extraction rate at high membrane area. For high catalyst concentration water production rate was higher, thus water content increased as catalyst content was increased.

David *et al.* (David, M.O., *et al.*, 1991) studied the esterification of 1-propanol and 2-propanol by propionic acid in an external pervaporation, equipped with PVA composite membrane, hybrid reactor. A basic kinetic model was established, which fits to the experimental results in (David, M.O., *et al.*, 1991, Part I). By using pervaporation, 90% conversion was achieved compared to 70% without pervaporation. One of the important observations reported was that the membrane that is several times used experienced esterification by the acid. The influence of several operating parameters on the system was investigated in (David, M.O., *et al.*, 1991, Part II).

Okomato *et al.* (Okamoto, K., *et al.*, 1993) studied the esterification of oleic acid with ethanol at two different temperatures in membrane reactor with two kind of asymmetric membranes, polyetherimide (PEI) and poly(4,4'-oxydiphenylene pyromellitimide) (POPMI). In the pervaporation experiments with quaternary reaction mixture neither acid nor ester permeation was observed through the membranes at low temperature, however at high temperature all of the components appeared in permeate, meaning that at high temperature plasticizing effect of the components become significant. A membrane reactor model was also established through investigation of effects of several operating parameters. As temperature increased, time required to attain 98% conversion decreased, as expected. As initial molar ratio of alcohol to acid increased the productivity increased after certain value productivity decreased, meaning that alcohol/acid ratio should be optimized for integrated pervaporation-reactor systems. It was concluded that for practical use, it is necessary to develop both a large-scale reactor with high membrane area to reaction volume ratio and a membrane with high water permeability with excellent long-term durability.

In all of the mentioned studies, a single hydrophilic membrane was integrated to the esterification reactor for the purpose of increasing conversion, while none of the studies was interested in obtaining of pure product together with increasing the conversion. Therefore, in the literature hybrid systems containing more than one pervaporation unit, i.e. the use of both hydrophobic and hydrophilic pervaporation units were not studied.

### *2.2.5. Pervaporation-Esterification Hybrid Systems for Ethyl Lactate*

In open literature, there is very limited number of studies on the production of ethyl lactate by pervaporation integrated hybrid processes, and there is only one report on integration of hydrophobic pervaporation unit(s) to the esterification reactor. In a patent by Datta and Tsai (Datta, R., and Tsai, S.P., 1998) a method for making high purity esters from fermentation derived organic acids using pervaporation processes was described. One of the examples given was the ethyl esterification of lactic acid by reacting ethanol with lactic acid. The lactic acid used was a commercial food grade fermentation-derived lactic acid. Amberlyst 15 at 3 weight percent of lactic acid was used as catalyst, and the membrane used was GFT PERVAP1005. The molar ratio of ethanol to lactic acid was 2.8 in the feed. The temperature of the reaction mixture was maintained at $80^0$C, and the permeate side pressure was 4-25 milibar. 90 percent conversion was achieved, compared with the 75 percent conversion for the batch esterification. A hydrophobic membrane GFT PerVap 1170 was used to separate ester from final product liquors, whereby mixture was subjected to pervaporation at $80^0$C, where permeate-side vacuum pressure was approximately 8 mbar. After 20.4 hours, separation of the ester by pervaporation was terminated, and a high selectivity but very low flux was obtained for ethyl lactate.

Tanaka *et al.* (Tanaka, K., *et al.*, 2002) and Jafar *et al.* (Jafar, J.J., *et al.*, 2002) studied lactic acid esterification in membrane reactor by using vapor permeation (VP) instead of pervaporation unit. In the study of Tanaka *et al.* (Tanaka, K., *et al.*, 2002) zeolite T membranes were used, since Zeolite T membranes are not stable at acidic conditions using VP ensured membrane stability, since vapor phase of reaction mixture composed of mainly ethanol and water. The reaction conversion for VP-aided reaction reached to almost completion using Amberlyst 15 cation exchange resin, at temperatures 90-$102^0$C, for the initial molar ratios of alcohol to lactic acid being 2.4 and 3.6. On the other hand, neither flux nor selectivity enhancement was observed for vapor permeation (VP) over pervaporation with ethanol-water mixtures.

Water content in the reactor was observed to increase in the early stage <1h, and then decreased, during the reaction water content never exceeded 10 wt%.

Similarly, Jafar *et al.* (Jafar, J.J., *et al.*, 2002) studied the lactic acid esterification with ethanol by using VP with Zeolite A membranes in a membrane reactor in a batch mode. In this study, 95% yield of ethyl lactate was achieved by using p-toluene sulphonic acid as catalyst, and reaction temperature of $70^0$C. Since the vapor phase of the reaction mixture does not contain acids, Zeolite A membrane observed to work steadily for a long time.

In the previous study of our group (Korkut, S., 2001, Korkut, S. *et al.*, 2003) pervaporation based hybrid process schemes for the production of ethyl lactate were developed, and performance of a commercial hydrophilic membrane, PERVAP©2201 for ethyl lactate-water-ethanol containing binary and ternary mixtures were evaluated. The variation of steady state flux and selectivities with feed composition was investigated for the ethyl lactate–water and the ethanol–water binary systems for a water concentration range of 0.8 to 60-wt %. In ternary mixture compositions of ethanol and ethyl lactate were kept equal in weight percents, whereas water concentration was changed from 0.8 to 60-wt%. This was the first concentration dependent pervaporation data for ethyl lactate-water and ethyl lactate-water-ethanol mixtures reported in the literature. It was shown that, as feed water concentration increases, flux increases and selectivity decreases.  Moreover, a linear relationship between feed water concentration and overall flux for the binary and ternary systems was found. On the other hand, the relationship between feed water concentration and water selectivity was found to follow a logarithmic trend. For ethanol-water system, the results were found to be completely consistent with the behavior of the hydrophilic PVA based Sulzer membranes reported in the literature. When ethyl lactate-water system was compared with ethanol-water system; similar flux but lower selectivity for the first system was observed. This result was explained by the structure of ethyl lactate and its high hydrophilicity as compared to other esters. It was pointed out that the interactions of ethyl lactate molecules with the hydrophilic membrane and with water might be more significant than that of ethanol, which results in higher ethyl lactate partial flux in ethyl lactate-water system than that of ethanol in the ethanol-water system. For the ternary system, due to coupling effects higher fluxes and lower selectivities were obtained with respect to binary systems studied. In other words, existing of all three components in feed solution caused swelling of the membrane more than in case of binary mixtures as a result of ternary interactions, known as ‘coupling effects’ in the literature.

As a conclusion, it was shown by (Korkut, S. 2001, Korkut S., *et al.* 2003) that pervaporative separation of ethyl lactate-water mixtures with hydrophilic PERVAP©2201 membrane could be carried out with high selectivities especially at low water concentrations. In order to better evaluate the performance of PERVAP©2201 membrane vapor-liquid equilibrium data of ethyl lactate mixtures is required. Moreover, water removal by hydrophilic pervaporation as a part of hybrid ethyl lactate production processes could be feasible, provided that water concentration of the feed stream entering to pervaporation unit is kept low. Finally, in the evaluation of the proposed hybrid layouts, especially third and fourth systems containing hydrophobic pervaporation units, investigation of pervaporation performance of hydrophobic membranes is essential, since the performance would mostly determine the product purity degree.

# CHAPTER 3

# EXPERIMENTAL

In this study, vapor pressure curve of ethyl lactate was measured with respect to the temperature by using the isoteniscope method (Shoemaker, D.P., 1974). Precision of the isoteniscope method was checked by measuring the vapor pressure curve of benzene as a reference component. In ethyl lactate vapor pressure data, the studied pressure range was between 12 and 74 mmHg, the corresponding temperatures were from 54 to $86^0$C.

VLE of ethyl lactate containing systems, that is ethyl lactate-ethanol and ethyl lactate-water VLE data were determined experimentally by using Gillespie still. Ethanol-water system was used as a reference system in order to evaluate the precision of the experimental set-up and procedure. Ethyl lactate-ethanol VLE data was determined at pressures 8cmHg and 68cmHg (atmospheric pressure at this altitude), and VLE curve of ethyl lactate-water mixture was determined only at 8cmHg pressure.

In membrane characterization studies, hydrophobic CMX-GF-010-D and PERVAP©1060, and an organoselective PERVAP©2256 membranes were used in the fractionation of ethanol-ethyl lactate mixtures.

## 3.1 Materials

Technical grade ethyl lactate, which has a purity of 98 %, from PURAC (Spain) and analytical grade ethyl lactate from Fluka (Switzerland), analytical grade ethanol having 99.5 % purity, from Deltalar (Turkey), 0.1N potassium hydroxide (prepared in the lab), and distilled water were used as chemicals for the experiments. Analytical grade ethyl lactate was used for calibration purposes. All of the chemicals were used without further purification. The filter paper of 25mm ashless type, liquid nitrogen, cotton, variable size plastic, silicon, PTFE hoses, glass and PTFE taps, silicon vacuum grease, from Ildam Kimya (Turkey), were used in the experiments. For pervaporation experiments, an organoselective PERVAP©2256 membrane were bought from Sulzer Chemtech, hydrophobic membranes CMX-GF-010-D from CM-CELFA and PERVAP©1060 from Sulzer were kindly supplied by the companies.

## 3.2 Experimental Methods

### 3.2.1 Experimental Set-up for Isoteniscope Method

Isoteniscope method was used in determining the vapor pressure curve. The experimental set up consists of a vacuum pump to reduce pressure, a 3-way stopcock, an isoteniscope filled with sample, a ballast tank used to reduce the pressure fluctuations, and an open-end mercury manometer to measure system pressure. A water bath with

Edmund Bühler th2 type-750W controllable heater-stirrer, and a cooling coil were used to control temperature of the liquid inside isoteniscope. A schematic diagram is shown in Fig. 3.1.

### 3.2.2 Experimental Set-Up For Gillespie Still

A Gillespie type of still was used in determination of binary phase diagrams. A schematic diagram is shown in Fig. 3.2. At vacuum Gillespie still with a sampling cell, which allows taking samples from the cell without interrupting the equilibrium, was used. An E2M0.7 Edwards type vacuum pump was used to regulate the pressure. A U-tube mercury manometer was used in measuring the pressure inside the still. Temperature was measured by ASTM 35C/IP +0°C-120°C 'nitrogen filled' type thermometer with a precision of 0.2 °C. LTD 6G Grant type circulated bath was used for cooling purpose. In the analysis of binary mixtures Bellingham Stanley 60/70 Abbe type refractometer was used. Determination of the free acidity in ethyl lactate-water mixtures was carried out by acid-base titration.

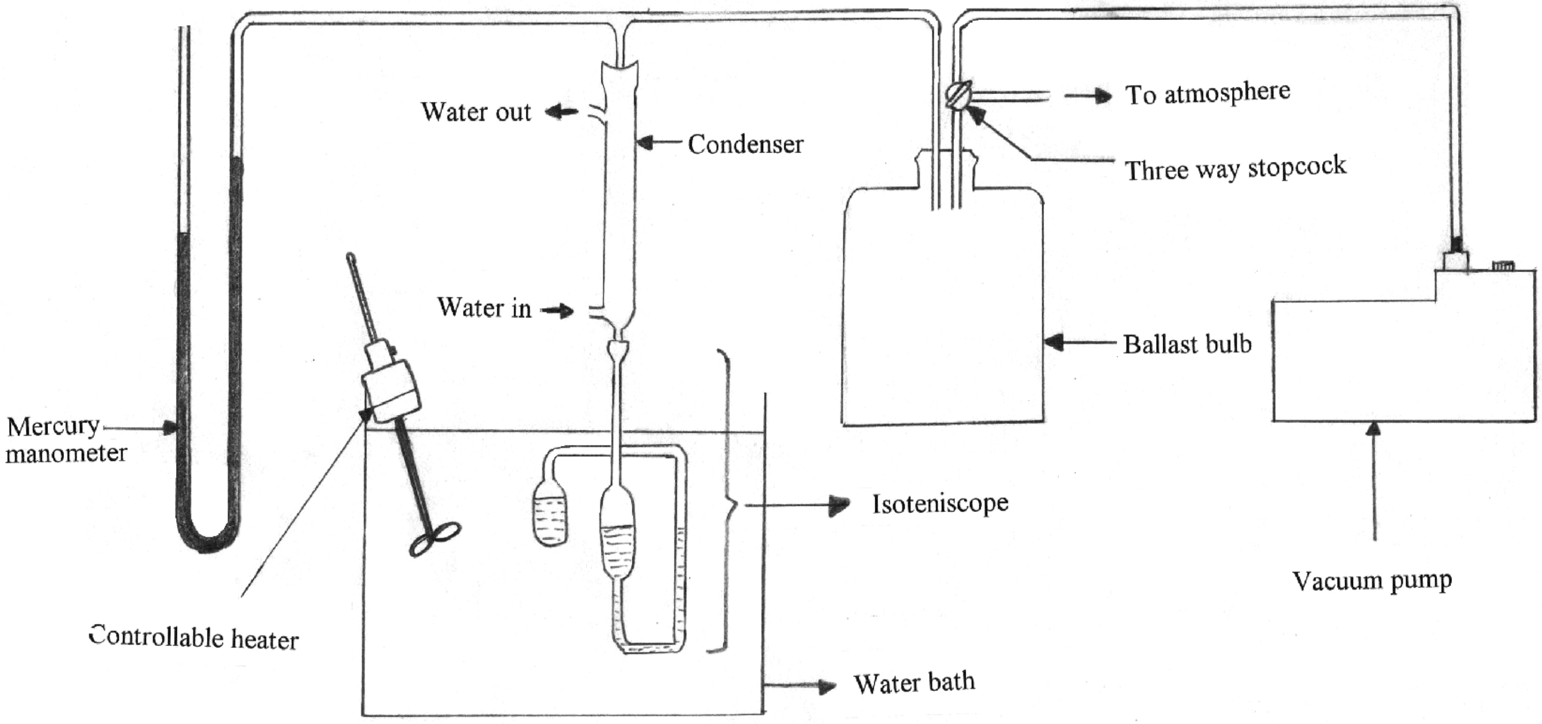

**Figure 3.1** Schematics of isoteniscope set-up

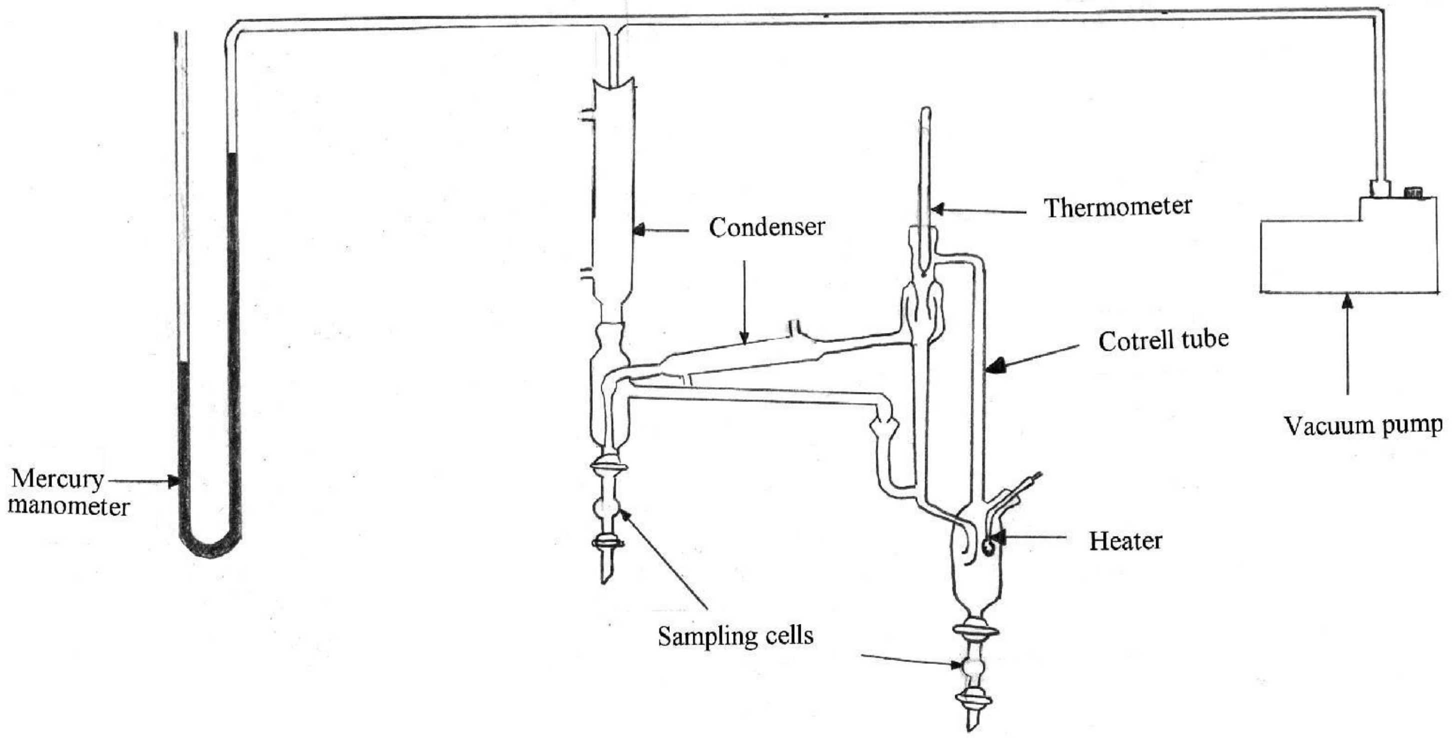

**Figure 3.2** Schematics of Gillespie still set-up

### 3.2.3 Experimental Set-up for Pervaporation

The apparatus for pervaporation experiments consisted of a permeation cell, which holds the membrane; a feed tank; a liquid pump to circulate the feed solution from feed tank to the pervaporation cell; a means of condensing and collecting permeate vapor which is evaporated at the downstream side; and a vacuum pump. The PV set-up, which is shown schematically in Fig. 3.3, was also used in the previous studies (Okumus, E. 1990, Okumus, E. *et al.,* 1994, Okumus, E. 1998, Korkut, S. 2001). The permeation cell is made up of stainless steel, circular construction having 10cm diameter. The Pyrex feed tank has a volume of about 5 L, large enough to ensure that the concentration of the feed solution remains constant during the experiment. The temperature of the solution is measured at retentate side before entering the feed tank by a thermocouple. Both the cell and the feed tank is placed in a constant temperature bath having dimensions 50*40*30cm. Downstream pressure measurement is done by a pressure transducer, shown digitally by a displayer and the controlling action is taken accordingly by the experimentalist. The value of the vacuum pressure can be adjusted by the help of two valves connected in series one of which is opened to the atmosphere.

To collect and condense vapors, cold traps immersed in liquid nitrogen were used on the vacuum side of the equipment. The traps were arranged such a way as to enable one trap to be removed with the collected permeate while the other was being used. In this way samples could be withdrawn at any time without interrupting the

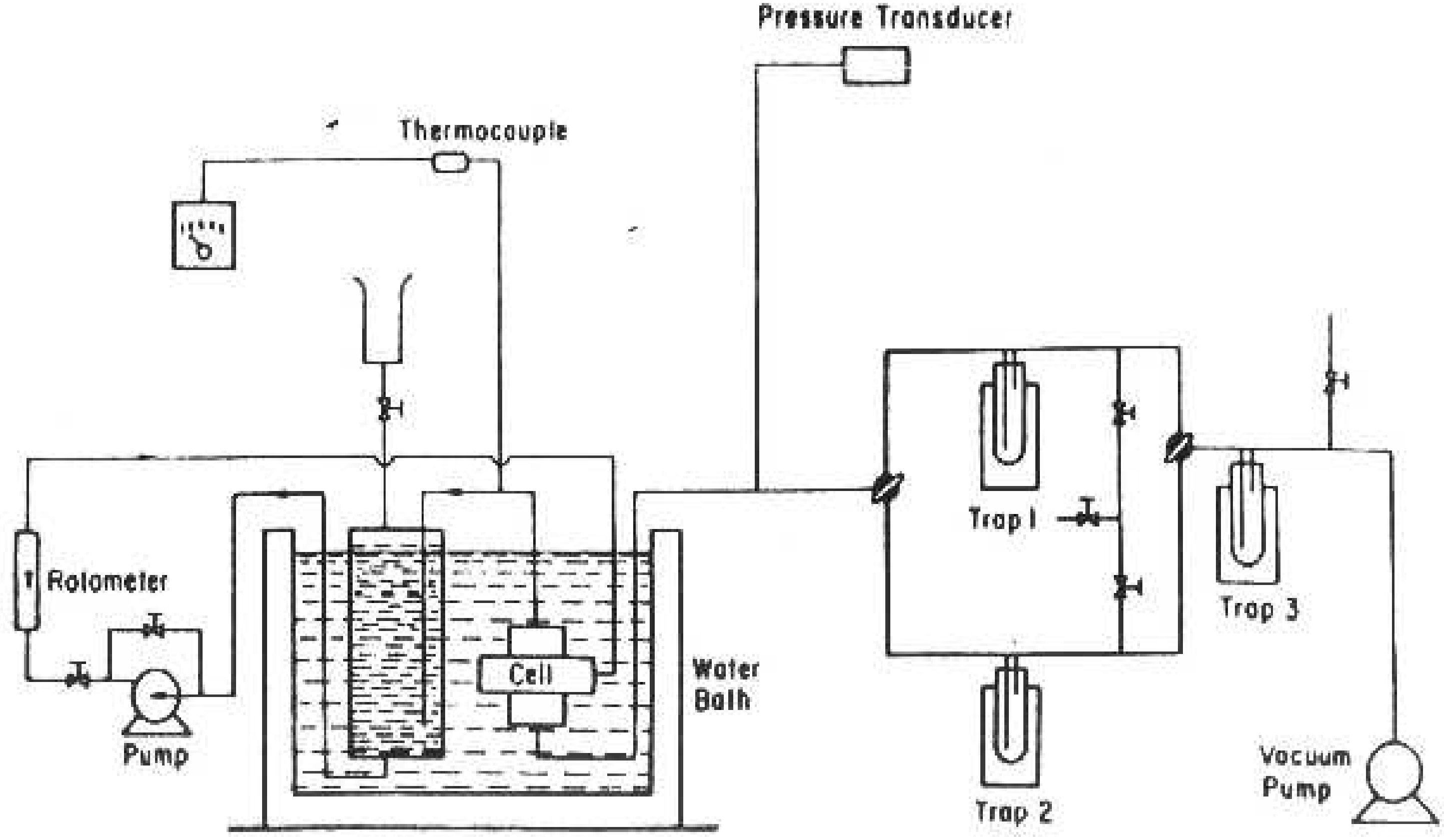

**Figure 3.3** Schematics of pervaporation set-up

permeation run. The third trap was connected in series to the previous two as a safety trap in order to prevent the permeate escape to the vacuum pump.

## 3.3 Experimental Procedure and Analysis Techniques

### 3.3.1 Experimental Procedure for Isoteniscope Method

Before starting the experiment isoteniscope is filled out and washed with ethanol and dried in a 50-60$^0$C oven for cleaning purpose. For the leak test, isoteniscope is connected to the condenser and vacuum is applied, if the level in U-tube manometer does not change significantly (1mm/20 min is acceptable) the test is completed, the system is opened up to the atmosphere slowly by means of the three-way valve. Then isoteniscope is removed from the condenser and filled with the sample liquid up to two thirds. Afterwards, cooling liquid is connected to the condenser and cooling is started. After connecting the isoteniscope to the condenser vacuum is applied for about 2-3 minutes then system is opened to atmosphere, by this way reservoir would be filled by the liquid. The same procedure is repeated until the level in the reservoir becomes just above the level in the main part. Atmospheric boiling point is to be measured at the beginning, heater and the stirrer are started and temperature is raised until liquid boils. The measured temperature at this point is recorded and boiling is continued for about 15 minutes in order to boil off the impurities present. Then, heater is turned off and cooling coil is placed inside the water-bath. The increase in the liquid level on the reservoir line is carefully observed, and when the same liquid levels are reached in both arms of the isoteniscope temperature is recorded. This would be the boiling point of the substance at atmospheric pressure. Afterwards, temperature is decreased a few more degrees and pressure is lowered by means of vacuum pump for about 5cmHg, then heater is turned on until the first bubble is observed. At this point, temperature is recorded and cooling coil is placed, after some time with cooling temperature drops and when liquid levels are equalized temperature is recorded at the level point. The average of these temperatures would give the boiling point of the substance at that pressure. The same procedure is repeated for each pressure, and complete vapor pressure curve would be obtained between the pressures studied.

The accuracy of the pressure and temperature readings was 1 mmHg and $0.5^0$C, respectively. The accuracy also depends on how well the water bath is mixed, which was checked by measuring the temperatures at different points of the bath. In all of the experiments stirring rate was high enough to ensure constant temperature inside the bath.

### 3.3.2 Experimental Procedure For The Operation of Gillespie Still

Before the experiment, system is checked for the leaks then both the vapor and liquid chambers are filled out with the binary solution prepared. Afterwards, vacuum is applied to the system until the desired pressure, and then heater is turned on. The heating and cooling rates are important in terms of the success of the equilibrium. The vapor, boiling from the liquid chamber should carry some liquid with it through the Cottrell tube and then completely condense into the vapor chamber. If no liquid comes to the Cottrell tube it means overheating, and if the bubbles occur in the vapor chamber it means the cooling is not sufficient. Moreover, the heating chamber and the Cottrell pump should be well insulated for a successful operation. The temperature should be recorded for about 10 minutes interval. If the temperature becomes constant for about 30-40 minutes the equilibrium is reached. The heater and cooler are turned off; the samples in the liquid and vapor chambers are analyzed.

### 3.3.3 Experimental Procedure for Pervaporation

Before the pervaporation experiments, the membranes are conditioned for two days by immersing them into the solution that has the same composition with the feed solution. Once they are wet, the membranes are always kept in these solutions; otherwise they may dry and loose their properties. The membranes are purchased in the form of 20*20cm flat sheets, to fit into the cell they are cut circularly to a diameter of 9.8 cm. Three filter papers are used as support. The placement in the cell is as follows: the perforated plate at the bottom, then the filter papers, then the membrane and finally two gaskets on the top. The upper part of the cell is placed on the gaskets and the cell is mounted and tightened by the help of three screws. Before the continuous mode of operation, the system is evacuated and tested for leaks. After vacuum check is complete, the system can be switched to the continuous mode.

The feed solution prepared in weight percents is put on the tank, and then the liquid pump, with a flow rate of 1 L/min, which is high enough to prevent concentration polarization (Okumuş, E., *et al.*, 1994), is turned on. The water bath, filled with water, is switched on; temperature controller is set from the panel of the bath. The vacuum pump is started and the pressure is kept constant at 4.5 mmHg. The collecting trap is weighed and recorded together with the starting time, and then put on to the equipment. This is the primary step whenever the traps are changed. After a time period determined based on the permeation rate, the next parallel trap is connected to the system, the second line is switched, and time is recorded. The second trap should immediately put into the dewar flask containing liquid nitrogen, the trap having the sample connected to the parallel line, which is not working, is removed after the frozen sample is converted into liquid. The collected permeate is filled in a 1 ml plastic sample tube leaving no empty spaces for the vapor phase to avoid possible evaporation and vapor liquid equilibrium. It is kept in the refrigerator until the analysis time. The flux is calculated by using the weight difference between the recorded empty and the sample filled trap weights and the time period. This procedure is repeated until the preceding flux values are almost the same, that is, until the steady state is achieved.

## 3.4 Analysis

The analysis of pervaporation permeate was carried out by using an Abbe type refractometer with Grant L60 water circulator. A calibration curve of refractive index versus percent composition was first prepared by accurately weighing out mixtures of the liquids for each binary solution. The calibration plots for ethanol-ethyl lactate, and ethyl lactate-water mixtures, showing weight percent ethyl lactate composition versus refractive index at $20^0$C, are shown in Appendix A. Approximate intervals of 3wt% were used for calibration, and 40-50 points were taken. All of the refractometer analyses were carried out at constant temperature of $20^0$C.

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Phase Diagrams

### 4.1.1 Vapor Pressure Curve for Reference Compound: Benzene

In order to check experimental set-up and the precision of the isoteniscope method vapor pressure curve of a reference component, which is selected as benzene, was measured. Benzene vapor pressure is calculated by using Antoine constants, which are given in Table 4.1 (Perry, R.H. and Green, D.W., 1998).

**Table 4.1:** Antoine equation constants of benzene

| *Name* | *A* | *B* | *C* |
|---|---|---|---|
| Benzene | 15.9008 | 2788.51 | -52.36 |

$\ln(P) = A - (B / (T + C))$, P (=mmHg), T (=K)

In figure 4.1 vapor pressure data is shown, together with literature data. In figure 4.2, benzene vapor pressure data is presented in lnP versus 1/T form. The calculated and experimentally found data points are, within the 99.5% confidence limits, so that experimental set-up and procedure is proved to be reliable.

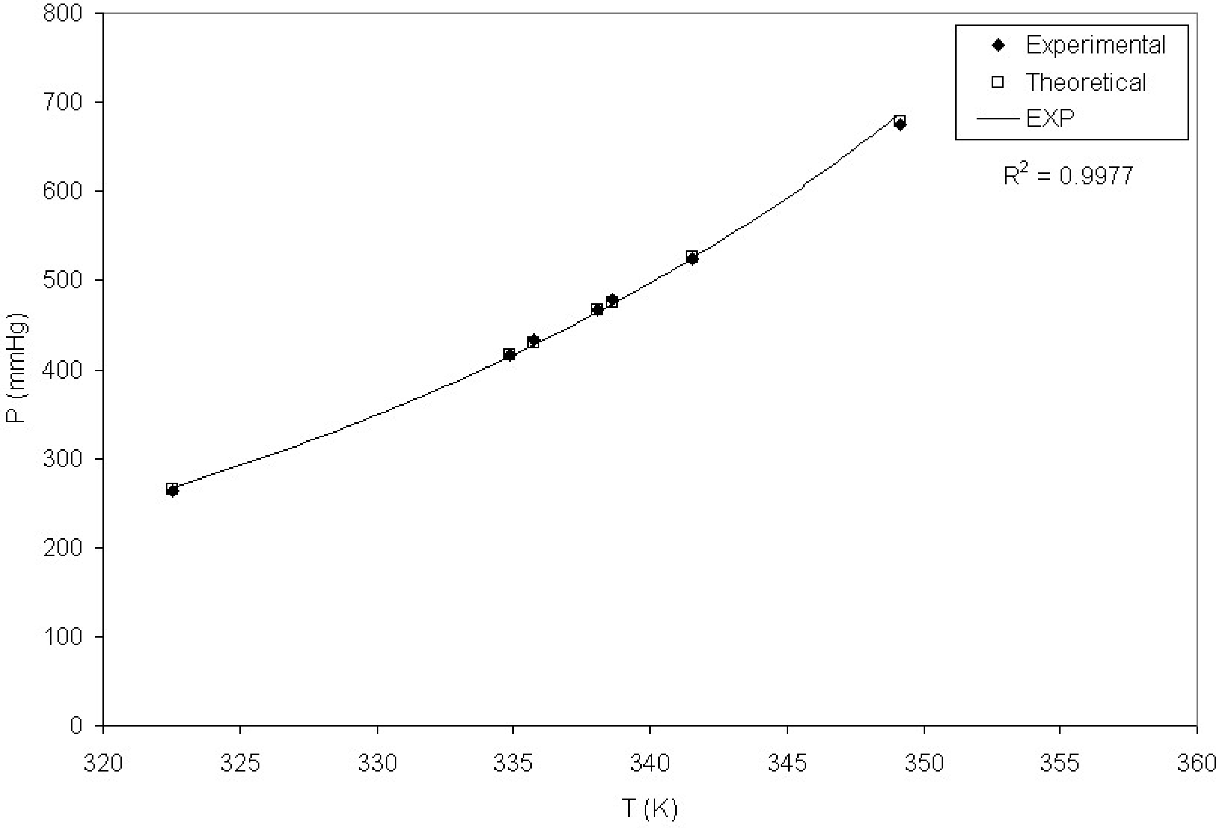

**Figure 4.1** Vapor pressure of benzene

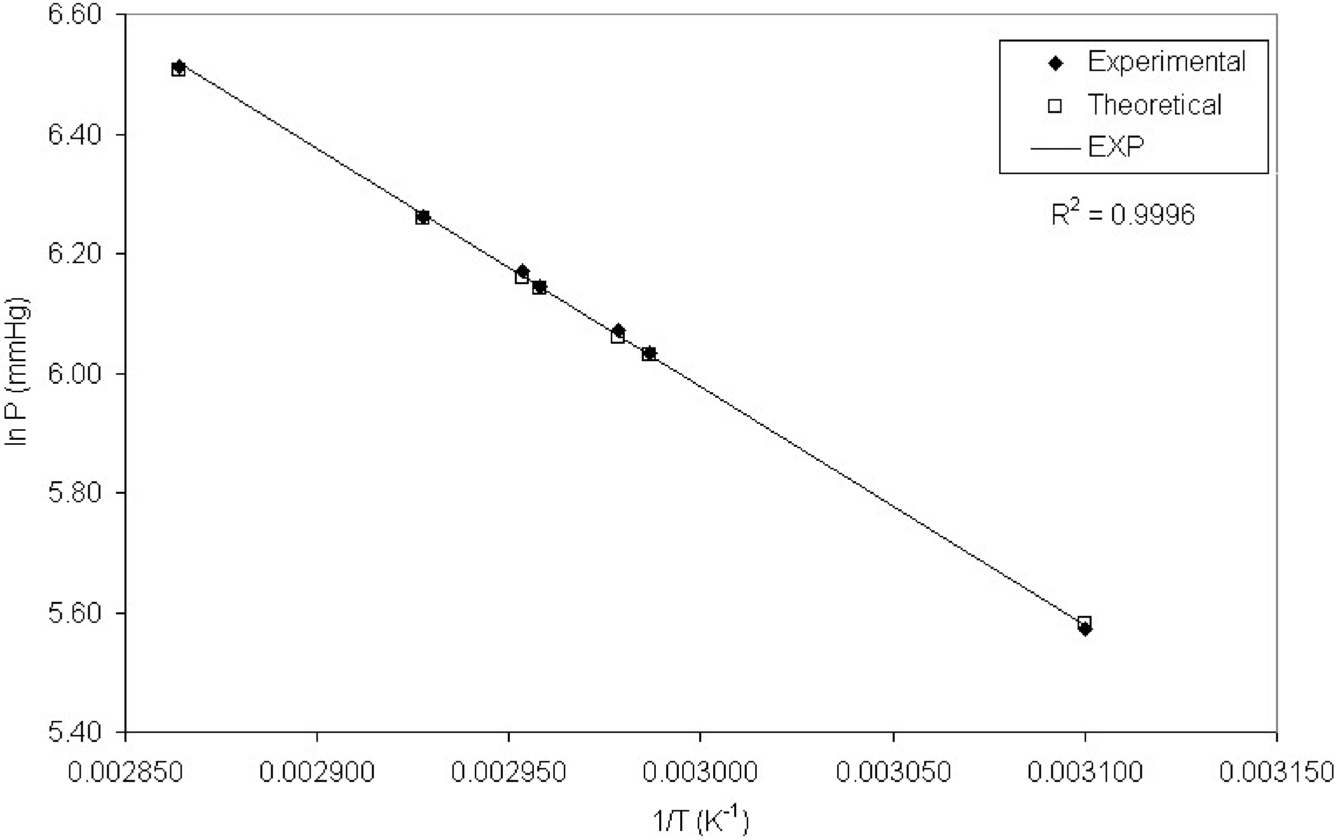

**Figure 4.2** Vapor pressure of benzene (lnP versus 1/T form)

### 4.1.2 Vapor Pressure Curve for Ethyl lactate

Vapor pressure curve of ethyl lactate is found between pressures, 12-74 mm-Hg and temperatures between 54-86$^0$C. Ethyl lactate vapor pressure curve is shown in Figure 4.3. For ethyl lactate, increase in temperature with pressure is very sharp, for example 60-mmHg-pressure change results in 30$^0$C increase in boiling point temperature. This result suggests a very high heat of vaporization value. The relationship between saturation temperature and pressure is exponential; but the same curve can not be extrapolated to atmospheric pressures, since there will be a shift in vapor pressure curves at higher pressures, as could be seen in the very beginning data points.

In figure 4.4 the same curve is plotted in lnP vs. 1/T form. Between 330K-366K a linear relationship between lnP and 1/T was found as suggested by Clasius-Clapeyron equation, with the correlation coefficient of 0.9876. The vapor pressure data is the fitted to Antoine equation to get the Antoine constants for ethyl lactate. It should be noted that these constants are applicable between temperature ranges of 54-86$^0$C and this is the first time they are reported in the literature (Table 4.2). Ethyl lactate heat of vaporization was calculated by the use of Clasius-Clapeyron equation, as 51.77 kJ/mol between 330K-366K. Ethyl lactate heat of vaporization was quite high as reported in Table 4.3, in comparison with propionic acid, ethyl ester. Due to the lactic acid origin, ethyl lactate has a hydroxyl group in its chemical structure, which accounts for its high boiling point and heat of vaporization value compared to ethyl propionate. The effect is apparent when the heat of vaporization values are compared with methyl acetate and its corresponding hydroxyl ester of acetic acid in Table 4.3. Based on this comparison criterion the results are in agreement with the literature.

**Table 4.2:** Antoine equation constants of ethyl lactate (Propionic acid, 2-hydroxy-, ethyl ester) compared to propionic acid, ethyl ester

| *Name* | *A* | *B* | *C* | *Reference* | *Applicable Temperature range* |
|---|---|---|---|---|---|
| Propionic acid, ethyl ester | 4.1453 | 1274.735 | -64.218 | Polak, J. and Mertl, L. (1965) | 307-371K |
| Propionic acid, 2-hydroxy-, ethyl ester (Ethyl lactate) | 5.5978 | 2113.610 | -39.695 | This study | 330-366 K |

**Table 4.3:** Heat of vaporization of ethyl lactate compared to other esters

| *Name* | *Chemical formula* | *Boiling Point ($^0C$)* | *Heat of Vaporization (kj/mol)* | *Reference* |
|---|---|---|---|---|
| Acetic acid, methyl ester | $C_3H_6O_2$ | 57 | 30.32 | Majer, V. and Svoboda, V. (1985) |
| Acetic acid, hydroxy-, methyl ester | $C_3H_6O_3$ | 151 | 52.5 | Steele, W.V. *et al.* (1996) |
| Propionic acid, ethyl ester | $C_5H_{10}O_2$ | 99 | 33.88 | Majer, V. and Svoboda, V. (1985) |
| Propionic acid, 2-hydroxy-, ethyl ester (Ethyl lactate) | $C_5H_{10}O_3$ | 154 | 51.77 | This study |

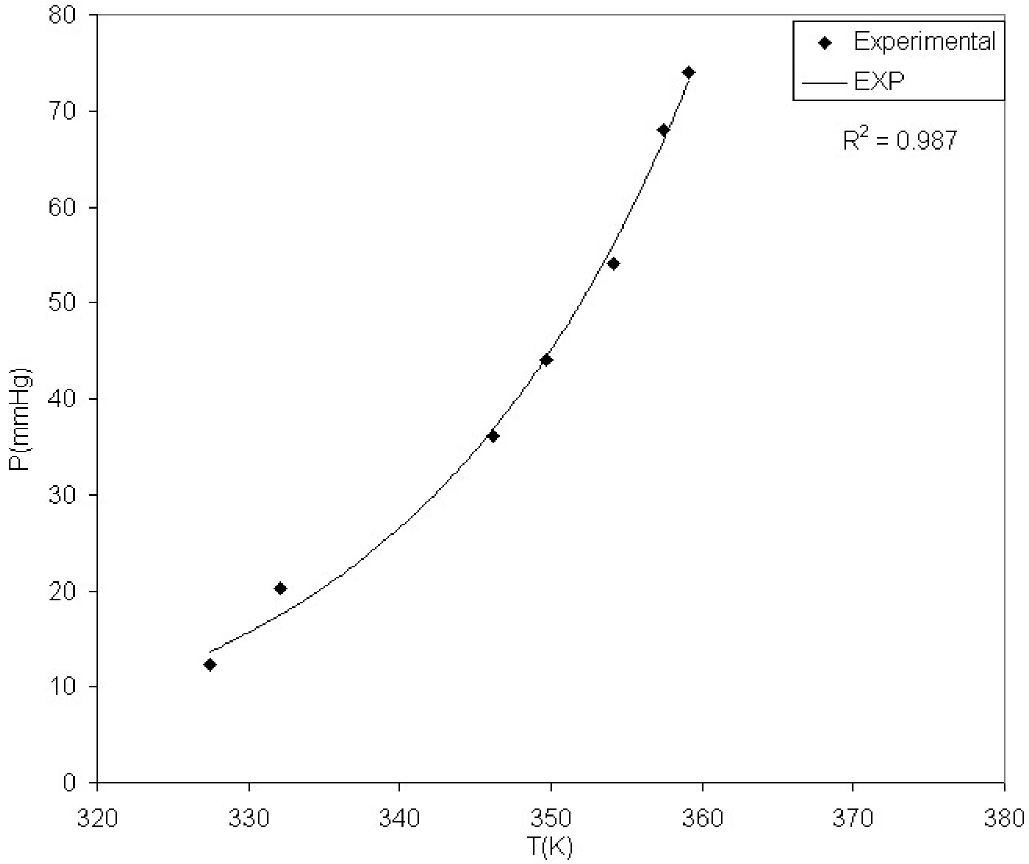

**Figure 4.3** Vapor pressure of ethyl lactate

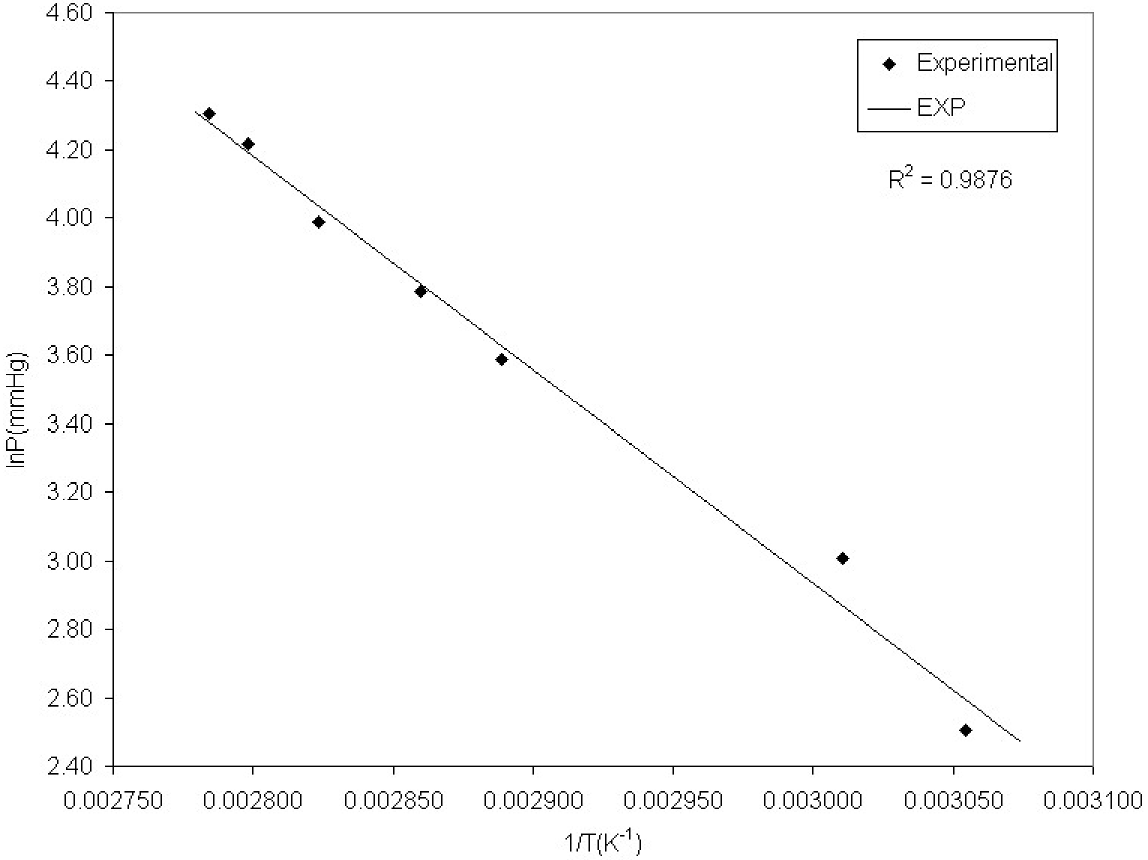

**Figure 4.4** Vapor pressure of ethyl lactate (lnP versus 1/T form)

### 4.1.3 Ethanol-Water VLE

Ethanol-water VLE curve was determined so as to check experimental set-up consistency. The literature data points were calculated, at the atmospheric pressure at this altitude (=680mmHg) according to the equations (4.1-4.3). Van-Laar activity coefficient model, represented by Eqns. 4.1 and 4.2 was used to calculate activity coefficients. In these equations $x_1$ and $x_2$ are mole fractions of species 1 and 2; $A_{12}$ and $A_{21}$ are Van-Laar activity coefficients as reported in the literature are tabulated in Table 4.4. Eqn. 4.3 is vapor-liquid phase equilibrium equation, which apply for the case of low-pressure, and ideal mixture. In eqn. 4.3, $y_i$ denotes vapor phase composition of species *i*, P is total pressure, $\gamma_i$ is activity coefficient of species *i*, $x_i$ is liquid mol fraction of species *i*, and $P_i^0$ is saturation vapor pressure of species *i*. In the evaluation of saturation pressures of ethanol and water Antoine constants, which are shown in Table 4.5, were used. The experimentally determined data points found in this study are compared with these points in Table 4.6. The difference between the calculated and experimentally determined data points was within the 95% confidence limits. Therefore, the resulted consistency between these points proved the accuracy of Gillespie set-up and procedure.

$$\ln\gamma_1 = \frac{A_{12}}{\left[1+\frac{A_{12}x_1}{A_{21}x_2}\right]^2} \text{ ..............................................................Eqn. 4.1}$$

$$\ln\gamma_2 = \frac{A_{21}}{\left[1+\frac{A_{21}x_2}{A_{12}x_1}\right]^2} \qquad \text{Eqn. 4.2}$$

$$y_i P = \gamma_i x_i P_i^0 \qquad \text{Eqn. 4.3}$$

**Table 4.4:** Van Laar activity coefficient constants for ethanol-water mixture (Perry, R.H. and Green, D.W., 1998)

| | $A_{12}$ | $A_{21}$ |
|---|---|---|
| Ethanol-Water | 1.54 | 0.97 |

**Table 4.5:** Antoine equation constants for ethanol and water (Perry, R.H. and Green, D.W., 1998)

| Component | A | B | C |
|---|---|---|---|
| Ethanol | 5.24677 | 1598.673 | -46.424 |
| Water | 5.08354 | 1663.125 | -45.622 |

*lnP (bar)=A-B/(C+T(K))*

**Table 4.6:** Literature and experimental vapor phase compositions for ethanol-water mixture

| $x_1$ (Wt%) | $y_1$ (exp) (wt%) | $y_1$ (Van Laar) (Wt%) | $T_{boil}$ (°C) |
|---|---|---|---|
| 0.24 | 0.53 | 0.51 | 81.4 |
| 0.36 | 0.58 | 0.60 | 78.6 |
| 0.58 | 0.68 | 0.69 | 76.6 |

### 4.1.4 Ethyl lactate-Ethanol and Ethyl lactate-Water VLE

Phase equilibrium data for ethyl lactate-ethanol mixtures at both atmospheric (680mm Hg) and 80mmHg pressure are reported in Figure 4.5. In determination of compositions, uncertainty of the refractometer analysis is not more than ±2.0%. Moreover, evaluating the data points several times with reproducibility experiments minimized experimental errors, the relative deviations were within the 98% confidence limits.

Temperature-xy data at 680mm Hg and 80 mm Hg are shown in figures 4.6 and 4.7. The corresponding bubble and dew points for the mixture are $90^0$C -$30^0$C at 80-mmHg and $155^0$C-$80^0$C at 680-mmHg pressures. When ethyl lactate-ethanol equilibrium curve is analyzed, a slight change in vapor composition was observed between pressures 680mmHg and 80mmHg. As pressure decreases, vapor composition decreases about 5% between 30-90 wt% ethanol, even higher about 15% decrease is observed at 20-wt% ethanol. The same equilibrium curve trend as in high pressure is followed by the lower pressure equilibrium curve. Although the result could change from one system to another, in the literature it was reported that pressure changes that do not exceed ±500 mmHg are too small to produce large shifts on the vapor liquid equilibrium diagrams (Majer V., and Svoboda, V., 1985), which is probably the case for ethyl lactate-ethanol system.

In VLE curve, it is seen that the highest slope at the high concentrations of ethyl lactate gets steeper when ethanol concentration is increased and after the inflection point at about 50-wt%, the curve bends smoothly to the x-y line. If the tie-lines are drawn, the same trend can be observed in Temperature-xy curves, maximum driving force for separation exist between 20wt% to 80wt% ethanol. Furthermore, tie-lines gets shorter as pressure decreases, which means that driving force for the separation is lower at low pressure. At 80-mmHg pressure, low and high ethanol region vapor-liquid equilibrium selectivity is around 1.1, therefore the separation is most difficult in these ranges.

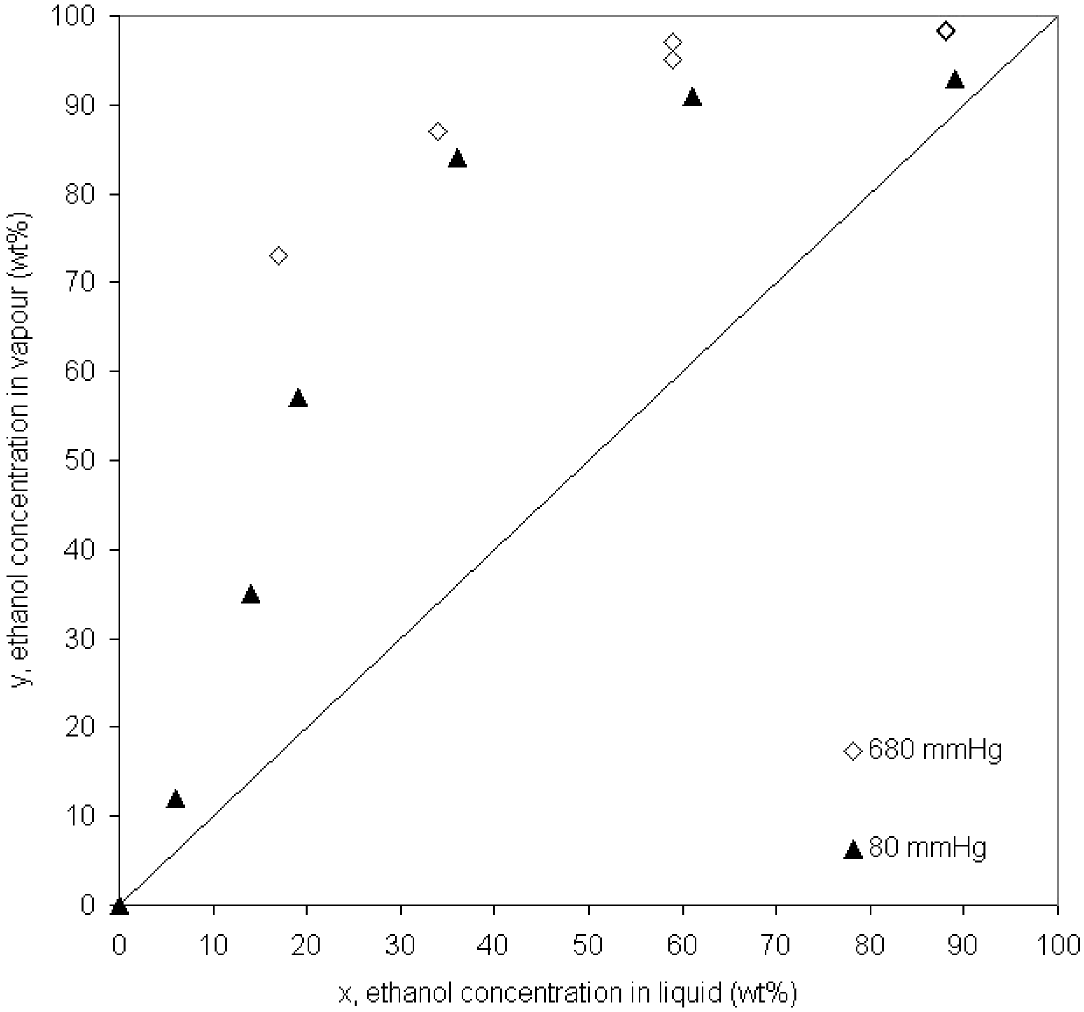

**Figure 4.5** x-y diagram of ethyl lactate-ethanol mixture at 680 and 80 mmHg

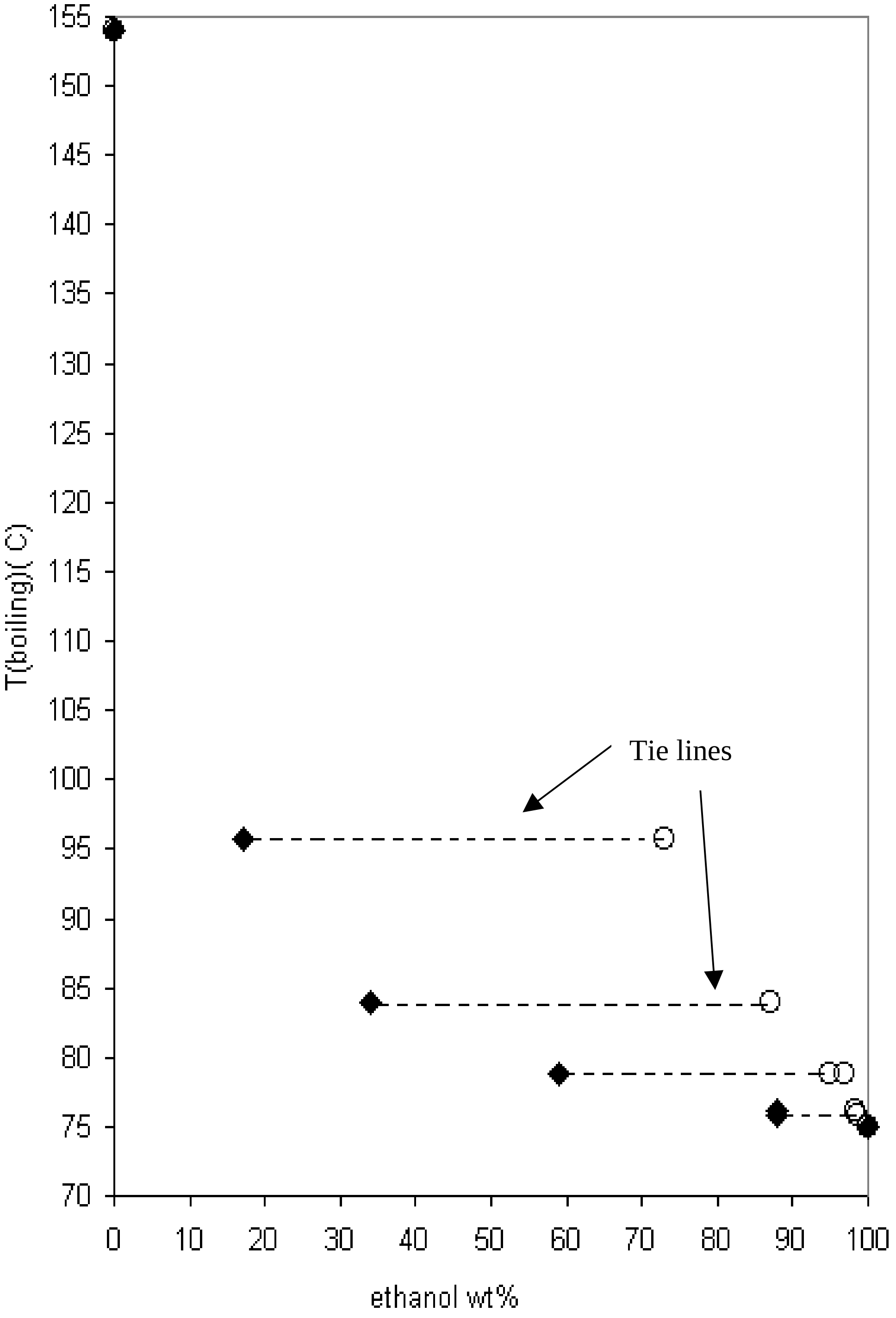

**Figure 4.6** Temperature-xy diagram for ethyl lactate-ethanol mixture at 680 mmHg

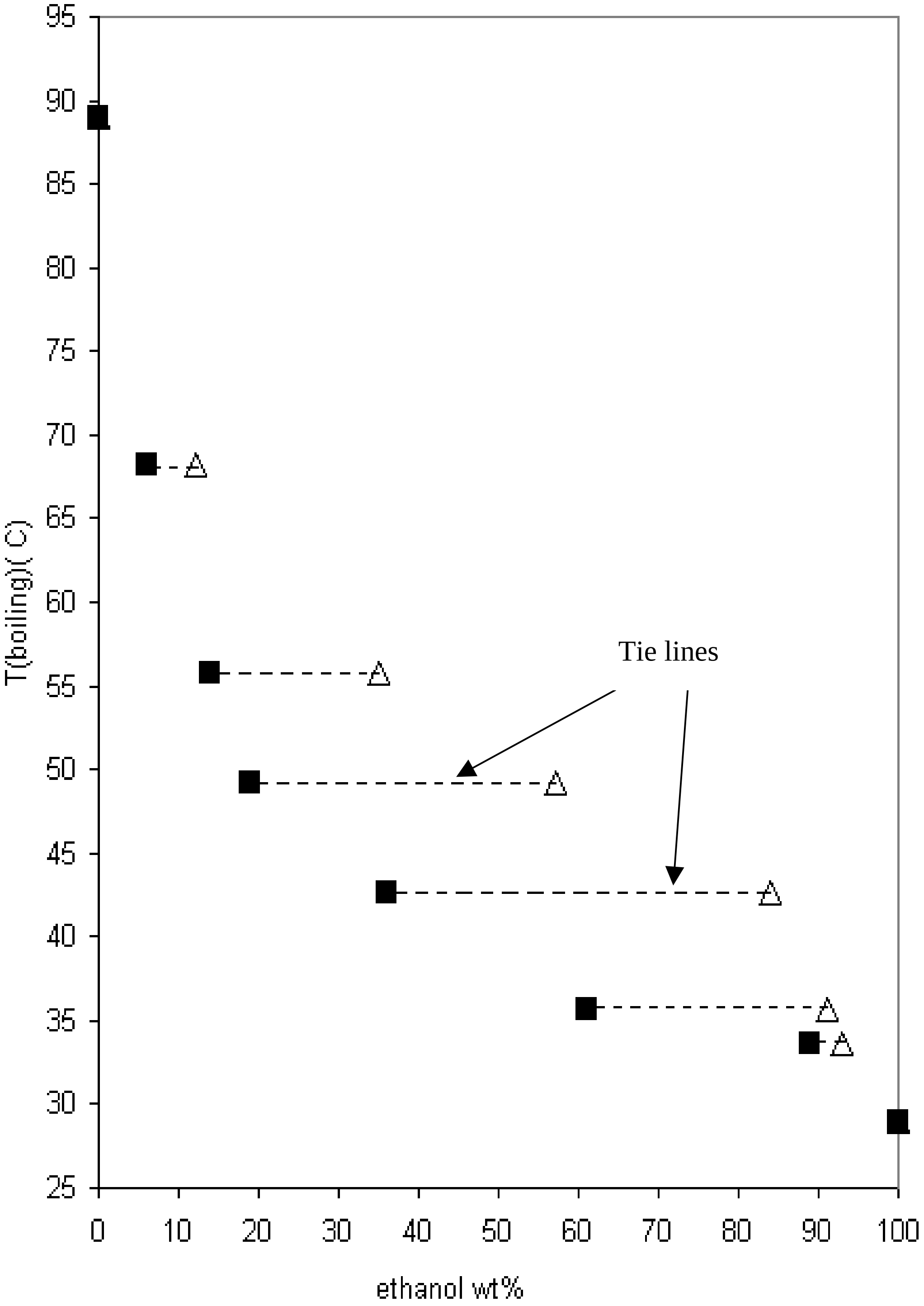

**Figure 4.7** Temperature-xy diagram for ethyl lactate-ethanol mixture at 80 mmHg

Furthermore, at 80 mmHg there is a nearly extreme point at T-xy curve, which could be a tangential azeotrope. This phenomenon is also called a tangent pinch (Doherty, M.F., and Knapp, J.F., 1993). Ethanol-ethyl lactate mixture exhibits a tangent pinch at the ethanol edge. Acetic acid-water and acetone-water systems are the common examples to tangentially azeotropic mixtures (Hilmen, E.K., 2000). The fact that the both liquid and vapor curves have inflection in T-xy curve is attributed to the high difference in the boiling point temperatures of ethanol and ethyl lactate and also to the dissimilarity of the components and their activity coefficients (Malesinski, W., 1965).

Being product pair of reaction system, ethyl lactate-water phase diagram was determined at 80mmHg pressure. Since this mixture is the product mixture of esterification reaction, the binaries are subject to the reverse esterification reaction, which may form lactic acid and ethanol impurities. The reverse reaction is an endothermic reaction and can be avoided only if temperature is lowered. In order to minimize the reverse reaction and the consecutive formation of lactic acid and ethanol impurities, the vapor liquid equilibrium of ethyl lactate and water binaries only measured at 80mmHg pressure where the corresponding bubble point of the binaries does not exceed $58^0$C. Under these conditions, the amounts of lactic acids in the binary samples were determined after each experiment by analysis. Free lactic acid amounts in the samples are shown in Table 4.7. The two factors affecting the formation of lactic acid were the residence time and the boiling point of the mixture. At 80 mmHg, the maximum reaction extend was as much as 2.3 wt% of lactic acid at $58^0$C in others it was much lower, which lead us to ignore the effect of reaction and presence of lactic acid on binary phase equilibrium curve. For ethyl lactate-water mixtures the uncertainty of the refractometer analysis, including the effect of the lactic acid, determined to be not more than ±3.0%.

**Table 4.7:** Free lactic acid amounts in liquid and vapor samples

| *(initial) ethyl lactate wt%* | *lactic acid wt% in liquid* | *lactic acid wt % in vapor* |
|---|---|---|
| 0.90 | 2.18 | 1.58 |
| 0.80 | 2.33 | 0.97 |
| 0.75 | 1.44 | 0.88 |
| 0.70 | 1.54 | 0.41 |

On the vapor-liquid equilibrium curve of ethyl lactate-water, shown in figure 4.8, a homogenous, minimum-boiling azeotrope was observed at 71wt% of water. It is well known that with the aliphatic alcohols and esters of medium volatility (examples are propyl, butyl, and amyl formats, ethyl, propyl, butyl, and amyl acetates, and the methyl and ethyl esters of propionic, butyric, and valeric acids), a variety of azeotropes are encountered on distillation (Malesinski, W., 1965). Binary azeotropes may be formed between alcohol and water, the alcohol and ester, and the ester and water (Othmer, K. and Kroschwitz, J.I., 1991). As Swietloslawski (Swietoslawski, W, 1963) pointed out that, the presence of specific polar groups, such as oxygen, nitrogen, etc. containing often results in the formation of azeotropes.

As it is seen from Temperature–xy curve in Figure 4.9, at the azeotropic composition the boiling point of the mixture is minimum. The formation of

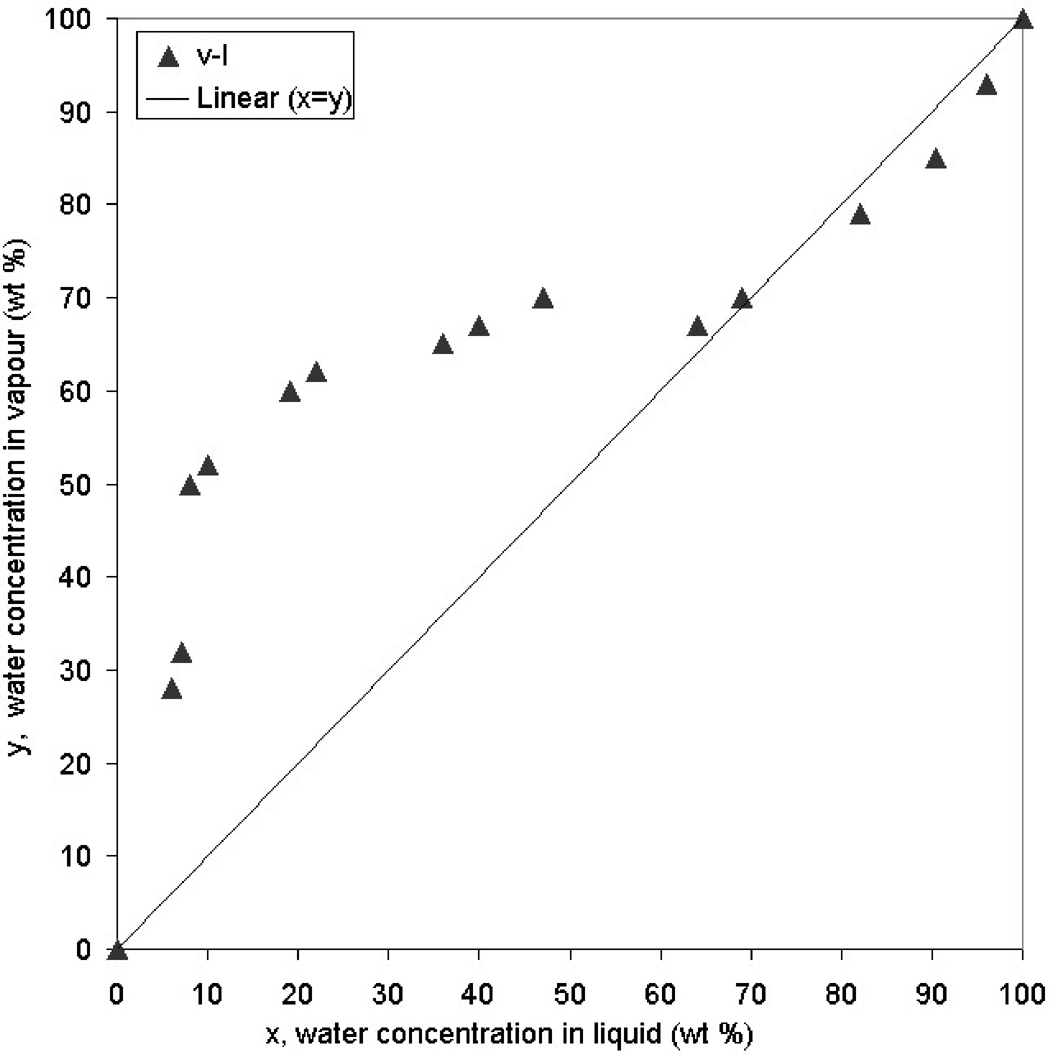

**Figure 4.8** x-y diagram of ethyl lactate-water mixture at 80 mmHg

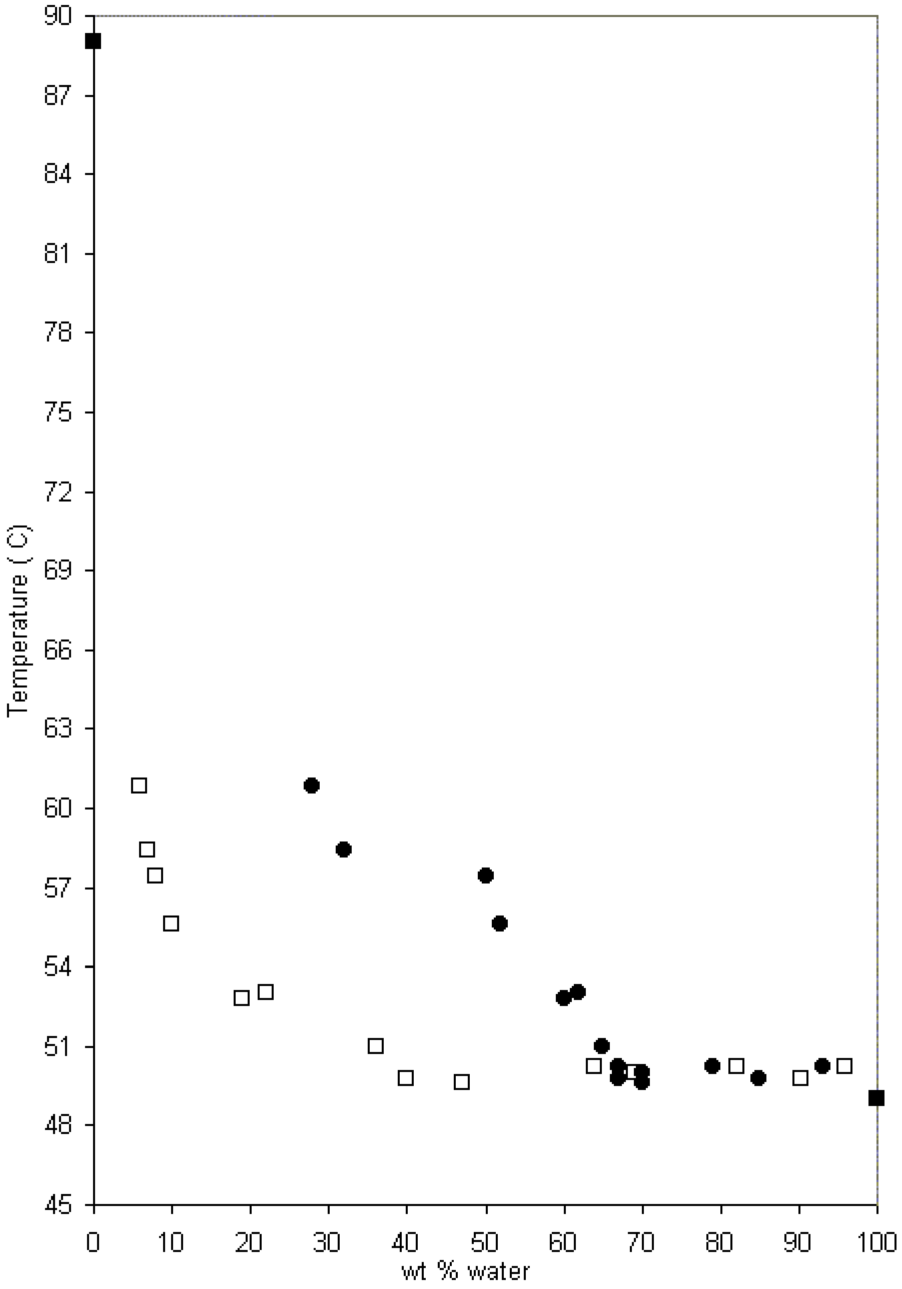

**Figure 4.9** Temperature-xy diagram for ethyl lactate-water mixture at 80 mmHg

minimum-boiling azeotrope shows that the components ethyl lactate and water ‘dislike’ each other, i.e. the attraction between identical molecules (A-A and B-B) is stronger than between different molecules (A-B). This behavior is known as positive deviation from Raoult’s law.

### 4.1.5 Comparison of VLE with Hydrophilic Membrane Performance

A hydrophilic membrane PERVAP©2201, produced by Sulzer, was used to separate ethyl lactate-water mixtures in the previous study of our group(Korkut, S., 2001, Korkut, S. *et al.*, submitted for publication). PERVAP©2201 is made of highly cross-linked polyvinylalcohol (PVA) and polyacrylonitrile (PAN) porous support (Jonquieres, A., *et al.*, 2002). Because of its high cross-linking degree, PERVAP©2201 is highly water selective, however its permeation rate is relatively small. The separation characteristics of PERVAP©2201 membrane for ethyl lactate-water mixture is compared, in terms of permeate and liquid compositions, with the VLE data in Figure 4.10. Pervaporation was carried out at 4.5 mm Hg downstream pressure and feed temperature of $30^0$C. When feed mixture or liquid composition versus permeate and saturated vapor composition data is plotted, membrane performance can be better understood.

In ethyl lactate-water/PERVAP©2201 system more volatile compound, water is selectively permeating component. Therefore, for this system VLE is said to be increasing the overall pervaporation selectivity, since low boiling water, whose saturation temperature is $29^0$C at 80mmHg, would also like to be more in the vapor phase than high boiling ethyl lactate, whose saturation temperature is $89^0$C at 80mmHg. In figure 4.10, permeate vapor composition at 4.5mmHg and $30^0$C temperature is compared to VLE at 80mmHg. Although for ethyl lactate-ethanol system saturation temperatures would be much lower at 4.5mmHg; the same vapor phase compositions at 80mmHg are used for comparison purposes, since it was shown for ethyl lactate-ethanol system that pressure effect on VLE selectivity is slight even for 600mmHg pressure difference.

It is seen that in 1-60 wt% feed water concentration range, permeate contains more water than the saturated vapor, i.e. with pervaporation water composition in saturated vapor is increased beyond thermodynamic limit. The very high water selectivity of membrane enables obtaining at least 90wt% pure water when feed water concentration is between 5-45 wt% water. On the other hand, permeate water concentration is observed to decrease after a maximum water concentration in permeate is observed, and then the permeate composition approaches to the azeotropic composition. This behavior is due to two phenomena, first the plasticizing effect of ethyl lactate and water on the membrane, and second an increase in VLE selectivity up to certain point and then a decrease with increasing water concentration. The former phenomenon, which is also known as swelling of membrane, is due to enlargement of transport channels by the permeating component. The latter, the effect of VLE, on the other hand is due to the selectivity definition of pervaporation, where total selectivity is the product of membrane selectivity and VLE selectivity as given in section 2.2.2.

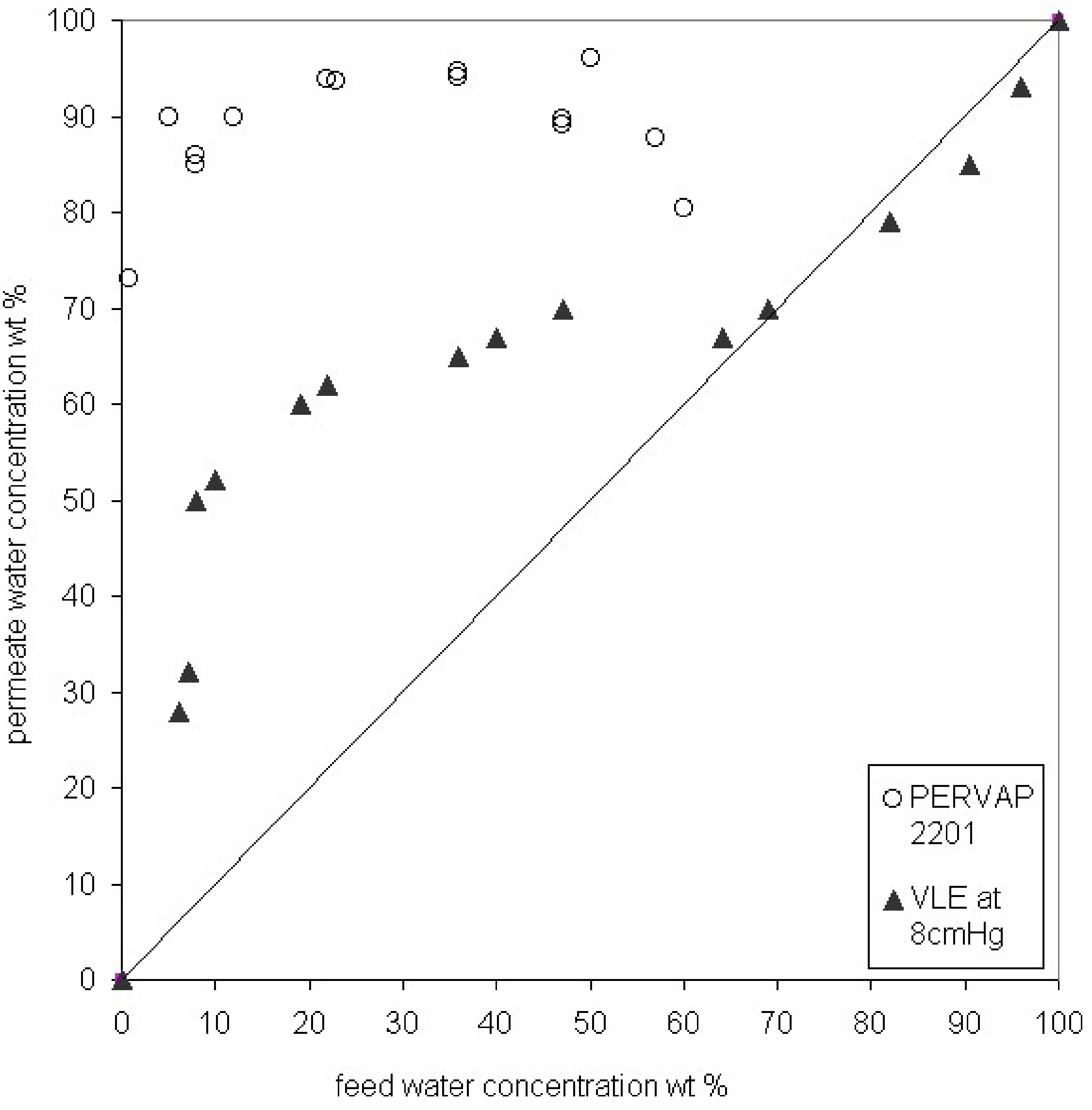

**Figure 4.10** Permeate concentration vs. feed concentration for water-ethyl lactate mixtures, as compared with the VLE data, for PERVAP©2201 membrane. Ref. Data is extracted from Korkut, S., 2001.

Finally, the effectiveness of pervaporation is more pronounced at low water concentration range; where almost one fold of increase in saturated vapor water concentration is obtained in permeate. In other words, membrane is most effective in the separation of ethanol-water mixture at low water concentration region, where the selectivity is around 300 (Korkut, S. *et al.*, submitted for publication). Therefore, removal of water from low water containing mixtures might be very advantageous with pervaporation unit(s) equipped with hydrophilic PERVAP©2201 membrane, where as high as 95wt% pure water could be obtained, and we might claim that comparison of pervaporation data with VLE clearly demonstrates hydrophilic pervaporation as a feasible option for by-product removal during ethyl lactate production.

## 4.2 Pervaporation Studies

### 4.2.1 Unsteady State Pervaporation Experiments

In all of the experiments performances of the pervaporation membranes are evaluated by using the steady state flux and selectivity values. However, steady state is preceded by a transient period during which flux and selectivity change with time. This transient period could change from several hours to days depending on the membrane material, initial state of membrane (dry or preswollen) and the experimental conditions. For each experiment, the data during transient period was taken at determined time intervals, which are selected such that amount of permeate collected was sufficient to be weighed and analyzed. Therefore, the longer time intervals between two data points were simply due to small membrane area used. An example of unsteady data in terms of flux and selectivity is shown at Table 4.8. In Table 4.8 unsteady state pervaporation data for a) hydrophilic membrane and b) hydrophobic membrane is given. It was observed that with hydrophobic membrane steady state is reached more quickly; due to high permeation rate of hydrophobic membrane compared to hydrophilic membrane. In other words, there is not a severe dependence of preconditioning to flux and selectivity for hydrophobic membranes, as also reported by Marin *et al.* (Marin, M., *et al.*, 1992); since there is a weaker interaction between components of the liquid feed mixture and the membrane.

During experiments it is tried to precondition each membrane under same conditions and time interval, since it is well known that, during preconditioning stage contact type between the liquid feed and the membrane that is under atmospheric pressure or under vacuum at the downstream side, affects the time required reaching steady state (Marin M., *et al.*, 1992). Furthermore, especially for hydrophilic membranes a long contact with the liquid without vacuum might give an undesirable extension of swelling inside the membrane. Marin *et al.* (Marin, M., *et al.*, 1992) reported about 50% decrease in both flux and selectivity when membrane is kept in liquid solution for 10 days.

Rautenbach and Hömmerich (Rautenbach, R., and Hömmerich, U., 1998) observed time-dependency for the permeate flux is more pronounced than for the permeate concentration, which was also observed in this study when unsteady data is analyzed. It is seen that for example, when flux decreases by 15%, corresponding relative increase in permeate is 3% for hydrophilic membrane. Therefore in all of the experiments the steady state points was evaluated by considering the change in fluxes between two consecutive data points, and in general permeate composition reached steady state before the fluxes.

**Table 4.8:** Unsteady state pervaporation data

a) Hydrophilic membrane

Membrane: PERVAP©2201 Temperature: 30$^0$C Downstream Pressure: 4.5mmHg
Concentration: 5%water-ethyl lactate

| Time (min) | Flux (g/m$^2$/min) | Water (wt.) in permeate | Water/Ethyl lactate Selectivity |
|---|---|---|---|
| 332 | 0.447 | 0.30 | 8 |
| 535 | 0.282 | 0.73 | 51 |
| 641 | 0.375 | 0.82 | 87 |
| 851 | 0.240 | 0.88 | 139 |
| 1083 | 0.233 | 0.91 | 192 |
| 1281 | 0.202 | 0.94 | 273 |
| 1483 | 0.201 | 0.94 | 298 |
| 1696 | 0.201 | 0.94 | 298 |

b) Hydrophobic membrane

Membrane: CMX-GF-010-D Temperature: 30$^0$C Downstream Pressure: 4.5mmHg
Concentration: 10% ethanol-ethyl lactate

| Time (min) | Flux (g/m$^2$/min) | Ethanol (wt.) in permeate | Ethanol/Ethyl lactate Selectivity |
|---|---|---|---|
| 115 | 11.47 | 0.49 | 9 |
| 160 | 11.97 | 0.46 | 8 |
| 205 | 11.87 | 0.46 | 8 |
| 250 | 12.19 | 0.46 | 8 |
| 295 | 11.74 | 0.48 | 8 |
| 346 | 11.95 | 0.47 | 8 |
| 388 | 11.22 | 0.48 | 8 |
| 439 | 11.81 | 0.46 | 8 |

### 4.2.2 Performance of Hydrophobic Membranes

In this study performances of commercial hydrophobic membranes, namely PERVAP©1060, produced by Sulzer, and CMX-GF-010-D, produced by CM-CELFA, were investigated in the separation of ethyl lactate-ethanol mixtures. Both membranes have selective skin layer made of Polydimethylsiloxane (PDMS), presumably with different membrane thickness and/or support layers. For, PERVAP©1060, the thickness of skin layer is approximately 8μm (Kujawski, W., 2000).

It is found that both membranes are selective to ethanol, as ethanol concentration in feed increase flux increases; correspondingly selectivity decreases as shown in Figure 4.11 and Table 4.9. Fluxes and selectivities of CMX-GF-010-D are given in Figure 4.11 and, Table 4.9 shows flux and selectivities for PERVAP©1060 membrane. The fact that both membranes are selective to more polar component, alcohol (ethanol) rather than assumedly less polar ester (ethyl lactate) could be explained by separation characteristics of hydrophobic membranes. In hydrophobic membranes, selectivity depends more on size and shape of the molecules, since the membrane interactions between the molecules are not as strong as those between hydrophilic membrane and water. Ethyl lactate is larger molecule than ethanol; and the existence of hydroxyl group in its structure might result in some molecular interactions. Therefore in addition to its large size, these interactions might hinder the passage of ethyl lactate molecules through the membrane. Moreover, ethyl lactate is much more polar than other esters and has higher hydrogen bonding capability, which probably makes the separation of alcohol-ester system more like a polar-polar system.

**Table 4.9:** Flux and selectivities for PERVAP1060 membrane compared to CMX-GF-010-D membrane in the separation of ethanol-ethyl lactate mixtures

| Feed (wt% ethanol) | **PERVAP©1060** | | **CMX-GF-010-D** | |
|---|---|---|---|---|
| | Flux (g/m$^2$/min) | $\alpha_{A/L}$ | Flux (g/m$^2$/min) | $\alpha_{A/L}$ |
| 5 | 5 | 10 | 7 | 17 |
| 50 | 15 | 5 | 28 | 7 |

Table 4.10 shows solubility parameters of ethyl lactate and some related compounds. In terms of pervaporation performance of membranes, a qualitative discussion could be made with the use of solubility parameter concept, which accounts for three type of interactions; permanent dipole, dispersion forces, and hydrogen bonding interactions. Accordingly, if a strong difference between solubility parameters of the components in the mixture exists, selectivity of the membrane would be high compared to the other system in which global solubility parameters ($\delta_t$) of the two components were close to each other (Roizard, D., *et al.*, 1999). For example, when solvent parameters of ethyl acetate and ethyl lactate are compared, as given in Table 4.10, ethyl lactate has both high polarity ($\delta_P$) and hydrogen bonding ($\delta_H$) value. Therefore, it could be estimated that separation of ethyl lactate-ethanol mixture, where $\delta_t$ values are 21.0 and 26.5 MPa$^{1/2}$, is more difficult than separation of ethyl

acetate-ethanol mixture, where $\delta_t$ values are 18.1 and 26.5 $MPa^{1/2}$, since both compounds in ethyl lactate-ethanol system may behave similarly.

**Table 4.10:** Solubility parameters of some compounds (extracted from Burton, A.F.M., 1983)

| | **Hansen Solubility Parameters ($MJ\ m^{-3})^{½}$** | | | | **Hildebrand Solubility Parameter ($MJm^{-3})^{1/2}$** |
|---|---|---|---|---|---|
| **Substance** | $\delta_P$ | $\delta_D$ | $\delta_H$ | $\delta_t$ | $\delta$ |
| Water | 27.3 | 12.2 | 47.8 | 47.8 | 48.0 |
| Ethanol | 8.8 | 15.8 | 19.4 | 26.5 | 26.2 |
| Ethyl lactate | 7.6 | 15.0 | 21.0 | 21.0 | 20.2 |
| Ethyl acetate | 5.3 | 15.8 | 18.1 | 18.1 | 18.2 |

CMX-GF-010-D membrane was tested in pervaporation of ethanol-ethyl lactate mixtures for the feed composition of ethanol between 1.0 and 50.0 wt%, at $30^0$C. It is observed that, as ethanol concentration in feed is increases flux increases in a logarithmic way, whereas in case of selectivity, when ethanol concentration in feed increases selectivity decreases in an exponential way as shown in Figure 4.11. Effect of feed concentration on flux and selectivity might be explained by solution-diffusion mechanism. As concentration of more permeating species in feed increases, transport channels gets larger by permeating species and transport of non-permeating species occur from these larger channels. In ethyl lactate-ethanol system, flux is quite high even for low concentration of ethanol in feed. High flux is

**Pressure:**
4.5 mmHg

**Temperature**:
$30^0C$

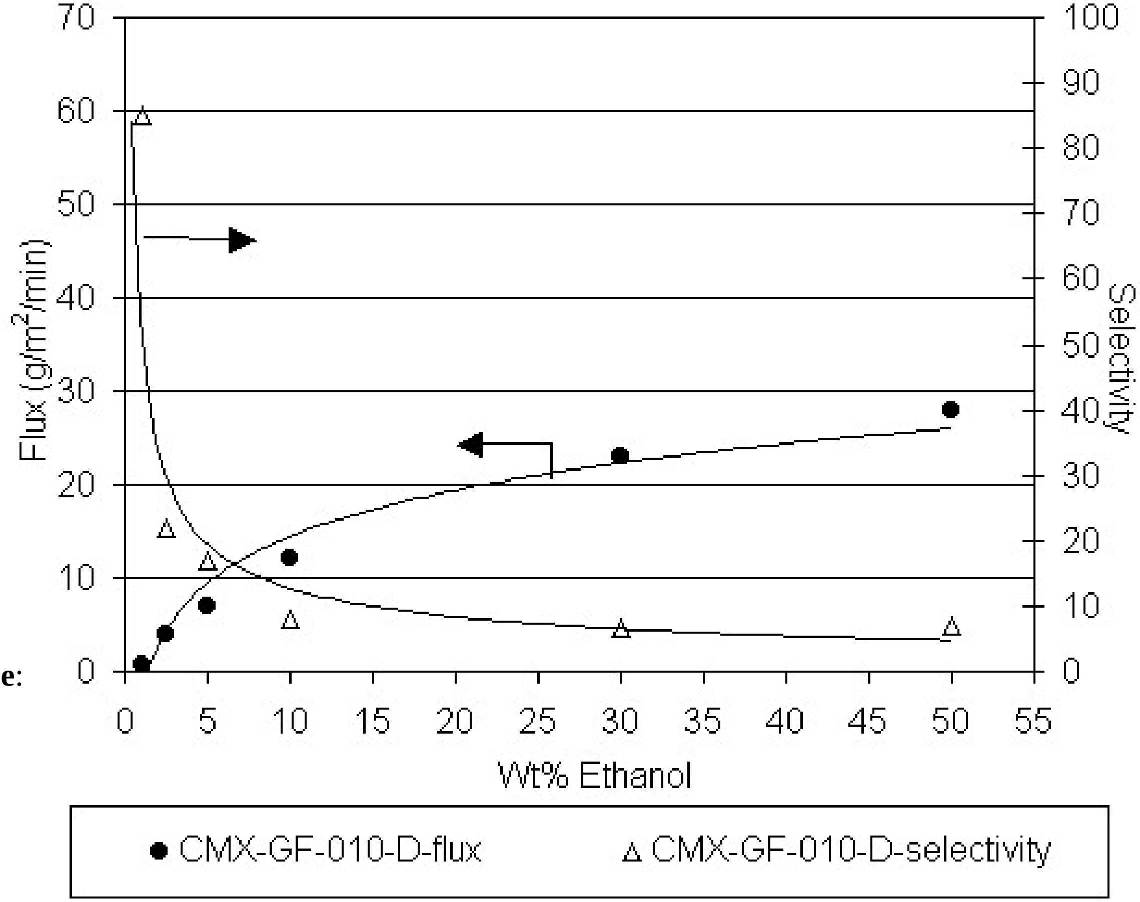

**Figure 4.11** Flux and selectivity versus ethanol feed concentration for CMX-GF-010-D for ethanol-ethyl lactate mixtures.

important in terms of the membrane area required for separation. On the other hand; although selectivity is quite high 85-15, between 1 and 10 wt% ethanol in feed, at higher ethanol concentrations selectivity is the same around 8. This might be due to the fact that swelling effect is more dominant than the other phenomena, such as selective sorption and diffusion at higher ethanol concentrations. This result shows that pervaporation is most effective at low ethanol concentration region. When feed contains less amount of preferentially permeating component (ethanol), CMX-GF-010-D membrane is more resistant to permeate the other compounds (ethyl lactate) in the mixture, which results in high selectivity when ethanol concentration of the mixture to be separated is less than 10-wt%. Moreover, at 1-50 wt% ethanol concentration range CMX-GF-010-D membrane exhibits very high flux although feed temperature is quite low ($30^0$C). As a result, in the separation of low ethanol containing mixtures the use of pervaporation with CMX-GF-010-D membrane is favorable.

In the literature there is limited information on alcohol/ester separation by hydrophobic membranes and ethyl lactate/ethanol system have not been studied before; therefore a direct comparison is not possible. Instead, separation performances of different membranes for alcohol/ester and alcohol/ether mixtures reported in the literature are compared (see Table 2.4). In the study of Pasternak *et al.* (Pasternak, M., *et al.*, 1989) dimethyl carbonate/methanol mixture was separated by PVA membranes prepared at different conditions. In this study, PVA membrane was selective to methanol, as expected, and even for high concentration of methanol high selectivity was obtained. The flux, on the other hand was very low when compared to our system. This is probably due to very thick selective layer of PVA membrane, through which swelling degree is much lower leading to high selectivity. In another study with the same mixture (Nickel, A., *et al.*, 1994) much higher fluxes and selectivity was obtained by using GFT No. 270 membrane. The flux for this system is comparable to our system; and in terms of selectivity higher selectivity is reported. High selectivity might be attributed to the functional groups on the hydrophilic membrane, and the high flux is due to the very thin membrane layer (0.5μm) obtained by plasma polymerization.

Other commercially avaliable hydrophobic membrane, PERVAP©1060 was also used in the separation of ethanol-ethyl lactate mixture for 5.0 and 50.0 wt% the ethanol composition in feed, at $30^0$C. Flux and selectivities at these concentrations are shown in Table 4.9 together with pervaporation data of CMX-GF-010-D membrane at the same feed concentrations. For PERVAP©1060 membrane, two pervaporation experiments, one with low ethanol and the other with high ethanol concentration were carried out. Since the general trend for flux and selectivity between these two points could be estimated by comparing pervaporation data of CMX-GF-010-D membrane, and the performance of CMX-GF-010-D membrane have been found to be superior to PERVAP©1060 membrane, two data points were found to be sufficient for characterization purposes.

In the studied concentration range and experimental conditions CMX-GF-010-D membrane has both higher flux and selectivity compared to PERVAP©1060 membrane, as shown in Table 4.9. This result might be interpreted from two perspectives as follows; first, selective skin layer of PERVAP©1060 might be such that ethyl lactate could be transported through the membrane easier than CMX-GF-010-D. Furthermore, since ethyl lactate diffusion coefficient through the membrane is smaller than that of ethanol, overall flux would be small since transport of ethyl lactate in membrane is the limiting step. Alternatively, low flux and selectivity could be due to the porous supporting sub layers of the membranes. The pores in PERVAP©1060 supporting sub layer could be smaller than that of CMX-GF-010-D membrane, so that support layer hinders both the transport of ethyl lactate and ethanol molecules. Similar to this discussion, Lipnizki *et al.* (Lipnizki, F., *et al.*, 2002) noted that support layer in hydrophobic membranes could affect both selectivity and flux and in some cases it even dominates and overturns the performance of the selective layer.

Figure 4.12 illustrates the permeate composition in comparison with the saturated vapor composition. This is again a case, in which more volatile component is also the preferentially permeating component through membrane. It is seen that at low ethanol concentration, ethanol concentration in permeate is higher than saturated vapor; however at middle range of concentrations, i.e. between 30-50 wt% ethanol, permeate concentration is almost same as saturated vapor concentration. Permeate is enriched more in ethanol with CMX-GF-010-D membrane, which results in high selectivity for CMX-GF-010-D as compared to PERVAP©1060 membrane. Permeate composition with vapor-liquid equilibrium (VLE) data was compared for the separation of dimethyl carbonate (DMC)/methanol in the study of Won *et al.* (Won, W., *et al.*, 2002), where cross-linked chitosan membranes, which are selective to methanol were used. It was found that permeate composition is higher in ethanol concentration than saturated vapor concentration over the entire feed range, which is expected for their system, due to several reasons. First, flux for DMC/Methanol system is much more lower than our system. The selectivity, in general could be increased by increasing thickness of separating layer or degree of cross-linking, which results in dramatic decrease in fluxes. Second, separation of ethanol-ethyl lactate is more difficult as mentioned before, due to small difference between solubility parameters. Finally, the types of membrane used are different, since it is reported that for hydrophobic membranes, permeate compositions are not much higher than those of saturated vapor compositions (Noble, R.D. and Stern, S.A., 1995). However, even at these conditions pervaporation is still advantageous than distillation process, since it is required to vaporize only the selectively removed compound in pervaporation.

It is important to note that at low ethanol concentration, where the use of pervaporation is most advantageous, permeate concentration is much higher than saturated vapor composition. Furthermore, pure ethanol could be obtained if multistage pervaporation units are used, where the cost of separation is expected to be lower than that of distillation. As another alternative, a hybrid separation system comprised of a pervaporation unit, to concentrate ethanol in low range, and a distillation column might be proposed in the separation of ethanol-ethyl lactate mixtures.

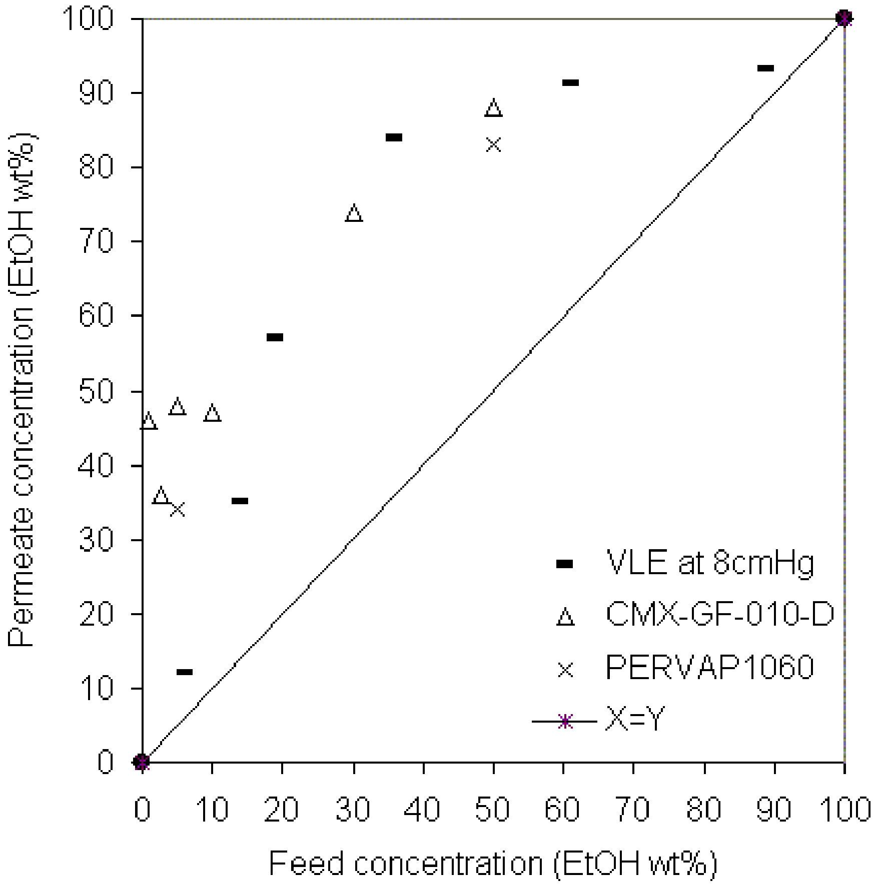

**Figure 4.12** Permeate concentration vs. feed concentration for ethanol-ethyl lactate mixtures, as compared with the VLE data.

### 4.2.3 Organoselective Membrane Performance

An organoselective selective PERVAP©2256 membrane, produced by Sulzer is used to extract ethanol from ethyl lactate-ethanol mixtures. PERVAP©2256 is an alcohol selective membrane comprising a chemically stable non-woven fabric as a substructure, a porous support of polyacrylonitrile and a separating layer of a proprietary polymer thickness about 2μm (Gonzalez, B.G. and Uribe, I.O., 2001).

With alcohol selective PERVAP©2256 membrane, flux and selectivity values were found to be 0.5-29.0 $g/m^2/min$ and 45-4 respectively for composition of ethanol between 5.0 and 50.0 wt%, at $30^0C$. Figure 4.13 shows flux and selectivity versus ethanol feed concentration for PERVAP©2256 membrane. Since PERVAP©2256 is selective to ethanol, as feed concentration increases permeation rate increases; correspondingly selectivity of alcohol to ethyl lactate decreases.

In literature there is not any reported concentration dependent pervaporation data on alcohol-ester separation with commercial PERVAP©2256 membrane, but the pervaporation performance for some alcohol/ether mixtures were reported. In the study of Ortiz *et al.* (Ortiz, I., *et al.*, 2002) ethanol-ethyl tert butyl ether (ETBE) mixtures were separated using PERVAP©2256 membrane. When compared to ethanol-ethyl lactate system ethanol-ETBE system results in much lower fluxes and higher selectivities. This is expected since; chemical structure dissimilarity between an alcohol and ether is much higher when compared to the dissimilarity between an alcohol and hydroxyl ester; and the swelling of membrane by hydroxyl ester is more pronounced than that of ether. In another study (Gonzalez, B.G., and Uribe, I.O., 2001) pervaporation performance of PERVAP©2256 for methanol-methyl tert butyl ether (MTBE) was investigated at low methanol concentration in feed. With methanol-MTBE mixtures, membrane showed high selectivity toward methanol and compared to ethanol-ethyl lactate system low fluxes were obtained. It is seen that ethanol-ethyl lactate/PERVAP©2256 system exhibit very high fluxes as compared to other alcohol-ether systems. This behavior might be attributed to the extensive swelling of membrane by ethyl lactate molecules, which are large in molecular size and shape. Moreover, there might be some interactions between the molecules in ethanol-ethyl lactate system, which may affect the polymer network in the membrane. These interpretations are also consistent with the previously mentioned arguments based on solubility parameter concept.

Figure 4.14 illustrates the permeation selectivity of all membranes, including PERVAP©2256 in comparison with the VLE data. It is seen that at low ethanol concentration permeate composition is richer in ethanol than that of saturated vapor composition; however at 30 and 50 wt% ethanol concentration in feed, permeate composition is lower in ethanol than that of saturated vapor. In fact, PERVAP©2256 selectivity is best among the other membranes at low ethanol region but is not as good as CMX-GF-010-D membrane at higher ethanol concentrations. This might be due to the extensive swelling of PERVAP©2256 membrane with ethanol; at 30 and 50 wt% ethanol concentration in feed swelling degree is most pronounced for PERVAP©2256 than that of the other membranes so that permeate contains more ethyl lactate when PERVAP©2256 membrane is used. When fluxes are compared, CMX-GF-010-D membrane has higher fluxes than PERVAP©2256 membrane for the studied feed concentration range. At low ethanol region, CMX-GF-010-D membrane has lower selectivity due to its higher flux, however at middle concentration range it has both high flux and selectivity as compared to PERVAP©2256 membrane. This result might be explained by the structure of the membranes, since PERVAP©2256 is designed for the extraction of alcohol from organic-alcohol mixtures; it is reported to be stable up to water concentration of 3 wt%. If the membrane instability is due to the hydrogen bonding capability of water, it is possible to realize that ethyl lactate molecules due to their $\delta_H$ value; might show the similar affect as water molecules show. Additionally, at high ethanol region there might be some interactions between ethyl lactate –ethanol and the membrane, which leads to PERVAP©2256 more selective to ethyl lactate than ethanol; therefore low flux might be due to the large molecular size of ethyl lactate.

Finally, it should be mentioned that for the separation of organic mixtures it is not yet very clear whether glassy or rubbery polymers are more appropriate and both types of polymers show some pervaporation selectivity. Therefore, in the future, development of new membranes having high selectivity and flux might make pervaporation to more easily compete with distillation or extraction for organic/organic separations.

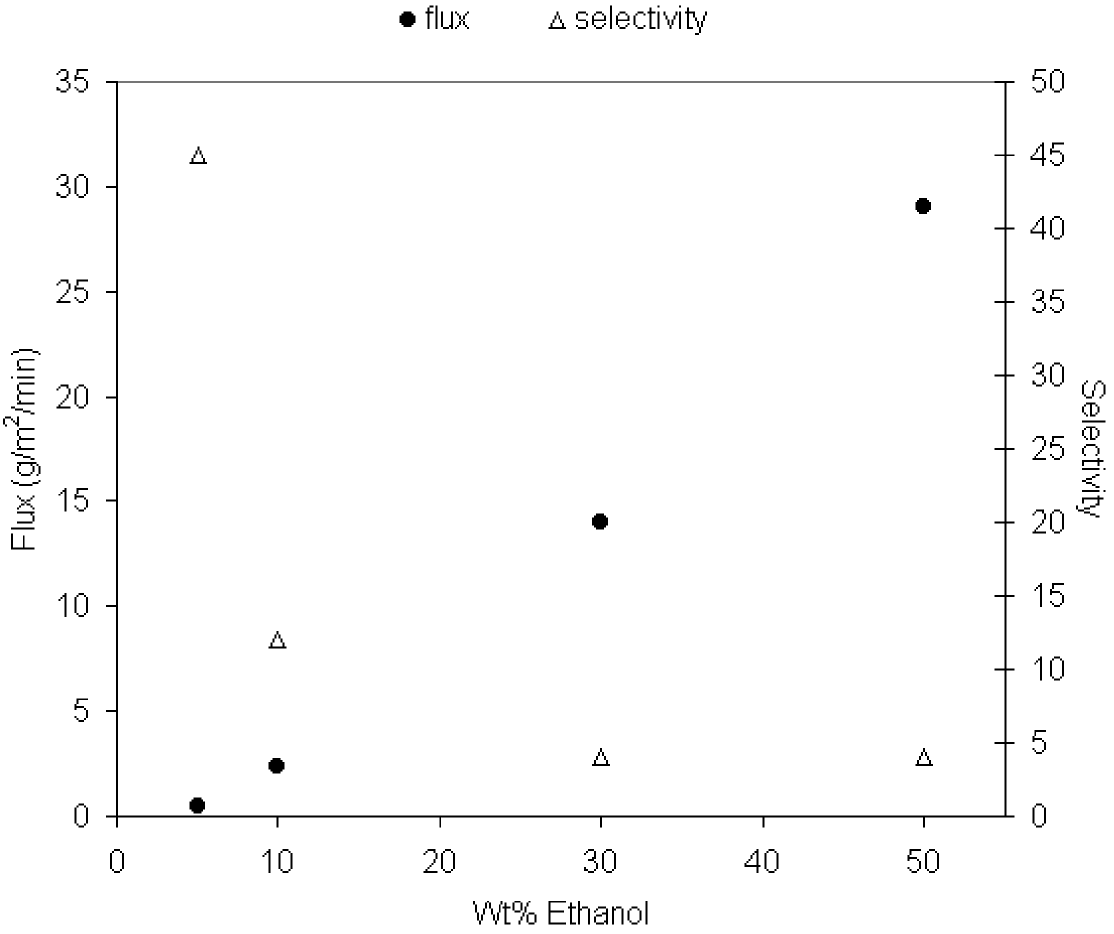

**Figure 4.13** Flux and selectivity versus ethanol feed concentration for PERVAP2256 for ethanol-ethyl lactate mixtures.

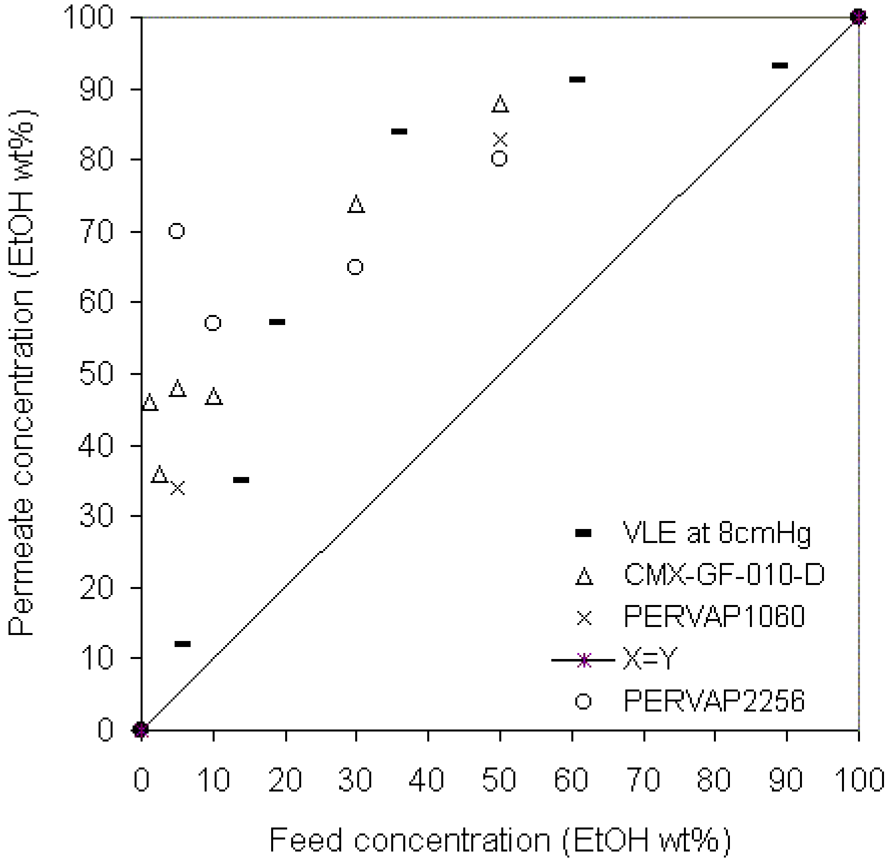

**Figure 4.14** Permeate concentration vs. feed concentration for ethanol-ethyl lactate mixtures, as compared with the VLE data, for all membranes studied.

### 4.2.4. Temperature Effect on Pervaporation

One very important operating parameter affecting pervaporation membrane performance is the temperature of feed mixture. Temperature affects the solubility and diffusivity of feed mixture components in polymeric membranes, hence pervaporation characteristics such as flux and selectivity changes accordingly with temperature. In general, permeation rates might increase several folds for each $10^0$C temperature increment. On the other hand, selectivity is not a strong function of temperature; in other words temperature affects the permeate composition very slightly. Furthermore, temperature might slightly increase or decrease selectivity, depending on the system or operating conditions. (Huang, R.Y.M. and Yeom, C.K., 1991). In most cases selectivity is reported to decrease with increasing temperature due to the increase of the thermal motion of the polymer chains, which creates larger transport channels for molecules to diffuse (Huang, R.Y.M., and Yeom, C.K., 1991).

In order to investigate temperature effect on pervaporation for the separation of ethanol-ethyl lactate mixtures; pervaporation experiments with hydrophobic CMX-GF-010-D membrane were conducted at $50^0$C. Figure 4.15 shows temperature effect on flux and selectivity of CMX-GF-010-D membrane. Table 4.11 shows flux and selectivities at $50^0$C. It is seen that $20^0$C temperature increase results in ten folds increase in flux when feed concentration is 1wt%, and about three folds when feed concentration is about 30wt%. However, on the contrary to tremendous increase in fluxes, selectivities decrease by a factor of one fourth from that of at lower temperature. In literature, selectivity decrease with increasing temperature is observed in the separation of alcohol-ester mixtures (Won, W. *et al.*, 2002), however it should be noted that both the membrane, feed type and feed composition affects the dependence of pervaporation parameters on temperature.

**Table 4.11** Flux and selectivities at $30^0$C and $50^0$C, for CMX-GF-010-D membrane in the separation of ethanol-ethyl lactate mixtures

| Feed (wt% ethanol) | **CMX-GF-010-D At 30 $^0$C** | | Feed (wt% ethanol) | **CMX-GF-010-D At 50 $^0$C** | |
|---|---|---|---|---|---|
| | Flux (g/m$^2$/min) | $\alpha_{A/L}$ | | Flux (g/m$^2$/min) | $\alpha_{A/L}$ |
| 1 | 0.6 | 85 | 1 | 6.5 | 45 |
| 30 | 23 | 7 | 23 | 60 | 5 |

Pervaporation results at $50^0$C show that structure of CMX-GF-010-D membrane is stable at this temperature so that further swelling does not occur, in fact for all of the membranes studied CMX-GF-010-D membrane was the most stable membrane, which is resistant to change of operating conditions. In terms of industrial viewpoint, this result is promising, since in industry generally low flux is a problem; therefore in the separation of ethyl lactate-ethanol mixtures with these membranes higher temperatures could be used to get high permeation rates, and using cascade pervaporation units may compensate the selectivity losses.

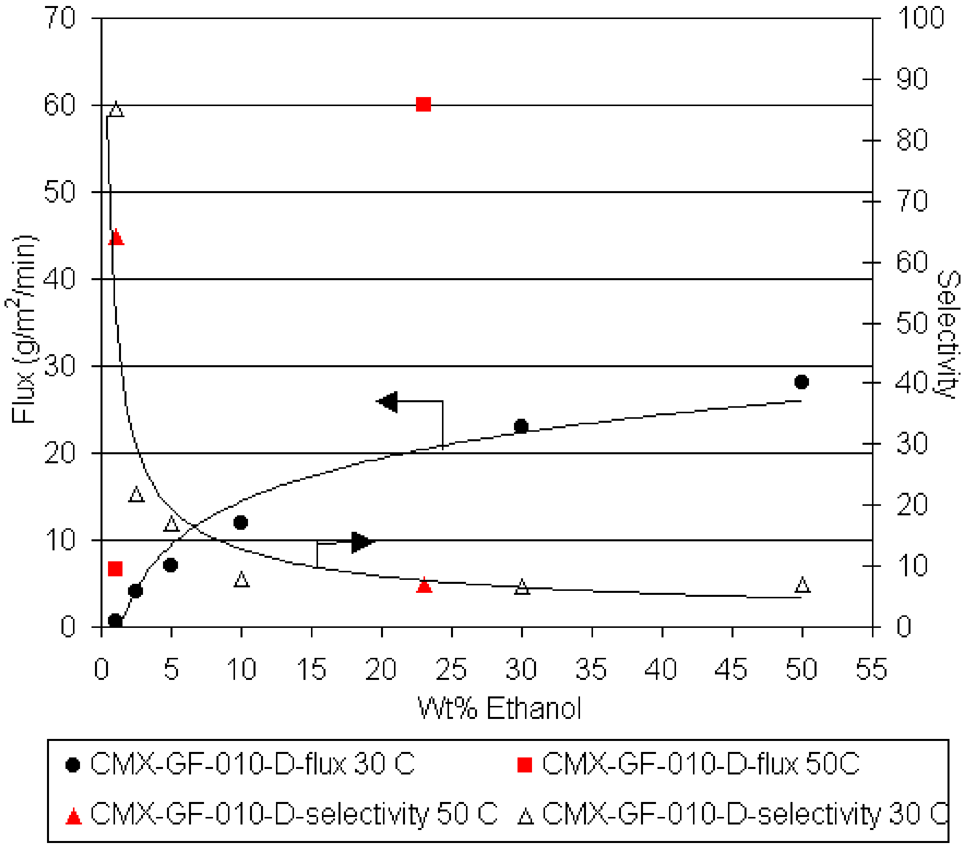

**Figure 4.15** Flux and selectivity versus ethanol feed concentration for PERVAP1060 and CMX-GF-010-D membranes for ethanol-ethyl lactate mixtures at 30$^0$C and 50$^0$C.

### 4.2.5 Hybrid System Selection

As a result of ethyl lactate-water and ethanol-ethyl lactate-water pervaporation experiments with hydrophilic PERVAP©2201 membrane it was shown that high water selectivity could be obtained provided that mixture entering to pervaporation unit has low water concentration. Moreover, separation of ethyl lactate-water mixtures with pervaporation might be more advantageous than distillation due to high selectivity exhibited by the hydrophilic membrane. Between the first and the second hybrid layouts, the use of vapor permeation (VP) could be an alternative, however membrane stability should be considered; since polymeric PVA membranes are stable up to $100^0$C as reported by the company's manufacturing sheets. Since PERVAP©2201 membrane is stable at acidic conditions the use of first layout is possible, due to high selectivity exhibited by membrane in the separation of ternary mixture. The evaluation of this hybrid layout requires investigation of hydrophilic membrane performance for real reaction mixtures. Moreover, in the second layout since feed mixture would contain mostly ethanol and water, pervaporation might be more advantageous since selectivity is two folds as compared to those of ternary mixture at low water concentrations. However, there is an additional condenser cost in this layout, therefore an economical analysis is essential to decide on the most feasible hybrid layout.

On the other hand, although satisfactory flux and selectivities were obtained in pervaporation experiments with hydrophobic and organoselective membranes, it could be said that in the separation of organic-organic mixtures, hybrid separation sequence involving hydrophobic pervaporation unit(s) and another type of separation unit(s), for example distillation could be advantageous than the use of pervaporation alone, when preferentially permeating component is also the more volatile one, as in this case. Furthermore, the use of hydrophobic or organoselective pervaporation with these commercial membranes alone could be made advantageous as compared to well-developed hydrophilic pervaporation, if the membrane performances are developed.

Therefore, the third and the fourth layouts might be improved by incorporation of a distillation column in addition to pervaporation unit(s). In determination of hybrid separation sequence VLE data would be used. For example, in the separation of ethanol from ethyl lactate a hybrid sequence comprising of a distillation and pervaporation unit(s) could be employed.  The use of pervaporation at lower concentration of alcohol, i.e. below 20-wt% alcohol or above 80-wt% ethyl lactate has two advantages. First, pervaporation permeate alcohol concentration is much higher than that of saturated vapor; 70wt% pure alcohol is obtained with PERVAP©2256 membrane. Afterwards, pervaporation permeate could be directly sent to distillation column where VLE selectivity is quite high, above 85wt%. By this way number of trays in distillation column is greatly reduced. Second, the overall energy cost significantly decreases since the vaporization of high boiling ethyl lactate is not required, i.e. since permeate of pervaporation contains mostly low boiling alcohol.

It may be possible to say that third hybrid system seems to be advantageous than the fourth system when the membrane performances and stability requirements are considered. It was shown before that hydrophilic PERVAP©2201 membrane is successful in the separation of ethyl lactate mixtures (S. Korkut, 2001), therefore the use of hydrophilic pervaporation unit first would make low water content feed to enter to hydrophobic pervaporation unit, where the performance is greatly effected by the presence of water. The fourth system is expected to have lower performance since it involves the separation of ethyl lactate-water and ethyl lactate-ethanol. In order to better evaluate these layouts, pervaporation experiments with hydrophobic membranes for the separation of ternary and quaternary reaction mixtures should be carried out.

Finally, in order to select the most efficient integrated sequence among the proposed layouts, there is a need for investigation of separation performance of pervaporation membranes for real reaction mixtures. By this way, coupling effects and the other important issues, such as acid stability and durability of the membranes could be investigated. Furthermore, if pervaporation performances of the membranes are found to be successful, a lab-scale hybrid system should be designed and operated to optimize hybrid system parameters. Afterwards, an economical analysis should be carried out to investigate the feasibility of the proposed hybrid system.

# CHAPTER 5

# CONCLUSIONS

The general conclusions obtained during this study are:

1. Heat of vaporization of ethyl lactate, which does not exist in the literature, was measured as 51.77 kj/mol.
2. In VLE curve of ethyl lactate-water mixture at 8cmHg pressure, a minimum boiling azeotrope exists at 71-wt% water.
3. Ethanol-ethyl lactate VLE selectivity shows slight dependence on pressure~~s~~ between 68-8 cm-Hg.
4. It is technically possible to produce ethyl lactate with high yield by using the previously proposed integrated pervaporation-esterification reactor systems, i.e. pervaporation could successfully separate ethyl lactate reaction mixtures; ethyl lactate-water, ethanol-ethyl lactate, ethyl lactate-ethanol-water.
5. The fact that both hydrophobic membranes are selective to ethanol, instead of ethyl lactate is attributed to high molecular weight and large molecular shape of ethyl lactate, and it’s relatively higher polarity and hydrogen bonding capability.

6. CMX-GF-010-D membrane has both high fluxes and selectivities as compared to PERVAP1060 membrane. On the other hand, PERVAP2256 is more selective than hydrophobic membranes at low concentrations of ethanol.
7. As temperature increase flux increases and selectivity decreases for the hydrophobic CMX-GF-010-D membrane.
8. The hydrophobic membranes showed much higher fluxes than hydrophilic membranes, with reasonable selectivities.
9. Pervaporation was found to enrich saturated vapor composition for ethyl lactate-water mixtures.
10. In the separation of ethanol-ethyl lactate mixtures, a hybrid separation sequence comprising of distillation column and pervaporation unit(s) is proposed as a result of comparison of VLE data and pervaporation performance since hydrophobic and organoselective membranes have higher permeate ethanol concentration than that of saturated vapor at low ethanol region and in the middle concentrations nearly equal ethanol composition as saturated vapor.

# CHAPTER 6

# RECOMMENDATIONS

For the selection of best hybrid sequence to produce ethyl lactate the following suggestions are implemented:

1. Pervaporation characteristics of real reaction mixtures should be investigated.

2. The hybrid system might be constructed and the membrane reactor performance might be evaluated.

3. Hydrophobic membranes should be developed in order to improve the performance of the commercially available membranes.

4. A catalytic membrane reactor might be developed and both the membrane development and reaction kinetics parameters should be evaluated. Furthermore, membrane reactor or hybrid system might be modeled.

5. Finally, the development of acid resistant PV membrane, which will show high selectivity and reasonable permeation rate, is needed.

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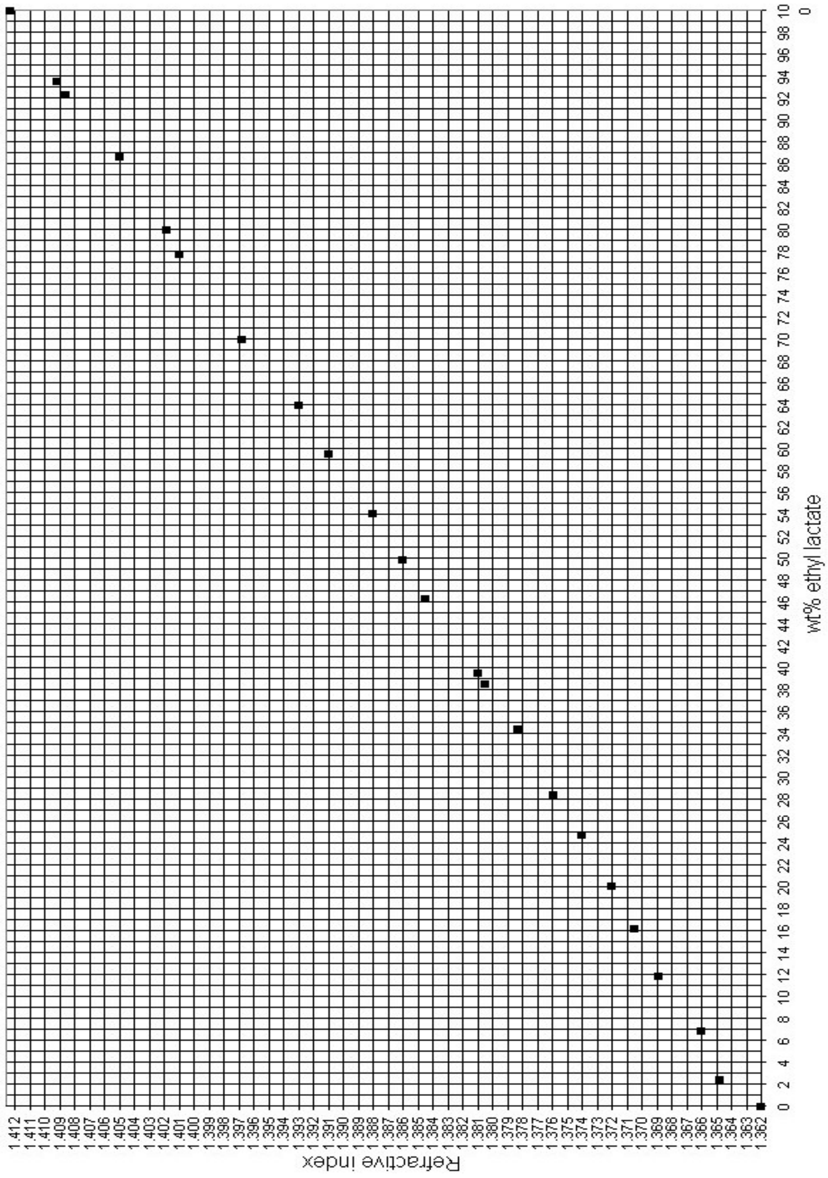
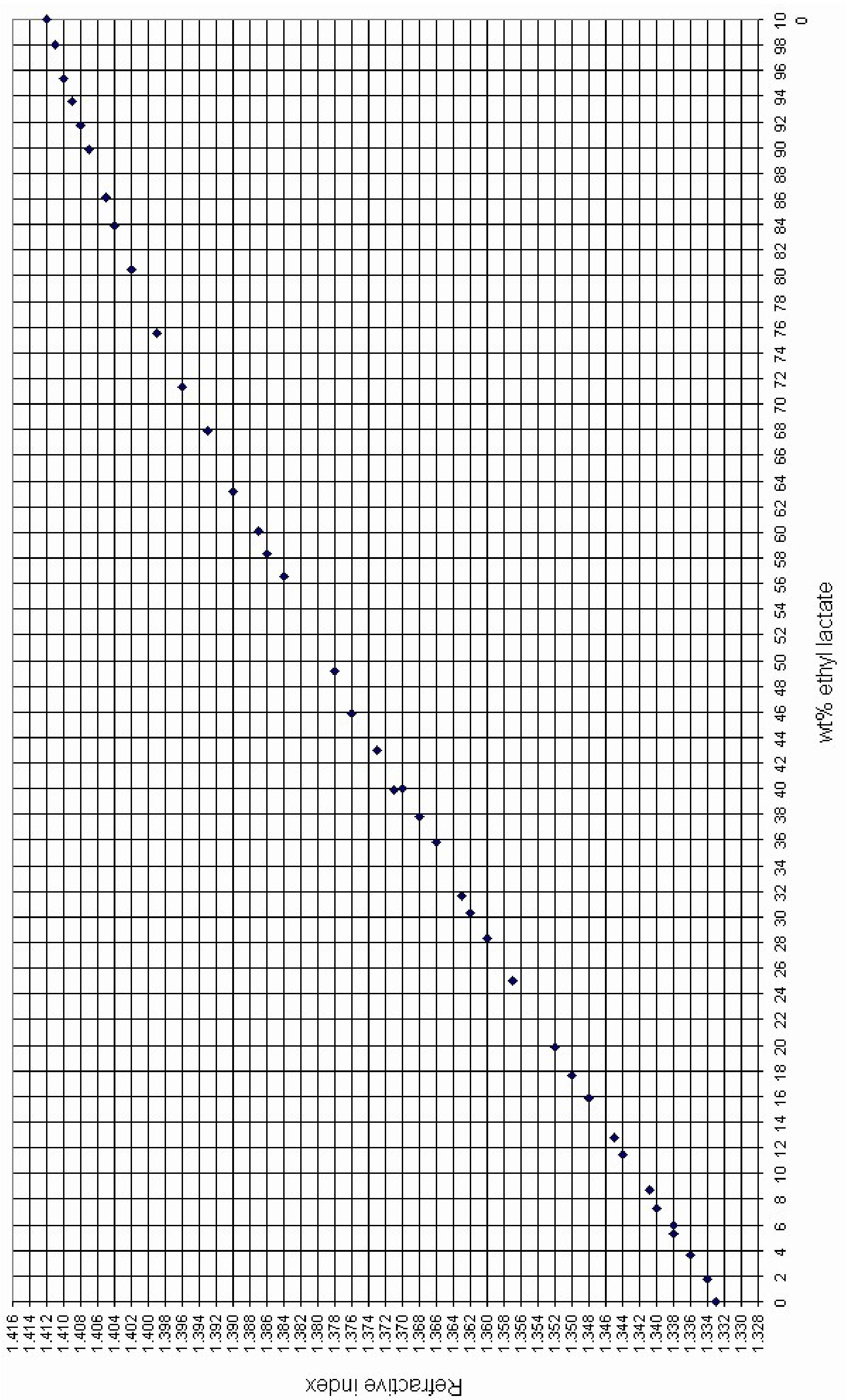
# APPENDIX A

# REFRACTOMETER CALIBRATION DATA

### 1. Calibration curve for ethyl lactate-ethanol solution, at $20^0$C



## 2. Calibration curve for ethyl lactate-water solution, at 20$^0$C



# APPENDIX B

## UNSTEADY STATE DATA

### 1. Hydrophobic membranes, CMX-GF-010-D and PERVAP1060 in the separation of ethyl lactate-ethanol mixtures

Date: 27.09.2002
Membrane: pervap 1060
concentration: 5%ethanol-lactate

| Sample # | Time (min) | Flux ($g/m^2/min$) | Ethanol wt. Fraction in permeate | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 98 | 3.087 | 0.40 | 13 |
| 2 | 146 | | 0.44 | 15 |
| 3 | 175 | 5.317 | 0.40 | 13 |
| 4 | 203 | 3.766 | 0.36 | 11 |
| 5 | 237 | 4.339 | 0.36 | 11 |
| 6 | 260 | 3.823 | 0.34 | 10 |
| 7 | | 5.179 | 0.23 | 6 |
| 8 | 322 | 3.986 | 0.36 | 11 |
| 9 | 356 | 4.769 | 0.33 | 9 |
| 10 | 385 | 4.014 | 0.33 | 9 |
| 11 | 413 | 5.031 | 0.34 | 10 |
| 12 | 434 | 4.301 | 0.33 | 9 |
| 13 | 459 | 5.046 | 0.33 | 9 |

Date: 10.09.2002
Membrane: pervap 1060
concentration: 50%ethanol-lactate

| **Sample #** | **Time (min)** | **Flux ($g/m^2/min$)** | **Ethanol wt. Fraction in permeate** | **$\alpha_{A/L}$** |
|---|---|---|---|---|
| 1 | 95 | 21.15 | 0.83 | 4.9 |
| 2 | 198 | 14.81 | 0.88 | 7.3 |
| 3 | 290 | 14.98 | 0.83 | 4.9 |
| 4 | 390 | 13.09 | 0.83 | 4.9 |
| 5 | 480 | 14.56 | 0.83 | 4.9 |
| 6 | 717 | 14.67 | 0.88 | 7.3 |
| 7 | 807 | 14.78 | | |
| 8 | 925 | 14.2 | | |
| 9 | 1091 | 15.27 | | |

Date: 23.09.2002
Membrane:CMX-GF-010-D
concentration: 1%ethanol-lactate

| **Sample #** | **Time (min)** | **Flux ($g/m^2/min$)** | **Ethanol wt. Fraction in permeate** | **$\alpha_{A/L}$** |
|---|---|---|---|---|
| 1 | 271 | 0.459 | 0.62 | 162 |
| 2 | 365 | 0.305 | 0.59 | 142 |
| 3 | 475 | | 0.42 | 72 |
| 4 | 562 | 0.702 | 0.42 | 72 |
| 5 | 620 | 0.429 | 0.40 | 66 |
| 6 | 738 | 0.504 | 0.50 | 99 |
| 7 | 880 | 0.518 | 0.51 | 103 |
| 8 | 970 | 0.568 | 0.45 | 81 |
| 9 | 992 | 0.588 | | |

Date: 29.09.2002
Membrane:CMX-GF-010-D
concentration: 2.5%ethanol-lactate

| **Sample #** | **Time (min)** | **Flux ($g/m^2/min$)** | **Ethanol wt. Fraction in permeate** | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 121 | 1.901 | 0.51 | 40.6 |
| 2 | 182 | 2.945 | 0.42 | 28.2 |
| 3 | 233 | 2.75 | 0.34 | 20.1 |
| | | | | |
| 5 | 342 | 2.858 | 0.42 | 28.2 |
| 6 | 395 | 3.54 | 0.38 | 23.9 |
| | | | | |
| 8 | 487 | 3.926 | 0.35 | 21.0 |
| 9 | 509 | 3.753 | 0.35 | 21.0 |
| 10 | 556 | 3.827 | 0.36 | 21.9 |

Date: 19.09.2002
Membrane:CMX-GF-010-D
concentration: 5%ethanol-lactate

| **Sample #** | **Time (min)** | **Flux ($g/m^2/min$)** | **Ethanol wt. Fraction in permeate** | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 154 | 4.314 | 0.48 | 18 |
| 2 | 255 | 6.329 | 0.48 | 18 |
| 3 | 337 | 6.571 | 0.47 | 17 |
| 4 | 371 | 6.554 | 0.47 | 17 |
| 6 | 433 | 6.656 | 0.45 | 16 |
| 7 | 499 | 6.894 | 0.45 | 16 |
| 8 | 542 | 7.218 | 0.45 | 16 |
| 9 | 659 | 6.625 | 0.47 | 17 |

Date: 04.10.2002
Membrane:CMX-GF-010-D
concentration: 10%ethanol-lactate

| **Sample #** | **Time (min)** | **Flux ($g/m^2/min$)** | **Ethanol wt. Fraction in permeate** | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 115 | 11.473 | 0.49 | 9 |
| 2 | 160 | 11.969 | 0.46 | 8 |
| 3 | 205 | 11.871 | 0.46 | 8 |
| 4 | 250 | 12.194 | 0.46 | 8 |
| 5 | 295 | 11.743 | 0.48 | 8 |
| 6 | 346 | 11.953 | 0.47 | 8 |
| 7 | 388 | 11.218 | 0.48 | 8 |
| 8 | 439 | 11.805 | 0.46 | 8 |

Date: 07.10.2002
Membrane:CMX-GF-010-D
concentration: 30%ethanol-lactate

| **Sample #** | **Time (min)** | **Flux ($g/m^2/min$)** | **Ethanol wt. Fraction in permeate** | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 102 | 22.274 | 0.74 | 7 |
| 2 | 146 | 22.641 | 0.74 | 7 |
| 3 | 190 | 22.324 | 0.72 | 6 |
| 4 | 236 | 22.971 | 0.74 | 7 |
| 5 | 280 | 22.473 | 0.74 | 7 |
| 6 | 327 | 23.219 | 0.74 | 7 |

Date: 11.09.2002
Membrane:CMX-GF-010-D
concentration: 50%ethanol-lactate

| **Sample #** | **Time (min)** | **Flux ($g/m^2/min$)** | **Ethanol wt. Fraction in permeate** | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 292 | 27.98 | 0.87 | 7 |
| 2 | 332 | 28.7 | 0.87 | 7 |

## 2. Organoselective Membrane, PERVAP2256 in the separation of ethyl lactate-ethanol mixtures

Date: 19.04.2003
Membrane: pervap 2256
concentration: 1%ethanol-lactate

| Sample # | Time (min) | Flux (g/m$^2$/min) | Ethanol wt. Fraction in permeate | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 526 | 0.077 | 0.7 | 231 |
| 2 | 782 | 0.024 | 0.98 | 4851 |
| 3 | 1232 | 0.031 | 0.99 | 9801 |
| 4 | 1600 | 0.027 | 0.99 | 9801 |
| 5 | 1944 | 0.0977 | 0.92 | 1139 |

Date: 15.04.2003
Membrane: pervap 2256
concentration: 5%ethanol-lactate

| Smp | time | flux | p.conc | selectivity |
|---|---|---|---|---|
| 1 | 266 | 0.41 | 0.75 | 57 |
| 2 | 478 | 0.421 | 0.7 | 44 |
| 3 | 675 | 0.457 | 0.7 | 44 |
| 4 | 859 | 0.436 | 0.69 | 42 |

Date: 28.01.2003
Membrane: pervap 2256
concentration: 30%ethanol-lactate

| Sample # | Time (min) | Flux (g/m$^2$/min) | Ethanol wt. Fraction in permeate | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 126 | 14.73 | 0.65 | 4 |
| 2 | 161 | 13.77 | 0.63 | 4 |
| 3 | 198 | 13.71 | 0.65 | 4 |
| 4 | 263 | 14.38 | 0.65 | 4 |
| 5 | 295 | 14.06 | 0.65 | 4 |
| 6 | 325 | 14.14 | 0.65 | 4 |
| 7 | 350 | 14.05 | 0.66 | 5 |

Date: 30.01.2003
Membrane: Pervap 2256
concentration: 50%ethanol-lactate

| Sample # | Time (min) | Flux (g/m$^2$/min) | Ethanol wt. Fraction in permeate | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 151 | 29.44 | 0.8 | 4 |
| 2 | 193 | 29.61 | 0.8 | 4 |
| 3 | 231 | 29.33 | 0.8 | 4 |
| 4 | 274 | 28.34 | 0.8 | 4 |
| 5 | 314 | 28.09 | 0.8 | 4 |
| 6 | 361 | 28.29 | 0.8 | 4 |
| 7 | 406 | 28.54 | 0.8 | 4 |

### 3. Hydrophobic Membrane, CMX-GF-010-D in the separation of ethyl lactate-ethanol mixtures at $50^0$C

Date: 03.11.2002
Membrane:CMX-GF-010-D
concentration: 1 %ethanol-lactate
T =$50^0$C

| Sample # | Time (min) | Flux ($g/m^2/min$) | Ethanol wt. Fraction in permeate | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 122 | 3.566 | 0.42 | 72 |
| 2 | 178 | 4.079 | 0.41 | 69 |
| 3 | 285 | 6.244 | 0.38 | 61 |
| 4 | 335 | 6.637 | 0.33 | 49 |
| 5 | 374 | 6.387 | 0.30 | 42 |

Date: 01.11.2002
Membrane:CMX-GF-010-D
concentration: 23 %ethanol-lactate
T =$50^0$C

| Sample # | Time (min) | Flux ($g/m^2/min$) | Ethanol wt. Fraction in permeate | $\alpha_{A/L}$ |
|---|---|---|---|---|
| 1 | 120 | 64.61 | 0.57 | 4 |
| 2 | 151 | 60.38 | 0.59 | 5 |
| 3 | 182 | 58.49 | 0.59 | 5 |
| 4 | 199 | 59.99 | 0.59 | 5 |
| 5 | 228 | 60.92 | 0.59 | 5 |
| 6 | 248 | 60.67 | 0.59 | 5 |