LIQUID-LIQUID EQUILIBRIA, SOLID-LIQUID EQUILIBRIA AND MIXTURE PROPERTIES FOR THE SEPARATION OF BIOBUTANOL FERMENTATION PRODUCTS

[1]SO-JIN PARK, [2]HA-YOUNG OH, [3]JI-EUN GU

[1,2,3] Department of Chemical Engineering and Applied Chemistry, College of Engineering Chungnam National University, Daejeon 305-764, Korea
E-mail: sjpark@cnu.ac.kr (S.-J. Park)

Abstract - Liquid-liquid equilibria (LLE) for extraction of butyric acid in aqueous system and in addition, solid-liquid equilibria (SLE), excess volume and deviation of molar refractivity for binary mixtures of acetic acid with C_3 to C_5 carboxylic acids: propionic, butyric and pentanoic acid, which are mostly biobutanol fermentation broth. LLE and SLE measurement was carried out under atmospheric pressure using self-made grass vessel while excess volume and deviation of molar refractivity were determined from directly measured density and refractive indices using precision densitometer and refractometer. All the determined LLE data for water+ butyric acid + heavy ether compound showed Treybal type II phase behavior, while SLE for binary mixtures of {acetic acid + C_3 - C_5 carboxylic acid} showed single eutectic point. The LLE and SLE data correlated well with common activity coefficient models within 0.6 K of root mean square standard deviation. The excess molar volumes (V^E) for the acetic acid + C_3 - C_5 carboxylic acid binary mixtures showed positive values for entire ranges of compositions, while the molar refractivity deviation (ΔR) showed negative values. The excess and deviation properties were modeled well by polynomial equations, namely Redlich-Kister within 0.006 $cm^3 \cdot mol^{-1}$ of standard deviation for V^E and 0.02 $cm^3 \cdot mol^{-1}$ for ΔR, respectively.

Keywords - Biobutanol, Phase Equilibria, Carboxyric Acid,Excess Volumes, Refractivity Deviation.

I. INTRODUCTION

Recently, bio fuels have been regaining popularity again due to the need of renewable resources and high price of petroleum feedstocks with growing concern about global warming and need of energy independence. In fact, it is not surprising because fossil fuels are also basically bio fuel, which are made from decomposed plants under the ground. Many countries around the world are using biofuels, mainly bio ethanol and biodiesel. Relatively new four carbonate bio butanol has some advantages compare to bioethanol: favorable higher density (29.2×10^6 kJ/m^3), easily mixing with gasoline, less corrosiveness and less emissivity of CO and NOx, etc.[1] Commercial problem for bio butanol fermentation process are mainly high feedstock cost, very low butanol yield caused by severe product inhibition during bioprocessing and increased separation cost, etc.[2] There are many reports for enhancing the fermentation yields by modification of microorganism and alternative cheaper biomass as renewable feedstock such as lignocellulosic materials: agricultural waste and wood chips. However, this is still an unrealized long term goal. Another approach is to develop the separation technology for the product recovery. Therefore, there are extensive review on the separation technologies for bio butanol from conventional ABE (acetone-butanol-ethanol) fermentation broth. In the industry, the equilibrium staged separation technologies are still popular and therefore concluded that adsorption, solvent extraction and membrane pervaporation are the most energy efficient process.[3,4] However the relate process design data was still worse off, even though they are indispensable for developing such equilibrium staged separation process. In a typical ABE fermentation, butyric (butanoic), propionic (propanoic) and acetic (ethanoic) acids are produced first by C. acetobutylicum and some other products, such as, isoamyl alcohol, acetaldehyde and 1-hexanol are also produced. That makes the separation process more complicate and challenging. Therefore, as a systematic study [5], we studied relate phase equilibrium and mixture property data for the systems containing C_2-C_4 and also with C_5 acid and other by product components.

In this work, we've determined ternary LLE for {water + butyric acid + Methyl tert butyl ether (MTBE)}, {tert-amyl methyl ether (TAME)} and {di isopropyl ether (DIPE)} at 298.15K and SLE (solid-liquid equilibrium) data for binary {acetic acid + propionic, butyric and pentanoic acid} systems under atmospheric pressure. LLE and SLE are important mainly for separation process development and safety assessment and also for the selection of solvents for product mixtures. In addition, these data provide information about the real mixture behavior at low temperatures, where the fugacity of a component cannot be easily determined. Density and refractive indices for the same binary mixtures are also reported and their excess and deviation properties were determined at 298.15 K. The phase equilibrium data were regressed with activity coefficient model: NRTL (nonrandom two liquids) and UNIQUAC (universal quasi chemical) model, in the meanwhile the excess and deviation properties were regressed with Redlich-

Kister polynomial. Their regression results are agreed very well with each model equations.

II. EXPERIMENT

2.1. Materials

Acetic acid was supplied by Samchun pure chemical Co. (Korea). Propionic acid, MTBE, TAME and DIPE were supplied by Sigma-Aldrich (USA), and butyric acid was supplied by Junsei chemical Co. (Japan), while pentanoic acid was supplied by Alfa Aesar (USA). The mass purities of all the chemicals were greater than 99.9 % by G.C. analysis. All chemicals were dried using molecular sieves with a pore diameter of 0.3 nm. The water content of the chemicals, determined using a Karl-Fischer titrator (Metrohm 684 KF-Coulometer), was less than 5×10^{-5} $g \cdot g^{-1}$. The determined physical properties of the chemicals at 298.15 K are summarized in Table 1, along with the reported literature values.

2.2. Apparatus and Procedure

LLE and SLE were determined using specially designed self-made double and triple jacketed glass still. These glass still was connected with a thermostat (cryostat) and a precision temperature measuring system. The heating or cryostat medium circulates through the outer jacket of glass still to insulate the equilibrium cell from changes in the environment via the contact medium. For LLE determination, the sample mixture was vigorously stirred for about 6 h and then were settled more 12 h at a constant temperature of 298.15K. On the other hand, SLE point (melting point of the crystal) of a given composition could be determined visually at the moment when the last crystal of the mixture disappeared. The overall uncertainty of the measurement was considered to be less than ± 0.1 K, and ΔR was determined from directly measured densities (ρ) and refractive indices (n_D). Densities of the pure and mixture components at atmospheric pressure were measured on a vibratingwith an accuracy of $\pm 1 \times 10^{-5}$g. The uncertainty in the mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$. $V^E$and ΔR was determined from directly measured densities (ρ) and refractive indices (n_D). Densities of the pure and mixture components at atmospheric pressure were measured on a vibrating tube densitometer (Anton Paar model DMA 5000). The temperature of the U-tube was controlled with in 0.001K and measured by a high-precision platinum resistance probe with an accuracy of 0.01 K. For thedensitometer calibration, standard bi-distilled water and air were used. The experimental systematic error in density and mass measurements was estimated to be less than $\pm 1 \times 10^{-5}$ g cm^{-3} and 1×10^{-4} in the mole fraction, respectively. The refractive indexes (n_D) of the pure components and mixtures were measured using a digital precision refractometer (KEM, model RA-520N, Kyoto, Japan). The time interval for recording the measurements was chosen to be 15 min to attain a constant temperature via sufficient heat transfer as well as for a stable condition of the measurement. And then ΔRwas obtained from the experimental n_D data. According to the manufacturer, the accuracy of the refractometer is less then $\pm 5 \times 10^{-5}$ and $\pm 1 \times 10^{-4}$ in the ranges of 1.32–1.40 and 1.40–1.58, respectively, and the accuracy of the temperature was $\pm 5 \times 10^{-2}$ K. The reproducibility of the measurement was checked periodically with double distilled water.

RESULTS AND DISCUSSION

The capability of heavy ether components as a solvent for butyric acid aqueous solution could be estimated LLE and solvent's selectivity. All the determined LLE showed type II phase behavior according to Treybal's classification for ternary system, which have 2 immiscible binaries. Fig. 1 showed LLE curve for water + butyric acid + TAME system among the determined ternary systems and calculated selectivity of different ethers to butyric acid in aqueous solution. The calculated selectivity are much greater than unity. That means ether componentscould be a good solvent for butyric acid in water. The experimental SLE data for the binary systems of the {acetic acid + propionic, butyric and pentanoic acid} are illustrated in Fig. 2. As shown in Fig. 2, all the systems in this work showed a single eutectic point. The experimental LLE and SLE data were correlated with two activity coefficient model: NRTL and UNIQUAC model. For the LLE data, UNIQUC model showed a slightly better correlation results than the UNIQUAC equation for all the determined systems, while the SLE data were correlated better with NRTL equation.

Chemical	GC (wt. %)	$\rho / g cm^{-1}$ (298.15K)		n_D (298.15 K)	
		Exp.	Ref.	Exp.	Ref.
acetic acid	>99.9	1.04774	1.04395 [a]	1.3729	1.36969 [a]
propionic acid	>99.9	0.98945	0.98833 [a]	1.3846	1.38484 [a]
butyric acid	>99.9	0.95349	0.95317 [a]	1.3967	1.39599 [a]
pentanoic acid	>99.9	0.93549	0.93485 [b]	1.4065	1.40641 [b]

Table1.Purity and physical properties of the chemicals

[a]Ref [6]. [b]Ref [7].

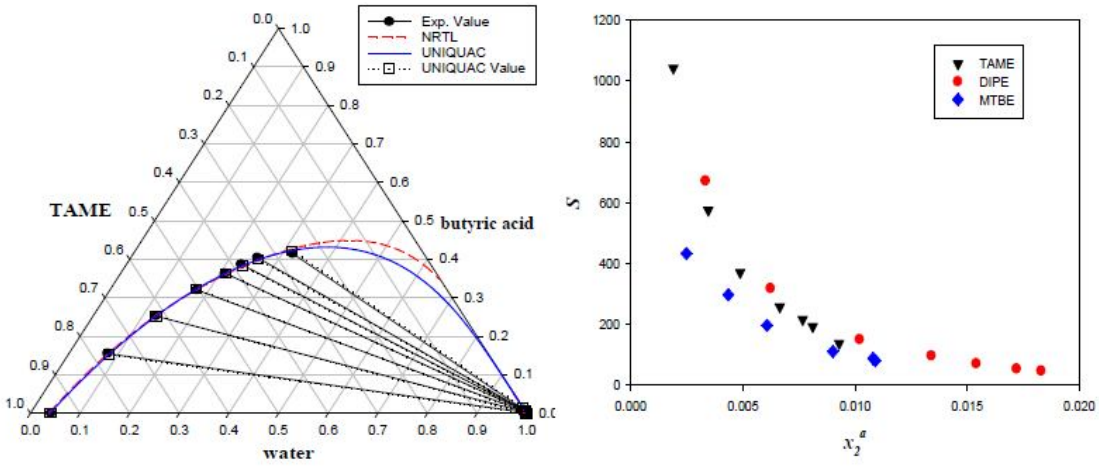

Fig. 1. LLE for water+butyric acid+TAME system and the selectivity of ether compounds to butyric acid

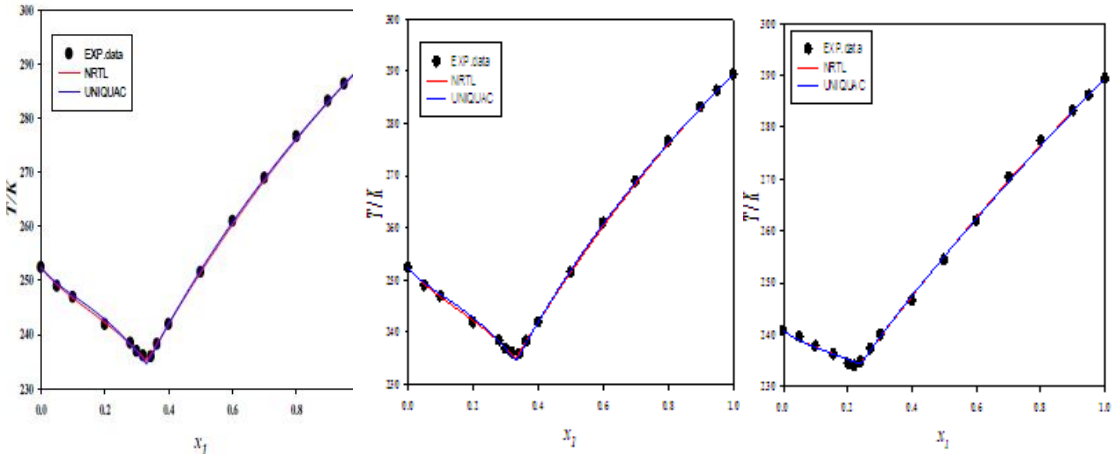

Fig. 2. The SLE diagram for the binary system of acetic acid + propionic acid (a); acetic acid + butyric acid (b);acetic acid + pentanoic acid (c); solid curves were calculated from NRTL model.

The root-mean-square deviation (RMSD) between the experimental data and calculated values from the correlated parameters were less than 0.6 K for all the determined LLE and SLE data. The RMSD was calculated from Eq. (1)

$$RMSD = \left[\frac{\sum_i \sum_\alpha \sum_k (x_{ik}^{\alpha\,(exp)} - x_{ik}^{\alpha\,(cal)})^2}{6N}\right]^{1/2} \quad (1)$$

The exact eutectic points were estimated with NRTL equation and on the basis of the NRTL parameters. They are x_1 = 0.3305 / T = 234.94 K, x_1 = 0.4026 / T = 246.26 K and x_1 = 0.2400 / T = 234.33 K for the system {acetic acid + propionic acid}, {acetic acid+ butyric acid} and {acetic acid+ pentanoic acid}, respectively. The uncertainty of the equilibrium temperature for SLE determination was estimated to be ± 0.2 K.

TheV^E value was calculated fromthe measureddensity using eq. (2)

$$V^E \,/\, cm^3 \cdot mol^{-1} = \frac{\sum_i x_i M_i}{\rho_m} - \sum_i \left[\frac{x_i M_i}{\rho_i}\right] \quad (2)$$

where ρ_i, ρ_m $and M_i$ are density of pure component and mixture and molar mass, respectively. The experimental V^E values showed positive deviation from the ideal behavior as illustrated in Fig. 3. Actually, smaller carboxylic acids (carbon number of 1-5) are basically polar and has hydrogen bonding, since they are hydrogen bond accepter and also hydrogen bond donor. However their mixtures showed positive deviation of V^E values. It may be caused by relatively low dielectric constant of these carboxylic acid. The dielectric constants of small carboxylic acids are relatively small: acetic acid; 6.20, propionic acid; 3.10, butyric acid; 2.80, pentanoic acid; 2.60. These low dielectric constant make the influence of non-polar alkyl group overwhelm the influence of carboxyl group in carboxylic acid. Therefore, the positive deviation increased with increasing the carbon number of 2nd component of carboxylic acid. In the meanwhile, ΔRshowed negative deviation in all the systems and the negativity increase with increasing the difference of molecular weight in the mixtures as also illustrated in Fig. 3. Namely, the negativity of deviation increased in the order of {acetic acid + propionic} <

{acetic acid + butyric acid} < {acetic acid + pentanoic acid}. ΔR was calculated from equation (3) using the molar refractivity of pure and mixed components and volume fraction of the component.

$$\Delta R / \ cm^3 \cdot mol^{-1} = R_m - \sum_i \phi_i R_i \quad (3)$$

$$R_m = \left[\frac{n_D^2-1}{n_D^2+1}\right]\left[\frac{\sum_i x_i M_i}{\rho_m}\right],\ R_i = \left[\frac{n_{D,i}^2-1}{n_{D,i}^2+1}\right]\left[\frac{M_i}{\rho_i}\right],$$

$$\phi_i = \frac{x_i V_i}{\sum_j x_j V_j}$$

where R_m, R_i,ϕ_i, n_D, $n_{D,i}$ and V_i represent the molar refractivity of mixture and pure component i, volume fraction of the pure component i in the mixture, the refractive index of the mixture and the pure component i and the molar volume of the pure component i, respectively.

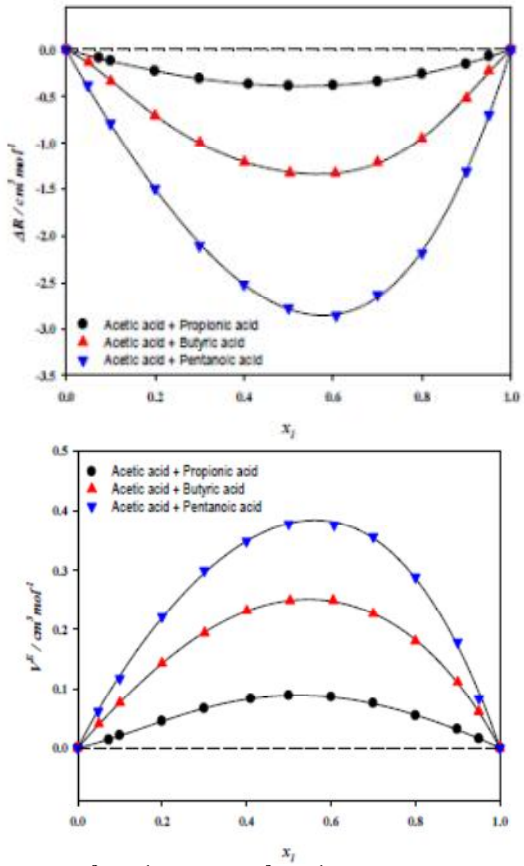

Fig. 3. V^E(cm^3·mol^{-1}) and ΔR(cm^3·mol^{-1}) for the binary systems at 298.15 K; ●, {acetic acid(1) + propionic acid(2)}; ▲, {acetic acid(1) + butyric acid(2)}; ▼, {acetic acid(1) + pentanoic acid(2)};solid curves were calculated using the Redlich-Kister equation

The V^E and ΔR was correlated with Redlich-Kister polynomial equation in order to correlate binary parameters and estimate standard deviation.

$$V^E,\ \Delta R = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \quad (4)$$

where x is the mole fraction, A_i, is fitted Redlich-Kister parameter and n signify a number of parameters. The corresponding standard deviations of the fit, σ_{st}, is then defined as:

$$\sigma_{st} = \sqrt{\frac{\sum_i^N \left(X_i^{calc} - X_i^{exp}\right)^2}{(N-n)}} \quad (5)$$

where X_i^{calc} and X_i^{exp} are the calculated and experimental value of component i, respectively. N is the number of experimental points, and n is the number of fitted parameters. The mean deviations of the V^E values were 0.0008, 0.0015 and 0.0056 $cm^3 \cdot mol^{-1}$ for the {acetic acid + propionic acid}, {acetic acid + butyric acid} and {acetic acid + pentanoic acid}, respectively. On the other hand, ΔR was 0.0037, 0.0144 and 0.0191 $cm^3 \cdot mol^{-1}$ for the {acetic acid + propionic acid}, {acetic acid + butyric acid} and {acetic acid + pentanoic acid}, respectively.

CONCLUSIONS

All the determined ternary LLE for {water+ butyric acid + ether compounds} showed Treybal type II phase behavior. The selectivity of ether compounds as solvent to butyric acid was much greater than unity. That means ether compounds in this work could be used as a good selective solvent for butyric acid in aqueous system. The SLE of determined {acetic acid + C_3-C_5 monocarboxylic acid} have single eutectic point. The estimated eutectic point by NRTL model are x_1 = 0.3305 / T = 234.94 K, x_1 = 0.4026 / T = 246.26 K and x_1 = 0.2400 / T = 234.33 K for the system {acetic acid + propionic acid}, {acetic acid+ butyric acid} and {acetic acid+ pentanoic acid}, respectively. They are correlated well with NRTL model. The values of V^E forC_2-C_5monocarboxylic acid mixtures were found to be positive for the whole composition ranges, whereas ΔR showed totally negative values for the same mixture systems. The positivity of V^E values increased in a regular way with increasing the carbon number of monocarboxylic acid. As in the same way, the negativity of ΔR increased also increasing the carbon number of constituent carboxylic acid. These results could be discussed in the light of the intermolecular interaction and molecular size and structure. The low dielectric constant of theC_2-C_5monocarboxylic acid make V^E values positively, i.e. non polarity of alkyl group overwhelm the low polarity of carboxyl group in carboxylic acid. In the meanwhile, the difference of molecular size and structure makes ΔR values to negative. They were correlated very well with Redlich-Kister polynomials within 0.006 $cm^3 \cdot mol^{-}$of standard deviation for V^E and 0.02 $cm^3 \cdot mol^{-1}$ for ΔR, respectively.

ACKNOWLEDGMENTS

This work was supported by the research fund of Chungnam National University, Korea.

REFERENCES

[1] Keikhoosro Karimi, Meisam Tabatabaei, Ilona sarvari Horvath and Rajeev Kumar, " Recent trends in acetone, butanol, and ethanol(ABE) production," Biofuel research journal, vol. 8, PP. 301-308, 2105

[2] Shoqu Xie, Conghua Yi, and Xueqing Qiu, "Energy-saving recovery of acetone, butanol, and ethanol from a prefractionator by the salting-out method," J. Chem. Eng. Data, vol. 58, PP. 3297-3303, 2013

[3] Dharamashi Rabari and Tamal Banerjee, "Biobutanol and n-propanol recovery using a low density phosphonium based ionic liquid at T=298.15K and p= 1atm," Fluid Phase Equilibria, vol. 355. PP. 26-33, 2013

[4] Shaohua Zheng, Hongye Cheng, Lifang Chen and Zhiwen Qi, "Feasibility of bio-based lactate esters as extractant for biobutanol recovery: (liquid + liquid) equilibria," J. Chem. Thermodynamics, vol. 93, PP. 127-131, 2016

[5] Kyungho lee and So-Jin Park, "Isothermal vapor-liquid equilibria, excess molar volume and the deviation of refractive indices for binary mixtures of 1-butanol, 1-hexanol, 3-methyl-1-butanol and butyl acetate," Fluid Phase Equilibria, vol.436, PP. 47-54, 2017

[6] Granados, K., Gracia-Fadrique, J.,Amigo, A., Bravo, R., "Refractive Index, Surface Tension, and Density of Aqueous Mixtures of Carboxylic Acids at 298.15 K", J. Chem. Eng. Data, vol. 51, PP. 1356-1360 (2006).

[7] Bahadur, I., Singh, S., Deenadayalu, N., Naidoo, P., Ramjugernath, D., "Influence of alkyl group and temperature on thermophysical properties of carboxylic acid and their binary mixtures", Thermochi. Acta, 590, PP. 151-159, 2014.

★★★