PAMUKKALE ÜNİVERSİTESİ MÜHENDİSLİK FAKÜLTESİ
PAMUKKALE UNIVERSITY ENGINEERING COLLEGE
MÜHENDİSLİK BİLİMLERİ DERGİSİ
JOURNAL OF ENGINEERING SCIENCES

YIL : 2003
CİLT : 9
SAYI : 1
SAYFA : 125-128

APPLICATION OF THE UNIFAC MODEL TO LIQUID-LIQUID EQUILIBRIA OF WATER-PROPIONIC ACID-SOLVENT TERNARIES*

Süheyla ÇEHRELİ
İstanbul University, Engineering Faculty, Department of Chemical Engineering, 34850-Avcılar/İstanbul

Geliş Tarihi : 09.08.2001

ABSTRACT

The liquid-liquid equilibria of Water-Propionic Acid-Benzyl Alcohol, Water-Propionic Acid-Benzyl Acetate and Water-Propionic Acid-Dibenzyl Ether ternary systems were predicted by means of UNIFAC Model. For this purpose, multivariable Newton-Raphson convergence procedure was used. Experimental and model results were compared.

Key Words : UNIFAC model, Liquid-Liquid equilibria, Propionic acid

SU-PROPİONİK ASİT-ÇÖZÜCÜ SİSTEMLERİ SIVI-SIVI DENGE VERİLERİNE UNIFAC MODELİNİN UYGULANMASI

ÖZET

Su-Propionik Asit-Benzil Alkol, Su-Propionik Asit-Benzil Asetat ve Su-Propionik Asit-Dibenzil Eter üçlü sistemlerine ait sıvı-sıvı denge verileri UNIFAC Modeli kullanılarak tahmin edilmiştir. Bunun için çok varyanslı Newton-Raphson yönteminin uygulandığı bir bilgisayar programı kullanılmıştır. Elde edilen model verileri deneysel verilerle karşılaştırılmıştır.

Anahtar Kelimeler : UNIFAC modeli, Sıvı-Sıvı dengesi, Propionik asit

1. INTRODUCTION

A large part of chemical engineering design is concerned with separation processes. Many of these are diffusional operations of the phase-contacting type; distillation, absorption and extraction are probably the most common. The liquid extraction process and the design of the corresponding equipment require the knowledge of the phase equilibrium data. Prediction and correlation of multicomponent liquid-liquid equilibrium (LLE) is of importance in chemical engineering applications. The UNIFAC Model (Fredenslund et al., 1975; Magnussen et al., 1981; Badakhshan et al., 1985; Correa et al., 1989; Solimo et al., 1989, Lo et al., 1991; Kyle, 1992; Solimo et al., 1994) is one of the useful model used for prediction of LLE Data.

LLE Data of Water-Propionic Acid-Solvent ternaries were estimated by UNIFAC Model. The experimental data were compared with the values calculated by the UNIFAC Model.

(*) : This work was presented at the IV. National Chemical Engineering Congress in September 2000, Istanbul, Turkey as a preliminary study.

2. MATERIAL AND METHOD

2. 1. Chemicals

All chemicals were furnished by Merck Co. (synthesis grade) and deionized water was further distilled before use.

2. 2. Procedure

Phase analysis was carried out by gas chromatography in a Hewlett Packard 6890 series chromatograph equipped with serial connected TCD and FID detectors. Separation used a 30m×0.32mm HP-INNOWAX column with a 0.5 µm film PGE: The injection was split (10:1) of volume 0.5 µL. The injector and detectors temperatures were held at 200 and 250 °C respectively. The oven temperature was 50 °C - 3 min, 10 °C/ min. 100 °C - 0 min., 50 °C / min. 250 °C – 15 min. The carrier gas was nitrogen (flow rate, 0.8 ml/min.). Quantitation was by the internal standard method. Water was analysed by the TCD, propionic acid and solvents were analysed by FID detector.

Conjugate phases were obtained by vigorously stirring mixtures having composition lying in the immiscible region for 1h in isothermal jacketed glass (298.15K), then leaving them to stand for 1h (the time necessary for attainment of equilibrium was established in preliminary experiments) before a sample of each phase was withdrawn and injected into GC column.

2. 3. UNIFAC Model

The multicomponent expressions for the activity coefficients for UNIFAC Model are given by the addition of the combinatorial and residual parts;

$$\mathbf{ln}\,\gamma_i = \mathbf{ln}\,\gamma_i^C + \mathbf{ln}\,\gamma_i^R \qquad (1)$$

Combinatorial residual

$$\mathbf{ln}\,\gamma_i^C = \mathbf{ln}\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \,\mathbf{ln}\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_j x_j l_j \qquad (2)$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \qquad (3)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \qquad \text{(area fraction)} \qquad (4)$$

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \qquad \text{(segment fraction)} \qquad (5)$$

x_i, is the mole fraction of component i; z = 10 (coordination number). Pure-component paremeters r_i and q_i are measures of molecular van der Waals volumes and molecular surface areas. They are calculated as the sum of the group volume and group area parameters, R_k and Q_k;

$$r_i = \sum_k v_k^i R_k \text{ and } q_i = \sum_k v_k^i Q_k \qquad (6)$$

Where v^i_k , is the number of groups k in molecule i.

The residual part is expressed by;

$$\mathbf{ln}\,\gamma_i^R = \sum_k v_k^i \left(\mathbf{ln}\,\tau_k - \mathbf{ln}\,\tau_k^i\right) \qquad (7)$$

$\ln\tau_k$ is the group residual activity coefficient and $\ln\tau_k^i$ is the residual activity coefficient of group k in reference solution containing only molecules of type i.

$$\mathbf{ln}\,\tau_k = Q_k\left[1 - \mathbf{ln}\left(\sum_m \theta_m \psi_{mk}\right) - \sum_m \frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}}\right] \qquad (8)$$

Equation (8) also holds for $\ln\tau_k^i$. θ_m is the area fraction of group m, and the sums are over all different groups. X_m is the mole fraction of group m in the mixture;

$$\theta_m = \frac{Q_m x_m}{\sum_n Q_n x_n} \qquad (9)$$

$$x_m = \frac{\sum_j v_k^j x_j}{\sum_j \sum_n v_n^j x_j} \qquad (10)$$

The group-interaction parameter ψ_{mn} is given by; ψ_{mn}= exp -[(u_{mn}-u_{nm})/RT]= exp -(a_{mn}/T) (11)

Where u_{mn} is a measure of the energy of interaction between groups m and n. The group- interaction parameters a_{mn} must be evaluated from experimental phase-equilibrium data and $a_{mn} \neq a_{nm}$.

3. RESULT AND DISCUSSION

The liquid-liquid equilibria of water-propionic acid-solvent (benzyl alcohol, benzyl acetate and dibenzyl ether) ternary systems were predicted by means of UNIFAC Model. For this purpose, multivariable Newton-Raphson convergence procedure was used. Paremeters r_i and q_i and group-interaction parameters are taken from Reid et al., (1987). The experimental and model results are listed in Table 1-3.

Table 1. Phase Compositions For Water(1)-Propionic Acid(2)-Benzyl Alcohol(3) System at 298.15 K

Experimental						UNIFAC					
W_{11}	W_{21}	W_{31}	W_{13}	W_{23}	W_{33}	W_{11}	W_{21}	W_{31}	W_{13}	W_{23}	W_{33}
95.19	2.13	2.68	9.40	4.48	86.12	95.71	3.33	0.96	8.30	8.51	83.19
92.36	4.65	2.99	10.48	10.22	79.30	92.94	6.04	1.02	9.08	14.71	76.21
89.02	7.59	3.39	13.95	17.45	68.60	89.68	9.22	1.10	10.09	21.34	68.57
81.90	12.44	5.66	17.70	21.87	60.43	83.03	15.65	1.32	12.44	33.06	54.50
79.63	14.17	6.20	23.20	25.66	51.14	80.85	17.74	1.41	13.31	36.38	50.31

W_{i1} : weight fraction of i th component in the aqueous phase; W_{i3} : weight fraction of i th component in the solvent-rich phase

Table 2. Phase Compositions For Water(1)-Propionic Acid(2)-Benzyl Acetate(3) System at 298.15 K

Experimental						UNIFAC					
W_{11}	W_{21}	W_{31}	W_{13}	W_{23}	W_{33}	W_{11}	W_{21}	W_{31}	W_{13}	W_{23}	W_{33}
91.47	8.43	0.10	2.65	10.87	86.48	91.48	8.43	0.09	1.15	5.54	93.31
85.24	14.65	0.11	3.31	20.86	75.83	84.95	14.91	0.14	1.68	11.34	86.98
78.78	20.27	0.95	6.40	28.37	65.23	79.08	20.71	0.21	2.38	17.65	79.97
73.11	25.00	1.89	11.00	37.08	51.97	73.71	25.98	0.31	3.23	23.99	72.78
67.29	29.60	3.11	14.01	41.81	44.18	68.21	31.34	0.45	4.30	30.57	65.13

Table 3. Phase Compositions for Water(1)-Propionic Acid(2)-Dibenzyl Ether(3) System at 298.15 K

Experimental						UNIFAC					
W_{11}	W_{21}	W_{31}	W_{13}	W_{23}	W_{33}	W_{11}	W_{21}	W_{31}	W_{13}	W_{23}	W_{33}
92.01	7.89	0.10	1.16	5.39	93.45	92.06	7.93	0.01	1.21	3.38	95.41
83.85	16.05	0.10	1.60	11.78	86.62	83.89	16.08	0.03	1.51	7.29	91.20
73.63	26.25	0.12	1.90	18.02	80.08	73.69	26.30	0.01	1.94	12.57	85.49
68.21	31.68	0.11	3.00	25.21	71.79	68.26	31.72	0.02	2.21	15.37	82.42
58.36	40.65	0.99	4.01	29.20	66.79	58.69	41.23	0.08	2.69	20.18	77.13
45.69	50.16	4.15	6.53	38.13	55.34	46.80	52.81	0.39	3.36	26.22	70.42

The experimental data along with the LLE and calculated results represented in Figure 1-3 comparatively.

Figure 1 and 3 show that the difference between experimental and UNIFAC calculated data become important by increasing the propionic acid content in the mixture. In Figure 2 it can be seen that all data show the same difference for each tie-line. According to the agreement of liquid-liquid equilibrium characteristics of the ternary systems, it can be said that UNIFAC model can predict the equilibrium data of water-propionic acid-solvent systems with a reasonable accuracy.

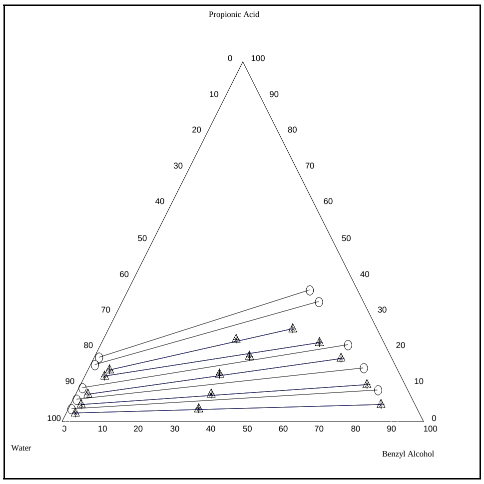

Figure 1. Liquid-Liquid Equilibria of Water-Propionic Acid-Benzyl Alcohol System at 298.15 K
— Δ — Experimental, – – 0 – – UNIFAC

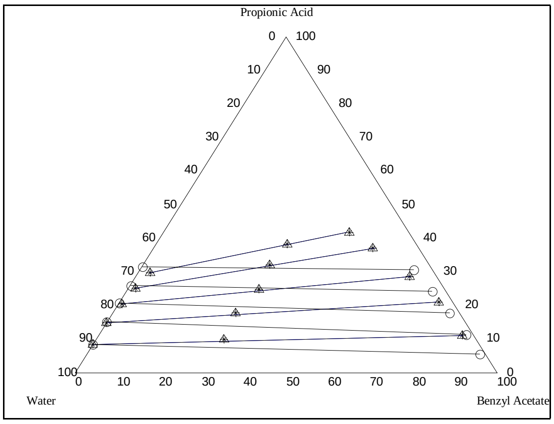

Figure 2. Liquid-Liquid Equilibria of Water-Propionic Acid-Benzyl Acetate System at 298.15 K —Δ— Experimental, – – 0 – – UNIFAC

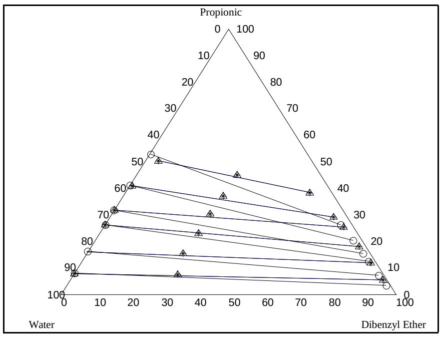

Figure 3. Liquid-Liquid Equilibria of Water-Propionic Acid-Dibenzyl Ether System at 298.15 K —Δ— Experimental, – – 0 – – UNIFAC

4. REFERENCES

Badakhshan, A., Chowdhury, A. I., Leung, R. 1985. Effect of Temperature on Liquid-Liquid Equilibria for Three Systems Containing Acetic Acid-Water-Toluene, Propionic Acid – Water - Cyclohexane, Propionic Acid-Water-Toluene at Atmospheric Pressure. J. Chem.Eng. Data. 30, 416-421.

Correa, J. M., Blanco, A. and Arce, A. 1989. Liquid-Liquid Equilibria for the System Water+Acetic Acid+Methtl Isopropyl Ketone between 25 and 55 °C. J.Chem.Eng.Data. (34), 415-419.

Fredenslund, A., Jones, R. L. and Prausnitz, M. 1975. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. AIChE Journal. 21 (6), 1086-1099.

Kyle, B. G. 1992. Chemical and Process Thermodynamics Second edition, ISBN 0-13-130030-X, Prentice Hall, Englewood Cliffs, New Jersey.

Lo, T. C., Baird, M. H. I., Hanson, C. 1991. Handbook of Solvent Extraction ISBN 0-89464-546-3, Krieger Publishing Company Malabar, Florida.

Magnussen, T., Rasmussen, P. And Fredenslund, A. 1981. UNIFAC Parameter Table for Prediction of Liquid-Liquid Equilibria. Ind. Eng. Chem. Process Des. Dev. 21, 331-339.

Reid, R. C., Prausnitz, J.M., Poling, B. E. 1987. The Properties of Gases and Liquids. 317-330. Fourth Edition, ISBN 0-07-051799-1, Mexico.

Solimo, H. N., Martinez, H. E., Riggio, R. 1989. Liquid-Liquid Extraction of Ethanol from Aqueous Solutions with Amyl Acetate, Benzyl Alcohol, and Methyl Isobutyl Ketone at 298.15 K. J. Chem.Eng.Data. 34, 176-179.

Solimo, H.N. and Arreguez, N. G. B. 1994. Liquid-Liquid Equilibria for Water + Ethanol + 2-Methylpropyl Ethanoate and Water + Ethanol + 1.2-Dibromoethane at 298.15 K. J. Chem. Eng. Data. (39), 8-11.