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

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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-PROPIONİK 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 gas by 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;

$$\ln \gamma_{i} = \ln \gamma_{i}^{C} + \ln \gamma_{i}^{R}$$
Combinatorial residual
(1)

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

$$l_{i} = \frac{z}{2}(r_{i} - q_{i}) - (r_{i} - 1)$$
(3)

$$\theta_{i} = \frac{q_{i}x_{i}}{\sum_{j} q_{j}x_{j}}$$
 (area fraction) (4)

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

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

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

The residual part is expressed by;

$$\ln \gamma_i^{\rm R} = \sum_k v_k^i \left(\ln \tau_k - \ln \tau_k^i \right) \tag{7}$$

 $ln\tau_k$ 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.

$$\ln \tau_{k} = Q_{k} \left[1 - \ln \left(\sum_{m} \theta_{m} \psi_{mk} \right) - \sum_{m} \frac{\theta_{m} \psi_{km}}{\sum_{n} \theta_{n} \psi_{nm}} \right]$$
(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;

$$\theta_{\rm m} = \frac{Q_{\rm m} x_{\rm m}}{\sum_{\rm n} Q_{\rm n} x_{\rm n}} \tag{9}$$

$$x_{m} = \frac{\displaystyle\sum_{j} v_{k}^{j} x_{j}}{\displaystyle\sum_{j} \displaystyle\sum_{n} v_{n}^{j} x_{j}}$$
(10)

The group-interaction parameter ψ_{mn} is given by; $\psi_{mn} = \exp -[(u_{mn}-u_{nm})/RT] = \exp -(a_{mn}/T)$ (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 acidsolvent (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 Com	positions For Wate	er(1)-Propionic	Acid(2)-Benzy	Alcohol(3) S	ystem at 298.15 K
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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

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