Thermochimica Acta, 164 (1990) 119–126
Elsevier Science Publishers B.V., Amsterdam

SIMULTANEOUS CORRELATION OF TERNARY VAPOUR–LIQUID AND LIQUID–LIQUID EQUILIBRIA

ISAMU NAGATA

Department of Chemical Engineering, Division of Physical Sciences, Kanazawa University, Kodatsuno 2, Kanazawa, Ishikawa 920 (Japan)

(Received 15 November 1989)

ABSTRACT

Ternary vapour–liquid equilibria (VLE) and liquid–liquid equilibria (LLE) for four systems are calculated using the UNIQUAC model in three cases: (1) binary parameters alone; (2) binary parameters plus ternary parameters obtained from only ternary LLE; and (3) binary parameters plus ternary parameters obtained from both ternary LLE and VLE. The most satisfactory results are obtained in case 3.

INTRODUCTION

Common activity coefficient equations based on the local composition concept contain only parameters due to the interactions between binary pairs of molecules and do not include any ternary parameters. These equations work considerably well for predicting ternary vapour–liquid equilibria (VLE) on the basis of binary data alone. On the contrary, the equations have difficulties in the prediction of ternary liquid–liquid equilibria (LLE), which imposes a severe test on the ability of solution models. In a ternary mixture there is an interaction among three unlike molecules. Hence, the original UNIQUAC model was modified to include three ternary parameters ascribed to the unlike ternary interaction [1]. When a ternary mixture degenerates to a binary, these ternary terms vanish. The newly modified UNIQUAC model greatly improves the correlation of ternary LLE for various ternary mixtures.

This paper presents some results obtained in the simultaneous correlation of ternary VLE and LLE for selected mixtures containing two completely miscible binaries and one partially miscible binary.

0040-6031/90/$03.50 © 1990 – Elsevier Science Publishers B.V.

SOLUTION MODEL

A modification of the UNIQUAC model [1] gives the ternary excess molar Gibbs energy and the activity coefficient of component 1 as follows

$$\frac{g^{\mathrm{E}}}{RT} = \sum_i^3 x_i \ln\frac{\Phi_i}{x_i} - \frac{Z}{2}\sum_i^3 q_i x_i \ln\frac{\Phi_i}{\theta_i} \tag{1}$$
$$- q_1' x_1 \ln(\theta_1'\tau_{11} + \theta_2'\tau_{21} + \theta_3'\tau_{31} + \theta_2'\theta_3'\tau_{231})$$
$$- q_2' x_2 \ln(\theta_1'\tau_{12} + \theta_2'\tau_{22} + \theta_3'\tau_{32} + \theta_1'\theta_3'\tau_{132})$$
$$- q_3' x_3 \ln(\theta_1'\tau_{13} + \theta_2'\tau_{23} + \theta_3'\tau_{33} + \theta_1'\theta_2'\tau_{123})$$

$$\ln \gamma_1 = \ln\frac{\Phi_1}{x_1} + 1 - \frac{\Phi_1}{x_1} - \left(\frac{Z}{2}\right) q_1 \left(\ln\frac{\Phi_1}{\theta_1} + 1 - \frac{\Phi_1}{\theta_1}\right) \tag{2}$$
$$- q_1' \ln(\theta_1'\tau_{11} + \theta_2\tau_{21} + \theta_3\tau_{31} + \theta_2\theta_3\tau_{231})$$
$$- q_1' \left[\theta_1' \frac{\tau_{11} - \theta_2'\theta_3'\tau_{231}}{\sum_J^3 \theta_j'\tau_{j1} + \theta_2'\theta_3'\tau_{231}} + \theta_2' \frac{\tau_{12} + (\theta_3' - \theta_1'\theta_3')\tau_{132}}{\sum_J^3 \theta_j'\tau_{j2} + \theta_1'\theta_3'\tau_{132}}\right.$$
$$\left. + \theta_3' \frac{\tau_{13} + (\theta_2' - \theta_1'\theta_2')\tau_{123}}{\sum_J^3 \theta_j'\tau_{j3} + \theta_1'\theta_2'\tau_{123}}\right]$$

where Z is the coordination number taken as 10. The segment fraction Φ_i, the surface fractions θ_i and θ_i', and the binary parameters, τ_{ij}, are expressed by

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{3}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{4}$$

$$\theta_i' = \frac{q_i' x_i}{\sum_j q_j' x_j} \tag{5}$$

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{T}\right) \tag{6}$$

τ_{231}, τ_{132} and τ_{123} are ternary parameters to be obtained from ternary experimental phase equilibrium data.

CALCULATED RESULTS AND DISCUSSION

Binary systems

The molecular structure constants of the pure components, r, q and q', were taken from ref. 2 and are shown in Table 1. The value of q' for

TABLE 1

Molecular structure constants for pure components

Component	r	q	q'
Acetonitrile	1.87	1.72	0.95
Benzene	3.19	2.40	2.40
n-Butanol	3.45	3.05	0.88
Ethanol	2.11	1.97	0.92
Ethyl acetate	3.48	3.12	3.12
n-Heptane	5.17	4.40	4.40
Methanol	1.43	1.43	0.96
n-Propanol	2.78	2.51	0.89
Water	0.92	1.40	1.00

acetonitrile was obtained empirically to give better agreement with ternary LLE for mixtures containing acetonitrile [3]. Binary VLE and mutual solubility data were used to obtain the UNIQUAC parameters. The computer program used for VLE data reduction is similar to that described by Prausnitz et al. [2], minimizing the objective function given by

$$F_1 = \sum_{i=1}^{N} \left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{1i} - \hat{x}_{1i})^2}{\sigma_x^2} + \frac{(y_{1i} - \hat{y}_{1i})^2}{\sigma_y^2} \right] \tag{3}$$

where the standard deviations are as follows; $\sigma_P = 1$ Torr for pressure; $\sigma_T = 0.05$ K for temperature; $\sigma_x = 0.001$ and $\sigma_y = 0.003$ for compositions. The binary parameters from the mutual solubilities were obtained by solving equations of isoactivity in two-liquid phases for components. The parameters are given in Table 2 and are used to calculate ternary LLE and VLE.

Ternary systems

For the simultaneous correlation of ternary LLE and VLE the following objective functions were used to obtain the ternary UNIQUAC parameters τ_{231}, τ_{132} and τ_{123}

$$F_2 = \sum_{k}^{M} \min \sum_{i}^{3} \sum_{j}^{2} (x_{ijk} - \hat{x}_{ijk})^2 + \sum_{m}^{N} \left(\frac{P_m - \hat{P}_m}{P_m} \right)^2 + \sum_{m}^{N} \sum_{n}^{3} (y_{mn} - \hat{y}_{mn})^2 \tag{4}$$

$$F_3 = \sum_{k}^{M} \min \sum_{i}^{3} \sum_{j}^{2} (x_{ijk} - \hat{x}_{ijk})^2 + \sum_{m}^{N} \left(\frac{T_m - \hat{T}_m}{T_m} \right)^2 + \sum_{m}^{N} \sum_{n}^{3} (y_{mn} - \hat{y}_{mn})^2 \tag{5}$$

where a circumflex represents the calculated value and min denotes minimum values. F_2 is for ternary LLE and isothermal VLE data and F_3 for ternary LLE and isobaric VLE data. Ternary phase equilibrium calculations

TABLE 2

Binary calculated results derived from phase equilibrium data reduction

System (1–2)	Type [a]	Number of data points	Temp. (°C)	UNIQUAC parameters		Root-mean-square deviations				Variance of fit [b]	Reference
				a_{12} (K)	a_{21} (K)	δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)		
Acetonitrile–benzene	VL	45	20	−101.78	448.89	0.74	0.01	0.6	4.2	10.27	[4]
Acetonitrile–*n*-heptane	MS	45	1	6.924	1502.7						[5]
Benzene–*n*-heptane	VL	15	45	19.07	31.35 [c]					1.77	[5]
Ethanol–*n*-butanol	VL	12	80–115	364.39	−197.11	0.55	0.04	0.7	5.0	5.10	[6]
Ethanol–ethyl acetate	VL	14	40	−148.29	594.60 [c]					3.09	[7]
Methanol–*n*-butanol	VL	21	25	295.88	−67.50	0.47	0.00	0.1	1.0	0.37	[8]
Water–*n*-butanol	MS	1	25	958.78	50.60						[9]
Water–*n*-butanol	MS	1	30	997.41	43.85						[9]
Water–ethanol	VL	10	25	164.24	49.20	0.67	0.00	1.3	5.7	7.22	[10]
Water–ethyl acetate	MS	1	40	58.58	618.91						[7]
Water–methanol	VL	10	25	167.17	−130.79	0.85	0.00	0.5	3.7	3.16	[10]

[a] VL, vapour–liquid equilibria; MS, mutual solubilities.

[b] Variance of fit = (sum of squared, weighted residuals)/(number of degrees of freedom) = F_1/(number of data points − number of parameters).

[c] Taken from ref. 2.

were performed using three different methods: method I correlates both LLE and VLE data simultaneously; method II correlates only LLE data and obtained ternary parameters are used to calculate VLE; method III predicts LLE and VLE using the binary parameters given in Table 2 without any ternary parameters. The ternary parameters were obtained for four systems and are listed in Table 3. An optimum-parameter searching program is based on the simplex method [14]. The ternary calculated results are given in Table 4 and are compared with the experimental results in Fig. 1. Table 4 shows that the calculated LLE based on binary data alone are not satisfactory (method III) and the best correlation of ternary LLE data is obtained by method II, which sometimes gives a little worse prediction of VLE than those of method III. For the acetonitrile–benzene–*n*-heptane system, meth-

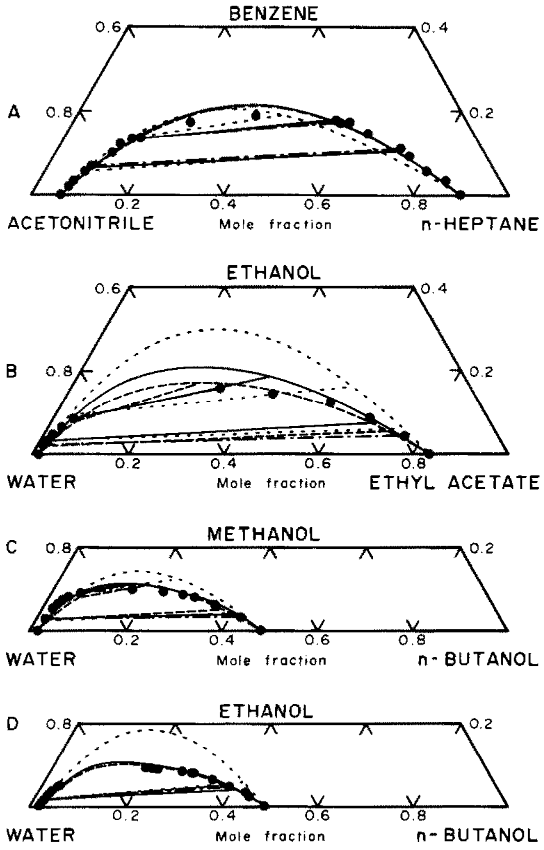

Fig. 1. Calculated and experimental liquid–liquid equilibria: A, acetonitrile–benzene–*n*-heptane at 45°C [5]; B, water–ethanol–ethyl acetate at 40°C [7]; C, water–methanol–*n*-butanol at 30°C [12]; D, water–ethanol–*n*-butanol at 25°C [13]. ●–·–●, Experimental tie-line. Calculated: - - -, based on binary data alone; — — —, fitted to ternary LLE data only; ———, fitted to both ternary LLE and VLE data.

TABLE 3

Ternary constants

System	Temp. (°C)	Number of data points	Method [a]	Ternary parameters			Reference
				τ_{231}	τ_{132}	τ_{123}	
Acetonitrile(1) -benzene(2) -*n*-heptane(3)	45 [b]	9 [b]	I	−0.1177	0.1825	0.0652	[5] [b]
	45 [c]	51 [c]	II	−0.0991	−0.1427	0.3993	[5] [c]
Water(1) -ethanol(2) -ethyl acetate(3)	40	5	I	0.0003	0.7756	0.3120	[7]
	40	8	II	0.0002	1.5703	0.6051	[7]
Water(1) -methanol(2) -*n*-butanol(3)	30	6	I	−4.1029	6.2153	−0.6188	[11]
	85–92	24	II	−0.1141	1.1137	0.1753	[12]
Water(1) -ethanol(2) -*n*-butanol(3)	25	10	I	−3.9887	10.681	−0.6611	[13]
	85–93	21	II	−3.7566	12.292	−0.5948	[12]

[a] Method I correlates both ternary LLE and VLE data. Method II correlates only ternary LLE data.

[b] Ternary LLE data.

[c] Ternary VLE data.

ods I and II give nearly the same results. For the other systems, method I yields the highest accuracy of vapour-phase mole fraction.

LIST OF SYMBOLS

a_{ij}	UNIQUAC binary interaction parameter related to τ_{ij}
F	objective function
g^E	excess molar Gibbs energy
P	total pressure
q_i	molecular-geometric area parameter for pure component i
q_i'	molecular-interaction area parameter for pure component i
r_i	molecular-geometric volume parameter for pure component i
R	universal gas constant
T	absolute temperature
x_i	liquid-phase mole fraction of component i
y_i	vapour-phase mole fraction of component i
Z	lattice coordination number, here equal to 10

Greek letters

γ_i	activity coefficient of component i
θ_i	area fraction of component i in combinatorial contribution

TABLE 4

Ternary calculated results

System	Data type	Property	Method I [a]		Method II [b]		Method III [c]	
			AAM [d]	RMS [e]	AAM	RMS	AAM	RMS
Acetonitrile(1)	LLE	δx [f]		0.79		0.81		3.06
–benzene(2)	VLE	δP(Torr)	2.36	3.82	2.93	4.43	4.69	6.61
–*n*-heptane(3)		$\delta y_1(\times 10^3)$	5.75	7.17	5.53	7.03	7.78	9.72
		$\delta y_2(\times 10^3)$	3.99	4.82	3.36	4.08	4.48	5.76
		$\delta y_3(\times 10^3)$	3.61	5.28	4.78	6.28	7.27	8.74
		Av. $\delta y(\times 10^3)$	4.45	5.76	4.56	5.80	6.51	8.07
Water(1)	LLE	δx		2.09		0.72		6.55
–ethanol(2)	VLE	δP(Torr)	8.88	12.45	18.74	20.98	14.06	17.87
–ethyl acetate(3)		$\delta y_1(\times 10^3)$	14.23	16.89	20.81	22.21	28.61	19.07
		$\delta y_2(\times 10^3)$	10.80	15.24	21.93	26.08	21.65	28.27
		$\delta y_3(\times 10^3)$	17.40	23.27	27.81	32.87	42.00	63.57
		Av. $\delta y(\times 10^3)$	14.10	18.47	23.52	27.05	30.75	36.97
Water(1)	LLE	δx		0.55		1.04		2.25
–methanol(2)	VLE	δT(°C)	0.57	0.70	1.24	1.47	0.79	0.96
–*n*-butanol(3)		$\delta y_1(\times 10^3)$	8.45	10.19	24.05	25.38	11.63	13.44
		$\delta y_2(\times 10^3)$	7.38	8.31	16.28	19.33	8.66	10.30
		$\delta y_3(\times 10^3)$	12.31	15.22	12.78	17.54	11.79	15.54
		Av. $\delta y(\times 10^3)$	9.38	11.24	17.70	20.75	10.69	13.09
Water(1)	LLE	δx		0.44		0.35		3.89
–ethanol(2)	VLE	δT(°C)	0.60	0.77	0.98	1.18	0.37	0.53
–*n*-butanol(3)		$\delta y_1(\times 10^3)$	9.35	11.03	9.72	13.27	12.22	13.89
		$\delta y_2(\times 10^3)$	5.97	7.66	13.30	15.14	4.61	7.03
		$\delta y_3(\times 10^3)$	13.35	16.82	13.50	17.14	12.73	15.93
		Av. $\delta y(\times 10^3)$	9.56	11.84	12.17	15.18	9.85	12.28

[a] Correlates both ternary LLE and VLE data.

[b] Correlates only ternary LLE data.

[c] Uses the binary parameters listed in Table 2.

[d] Absolute arithmetic mean deviation between the experimental values and calculated results.

[e] Root-mean-square mean deviation.

[f] Given by $100\left[\sum_{k} \min \sum_{i} \sum_{j} (x_{ijk} - \hat{x}_{ijk})^2/6M\right]^{0.5}$, $i = 1, 2, 3$; $j =$ I, II; $k = 1, \ldots, M$.

	to the excess molar Gibbs energy
θ_i'	area fraction of component i in residual contribution to the excess molar Gibbs energy
σ_P, σ_T, σ_x, σ_y	standard deviations for the pressure, temperature, liquid composition and vapour composition measurements, respectively
τ_{ij}	UNIQUAC binary parameter
τ_{ijk}	UNIQUAC ternary parameter
Φ_i	segment fraction of component i

REFERENCES

1 I. Nagata and Y. Usui, Thermochim. Acta, 140 (1989) 121.
2 J.M. Prausnitz, T.F. Anderson, E.A. Grens, C.A. Eckert, R. Hsieh and J.P. O'Connell, Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice–Hall, Englewood Cliffs, NJ, 1980.
3 I. Nagata and S. Nakamura, J. Chem. Thermodyn., 17 (1985) 1103.
4 G. Werner and H. Schuberth, J. Prakt. Chem., 31 (1966) 225.
5 D.A. Palmer and B.D. Smith, J. Chem. Eng. Data, 17 (1972) 71.
6 L. Gay, Chim. Ind. (Milan), 18 (1927) 187.
7 I. Mertl, Collect. Czech. Chem. Commun., 37 (1972) 366.
8 J. Polak, S. Murakami, H.D. Pflug and G.C. Benson, Can. J. Chem., 48 (1970) 2457.
9 J.M. Sørensen and W. Arlt, Liquid–Liquid Equilibrium Data Collection, Binary Systems, Chemistry Data Series Vol. V, Part 1, DECHEMA, Frankfurt am Main, 1979.
10 D.J. Hall, C.J. Mash and R.C. Pemberton, NPL Report Chem. No. 95, January 1979 (U.K. National Physical Laboratory, Division of Chemistry Standards).
11 A.J. Mueller, L.I. Pugsley and J.B. Ferguson, J. Phys. Chem., 35 (1931) 1314.
12 D.M.T. Newsham and N. Vahdat, Chem. Eng. J., 13 (1977) 27.
13 V.P. Solomko, V.D. Panasyuk and A.M. Zelenskaya, Zh. Prikl. Khim. (Leningrad), 35 (1962) 628.
14 J.A. Nelder and R. Mead, Computer J., 8 (1965) 308.