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AN EMPIRICAL METHOD TO CORRELATE AND PREDICT SOLUTE DISTRIBUTION IN TERNARY LIQUID-LIQUID SYSTEMS

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Abstract - This paper presents a method that combines activity coefficient models with Hand's equation for tie lines. The proposed method calculates solute distribution in liquid-liquid ternary systems. The combination improves the calculated solute distributions using activity coefficient models while Hand's equation gives a good correlation of the experimental tie lines. The method could be used to extrapolate experimental information.
Keywords: liquid-liquid equilibrium, distribution coefficients, UNIQUAC, UNIFAC, Hand.

INTRODUCTION

Prediction and correlation of ternary liquid-liquid equilibrium is important in chemical engineering applications, such as extraction and heterogeneous azeotropic distillation. Several methods of equilibrium data correlation/prediction have been presented in the literature. A series of articles (Sørensen et al., 1979a, 1979b; Magnussen et al., 1980) gives an excellent review of experimental data sources, correlation models and prediction methods. Basically, there are two approaches to correlating data. One of them uses equality of activity with a model for the activity coefficient; the other correlates data with equations such as that of Hand (Treybal, 1963). For practical utilization of equilibrium data in calculations of separation processes, sometimes it is convenient to describe equilibrium in terms of the distribution coefficients for each component. As the distribution coefficients are composition-dependent, they are normally represented as polynomials (Rod, 1976).

In previous work (Mandagarán and Campanella, 2001), the two approaches to correlating data were combined in a way that the resulting method for calculating distribution coefficients produces results that improve results obtained with UNIQUAC. In this article we present results obtained by applying the proposed mixed method to a wide range of ternary systems.

MODELS AND METHOD

Hand's method is a well-known empirical correlation for tie lines in liquid-liquid equilibrium (Treybal, 1963). Consisting of a molar fraction and a natural logarithm, Hand's equation is given by

$$\ln (y_2/y_1) = k \ln (x_2/x_3) + C \qquad (1)$$

where component 2 is the solute, y_i is the composition of component i in the phase rich in component 1, x_i is the composition of component i in

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the phase rich in component 3, and k and C are ternary-system-dependent constants.

Another way to calculate liquid-liquid equilibrium is using the equality of chemical potentials for each component in both phases. The equality is normally rewritten in terms of activities. Using a model for the activity coefficients calculations can be carried out to obtain liquid-liquid compositions (Sørensen et al., 1979b). Two models were used in our calculations: UNIQUAC (Abrams and Prausnitz, 1975) and UNIFAC (Fredenslund et al., 1975). The data, equations, parameters and programs were taken from Sørensen and Arlt (1980) and Magnussen et al. (1981).

To obtain the distribution coefficients, mi, we combined Hand's equation and activity coefficient models in the following way:

1) k and C constants of Hand's equation (Eqn. 1) were obtained using experimental liquid-liquid ternary equilibrium data.
2) The binodal curve of the ternary system under study was obtained using an activity coefficient model.
3) x_1 and x_3 were obtained from the binodal curve calculated in step 2 using a chosen value of x_2.
4) y_2/y_1 was obtained using Eqn. 1 with x_2/x_3 , k and C from previous steps.
5) y_1,y_2 and y_3 were calculated with y_2/y_1 and the binodal curve was calculated in step 2.
6) $mi = y_i / x_i$ was computed.

RESULTS AND DISCUSSIONS

Tables 1 and 2 contain the systems studied in this work. The type of mixture, reference and temperature are recorded in the tables. The systems under study listed in Table 1 encompasses ternary mixtures with and without water, with one or two inmiscible binaries. The systems under study listed in Table 2 have inusual binodal curve and/or tie lines. Tables 1 and 2 and Figures 1 through 8 compare and display results from the calculations described in item Models and Method. In the last column of Tables 1 and 2 calculated distribution coefficients for the solute, component 2, are shown quantitatively. The last column in the tables reflects the agreement between the model/method and the experimental data. The first model in the list is the one that shows the best agreement with the experiments. The numbers in parenthesis are average absolute relative deviations.

As expected, correlation of data (UNIQUAC) is better than prediction (UNIFAC) for phase envelope and tie-line determination. Those results are not shown in Tables 1 and 2. In addition, depending on the system, results from UNIQUAC belong to different sets of parameters (Sørensen and Arlt, 1980). The parameters are "specific" (SP) when they are fitted to one particular system. The parameters are "common" (CO) when they are determined by simultaneous correlation of experimental data from different systems. The values of the specific parameters used are from Sørensen and Arlt (1980), Table 1 indicates the pages where to find them. Table 3 displays the common parameters used in this work. In Tables 1 and 2 it is possible to observe under the last heading that the calculation method that combines UNIQUAC with Hand´s correlation gives better coefficient distributions than the one calculated using UNIQUAC alone. In some cases the combination UNIFAC plus Hand is even better than correlation of data using UNIQUAC.

To get a better picture of the agreement, results for one representative system in Table 1(1-Butanol(1)/Acetic Acid(2)/Water(3), system nº 4) are shown in Figures 1 to 4. In Figure 1 Hand´s correlation is shown graphically for several systems in Table 1, including 1-Butanol(1)/Acetic Acid(2)/Water(3). Figure 2 shows experimental, UNIQUAC and UNIFAC results. Figure 3 shows several tie lines. The tie lines are from experimental data, UNIQUAC with specific parameters and UNIFAC. In Figures 2 and 3 it is possible to observe the fact that UNIQUAC better represents the binodal curve of liquid-liquid equilibrium in ternary mixtures than the corresponding tie lines. For many cases in Table 1, the fact that binodal representation is better than tie-line representation is true for UNIFAC too. The association of Hand with UNIQUAC/UNIFAC proposed in this paper is based on those observations. Figure 4 displaying acetic acid concentrations in the 1-Butanol-rich phase and in the water-rich phase shows that a combination of UNIQUAC with Hand gives better results than UNIQUAC with specific parameters.

Figures 5 to 8 display results identical to those in Figures 1 to 4. The results shown in Figures 5 to 8 are representative of results obtained for the systems in Table 2. Figure 5 illustrates Hand's correlation graphically for several systems in Table 2, including Water(1)/1-Propanol(2)/Diphenylether(3) (system nº 13 in Table 2). Figure 6 shows the phase envelope for Water(1)/1-Propanol(2)/Diphenylether(3). Figure 7 displays tie lines for the same system. Figures 6 and 7 show results for experimental, UNIQUAC with specific parameters, and UNIQUAC with common parameters. Figure 8 displays 1-Propanol

concentrations in both phases; here UNIQUAC with specific parameters gives better results than it does when combined with Hand. This last situation is similar for many systems in Table 2. For the Hand plus UNIQUAC/UNIFAC combination to work, Hand's equation must correlate data very well. The value of r for the correlation, written in a column in Tables 1 and 2, indicates how good the correlation is. When the value of r is larger than 0.98, Hand provides a good correlation of the tie lines, as can be seen in Figure 1 for the systems in Table 1 and in Figure 5 for the systems in Table 2. Then, when r is larger than 0.98, the combination of models (Hand + UNIQUAC) gives better results than UNIQUAC alone. A way to improve the method for the systems in Table 2 is by replacing the linear correlation of Hand's equation by a nonlinear correlation, as suggested by Carniti et al. (1978) for a more correct extrapolation for estimating the location of the plait point.

The proposed combination seems to work because it uses the best of the approaches cited earlier in this work. The orientation of the tie-lines is set by Hand's equation and the binodal curve is set by UNIQUAC/UNIFAC. It is to be expected that the proposed method will work better in cases where tie line differences between UNIQUAC and experiments are larger. Also, we could use the proposed combination to obtain improved distribution coefficients, which in a later step are fitted with polynomials, as recommended in the literature (Rod, 1976). The combination works even when the available experimental information is minimal, allowing for extrapolation of data. The minimum experimental data required for the combination to work is the two tie lines that are needed to obtain Hand's parameters k and C in Eqn. 1.

Table 1: Model performance for several ternary systems

N°	System	Type	Temperature (K)	Reference	Hand's Correlation (r)	m_2 Calculation Performance[a)]
1	Water (1) Ethanol (2) Hexane (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.364	0.9911	UNIQUAC SP+Hand (7.5) UNIFAC+Hand (7.7) UNIQUAC SP (16.3) UNIFAC (58.3)
2	1 – Butanol (1) Ethanol (2) Water (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.340	0.9911	UNIQUAC SP+Hand (4.7) UNIQUAC SP (6.5) UNIFAC+Hand (13.7) UNIFAC (35.4)
3	Water (1) Ethanol (2) Benzene (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.350	0.9999	UNIQUAC SP+Hand (1.8) UNIQUAC SP (6.5) UNIFAC+Hand (3.4) UNIFAC (8.7)
4	1 – Butanol (1) Acetic Acid (2) Water (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.227	0.9995	UNIQUAC SP+Hand (2.2) UNIQUAC SP (3.1) UNIFAC (9.2) UNIFAC+Hand (13.9)
5	Water (1) 1,2 – Ethanediol (2) Formic Acid, Ethyl Ester (3)	2	303.15	Sørensen and Arlt, 1980 Vol.5/2, p.417	0.9823	UNIQUAC CO+Hand (14.9) UNIQUAC CO (96.8)
6	Ethane, 1,2– Dichloro (1) 2 – Propanol (2) Water (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.207	0.9850	UNIQUAC SP (6.1) UNIQUAC SP+Hand (11.9) UNIFAC+Hand (14.4) UNIFAC (97.1)
7	1 – Hexanol (1) Methane, Nitro (2) Water (3)	2	313.15	Sørensen and Arlt, 1980 Vol.5/2, p.71	0.9244	UNIQUAC SP (10.3) UNIQUAC SP+Hand (31.4)
8	Hexane (1) 2- Propanone (2) Water (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.487	0.9995	UNIQUAC SP+Hand (1.2) UNIFAC+Hand (2.0) UNIQUAC SP (4.9) UNIFAC (18.3)

Continuation Table 1

9	Acetic Acid, Ethyl Ester (1) Acetic Acid (2) Water (3)	1	303.15	Sørensen and Arlt, 1980 Vol.5/2, p.220	0.9997	UNIQUAC SP+Hand (1.4) UNIQUAC SP (1.9) UNIFAC+Hand (6.4) UNIFAC (37.4)
10	Ethane, 1,1,2 – Trichloro (1) 2 – Propanone (2) Water (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.167	0.9997	UNIQUAC SP (1.8) UNIQUAC SP+Hand (2.0) UNIFAC+Hand (2.0) UNIFAC (4.4)
11	Ethane, 1,1,2 – Trichloro (1) 2- Butanone (2) Water (3)	2	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.168	0.9911	UNIQUAC SP (2.5) UNIQUAC SP+Hand (7.1) UNIFAC+Hand (7.1) UNIFAC (9.3)
12	Water (1) Acetic Acid (2) Aniline, N,N– Dimethyl (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.301	0.9789	UNIQUAC SP+Hand (2.6) UNIQUAC SP(7.8)
13	Benzene (1) 2 – Propanone (2) Water (3)	1	293.15	Sørensen and Arlt, 1980 Vol.5/2, p.481	0.9997	UNIQUAC SP+Hand (1.5) UNIQUAC SP (3.0) UNIFAC+Hand (4.5) UNIFAC (15.9)
14	Water (1) Formic Acid (2) Benzene (3)	2	303.15	Sørensen and Arlt, 1980 Vol.5/2, p.54	0.9986	UNIQUAC SP+Hand (1.9) UNIFAC+Hand (1.9) UNIQUAC SP (7.6) UNIFAC (29.5)
15	Heptane (1) Benzene (2) Diethylene Glycol (3)	1	423.15	Sørensen and Arlt, 1980 Vol.5/3 p.163	0.9943	UNIQUAC SP+Hand (3.9) UNIQUAC SP (3.5) UNIFAC+Hand (4.9) UNIFAC (35.1)
16	Heptane (1) Toluene (2) Diethylene Glicol (3)	2	298.15	Sørensen and Arlt, 1980 Vol.5/3 p.165	0.9925	UNIQUAC SP+Hand (6.0) UNIFAC+Hand (6.1) UNIQUAC SP (6.5) UNIFAC (6.8)
17	Decane (1) 1-Octanol (2) Diethylene Glicol (3)	1	293.15	Sørensen and Arlt, 1980 Vol.5/3 p.172	0.9951	UNIQUAC SP+Hand (8.0) UNIFAC+Hand (8.1) UNIQUAC SP (12.3) UNIFAC (51.1)
18	Heptane (1) Benzene (2) Methanol (3)	1	286.95	Sørensen and Arlt, 1980 Vol.5/2, p.119	0.9975	UNIQUAC SP+Hand (1.7) UNIQUAC SP (1.7) UNIFAC+Hand (8.4) UNIFAC (18.5)
19	Heptane (1) Hexane (2) Methanol (3)	2	305.95	Sørensen and Arlt, 1980 Vol.5/2, p.133	0.9707	UNIQUAC SP (2.7) UNIFAC+Hand (4.1) UNIQUAC SP+Hand (8.3) UNIFAC (21.6)

a) m_2 = distribution coefficient of component 2 = y_2/x_2 , SP=specific parameter
CO=common parameter, in parenthesis (Absolute Average Deviation %).

Table 2: Model performance for several ternary systems with unusual behavior

N°	System	Type	Temperature (K)	Reference	Hand's Correlation (r)	m_2 Calculation Performance[a)]
1	Acetic acid, ethyl ester (1) 1-Butanol (2) Water (3)	2	293.15	Sørensen and Arlt, 1980 Vol.5/3, p.50	0.985	UNIQUAC SP(12.4) UNIFAC+Hand (14.6) UNIQUAC SP+Hand (15.7) UNIFAC (26.1)
2	Hypochlorous acid, tertbutyl ester (1) 2-propanol, 2-methyl (2) Water (3)	1	333.15	Sørensen and Arlt, 1980 Vol.5/3, p.101	0.9744	UNIQUAC SP+Hand (27.5) UNIQUAC SP (35.4)
3	Water (1) Morpholine (2) Benzene (3)	1	293.15	Sørensen and Arlt, 1980 Vol.5/3, p.105	0.9948	UNIQUAC SP+Hand (1.6) UNIQUAC SP (7.8)
4	Water (1) Etanol, 2-ethoxy (2) Styrene (3)	1	293.15	Sørensen and Arlt, 1980 Vol.5/3, p.157	0.9817	UNIQUAC SP+Hand (5.8) UNIFAC+Hand (5.8) UNIQUAC SP (7.4) UNIFAC (79.3)
5	Benzene (1) Pyridine (2) Water (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/3, p.228	0.9793	UNIQUAC SP+Hand (6.1) UNIFAC+Hand (6.2) UNIQUAC SP (8.2) UNIFAC (10.3)
6	Heptane (1) Toluene (2) Diethylene glycol (3)	2	298.15	Sørensen and Arlt, 1980 Vol.5/3, p.165	0.9925	UNIQUAC SP+Hand (6.0) UNIFAC+Hand (6.2) UNIQUAC SP (6.5) UNIFAC (6.8)
7	Water (1) Formic acid (2) 2-Pentanol, 4-methyl (3)	1	303.15	Sørensen and Arlt, 1980 Vol.5/2, p.60	0.9963	UNIQUAC SP (5.9) UNIQUAC SP+Hand (6.1) UNIFAC+Hand (17.2) UNIFAC (212.1)
8	Hexadecanoic acid, methyl ester (1) 9-octadecenoic acid(cis), methyl ester (2)	2	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.200	0.8437	UNIQUAC CO (2.3) UNIQUAC CO+Hand (14.6)
9	Water (1) Ethanol (2) Heptane (3)	1	303.15	Sørensen and Arlt, 1980 Vol.5/2, p.376	0.8768	UNIQUAC SP+Hand (31.0) UNIFAC+Hand (31.9) UNIQUAC SP (235.0) UNIFAC (258.6)
10	Propanoic acid, nitrile (1) Heptane (2) Octane, 1,8-oxy, Perfluoro (3)	2	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.460	0.8696	UNIQUAC SP (6.7) UNIQUAC SP+Hand (37.0)
11	1-Propanol, 2-methyl (1) Propanal (2) Water (3)	2	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.461	0.9916	UNIQUAC SP+Hand (9.1) UNIFAC+Hand (9.2) UNIQUAC SP (58.8) UNIFAC (170.1)
12	Water (1) 1-Propanol (2) Heptane (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.584	0.9429	UNIQUAC SP (14.9) UNIQUAC SP+Hand (15.1) UNIFAC+Hand (15.6) UNIFAC (86.3)
13	Water (1) 1-Propanol (2) Ether diphenyl (3)	1	298.15	Sørensen and Arlt, 1980 Vol.5/2, p.587	0.8615	UNIQUAC SP(3.1) UNIQUAC SP+Hand (55.9)
14	1-Hexanol (1) Methane, nitro (2) Water (3)	2	313.15	Sørensen and Arlt, 1980 Vol.5/2, p.71	0.9348	UNIQUAC SP (10.3) UNIQUAC SP+Hand (31.4)

b) m_2 = distribution coefficient of component 2 = y_2/x_2 , SP=specific parameter, CO=common parameter, in parenthesis (Absolute Average Deviation %).

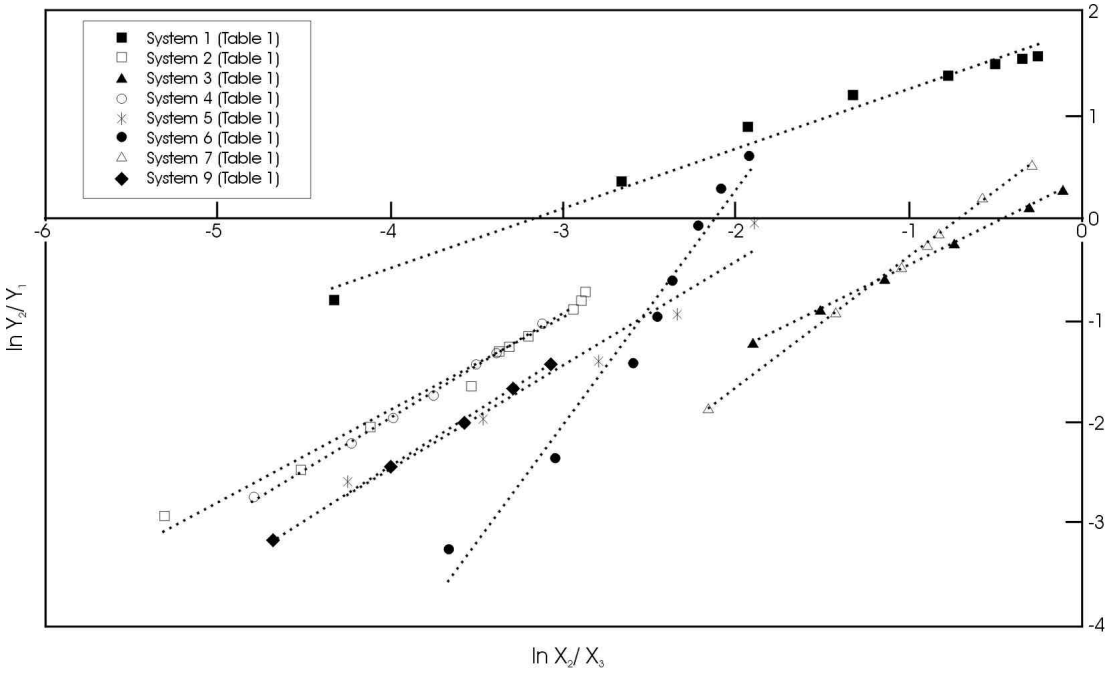

Figure 1: Representation of Hand's correlation for some systems in Table 1.

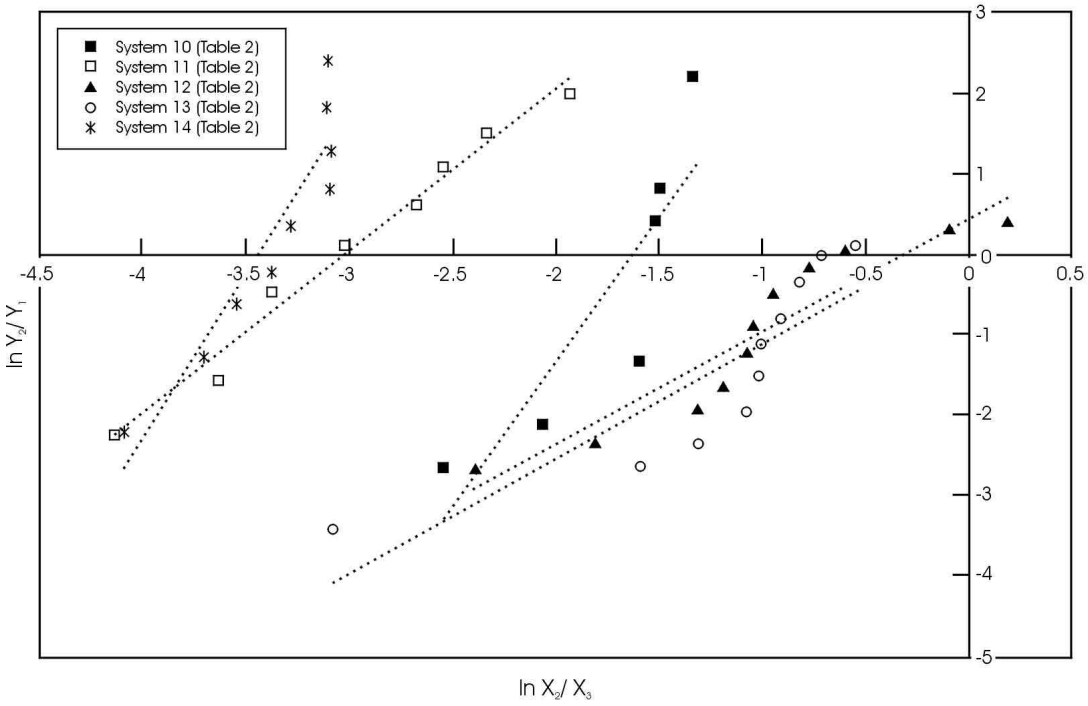

Figure 2: Binodal curve for 1-Butanol(1)-Acetic Acid(2)-Water(3). System nº2 in Table 1.

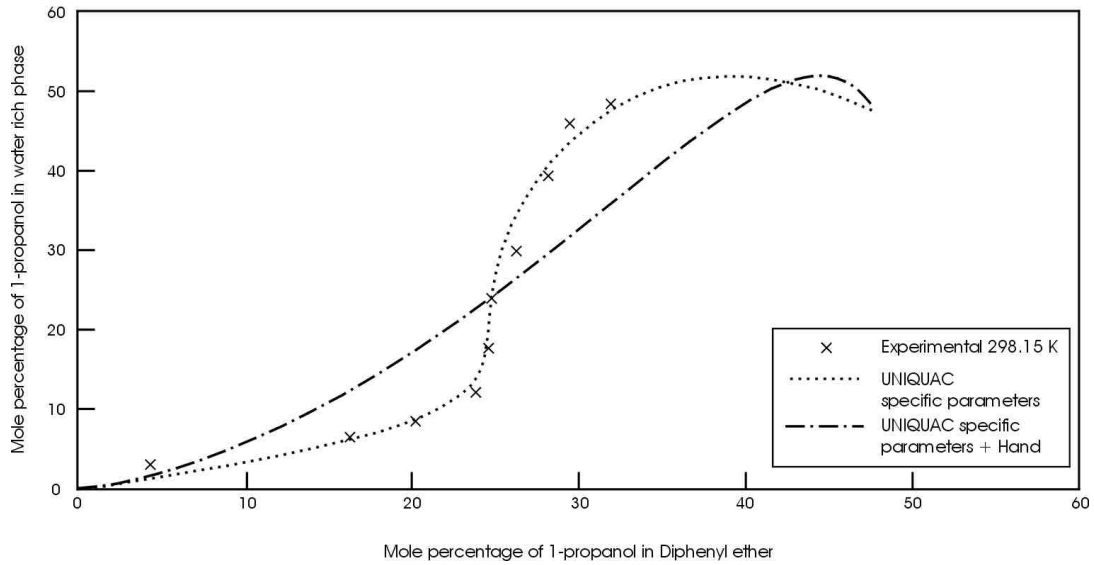

Figure 3: Tie lines for 1-Butanol(1) - Acetic Acid(2) - Water(3). System nº 2 in Table 1.

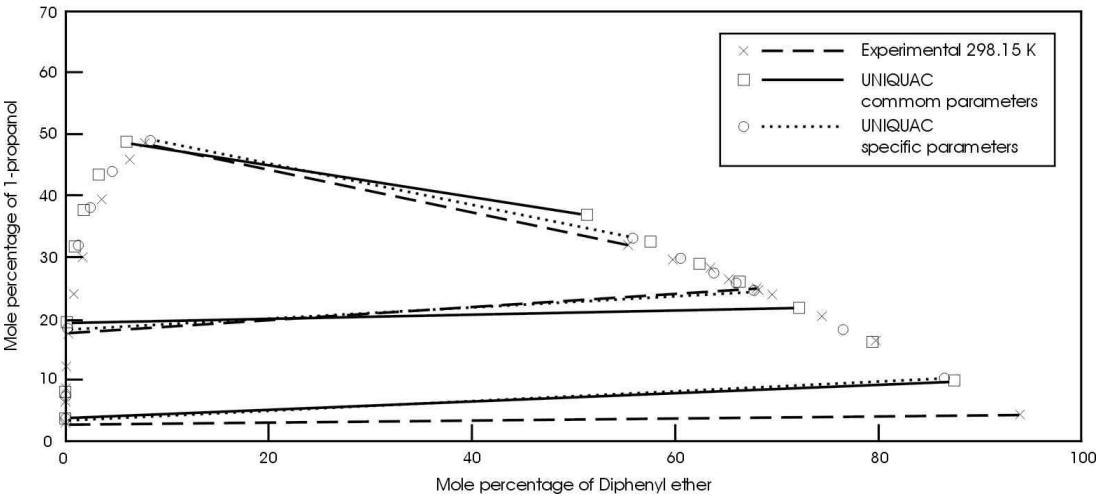

Figure 4: Distribution of acetic acid(2) between the water(3)-rich phase and the 1-butanol(1)-rich phase. System nº 2 in Table 1.

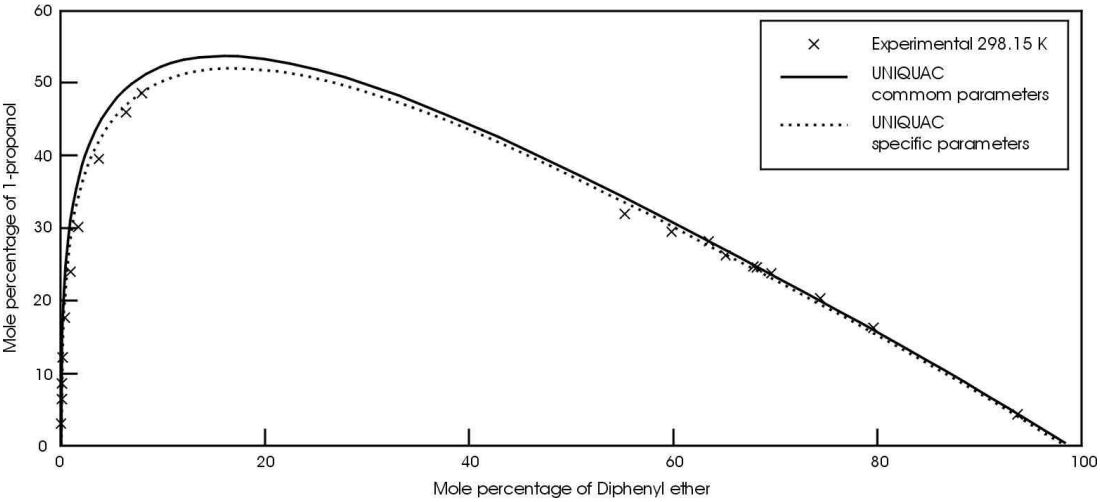

Figure 5: Representation of Hand's correlation for some systems in Table 2.

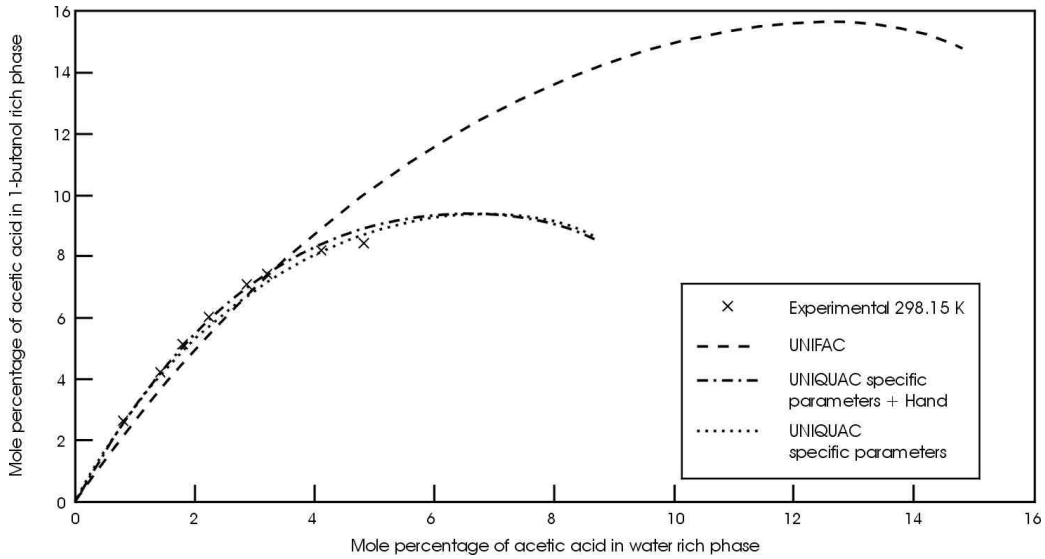

Figure 6: Binodal curve for Water(1) - 1-Propanol(2) - Diphenyl ether(3). System nº 13 in Table 2.

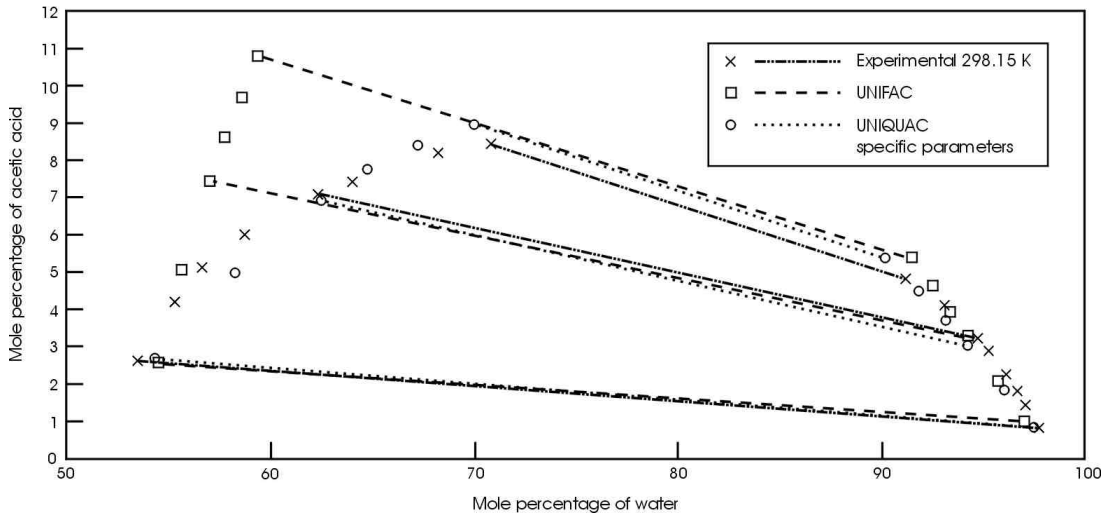

Figure 7: Tie lines for Water(1) - 1-Propanol(2) - Diphenyl ether(3). System nº 13 in Table 2.

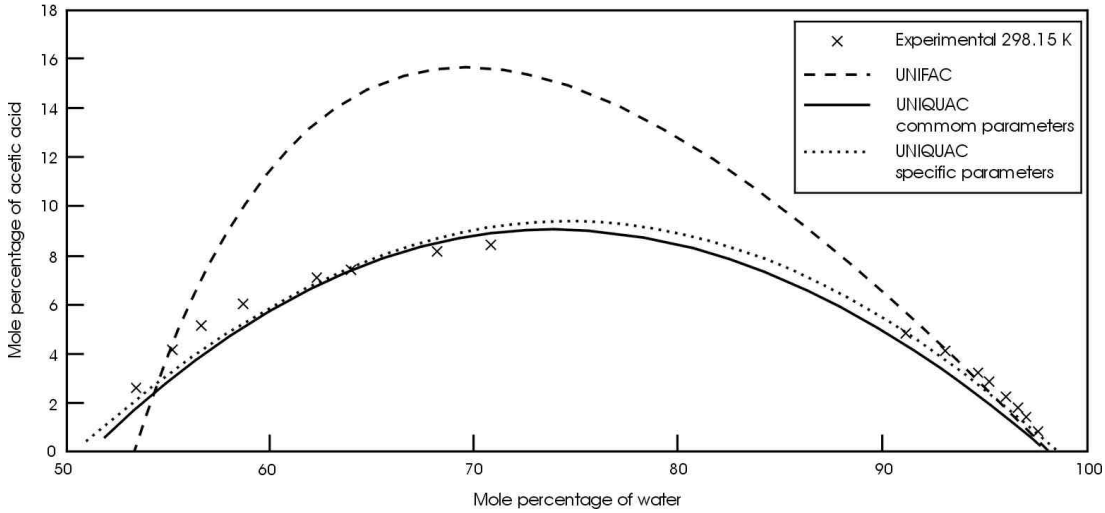

Figure 8: Distribution of 1-propanol (2) between the water(1)-rich phase and the diphenyl ether(3)-rich phase. System nº 13 in Table 2.

Table 3: Common UNIQUAC interaction parameters

i	j	a_{ij}, K	a_{ji}, K
Water (1) - 1, 2 Ethanediol (2) - Formic Acid, Ethyl Ester (3)			
1	2	- 221.13	- 39.881
2	3	170.57	363.06
3	3	211.84	104.70
Hexadecanoic Acid, Methyl Ester (1) – 9 Octadecenoic Acid (Cis), Methyl Ester 82) – Acetic Acid, Nitrile (3)			
1	2	- 4.6931	25.370
1	3	260.96	22.177
2	3	235.50	28.275

CONCLUSIONS

This paper presents a method to calculate coefficient distributions in ternary liquid-liquid systems. The proposed method combines Hand's equation with both the UNIQUAC and the UNIFAC models. When experimental tie lines are well correlated with Hand's equation, the combination allows obtaining distribution coefficients that describe experimental distribution coefficients better than the coefficients calculated using UNIQUAC alone.

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NOMENCLATURE

C [-] constant in Hand's equation (Eqn. 1)
k [-] constant in Hand's equation (Eqn. 1)
x [-] liquid molar fraction phase rich in component 3
y [-] liquid molar fraction phase rich in component 1

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APPENDIX A: UNIFAC Equation

The UNIFAC model expresses the component activity coefficient γ_i as a function of temperature and composition as follows:

$$\begin{aligned} n\ \gamma_i &= 1 - RI_i + n\ RI_i + \\ &+ q_i\left[1 - n\ QI_i - z\left(1 - \frac{RI_i}{QI_i} + n\frac{RI_i}{QI_i}\right)\right] \\ &- \sum_{(\text{all groups})}^{k}\left[\theta_k \frac{S_{ki}}{\eta_k} - G_{ki}\ n\ \frac{S_{ki}}{\eta_k}\right] \end{aligned} \tag{A1}$$

$$RI_j = r_j / \sum_{(\text{all components})}^{i} x_i r_i, \tag{A.2}$$

$$QI_j = q_j / \sum^{i} x_i q_i$$

$$R_j = \sum^{k} v_k^{(j)} R_k, \qquad q_j = \sum^{k} v_k^{(j)} Q_k \tag{A.3}$$

$$G_{ki} = Q_k\, v_k^{(i)}, \quad \theta_k = \sum^{i} G_{ki}\, x_i \tag{A.4}$$

$$S_{ki} = \sum_{(\text{all groups})}^{m} G_{mi}\,\tau_{mk}, \quad \eta_k = \sum^{i} S_{ki}\, x_i \tag{A.5}$$

$$\tau_{mk} = \exp(-a_{mk}/T), \quad z = 10 \tag{A.6}$$

In (A.3), r_j and q_j are the molecular (UNIQUAC) volumes and surfaces areas. They are calculated from the appropriate group properties R_j and Q_k; $v_k^{(i)}$ is the number of groups of type k in molecule i. In (A.6), the group interaction parameter a_{mk} has the unit Kelvin. The coordination number z is arbitrarily s et equal to ten. UNIFAC group interaction parameters a_{mk} are given by Magnussen et al. (1981).

APPENDIX B: UNIQUAC Equation

The UNIQUAC equation for G^E consists of two parts, a combinatorial part that attemps to describe the dominant entropic contribution, and a residual part due primarily to intermolecular forces that are responsible for the enthalpy of mixing.

$$\frac{G^E}{RT} = \frac{G^E(\text{combinatorial})}{RT} + \frac{G^E(\text{residual})}{RT} \tag{B.1}$$

$$\begin{aligned} \frac{G^E(\text{combinatorial})}{RT} &= \sum_i x_i\ n\ \frac{\Phi_i}{x_i} + \\ &+ \frac{z}{2}\sum q_i x_i\ n\frac{\Theta_i}{\Phi_i} \end{aligned} \tag{B.2}$$

$$\begin{aligned} \frac{G^E(\text{residual})}{RT} &= -\sum_i q_i x_i\ n\sum_j \Theta_j \tau_{ji} \\ i, j &= 1, 2, ..., N\,(\text{components}) \end{aligned} \tag{B.3}$$

$$\Theta_i = \frac{x_i q_i}{\sum_j x_j q_j}\ , \quad \Theta_i = \frac{x_i r_i}{\sum_j x_j r_j} \tag{B.4}$$

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right) \tag{B.5}$$

In (B.4) parameters r_i, q_i are pure-component molecular-structure constants depending on molecular size and external surface areas. The coordination number z is set equal to ten. In (B.5) the interaction parameter a_{ji} has the unit Kelvin. ”Specific” parameters are UNIQUAC parameters fitted individually to each ternary system. Table 1 indicates the page of Sϕrensen and Arlt (1980) where to find the specific parameter values. “Common” parameters are reported in Table 3.

APPENDIX C: Hand Equation

The Hand correlation derives from the mass-action law assuming that components 1 and 3 are scarcely soluble in each other, and that the solute (component 2) is at low concentration in 1- and 3-rich phases; but it also applied to systems with partly miscibles non consolute liquids:

$$n\,\frac{X_{21}}{X_{11}} = k \quad n\,\frac{X_{23}}{X_{33}} + \; C \tag{C.1}$$

where X_{ij} is the molar fraction of the component i in the $j-$rich phase and k and C are constants.

APPENDIX D: The linear correlation coefficient r

The correlation coefficient r can be computed from

$$r = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2}\sqrt{\sum (y-\bar{y})^2}} \tag{D.1}$$

where x is $n\,y_2/y_1$ of equation (1), y is $n\,x_2/x_3$ of equation (1), and $\bar{x}$ and $\bar{y}$ are mean values of x and y. The formula (D.1) is often referred to as the product-moment formula for linear correlation. If $r = \pm 1$, we say that there is perfect linear regression.