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Liquid Data Systems Correlation

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Abstract

Four simple polynomials of the fourth degree have been developed based on thermodynamic analysis to be used for correlating ternary and pseudoternary liquid–liquid systems. The correlations make use of a parameter, x, which is in effect the concentration of one of the solvents at zero solute concentration distorted by a certain function of the solute present in the system. Data generated by this technique were found to be in excellent agreement with the experimental published data for 12 systems tested by the model and published in a previous paper. In this work, 19 other liquid systems have been tested by the same model. The excellent agreement between published and estimated data proves the suitability of such a model for generally correlating liquid data systems. Such a model can therefore be recommended to be incorporated in simulating models for liquid extraction and extractive distillation processes computations.

1. INTRODUCTION

Analytical procedures for the computation of extraction processes are usually based only on solute balances between the phases. Therefore, such procedures are less accurate than graphical methods which take into account the balance of the other components in the system. Hence, models correlating the solvents concentrations in the two phases of an extraction system are very desirable. Such models will render analytical computation of these systems more accurate than graphical methods, especially in systems with very small distribution coefficients.

In a previous paper (*1*) the authors introduced a model initially based on thermodynamic principles. The model was used to correlate successfully the data of 12 liquid systems. In this work, 19 other liquid systems are correlated by the same model. Such correlations will be used in subsequent work to simulate and optimize extraction processes.

2. THE MODEL USED

The developed model was based on an analysis of the most famous UNIQUAC equation (*2*, *3*). Development of the model is found elsewhere (*1*). This model makes use of a parameter x for correlating the solubility data of a liquid–liquid system where

$$x = \frac{W_B + KW_C - W^\circ_{BA}}{W^\circ_{BB} - W^\circ_{BA}} \tag{1}$$

A, B, and C are the components of the liquid system. C is a solute which is completely miscible with Solvents A and B. The composition is expressed as mass percentage, so W_A, W_B, and W_C are the relative proportions of A, B, and C, respectively (g/100 g), in the system.

W°_{BB} is the mass percent of Component B in Phase B saturated with A. W°_{AB} is the mass percent of Component B in the coexisting Phase A saturated with B. Thus W°_{BA} and W°_{BB} are the $W_C = 0$ end-points of the binodial curve. K is a constant developed by trial and error to get the best correlation. Investigation of Eq. (1) shows that x is a scale defined as follows:

$$\text{At } x = 0, \qquad W_B = W^\circ_{BA}$$

$$\text{At } x = 1, \qquad W_B = W^\circ_{BB}$$

These values of W_B are distorted by the value of $[KW_C/(W^\circ_{BB} - W^\circ_{BA})]$ so that x remains single-valued along the binodial locus. However, for every system there is a value of K, say K_m, such that for $K > K_m$, x has values > 1. Thus K must be kept less than K_m characteristic of the system. Therefore, every value of x locates a unique point on the binodial line for all $K < K_m$.

The concentrations of the solvents W_A and W_B in the system were correlated by

$$W_A = P_1(x) = \sum_i a_i x^i \tag{2}$$

$$W_B = P_2(x) = \sum_j a_j x^j \tag{3}$$

where a_i and a_j are the coefficients of the polynomials. These coefficients can be obtained for any liquid system by a least-squares technique.

Nineteen liquid–liquid data systems published in the literature have been tested by the model. The systems used are displayed in Table 1, and the corresponding correlations for W_A and W_B against the parameter x for the system water–hexane–acetic acid are given in Table 2. Similar tables for the other 18 systems are available and will be furnished on request. Excellent agreement has been obtained for both ternary and pseudoternary systems. In some polynomials the variance was relatively large due to the first few points.

The value of K was taken as starting from 0.01. The optimum values of K and the degree of the polynomial, n, are found in the corresponding tables.

Equations (2) and (3) have been successfully used to develop the solu-

TABLE 1
Systems Tested by the Model

No.	System: A–B–C	Temperature (°C)	Ref.	Agreement[a] P_1	P_2	P_3	P_4
1	Water–hexane–acetic acid	31	*4*	E	E	E	E
2	Water–cyclohexane–methyl ethyl ketone	25	*5*	E	E	E	E
3	Water–cyclohexane–methyl ethyl ketone	30	*4*	E	E	B	B
4	Water–methyl ethyl ketone–ethylene glycol	30	*4*	E	E	E	E
5	Water–1,1,2-trichloroethane–acetone	25	*6*	E	E	B	E
6	Water–methyl butyrate–acetic acid	30	*7*	E	E	G	E
7	Water–methyl butyrate–propionic acid	30	*7*	E	E	E	G
8	Water–methyl *n*-butyl ketone–*n*-butanol	38	*4*	E	E	E	E
9	Water–methyl butyrate–butyric acid	30	*7*	E	E	E	B
10	Acetonitrile–cyclohexane–benzene	30	*8*	E	E	E	E
11	Acetonitrile–cyclohexane–benzene	45	*8*	E	E	E	G
12	Acetonitrile–cyclohexane–toluene	25	*8*	E	E	E	B
13	Acetonitrile–cyclohexane–toluene	45	*8*	E	E	E	B
14	*n*-Heptane–sulfolane–toluene	30	*9*	E	E	B	B
15	*n*-Heptane–(sulfolane + 10% 2-propanol)–toluene	30	*9*	E	E	G	E
16	*n*-Heptane–(sulfolane + 20% 2-propanol)–toluene	30	*9*	E	E	G	B
17	*n*-Heptane–(sulfolane + 2% water)–toluene	30	*9*	E	E	B	B
18	*n*-Heptane–(sulfolane + 4% water)–toluene	30	*9*	E	E	B	B
19	Toluene–water–sulfolane	30	*9*	E	E	F	E

[a] E = Excellent, variance < 1.
G = Good, variance = 1–3
F = Fair, variance = 3–10.
B = Bad and should not be used, variance > 10.
P = Polynomials defined by Eqs. (2), (3), (4), and (5).

TABLE 2

System 1: Water–Hexane–Acetic Acid at 31°C (*4*)

No.	Polynomial	n	Coefficients a_0	a_1	a_2	a_3	a_4	K	l	Variance
1	$W_A = P_1(x)$	4	99.8779	−99.7191	−1.2193	−3.7271	4.1941	0.99	7	0.0238
2	$W_B = P_2(x)$	4	−0.3373	92.0675	26.4819	−6.267	−11.9425	0.01	5	0.0226
3	$W_{CB} = P_3(W_{CA})^a$	2	0.0065	0.0037	0.0013			—	5	0.66315
4	$W_{BB} = P_4(W_{BA})$	4	99.8008	−3.6233	−2.433	2.5104	−0.5784	—	5	0.0097

Selectivities at minimum concentrations			Selectivities at maximum concentration			
m_{AB}	$\beta_{AB}{}^b$	$\beta_{BA}{}^c$	m_{AB}	β_{AB}	β_{BA}	
0.017	—	—	0.147	44.597	199.842	$\%(S_B/S_T)^d$
$\beta_{AB}/\beta_{BA} = 1$			$\beta_{AB}/\beta_{BA} = 1{:}4.48$			95.1358

[a] Valid in the range of $W_{CA} = 18.8–81.8$.

[b] Direction of mass transfer is from A to B.

[c] Direction of mass transfer is from B to A.

[d] S_B = area under the binodal curve, S_T = area of the equilateral triangle.

bility data for any liquid system. However, for extraction computations and optimization, equilibrium data also have to be accurately developed. This has been done through the following correlations:

$$W_{CB} = P_3(W_{CA}) = \sum_i b_i W_{CA}^i \tag{4}$$

$$W_{BB} = P_4(W_{BA}) = \sum_j b_j W_{BA}^j \tag{5}$$

The coefficients of these correlations for the systems studied are also given in the mentioned tables. Table 2 is incorporated here as an example.

3. SOLUBILITY AND TIE LINES DATA GENERATION

The four polynomial correlations 2, 3, 4, and 5 form the basis for the model used to generate the ternary and tie lines data for any liquid system. The steps used to generate these data for a certain system by using the coefficients of the tables are explained as follows:

1. Mutual solubility data can be obtained by using Eq. (3), $W_B = P_2(x)$. Putting $x = 0$ in this equation gives W_{BA}°. W_{AA}° can be obtained by

   $$W_{AA}^\circ = 100 - W_{BA}^\circ \tag{6}$$

   Putting $x = 1$ in the same equation gives W_{BB}°. Then W_{AB}° is given by

   $$W_{AB}^\circ = 100 - W_{BB}^\circ \tag{7}$$

2. Ternary data can be obtained by using values of x where $0 < x < 1$ in Eq. (3) to get W_B. Then W_C can be estimated from Eq. (1) as follows:

   $$W_C = \frac{1}{K}[x(W_{BB}^\circ - W_{BA}^\circ) + W_{BA}^\circ - W_B] \tag{8}$$

   Then W_A can be estimated by

   $$W_A = 100 - (W_B + W_C) \tag{9}$$

   W_A can also be estimated by Polynomial 2, considering that the value of K of this polynomial may be different from that of Polynomial 3.
3. Tie lines data are obtained by similar prcoedures as follows for any value of x where $0 < x < 1$.

a. For Phase A: W_{BA} can be estimated from Eq. (3), W_{CA} from Eq. (8), and W_{AA} from Eq. (9).
b. For Phase B: W_{CB} is estimated from Polynomial 4, and W_{BB} from Polynomial 5. Then W_{AB} is estimated from Eq. (9).

Other related data, such as the distribution ratios and the selectivities of both solvents to solute at minimum and maximum concentrations in both directions of mass transfer, can also be easily estimated. These data have been also incorporated in the same tables for the systems studied.

The area of immiscibility of liquid systems has been estimated by a modified Simpson's rule which allows for projecting the area under the binodial curve from an equilateral triangular form into two perpendicular axes suitable for applying Simpson's rule of integration. A small subroutine has been incorporated in the computer program of this technique to calculate the area of immiscibility and to estimate its percentage relative to the area of the equilateral triangle. The objective was to try to relate the selectivity of solvents to the area under the binodial curve. These values are also given in the same tables.

4. DISCUSSION

Table 1 shows the 19 systems tested by the developed technique. The table also summarizes the results obtained and shows the agreement between the generated and the experimental published data. Agreement in the case of the generated solubility data is excellent as shown in P_1 and P_2 where the variance is less than 1. However, the equilibrium data in some systems (3, 14, 17, and 18) behaved very badly. This might be due to the fact that turbidity determination of the binodial curve is much easier than determination of the equilibrium data, which usually depends on Othmar and Tobias or Hand correlations (*2*). However, Table 1 shows that the developed technique has a screening power and can be used for proving and checking the published experimental data in liquid equilibria fields.

In most systems it was found that a polynomial of degree 4 is sufficient to produce excellent agreement between the generated and experimental data. Polynomials of higher degrees were also tried for the ill-behaved Systems 17, 18, and 19, as shown in Table 1. However, System 17 data showed a higher dispersion. We also tried to relate the effect of any change in a liquid system with the main parameters of the system; for example, the capacity of the solvent indicated by the distribution coefficient, the selectivity of the system, and the area under the binodial locus. Table 3 summarizes such effects due to an increase of temperature or the addition of a certain amount of a component to the system. The table does not show any concrete trend for such effects, although reading out such figures

TABLE 3

Effect of Temperature and Additives on the Liquid Systems Parameters

			% Change					
		% Change in area of immiscibility	Minimum concentration			Maximum concentration		
Systems	Variable studied		m_{AB}	β_{AB}	β_{BA}	m_{AB}	β_{AB}	β_{BA}
10, 11	6.7% increase in temperature	−43.5	−9	−68	−38	+7.7	+43	+26
12, 13	6.7% increase in temperature on an absolute basis	−40.6	−7	−45	−21	−9	−26	−10.8
14, 15	10% addition of 2-propanol	−13.9	−45.7	+1551	+2997	+98	−19.5	−99
14, 16	20% addition of 2-propanol	−22.6	−12.6	+93	+95	−58.8	−80	+73
14, 17	Addition of water	+7	−11.3	+26.3	+16.3	−6	+90.4	+169
14, 18	4% addition of water	+10.4	−26	+64.7	+70.2	−17.4	+129.3	+518

can tell that a 6.7% increase of temperature, on an absolute basis, in Systems 10 to 13 causes large changes in the parameters of the system. However, more data are required in order to draw better conclusions. Nevertheless, the technique has the ability to screen the published data in this important chemical engineering field, to analyze them in a very comprehensive and constructive way, and to pave the road toward including these techniques in computation systems for designing and optimizing extraction systems without the need for simplification approaches.

However, it should be stated that the polynomial approach is only a mathematical tool to approximate experimental data. Predictions for values outside the ranges of the tie-line data stated in the tables are not recommended unless some other experimental results are provided to justify such predictions. Nevertheless, work is now underway to use this technique for rigorous computation of extraction processes to prove its usefulness.

5. CONCLUSIONS

Simple polynomial models have been developed by using a complex parameter which is a function of two components concentrations in liquid–liquid ternary systems. These polynomials have been used to correlate a number of ternary and pseudoternary liquid systems with a great deal of success. This technique may prove to be more simple and accurate than any other available technique when it is included in simulation programs for extraction and azeotropic and extractive distillation processes. However, since this model is used only to approximate available experimental data, care should be taken if it is used outside such a range of data.

Analysis of such data can then lead to the optimum selection of a solvent for a certain duty. By using additives to the systems, temperature differences or salting out can also be incorporated in such an analysis. Including such a technique in extraction process design and optimization will produce accurate results because there will be no need to use classical simplifications.

NOMENCLATURE

A	carrier solvent, raffinate phase
a_i	coefficients of polynomial P_1
B	extracting solvent, extract phase
b_i	coefficients of polynomial P_2
C	solute
I	iteration number
K	constant in Eq. (1), obtained by trial and error
K_m	maximum value for K, characteristic for each system
m	distribution coefficient

n	degree of polynomial
P	polynomial
S_B	area under the binodal curve, unit square
S_T	area of the equilateral triangle, unit square
W	weight, g/100 g
W_0	weight at zero solute concentration, g/100 g
x	parameter defined by Eq. (1)
β_{AB}	selectivity of Solvent B to Solute C $m_{AB} \cdot W_{AA}/W_{AB}$
β_{BA}	selectivity of Solvent A to Solute C $m_{BA} \cdot W_{BB}/W_{BA}$

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