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General Correlations for Liquid-Liquid Data Systems

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Abstract

An efficient algorithm based on simple correlations for generating the solubility, tie line, and solvent selectivity data for ternary and pseudoternary liquid systems has been developed. The experimental data of 12 different systems have been tested with the model formulated, and excellent agreement has been verified. Simpson's rule has been also incorporated in the model to enable the area under the binodal curve to be calculated for comparison with the area of the equilateral triangle. The relationship between the area of immiscibility and the selectivity of a solvent toward a certain solute is discussed. Simulation of such data is important in extraction, azeotropic and extractive distillations, computations, and optimization. This model may prove to be more simple and accurate than the other available thermodynamic correlations when included in computation algorithms for design and optimization of processes involving multicomponent liquid systems. However this technique has limited predictive power since it is based on experimental data approximation.

1. INTRODUCTION

Analytical procedures for computation of extraction processes are usually less accurate than graphical computation methods. The reason may be that analytical techniques use only solute balance as the basis for their computation, while graphical methods take into account the balance of the other components (solvents) in the systems. Therefore, if it were possible to build models correlating the solvents concentrations in the two coexisting phases of an extraction system, digital simulation and analytical computation of these processes would be at least as accurate as the graphical techniques, depending upon the quality of the model.

Different trials based on thermodynamic principles have been made for correlating these data systems, with varying degrees of success (*1*, *2*). The UNIQUAC equation is considered to be more accurate than the other expressions. However, this correlation is still under development to improve its ability to predict and/or to correlate available data sytems (*3*).

A modified version of the UNIQUAC equation proposed by Anderson and Prausnitz and recommended by Perry (*1*) was found to produce an average absolute error in distribution coeffiicents of 5.9% in correlating some Type 1 systems as reported by Simonetty et al. (*2*).

It was also stated (*1*) that a 5% error in the prediction of the activity coefficient can represent a 10 to 50% error in the separation per stage.

The object of this work is to develop a simple, efficient, and accurate technique based on the well-known expressions of the excess Gibbs energy function for correlating liquid–liquid systems by simple models which can be easily computerized for purposes of comprehensive analysis of extraction processes and the optimum selection of solvents.

2. THERMODYNAMIC BACKGROUND

When a solute, C, is distributed between two liquid phases, A and B, then at equilibrium the activity of the solute will be the same in each phase. Therefore, the activity coefficients of a solute in the liquid phases can be used to describe the thermodynamic basis for the distribution coefficients and also for the concentrations of the components in the liquid phases.

The activity coefficients, γ, can be determined by knowledge of the dimensionless excess Gibbs function, g:

$$g = G^E/RT \tag{1}$$

According to Perry (*1*) γ is given for a multicomponent liquid mixture by

$$\ln \gamma_i = \ln\left(\frac{\phi_i}{C_i}\right) + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{C_i} \sum_j C_i l_j - q_i \ln \sum_j \theta_j \tau_{ij} + q_i'$$

$$- q_i' \sum \left(\frac{\theta_i' \tau_{ij}}{\sum_k \theta_k' \tau_{kj}} \right) \tag{2}$$

where

$$\phi_i = -\frac{C_i r_i}{\sum_j C_j r_j}, \qquad \theta_i = \frac{C_i q_i}{\sum_j C_j q_j}$$

$$\tau_{ij} = \exp\left(-\frac{\Delta u_{ij}}{RT}\right), \quad \tau_{ij} = 1 \text{ for } i = j \tag{3}$$

$$\Delta u_{ij} = u_{ij} - u_{jj}, \qquad \theta_i' = \frac{q_i' C_i}{\sum_j q_j' C_j}$$

$$l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1)$$

r and q are the pure component molecular structure constants, q' is an empirical value, and z is a coordination number, usually taken as 10 for all mixtures.

Equation (2) is a complicated function which contains a large number of parameters. Some of them are empirical (e.g., q') and others, such as z, have to be obtained by trial and error. However, these parameters are all dependent upon the component concentrations, molecular physical constants, and the temperature and pressure of the system.

Since the pressure has little effect on liquid systems, then at constant temperature Eq. (2) can simply be written as

$$\gamma_i = f(C_i) \tag{4}$$

where the molecular physical constants will be inherent in the coefficients of this correlation. For a ternary system A, B, and C, Eq. (4) can be written for Component A as

$$\gamma_A = f(C_A, C_B, C_C) \tag{4a}$$

and since

$$C_A + C_B + C_C = 1 \tag{5}$$

$$\gamma_A = f(C_B, C_C) \tag{6}$$

Now, introducing a new parameter x, which is a complex function defined by

$$x = \psi(C_B,C_C) \tag{7}$$

then

$$\gamma_A = f_1(x) \tag{8}$$

$$\gamma_C = f_2(x) \tag{9}$$

However, since any component concentration in one phase can be determined by the ratio of the activity coefficient of this component to another component in the same phase, therefore

$$C_{AA} = f_3(\gamma_{AA},\gamma_{CA}) \tag{10}$$

and hence Eq. 10 can be written as

$$C_{AA} = f_4(x) \tag{11}$$

Equation (11) can be used to calculate the component concentrations in both phases.

Similar analysis of the most widely used thermodynamic equations, such as Margules, van Laar, and Wilson's (*1*), lead to the same conclusion.

3. FORMULATION OF THE MODEL

Initially, trials were made to select a suitable parameter, x, which can satisfy Eq. (7) and does not violate Eq. (5). This parameter will serve as the independent variable in correlating liquid–liquid data.

A survey of the related literature revealed that Hlavaty (*4*, *5*) suggested a correlation for systems in which ethanoic acid is the third component, the other two being widely immiscible. The Hlavaty correlation takes the form

$$W_C = A_0 + A_1 \ln x_1 + A_2 \ln x_2 + x_1x_2 \sum A_i(x_2 - x_1)^{i-3} \tag{12}$$

where

$$x_1 = \frac{W_B + KW_C - W^0_{BA}}{W^0_{BB} - W^0_{BA}} \tag{13}$$

$$x_2 = \frac{W^0_{BB} - W_B - KW_C}{W^0_{BB} - W^0_{BA}} \tag{14}$$

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^0_{BB} is the mass percent of Component B in Phase B saturated with A. W^0_{AB} is the mass percent of Component B in the co-existing Phase A saturated with B. Thus W^0_{BA} and W^0_{BB} are the $W_C = 0$ end-points of the binodal curve.

Although Hlavaty's Eq. (12) has been discussed, it has not been widely used, perhaps due to its computational difficulties. It has also had limited application since it can generate only the solubility data of a liquid system. However, equilibrium data are much more important for computation and optimization purposes. These data cannot be obtained by Eq. (12) because it represents a continuous binodal locus. On the other hand, addition of Eqs. (13) and (14) shows that

$$x_1 + x_2 = 1 \tag{15}$$

This simply means that Eq. (12) could have been represented by

$$W_C = f(x) \tag{16}$$

which is similar to Eq. (11) where x is equal either to x_1 or x_2 of Eqs. (13) and (14).

According to the previous discussion, a parameter x can be used for correlating the solubility data for a liquid–liquid system. This means that each component in the system can be represented by Eq. (16) where

$$x = \frac{W_B + KW_C - W^0_{BA}}{W^0_{BB} - W^0_{BA}} \tag{17}$$

which means that x is a scale defined as follows:

$$\text{at } x = 0,\ W_B = W^0_{BA}$$

$$\text{at } x = 1,\ W_B = W^0_{BB}$$

These values of W_B are distorted by the value of $KW_C/(W^0_{BB} - W^0_{BA})$ so that x remains single valued along the binodal 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 binodal line for all $K < K_m$.

In order to explore the shape of the Function (17), the values for a pseudoternary system, *n*-heptane (A), sulfolane + 10% 2 propanol (B), and toluene (C) data at 30°C (*2*), was calculated by Eq. (17) and the solubility data were then plotted against x as shown in Fig. 1. This figure indicates that W_C is still of the Hlavaty form but W_A and W_B are single-valued functions. So, to describe binodal locus data, it is sufficient to correlate $W_A(x)$ and $W_B(x)$. In this case W_C can be obtained from Eq. (5) or Eq. (17).

Correlating W_A and W_B by using the independent variable x has been tried in this work by the polynomial approximation technique. Polynomials have been adopted since they are simple in computations and can be truncated at any suitable degree to give the accuracy required.

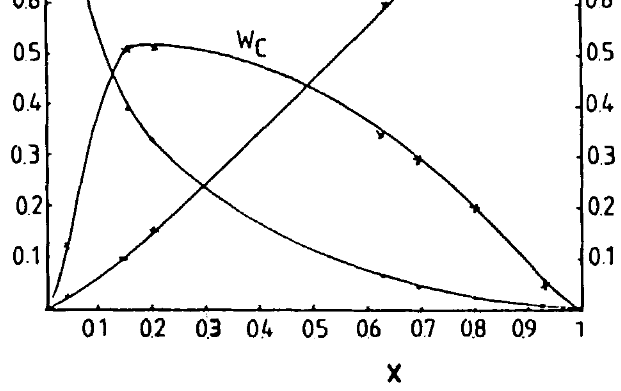

FIG. 1. Representation of the *n*-heptane, sulfolane + 10% 2-propanol, toluene system at 30°C on rectangular coordinates vs x.

However, although UNIQUAC Eq. (2) and Hlavaty's Eq. (12) are both complicated logarithmic functions, they can be mathematically expanded to take the form of a polynomial.

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

$$W_A = P_1(x) = \sum_i a_i x^i \tag{18}$$

$$W_B = P_2(x) = \sum_j a_j x^j \tag{19}$$

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.

Twelve liquid-liquid data systems published in the literature have been used to test the applicability of the model. The systems used are displayed in Table 1, and their corresponding correlations for W_A and W_B against the parameter x are given in Tables 2 through 13. Excellent agreement has been obtained for both ternary and pseudoternary systems. In some polynomials the variance is relatively large due to the first few points.

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

Equations (18) and (19) have been successfully used to develop the solubility 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:

$$W_{CB} = P_3(W_{CA}) = \sum_i b_i W^i_{CA} \tag{20}$$

$$W_{BB} = P_4(W_{BA}) = \sum_j b_j W^j_{BA} \tag{21}$$

Since the ends of the tie lines inevitably lie on the binodal locus, only one of these relations is required; W_{CB} vs W_{CA} generally has the greatest discriminatory power and therefore the highest precision. However, there is a computational problem in that either this relation or its inverse is two valued as shown in Fig. 2. The values of W_{BB} vs W_{BA} or W_{AA} vs W_{AB} are usually well behaved but rather less precise, as shown in Fig. 3.

Hence, it is necessary to use Correlations (20) and (21) together. The coefficients of these correlations for the 12 systems are also given in Tables 2 to 13.

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	Methyl isobutyl ketone	Acetic acid	25	*6*	E	E	E	E
2	Water	Isopropyl ether	Acetic acid	20	*7*	E	E	E	G
3	Water	Mesityl oxide	Acetic acid	30	*8*	E	E	E	E
4	Water + 10.9% NaCl	Mesityl oxide	Acetic acid	30	*8*	E	E	E	G
5	Water	Toluene	Acetic acid	30	*9*	E	E	E	E
6	*n*-Heptane	Sulfolane + 2-propanol	Toluene	30	*10*	E	E	E	B
7	Water	Toluene	Acetic acid	45	*9*	E	E	E	E
8	Water	Toluene	Acetic acid	60	*9*	E	E	E	E
9	Furfural	Docosane	Diphenyl hexane	45	*11*	E	E	E	E
10	Methanol	Cyclohexane	Ethanol	25	*3*	E	E	E	B
11	Propane	Cottonseed oil	Oleic acid	98.5	*12*	E	E	B	F
12	*n*-Heptane	Sulfolane + 7% water	Toluene	30	*10*	E	E	E	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. (18), (19), (20), and (21).

TABLE 2

System 1: Water (A)-Methyl Isobutyl Ketone (B)-Acetic Acid (C) at 25°C (*6*)

No.	Polynomial	n	Coefficients a_0	a_1	a_2	a_3	a_4	K	I	Variance
1	$W_A = P_1(x)$	3	98.4617	−96.2738	−0.2382	0.1744		1	25	0.0003
2	$W_B = P_2(x)$	4	1.4869	93.2954	8.8301	−9.1741	3.4383	0.01	12	0.0016
3	$W_{CB} = P_3(W_{CA})^a$	3	0.1803	0.5294	0.0187	−0.0002		—	5	0.2111
4	$W_{BB} = P_4(W_{BA})$	4	123.2056	−19.71	2.1322	−0.1084	0.002	—	34	0.0082

Selectivities at minimum concentrations m_{AB}	β_{AB}	$\beta_{BA}{}^b$	Selectivities at maximum concentrations m_{AB}	β_{AB}	β_{BA}	% $(S_B/S_T)^c$
0.6561	22.37	85.46	0.9711	1.34	1.62	
β_{AB}/β_{BA} = 1:3.82			β_{AB}/β_{BA} = 1:1.2			45.706

[a] Valid in the range of $W_{CA} = 2.85 - 34.6\%$.

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

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

TABLE 3

System 2: Water (A)–Isopropyl Ether (B)–Acetic Acid (C) at 20°C (7)

			Coefficients							
No.	Polynomial	n	a_0	a_1	a_2	a_3	a_4	K	I	Variance
1	$W_A = P_1(x)$	3	99.2827	−98.5085	−0.6481	0.3628		1	15	0.001
2	$W_B = P_2(x)$	4	0.6704	93.8379	14.0367	−13.6207	4.5674	0.01	13	0.0027
3	$W_{CB} = P_3(W_{CA})^a$	3	−0.00123	0.2567	0.0058	0.00012		—	5	0.7365
4	$W_{BB} = P_4(W_{BA})$	4	90.963	14.575	−7.49	0.8459	−0.0276	—	5	3.3036

Selectivities at minimum concentrations			Selectivities at maximum concentrations			
m_{AB}	β_{AB}	$\beta_{BA}{}^b$	m_{AB}	β_{AB}	β_{BA}	% $(S_B/S_T)^c$
0.2609	51.18	317.21	0.7802	1.92	3.78	57.58
	β_{AB}/β_{BA} = 1:6.2			β_{AB}/β_{BA} = 1:2		

[a] Valid in the range of W_{CA} = 0.69 – 46.4%.

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

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

TABLE 4

System 3: Water (A)–Mesityl Oxide (B)–Acetic Acid (C) at 30°C (*8*)

			Coefficients							
No.	Polynomial	n	a_0	a_1	a_2	a_3	a_4	K	I	Variance
1	$W_A = P_1(x)$	3	97.0687	−91.0181	−0.2196	0.1331		1	50	0.00001
2	$W_B = P_2(x)$	4	2.8906	88.8566	6.7055	−7.4196	3.0081	0.01	15	0.0004
3	$W_{CB} = P_3(W_{CA})^a$	3	0.0806	1.3865	−0.0304	0.00064		—	5	0.3701
4	$W_{BB} = P_4(W_{BA})$	5	86.1797	−1.0906	2.1763	−0.9441	0.1160	—	16	0.5237

Selectivities at minimum concentrations			Selectivities at maximum concentrations			
m_{AB}	β_{AB}	$\beta_{BA}{}^b$	m_{AB}	β_{AB}	β_{BA}	% $(S_B/S_T)^c$
1.28	13.04	20.03	1.0337	2.87	4.219	32.5
	β_{AB}/β_{BA} = 1:1.54			β_{AB}/β_{BA} = 1:1.47		

[a] Valid in the range of $W_{CA} = 5 - 20.8\%$.

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

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

TABLE 5

System 4: Water + 10.9% NaCl (A)-Mesityl Oxide (B)-Acetic Acid (C) at 30°C (*8*)

			Coefficients							
No.	Polynomial	n	a_0	a_1	a_2	a_3	a_4	K	I	Variance
1	$W_A = P_1(x)$	3	98.5854	−94.6056	−0.2851	−0.2851	0.1703	1	50	0.00001
2	$W_B = P_2(x)$	4	1.3382	92.1751	6.3922	−5.6269	1.8598	0.01	11	0.0007
3	$W_{CB} = P_3(W_{CA})^a$	3	−0.3085	2.4305	−0.1172	0.0041		—	5	0.6409
4	$W_{BB} = P_4(W_{BA})$	4	93.5274	−8.7458	14.2742	−9.0182	1.3563	—	5	1.1133

Selectivities at minimum concentrations			Selectivities at maximum concentrations			
m_{AB}	β_{AB}	$\beta_{BA}{}^b$	m_{AB}	β_{AB}	β_{BA}	% $(S_B/S_T)^c$
1.89	36.68	44.09	1.58	10.13	9.4	48.029
	β_{AB}/β_{BA} = 1:1.2			β_{AB}/β_{BA} = 1:0.93		

[a] Valid in the range of $W_{CA} = 1.8 - 15.8\%$.

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

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

TABLE 6
System 5: Water (A)–Toluene (B)–Acetic Acid (C) at 30°C (9)

			Coefficients							
No.	Polynomial	n	a_0	a_1	a_2	a_3	a_4	K	I	Variance
1	$W_A = P_1(x)$	3	99.6747	−97.27	−6.8104	4.5535		1	6	0.017
2	$W_B = P_2(x)$	4	−0.1252	95.0802	14.5678	−14.9456	5.3011	0.01	8	0.013
3	$W_{CB} = P_3(W_{CA})^a$	3	−2.926	0.3502	−0.0095	0.00014		—	21	0.2415
4	$W_{BB} = P_4(W_{BA})$	4	98.672	−3.601	0.4527	0.2367	−0.033	—	5	0.0715

Selectivities at minimum concentrations			Selectivities at maximum concentrations			
m_{AB}	β_{AB}	$\beta_{BA}{}^b$	m_{AB}	β_{AB}	β_{BA}	% $(S_B/S_T)^c$
0.08	38.34	4376.9	0.3177	9.8	47.06	84.08
	β_{AB}/β_{BA} = 1:114			β_{AB}/β_{BA} = 1:4.8		

[a] Valid in the range of W_{CA} = 23.01 – 69.85%.

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

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

TABLE 7

System 6: *n*-Heptane (A)–Sulfolane (B)–2-Propanol (C) at 30°C (*10*)

			Coefficients								
No.	Polynomial	n	a_0	a_1	a_2	a_3	a_4	a_5	K	I	Variance
1	$W_A = P_1(x)$	3	99.73	−97.81	−3.03	1.925	—	—	1	4	0.0012
2	$W_B = P_2(x)$	4	−0.066	64.7	76.11	−57.22	15.6		0.1	20	0.046
3	$W_{CB} = P_3(W_{CA})^a$	3	1.436	1.615	−0.06	0.0008			—	4	0.5
4	$W_{BB} = P_4(W_{BA})$	5	104.89	−29.53	11.8	−1.97	0.132	−0.0027		50	Large

Selectivities at minimum concentrations			Selectivities at maximum concentrations			
m_{AB}	$\beta_{AB}{}^b$	$\beta_{BA}{}^c$	m_{AB}	β_{AB}	β_{BA}	
5.67	625.85	57.29	0.587	4.15	5.73	$\% (S_B/S_T)^d$
$\beta_{AB}/\beta_{BA} = 1:0.09$			$\beta_{AB}/\beta_{BA} = 1:1.38$			55.64

[a] Valid in the range of $W_{CA} = 0.3 - 43.4\%$.

[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.

TABLE 8
System 7: Water (A)-Toluene (B)-Acetic Acid (C) at 45°C (9)

			Coefficients								
No.	Polynomial	n	a_0	a_1	a_2	a_3	a_4	a_5	K	I	Variance
1	$W_A = P_1(x)$	3	99.8411	−99.3535	−0.5932	0.3764			1	42	0.0001
2	$W_B = P_2(x)$	5	−0.0946	94.0406	16.3645	−11.1991	−5.479	6.1049	0.01	7	0.0113
3	$W_{CB} = P_3(W_{CA})^a$	3	0.006	−0.0578	0.0128	−0.00033			—	5	0.0616
4	$W_{BB} = P_4(W_{BA})$	4	100.8546	−7.5625	1.3581	−0.1311	0.0037		—	5	0.0833

Selectivities at minimum concentrations			Selectivities at maximum concentrations			
$m_{AB}{}^b$	β_{AB}	$\beta_{BA}{}^c$	m_{AB}	β_{AB}	β_{BA}	% $(S_B/S_T)^c$
0.086	23.3	3274.7	0.336	7.4	30.8	80.4
	β_{AB}/β_{BA} = 1:140.5			β_{AB}/β_{BA} = 1:4.2		

[a] Valid in the range of W_{CA} = 18.1 − 64.62%.

[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.

TABLE 9

System 8: Water (A)-Toluene (B)-Acetic Acid (C) at 60°C (9)

			Coefficients							
No.	Polynomial	n	a_0	a_1	a_2	a_3	a_4	K	I	Variance
1	$W_A = P_1(x)$	3	99.6904	−115.3187	−60.3553	76.3465		0.78	5	0.1554
2	$W_B = P_2(x)$	4	−0.0661	94.5313	14.625	−14.2319	4.6949	0.01	10	0.0095
3	$W_{CB} = P_3(W_{CA})^a$	3	−0.5648	0.1642	−0.00072	0.00004		—	5	0.0147
4	$W_{BB} = P_4(W_{BA})$	4	99.7522	−2.5719	−10.886	12.2967	−4.3674	—	5	0.0526

Selectivities at minimum concentrations			Selectivities at maximum concentrations			
$m_{AB}{}^b$	β_{AB}	$\beta_{BA}{}^c$	m_{AB}	β_{AB}	β_{BA}	% $(S_B/S_T)^d$
0.1165	23.69	2340.5	0.2386	12.58	204.39	80.5
	β_{AB}/β_{BA} = 1:99			β_{AB}/β_{BA} = 1:16		

[a] Valid in the range of W_{CA} = 12.19 − 53.91%.

[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.

TABLE 10

System 9: Furfural (A)-Docosane (B)-Diphenyl Hexane (C) at 45°C (*11*)

No.	Polynomial	n	Coefficients a_0	a_1	a_2	a_3	a_4	K	I	Variance
1	$W_A = P_1(x)$	4	99.26	−95.70	−0.415	−1.83	2.603	0.99	20	0.0019
2	$W_B = P_2(x)$	4	0.602	91.4076	10.654	−10.0017	3.3265	0.01	11	0.0031
3	$W_{CB} = P_3(W_{CA})^a$	4	0.0044	0.0289	0.1671	−0.0078	0.0001	—	11	0.0000
4	$W_{BB} = P_4(W_{BA})$	4	44.3	37.0196	17.1762	−17.8275	2.1324	—	30	0.0000

Selectivities at minimum concentrations			Selectivities at maximum concentrations			
m_{AB}	$\beta_{AB}{}^b$	$\beta_{BA}{}^c$	m_{AB}	β_{AB}	β_{BA}	$\% (S_B/S_T)^d$
1.02	18.941	75.905	1.042	4.096	6.226	61.062
β_{AB}/β_{BA} = 1:4.007			β_{AB}/β_{BA} = 1:1.52			

[a] Valid in the range of $W_{CA} = 24.2 - 40.9\%$.

[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.

TABLE 11
System 10: Methanol (A)-Cyclohexane (B)-Ethanol (C) at 25°C (*3*)

No.	Polynomial	n	Coefficients a_0	a_1	a_2	a_3	a_4	K	I	Variance
1	$W_A = P_1(x)$	4	82.858	−70.557	−0.6987	1.7886	−0.894	0.99	30	0.00003
2	$W_B = P_2(x)$	4	17.1364	69.3262	2.9335	−3.1053	1.2122	0.01	30	0.00001
3	$W_{CB} = P_3(W_{CA})^a$	4	9.5778	−6.9113	1.8593	−0.2019	0.0079	—	5	0.094
4	$W_{BB} = P_4(W_{BA})$	4	4.4209	29.1871	−2.5576	0.0834	−0.0009	—	30	98.8

Selectivities at minimum concentrations			Selectivities at maximum concentrations			
m_{AB}	$\beta_{AB}{}^b$	$\beta_{BA}{}^c$	m_{AB}	β_{AB}	β_{BA}	% $(S_B/S_T)^d$
0.21	1.106	20.609	0.627	1.037	2.537	
β_{AB}/β_{BA} = 1:18.634			β_{AB}/β_{BA} = 1:2.446			9.874

[a] Valid in the range of W_{CA} = 5.57 − 11.17%.
[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.

TABLE 12
System 11: Propane (A)–Cottonseed Oil (B)–Oleic Acid (C) at 45°C (*12*)

			Coefficients							
No.	Polynomial	n	a_0	a_1	a_2	a_3	a_4	K	I	Variance
1	$W_A = P_1(x)$	4	99.755	−62.0232	−2.4916	4.8361	−3.5877	1.01	30	0.00007
2	$W_B = P_2(x)$	4	0.1823	60.5088	6.7104	−5.0137	1.0977	0.01	5	0.008
3	$W_{CB} = P_3(W_{CA})^a$									
4	$W_{BB} = P_4(W_{BA})$	4	−13.0669	69.345	−26.3361	5.7439	−0.4345		5	4.55^b

Selectivities at minimum concentrations			Selectivities at maximum concentrations			
m_{AB}	$\beta_{AB}{}^c$	$\beta_{BA}{}^d$	m_{AB}	β_{AB}	β_{BA}	% $(S_B/S_T)^e$
1	2.652	29.279	7.727	12.874	0.582	26.70255
β_{AB}/β_{BA} = 1:11.04			β_{AB}/β_{BA} = 1:0.045			

[a] W_{CA} = 0.25 – 55%.

[b] Large errors are due to 7 data points.

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

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

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

TABLE 13

System 12: *n*-Heptane (A)–Sulfolane + 7% Water (B)–Toluene (C) at 25°C (*10*)

No.	Polynomial	n	Coefficients a_0	a_1	a_2	a_3	a_4	K	I	Variance
1	$W_A = P_1(x)$	3	99.68552	99.45781	0.030158	0.17637		1	50	0.00002
2	$W_B = P_2(x)$	4	0.04357	−4.73127	238.85643	−184.12569	49.6949	0.2		0.08765
3	$W_{CB} = P_3(W_{CA})^a$	3	−10.09999	1.15562	−0.02992	0.00029				8.864
4	$W_{BB} = P_4(W_{BA})$	4	100.75343	−9.42131	1.92080	−0.15736	0.00373			0.978

Selectivities at minimum concentrations m_{AB}	$\beta_{AB}{}^b$	$\beta_{BA}{}^c$	Selectivities at maximum concentrations m_{AB}	β_{AB}	β_{BA}	% $(S_B/S_T)^d$
0.18	68.6	591.32	0.415	2.67	6.71	84.85
β_{AB}/β_{BA} = 1:8.52			β_{AB}/β_{BA} = 1:2.51			

[a] Valid in the range of W_{CA} = 22.8 − 69.9%.

[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.

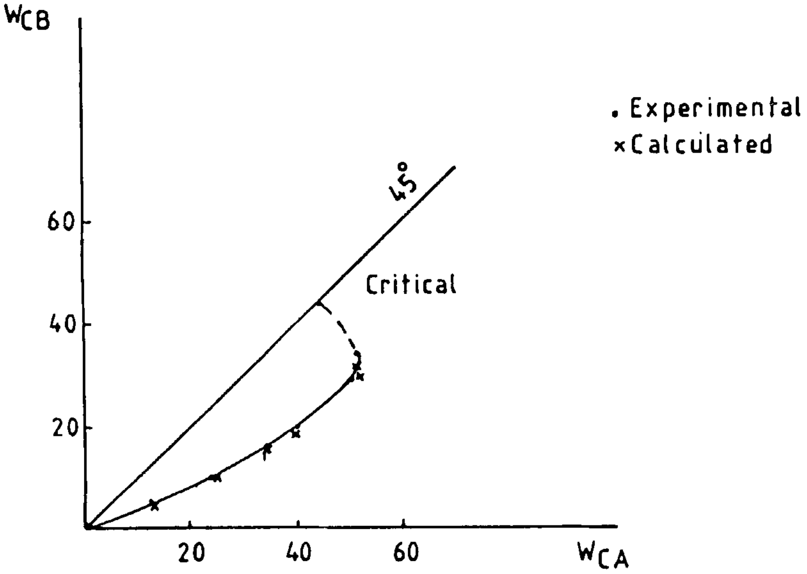

FIG. 2. W_{CB} vs W_{CA} for the *n*-heptane, sulfolane + 10% 2-propanol, toluene system at 30°C.

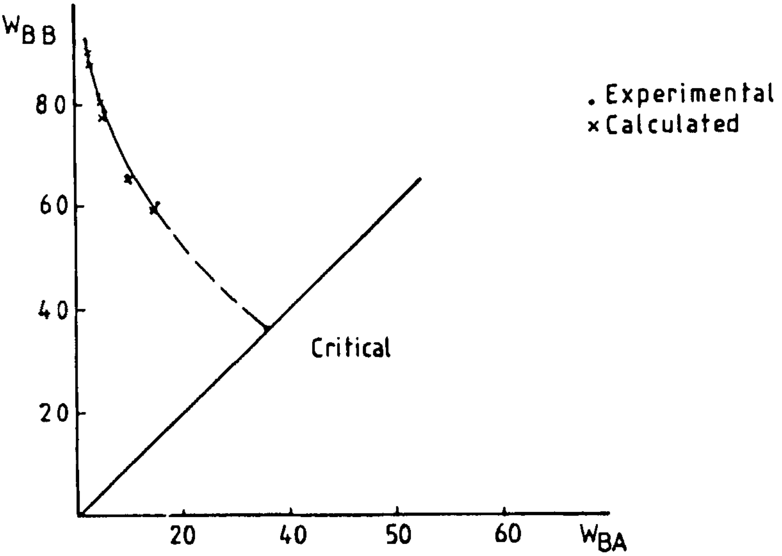

FIG. 3. W_{BB} vs W_{BA} for the *n*-heptane, sulfolane + 10% 2-propanol, toluene system at 30°C.

4. SOLUBILITY AND TIE LINES DATA GENERATION

The four polynomial correlations (18), (19), (20), and (21) form the basis of the model used for generating the ternary and tie lines data for any liquid system. The steps for generating these data for a certain system using the coefficients of the tables can be explained as follows.

1. Mutual solubility data can be obtained by using Eq. (19), $W_B = P_2(x)$. Putting $x = 0$ in this equation gives W_{BA}. Then W^0_{AA} can be obtained by

$$W^0_{AA} = 100 - W^0_{BA} \tag{22}$$

Putting $x = 1$ in Eq. (19) gives W^0_{BB}. Then W^0_{AB} is given by

$$W^0_{AB} = 100 - W^0_{BB} \tag{23}$$

2. Ternary data can be obtained by using values of x, where $0 < x < 1$, in Eq. (19) to get W_B. Then W_C can be estimated from Eq. (18) as follows:

$$W_C = \frac{1}{K}\left[x(W^0_{BB} - W^0_{BA}) + W^0_{BA} - W_B\right] \tag{24}$$

Then W_A can be estimated by

$$W_A = 100 - (W_B + W_C) \tag{25}$$

W_A can also be estimated by Polynomial (18), considering that the value of K of this polynomial may be different from that of the Polynomial (19).

3. Tie line data are obtained by similar procedures as follows for any value of x, where $0 < x < 1$. (a) For Phase A: W_{BA} can be estimated from Eq. (19), W_{CA} from Eq. (24), and W_{AA} from Eq. (25). (b) For Phase B: W_{CB} is estimated from Polynomial (20) and W_{BB} from Polynomial (21). Then W_{AB} is found from Eq. (25).

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.

5. AREA OF IMMISCIBILITY

The area of immiscibility of liquid systems can be estimated by a modified Simpson's rule which allows for projecting the area under the binodal 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 binodal curve.

6. DISCUSSION

Table 1 shows the 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. The 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 (6, 10, and 11) behaved very badly. This might be due to the fact that turbidity determination of the binodal curve is easier than determination of the equilibrium data which usually depends on Othmar and Tobias or Hand correlations. However, Table 1 proves 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 four is sufficient to produce excellent agreement between the generated and experimental data. Polynomials of higher degrees were also tried for ill-behaved systems as shown in Tables 7 and 8 for Systems 6 and 7. However, System 6 data showed a high 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 as indicated by the distribution coefficient, the selectivity of the system, and the area under the binodal locus. Table 14 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 can tell that a 9.9% increase of temperature, on an absolute basis, in Systems 5 and 8 causes large changes in the parameters of the system.

On the other hand, the addition of other materials to the liquid sys-

TABLE 14

Effect of Temperature and Additives on the Parameters of Liquid Systems

			% Change			
			Minimum concentration		Maximum concentration	
Systems	Variable studied	% Change in area[a]	m_{AB}	β_{AB}	m_{AB}	β_{AB}
3 and 4	10.9% addition of NaCl	+48.0	+48.0	+181.0	+53.0	+264.0
6 and 12	7% addition of water	+52.5	−97.0	+89.0	−29.0	−36.0
5 and 8	9.9% increase of temperature[b]	−4.0	+46.0	−38.0	−25.0	−28.0

[a] Area of immiscibility.

[b] On an absolute basis.

tems, such as the addition of salt to System 3 or of water to System 6, largely affects the area of immiscibility and selectivity, but no concrete conclusion can be drawn, as shown in Table 14. This table shows that addition of 10.9% salt to Solvent A has increased the area of immiscibility by 48%. A corresponding increase in the distribution coefficient and the selectivity at minimum and maximum concentrations also has been obtained. However, an increase of the area of immiscibility of System 6 due to the addition of 7% water to Solvent B resulted in a sharp decrease in the parameters of the system.

Table 14 also indicates that raising the temperature of System 5 resulted in a decrease in the area of immiscibility. A corresponding decrease in the other parameters of the system, except for the distribution coefficient at the minimum concentration, has occurred.

A trial has been made to relate the selectivity of solvents to the area of immiscibility. This is shown in Fig. 4. This figure indicates that System 2 has the highest selectivity among the systems plotted, while its area is

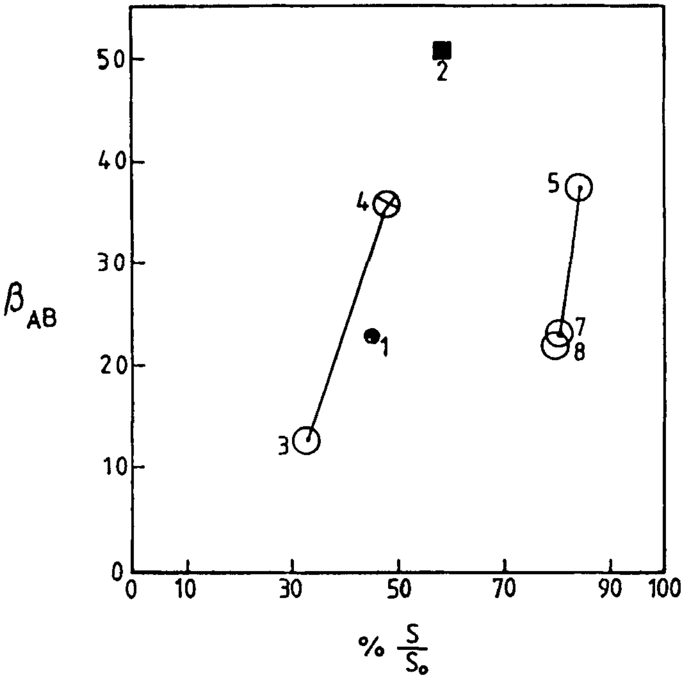

FIG. 4. Selectivity at minimum concentration vs percentage relative area for the different systems.

about 58%. System 5 has the largest area, 84%, while its selectivity is less than 40%. Raising the temperature of this system has lowered the area and selectivity, as shown at Points 7 and 8.

Salting out of System 3 has increased the area and the selectivity, which suggests that the addition of salt favors the extraction of acetic acid from water by mesityl oxide. However, more data are required in order to draw better conclusions. Nevertheless, the technique introduced may be the first which has the ability to screen the published data in this important chemical engineering field, to analyze data 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 in order to test its usefulness.

7. 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 included in simulation programs for both 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 lead to the optimum selection of a solvent for a certain duty. 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 without the need for classical simplifications.

NOMENCLATURE

A	carrier solvent, raffinate phase
A_0, A_1, A_2, A_i	coefficients of Correlation (12)
a_i	coefficients of polynomial P_1
B	extracting solvent, extract phase
b_i	coefficients of polynomial P_2
C	solute
C_i, C_j, C_k	mole fraction of the Components i, j, and k in the system or phase
G^E	excess Gibbs energy
g	dimensionless excess Gibbs energy
I	iteration number
K	constant in Eq. (17), obtained by trial and error
K_m	maximum value for K, characteristic for each system
l	parameter, defined by Eq. (3)
m	distribution coefficient
n	degree of polynomial
P	polynomial
q_i, q_i'	surface parameters for pure Component i
R	gas constant
r_i	molecular volume parameter for pure Component i
S_B	area under the binodal curve, unit square
S_T	area of the equilateral triangle, unit square
T	temperature, K
u_{ij}	binary interaction parameter, cal/mol
W	weight, g/100 g
W^0	weight at zero solute concentration, g/100 g
x	parameter defined by Eq. (17)
z	liquid-phase coordination number, usually taken as 10 for all mixtures

Greek Letters

β_{AB}	selectivity of Solvent B to Solute C

$$m_{AB} \cdot \frac{W_{AA}}{W_{AB}}$$

β_{BA}	selectivity of Solvent A to Solute C $m_{BA} \cdot \frac{W_{BB}}{W_{BA}}$
γ	activity coefficient
ϕ_i	segment fraction of Component *i*
θ, θ'	area fractions
τ_{ij}	UNIQUAC binary parameter
ψ	function defined by Eq. (7)

REFERENCES

1. R. H. perry and D. Green, *Perry's Chemical Engineer's Handbook,* 6th ed., 1984, p. 4-76.
2. J. Simonetty, D. Yee, and D. Tassios, *Ind. Eng. Chem., Process Des. Dev., 21,* 174–180 (1982).
3. I. Nagata and T. Ohta, *J. Chem. Eng. Data, 28,* 256–259 (1983).
4. K. Hlavaty, *Collect. Czech. Chem. Commun., 37,* 4005 (1972).
5. K. Hlavaty, *Ibid., 38,* 374 (1973).
6. T. Sherwood, G. Evans, and R. Longcor, *Ind. Eng. Chem., 31,* 599 (1939).
7. R. Treybal, *Trans. AIChE, 36,* 628 (1940).
8. M. F. Hegazi and A. B. Salem, *J. Chem. Biotechnol., 33A,* 145–150 (1983).
9. A. B. Salem, *J. Chem. Eng. Jpn., 12,* 236 (1979).
10. S. J. Aschraft, A. D. Clayton, and R. B. Shearn, *J. Chem. Eng. Data, 27,* 148 (1982).
11. S. W. Briggs and E. W. Comings, *Ind. Eng. Chem., 35*(4), 411 (1943).
12. A. W. Hixson and J. B. Bockelmann, *Trans. AIChE, 38,* 891 (1942).

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