CORRELATION OF THE BINODAL CURVE IN A TERNARY LIQUID MIXTURE WITH ONE PAIR OF IMMISCIBLE LIQUIDS

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A new equation was proposed for correlating the binodal curve in a ternary liquid mixture with one pair of immiscible liquids. The equation is capable of expressing the binodal curve within experimental accuracy with relatively few constants. It has an additional advantage of passing automatically through both binary solubility points.

Several attempts have been made to correlate the binodal curve in a ternary liquid mixture containing one pair of immiscible liquids[1,2]. None of them was very successful. Spalding[1] divided the binodal curve in two parts separated by the ternary plaint point region and correlated both segments separately by equations ranging in complexity from linear equations to hyperbolic functions. The error of his correlations was of the order of $\sim 1\%$. Bulatov and Jachmenev[2] used polynomials and rational, exponential or logarithmic functions with which they were able to achieve an accuracy of $0.8-3\%$ depending on the number of empirical constants used.

As it would be very useful to have a good empirical correlation for practical calculations and interpolations of ternary solubility data, we have made several attempts to correlate the binodal curve. We started with polynomials or rational functions with up to seven constants using the double precision computer technique but the results were not encouraging. Subsequently we were stricken by the similarity in shape between the binodal curve and the Gibbs free energy of mixing of a binary solution. The two curves usually have a flat central portion with abruptly changing slopes towards one end. Thus we propose for correlating the binodal curve the following equation

$$w_C = A_1 x_1 \ln (x_1) + A_2 x_2 \ln (x_2) + x_1 x_2 \sum_{i=3}^{n} A_i (x_2 - x_1)^{i-3} \qquad (1)$$

with

$$x_1 = (w_B + w_C k - w_{BA}^0)/(w_{BB}^0 - w_{BA}^0)$$

and

$$x_2 = (w_{BB}^0 - w_B - w_C k)/(w_{BB}^0 - w_{BA}^0).$$

The different symbols stand for the weight fractions of the homogenizing component (w_C) and of solvent B (w_B) in the ternary systems along the binodal curve and for the weight fractions of solvent B in the solvent B-rich (w_{BB}^0) or solvent A-rich (w_{BA}^0)

TABLE I

Empirical Correlation of Binodal Curves in 5 Ternary Liquid Systems

Number of experimental points analyzed	n(Eq. (I))	k(Eq. (I))	Root mean square deviation weight %
	Water–ethylene glycol–cyclohexane, 30°C		
12	3	0	2·25
	5	0	1·25
	3	0·3	0·58
	3	0·5	0·91
	4	0·5	0·38
	2[a]	—	2·71
	Water–dichloroacetic acid–benzene, 25°C		
25	3	0	1·94
	4	0	1·24
	3	0·3	1·20
	5	0·3	0·29
	Water–acetic acid–diethyl ether, 15°C		
20	3	0	0·59
	6	0	0·30
	3	0·3	0·59
	3	0·5	0·70
	5[a]	—	0·80
	Butanol–acetone–water, 25°C		
8	3	0	0·98
	3	0·5	0·68
	3	1	0·61
	4	1	0·28
	Chloroform–acetone–water, 25°C		
19	3	0·5	0·93
	4	0·5	0·67

[a] Cf. the Bulatov's work[2].

phase of the immiscible binary system at equilibrium conditions. The k is an empirical constant from interval $\langle 0.1 \rangle$, the value of which was determined prior to least squares calculations to obtain constants A_i. The equation could be extended easily to describe

the saturation surfaces in multicomponent liquid system with one pair of immiscible liquids bur we do not follow this line of approach here.

The proposed equation has an advantage of passing automatically through both binary solubility points, *i.e.* it holds $w_C \to 0$ for $w_B \to w_{BB}^0$ or $w_B \to w_{BA}^0$, resp. The choice of solvent B in Eq. (*1*) was arbitrary; we could have as well chosen solvent A. To make this new equation identical with Eq. (*1*), it would be only necessary to put $(1 - k)$ instead of k into the expressions for x_1 and x_2. The only limitation on binodal experimental data is that $w_{BA}^0 < w_B + w_C k < w_{BB}^0$ for the whole concentration range; this condition is in most cases satisfied. It may be seen that the right hand side of Eq. (*1*) is an explicit function of w_B (resp. w_A) only for $k = 0$ (resp. $k = 1$). Although the best results were obtained with k from interval $(0\cdot3, 0\cdot7)$, the experimental accuracy with which a binodal curve could be determined was achieved in most cases with $k = 0$ or $k = 1$ as well. For $k \neq 0$ or for $k \neq 1$ it is necessary to adopt some iteration scheme: the right hand side of Eq. (*1*) is calculated with an initial value of w_C, the calculated value of w_C is substituted again into the right-hand side and so on until the difference between two successive steps becomes negligible. This process converges very rapidly.

RESULTS AND DISCUSSION

We correlated the solubility data in some 20 ternary liquid systems by Eq. (*1*). Most of the experimental data were taken from Kogan's compilation[3], the rest from other works[4,5]. The calculations were performed on a Minsk 22 computer. Some of the results are given in Table I. Results of Bulatov and Jachmenev[2] are also included in the table. It may be seen that Eq. (*1*) is somewhat superior to the Bulatov correlation, especially in the case of the water–acetic acid–diethyl ether system for which Eq. (*1*) with only 3 empirical constants yields better agreement than a fourth order polynomial. We may conclude this by stating that Eq. (*1*) could become a useful tool for correlating solubility data and subsequent computer interpolations needed in chemical engineering applications.

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