

EQUILIBRIUM OF ISOBUTYL ACETATE-ACETIC ACID-WATER

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The equilibrium of the system isobutyl acetate-acetic acid-water was measured at 25 and 50°C. The data for the binodal curve were correlated using the method proposed by Hlavatý, the distribution of acetic acid in both solvents was correlated according to Hand and also Othmer and Tobias. Both types of data were also approximated by means of orthogonal polynomials and the results compared with the correlation procedures mentioned.

The ternary liquid system isobutyl acetate-acetic acid-water is interesting from the industrial point of view. At normal (usual) temperatures it forms a heterogeneous system of the 1st type (with one restrictedly soluble pair). The equilibrium data for this system have not been published to our knowledge. In this paper the data were measured for a binodal curve and the composition of the equilibrium phases for temperatures of 25 and 50°C.

Various relations have been proposed for the correlation of equilibrium data for ternary systems. In this paper the correlation by Hlavatý¹ was used for binodal data,

$$w_C = A_1 x_1 \ln(x_1) + A_2 x_2 \ln(x_2) + x_1 x_2 \sum_{i=3}^n A_i (x_2 - x_3)^{i-3}; \quad i = 3, 4, \dots \quad (1)$$

where

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

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

for distribution the correlation by Hand²

$$w_{CB}/w_{BB} = r(w_{CA}/w_{AA})^S \quad (2)$$

and by Tobias³

$$(1 - w_{AA})/w_{AA} = m[(1 - w_{BB})/w_{BB}]^n, \quad (3)$$

where w_I is the concentration of component I (weight %), w_{IJ} the weight % of com-

ponent I in the phase rich in solvent J , w_D^0 the solubility of the component I in the component J in weight %; Indices of I: A water, B isobutyl acetate, C acetic acid.

For both types of data the correlation by orthogonal polynomials has also been used⁴. One of the advantages of this method of approximation of functions consists in the fact that it enables a decrease to a minimum of the systematic error of approximation, when a sufficient number of experimental data is available, by using polynomial of a sufficiently high degree. The high number of empirical constants comprized in such an approximation formula represents no difficulty at the present state of computer technique. However, as high requirements are put on the accuracy of equilibrium data for computation of countercurrent extractors, the ability of the approximation relation to smooth out the random error of measurement and decrease the systematic error of correlation to a minimum is very important. On the contrary the advantages of the previously mentioned approximations by semiempirical functions and empirical functions of a specific form apply primarily in the predictions of the equilibrium composition from a small number of experimental data. In such a case only orthogonal polynomials of a lower degree can be constructed, while in the case of curves of complex form, as for example a binodal, their use necessarily fails. It should also be stated that not merely the number of experimental points is decisive for the utilizability of orthogonal polynomials, but also the value of the random error superimposing them.

EXPERIMENTAL

Materials used: acetic acid, *a.g.* purity, a product of Lachema, Brno; density 1.0417 g/cm³; refractive index 1.3715. Water content was determined by titration according to Karl Fischer. Isobutyl acetate, technical grade, was purified from free acid by shaking with aqueous sodium carbonate solution and from water by azeotropic distillation after addition of chloroform. Density 0.8673 g/cm³; refractive index 1.3909.

Analytical methods. Acetic acid concentration in the aqueous and the organic phase was determined by titration with 0.1M-NaOH using potentiometric indication. Samples of organic phase were diluted with aqueous methanol before titration. The composition of the points of the binodal curve was determined by the turbidity method; a weighed solution of acetic acid in that solvent, occurring in excess, was titrated with the second solvent until a turbidity or droplets of the second phase appeared. The distribution of acetic acid was determined by shaking aqueous solutions of the acid with isobutyl acetate at various ratios in a thermostated bath for 1 h. The concentration of acetic acid was then determined in the samples taken of the equilibrated phase by the above described method.

RESULTS

The measured values of w_C and w_B for the binodal are given in Table I, the distribution data w_{CA} and w_{CB} are in Table II. In the determination of the binodal data using equation (1) the number and the values of empirical constants A_i and k were

TABLE I
Measured Points (weight %) of the Binodal Curve

w_B	w_C	W	w_B	w_C	W
$t = 25^\circ\text{C}; w_{BA}^0 = 0.400; w_{BB}^0 = 98.640$					
0.55	2.17	0.10	27.40	40.14	1.00
0.58	2.17	0.10	31.63	39.10	1.00
0.60	4.24	0.10	31.70	39.06	1.00
0.65	4.24	0.10	31.65	38.19	1.00
0.95	10.34	0.10	32.65	38.59	1.00
1.00	10.33	0.10	36.78	37.63	1.00
1.13	14.56	0.10	36.78	37.63	1.00
1.20	14.53	0.10	40.66	36.39	1.00
1.27	18.36	0.10	46.16	33.93	1.00
1.29	18.36	0.10	46.58	34.25	1.00
1.39	21.96	0.10	51.86	32.02	1.00
1.44	21.95	0.10	51.94	32.05	1.00
2.41	29.86	0.10	55.95	30.08	1.00
2.49	29.83	0.10	56.01	30.12	1.00
3.55	31.12	0.10	61.10	27.43	1.00
3.73	31.07	0.10	61.12	27.43	1.00
4.08	32.92	1.00	67.04	23.78	1.00
4.10	32.91	1.00	67.06	23.79	1.00
5.24	36.35	1.00	72.77	20.33	1.00
5.33	36.10	1.00	72.85	20.35	1.00
6.83	39.35	1.00	77.80	16.47	1.00
7.14	39.22	1.00	77.94	16.51	1.00
8.56	39.60	1.00	83.45	12.39	1.00
8.59	39.59	1.00	88.58	8.04	1.00
10.94	40.96	1.00	88.61	8.04	1.00
11.22	41.70	1.00	89.88	7.14	1.00
16.68	41.58	1.00	89.96	7.15	1.00
16.96	41.38	1.00	94.35	3.59	1.00
23.78	40.92	1.00	94.54	3.59	1.00
24.35	40.61	1.00	97.48	1.03	1.00
27.37	40.10	1.00	97.53	1.02	1.00
$t = 50^\circ\text{C}; w_{BA}^0 = 0.670; w_{BB}^0 = 96.400$					
0.69	2.33	0.10	21.24	39.64	1.00
0.69	2.33	0.10	30.89	37.84	1.00
0.70	6.70	0.10	31.03	38.01	1.00
0.71	6.70	0.10	41.65	35.00	1.00
0.79	8.37	0.10	41.74	35.07	1.00
0.84	8.37	0.10	54.81	29.72	1.00

TABLE I
(Continued)

w_B	w_C	W	w_B	w_C	W
0.89	14.40	0.10	54.93	29.78	1.00
0.91	14.40	0.10	67.53	22.43	1.00
0.98	20.33	0.10	67.81	22.52	1.00
1.13	20.29	0.10	76.19	16.32	1.00
3.21	31.20	0.10	76.30	16.34	1.00
3.25	31.11	0.10	83.10	11.49	1.00
7.09	37.47	1.00	83.29	11.52	1.00
7.12	37.48	1.00	91.79	4.07	1.00
18.48	40.28	1.00	91.82	4.07	1.00
19.86	39.61	1.00	95.12	0.99	1.00
21.23	39.62	1.00	95.51	0.99	1.00

TABLE II
Measured Points (weight %) of the Distribution Curve

$t = 25^\circ\text{C}$		$t = 50^\circ\text{C}$	
w_{CB}	w_{CA}	w_{CB}	w_{CA}
31.37	41.68	30.57	39.67
27.97	38.58	30.26	39.09
26.77	37.75	24.74	35.39
24.49	35.56	21.75	32.95
17.46	29.05	17.36	28.71
14.73	25.41	17.26	28.41
10.69	20.12	13.72	24.07
7.87	15.71	11.98	21.69
6.86	14.00	8.24	16.01
4.86	10.53	6.99	13.88
3.69	8.40	4.70	9.98
2.85	6.69	2.81	6.53
1.90	4.79	1.95	4.64
1.47	3.81	1.12	2.80
1.07	2.83	0.72	1.84
0.67	1.82		

determined by optimization. As the first calculations showed that the points of the binodal for the aqueous phase and low concentrations of acetic acid are obstructed by a systematic error caused by the unclearness of the formed turbidity, a new calculation was undertaken at which a lower weight was assigned to the mentioned points. The values for weights of individual points are also listed in Table I. The values of the constants for both temperatures are in Table III where the value of the relative mean error is also given, defined by the equation

$$\sigma = 100 \left[\sum_{i=1}^N W_i (w_{Ci} - \bar{w}_{Ci})^2 / \bar{w}_{Ci}^2 \right]^{1/2} \left[\sum_{i=1}^N W_i - v \right]^{-1/2}, \quad (4)$$

where N is the number of the correlated points, w_{Ci} the concentration calculated from the respective correlation, W are the weights of the points, and the number

TABLE III
Constants for the Calculation of the Binodal Curve

Constants for equation (1)	Constants for equation (10)	
$t = 25^\circ\text{C}$		
$k = 0.7$	$B'_0 = -1.07717 \cdot 10^{+1}$	$B'_8 = 6.15749 \cdot 10^{-7}$
$A_1 = -22.605$	$B'_1 = 3.03180 \cdot 10^1$	$B'_9 = 1.17700 \cdot 10^{-8}$
$A_2 = 51.325$	$B'_2 = -9.02897$	$B'_{10} = 1.64512 \cdot 10^{-10}$
$A_3 = 205.400$	$B'_3 = 1.59107$	$B'_{11} = 1.66167 \cdot 10^{-12}$
$A_4 = -22.337$	$B'_4 = -1.76137 \cdot 10^{-1}$	$B'_{12} = 1.18026 \cdot 10^{-14}$
$A_5 = 25.019$	$B'_5 = 1.29152 \cdot 10^{-2}$	$B'_{13} = 5.59013 \cdot 10^{-17}$
$A_6 = -127.421$	$B'_6 = -6.54087 \cdot 10^{-4}$	$B'_{14} = 1.58462 \cdot 10^{-19}$
	$B'_7 = 2.35689 \cdot 10^{-5}$	$B'_{15} = 2.03307 \cdot 10^{-22}$
$t = 50^\circ\text{C}$		
$k = 0.0$	$B'_0 = -6.77366 \cdot 10^1$	$B'_8 = -9.97490 \cdot 10^{-6}$
$A_1 = -709.708$	$B'_1 = 1.41203 \cdot 10^2$	$B'_9 = 1.96220 \cdot 10^{-7}$
$A_2 = -45.164$	$B'_2 = -6.96754 \cdot 10^1$	$B'_{10} = -2.80026 \cdot 10^{-9}$
$A_3 = -789.309$	$B'_3 = 1.63798 \cdot 10^1$	$B'_{11} = 2.87059 \cdot 10^{-11}$
$A_4 = -376.259$	$B'_4 = -2.15432$	$B'_{12} = -2.05982 \cdot 10^{-13}$
$A_5 = -214.338$	$B'_5 = 1.76554 \cdot 10^{-1}$	$B'_{13} = 9.82079 \cdot 10^{-16}$
$A_6 = -178.934$	$B'_6 = -9.64960 \cdot 10^{-3}$	$B'_{14} = -2.79465 \cdot 10^{-18}$
	$B'_7 = -3.67080 \cdot 10^{-4}$	$B'_{15} = -3.59186 \cdot 10^{-21}$

At 25°C or 50°C and for $A_1\sigma = 7.42$ or 15.84% , respectively, and for $B_1\sigma = 6.84$ or 16.97% , respectively.

of constants in the correlation relationship. The comparison of the relative mean error for the weighed and non-weighed binodal data correlated by the equation (1) gives the following values: at temperatures 25 or 50°C the errors of the non-weighed points were 13.89 or 28.61%, respectively, and of the weighed points 7.42 or 15.84%, respectively.

In the case of orthogonal polynomials the approximation function has the form⁴

$$y(x) = \sum_{j=0}^m b_j P_j(x), \quad (5)$$

while the relationships for coefficients b_j can be obtained by the method of least squares in the form

$$b_j = \omega_k / \gamma_j, \quad (6a)$$

where

$$\omega_j = \sum_{i=1}^N W_i y_i P_j(x_i), \quad (6b)$$

$$\gamma_j = \sum_{i=1}^N W_i [P_j(x_i)]^2. \quad (6c)$$

The values of the polynomials P_j , orthogonal to the set of points $\{x_i\}$, $i = 1, \dots, N$ are calculated using the recurrent relationship where

$$P_{j+1}(x_i) = (x_i - \alpha_{j+1}) P_j(x_i) - \beta_j P_{j-1}(x_i), \quad (7)$$

$$\alpha_{j+1} = \frac{\sum_{i=1}^N x_i W_i [P_j(x_i)]^2}{\sum_{i=1}^N W_i [P_j(x_i)]^2},$$

$$\beta_j = \frac{\sum_{i=1}^N W_i [P_j(x_i)]^2}{\sum_{i=1}^N W_i [P_{j-1}(x_i)]^2}.$$

The equation (5) obtained by correlation can be rewritten to the form (8) that is more suitable for practical computations.

$$y = \sum_{j=0}^m B_j x^j. \quad (8)$$

The values of the coefficients B_j are then determined on the basis of the knowledge of the values of coefficients α_j , β_j , b_j by calculating the n^{th} derivations of the orthogonal polynomials at the zero point, because it applies⁵ that

$$B_M = \frac{1}{M!} \sum_{j=0}^m b_j P_j^{(M)}(0). \quad (9)$$

The binodal data were correlated satisfactorily only by orthogonal polynomials of the 15th degree. For the calculation of the binodal the correlation was adjusted to the form (10). The values of the constants B'_j are given in Table III.

$$w_c = \sum_{j=0}^{15} B'_j w_B^j. \quad (10)$$

In the correlation of the distribution data an accuracy was achieved that already corresponded to the random error of the measurement in polynomials of the 3rd degree. The adjusted correlation of the distribution data assumes the form (11) in this case:

$$w_{cB}/w_{BB} = \sum_{j=0}^3 B''_j (w_{cA}/w_{AA})^j. \quad (11)$$

The values of the constants for the distribution data correlation using the equations (2), (3) and the orthogonal polynomials (after adjustment to the equation 11) are given in Table IV. In both tables the corresponding mean relative errors are also given.

DISCUSSION

When binodal data were correlated by means of equation (1) with 7 constants the same accuracy was achieved as with orthogonal polynomials of the 15th degree. This means that the equation (1) is not hampered by a systematic error. In view of the lower

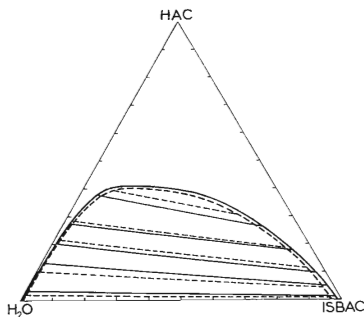


FIG. 1
Equilibrium Diagram of the System Isobutyl
Acetate (ISBAC)–Acetic Acid (HAC)–Water;
Full Curve 25°C, Dashed Curve 50°C

TABLE IV
 Constants for the Calculation of the Distribution Curves

Equation	Constants, 25°C	σ , %	Constants, 50°C	σ , %
(2)	$r = 0.30654$ $s = 1.1614$	4.90	$r = 0.32382$ $s = 1.1609$	8.39
(3)	$m = 1.3563$ $n = 1.0149$	15.56	$m = 0.82228$ $n = 1.1144$	28.52
(11)	$B_0'' = 4.66934 \cdot 10^{-1}$ $B_1'' = 2.30299$ $B_2'' = -4.91905 \cdot 10^{-2}$ $B_3'' = 5.65139 \cdot 10^{-4}$	2.84	$B_0'' = 4.31804 \cdot 10^{-1}$ $B_1'' = 2.18880$ $B_2'' = -3.69769 \cdot 10^{-2}$ $B_3'' = 2.33661 \cdot 10^{-4}$	2.64

number of constants the equation (1) is more suitable for the correlation of the binodal data, although the circumstance that it is implicit in w_c is a certain disadvantage, and therefore the calculation of this value requires an iterative procedure. In both instances it was found that decreasing the weight of the points in aqueous phase in the region of low w_c values brought about a decrease of the error to one half of its value. This strengthened the assumption that these points are hampered by a systematic error.

In the correlation of the distribution data a better agreement with experimental data was achieved with orthogonal polynomials than when the other two correlations were employed.

Equilibrium data, smoothed out using the best correlations are represented graphically in Fig. 1. It is evident that the effect of the temperature within the investigated range is relatively small.

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