PHASE EQUILIBRIA IN THE METHANOL–WATER–1-BUTANOL SYSTEM

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The mutual solubility of components in the water–1-butanol system as a function of temperature (from 80°C up to the critical solution temperature) and the mutual solubility of components in the methanol–water–1-butanol system at 25, 45, and 65°C were measured. Simultaneously, the vapour–liquid equilibrium in the methanol–water–1-butanol at a pressure of 760 Torr in homogeneous region was determined. The vapour–liquid equilibrium data were correlated by the Redlich–Kister equation.

In connection with a systematic study of phase equilibria of multicomponent systems, the behaviour of the system of three strongly polar substances was studied.

EXPERIMENTAL AND RESULTS

Preparation of pure substances. Methanol, an analytical reagent, was dried with Grignard's reagent and distilled over on a packed column; b.p. 64·7°C/760 Torr, d_4^{25} 0·7865, n_D^{25} 1·3267 (ref.[1] gives 64·50—64·75, 0·7865—0·7867, 1·32657). 1-Butanol, an analytical grade reagent, was distilled over on a forty-plate bubble-cup column; b.p. 117·9°C/760 Torr, d_4^{25} 0·8057, n_D^{25} 1·3974 (ref.[1] gives 117·7—118·0, 0·80567—0·80572, 1·3970—1·3974). Redistilled water was used.
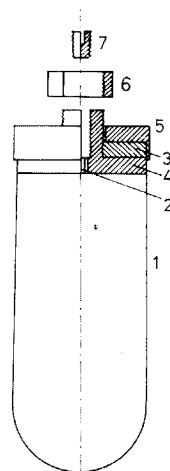

Fig. 1

Polypropylene Measuring Cell

1 Core of polypropylene cell, 2 hole for syringe needle, 3 packing, 4 closure body, 5 closure cover, 6 tightened nut, 7 plug screw.

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TABLE I

Mutual Solubility of Components in the Water(2)–1-Butanol(3) System

w_3	t, °C	w_3	t, °C
0·073	82·7	0·365	124·3
0·083	94·0	0·380	124·2
0·089	98·5	0·414	123·9
0·103	107·2	0·455	123·1
0·117	111·6	0·500	121·0
0·126	114·0	0·521	119·8
0·149	117·8	0·526	119·3
0·184	121·7	0·568	115·2
0·186	121·9	0·604	110·2
0·207	123·1	0·629	106·1
0·261	124·1	0·634	105·2
0·297	124·3	0·666	98·7
0·318	124·4	0·672	97·3
0·325	124·4	0·698	90·1
0·340	124·4	0·705	87·1

TABLE II

Smoothed Solubility Data in the Water(2)–1-Butanol(3) System

t, °C	w_2	$\overline{w}_2$
90	0·301$_5$	0·919$_5$
92·7[a]	0·310$_5$	0·916$_5$
95	0·319	0·91
100	0·341	0·909
105	0·366	0·901$_5$
110	0·395	0·888$_5$
115	0·434	0·869
120	0·483	0·833$_5$
122	0·519	0·813
124	0·594	0·749
124·4[b]	0·675	—

[a] Normal boiling point of heteroazeotrope. [b] Critical point.

Composition of Coexisting Phases in the Methanol(1)–Water(2)–1-Butanol(3) System at 25°C

Water phase		Butanol phase	
w_1	w_2	$\overline{w}_1$	$\overline{w}_2$
0·015	0·912	0·010	0·214
0·023	0·904	0·014	0·219
0·041	0·882	0·027	0·230
0·060	0·859	0·043	0·258
0·071	0·847	0·054	0·265
0·082	0·831	0·063	0·281
0·101	0·808	0·081	0·323
0·112	0·783	0·093	0·351
0·120	0·763	0·101	0·378

Mutual solubility of components in the water–1-butanol system was determined by the turbidity method with visual indication of turbidity in an apparatus described in another paper[2]. The measured values are presented in Table I. A smooth curve was plotted through the experimental points and the composition of coexisting phases was determined at various temperatures (Table II). The coordinates of the critical point ($t_c = 124\cdot4°C$, $w_{2c} = 0\cdot675$, and/or $x_{2c} = 0\cdot895$) were established by means of the Cailletet–Mathias rule.

Mutual solubility of components in the three-component system methanol–water–1-butanol was determined at temperatures 25, 45, and 65°C and the measured values are given in Tables III, IV, and V. For establishing the equilibrium, polypropylene measuring cells with a special aluminium-steel closure (Fig. 1), usually used with preparative ultracentrifuge Spinco, were used.

Composition of Coexisting Phases in the Methanol(1)–Water(2)–1-Butanol(3) System at 45°C

Water phase		Butanol phase	
w_1	w_2	$\overline{w}_1$	$\overline{w}_2$
0·015	0·925	0·011	0·235
0·021	0·921	0·017	0·248
0·038	0·896	0·031	0·264
0·055	0·872	0·045	0·294
0·078	0·839	0·069	0·338
0·091	0·812	0·082	0·369
0·096	0·798	0·088	0·391

These cells filled with corresponding solutions were tempered and after establishing equilibrium both phases were analyzed.

Analysis of equilibrium samples was carried out by a Giede gas chromatograph on a combined column: 1·5 m of the column filled with pulverized Teflon coated with 13% cetyl alcohol and 0·5 m of the column filled also with pulverized Teflon coated with 13% polyethylene glycol 600. Teflon appeared to be a very suitable support for chromatographic separation of water for other supports with the same stationary phases cause a considerable tailing of water peaks. On the other hand the Teflon columns are difficult to prepare[3]. Electrolytic hydrogen was used as a carrier gas. The optimum temperature of separation was 80°C and the pressure drop over the columns 0·1 atm/m. The analysis of every sample was repeated minimally four times to increase its accuracy. By using samples of a known composition, the accuracy of single component determina-

TABLE V

Composition of Coexisting Phases in the Methanol(1)–Water(2)–1-Butanol(3) System at 65°C

	Water phase		Butanol phase	
	w_1	w_1	$\overline{w}_1$	$\overline{w}_2$
	0·015	0·922	0·013	0·264
	0·020	0·917	0·018	0·273
	0·038	0·897	0·034	0·295
	0·054	0·871	0·051	0·338
	0·077	0·833	0·074	0·419

TABLE VI

Binodal Curve in the Methanol(1)–Water(2)–1-Butanol(3) System at 25°C

w_1	w_2	w_3
—	0·203	0·797
0·014	0·219	0·767
0·034	0·240	0·726
0·064	0·287	0·649
0·092	0·355	0·554
0·097	0·362	0·541
0·100	0·379	0·521
0·115	0·463	0·422
0·124	0·544	0·332
0·128	0·616	0·256
0·124	0·703	0·173

TABLE VII

Vapour–Liquid Equilibrium in the Methanol(1)–Water(2)–1-Butanol(3) System at a Pressure of 760 Torr

x_1	x_2	y_1	y_2	$t, °C$	$\Delta y_1{}^a$	$\Delta y_2{}^b$
0·437	0·531	0·708	0·277	75·46	−0·009	0·012
0·426	0·507	0·678	0·297	76·58	−0·011	0·018
0·390	0·500	0·595	0·352	77·59	−0·048	0·045
0·302	0·614	0·563	0·382	79·48	−0·008	0·013
0·295	0·586	0·542	0·395	80·11	−0·003	0·012
0·268	0·573	0·513	0·415	81·33	0·016	0·001
0·202	0·679	0·423	0·484	83·28	−0·001	0·013
0·187	0·643	0·395	0·498	83·88	0·015	−0·002
0·172	0·614	0·359	0·522	85·03	0·014	−0·001
0·164	0·576	0·332	0·539	85·40	0·006	0·006
0·145	0·534	0·306	0·550	86·16	0·014	0·011
Mean deviations					*0·013*	*0·011*

$^a \Delta y_1 = y_{1,\text{exp}} - y_{1,\text{calc}}.$ $^b \Delta y_2 = y_{2,\text{exp}} - y_{2,\text{calc}}.$

tion was estimated at approximately ±1·2 weight percent. At 25°C the course of the binodal curve, established on the basis of direct analytical determination of composition of conjugated phases, was checked by titration. The data measured in this way are given in Table VI.

Measurement of the vapour–liquid equilibrium data in the three-component system was carried out in a modified Gillespie still[4] at a constant pressure of 760 Torr and in the concentration regions where the liquid and vapour phase is homogeneous. The pressure was maintained at a constant value by the inert nitrogen atmosphere by means of a water tube manostat. The temperature was measured by standard thermometers with an accuracy of ±0·01°C. The analysis of the liquid and vapour phase samples was carried out in the same way as in case of the solubility determination. The experimental values are given in Table VII.

The binary constants needed for calculating the ternary system were calculated from the literature data (for the methanol(1)–water (2) system from[5], for the methanol(1)–1-butanol(3) system from[6], and for the water(2)–1-butanol(3) system from[7]) in terms of the Redlich–Kister equation[8]

$$\log (\gamma_1/\gamma_2) = b_{12}(x_2 - x_1) + c_{12}(6x_1x_2 - 1) + d_{12}(x_1 - x_2)(8x_1x_2 - 1) +$$
$$+ e_{12}(x_1 - x_2)^2 (10x_1x_2 - 1). \tag{1}$$

The following set of binary constants was calculated:

$$b_{12} = 0.2620, \quad c_{12} = 0.0938, \quad d_{12} = -0.0380,$$
$$b_{13} = 0.0672, \quad c_{13} = 0.0121,$$
$$b_{23} = 0.8440, \quad c_{23} = 0.2804, \quad d_{23} = 0.3481, \quad e_{23} = 0.2300.$$

By using the relations valid for the ternary system

$$
\begin{aligned}
\log\left(\gamma_1/\gamma_2\right) = {} & b_{12}(x_2 - x_1) + c_{12}\left[2x_1x_2 - (x_1 - x_2)^2\right] + \\
& + d_{12}(x_1 - x_2)\left[4x_1x_2 - (x_1 - x_2)^2\right] + b_{13}x_3 + c_{13}x_3(2x_1 - x_3) - \\
& - b_{23}x_3 + c_{23}x_3(x_3 - 2x_2) + d_{23}x_3(x_2 - x_3)(x_3 - 3x_2) + \\
& + e_{23}x_3(x_2 - x_3)^2 - C_{123}x_3(x_1 - x_2),
\end{aligned}
\tag{2}
$$

$$
\begin{aligned}
\log\left(\gamma_1/\gamma_3\right) = {} & b_{12}x_2 + c_{12}x_2(2x_1 - x_2) + d_{12}(x_1 - x_2)x_2(3x_1 - x_2) - \\
& - b_{13}(x_1 - x_3) + c_{13}\left[2x_1x_3 - (x_1 - x_3)^2\right] - b_{23}x_2 + \\
& + c_{23}x_2(2x_3 - x_2) + d_{23}(x_2 - x_3)x_2(3x_3 - x_2) + \\
& + e_{23}(x_2 - x_3)^2 x_2(4x_3 - x_2) - C_{123}x_2(x_1 - x_3)
\end{aligned}
\tag{3}
$$

the ternary constant $C_{123} = -0.1363$ was calculated. The correlation of the experimental data gave a satisfactory agreement of measured and calculated values.

REFERENCES

1. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, New York 1950.
2. Matouš J., Novák J. P., Šobr J., Pick J.: This Journal *37*, 2653 (1972).
3. Kohoutová J., Samohýl I.: Sborník Vysoké školy chemickotechnologické v Praze B 9 (1966).
4. Boublík T., Benson G. C.: Can J. Chem. *47*, 539 (1969).
5. Kohoutová J., Suška J., Novák J. P., Pick J.: This Journal *35*, 3210 (1970).
6. Polák J., Murakami S., Lam V. T., Pflug H. D., Benson G. C.: Can. J. Chem. *48*, 2457 (1970).
7. Stockhardt J. S., Hull C. M.: Ind. Eng. Chem. *23*, 1438 (1931).
8. Redlich O., Kister A. T.: Ind. Eng. Chem. *40*, 345 (1948).

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