

## LIQUID-LIQUID EQUILIBRIA IN THE TERNARY ACRYLIC ACID-EXTRACTION SOLVENT-WATER SYSTEMS

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Binodal curves and tie-lines have been determined in the acrylic acid-diisopropyl ether-water, acrylic acid-isopropyl acetate-water, acrylic acid-2-ethylhexanol-water, and acrylic acid-methyl isobutyl ketone-water systems at 24.6°C. The tie-lines have been correlated by the Othmer-Tobias and Bachman equations and the binodal curves by a new correlation equation, the deviations being within the experimental error.

As part of a systematic study of thermodynamic properties of ternary mixtures whose components belong to various groups of Ewell's classification of liquids, the liquid-liquid equilibria were measured for four acrylic acid-extraction solvent-water systems.

### EXPERIMENTAL

*Materials used.* The methods of purification and physical constants of all substances used were given in previous communications<sup>1,2</sup>.

*Analytical method.* The content of acrylic acid in equilibrium samples (for the tie-lines determination) was determined by visual alkalimetric titration. The ethanolic 0.1M-NaOH solution prepared from distilled ethanol and metallic sodium and Thymol Blue indicator were used. The titrations were carried out in a nitrogen atmosphere. The accuracy of the acid determination was  $\pm 0.2$  per cent.

*Experimental procedure.* The binodal (solubility) curves were determined by titration of prepared binary heterogeneous mixtures of water and organic solvent with acrylic acid until the turbidity disappeared. For the details of the method see<sup>3</sup>.

The composition of conjugate phases was determined from the known binodal curve and the measured concentrations of acrylic acid in both phases. For this purpose, the suitably chosen mixture of acid, water, and solvent were sealed into glass ampoules together with a glass ball to ensure good mixing of both phases and a set of such ampoules of different composition was rotated in a thermostat for about five hours at  $24.6 \pm 0.1^\circ\text{C}$ . After separating both phases, the samples were taken by syringes, weighed, diluted with distilled ethanol into volumetric flasks, pipetted and analyzed in the above mentioned way. The tie-lines were found in terms of the intersection points of the two branches of the binodal curve with the measured acrylic acid

concentrations. The plait point was then determined as the point of intersection of the binodal curve and the line connecting centres of the tie-lines.

## RESULTS AND DISCUSSION

The measured points of the binodal curves are given in Table I, the compositions of the conjugate phases and the plait points in Table II.

For numerical correlation of the measured solubility data, the equation was proposed<sup>4</sup>

$$w_C = x_1 x_2 \sum_{i=1}^n A_i (x_2 - x_1)^{i-1} + A_{n+1} x_1 \ln x_1 + A_{n+2} x_2 \ln x_2, \quad (1)$$

where  $x_1 = (w_B + kw_C - w_{BA}^0)/(w_{BB}^0 - w_{BA}^0)$  and  $x_2 = (w_{BB}^0 - w_B - kw_C)/(w_{BB}^0 + w_{BA}^0)$ , the symbol  $w$  denotes weight fractions as follows:  $w_C$  of acrylic acid and  $w_B$  or organic solvent in the ternary system,  $w_{BB}^0$  of organic solvent in the solvent-rich phase and  $w_{BA}^0$  of organic solvent in water-rich phase of the respective binary system. The  $k$  is an empirical constant from the interval  $\langle 0,1 \rangle$  whose value is to be determined in advance and  $A_i$  empirical constants determined by the least squares method. The values of the computed empirical constants together with the deviations of the calculated and measured data are given in Table III.

For correlation of tie-lines, a number of empirical relations had been proposed<sup>5</sup>. The graphic treatment of the data showed that the most suitable are: the Othmer-Tobias equation<sup>6</sup>

$$(1 - w_B)/w_B = c[(1 - w_A)/w_A]^r \quad (2)$$

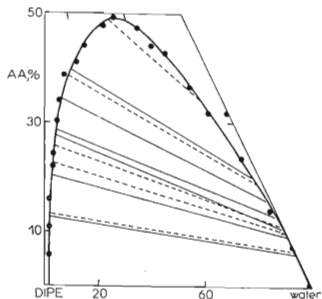


FIG. 1

Liquid-Liquid Equilibrium in the Acrylic Acid (AA)-Diisopropyl Ether (DIPE)-Water System at 20.0°C

Composition in weight per cent. ● Frolov and coworkers<sup>8</sup>, --- this work.

and the Bachman equation<sup>7</sup>

$$w_B = r + cw_B/w_A, \quad (3)$$

where  $w_A$ ,  $w_B$  are weight fractions of water in the water-rich phase and the organic solvent in the solvent-rich phase, resp., and  $c$  and  $r$  are empirical constants characteristic for the given equation and the given system. Whereas the former equation

TABLE I  
Binodal Curves in the Acrylic Acid-Extraction Solvent-Water Systems at 24°C (weight fractions)

Acrylic acid	Diisopropyl ether	Water	Acrylic acid	2-Ethylhexanol	Water
0.000	0.991	0.009	0.000	0.980	0.020
0.196	0.761	0.043	0.111	0.855	0.033
0.322	0.598	0.080	0.272	0.668	0.060
0.412	0.471	0.116	0.402	0.486	0.112
0.474	0.331	0.195	0.468	0.349	0.183
0.472	0.223	0.305	0.481	0.237	0.282
0.431	0.134	0.435	0.469	0.140	0.391
0.367	0.067	0.566	0.427	0.059	0.515
0.297	0.036	0.667	0.393	0.037	0.569
0.222	0.021	0.757	0.349	0.021	0.630
0.000	0.014	0.986	0.318	0.014	0.668
			0.235	0.005	0.760
			0.000	>0.000	<1.000

Acrylic acid	Isopropyl acetate	Water	Acrylic acid	Methyl isobutyl ketone	Water
0.000	0.978	0.022	0.000	0.976	0.024
0.089	0.862	0.049	0.133	0.811	0.056
0.206	0.703	0.091	0.232	0.676	0.092
0.317	0.535	0.148	0.354	0.489	0.157
0.361	0.446	0.193	0.393	0.406	0.201
0.396	0.286	0.318	0.410	0.267	0.323
0.386	0.286	0.328	0.361	0.164	0.475
0.341	0.184	0.475	0.322	0.115	0.563
0.304	0.128	0.568	0.260	0.060	0.680
0.243	0.071	0.686	0.196	0.033	0.771
0.152	0.037	0.811	0.146	0.024	0.830
0.118	0.030	0.852	0.000	0.019	0.981
0.000	0.022	0.978			

TABLE II  
Compositions of Conjugate Phases in the Acrylic Acid-Extraction Solvent-Water Systems at 24.6°C (weight fractions)

Organic phase			Water phase		
Water	acrylic acid	diisopropyl ether	water	acrylic acid	diisopropyl ether
0.009	0.000	0.991	0.986	0.000	0.014
0.034	0.148	0.818	0.918	0.073	0.009
0.059	0.256	0.685	0.874	0.117	0.009
0.109	0.394	0.497	0.781	0.202	0.017
0.122	0.422	0.456	0.745	0.233	0.022
0.156	0.457	0.387	0.683	0.284	0.033
0.394 <sup>a</sup>	0.446	0.160	0.394	0.446	0.160
Water	acrylic acid	isopropyl acetate	water	acrylic acid	isopropyl acetate
0.022	0.000	0.978	0.978	0.000	0.022
0.068	0.143	0.789	0.925	0.052	0.023
0.116	0.260	0.624	0.872	0.100	0.028
0.148	0.317	0.535	0.833	0.134	0.033
0.235	0.381	0.384	0.745	0.203	0.052
0.378	0.375	0.246	0.596	0.291	0.113
0.488 <sup>a</sup>	0.336	0.176	0.488	0.336	0.176
Water	acrylic acid	2-ethylhexanol	water	acrylic acid	2-ethylhexanol
0.020	0.000	0.980	<1.000	0.000	>0.000
0.036	0.137	0.827	0.935	0.064	0.001
0.053	0.242	0.705	0.864	0.135	0.001
0.075	0.316	0.609	0.796	0.201	0.003
0.093	0.361	0.546	0.744	0.249	0.007
0.111	0.398	0.491	0.686	0.302	0.012
0.333 <sup>a</sup>	0.478	0.189	0.333	0.478	0.189
Water	acrylic acid	methyl isobutyl ketone	water	acrylic acid	methyl isobutyl ketone
0.024	0.000	0.976	0.981	0.000	0.019
0.066	0.163	0.771	0.927	0.054	0.019
0.103	0.258	0.639	0.888	0.093	0.019
0.152	0.348	0.500	0.830	0.145	0.025
0.188	0.383	0.429	0.796	0.175	0.029
0.189	0.384	0.427	0.794	0.177	0.029
0.487 <sup>a</sup>	0.355	0.158	0.487	0.355	0.158

<sup>a</sup> Plait point.

TABLE III

Correlation of Binodal Curves in Four Ternary Acrylic Acid-Extraction Solvent-Water Systems at 24.6°C

Quantity	Diisopropyl ether	Isopropyl acetate	2-Ethylhexanol	Methyl isobutyl ketone
$n^a$	1	2	3	3
$k$	0.3	0.5	0.7	1
$A_1$	0.990	1.558	5.484	2.663
$A_2$	-0.911	-0.560	0.244	0.266
$A_3$	0.306	-0.436	1.674	1.657
$A_4$	—	0.455	1.849	1.394
$A_5$	—	—	0.735	-0.476
$w_{BB}^0$	0.991	0.978	0.980	0.976
$w_{BA}^0$	0.014	0.022	0.0007 <sup>b</sup>	0.019
Mean <sup>c</sup>	0.0044	0.0041	0.0022	0.0023
Rms <sup>c</sup>	0.0059	0.0062	0.0035	0.0038

<sup>a</sup> For explanation of the symbols see Eq. (1) and the text. <sup>b</sup> This value was taken from another work<sup>9</sup>. <sup>c</sup> Mean and rms deviations were calculated according to the formulas: mean =  $\sum |w_{calc.} - w_{exp.}|/n_{exp.}$  and rms =  $(\sum (w_{calc.} - w_{exp.})^2 / (n_{exp.} - n_{const.}))^{1/2}$ , where  $w$ 's are the weight fractions,  $n_{exp.}$  is the number of experimental points and  $n_{const.}$  is the number of empirical constants.

TABLE IV

Correlation of Tie-Lines in Four Ternary Acrylic Acid-Extraction Solvent-Water Systems at 24.6°C

Quantity	Diisopropyl ether	Isopropyl acetate	2-Ethylhexanol	Methyl isobutyl ketone
Eq.	(3)	(3)	(2)	(3)
$c^a$	-0.3492	-0.2545	2.0458	-0.2046
$r^a$	1.3149	1.2267	0.8552	1.1732
Mean <sup>b</sup>	0.005	0.003	0.002	0.001
Rms <sup>b</sup>	0.008	0.005	0.003	0.002

<sup>a</sup> For explanation of the symbols see Eqs (2), (3). <sup>b</sup> For explanation see note c in Table III.

gave the best results with the system acrylic acid-2-ethylhexanol-water, the latter was better for the other systems. The values of the constants computed by the least squares method and the deviations of the calculated and measured values are given in Table IV.

It is seen from Tables III and IV that the agreement of the calculated and experimental values is very good and comparable with the experimental error. Thus, Eqs (1)–(3) together with the values of the empirical constants in Tables III and IV can be considered adequate for the description of the liquid-liquid equilibria in the ternary systems.

The only data found in the literature, concerning the equilibria mentioned, are those on the system acrylic acid-diisopropyl ether-water at 20°C published by Frolow and coworkers<sup>8</sup>. Because of some discrepancies between that and our measurement, we remeasured five equilibrium concentrations of acrylic acid (as well at 20.0°C) and these points entered into the triangle diagram of the authors<sup>8</sup>. From Fig. 1 it is evident that the course of tie-lines of both measurements is in the main in good agreement. Nevertheless, several points of the binodal curve and one tie-line of the paper<sup>8</sup> are evidently in error.

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