DISTRIBUTION OF ACRYLIC AND ACETIC ACIDS IN WATER–ORGANIC SOLVENT SYSTEMS

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The distribution of acrylic and acetic acids in ternary water–acid–solvent systems was investigated at low concentrations and at 25°C with 2-ethylhexanol and isopropyl acetate as solvents. The interaction of both acids in quaternary water–acrylic acid–acetic acid–solvent systems was also studied. The concentration of acetic acid could be correlated in the concentration range studied with sufficient accuracy by linear relationships in both the Hand and Othmer–Tobias coordinates. The concentration range in the systems containing acrylic acid was divided into two parts. The region of lower or higher concentrations was correlated by linear or power-law relations, respectively.

This work is a continuation of studies performed by Hlavatý, Linek and Wichterle[1,2] in which ternary equilibria of acrylic and acetic acids in systems containing water and an organic solvent had been studied. Correlations of binodal curves and tie lines in these systems are given in the cited papers. In this work, the region of relatively low concentrations has been investigated, which is of special practical importance. The distribution of the acids in conjugated phases of both ternary systems containing only one of the acids and in the quaternary systems with both acids together was measured with 2-ethylhexanol and isopropyl acetate as solvents. As far as the binodal curves are concerned, the data in the preceding works[1,2] are sufficient even for calculating the composition in the quaternary systems due to a low mutual solubility of the solvents in this region and to similar behaviour of both acids in ternary systems.

EXPERIMENTAL

Materials used. Acrylic acid (pure) was rectified at 40 Torr in a 1 000 mm-long column filled by copper spirals. The distillate was stabilized by addition of 0·05% hydroquinone. Acetic acid (AR grade) was rectified on a bubble cap column with 40 plates. According to a chromatographic analysis, 2-ethylhexanol contained 0·5 wt.% 4-ethyl-2-methylpentanol. Isopropyl acetate contained by the chromatographic analysis 0·8 wt.% diisopropyl ether. Ethanol needed for the analytical determinations was rectified on a 40-plate bubble cap column in the presence of NaOH.

Analytical methods. The concentration of acid in ternary water–acid–solvent systems was determined alkalimetrically. A simultaneous determination of acrylic and acetic acids is impossible due to similar values of their dissociation constants. To find the concentration of the individual

acids in quaternary systems, therefore, the total amount of both acids was determined by titration and combined with the ratio of the acids found from chromatographic record. As the analyzed solutions including aqueous ones contained organic solvents, the titrations were performed in an ethanolic medium containing 0·1M ethanolic solution of NaOH and with bromothymol blue as indicator. Nitrogen atmosphere was used. The gas-chromatographical determinations were performed on a Chrom 4 apparatus produced by Laboratorní přístroje and provided with a flame ionization detector. Samples containing 2-ethylhexanol were analyzed on a 2500 mm-long column of the diameter of 3 mm. Polytetrafluoroethylene (ICI fluon) of the grain size of 0·2—0·4 mm with 8% Apiezone and 2% Carbowax M20 was used as packing. The temperatures of the column and the preheating section were 125°C and 150°C, resp. Nitrogen was used as carrier gas with the flow rate of 66 ml/min; the flow rates of hydrogen and air were 44 ml/min and 0·5 l/min. Samples containing isopropyl acetate were analyzed on a stainless 1200 mm-long column of the diameter of 3 mm with poly(cyanoethyl methacrylate)[3] (KEM) of the grain size of 0·2—0·3 mm as packing. The temperatures of the column and the preheating section were 145°C and 150°C, resp. Nitrogen was used as carrier gas with the flow rate of 60 ml/min; the flow rates of hydrogen and air were 30 ml/min and 0·5 l/min, resp. Calibration factors for recalculating the ratio of peak areas to the ratio of weight fractions of both acids were determined with the help of weighed samples.

Measurements of the equilibria. All measurements were performed at 25°C. Equilibrium concentrations in ternary systems were obtained by shaking aqueous solutions of the acids of different initial concentrations with the corresponding solvent in a thermostated bath for 50 min. In quaternary systems, the initial aqueous solution with the weight ratio of acrylic to acetic acid of 10 : 1 was repeatedly treated with the pure solvent.

RESULTS

The results of the measurements are given in Tables I — VI. Weight fractions of the second solvent in the ternary systems were calculated from the relation for the binodal curves from the work of Linek and coworkers[1,2], which are sufficiently accurate for this purpose even in the region of very low concentrations. The same procedure has been adopted for quaternary systems, for which binodal curves of the ternary acrylic acid-containing system have been used for the calculations.

The Hand[4]

$$x_{CB}/x_{BB} = k(x_{CA}/x_{AA})^r, \quad Y = kX^r \qquad (1)$$

and Othmer–Tobias[5]

$$(1 - x_{BB})/x_{BB} = k[(1 - x_{AA})/x_{AA}]^r \qquad (2)$$

relations were used for correlating the data. The following relations have been also tested for ternary acetic acid-containing systems

$$x_{CB}/x_{BB} = k(x_{CA}/x_{AA}) + r, \quad Y = kX + r, \qquad (3)$$

and

$$(1 - x_{BB})/x_{BB} = k(1 - x_{AA})/x_{AA} + r. \qquad (4)$$

Here x_{IJ} stands for the weight fraction of component I in the phase rich on solvent J (weight of I in the weight unit of the solution); X or Y is the weight ratio of the dissolved component in the aqueous or organic phase, resp.; k and r are constants; A, B and C denote water, solvent and solute, respectively.

Relations (1) and (3) may be easily rearranged to a form in which the distribution

TABLE I

Equilibrium Concentrations in 2-Ethylhexanol-Containing Systems
It was found in all cases that $x_{BA} = 0.00000$.

2-Ethylhexanol–acrylic acid–water			2-Ethylhexanol–acetic acid–water		
x_{CA}	x_{CB}	x_{BB}	x_{CA}	x_{CB}	x_{BB}
0·00018	0·00032	0·9784	0·00112	0·00069	0·9794
0·00035	0·00043	0·9782	0·00285	0·00176	0·9785
0·00070	0·00175	0·9762	0·00441	0·00270	0·9776
0·00080	0·00182	0·9761	0·00483	0·00298	0·9774
0·00220	0·00548	0·9713	0·00692	0·00413	0·9763
0·00250	0·00627	0·9703	0·00729	0·00438	0·9761
0·00700	0·01780	0·9568	0·00959	0·00565	0·9749
0·00770	0·01960	0·9547	0·00990	0·00578	0·9748
0·01960	0·04980	0·9213	0·01070	0·00639	0·9742
0·02000	0·05030	0·9207	0·01070	0·00646	0·9742
0·02270	0·05610	0·9144	0·01310	0·00780	0·9729
0·02290	0·05710	0·9133	0·01310	0·00772	0·9730
0·03400	0·08110	0·8872	0·01490	0·00893	0·9718
0·03690	0·08630	0·8815	0·01500	0·00902	0·9718
0·04460	0·10240	0·8640	0·01560	0·00927	0·9715
0·04510	0·10820	0·8577	0·01560	0·00939	0·9714
0·06230	0·13440	0·8290	0·01790	0·01070	0·9702
0·06380	0·13700	0·8260	0·01790	0·01060	0·9702
0·06450	0·13790	0·8250	0·02160	0·01280	0·9681
0·06490	0·14050	0·8221	0·02300	0·01390	0·9671
0·08920	0·18380	0·7735	0·03080	0·01800	0·9630
0·09100	0·18650	0·7704	0·03140	0·01860	0·9625
0·10060	0·19430	0·7615	0·03760	0·02200	0·9591
0·10540	0·19890	0·7562	0·03790	0·02220	0·9588
0·14970	0·26161	0·6819	0·04430	0·02530	0·9557
0·15030	0·26150	0·6821	0·04450	0·02560	0·9554

factor, m, depends on the weight ratio of the component in the aqueous phase, X. We obtain from Eq. (1)

$$m = kX^{r-1} \qquad (5)$$

and from Eq. (3)

$$m = k + rX^{-1}. \qquad (6)$$

Values of constants k and r for these relations are given in Table V together with the standard deviation s of a single measurement from these correlations. It may be seen that the ternary acetic acid-containing systems exhibit for all relations an error by an order less than that for the acrylic acid-containing systems. It is probably caused by a narrow concentration range in the case of acetic acid.

TABLE II
Equilibrium Concentrations in Isopropyl Acetate-Containing Systems

x_{CA}	x_{BA}	x_{CB}	x_{BB}	x_{CA}	x_{BA}	x_{CB}	x_{BB}
Isopropyl acetate–acrylic acid–water				Isopropyl acetate–acrylic acid–water			
0·00058	0·0218	0·00109	0·9719	0·00293	0·0255	0·00167	0·9761
0·00062	0·0218	0·00128	0·9715	0·00481	0·0262	0·00285	0·9748
0·00113	0·0217	0·00301	0·9684	0·00640	0·0266	0·00383	0·9737
0·00126	0·0217	0·00328	0·9679	0·00714	0·0268	0·00418	0·9733
0·00232	0·0214	0·00739	0·9614	0·00915	0·0272	0·00541	0·9719
0·00238	0·0214	0·00720	0·9617	0·01070	0·0275	0·00653	0·9706
0·00432	0·0210	0·01430	0·9516	0·01120	0·0276	0·00671	0·9704
0·00448	0·0210	0·01470	0·9511	0·01280	0·0278	0·00738	0·9696
0·00758	0·0205	0·02650	0·9354	0·01460	0·0280	0·00854	0·9682
0·00793	0·0204	0·02680	0·9350	0·01470	0·0281	0·00901	0·9677
0·01570	0·0195	0·05210	0·9034	0·01840	0·0284	0·01140	0·9648
0·01580	0·0195	0·05120	0·9045	0·02140	0·0286	0·01310	0·9628
0·03020	0·0186	0·09670	0·8489	0·02280	0·0287	0·01390	0·9618
0·03070	0·0186	0·09970	0·8452	0·02740	0·0289	0·01790	0·9571
0·06110	0·0194	0·18370	0·7392	0·02860	0·0289	0·01690	0·9583
0·06150	0·0194	0·17930	0·7450	0·03340	0·0290	0·02090	0·9534
0·11430	0·0272	0·28900	0·5853	0·03470	0·0291	0·02180	0·9523
0·11510	0·0274	0·28620	0·5899	0·03960	0·0291	0·02510	0·9483
				0·04060	0·0291	0·02590	0·9473
				0·04780	0·0292	0·03050	0·9415
				0·04780	0·0292	0·03010	0·9420
				0·05550	0·0292	0·03560	0·9351
				0·05580	0·0292	0·03540	0·9354

As the region of low acrylic acid concentrations displayed on the graphs a linear dependence, we decided to correlate this region by linear relations (3) and (4) and the region of higher concentrations by power-law relations (1) and (2). The transition from the linear to the power-law relation securing the best fit has been found to be at the value of the mole fraction of the solute in the aqueous phase equal to 0·03. The values of k, r and s for these correlations are given in Table V. It is seen that the accuracy of the correlations has been increased by an order.

TABLE III

Equilibrium Concentrations in the Isopropyl Acetate–Acrylic Acid–Acetic Acid–Water System

Acrylic acid		Acetic acid			
x_{CA}	x_{CB}	x_{CA}	x_{CB}	x_{BA}	x_{BB}
0·00085	0·00589	0·00163	0·00135	0·0217	0·9637
0·00196	0·00471	0·00057	0·00061	0·0215	0·9656
0·00219	0·00609	0·00276	0·00264	0·0215	0·9634
0·00375	0·00834	0·00431	0·00324	0·0211	0·9600
0·00501	0·01080	0·00139	0·00118	0·0209	0·9565
0·00537	0·01200	0·00128	0·00116	0·0209	0·9548
0·00668	0·01240	0·00543	0·00660	0·0206	0·9542
0·00821	0·01800	0·00508	0·00586	0·0204	0·9465
0·01180	0·02960	0·00242	0·00144	0·0199	0·9314
0·01180	0·02990	0·00237	0·00162	0·0199	0·9311
0·01300	0·03490	0·00799	0·00693	0·0198	0·9247
0·01320	0·03450	0·00675	0·00706	0·0198	0·9253
0·02520	0·06960	0·00329	0·00209	0·0188	0·8820
0·02590	0·06260	0·00280	0·00167	0·0188	0·8905
0·02840	0·08050	0·00863	0·00640	0·0187	0·8687
0·02930	0·08090	0·00804	0·00616	0·0186	0·8682
0·04980	0·14200	0·00385	0·00300	0·0187	0·7928
0·05000	0·14050	0·00368	0·00274	0·0187	0·7947
0·05380	0·15700	0·01020	0·00876	0·0189	0·7738
0·05520	0·14960	0·00989	0·00990	0·0190	0·7832
0·08270	0·23110	0·00456	0·00383	0·0216	0·6743
0·08350	0·22620	0·00440	0·00380	0·0218	0·6813
0·09830	0·25920	0·01170	0·01160	0·0241	0·6329
0·09970	0·25400	0·01160	0·01110	0·0243	0·6408
0·13430	0·31910	0·00546	0·00488	0·0321	0·5311
0·14860	0·31650	0·00564	0·00492	0·0363	0·5361
0·16320	0·34500	0·01610	0·01390	0·0411	0·4758
0·16460	0·32900	0·01350	0·01270	0·0416	0·5113

It is possible to perform a mutual comparison of accuracy of relations $(1)-(4)$ with the help of a statistical test. In view of the fact that the mean values expressed in the Hand and Othmer–Tobias coordinates are different, relative standard deviations related to the corresponding mean value have been employed. The one-sided F-test[6] is appropriate in this case. For acetic acid it was applied to the variances calculated from the linear and power-law relations, resp. For acrylic acid, relations (3) and (4) at $x_{CA} < 0.03$ or (1) and (2) at $x_{CA} > 0.03$ have been mutually compared.

TABLE IV

Equilibrium Concentrations in the 2-Ethylhexanol–Acrylic Acid–Acetic Acid–Water System

It was found in all cases that $x_{BA} = 0.0000$.

Acrylic acid		Acetic acid		
x_{CA}	x_{CB}	x_{CA}	x_{CB}	x_{BB}
0.00115	0.00117	0.00111	0.00106	0.9770
0.00183	0.00242	0.00193	0.00151	0.9753
0.00212	0.00270	0.00302	0.00280	0.9739
0.00359	0.00632	0.00522	0.00382	0.9703
0.00378	0.00823	0.00360	0.00225	0.9679
0.00754	0.02080	0.00827	0.00577	0.9533
0.00761	0.02055	0.00817	0.00531	0.9536
0.01100	0.02860	0.00620	0.00338	0.9446
0.01490	0.04100	0.01100	0.00597	0.9309
0.01580	0.03950	0.01100	0.00699	0.9325
0.01600	0.04130	0.00725	0.00345	0.9306
0.01710	0.04120	0.00740	0.00326	0.9307
0.02810	0.06850	0.00842	0.00425	0.9009
0.03300	0.07650	0.01310	0.00745	0.8923
0.03350	0.07730	0.01340	0.00729	0.8913
0.03360	0.07850	0.00757	0.00476	0.8900
0.04960	0.11400	0.00838	0.00403	0.8513
0.05040	0.11550	0.00824	0.00399	0.8497
0.05800	0.13080	0.01490	0.00886	0.8328
0.06050	0.12630	0.01560	0.00958	0.8378
0.09900	0.18920	0.01500	0.00950	0.7674
0.09960	0.19130	0.01800	0.00994	0.7650
0.10720	0.19520	0.00947	0.00571	0.7605
0.11110	0.20320	0.01000	0.00590	0.7513
0.13730	0.24850	0.01830	0.01140	0.6979
0.14980	0.26830	0.01840	0.01290	0.6737

The results are summarized in Table VI. According to this table, the following relations may be recommended for the systems studied:

2-ethylhexanol–acrylic acid–water: $x_{CA} < 0.03$, relation (3) or (4)
$x_{CA} > 0.03$, relation (1) or (2)

2-ethylhexanol–acetic acid–water: relation (4)

isopropyl acetate–acrylic acid–water: $x_{CA} < 0.03$, relation (3)
$x_{CA} > 0.05$, relation (1) or (2)

isopropyl acetate–acetic acid–water: relations (1), (2), (3) or (4).

TABLE V

Values of Constants k and r and Standard Deviations s for Relations (1) to (4)

System	Relations	k	r	s
	Overall dependence			
2-Ethylhexanol–acrylic acid–water	(1)	2·704	1·030	0·02249
	(2)	0·7420	0·4828	0·04984
2-Ethylhexanol–acetic acid–water	(1)	0·5451	0·9765	0·0002
	(2)	0·08482	0·2420	0·00276
	(3)	0·5761	0·0003363	0·00022
	(4)	0·5689	0·02033	0·00014
Isopropyl acetate–acrylic acid–water	(1)	4·949	1·093	0·02170
	(2)	14·956	1·573	0·06706
Isopropyl acetate–acetic acid–water	(1)	0·6805	1·031	0·00034
	(2)	0·6138	0·9305	0·00108
	(3)	0·6297	−0·0004183	0·00036
	(4)	0·7160	0·001786	0·00086
	Dependences for regions of lower and higher concentrations			
2-Ethylhexanol–acrylic acid–water	(1)	1·790	0·8839	0·00462
	(2)	1·8520	0·8030	0·00564
	(3)	2·681	−0·0002457	0·00033
	(4)	3·177	0·02228	0·00079
Isopropyl acetate–acrylic acid–water	(1)	3·638	0·9970	0·00791
	(2)	5·141	1·107	0·01171
	(3)	3·645	−0·001184	0·00079
	(4)	5·238	−0·08732	0·00310

Tables III and IV contain results of the measurements of equilibrium concentrations in the quaternary systems. For comparison, equilibrium weight fractions of acrylic acid in the quaternary mixture are plotted in Figs 1 and 2 and compared

TABLE VI

F-Test

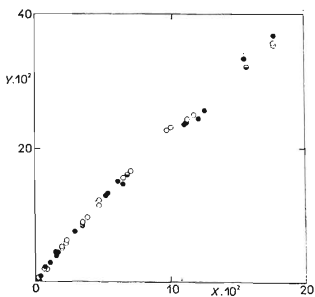| Compared relations $(A), (B)$	$s^2 \cdot 10^4$	Number of degrees of freedom	s_A^2/s_B^2	F_{AB}
		2-Ethylhexanol–acrylic acid–water		
$(A) = (1)$	5·10	12	1·05	2·15
$(B) = (2)$	4·84			
$(A) = (4)$	2·45	10	1·30	2·32
$(B) = (3)$	1·89			
		2-Ethylhexanol–acetic acid–water		
$(A) = (2)$	80·7	24	23·8	1·70
$(B) = (1)$	3·39			
$(A) = (2)$	80·7	24	389	1·70
$(B) = (4)$	0·208			
$(A) = (3)$	4·10	24	1·21	1·70
$(B) = (1)$	3·39			
$(A) = (3)$	4·10	24	19·7	1·70
$(B) = (4)$	0·208			
		Isopropyl acetate–acrylic acid–water		
$(A) = (2)$	4·98	2	1·07	9·00
$(B) = (1)$	4·65			
$(A) = (4)$	18·2	12	3·11	2·15
$(B) = (3)$	5·84			
		Isopropyl acetate–acetic acid–water		
$(A) = (2)$	6·61	21	1·50	1·78
$(B) = (1)$	4·40			
$(A) = (2)$	6·61	21	1·58	1·78
$(B) = (4)$	4·19			
$(A) = (3)$	4·93	21	1·12	1·78
$(B) = (1)$	4·40			
$(A) = (3)$	4·93	21	1·18	1·78
$(B) = (4)$	4·19			

FIG. 1

Comparison of Equilibrium Concentrations of Acrylic Acid in 2-Ethylhexanol–Acrylic Acid–Water and 2-Ethylhexanol–Acrylic Acid–Acetic Acid–Water Systems

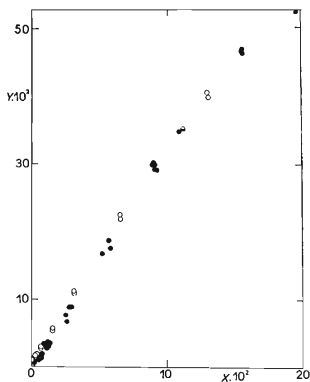○ Ternary system; ● quaternary system; ◐ points from ref.[2].

FIG. 2

Comparison of Equilibrium Concentrations of Acrylic Acid in Isopropyl Acetate–Acrylic Acid–Water and Isopropyl Acetate–Acrylic Acid–Acetic Acid–Water Systems

○ Ternary system; ● quaternary system; ◐ points from ref.[2].

with the values for the ternary mixture from Tables I and II. We may contend that the fourth component does not affect the equilibrium in the case of 2-ethylhexanol. A distinct shift in the data for the quaternary system is observed for the system containing isopropyl acetate. It is not certain, however, whether this is not due to a systematic error in the chromatographic determinations which are rather difficult in the case of isopropyl acetate.

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Translated by K. Hlavatý.