

LIQUID-LIQUID EQUILIBRIA IN FOUR TERNARY ACETIC ACID-ORGANIC SOLVENT-WATER SYSTEMS AT 24.6°C

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Solubilities and tie lines were determined in four ternary acetic acid-organic solvent-water systems at 24.6°C. The organic solvents used were diisopropyl ether, isopropyl acetate, 2-ethylhexanol and methyl isobutyl ketone. The tie lines were correlated by the Othmer-Tobias equation and the solubility data by a new correlation, both within the experimental error.

As a part of the systematic study¹ of thermodynamic properties of ternary mixtures whose components belong to various groups of Ewell's classification of liquids, the liquid-liquid equilibria were measured in four acetic acid-organic solvent-water systems.

EXPERIMENTAL

Materials. Preparation and properties of all chemicals used were described in previous communications²⁻³.

Binodal curves. The binodal curves were determined by titrating mixtures of water and the organic solvent with acetic acid until the mixture became homogeneous. The titrations were performed in a titration vessel according to Merti⁴ which can be thermostated during the titration. Both the vessel and the burette with acetic acid were thermostated to $24.6 \pm 0.1^\circ\text{C}$. The mixture was agitated vigorously by a magnetic stirrer during the titration. The equilibrium point could be determined easily by observing a distinctly printed text pasted on the opposite side of the titrating vessel with a narrow 35 W light beam passing simultaneously through the liquid mixture perpendicular to the line connecting the observer's eye and the text. The accuracy of the titration was somewhat lower for mixtures of compositions remote from the ternary plait point but in any case it was not lower than ± 0.3 weight %. The solubilities in the binary water-organic solvent mixtures were determined in the same manner.

Tie lines. A ternary liquid-liquid mixture was sealed into a glass ampule together with a glass ball to secure a good emulsification of both phases during rotating the ampule in the thermostat at $24.6 \pm 0.1^\circ\text{C}$; after 5 h the rotation was stopped and after both phases had separated, samples for analysis were withdrawn by a hypodermic syringe. The acetic acid concentration in the co-existing equilibrium phases was determined alkalimetrically by a 0.1M-NaOH solution in ethanol with thymol blue as indicator (yellow \rightarrow blue transition). The titration was performed in a nitrogen atmosphere with an accuracy of $\pm 0.2\%$. The tie lines were then found as intersections of the binodal curve with the respective acetic acid concentrations. The plait point was obtained as the

intersection point of the binodal curve and the line connecting centres of the tie lines on the weight fraction basis.

TABLE I
Binodal Curves in the Ternary Systems at 24.6°C (weight fractions)

Acetic acid	Diisopropyl ether	Water	Acetic acid	2-Ethylhexanol	Water
0.000	0.991	0.009	0.535	0.123	0.341
0.156	0.804	0.040	0.513	0.040	0.447
0.167	0.795	0.038	0.465	0.020	0.515
0.178	0.777	0.044	0.404	0.011	0.586
0.212	0.731	0.057	0.000	0.00	1.000
0.231	0.706	0.063			
0.258	0.669	0.074	Acetic acid	Isopropyl acetate	Water
0.258	0.668	0.074	0.000	0.978	0.022
0.356	0.517	0.128	0.138	0.789	0.075
0.403	0.420	0.177	0.215	0.660	0.125
0.433	0.343	0.225	0.295	0.472	0.233
0.456	0.274	0.270	0.319	0.316	0.364
0.471	0.214	0.315	0.320	0.187	0.494
0.475	0.159	0.365	0.294	0.114	0.592
0.464	0.109	0.427	0.230	0.064	0.706
0.461	0.107	0.432	0.043	0.029	0.928
0.397	0.061	0.542	0.000	0.022	0.978
0.373	0.043	0.584			
0.335	0.039	0.626	Acetic acid	Methyl isobutyl ketone	Water
0.000	0.014	0.986	0.000	0.976	0.024
Acetic acid	2-Ethylhexanol	Water	0.099	0.844	0.057
0.000	0.980	0.020	0.181	0.722	0.098
0.070	0.908	0.022	0.253	0.603	0.145
0.166	0.786	0.048	0.315	0.454	0.231
0.269	0.652	0.079	0.346	0.271	0.383
0.329	0.568	0.103	0.343	0.157	0.500
0.444	0.373	0.183	0.289	0.069	0.643
0.445	0.370	0.185	0.159	0.029	0.812
0.505	0.225	0.270	0.000	0.019	0.981

RESULTS AND CORRELATIONS

All results were expressed on the weight fraction basis and they are given in Tables I and II. The binodal curves were correlated by the equation⁵

TABLE II
Composition of the Coexisting Phases at 24.6°C (weight fractions)

Organic phase			Water phase		
Water	Acetic acid	Diisopropyl ether	Water	Acetic acid	Diisopropyl ether
0.009	0.000	0.991	0.986	0.000	0.014
0.013	0.036	0.951	0.868	0.112	0.020
0.015	0.049	0.936	0.834	0.146	0.020
0.032	0.133	0.835	0.674	0.295	0.031
0.055	0.206	0.739	0.563	0.384	0.053
0.066	0.236	0.698	0.519	0.414	0.067
0.240 ^a	0.441	0.319	0.240	0.441	0.319
Water	Acetic acid	2-Ethylhexanol	Water	Acetic acid	2-Ethylhexanol
0.020	0.000	0.980	1.000	0.000	0.000
0.032	0.094	0.874	0.832	0.167	0.001
0.041	0.138	0.821	0.750	0.249	0.001
0.048	0.167	0.785	0.700	0.298	0.002
0.063	0.219	0.718	0.605	0.387	0.008
0.086	0.289	0.625	0.503	0.474	0.023
0.242 ^a	0.488	0.270	0.242	0.488	0.270
Water	Acetic acid	Isopropyl acetate	Water	Acetic acid	Isopropyl acetate
0.022	0.000	0.978	0.978	0.000	0.022
0.051	0.083	0.866	0.848	0.115	0.037
0.094	0.169	0.737	0.736	0.206	0.058
0.144	0.235	0.621	0.645	0.268	0.087
0.218	0.286	0.501	0.549	0.308	0.143
0.260	0.304	0.436	0.477	0.321	0.202
0.376 ^a	0.320	0.304	0.376	0.320	0.304
Water	Acetic acid	Methyl isobutyl ketone	Water	Acetic acid	Methyl isobutyl ketone
0.024	0.000	0.976	0.981	0.000	0.019
0.056	0.095	0.849	0.849	0.127	0.024
0.094	0.174	0.732	0.753	0.208	0.039
0.133	0.238	0.629	0.674	0.268	0.058
0.180	0.287	0.533	0.607	0.310	0.083
0.189	0.292	0.519	0.592	0.317	0.091
0.384 ^a	0.346	0.270	0.384	0.346	0.270

^aPlait point.

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

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 acetic acid (w_C) and of the organic solvent (w_B) in the ternary system and of the organic solvent in the solvent-rich (w_{BB}^0) or water-rich (w_{BA}^0) phase of the respective binary system. The k is an empirical constant from interval $\langle 0.1 \rangle$, the value of which was determined prior to the least squares calculations to obtain constants A_i . The values of the constants as well as mean and rms deviations between experimental and calculated values are given in Table III. The tie lines were correlated by the Othmer-Tobias equation⁶

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

where w_A and w_B are the weight fractions of water in the water-rich phase and of the organic solvent in the solvent-rich phase. The values of c and r were determined by the least squares method and they are given in Table IV together with the respective deviations.

TABLE III

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

Solvent	Diisopropyl ether	Isopropyl acetate	2-Ethylhexanol	Methyl isobutyl ketone
n^a	3	2	2	1
k	0.5	1	0.7	0.7
A_1	5.734	0.099	4.344	0.963
A_2	1.755	0.408	1.777	-0.136
A_3	1.509	0.224	2.289	-0.198
A_4	2.304	-1.068	-0.694	—
A_5	0.508	—	—	—
w_{BB}^0	0.991	0.978	0.980	0.976
w_{BA}^0	0.014	0.022	0.0007 ^b	0.019
Mean ^c	0.0025	0.0030	0.0038	0.0051
Rms ^c	0.0035	0.0051	0.0063	0.0080

^aFor explanation of the symbols see Eq. (1) and the text. ^bThis value was taken from another work⁷. ^cMean and rms deviations were calculated according to the formulas $\text{mean} = \sum |w_{\text{calc.}} - w_{\text{expt.}}|/n_{\text{expt.}}$ and $\text{rms} = (\sum (w_{\text{calc.}} - w_{\text{expt.}})^2 / (n_{\text{expt.}} - n_{\text{const.}}))^{1/2}$, where the w 's are the weight fractions, $n_{\text{expt.}}$ is the number of experimental points analyzed and $n_{\text{const.}}$ is the number of empirical constants.

TABLE IV
Correlation of Tie Lines in Four Ternary Acetic Acid–Organic Solvent–Water Systems at 24·6°C

Solvent	Diisopropyl ether	Isopropyl acetate	2-Ethyl- hexanol	Methyl isobutyl ketone
c^a	0·4728	1·2127	0·5898	1·4634
r	1·1867	1·1901	0·8938	1·2279
Mean ^b	0·001	0·006	0·004	0·003
Rms	0·002	0·009	0·005	0·004

^aFor explanation of the symbols see Eq. (2). ^bFor explanation *cf.* note *c* in Table III.

It is seen from Tables III and IV that agreement between the experimental and calculated values is very good, almost within the experimental error. Thus we may say that Eqs (1)–(2) together with the values of the empirical constants in Tables III and IV describe the liquid–liquid equilibria in the four ternary systems at 24·6°C completely.

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