

LIQUID-VAPOUR EQUILIBRIUM IN THE TERNARY ISOPROPYL ACETATE-WATER-ACETIC ACID AND ISOPROPYL ACETATE-WATER-ACRYLIC ACID SYSTEMS AT 200 TORR*

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Isobaric vapour-liquid equilibria were determined in the ternary systems isopropyl acetate-water-acetic acid and isopropyl acetate-water-acrylic acid and in the corresponding binary systems at 200 Torr. A modified circulation still of the Gillespie type was used for measurements. The Margules third and fourth order equations and the Renon-Prausnitz (NRTL) equation were used for the correlation of experimental data.

The phase liquid-liquid^{1,2} and vapour-liquid^{3,4} equilibria measurements in systems containing acetic acid or acrylic acid and organic solvents, or organic solvents and water were extended to two ternary systems of the acids with water and isopropyl acetate.

EXPERIMENTAL

The methods of purification and physical constants of all substances used were given in previous communications^{3,4}.

Analytical method. The analysis of the equilibrium phase samples was made by means of a gas chromatograph Chrom-4 with heat conductivity detection using hydrogen as a carrier gas. The conditions of the analyses were as follows: temperature 150°C, a 120 cm long column filled with KEM [poly(cyanomethyl methacrylate)] of 0.2–0.4 mm particle size. Heterogeneous samples (usually of the vapour phase) were homogenized before analyzing by adding an amount of the other acid (*e.g.* the samples of the isopropyl acetate-water-acetic acid were homogenized by adding acrylic acid). This addition showed no apparent effect on the results of analyses.

Apparatus and procedure. The appropriate equilibrium still for the measurements of the ternaries and corresponding binaries was chosen according to the character of measured system. For the systems in which acrylic acid occurred in the vapour phase, the specially modified apparatus⁴ with copper sheets had to be used to prevent the polymerization of acrylic acid in the parts of the still where the mixture was not stabilized by hydroquinone. The other systems were measured

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TABLE I
Vapour-Liquid Equilibrium in the Water(1)-Acetic Acid(2) System at 200 Torr

x_1	y_1	$t, ^\circ\text{C}$	$y_{1,\text{calc}} - y_{1,\text{exp}}$			
			Marg. 3	Marg. 4	NRTL 2	NRTL 3
0.302	0.387	71.75	0.035	0.025	0.018	0.003
0.469	0.560	70.00	0.012	0.004	0.002	0.006
0.579	0.681	68.95	-0.012	-0.015	-0.014	-0.010
0.632	0.731	68.40	-0.016	-0.016	-0.014	-0.012
0.707	0.781	67.85	-0.001	0.001	0.004	0.002
0.761	0.815	67.65	0.011	0.013	0.016	0.012
0.796	0.853	67.50	0.002	0.004	0.006	0.002
0.839	0.886	67.10	0.004	0.004	0.007	0.001
0.872	0.912	66.90	0.003	0.003	0.005	0.000
0.947	0.968	66.70	0.000	-0.002	0.000	-0.004
<i>Mean</i>			<i>0.010</i>	<i>0.009</i>	<i>0.009</i>	<i>0.005</i>

Constants of correlation equations: Marg. 3 $A_{12} = 0.1665$, $A_{21} = -0.0242$; Marg. 4 $A_{12} = 0.2494$, $A_{21} = 0.0105$, $D_{12} = 0.2049$; NRTL 2 $(g_{12} - g_{22}) = -821.1$, $(g_{12} - g_{11}) = 1619.3$, $\alpha_{12} = 0.3$; NRTL 3 $(g_{12} - g_{22}) = -24.2$, $(g_{12} - g_{11}) = 8236.4$, $\alpha_{12} = 0.3796$.

TABLE II
Vapour-Liquid Equilibrium in the Water(1)-Acrylic Acid(2) System at 200 Torr

x_1	y_1	$t, ^\circ\text{C}$	$y_{1,\text{calc}} - y_{1,\text{exp}}$			
			Marg. 3	Marg. 4	NRTL 2	NRTL 3
0.691	0.888	68.00	0.001	0.000	0.000	0.000
0.762	0.902	67.50	0.000	0.001	0.000	0.000
0.879	0.933	66.90	-0.001	0.000	0.000	0.000
0.932	0.954	66.60	0.000	0.000	0.000	0.000
<i>Mean</i>			<i>0.001</i>	<i>0.000</i>	<i>0.000</i>	<i>0.000</i>

Constants of correlation equations: Marg. 3 $A_{12} = 0.2235$, $A_{21} = 0.6029$; Marg. 4 $A_{12} = 0.3602$, $A_{21} = 0.6233$, $D_{12} = 0.2606$; NRTL 2 $(g_{12} - g_{22}) = 1225.8$, $(g_{12} - g_{11}) = -228.4$, $\alpha_{12} = 0.3$; NRTL 3 $(g_{12} - g_{22}) = 1097.0$, $(g_{12} - g_{11}) = -113.2$, $\alpha_{12} = 0.3685$.

TABLE III
Vapour-Liquid Equilibrium in the Isopropyl Acetate(1)-Acetic Acid(2) System at 200 Torr

x_1	y_1	$t, ^\circ\text{C}$	$y_{1,\text{calc}} - y_{1,\text{exp}}$			
			Marg. 3	Marg. 4	NRTL 2	NRTL 3
0.136	0.291	71.95	-0.017	-0.001	-0.026	-0.009
0.346	0.559	64.95	0.001	-0.011	0.022	-0.007
0.497	0.722	60.70	0.000	0.009	0.021	0.002
0.724	0.911	55.95	-0.012	-0.003	-0.007	-0.007
<i>Mean</i>			<i>0.008</i>	<i>0.006</i>	<i>0.019</i>	<i>0.006</i>

Constants of correlation equations: Marg. 3 $A_{12} = -0.0292$, $A_{21} = -0.2608$; Marg. 4 $A_{12} = 0.1887$, $A_{21} = 0.0383$, $D_{12} = 0.8303$; NRTL 2 ($g_{12} - g_{22}$) = 589.2, ($g_{12} - g_{11}$) = -640.9, $\alpha_{12} = 0.3$; NRTL 3 ($g_{12} - g_{22}$) = -1837.3, ($g_{12} - g_{11}$) = 2877.3, $\alpha_{12} = 0.1481$.

TABLE IV
Vapour-Liquid Equilibrium in the Isopropyl Acetate(1)-Acrylic Acid(2) System at 200 Torr

x_1	y_1	$t, ^\circ\text{C}$	$y_{1,\text{calc}} - y_{1,\text{exp}}$			
			Marg. 3	Marg. 4	NRTL 2	NRTL 3
0.014	0.062	101.00	-0.006	0.002	0.005	0.006
0.034	0.159	98.65	-0.023	-0.011	-0.003	-0.001
0.052	0.234	97.00	-0.025	-0.013	-0.006	-0.003
0.084	0.339	93.80	-0.013	-0.005	0.004	0.006
0.116	0.418	91.05	0.015	0.017	0.022	0.024
0.195	0.624	83.65	0.010	0.004	0.002	0.001
0.245	0.725	80.25	-0.006	-0.010	-0.016	-0.017
0.468	0.902	67.05	-0.002	0.005	0.005	0.004
0.629	0.959	61.05	-0.015	-0.008	-0.001	0.002
0.907	0.995	53.65	-0.011	-0.015	-0.013	-0.002
<i>Mean</i>			<i>0.012</i>	<i>0.009</i>	<i>0.008</i>	<i>0.007</i>

Constants of correlation equations: Marg. 3 $A_{12} = -0.1474$, $A_{21} = 0.2778$; Marg. 4 $A_{12} = -0.0791$, $A_{21} = 0.5184$, $D_{12} = 0.5217$; NRTL 2 ($g_{12} - g_{22}$) = 3095.0, ($g_{12} - g_{11}$) = -985.3, $\alpha_{12} = 0.3$; NRTL 3 ($g_{12} - g_{22}$) = 13415.6, ($g_{12} - g_{11}$) = -486.3, $\alpha_{12} = 0.1947$.

by means of the Gillespie still slightly modified to prevent distilling over isopropyl acetate from mixing vessel into the cooled receiver for condensate. The description of the measuring procedure including the vacuum system can be found in the literature⁵. The pressure in the measuring system was determined indirectly, *i.e.* by measuring the boiling point of water in an ebulliometer connected parallel to the equilibrium still. Temperature was measured by mercury standards calibrated by means of a Mueller bridge with platinum resistance thermometer Leeds and Northrup. The equilibrium samples were taken for analysis only if the boiling point in the still did not change for 20 minutes.

RESULTS AND DISCUSSION

The experimental binary vapour-liquid equilibrium data were correlated by using the following equations for the concentration dependence of activity coefficients: the Margules third order equation⁵

$$\log (\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 (A_{12} - A_{21}), \quad (1)$$

the Margules fourth order equation⁵

$$\log (\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 [A_{12} - A_{21} + (x_2 - x_1) D_{12}], \quad (2)$$

and the Renon-Prausnitz (NRTL) equation^{6,7}

$$\begin{aligned} \ln \gamma_1 &= x_2^2 \left\{ \frac{\tau_{12} \exp(-\alpha_{12}\tau_{12})}{[x_1 \exp(-\alpha_{12}\tau_{12}) + x_2]^2} + \frac{\tau_{21} \exp(-2\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} \right\}, \\ \ln \gamma_2 &= x_1^2 \left\{ \frac{\tau_{12} \exp(-2\alpha_{12}\tau_{12})}{[x_1 \exp(-\alpha_{12}\tau_{12}) + x_2]^2} + \frac{\tau_{21} \exp(-\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} \right\}, \end{aligned} \quad (3)$$

$$\tau_{12} = (g_{12} - g_{22})/RT, \quad \tau_{21} = (g_{12} - g_{11})/RT,$$

where x_1, x_2 are mole fractions of the components 1, 2 in the liquid phase and y_1, y_2 those in the vapour phase, γ_1, γ_2 activity coefficients, R is gas constant, T absolute temperature, and $A_{12}, A_{21}, D_{12}, g_{12}, g_{22}, g_{11}, \alpha_{12}$ are adjustable parameters characteristic of the given equation and the binary mixture. The constant α_{12} of the NRTL equation was determined both by means of general rules^{6,7} (NRTL 2) and by computing as the third adjustable parameter (NRTL 3).

The values of constants were obtained by minimizing the function

$$Q = \sum_{i=1}^n W_i F_i^2, \quad (4)$$

where n is the number of experimental points and F_i is a function defined by

$$F_i = \ln(\gamma_1/\gamma_2)_{i,\text{exp}} - \ln(\gamma_1/\gamma_2)_{i,\text{calc}} \quad (5)$$

TABLE V

Vapour-Liquid Equilibrium in the Ternary Isopropyl Acetate(1)-Water(2)-Acetic Acid(3) System at 200 Torr

x_1	x_2	y_1	y_2	$t, ^\circ\text{C}$	Marg. 3		NRTL	
					Δy_1	Δy_2	Δy_1	Δy_2
0.057	0.371	0.217	0.438	64.60	-0.018	0.015	0.001	-0.025
0.059	0.353	0.207	0.420	65.30	-0.013	0.022	0.009	-0.019
0.092	0.317	0.274	0.386	63.85	0.010	0.012	0.018	-0.026
0.081	0.296	0.240	0.373	65.35	-0.006	0.018	0.013	-0.019
0.056	0.432	0.241	0.480	63.80	0.001	-0.002	0.001	-0.032
0.041	0.531	0.233	0.552	63.10	0.032	-0.036	0.001	-0.035
0.027	0.423	0.137	0.506	66.65	-0.032	0.006	-0.012	-0.027
0.050	0.424	0.216	0.474	64.70	-0.009	0.011	0.000	-0.023
0.090	0.403	0.314	0.445	61.60	0.044	-0.022	0.019	-0.045
0.153	0.371	0.385	0.437	58.55	0.145	-0.092	0.073	-0.090
0.116	0.314	0.322	0.383	62.55	0.037	-0.004	0.026	-0.036
0.109	0.298	0.293	0.372	63.50	0.031	0.005	0.030	-0.029
0.091	0.260	0.241	0.340	65.65	0.002	0.020	0.020	-0.011
0.155	0.236	0.355	0.319	62.50	0.046	0.001	0.028	-0.020
0.242	0.202	0.463	0.293	59.70	0.076	-0.003	0.031	-0.019
0.180	0.367	0.411	0.445	57.20	0.179	-0.126	0.092	-0.112
0.152	0.380	0.373	0.462	58.40	0.165	-0.118	0.089	-0.112
0.151	0.541	0.466	0.466	52.80	0.283	-0.242	0.099	-0.106
0.100	0.679	0.364	0.614	50.40	0.445	-0.439	0.216	-0.237
0.004	0.491	0.030	0.586	68.65	-0.010	0.000	-0.006	-0.013
0.010	0.513	0.078	0.588	67.65	-0.022	0.005	-0.015	-0.010
0.004	0.597	0.055	0.689	67.20	-0.018	-0.022	-0.021	-0.023
0.004	0.505	0.035	0.600	68.75	-0.014	-0.002	-0.010	-0.014
0.001	0.669	0.028	0.739	67.50	-0.013	-0.001	-0.016	0.004
0.002	0.937	0.042	0.941	61.45	0.239	-0.249	0.178	-0.189
0.001	0.650	0.013	0.755	67.85	0.000	0.032	-0.002	-0.028
<i>Mean</i>					<i>0.073</i>	<i>0.058</i>	<i>0.040</i>	<i>0.050</i>

Constants of correlation equations: Marg. 3 $A_{12} = 2.328$, $A_{21} = 4.229$, $A_{13} = -0.0292$, $A_{31} = -0.2608$, $A_{23} = 0.1665$, $A_{32} = -0.0242$, $C = 4.8081$; NRTL $(g_{12} - g_{22}) = 3060.2$, $(g_{12} - g_{11}) = 3081.4$, $(g_{13} - g_{33}) = 589.2$, $(g_{13} - g_{11}) = -640.9$, $(g_{23} - g_{33}) = -821.1$, $(g_{23} - g_{22}) = 1619.3$, all $\alpha_{ij} = 0.3$.

and W_i is a weight factor given by

$$W_i = \{[(\partial F/\partial x_i)_{y_i}]^2 + [(\partial F/\partial y_i)_{x_i}]^2\}^{-1}. \quad (6)$$

The function Q was minimized by the least square method (in case of Eqs (1) and (2)) or by the Marquardt method⁸ (for the NRTL equation).

The ternary experimental data were fitted to the third order Margules equation⁵

$$\begin{aligned} \log \gamma_1 = & x_2^2[A_{12} + 2x_1(A_{21} - A_{12})] + x_3^2[A_{13} + 2x_1(A_{31} - A_{13})] + \\ & + x_2x_3[A_{21} + A_{13} - A_{32} + 2x_1(A_{31} - A_{13}) + 2x_3(A_{32} - A_{23}) - \\ & - C(1 - 2x_1)] \end{aligned} \quad (7)$$

(the expressions for γ_2 and γ_3 are obtained by cyclic permutation of indices)

and to the NRTL equation (with $c = 3$)

$$\begin{aligned} \ln \gamma_i = & \frac{\sum_{j=1}^c x_j \tau_{ji} \exp(-\alpha_{ij} \tau_{ji})}{\sum_{j=1}^c x_j \exp(-\alpha_{ij} \tau_{ji})} + \frac{\sum_{j=1}^c x_j \exp(-\alpha_{ij} \tau_{ji})}{\sum_{k=1}^c x_k \exp(-\alpha_{kj} \tau_{kj})} \cdot \\ & \cdot \left[\tau_{ij} - \frac{\sum_{l=1}^c x_l \tau_{lj} \exp(-\alpha_{il} \tau_{lj})}{\sum_{k=1}^c x_k \exp(-\alpha_{kj} \tau_{kj})} \right]. \end{aligned} \quad (8)$$

In Eq. (7) only the ternary constant C was determined by the least square method, the other constants are parameters of corresponding binary systems. The parameters α_{ij} of Eq. (8) were estimated in terms of general rules^{6,7}. This simplification was chosen in accordance with the recommendation in the literature⁹.

The temperature dependence of the vapour pressures of pure substances which was needed for the computations was taken over from the literature^{3,10}. The constants of the Antoine vapour pressure equation

$$\log P^\circ = A - B/(t + C), \quad (9)$$

(P° is vapour pressure in Torr, t is temperature, °C) are as follows: isopropyl acetate $A = 7.33395$, $B = 1436.53$, $C = 233.66$; acetic acid $A = 7.18807$, $B = 1416.70$, $C = 211.00$; acrylic acid $A = 7.80806$, $B = 1827.90$, $C = 230.00$; water $A = 7.96681$, $B = 1668.21$, $C = 228.00$. The ideal behaviour of the vapour phase was assumed when computing the constants of correlating equations.

TABLE VI
Vapour-Liquid Equilibrium in the Ternary Isopropyl Acetate(1)-Water(2)-Acrylic Acid(3)
System at 200 Torr

x_1	x_2	y_1	y_2	$t, ^\circ\text{C}$	Marg. 3		NRTL	
					Δy_1	Δy_2	Δy_1	Δy_2
0.077	0.282	0.188	0.555	70.85	-0.067	0.130	0.017	0.067
0.106	0.140	0.236	0.417	76.35	0.018	-0.007	0.053	0.036
0.096	0.168	0.209	0.455	75.30	-0.004	0.033	0.050	0.046
0.104	0.318	0.233	0.596	67.65	-0.040	0.077	0.035	0.005
0.094	0.435	0.255	0.629	64.30	-0.053	0.088	0.016	0.006
0.102	0.506	0.205	0.741	60.80	0.092	-0.086	0.117	-0.130
0.112	0.602	0.164	0.816	56.80	0.345	-0.344	0.250	-0.269
0.017	0.906	0.282	0.700	51.45	0.369	-0.364	0.228	-0.228
0.000 ₂	0.938	0.108	0.852	66.10	-0.090	0.088	-0.089	0.087
0.000 ₃	0.881	0.005	0.899	66.80	0.008	0.022	0.006	0.025
0.000 ₃	0.883	0.009	0.908	66.40	0.004	0.013	0.002	0.016
0.000 ₂	0.756	0.008	0.899	67.30	-0.006	0.000	-0.005	0.000
0.000 ₇	0.780	0.016	0.870	66.80	-0.008	0.029	-0.007	0.029
0.000 ₅	0.702	0.002	0.895	67.00	0.001	-0.006	0.002	-0.008
0.002 ₆	0.686	0.023	0.877	66.70	-0.012	0.004	-0.004	-0.004
<i>Mean</i>					<i>0.074</i>	<i>0.086</i>	<i>0.059</i>	<i>0.069</i>

Constants of correlation equations: Marg. 3 $A_{12} = 2.328$, $A_{21} = 4.229$, $A_{13} = -0.1474$, $A_{31} = 0.2778$, $A_{23} = 0.2235$, $A_{32} = 0.6029$, $C = 7.1295$; NRTL $(g_{12} - g_{22}) = 3060.2$, $(g_{12} - g_{11}) = 3081.4$, $(g_{13} - g_{33}) = 3095.0$, $(g_{13} - g_{11}) = -985.3$, $(g_{23} - g_{33}) = 1225.8$, $(g_{23} - g_{22}) = -228.4$, all $\alpha_{ij} = 0.3$.

The experimental data on the vapour-liquid equilibrium in the water-acetic acid system at 200 Torr and their comparison with calculated ones are given in Table I. The data on the water-acrylic acid system are presented in Table II and the data on the isopropyl acetate-acetic acid in Table III. The experimental data on the isopropyl acetate-acrylic acid system at 200 Torr have been published formerly³; their correlation is presented in Table IV. With regard to the limited miscibility in the isopropyl acetate(1)-water(2) system (the isopropyl acetate solubility in water amounts to 0.54 mol %), the constants of correlation equations were only estimated⁵ on the basis of the measured and published data on solubilities^{1,2} and on azeotropic point¹¹, and in this way calculated vapour-liquid equilibrium data were checked by an orienting measurement of several equilibrium points at 760 Torr, the agreement being reasonable. The estimated constants are as follows: the Margules third order

equation $A_{12} = 2.328$, $A_{21} = 4.229$ and the NRTL equation $(g_{12} - g_{22}) = 3060.2$, $(g_{12} - g_{11}) = 3081.4$, $\alpha_{12} = 0.3$.

The experimental and calculated data in the ternary isopropyl acetate–water–acetic acid and isopropyl acetate–water–acrylic acid systems are presented in Tables V and VI, respectively.

As it can be seen from the two last tables the Margules third order equation is not able to fit well the data in these systems with strong associations in the vapour phase. Somewhat better correlation, especially as for the maximum deviations, is obtained with the NRTL equation. In spite of it the results are appropriate and sufficient for the industrial design and optimum performance of rectification units.

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