

LIQUID-VAPOUR EQUILIBRIUM IN THE TERNARY WATER-ACETIC ACID-2-ETHYLHEXANOL AND WATER-ACRYLIC ACID-2-ETHYLHEXANOL SYSTEMS AT 50 TORR*

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Isobaric vapour-liquid equilibria were measured in the ternary systems water-acetic acid-2-ethylhexanol and water-acrylic acid-2-ethylhexanol and in some of corresponding binary systems at 50 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 the ternary systems of the acids with water and 2-ethylhexanol.

EXPERIMENTAL

The methods of purification and physical constants of all substances used were given in foregoing papers^{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 140°C, a 250 cm long column filled with Fluon coated by 8% Apiezon L and 2% Carbowax 20M. 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 water-acetic acid-2-ethylhexanol system were homogenized by adding a needed amount of 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 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 by means of a slightly modified Gillespie still. The description of the measuring procedure including

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TABLE I

Vapour-Liquid Equilibrium in the Acetic Acid(1)-2-Ethylhexanol(2) System at 50 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
0.204	0.649	91.60	0.053	-0.003	0.059	0.021
0.286	0.786	87.35	-0.015	0.013	-0.034	-0.017
0.491	0.915	68.70	-0.009	-0.006	-0.014	-0.003
0.688	0.963	58.55	0.009	0.002	0.008	0.001
<i>Mean</i>			<i>0.021</i>	<i>0.006</i>	<i>0.029</i>	<i>0.011</i>

Constants of correlation equations: Marg. 3 $A_{12} = 0.1945$, $A_{21} = -0.4910$; Marg. 4 $A_{12} = -1.3705$, $A_{21} = -2.0368$, $D_{12} = -4.2110$; NRTL 2 ($g_{12} - g_{22}$) = -912.7, ($g_{12} - g_{11}$) = 3764.2, $\alpha_{12} = 0.3$; NRTL 3 ($g_{12} - g_{22}$) = -32677.3, ($g_{12} - g_{11}$) = 115.9, $\alpha_{12} = -0.1032$.

TABLE II

Vapour-Liquid Equilibrium in the Acrylic Acid(1)-2-Ethylhexanol(2) System at 100 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
0.138	0.352	121.90	-0.007	0.008	0.039	0.023
0.161	0.423	120.90	-0.015	-0.007	0.020	0.007
0.166	0.423	120.70	0.000	0.006	0.030	0.018
0.224	0.583	118.70	-0.020	-0.026	-0.017	-0.021
0.289	0.683	114.60	0.004	-0.003	-0.013	-0.008
0.306	0.707	115.10	0.002	-0.003	-0.015	-0.007
0.331	0.729	113.30	0.014	0.011	-0.004	0.005
0.341	0.758	112.70	-0.002	-0.004	-0.022	-0.011
0.461	0.857	107.70	-0.005	0.006	-0.010	0.007
0.637	0.941	98.45	-0.027	-0.014	-0.006	0.008
0.757	0.969	93.85	-0.036	-0.032	-0.008	0.002
0.855	0.986	90.05	-0.037	-0.047	-0.018	-0.013
<i>Mean</i>			<i>0.014</i>	<i>0.014</i>	<i>0.017</i>	<i>0.011</i>

Constants of correlation equations: Marg. 3 $A_{12} = -0.3349$, $A_{21} = 0.5178$; Marg. 4 $A_{12} = -0.1275$, $A_{21} = 0.9367$, $D_{12} = 0.9768$; NRTL 2 ($g_{12} - g_{22}$) = 5322.0, ($g_{12} - g_{11}$) = -780.8, $\alpha_{12} = 0.3$; NRTL 3 ($g_{12} - g_{22}$) = 7457.8, ($g_{12} - g_{11}$) = -1142.0, $\alpha_{12} = 0.2179$.

TABLE III

Vapour-Liquid Equilibrium in the Ternary Water(1)-Acetic Acid(2)-2-Ethylhexanol(3) System at 50 Torr

x_1	x_2	y_1	y_2	$t, ^\circ\text{C}$	Marg. 3		NRTL	
					Δy_1	Δy_2	Δy_1	Δy_2
0.197	0.666	0.409	0.588	43.85	0.024	-0.025	-0.066	0.064
0.198	0.663	0.399	0.598	44.15	0.039	-0.040	-0.054	0.052
0.220	0.633	0.446	0.551	43.40	0.051	-0.052	-0.066	0.064
0.261	0.598	0.504	0.494	42.50	0.070	-0.072	-0.073	0.070
0.306	0.559	0.553	0.443	42.25	0.096	-0.096	-0.066	0.065
0.168	0.684	0.370	0.627	44.60	0.008	-0.010	-0.061	0.058
0.252	0.616	0.483	0.514	42.75	0.059	-0.060	-0.071	0.069
0.328	0.552	0.564	0.433	41.75	0.094	-0.095	-0.062	0.061
0.428	0.471	0.659	0.338	40.50	0.099	-0.102	-0.049	0.048
0.511	0.399	0.738	0.258	39.75	0.083	-0.088	-0.039	0.039
0.091	0.825	0.159	0.837	46.60	0.022	-0.019	0.025	-0.024
0.163	0.761	0.317	0.681	43.80	-0.008	0.008	-0.044	0.044
0.287	0.648	0.444	0.555	42.25	0.051	-0.052	-0.038	0.037
0.391	0.555	0.558	0.439	41.20	0.054	-0.053	-0.043	0.043
0.482	0.473	0.656	0.341	40.20	0.036	-0.036	-0.048	0.049
0.560	0.400	0.729	0.267	40.00	0.026	-0.028	-0.040	0.042
0.675	0.310	0.792	0.206	39.90	-0.008	0.001	-0.018	0.019
0.080	0.872	0.172	0.827	45.40	-0.017	0.017	-0.010	0.010
0.179	0.778	0.304	0.695	43.50	0.007	-0.007	-0.025	0.025
0.308	0.656	0.440	0.559	42.00	0.034	-0.034	-0.031	0.031
0.418	0.553	0.547	0.451	40.90	0.037	-0.036	-0.027	0.028
0.470	0.505	0.602	0.396	40.50	0.026	-0.025	-0.030	0.031
0.540	0.439	0.676	0.322	40.10	0.009	-0.009	-0.033	0.034
0.576	0.402	0.714	0.283	37.25	0.006	-0.006	-0.032	0.034
0.648	0.339	0.768	0.229	39.45	-0.011	0.009	-0.024	0.026
0.648	0.350	0.764	0.233	39.70	-0.039	0.041	-0.035	0.038
0.600	0.368	0.773	0.223	39.80	-0.004	0.001	-0.051	0.054
0.109	0.305	0.473	0.499	61.90	0.210	-0.245	0.021	-0.082
0.040	0.527	0.207	0.779	59.20	-0.079	0.037	-0.072	0.032
0.141	0.485	0.544	0.449	57.30	0.005	-0.028	-0.140	0.114
0.021	0.148	0.090	0.468	95.40	0.216	-0.045	0.066	0.102
0.029	0.445	0.060	0.861	69.85	0.052	-0.073	0.052	-0.073
0.043	0.628	0.088	0.879	58.70	0.022	-0.020	0.040	-0.037
0.020	0.246	0.237	0.568	84.20	-0.067	0.046	-0.131	0.089
<i>Mean</i>					<i>0.049</i>	<i>0.045</i>	<i>0.049</i>	<i>0.049</i>

Constants of correlation equations: Marg. 3 $A_{12} = 0.1665$, $A_{21} = -0.0242$, $A_{13} = 0.783$, $A_{31} = 3.940$, $A_{23} = 0.1945$, $A_{32} = -0.4910$, $C = 2.2056$; NRTL $(g_{12} - g_{22}) = -821.1$, $(g_{12} - g_{11}) = 1619.3$, $(g_{13} - g_{33}) = 4754.6$, $(g_{13} - g_{11}) = 1325.8$, $(g_{23} - g_{33}) = -912.7$, $(g_{23} - g_{22}) = 3764.2$, all $\alpha_{ij} = 0.3$.

the vacuum system can be found in the literature⁵. The pressure in the measuring system was determined indirectly by measuring boiling point of water in an ebulliometer with water 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.

TABLE IV

Vapour-Liquid Equilibrium in the Ternary Water(1)-Acrylic Acid(2)-2-Ethylhexanol(3) System at 50 Torr

x_1	x_2	y_1	y_2	$t, ^\circ\text{C}$	Marg. 3		NRTL	
					Δy_1	Δy_2	Δy_1	Δy_2
0.008	0.819	0.133	0.759	71.30	-0.058	0.120	-0.036	0.122
0.016	0.799	0.305	0.686	66.85	-0.159	0.125	-0.123	0.113
0.026	0.794	0.449	0.544	61.25	-0.223	0.192	-0.180	0.171
0.039	0.782	0.538	0.456	56.90	-0.219	0.192	-0.175	0.168
0.347	0.542	0.870	0.128	42.10	0.013	-0.025	-0.024	0.020
0.485	0.429	0.919	0.080	39.70	-0.013	-0.009	-0.036	0.029
0.375	0.500	0.891	0.106	40.70	0.011	-0.023	-0.026	0.023
0.404	0.476	0.907	0.092	40.20	0.002	-0.017	-0.033	0.028
0.001 ₅	0.100	0.044	0.228	106.60	0.081	-0.003	0.138	0.020
0.002 ₁	0.296	0.034	0.640	104.20	0.059	0.005	0.082	-0.033
0.001 ₂	0.296	0.063	0.616	98.90	-0.007	0.062	0.010	0.024
0.002 ₁	0.412	0.060	0.784	92.75	0.002	0.001	0.023	-0.032
0.002 ₃	0.412	0.071	0.761	92.30	-0.003	0.020	0.019	-0.014
0.002 ₂	0.196	0.057	0.476	103.90	0.082	-0.024	0.119	-0.044
0.001 ₆	0.195	0.074	0.450	103.15	0.031	0.019	0.062	0.001
0.001 ₁	0.458	0.027	0.865	90.70	0.001	-0.024	0.012	-0.042
0.001 ₄	0.450	0.040	0.850	90.10	-0.003	-0.020	0.010	-0.042
0.001 ₈	0.570	0.068	0.875	88.25	-0.037	0.002	-0.025	0.002
0.001 ₆	0.544	0.094	0.843	86.10	-0.063	0.030	-0.051	0.025
0.001 ₆	0.550	0.090	0.857	85.15	-0.060	0.018	-0.048	0.015
<i>Mean</i>					<i>0.056</i>	<i>0.046</i>	<i>0.062</i>	<i>0.048</i>

Constants of correlation equations: Marg. 3 $A_{12} = 0.2235$, $A_{21} = 0.6029$, $A_{13} = 0.783$, $A_{31} = 3.940$, $A_{23} = -0.3349$, $A_{32} = 0.5178$, $C = 0.2810$; NRTL $(g_{12} - g_{22}) = 1225.8$, $(g_{12} - g_{11}) = -228.4$, $(g_{13} - g_{33}) = 4754.6$, $(g_{13} - g_{11}) = 1325.8$, $(g_{23} - g_{33}) = 5322.0$, $(g_{23} - g_{22}) = -780.8$, all $\alpha_{ij} = 0.3$.

RESULTS AND DISCUSSION

The experimental data were correlated by using the same correlation relations as in a previous paper⁶ (Eqs (1)–(8)).

The temperature dependence of vapour pressures of pure substances which was needed for the computations was taken over from the literature^{3,7}. 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: acetic acid $A = 7.18807$, $B = 1416.70$, $C = 211.00$; acrylic acid $A = 7.80806$, $B = 1827.90$, $C = 230.00$; water $A = 7.96681$, $B = 1668.21$, $C = 228.00$; 2-ethylhexanol $A = 8.16793$, $B = 2156.14$, $C = 230.00$. The ideal behaviour of the vapour phase was assumed during computations.

The experimental data on the vapour-liquid equilibrium in the binary system acetic acid-2-ethylhexanol at 50 Torr and their comparison with calculated ones are given in Table I. The experimental data on the acrylic acid-2-ethylhexanol system (at 100 Torr) have been published formerly³; their correlation is given in Table II. The binary constants of the other binary systems were taken from a previous paper⁶. Even if the data were measured at 200 Torr the constants are considered to be a good approximation for the pressure of 50 Torr. With regard to the limited (and very low) mutual solubility of water and 2-ethylhexanol, the constants of correlation equations for this system were only estimated⁵ on the basis of the measured and published data on solubilities^{1,2}. The estimated constants are as follows: the Margules third order equation $A_{12} = 0.783$, $A_{21} = 3.940$; the NRTL equation $(g_{12} - g_{22}) = 4754.6$, $(g_{12} - g_{11}) = 1325.8$, $\alpha_{12} = 0.3$.

The experimental and calculated data in the ternary water-acetic acid-2-ethylhexanol and water-acrylic acid-2-ethylhexanol systems are presented in Tables III and IV, respectively.

It is seen from the two last tables that the Margules third order equation is not able to correlate 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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