

Phase-Equilibria in Methanol-Ethyl Acetate-Water System

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Vapor-liquid equilibrium data at atmospheric pressure were obtained for the binary and ternary systems containing methanol, ethyl acetate and water. This ternary system forms heterogeneous liquid mixtures in the region where methanol content is low. The methanol-ethyl acetate binary system forms a minimum boiling azeotrope. Activity coefficients were calculated, and checks of thermodynamic consistencies were made.

VAPOR-LIQUID equilibrium data at atmospheric pressure were determined for the binary and ternary systems containing methanol, ethyl acetate and water. Since this ternary system forms heterogeneous liquid mixtures at a certain composition region, vapor-liquid equilibria were determined only for homogeneous liquid mixtures, and liquid-liquid equilibrium data were taken for the heterogeneous region.

EXPERIMENTAL

Purity of Compounds. Methanol and ethyl acetate used were prepared from special reagent grade materials by fractional distillation with a laboratory column 150 cm. in height packed with McMahan packings, and heart cuts were taken.

The properties of the materials as used in the experimental work are:

	Boiling Point [° C.]		Density at 25° C. [G./Cm. ³]		Refractive Index at 25° C.	
	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.
Methanol	64.7(10)	64.7	0.7866(4)	0.7870	1.32668(6)	1.3265
Ethyl Acetate	77.15(4)	77.1	0.89446(4)	0.8945	1.36984(8)	1.3697

Procedure. Vapor-liquid equilibrium data were obtained by use of a modified Braun type still (5) at atmospheric pressure. Temperatures were measured by copper-constantan thermocouples used in conjunction with a potentiometer. Boiling temperature readings were corrected for variation of the atmospheric pressure by the Crafts rule (2) based on the Clausius-Clapeyron equation.

The binary mixtures were analyzed by measuring their densities at 25° C. The smoothed binary density tables, Table I, were prepared by measuring densities of liquid samples of known compositions. The ternary samples were analyzed by density at 25° C. and chemical analysis of ethyl acetate based on the saponification of the ester with standard sodium hydroxide solutions. The smoothed ternary density data are given in Table II and are plotted in Figure 1.

Mutual solubilities of heterogeneous liquid mixtures at 25° C. were determined by cloud point measurements. Liquid-liquid equilibria and mutual solubilities at 70° C.

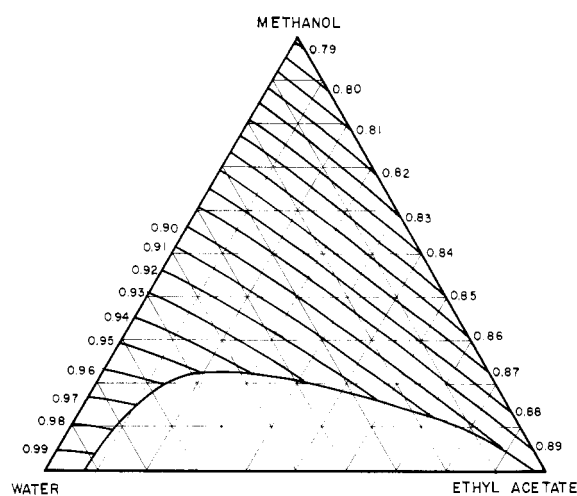


Figure 1. Ternary density data.

were measured by analyzing separately the two liquid phases in equilibrium.

EXPERIMENTAL DATA

Binary Systems. Seventeen runs were made on the methanol-water system to check the performance of the apparatus and for its calibration. Boiling points and x - y values for this system checked the data in Perry (1) to within analytical accuracy.

The methanol-ethyl acetate system forms a minimum boiling azeotrope. The azeotropic data reported by several investigators and obtained in the present work are given below:

Investigator	Mole Fraction Methanol	Boiling Point [° C.]
Ryland (3)	0.668	62.3
Murti (8)	0.705	62.3
Present data	0.710	62.3

Table I. Smoothed Binary Density Data at 25° C. and 1 atm.

Methanol-Water		Methanol-Ethyl Acetate	
Wt. fraction methanol	Density [g./cm. ³]	Wt. fraction methanol	Density [g./cm. ³]
0.000	0.9971	0.000	0.8945
0.050	0.9887	0.050	0.8886
0.100	0.9807	0.100	0.8827
0.150	0.9729	0.150	0.8770
0.200	0.9650	0.200	0.8712
0.250	0.9571	0.250	0.8658
0.300	0.9488	0.300	0.8604
0.350	0.9402	0.350	0.8549
0.400	0.9312	0.400	0.8493
0.450	0.9220	0.450	0.8439
0.500	0.9134	0.500	0.8384
0.550	0.9024	0.550	0.8330
0.600	0.8913	0.600	0.8276
0.650	0.8798	0.650	0.8223
0.700	0.8677	0.700	0.8171
0.750	0.8554	0.750	0.8120
0.800	0.8426	0.800	0.8069
0.850	0.8293	0.850	0.8020
0.900	0.8154	0.900	0.7971
0.950	0.8014	0.950	0.7922
1.000	0.7870	1.000	0.7870

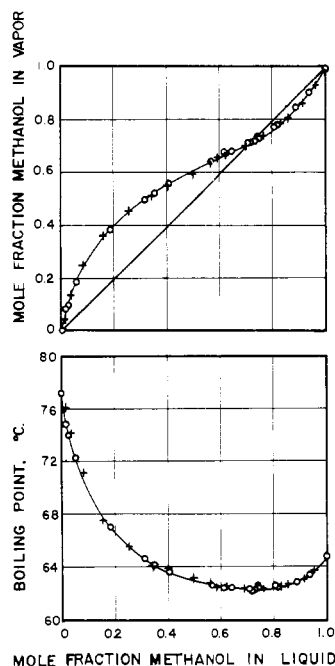


Figure 2. *x*-*y* data and boiling points at 1 atm., methanol-ethyl acetate system.

○ Present data
+ Data of Murti

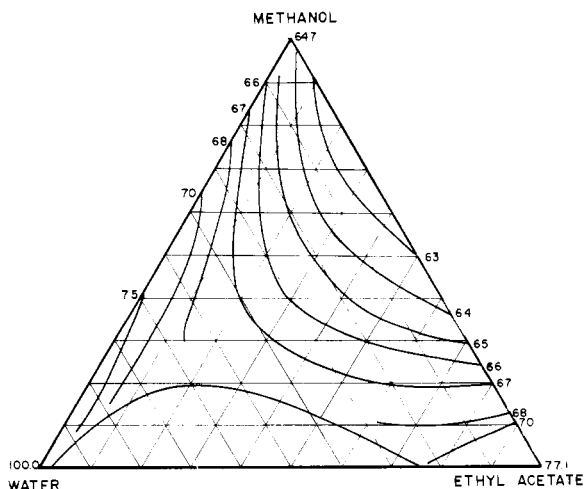


Figure 3. Ternary boiling point data at 1 atm.

The experimental *x*-*y* data and boiling points for the methanol-ethyl acetate system are given in Table III and are shown in Figure 2. These agree with the data of Murti (8) except in the 0 to 10 mole % methanol region where the present data show slightly lower boiling points.

Ternary System. The ternary boiling points and the experimental *x*-*y* data are given in Table IV. Boiling points are plotted in Figure 3, and the *x*-*y* data in Figure 4, which shows mole fraction of methanol in vapor *y_M* and mole fraction of ethyl acetate in vapor *y_E* in equilibrium with liquid compositions *x*.

As seen from these figures, there exists no ternary homogeneous azeotrope for this system. Data on mutual solubilities and liquid-liquid equilibria are given in Tables V and VI, respectively, and are plotted in Figure 5.

DISCUSSION

Calculation of Activity Coefficients. The activity coefficients were evaluated by the following equation (2) on the assumption that the vapor phase is an ideal mixture.

$$\log \gamma_i = \log \left(\frac{y_i}{x_i} \right) + \log \left(\frac{\pi}{p_i^s} \right) + \frac{(\pi - p_i^s)(B_i - V_i^s)}{2.303RT} \quad (1)$$

The second virial coefficient *B_i* was estimated by the following equation of Wohl (11).

$$B_i = \frac{RT_c}{p_c} \left(0.197 - 0.012T_r - \frac{0.4}{T_r} - \frac{0.146}{T_r^{3.27}} \right) \quad (2)$$

The values of the activity coefficients for the binary and ternary system are given in Tables 3 and 4, respectively.

The activity coefficients for the binary methanol-ethyl acetate system were excellently correlated by the 3-suffix van Laar equation and the 4-suffix Margules equation and also by the 4-suffix Redlich-Kister equation. Thus,

van Laar:

$$\log \gamma_M = \frac{0.42}{\left(1 + 0.93 \frac{x_M}{x_E} \right)^2} \quad (3)$$

$$\log \gamma_E = \frac{0.45}{\left(1 + 1.07 \frac{x_E}{x_M} \right)^2}$$

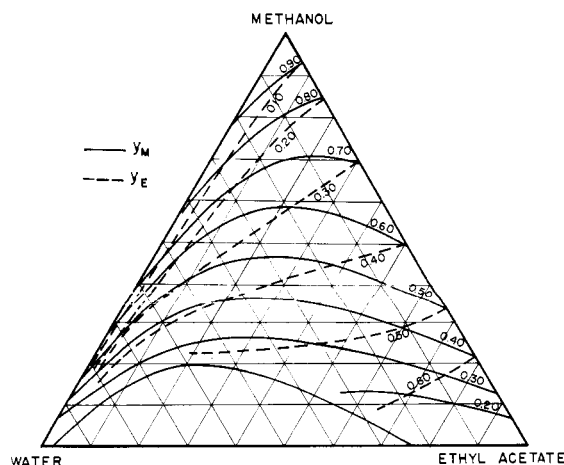


Figure 4. Ternary *x*-*y* data at 1 atm.

Table II. Smoothed Ternary Density Data at 25° C. and 1 atm.

Wt. Fraction Ethyl Acetate	Wt. Fraction Water	Density G./Cm. ³	Wt. Fraction Ethyl Acetate	Wt. Fraction Water	Density G./Cm. ³
0.020	0.936	0.9900	0.100	0.346	0.8900
0.040	0.918	0.9900	0.200	0.302	0.8900
			0.300	0.259	0.8900
0.020	0.875	0.9800	0.400	0.218	0.8900
0.040	0.857	0.9800	0.500	0.176	0.8900
0.060	0.842	0.9800	0.600	0.136	0.8900
0.080	0.827	0.9800	0.700	0.098	0.8900
			0.800	0.060	0.8900
0.020	0.814	0.9700	0.900	0.023	0.8900
0.040	0.797	0.9700			
0.060	0.781	0.9700	0.050	0.328	0.8800
0.080	0.766	0.9700	0.100	0.307	0.8800
0.100	0.750	0.9700	0.200	0.265	0.8800
			0.300	0.223	0.8800
0.020	0.752	0.9600	0.400	0.182	0.8800
0.060	0.722	0.9600	0.500	0.142	0.8800
0.100	0.694	0.9600	0.600	0.103	0.8800
0.120	0.680	0.9600	0.700	0.064	0.8800
			0.800	0.028	0.8800
0.020	0.690	0.9500			
0.060	0.661	0.9500	0.050	0.287	0.8700
0.100	0.637	0.9500	0.100	0.266	0.8700
0.140	0.615	0.9500	0.200	0.224	0.8700
0.180	0.594	0.9500	0.300	0.184	0.8700
			0.400	0.145	0.8700
0.050	0.613	0.9400	0.500	0.106	0.8700
0.100	0.584	0.9400	0.600	0.068	0.8700
0.150	0.557	0.9400	0.700	0.030	0.8700
0.200	0.532	0.9400			
0.250	0.509	0.9400	0.050	0.248	0.8600
			0.100	0.226	0.8600
0.050	0.560	0.9300	0.200	0.186	0.8600
0.100	0.533	0.9300	0.300	0.146	0.8600
0.150	0.507	0.9300	0.400	0.108	0.8600
0.200	0.483	0.9300	0.500	0.071	0.8600
0.250	0.459	0.9300	0.600	0.034	0.8600
0.300	0.436	0.9300			
0.350	0.413	0.9300	0.050	0.208	0.8500
0.400	0.391	0.9300	0.100	0.188	0.8500
			0.200	0.150	0.8500
0.050	0.510	0.9200	0.300	0.112	0.8500
0.100	0.483	0.9200	0.400	0.074	0.8500
0.200	0.437	0.9200	0.500	0.036	0.8500
0.300	0.389	0.9200			
0.400	0.345	0.9200	0.050	0.170	0.8400
0.500	0.301	0.9200	0.100	0.151	0.8400
			0.200	0.112	0.8400
0.050	0.461	0.9100	0.300	0.076	0.8400
0.100	0.436	0.9100	0.400	0.040	0.8400
0.200	0.389	0.9100	0.500	0.005	0.8400
0.300	0.344	0.9100			
0.400	0.300	0.9100	0.050	0.134	0.8300
0.500	0.258	0.9100	0.100	0.115	0.8300
0.600	0.218	0.9100	0.200	0.078	0.8300
0.650	0.198	0.9100	0.300	0.043	0.8300
			0.400	0.008	0.8300
0.050	0.414	0.9000			
0.100	0.391	0.9000	0.050	0.097	0.8200
0.200	0.346	0.9000	0.100	0.079	0.8200
0.300	0.302	0.9000	0.200	0.043	0.8200
0.400	0.258	0.9000	0.300	0.009	0.8200
0.500	0.217	0.9000			
0.600	0.176	0.9000	0.050	0.062	0.8100
0.700	0.136	0.9000	0.100	0.044	0.8100
0.800	0.097	0.9000	0.150	0.026	0.8100
0.850	0.078	0.9000	0.200	0.010	0.8100
• 0.050	0.368	0.8900	0.050	0.028	0.8000
			0.100	0.010	0.8000

Margules:

$$\log \gamma_M = (1 - x_M)^2 [0.430 + 0.023 (1 - 2x_M) (1 - 6x_M)] \quad (4)$$

$$\log \gamma_E = x_M^2 [0.430 + 0.023 (2x_M - 1) (6x_M - 5)]$$

Redlich-Kister:

$$\log \frac{\gamma_M}{\gamma_E} = 0.430 (1 - 2x_M) + 0.023 (1 - 2x_M) [1 - 8x'_M (1 - x_M)] \quad (5)$$

Figure 6 shows a Redlich-Kister plot for this binary mixture.

The values of the logarithms of activity coefficients in the ternary system are plotted in Figure 7, 8, and 9 as function of the liquid composition. The smoothed ternary vapor-liquid equilibria and boiling points data are listed in Table 7. Thermodynamic consistencies of the ternary

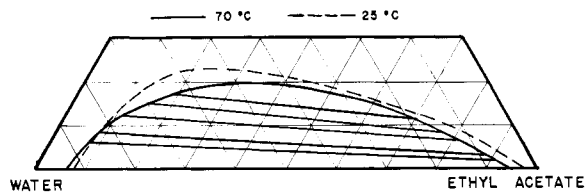


Figure 5. Mutual solubilities and liquid-liquid equilibria.

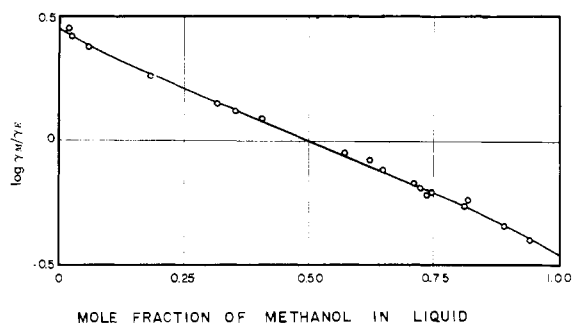


Figure 6. Redlich-Kister plot for methanol-ethyl acetate system.

data were checked by the method of Krishnamurty and Rao (7). The Q term is defined as:

$$Q = \frac{\Delta G^E}{2.303RT} = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3 \quad (6)$$

If this equation is differentiated with respect to x_1 , holding x_3 constant, and combined with the Gibbs-Duhem equation:

$$\left(\frac{\partial Q}{\partial x_1} \right)_{x_3} = \log \left(\frac{\gamma_1}{\gamma_2} \right)$$

Upon integration:

$$\left[Q'' - Q' = \int_{x_1' \geq 0}^{x_1'' \leq 1-x_1} \log \left(\frac{\gamma_1}{\gamma_2} \right) dx_1 \right]_{x_3 = \text{const.}} \quad (7)$$

Rigorously, this equation applies only to isothermal and isobaric conditions but is considered to hold approximately for isobaric conditions. The right member of Equation 7 was evaluated graphically, while the left member analytically. By comparing the values of the two members of Equation 7, 13 checks for thermodynamic consistencies were made at constant water mole percentages of 10, 20, 30, 40, 50 and 60 and also at constant methanol mole percentages of 10, 20, 30, 40, 50, 60 and 70.

The percentage difference between the two members of Equation 7 is defined by the following relationship:

$$\% \text{ Diff.} = \left| \frac{(Q'' - Q') - \int_{x_1' \geq 0}^{x_1'' \leq 1-x_1} \log \left(\frac{\gamma_1}{\gamma_2} \right) dx_1}{\sum} \right| \quad (8)$$

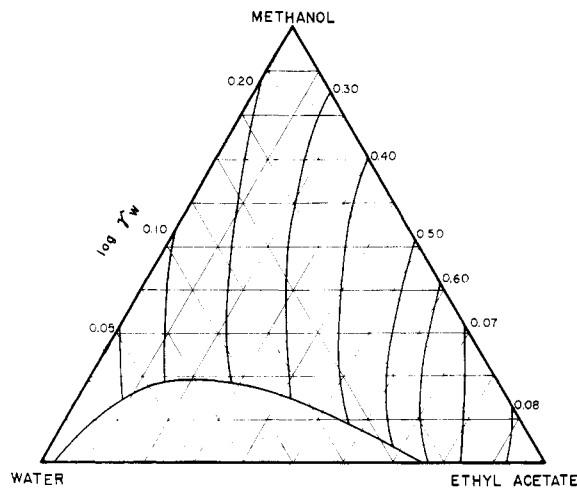


Figure 7. Logarithm of activity coefficient of water in ternary mixture.

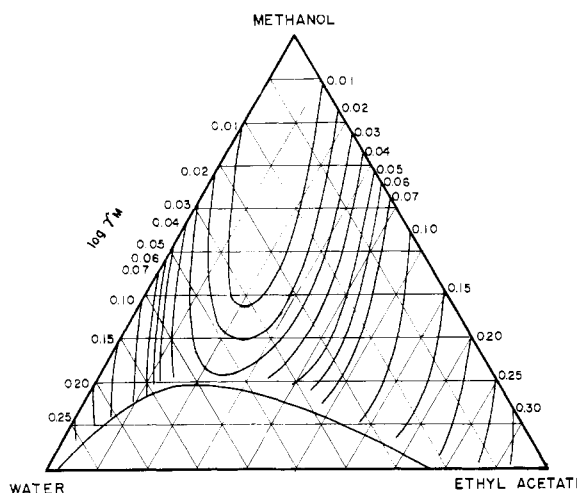


Figure 8. Logarithm of activity coefficient of methanol in ternary mixture.

Table III. Vapor-Liquid Equilibrium Data for Methanol-Ethyl Acetate at 1 atm.

Boiling Point [° C.]	Mole Fraction of Methanol in Liquid	Mole Fraction of Methanol in Vapor	Activity Coefficient	
			Methanol	Ethyl acetate
74.8	0.019	0.079	2.856	1.014
74.0	0.024	0.093	2.742	1.030
72.3	0.056	0.181	2.429	1.014
67.1	0.181	0.384	1.933	1.048
64.7	0.311	0.492	1.582	1.116
64.2	0.350	0.520	1.511	1.138
63.6	0.403	0.557	1.440	1.167
62.6	0.566	0.640	1.228	1.364
62.4	0.616	0.675	1.167	1.390
62.4	0.646	0.678	1.148	1.494
62.3	0.708	0.711	1.103	1.631
62.1	0.720	0.716	1.101	1.684
62.3	0.734	0.717	1.073	1.753
62.5	0.743	0.732	1.074	1.707
62.6	0.744	0.733	1.070	1.701
62.5	0.810	0.779	1.048	1.904
62.4	0.815	0.784	1.053	1.819
62.8	0.889	0.846	1.025	2.246
63.3	0.939	0.903	1.014	2.529

Table IV. Experimental Vapor-Liquid Equilibrium Data for Methanol-Ethyl Acetate-Water at 1 atm.

Boiling Point, °C.	Liquid Mole Fraction		Vapor Mole Fraction		Activity Coefficient		
	Methanol	Ethyl acetate	Methanol	Ethyl acetate	Methanol	Ethyl acetate	Water
63.2	0.639	0.288	0.656	0.304	1.086	1.685	2.389
63.3	0.707	0.211	0.708	0.258	1.056	1.935	1.844
63.7	0.783	0.136	0.769	0.196	1.019	2.259	1.841
63.7	0.547	0.367	0.595	0.357	1.126	1.525	2.378
63.8	0.608	0.284	0.621	0.316	1.056	1.738	2.435
63.9	0.697	0.178	0.681	0.261	1.006	2.283	1.960
65.2	0.514	0.256	0.544	0.339	1.042	1.969	2.026
65.3	0.306	0.632	0.429	0.514	1.369	1.205	3.588
65.3	0.378	0.444	0.457	0.435	1.185	1.452	2.415
65.5	0.830	0.047	0.858	0.088	1.001	2.756	1.725
65.9	0.626	0.126	0.659	0.238	1.004	2.737	1.604
66.1	0.405	0.275	0.445	0.394	1.040	2.060	1.799
66.2	0.438	0.221	0.480	0.361	1.033	2.347	1.777
66.4	0.297	0.422	0.350	0.468	1.139	1.582	2.459
66.4	0.666	0.083	0.720	0.184	1.116	3.120	1.070
66.8	0.219	0.562	0.289	0.520	1.215	1.333	3.235
66.8	0.287	0.357	0.333	0.461	1.068	1.818	1.873
66.8	0.260	0.430	0.312	0.490	1.105	1.604	2.374
66.8	0.313	0.325	0.361	0.441	1.080	1.910	2.029
66.9	0.329	0.288	0.371	0.429	1.032	2.089	1.919
66.9	0.196	0.726	0.302	0.596	1.414	1.152	4.832
67.0	0.381	0.208	0.427	0.382	1.025	2.567	1.709
67.1	0.204	0.528	0.290	0.522	1.206	1.377	2.854
67.1	0.552	0.106	0.605	0.245	0.998	3.220	1.616
67.3	0.324	0.218	0.374	0.421	1.043	2.672	1.624
67.4	0.528	0.097	0.594	0.250	1.013	3.554	1.503
67.4	0.425	0.138	0.486	0.329	1.030	3.287	1.534
67.5	0.328	0.180	0.383	0.411	1.048	3.136	1.506
67.7	0.533	0.080	0.622	0.222	1.039	3.787	1.446
67.7	0.368	0.137	0.434	0.357	1.050	3.557	1.509
67.8	0.589	0.063	0.680	0.173	1.009	3.734	1.447
68.1	0.289	0.138	0.356	0.419	1.083	4.075	1.375
68.1	0.670	0.028	0.797	0.082	1.046	3.931	1.417
68.2	0.119	0.706	0.204	0.590	1.498	1.119	4.111
68.6	0.388	0.087	0.488	0.309	1.083	4.696	1.327
68.7	0.471	0.068	0.580	0.237	1.056	4.592	1.364
69.4	0.294	0.065	0.413	0.349	1.174	6.907	1.230
69.5	0.385	0.059	0.522	0.264	1.129	5.739	1.270
70.1	0.570	0.021	0.735	0.084	1.051	5.027	1.428
70.2	0.067	0.838	0.146	0.690	1.768	1.031	5.529
70.6	0.082	0.867	0.188	0.716	1.835	1.021	5.808
71.1	0.419	0.031	0.613	0.175	1.149	6.868	1.188
71.8	0.487	0.015	0.714	0.083	1.122	6.577	1.220
71.9	0.058	0.901	0.146	0.777	1.920	1.022	5.595
72.4	0.061	0.911	0.171	0.778	2.101	0.993	5.311
73.1	0.330	0.019	0.572	0.173	1.267	10.38	1.105
73.7	0.021	0.942	0.057	0.850	1.941	1.009	2.303
74.6	0.357	0.009	0.654	0.080	1.268	99.76	1.113
76.0	0.248	0.011	0.536	0.155	1.424	14.65	1.044
77.4	0.262	0.004	0.614	0.062	1.471	15.41	1.047
80.0	0.139	0.005	0.431	0.172	1.779	31.55	0.990
82.0	0.158	0.014	0.526	0.047	1.787	2.896	1.014
64.9	0.329	0.593	0.445	0.481	1.788	1.219	3.829
66.2	0.304	0.463	0.379	0.482	1.235	1.399	2.751
67.4	0.220	0.387	0.235	0.547	0.962	1.949	2.003
67.4	0.254	0.297	0.301	0.481	1.067	2.233	1.753
67.5	0.216	0.376	0.269	0.519	1.117	1.896	1.868
67.7	0.120	0.734	0.228	0.618	1.692	1.159	3.760
67.7	0.121	0.743	0.219	0.617	1.611	1.033	4.299
67.8	0.115	0.689	0.194	0.604	1.497	1.192	3.662
67.9	0.131	0.554	0.183	0.572	1.235	1.399	2.751
69.1	0.524	0.050	0.654	0.179	1.055	4.650	1.324
69.4	0.122	0.833	0.260	0.681	1.781	1.052	4.250
69.5	0.064	0.874	0.152	0.709	1.763	1.041	7.400
69.6	0.067	0.843	0.099	0.694	1.226	1.052	7.555

Table V. Mutual Solubility Data at 25° C. and 1 atm.

Fraction of Methanol		Fraction of Ethyl Acetate	
Wt.	Mole	Wt.	Mole
0.000	0.000	0.075	0.016
0.098	0.062	0.090	0.021
0.132	0.087	0.098	0.023
0.203	0.142	0.136	0.035
0.228	0.184	0.253	0.074
0.223	0.185	0.281	0.085
0.204	0.196	0.412	0.145
0.168	0.200	0.570	0.246
0.128	0.196	0.726	0.406
0.112	0.174	0.741	0.419
0.000	0.000	0.978	0.899

Table VI. Tie Line Data at 70° C. and 1 atm.

Methanol Fraction		Ethyl Acetate Fraction	
Wt.	Mole	Wt.	Mole
Ethyl Acetate Phase			
0.000	0.000	0.940	0.762
0.020	0.042	0.908	0.690
0.032	0.063	0.885	0.641
0.058	0.103	0.826	0.531
0.079	0.130	0.781	0.463
0.116	0.163	0.690	0.352
0.125	0.171	0.673	0.335
Water Phase			
0.000	0.000	0.062	0.013
0.063	0.039	0.072	0.016
0.080	0.050	0.089	0.020
0.119	0.078	0.115	0.028
0.149	0.103	0.146	0.036
0.169	0.123	0.189	0.050
0.206	0.154	0.194	0.053

Table VII. Smoothed Ternary Vapor-Liquid Equilibrium Data at 1 atm.

Boiling point, ° C.	Liquid Mole Fraction		Vapor Mole Fraction	
	Methanol	Ethyl acetate	Methanol	Ethyl acetate
68.5	0.100	0.600	0.152	0.586
68.5	0.100	0.700	0.169	0.610
68.9	0.100	0.800	0.195	0.660
68.0	0.200	0.200	0.245	0.512
67.8	0.200	0.300	0.249	0.512
67.8	0.200	0.400	0.253	0.512
67.2	0.200	0.500	0.262	0.524
66.8	0.200	0.600	0.284	0.535
66.6	0.200	0.700	0.324	0.559
68.5	0.300	0.100	0.381	0.393
67.1	0.300	0.200	0.348	0.438
67.1	0.300	0.300	0.345	0.454
66.5	0.300	0.400	0.356	0.463
66.0	0.300	0.500	0.376	0.477
65.2	0.300	0.600	0.416	0.490
68.2	0.400	0.100	0.482	0.320
67.0	0.400	0.200	0.440	0.375
65.9	0.400	0.300	0.444	0.397
65.1	0.400	0.400	0.459	0.415
64.3	0.400	0.500	0.492	0.433
67.6	0.500	0.100	0.571	0.262
66.0	0.500	0.200	0.530	0.328
64.8	0.500	0.300	0.536	0.355
63.9	0.500	0.400	0.559	0.377
66.8	0.600	0.100	0.652	0.219
64.9	0.600	0.200	0.615	0.289
63.6	0.600	0.300	0.624	0.321
65.6	0.700	0.100	0.726	0.189
63.6	0.700	0.200	0.690	0.260
64.2	0.800	0.100	0.791	0.165

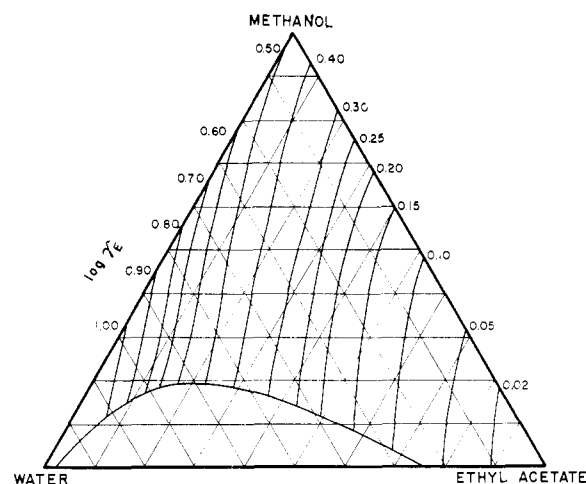


Figure 9. Logarithm of activity coefficient of ethyl acetate in ternary mixture.

where, Σ is the total area enclosed by the abscissa and a plot of $\log \gamma_1/\gamma_2$ vs. x_1 . In the 13 cases above listed, the differences of Equation 8 were 9% maximum and 0.9% minimum, except for one case of 70 mole per cent methanol for which the difference was 30%. For this particular case, the range of integration was so narrow and the value of Σ is so small that the percentage error involved in the calculation of Equation 8 was considered to be large. Thus, the ternary data appear to be thermodynamically consistent.

ACKNOWLEDGMENT

Shigeyoshi Takaoka constructed the equilibrium still and performed some preliminary experiments.

NOMENCLATURE

- B = second virial coefficient
- ΔG^E = excess molar free energy
- p^o = vapor pressure of pure component
- p_c = critical pressure
- Q = Redlich-Kister function, defined by Equation 6
- R = gas constant
- T = absolute temperature
- T_c = critical temperature
- T_r = reduced temperature
- V^o = molar volume of pure component
- x = mole fraction in liquid phase
- y = mole fraction in vapor phase
- γ = activity coefficient
- π = total pressure
- Σ = total area enclosed by the abscissa and a plot of $\log \gamma_1/\gamma_2$ vs. x_1

Subscripts:

- E = refers to ethyl acetate
- i = refers to i -component
- M = refers to methanol
- 1,2,3 = refer to 1-, 2-, 3- component, respectively

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RECEIVED for review October 22, 1962. Accepted May 6, 1963. This paper is based on the M. Eng. thesis submitted by K. Akita to Kyoto University in March, 1960.

Polarizations and Refractions of Some *N*-Methylacetamide-*n*-Alcohol Systems

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The dependence of polarization on concentration and temperature has been determined for five *N*-methylacetamide-*n*-alcohol systems and the *N*-methylacetamide-water system. Within the homologous alcohol series, departures from Debye behavior in regard to concentration dependence are greatest for the *n*-amyl alcohol system and least for the methyl alcohol system. The departures from Debye temperature dependence however, are greatest for the methyl alcohol system and least for the *n*-amyl alcohol system. The water system displays almost linear concentration dependence, but exhibits a temperature dependence intermediate between those of ethyl and *n*-alcohol. Association by hydrogen bonding is displayed to a high degree by these components and systems. The association in *N*-methylacetamide appears approximately equal to that in methyl alcohol but less than that in water. Within the homologous alcohol series, association characteristics decrease steadily from methyl alcohol to *n*-amyl alcohol.

THE POLARIZATION behavior of alcohol-non-polar solvent systems has been investigated extensively (3, 4, 12, 13). Large deviations from Debye behavior have been observed and accredited to association. However, few if any investigations concerned with the polarization behavior of alcohols in extremely polar solvents have been carried out. In 1951, Leader and Gormley (6) reported that *N*-methylacetamide was characterized by an exceptionally high dielectric constant which exceeds more than twice that of water at a comparable temperature. With this very polar solvent available, the present investigation concerned with determination of polarization dependence on temperature and concentration for *N*-methylacetamide-*n*-alcohol systems was initiated. Water and the first five normal

alcohols (methanol-*n*-amyl alcohol) were chosen for use as the *n*-alcohol components. This selection enables one to make comparisons of polarization behavior within the homologous series and also allows a comparison of effects apparent in polar and non-polar solvents.

EXPERIMENTAL

Purification of Materials. *N*-Methylacetamide was obtained from a departmental supply and purified by fractional distillation at reduced pressure, followed by fractional freezing (2). The physical properties of the final product at 30°C. were as follows: density, 0.9498 gram/ml.; viscosity, 0.03885 poise; dielectric constant, 178.6.

Methanol (Fisher Scientific Co. Reagent grade) was refluxed for several hours in contact with activated alumina and fractionally distilled. The retained middle fraction

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