Vapor-Liquid Equilibria for Binary Systems of Methanol, Ethyl Alcohol, 1-Propanol, and 2-Propanol with Ethyl Acetate and 1-Propanol-Water

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The design and economic operation of fractionating equipment require knowledge of vapor-liquid equilibrium relations of the systems involved in the separation process. Equilibrium data at two or more temperatures for binary systems composed of a common component and several in a series of homologous compounds allow calculation of thermodynamic properties and interpretation of behavior of the mixtures in relation to the chain length or structure of the homologs. Few experimental investigations of such a series of systems have been reported. Scatchard and his coworkers (*25-29*) calculated the thermodynamic properties of binary mixtures and, in some instances, the extent of association and hydrogen bond strength from vapor-liquid equilibrium measurements. Mertes and Colburn (*19*) reported results of isothermal vapor-liquid equilibrium measurements on some of the industrially important systems of hydrocarbons with furfural and made use of the variation of activity coefficients with temperature to calculate the heats of solution of the hydrocarbons in furfural. Thus, isothermal vapor-liquid equilibrium data can be utilized to calculate the heats of mixing for those systems for which experimental data cannot be taken conveniently in a laboratory.

Binary systems of methanol, ethyl alcohol, 1-propanol, and 2-propanol with ethyl acetate and 1-propanol with water were studied in this investigation. Selection of these particular systems was based upon the availability of information on solution behavior from other studies (*1*).

MATERIALS

The physical properties of the purified materials are given in Table I. Refined methanol was first treated with Drierite, allowed to stand for 36 hours, and then distilled in a 4-foot glass column packed with 0.25-inch glass helices with a reflux ratio of approximately 20 to 1. The heart cut was treated with calcium turnings and a portion of this material was distilled in the same column and a heart cut was taken for experimental work. Because of the tendency of anhydrous alcohol to absorb moisture from the atmosphere, the distillate was collected in such quantity that it was not stored for more than a day and the material was exposed to the atmosphere only momentarily while charging the equilibrium still.

U.S.P. grade absolute alcohol was used without any further purification.

Eastman Kodak Co. 1-propanol and Baker's analyzed 2-propanol were subjected to the same treatment as the methanol and similar precautions were taken against possible contamination from atmospheric moisture.

Baker's analyzed ethyl acetate was fractionated in the column and a heart-cut was collected and used in the experiments.

Distilled water was boiled to dispel dissolved gases.

APPARATUS

A Bausch & Lomb precision refractometer was used to determine the refractive indices of the equilibrium liquid and vapor samples of methanol-ethyl acetate mixtures. Prism temperature was maintained constant within ±0.05 °C. by circulating water from a constant temperature bath. Monochromatic light for the optical system was obtained from a sodium lamp.

A 10.0-ml. pycnometer was used to determine the densities of the mixtures when density was used as a means of analyzing unknown mixtures.

Temperatures were measured by an iron-constantan thermocouple which was calibrated against Bureau of Standards thermometers using a Leeds & Northrup precision potentiometer.

The vapor-liquid equilibria were determined in a Colburn still (*10*) modified by introducing an extra heater and increasing the size (*7*). The still consisted of a residue chamber, a condenser, a condensate chamber, and a flash tube. An ice-water condenser with sufficient heat transfer area ensured complete condensation of the vapors rising from the condensate chamber. The still was encased in a wooden cabinet to reduce the effect of convection currents. The door was fitted with a glass window for visual observation of distillation during a run. Residue, condensate, and flash chambers were wound with 28-gage Nichrome wire covered with glass insulation. Each heating arrangement was independently controlled through a powerstat and the power supply was obtained from a Solo constant voltage transformer. A 200-watt bulb was placed in series with the residue and flash chamber heaters to obtain voltage control sensitivity.

Table I. Physical Properties of Compounds (*30*)

Compound	Boiling Point, °C.		Density 25/4		Refr. Index, D/25 °C.	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Methanol	64.5	64.509	0.78682	0.78675	1.32668	1.32663
Ethyl alcohol	78.3	78.325	0.78512	0.78506	1.35936	1.35941
1-Propanol	97.2	97.15	0.79936	0.79950	1.38347	1.38350
2-Propanol	82.4	82.4	0.78100	0.78095	1.37475	1.37470
Ethyl acetate	77.1	77.114	0.89462	0.89455	1.36984	1.36979

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Pressure control was obtained either manually by bleeding off through a $\frac{1}{8}$-inch needle valve or mechanically using a Cartesian manostat.

PROCEDURE

About 40 ml. of the sample were transferred to the equilibrium still through the funnel attached to the top of the vent condenser. The three-way stopcock was opened to the flash tube and the liquid was allowed to flow into the residue chamber. The stopcock was closed when the liquid level in the condensate chamber reached 1.5 to 2.0 cm. above the three-way stopcock. The still was then connected to the pressure (or vacuum) system, and the residue heater was turned on. It was necessary to turn on the heater of the flash tube simultaneously, to avoid the back suction of the liquid into the flash tube from the residue chamber. When the liquid in the latter reached its boiling point, the three-way stopcock was opened in all directions, and kept partially open if necessary. In the case of all isothermal runs, the pressure was fixed by trial and error, which required from 0.5 to 1 hour. When the correct pressure was thus fixed, it was regulated by the Cartesian manostat which was operated under throttling instead of "on and off" control. This was accomplished by careful adjustment of the nozzle in relation to the float and by adjustment of a fine needle valve on the still side of the manostat. When equilibrium temperature and hence the pressure were maintained constant, 2 to 3 hours were allowed for attainment of equilibrium.

Periodic checks were made during this time interval for constancy in temperature. After it was certain that no variation in temperature was noticeable during the latter half of the run, the three-way stopcock was closed to the flash tube and the few drops of liquid in the latter were vaporized completely to prevent contamination of the liquid sample. The main power switch was then opened. The liquid and vapor samples were collected from the residue and condensate chambers respectively, in clean, dry, cold sampling tubes placed in ice. Liquid and vapor samples were then analyzed using either refractive index or density for estimating the composition of unknown mixtures. Calibration charts for each of the binary systems were obtained by weighing one of the pure components by means of a Chainomatic balance, adding the second component, weighing, mixing, and finding the physical property of this mixture. The data thus obtained are given in Tables II and III.

Table II. Refractive Index vs. Composition of Methanol-Ethyl Acetate

x_1[a]	n_{30}^{D}
0.8386	1.33874
0.7725	1.34316
0.7089	1.34662
0.6790	1.34848
0.6632	1.35040
0.6095	1.35160
0.5626	1.35356
0.5267	1.35533
0.4895	1.35646
0.4150	1.35855
0.2861	1.36214
0.1948	1.36390
0.1052	1.36566
0.000	1.36759
	n_{20}^{D}
1.000	1.32861
0.9801	1.33060
0.9475	1.33390
0.9370	1.33829

[a] Mole fraction of alcohol.

The estimated experimental and analytical precision for the various measurements are as follows:

Temperature, ±0.05 °C.
Pressure, ±0.5 mm. Hg
Composition, mole fraction units
  Methanol-ethyl acetate, 0.002
  Ethyl alcohol-ethyl acetate, 0.003
  1-Propanol-ethyl acetate, 0.004
  2-Propanol-ethyl acetate, 0.003

ACTIVITY COEFFICIENTS

Scatchard and others (*25, 27*), Wohl (*31*), and Wood (*32*) have developed expressions relating activity coefficients to the equilibrium compositions of the liquid and vapor. The final equation is

$$\log_{10}\gamma_1 = \log_{10}\frac{P_T y_1}{P_1 x_1} + \frac{(\beta_{11} - V_{11})(P_T - P_1)}{2.303\,RT} + \frac{\delta_{12} P_T (1 - y_1)^2}{2.303\,RT} \qquad (1)$$

where

γ_1 = activity coefficient of component 1
P_T = total pressure in atmospheres
P_1 = saturated vapor pressure of the pure component 1 in atmospheres
x_1, y_1 = mole fraction of component 1 in the equilibrium liquid and vapor phases, respectively
β_{11} = second virial coefficient of the pure component 1 in the gas phase (function of temperature only)
δ_{12} = evaluated by the relation, $\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{22}$
R = gas constant
T = absolute temperature

The derivation of the above relationship was fully illustrated by Wood (*32*) and involves the following assumptions: that the effect of pressure on the volume of the liquid is negligible, that the gas law deviation for pure vapors involves only the second virial coefficients, and that the P-V-T relation of the gas mixture can be represented by an equation of the form:

$$V = (n_1 + n_2)\left(\frac{RT}{P_T} + y_1^2\beta_{11} + 2\,y_1 y_2 \beta_{12} + y_2^2\beta_{22}\right) \qquad (2)$$

Table III. Density Versus Composition

Ethyl Alcohol-Ethyl Acetate		1-Propanol-Ethyl Acetate		2-Propanol-Ethyl Acetate		1-Propanol-Water	
x_1	d_4^{30}	x_1[a]	d_4^{30}	x_1	d_4^{30}	x_1	d_4^{30}
1.000	0.78134	1.0000	0.79524	1.000	0.77689	1.000	0.79524
0.8609	0.79404	0.8633	0.80548	0.8595	0.78821	0.8505	0.80674
0.7256	0.80721	0.7286	0.81678	0.7209	0.80107	0.7288	0.81814
0.5947	0.81923	0.5983	0.82659	0.5938	0.81389	0.5710	0.83547
0.4796	0.83179	0.4733	0.83835	0.4656	0.72948	0.4138	0.85905
0.3539	0.84562	0.3453	0.84962	0.3390	0.84359	0.2846	0.88681
0.2313	0.85847	0.2065	0.86360	0.2245	0.85856	0.1923	0.91391
0.1119	0.87536	0.1147	0.87425	0.1123	0.87307	0.1252	0.93893
0.000	0.88719	0.000	0.88719	0.000	0.88719	0.0729	0.96294

[a] Mole fraction of alcohol.

Table IV. Experimental Vapor-Liquid Equilibrium Data at 760 Mm. of Mercury Pressure for System Methanol-Ethyl Acetate

x_1[a]	y_1[b]	t, °C.[c]	γ_1	γ_2
0.0000	0.000	77.10	. . .	1.000
0.0125	0.0475	76.10	2.570	0.990
0.0320	0.1330	74.15	2.912	1.001
0.0800	0.2475	71.24	2.414	1.001
0.1550	0.3650	67.75	2.097	1.043
0.2510	0.4550	65.60	1.754	1.091
0.3465	0.5205	64.10	1.563	1.142
0.4020	0.5560	64.00	1.424	1.186
0.4975	0.5970	63.25	1.275	1.325
0.5610	0.6380	62.97	1.253	1.378
0.5890	0.6560	62.50	1.216	1.424
0.6220	0.6670	62.65	1.165	1.487
0.6960	0.7000	62.50	1.096	1.665
0.7650	0.7420	62.35	1.066	1.868
0.8250	0.7890	62.60	1.043	2.028
0.8550	0.8070	62.80	1.020	2.229
0.9160	0.8600	63.21	0.9458	2.176
0.9550	0.9290	63.90	1.006	2.539
1.0000	1.000	64.70	1.0000	. . .
		P_T[c]		
0.0190	0.0950	456	3.770	1.010
0.0495	0.1785	490.5	2.909	1.017
0.1090	0.3100	545	2.527	1.013
0.1360	0.3450	558	2.301	1.015
0.1900	0.4160	591.5	2.095	1.025
0.2375	0.4350	611	1.806	1.088
0.3590	0.5320	644	1.531	1.134
0.4020	0.550	660	1.460	1.184
0.4950	0.5940	673	1.290	1.308
0.590	0.6430	684.5	1.189	1.444
0.6990	0.7020	690	1.101	1.662
0.7350	0.7280	687.5	1.082	1.720
0.7480	0.7320	688	1.07	1.785
0.8980	0.8470	677	1.014	2.502
0.9100	0.8535	674.5	1.003	2.706
0.0525	0.1700	330.5	3.635	1.049
0.1260	0.3375	373.5	2.608	1.027
0.2315	0.4360	405.5	1.943	1.031
0.3435	0.5125	435	1.644	1.177
0.4500	0.5685	455.5	1.454	1.302
0.5425	0.6170	459.5	1.317	1.404
0.5680	0.6325	460.5	1.292	1.431
0.6350	0.6640	461.5	1.215	1.554
0.7060	0.6975	463	1.150	1.746
0.7580	0.7290	461.5	1.118	1.891
0.8215	0.7655	457.5	1.071	2.212
0.8755	0.8100	452.5	1.051	2.549
0.9250	0.8550	444.5	1.032	3.178
0.0500	0.2115	231.5	3.750	1.017
0.0670	0.2130	231.5	3.021	1.066
0.0970	0.2620	240.0	2.490	1.023
0.1540	0.3718	259.0	2.363	1.030
0.2175	0.4242	268.5	1.979	1.060
0.2620	0.4695	284.0	1.937	1.105
0.3000	0.4912	289.5	1.791	1.130
0.3820	0.5356	296.5	1.571	1.194
0.4500	0.5360	298.0	1.346	1.363
0.5680	0.615	304.0	1.244	1.477
0.6560	0.6600	305.0	1.163	1.652
0.7190	0.694	302.0	1.101	1.800
0.7800	0.7300	303.5	1.073	2.089
0.8100	0.7495	301.5	1.053	2.180

[a] Mole fraction of methanol in liquid.
[b] Mole fraction of methanol in vapor.
[c] Total pressure in millimeters of mercury.

where

V = molal volume of the mixture
n_1, n_2 = number of moles of components 1 and 2
y_1, y_2 = mole fractions of components 1 and 2 in the vapor phase
β_{11}, β_{22} = second virial coefficients of the pure components in the vapor phase
β_{12} = second virial coefficient of the 1-2 mixture in the vapor phase

Table V. Experimental Vapor-Liquid Equilibrium Data at 760 Mm. of Mercury Pressure for System Ethyl Alcohol-Ethyl Acetate

x_1[a]	y_1[b]	t, °C.	γ_1	γ_2
0.0505	0.1036	75.55	2.300	0.9925
0.1260	0.2146	73.82	2.037	1.003
0.1343	0.2146	73.78	1.918	1.008
0.2271	0.2960	73.04	1.614	1.047
0.3128	0.3634	72.5	1.453	1.089
0.3358	0.3643	72.28	1.385	1.128
0.5052	0.4803	72.18	1.218	1.240
0.5441	0.5074	72.35	1.187	1.273
0.6442	0.5618	72.7	1.092	1.431
0.6828	0.6092	72.9	1.110	1.417
0.786	0.6819	74.14	1.026	1.633
0.8774	0.7908	75.5	1.009	1.792
0.9482	0.8924	76.7	1.004	2.095
		P_T[c]		
0.0505	0.1107	444.0	2.858	0.000
0.0595	0.1100	444.5	2.410	1.011
0.1319	0.2023	464.0	2.084	1.024
0.2286	0.2801	478.0	1.700	1.074
0.2286	0.2889	478.5	1.754	1.062
0.3279	0.3257	484.5	1.504	1.126
0.4437	0.4244	485.0	1.334	1.213
0.5011	0.4578	481.0	1.282	1.266
0.5229	0.4625	479.5	1.190	1.309
0.5860	0.4865	474.0	1.128	1.426
0.6200	0.5294	473.0	1.155	1.424
0.6870	0.5880	466.0	1.139	1.496
0.7541	0.6285	454.0	1.055	1.677
0.8064	0.6800	444.5	1.067	1.802
0.8559	0.7260	421.5	1.018	1.966
0.8940	0.7730	411.0	1.011	2.172
0.9247	0.8491	389.0	1.015	1.933
0.9760	0.9393	361.5	0.990	2.280
0.9565	0.8849	375.0	0.987	2.466
0.0757	0.1226	206.0	2.530	1.048
0.1285	0.1874	212.0	2.333	1.060
0.2256	0.2745	213.5	1.956	1.073
0.2316	0.2614	216.0	1.838	1.113
0.3441	0.3414	216.0	1.611	1.165
0.3554	0.3307	215.5	1.507	1.202
0.4389	0.4022	216.0	1.484	1.238
0.5410	0.4317	211.0	1.285	1.407
0.6359	0.4910	204.5	1.182	1.542
0.7166	0.5315	200.5	1.111	1.790
0.7576	0.5760	191.5	1.087	1.812
0.7715	0.5830	191.5	1.081	1.891
0.8260	0.6442	184.0	1.071	2.039
0.8638	0.6921	176.0	1.052	2.160
0.9009	0.7544	165.0	1.031	2.225
0.9312	0.8164	158.0	1.032	2.246
0.9636	0.8868	151.5	1.116	2.575
0.9776	0.9192	146.0	1.025	2.881

[a] Mole fraction of ethyl alcohol in liquid.
[b] Mole fraction of ethyl alcohol in vapor.
[c] Total pressure in millimeters of mercury.

Many investigators (*19, 25, 27-29*) assumed the additivity of partial volumes in a gaseous mixture to be valid, which means that

$$\delta_{12} = 0 \quad \text{or} \quad \beta_{12} = \frac{\beta_{11} + \beta_{22}}{2} \tag{3}$$

However, Scatchard and others (*27*) showed that it was necessary to include δ in calculating activity coefficients, especially when the vapor phase contains polar vapors.

Evaluation of β_{11} and β_{22}. The literature revealed that only a limited number of experimental measurements on *P-V-T* properties are available for polar vapors and much less on their mixtures; therefore it became necessary to estimate the second virial coefficients based on certain simplifying assumptions. Scatchard and others assumed that they have the same values at their corresponding states. Keyes, Smith, and Gerry (*12*) presented Equation 4 to evaluate the second virial coefficient for water.

$$\beta = \frac{T_c}{P_c}\left[11.5 - \frac{24.78}{T_r}\,10^{\frac{0.1930}{T_r}}\right] \tag{4}$$

Table VI. Experimental Vapor-Liquid Equilibrium Data at 760 Mm. of Mercury Pressure for System 1-Propanol–Ethyl Acetate

x_1[a]	y_1[b]	t, °C.	γ_1	γ_2
0.0926	0.0699	78.0	1.592	1.002
0.1667	0.1209	78.5	1.564	1.013
0.2680	0.1764	79.5	1.359	1.047
0.3623	0.2381	80.38	1.306	1.082
0.5316	0.3373	82.8	1.138	1.188
0.6178	0.4130	84.15	1.132	1.237
0.6779	0.4566	85.47	1.070	1.306
0.7560	0.5392	87.5	1.052	1.374
0.8198	0.6116	89.2	1.026	1.468
0.8506	0.6565	90.55	1.006	1.530
0.9062	0.7678	93.25	0.991	1.521
0.8863	0.7269	91.95	1.011	1.533
0.9477	0.8669	94.9	1.003	1.490
0.9762	0.9237	96.00	0.995	1.817
		P_T[c]		
0.0843	0.0560	402.0	1.777	0.9982
0.1860	0.1120	393.0	1.574	1.033
0.2977	0.1660	379.0	1.405	1.085
0.3738	0.2122	362.5	1.369	1.101
0.4716	0.2500	343.0	1.211	1.177
0.5842	0.3109	324.5	1.150	1.302
0.6375	0.3528	305.5	1.126	1.322
0.7230	0.4097	285.5	1.079	1.477
0.7811	0.4768	262.0	1.068	1.522
0.8404	0.5405	239.5	1.030	1.678
0.8825	0.6235	222.0	1.049	1.734
0.9095	0.6900	205.0	1.041	1.714
0.9362	0.7575	289.0	1.024	1.754
0.9520	0.8050	179.0	1.015	1.778
0.0857	0.0477	185.0	1.989	1.034
0.1476	0.0825	178.0	1.902	1.058
0.1799	0.100	176.5	1.824	1.041
0.2550	0.1300	171.0	1.621	1.073
0.2777	0.1416	170.0	1.612	1.086
0.3519	0.1695	165.0	1.475	1.137
0.3851	0.1802	161.5	1.405	1.158
0.4874	0.2285	154.0	1.343	1.247
0.6913	0.3344	127.5	1.149	1.483
0.7988	0.4130	109.0	1.050	1.719
0.8500	0.4869	95.0	1.014	1.758
0.8990	0.5715	84.0	0.9954	1.929

[a] Mole fraction of 1-propanol in liquid.
[b] Mole fraction of 1-propanol in vapor.
[c] Total pressure in millimeters of mercury.

In the absence of experimental data for ethyl alcohol, 1-propanol, and 2-propanol, this equation was used to calculate the second virial coefficient. For methanol, however, the experimental results of Lambert, Roberts, Rowlinson, and Wilkinson (*15*) were extrapolated slightly and used in the calculations. β for methanol at 45 °C. from Equation 4 was 755.8 while from (*15*) the value was 551.3.

Ethyl acetate was considered to be nonpolar for the purposes of computing the virial coefficient. The reasons for this assumption are based on the explanation of Beech and Glasstone (*1*) for the solubility behavior of ethyl acetate and water, "......although ethyl acetate contains polar groupings it behaves virtually as a nonpolar substance from the standpoint of solubility......" Lambert and others (*15*) stated that the virial coefficients calculated by the Berthelot equation represented the experimental values fairly well for a number of nonpolar compounds including ethyl chloride and failed to represent the data for certain other compounds including methanol. Ethyl chloride has a dipole moment of 1.98 while methanol has a dipole moment of 1.66.

The Berthelot equation of state in reduced form, Equation 5, was used to calculate the second virial coefficient for ethyl acetate.

$$\beta = B - \frac{A}{T^2} = \frac{9RT_c}{128P_c} - \frac{27RT_c^3}{64P_cT^2} \tag{5}$$

where B and A are constants, functions of the properties of the compounds.

Table VII. Experimental Vapor-Liquid Equilibrium Data at 760 Mm. of Mercury Pressure for System 2-Propanol–Ethyl Acetate

x_1[a]	y_1[b]	t, °C.	γ_1	γ_2
0.0960	0.1114	76.85	1.450	0.985
0.3850	0.3538	75.92	1.196	1.083
0.5390	0.4662	76.40	1.103	1.174
0.5985	0.5240	76.85	1.094	1.188
0.6555	0.5750	77.25	1.076	1.215
0.7710	0.6750	78.70	1.013	1.335
0.8295	0.7410	79.38	1.005	1.388
0.8815	0.8068	80.30	0.9923	1.446
		P_T[c]		
0.0775	0.1068	425.0	2.017	1.013
0.0805	0.100	432.0	1.845	1.019
0.1650	0.1795	430.5	1.612	1.019
0.2475	0.2555	434.0	1.542	1.034
0.3200	0.3023	432.0	1.404	1.068
0.4095	0.3578	430.5	1.294	1.128
0.5085	0.4168	420.0	1.186	1.199
0.5680	0.4587	413.0	1.150	1.246
0.5725	0.4631	411.5	1.147	1.244
0.6400	0.5119	404.5	1.115	1.319
0.6865	0.5387	394.0	1.066	1.394
0.7335	0.5787	385.0	1.049	1.462
0.8245	0.6795	358.5	1.022	1.571
0.8410	0.7020	355.0	1.024	1.596
0.8705	0.7372	343.0	1.004	1.668
0.9065	0.7824	330.5	1.012	1.672
0.9145	0.8100	329.5	1.010	1.754
0.9260	0.8415	321.5	1.011	1.644
0.9545	0.8746	312.5	1.017	1.692
0.9620	0.8653	118.0	1.005	2.203
0.9500	0.8340	120.5	1.004	2.151
0.9300	0.7825	126.0	1.005	2.103
0.8845	0.6935	137.0	1.014	1.952
0.8500	0.6270	148.5	1.038	1.840
0.8010	0.5770	152.5	1.043	1.738
0.7300	0.5050	161.5	1.059	1.588
0.7100	0.4960	164.0	1.082	1.530
0.6150	0.4220	174.0	1.133	1.403
0.5385	0.3775	178.0	1.181	1.288
0.4600	0.3335	183.5	1.259	1.214
0.3595	0.2880	191.0	1.446	1.141
0.1860	0.1850	194.0	1.828	1.043
0.0915	0.1014	192.0	2.014	1.019

[a] Mole fraction of 2-propanol in liquid.
[b] Mole fraction of 2-propanol in vapor.
[c] Total pressure in millimeters of mercury.

Evaluation of δ_{12}. The simplified procedure adopted by Scatchard and others was used to calculate the correction term, δ_{12}. In this method, it was assumed that B is proportional to the molal volume of the liquid and that A/B^2 is proportional to 5/3 power of the refraction

$$r = \frac{n^2 - 1}{n^2 + 2}$$

Thus

$$B = V/k_1 \tag{6}$$

and

$$A = \frac{(V)^2(r)^{5/3}}{k_2} \tag{7}$$

where k_1 and k_2 are constants.

A and B are the same constants as those in Equation 5. The values of k_1 and k_2 given by Scatchard and others for nonpolar molecules are assumed to be applicable to polar molecules. The values of A and B for alcohols were calculated using Equations 6 and 7 while, for ethyl acetate, values obtained from Equation 5 were used.

The values of A and B for the two components of a binary system were then combined by a method which is very similar to the combinations generally employed for the constants in the van der Waals equation or Beattie-Bridgeman equation of state.

$$B_{12} = {}^1\!/_8[(B_{11})^{1/3} + (B_{22})^{1/3}]^3 \tag{8}$$

Table VIII. Experimental Vapor-Liquid Equilibrium Data at 760 Mm. of Mercury Pressure for System 1-Propanol-Water

x_1[a]	y_1[b]	t, °C.	γ_1	γ_2
0.0390	0.2810	92.35	8.735	0.990
0.0720	0.3600	88.85	6.986	1.042
0.0750	0.3750	89.05	6.921	1.014
0.1790	0.3880	87.95	3.135	1.163
0.2000	0.3790	88.00	2.738	1.211
0.4250	0.4260	87.50	1.478	1.588
0.4820	0.4380	87.80	1.323	1.706
0.7120	0.560	89.20	1.092	2.079
0.8500	0.6850	91.70	1.003	2.847
0.9400	0.8550	95.0	0.994	3.006
		P_T[c]		
0.0390	0.2800	202.5	9.732	1.014
0.0650	0.3575	223.0	8.140	1.024
0.1545	0.3670	228.5	3.600	1.140
0.1790	0.3735	230.5	3.190	1.173
0.1960	0.3750	228.5	2.900	1.184
0.2620	0.3920	229.0	2.309	1.271
0.3000	0.3940	229.5	2.000	1.328
0.4090	0.4120	231.0	1.555	1.535
0.4260	0.4175	231.0	1.502	1.566
0.4895	0.4455	230.0	1.406	1.691
0.5660	0.5030	229.0	1.360	1.752
0.7050	0.5530	216.0	1.133	2.188
0.7350	0.5575	215.0	1.083	2.400
0.7960	0.6210	204.5	1.067	2.540
0.8800	0.7460	184.5	1.040	2.612
0.8940	0.7600	178.5	1.017	2.579
0.9250	0.7850	182.5	1.038	3.499
0.9500	0.8500	169.5	1.017	3.401
0.0805	0.3410	85.75	6.770	1.122
0.1295	0.3555	86.50	4.426	1.168
0.1525	0.3615	86.50	3.822	1.189
0.3050	0.3870	86.50	2.046	1.392
0.3980	0.3995	86.75	1.622	1.578
0.4700	0.4225	86.50	1.450	1.719
0.5755	0.4540	86.00	1.265	2.017
0.6660	0.4995	83.50	1.168	2.282
0.7385	0.5405	81.50	1.120	2.612
0.8440	0.6625	72.50	1.062	2.862
0.8500	0.7260	69.50	1.108	2.317
0.8975	0.7535	69.00	1.082	3.029

[a] Mole fraction of 1-propanol in liquid.
[b] Mole fraction of 1-propanol in vapor.
[c] Total pressure in millimeters of mercury.

and

$$A_{12}/B_{12}^2 = \left[\frac{(A_{11})(A_{22})}{(B_{11})^2(B_{22})^2}\right]^{1/2} \tag{9}$$

With the aid of Equations 8 and 9, it was possible to calculate A_{12} and B_{12} and hence β_{12} and δ_{12} because

$$\beta_{12} = B_{12} - \frac{A_{12}}{T^2} \tag{10}$$

$$\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{22} \tag{11}$$

VAPOR PRESSURE DATA

The vapor pressure data for methanol, ethyl alcohol, and 1-propanol were calculated using the Antoine equations presented by Weissberger, Proskauer, and Riddick (*30*).

Methanol. $\log_{10}P_{\text{mm.Hg}} = 7.87863 - 1473.11/(t\,^\circ\text{C.} + 230)$
Ethyl alcohol. $\log_{10}P_{\text{mm.Hg}} = 8.04494 - 1554.30/(t\,^\circ\text{C.} + 222.65)$
1-Propanol. $\log_{10}P_{\text{mm.Hg}} = 7.99733 - 1569.70/(t\,^\circ\text{C.} + 209.5)$

The vapor pressure data for ethyl acetate by Jordan (*11*) and those presented for 2-propanol by Parks and Barton (*21*) were used in this work.

The critical properties of all the compounds were taken from the review of Kobe and Lynn (*13*). The molal volumes of the liquids were calculated using the density equations given in the International Critical Tables (*9*) and the refractive indices used to calculate the molar refraction were taken from the same source.

Table IX. Van Laar Constants

		P_T = 760 Mm.Hg	T = 60 °C.	T = 50 °C.	T = 40 °C.
Methanol-ethyl acetate	A.	0.4530	0.4700	0.4940	0.5220
	B.	0.4600	0.4791	0.4940	0.5120
Ethyl alcohol-ethyl acetate	A.	0.3720	0.3960	...	0.4640
	B.	0.3840	0.4040	...	0.4550
1-Propanol-ethyl acetate	A.	0.2400	0.300	...	0.375
	B.	0.2460	0.307	...	0.364
2-Propanol-ethyl acetate	A.	0.2010	0.2980	...	0.3760
	B.	0.2060	0.3040	...	0.3680
1-Propanol-water	A.	1.160	1.000	...	1.050
	B.	0.503	0.563	...	0.600

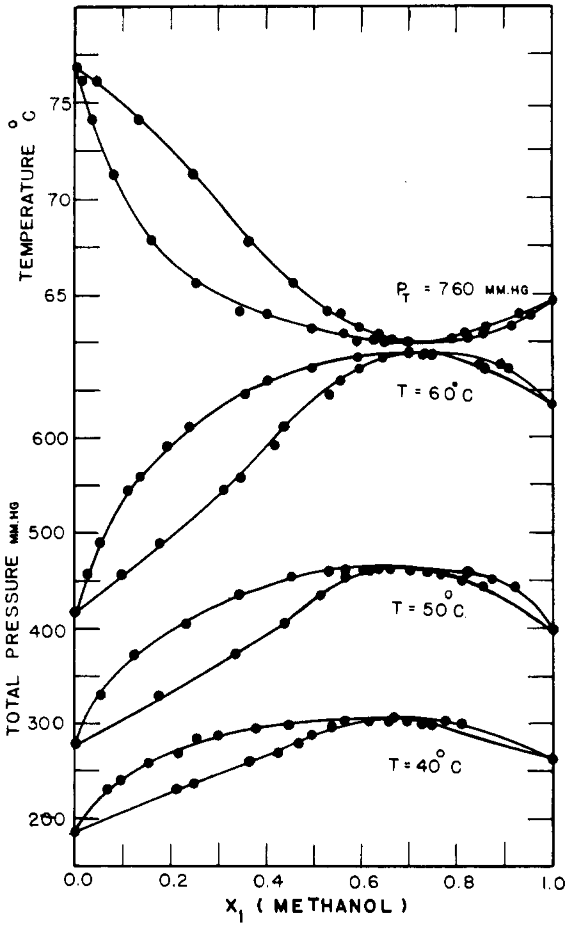

Figure 1. T-X-Y and P_T-X-Y diagrams for methanol-ethyl acetate

SMOOTHING OF DATA

The van Laar (*14*), Margules (*17*), and Wohl suffix equations (*31*) were applied to the experimental data and the van Laar equations as modified by Carlson and Colburn (*3*) were found to describe the data satisfactorily:

$$\log \gamma_1 = \frac{Ax_2^2}{\left[\frac{A}{B}x_1 + x_2\right]^2} \tag{12}$$

$$\log \gamma_2 = \frac{Bx_1^2}{\left[x_1 + \frac{Bx_2}{A}\right]^2}$$

Another test for thermodynamic consistency of experimental vapor-liquid equilibrium data was presented by Redlich and

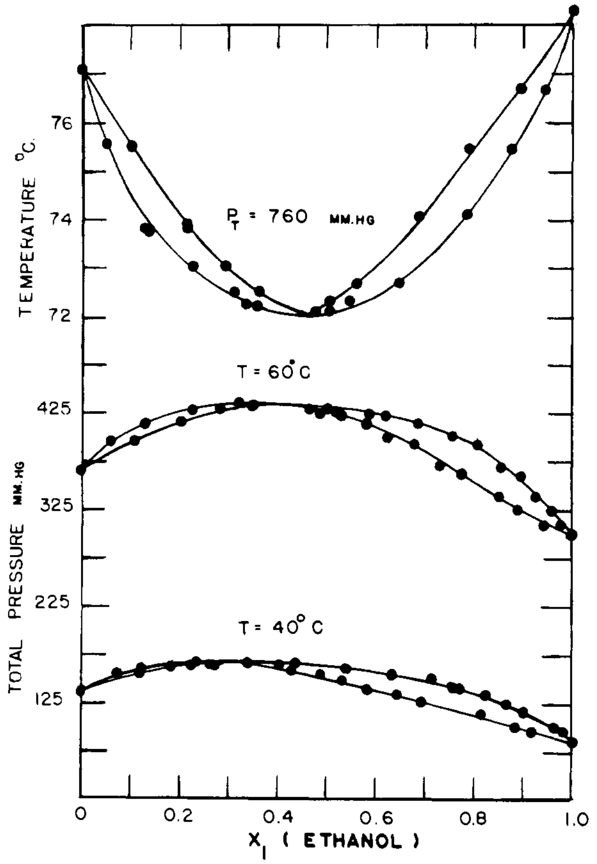

Figure 2. *T-X-Y* and P_T-*X-Y* diagrams for ethyl alcohol–ethyl acetate

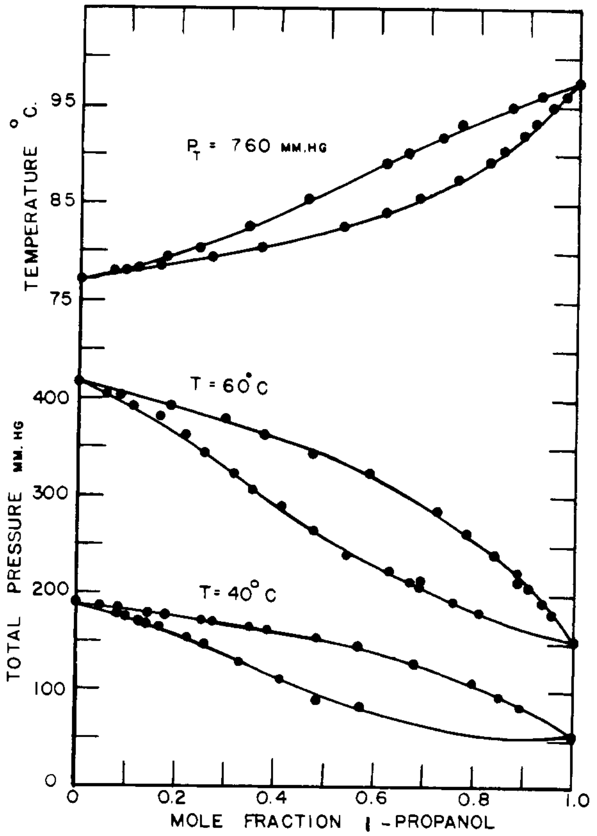

Figure 3. *T-X-Y* and P_T-*X-Y* diagrams for 1-propanol–ethyl acetate

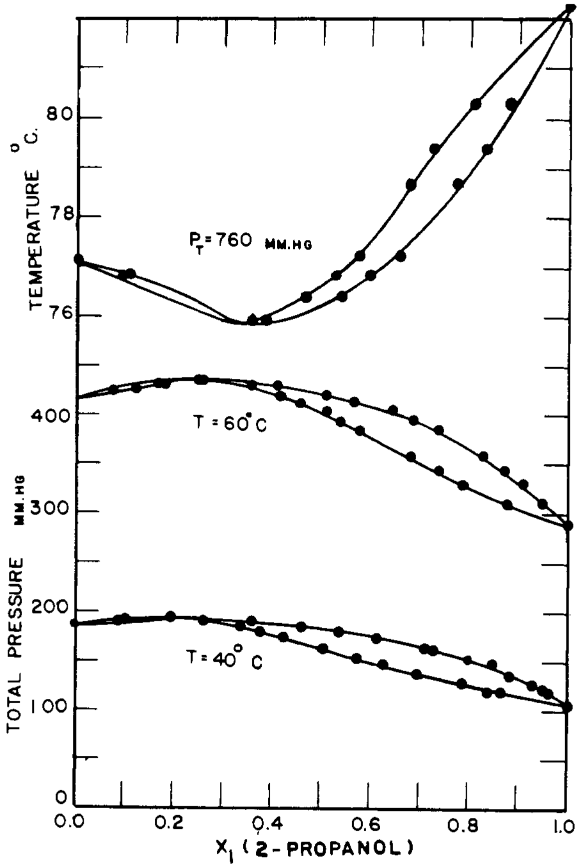

Figure 4. *T-X-Y* and P_T-*X-Y* diagrams for 2-propanol–ethyl acetate

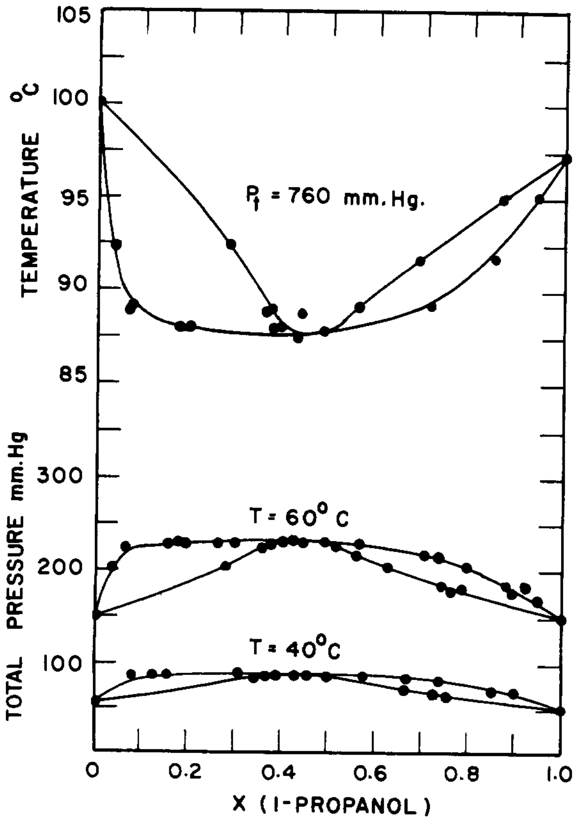

Figure 5. *T-X-Y* and P_T-*X-Y* diagrams for 1-propanol–water

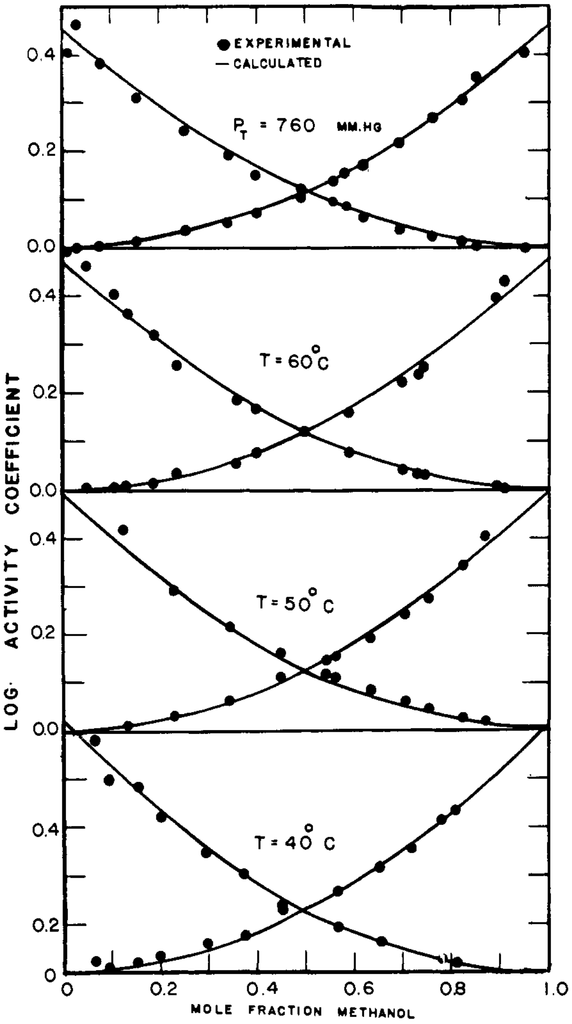

Figure 6. Activity coefficients, methanol–ethyl acetate

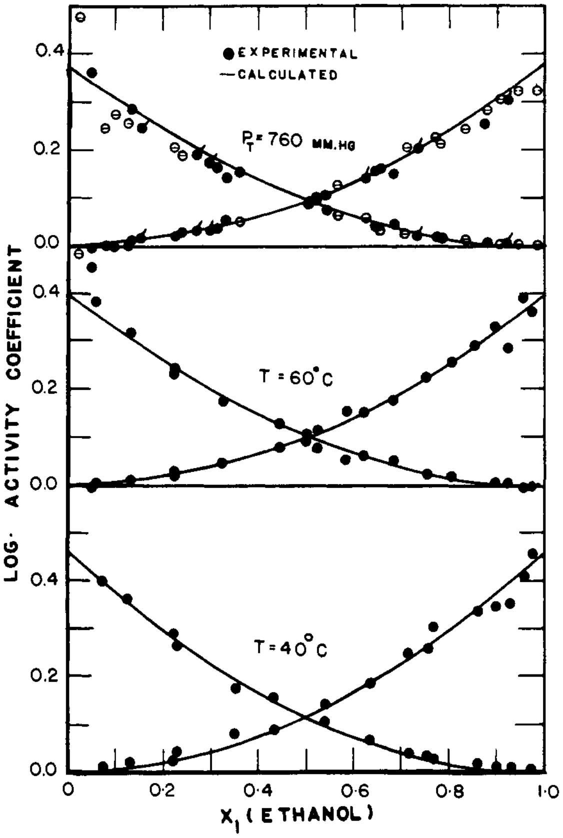

Figure 7. Activity coefficients, ethyl alcohol–ethyl acetate

● This work
♂ Griswold, *et al.* (*8*)
⊖ Furnas, *et al.* (*5*)

Kister (*23*) and all isothermal data were tested by this method:

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \tag{13}$$

This is strictly valid only for data obtained under constant temperature and pressure conditions. It can be used safely for isothermal data, since the pressure correction for γ is generally small over small pressure ranges.

RESULTS AND DISCUSSION

The experimental results of vapor-liquid equilibrium measurements are presented in Tables IV through VIII. The experimental data are shown plotted in Figures 1 through 5. The activity coefficients as functions of liquid composition are shown in Figures 6 through 10, in which the curves calculated by the van Laar equations as modified by Carlson and Colburn (*3*) are shown. The van Laar constants for all the systems studied in this work are listed in Table IX. The isothermal data were tested for consistency by the method of Redlich and Kister (*23*) and are shown in Figures 11 through 15. The equal area condition is satisfied within limits of experimental accuracy. No attempt was made to test the isopiestic data by this method.

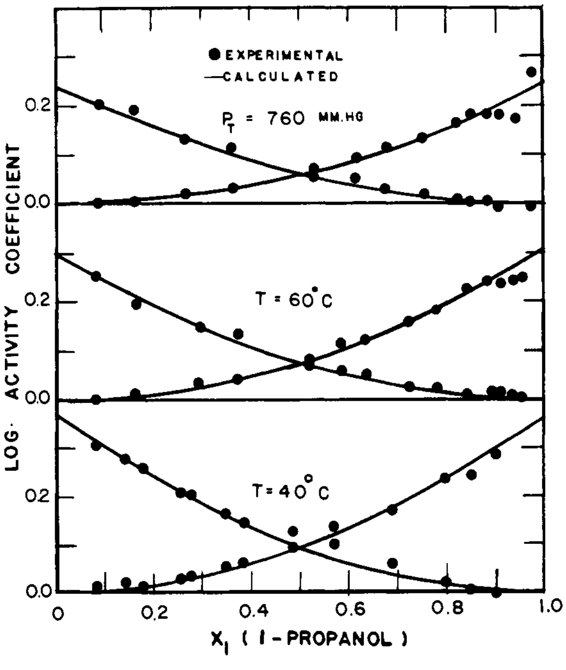

Figure 8. Activity coefficients, 1-propanol–ethyl acetate

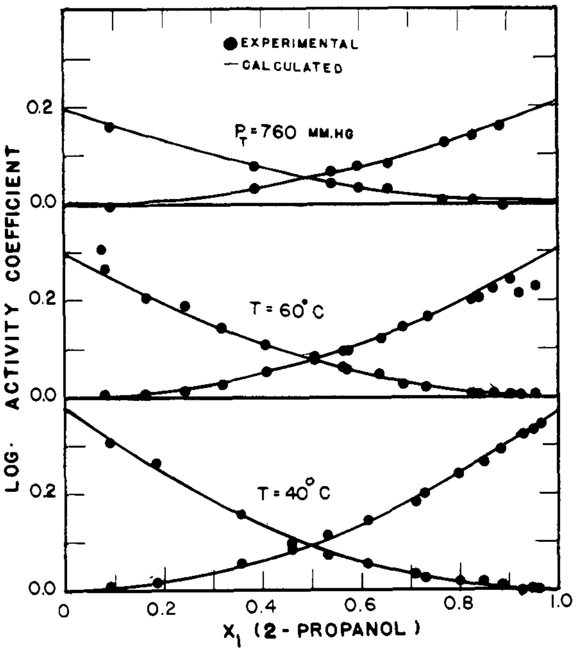

Figure 9. Activity coefficients, 2-propanol–ethyl acetate

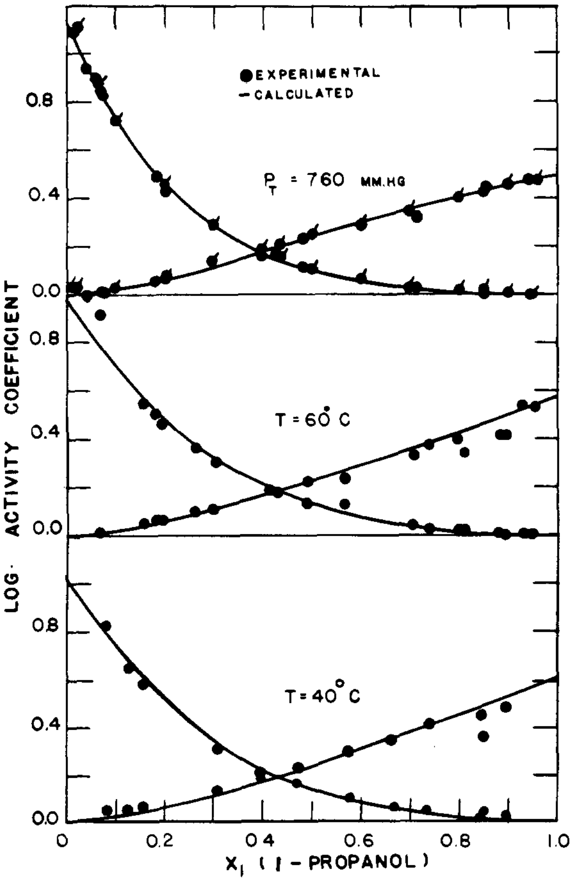

Figure 10. Activity coefficients, 1-propanol–water

● This work
ό Gadwa (*6*)

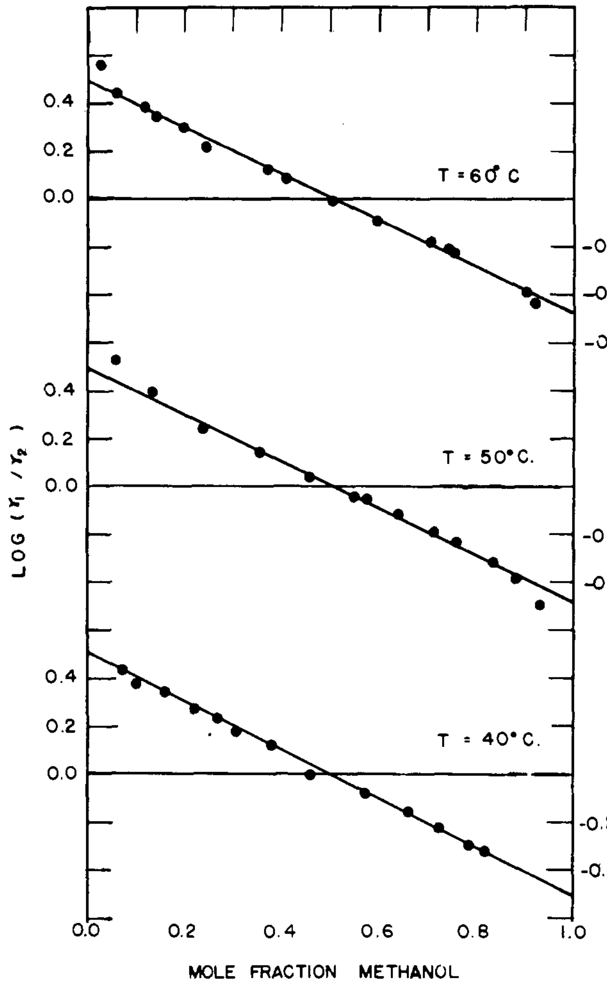

Figure 11. Thermodynamic consistency test, methanol–ethyl acetate

Methanol-Ethyl Acetate System. Experimental vapor-liquid equilibrium data at 39.6°C. were reported by Bredig and Bayer (*2*), who used the differential distillation technique. The results obtained by this method can be of doubtful accuracy and hence new data were determined in this investigation. The data indicate that the system exhibits nonideality and azeotropism. The azeotrope composition increases with respect to the more volatile component, methanol, as the pressure on the system is increased. The degree of nonideality, as shown by the value of activity coefficient, increases with decrease in temperature. The azeotropic data obtained here agree well with those reported by Lecat (*16*) at atmospheric pressure.

Ethyl Alcohol-Ethyl Acetate System. Experimental data on this system were reported at atmospheric pressure by Furnas and Leighton (*5*) and Griswold, Chu, and Winsauer (*8*) and at 60°C. by Mund and Heim (*20*). The atmospheric pressure data developed in this investigation compare satisfactorily with those of Griswold and others. At 60°C. the data of Mund and Heim were fitted by Redlich, Kister, and Turnquist (*24*) into a symmetrical equation and the constant in their equation was found to be slightly low for the data of this work. The behavior of this system is similar to that of the methanol-ethyl acetate binary in regard to azeotropic behavior and nonideality. The azeotropic data agree well with those of Merriman (*18*) at atmospheric pressure.

1-Propanol-Ethyl Acetate System. Vapor-liquid equilibrium data on this system are not reported in the literature. Although the behavior of this system is similar to that of

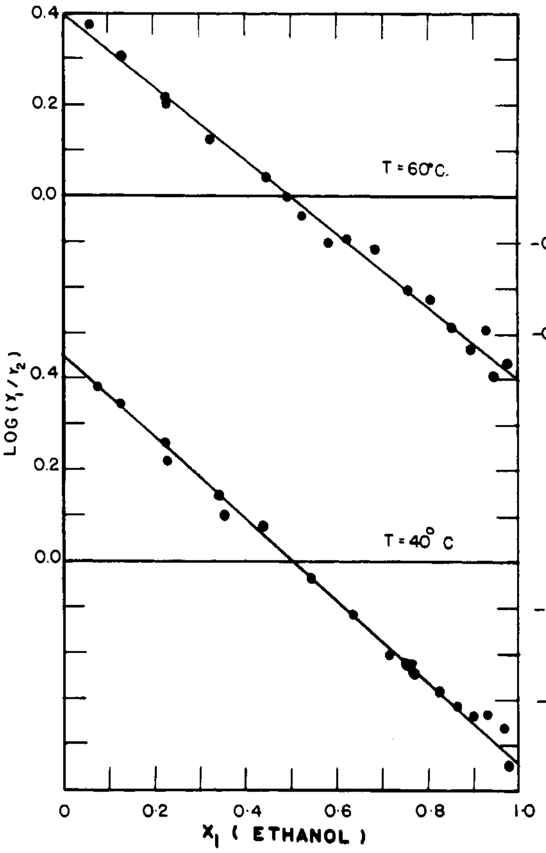

Figure 12. Thermodynamic consistency test, ethyl alcohol-ethyl acetate

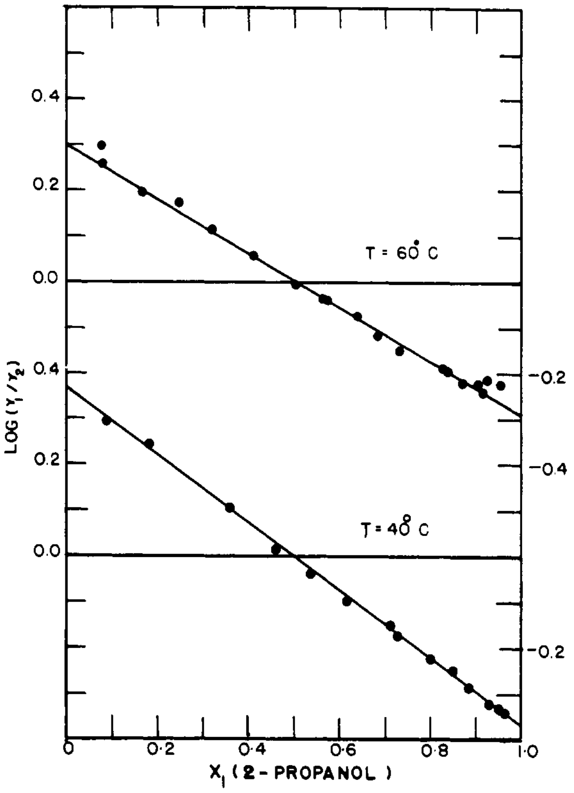

Figure 14. Thermodynamic consistency test, 2-propanol-ethyl acetate

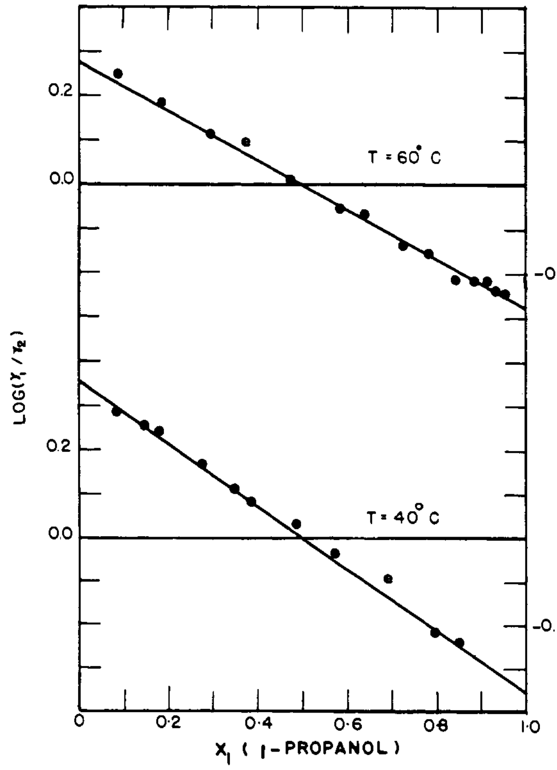

Figure 13. Thermodynamic consistency test, 1-propanol-ethyl acetate

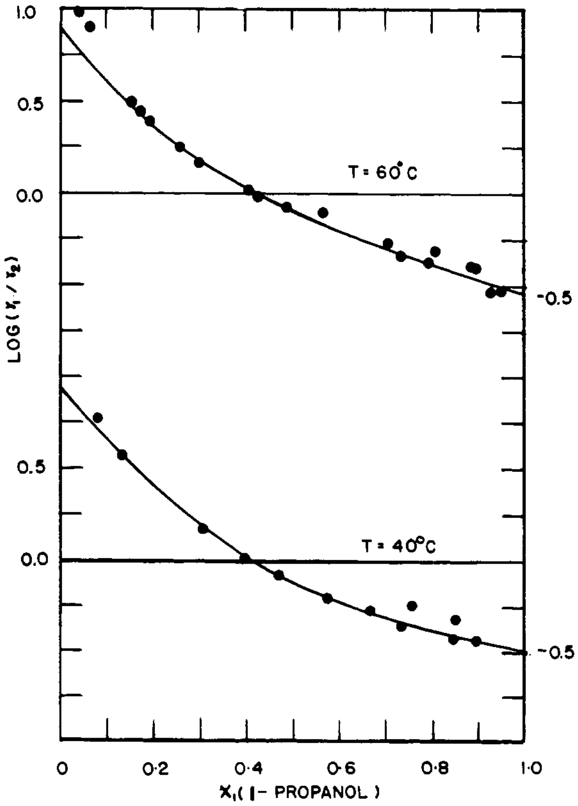

Figure 15. Thermodynamic consistency test, 1-propanol-water

the above two systems with respect to nonideality, it does not exhibit azeotropism within the conditions of this experimental work. This may be the result of increased chain length of the alkyl group in the alcohol molecule.

2-Propanol-Ethyl Acetate System. Data on this system are not reported in the literature. The behavior of this system is similar to the methanol-ethyl acetate system in regard to both nonideality and azeotropism.

1-Propanol-Water System. Data on this system were reported at 79.8°, 65.94°, 49.92°, and 30.35°C., by Wrewsky (*33*) and at atmospheric pressure by Gadwa (*6*) and Fowler and Hunt (*4*). Wrewsky used the differential distillation technique for all of his isothermal experiments. In this work, a few runs were made at 760 mm. of mercury and complete data were taken at 60° and 40°C. The data were correlated by the van Laar equations and the constants in the equation agree closely with those given by Carlson and Colburn (*3*), who fitted Gadwa's experimental results at atmospheric pressure.

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NOMENCLATURE

A, B = constants
k_1, k_2 = constants
n = number of moles
P_T = total pressure
P = vapor pressure
P_c = critical pressure
R = gas constant
r = refraction
T = absolute temperature
T_c = critical temperature
T_r = reduced temperature = T/T_c
V = molal volume
x, y = mole fraction of a component in the liquid and vapor

Greek Letters

γ = activity coefficient
β = second virial coefficient
δ_{12} = related by the equation $(2\beta_{12} - \beta_{11} - \beta_{22})$, also the differential operator

Subscripts

1, 2 = refer to components 1 and 2, respectively
11, 22 = refer to pure components 1 and 2, respectively
12 = refer to mixture of 1 and 2 components

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