Table V. Activity of Methyl Ethyl Ketone in Organic and Aqueous Phases

Mole Fraction Methyl Ethyl Ketone, x_A	Mole Fraction Water, x_B	Mole Fraction Cyclohexane, x_c	Activity Coefficient, γ_{AC}	Activity, a_{AC}
		Organic Phase		
0.725	0.234	0.041	1.088	0.788
0.730	0.180	0.090	1.084	0.790
0.703	0.152	0.145	1.102	0.775
0.652	0.079	0.269	1.134	0.740
0.550	0.053	0.397	1.244	0.684
0.367	0.030	0.603	1.578	0.579
0.229	0.014	0.757	2.128	0.487
0.119	0.004	0.877	2.891	0.334

Mole Fraction Methyl Ethyl Ketone, x_A	Mole Fraction Water, x_B	Mole Fraction Cyclohexane, x_c	Activity Coefficient, γ_{AB}	Activity, a_{AB}
		Aqueous Phase		
0.072	0.928	...	10.59	0.762
0.060	0.940	...	11.72	0.703
0.042	0.958	...	13.03	0.547
0.028	0.972	...	15.96	0.445
0.014	0.986	...	18.58	0.260

NOMENCLATURE

A = end value constants in the double suffix van Laar equation
a = activity
T = temperature
x = mole fraction

Subscripts

A = methyl ethyl ketone
B = water
c = cyclohexane
AB = methyl ethyl ketone in water
AC = methyl ethyl ketone in cyclohexane

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Densities and Viscosities of 1-Propanol–Water Mixtures

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Densities and viscosities of 1-propanol water mixtures obtained at 25°, 30°, 35°, 40°, and 50° C. are reported experimentally and presented empirically using a power series equation. Constants a_i were determined by the least squares procedure using the IBM 650 digital computer except a_0 which was, in some cases, chosen to agree with accepted values of density and viscosity of water. Tables of the computed constants of various equations at different temperatures are included. The maximum deviation of the calculated values as compared with the experimental values was always less than 0.15 and 0.88% for density and viscosity data, respectively.

IN A PREVIOUS article (*11*) the densities and viscosities of methanol-water mixtures were reported. The data were also reported empirically with a power series equation of the form

$$y = \sum_{i=0}^{n} a_i x^i \tag{1}$$

where y denoted the density d, viscosity η, or molal volume, V; and x, the independent variable, denoted the alcohol weight percentage W, alcohol mole percentage N, or temperature t, °C. The constants, a_i, were determined by the least squares procedure using the IBM 650 digital computer except a_0 which was, in some cases, chosen to agree with accepted values of density and viscosity of water.

In this paper the results for the densities and viscosities of 1-propanol-water mixtures obtained at 25°, 30°, 35°, 40°, and 50° C. are reported experimentally and presented empirically using the same power series Equation 1.

Densities of these mixtures at 0°, 15°, and 30° C. are available from the International Critical Tables (*6*). Gallart (*3*) determined their densities at 25°, 30°, and 35° C.; Chu and Thompson (*1*) obtained their densities at 25° C. Our values at 30° C. were in almost all cases lower than the I.C.T. values by 1 to 3 × 10^{-4} gram per ml. Although Gallart's and Chu and Thompson's values were determined at different weight percentages it can be concluded from graphical comparison that our values were almost invariably less than Gallert's by 1 to 4 × 10^{-4} gram per ml., but in excellent agreement with Chu and Thompson's values. Viscosities of only a few of these mixtures are available from the I.C.T. (*7*).

The maximum deviation of the calculated values from Equation 1 as compared with the experimental values was always less than 0.15 and 0.88% for density and viscosity data, respectively. This deviation can be further reduced to any reasonable arbitrary minimum by adding more terms to Equation 1.

In particular, it is noted that experimental values of density were reproducible within ±0.0001 gram per ml. and viscosity values within ±0.01 millipoise. It was considered impractical to add enough terms to make the empirical representation compatible with the experimental determination of each point.

EXPERIMENTAL

Chemically pure 1-propanol was further purified from allyl alcohol traces by addition of bromine and then fractionally distilled through an efficient column with several grams of anhydrous K_2CO_3. The middle fraction was then collected, dried with clean magnesium ribbon, treated with 2,4-dinitrophenylhydrazine to react with any propionaldehyde from the bromine treatment, and vacuum distilled after the method recommended by Kretschner (*8*). The resulting product had no perceptible odor of propionaldehyde, and had a density d_4^{25} of 0.7995 gram per ml. compared to the International Critical Tables value of 0.8001 gram per ml. (*5*) and to Gallart's (*3*) extrapolated value of 0.8000 gram per ml. but in perfect agreement with Kretschner's value (*8*) of 0.7995 gram per ml. and with the Manufacturing Chemists' Association value of 0.7995 gram per ml. (*10*). Densities obtained at higher temperatures were always less than either the International Critical Tables' and Gallart's values but agreed within ±0.0001 with Kretschner's values.

Methods of preparation of solutions and measurement of densities and viscosities were the same as described in the authors' previous article (*11*).

RESULTS

Tables I and II summarize the experimental results obtained. Empirical equations relating the different parameters follow.

Density of the Mixtures, d_4^t, as a Function of Weight Per Cent 1-Propanol, W.

$$d_4^t \text{ (g./ml. in vacuo)} = \sum_{i=0}^{6} a_i W^i \qquad (2)$$

In this equation, a_0 was chosen to agree with the density values of water given in the International Critical Tables (*4*). Values of a_0 through a_6 evaluated at the five different working temperatures are recorded in Table III. The maximum percentage error given in column 9 is:

$$\text{Max. } (d_{\text{obsd}} - d_{\text{calcd}})\, 100/d_{\text{obsd}}$$

The mean percentage error given in column 10 is:

$$1/m \sum_{i=1}^{m} \left| d_{i\,\text{obsd}} - d_{i\,\text{calcd}} \right| \, 100/d_{i\,\text{obsd}}$$

where m denotes the number of experimental values obtained between pure alcohol and pure water at one and and the same temperature.

Figure 1 graphically illustrates the closeness of fit between Equation 2 and typical experimental density data.

Density of Mixtures, d_4^t, as a Function of Mole Per Cent 1-Propanol, N.

$$d_4^t \text{(g./ml. in vacuo)} = \sum_{i=0}^{6} a_i N^i \qquad (3)$$

In this equation, a_0 is the same as a_0 of Equation 2. Constants a_0 through a_6 are given in Table III.

Figure 2 illustrates the closeness of fit between Equation 3 and typical experimental density data.

Table II. Viscosities of 1-Propanol–Water Mixtures at Different Temperatures

1-Propanol, Wt. %	1-Propanol, Mole %[a]	Viscosity, Millipoises 25° C.	30° C.	35° C.	40° C.	50° C.
0[b]	0.0000	8.95	8.00	7.21	6.54	5.49
10	3.2235	13.47	11.64	10.19	9.02	7.26
20	6.9720	18.36	15.46	13.30	11.59	9.07
30	11.385	22.26	18.68	16.00	13.84	10.72
40	16.656	24.97	21.01	17.93	15.45	11.91
50	23.064	26.50	22.37	19.13	16.55	12.74
60	31.019	26.61	22.59	19.40	16.82	12.97
70	41.159	25.92	22.16	19.02	16.51	12.76
80	54.527	23.94	20.71	18.02	15.74	12.33
90	72.959	21.62	18.91	16.62	14.67	11.65
95	85.065	20.43	18.05	15.93	14.14	11.32
100	100.000	19.38	17.23	15.34	13.79	11.10

[a] Molecular weight = 60.097.
[b] Reference (*9*).

Table I. Densities, d_4^t, Molal Volumes, V, of 1-Propanol–Water Mixtures at Different Temperatures

		25° C.		30° C.		35° C.		40° C.		50° C.	
1-Propanol, Wt. %	1-Propanol, Mole %[a]	d, g./ml.	Vol., ml.	d, g./ml.	Vol., ml.	d, g./ml.	Vol., ml.	d, g./ml.	Vol., ml.	d, g./ml.	Vol., ml.
0[b]	0.0000	0.9971	18.068	0.9957	18.094	0.9941	18.123	0.9923	18.156	0.9881	18.233
5	1.5533	0.9890	18.877	0.9875	18.906	0.9857	18.940	0.9836	18.981	0.9790	19.070
10	3.2235	0.9824	19.719	0.9804	19.760	0.9783	19.802	0.9761	19.847	0.9709	19.953
15	5.0245	0.9755	20.636	0.9732	20.685	0.9708	20.736	0.9673	20.811	0.9616	20.934
20	6.9720	0.9672	21.660	0.9642	21.728	0.9613	21.793	0.9582	21.864	0.9517	22.013
30	11.385	0.9473	24.076	0.9437	24.168	0.9404	24.252	0.9370	24.340	0.9297	24.531
40	16.656	0.9263	27.016	0.9225	27.127	0.9192	27.225	0.9157	27.329	0.9081	27.558
50	23.064	0.9051	30.628	0.9014	30.754	0.8973	30.894	0.8936	31.022	0.8856	31.303
60	31.019	0.8845	35.126	0.8806	35.282	0.8766	35.443	0.8726	35.605	0.8640	35.960
70	41.159	0.8640	40.898	0.8600	41.088	0.8558	41.290	0.8517	41.489	0.8430	41.917
80	54.527	0.8434	48.567	0.8392	48.810	0.8350	49.056	0.8310	49.292	0.8222	49.819
90	72.959	0.8224	59.239	0.8183	59.535	0.8140	59.850	0.8097	60.168	0.9010	60.821
95	85.065	0.8117	66.296	0.8075	66.640	0.8031	67.006	0.7990	67.349	0.7902	68.099
100	100.00	0.7995	75.168	0.7955	75.546	0.7914	75.938	0.7873	76.333	0.7790	77.146

[a] Molecular weight = 60.097.
[b] Reference (*6*).

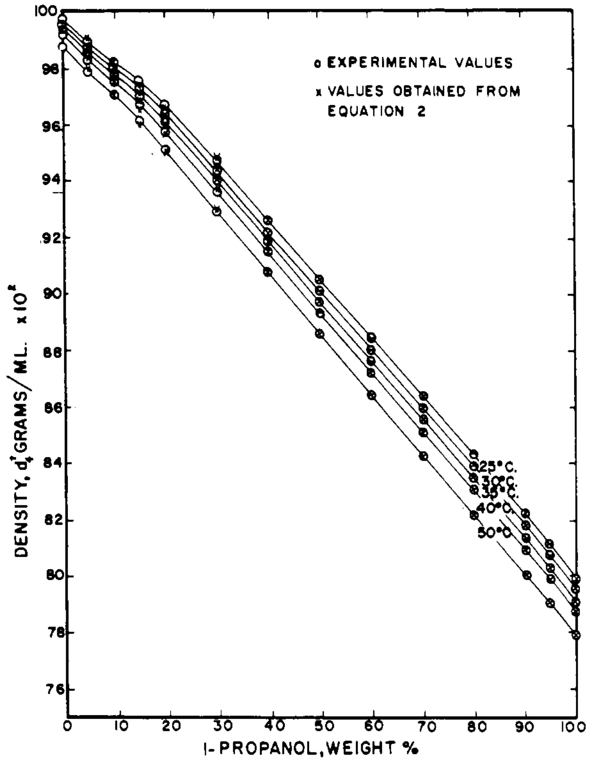

Figure 1. Comparison of experimental and computed data for density, d_4^t, vs. percentage 1-propanol by weight, *W*.

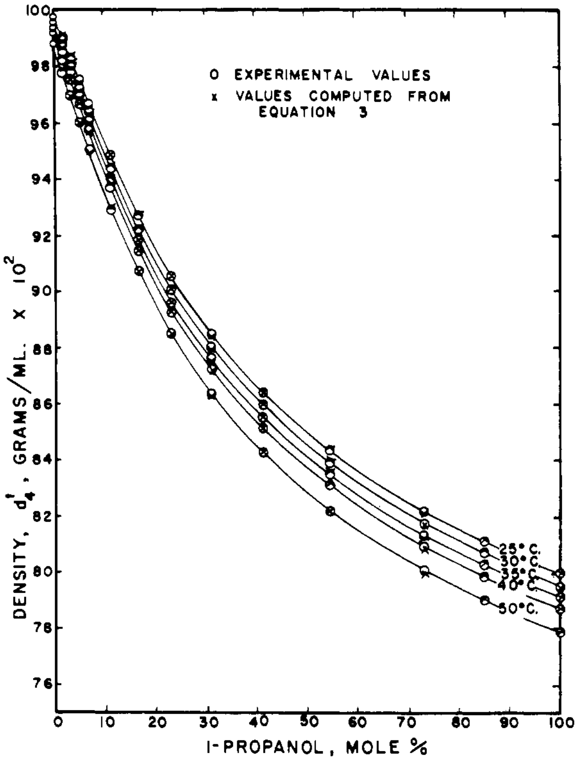

Figure 2. Comparison of experimental and computed data for density, d_4^t, vs. mole per cent 1-propanol.

Table III. Computed Constants of Various Equations at Different Temperatures

Temp., °C.	a_0	a_1	a_2	a_3	a_4	a_5	a_6	Max., % Error	Mean, % Error
				Equation 2: d_4^t vs. *W*					
		$\times10^{3}$	$\times10^{6}$	$\times10^{7}$	$\times10^{8}$	$\times10^{10}$	$\times10^{13}$		
25	0.9971	−1.5637	24.327	−16.722	3.3368	−2.8011	8.5221	+0.07	0.04
30	0.9957	−1.4964	7.1420	−9.7042	2.1128	−1.8196	5.5541	+0.08	0.04
35	0.9941	−1.5370	5.2295	−8.9954	2.0222	−1.7733	5.4939	+0.07	0.03
40	0.9923	−1.6311	6.1225	−8.5715	1.8923	−1.6437	5.0554	+0.06	0.02
50	0.9881	−1.6417	−6.8527	−2.8465	0.84336	−0.7651	2.2996	+0.07	0.02
				Equation 3: d_4^t vs. N^a					
		$\times10^{3}$	$\times10^{5}$	$\times10^{6}$	$\times10^{8}$	$\times10^{10}$	$\times10^{12}$		
25	0.9971	−4.2496	−4.6263	4.0238	−8.1203	7.1064	−23.200	+0.14	0.05
30	0.9957	−4.4770	−4.2112	4.1528	−8.6575	7.7379	−25.646	+0.12	0.06
35	0.9941	−4.6863	−3.4212	3.9645	−8.3710	7.4953	−24.808	+0.11	0.05
40	0.9923	−5.0236	−0.91843	3.0540	−6.7305	6.0832	−20.176	+0.09	0.03
50	0.9881	−5.3972	+0.37936	2.8190	−6.5028	5.9720	−19.956	−0.08	0.04
				Equation 4: *V* vs. N^a					
25	18.068	50.277	27.633	−53.969	50.351	−17.196		+0.14	0.05
30	18.094	50.831	27.267	−54.419	51.819	−18.050		+0.12	0.05
35	18.123	51.325	27.143	−55.044	53.249	−18.861		+0.13	0.05
40	18.156	51.965	25.452	−50.853	48.779	−17.171		+0.10	0.04
50	18.233	52.951	25.298	−51.942	50.919	−18.316		+0.08	0.04
				Equation 8: η vs. *W*					
			$\times10^{3}$	$\times10^{4}$	$\times10^{7}$	$\times10^{9}$			
25	8.95	0.43069	5.2093	−2.0423	15.413	−3.4680		+0.88	0.35
30	8.00	0.34270	3.9800	−1.4759	10.100	−1.8276		+0.41	0.21
35	7.21	0.27673	3.5181	−1.2480	8.6173	−1.6125		−0.22	0.17
40	6.54	0.23449	2.3394	−0.82507	4.4240	−0.13499		+0.33	0.17
50	5.49	0.16119	2.1487	−0.70283	4.3962	−0.56863		−0.29	0.16
				Equation 9: η vs. N^a					
			$\times10^{2}$	$\times10^{4}$	$\times10^{6}$	$\times10^{8}$	$\times10^{10}$		
25	8.95	1.6606	−5.0833	5.1903	1.2599	−5.5269	2.6039	+2.39	0.74
30	8.00	1.3122	−3.8111	3.4179	1.9208	−4.9245	2.1772	+1.76	0.62
35	7.21	1.0618	−2.8984	1.8454	3.4718	−5.7955	2.3962	+1.45	0.56
40	6.54	0.87179	−2.2652	1.0050	3.8108	−5.5922	2.2424	+1.09	0.47
50	5.49	0.61321	−1.4657	0.08560	3.9444	−5.0918	1.9705	+0.76	0.40

[a] Molecular weight = 60.097.

Molal Volumes of Mixtures, V, as Functions of Mole Fraction 1-Propanol, N.

$$V\text{ (ml.)} = \sum_{i=0}^{5} a_i N^i \tag{4}$$

In this equation, a_0 was chosen to agree with the molal volumes of water computed from density values of water given above. Equation 4 can also be used to derive the expressions of the partial molal volumes (*9*) as follows:

$$\text{1-Propanol partial molal volume } v_m = V + (1 - N)\frac{dV}{dN} \tag{5}$$

$$\text{Water partial volume } v_w = V - N\frac{dV}{dN} \tag{6}$$

Temperature Dependence of Density, d_4^t, for Mixtures, between t = 25° and 50° C.

$$d_4^t = \sum_{i=0}^{4} a_i t^i \tag{7}$$

An equation of the fourth degree was found to give the same order of accuracy as Equations 2, 3, and 4 in this case. Constants a_0 through a_4 were determined for different 1-propanol percentage by weight and recorded in Table IV.

Absolute Viscosity of Mixtures, η, as a Function of Weight Per Cent 1-Propanol, W.

$$\eta\text{ (millipoise)} = \sum_{i=0}^{5} a_i W^i \tag{8}$$

In this equation, as in the case of methanol (*11*), a_0 was chosen to agree with the values of the viscosity from Dorsey's selection (*2*). Consideration was given in the previous article (*11*) to the correction of Dorsey's values to the new National Bureau of Standards basis of 10.02 millipoises for the viscosity of water at 20° C.; however, it was decided in view of the lack of agreement in the literature to keep Dorsey's values as they are. Aside from the viscosity values of water, all the viscosities recorded in Table II are based on 10.02 millipoises for water at 20° C. Constants a_0 through a_5 are given in Table III. Figure 3 illustrates the closeness of fit between Equation 8 and typical viscosity data.

Absolute Viscosity of Mixtures, η, as a Function of Mole Per Cent 1-Propanol, N.

$$\eta\text{ (millipoises)} = \sum_{i=0}^{6} a_i N^i \tag{9}$$

In this equation, a_0 is the same as a_0 of Equation 8. Viscosity values computed from this equation had a maximum error of 2.39% and a maximum mean error of 0.74% compared to the corresponding values of 0.88 and 0.35% obtained from Equation 8 using the constants given in Table III. The difference in maximum error in these two cases, as has been indicated before (*11*), is a natural result of the least squares analysis, since the data in the two cases are different and the number of parameters is identical. The closeness of fit in such analyses of experimental data, with a given number of parameters, generally becomes better as the number of inflection points in the data decreases. Inspection of Figure 4 reveals one additional inflection point compared with Figure 2; therefore the closeness of fit is expected to be better in the relation represented by Equation 8 than that represented by Equation 9. Readers interested in computing viscosity values for solution mixtures of known mole percentages are therefore advised to calculate the corresponding weight

Table IV. Computed Constants for Different Weight Per Cents of 1-Propanol

1-Propanol, Wt. %	a_0	a_1	a_2	a_3	a_4	%, Error Max.	%, Error Mean
			Equation 7: d_4^t *vs.* t				
		× 10^3	× 10^5	× 10^6	× 10^9		
0	0.97911	2.4933	−11.286	2.0197	−13.759	0.00	0.00
5	0.98839	0.38665	−1.7794	0.13813	−0.24065	0.00	0.00
10	0.98088	0.95554	−5.9321	1.1587	−8.6851	0.00	0.00
15	0.86144	13.424	−56.038	9.8253	−63.720	−0.04	0.02
20	1.0597	−9.6346	38.583	−7.1442	48.355	0.01	0.00
30	0.92035	4.7350	−24.472	4.7975	−34.447	−0.01	0.01
40	1.0633	−14.240	56.195	−10.140	67.097	0.01	0.00
50	1.0361	−13.843	56.151	−10.485	71.756	0.03	0.02
60	0.90258	−0.59627	−0.90781	0.20909	−1.9528	0.00	0.00
70	0.98609	−12.725	51.162	−9.5449	65.158	0.02	0.01
80	0.90099	−4.8742	16.144	−2.776	17.301	0.01	0.01
90	0.85094	−1.8649	5.0023	−1.0326	7.5705	0.00	0.00
95	0.96731	−16.451	66.486	−12.323	83.791	0.03	0.02
100	0.78505	3.1786	−16.840	3.1014	21.063	0.00	0.00
			Equation 10: η *vs.* t				
		× 10	× 10^2	× 10^4	× 10^6		
0	14.579	−1.8040	−0.53942	1.8089	−1.4710	−0.07	0.04
10	26.013	−4.8260	−0.75540	3.4883	−3.0947	−0.09	0.05
20	40.490	−9.3966	−0.88411	5.7960	−5.5660	−0.22	0.11
30	38.570	0.88006	−6.2672	16.474	−13.041	−0.35	0.17
40	46.809	−4.1665	−4.3630	12.672	−10.143	−0.22	0.11
50	40.977	5.5073	−8.8487	21.389	−16.307	−0.21	0.11
60	54.111	−10.647	−1.5880	7.4226	−6.5587	−0.12	0.06
70	60.018	−20.456	3.3990	−2.9754	1.1589	0.11	0.05
80	40.821	−3.7472	−2.7259	7.5128	−5.6829	−0.13	0.06
90	38.416	−6.3151	−0.88441	3.6281	−2.9492	−0.06	0.03
95	41.002	−12.829	2.5998	−3.6293	2.3740	0.11	0.06
100	45.329	−19.445	5.3505	−8.1238	4.9254	0.22	0.11

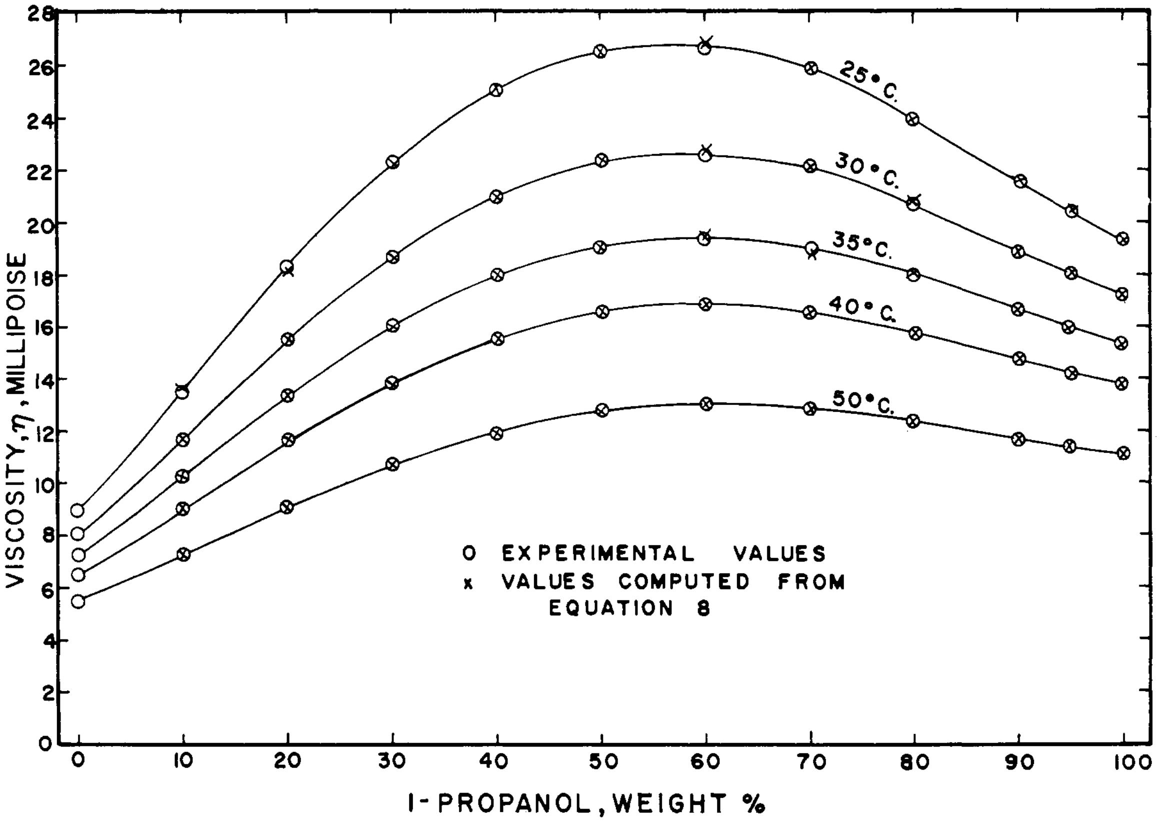

Figure 3. Comparison of experimental and computed data for viscosity η, vs. percentage 1-propanol by weight, W.

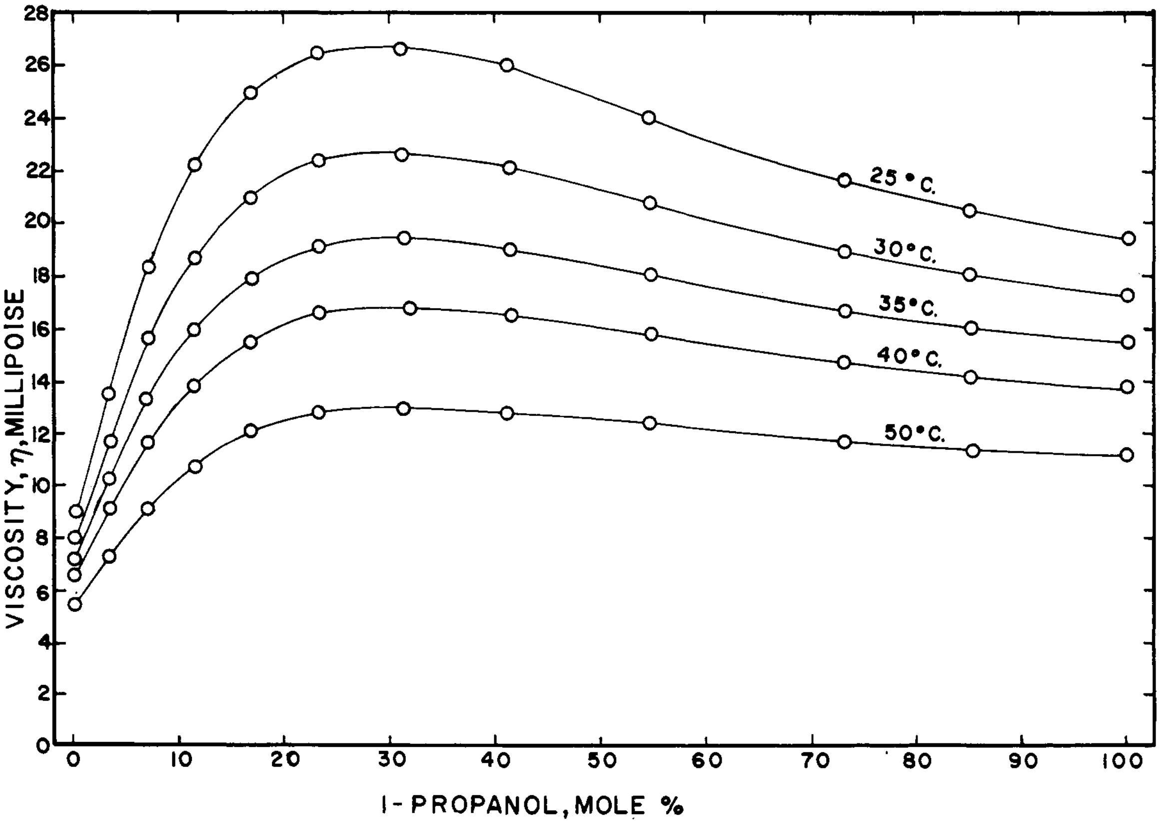

Figure 4. Viscosities of water -1-propanol mixtures, η, vs. mole per cent 1-propanol.

percentages and use Equation 8, rather than use Equation 9 directly unless ±2.39% maximum error is tolerable.

Temperature Dependence of Viscosity, η, for Mixtures, between t = 25° and 50° C.

$$\eta \text{ (millipoises)} = \sum_{i=0}^{4} a_i t^i \qquad (10)$$

An equation of the fourth degree gave fairly precise computed values in this case also. Constants a_0 through a_4 were determined for different 1-propanol percents by weight and recorded in Table IV.

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Consolute Temperatures for *m*-Fluoroaniline–Hydrocarbon Systems

Coexistence Data for the Isomeric Hexanes and Pentanes

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Phase diagrams of binary liquid liquid systems involving *m*-fluoroaniline in the isomeric pentanes and hexanes were obtained, and coexistence data is presented. Consolute temperatures were determined by the cloud point method. The data was better fitted to a cubic than a quadratic equation. However, neither equation would permit theoretical predictions of solubility without empirical measurements as shown by the drift in the collected constants of both equations.

THIS STUDY was undertaken to supplement the rather fragmentary data available on the solvent power of the fluorocarbons. The critical solution temperature may be used to characterize hydrocarbons in the same manner as the melting point, specific gravity, or any representative physical property. It is useful in selecting a proper solvent for extractions and separations. Further, coexistence equilibria may be utilized to predict solubilizing effects of traces which produce a ternary system by the Crismer method (*2*). The recent ACS Monograph (*1*) stimulates interest in this area and indicates the need for further study of univestigated systems.

EXPERIMENTAL

Materials. Spectrophotometric grade, *n*-pentane, *n*-hexane 2-methylbutane, 2,3-dimethylbutane, and 2,2-dimethylbutane, were obtained from Matheson, Coleman, and Bell Division, Norwood, Ohio. Research grade 2-methylpentane, 3-methylpentane, and *m*-fluoroaniline were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin. Degree of purity was confirmed by refractive indices using an Abbē refractometer.

Procedure. The usual cloud point method was used with the aid of a mechanical agitating device. Samples were measured volumetrically to within ±0.005 ml., corresponding to a maximum error of 0.005 ml. at the mole fraction 0.870. Microburets equipped with Teflon stopcocks and water jacketed when necessary were employed. Quadruplicate reproducible analyses were run. Tubes were filled almost completely and stoppered securely to minimize changes in composition caused by large vapor accumulations. Samples were thermostated at once. Mayer found that consolute temperatures rose 1° C. if solutions stood 24 to 48 hours before use (*5*). In the present study, delay also seemed to interfere with reproducibility. Heating was accomplished in a water bath with auxiliary heaters at the rate of ⅓° C. per minute. Equilibrium was approached both from the direction of increasing and decreasing temperature until confirmation was obtained from the appearance and from the disappearance of turbidity from within the limiting uncertainty determined by volumetric tolerances. A National Bureau of Standards thermometer graduated to 0.1° C. was used.

RESULTS AND DISCUSSION

Coexistence data are presented in Tables I through III with the critical solution temperature as determined by