are one, although values of 2 and 3 sometimes occur; one to five different groups are present.

LIMITATION

Insufficiency of examples causes exclusion of compounds with only one or more than five carbon atoms, or with branched or cyclic structure. Occurrence of the CHF group only five times and the CH_2F group only eight times (Tables I and II) limits the accuracy of fit of the new b.p.n.'s. Assumption that each group in the molecule is independent of any other group present involves some approximation. Group b.p.n.'s herein do not properly fit compounds with a lone hydrogen atom such as $CF_3CF_2CHF_2$ (*5*). Myer's equation (*30*) introduces rather minor errors in normal boiling points corrected from the usual pressures above 700 mm. pressure.

DISCUSSION OF RESULTS

New Equation 3 is for calculations of total boiling point number of *n*-chlorofluoroalkanes through use of the new boiling point numbers of 16 groups, such as CH_2Cl. Then the Kinney equation, Equation 1, serves in calculation of 153 normal boiling points of *n*-chlorofluoroalkanes, with a simple average error of 4.9°, a root mean square error of 6.2°, a standard deviation of 0.65 in the total boiling point number, and 90.8% of the calculated boiling points within 10° of the observed b.p.'s. Kinney (*20*) has 87.4% of 437 calculated boiling points within 10° of the observed b.p.'s of aliphatic, alicyclic, and aromatic monohalogen derivatives.

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RECEIVED for review January 6, 1966. Accepted February 10, 1967.

Thermodynamic Excess Properties of Three Alcohol-Hydrocarbon Systems

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The thermodynamic functions ΔC_p, ΔH, ΔS^E, and ΔG^E are presented as functions of temperature over the entire composition range for three binary liquid systems. The pressure dependency of ΔH, ΔS^E, and ΔG^E is determined from measurements of ΔV.

THE PURPOSE of this paper is to present an extensive correlation of thermodynamic data for the binary liquid systems: ethanol-toluene, 1-propanol-*n*-heptane, and 2-propanol-*n*-heptane. The results presented provide data over a considerable temperature range on the excess heat capacities, enthalpies, entropies, Gibbs free energies, and volumes of three highly nonideal alcohol-hydrocarbon solutions.

The complexity of systems such as these on a molecular scale is demonstrated in another paper (*24*), where heat-of-mixing data are used in conjunction with infrared spectral data. The present paper is devoted to simple publication of results so that they may be of aid to anyone who wishes to test or to develop a theory.

The usual correlation of excess properties of mixing for binary systems represents a property, say ΔM^E, as a function of mole fraction for a particular temperature by an equation such as

$$\frac{\Delta M^E}{x_1 x_2} = \sum_{n=0}^{n} A_n (x_1 - x_2)^n$$

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As has been pointed out (*9, 17*), this procedure is not satisfactory for alcohol-hydrocarbon systems, which exhibit marked departures from ideality, primarily as a result of hydrogen-bonding of the alcohol. Where data are available as a function of temperature, an alternative means of correlation is attractive, because it provides both a concise means for representing much information and a direct expression of the influence of temperature.

The temperature dependency of the heat capacity change of mixing for a solution of given composition can usually be represented by an equation of the form,

$$\frac{\Delta C_p}{x_1 x_2 R} = A + BT \text{ (constant composition)} \qquad (1)$$

where T is absolute temperature, and A and B are constants. Then since $\Delta C_p = \partial \Delta H / \partial T$, integration gives:

$$\frac{\Delta H}{x_1 x_2 R} = AT + \frac{BT^2}{2} + C \qquad (2)$$

where C is a constant of integration. The excess Gibbs function is related to ΔH by the Gibbs-Helmholtz equation

$$\frac{\partial(\Delta G^E/RT)}{\partial T} = \frac{-\Delta H}{RT^2}$$

Integration yields

$$\frac{\Delta G^E}{x_1 x_2 R} = -AT \ln T - \frac{BT^2}{2} + C + IT \qquad (3)$$

where again I is a constant of integration. The basic relation $\Delta S^E = -\partial(\Delta G^E)/\partial T$ provides

$$\frac{\Delta S^E}{x_1 x_2 R} = A \ln T + BT + (A - I) \qquad (4)$$

In these equations B has the dimension of T^{-1}; and C, the dimensions of T. A and I are dimensionless.

Thus, assuming the validity of Equation 1, the temperature dependence of ΔC_p, ΔH, ΔG^E, and ΔS^E for a particular composition is determined by the values of four constants. The enumeration of sets of these constants for a sufficient number of compositions provides both the temperature and composition dependence of the system. The purpose of this paper is to present sets of these constants for the three systems considered.

Volume changes of mixing, also measured during the course of this work, cannot be included in this scheme. Such data are useful for showing the effect of pressure on the other excess functions, as discussed below.

Sets of constants for Equation 2 were determined from heat-of-mixing data as a function of temperature. These data were taken by isothermal dilution calorimetry in an apparatus which is described elsewhere (*15, 16*). Results for a number of alcohol-hydrocarbon systems have been published, and their reliability has been thoroughly established (*9, 16, 17*). Thus heat-of-mixing data provide three of the four constants (A, B, and C) necessary for the representation of results. Values for I were determined from isothermal vapor-liquid equilibria. Total solution vapor pressures were measured at one or more temperatures as a function of liquid composition in a static cell. The apparatus and experimental procedure are described by Ljunglin and Van Ness (*7*). The resulting isothermal *P-x* data were used for numerical integration of the coexistence equation as discussed by Van Ness (*21*). This provided isothermal *P-x-y* data from which liquid-phase activity coefficients were calculated by the equations (*20*):

$$\left.\begin{aligned} \ln \gamma_1 &= \ln \frac{y_1 P}{x_1 P_1} + \frac{(B_{11} - V_1^L)(P - P_1) + P\delta_{12} y_2^2}{RT} \\ \ln \gamma_2 &= \ln \frac{y_2 P}{x_2 P_2} + \frac{(B_{22} - V_2^L)(P - P_2) + P\delta_{12} y_1^2}{RT} \end{aligned}\right\} \qquad (5)$$

In all cases the vapor pressures of the pure components, P_1 and P_2, were determined in the same apparatus as the solution vapor pressures. The second virial coefficients, B_{11}, B_{22}, and B_{12} ($\delta_{12} = 2B_{12} - B_{11} - B_{22}$), when not available in the literature, were estimated by generalized correlations (*1, 2, 14*). Since

$$\Delta G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad (6)$$

a value of $\Delta G^E/RT$ is known for substitution into Equation 3 for the determination of I.

With sets of constants known for a sufficient number of compositions, one has all the information needed to determine ΔC_p, ΔH, ΔS^E, and ΔG^E at any composition and at any temperature within the range covered. Extrapolation of 10° to 20° C. outside the range of the data should give reliable results at least for ΔH and ΔG^E. Since ΔC_p and ΔS^E depend on differentiation of the data, extrapolation is less certain.

Partial molar properties must be found from calculated values of the total property as a function of x at the temperature of interest. It is best to deal with the quantity $\Delta M/x_1 x_2$ rather than with ΔM itself, and to determine $\overline{\Delta M}_1$ and $\overline{\Delta M}_2$ by the method of Van Ness and Mrazek (*19, 22*). This can be done graphically or numerically. Numerical operations are facilitated if the composition dependence of $\Delta M/x_1 x_2$ is represented by the spline-fit technique (*5*).

The materials used in this work were all of high purity as received from the vendors, whose specifications are given in Table I. Chromatographic analyses indicated a purity of at least 99.5 mole % for all of them, and they were used in the "as received" condition for all heat-of-mixing and volume-change-of-mixing measurements. The question of purity is much more critical with respect to vapor pressure measurements. For this work, all materials were thoroughly degassed and transferred to the measuring cell by distillation. Unfortunately, for 1-propanol and 2-propanol this distillation process effected a considerable concentration of the small amounts of water initially present. Therefore, during distillation of these materials the vapors were passed through a 4-foot column of activated Linde Type 3A Molecular Sieves, which reduced the water content to a negligible level.

Table I. Materials Employed

Material	Vendor's Specification	Refractive Index at 25° C.	
		Exptl.	Lit.[a]
Toluene	Certified, Fisher Scientific Co.	1.49404	1.49413
n-Heptane	99 + mole %, Phillips Petroleum Co.	1.38508	1.38511
Ethanol	Reagent quality, 200 proof, U.S. Industrial Chemicals	1.35920	1.35941
1-Propanol	Certified, Fisher Scientific Co., boiling range, 96.9–97.4° C.	1.38337	1.38355
2-Propanol	Certified, Fisher Scientific Co., boiling range, 82.1–82.2° C.	. . .	. . .

[a] American Petroleum Institute, Research Project 44.

Vapor pressures taken as a function of temperature for each of the pure materials were fitted by the Antoine equation:

$$\log_{10}P = a - \frac{b}{t + c}$$

where t is in °C. and P is in mm. Hg. The constants so determined are listed in Table II. Vapor pressures calculated from these equations are in substantial agreement with values reported by Research Project 44 of the American Petroleum Institute.

ETHANOL-TOLUENE

For the ethanol-toluene system heats of mixing at 25° and 45° C. were reported by Mrazek (*9*). Additional data at these temperatures together with data at 60° C. were given by Savini (*15*). In this temperature range these data are not far from being linear with temperature. Thus they were fitted closely by a parabola, represented by Equation 2. The values of A, B, and C so determined are included in Table V. The raw data upon which this correlation is based are given in Table III.

Vapor pressure data for a number of liquid compositions were taken over a temperature range of 25° to 65° C. All experimental values (*6*) are recorded in Table IV. These data for each liquid composition were used to determine the best constants in the Antoine equation for their correlation, and these equations were then used to interpolate the vapor pressures at 55° C. The resulting P-x relationship together with the coexistence equation provided P-x-y data, which allowed the calculation of $\Delta G^E/RT$ as a function of composition at 55° C. through Equations 5 and 6.

The temperature of 55° C. was chosen to permit direct comparison of results with the data of Kretschmer and Wiebe (*4*). The excellent agreement was shown by Ljunglin and Van Ness (*7, 21*). The values of I obtained by substitution of the data for 55° C. in Equation 3 are included in Table V.

From the general relation for $\Delta G^E/RT$ as a function of temperature, values for this function were calculated at 30°, 45°, and 60° C. At each of these temperatures the calculated values of $\Delta G^E/x_1x_2RT$ were spline-fit as a function of ethanol mole fraction, and values of $\ln \gamma_i = \overline{\Delta G}_i^E/RT$ were determined as functions of liquid composition through a computer program based on the method of Van Ness

Table II. Coefficients in the Antoine Equation for Pure Materials at 15°–75° C.

	a	b	c
Toluene	7.335234	1580.415	244.566
n-Heptane	7.080171	1363.355	226.669
Ethanol	8.295981	1699.501	235.539
1-Propanol	8.367686	1792.823	229.880
2-Propanol	8.009859	1506.916	211.571

Table III. Experimental Heat-of-Mixing Data, (Joules/Gram Mole) for Ethanol-Toluene

25° C.		45° C.		60° C.	
x_{EtOH}	$\Delta H/x_1x_2$	x_{EtOH}	$\Delta H/x_1x_2$	x_{EtOH}	$\Delta H/x_1x_2$
0.0054	14620	0.0166	14100	0.0224	14340
0.0098	14230	0.0247	13600	0.0291	14050
0.0144	13740	0.0333	13020	0.0368	13700
0.0195	13110	0.0402	12490	0.0472	13180
0.0253	12380	0.0458	12060	0.0541	12840
0.0315	11640	0.073	10580	0.0658	12250
0.0366	11060	0.101	9330	0.0828	11420
0.0410	10600	0.130	8330	0.100	10640
0.0449	10220	0.176	7200	0.116	10110
0.0500	9770	0.224	6360	0.135	9520
0.060	8980	0.252	6020	0.159	8900
0.098	7120	0.280	5690	0.192	8180
0.152	5660	0.306	5440	0.223	7640
0.222	4630	0.329	5230	0.280	6870
0.312	3820	0.363	4980	0.330	6350
0.364	3490	0.410	4640	0.373	5980
0.407	3260	0.466	4340	0.411	5700
0.463	3010	0.512	4120	0.446	5480
0.510	2830	0.550	3960	0.476	5300
0.551	2690	0.584	3830	0.504	5150
0.591	2570	0.641	3610	0.528	5030
0.628	2460	0.704	3400	0.550	4920
0.656	2380	0.795	3120	0.589	4750
0.698	2260	0.882	2880	0.622	4620
0.756	2120	0.974	2660	0.684	4420
0.823	1930			0.749	4210
0.854	1870			0.807	4030
0.896	1740			0.868	3850
0.943	1640			0.913	3730
				0.979	3570

Table IV. Experimental Vapor Pressures of Ethanol-Toluene

x_{EtOH}	t, °C.	P, Mm. Hg	x_{EtOH}	t, °C.	P, Mm. Hg
0.0000	27.06	32.91	0.6879	27.93	82.63
	44.20	72.60		43.82	183.63
	58.88	134.30		54.99	308.70
	72.43	223.55		66.89	509.40
0.0105	27.49	44.03	0.7594	27.23	79.64
	43.45	88.37		43.17	177.94
	55.00	143.42		55.03	310.13
	65.34	206.27		66.01	491.96
0.0334	27.63	57.91	0.8688	27.41	78.73
	43.67	118.11		43.36	176.59
	55.01	182.23		55.00	304.24
	66.62	282.86		66.07	487.66
0.0514	27.11	61.65	0.9321	27.44	74.98
	43.31	129.32		43.91	176.12
	55.00	207.56		54.99	296.50
	68.31	335.96		70.21	569.19
0.1277	27.43	71.17	0.9557	28.83	79.21
	43.81	156.33		42.98	164.94
	54.99	253.12		55.00	292.46
	62.57	341.25		65.90	469.64
0.2681	27.69	79.01	0.9777	27.12	71.10
	43.28	166.86		42.57	158.79
	54.99	281.98		54.99	287.54
	66.38	447.92		65.89	461.25
0.4252	24.91	68.47	1.0000	25.67	61.60
	42.91	170.88		32.92	92.41
	55.00	296.24		45.93	180.96
	63.13	419.62		57.89	319.38
0.6490	25.62	72.78			
	42.61	173.28			
	57.48	341.33			
	70.53	585.19			

Table V. Ethanol-Toluene Constants for Equations 1 through 4

x_{EtOH}	A	B, °K.$^{-1}$	C, °K.	I
0.000	0.0000	0.000000	1796.97	−3.1191
0.010	6.2128	−0.014892	517.53	34.3051
0.020	35.2633	−0.097944	−4591.42	204.5227
0.050	34.4737	−0.072743	−5871.23	207.9191
0.075	83.0882	−0.223382	−13865.09	489.1580
0.100	76.6662	−0.203908	−12947.05	452.3018
0.200	26.0122	−0.048114	−5029.48	160.1153
0.300	21.6245	−0.038949	−4245.89	133.7024
0.400	12.4832	−0.012602	−2764.83	80.4807
0.500	4.5812	0.010309	−1477.09	34.4878
0.600	3.6608	0.012028	−1319.94	28.9276
0.700	−0.9360	0.025774	−595.27	2.3240
0.800	−7.2377	0.045248	386.14	−33.9892
0.900	−13.2727	0.064150	1315.89	−68.6896
1.000	−20.0137	0.085342	2354.31	−107.4286

and Mrazek (*19, 22*). Equation 5 together with the condition $y_1 + y_2 = 1$ was then solved for the P-x-y relationships at 30°, 45°, and 60° C. Since these operations involve considerable effort, the results are reported here in Table VI. In addition, the computed P-x curves are compared with the smoothed vapor pressure data in Figure 1. The excellence of agreement demonstrates the thermodynamic consistency of the heat-of-mixing and phase-equilibrium data.

Table VI. Ethanol(1)-Toluene(2) Phase Equilibria and Acitivity Coefficients

x_1	y_1	P, Mm.	$\ln\gamma_1$	$\ln\gamma_2$
		30° C.		
0.000	0.000	37.95	2.818	0.000
0.005	0.138	43.8	2.739	0.000
0.010	0.230	48.85	2.664	0.001
0.015	0.295	53.2	2.593	0.002
0.020	0.343	56.9	2.524	0.003
0.040	0.449	66.95	2.261	0.011
0.060	0.502	73.3	2.057	0.022
0.080	0.531	77.2	1.875	0.035
0.100	0.547	79.5	1.712	0.051
0.150	0.572	83.05	1.393	0.096
0.200	0.588	85.4	1.161	0.145
0.300	0.611	88.3	0.827	0.256
0.400	0.628	90.0	0.586	0.386
0.500	0.645	91.3	0.404	0.533
0.600	0.665	92.1	0.260	0.709
0.700	0.691	92.4	0.147	0.919
0.800	0.735	91.55	0.066	1.162
0.850	0.770	90.3	0.038	1.297
0.900	0.818	88.1	0.017	1.442
0.950	0.889	84.45	0.004	1.598
1.000	1.000	78.65	0.000	1.765
		45° C.		
0.000	0.000	75.40	2.531	0.000
0.005	0.119	85.2	2.474	0.000
0.010	0.204	94.0	2.418	0.001
0.015	0.268	101.8	2.364	0.001
0.020	0.318	108.8	2.312	0.002
0.040	0.438	130.1	2.114	0.008
0.060	0.497	143.9	1.936	0.018
0.080	0.532	153.15	1.778	0.030
0.100	0.555	159.6	1.637	0.043
0.150	0.588	169.55	1.348	0.084
0.200	0.608	175.7	1.129	0.131
0.300	0.634	183.1	0.806	0.237
0.400	0.653	187.8	0.573	0.362
0.500	0.672	191.3	0.397	0.506
0.600	0.693	193.65	0.256	0.677
0.700	0.719	194.9	0.146	0.881
0.800	0.761	194.3	0.066	1.123
0.850	0.794	192.55	0.038	1.256
0.900	0.838	189.1	0.017	1.403
0.950	0.902	183.0	0.004	1.558
1.000	1.000	172.95	0.000	1.725
		60° C.		
0.000	0.000	140.0	2.271	0.000
0.005	0.103	155.4	2.227	0.000
0.010	0.181	169.55	2.185	0.000
0.015	0.242	182.55	2.144	0.001
0.020	0.291	194.4	2.103	0.002
0.040	0.416	232.6	1.943	0.007
0.060	0.485	260.4	1.801	0.014
0.080	0.529	281.2	1.675	0.024
0.100	0.557	296.45	1.556	0.035
0.150	0.597	319.7	1.294	0.072
0.200	0.620	333.5	1.084	0.117
0.300	0.652	351.65	0.780	0.217
0.400	0.675	363.7	0.560	0.334
0.500	0.695	371.6	0.387	0.476
0.600	0.717	377.7	0.250	0.642
0.700	0.743	381.7	0.143	0.843
0.800	0.785	382.65	0.066	1.076
0.850	0.814	380.7	0.037	1.211
0.900	0.856	375.9	0.017	1.352
0.950	0.914	366.8	0.004	1.507
1.000	1.000	351.1	0.000	1.672

Hwa and Ziegler (*3*) have recently reported extensive measurements of heat capacity for this system at temperatures from −95° to 35° C. Their results for ΔC_p at 30° C. are compared with those determined from Equation 1 and the constants of Table V in Figure 2. The agreement is entirely reasonable in view of the fact that the ΔC_p values reported in this work depend on a differentiation of the data with respect to temperature, and data are available for only three temperatures.

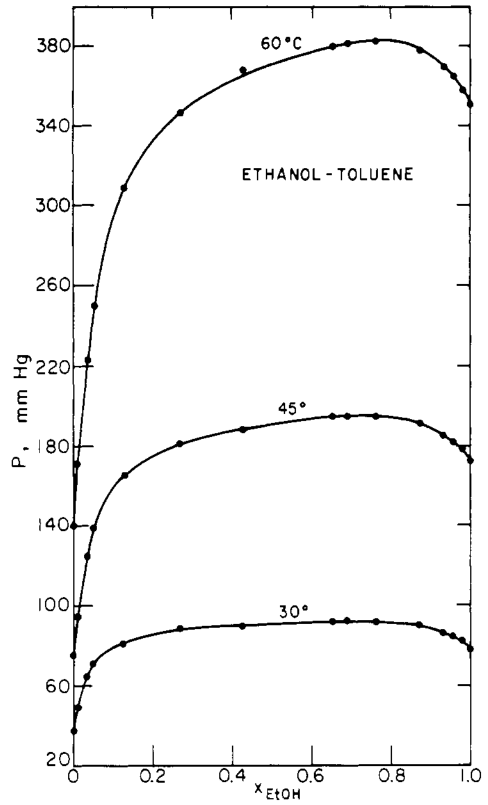

Figure 1. Vapor pressures as a function of ethanol mole fraction for ethanol-toluene

All points experimental. Curves represent values calculated from correlation of all data

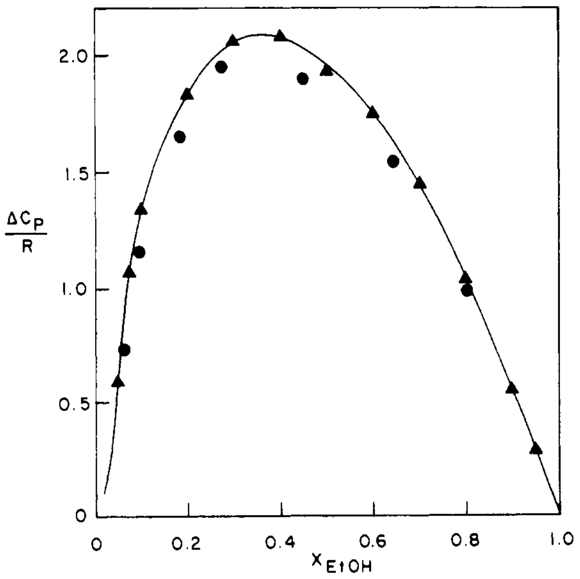

Figure 2. Excess heat capacity for ethanol-toluene at 30° C.

▲ Values calculated from correlation of data

● Data of Hwa and Ziegler (3)

1-PROPANOL–*n*-HEPTANE

Heat-of-mixing data for the 1-propanol-*n*-heptane system at 30° and 45° C. have been published by Savini, Winterhalter, and Van Ness (*17*). Since the 1-propanol-*n*-heptane system is very similar chemically to ethanol-*n*-heptane, the data were extrapolated to 60° C. upon the assumption that the ΔH *vs.* T curves are parabolic (Equation 2) and similar in shape to those for ethanol-*n*-heptane (*23*). The constants A, B, and C which provided reasonable results are listed in Table VIII. Since the temperature dependency of ΔH is not far from linear in the range from 30° to 60° C., this procedure should provide entirely reliable values of ΔH and ΔG^E. A bit less certain are the results for ΔC_p and ΔS^E, which depend upon differentiation.

Vapor pressure data for this system have been measured at 30°, 40°, 50°, and 60° C. by Peloquin (*12*) and are given in Table VII. Integration of the coexistence equation provided P-x-y data for each of these temperatures and through Equations 5 and 6 values of $\Delta G^E/RT$ as a function of composition at each temperature. Values of the constant I were determined so as to achieve the best fit of Equation 3 to all the $\Delta G^E/RT$ data at various compositions, and the resulting values of I are included in Table VIII.

Phase equilibrium data, calculated as described above are listed for 30°, 45°, and 60° C. in Table IX. Again, the calculated P-x curves correlate the experimental P-x data very well.

2-PROPANOL–*n*-HEPTANE

The experience gained in taking data for the systems already discussed led to considerable confidence in the methods employed, and demonstrated that maximum use should be made of heat-of-mixing data. Such data, taken over an adequate temperature range, provide reliable values for all of the constants in Equations 1 through 4 with the exception of I. All that is required for the determination of this last constant is phase-equilibrium data at one temperature. This being the case, the most expedient procedure is to focus attention on obtaining the best possible set of P-x data at a single temperature. This course was adopted for the 2-propanol–*n*-heptane system.

Table VII. Experimental Vapor Pressures of l-Propanol–*n*-Heptane

x_{PrOH}	Vapor Pressure, P, Mm. Hg 30° C.	40° C.	50° C.	60° C.
0.0000	58.75	92.79	142.08	211.00
0.0126	67.84	107.30	161.85	236.96
0.0246	70.64	112.23	171.54	253.86
0.0627	73.61	118.38	183.92	276.09
0.1583	75.63	122.74	193.01	292.64
0.2156	76.03	...	194.63	296.09
0.2886	76.15	123.92	195.35	298.08
0.3237	...	123.89	...	...
0.3867	76.03	123.68	195.04	298.62
0.4988	75.42	123.01	193.90	297.48
0.6843	72.68	119.05	187.75	288.00
0.8168	65.87	108.58	172.94	267.25
0.9108	54.43	91.00	147.11	230.67
0.9547	44.89	76.52	126.00	202.74
0.9723	39.49	68.33	114.13	184.37
1.0000	29.44	53.04	91.65	152.46

Table VIII. 1-Propanol–*n*-Heptane Constants for Equations 1 through 4

x_{PrOH}	A	B, °K.$^{-1}$	C, °K.	I
0.000	−3.2073	0.000000	3774.82	−27.0598
0.010	249.5127	−0.759057	−38469.81	1441.1877
0.020	214.5862	−0.604037	−35569.15	1255.3782
0.050	22.3140	0.005349	−5968.65	151.0550
0.075	7.7401	0.037421	−3235.98	63.4355
0.100	−32.8185	0.160367	3287.32	−171.3498
0.200	−29.7275	0.133639	3363.14	−158.3193
0.300	−32.8430	0.136311	4098.80	−178.3203
0.400	−30.7647	0.125620	3909.50	−167.5468
0.500	−28.1652	0.114929	3577.83	−153.2832
0.600	−25.4454	0.104238	3219.93	−138.2181
0.700	−21.6949	0.090874	2679.58	−117.0456
0.800	−19.6450	0.082856	2414.58	−105.6738
0.900	−24.1974	0.096220	3173.95	−132.1504
1.000	−23.7680	0.093547	3162.99	−130.0373

Table IX. 1-Propanol(1)–*n*-Heptane(2) Phase Equilibria and Activity Coefficients

x_1	y_1	P, Mm.	$\ln\gamma_1$	$\ln\gamma_2$
		30° C.		
0.000	0.000	58.67	3.719	0.000
0.005	0.079	63.49	3.536	0.0005
0.010	0.125	66.59	3.344	0.002
0.020	0.166	69.56	2.976	0.007
0.040	0.199	72.02	2.500	0.022
0.100	0.238	74.63	1.795	0.072
0.200	0.270	76.04	1.246	0.166
0.300	0.281	76.13	0.883	0.285
0.400	0.296	75.81	0.640	0.415
0.500	0.308	75.15	0.449	0.571
0.600	0.322	73.96	0.297	0.757
0.700	0.343	71.81	0.174	0.986
0.800	0.382	67.10	0.082	1.262
0.850	0.419	62.83	0.048	1.423
0.900	0.482	56.34	0.022	1.606
0.920	0.522	52.76	0.014	1.684
0.940	0.577	48.44	0.008	1.765
0.960	0.657	43.27	0.004	1.849
0.980	0.781	37.03	0.001	1.940
0.990	0.873	33.42	0.0002	1.986
1.000	1.000	29.45	0.000	2.033
		45° C.		
0.000	0.000	115.27	3.287	0.000
0.005	0.067	123.08	3.162	0.0003
0.010	0.114	129.10	3.044	0.001
0.020	0.171	137.20	2.818	0.005
0.040	0.216	143.96	2.404	0.017
0.100	0.266	151.38	1.747	0.065
0.200	0.305	155.57	1.215	0.156
0.300	0.320	156.26	0.864	0.271
0.400	0.338	156.02	0.628	0.398
0.500	0.353	154.92	0.441	0.550
0.600	0.370	152.73	0.292	0.733
0.700	0.393	148.70	0.171	0.957
0.800	0.436	139.85	0.081	1.229
0.850	0.475	131.89	0.047	1.388
0.900	0.540	119.78	0.022	1.567
0.920	0.580	113.14	0.014	1.664
0.940	0.633	105.13	0.008	1.723
0.960	0.708	95.55	0.004	1.807
0.980	0.819	84.03	0.001	1.896
0.990	0.897	77.38	0.0002	1.941
1.000	1.000	70.06	0.000	1.987
		60° C.		
0.000	0.000	211.02	2.901	0.000
0.005	0.056	222.79	2.807	0.0002
0.010	0.099	232.66	2.725	0.001
0.020	0.162	248.25	2.580	0.003
0.040	0.226	266.09	2.288	0.012
0.100	0.289	284.32	1.682	0.057
0.200	0.337	295.79	1.181	0.143
0.300	0.357	298.30	0.841	0.254
0.400	0.379	298.86	0.613	0.377
0.500	0.397	297.42	0.431	0.525
0.600	0.417	293.83	0.286	0.703
0.700	0.443	286.86	0.168	0.922
0.800	0.489	271.61	0.079	1.188
0.850	0.529	257.93	0.046	1.344
0.900	0.594	237.10	0.021	1.521
0.920	0.633	225.72	0.014	1.596
0.940	0.684	212.04	0.008	1.673
0.960	0.753	195.70	0.004	1.755
0.980	0.851	176.12	0.001	1.843
0.990	0.917	164.82	0.0002	1.888
1.000	1.000	152.40	0.000	1.933

Heat-of-mixing data at 30°, 45°, and 60° C., and the P-x relationship at 30° C. were determined by Soczek (*18*). All experimental values are listed in Tables X and XI. The constants A, B, and C were determined by heat-of-mixing data, and the constant I from the phase equilibrium data. Values for these constants are listed in Table XII. As before, phase equilibrium data have been computed for 30°, 45°, and 60° C., and are presented in Table XIII. Since no unnecessary data were taken for this system, no consistency check is possible. However, a few experimental P-x-y data points at low alcohol concentrations at 60° C. are given in the literature (*13*). These are shown in Figure 3 along with calculated values from Table XIII. The excellence of agreement is particularly remarkable in view of the fact that both experimental measurements and correlation techniques have their greatest uncertainty in the dilute alcohol region.

Table X. Experimental Heat-of-Mixing Data (Joules/Gram Mole) for 2-Propanol–*n*-Heptane

30° C.		45° C.		60° C.	
x_{PrOH}	$\Delta H/x_1x_2$	x_{PrOH}	$\Delta H/x_1x_2$	x_{PrOH}	$\Delta H/x_1x_2$
0.0019	24717	0.0023	22447	0.0058	21764
0.0061	22067	0.0050	22311	0.0136	20969
0.0121	18774	0.0072	21967	0.0187	20390
0.0188	15810	0.0277	16630	0.0297	18545
0.0250	13896	0.0430	13763	0.0439	16385
0.0400	10943	0.0786	10206	0.0841	12415
0.0642	8499	0.1270	7687	0.1182	10553
0.1157	6286	0.1843	6707	0.1638	9017
0.1931	4984	0.2457	5921	0.2044	8142
0.2614	4427	0.3068	5430	0.2998	6907
0.3126	4154	0.3753	5060	0.3625	6430
0.3676	3935	0.4383	4814	0.4117	6155
0.4195	3769	0.4955	4639	0.5050	5779
0.5086	3548	0.5430	4521	0.5888	5553
0.5744	3413	0.5814	4436	0.6300	5464
0.6140	3345	0.6181	4360	0.6605	5406
0.6425	3311	0.6510	4303	0.6962	5363
0.6666	3278	0.6961	4207	0.7356	5308
0.7122	3219	0.7184	4176	0.7832	5251
0.7590	3170	0.7668	4110	0.8281	5193
0.7938	3139	0.8035	4068	0.8875	5171
0.8466	3106	0.8296	4045	0.9125	5168
0.8928	3090	0.8744	4004	0.9443	5164
0.9114	3086	0.9091	3983	0.9670	5163
0.9492	3051	0.9593	3936	0.9891	5136
0.9894	2937				

Table XI. Experimental Vapor Pressures of 2-Propanol–*n*-Heptane at 30° C.

x_{PrOH}	P, Mm. Hg	x_{PrOH}	P, Mm. Hg
0.00000	58.68	0.5167	97.26
0.00949	72.23	0.6944	95.45
0.0229	80.02	0.8309	90.07
0.0683	88.27	0.9208	81.22
0.1118	91.44	0.9788	66.92
0.2440	95.52	1.0000	59.13
0.4019	97.25		

Table XII. 2-Propanol–*n*-Heptane Constants for Equations 1 through 4

x_{PrOH}	A	B, ° K.$^{-1}$	C, ° K.	I
0.000	−31.4371	0.090873	8151.03	−189.3122
0.010	203.1305	−0.620075	−30684.61	1171.3257
0.020	444.1694	−1.336368	−71402.44	2574.3100
0.050	14.6543	0.032071	−4779.45	107.2979
0.075	−20.9074	0.133640	1121.07	−100.1533
0.100	−101.5435	0.379542	14150.52	−566.7676
0.200	−41.2714	0.171057	5243.11	−224.8914
0.300	−8.0029	0.058802	230.53	−35.4341
0.400	−7.4649	0.053456	266.15	−33.3817
0.500	−6.3255	0.048111	133.90	−27.3008
0.600	−25.5139	0.106911	3232.16	−138.2814
0.700	−28.8351	0.117602	3724.86	−157.2670
0.800	−32.3968	0.128293	4302.52	−177.8774
0.900	−37.3785	0.144329	5066.23	−206.3757
1.000	−46.1625	0.171057	6499.76	−257.1726

Table XIII. 2-Propanol(1)–*n*-Heptane(2) Phase Equilibria and Activity Coefficients

x_1	y_1	P, Mm.	$\ln\gamma_1$	$\ln\gamma_2$
		30° C.		
0.000	0.000	58.68	3.440	0.000
0.005	0.121	66.50	3.331	0.0003
0.010	0.194	72.33	3.201	0.001
0.030	0.302	82.75	2.630	0.013
0.050	0.328	85.61	2.273	0.027
0.100	0.374	90.61	1.749	0.068
0.150	0.399	93.23	1.433	0.113
0.200	0.414	94.64	1.200	0.162
0.300	0.440	96.38	0.870	0.270
0.400	0.459	97.18	0.635	0.397
0.500	0.476	97.28	0.449	0.548
0.600	0.496	96.81	0.301	0.729
0.700	0.523	95.30	0.184	0.947
0.800	0.567	91.80	0.094	1.219
0.850	0.600	88.80	0.056	1.395
0.900	0.652	83.94	0.026	1.606
0.950	0.753	75.20	0.007	1.848
0.980	0.870	66.76	0.001	2.008
0.990	0.927	63.18	0.0003	2.065
1.000	1.000	59.13	0.000	2.123
		45° C.		
0.000	0.000	115.27	3.009	0.000
0.005	0.101	127.75	2.945	0.0002
0.010	0.173	138.51	2.874	0.0007
0.030	0.307	163.45	2.508	0.008
0.050	0.347	172.33	2.171	0.022
0.100	0.399	184.57	1.685	0.061
0.150	0.429	191.31	1.386	0.103
0.200	0.449	195.59	1.166	0.150
0.300	0.476	200.09	0.840	0.256
0.400	0.500	202.93	0.616	0.377
0.500	0.520	203.84	0.435	0.524
0.600	0.542	203.50	0.293	0.698
0.700	0.571	201.17	0.169	0.933
0.800	0.617	195.17	0.092	1.174
0.850	0.650	189.85	0.055	1.346
0.900	0.700	181.21	0.026	1.552
0.950	0.793	165.59	0.007	1.789
0.980	0.894	150.53	0.001	1.946
0.990	0.941	144.16	0.0003	2.002
1.000	1.000	136.95	0.000	2.059
		60° C.		
0.000	0.000	211.00	2.622	0.000
0.005	0.082	229.10	2.582	0.0001
0.010	0.147	245.78	2.542	0.0004
0.030	0.297	294.64	2.322	0.005
0.050	0.356	318.61	2.066	0.016
0.100	0.419	347.43	1.621	0.051
0.150	0.452	362.44	1.331	0.092
0.200	0.474	373.32	1.116	0.137
0.300	0.507	384.23	0.809	0.238
0.400	0.534	391.83	0.592	0.354
0.500	0.558	395.30	0.419	0.495
0.600	0.583	396.17	0.283	0.662
0.700	0.614	393.29	0.174	0.866
0.800	0.661	384.11	0.089	1.122
0.850	0.693	375.54	0.054	1.288
0.900	0.741	361.39	0.025	1.488
0.950	0.826	335.93	0.007	1.719
0.980	0.913	311.31	0.001	1.872
0.990	0.952	300.92	0.0003	1.926
1.000	1.000	289.17	0.000	1.982

PRESSURE DEPENDENCY THROUGH ΔV

Volume changes of mixing were also measured during the course of this work (*8*, *10*). Data for the ethanol-toluene system have been published by Pardo and Van Ness (*11*). Results for the propanol-*n*-heptane systems at

25° C. are reported in Table XIV. Additional data taken for these systems at 30° C. show that ΔV increases with increasing temperature over the entire composition range. To a first approximation, $\partial(\Delta V/x_1x_2)/\partial T = 0.03$ cc. per gram mole-° K. for both systems between 25° and 30° C.

These data are useful for showing the effect of pressure on the other excess functions. Thus at constant composition and temperature:

$$\frac{\partial \Delta G^E}{\partial P} = \Delta V$$

$$\frac{\partial \Delta S^E}{\partial P} = \frac{-\partial \Delta V}{\partial T}$$

and

$$\frac{\partial \Delta H}{\partial P} = \Delta V - T(\partial \Delta V/\partial T)$$

Application of these equations to the 2-propanol–*n*-heptane system at 25° C. yields the results shown in Table XV. The maximum effect of pressure amounts to no more than several hundredths of 1% per atmosphere.

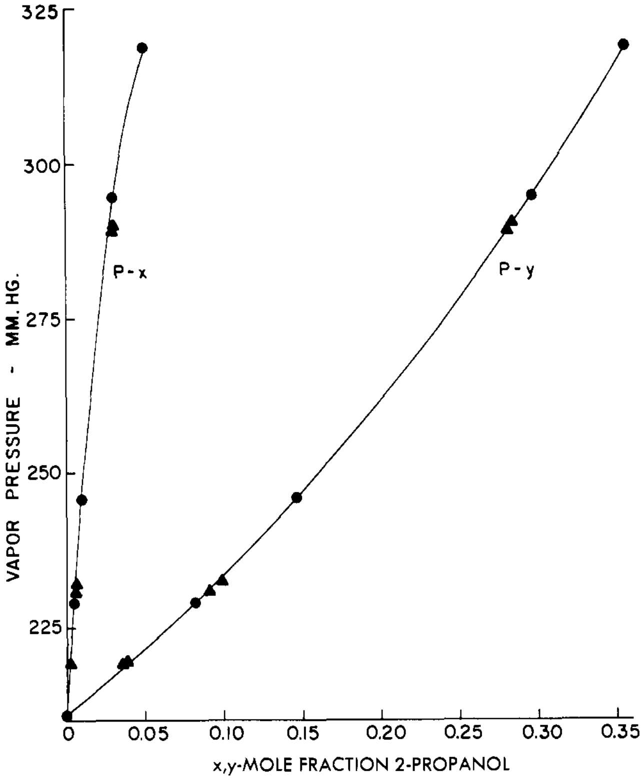

Figure 3. Vapor-liquid equilibria for 2-propanol–*n*-heptane at 60° C.
● Values calculated from correlation of data
▲ Data of Pierotti, Deal, and Derr (13)

Table XIV. Volume Change of Mixing $\Delta V/x_1x_2$ in Cubic Centimeters per Gram Mole at 25° C.

Mole Fraction Alcohol	1-Propanol–*n*-Heptane	2-Propanol–*n*-Heptane
0.000	(8.0)[a]	(9.1)[a]
0.010	6.06	7.97
0.025	4.23	5.58
0.050	3.12	3.98
0.075	2.65	3.55
0.100	2.40	3.35
0.150	2.05	3.13
0.200	1.84	2.98
0.300	1.55	2.72
0.400	1.36	2.51
0.500	1.22	2.34
0.600	1.12	2.21
0.700	1.06	2.12
0.800	1.04	2.10
0.900	1.05	2.12
1.000	1.13	2.24

[a] Extrapolated values.

Table XV. Effect of Pressure on Excess Functions for 2-Propanol–*n*-Heptane at 25° C.

Mole fraction alcohol	0.2	0.5	0.8
ΔV, cc./gram mole	0.48	0.58	0.34
$\partial\Delta V/\partial T$, cc./gram mole-° K.	0.0048	0.0075	0.0048
ΔH, cal./gram mole	170	190	110
$\partial\Delta H/\partial P$, cal./gram mole-atm.	−0.023	−0.040	−0.026
ΔS^E, cal./gram mole-° K.	−0.164	−0.370	−0.268
$\partial\Delta S^E/\partial P$, cal. /gram mole-° K.-atm.	−0.00012	−0.00018	−0.00012
ΔG^E, cal./gram mole	220	300	190
$\partial\Delta G^E/\partial P$, cal./gram mole-atm.	0.011	0.014	0.008

NOMENCLATURE

A = constant
B = constant
B_{ii} = second virial coefficient for pure i
B_{ij} = second cross virial coefficient
C = constant
C_p = molar heat capacity at constant pressure
E = as superscript, designation of an excess function
G = molar Gibbs function or free energy
H = molar enthalpy
I = constant
M = general molar thermodynamic property
P = vapor pressure
R = universal gas constant
S = molar entropy
T = absolute temperature
V = molar volume
a, b, c = constant in Antoine equation
t = Celsius temperature
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = activity coefficient
Δ = designation of property change of mixing, $\Delta M = M - x_1M_1 - x_2M_2$
$1, 2$ = as subscripts, designation of alcohol or hydrocarbon, respectively
— = designation of partial molar property when placed over a symbol

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Received for review April 14, 1966. Accepted November 21, 1966. Work supported in large part by National Science Foundation Research Grant GP-2199. A Procter and Gamble fellowship was awarded to C.A. Soczek, and an Arthur J. Schmidt Foundation fellowship to R.L. Machado.

Synthesis and Proton Dissociation Constants of 2,2′-Iminodimethylene Dipyridine (2,2′-Dipicolylamine)

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Synthesis of 2,2′-iminodimethylene dipyridine has been accomplished in good yield by reaction of 2-chloromethyl pyridine with excess 2-aminomethyl pyridine. Stepwise proton dissociation constants have been determined. At 25° C. and at an ionic strength of 0.10 in KNO_3, $pK_1 = 7.30 \pm 0.02$, $pK_2 = 2.60 \pm 0.02$, and $pK_3 = 1.12 \pm 0.04$.

WHILE the literature describes the synthesis of such substituted pyridines as *N*-picolyl-1,2-diaminoethanes (*2*), 2,2′-dipyridylmethane (*6*), di-(3-pyridylmethyl) amine (*3*), and others (*4*), the synthesis of 2,2′-iminodimethylene dipyridine (2,2′-dipicolylamine) has not been previously reported. This work describes the synthesis of the latter by reaction of 2-chloromethyl pyridine with a fivefold excess of 2-aminomethyl pyridine.

EXPERIMENTAL

The NMR spectra were obtained on the Varian A-60 spectrometer. The samples were run in carbon tetrachloride solution using tetramethylsilane as an internal reference standard. Infrared spectra were obtained with a Perkin-Elmer Model 521 Spectrophotometer using KBr plates. Potentiometric titrations were made with a Metrohm Hereassau 388 research pH meter with a Beckman E-2 glass electrode. Melting points were taken with a Thomas-Hoover melting point apparatus. Elemental analyses and molecular weight determinations were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. The aminomethyl pyridine and the 2-chloromethyl pyridine monohydrochloride were obtained from Aldrich Chemical Co.

Chloromethyl pyridine hydrochloride (25 grams; 0.15 mole) was dissolved in 50 ml. of water and neutralized slowly (with cooling in an ice bath) with 15 ml. of saturated aqueous K_2CO_3. The chloromethyl pyridine free base, which separates as a straw yellow oil, was removed from the aqueous layer and used immediately without further purification in order to minimize decomposition. The free base was added directly to 82.5 grams (0.75 mole) of 2-aminomethyl pyridine, which had been previously cooled to 5° C. by immersion in an ice bath. During the addition, the reactants were vigorously stirred and kept at 5° C. The reaction mixture was then removed from the ice bath and allowed to warm up to room temperature while vigorous stirring was continued. Chemical reaction began at about 15° C. as evidenced by a gradual color change from light yellow to reddish brown. If no additional cooling was employed, the temperature gradually rose to a maximum of 35° C.

When the reaction was complete, the product mixture was acidified with aqueous tartaric acid, extracted several times with ether, and neutralized with 30% aqueous KOH. To separate the aqueous and organic layers, KOH pellets were added with stirring and cooling. The pH of the mixture reached 9-10. The separated organic layer was removed and further dried with anhydrous $MgSO_4$. The liquid at this point was wine-red and clear. The secondary amine product and the unreacted primary amine were then separated by distillation at reduced pressure. This separation was easily accomplished owing to the 80° boiling point difference.

The product, redistilled at 1.05 mm., had a boiling point of 148–149° C. The yield was 73%. The very light yellow liquid product was somewhat viscous, had a slight pyridine-type odor, and was highly soluble in water, alcohol, chloroform, and carbon tetrachloride, but only slightly soluble in ether. Under the reaction conditions used, formation of the corresponding trisubstituted amine was not observed.

Although there was a tendency for the chloromethyl pyridine to remain in the aqueous K_2CO_3 phase after neutralization, this could be largely overcome by using a 10% excess of K_2CO_3, keeping the temperature as low as possible, and by repeated vigorous agitation. Also, the use of alcoholic KOH for the neutralization of the acidified amine mixture led to undesirable side reactions which drastically cut the