Results and Discussion

Experimental measurements of the solubility of CO_2 and H_2S in a Sulfinol solution have been made at 40 and 100 °C. Partial pressures of CO_2 ranged from 2.4 to 5688 kPa while partial pressures of H_2S ranged from 4.6 to 3862 kPa. The results are presented in Tables I and II for CO_2 and H_2S, respectively. No comparisons with data from the literature are possible for this solution, but comparisons with a 2.5 kmol m^{-3} DIPA solution are shown on Figures 2 and 3 for H_2S and CO_2, respectively. The amount of DIPA in the Sulfinol solution is equivalent to that in a 3.4 kmol m^{-3} solution so that the somewhat lower solubility in the Sulfinol solution is consistent with the effect of amine concentration on solubility behavior. At high partial pressures, however, the effect of the physical solvent, sulfolane, becomes paramount and leads to high solubilities of the acid gases in the liquid. The present results are consistent with the statement (*4*) that Sulfinol solutions are attractive solvents at acid gas partial pressures of 760 kPa or greater.

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Vapor–Liquid Equilibria at 25 °C for Nine Alcohol–Hydrocarbon Binary Systems

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Solution vapor pressures at 25 °C were measured over the complete composition range for the nine alcohol–hydrocarbon binary systems formed among methanol, ethanol, 1-propanol, *n*-hexane, cyclohexane, and benzene. Vapor compositions and excess Gibbs energies were calculated from these data by the method of Mixon, Gumowski, and Carpenter. Heat-of-mixing data from the literature were combined with the present data to permit presentation of complete information on the excess properties G^E, H^E, and S^E for each system.

Recent interest in prediction of the phase behavior of nonideal solutions has led to the introduction of numerous models to represent this behavior. To develop and/or evaluate such models, especially those of the group-contribution type, requires accurate, systematic data on homologous series of substances with limited numbers of functional groups. Such data are surprisingly scarce. The present study was designed to produce data on the behavior of normal alcohols with an aliphatic, a naphthenic, and an aromatic six-carbon hydrocarbon. The particular systems were selected, in part, because heat-of-mixing data are available for each system, thus rather complete excess properties (G^E, H^E, S^E) could be calculated from the combined data.

Experimental Section

Apparatus. Detailed description of the experimental work is given elsewhere (*7*). Basically, the apparatus is similar in many features to that used by Gibbs and Van Ness (*5*). As shown in Figure 1, the major components of the system included a degassing assembly and storage bulb for each component of a binary system under study, a liquid measurement and injection assembly, an equilibrium cell, and a pressure measurement facility. All components other than the degassing assemblies were housed in a constant-temperature air bath where temperature was controlled at 26.0 ± 0.2 °C. The equilibrium cell was further immersed in a liquid (water) bath where the temperature was controlled at 25.0 ± 0.01 °C. Temperatures were measured by mercury-in-glass thermometers which had been calibrated against an NBS-certified platinum-resistance thermometer.

The equilibrium cell (Figure 2) is patterned after that of Gibbs and Van Ness. However, the pressure measurement and liquid measurement and injection apparatus differed from their design. Pressures were measured by a mercury manometer with levels determined by cathetometer. The manometer was maintained at a temperature of 28–29 °C to prevent condensation of vapor

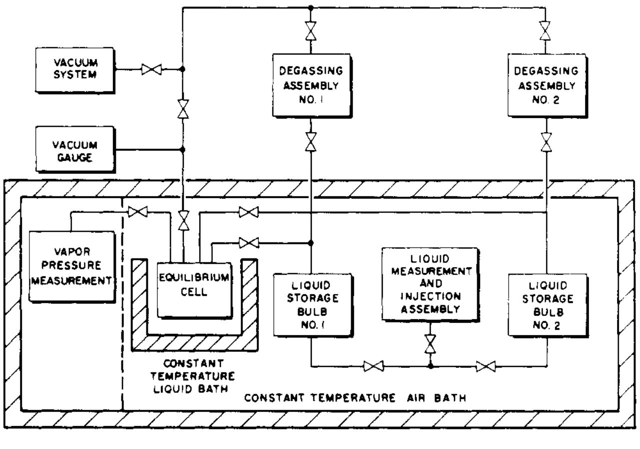

Figure 1. Schematic diagram of apparatus.

Table I. Organic Chemicals Used in This Investigation

Compound	Manufacturer	Specified min purity	Most probable impurity
Methanol	Fisher Scientific Co.	99.9 mole %	—
Ethanol	U.S. Industrial Chemical Co.	Reagent quality 200 proof	—
1-Propanol	Fisher Scientific Co.	Certified grade, bp 96.9–97.3 °C	—
Benzene	Phillips Petroleum Co.	99.91 mole %	Toluene
Cyclohexane	Phillips Petroleum Co.	99.94 mole %	2,4-Dimethylpentane and 2,2-dimethylpentane
n-Hexane	Phillips Petroleum Co.	99.99 mole %	Methyl cyclopentane

Table II. Pure Component Densities at 26 °C

Compound	Density, ρ, g cm^{-3}	
	This work	Lit.[a]
Methanol	0.7857	0.7856–0.7858
Ethanol	0.7842	0.7842–0.7844
1-Propanol	0.7989	0.7989–0.7991
Benzene	0.8727	0.8725–0.8727
Cyclohexane	0.7729	0.7728–0.7731
n-Hexane	0.6537	0.6539–0.6542

[a] Linear interpolation between 25 and 30 °C. Reference 17.

Table III. Pure Component Vapor Pressures at 25 °C

Compound	Vapor pressure, mmHg	
	This work	Lit. (*17*)
Methanol	127.14 (0.09[a])	125.40–127.18
Ethanol	58.96 (0.09)	58.90–59.80
1-Propanol	20.96 (0.01)	20.44–20.90
Benzene	95.11 (0.01)	95.03–95.25
Cyclohexane	97.69 (0.10)	97.41–98.25
n-Hexane	151.79 (0.11)	151.05–152.85

[a] Average absolute deviation from mean of three measurements.

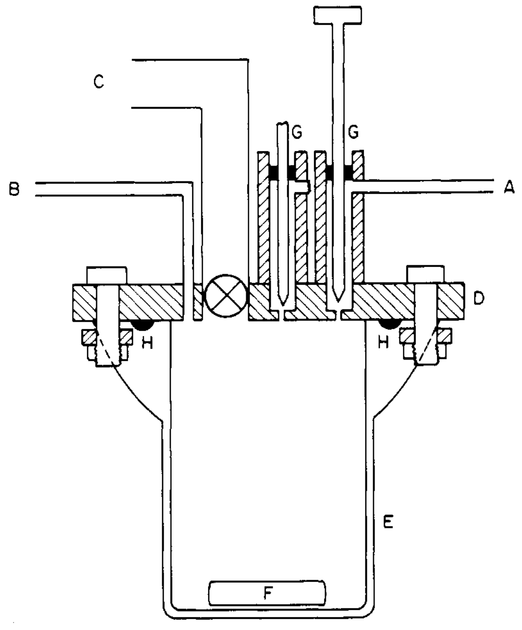

Figure 2. Equilibrium cell.

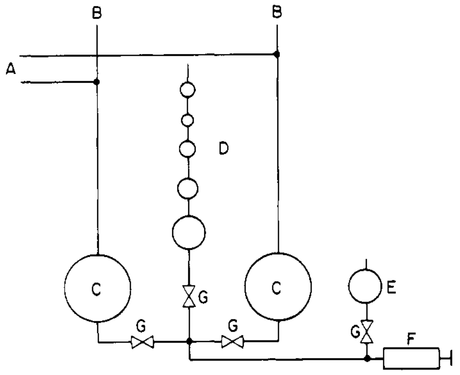

Figure 3. Liquid storage, measurement, and injection assembly.

in the manometer. The injection and measurement facility is shown in Figure 3. The degassed liquids were stored over mercury in the storage bulbs (C) of 200 cm^3 capacity. The mercury was also in communication with a set of calibrated measuring bulbs (D) and a screw pump. The bulbs had nominal volumes of 20, 4, 2, and 1 cm^3 with average uncertainties of 0.004 cm^3. A fifth, uppermost bulb served as an overflow reservoir.

The degassing assembly employed the technique of molecular sublimation as described by Bell et al. (*1*).

Procedure. The experimental runs were begun by degassing the pure components. Each component was sublimed and condensed two or three times to ensure thorough degassing. The degassed liquid was then allowed to drain into the evacuated storage bulbs. This degassing technique proved definitely superior to the bulk freezing, evacuation, and melting technique used previously in this laboratory (*16*).

When the degassed liquids were in place in the storage bulbs, mercury was injected into each bulb until the bulb was completely liquid-filled. Components were metered from the storage bulbs into the equilibrium cell as follows. First, mercury was injected into the measuring bulb assembly to the desired level, with valve G (Figure 3) open. The needle valve G (Figure 2) on the equilibrium cell was then slightly opened, allowing the mercury level in the measuring bulbs to drop and force degassed liquid into the equilibrium cell. The decrease in volume of mercury in the measuring bulbs was then identical with the volume of liquid displaced from the storage bulb C (Figure 3) into the equilibrium cell.

Vapor pressure measurements were begun by injecting 25 cm^3 of one component and measuring its vapor pressure. A second injection of 25 cm^3 was then made and the pressure remeasured. This procedure served as a partial test for incom-

Table IV. Experimental Vapor Pressures at 25 °C

x_1	π, mmHg	x_1	π, mmHg
	Methanol (1)-Benzene (2)		
0.000	95.1	0.561	183.0_5
0.010	129.1	0.619	182.5
0.034	157.5_5	0.656_5	182.4
0.059_5	168.3	0.699	181.7
0.087_5	173.6_5	0.747	180.0
0.118	176.3_5	0.802	177.5_5
0.149_5	177.8	0.847	173.7_5
0.201	179.3	0.897_5	166.3_5
0.247	180.3_5	0.918_5	161.7
0.288_5	180.8_5	0.940_5	155.4_5
0.376_5	181.9_5	0.963_5	147.9
0.445	182.4_5	0.977	141.2_5
0.500_5	183.0	0.990	133.9_5
0.505_5	183.0	1.000	127.1_5
	Ethanol (1)-Benzene (2)		
0.000	95.1	0.539	121.3_5
0.006_5	101.9	0.573	120.1_5
0.015	107.6	0.590	120.3
0.029_5	113.1	0.623	118.9_5
0.053_5	117.2	0.682_5	116.0
0.087	119.9_5	0.733	112.7_5
0.145	122.4_5	0.792	108.2
0.196_5	123.3	0.861	99.9_5
0.242	123.4	0.890_5	94.4
0.283	123.4	0.922_5	87.1
0.370	122.9	0.956_5	78.3
0.439	122.5	0.976	70.5
0.493_5	122.1_5	0.990	63.9_5
0.530	121.1	1.000	58.8
	1-Propanol (1)-Benzene (2)		
0.000	95.1	0.537_5	87.7
0.010_5	97.0_5	0.563_5	86.6_5
0.024_5	97.2_5	0.584	85.2_5
0.042	97.8	0.608	84.2
0.063_5	97.7_5	0.660	81.4_5
0.089	97.1_5	0.722	77.7_5
0.117_5	97.1	0.796_5	71.6
0.166_5	96.7_5	0.829_5	67.6
0.210	96.0	0.865_5	61.6
0.250_5	95.4	0.904	54.3
0.287	94.7	0.928	47.9
0.365_5	92.9	0.953_5	39.8_5
0.428	91.3_5	0.975_5	31.8
0.480	89.8_5	0.988	26.6
0.525	87.9_5	0.995	23.7
		1.000	20.9_5
	Methanol (1)-Cyclohexane (2)		
0.000	97.6_5	*a*	213.6_5
0.009_5	183.0_5	*a*	213.6
0.020_5	199.4_5	*a*	213.6_5
0.047_5	208.9_5	*a*	213.6_5
0.085_5	212.6_5	*a*	213.6_5
0.125_5	213.7	*a*	213.6
a	213.8_5	0.828	213.6
a	213.8_5	0.865_5	212.8_5
a	213.8_5	0.906	209.8
a	213.8_5	0.929_5	204.5
a	213.7_5	0.952_5	193.8
a	213.7	0.976_5	171.8
a	213.6_5	0.990_5	149.1
a	213.6	1.000	127.2_5
	Ethanol (1)-Cyclohexane (2)		
0.000	97.6	0.645	138.0
0.028	130.9	0.655	137.9_5
0.055	134.9_5	0.693_5	137.0_5
0.081_5	136.7_5	0.736_5	135.3_5
0.131	138.8_5	0.785	132.4
0.175	139.4_5	0.832_5	128.1
0.233	139.5_5	0.867_5	121.5
0.284	139.5_5	0.895	114.9

x_1	π, mmHg	x_1	π, mmHg
	Ethanol (1)-Cyclohexane (2)		
0.344	139.4_5	0.924	106.0_5
0.416_5	139.4	0.944	98.2
0.483	139.3	0.965_5	87.3
0.536	139.0_5	0.977	79.7
0.556_5	139.0_5	0.988_5	70.5_5
0.579	138.6_5	1.000	59.0_5
0.615	138.1		
	1-Propanol (1)-Cyclohexane (2)		
0.000	97.8_5	0.502	102.0
0.010	104.6_5	0.539	101.1_5
0.020_5	105.8	0.547_5	101.0
0.050_5	107.0	0.573_5	99.8
0.082	107.1_5	0.602_5	99.6
0.112_5	107.1	0.669_5	96.5_5
0.162_5	106.8_5	0.753	90.8
0.207_5	106.6	0.791_5	86.4_5
0.247_5	106.4	0.834	79.9_5
0.284_5	105.9	0.881	69.8
0.318_5	105.4	0.933_5	55.4
0.391	104.4_5	0.962_5	42.9_5
0.450	103.3_5	0.985_5	30.3_5
0.450	103.5	1.000	20.9_5
0.498_5	102.3		
	Methanol (1)-*n*-Hexane (2)		
0.000	151.7_5	*a*	265.8
0.004	205.6_5	*a*	265.8_5
0.010	230.5_5	*a*	265.8_5
0.018_5	243.0	*a*	265.8_5
0.035	253.8_5	*a*	265.8_5
0.058	259.8	*a*	265.8_5
0.092	263.6_5	0.820	265.9
0.130_5	264.2	0.850	264.9_5
0.174_5	265.4_5	0.882	263.8
0.216_5	265.9	0.916_5	259.5_5
a	265.8_5	0.936	252.9
a	265.8_5	0.954_5	241.1
a	265.8_5	0.970	223.3
a	265.8_5	0.981_5	203.7
a	265.8_5	0.989_5	183.1_5
a	265.8_5	0.995_5	149.1
		1.000	127.0
	Ethanol (1)-*n*-Hexane (2)		
0.000	151.9_5	0.518_5	188.4_5
0.025_5	183.2_5	0.553	188.8
0.050_5	185.7	0.629	187.1_5
0.097	188.9	0.667_5	185.6_5
0.139_5	189.9	0.710_5	183.5
0.197	190.2	0.760	179.5_5
0.247	190.2_5	0.797_5	175.1
0.307	190.2_5	0.838_5	168.0
0.358	189.9_5	0.884	156.1_5
0.421_5	189.8_5	0.908	145.9
0.440_5	190.2	0.932_5	132.3
0.473	188.9_5	0.958_5	112.8
0.516_5	188.9_5	0.986	82.3
		1.000	59.0_5
	1-Propanol (1)-*n*-Hexane (2)		
0.000	151.6_5	0.524_5	150.1_5
0.006_5	157.5	0.548_5	149.6_5
0.024_5	159.3_5	0.570	148.1
0.052_5	159.8	0.593_5	147.7
0.105	159.4_5	0.646	144.9
0.151_5	158.6_5	0.709	139.6_5
0.194	157.9_5	0.785	130.5_5
0.232_5	157.2_5	0.819	124.1
0.316_5	155.7_5	0.856_5	114.9_5
0.383_5	154.5_5	0.897	101.9
0.439	153.0_5	0.941	80.6_5
0.485_5	151.7_5	0.964	63.2_5
0.510	150.6_5	0.987	38.9
		1.000	20.9_5

[a] Two-liquid phases.

Table V. Vapor-Liquid Equilibrium Data and Excess Properties at 25 °C

x_1	π, mmHg	y_1	γ_1	γ_2	G^E, cal g-mol^{-1}	H^E [a] cal g-mol^{-1}	TS^E, cal g-mol^{-1}
System Methanol-Benzene (*2, 11, 18*)							
0.1	174.9	0.476	6.536	1.061	142.8	136.0	−6.8
0.2	179.2_5	0.494	3.480	1.179	225.9	167.0	−58.9
0.3	181.0	0.504	2.390	1.334	274.3	171.5	−102.8
0.4	182.0	0.514	1.838	1.534	296.3	166.1	−130.2
0.5	182.9	0.532	1.530	1.778	296.5	148.6	−147.9
0.6	182.7	0.564	1.350	2.072	279.3	126.5	−152.8
0.7	181.3	0.593	1.208	2.557	245.2	100.0	−145.2
0.8	177.5	0.627	1.095	3.438	189.3	69.1	−120.3
0.9	165.4	0.709	1.026	4.999	108.8	35.8	−73.0
System Ethanol-Benzene (*2, 11*)							
0.1	120.4	0.249	5.075	1.054	124.2	161.0	36.8
0.2	123.0	0.283	2.956	1.155	196.5	201.2	4.7
0.3	123.5	0.310	2.167	1.274	238.0	208.0	−30.0
0.4	123.2	0.336	1.755	1.430	260.5	204.0	−56.5
0.5	122.0	0.357	1.478	1.644	263.0	187.9	−75.1
0.6	119.8	0.380	1.289	1.945	248.0	153.0	−95.0
0.7	115.0	0.419	1.169	2.335	215.4	117.4	−98.0
0.8	107.4	0.474	1.081	2.962	165.6	80.0	−85.6
0.9	92.8	0.583	1.022	4.059	94.7	39.0	−55.4
System 1-Propanol-Benzene (*2, 11*)							
0.1	97.5	0.090	4.142	1.037	103.4	174.0	70.6
0.2	96.5	0.120	2.753	1.116	171.9	229.8	57.9
0.3	94.4	0.140	2.096	1.219	213.7	248.4	34.7
0.4	91.9	0.156	1.707	1.359	235.9	245.9	10.0
0.5	88.9	0.172	1.455	1.549	240.7	224.5	−16.2
0.6	84.6	0.192	1.288	1.798	229.0	193.1	−35.9
0.7	79.0	0.217	1.165	2.171	201.0	150.5	−50.5
0.8	71.2	0.253	1.070	2.803	154.2	101.0	−53.2
0.9	54.8	0.350	1.017	3.754	87.3	51.6	−35.7
System Methanol-Cyclohexane (*9*)							
0.05	209.2	0.542	17.841	1.018	95.1	65.0	−30.1
0.10	213.2	0.550	9.235	1.074	169.7	90.0	−79.0
0.85	213.4	0.562	1.111	6.281	216.4	115.0	−101.4
0.90	210.5	0.571	1.052	9.095	157.9	95.5	−62.4
0.95	195.0	0.629	1.017	14.599	88.6	63.1	−25.5
System Ethanol-Cyclohexane (*6, 18*)							
0.1	137.8	0.318	7.413	1.064	151.8	108.0	−43.8
0.2	139.4	0.333	3.931	1.184	242.3	141.5	−100.8
0.3	139.5	0.337	2.648	1.347	296.6	153.2	−143.4
0.4	139.4	0.352	2.074	1.535	325.2	156.7	−168.5
0.5	139.2	0.356	1.678	1.825	331.6	153.3	−178.3
0.6	138.5	0.362	1.414	2.249	315.3	142.5	−172.8
0.7	136.5	0.374	1.234	2.904	276.6	125.1	−151.5
0.8	131.5	0.398	1.107	4.033	213.4	99.8	−113.6
0.9	113.6	0.483	1.032	5.994	122.3	61.2	−61.1
System 1-Propanol-Cyclohexane (*18*)							
0.1	107.1	0.119	6.043	1.070	142.8	97.3	−45.5
0.2	106.6	0.134	3.381	1.179	222.2	126.0	−96.2
0.3	105.5	0.143	2.384	1.319	269.3	140.1	−129.2
0.4	104.1	0.151	1.867	1.504	293.0	141.3	−151.7
0.5	102.1	0.160	1.547	1.753	295.5	134.0	−161.5
0.6	99.4	0.169	1.329	2.110	278.0	118.7	−159.3
0.7	94.9	0.183	1.178	2.642	240.5	94.9	−145.6
0.8	85.1	0.214	1.080	3.422	182.4	69.3	−113.1
0.9	65.0	0.298	1.024	4.678	104.2	38.0	−66.2
System Methanol-*n* Hexane (*13*)							
0.05	258.2	0.424	17.242	1.017	93.8	73.9	−19.9
0.10	263.7	0.436	9.062	1.072	167.7	92.5	−75.2
0.15	265.2	0.445	6.211	1.122	220.2	106.1	−114.1
0.20	265.5	0.449	4.614	1.204	269.1	115.7	−153.4
0.85	265.3	0.456	1.124	6.235	221.3	98.7	−122.6
0.90	262.4	0.461	1.060	9.170	162.5	77.9	−84.6
0.95	245.1	0.502	1.021	15.868	93.5	46.9	−46.6

Table V *(Continued)*

x_1	π, mmHg	y_1	γ_1	γ_2	G^E, cal g-mol^{-1}	$H^{E\,a}$ cal g-mol^{-1}	TS^E, cal g-mol^{-1}
			System Ethanol-*n*-Hexane (*3*, *8*)				
0.1	188.8	0.226	7.204	1.064	149.8	101.5	−48.3
0.2	190.2	0.242	3.890	1.180	239.4	126.4	−113.0
0.3	109.2_5	0.258	2.762	1.321	295.8	136.4	−159.4
0.4	190.1	0.259	2.081	1.536	326.1	138.0	−188.1
0.5	189.4	0.262	1.679	1.830	332.4	133.0	−199.4
0.6	187.8	0.268	1.418	2.250	316.3	122.0	−194.3
0.7	184.1	0.278	1.237	2.902	277.5	106.0	−171.5
0.8	174.6	0.301	1.113	3.998	214.8	82.0	−132.8
0.9	149.0	0.368	1.032	6.186	124.7	48.0	−76.7
			System 1-Propanol-*n*-Hexane (*3*)				
0.1	159.3	0.084	6.339	1.068	144.4	97.0	−47.4
0.2	157.8	0.096	3.573	1.175	227.4	134.7	−92.7
0.3	156.0	0.102	2.511	1.319	278.5	145.4	−133.1
0.4	153.9	0.107	1.952	1.509	304.8	146.6	−158.2
0.5	150.8	0.113	1.611	1.765	309.5	137.5	−172.0
0.6	146.9	0.119	1.379	2.134	293.9	120.6	−173.3
0.7	140.4	0.128	1.217	2.695	247.6	99.5	−158.1
0.8	128.0	0.145	1.104	3.614	199.1	72.8	−126.3
0.9	100.9	0.193	1.031	5.397	116.3	40.0	−76.3

[a] Data sources shown after each system title.

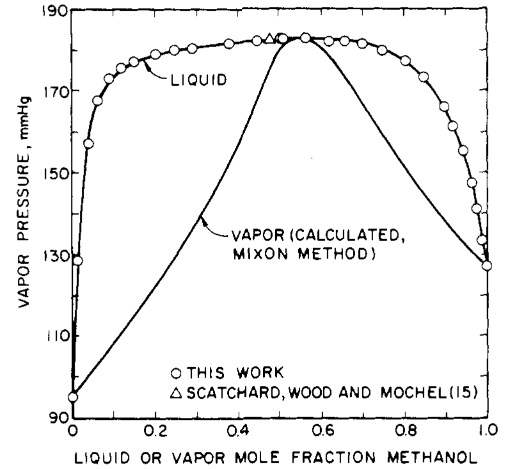

Figure 4. Vapor pressure at 25 °C for the methanol-benzene system.

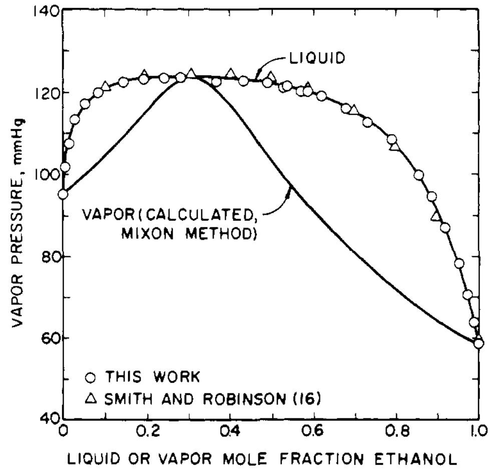

Figure 5. Vapor pressure at 25 °C for the ethanol-benzene system.

plete degassing, since subsequent injections (of a pure component) should result in increased pressures if more dissolved gases were injected into the constant-volume equilibrium cell.

If degassing was deemed adequate, a small amount of the second component was injected into the cell. After the pressure stabilized (usually 20–30 min) a pressure reading was recorded. This injection procedure was repeated until the equilibrium cell contained approximately equal volumes of the two components. The cell was then emptied, cleaned, and leak-tested and the above procedure repeated with the components injected in reverse order.

Materials. The suppliers and purities of the components used in this study are summarized in Table I. All chemicals were used as received, without further purification.

Results

Two properties of each pure substance were measured in this study. In addition to the vapor pressures described above, the densities at 26 °C were determined pycnometrically by the technique described by Robinson (*12*). These densities were required because the materials were injected volumetrically into

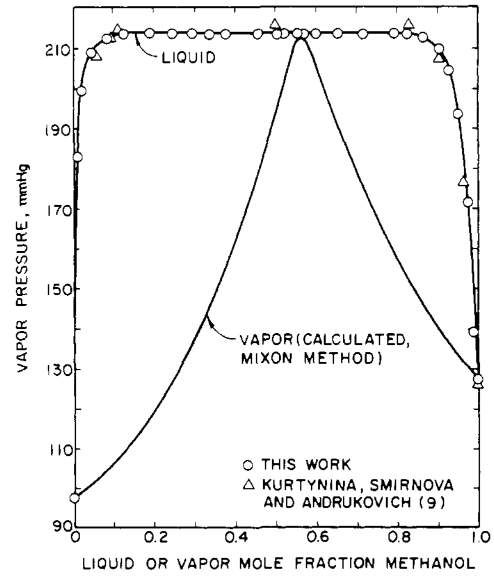

Figure 6. Vapor pressure at 25 °C for the methanol-cyclohexane system.

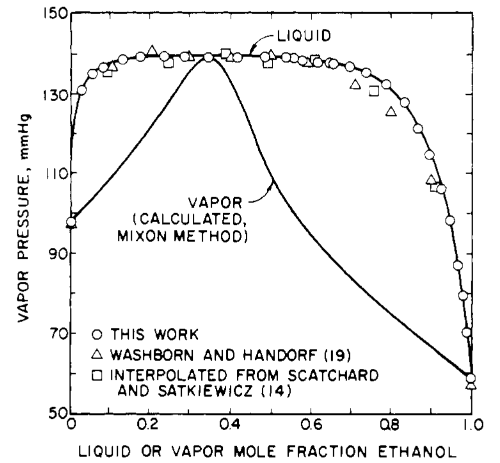

Figure 7. Vapor pressure at 25 °C for the ethanol–cyclohexane system.

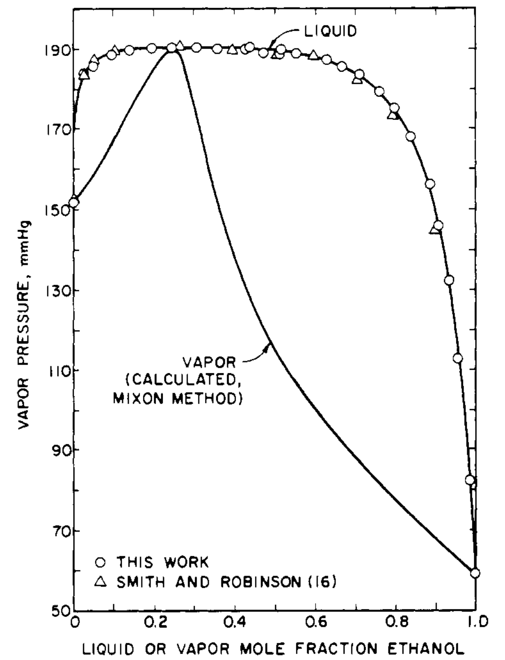

Figure 8. Vapor pressure at 25 °C for the ethanol–*n*-hexane system.

the equilibrium cells. The pure component properties are given in Tables II and III. Also shown are the ranges of literature data as compiled by Timmermans (*17*).

Experimental vapor pressures over the composition range for each of the nine binary systems are given in Table IV. Total mole fractions in the equilibrium cell were determined from measured injection volumes; liquid mole fractions were calculated by an iterative technique (*7*) which accounted for vaporization of a portion of the mixture to fill the vapor space in the cell. Figures 4–8 show experimental results for the five systems for which some literature data are available. Also shown in the figures are vapor compositions calculated by methods described below.

Based on the system calibrations, pure component measurements, and data replication conducted in this study, uncertainties in the measurements are estimated to be 0.01 °C, 0.2 mmHg, and 0.0008 mole fraction unit.

Data Reduction

The experimental π–x data were utilized to determine values of y, G^E, and γ by the technique of Mixon, Gumowski, and Carpenter (*10*) using relations described in previous studies (*16*).

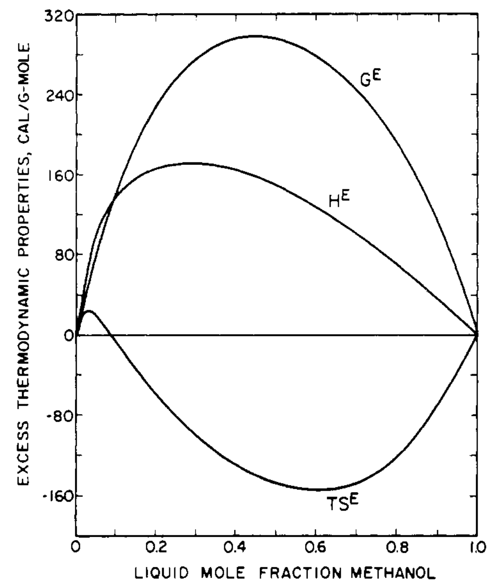

Figure 9. Excess thermodynamic properties at 25 °C for the methanol–benzene system.

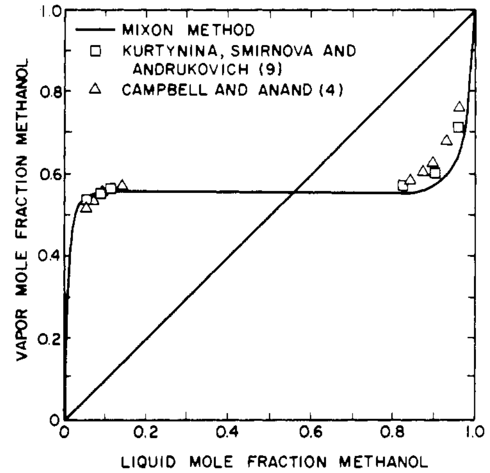

Figure 10. Vapor–liquid composition data at 25 °C for the methanol–cyclohexane system.

These properties were combined with (smoothed) literature data on heat of mixing (H^E) to calculate excess entropies, $TS^E = H^E - G^E$. Table V contains the complete results. Figure 9 presents excess properties for the methanol–benzene system whose behavior is qualitatively similar to the other miscible systems.

Discussion

Figures 4–8 show comparisons of the data from the present study with those of previous authors. The single data point of Scatchard et al. (*15*) for methanol–benzene is in excellent agreement with the present data. The data of Smith and Robinson (*16*) for ethanol–benzene and ethanol–*n*-hexane are also in reasonable agreement with the present results but show pressures about 3 mmHg lower at 0.9 liquid mole fraction ethanol and, for ethanol–benzene, 2 mmHg lower at 0.5 mole fraction ethanol. For both the methanol–cyclohexane and ethanol–cyclohexane systems, the present data demonstrate higher pressures in the dilute regions than prior studies (*9, 14, 19*), but they are significantly lower (for methanol–cyclohexane) in the midcomposition region.

Figure 10 shows a typical comparison of the vapor compositions calculated from the vapor pressures of this work with directly measured values for methane–cyclohexane from the

Table VI. Azeotrope Compositions at 25 °C

System	Azeotrope composition, mole fraction alcohol	
	This work	Lit.
Methanol–benzene	0.539	NA[a]
Ethanol–benzene	0.313	0.312 (*16*)
1-Propanol–benzene	0.080	NA
Ethanol–cyclohexane	0.340	0.336 (*19*)
1-Propanol–cyclohexane	0.121	NA
Ethanol–*n*-hexane	0.249	0.245 (*16*)
1-Propanol–*n*-hexane	0.085	NA

[a] Not available in literature.

literature. This figure includes vapor mole fractions of Campbell and Anad (*4*) who did not present π–x data.

Of the nine systems studied, two exhibit partial miscibility. The present data indicate solubility limits of 0.120 and 0.830 mole fraction methanol in the methanol–cyclohexane system. Kurtynina et al. (*9*) report values of 0.112 and 0.830. For methanol–*n*-hexane, the present data give solubility limits of 0.210 and 0.810 mole fraction methanol while Savini et al. (*13*) report values of 0.270 and 0.791 mole fraction from heat-of-mixing data.

The seven miscible systems studied all exhibited azeotropes. Table VI lists the azeotropic compositions, including literature data for three systems.

The excess properties of the systems studied in this work are similar qualitatively for the miscible systems. Heats of mixing are positive and reach maxima in the alcohol-dilute portion of the composition range. Excess Gibbs energies are positive and nearly symmetric in composition. Excess entropies show positive values in the dilute alcohol regions. This behavior is probably due to the loss of orientation order that accompanies the breaking of hydrogen bonds in the alcohols. The benzene systems exhibit the highest heats of mixing and excess entropies due to the favorable interaction energies between hydroxyl groups and the more polarizable electrons in the aromatic molecule (relative to the normal and cycloparaffins). This interaction leads to increased breakage of hydrogen bonds among the alcohols.

Glossary

G^E	excess Gibbs free energy
H^E	excess enthalpy
S^E	excess entropy
T	absolute temperature
x	liquid-phase mole fraction
y	vapor-phase mole fraction
γ	activity coefficient
π	system pressure

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