The quantity of XeF_4 produced by thermal dissociation was estimated from the equilibrium data (*6*). At the critical temperature of 502 K and critical pressure of 4.70 MPa, the degree of dissociation is about 10%. Kinetically only about 6.5% of the final equilibrium value dissociates in the first 8 min at 566 K, as was determined by measurements of the thermal dissociation of XeF_6 (*7*). On the basis of all these data, it could be concluded that the degree of dissociation of XeF_6 at 502 K in the first 5 min of heating should be smaller than 0.5%.

Therefore it seems reasonable to consider $XeOF_4$ and SiF_4 as the main impurities in XeF_6. Their origin is the reaction

$$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$$

The slow rise of critical temperature during prolonged heating (at least 3 times longer than the duration of the measurement) could be explained by the increasing influence of $XeOF_4$. In view of the lack of reliable data concerning the value of the critical temperature of $XeOF_4$, this was estimated from the vapor pressure at about room temperature (*8*) via the estimated boiling point at about 373 K to be somewhat higher than the critical temperature of XeF_6. The influence of SiF_4, with a critical temperature of 259.0 K (*9*), is lower than that of $XeOF_4$ because of the relatively lower concentration.

On the basis of these evaluations the critical temperature of XeF_6 can be confidently given as 502 ± 0.5 K.

Registry No. XeF_6, 13693-09-9.

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Received for review July 31, 1986. Accepted June 11, 1987. The authors are grateful to the Research Community of Slovenia for financial support.

Excess Gibbs Energy for Binary Mixtures Containing Carboxylic Acids. 3. Excess Gibbs Energy for Isobutyric Acid and Trimethylacetic Acid + Cyclohexane and + *n*-Heptane

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Total vapor pressures for the binary mixtures containing isobutyric and trimethylacetic acids with cyclohexane and *n*-heptane at 298.15 and 318.15 K have been measured for the entire composition range by using the static manometric method. Positive deviations from Raoult's law for all the systems decrease with the increase of methylation of the acids and increase with the rise of temperature. Activity coefficients have been calculated by taking into consideration the dimerization of the acids in the vapor phase. Estimated TS^E values from experimental H^E values are negative and have about the same magnitude for all the systems. Negative TS^E values have been attributed to the increasing proportion of acid dimers with increasing proportion of the nonpolar component.

Introduction

In continuation of our studies (*1*, *2*) on the excess Gibbs free energies of the binary mixtures containing carboxylic acids, in this paper we report such studies for two higher acids, i.e., isobutyric acid (IBA) and trimethylacetic acid (TMA), with either cyclohexane or *n*-heptane as the second component. Total vapor pressures of the mixtures over the entire composition range at 298 .15 and 318.15 K have been measured by using a static manometer. Activity coefficients have been calculated by taking into consideration the dimerization of these acids in the vapor phase (*1*-*3*). Estimated TS^E values are compared with the already reported (*1*, *2*) corresponding results for the lower acids, i.e., acetic acid (AA) and propionic acid (PA). The magnitude and the sequence of the results have been interpreted in terms of both increasing dimerization constant and steric hindrance with the complexity of the acid molecule.

Table I. Physical Constants of Pure Compounds

compd	refractive index obsd	refractive index lit.	density/g cm^{-3} obsd	density/g cm^{-3} lit.
isobutyric acid	1.3933[a]		0.94428[b]	
trimethylacetic acid	1.3925[c]		0.90396[c]	0.90401[c]

Dimerization Constants K_p, Torr^{-1}

T/K	AA	PA	IBA	TMA
298.15	1.982	2.301	7.755	842.9
318.15	0.379	0.388	1.208	15.58

[a] At 293.15 K. [b] At 298.15 K. [c] At 313.15 K (from ref *4*).

Experimental Section

Cyclohexane and *n*-heptane were the same as used in earlier reports (*1*, *2*).

Isobutyric acid (L.R., SRL) was dried by refluxing it over phosphorus pentoxide and then fractionally distilled. The middle fraction was further refluxed over potassium permanganate and fractionally distilled. The fraction distilling at 427.5 K was collected. Trimethylacetic acid (G.R., Tokyo Kasei Kogyo Co. Ltd., Japan) was first fractionally crystallized and the liquid layer was discarded. The solid portion (mp 308.55 K) was then distilled under reduced pressure. The refractive index and

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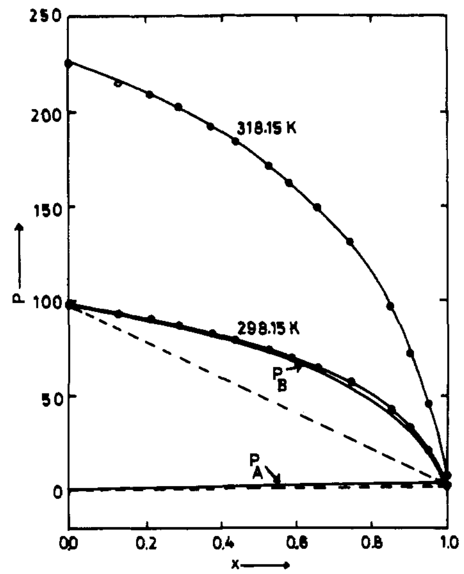

Figure 1. Plot of total pressure (P) and partial pressures (P_A, P_B) in Torr against mole fraction (x) for the isobutyric acid + cyclohexane system.

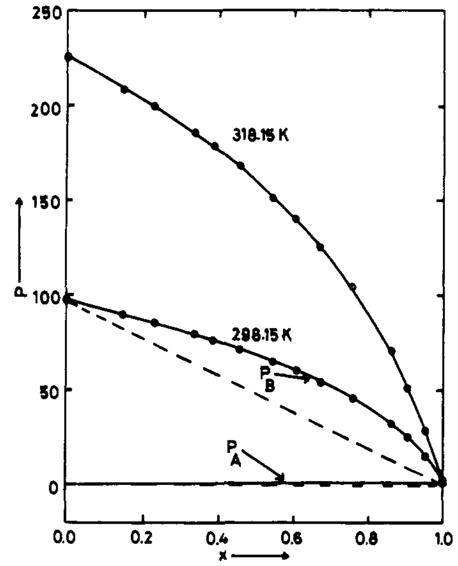

Figure 2. Plot of total pressure (P) and partial pressures (P_A, P_B) in Torr against mole fraction (x) for the trimethylacetic acid + cyclohexane system.

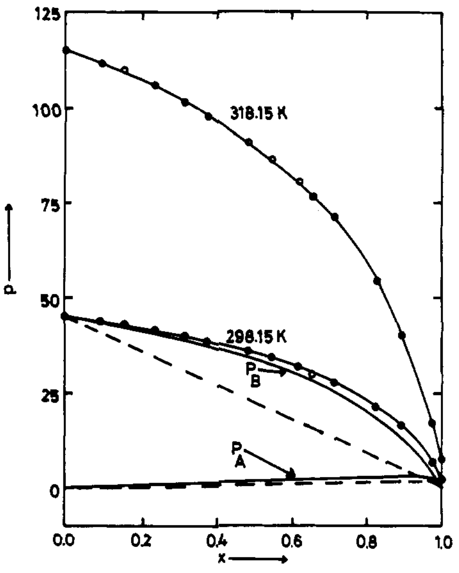

Figure 3. Plot of total pressures (P) and partial pressure (P_A, P_B) in Torr against mole fraction (x) for the isobutyric acid + n-heptane system.

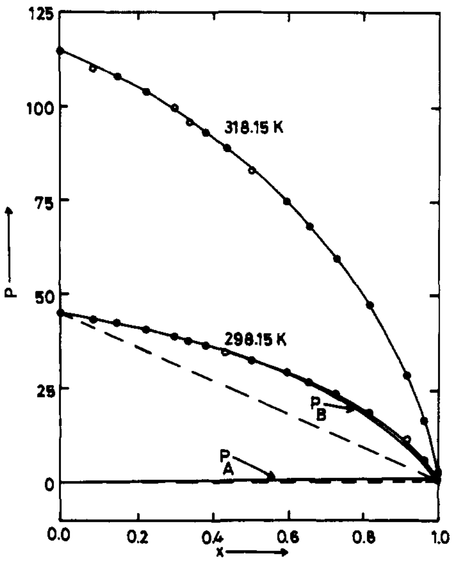

Figure 4. Plot of total pressure (P) and partial pressures (P_A, P_B) in Torr against mole fraction (x) for the trimethylacetic acid + n-heptane system.

density have been used as the criteria of purity and results are compared with the literature (*4*, *5*) values which are in good agreement (Table I).

Total vapor pressure measurements have been made by using the static manometric method described previously (*1*, *2*).

Results and Discussion

Total vapor pressures measured at 298.15 and 318.15 K for all the systems are summarized in Table II and illustrated in Figures 1–4. All the systems show positive deviations from Raoult's law and these decrease from IBA to TMA. Deviations, however, increase with the rise of temperature which may be due to the greater depolymerization of the acid at higher temperature. Partial pressures have also been plotted at 298.15 K only and it may be seen that ideality increases from AA (*1*, *2*) to TMA in both the solvents.

For determining activity coefficients, a method similar to Kohler's method was used (*3*). The dimerization constants of these acids being not available in literature were determined by the method described by Taylor (*5*) and are summarized in Table I. The details will be published later. Estimated activity coefficients fitted to the equations

$$\ln \gamma_A = Al_1 + Bm_1 + Cn_1 + Do_1 + Ep_1 + \ldots \quad (1)$$

$$\ln \gamma_B = Al_2 + Bm_2 + Cn_2 + Do_2 + Ep_2 + \ldots \quad (2)$$

by the method of least squares are included in Table II. Equations 1 and 2 satisfy Gibbs–Duhem equation and the values of constants A, B, C, ... are given in Table III. l_1, m_1, n_1 and l_2, m_2, n_2, ... are functions of mole fractions only (*1*, *2*). Residual pressures, i.e., differences between the observed and calculated pressures, mole fraction of acid in the vapor phase, and standard deviations are also included in Table II. The negligible area under the plots of ln (γ_A/γ_B) vs. x shows the consistency of the activity data.

The excess Gibbs free energies calculated at 298.15 and 318.15 K are summarized in Table IV along with the experimental excess enthalpies (*7*, *8*). TS^E values for the systems containing IBA have been calculated by utilizing the mean G^E,

Table II. Vapor Pressures, Activity Coefficients, and Mole Fraction of Acid in the Vapor Phase for Various Systems

	298.15 K					318.15 K				
x	P/Torr	$\ln \gamma_A$	$\ln \gamma_B$	y	P^R	P/Torr	$\ln \gamma_A$	$\ln \gamma_B$	y	P^R
				$x(CH_3)_2CHCOOH + (1 - x)c\text{-}C_6H_{12}$						
0.0000	97.51	2.3805	0.0000	0.0000	0.00	225.85	2.3994	0.0000	0.0000	0.00
0.1276	92.30	1.2028	0.0705	0.0086	0.52	214.08	1.1954	0.0721	0.0128	0.51
0.2131	89.68	0.8210	0.1470	0.0111	0.18	208.90	0.8046	0.1504	0.0161	0.14
0.2888	86.20	0.6224	0.2127	0.0139	−0.32	202.03	0.0008	0.2178	0.0198	−0.25
0.3723	81.74	0.4802	0.2824	0.0179	−0.32	191.96	0.4556	0.2890	0.0250	−0.35
0.4352	78.15	0.3978	0.3381	0.0214	−0.07	183.40	0.3731	0.3447	0.0298	−0.09
0.5241	73.10	0.2956	0.4326	0.0268	0.43	170.65	0.2737	0.4365	0.0373	0.41
0.5831	69.33	0.2323	0.5112	0.0305	0.31	161.62	0.2140	0.5106	0.0428	0.47
0.6555	64.09	0.1600	0.6291	0.0355	−0.26	148.65	0.1473	0.6193	0.0504	−0.51
0.7428	56.94	0.0861	0.8011	0.0436	−0.40	130.96	0.0802	0.7754	0.0632	−0.27
0.8524	43.15	0.0243	1.0432	0.0670	0.63	96.83	0.0239	0.9963	0.0985	0.71
0.9033	31.19	0.0091	1.1519	0.0962	−0.44	71.28	0.0095	1.0996	0.1399	−0.59
0.9492	19.15	0.0021	1.2388	0.1675	0.11	44.61	0.0024	1.1882	0.2345	0.20
1.0000	2.12	0.0000	1.3137	1.0000	0.00	7.36	0.0000	1.2770	1.0000	0.00
					$\sigma = 0.48$					$\sigma = 0.55$
				$x(CH_3)_3CCOOH + (1 - x)c\text{-}C_6H_{12}$						
0.0000	97.51	1.8539	0.0000	0.0000	0.00	225.85	1.9103	0.0000	0.0000	0.00
0.1438	89.53	0.9329	0.0627	0.0017	0.56	208.38	0.9114	0.0686	0.0035	0.84
0.2295	85.18	0.6580	0.1246	0.0025	−0.03	199.79	0.6099	0.1365	0.0049	−0.25
0.3382	78.96	0.4508	0.2053	0.0039	−0.44	186.86	0.3943	0.2201	0.0072	−0.18
0.3874	76.18	0.3858	0.2423	0.0046	−0.11	179.10	0.3313	0.2559	0.0086	−0.48
0.4558	71.76	0.3119	0.2960	0.0059	0.19	168.28	0.2624	0.3060	0.0109	0.34
0.5475	64.91	0.2307	0.3778	0.0080	0.27	151.14	0.1872	0.3817	0.0149	0.19
0.6061	59.96	0.1855	0.4394	0.0096	0.06	140.05	0.1444	0.4402	0.0180	0.49
0.6754	53.97	0.1370	0.5261	0.0120	0.07	124.93	0.0979	0.5232	0.0225	−0.34
0.7607	44.99	0.0842	0.6612	0.0161	−0.59	104.38	0.0499	0.6456	0.0306	−0.48
0.8664	32.90	0.0316	0.8943	0.0263	0.60	70.61	0.0118	0.8105	0.0541	0.64
0.9097	24.77	0.0158	1.0206	0.0363	−0.13	51.04	0.0042	0.8703	0.0794	0.07
0.9536	15.02	0.0046	1.1742	0.0632	−0.13	28.23	0.0007	0.9167	0.1484	−0.45
1.0000	0.55	0.0000	1.3721	1.0000	0.00	2.69	0.0000	1.0000	1.0000	0.00
					$\sigma = 0.44$					$\sigma = 0.58$
				$x(CH_3)_2CHCOOH + (1 - x)n\text{-}C_7H_{16}$						
0.0000	45.15	2.5807	0.0000	0.0000	0.00	114.89	2.5012	0.0000	0.0000	0.00
0.0988	44.11	1.3853	0.0553	0.0160	0.67	111.70	1.3342	0.0536	0.0203	0.94
0.1540	43.37	1.0212	0.1072	0.0185	0.35	110.12	0.9897	0.1026	0.0242	0.65
0.2332	41.69	0.7099	0.1803	0.0227	−0.36	106.01	0.7005	0.1705	0.0307	−0.61
0.3149	40.09	0.5291	0.2476	0.0293	−0.25	101.48	0.5312	0.2336	0.0400	−0.58
0.3774	38.55	0.4353	0.2970	0.0356	−0.12	97.87	0.4392	0.2822	0.0485	−0.02
0.4820	35.62	0.3117	0.3901	0.0480	0.05	90.77	0.3103	0.3795	0.0638	0.14
0.5470	33.93	0.2446	0.4613	0.0565	0.36	86.59	0.2385	0.4556	0.0737	0.52
0.6172	31.45	0.1793	0.5524	0.0668	0.18	80.70	0.1697	0.5515	0.0858	0.01
0.6560	29.49	0.1470	0.6089	0.0736	−0.37	76.87	0.1367	0.6093	0.0939	−0.37
0.7116	27.45	0.1063	0.6970	0.0854	−0.10	71.23	0.0963	0.6965	0.1087	−0.13
0.8261	21.11	0.0433	0.9071	0.1284	0.03	54.44	0.0382	0.8894	0.1643	0.14
0.8940	15.72	0.0183	1.0618	0.1864	0.09	40.18	0.0164	1.0243	0.2382	0.01
0.9743	6.13	0.0014	1.3117	0.4558	−0.20	17.07	0.0013	1.2482	0.5399	−0.27
1.0000	2.12	0.0000	1.4173	1.0000	0.00	7.36	0.0000	1.3480	1.0000	0.00
					$\sigma = 0.38$					$\sigma = 0.56$
				$x(CH_3)_3CCOOH + (1 - x)n\text{-}C_7H_{16}$						
0.0000	45.15	2.1417	0.0000	0.0000	0.00	114.89	2.2408	0.0000	0.0000	0.00
0.0867	43.05	1.2910	0.0351	0.0026	0.28	110.02	1.2739	0.0393	0.0051	0.54
0.1467	42.18	0.9467	0.0797	0.0038	0.37	107.80	0.9082	0.0866	0.0070	0.45
0.2213	40.25	0.6825	0.1382	0.0052	−0.23	103.79	0.6455	0.1446	0.0094	−0.17
0.2892	38.77	0.5335	0.1888	0.0069	−0.13	99.59	0.5059	0.1920	0.0124	−0.07
0.3365	37.60	0.4583	0.2230	0.0082	0.00	95.63	0.4366	0.2234	0.0150	−0.51
0.3791	36.39	0.4023	0.2541	0.0096	0.06	92.67	0.3844	0.2525	0.0176	−0.08
0.4325	34.60	0.3416	0.2956	0.0116	−0.04	88.69	0.3266	0.2920	0.0212	0.32
0.5031	32.23	0.2709	0.3577	0.0145	−0.10	82.66	0.2575	0.3527	0.0264	0.20
0.5984	29.23	0.1875	0.4602	0.0193	0.21	74.10	0.1762	0.4526	0.0349	0.10
0.6580	26.95	0.1421	0.5369	0.0230	0.21	67.85	0.1335	0.5246	0.0418	−0.14
0.7280	23.40	0.0961	0.6409	0.0289	−0.27	59.68	0.0920	0.6183	0.0530	−0.09
0.8153	18.72	0.0501	0.7972	0.0411	−0.19	47.14	0.0512	0.7571	0.0761	−0.13
0.9194	11.54	0.0119	1.0520	0.0822	0.64	28.34	0.0139	1.0099	0.1466	0.51
0.9607	5.86	0.0032	1.1907	0.1462	−0.49	16.60	0.0039	1.1688	0.2429	−0.45
1.0000	0.55	0.0000	1.3547	1.0000	0.00	2.69	0.0000	1.3740	1.0000	0.00
					$\sigma = 0.36$					$\sigma = 0.41$

at 308.15 K, of that measured at 298.15 and 318.15 K and for TMA G^E values at 318.15 K have been used as such. (Plots of G^E, H^E, and TS^E vs. x are shown in Figure 5.) All the systems possess negative TS^E values which for equimolar mixtures with cyclohexane are −696, −394, −443, and −456 J mol^{-1} and for mixtures with n-heptane are −727, −542, −479, and −469 J mol^{-1} with AA(1), PA(2), IBA, and TMA, respectively. It may be seen that the decrease in values from AA to PA is quite sharp and after that the values virtually remain of the same order may be arising due to the onset of steric hin-

Table III. Values of Parameters of Eq 1 and 2

T/K	A	B	C	D	E
		$(CH_3)_2CHCOOH + c\text{-}C_6H_{12}$			
298.15	1.4537	–0.1641	0.3307	–0.3693	0.0627
318.15	1.4178	–0.2203	0.3359	–0.3409	0.0845
		$(CH_3)_3CCOOH + c\text{-}C_6H_{12}$			
298.15	1.2088	–0.1257	0.3247	–0.1152	0.0795
318.15	1.1303	–0.2321	0.3137	–0.2531	–0.0189
		$(CH_3)_2CHCOOH + n\text{-}C_7H_{16}$			
298.15	1.4023	–0.2323	0.3494	–0.3494	0.2473
318.15	1.3780	–0.2190	0.2516	–0.3576	0.2950
		$(CH_3)_3CCOOH + n\text{-}C_7H_{16}$			
298.15	1.2572	–0.1617	0.3096	–0.2318	0.1814
318.15	1.2204	–0.1788	0.2882	–0.2546	0.2988

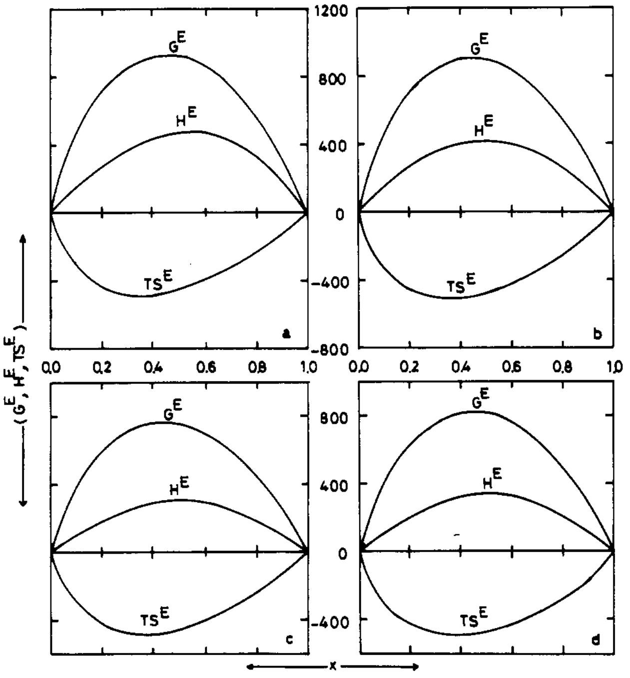

Figure 5. Plots of (G^E, H^E, TS^E) in J/mol against mole fractions (x): (a) isobutyric acid + cyclohexane; (b) isobutyric acid + n-heptane; (c) trimethylacetic acid + cyclohexane; (d) trimethylacetic acid + n-heptane.

Table IV. G^E, H^E, and TS^E Values[a]

x	G^E/(J mol^{-1}) 298.15 K	G^E/(J mol^{-1}) 318.15 K	H^E/(J mol^{-1}) 308.15 K	TS^E/(J mol^{-1}) 308.15 K
		$x(CH_3)_2CHCOOH + (1 - x)c\text{-}C_6H_{12}$		
0.1	448.7	480.5	151.2 (–25.4)	–313.4
0.2	697.7	743.0	270.0 (22.4)	–450.4
0.3	831.6	879.7	365.6 (114.7)	–490.1
0.4	894.1	938.4	436.8 (233.9)	–479.5
0.5	900.9	937.6	475.9 (354.2)	–443.4
0.6	851.5	879.0	472.9 (442.0)	–392.4
0.7	738.7	757.6	420.0 (457.4)	–328.2
0.8	556.3	568.8	315.3 (370.3)	–247.0
0.9	305.8	313.4	167.6 (192.7)	–142.0
		$x(CH_3)_3CCOOH + (1 - x)c\text{-}C_6H_{12}$[b]		
0.1	358.9	390.1	98.9[c] (–106.3)	–291.2
0.2	569.7	607.2	180.4 (10.7)	–426.8
0.3	687.4	716.1	241.5 (259.8)	–474.6
0.4	742.5	756.3	279.1 (537.3)	–477.2
0.5	749.1	747.5	291.1 (773.8)	–456.4
0.6	711.5	694.8	276.6 (961.5)	–418.2
0.7	627.4	594.9	236.2 (1113.1)	–358.7
0.8	490.1	443.1	172.6 (1192.0)	–270.5
0.9	287.7	240.0	91.2 (999.8)	–148.8
		$x(CH_3)_2CHCOOH + (1 - x)n\text{-}C_7H_{16}$		
0.1	466.7	480.5	149.0 (261.2)	–324.6
0.2	704.0	726.0	263.5 (376.4)	–451.5
0.3	822.4	853.4	344.9 (360.6)	–493.0
0.4	872.1	911.1	394.1 (291.0)	–497.5
0.5	869.0	911.3	411.3 (238.7)	–478.9
0.6	813.5	851.9	396.5 (241.3)	–436.2
0.7	702.4	730.7	349.2 (280.8)	–367.4
0.8	533.6	549.4	268.4 (298.4)	–273.1
0.9	304.0	309.9	152.7 (216.3)	148.3
		$x(CH_3)_3CCOOH + (1 - x)n\text{-}C_7H_{16}$[b]		
0.1	396.6	428.7	112.7[c] (–820)	–316.0
0.2	610.5	645.5	207.2 (88.8)	–438.3
0.3	724.1	756.6	278.5 (239.8)	–478.1
0.4	775.8	806.4	322.8 (320.0)	–483.6
0.5	779.1	807.1	338.1 (362.1)	–469.0
0.6	735.2	758.4	323.3 (389.8)	–435.1
0.7	641.3	659.0	279.4 (377.8)	–379.6
0.8	493.8	508.1	208.2 (280.9)	–299.9
0.9	285.9	298.5	113.4 (98.2)	–185.1

[a] Calculated H^E values in parentheses. [b] G^E at 318.15 K have been used for TS^E values. [c] H^E at 313.15 K.

drance from PA onwards.

The H^E values have also been calculated from the temperature dependence of G^E values for the present systems and are included in Table IV. The agreement between these and the experimental values is quite good except in case of TMA + cyclohexane where it is within the uncertainty of the order of 1% in G^E values.

As reported earlier (*1*, *2*) the negative magnitude of TS^E values may be attributed to the predominant breaking of dimer–monomer interactions of acid molecules in favor of the formation of dimers with increasing mole fraction of the nonpolar component. The decreasing magnitude of negative TS^E values from AA to TMA again suggests the increased ideal mixing behavior which is due to (i) the increased alkyl part of the acid, (ii) the systematic increase of dimerization constants of these acids (Table I), and (iii) steric hindrance. In the case of mixtures containing n-heptane, the additional factor responsible for the increased ideal mixing behavior from AA to TMA may be increasing likeness between the alkyl part of the acid and n-heptane molecules. This is in line with the explanation given for the excess volume and excess enthalpy results reported earlier (*6*–*8*).

The sharp fall of G^E values from AA to PA followed by the flattening trend in IBA and TMA is also quite similar to the behavior found in the other properties reported earlier (*6*–*8*).

Glossary

A, B, C, ...	constants used in eq 1 and 2
γ_A, γ_B	activity coefficients of the acid and solvent
G^E	excess Gibbs free energy of mixing, J mol^{-1}
H^E	excess enthalpy of mixing, J mol^{-1}
K_p	dimerization constant of acids in the vapor phase
l_1	$= x_2^2$
m_1	$= -x_2^2 (1 - 4x_1)$
n_1	$= x_2^2 (1 - 8x_1 + 12x_1^2)$
o_1	$= -x_2^2 (1 - 12x_1 + 36x_1^2 - 32x_1^3)$
p_1	$= x_2^2 (1 - 16x_1 + 72x_1^2 - 128x_1^3 + 80x_1^4)$
l_2	$= x_1^2$
m_2	$= x_1^2 (1 - 4x_2)$
n_2	$= x_1^2 (1 - 8x_2 + 12x_2^2)$
o_2	$= x_1^2 (1 - 12x_2 + 36x_2^2 - 32x_2^3)$
p_2	$= x_1^2 (1 - 16x_2 + 72x_2^2 - 128x_2^3 + 80x_2^4)$
P	total pressure of the mixture, Torr
P_A, P_B	partial pressure of acetic acid and solvent, Torr
P^R	residual pressure, Torr
S^E	excess entropy of mixing, J/(K mol)
T	temperature, K
x	mole fraction of acid in liquid phase
x_1	mole fraction of the first component, i.e., acid

x_2 mole fraction of the second component, i.e., solvent
y mole fraction of the acid in vapor phase

Registry No. $(CH_3)_2CHCOOH$, 79-31-2; $(CH_3)_3CCOOH$, 75-98-9; c-C_6H_{12}, 110-82-7; n-C_7H_{16}, 142-82-5.

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Received for review August 14, 1986. Accepted June 29, 1987. T.S.B. is grateful to the CSIR, New Delhi, India, for the award of senior research fellowship.

Predicting Refractive Index and Density Increments of Binary Solvent Mixtures

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Refractive indices and densities of six binary liquid mixtures measured at 20 °C for three wavelengths (589, 546, and 436 nm) have been used to predict their increments. Dependence of refractive index and density increments has been discussed as a function of composition of the mixture.

For a satisfactory thermodynamic treatment of polymers in mixed solvents it seemed important to have accurate values of refractive index and density increments (*1*-*3*). While these increments can be measured experimentally for polymer solutions, no accurate procedure exists to measure them in neat solvent mixtures. In this study, an attempt is made to present equations which could be successfully used to predict both refractive index and density increments of solvent mixtures by using refractive index and density data on pure solvents and their mixtures. Accordingly, refractive indices and densities have been measured for six binary mixtures comprising benzene, cyclohexane, ethyl acetate, and carbon tetrachloride at 20 °C over the entire range of composition for each mixture. The data are used to predict refractive index and density increments of solvent mixtures; a dependence of these quantities on mixture composition is also discussed.

Theory

To incorporate the changes of volume and refractivity, we use the following relations (*2*, *4*)

$$\Delta V_{\text{mix}} = \left(\sum_{i=1}^{2} N_i V_i\right) A_{12}\phi_1\phi_2 \tag{1}$$

$$\Delta R_{\text{mix}} = \left(\sum_{i=1}^{2} N_i V_i\right) B_{12}\phi_1\phi_2 \tag{2}$$

where A_{12} and B_{12} are the empirical parameters which depend on composition of the mixture; ϕ_i is the volume fraction of the ith component in a mixture.

Lorentz-Lorenz relation leads to the definition of molar refractivity, R_i, of pure substance i as (*5*)

$$R_i = [(n_i^2 - 1)/(n_i^2 + 2)](M_i/\rho_i) \tag{3}$$

where n_i, M_i, and ρ_i represent the refractive index, molecular weight, and density of the ith component in the mixture. However, the refractivity, R, of a mixture is defined as the product of polarizability P and volume V of the system (*6*). Thus

$$R \equiv PV \tag{4}$$

so that

$$P \equiv (n^2 - 1)/(n^2 + 2) \tag{5}$$

where n is the refractive index of the mixture. For binary mixtures the following relations are feasible

$$\rho = (\phi_1\rho_1 + \phi_2\rho_2)/(1 + A_{12}\phi_1\phi_2) \tag{6}$$

$$P = (\phi_1P_1 + \phi_2P_2 + B_{12}\phi_1\phi_2)/(1 + A_{12}\phi_1\phi_2) \tag{7}$$

where P_1, P_2 are the polarizability of component 1 and 2 of the mixture; ρ_1, ρ_2 and ϕ_1, ϕ_2 represent their respective densities and volume fractions. Routine calculations from eq 6 and 7 lead to the desired quantities

$$(\mathrm{d}\rho/\mathrm{d}\phi_1) = \frac{(\rho_1 - \rho_2) + \rho D}{(1 + A_{12}\phi_1\phi_2)} \tag{8}$$

$$(\mathrm{d}n/\mathrm{d}\phi_1) = \left[(n^2 + 2)\left\{\left[(P_1 - P_2) + B_{12}(\phi_2 - \phi_1) + \frac{\mathrm{d}B_{12}}{\mathrm{d}\phi_1}(\phi_1\phi_2)\right] - PD\right\}\right] \Big/ [6n(1 + A_{12}\phi_1\phi_2)] \tag{9}$$

where

$$D = \left[A_{12}(\phi_2 - \phi_1) + \frac{\mathrm{d}A_{12}}{\mathrm{d}\phi_1}(\phi_1\phi_2)\right]$$

Experimentally calculated values of A_{12} and B_{12} (using eq 6 and 7) may be fitted to the following quadratic equations in order to evaluate the coefficients a_0, a_1, a_2, and b_0, b_1, and b_2.

$$A_{12} = a_0 + a_1(\phi_2 - \phi_1) + a_2(\phi_2 - \phi_1)^2 \tag{10}$$

$$B_{12} = b_0 + b_1(\phi_2 - \phi_1) + b_2(\phi_2 - \phi_1)^2 \tag{11}$$

Equations 10 and 11 are used to compute the derivatives $(\mathrm{d}A_{12}/\mathrm{d}\phi_1)$ and $(\mathrm{d}B_{12}/\mathrm{d}\phi_1)$ whose values are then inserted into eq 8 and 9 along with others to predict the incremental values

0021-9568/87/1732-0406$01.50/0