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Excess Gibbs Energy for Binary Mixtures Containing Carboxylic Acids. 2. Excess Gibbs Energy for Propionic Acid + Cyclohexane and + *n*-Heptane

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Total vapor pressures have been measured for propionic acid + cyclohexane and + *n*-heptane systems at 298.15 and 318.15 K for the entire mole fraction range. Both systems show positive deviations from Raoult's law. Activity coefficients have been calculated by taking into consideration the dimerization of the acid in the vapor phase. As with the corresponding mixtures of acetic acid, the estimated TS^E values are very negative, indicative of increased population of dimers in the presence of the title solvents.

Introduction

Mixtures of acetic acid in nonpolar solvents such as cyclohexane, benzene, *n*-heptane (*1*), and carbon tetrachloride (*2*) have been shown to possess large positive free energy and negative entropy of mixing. This has been attributed to the increasing population of cyclic dimers with the increasing concentration of the nonpolar component (*2*). Propionic acid has a dimerization constant slightly greater than that of acetic acid. It would be of interest to compare the behavior of similarly constituted mixtures of the two acids and divulge the nature of interactions in terms of the increased dimerization constant and length of the alkyl chain. Consequently, in this paper we report the total vapor pressure of propionic acid + cyclohexane and + *n*-heptane mixtures at 298.15 and 318.15 K for the entire concentration range. Taking into consideration the dimerization of the acid in the vapor phase, we have calculated activity coefficients and thereupon excess free energies and entropies of mixing.

Experimental Section

Propionic acid (AR, BDH) was kept over anhydrous sodium sulfate for about 24 h and then distilled. Finally, it was fractionally distilled over potassium permanganate and the middle fraction distilling at 414.35 K was collected. Its refractive index and vapor pressure at 298.15 K were 1.3845 and 3.90 torr, which agreed very well with the literature values of 1.3843 (*3*) and 3.90 torr (*4*), respectively. The purity and its check for other solvents are as reported in the previous paper (*1*).

The static manometric method used in the present studies (*5*) for measuring vapor pressures consists of two distillation assemblies for degassing and storage of the solvents, three calibrated measuring bulbs of capacity ca. 0.58, 1.95, and 4.80 cm^3, and a mixing bulb of suitable capacity. The manometer is made from 14 mm i.d. U-shaped Corning glass tubing, filled with freshly distilled mercury. Diferent parts are connected or disconnected with the help of mercury cutoffs except at one place where a greased stopcock has been used. The vapor pressures have been read with a cathetometer having a least count of 0.001 cm. Different mole fractions were prepared by transferring measured aliquots of one liquid into the other already transferred in the mixing bulb and covering more than half the composition range. Similarly the mole fractions from the other side were covered. The consistency of the measured vapor pressures is apparent from falling of the points on the same smooth curve irrespective of the direction from which they started.

The temperature of the thermostat housing the mixing bulb was controlled to ±0.005 K with the help of a 0.001 K (1 °C) Beckmann thermometer. The temperature of the air thermostat was kept at 323.15 ± 0.1 K and the necessary correction to convert the pressures to 273.15 K was employed. Absoluteness of the temperature was checked by determining the transition temperature of Glauber's salt (305.534 K). The vapor pressures are reproducible to ±0.50 torr.

Systematic error analysis carried out for the uncertainties due to volumes of calibrated bulbs, the temperature of measuring the volumes in the bulbs, and repeated additions shows that the mole fractions are precise to ±0.0001.

Methods of Calculations

The activity coefficients of the components in the mixtures were determined from the total vapor pressure, the composition in the liquid phase, and the dimerization constant of the acid in the vapor phase, by the procedure as outlined in previous reports (*1*, *2*). The dimerization constant of the acid used at 298.15 and 318.15 K was 2.301 and 0.388 $torr^{-1}$, respectively (*4*).

Results and Discussion

The measured vapor pressures for the title systems as a function of mole fraction of acid and calculated activity coefficients at 298.15 and 318.15 K as least-square fitted to the equations (*6*)

$$\ln \gamma_A = Al_1 + Bm_1 + Cn_1 + Do_1 + Ep_1 + ... \qquad (1)$$

$$\ln \gamma_B = Al_2 + Bm_2 + Cn_2 + Do_2 + Ep_2 + ... \qquad (2)$$

are summarized in Table I. These equations satisfy the Gibbs-Duhem equation and the values of corresponding l_1, m_1, ... and l_2, m_2, ... parameters are given in the Glossary. Negligible areas under the plots of $\ln \gamma_A/\gamma_B$ vs. x ensure that the fit is satisfactory. The small differences between the experimental and calculated total pressures (called residual pressures) as depicted in Table I, are mostly smaller than the reproducibility of the measured vapor pressures (0.50 torr) and seldom exceed the standard deviations (σ). Plots of total pressure (P) and the partial pressures (P_A, P_B) against mole fraction (x) are given in Figures 1 and 2. Both systems show positive deviations and unlike in acetic acid do not show any maximum. Excess free energies at rounded mole fractions as obtained from the A, B, C, D, ... parameters of eq 1 and 2 (Table II) are given in Table III and illustrated in Figure 3. From the temperature dependence of present G^E values, H^E values at the mean temperature of 308.15 K and at rounded mole fractions have been estimated and for the system propionic acid + cyclohexane only, for which the experimental H^E values are available (*7*), a comparison has been made in Table IV. The

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Table I. Vapor Pressures, Activity Coefficients, and Mole Fraction of Acid in the Vapor Phase for Propionic Acid + Solvent System at 298.15 and 318.15 K

	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
					CH_3CH_2COOH + c-C_6H_{12}					
0.0000	97.51	2.565	0.000	0.0000	0.00	225.85	2.512	0.000	0.0000	0.00
0.1407	92.78	1.300	0.084	0.0221	0.37	216.07	1.253	0.083	0.0287	0.97
0.2080	91.06	0.989	0.148	0.0257	–0.02	211.56	0.948	0.147	0.0334	–0.35
0.2201	90.62	0.945	0.160	0.0264	–0.18	210.74	0.905	0.158	0.0343	–0.50
0.3068	88.10	0.701	0.247	0.0316	–0.16	204.83	0.669	0.242	0.0414	–0.17
0.3935	84.88	0.532	0.337	0.0378	0.05	196.90	0.509	0.328	0.0500	0.33
0.4702	81.45	0.414	0.427	0.0437	0.08	188.32	0.396	0.414	0.0581	0.21
0.5248	78.76	0.340	0.501	0.0479	–0.02	181.69	0.324	0.485	0.0641	–0.16
0.5557	77.40	0.300	0.547	0.0504	0.14	178.01	0.286	0.529	0.0675	–0.20
0.6071	74.42	0.239	0.632	0.0547	–0.18	171.84	0.226	0.612	0.0734	–0.02
0.6229	73.79	0.221	0.660	0.0562	0.07	169.76	0.209	0.640	0.0753	–0.02
0.6869	69.55	0.155	0.786	0.0627	–0.13	160.34	0.145	0.762	0.0842	0.10
0.7647	62.72	0.089	0.961	0.0745	–0.14	144.09	0.081	0.931	0.1003	–0.11
0.7949	59.63	0.068	1.036	0.0813	0.34	135.99	0.061	1.001	0.1097	0.19
0.8608	48.53	0.032	1.210	0.1060	–0.17	110.85	0.027	1.163	0.1434	–0.19
0.9689	21.65	0.003	1.501	0.2574	0.02	50.25	0.002	1.445	0.3379	0.11
0.9827	12.05	0.001	1.579	0.4425	0.08	29.51	0.000	1.477	0.5426	0.01
1.0000	3.90	0.000	1.638	1.0000	0.0	12.75	0.000	1.5217	1.0000	0.00
					$\sigma = 0.20$					$\sigma = 0.39$
					CH_3CH_2COOH + n-C_7H_{16}					
0.0000	44.15	2.480	0.000	0.0000	0.00	114.89	2.316	0.000	0.0000	0.00
0.0509	44.29	1.955	0.013	0.0252	0.11	113.23	1.858	0.012	0.0285	0.56
0.0950	43.66	1.607	0.040	0.0402	–0.03	112.02	1.548	0.036	0.0469	0.59
0.1635	43.09	1.216	0.097	0.0526	0.00	109.78	1.188	0.088	0.0639	–0.01
0.2064	42.81	1.040	0.137	0.0584	0.11	108.45	1.021	0.126	0.0717	–0.28
0.2671	42.00	0.853	0.195	0.0670	0.00	106.54	0.839	0.182	0.0824	–0.04
0.3137	41.22	0.744	0.239	0.0744	–0.09	104.88	0.731	0.226	0.0912	–0.46
0.3785	40.05	0.624	0.303	0.0859	–0.10	102.15	0.610	0.290	0.1042	–0.47
0.4777	38.17	0.474	0.415	0.1040	–0.02	98.01	0.461	0.402	0.1253	0.19
0.5686	36.55	0.351	0.551	0.1184	0.05	93.75	0.342	0.532	0.1435	0.46
0.6764	34.76	0.213	0.780	0.1319	0.02	87.89	0.213	0.747	0.1629	–0.15
0.7706	32.62	0.110	1.050	0.1466	0.00	81.96	0.115	1.005	0.1832	–0.13
0.8138	30.87	0.072	1.195	0.1588	0.00	77.60	0.077	1.148	0.1981	–0.16
0.8692	27.03	0.034	1.393	0.1883	–0.02	69.21	0.039	1.352	0.2313	0.30
0.9322	19.10	0.009	1.627	0.2775	0.02	50.43	0.011	1.610	0.3255	–0.11
1.0000	3.90	0.000	1.863	1.0000	0.00	12.75	0.000	1.909	1.0000	0.00
					$\sigma = 0.07$					$\sigma = 0.42$

Table II. Values of Parameters of Eq 1 and 2

T/K	A	B	C	D	E
		CH_3CH_2COOH + c-C_6H_{12}			
298.15	1.6768	–0.1869	0.3193	–0.2769	0.1054
318.15	1.6136	–0.1904	0.3069	–0.3048	0.0964
		CH_3CH_2COOH + n-C_7H_{16}			
298.15	1.7747	–0.0019	0.3971	–0.3067	
318.15	1.7223	0.0009	0.3998	–0.2045	

agreement is excellent, taking into view the inherent large uncertainties associated with the H^E values as obtained from G^E data.

TS^E values at 298.15 K have been obtained for the propionic acid + cyclohexane system from the present G^E and experimental H^E values by using the equation

$$TS^E = H^E - G^E$$

However, for TS^E values of the second system, estimated H^E values at 308.15 K without any temperature correction have been used. The TS^E values are summarized in Table IV. It is apparent that these are very negative and may, as in the case of acetic acid, be attributed to the increased proportion of acid dimers in nonpolar solvents. On comparing the G^E and TS^E values determined presently of propionic acid + cyclohexane mixtures with those of corresponding acetic acid mixtures reported earlier (*1*) one finds that G^E becomes less positive by about 17–41% and TS^E values less negative by 21–73% for the variation of acid mole fraction from 0.1 to 0.9, which shows that nonideality flattens off more steeply in the acid-rich region in the case of propionic acid mixtures. This points out the increased ideality due to increased alkyl chain length. This finds further support from the higher dimerization constant of propionic acid, which is 2.301 $torr^{-1}$ (*4*), vs. 1.9824 $torr^{-1}$ (*1*) for acetic acid (at 298.15 K), leading to a lesser number of available monomers to be dimerized in the presence of the solvent.

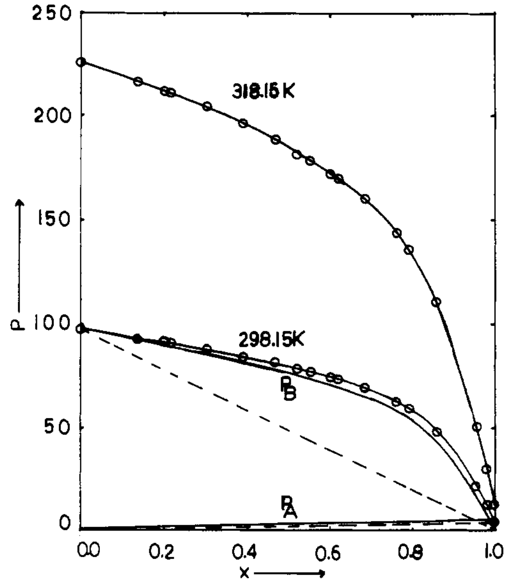

Figure 1. Plot of total pressure (P) and partial pressures (P^A, P^B) in torr against mole fraction (x) for propionic acid + cyclohexane system.

Table III. G^E, H^E, and TS^E Values for Propionic Acid + Solvent Systems at 298.15 K

	CH_3CH_2COOH + c-C_6H_{12}			CH_3CH_2COOH + n-C_7H_{16}		
x	G^E/(J/mol)	H^E/(J/mol)	TS^E/(J/mol)	G^E/(J/mol)	H^{Ea}/(J/mol)	TS^E/(J/mol)
0.1	494	177	-318	488	396	-92
0.2	784	360	-424	787	496	-222
0.3	949	527	-422	968	509	-459
0.4	1029	657	-372	1067	512	-556
0.5	1039	729	-310	1100	518	-582
0.6	982	731	-251	1064	487	-576
0.7	853	654	-198	946	380	-566
0.8	648	499	-149	734	199	-535
0.9	364	275	-90	417	7	-410

[a] H^E has been calculated from the temperature dependence of G^E at 308.15 K and has been used as such.

Table IV. Comparison of Experimental and Calculated H^E Values for Propionic Acid + Cyclohexane System at 318.15 K

x	$H^E_{exptl}{}^a$/(J/mol)	H^E_{calcd}/(J/mol)	x	$H^E_{exptl}{}^a$/(J/mol)	H^E_{calcd}/(J/mol)
0.1	215	207	0.6	662	611
0.2	385	387	0.7	609	569
0.3	516	516	0.8	489	486
0.4	609	593	0.9	290	329
0.5	659	624			

[a] These values are taken from ref 7 and are accurate to ±1% of the observed values.

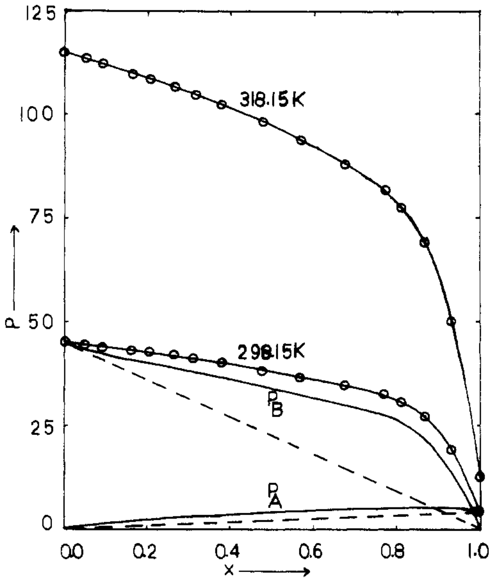

Figure 2. Plot of total pressure (P) and partial pressures (P^A, P^B) in torr against mole fraction (x) for propionic acid + n-heptane system.

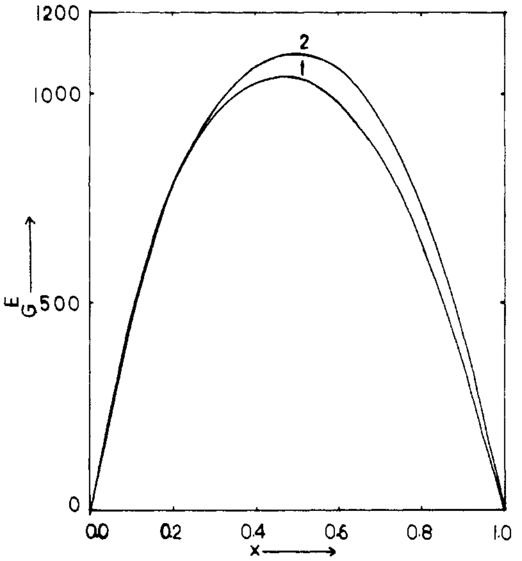

Figure 3. Plot of excess Gibbs free energy (G^E) in J/mol against mole fraction (x) at 298.15 K: (1) propionic acid + cyclohexane, (2) propionic acid + n-heptane.

Glossary

$A, B, C, \ldots$	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
H^E	excess enthalpy of mixing, J/mol
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. Propionic acid, 79-09-4; cyclohexane, 110-82-7; n-heptane, 142-82-5.

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