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EXCESS ENTHALPIES AND EXCESS VOLUMES OF SOME CARBOXYLIC ACID MIXTURES WITH *n*-HEPTANE

B.S. LARK and T.S. BANIPAL

Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005 (India)

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ABSTRACT

Excess enthalpies of the binary mixtures consisting of *n*-heptane + acetic acid (AA), + propionic acid (PA), + iosbutyric acid (IBA) at 308.15 K and + trimethylacetic acid (TMA) at 313.15 K have been measured over the whole composition range using an adiabatic calorimeter. Excess volumes for the first three mixtures at 298.15 and 308.15 K and for the last at 313.15 K have also been measured using a batch dilatometer. Both the excess functions are found to be positive for all the systems over the entire composition range. Excess entropies for the first two systems, for which free energy data are available in the literature, have also been estimated and found to be negative. Results have been discussed in terms of depolymerization of acids and increase in steric hindrance due to the increasing methylation of acetic acid.

INTRODUCTION

In the recent few years some reports have appeared about the excess thermodynamic properties of some binary mixtures containing a carboxylic acid as one of the components [1–13]. Incidentally, most of the studies are related to the measurement of excess volumes and excess free energies, and such data on excess heats of mixing are so far lacking. Carboxylic acids have interesting mixing properties and with non-polar solvents yield large, positive excess volumes and negative excess entropies. To correlate the previous findings [1–5] and to ascertain the effect of increasing methylation of acetic acid on its mixing properties with non-polar solvents, in the present paper we report excess heats of mixing of *n*-heptane + acetic acid (AA), + propionic acid (PA), + isobutyric acid (IBA) at 308.15 K and + trimethylacetic acid (TMA) at 313.15 K, since it is a solid up to 308.55 K. The H^E values for acetic and propionic acids have been combined with earlier reported [4,5] G^E values to yield excess entropies of mixing. Excess volumes of these mixtures at 298.15 and 308.15 K for AA, PA, IBA and at 313.15 K for TMA

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are also reported. A comparison with earlier reported results of similar studies in other non-polar solvents is presented.

EXPERIMENTAL

Acetic and propionic acids (AR, BDH) and *n*-heptane (GR, Tokyo Kasei Kogyo Co. Ltd., Japan) were purified by the methods reported earlier [4,5]. Isobutyric acid (LR, SRL) was dried by refluxing it over phosphorus pentaoxide and then fractionally distilled over a 1.2 m long column. The middle fraction was further refluxed over potassium permanganate and fractionally distilled. The fraction distilling at 427.5 K was collected. Trimethyl acetic acid (GR, Tokyo Kasei Kogyo Co. Ltd., Japan) was first fractionally crystallised and the liquid layer was discarded. The solid portion (m.p. 308.55 K) was then distilled under reduced pressure. The purity of the chemicals was checked by measuring their densities and refractive indices which have been compared with the literature values [14–16] in Table 1. The agreement is quite good. For excess volume measurements the purified solvents were thoroughly degassed before use.

Excess volumes have been measured directly by using a batch dilatometer introduced by Lark and Palta [17] while excess heats have been measured using an adiabatic calorimeter designed by Larkin and McGlashan [18] and later modified by Nigam and Mahl [19]. The two-limbed calorimeter has the advantage of the absence of the vapour phase and at the same time allows for volume change accompanied with mixing of the components. A water thermostat of suitable capacity, controlled to ±0.01 K with the help of a 0.01 K Beckmann thermometer (calibrated by determining the transition temperature of Glauber's salt), was used.

TABLE 1

Physical constants of pure compounds

Compound	Refractive index		Density (g cm^{-3})	
	Obs.	Lit.	Obs.	Lit.
IBA	1.3933 [a]	1.3930 [a]	0.94428 [b]	0.94423 [b]
TMA	1.3925 [c]	—	0.90396 [c]	0.90401 [c]

Dimerization constants (Torr^{-1})

Temp. (K)	AA [9]	PA [8]
298.15	1.982	2.301
318.15	0.379	0.388

[a] At 293.15 K. [b] At 298.15 K. [c] At 313.15 K.

RESULTS AND DISCUSSION

Measured excess volumes and excess heats for the various systems as a function of mole fraction of the acid are summarized in Tables 2 and 3, respectively. The results have been fitted by the least-squares method to the equation

$$X^{\mathrm{E}} = x(1-x)\left[A + B(1-2x) + C(1-2x)^2 + \ldots\right] \qquad (1)$$

where X^{E} may be excess volume or excess enthalpy, A, B, C, etc., are

TABLE 2

Excess volumes for acetic and its methylsubstituted acids with n-heptane

298.15 K			308.15 K		
x	V^{E} (cm^3 mol^{-1})	$10^4\delta V^{\mathrm{E}}$ (cm^3 mol^{-1})	x	V^{E} (cm^3 mol^{-1})	$10^4\delta V^{\mathrm{E}}$ (cm^3 mol^{-1})
$x\mathrm{CH_3COOH} + (1-x)n\text{-}\mathrm{C_7H_{16}}$					
0.0752	0.3290	−8	0.0961	0.4646	−4
0.1748	0.6877	−10	0.2119	0.8972	−3
0.2480	0.9004	−13	0.2838	1.1014	−8
0.2727	0.9656	12	0.3007	1.1447	12
0.3353	1.1035	8	0.3681	1.2828	2
0.3910	1.2017	9	0.4589	1.4045	6
0.4589	1.2880	10	0.5315	1.4428	−5
0.5547	1.3410	5	0.5793	1.4391	0
0.5895	1.3371	−8	0.6540	1.3796	−5
0.6584	1.2918	−17	0.7135	1.2820	−5
0.7187	1.2060	−7	0.7608	1.1692	−3
0.7586	1.1209	−6	0.8132	1.0048	9
0.8536	0.8178	15	0.8738	0.7547	7
0.9369	0.4111	12	0.9460	0.3638	−7
0.9518	0.3220	11			
$x\mathrm{CH_3CH_2COOH} + (1-x)n\text{-}\mathrm{C_7H_{16}}$					
0.0871	0.1724	−14	0.1056	0.2363	−17
0.1301	0.2535	−12	0.1651	0.3525	−12
0.1908	0.3613	6	0.2198	0.4472	2
0.2291	0.4226	10	0.2730	0.5262	10
0.2994	0.5198	7	0.2978	0.5578	7
0.3297	0.5536	−12	0.3668	0.6315	12
0.4146	0.6324	10	0.4606	0.6914	10
0.4681	0.6616	10	0.5277	0.7024	−15
0.5529	0.6733	−6	0.5954	0.6902	−9
0.6080	0.6588	−7	0.6661	0.6476	−5
0.7147	0.5759	−17	0.7209	0.5925	−7
0.7641	0.5152	2	0.7869	0.5015	14
0.8056	0.4508	6	0.8530	0.3793	−3
0.8575	0.3542	8	0.9404	0.1738	13
0.9409	0.1629	10	0.9778	0.0682	9

TABLE 2 (continued)

298.15 K			308.15 K		
x	V^E (cm^3 mol^{-1})	$10^4\delta V^E$ (cm^3 mol^{-1})	x	V^E (cm^3 mol^{-1})	$10^4\delta V^E$ (cm^3 mol^{-1})
$x(CH_3)_2CHCOOH+(1-x)n$-C_7H_{16}					
0.0529	0.0854	−4	0.0626	0.0933	11
0.1309	0.1925	7	0.1137	0.1588	−12
0.1787	0.2443	−11	0.1843	0.2418	0
0.2659	0.3237	10	0.2382	0.2932	−13
0.3329	0.3641	−9	0.3263	0.3621	8
0.4239	0.4009	8	0.3931	0.3956	2
0.4970	0.4091	−9	0.4345	0.4103	12
0.5549	0.4079	15	0.5058	0.4201	10
0.6006	0.3962	−1	0.5754	0.4114	−5
0.6875	0.3584	−5	0.6155	0.3992	−8
0.7519	0.3137	−14	0.6582	0.3806	−5
0.8413	0.2311	12	0.7167	0.3438	−10
0.8996	0.1572	−7	0.7445	0.3229	−4
0.9073	0.1479	6	0.7793	0.2922	−3
0.9647	0.0617	11	0.8497	0.2181	8
			0.8806	0.1801	12
			0.9209	0.1244	5
$x(CH_3)_3CCOOH+(1-x)n$-C_7H_{16}					
0.0764	0.1071	−26	0.5649	0.3911	−10
0.1580	0.2096	14	0.5766	0.3887	−8
0.2055	0.2580	16	0.6933	0.3405	10
0.2278	0.2745	−22	0.7910	0.2619	19
0.2872	0.3228	−4	0.8262	0.2306	16
0.3721	0.3730	25	0.8847	0.1621	−3
0.4541	0.3933	−10	0.9371	0.0955	18
0.5204	0.3983	5	0.9782	0.0317	−21

constants, and x is the mole fraction of the acid. The constants for various systems along with the standard deviations are given in Table 4. It may be seen that the observed excess volumes are quite precise and standard deviation, except in the case of TMA where it is ±0.002, is never more than 0.0013 cm^3 mol^{-1} for any system. The scatter in the H^E values is also quite small. Individual deviations seldom exceed the standard deviation in any system which itself is not more than ±1% of the observed magnitude for a mixture.

V^E and H^E values for the various systems as illustrated in Figs. 1 and 2 reveal their symmetrical disposition with respect to composition coordinate. The positive magnitude of V^E decreases in the order AA > PA > IBA ≈ TMA, and increases slightly with the increase in temperature. The observed behaviour may be explained by looking into the structure of carboxylic

TABLE 3

Excess enthalpies for acetic and its methylsubstituted acids with n-heptane

308.15 K			308.15 K		
x	H^E (J mol^{-1})	δH^E (J mol^{-1})	x	H^E (J mol^{-1})	δH^E (J mol^{-1})
$x CH_3COOH + (1-x) n\text{-}C_7H_{16}$			$x CH_3CH_2COOH + (1-x) n\text{-}C_7H_{16}$		
0.1674	402.9	−0.1	0.1371	230.4	4.0
0.2638	536.4	−2.0	0.1790	291.3	11.8
0.3598	625.0	2.9	0.2215	353.6	−2.8
0.3969	643.3	0.3	0.3081	467.2	1.3
0.4816	664.5	−4.4	0.3445	497.9	−4.3
0.5203	677.1	6.1	0.4087	552.3	2.6
0.5777	661.3	−1.4	0.4684	576.3	3.0
0.6776	608.0	−4.9	0.5405	577.0	2.8
0.7603	537.2	5.3	0.6051	545.9	−3.0
0.7915	489.1	−1.1	0.6957	472.0	−2.3
0.8610	369.2	−2.3	0.7797	368.0	−1.3
0.9223	234.7	2.3	0.8288	295.6	0.5
			0.9155	152.5	3.5
$x (CH_3)_2CHCOOH + (1-x) n\text{-}C_7H_{16}$			$x (CH_3)_3CCOOH + (1-x) n\text{-}C_7H_{16}$		
0.1288	182.1	−3.3	0.1145	128.7	1.1
0.2136	278.2	1.7	0.1385	153.3	1.8
0.2153	278.7	0.6	0.1821	190.7	−1.2
0.2572	315.4	1.3	0.2968	275.2	−1.4
0.3618	379.3	0.2	0.4143	325.1	−1.7
0.3639	382.0	2.0	0.4810	339.1	1.7
0.4419	402.4	−2.8	0.5791	330.9	2.0
0.5008	411.1	−0.2	0.6147	318.7	0.0
0.5104	410.0	−1.3	0.6617	297.0	−2.6
0.5785	400.6	−1.8	0.6954	283.9	1.9
0.6811	362.7	2.0	0.7955	210.5	−1.5
0.7311	332.1	4.3	0.8241	188.4	1.0
0.8112	254.6	−2.6	0.8630	149.7	−1.3
0.9063	141.8	−2.3	0.9308	81.4	0.9
0.9506	81.6	1.4			

acids, which mainly exist as ring dimers. These dimers (D) interact with acid monomers (M) and pass as (D–M) trimers. In the case of acetic acid, Kohler and co-workers [9] have shown that when a non-polar solvent is added, the trimers break up with larger positive excess volumes and the monomers, thus set free, change isochorically into dimers

$$\text{D–M} \rightleftharpoons \text{D} + \text{M} \tag{2}$$

$$2\text{M} \rightleftharpoons \text{D} \tag{3}$$

Because of +I effect of methyl groups, the successive methylation of acetic acid is expected to result in a higher dimerization constant. With the

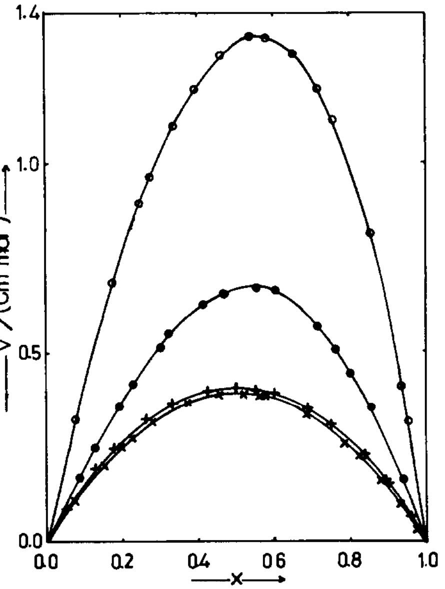
TABLE 4

Constants *A*, *B* and *C* of eqn. (1)

T (K)	V^E			$\sigma(V^E)$ (cm^3 mol^{-1})
	A	*B*	*C*	
$CH_3COOH + n\text{-}C_7H_{16}$				
298.15	5.2812	−1.2530	0.7292	0.0012
308.15	5.7310	−0.9939	0.6505	0.0007
$CH_3CH_2COOH + n\text{-}C_7H_{16}$				
298.15	2.6820	−0.4366	−0.1988	0.0011
308.15	2.8057	−0.3369	−0.0319	0.0012
$(CH_3)_2CHCOOH + n\text{-}C_7H_{16}$				
298.15	1.6403	−0.0327	0.1278	0.0010
308.15	1.6758	−0.0740	−0.0525	0.0009
$(CH_3)_3CCOOH + n\text{-}C_7H_{16}$				
313.15	1.5930	−0.0213	−0.0290	0.0018
	H^E			$\sigma(H^E)$ (J mol^{-1})
	A	*B*	*C*	
$CH_3COOH + n\text{-}C_7H_{16}$				
308.15	2682.8	−116.4	646.5	3.9
$CH_3CH_2COOH + n\text{-}C_7H_{16}$				
308.15	2309.9	−75.7	−647.0	3.2
$(CH_3)_2CHCOOH + n\text{-}C_7H_{16}$				
308.15	1645.2	−25.6	47.6	2.4
$(CH_3)_3CCOOH + n\text{-}C_7H_{16}$				
313.15	1352.2	−5.02	−149.9	1.7

data in the liquid phase not being available, the actual trend cannot be stated with finality. However, the vapour phase dimerization constant of PA is more than that of AA (Table 1). The increasing dimerization constant will leave a lower number of monomers to give a corresponding lower number of (D–M) trimers. The formation of trimers is further checked by the increasing steric hindrance of crowding methyl groups. Consequently, the addition of a non-polar solvent results in less positive V^E values. The increase in temperature results in a decrease in the dimerization constant of the acid and a greater number of available monomers to give a higher number of D–M trimers and, consequently, larger positive V^E values.

The V^E values for equimolar mixtures of the presently studied systems are compared with earlier reported [1–3] corresponding results in other non-polar solvents in Table 5. It may be seen that the behaviour of mixing of the title acids with *n*-heptane is more or less similar to that with cyclohexane. However, systematically smaller V^E values may be ascribed to the greater



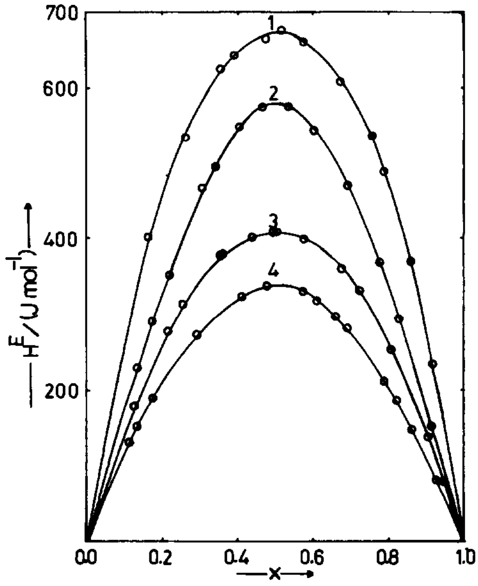


Fig. 1. Plot of V^E vs. x: n-C_7H_{16} + AA (○), + PA (●), + IBA (+) at 298.15 K and + TMA (×) at 313.15 K.

Fig. 2. Plot of H^E vs. x: n-C_7H_{16} + AA (1), PA (2), + IBA (3) at 308.15 K and + TMA (4) at 313.15 K.

likeness of n-heptane with the non-polar part of the acids. Greatly decreased V^E values in the case of benzene and carbon tetrachloride may be ascribed to specific interactions between these molecules and acid dimers, which are, however, slightly offset in the case of TMA because of steric hindrance caused by its three methyl groups.

The above conclusions receive sufficient, appropriate support from the excess enthalpies. H^E values are all positive for the title systems with the magnitude decreasing as the successive methylation of acetic acid increases. This shows that the equilibrium (2) is pushed to the right in the presence of non-polar solvents, and contributes more endothermally than the second

TABLE 5

Excess volumes for equimolar mixtures for various systems

Acid	c-C_6H_{12}		C_6H_6		CCl_4		n-C_7H_{16}	
	298.15 K	308.15 K	298.15 K	308.15 K	298.15 K	308.15 K	298.15 K	308.15 K
AA	1.564	1.643	0.815	0.854	0.725	0.782	1.320	1.433
PA	1.070	1.108	0.388	0.392	0.267	0.293	0.671	0.701
IBA	0.741	0.759	0.333	0.324	0.155	0.159	0.410	0.419
TMA	—	0.504 [a]	—	0.510 [a]	—	0.298 [a]	—	0.398 [a]

[a] At 313.15 K.

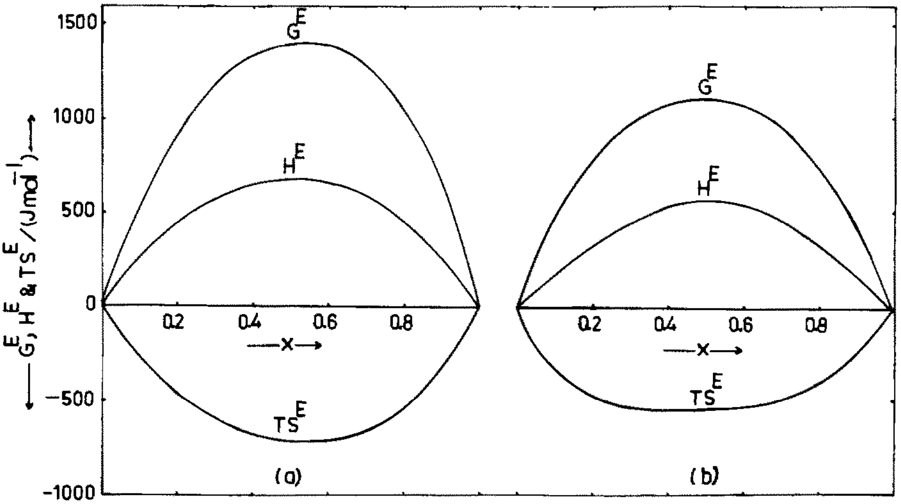


Fig. 3. Plots of G^E, H^E and TS^E vs. x at 308.15 K: n-C_7H_{16} + AA (a) and + PA (b).

exothermic step, so that overall endothermic mixing is observed. Even dispersion forces would contribute to some extent to the endothermic mixing.

Activity coefficients for the two systems AA and PA with n-heptane at 298.15 and 318.15 K have been reported earlier [4,5]. Assuming a linear dependence, excess free energies estimated at the mean temperature of 308.15 K have been combined with the present experimental excess enthalpies to give excess entropies as per the relation

$$G^E = H^E - TS^E \tag{4}$$

G^E, H^E and TS^E values for these two systems at 308.15 K are illustrated in Fig. 3. TS^E values for equimolar mixtures have been compared with those of other similar systems [4,5] in Table 6.

It is evident that these systems are characterized by large negative entropies of mixing arising from large positive free energies as compared to H^E values. These, as assigned by Kohler and coworkers [6], are due to the formation of dimers with increasing mole fraction of the non-polar component. In the case of mixtures with benzene and carbon tetrachloride the specific interactions might also contribute to the observed magnitude of TS^E values.

TABLE 6

TS^E values (J mol^{-1}) for equimolar mixtures for various systems at 308.15 K

Acid	c-C_6H_{12}	C_6H_6	CCl_4	n-C_7H_{16}
AA	−721.9	−715.3	−771.718	−727.3
PA	−324.0	—	—	−542.0

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