

MOLAR EXCESS ENTHALPIES, MOLAR EXCESS VOLUMES AND MOLAR ISENTROPIC COMPRESSIONS OF MIXTURES OF 2-PROPANONE WITH HEPTANE, BENZENE AND TRICHLOROMETHANE AT 298.15 K

YUTAKA AKAMATSU, HIDEO OGAWA and SACHIO MURAKAMI *

*Department of Chemistry, Faculty of Science, Osaka City University, 3-3-138 Sugimoto,
Sumiyoshi-ku, Osaka 558 (Japan)*

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ABSTRACT

Molar excess enthalpies, densities and speeds of sound of mixtures of 2-propanone with heptane, benzene and trichloromethane have been measured at 298.15 K by using a LKB flow microcalorimeter, a Picker vibrating densimeter and a “sing-around” technique, respectively. Molar excess volumes and pseudo-excess isentropic compressions of these mixtures have been also determined from the experimental results of densities and speeds of sound. These excess functions for the 2-propanone/heptane mixture are positive. Molar excess enthalpies are positive but molar excess volumes and pseudo-excess isentropic compressions are negative for the 2-propanone/benzene mixture. For the 2-propanone/trichloromethane mixture, molar excess enthalpies and molar excess volumes are negative, except for the ketone-rich region, in which molar excess volumes are positive, while pseudo-excess isentropic compression are positive. These experimental results are discussed qualitatively.

INTRODUCTION

There have been many thermodynamic investigations on binary mixtures containing a dipolar liquid such as a ketone or amide. In most of these investigations, experimental results have been analyzed on the basis of the associated solution theory. However, general discussion about the second derivatives of chemical potential to temperature and pressure, heat capacity and compression, has scarcely been carried out. We are interested in these thermodynamic functions because they closely reflect the behaviour of the component molecules in solution, as well as excess enthalpy and excess volume. Recently, experimental excess enthalpies and excess volumes for binary mixtures including 2-propanone (C_3H_6O) have been measured by many investigators; however, these results vary widely. In addition, we have

* To whom correspondence should be addressed.

found very little data on excess heat capacities and excess isentropic compressions for these mixtures. As a part of a series of studies on the thermodynamic properties of binary mixtures which include a polar liquid, the present paper reports the experimental results of excess enthalpies, H^E , excess volumes, V^E and isentropic compressions, K_S for binary mixtures of C_3H_6O with heptane (C_7H_{16}), benzene (C_6H_6) and trichloromethane ($CHCl_3$).

EXPERIMENTAL

C_7H_{16} , C_6H_6 and $CHCl_3$ were purified by the usual procedure [1]. The purity of the purified samples was checked by gas-liquid chromatography (GLC) with a silicon column. No peak ascribed to impurity was seen on the chart sheet, except for C_7H_{16} in which a trace impurity was found. Purities of these samples were more than 99.97 mol%.

C_3H_6O was purified by transfer in vacuum on 3 Å molecular sieves, to avoid moisture in the air. No trace impurities were found in a GLC analysis with a TSG-1 column, which is highly sensitive to ketones and water. The water content was believed to be less than 0.02 mol%. The purified C_3H_6O and $CHCl_3$ were stored in sealed and coloured bottles, respectively, to prevent the water contamination and decomposition by air and light.

The densities, ρ , and speeds of sound, u , of these samples are presented in Table 1 along with literature values. The inaccuracy of u , $\epsilon(u)$, for each sample in Table 1 was found by the procedure described previously [4]. The density results do not differ very much from the literature values, except in the case of $CHCl_3$.

TABLE 1

Densities, ρ , speeds of sound, u , inaccuracies of u , $\epsilon(u)$ and isentropic compressibilities, κ_S for component liquids at 298.15 K

Liquid	ρ (g cm ⁻³)		u (m s ⁻¹)	$\epsilon(u)$ (m s ⁻¹)	κ_S (TPa ⁻¹)
	Observed	Lit.			
C_3H_6O	0.784431	0.7844 ^a 0.78508 ^b	1161.72	0.59	944.59
C_7H_{16}	0.679475	0.67951 ^a	1131.25	0.64	1150.03
C_6H_6	0.873657	0.87370 ^a 0.87360 ^b 0.87368 ^c	1299.73	0.37	677.57
$CHCl_3$	1.479010	1.47988 ^a	984.38	0.89	697.76

^a Ref. 1.

^b Ref. 2.

^c Ref. 3.

Excess enthalpies, H^E , for liquid mixtures containing C_3H_6O were measured at 298.15 K by a LKB flow microcalorimeter (LKB 107001) immersed in a water bath. The temperature of the bath was controlled to within ± 1 mK. The component liquids were delivered into the mixing cell by a pair of piston displacement pumps, which were newly constructed in our laboratory. The errors in the flow rate of the pumps were less than 0.05% over the mole fraction used in the present study. The uncertainty of H^E was estimated to be less than 0.5%.

Excess volumes, V^E , and isentropic compressibilities, κ_S for these mixtures were determined at 298.15 K from the density and speed-of-sound measurements. A Picker vibrating densimeter (Sodev 01D, Canada) was used to measure density and a "Sing-around" technique was used to measure speed of sound. The procedures used for both measurements are described elsewhere [4]. Reproducibilities of the measurements were estimated to be less than $\pm 3 \times 10^{-6}$ g cm $^{-3}$ for ρ and less than ± 0.1 m s $^{-1}$ for μ .

RESULTS AND DISCUSSION

Experimental H^E results for the liquid mixtures of $C_3H_6O(1)$ with $C_7H_{16}(2)$, $C_6H_6(2)$, and $CHCl_3(2)$ are listed in Table 2.

It is rather complicated to evaluate excess isentropic compressibility, κ_S^E , so the change of molar isentropic compression on mixing (pseudo-excess isentropic compression), ΔK_S , will be used to discuss the dependence of the molar volumes of mixtures on pressure. The values of the quantity ΔK_S refer to deviations of the experimental values of K_S for the various mixtures from the mole-fraction mixture law values. Molar isentropic compression, K_S , is defined by the thermodynamic relation,

$$K_S = -(\partial V / \partial P)_S = V \kappa_S \quad (1)$$

where V is the molar volume of liquid. ΔK_S is represented by the following equation,

$$\Delta K_S = K_S - x K_{S,1}^* - (1 - x) K_{S,2}^* \quad (2)$$

where K_S and $K_{S,i}^*$ are the molar isentropic compressions of the mixture and the pure component, i , respectively. The calculated V^E and ΔK_S results are listed in Table 3, along with ρ , u and κ_S values.

The results of the excess thermodynamic functions, X^E (or ΔX) were fitted to the following equation,

$$X^E = x(1 - x) \sum_{i=1}^n A_i (1 - 2x)^{i-1} \quad (3)$$

by the least-squares method; x is the mole fraction of C_3H_6O . The values of the coefficients, A_i , of eqn. (3) are summarized in Table 4, along with the

TABLE 2

Molar excess enthalpies, H^E , for binary liquid mixtures at 298.15 K

x	H^E (J mol ⁻¹)	x	H^E (J mol ⁻¹)
$x\text{C}_3\text{H}_6\text{O} + (1-x)\text{C}_7\text{H}_{16}$			
0.05000	411.0	0.55001	1658.7
0.10001	725.2	0.60001	1617.5
0.15000	977.0	0.65002	1549.3
0.20001	1184.3	0.70001	1452.0
0.25001	1343.5	0.75001	1318.9
0.30001	1469.3	0.80001	1153.1
0.35002	1563.0	0.85001	945.5
0.40002	1630.5	0.90000	690.8
0.45002	1667.4	0.95000	378.6
0.50002	1674.0		
$x\text{C}_3\text{H}_6\text{O} + (1-x)\text{C}_6\text{H}_6$			
0.05000	39.7	0.55001	136.8
0.10001	67.9	0.60001	132.7
0.15001	89.0	0.65001	126.5
0.20001	105.1	0.70001	118.0
0.25001	117.6	0.75001	106.7
0.30001	126.7	0.80001	92.7
0.35001	133.2	0.85000	76.1
0.40001	135.9	0.90000	55.0
0.45002	138.2	0.95000	27.0
0.50001	138.4		
$x\text{C}_3\text{H}_6\text{O} + (1-x)\text{CHCl}_3$			
0.05003	-402.1	0.55015	-1822.0
0.10005	-764.6	0.60014	-1705.7
0.15008	-1091.4	0.65013	-1554.0
0.20010	-1362.4	0.70012	-1381.6
0.25011	-1588.7	0.75011	-1179.2
0.30013	-1756.8	0.80009	-970.5
0.35014	-1870.7	0.85008	-741.6
0.40014	-1933.5	0.90005	-501.2
0.45015	-1941.0	0.95003	-227.7
0.50015	-1904.4		

standard deviations, s , of the fits. The results and the smoothed curves of H^E , V^E and ΔK_S are shown in Figs. 1–3, respectively.

Our H^E results for the $\text{C}_3\text{H}_6\text{O}/\text{C}_7\text{H}_{16}$ mixture were positive over the whole concentration range and the large parabolic curve was maximum at $x = 0.5$. Values of H^E for the $\text{C}_3\text{H}_6\text{O}/\text{C}_6\text{H}_6$ mixture were positive but not so large in magnitude. On the other hand, H^E values for the $\text{C}_3\text{H}_6\text{O}/\text{CHCl}_3$ mixture were large negative values. Several investigators have measured H^E for these mixtures [5–10], but the agreement between their results and ours is not very good and their data vary widely.

TABLE 3

Densities, ρ , speeds of sound, u , isentropic compressibilities, κ_S , molar excess volumes, V^E and molar excess compressions, ΔK_S , for binary liquid mixtures at 298.15 K

x	ρ (g cm ⁻³)	u (m s ⁻¹)	κ_S (TPa ⁻¹)	V^E (cm ³ mol ⁻¹)	ΔK_S (cm ³ TPa ⁻¹ mol ⁻¹)
$x\text{C}_3\text{H}_6\text{O} + (1-x)\text{C}_7\text{H}_{16}$					
0.05018	0.680913	1125.75	1158.85	0.2690	2343
0.20252	0.687214	1114.15	1172.25	0.7969	6960
0.30031	0.692616	1109.49	1172.90	0.9900	8597
0.33384	0.694707	1108.32	1171.85	1.0385	8977
0.33517	0.694815	1108.26	1171.78	1.0362	8985
0.50074	0.707389	1105.97	1155.72	1.1326	9555
0.59977	0.716993	1107.51	1137.07	1.0885	9020
0.70731	0.729687	1112.58	1107.13	0.9587	7722
0.79801	0.742817	1120.84	1071.59	0.7700	5993
0.89487	0.760194	1135.46	1020.32	0.4663	3482
0.94913	0.771872	1147.33	984.19	0.2454	1780
$x\text{C}_3\text{H}_6\text{O} + (1-x)\text{C}_6\text{H}_6$					
0.05388	0.869770	1295.05	685.52	-0.0134	-370
0.19760	0.859017	1281.17	709.23	-0.0477	-1206
0.26370	0.853894	1274.01	721.52	-0.0647	-1509
0.30095	0.850864	1269.63	729.10	-0.0656	-1629
0.40211	0.842499	1257.07	751.13	-0.0752	-1884
0.50313	0.833740	1243.38	775.82	-0.0764	-1982
0.60173	0.824799	1229.05	802.63	-0.0713	-1929
0.70141	0.815322	1213.42	833.01	-0.0576	-1693
0.79825	0.805717	1197.44	865.58	-0.0405	-1313
0.90098	0.795088	1179.60	903.90	-0.0193	-729
0.94999	0.789859	1170.81	923.59	-0.0090	-386
$x\text{C}_3\text{H}_6\text{O} + (1-x)\text{CHCl}_3$					
0.05228	1.446527	986.23	710.76	-0.0539	51
0.10027	1.416263	988.18	723.08	-0.0948	125
0.20483	1.348892	944.04	750.27	-0.1553	306
0.30833	1.280160	1001.98	778.07	-0.1688	551
0.39997	1.217773	1011.35	802.85	-0.1493	772
0.50203	1.146799	1024.69	830.47	-0.1022	1007
0.60111	1.076737	1041.47	856.24	-0.0543	1123
0.69799	1.007128	1062.14	880.14	-0.0068	1109
0.79790	0.934439	1088.40	903.39	0.0224	940
0.90066	0.858651	1121.84	925.38	0.0288	570
0.95016	0.821843	1140.67	935.18	0.0139	306

V^E results were positive and large for the $\text{C}_3\text{H}_6\text{O}/\text{C}_7\text{H}_{16}$ mixture and small and negative for the $\text{C}_3\text{H}_6\text{O}/\text{C}_6\text{H}_6$ mixture. On the other hand, V^E for the $\text{C}_3\text{H}_6\text{O}/\text{CHCl}_3$ mixture changed in sign from negative to positive, as the mole fraction of $\text{C}_3\text{H}_6\text{O}$ increased. Values of V^E for these mixtures have

TABLE 4

Coefficients, A_i , standard deviations, s and maximum deviations, $s(\max)$ of excess thermodynamic functions, X^E for binary liquid mixtures at 298.15 K ^a

X^E	A_1	A_2	A_3	A_4	A_5	s	$s(\max)$
$x\text{C}_3\text{H}_6\text{O} + (1-x)\text{C}_7\text{H}_{16}$							
H^E	6705.5	70.7	1428.9	266.0	618.6	2.6	6.0
V^E	4.5180	0.0680	0.9760	0.2454		0.0029	0.0046
ΔK_S	38225	4043	5606	3074		16	27
$x\text{C}_3\text{H}_6\text{O} + (1-x)\text{C}_6\text{H}_6$							
H^E	552.7	32.4	189.8	98.5		0.8	1.8
V^E	-0.3091	-0.0504	0.0827			0.0015	0.0036
ΔK_S	-7948	427	182			7	13
$x\text{C}_3\text{H}_6\text{O} + (1-x)\text{CHCl}_3$							
H^E	-7617.9	-2344.2	940.3	725.3		6.8	22.7
V^E	-0.4239	-1.0105	0.0575	0.2593		0.0020	0.0029
ΔK_S	3965	-3588	-268	731		8	12

^a Units of H^E in J mol^{-1} , V^E in $\text{cm}^3 \text{mol}^{-1}$ and ΔK_S in $\text{cm}^3 \text{TPa}^{-1} \text{mol}^{-1}$.

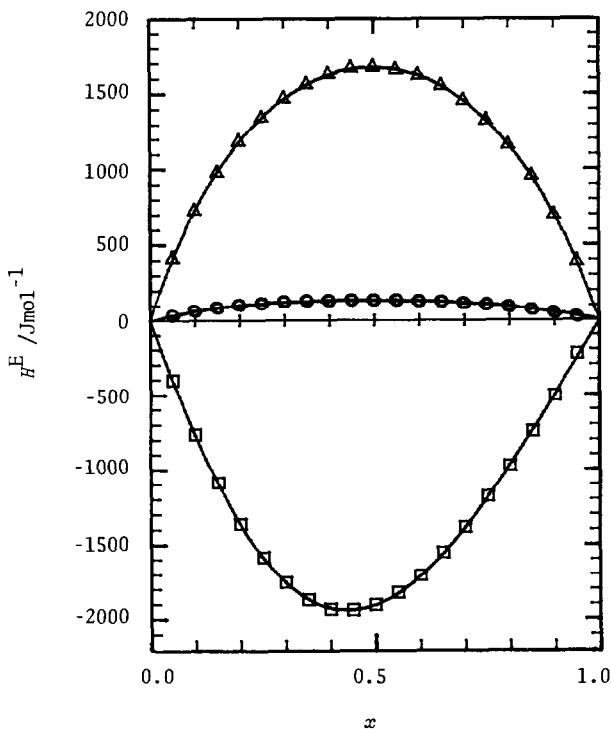


Fig. 1. Molar excess enthalpies for the binary liquid mixtures at 298.15 K. (Δ) $\text{C}_3\text{H}_6\text{O}/\text{C}_7\text{H}_{16}$; (\circ) $\text{C}_3\text{H}_6\text{O}/\text{C}_6\text{H}_6$; (\square) $\text{C}_3\text{H}_6\text{O}/\text{CHCl}_3$.

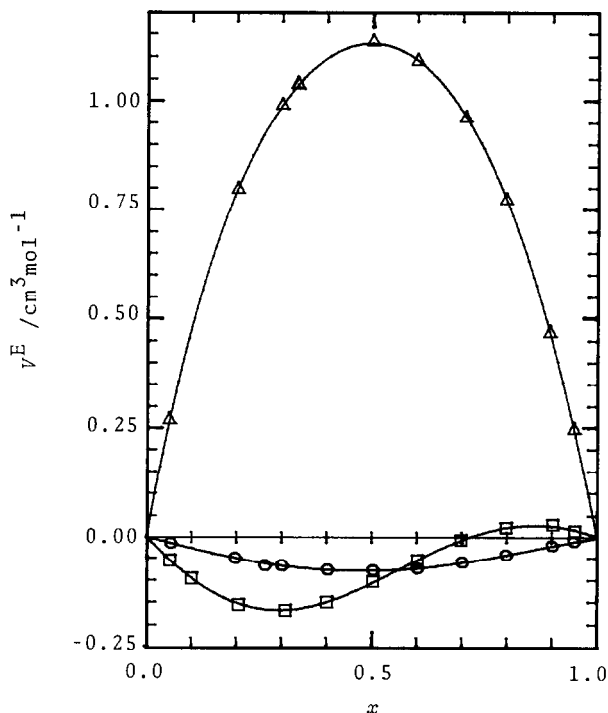


Fig. 2. Molar excess volumes for the binary liquid mixtures at 298.15 K. (Δ) $\text{C}_3\text{H}_6\text{O}/\text{C}_7\text{H}_{16}$; (O) $\text{C}_3\text{H}_6\text{O}/\text{C}_6\text{H}_6$; (\square) $\text{C}_3\text{H}_6\text{O}/\text{CHCl}_3$.

been also measured by several investigators [11–15]; their results tend to the more positive side than ours.

Values of ΔK_S were positive and large for the $\text{C}_3\text{H}_6\text{O}/\text{C}_7\text{H}_{16}$ mixture, and positive and small for the $\text{C}_3\text{H}_6\text{O}/\text{CHCl}_3$ mixture. On the other hand, ΔK_S values for the $\text{C}_3\text{H}_6\text{O}/\text{C}_6\text{H}_6$ mixture were negative and not so large. The differences of isentropic compressibilities between the solution and the pure liquids, $\Delta\kappa_S$, for the $\text{C}_3\text{H}_6\text{O}/\text{C}_6\text{H}_6$ and $\text{C}_3\text{H}_6\text{O}/\text{CHCl}_3$ mixtures were found in the literature [16]. Our results for the above quantities were the same sign as that of Nath and Dixit [15]. For the $\text{C}_3\text{H}_6\text{O}/\text{C}_7\text{H}_{16}$ mixture, there are no data available in the literature for comparison with our result.

Values of V^E and excess isentropic compressibilities for aliphatic ketone/ C_7H_{16} mixtures have been measured previously [17]. It was found from these data that the value of κ_S^E decreases with increasing alkyl chain length of the ketone molecule and the maximum value shifts to the lower mole fractions of ketone; this is in addition to an observed dependence of V^E on the concentration in these mixtures. This is attributed to the less attractive interactions between the carbonyl group in ketone molecules relative to the total intermolecular interactions, because the molecule becomes more bulky as the alkyl chain length in the ketone molecule increases.

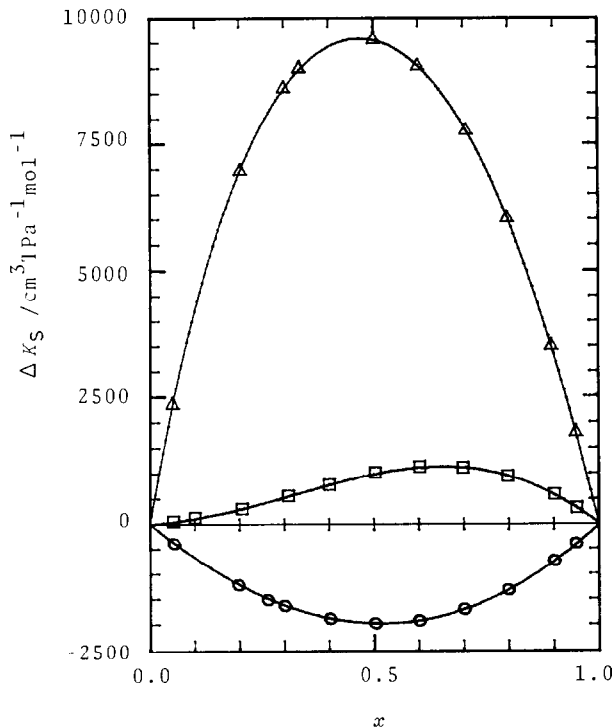


Fig. 3. Pseudo-excess isentropic compressions for the binary liquid mixtures at 298.15 K. (Δ) $\text{C}_3\text{H}_6\text{O}/\text{C}_7\text{H}_{16}$; (\circ) $\text{C}_3\text{H}_6\text{O}/\text{C}_6\text{H}_6$; (\square) $\text{C}_3\text{H}_6\text{O}/\text{CHCl}_3$.

Normally, excess thermodynamic functions, X^E , for binary mixtures give rise to any one, or a combination, of the following factors. (1) Difference in the molecular interaction energy between like and unlike molecules. (2) Formation of strong interaction between the unlike molecules (for example, hydrogen bonding). (3) Difference in size and shape of the component molecules.

The first factor makes a positive contribution to H^E , V^E and ΔK_S in consideration of the van der Waals interaction in solution. On the other hand, the second factor gives a negative contribution. The third depends on the ease of the geometrical fit of the component molecules in the solution state.

In addition to the dispersion force in pure $\text{C}_3\text{H}_6\text{O}$, there is a dipolar interaction. In the solution state, disruption of the dipolar interaction occurs by adding another component. With C_7H_{16} as the other component, only the dispersion force is considered in the pure state; H^E , V^E and ΔK_S in the $\text{C}_3\text{H}_6\text{O}/\text{C}_7\text{H}_{16}$ mixture will then be positive. C_6H_6 is a non-polar molecule but said to be ordered by the " π - π " interaction in the presence of the π orbital in the molecule. In the $\text{C}_3\text{H}_6\text{O}/\text{C}_6\text{H}_6$ mixture, disruption of the

dipolar interaction in pure C_3H_6O and disorder of "benzene structure" in pure C_6H_6 occur and the strong interaction will be newly formed between the dipole in C_3H_6O and the benzene ring of C_6H_6 . As a result, H^E tends to be more negative in direction than it would be for a ketone/non-polar molecule mixture, such as the C_7H_{16} system. In addition to the above contribution, V^E will be negative due also to the good geometrical fit of unlike molecules. In a mixture with negative V^E , the solution state will be less compressible, relative to the pure liquid state, by exerting pressure. Then, ΔK_S will take a negative value.

We are now calculating the stabilization energy, ΔE , between a ketone molecule and a C_6H_6 molecule by carrying out ab initio MO calculations, in which the 4-31G basis set was adopted. We found from the preliminary calculation that ΔE is $-7.95 \text{ kJ mol}^{-1}$ at $R = 4.0 \text{ \AA}$, the distance of the oxygen atom of the carbonyl group in ketone right over the hydrogen atom of benzene in the "stacking structure" [18].

The $C_3H_6O/CHCl_3$ mixture has been treated theoretically by many investigators as a typical system in the ideal associated solution. In this treatment the hydrogen bond is considered to be newly formed between the carbonyl group in C_3H_6O and the hydrogen atom in $CHCl_3$ in solution. Therefore, H^E and V^E in this mixture give large negative values. In such a mixture, ΔK_S is predicted to be negative. However, the experimental ΔK_S was positive. A positive ΔK_S means that the liquid is compressible in the solution state, compared with the pure liquid state, which suggests an increase of the hydrogen-bonded interaction between the unlike molecules on exerting the pressure. Interest will be taken in H^E at high pressure. The positive V^E value in the C_3H_6O rich region of the $C_3H_6O/CHCl_3$ mixture may be attributed to the very bad geometrical fit of the unlike molecules in the presence of a small amount of the bulky $CHCl_3$ molecule.

Excess heat capacity measurements on these mixtures are being undertaken. With these results we will quantitatively discuss the thermodynamic properties of these mixtures.

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