EXCESS MOLAR ISOBARIC HEAT CAPACITIES OF MIXTURES OF 2-PROPANONE WITH HEPTANE, BENZENE, AND TRICHLOROMETHANE AT 298.15 K *

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(Received 25 August 1989)

ABSTRACT

Excess molar isobaric heat capacities of 2-propanone + heptane, + trichloromethane and + benzene were measured at 298.15 K. They were positive for the former two mixtures and changed the sign from positive to negative with increase of 2-propanone for the latter mixture. The results were discussed in relation to the local fluctuation of concentration. Excess isothermal compressions for these mixtures were calculated by using the present heat capacity data and isentropic compression results measured previously. The excess isothermal compressions were found to have similar composition dependence as those of the excess volumes for these mixtures.

INTRODUCTION

Thermodynamic properties of binary mixtures which include a polar liquid are of considerable interest because of the unusual complexity of the interactions between the component molecules over the composition range. We reported previously experimental results of excess molar enthalpies, H^E, excess molar volumes, V^E, and changes of molar isentroic compression on mixing, ΔK_s, for binary mixtures of 2-propanone (C_3H_6O) with heptane (C_7H_{16}), benzene (C_6H_6) and trichloromethane ($CHCl_3$) at 298.15 K [1]. In this report, we present the calorimetric excess molar isobaric heat capacities, C_p^E for these mixtures at 298.15 K.

Recently, two groups (Grolier et al. and Patterson et al.) have discussed the thermodynamic properties of mixtures and have shown that the composition dependence of C_p^E has a "W-shape", i.e. two minima occur separated by a maximum [2–6]. One of the present mixtures, C_3H_6O–C_7H_{16},

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* Presented at the International Conference on Chemical Thermodynamics and Calorimetry, Beijing, P.R. China, 25–28 August 1989.
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may be included in this class: two regions of positive C_p^E curvature occur separated by a region of negative curvature. We will discuss these mixtures in relation to the local fluctuation of concentration.

EXPERIMENTAL

Values of C_p^E were measured by using a type of flow microcalorimeter constructed recently in our laboratory [7,8]. The molar isobaric heat capacities for pure components, C_p, were estimated from a ratio of C_p to the molar volume, C_p/V values, obtained in a similar manner to that reported by Fortier et al. [9]. We employed the value of C_p for C_7H_{16} reported by Kalinowska et al. [10] as the reference value needed in this method. On the other hand, C_p^E values were determined by the "direct mixing method" in which two sample liquids were delivered into a mixing cell by a pair of piston displacement pumps. The mole fraction of the mixture was determined by a ratio of flow rates of the two pumps. The details of the apparatus are described elsewhere [7,8]. The error in the C_p^E measurement is estimated to be less than 1% for a mixture with $C_p^E/C_p = 0.01$.

All the samples used here were purified by the method described previously [1]. Impurities of the sample liquids were checked by an analytical GLC (Shimazu, GC-3BT). A similar analytical result to that obtained previously was found.

The C_p/V and C_p values of these pure liquids at 298.15 K are listed in Table 1.

RESULTS AND DISCUSSION

The experimental C_p^E results at 298.15 K are listed in Table 2. The equation

$$C_p^E = x_1(1 - x_1)\Sigma A_i(1 - 2x_1)^{i-1} \tag{1}$$

TABLE 1

Volumetric heat capacities, C_p/V and molar heat capacities, C_p for the component liquids at 298.15 K

Liquid	C_p/V (J K^{-1} cm^{-3})	C_p (J K^{-1} mol^{-1})
C_3H_6O	1.6687	123.55
C_7H_{16}	1.5240	224.73 [a]
C_6H_6	1.5123	135.21
$CHCl_3$	1.4106	113.84

[a] Standard value by Kalinowska et al. [10].

TABLE 2

Excess molar isobaric heat capacities, C_p^E, for binary liquid mixtures at 298.15 K

x_1	C_p^E (J K^{-1} mol^{-1})	x_1	C_p^E (J K^{-1} mol^{-1})
$C_3H_6O(1)+C_7H_{16}(2)$			
0.05001	0.029	0.60003	2.720
0.10001	0.393	0.70003	2.150
0.20002	1.326	0.80002	1.316
0.30003	2.126	0.90001	0.400
0.40004	2.698	0.95001	0.072
0.50004	2.914		
$C_3H_6O(1)+C_6H_6(2)$			
0.05000	0.109	0.60001	−0.235
0.10001	0.160	0.70002	−0.303
0.20001	0.154	0.80001	−0.367
0.30002	0.108	0.90001	−0.322
0.40002	−0.003	0.95000	−0.218
0.50002	−0.137		
$C_3H_6O(1)+CHCl_3(2)$			
0.05003	1.290	0.60016	3.824
0.10006	2.402	0.70014	2.541
0.20011	4.262	0.80011	1.364
0.30014	5.410	0.90006	0.480
0.40016	5.601	0.95003	0.200
0.50017	4.941		

where x_1 is the mole fraction of C_3H_6O, was fitted to each set of results by the least squares method. The coefficients A_i of eqn. (1) are summarized in Table 3 along with the standard deviation, s, and the maximum deviation,

TABLE 3

Coefficients, A_i, standard deviations, s, and maximum deviations, s(max), of excess molar heat capacities, C_p^E, for binary liquid mixtures at 298.15 K [a]

A_1	A_2	A_3	A_4	A_5	s	s(max)
$C_3H_6O(1)+C_7H_{16}(2)$						
11.583	−0.06	−7.05	−0.08	−6.77	0.024	0.034
$C_3H_6O(1)+C_6H_6(2)$						
−0.462	2.14	−0.59	1.87		0.017	0.021
$C_3H_6O(1)+CHCl_3(2)$						
19.833	18.10	−5.89	−7.58		0.037	0.059

[a] Units of C_p^E are J K^{-1} mol^{-1}.

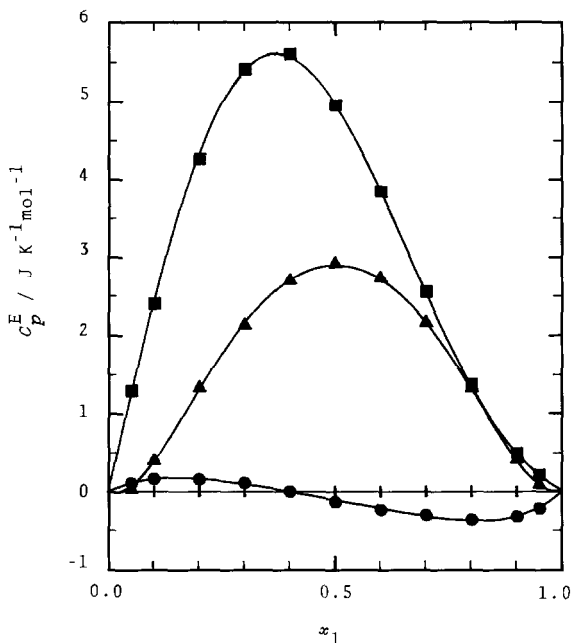Fig. 1. Excess molar isobaric heat capacities for binary liquid mixtures containing 2-propan-one(1) at 298.15 K. ▲, $C_3H_6O-C_7H_{16}$; ●, $C_3H_6O-C_6H_6$; ■, $C_3H_6O-CHCl_3$.

s(max). The experimental results and the smoothed curves calculated from eqn. (1) are also represented graphically in Fig. 1.

As shown in Fig. 1, C_p^E revealed the interesting composition dependence in all the mixtures. For the $C_3H_6O-CHCl_3$ and $C_3H_6O-C_7H_{16}$ mixtures, C_p^E values are positive. On the other hand, the sign changes from positive to negative for the $C_3H_6O-C_6H_6$ mixture with increasing x_1.

We reported previously the changes of molar isentropic compression on mixing ΔK_S, for the present mixtures [1]. Then, we can estimate molar excess isothermal compressions, K_T^E, for these mixtures in connection with the C_p^E results found in the present work. The procedure for finding K_T^E values is described in an earlier report from our laboratory [11]. In the calculations, the thermal expansion coefficients of mixtures, α, were found by assuming the volume fraction additivity of the component liquids. The results are shown in Fig. 2 with those of ΔK_S for these mixtures. K_T^E, considered as the pressure dependence of V^E, reveals a similar composition dependence to that of V^E even for the $C_3H_6O-CHCl_3$ mixture, for which $\Delta K_S > 0$ in the region of $V^E < 0$. This result supports the previous discussion [1].

Normally, the attractive intermolecular interaction between like molecules would be weakened more strongly in the pure state than in the solution state by the developed thermal motions of the component molecules at higher temperature. Therefore H^E becomes less positive at higher temperatures and
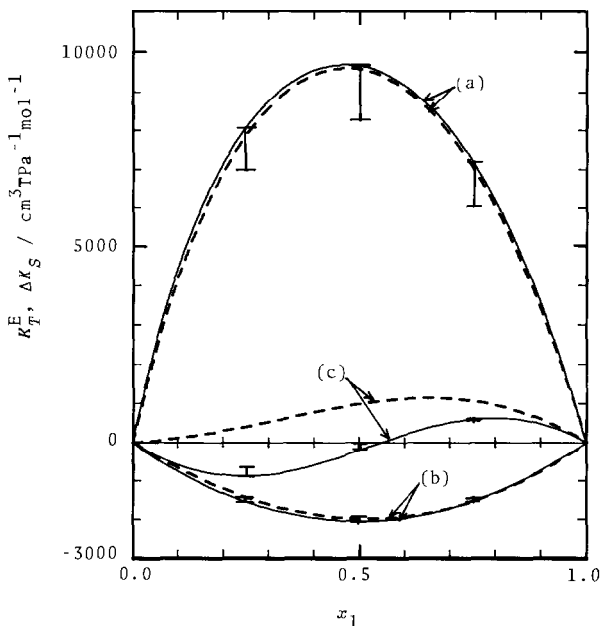
Fig. 2. Excess isothermal compressions and change of molar isentropic compressions on mixing for binary liquid mixtures containing 2-propanone(1) at 298.15 K. (a), $C_3H_6O-C_7H_{16}$; (b) $C_3H_6O-C_6H_6$; (c) $C_3H_6O-CHCl_3$. Solid lines are K_T^E at $\alpha^E = 0$ and errors bars show the difference from the other assumption of α^E by $(\partial V^E/\partial T) = -(\partial V^{id}/\partial T)(V^E/V^{id})$; broken lines are ΔK_S estimated previously [1].

C_p^E will be negative. On the other hand, the attractive intermolecular interaction acting between unlike molecules in the solution state would be weakened and H^E becomes less negative at higher temperatures. Then, C_p^E will be positive. The above prediction is in qualitative agreement with the experimental C_p^E results for the $C_3H_6O-CHCl_3$ and $C_3H_6O-C_6H_6$ mixtures at $x_1 > 0.4$. However, C_p^E for the $C_3H_6O-C_7H_{16}$ mixture is inconsistent with the above prediction. It means that the attractive intermolecular interaction between C_3H_6O molecules may be more weakened in the solution state than in the pure state at higher temperatures. This suggests large local fluctuation of concentration in this mixture as well as in the alcohol–non-polar liquid mixtures.

In order to understand the state of mixing for these mixtures, we calculated the mean square concentration fluctuation, $N\langle \Delta x_1^2 \rangle$. The excess mean square concentration fluctuation, $N\langle \Delta x_1^2 \rangle^E$ is related to molar excess Gibbs energy, G^E, by

$$N\langle \Delta x_1^2 \rangle^E = N\langle \Delta x_1^2 \rangle - N\langle \Delta x_1^2 \rangle^{id} \tag{2}$$

$$N\langle \Delta x_1^2 \rangle = \frac{x_1 x_2}{\left\{ 1 + (x_1 x_2/RT)(\partial^2 G^E/\partial x_1^2)_{T,p} \right\}} \tag{3}$$

$$N\langle \Delta x_1^2 \rangle^{id} = x_1 x_2 \tag{4}$$

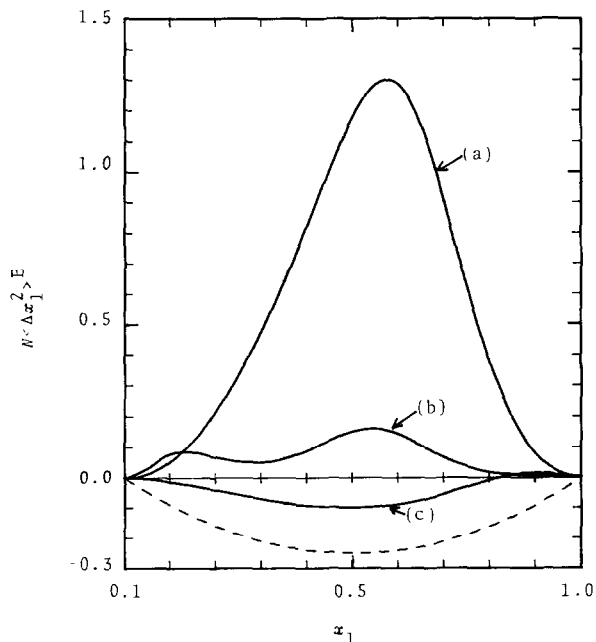where the superscript id indicates the thermodynamic ideal state.

Fig. 3. Excess mean square concentration fluctuation for binary liquid mixtures containing 2-propanone(1) at 298.15 K. Solid lines: (a), $C_3H_6O-C_7H_{16}$; (b) $C_3H_6O-C_6H_6$; (c) $C_3H_6O-CHCl_3$. The broken line denotes the zero fluctuation.

The excess molar Gibbs energies, G^E, in the literature [12,13] were those at different temperatures from 298.15 K. The values of G^E at 298.15 K were determined by using the following equation obtained from the Gibbs–Helmholtz relation

$$\frac{G^E(T_0)}{RT_0} = \frac{G^E(T^+)}{RT^+} - \frac{1}{R}\left\{\left(\frac{H^E(T_0)}{T_0} - C_p^E\right)\left(\frac{T_0}{T^+} - 1\right) + C_p^E \ln\left(\frac{T_0}{T^+}\right)\right\} \quad (5)$$

where the temperature dependence of C_p^E was assumed to be zero. H^E and C_p^E values from the previous [1] and the present reports were used. $N\langle\Delta x_1^2\rangle^E$ for the present mixtures are shown in Fig. 3.

As shown in Fig. 3, $N\langle\Delta x_1^2\rangle^E < 0$ except for $x_1 > 0.8$ in the C_3H_6O-CHCl$_3$ mixture. At $N\langle\Delta x_1^2\rangle = 0$, the local fluctuation of concentration does not occur and the negative $N\langle\Delta x_1^2\rangle^E$ means that the component molecules distribute homogeneously in solution due to the attractive intermolecular interaction between unlike molecules. The negative value for this mixture may not be as large as expected from the large negative H^E values for the mixture with hydrogen bonding between the unlike molecules but it seems not to be small relative to $N\langle\Delta x_1^2\rangle = 0$, and the minimum point of $N\langle\Delta x_1^2\rangle^E$ in Fig. 3 shifts to the lower composition of x_1. Such a result will not predict the $2:1$ associated species between the unlike molecules. We are interested in the similar composition behaviour of $N\langle\Delta x_1^2\rangle^E > 0$ to that of V^E. This

may suggest an excess gathering of like molecules and a decrease of the formation of hydrogen bonding between C_3H_6O and $CHCl_3$ molecules at $x_1 > 0.8$, although this should not be discussed in detail because of the lower confidence of the experimental G^E values in this region.

For the $C_3H_6O-C_6H_6$ mixture, the H^E values are slightly positive and it seems to be nearly an athermal solution. On the other hand, G^E is positive and larger than H^E [1,13]. Then, S^E will be negative, resulting in lower stabilization entropically in the mixing process. $N\langle \Delta x_1^2 \rangle^E$ is small and positive. This means an excess gathering of the component molecules in this mixture and leading to $C_p^E > 0$ at $x_1 < 0.4$. On the other hand, $H^E > 0$ over the whole composition range in this mixture. From this, C_p^E seems to reflect the solution state more strongly than does H^E.

C_p^E for the $C_3H_6O-C_7H_{16}$ mixture indicates an unusually complicated dependence with a point of inflection, especially in the dilute region of both the component liquids. Grolier et al. and Patterson et al. have found similar behaviour for the mixtures, for which G^E and H^E have extremely large positive values and the composition dependence of C_p^E has a "W-shape". They have discussed this in terms of cooperative induced molecular arrangement or non-randomness in the solution using the Guggenheim treatment [2–6,14]. The simple Guggenheim quasi-chemical treatment gives the expression for C_p^E

$$C_p^E = -Ax_1x_2 + B(x_1x_2)^2 \tag{6}$$

where A and B are coefficients representing the random and non-random terms, respectively. The larger non-random contribution tends to shift C_p^E to the more positive side. This contribution for the $C_3H_6O-C_7H_{16}$ mixture is 98.7% ($A = 0.68 \pm 0.2$, $B = 51.3 \pm 6.2$). This suggests high non-randomness in the solution state for this mixture.

$N\langle \Delta x_1^2 \rangle^E$ is large and positive in this mixture. This suggests a strong repulsive interaction between the unlike molecules and a large excess gathering of the component molecules. From a consideration of the G_{ij} integral by the Kirkwood–Buff theory [15], although we do not show the figure of the composition dependence of G_{ij}, C_3H_6O molecules seem to gather spontaneously and form the associated state in the region of $x_1 = 0.1$. On the other hand, C_7H_{16} molecules are excluded by the large number of C_3H_6O molecules in the region of $x_1 = 0.8$ because of the non-associative character in the C_7H_{16} molecules.

Excess partial molar isobaric heat capacities, $C_{p,i}^E$, are one of the most suitable thermodynamic functions used to observe the behaviour of the component species in the mixture. C_p^E will be represented by $C_{p,i}^E$

$$C_p^E = x_1 C_{p,1}^E + (1 - x_1) C_{p,2}^E \tag{7}$$

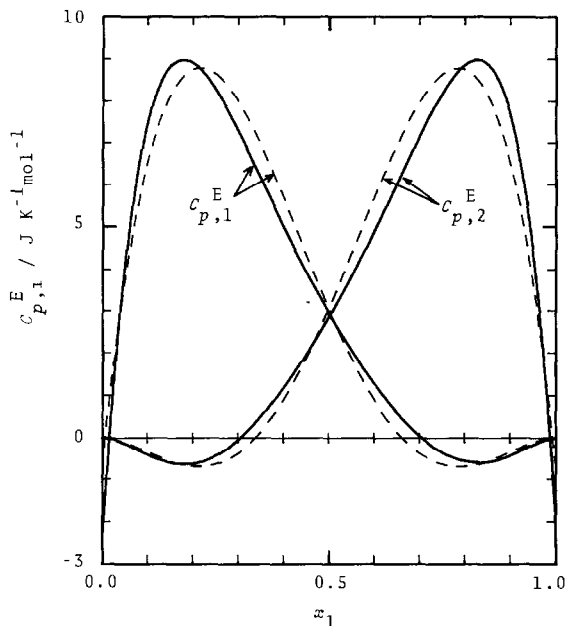$$= x_1 (C_{p,1} - C_{p,1}^*) + (1 - x_1)(C_{p,2} - C_{p,2}^*) \tag{8}$$

Fig. 4. Excess partial molar isobaric heat capacities for $C_3H_6O(1) + C_7H_{16}(2)$ mixture at 298.15 K. The solid lines were calculated using the A_i coefficients in Table 3. The broken lines were obtained by differentiating eqn. (6) with the parameters A and B given in the text.

where $C_{p,i}$ and $C_{p,i}^*$ are the partial molar isobaric heat capacity of the component i of the mixture and of the pure liquid, respectively.

Figure 4 shows $C_{p,i}^E$ for these mixtures calculated from the C_p^E results using the A_i coefficients of eqn. (1). $C_{p,i}^E > 0$ means that more energy is required to weaken the interaction between the component molecules i in the mixture than in the pure state with an increment of temperature. It is considered from the maximum values of $C_{p,1}^E$ at $x_1 = 0.2$ and $C_{p,2}^E$ at $x_1 = 0.8$ in the $C_3H_6O-C_7H_{16}$ mixture that most energy is required to weaken the interaction between the like component molecules in these regions of the mixture. It is qualitatively related to the gathering of the component molecules.

As shown in this figure, $C_{p,1}^E$ seems to be negative at the extreme dilution, though we have no experimental result. This suggests that C_3H_6O molecules are dispersed by the large amount of C_7H_{16} molecules at this region, and this is also supported by the similar composition dependence of $C_{p,i}^E$ obtained by differentiating eqn. (6).

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