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EXCESS THERMAL EXPANSION FACTORS OF POLAR MIXTURES AND AQUEOUS SOLUTIONS

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Abstract

Excess thermal expansion factor of non-polar mixtures is the order of 10^{-6} K^{-1} and within an experimental error. On the other hand, those of polar mixtures and aqueous solutions are very large and the order of 10^{-5} K^{-1}, up to the order of 10^{-4} K^{-1} in an extreme case. The excess thermal expansion factors express well the excesses of entropy volume cross fluctuation and enthalpy volume cross fluctuation estimated from thermal expansion factor and molar volume. Those of aqueous solutions are, however, reduced by small molar volume of water.

Keywords: aqueous solution, excess thermal expansion factor, polar mixture, the cross entropy volume fluctuation

Introduction

We have study thermodynamic properties of binary mixtures of polar solvent and aqueous solution of organic solvents. Our group were aware of the importance of excess expansion factor in the estimation of the isothermal compressibility from the isentropic compressibility about ten years ago. In the polar mixtures and aqueous solution the excess thermal expansion factor is very large and often reached to more than 10 percent of total value [1]. Consequently, the estimated values of isothermal compressibility by neglecting the excess thermal expansion factor is often deviated a several percent from the true value. Moreover, thermal expansion factor is a measure of fluctuation together with isothermal compressibility and heat capacity [2]. $RT\alpha<V_m>$ represents the entropy volume cross fluctuation and also $RT^2\alpha<V_m>$ represents the enthalpy volume cross fluctuation [3].

Results and discussion

The excess thermal expansion factor α^E is estimated by the following thermodynamically rigorous equation:

$$\alpha^E = [(\partial V_m^E/\partial T)_p - \alpha^{id} V_m^E]/(V_m^{id} + V_m^E) \qquad (1)$$

from the molar volumes, V_m, and the excess volumes, V_m^E, measured at a few different temperatures. In the case of the number of the measured temperatures less than four, $(\partial V_m^E/\partial T)_p$ is replaced by the temperature difference of excess volumes.

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The excess entropy volume cross fluctuation, Δ^E, is expressed by the following equation;

$$\Delta^E = (\alpha V_m - \alpha^{id} V_m^{id})RT \qquad (2)$$

where *id* represents ideal mixing. The excess enthalpy volume cross fluctuation is only multiplied by T and the curve is similar shape.

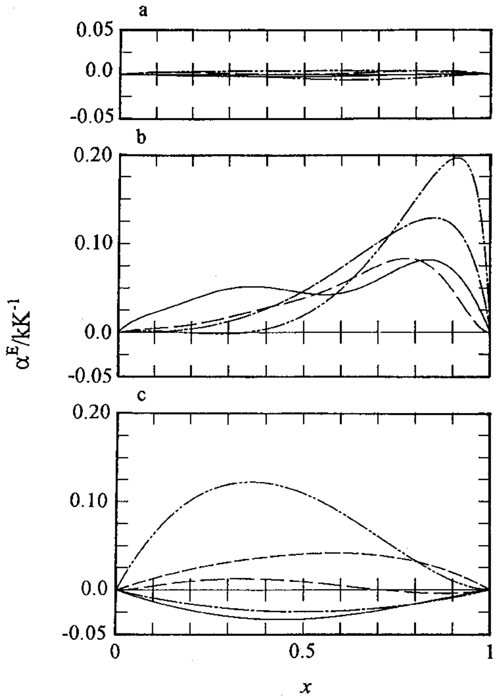

Fig. 1 Excess thermal expansion factors of the mixtures: (The scale of axis of a, b and c is the same to each other for the convenience)
a – non polar solutions:
— x cyclohexane+(1–x) benzene [1, 6]
– – x cyclohexane+(1–x) toluene [1, 7]
– . – x heptane+(1–x) benzene [1, 6]
– .. – x methylcyclohexane+(1–x) benzene [1, 7]
b – aqueous solutions:
— x water+(1–x) acetonitrile [1, 9]
– – x water+(1–x) dimethylsulfoxide [1, 11]
– . – x water+(1–x) ethoxyethanol [13]
– .. – x water+(1–x) isopropoxyethanol [14]
c – polar solutions:
— x cyclohexanone+(1–x) benzene [10]
– – x cyclohexanone+(1–x) cyclohexane [5]
– . – x cyclohexanone+(1–x) heptane [5]
– .. – x methoxyethanol+(1–x) cyclohexane [4]
- - - - x trifluoroethanol+(1–x) acetonitrile [8, 12]

The values of α, V_m, entropy volume cross fluctuation, Δ_{SV}, and enthalpy volume cross fluctuation, Δ_{HV}, of pure components are given in table for comparison with the amount of excess values.

Some of the excess thermal expansion factors already reported by us are plotted in Fig. 1. They are a) four non-polar mixtures, b) four aqueous solutions, and c) five polar mixtures, one of which is polar polar mixture.

Non-polar–non-polar mixtures show negligible amount of α^E, an order of 10^{-6} at maximum and the values are almost in the limit of experimental errors [1]. Since the accuracy of density is some of 10^{-6} at best and the estimated α is about unit of the order of 10^{-3} in many cases, then the digit of 10^{-6} of the ratio of densities is considered experimental error. Many of polar non polar mixtures show a considerable amount of α^E, an order of 10^{-5}, up to an order of 10^{-4}, which corresponds almost ten percent of total value of mixture, α. Polar polar mixture, however, reduced the value. On the other hand, aqueous solutions show large α^E declined to water-rich composition, more than 10^{-4} at maximum. Positive large value of α^E in water-rich region is originated to the breaking of the hydrogen bond network of water having in pure state and the ordinary expansiveness of water molecules free from the network.

The curves of the excess entropy volume cross fluctuation, Δ^E, are plotted in Fig. 2 a), b), and c). The curves of Δ^E are very similar to α^E, though the group of aqueous solutions are smaller than the group of polar solutions. The values of Δ^E of aqueous solutions are reduced by the smaller molar volume of water, especially, in the water-rich region, where α^E curve has a large peak.

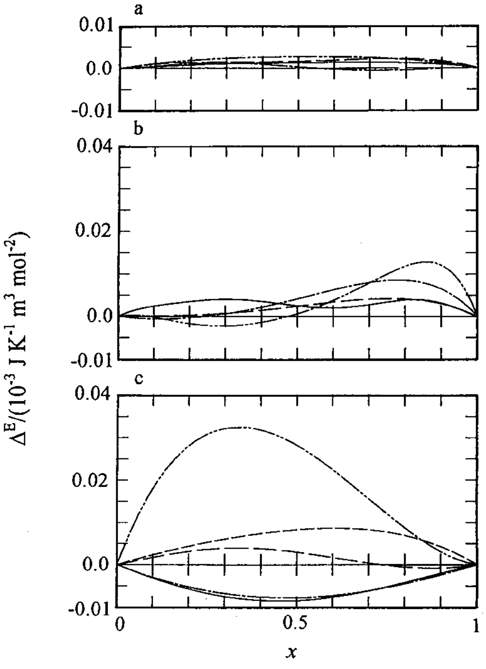

Fig. 2 Excess entropy volume cross fluctuations of the mixtures: notations are same as Fig. 1

Table 1 Molar volumes, V_m, thermal expansion factor, α, entropy volume cross fluctuation, Δ_{SV}, and enthalpy volume cross fluctuation, Δ_{HV}, of pure components

Component	V_m/(cm^3 mol^{-1})	α/kK^{-1}	Δ_{SV}/(J K^{-1} m^3 mol^{-2})	Δ_{HV}/(J m^3 mol^{-2})
Heptane	147.464	1.251	0.000457	0.136
Cyclohexane	108.756	1.220	0.000329	0.0981
Methylcyclohexane	128.355	1.156	0.000368	0.110
Benzene	89.411	1.228	0.000272	0.0812
Toluene	106.864	1.087	0.000288	0.0859
Cyclohexanone	104.202	0.966	0.000250	0.0744
Acetonitrile	52.866	1.368	0.000179	0.0535
Dimethylsulfoxide	71.339	0.998	0.000176	0.0526
Methoxyethanol	79.253	0.956	0.000188	0.0560
Ethoxyethanol	97.426	0.978	0.000236	0.0704
Isopropoxyethanol	115.764	1.010	0.000290	0.0864
Trifluoroethanol	72.336	1.450	0.000260	0.0775
Water	18.069	0.25705	0.0000115	0.00343

The increase of entropy volume cross fluctuation probably means the increment of the randomness of the direction of molecular interaction and the volume related to interaction field. On the other hand, the decrease of that also means the fixing the direction of molecular interaction or molecular orientation. The large peak of the aqueous solutions in water-rich region is reasonable that the hydrogen bond network existing in pure state of water is broken by mixing with the other component to separated water molecule. In the polar mixtures, methoxyethanol+cyclohexane mixture shows large and positive parabola one, and this mixture shows non-random mixing due to the concentration fluctuation producing phase separation at the temperature just below 298.15 K. This is an example that the concentration fluctuation causes a large Δ^E. The mixture {cyclohexanone+benzene} shows negative because of the formation of dipole-induce dipole interaction. The negative values of the mixture {cyclohexanone+heptane} may be due to some molecular orientational correlation. The values of the mixture {cyclohexanone+cyclohexane} change from positive to negative and are small as non-polar mixtures, positive region is due to the breaking of dipole interaction and negative region is due to the reorientation of dipole moments. The values of the mixture {trifluoroethanol+acetonitrile} are not so large that the breaking of dipolar interaction between like molecules is compensated by the formation of dipolar interaction between unlike molecules.

As the results, it is concluded that α^E well reflects the behavior of Δ^E and that α is reasonably representative of molecular orientational structure of mixtures or liquids. Positive α^E corresponds to the break-down of the molecular association or complex in pure states and negative one corresponds to the formation of molecular association or complex in mixtures.

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