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# Thermodynamic properties of the binary mixtures of cyclohexanone with globular species

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## Abstract

Excess heat capacities $C_p^E$ of the mixtures of cyclohexanone with toluene, chlorobenzene, methylcyclohexane and 1,4-dioxane and excess enthalpies $H^E$ of the mixtures with chlorobenzene and 1,4-dioxane were measured at 298.15 K. Density and speed of sound of the mixture of cyclohexanone with 1,4-dioxane were also measured at 298.15 K. Thermodynamic properties of the mixtures of cyclohexanone with globular solvents are discussed with reference to the heptane systems. $H^E$ of aliphatic systems is highly positive and their $C_p^E$ show various steps of W-shaped curves. $H^E$ of 1,4-dioxane system is positive but a third of aliphatic ones and its $C_p^E$ is negative. $H^E$ of aromatic systems is negative to form strong induced dipole–dipole interaction between aromatic and cyclohexanone molecules. $C_p^E$ of these systems changes from negative to positive with the increase of the mole fraction of aromatics. However that of chlorobenzene is large and has no negative part.

*Keywords:* Excess enthalpy; Excess isobaric heat capacity; Cyclohexanone mixtures; Globular solvents

## 1. Introduction

We have studied the effects of molecular shape and size on the thermodynamic properties of the mixtures. The shape and size of the components strongly affects the volumetric properties, such as excess volume and isentropic and isothermal compressibilities through the molecular packing. Globular polar molecule, cyclohexanone is rigid and bulky and results in small change in volume and compressibility on mixing [1–3]. In this paper, we make up the lack of thermal properties, excess enthalpy and excess heat capacity, of some systems reported on excess volume and isentropic compressibility and discuss on intermolecular interaction.

Thermodynamic properties of the mixtures of cyclohexanone with globular solvents, cyclohexane, methylcyclohexane, 1,4-dioxane, benzene, toluene, and chlorobenzene, are discussed with reference to heptane systems. The mixtures are classified into two groups; aliphatic systems, heptane as reference, cyclohexane, methylcyclohexane, and 1,4-dioxane, and aromatic systems, benzene, toluene, and chlorobenzene.

Excess heat capacities $C_p^E$ of the toluene, chlorobenzene, methylcyclohexane and 1,4-dioxane systems and excess enthalpies $H^E$ of the chlorobenzene and 1,4-dioxane systems were measured at 298.15 K. $C_p^E$ of the benzene [1] and cyclohexane [2] systems and $H^E$ of

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the benzene [4], toluene [4], cyclohexane [2], and methylcyclohexane [4] systems had been published. Excess volumes $V^E$ and excess isentropic compressibilities $\kappa_S^E$ of the mixtures except 1,4-dioxane system had also been published [1–3]. They are compared with the mixture of cyclohexanone+heptane system [2] too.

## 2. Experimental

Cyclohexanone, methylcyclohexane, 1,4-dioxane, toluene, and chlorobenzene were supplied from Wako Pure Chemical as special grade reagents and used by no further purification, the purity of solvents was determined by g.l.c. The purity of cyclohexanone was better than 99.8 mol%, that of methylcyclohexane better than 99.85 mol%, that of 1,4-dioxane better than 99.95 mol%, that of toluene better than 99.95 mol%, and that of chlorobenzene better than 99.96 mol%.

Excess enthalpies of mixtures were measured by a flow microcalorimeter (LKB 10700). The details of the measurement are described elsewhere [5].

Excess isobaric heat capacities of mixtures were measured by a flow microcalorimeter constructed in our laboratory of Osaka City University. The precision is better than ±0.01 J K$^{-1}$ mol$^{-1}$. The details of the measurement are described elsewhere [6].

Densities of the components and the mixture {$x$ 1,4-dioxane+(1−$x$)cyclohexanone} were measured by a vibrating-tube densimeter (Anton Paar DMA602). The accuracy is ±0.00001 g cm$^{-3}$ restricted by the accuracy of pycnometry of standard samples, and the reproducibility is ±0.000003 g cm$^{-3}$. The details of measurement are described elsewhere [7].

Speed of sound of the mixture {$x$ 1,4-dioxane+(1−$x$)cyclohexanone} was measured by a sing-around method. The accuracy is better than ±0.1 m s$^{-1}$ and the details of the measurement are described elsewhere [8].

The densities and isobaric heat capacities of pure components used are given in Table 1.

Table 1
The densities $\rho$ and isobaric heat capacities $C_p$ of pure components at 298.15 K

| Material | $\rho$ (g cm$^{-3}$) | $C_p$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|
| Cyclohexanone | 0.94204 | 177.97 [1] |
| Heptane [2] | 0.67957 | 224.75 |
| Cyclohexane [2] | 0.77385 | 156.01 |
| Methylcyclohexane | 0.76497 | 184.73 |
| 1,4-Dioxane | 1.02792 | 150.75 [9] |
| Benzene [1] | 0.87366 | 135.21 |
| Toluene | 0.86229 | 156.37 [10] |
| Chlorobenzene | 1.10114 | 149.33 |

## 3. Results and discussion

The values of $H^E$ obtained for the mixtures {$x$chlorobenzene+(1−$x$)cyclohexanone} and {$x$ 1,4-dioxane+(1−$x$)cyclohexanone} are given in Table 2 and the values of $C_p^E$ for the mixtures {$x$ methylcyclohexane+(1−$x$)cyclohexanone}, {$x$ 1,4-dioxane+(1−$x$)-cyclohexanone}, {$x$ toluene+(1−$x$)cyclohexanone}, and {$x$ chlorobenzene+(1−$x$)cyclohexanone} are given in Table 3. The values of density $\rho$ and speed of sound $u$ for the mixture {$x$ 1,4-dioxane+(1−$x$)-cyclohexanone} are given in Table 4, together with the values of excess volume $V^E$ and excess isentropic compressibility $\kappa_S^E$ obtained therefrom. The $\kappa_S^E$ is calculated by

$$\kappa_S = \frac{1}{(\rho u^2)} \tag{1}$$

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{2}$$

where superscript id means ideal mixing value and

$$\kappa_S^{id} = \kappa_T^{id} - (\alpha^{id})^2 V^{id} \frac{T}{C_p^{id}} \tag{3}$$

where $\kappa_T$ is isothermal compressibility, $\alpha$ is isobaric thermal expansivity, $V$ is molar volume, and $C_p$ is molar isobaric heat capacity. The ideal mixing values of them are

$$\kappa_T^{id} = \phi\kappa_{T,1} + (1-\phi)\kappa_{T,2} \tag{4}$$

$$\alpha^{id} = \phi\alpha_1 + (1-\phi)\alpha_2 \tag{5}$$

$$V^{id} = xV_1 + (1-x)V_2 \tag{6}$$

$$C_p^{id} = xC_{p,1} + (1-x)C_{p,2} \tag{7}$$

where $x$ and $\phi$ are the mole fraction and volume fraction of first component, and subscript 1 and 2 correspond to the first and second components, respectively. The volume fraction is defined by

$$\phi = \frac{xV_1}{V^{id}} \tag{8}$$

Table 2
Excess enthalpies of the mixtures {$x$ 1,4-dioxane+(1−$x$)cyclohexanone} and {$x$ chlorobenzene+(1−$x$)cyclohexanone} at 298.15 K

| $x$ | $H^E$ (J mol$^{-1}$) | $x$ | $H^E$ (J mol$^{-1}$) | $x$ | $H^E$ (J mol$^{-1}$) | $x$ | $H^E$ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $x$ 1,4-dioxane+(1−$x$)cyclohexanone | | | | | | | |
| 0.02500 | 22.4 | 0.25000 | 194.6 | 0.50001 | 277.8 | 0.75000 | 229.9 |
| 0.05000 | 46.1 | 0.30000 | 220.4 | 0.55001 | 279.7 | 0.80001 | 201.9 |
| 0.10001 | 90.2 | 0.35000 | 241.7 | 0.60000 | 275.7 | 0.84999 | 166.1 |
| 0.15001 | 129.3 | 0.40000 | 258.2 | 0.65000 | 266.3 | 0.89999 | 121.2 |
| 0.20001 | 164.0 | 0.45000 | 270.2 | 0.70000 | 251.1 | 0.95000 | 67.0 |
| | | | | | | 0.97500 | 35.2 |
| $x$ chlorobenzene+(1−$x$)cyclohexanone | | | | | | | |
| 0.02495 | −47.5 | 0.24962 | −409.3 | 0.49949 | −527.8 | 0.74963 | −379.6 |
| 0.04991 | −103.1 | 0.29958 | −452.7 | 0.54951 | −519.0 | 0.79967 | −320.3 |
| 0.09983 | −198.5 | 0.34955 | −488.4 | 0.59952 | −499.8 | 0.84974 | −252.8 |
| 0.14975 | −282.4 | 0.39952 | −512.5 | 0.64954 | −469.3 | 0.89981 | −176.4 |
| 0.19968 | −350.1 | 0.44051 | −525.5 | 0.69957 | −429.4 | 0.94990 | −92.4 |
| | | | | | | 0.97495 | −46.1 |

Table 3
Excess molar isobaric heat capacities of the mixtures containing cyclohexanone at 298.15 K

| $x$ | $C_p^E$ (J K$^{-1}$ mol$^{-1}$) | $x$ | $C_p^E$ (J K$^{-1}$ mol$^{-1}$) | $x$ | $C_p^E$ (J K$^{-1}$ mol$^{-1}$) | $x$ | $C_p^E$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $x$ methylcyclohexane+(1−$x$)cyclohexanone | | | | | | | |
| 0.02495 | 0.017 | 0.24960 | 0.748 | 0.49946 | 1.130 | 0.74959 | 0.829 |
| 0.04990 | 0.048 | 0.29955 | 0.887 | 0.54947 | 1.150 | 0.79965 | 0.756 |
| 0.09981 | 0.214 | 0.34951 | 0.969 | 0.59948 | 1.107 | 0.84972 | 0.510 |
| 0.14973 | 0.389 | 0.39948 | 1.059 | 0.64951 | 1.061 | 0.89981 | 0.350 |
| 0.19965 | 0.580 | 0.44946 | 1.102 | 0.69954 | 0.956 | 0.94990 | 0.184 |
| | | | | | | 0.97495 | 0.075 |
| $x$ 1,4-dioxane+(1−$x$)cyclohexanone | | | | | | | |
| 0.02500 | −0.164 | 0.25001 | −1.292 | 0.50001 | −1.511 | 0.75001 | −1.044 |
| 0.05000 | −0.325 | 0.30002 | −1.400 | 0.55001 | −1.467 | 0.80001 | −0.898 |
| 0.10001 | −0.651 | 0.35001 | −1.465 | 0.60001 | −1.389 | 0.85001 | −0.726 |
| 0.15001 | −0.921 | 0.40001 | −1.515 | 0.65001 | −1.290 | 0.90001 | −0.529 |
| 0.20001 | −1.132 | 0.45001 | −1.532 | 0.70001 | −1.172 | 0.95000 | −0.311 |
| | | | | | | 0.97500 | −0.178 |
| $x$ toluene+(1−$x$)cyclohexanone | | | | | | | |
| 0.02500 | −0.023 | 0.25001 | 0.473 | 0.50001 | 1.138 | 0.75001 | 1.261 |
| 0.05000 | −0.024 | 0.30001 | 0.622 | 0.55001 | 1.237 | 0.80000 | 1.145 |
| 0.10000 | 0.056 | 0.35001 | 0.758 | 0.60001 | 1.304 | 0.85000 | 1.007 |
| 0.15000 | 0.176 | 0.40001 | 0.891 | 0.65001 | 1.337 | 0.90000 | 0.795 |
| 0.20001 | 0.318 | 0.45001 | 1.015 | 0.70001 | 1.316 | 0.95000 | 0.463 |
| | | | | | | 0.97500 | 0.237 |
| $x$ chlorobenzene+(1−$x$)cyclohexanone | | | | | | | |
| 0.02500 | 0.148 | 0.25000 | 1.512 | 0.50000 | 2.040 | 0.75000 | 1.557 |
| 0.05000 | 0.307 | 0.30000 | 1.708 | 0.55000 | 2.026 | 0.80000 | 1.331 |
| 0.10000 | 0.656 | 0.35000 | 1.856 | 0.60000 | 1.971 | 0.85000 | 1.095 |
| 0.15000 | 0.959 | 0.40000 | 1.957 | 0.65000 | 1.866 | 0.90000 | 0.818 |
| 0.19991 | 1.265 | 0.45000 | 2.019 | 0.70000 | 1.734 | 0.95000 | 0.470 |
| | | | | | | 0.97500 | 0.239 |

Table 4
Densities, speeds of sound, excess volumes and excess isentropic compressibilities of the mixture {$x$ 1,4-dioxane+(1−$x$)cyclohexanone} at 298.15 K

| $x$ | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $V^E$ (cm$^3$ mol$^{-1}$) | $\kappa_S^E$ (TPa$^{-1}$) |
|---|---|---|---|---|
| 0 | 0.942017 | 1407.60 | | |
| 0.02662 | 0.943665 | 1405.55 | 0.0268 | 0.51 |
| 0.05232 | 0.945266 | 1403.57 | 0.0530 | 1.01 |
| 0.10313 | 0.948565 | 1399.73 | 0.0949 | 1.88 |
| 0.16023 | 0.952369 | 1395.37 | 0.1391 | 2.85 |
| 0.16726 | 0.952842 | 1394.91 | 0.1446 | 2.92 |
| 0.21422 | 0.956113 | 1391.45 | 0.1729 | 3.58 |
| 0.26816 | 0.959954 | 1387.58 | 0.2036 | 4.24 |
| 0.37646 | 0.968118 | 1380.05 | 0.2430 | 5.21 |
| 0.43149 | 0.972516 | 1376.45 | 0.2508 | 5.41 |
| 0.47999 | 0.976480 | 1373.04 | 0.2566 | 5.79 |
| 0.53387 | 0.981063 | 1369.59 | 0.2542 | 5.83 |
| 0.58731 | 0.985730 | 1366.24 | 0.2493 | 5.83 |
| 0.63776 | 0.990340 | 1363.01 | 0.2341 | 5.74 |
| 0.68455 | 0.994691 | 1360.42 | 0.2210 | 5.40 |
| 0.74899 | 1.000955 | 1356.74 | 0.1907 | 4.80 |
| 0.80139 | 1.006214 | 1353.95 | 0.1626 | 4.21 |
| 0.86299 | 1.012607 | 1350.74 | 0.1242 | 3.25 |
| 0.88282 | 1.014757 | 1349.86 | 0.1071 | 2.88 |
| 0.92461 | 1.019324 | | 0.0731 | |
| 0.97512 | 1.025031 | 1345.74 | 0.0258 | 0.69 |
| 0.99529 | 1.027379 | 1344.96 | 0.0042 | 0.10 |
| 1 | 1.027921 | 1344.73 | | |

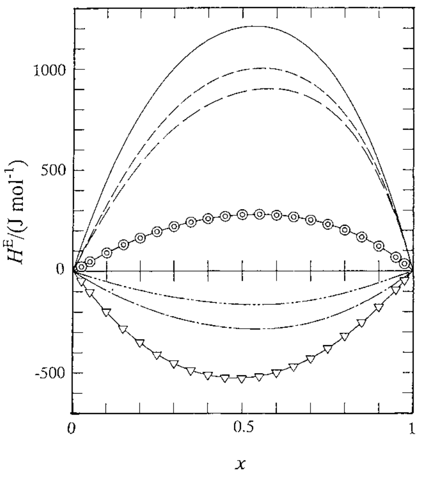

Fig. 1. Excess molar enthalpies of the mixtures at 298.15 K. ——, {$x$ heptane+(1−$x$)cyclohexanone} [2]; — —, {$x$ cyclohexane+(1−$x$)cyclohexanone} [2]; – – –, {$x$ methylcyclohexane+(1−$x$)cyclohexanone} [4]; ◎, {$x$ 1,4-dioxane+(1−$x$)cyclohexanone}; — · —, {$x$ benzene+(1−$x$)cyclohexanone} [4]; — ·· —, {$x$ toluene+(1−$x$)cyclohexanone} [4]; and ▽, {$x$ chlorobenzene+(1−$x$)cyclohexanone}.

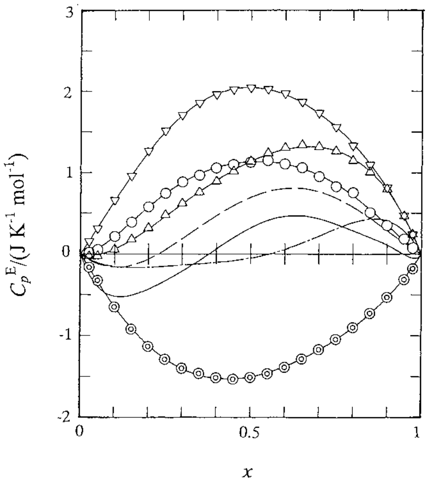

Fig. 2. Excess molar isobaric heat capacities of the mixtures at 298.15 K. ——, {$x$ heptane+(1−$x$)cyclohexanone} [2]; — —, {$x$ cyclohexane+(1−$x$)cyclohexanone} [2]; ○, {$x$ methylcyclohexane+(1−$x$)cyclohexanone}; ◎, {$x$ 1,4-dioxane+(1−$x$)cyclohexanone}; — · —, {$x$ benzene+(1−$x$)cyclohexanone} [1]; △, {$x$ toluene+(1−$x$)cyclohexanone}; and ▽, {$x$ chlorobenzene+(1−$x$)cyclohexanone}.

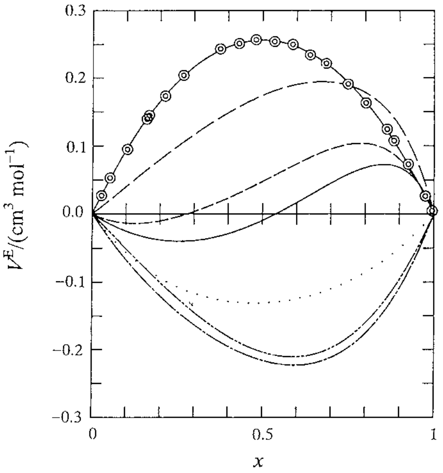

Fig. 3. Excess molar volumes of the mixtures at 298.15 K. ——, {$x$ heptane+(1−$x$)cyclohexanone} [2]; — —, {$x$ cyclohexane+(1−$x$)cyclohexanone} [3]; – – –, {$x$ methylcyclohexane+(1−$x$)cyclohexanone} [3]; ◎, {$x$ 1,4-dioxane+(1−$x$)cyclohexanone}, — · —, {$x$ benzene+(1−$x$)cyclohexanone} [1]; — ·· —, {$x$ toluene+(1−$x$)cyclohexanone} [3]; and ····, {$x$ chlorobenzene+(1−$x$)-cyclohexanone} [3].

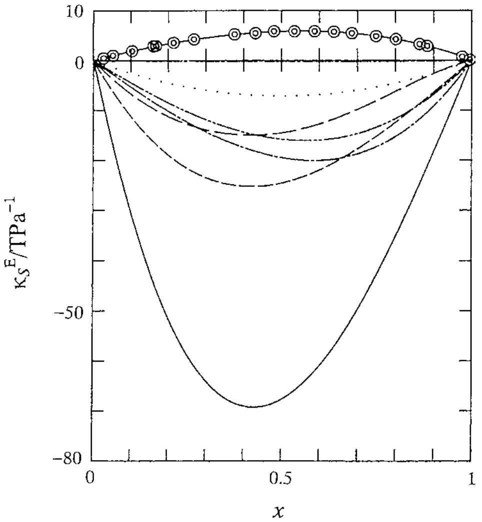

Fig. 4. Excess isentropic compressibilities of the mixtures at 298.15 K. ——, {$x$ heptane+(1−$x$)cyclohexanone} [2]; — —, {$x$ cyclohexane+(1−$x$)cyclohexanone} [3]; – – –, {$x$ methylcyclohexane+(1−$x$)cyclohexanone} [3]; ◎, {$x$ 1,4-dioxane+(1−$x$)-cyclohexanone}, – · –, {$x$ benzene+(1−$x$)cyclohexanone} [1]; – ·· –, {$x$ toluene+(1−$x$)cyclohexanone} [3]; and ····, {$x$ chlorobenzene+(1−$x$)cyclohexanone} [3].

In the calculations of $\kappa_S^E$, the values of $\alpha$ of the pure components of the 1,4-dioxane system measured at present time are 0.001115 $\mathrm{K^{-1}}$ for 1,4-dioxane and 0.000955 $\mathrm{K^{-1}}$ for cyclohexanone [11].

The values of $H^E$, $C_p^E$, $V^E$, and $\kappa_S^E$ are plotted in Figs. 1–4, respectively, together with the smoothed curves calculated by Redlich–Kister type equation.

$$H^E \text{ or } C_p^E \text{ or } V^E \text{ or } \kappa_S^E = x(1-x)\Sigma A_i(1-2x)^{i-1} \tag{9}$$

where $x$ is mole fraction of the first component, and the fitting parameters $A_i$ are determined by a least square method. Parameters are given in Table 5, together with estimated standard deviation $s$.

Table 5
Parameters and standard deviation of Eq. (9)

| | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $A_5$ | $S$ |
|---|---|---|---|---|---|---|
| $x$ methylcyclohexane+(1−$x$)cyclohexanone | | | | | | |
| $C_p^E$ | 4.535 | −0.361 | −0.432 | −0.976 | −2.769 | 0.018 |
| $x$ 1,4-dioxane+(1−$x$)cyclohexanone | | | | | | |
| $H^E$ | 1108.8 | −171.1 | 97.0 | −76.9 | | 0.5 |
| $C_p^E$ | −6.018 | −1.559 | −0.851 | 1.200 | | 0.013 |
| $V^E$ | 1.0237 | 0.0073 | 0.0206 | | | 0.0014 |
| $\kappa_S^E$ | 23.15 | −4.49 | 1.81 | | | 0.04 |
| $x$ toluene+(1−$x$)cyclohexanone | | | | | | |
| $C_p^E$ | 4.568 | −3.876 | 0.145 | −1.752 | | 0.015 |
| $x$ chlorobenzene+(1−$x$)cyclohexanone | | | | | | |
| $H^E$ | −2104.0 | −153.7 | | | | 2.3 |
| $C_p^E$ | 8.184 | 0.218 | −0.108 | −2.086 | | 0.013 |

The mixtures are classified into two groups; mixing with aliphatic non-polar solvents, heptane, cyclohexane, methylcyclohexane, and 1,4-dioxane, and mixing with aromatic solvents, benzene, toluene, and chlorobenzene.

$H^E$ of aliphatic systems is very large and positive, as shown in Fig. 1. The $C_p^E$ curves of them show the various steps of W shaped curve, as shown in Fig. 2, from a typical W shaped curve for heptane system to the one having no negative part but negative curvatures in both sides for methylcyclohexane system. That of cyclohexane system is intermediate one having a small negative part in cyclohexanone rich region. The large and positive $H^E$ and W-shaped $C_p^E$ indicate 'non-randomness' proposed by Patterson et al. [12]. These systems are considered to be non-random mixing that the gathering of the cyclohexanone molecules by a very strong dipole–dipole interaction between them makes local concentration fluctuate. The degree of positive tendency in the middle region of negative $C_p^E$ may express the extent of the non-randomness, which is in order of cyclohexane>methylcyclohexane>heptane systems.

Excess volume $V^E$ of all systems is rather small, as shown in Fig. 3. The molecular packing in the mixtures hardly changes from that in pure state because of the similarity of molecular shape of the components. The values of $V^E$ of aliphatic systems change the sign from negative to positive with the decrease of mole fraction of cyclohexanone, though cyclohexane system shifts to positive and has no negative part. The more favorite orientation for dipole–dipole interaction of cyclohexanone molecules increases in the mixture by the lubrication effect of opposite components on the packing of cyclohexanone molecules in the cyclohexanone-rich region, which results in the negative $V^E$.

Excess isentropic compressibility $\kappa_S^E$ of the systems except the 1,4-dioxane system is negative and is small except the heptane system. The globular molecule systems show small $\kappa_S^E$ because of the reason described in $V^E$ and is negative because the rigid globular molecules may be less compressible. The large negative $\kappa_S^E$ of heptane system may be due to the molecular correlation of orientation; the flexible heptane molecules squeeze to the room formed by globular cyclohexanone and the mixture is not afford to be compressed.

$H^E$ of 1,4-dioxane system is positive but a third of aliphatic ones and its $C_p^E$ is negative. At a glance, this system is an ordinary non-polar mixture, which shows positive $H^E$ and negative $C_p^E$. 1,4-Dioxane used to be classified under non-polar solvent, but the local dipole moment due to ether groups of 1,4-dioxane molecule makes the dipole–dipole interaction between cyclohexanone molecules weak by interacting with the dipole of cyclohexanone molecules. Then, it seems like a random mixing of a weak polar solvent with non-polar liquid.

Positive $V^E$ of 1,4-dioxane corresponds with positive $H^E$, and $\kappa_S^E$ is also positive and extremely small. 1,4-Dioxane system is less compressible because the solid molecular packing due to dipolar interaction between both globular solid components. These are consistent with the above interpretations.

On the other hand, $H^E$ of aromatic systems is negative because of the formation of the stronger induced dipole–dipole interaction between aromatic and cyclohexanone molecules, as shown in Fig. 1. Molecular polarization of toluene is slightly larger than that of benzene but it may be canceled out by the hindrance of bulky methyl group. Then the negativity of $H^E$ is in the order of chlorobenzene>benzene>toluene. $C_p^E$ of the benzene and toluene systems changes the sign from negative to positive with the increase of the mole fraction of aromatics, however that of chlorobenzene is large and positive. The magnitude of $C_p^E$ of these systems is in the order of chlorobenzene>toluene>benzene according to the strength of the molecular interaction formed between aromatic and cyclohexanone molecules in the most favorable orientation of molecules, that is, molecular polarization. As temperature rises, the induced dipole–dipole interaction formed more in aromatics rich region is broken to absorb heat and then $C_p^E$ becomes positive. In the cyclohexanone rich region, the dipole–dipole interaction between cyclohexanone in pure state is broken by mixing but aromatics is not enough to form thoroughly an induced dipole–dipole interaction, then $C_p^E$ shows negative due to a random orientation of dipoles.

The values of $V^E$ of aromatic systems are negative in the whole concentration range. Attractive interaction makes unlike molecules draw near to each other. The order of negativity is benzene>toluene>chlorobenzene, corresponding to the bulkiness of substitute groups for molecular packing. According to negative

$V^E$, the values of $\kappa_S^E$ of these systems are also negative and the order of negativity is the same.

As conclusions, the properties related to the core volume of all systems mixing with globular solvents are small and less compressible, because of the rigid and bulky shape of both globular components in comparison with heptane system. Globular molecule seems to enhance the non-randomness of mixing state than linear molecule, when globular cyclohexanone is mixed with them. 1,4-Dioxane is not a normal non-polar solvent. It interacts with dipole moment of polar components through the local dipole moments due to bond dipoles of ether binding.

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