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ENTHALPIES OF DILUTION AND HOMOTACTIC ENTHALPIC INTERACTION COEFFICIENTS OF THF AND 1,4-DIOXANE AT 298.15 K

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Enthalpies of dilution at 298.15 K of aqueous solutions of THF and 1,4-dioxane have been determined using flow microcalorimetry. The results obtained were used to determine the homotactic enthalpic interaction coefficients that characterize pair interactions of THF and 1,4-dioxane in aqueous solution. These are briefly discussed from the point of view of intermolecular interaction between the hydrated solute species.

Keywords: *1,4-dioxane, homotactic enthalpic interaction coefficient, hydrated solute species, THF*

Introduction

Heterocyclic compounds exist extensively in nature, such as in the chlorophyl of plants and hemachrome of animals. Many alkaloids and important natural products contain one or more heterocycles. Thus, the importance of studying the thermodynamic properties of heterocyclic compounds is apparent; however, the great structural diversity of heterocycles makes this a daunting challenge. Tetrahydrofuran (THF) and 1,4-dioxane are both two kinds of heterocyclic compound containing oxygen atom familiar to all of us.

The study of hydrophobic hydration and hydrophobic ‘non-bonding’ solute-solute interactions is an important step for understanding several phenomena in biological systems. Enthalpic pairwise interaction coefficients of the virial expansion of the excess enthalpies are particularly useful for obtaining information about the interaction mechanism [1–4]. They can be easily derived from enthalpies of dilution of binary solutions [5–10]. The physical meaning of the pair interaction coefficient of an excess property is linked to the variation of the thermodynamic property when two hydrated molecules ate brought from an infinite distance, where solute–solvent interactions prevail, to a finite distance where solute–solute, water-mediated interactions are operating [11].

As an extension to our previous study [9, 12–18], in this paper the enthalpies of dilution in water of binary aqueous solutions of THF and 1,4-dioxane have been reported. According to the excess enthalpy concept, the homotactic enthalpic coefficients of interactions between THF or 1,4-dioxane molecules in aqueous solution have been obtained. The analysis of the enthalpic coefficients obtained leads to a better understanding of the behavior of the binary solutions of THF and 1,4-dioxane.

Experimental

Materials

Analytical reagent grade (with a mole fraction purity >99%), THF and 1,4-dioxane were used without any pretreatment. The water used for the preparation of solutions was deionized and distilled using a quartz sub-boiling purifier. Both THF and 1,4-dioxane aqueous solutions were prepared immediately before the microcalorimetric experiment by mass with a Mettler AE 200 balance with a precision of (±0.0001 g).

Instrumentation and methods

The calorimetric system was a 2277-Thermal Activity Monitor produced by Thermometric AB (Thermometric AB is a company in Stockholm, Sweden, working in the field of thermal measurements) [19]. The 2277-Thermal Activity Monitor is an isothermally thermostated 23 L water bath holding up to four independent calorimetric units and operating at working temperatures between 10 to 90°C. With an external water circulator, its stability over 24 h is better than $\pm 10^{-4}$°C. This monitor is very sensitive, the detection limit is 0.15 μW and the baseline stability (over a period of 24 h) is 0.20 μW.

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The calorimetric measurements were performed by a 2277-Thermal Activity Monitor. All measurements were carried out at 298.15±0.01 K. Errors in the determinations of the molar enthalpies of dilution and mixing were estimated to be <1%. The solutions were pumped into the mixing cell of the calorimeter by two LKB-2132 microperpex peristaltic pumps. The variation in flow rates was less than 0.1% both before and after a complete dilution experiment. The flow rates were determined by weighing the masses of the liquids through each pump within 8 min. The liquid passing through pumps A and B were changed in the following sequence:

- A (water)+B (water) baseline determined
- A (aqueous pyridine or methylpyridine solution)+B (water) dilution thermal power determined
- A (water)+B (water) baseline re-established

The molar dilution enthalpies $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ (J kg^{-1}) were calculated by the equation

$$\Delta_{\mathrm{dil}}H_{\mathrm{m}}=P(1+m_{\mathrm{i}}M)/m_{\mathrm{i}}f_2 \qquad (1)$$

P is the dilution thermal power (μW), m_{i} is the initial molality of the solution (mol kg^{-1}), M is the molar mass of THF or 1,4-dioxane (kg mol^{-1}) and f_2 is the flow rate of THF or 1,4-dioxane solution (mg s^{-1}). The final molality m_{f} was calculated from the equation

$$m_{\mathrm{f}}=m_{\mathrm{i}}f_2/[f_1(m_{\mathrm{i}}M_2+1)+f_2] \qquad (2)$$

f_1 is the flow rate of water.

Results and discussion

The thermodynamic procedures used, which are based on the excess function concept, have been described previously [20–22] and only a summary will be given here. The excess enthalpy, h^{E}, for a binary aqueous solution can be defined as [23]

$$h^{\mathrm{E}}=h-h_{\mathrm{W}}^{*}-mH_2 \qquad (3)$$

where h the absolute enthalpy, and h^{E} both refer to an amount of solution containing 1 kg of water and m moles of the solute. h_{w}^{*} is the standard enthalpy of 1 kg of water and H_2 is the partial molar enthalpy of the solute at infinite dilution. h^{E} can be expressed as a virial expansion of the molality [24, 25]

$$h^{\mathrm{E}}=h_{\mathrm{xx}}m^2+h_{\mathrm{xxx}}m^3+h_{\mathrm{xxxx}}m^4+\ldots \qquad (4)$$

where h_{xx}, etc., are homotactic interaction coefficients that represent, at least notionally, interactions between the subscribed species. For the dilution of a solution of initial molality m_{i} to give a solution of final molality m_{f}, the molar enthalpy of dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ is given by [25, 26]

$$\Delta_{\mathrm{dil}}H_{\mathrm{m}}=[h^{\mathrm{E}}(m_{\mathrm{f}})/m_{\mathrm{f}}]-[h^{\mathrm{E}}(m_{\mathrm{i}})/m_{\mathrm{i}}] \qquad (5)$$

where $h^{\mathrm{E}}(m_{\mathrm{f}})$ is the excess enthalpy for the solution of molality m_{f} and $h^{\mathrm{E}}(m_{\mathrm{i}})$ is that for the solution of molality m_{i}. From Eqs (4) and (5), it follows that

Table 1 Enthalpies of dilution of aqueous THF and 1,4-dioxane solutions at 298.15 K

m_{i}/	m_{f}/	$\Delta_{\mathrm{dil,exp}}H_{\mathrm{m}}$/	$\Delta_{\mathrm{dil,calc}}H_{\mathrm{m}}$/	m_{i}/	m_{f}/	$\Delta_{\mathrm{dil,exp}}H_{\mathrm{m}}$/	$\Delta_{\mathrm{dil,calc}}H_{\mathrm{m}}$/
mol kg^{-1}		J mol^{-1}		mol kg^{-1}		J mol^{-1}	
THF							
0.1000	0.0493	–74.0 (0.74)	–71.4	0.3200	0.1564	–221 (2.20)	–220
0.1500	0.0737	–99.1 (0.99)	–102	0.3500	0.1708	–243 (2.42)	–242
0.1800	0.0884	–119 (1.19)	–121	0.3800	0.1853	–259 (2.60)	–265
0.2000	0.0981	–134 (1.34)	–135	0.4000	0.1949	–276 (2.76)	–280
0.2200	0.1079	–146 (1.46)	–149	0.4200	0.2045	–294 (2.95)	–295
0.2500	0.1225	–173 (1.73)	–169	0.4500	0.2189	–321 (3.21)	–318
0.2800	0.1370	–194 (1.94)	–191	0.5000	0.2427	–356 (3.55)	–356
0.3000	0.1467	–208 (2.08)	–205				
1,4-dioxane							
0.1000	0.0493	–62.4 (0.63)	–61.4	0.3200	0.1562	–187 (1.87)	–186
0.1500	0.0737	–88.0 (0.88)	–89.2	0.3500	0.1706	–206 (2.07)	–204
0.1800	0.0884	–105 (1.06)	–106	0.3800	0.1849	–218 (2.18)	–221
0.2000	0.0981	–116 (1.16)	–118	0.4000	0.1945	–230 (2.31)	–232
0.2200	0.1078	–131 (1.30)	–129	0.4200	0.2041	–241 (2.42)	–244
0.2500	0.1224	–146 (1.45)	–146	0.4500	0.2183	–262 (2.62)	–261
0.2800	0.1369	–162 (1.63)	–163	0.5000	0.2421	–289 (2.89)	–289
0.3000	0.1465	–176 (1.77)	–175				

*m_{i} and m_{f} are the initial and final molalities of solute; **The values in parentheses are the experimental errors

Table 2 Homotactic enthalpic interaction coefficients of THF and 1,4-dioxane in pure water at 298.15 K

Compounds	$h_{xx}\cdot 10^2$/J kg mol^{-2}	$h_{xx}\cdot 10^2$/J kg^2 mol^{-3}	$h_{xxxx}\cdot 10^2$/J kg^3 mol^{-4}	R^2	SD
THF	9.6	7.8	–5.2	0.9989	3.2
1,4-dioxane	11	15	–1.6	0.9995	1.8

*SD: Standard derivation; R^2: Square of relation coefficient

$$\Delta_{\rm dil} H_{\rm m} = h_{\rm xx}(m_{\rm f} - m_{\rm i}) + \\ + h_{\rm xxx}(m_{\rm f}^2 - m_{\rm i}^2) + h_{\rm xxxx}(m_{\rm f}^3 - m_{\rm i}^3) + \ldots \tag{6}$$

or

$$\Delta_{\rm dil} H_{\rm m} / (m_{\rm f} - m_{\rm i}) = h_{\rm xx} + h_{\rm xxx}(m_{\rm f} + m_{\rm i}) + \\ + h_{\rm xxxx}(m_{\rm f}^2 + 2m_{\rm f} m_{\rm i} + m_{\rm i}^2) \tag{7}$$

Table 1 gives the experimental results obtained for the dilutions $\Delta_{\rm dil,exp}H_{\rm m}$ for THF and 1,4-dioxane aqueous solutions, together with the initial and final molalities. The results were fitted to Eq. (7) using the least-squares procedure. Values of the homotactic enthalpic interaction coefficients of THF and 1,4-dioxane in water are collected in Table 2. The calculated values $\Delta_{\rm dil,cal}H_{\rm m}$ according to Eq. (6) are also listed in Table 1.

It is generally accepted that the excess enthalpies, and hence the *h* coefficients, are attributable to the solvent-mediated interactions between solvated solute molecules [27]. In the discussion that follows, attention will be directed only to the pairwise coefficients $h_{\rm xx}$, for reasons that can be interpreted relatively easily.

The process of interaction of two solvated species can be represented as consisting of two successive stages: the partial dehydration of the solutes and the further direct interaction caused by the short-range molecular forces [28, 29]. Among them, the direct solute–solute interaction plays the dominant role in the process of interaction. The direct interaction between the homotactic molecules of THF or 1,4-dioxane comprises three kinds of interactions: (a) the hydrophobic–hydrophobic interaction between the rings, making positive contributions to $h_{\rm xx}$; (b) the hydrophobic–hydrophilic interaction between the ring and the ether oxygen atom, making positive contributions to $h_{\rm xx}$; (c) the hydrophilic–hydrophilic interaction between the ether oxygen atoms, making negative contributions to $h_{\rm xx}$.

In the binary solutions under investigation (THF+water and 1,4-dioxane+water), the enthalpic pairwise interaction coefficients, $h_{\rm xx}$, represent the result of the balance between the above effects. As can be seen from Table 2, the positive sign of $h_{\rm xx}$ coefficients is an indication that, upon homotactic interaction between THF or 1,4-dioxane molecules, endothermic processes play a predominant role. The relative magnitudes of $h_{\rm xx}$ are closely related with the differences in the structures of THF and 1,4-dioxane.

The oxygen atom of THF and 1,4-dioxane employs the hybrid mode of sp^2 and has a pair of lone-pair electrons. So to a certain extent, the THF and 1,4-dioxane molecules display hydrophilicity. It should be noted that THF is a polar molecule in itself. But 1,4-dioxane, an aprotic solvent, used to be classified under non-polar solvent [30]. It exhibits the polar property similar to 1,3-dioxane because of the local dipole moment caused by the bond dipole [31].

During the processes of homotactic interaction of THF and 1,4-dioxane, since both the two kinds of molecules have four methylene groups (–CH$_2$) in structures, interaction (a) may be roughly considered as equality. THF only has one ether oxygen atom (–O–), however, 1,4-dioxane has two. Compared with THF, interactions (b) and (c) increase for 1,4-dioxane. So the comparative magnitude of $h_{\rm xx}$ (1,4-dioxane) and $h_{\rm xx}$ (THF) depends on the competitive balance of the above two kinds of interactions. In water there exists $h_{\rm xx}$ (1,4-dioxane)>$h_{\rm xx}$ (THF), which indicates that the former effect is relatively stronger.

Conclusions

- The homotactic enthalpic pairwise interaction coefficients, $h_{\rm xx}$, between THF or 1,4-dioxane molecules show the differences in the total energetic effects of interactions between two identical molecules with the participation of water molecules. The experimentally observed positive values of $h_{\rm xx}$ indicate that endothermic processes are dominant during the homotactic interaction processes of THF or 1,4-dioxane.
- The relative magnitudes of $h_{\rm xx}$ values between THF or 1,4-dioxane are in the following order: $h_{\rm xx}$(1,4-dioxane)>$h_{\rm xx}$(THF), which can be attributed to the discrepancies of the structures of 1,4-dioxane and THF.

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References

1 H. L. Friedman and C. V. Krishnan, J. Solution Chem., 2 (1973) 119.

2 T. Kimura, M. A. Khan and T. Kamiyama, J. Therm. Anal. Cal., 85 (2006) 575.

3 T. Kimura, Y. Takahashi, T. Kamiyama and M. Fujisawa, J. Therm. Anal. Cal., 88 (2007) 587.

4 M. W. Rylik and W. Zielenkiewicz, J. Therm. Anal. Cal., 83 (2006) 607.

5 F. Franks, M. Pedley and S. Reid, J. Chem. Soc., Faraday Trans., 72 (1976) 1359.

6 G. Barone, G. Castronuovo, V. Elia and A. Menna, J. Solution Chem., 8 (1976) 152.

7 P. Fini and M. Castagnolo, J. Therm. Anal. Cal., 66 (2001) 91.

8 L. Li, L. Y. Zhu, X. M. Qiu, D. Z. Sun and Y. Y. Di, J. Therm. Anal. Cal., 89 (2007) 295.

9 Y. Li, H. Xingen, L. Ruisen and X. Guiying, J. Therm. Anal. Cal., 83 (2006) 269.

10 N. G. Manin, A. Fini, A. N. Manin and G. L. Perlovich, J. Therm. Anal. Cal., 90 (2007) 147.

11 G. Castronuovo, V. Elia and F. Velleca, J. Solution Chem., 25 (1996) 971.

12 S. Shuang, H. Xingen and L. Ruisen, Thermochim. Acta, 360 (2000) 93.

13 Y. Li, H. Xingen, L. Ruisen and X. Guiying, J. Chem. Thermodyn., 36 (2004) 481.

14 Y. Li, L. Ruisen, H. Xingen, Z. Honglin and X. Guiying, J. Chem. Eng. Data, 48 (2003) 990.

15 Y. Li, H. Xingen, L. Ruisen and X. Guiying, J. Solution Chem., 32 (2003) 273.

16 Y. Li, H. Xingen, L. Ruisen and X. Guiying, J. Therm. Anal. Cal., 76 (2004) 443.

17 L. Huaji, L. Ruisen and Z. Honglin, J. Chem. Eng. Data, 49 (2004) 416.

18 Y. Li, H. Xingen, L. Ruisen and X. Guiying, J. Solution Chem., 32 (2004) 131.

19 Z. Honglin, Y. Xiufang, L. Xiangyang, S. Haitao, N. Yi, W. Lili and L. Chengxue, J. Therm. Anal. Cal., 68 (2002) 931.

20 P. J. Cheek and T. H. Lilley, J. Chem. Soc., Faraday Trans., 84 (1988) 1927.

21 T. H. Lilley, E. Moses and I. R. Tasker, J. Chem. Soc., Faraday Trans. 1, 76 (1980) 906.

22 T. H. Lilley and I. R. Tasker, J. Chem. Soc., Faraday Trans., 78 (1982) 1.

23 H. L. Friedman and C. V. Krishnan, J. Solution Chem., 2 (1973) 119.

24 T. H. Lilley, Biochemical Thermodynamics, M. N. Jones, Ed., 2nd Edn., Elsevier, Amsterdam 1988, Chapter 1.

25 J. E. Desnoyers, G. Perron, L. Avedikan and J. P. Morel, J. Solution Chem., 5 (1976) 631.

26 G. Barone, G. Castronuovo, V. Crescenzi, V. Elia and E. Rizzo, J. Solution Chem., 7 (1978) 179.

27 H. Piekarski, J. Chem. Soc. Faraday Trans., 84 (1988) 591.

28 K. G. Davis and T. H. Lilley, Thermochim. Acta, 107 (1986) 267.

29 F. Franks and M. D. Pedley, J. Chem. Soc., Faraday Trans., 77 (1981) 1341.

30 K. Tamura and A. Osaki, Thermochim. Acta, 352–353 (2000) 11.

31 T. Takigawa, J. Chem. Thermodyn., 32 (2000) 1045.

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