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Enthalpies of mixing of tetrachloroethane with furan, methylfuran, tetrahydrofuran, cyclopentanone and 1,4-dioxane[☆]

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Abstract

Enthalpies of mixing of furan, methylfuran, tetrahydrofuran (THF), 1,4-dioxane and cyclopentanone with tetrachloroethane (TCE) were determined by microcalorimetry. All the systems were exothermic in nature, showing the following trend: THF > cyclopentanone > 1,4-dioxane > methylfuran > furan. Saturation of the ring led to a marked increase in the energy of intermolecular interaction. This was attributed to the specific interactions between oxygen and the H of TCE, oxygen and the Cl of TCE, and between the CH_2 group and the Cl of TCE. This hypothesis was confirmed by a downfield shift in the NMR spectra on addition of TCE to pure THF, 1,4-dioxane and cyclopentanone.

Keywords: Binary mixture; Enthalpy of complex formation; Enthalpy of mixing; Hydrogen bonding

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1. Introduction

In the investigations of intermolecular interactions between molecules having different functional groups and of the effect of structure on them, we have studied the aliphatic alcohols, aliphatic amines, aliphatic ethers, acetonitrile and chloroform systems [1–4]. In continuation, we have undertaken the study of binary mixtures of cyclic oxy-compounds.

The study of cyclic ethers such as furan, tetrahydrofuran (THF) and dioxane is of interest, not only because the compounds are of industrial importance, but also because

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their interactions are more pronounced than those of the aliphatic ethers, actually making them better solvents. Thus the enthalpy of mixing of diethyl ether with benzene shows an S-type curve for the H^E vs. X plot, having maximum values of the order of only $+22$ and $-25\,\mathrm{J\,mol^{-1}}$, whereas the enthalpy of mixing of THF with benzene is exothermic throughout the concentration range with a maximum value of $\approx -366\,\mathrm{J\,mol^{-1}}$ [5,6]. In the present investgation we have studied the enthalpies of mixing of 1,1,2,2-tetrachloroethane (TCE) with furan, methylfuran, THF, cyclopentanone and 1,4-dioxane. These systems were selected in order to find out the effect of substitution of a methyl group in the furan ring and that of saturation of the furan ring on the interactions. And also to establish the effect of one oxygen (THF) or two oxygens (dioxane) in the ring and oxygen outside the ring (cyclopentanone).

2. Experimental

Cyclopentanone and 1,4-dioxane (S.D. Chemicals AnalaR) were further purified by fractional distillation, and the constant boiling middle fraction was used for the experiment. Furan, methylfuran and THF (Fluka A.R.) were used without further purification. All the compounds were dried over freshly activated molecular sieve.

2.1. *Enthalpies of mixing*

The enthalpies of mixing were determined by means of a heat flux calorimeter (C-80 model from Setaram, France). Experimental details are given in an earlier communication [2]. The enthalpy of mixing of TCE + furan was measured at 298.15 K, and those of other systems were determined at 303.15 K.

2.2. *NMR*

The NMR spectra were recorded at room temperature by means of a Bruker WH 90 FT-NMR instrument with a data system.

3. Results and discussion

Enthalpies of mixing of TCE (1) with furan, methylfuran, THF, cylopentanone or 1,4-dioxane (2) are given in Table 1. The data were fitted to the least squares equation

$$\Delta H = X_1 X_2 \sum_{i=0}^{3} A_i (X_1 - X_2)^i \tag{1}$$

The least squares parameters and the standard deviations are given in Table 2. The plots of enthalpies of mixing as a function of the mole fraction x_1 of TCE are given in Fig. 1.

All the systems are exothermic in nature, and the electronic environment around the oxygen atom showed a marked effect on the enthalpies of mixing.

Table 1
Excess enthalpies of mixing of TCE with furan, methylfuran, THF, cyclopentanone and 1,4-dioxane

x_1	$\Delta H/(\mathrm{J\,mol^{-1}})$	x_1	$\Delta H/(\mathrm{J\,mol^{-1}})$
	Tetrachloroethane(1) + Furan(2)		
0.0445	−44	0.4722	−230
0.1097	−90	0.5938	−218
0.1545	−118	0.6712	−192
0.2878	−192	0.7812	−138
0.3698	−218	0.8972	−74
	Tetrachloroethane(1) + Methylfuran(2)		
0.0738	−67	0.6163	−476
0.1443	−155	0.6778	−448
0.4445	−274	0.7753	−354
0.3454	−381	0.8759	−203
0.4406	−451		
	Tetrachloroethane(1) + Tetrahydrofuran(2)		
0.0557	−659	0.5262	−3083
0.1139	−1242	0.6242	−2837
0.2289	−2181	0.7052	−2460
0.3134	−2614	0.8143	−1598
0.3850	−2942	0.8903	−948
0.4351	−3088	0.9531	−401
0.4665	−3094		
	Tetrachloroethane(1) + Cyclopentanone(2)		
0.0482	−420	0.4434	−2767
0.0914	−796	0.5625	−2784
0.1315	−1084	0.7181	−2188
0.2021	−1659	0.8000	−1668
0.3112	−2360	0.9303	−657
0.3868	−2681		
	Tetrachloroethane(1) + 1,4-Dioxane(2)		
0.0146	−129	0.5184	−2748
0.0517	−433	0.5419	−2742
0.1043	−903	0.6149	−2677
0.1394	−1190	0.7038	−2305
0.1879	−1446	0.7731	−1938
0.2905	−2079	0.8693	−1179
0.3986	−2530	0.9326	−653

The enthalpy of mixing of furan is small, $\approx -230\,\mathrm{J\,mol^{-1}}$ at the maximum, indicating only slight specific interaction between the furan and TCE molecules. The ether oxygen is a weak proton acceptor and can interact to form a hydrogen bond with a proton donor molecule. However, owing to the presence of two double bonds in the ring, the oxygen becomes less basic, and therefore the possibility of hydrogen bonding

Table 2
The least squares parameters for enthalpies of mixing of TCE (1) with furan, methylfuran, THF, cyclopentanone and 1,4-dioxane (2)

System	$A_0/(\mathrm{J\,mol^{-1}})$	$A_1/(\mathrm{J\,mol^{-1}})$	$A_2/(\mathrm{J\,mol^{-1}})$	$A_3/(\mathrm{J\,mol^{-1}})$	Std. Dev./ $(\mathrm{J\,mol^{-1}})$
Tetrachloroethane + furan	−905.26	39.75	52.92	119.24	3.9
Tetrachloroethane + methylfuran	−1982.7	−651.05	808.89	300.85	13.7
Tetrachloroethane + tetrahydrofuran	−12380.8	502.81	2109.39	1848.08	21.1
Tetrachloroethane + cyclopentanone	−11256.7	64.52	2180.55	−753.53	20.8
Tetrachloroethane + 1,4-dioxane	−10922.2	−1399.98	1680.20	1019.50	19.3

is much reduced. The enthalpy of mixing of methylfuran is a little higher than that of furan ($\Delta H_{\mathrm{max}} = -400\,\mathrm{J\,mol^{-1}}$). This is attributed to an increase in the basic character of the ether oxygen owing to the presence of an electron donor methyl group at the α-carbon atom. The effect of saturation of the furan ring is marked and the THF–TCE system is highly exothermic ($\Delta H_{\mathrm{max}} = -3100\,\mathrm{J\,mol^{-1}}$). The enthalpies of mixing of 1,4-dioxane and cyclopentanone are also highly negative. The highly exothermic mixing of these systems indicates strong specific interactions involving the heteromolecules. In these three systems, two types of interactions are expected. First, the hydrogen bonding between the hydrogen of TCE and the keto or ether oxygen. Hydrogen bonded complex formation of chloroform with tetrahydrofuran and dioxane has been reported [7,8]. In the present systems the interactions are more complicated than those with chloroform, as TCE (A) has two equivalent proton donors and can thus form AB and A_2 types of complexes with THF or cyclopentanone (B). In the case of dioxane, it can form AB, A_2B and AB_2 types of complexes.

It may be noted that the maximum heats of mixing for these three systems show the trend: THF > cyclopentanone > 1,4-dioxane. In the case of binary hydrogen bond forming systems the number of H-bonds formed, the enthalpy of H-bond formation and other specific interactions are the chief contributors to the enthalpy of mixing. As far as hydrogen bond formation is concerned, dioxane can form more numerous H-bonded species than THF owing to the presence of two oxygens. So from the viewpoint of H-bond formation the 1,4-dioxane system should be more exothermic than the THF system, but the reverse is observed. Wilhelm et al. [9,10] studied the heats of mixing of carboxylic acids with THF and 1,4-dioxane and found the same trend of interaction. This indicates that the interactions other than H-bonding contribute significantly to the enthalpies of mixing of these systems.

Dincer and Van Ness [11,12] determined the enthalpies of mixing of dichloromethane with THF and 1,4-dioxane. Both the systems were exothermic and the maximum enthalpy changes were −1343 and $-1080\,\mathrm{J\,mol^{-1}}$. In the case of tetra-

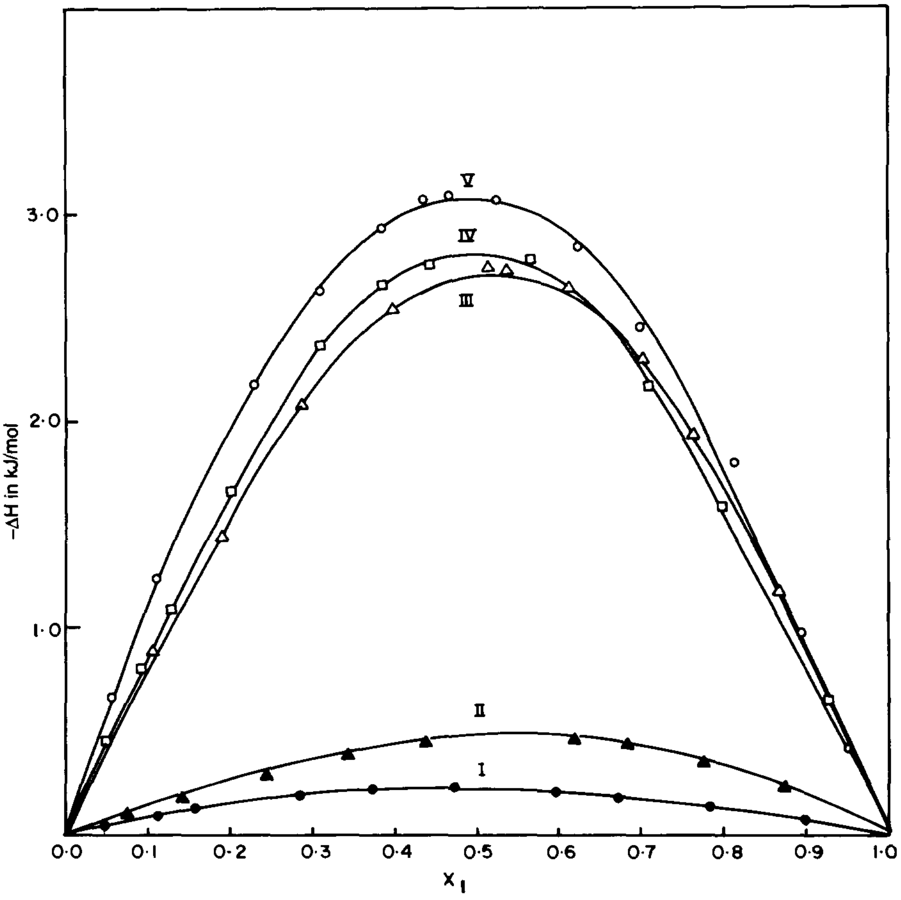

Fig. 1. ΔH vs. x_1 plots for tetrachloroethane TCE (1)+furan, methylfuran, THF, cyclopentanone and 1,4-dioxane (2): I, furan; II, methylfuran; III, 1,4-dioxane; IV, THF.

chloro systems, the maximum enthalpy changes are nearly twice that of dichloro systems. This clearly indicates that the chlorine atom makes a significant contribution to the energy of interaction. Williamson and co-workers [13, 14] investigated the ether + CCl_4, ether + $CHCl_3$ and ether + CH_2Cl_2 systems and quantified the relative strengths of O···H and O···Cl interactions.

Considering the fact that the small electronegativity difference (0.5) between O and Cl leads to specific interactions, there is a strong possibility of hydrogen bond-type specific interaction between the hydrogen of a cyclic ether and the Cl of TCE. In order to confirm the existence of such interaction, the NMR spectra of neat cyclopentanone, THF and 1,4-dioxane and those of 1:1 mixtures of these compounds with TCE were recorded at room temperature. In the case of 1,4-dioxane all four CH_2 groups are equivalent and a singlet is observed, whereas in the case of THF the CH_2 groups at positions 2 and 5 and those at positions 3 and 4 are equivalent, so a triplet and a pentate

Table 3
Proton chemical shifts in Hz[a] before and after addition of TCE (1 : 1 by volume) to cyclopentanone, THF and 1,4-dioxane

Compound	Neat	After addition	Shift
Cyclopentanone			
2, 5 carbon	154.0	192.8	38.8
3, 4 carbon	143.9	178.3	34.4
THF			
2, 5 carbon	308.7	340.0	31.3
3, 4 carbon	142.6	171.7	29.1
1,4 dioxane	303.9	337.4	34.5

[a] With respect to peak of HOD at 432.1 Hz.

are observed. A similar pattern is observed for cyclopentanone also. All the lines and their positions in hertz units are recorded in the spectra. The spectral lines for different protons of the neat samples and the positions of corresponding lines after addition of TCE in terms of Hz are given in Table 3. In the two sets of spectral recordings the position of the internal standard did not show any change. It may be noted that in the case of cyclopentanone the spectral line for protons at the 2 and 5 positions has moved downfield by 38.8 Hz, and that for the protons at the 3 and 4 positions has moved downfield by 35.4 Hz. In the case of THF the spectral lines for the protons at the 2 and 5 and at the 3 and 4 positions have moved downfield by 31.3 and 29.1 Hz respectively. In the case of 1,4-dioxane also, a downfield shift of 34.5 Hz is observed. This clearly establishes [15] the strong interactions between the protons of cyclopentanone, THF and 1,4-dioxane and the chlorine of TCE.

4. Conclusions

The interactions between cyclic ethers or ketones and chloro compounds are governed essentially by the saturation or unsaturation of the ring. When the ring is unsaturated, the interactions are weak and substitution of a methyl group at the α-carbon atom enhances the interactions. For cyclic ethers with a saturated ring, the interactions become many times stronger. In these systems not only the O···H and O···Cl interactions [14] but interactions between CH_2 groups and chlorine atoms contribute to the enthalpies of mixing. The interaction of TCE with aliphatic ketones is much stronger than with aliphatic ethers [4]. However, in the case of a cyclic ether or ketone, the interactions of hydrogen and chlorine atoms are so dominant that the presence of a functional group or the position of oxygen within or external to the ring does not make any significant difference to the enthalpy of mixing.

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