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# Thermodynamics of hydrogen-bonded complex formation in chloroform + cyclic ether mixtures [1]

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## Abstract

The molar excess enthalpies $H^E$ for the binary mixtures chloroform + oxolane, + 1,3-dioxolane, + oxane, + 1,4-dioxane, and + 1,3-dioxane have been measured as a function of mole fraction at atmospheric pressure and 298.15 K using a Picker flow microcalorimeter. The imprecision at the maximum value of $H^E$ is about ±0.5%. Values of $H^E$ were strongly negative for all mixtures. The magnitude and the symmetry of the $H^E$ curves depended on ring size and number of oxygen atoms. These results and the literature vapour pressure data for the chloroform + oxolane, chloroform + 1,3-dioxolane, and chloroform + 1,4-dioxane mixtures have been analyzed with the ideal associated solution model. The $A + B + AB + AB_2$ model, where complexes AB and $AB_2$ are expected to form by the simultaneous chemical equilibria $A + B \rightleftarrows AB$ and $A + 2B \rightleftarrows AB_2$, was used for the diether mixtures. The simpler association model $A + B + AB$ with formation of the AB complex was employed for the monoether mixtures. The equilibrium constants and enthalpies of formation of the AB and $AB_2$ complexes have been calculated from this analysis.

## INTRODUCTION

We have recently determined the thermodynamic properties ($H^E$, $C_p^E$, $V^E$) of binary mixtures formed by a cyclic ether with an organic solvent having specific structural and interactional properties [1–7] to provide information on the molecular interactions characteristic of pure cyclic ethers and their binary mixtures. The effects of ring size, number of oxygen atoms and their positions on these interactions were also investigated. Basic information has been obtained from the analysis of the thermodynamic properties of the cyclic ether + *n*-alkane, + cycloalkane, + benzene, + tetrachloromethane, + cyclohexene, and + 1,1,1-trichloroethane binary mixtures.

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This line of research has now been extended to mixtures in which the cyclic ethers act as bases and form hydrogen-bonded complexes. We have determined the molar excess volumes and molar excess heat capacities of chloroform + cyclic ether mixtures. Both the thermal and the volumetric data are indicative of strong intermolecular interactions through the formation of hydrogen-bonded complexes in all these mixtures.

This paper reports the molar excess enthalpies $H^E$ at 298.15 K of mixtures formed by chloroform with oxolane ($C_4H_8O$, tetrahydrofuran), 1,3-dioxolane (1,3-$C_3H_6O_2$), oxane ($C_5H_{10}O$, tetrahydropyran), 1,4-dioxane (1,4-$C_4H_8O_2$) and 1,3-dioxane (1,3-$C_4H_8O_2$).

Quantitative information on the strength of hydrogen bonds cannot be obtained directly from the $H^E$ values. We therefore combined our data with the vapour pressure measurements available in the literature [8,9] and calculated, using the ideal associated model proposed by McGlashan and Rastogi [10], the equilibrium constants and enthalpies of formation of the hydrogen-bonded complexes.

## EXPERIMENTAL

### *Materials*

All liquids were from Fluka. Oxolane (puriss., > 99.5 mol%), oxane (purum, > 99 mol%), 1,3-dioxolane (purum, > 99 mol%) and 1,4-dioxane (puriss., > 99.5 mol%) were further purified by fractional distillation over sodium wire and stored in the dark. Chloroform (puriss., 99.5 mol%) and 1,3-dioxane (purum, > 99 mol%) were used without further purification. All liquids were carefully dried with molecular sieves (Union Carbide type 4A, from Fluka) before use.

### *Calorimetry*

Molar excess enthalpies were measured with a Picker flow calorimeter [11–13] equipped with separators in the liquid feed system [14]. The calorimeter was used in the discontinuous mode [15] to obtain more precise values of $H^E$ and mole fraction. For each selected position of the two bent axis Picker pumps, the density of the solution at the exit of the calorimeter was measured by means of a vibrating tube densimeter (model 0.3, Sodev, Canada) mounted in series. In this way, the mole fractions were determined with greater accuracy than in the conventional method.

All measurements were carried out at 298.15 K and atmospheric pressure with the calorimeter thermostatted at ±0.005 K. The performance of the calorimeter was checked by determining the $H^E$ of some well investigated mixtures, such as tetrachloromethane + benzene and benzene +

TABLE 1

Experimental results of molar excess enthalpies $H^E$ of chloroform (B)+cyclic ether (A) mixtures at 298.15 K and atmospheric pressure

| $x_B$ | $H^E$ (J mol$^{-1}$) | $x_B$ | $H^E$ (J mol$^{-1}$) | $x_B$ | $H^E$ (J mol$^{-1}$) |
|---|---|---|---|---|---|
| Chloroform (B)+oxolane (A) | | | | | |
| 0.0216 | −119.4 | 0.3943 | −2550.8 | 0.7569 | −2030.6 |
| 0.0755 | −567.3 | 0.4467 | −2711.6 | 0.8079 | −1709.4 |
| 0.1826 | −1466.4 | 0.4989 | −2740.3 | 0.8587 | −1311.4 |
| 0.2358 | −1859.0 | 0.5509 | −2730.8 | 0.9094 | −863.3 |
| 0.2888 | −2153.2 | 0.6027 | −2645.2 | 0.9598 | −389.1 |
| 0.3417 | −2358.1 | 0.6543 | −2484.1 | 0.9799 | −194.4 |
| Chloroform (B)+1,3-dioxolane (A) | | | | | |
| 0.0221 | −81.0 | 0.3359 | −1298.9 | 0.7041 | −1544.1 |
| 0.0411 | −163.9 | 0.3868 | −1464.1 | 0.7589 | −1376.1 |
| 0.0889 | −400.4 | 0.4383 | −1573.4 | 0.8144 | −1158.4 |
| 0.1374 | −611.1 | 0.4903 | −1654.8 | 0.8705 | −866.9 |
| 0.1862 | −817.3 | 0.5429 | −1699.8 | 0.9272 | −506.7 |
| 0.2356 | −993.0 | 0.5961 | −1701.4 | 0.9502 | −348.7 |
| 0.2855 | −1166.3 | 0.6497 | −1644.9 | 0.9731 | −181.9 |
| Chloroform (B)+oxane (A) | | | | | |
| 0.0346 | −203.9 | 0.4152 | −2618.2 | 0.7699 | −1842.8 |
| 0.0602 | −441.8 | 0.4695 | −2657.7 | 0.8162 | −1530.6 |
| 0.1231 | −943.9 | 0.5225 | −2659.5 | 0.8615 | −1196.0 |
| 0.1845 | −1430.6 | 0.5743 | −2644.4 | 0.9058 | −843.8 |
| 0.2443 | −1849.4 | 0.6249 | −2550.1 | 0.9492 | −457.6 |
| 0.3027 | −2156.0 | 0.6743 | −2360.2 | 0.9663 | −300.6 |
| 0.3596 | −2447.1 | 0.7227 | −2124.3 | 0.9832 | −150.9 |
| Chloroform (B)+1,4-dioxane (A) | | | | | |
| 0.0195 | −87.9 | 0.3470 | −1701.6 | 0.7152 | −1959.8 |
| 0.0312 | −142.8 | 0.4014 | −1883.8 | 0.7656 | −1831.1 |
| 0.0660 | −338.2 | 0.4551 | −1977.7 | 0.8154 | −1569.8 |
| 0.1235 | −700.3 | 0.5083 | −2067.3 | 0.8647 | −1242.6 |
| 0.1803 | −975.3 | 0.5608 | −2125.9 | 0.9135 | −847.2 |
| 0.2365 | −1240.4 | 0.6129 | −2131.0 | 0.9617 | −402.8 |
| 0.2921 | −1485.4 | 0.6643 | −2073.4 | 0.9809 | −216.4 |
| Chloroform (B)+1,3-dioxane (A) | | | | | |
| 0.0785 | −366.5 | 0.5095 | −2011.3 | 0.9128 | −731.9 |
| 0.1340 | −721.6 | 0.6128 | −2041.6 | 0.9614 | −351.3 |
| 0.2436 | −1248.9 | 0.7145 | −1825.9 | | |
| 0.3513 | −1668.6 | 0.8144 | −1429.1 | | |

cyclohexane. At $x = 0.5$ the agreement of our results with those of Marsh et al. [16] was better than 1%.

The $H^E$ values of chloroform + cyclic ether mixtures are given in Table 1 and plotted against the chloroform mole fraction in Figs. 1–3.

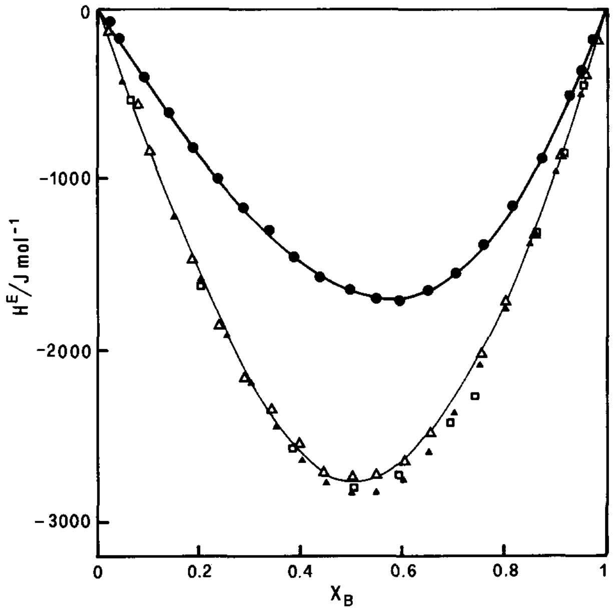

Fig. 1. Experimental molar excess enthalpies $H^E$ of chloroform (B) + cyclic ether (A) mixtures at 298.15 K. Chloroform + oxolane: Δ, present work; □, Murakami et al. [18]; ▲, Becker et al. [17]. Chloroform + 1,3-dioxolane, ●. The solid curves were calculated from eqn. (1) with coefficients from Table 2.

The experimental results of $H^E$ for each mixture were fitted by the least squares method to the equation

$$H^E = x_B x_A \sum_{i=1}^{l-1} A_i (x_B - x_A)^i \tag{1}$$

where $x_B$ is the mole fraction of chloroform. The appropriate number of coefficients was chosen according to the variation of the standard deviation

$$\sigma(H^E) = \left\{ \sum_{1}^{n} \delta_i^2/(n-m) \right\}^{1/2} \tag{2}$$

where $\delta_i = [H^E(\text{expt}) - H^E(\text{calc})]$ is the deviation of the $i$-th experimental point from the smooth curve, $n$ is the number of experimental points and $m$ is the number of coefficients. The $A_i$ and $\sigma(H^E)$ values thus obtained are given in Table 2.

As shown in Figs. 1 and 2, the $H^E$ values for the two monoether mixtures are strongly exothermic, with a maximum at $x \approx 0.5$. Our results are in good agreement with those of Becker and Kiefer [17]: the discrepancies, over a large concentration range, are 1.5% for the chloroform + oxane mixture and about 3% for that containing oxolane. The results of Murakami et al. [18] for chloroform + oxolane show differences of the same

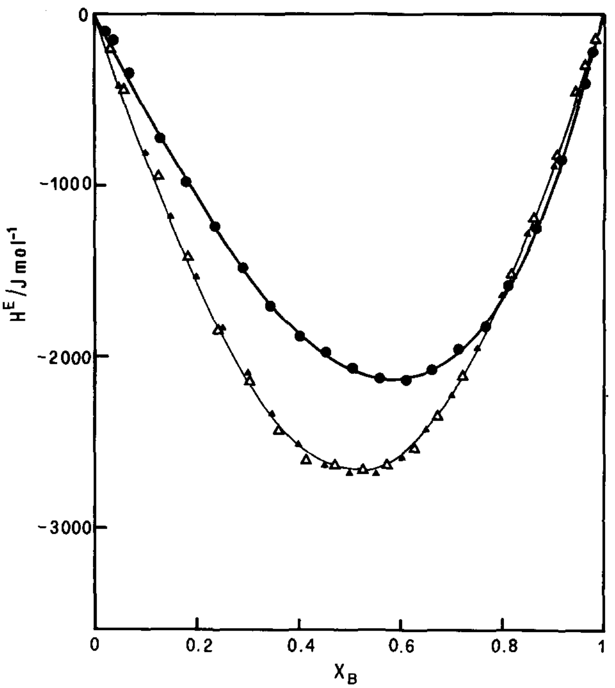

Fig. 2. Experimental molar excess enthalpies $H^E$ of chloroform (B)+cyclic ether (A) mixtures at 298.15 K. Chloroform+oxane: Δ, present work, ▲, Becker et al. [17]. Chloroform+1,4-dioxane, ●. The solid curves were calculated from eqn. (1) with coeffecients from Table 2.

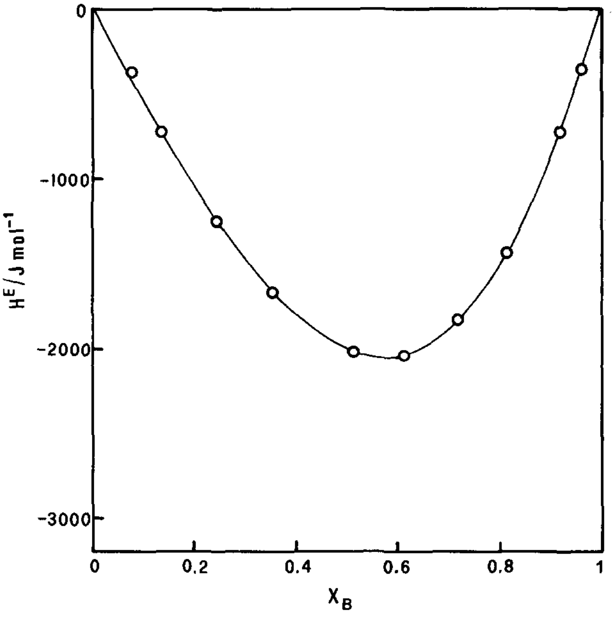

Fig. 3. Experimental molar excess enthalpies $H^E$ of chloroform (B)+1,3-dioxane (A) mixture at 298.15 K. The solid curve was calculated from eqn. (1) with coefficients from Table 2.

TABLE 2

Values of the parameters $A_i$ of eqn. (1) and standard deviation $\sigma(H^E)$ of the experimental molar excess enthalpies $H^E$ for chloroform (B)+cyclic ether (A) mixtures at 298.15 K

| Mixture | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma(H^E)$ |
|---|---|---|---|---|---|---|
| $CHCl_3$ + oxolane | −10927 | −545 | 349 | −1013 | −2683 | 20 |
| $CHCl_3$ + 1,3-dioxolane | −6668 | −2171 | 373 | 816 | | 12 |
| $CHCl_3$ + oxane | −10778 | −255 | 1501 | −998 | 1874 | 19 |
| $CHCl_3$ + 1,3-dioxane | −8084 | −2330 | 691 | | | 25 |
| $CHCl_3$ + 1,4-dioxane | −8250 | −2858 | −1462 | −264 | 1944 | 15 |

magnitude in the central concentration range, but they are in better agreement in the dilute region.

The $H^E$ values of the three diether mixtures are less negative (≈ 20% for six-membered and ≈ 40% for five-membered rings) than those of the corresponding monoethers. Moreover, the minimum of their $H^E$ vs. $x_B$ curves is skewed towards a high chloroform mole fraction ($x_{CHCl_3} \approx 0.63$).

## DISCUSSION

As shown in Figs. 1–3, the $H^E$ values were always strongly exothermic owing to the strong interactions between the hydrogen atom of chloroform and the oxygen atom of the cyclic ether, with the formation of a hydrogen-bonded complex.

For the monoether (oxolane and oxane) mixtures the $H^E$ vs. $x_{CHCl_3}$ curves are symmetrical with the minimum at $x \approx 0.5$. For the same mixtures the molar excess heat capacities and molar excess volumes [7] show, as a function of the mole fraction of $CHCl_3$, a maximum and a minimum respectively at $x \approx 0.5$. These trends suggest that an equimolecular hydrogen-bonded complex AB is the predominant type of association.

Qualitative analysis indicates that the extent of the hydrogen bond is influenced by the shape and size of the cyclic ether ring. The value of $H^E$ at $x = 0.5$ of the chloroform + oxolane mixture, in fact, is higher (≈ 5%) than that of the chloroform + oxane mixture. For comparative analysis these results must be combined with the enthalpic contribution derived from the destruction in the mixing process of the molecular interactions in the pure liquids, since the thermodynamic excess functions of a mixture are the result of a series of structural and energetic factors characteristic of the solution and of the pure liquids. In our case, the $H^E$ values of mixtures of oxolane and oxane with an inert solvent, such as $n$-heptane, are endothermic [1] (790 J $mol^{-1}$ for oxolane and 598 J $mol^{-1}$ for oxane at $x = 0.5$). Molecular interactions between oxolane molecules are thus stronger than those between oxane molecules. This result and the molar excess enthalpies of the two mixtures indicate that the exothermic effect deriving from the hydrogen bond O · · · H–C is stronger in the case of the mixture containing oxolane. This conclusion is in agreement with the spectroscopic and thermodynamic results of Searles and co-workers [19,20], who studied the electron-donor ability of a series of saturated cyclic monoethers in hydrogen bond formation. Their results show that the extent of hydrogen bonding in chloroform + cyclic monoether mixtures decreases in the order trimethylene oxide > oxolane > oxane > propylene oxide > ethylene oxide.

For the cyclic diether mixtures (1,3-dioxolane, 1,3-dioxane, and 1,4-dioxane) the curves of the molar excess thermodynamic functions ($H^E$, $C_p^E$, $G^E$ and $TS^E$) are skewed towards high mole fractions of chloroform, with the minimum or the maximum at $x_{CHCl_3} \approx 0.65$. These trends may be ascribed to the simultaneous formation of AB and $AB_2$ complexes (A = cyclic ether, B = chloroform) as suggested by McGlashan and Rastogi [10] for the chloroform + 1,4-dioxane mixture.

Formation of $AB_2$ complexes in this mixture is also confirmed by the liquid–solid phase diagram [21] which shows two eutectics at 196.9 K and $x_{CHCl_3} = 0.874$ and at 213.2 K and $x_{CHCl_3} = 0.625$. The liquidus curve shows a maximum between the two eutectics at $x_{CHCl_3} = 0.666$. This behaviour is characteristic for the formation of an $AB_2$ complex in the solid state.

Comparative analysis of the $H^E$ of the chloroform + six-membered cyclic diether (1,3-dioxane and 1,4-dioxane) mixtures shows that the value for the mixture containing 1,4-dioxane is more exothermic by about 100 J mol$^{-1}$ at the minimum of the $H^E$ vs. $x_{CHCl_3}$ curve. This result, and the fact that the endothermic contribution to the enthalpy of mixing resulting from the destruction of the molecular interactions between cyclic diether molecules in the pure state is stronger in the case of 1,4-dioxane [1], indicate that the strength of the O · · · H–C hydrogen bond is influenced by the relative position of the oxygen atoms in the ring (proximity effect).

We used McGlashan and Rastogi's model [10] to evaluate the thermodynamic parameters characterizing the chemical equilibrium in our mixtures. In the case of mixtures containing cyclic monoethers, we assumed that the only significant reaction is formation of the AB complex (A + B + AB model), as represented by the chemical equilibrium

$$A + B \rightleftharpoons AB$$

The corresponding equilibrium constant is

$$K_{AB} = \frac{Z_{AB}}{Z_A Z_B} \tag{3}$$

with

$$Z_A + Z_B + Z_{AB} = 1 \tag{4}$$

where $Z_A$, $Z_B$, and $Z_{AB}$ are the equilibrium mole fractions of cyclic monoether, chloroform and hydrogen-bonded complex respectively. Assuming that all species mix ideally, eqns. (3) and (4) give

$$K_{AB}a_B = \frac{1 - a_A - a_B}{a_A} \tag{5}$$

where $a_A$ and $a_B$ are the activities of A and B, and $K_{AB}$ is the equilibrium constant.

For the cyclic diether mixtures, where both $AB_2$ and AB complexes are expected ($A + B + AB + AB_2$ model), two equilibrium reactions and two equilibrium constants were considered

$$A + B \rightleftharpoons AB$$

$$A + 2B \rightleftharpoons AB_2$$

$$K_{AB} = \frac{Z_{AB}}{Z_A Z_B} \tag{6}$$

$$K_{AB_2} = \frac{Z_{AB_2}}{Z_A Z_B^2} \tag{7}$$

with

$$Z_A + Z_B + Z_{AB} + Z_{AB_2} = 1 \tag{8}$$

The corresponding equation relating the activities of the chemical species at equilibrium to the equilibrium constants ($K_{AB}$ and $K_{AB_2}$) is

$$K_{AB} + K_{AB_2}a_B = \frac{1 - a_A - a_B}{a_A a_B} \tag{9}$$

Equations (5) and (9) can be used to calculate $K_{AB}$ and $K_{AB_2}$ by plotting the right side term vs. $a_B$.

Activities $a_A$ and $a_B$ can be calculated from vapour pressure–composition data. Unfortunately, the only results published are those of McGlashan and Rastogi [10] at 323.15 K for the chloroform + 1,4-dioxane mixture, those of Van Ness and Abbott [8] at 303.15 K for the chloroform + 1,4-dioxane and chloroform + oxolane mixtures and those of Wu and Sandler [9] at 308.15 and 323.15 K for the chloroform + 1,3-dioxolane mixture. From these results, the dependence of the equilibrium constants on temperature and the enthalpies of formation of AB and $AB_2$ complexes have been obtained.

The activities ($a_A$ and $a_B$) have been obtained from the experimental vapour pressure data with the equation

$$a_i = \frac{y_i P}{P_i^{\circ}} \exp\left[(P - P^{\circ})(B_{ii} - V_i^{\circ})/RT\right] \exp\left[(1 - y_i)^2 P\, \delta_{1,2}/RT\right] \tag{10}$$

TABLE 3

Second virial coefficients and liquid molar volumes

| Mixture | $T$ (K) | $B_{AA}$ | $B_{BB}$ | $B_{AB}$ | $\delta_{1.2}$ | $V_A^{\circ}$ | $V_B^{\circ}$ |
|---|---|---|---|---|---|---|---|
| $CHCl_3$ (B) + oxolane (A) | 303.15 | −1540 | −1180 | −3490 | −4260 | 81 | 80 |
| $CHCl_3$ (B) + 1,4-dioxane (A) | 303.15 | −2070 | −1180 | −4860 | −6470 | 85 | 80 |
| $CHCl_3$ (B) + 1,3-dioxolane (A) | 308.15 | −2046 | −1070 | −4400 | −5680 | 79 | 81 |
| $CHCl_3$ (B) + 1,3-dioxolane (A) | 323.15 | −1670 | −950 | −2950 | −3280 | 81 | 84 |

Units of $B_{AA}$, $B_{BB}$, $B_{AB}$, $\delta_{1.2}$, $V_A^{\circ}$ and $V_B^{\circ}$ are $cm^3\ mol^{-1}$.

with

$i = \text{A or B}$

$\delta_{1,2} = 2B_{AB} - B_{AA} - B_{BB}$

where $y_i$ is the mole fraction of component $i$ in the vapour phase, $P$ is the equilibrium pressure, $V_i^{\circ}$ the molar volume of pure liquid under saturation pressure, and $B_{ii}$ is the second virial coefficient that takes into account the imperfections of the vapour phase. The second virial coefficients have been

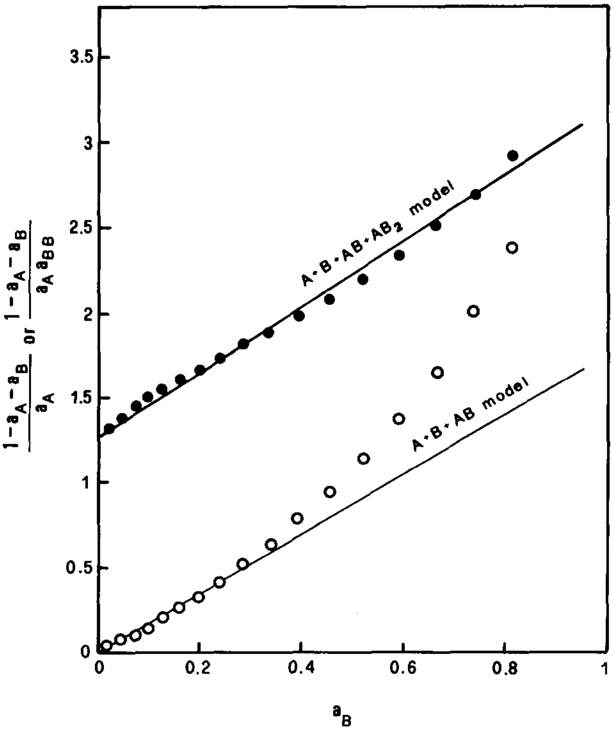

Fig. 4. Verification of the appropriate association model for the chloroform (B) + 1,4-dioxane (A) mixture at 303.15 K. Right-hand term of eqn. (5) or (9) vs. chloroform activity.

TABLE 4

Equilibrium constants at different temperatures for AB and $AB_2$ hydrogen-bonded complex formation in the chloroform + cyclic ether mixtures

| Mixture | $T$ (K) | $K_{AB}$ | $K_{AB_2}$ | Ref. |
|---|---|---|---|---|
| $CHCl_3$ (B) + 1,4-dioxane (A) | 298.15 | 1.38 | 1.89 | Eqns. (11), (12) |
| | 303.15 | 1.32 | 1.72 | 8 |
| | 323.15 | 1.11 | 1.24 | 10 |
| $CHCl_3$ (B) + 1,3-dioxolane (A) | 298.15 | 0.916 | 0.906 | Eqns. (13), (14) |
| | 308.15 | 0.836 | 0.764 | 9 |
| | 323.15 | 0.736 | 0.604 | 9 |
| $CHCl_3$ (B) + oxolane (A) | 303.15 | 3.56 | - | 8 |

estimated according to Tsonopoulos [22,23] and are reported along with $V_i^\circ$ and $\delta_{1,2}$ in Table 3.

The equilibrium constants and the appropriate association model have been obtained by plotting $(1 - a_A - a_B)/a_A$ vs. $a_B$ and $(1 - a_A - a_B)/a_A a_B$ vs. $a_B$ for $A + B \rightleftarrows AB$ and $A + 2B \rightleftarrows AB_2$. An association model is appropriate when the points lie on a straight line. The equilibrium constants can then be calculated from the slope and intercept by the least squares method.

In Fig. 4 are reported the results obtained from this analysis for chloroform + 1,4-dioxane mixture at 303.15 K. As can be seen, the $A + B + AB + AB_2$ model is more appropriate. The $A + B + AB$ model is valid only for dilute solutions of chloroform in 1,4-dioxane. According to eqn. (9) the equilibrium constants $K_{AB}$ and $K_{AB_2}$ have been calculated, and are reported along with the values obtained by McGlashan and Rastogi [10] at 323.15 K in Table 4. The $K_{AB}$ and $K_{AB_2}$ values calculated by Barta et al. [24] using McGlashan and Rastogi's [10] vapour pressure data at 323.15 K are 1.10 and 0.91 respectively.

Comparison with the results of McGlashan and Rastogi shows that agreement is excellent for $K_{AB}$ but not for $K_{AB_2}$. The smaller $K_{AB_2}$ value obtained by Barta et al. [24] may be attributed to approximations in determination of the activities of the chemical species at equilibrium. We therefore used McGlashan and Rastogi's $K_{AB}$ and $K_{AB_2}$ values.

The dependence of the equilibrium constant on temperature is described by the van 't Hoff equation. If the enthalpy of formation of the complex $\Delta H^\circ$ is assumed independent of temperature, the equations for the two equilibrium constants are

$$\ln K_{AB} = 851.1/T - 2.529 \quad (11)$$

$$\ln K_{AB_2} = 1615.6/T - 4.784 \quad (12)$$

The enthalpies of formation $\Delta H^\circ_{AB}$ and $\Delta H^\circ_{AB_2}$ have been calculated from the slope $(-\Delta H^\circ/R)$ of the straight lines represented by eqns. (11) and

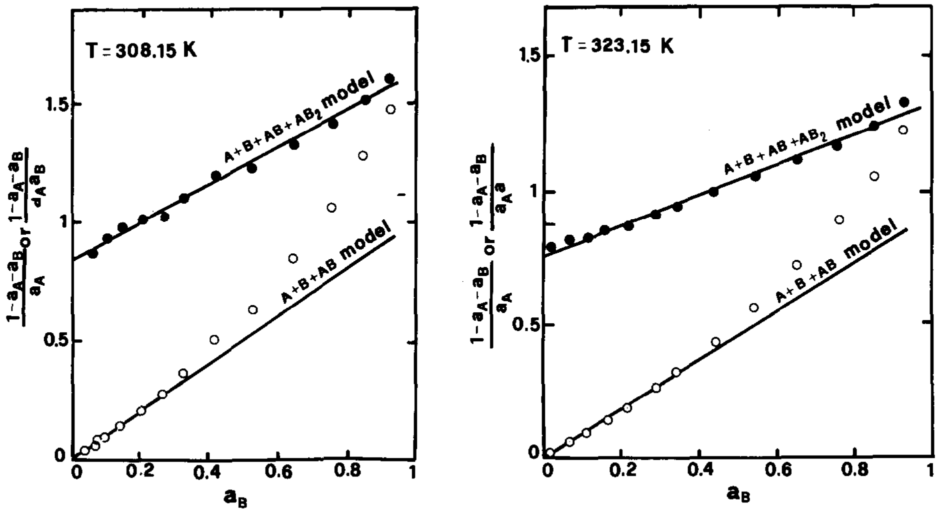

Fig. 5. Verification of the appropriate association model for the chloroform (B) + 1,3-dioxolane (A) mixture at 308.15 and 323.15 K. Right-hand term of eqn. (5) or (9) vs. chloroform activity.

(12). Their values ($\Delta H^\circ_{AB} = -7.1$ kJ mol$^{-1}$ and $\Delta H^\circ_{AB_2} = -13.5$ kJ mol$^{-1}$) may be considered as average in the range of temperature considered (303.15–323.15 K). The difference $\Delta H^\circ_{AB_2} - \Delta H^\circ_{AB} = -6.4$ kJ mol$^{-1}$ represents the heat evolved during formation of the second hydrogen bond of the $AB_2$ complex. Within the estimated uncertainties (10%), this quantity is very close to $\Delta H^\circ_{AB}$. The two hydrogen bonds in the $AB_2$ complex can thus be regarded as equivalent, which means that the first bond has no significant influence on the formation of the second.

The values of $K_{AB}$ and $K_{AB_2}$ at 298.15 K (from eqns. (11) and (12)) are in agreement with the values calculated ($K_{AB} = 1.41$ and $K_{AB_2} = K_1 K_2 = 1.55$) by Barta et al. [24] using the ideal associated solution model. The agreement is also good for the enthalpies of formation $\Delta H^\circ_{AB}$ and $\Delta H^\circ_{AB_2}$, for which the differences are within the experimental uncertainties (10%) for $\Delta H^\circ_{AB}$ and slightly higher (16%) for $\Delta H^\circ_{AB_2}$.

Analysis of the chloroform + 1,4-dioxane mixture has been extended to the other binary mixtures for which vapour pressure data were available: chloroform + 1,3-dioxolane and chloroform + oxolane.

In Figs. 5 and 6, the right hand terms of eqns. (5) and (9) are reported as a function of $a_B$ at 308.15 and 323.15 K for the chloroform + 1,3-dioxolane mixture and at 303.15 K for the chloroform + oxolane mixture. The trends show that for the 1,3-dioxolane mixture the A + B + AB + $AB_2$ model is the more appropriate, since the A + B + AB model is valid only in the dilute region. The opposite is obtained for the oxolane mixture (Fig. 6). Equation (5) satisfactorily reproduces the experimental results in the whole

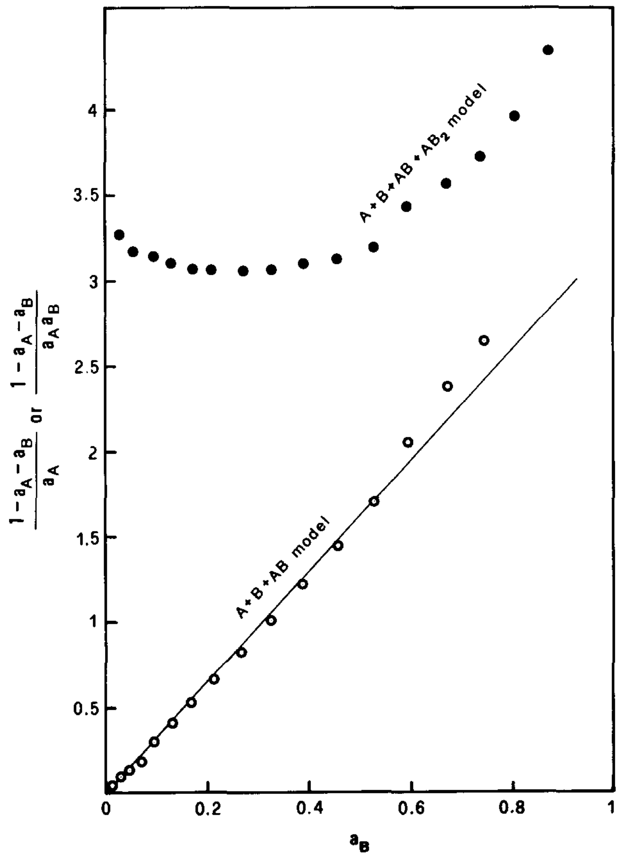

Fig. 6. Verification of the appropriate association model for the chloroform (B)+oxolane (A) mixture at 303.15 K. Right-hand term of eqn. (5) or (9) vs. chloroform activity.

concentration range and, according to the theory, the AB complex should be the only type of association in this mixture.

The equilibrium constants obtained from the slope and the intercept of the straight line are reported in Table 4.

The equivalents of eqns. (11) and (12) for the chloroform + 1,3-dioxolane mixture are

$$\ln K_{AB} = 844.0/T - 2.919 \tag{13}$$

$$\ln K_{AB_2} = 1561.4/T - 5.336 \tag{14}$$

The values of $\Delta H^\circ_{AB}$ ($-7.0$ kJ mol$^{-1}$) and $\Delta H^\circ_{AB_2}$ ($-13.0$ kJ mol$^{-1}$) have been obtained from the slope of the straight lines represented by eqns. (13) and (14). The heat evolved during formation of the first hydrogen bond ($\Delta H^\circ_{AB} = -7.0$ kJ mol$^{-1}$) is about 17% higher than that evolved during the formation of the second hydrogen bond ($\Delta H^\circ = \Delta H^\circ_{AB_2} - \Delta H^\circ_{AB} = -6.0$ kJ mol$^{-1}$). This difference cannot be ascribed completely to the estimated uncertainties (10%). It is due to the mutual influence of the two oxygen atoms (proximity effect) and to steric hindrance.

The lack of experimental vapour pressure–composition data prevents extension of this quantitative analysis to the other mixtures. Nevertheless, the results obtained with 1,3-dioxolane and 1,4-dioxane corroborate the conclusions derived from the qualitative analysis of the experimental molar excess enthalpies. As expected, the calculated $\Delta H^\circ_{AB_2}$ values for chloroform + 1,3-dioxolane and chloroform + 1,4-dioxane indicate that the mutual influence between the oxygen atoms is more important when they are in the 1,3-position. Consequently, the hydrogen bond is stronger with 1,4-dioxane than with 1,3-dioxolane, and hence with 1,3-dioxane, as evinced by the qualitative analysis.

The $\Delta H^\circ_{AB}$ value is about the same for both 1,3-dioxolane and 1,4-dioxane mixtures. We think that this result is a consequence of two opposite effects when changing from 1,3-dioxolane to 1,4-dioxane. The more substantial proximity effect with 1,3-dioxolane provides a negative contribution to the enthalpy of formation that is balanced by the positive contribution deriving from the structure of the five-membered cyclic ethers, which renders the oxygen atom more exposed. Consequently, the enthalpy of formation of the AB complex in the monoether mixtures can be expected to be higher with oxolane than with oxane. This result is in agreement with the qualitative interpretation of the $H^E$ of the monoether mixtures.

Using the $K_{AB}$, $K_{AB_2}$, $\Delta H^\circ_{AB}$ and $\Delta H^\circ_{AB_2}$ values, $H^E$ can be calculated in the McGlashan and Rastogi approach by means of the equation

$$H^E = \frac{(1-x_B)Z_B(K_{AB}\Delta H^\circ_{AB} + K_{AB_2}Z_B\Delta H^\circ_{AB_2})}{1 + Z_B K_{AB} + Z_B^2 K_{AB_2}} \tag{15}$$

where $x_B$ and $Z_B$ are the stoichiometric and equilibrium mole fractions of chloroform respectively.

We have calculated $H^E$ at 308.15 K for chloroform + 1,3-dioxolane and at 303.15 K for the chloroform + 1,4-dioxane mixtures. The choice of these temperatures was conditioned by the availability of the vapour pressure data. Figure 7 compares the calculated results with the $H^E$ at the same temperatures, those obtained from our experimental results at 298.15 K (this paper) and the $C_p^E$ results at 298.15 K [6]. The $H^E$ values calculated in this way at 303.15 K for chloroform + 1,4-dioxane are in good agreement (within 1.5%) with the experimental results of Van Ness and Abbott [8] in a wide concentration range ($0.4 < x_{CHCl_3} < 0.8$).

Figure 7 shows that the model used in this approach perfectly reproduces the symmetry of the $H^E$ vs. $x_{CHCl_3}$ curves. Systematic deviations between experimental and calculated values of $H^E$ are shown by both systems in the whole concentration range. At the maximum value of $H^E$ the differences are about 11% for chloroform + 1,4-dioxane and about

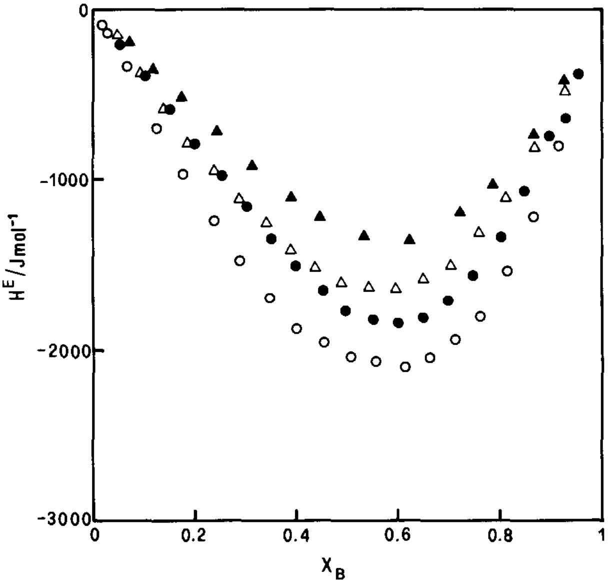

Fig. 7. Molar excess enthalpies of chloroform (B) + 1,4-dioxane (A) (o, ●) at 303.15 K and chloroform (B) + 1,3-dioxolane (A) (△, ▲) at 308.15 K. Open symbols represent the experimental data; solid symbols are the values predicted by the ideal associated solution model.

15% for chloroform + 1,3-dioxolane. These deviations are due to approximations and uncertainties of the enthalpies of formation and the equilibrium constants used in eqn. (15).

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