Thermochimica Acta, 99 (1986) 317–324
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMIC INVESTIGATION OF COMPLEX FORMATION IN 1,4-DIOXANE + BROMOFORM MIXTURE

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(Received 13 September 1985)

ABSTRACT

Molar excess enthalpies, H^E, have been measured for mixtures of 1,4-dioxane (A) and bromoform (B) at 298.15 K and the same have been interpreted to indicate the presence of A, AB and B molecular species in mutual equilibrium. The equilibrium constant and the molar enthalpy of formation, ΔH, of the AB complex have also been evaluated from the measured H^E values. The equilibrium constant, K, value has been further substantiated by K values determined for the AB molecular complex from NMR studies on this mixture. A tentative molecular geometry of the AB molecular complex consistent with NMR and UV spectral studies has also been proposed.

INTRODUCTION

1,4-Dioxane (A) contains two oxygen atoms, with two free lone pairs of electrons on each, in its structure. It would thus be expected to form weak molecular complexes of the type AB and AB_2 in its binary mixtures with bromoform (B). However, very few spectroscopic studies have been made to yield precise equilibrium constant data for such weak molecular complexes to enable one to evaluate their molar enthalpy of formation. A number of workers [1–3] have, however, suggested that it is possible to evaluate both the equilibrium constant and the enthalpy of formation of the AB and AB_2 type complexes that may characterize (A + B) binary mixtures if the integral molar enthalpy of mixing, H^E, data for these binary mixtures are available. In this communication we have determined the equilibrium constant, K, and the molar enthalpy, ΔH, of the AB complex, characterizing this (A + B) mixture, from the measured H^E data at 298.15 K for this mixture. We have further utilized proton magnetic resonance studies on this mixture to understand not only the nature of molecular interactions that characterize this mixture but also to evaluate K, by an independent method. This has been done in order to compare K values determined from calorimetric and NMR studies.

0040-6031/86/$03.50

EXPERIMENTAL

Materials and method

1,4-Dioxane (Merck, Analar grade) was dried by refluxing it over sodium wire as suggested by Rastogi and McGlashan [4]. It was then fractionally distilled.

Bromoform (Merck, Analar grade) was washed [5] repeatedly with distilled water and then dried over anhydrous calcium chloride. It was then distilled.

The purities of the final samples were checked by determining their densities at (298.15 ± 0.01) K, and these agreed to within ± 0.00005 g cm^{-3} with their corresponding literature values [6,7].

Molar excess enthalpies, H^{E}, at 298.15 K were measured by an LKB flow microcalorimeter (LKB-2107, M/S LKB, Broma, Sweden) in the manner described by Monk and Wadsö [8]. According to the specifications of the instrument, the temperature can be set with a precision of 0.1 K and its stability is ± 0.02 K/24 h. Two identical Braun perfusor pumps (B. Braun Melsungen AG, W. Germany) and gas-tight Hamilton syringes were employed to pump liquids through the calorimeter. Using 10-, 20- and 50-cm^3 syringes and 10-speed gear boxes of the perfusor pumps, different mixing ratios were achieved. The flow rates were determined by pumping distilled water through the calorimeter and weighing the amounts collected in a specific time interval. For each typical H^{E} measurement, different calibration constants were determined according to the flow rate, the amplification needed and the composition of the mixture.

Samples for NMR studies were prepared by mixing (by weight) bromoform with 1,4-dioxane in NMR tubes followed by dilution with a fixed quantity of an inert solvent (cyclohexane). Immediately after preparation, a fixed quantity of tetramethylsilane (TMS) (internal reference) was added to each tube and the chemical shift of bromoform relative to TMS was detected on a Varian 90 MHz spectrometer using the side band method [9]. The chemical shifts for the various mixtures were averaged over three determinations and were reproducible to ± 0.5 Hz.

UV absorption studies on this (A + B) mixture were performed by mixing 10^{-4} M solutions of bromoform and 1,4-dioxane (in analytical grade cyclohexane) according to Job's method of continuous variation [10] in the UV region. The UV absorption spectra of each of these solutions were recorded on a spectronic 2000 spectrophotometer (Bausch and Lomb) and the optical density corresponding to the absorption maximum (which was found to be 222.3 nm) for each of these solutions was also noted.

RESULTS

Molar excess enthalpy, H^{E}, data for this mixture as a function of composition at 298.15 K (reported in Table 1) were fitted to the equation

$$H^{E}(\mathrm{J\ mol^{-1}}) = X_{A}X_{B}\Sigma H_{0}^{n}(2X_{A}-1)^{n} \tag{1}$$

where H_{0}^{n} ($n = 0$–2) are disposable parameters and X_{A} is the mole fraction of 1,4-dioxane. These parameters were evaluated by fitting $H^{E}/X_{A}X_{B}$ to

TABLE 1

Measured H^{E} (J mol^{-1}) data for 1,4-dioxane (A)+bromoform (B) mixtures at 298.15 K for various mole fractions, X_{A}

X_A	H^E
0.0530	−436.7
0.1028	−780.6
0.1812	−1260.1
0.3493	−1920.9
0.4980	−2080.1
0.5315	−2061.1
0.6766	−1761.1
0.7095	−1645.1
0.8014	−1236.9
0.8374	−1045.7
0.8809	−793.8
0.9538	−323.9

$H_{0}^{0} = -8320.0$ J mol^{-1}, $H_{0}^{1} = 595.24$ J mol^{-1}, $H_{0}^{2} = 511.91$ J mol^{-1}, $\sigma\ (H^{E}) = 0.62$ J mol^{-1}

TABLE 2

Proton resonance shifts, δ, of 1,4-dioxane (A)+bromoform (B) mixtures with respect to pure bromoform and the optical density (OD) at 222.3 nm of the (A + B) mixtures as a function of X_{B}

X_B	δ(Hz)	OD
0.1198	–	0.275
0.1609	−26.1	–
0.2390	–	0.626
0.2741	−24.3	–
0.3630	–	0.788
0.4055	−18.0	–
0.4841	–	1.086
0.5182	−15.3	–
0.6148	−12.6	–
0.7410	–	0.580
0.8690	–	0.270
0.8701	−0.04	–

eqn. (1) by the method of least squares and are recorded in Table 1, together with the standard deviations, $\sigma(H^{E})$, of H^{E} defined by

$$\sigma(H^{E})\ (\mathrm{J\ mol^{-1}}) = \left[\frac{\Sigma\left(H^{E}_{\mathrm{exp}} - H^{E}_{\mathrm{calc.eqn.(1)}}\right)^{2}}{m-t} \right]^{0.5} \tag{2}$$

where m is the number of data points and t is the number of adjustable parameters in eqn. (1).

The proton chemical shifts of bromoform in its binary mixtures with 1,4-dioxane relative to pure bromoform are recorded in Table 2. Table 2 also contains optical density (in the UV region) vs. X_{B} data for this (A + B) mixture.

DISCUSSION

H^{E} for this mixture is negative over the entire 1,4-dioxane composition range. This suggests that this (A + B) mixture is characterized by specific interactions [11] between A and B. Again, since H^{E} is almost symmetrical about $X_{A} = 0.5$, this indicates that a 1:1 molecular complex is formed between A and B in this binary mixture. The complexation reaction between A and B in this mixture may thus be described by the equilibrium

$$\mathrm{A + B = AB} \tag{3}$$

It has, however, been shown [1–3] that in a complexation reaction of the type represented by equilibrium (3), $X_{A}X_{B}/H^{E}$ is related to the equilibrium constant, K, and the molar enthalpy of formation, ΔH, of the AB complex by the equation

$$\frac{X_{A}X_{B}}{H^{E}} = -\left[(K+1)/K(\Delta H)^{2}\right]H^{E} + \left[\frac{(K+1)}{K(\Delta H)}\right] \tag{4}$$

so that both K and ΔH for the complexation reaction (3) can be readily evaluated from the measured H^{E} data provided $X_{A}X_{B}/H^{E}$ is a linear function of H^{E}. In deriving eqn. (4) it has been tacitly assumed [1] that the measured H^{E} for this (A + B) mixture is due primarily to the "chemical" interactions represented by equilibrium (3) and the "physical" interactions between A and B being negligibly small compared to the "chemical" interactions. Matsui et al. [1] suggested that this requirement is met if the measured $-H^{E}$ is greater than about 1.5 kJ at $X_{A} = 0.5$. Since the measured $-H^{E}$ in the present system fills this requirement the present mixture provides an ideal test of eqn. (4).

For this purpose $X_{A}X_{B}/H^{E}$ was plotted against H^{E} and it was found that $X_{A}X_{B}/H^{E}$ was indeed a linear function of H^{E}. From the intercept (-1.45×10^{-4} kJ mol^{-1}) and the slope ($= -1.17 \times 10$ (kJ mol^{-1})$^{-2}$) we evaluated $K = 1.255$ and $\Delta H = -12.39$ kJ mol^{-1}.

In order to further supplement the K value so obtained for the equilibria represented by eqn. (4), we studied the proton chemical shift, δ, of bromoform relative to that of pure bromoform in its binary mixtures with 1,4-dioxane.

Examination of Table 2 clearly shows that there is a net shift of the bromoform proton towards low magnetic fields. The proton magnetic resonance studies on this mixture thus clearly show that the proton of bromoform is deshielded in its interactions with 1,4-dioxane in this (A + B) mixture.

The proton chemical shift data of bromoform in the bromoform (B) + 1,4-dioxane (A) mixture were then utilized to evaluate K for the equilibria represented by eqn. (4).

If ξ_{A}, ξ_{B}, and ξ_{AB} denote, respectively, the actual mole fractions of 1,4-dioxane (donor), bromoform (acceptor) and the complex AB, respectively, then

$$K = \xi_{\mathrm{AB}}/\xi_{\mathrm{A}}\xi_{\mathrm{B}} \tag{5}$$

Further, ξ_{A}, ξ_{B} and ξ_{AB} are related [4] to the stoichiometric mole fractions of A and B by

$$X_{\mathrm{B}} = (\xi_{\mathrm{B}} + \xi_{\mathrm{AB}})/(\xi_{\mathrm{A}} + \xi_{\mathrm{B}} + 2\xi_{\mathrm{AB}}) \tag{6}$$

and

$$X_{\mathrm{A}} = (\xi_{\mathrm{AB}} + \xi_{\mathrm{A}})/(\xi_{\mathrm{A}} + \xi_{\mathrm{B}} + 2\xi_{\mathrm{AB}}) \tag{7}$$

$$= (1 + K)\xi_{\mathrm{A}}/[1 + K\xi_{\mathrm{A}}(2_{\mathrm{A}} - \xi_{\mathrm{A}})] \tag{8}$$

In deriving eqns. (6)–(8) it has been assumed that $\gamma_{\mathrm{A}}\ \gamma_{\mathrm{B}}/\gamma_{\mathrm{AB}} \approx 1$ and this assumption has been shown [12] to be unlikely to lead to serious errors in K. If now the observed chemical shift, δ_{obs}, of the bromoform proton in its mixtures with 1,4-dioxane relative to that of the pure bromoform is assumed to be the weighted average of the shifts in the complexed, δ_{AB}, state and the uncomplexed, δ_{B}, state, then

$$\delta_{\mathrm{obs}} = \xi_{\mathrm{B}}[\xi_{\mathrm{B}}/(\xi_{\mathrm{B}} + \xi_{\mathrm{AB}})] + \xi_{\mathrm{AB}}[\xi_{\mathrm{AB}}/(\xi_{\mathrm{B}} + \xi_{\mathrm{AB}})] \tag{9}$$

$$= \delta_{\mathrm{B}} + x(\delta_{\mathrm{AB}} - \delta_{\mathrm{B}}) \tag{10}$$

where

$$x = \xi_{\mathrm{AB}}/(\xi_{\mathrm{B}} + \xi_{\mathrm{AB}}) = \mathrm{K}\xi_{\mathrm{A}}/(1 + \mathrm{K}\xi_{\mathrm{A}}) \tag{11}$$

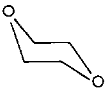
In order to evaluate K from eqns. (5)–(11), a series of values were assumed for K. For each K value, ξ_{A} was evaluated from the corresponding experimental X_{A} value from eqn. (8) and, hence, the corresponding value of x was obtained from eqn. (11). Only that value of K was retained that gave the best straight line of δ_{obs} against x. The best value of K was taken to be that for which $\sigma = (\delta_{\mathrm{obs}} - \delta_{\mathrm{calc}})^2$ is minimum. This analysis of our δ_{obs} data yielded $K = 1.3$. The uncertainty in our K value is of the order of ± 0.05.

The $K = 1.3 \pm 0.05$ obtained from an analysis of the proton chemical shift of bromoform relative to that of the pure bromoform in its binary mixtures with 1,4-dioxane is thus very close to the $K = 1.255$ value determined for equilibria (3) from the measured H^E data by means of eqn. (4).

In order to further investigate the type of molecular complex(es) that may characterize this binary mixture, we utilized its activity coefficient, a_i (i = A or B), data [13] at 308.15 K. If this mixture is assumed to contain A, AB, AB_2 and B molecular species in mutual equilibrium, then $(1 - a_A - a_B)/a_A a_B$ should be linear [4] in a_B. It was, however, observed that this was not true. On the other hand, when we assumed that this mixture contains A, AB and B molecular species in mutual equilibrium $(1 - a_A - a_B)/a_A$ was indeed found to be linear in a_B. Such an analysis also suggests that A interacts with B in 1:1 proportion to yield an AB molecular complex; it being assumed (during this analysis) that a rise of 10 K in temperature from 298.15 to 308.15 K does not basically change the equilibria that characterize this mixture.

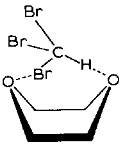
The above assertion that an AB molecular entity is formed between A and B in this mixture is further substantiated by Job's method of continuous variation (in the UV region), studies which clearly showed that A interacts with B in 1:1 (optical density vs. X_{CHBr_3} plot had maxima at $X_{CHBr_3} = 0.5$) proportions to yield an AB molecular complex.

The interaction between A and B moieties to yield and AB molecular complex alone and not AB and AB_2 molecular complexes may then be explained on the basis of the conformation of 1,4-dioxane. It is well known that 1,4-dioxane exists in the chair (a) and the boat (b) forms and that the chair form (a) is the more stable of these two conformations. It may so happen that when bromoform (B) interacts with A (i.e., 1,4-dioxane), either (a) or (b) forms of A interact with B. Since in the present analysis only an AB molecular complex is indicated to be present, it suggests that it is the boat form of A that interacts with B. Such a conjecture would then require that the proton of B should get deshielded in its interactions with A. The present NMR studies on this (A + B) mixture do lend credence to this hypothesis. At the same time the vacant 3*d* levels in one of the bulky bromine atoms of bromoform may also tend to accommodate the lone pairs of electrons on the other oxygen atoms of 1,4-dioxane yielding the following geometry to the AB molecular complex.



(a) Chair form

(b) Boat form



Such a scheme of the nature of molecular interactions between A and B to yield an AB molecular complex would of necessity require that only an AB molecular complex should be formed in this mixture; the O---Br and O---H interactions between A and B in this AB molecular complex compensate for the instability of the boat conformation of 1,4-dioxane.

The above geometry of the AB molecular complex requires that one bromine atom of bromoform must also be involved in interaction with the other oxygen atom of 1,4-dioxane.

Now the absorption band maximum for the bromine atom (core plus σ^2 π^4 π^{*4}) in bromoform occurs at about 256 nm in cyclohexane and is assigned to a $\pi^* \rightarrow \sigma^*$ transition. When 1,4-dioxane (donor) is now added to bromoform, the absorption band shifts to 222.3 nm. The present UV spectral studies thus clearly point out that the bromine atom of bromoform (B) accepts electrons [14] from the donor (A), i.e., 1,4-dioxane. During these interactions with A the molecular orbital of the bromine atom becomes destabilized [14] and acquires higher energy than the corresponding bromine atom in bromoform so that a blue shift in the bromoform peak in the UV region is obtained.

Again for this "ideal associated" solution, Matsui et al. [1] have shown that the molar enthalpy, ΔH, of AB complex formation is given by

$$\Delta H = \overline{L_{\mathrm{B}}^{0}}(1+K)/K = \overline{L_{\mathrm{A}}^{0}}(1+K)/K \qquad (12)$$

where $\overline{L_{\mathrm{B}}^{0}}$, etc., represent the partial molar enthalpy of solution of B (at infinite dilution) in A. In order to evaluate the ΔH value of the AB complex from eqn. (12) utilizing the K (= 1.3) value determined from NMR studies, we, following Van Ness and Mrazek [15,16], constructed a graph of $H^{\mathrm{E}}/X_{\mathrm{A}}X_{\mathrm{B}}$ vs. X_{A} to yield $\overline{L_{A}^{0}}$ and $\overline{L_{B}^{0}}$ from the extrapolated intercepts corresponding to $X_{\mathrm{A}} = 0$ and $X_{\mathrm{A}} = 1$, respectively. Such a procedure yielded $\overline{L_{\mathrm{A}}^{0}} = -9.45$ kJ mol^{-1} and $\overline{L_{\mathrm{B}}^{0}} = -7.1$ kJ mol^{-1}. The ΔH values obtained from eqn. (12) range between -16.73 and -12.37 kJ mol^{-1}. If we use the average values of $\overline{L_{A}^{0}}$ and $\overline{L_{B}^{0}}$ to evaluate ΔH from eqn. (12) we get $\Delta H = -14.65$ kJ mol^{-1}. The ΔH values determined from eqns. (12) and (4) thus differ by about 16%. Nevertheless, they are of the right order of magnitude.

ACKNOWLEDGEMENTS

The authors express their thanks to the Authorities of M.D. University, Rohtak for providing the necessary facilities.

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