Thermochimica Acta, 17 (1976) 113–118

THERMODYNAMIC INVESTIGATION OF AB AND AB_2 MOLECULAR SPECIES IN BINARY LIQUID SYSTEMS

EXCESS ENTHALPIES OF 1,4-DIOXANE WITH CHLOROFORM AND BROMOFORM

P. P. SINGH*
Department of Chemistry and Biochemistry, Panjab Agricultural University, Ludhiana (India)
(Received 20 February 1976)

ABSTRACT

Excess enthalpies have been measured at 308.15 K for 1,4-dioxane (A)+chloroform (B) and 1,4-dioxane (A)+bromoform (B). The data have been examined on the basis of Barker's theory. Interaction energies between the components have been determined and the study suggests that these mixtures contain both AB and AB_2 molecular species.

INTRODUCTION

Complex formation equilibria in dilute non-electrolyte solutions involving reactions of the type

$$A+B \rightleftharpoons AB \qquad (1)$$

in some more or less "inert" solvents have been investigated by various spectroscopic methods as also by such classical thermodynamic methods as distribution between immiscible solvents etc. Hepler and Fenby[1] have recently shown that it is possible to analyse molar excess enthalpies for a binary liquid mixture in terms of equilibrium constant and the molar enthalpy of reaction, ΔH_1°, for the complex formation represented by reaction (1). In a subsequent paper[2] these workers have extended this method to analyse H^E for mixtures assumed to have AB and AB_2 complexes. In another realistic approach McGlashan and Rastogi[3] have shown that K_1 and K_2 for the reaction

$$A+B \overset{K_1}{\rightleftharpoons} AB$$

$$A+2B \overset{K_2}{\rightleftharpoons} AB_2$$

evaluated from vapour pressure measurements can be combined with H^E data to

---

*Present address: Dept. of Chemistry, University of Lethbridge, Alberta, Canada.

yield ΔH_1° and ΔH_2°. While the most compelling evidence for the presence of AB and AB_2 type molecular species in these mixtures is usually spectroscopic, this is often supplemented by thermodynamic excess functions and their temperature dependence. Excess enthalpies are potentially rich sources of information about complex formation in solution[4–7]. The work described here shows that Barker's theory[8] can be utilized to analyse H^E data for a binary non-electrolyte mixture to decide whether it contains AB or AB and AB_2 molecular species.

EXPERIMENTAL

Dioxane, chloroform and bromoform were purified as suggested by Vogel[9] and the purities of the final samples were checked by measuring their densities as described earlier[10,11].

Heats of mixing measurements were made in an adiabatic calorimeter[12].

RESULTS

Heats of mixing data for various systems are recorded in Table 1. The results were fitted to the expression

$$H^E/x_1(1-x_1)\ \mathrm{J\ mol^{-1}} = h_0 + h_1(2x_1-1) + h_2(2x_1-1)^2 \tag{2}$$

where x_1 is the mole fraction of component 1. The constants h_0, h_1 and h_2 were evaluated by fitting $H^E/x_1(1-x_1)$ to expression (2) by the method of least squares. They are recorded in Table 2 together with the standard deviations $\sigma(H^E)$.

DISCUSSION

Excess enthalpies for 1,4-dioxane (1)+chloroform (2) have been measured at 303.15 and 318.15 K by Van Ness and Abbott[13]. The heats of mixing values for this mixture at 308.15 K interpolated from their data[13] gave values that have a maximum at $x_2 = 0.6$, ($H^E_{max} = -2080$ J mol^{-1}) while our H^E values have a maximum of -2100 J mol^{-1} at $x_2 = 0.55$. Further, while their H^E values[13] are considerably more endothermic than ours in the composition range $x_2 = 0.25$ to $x_2 = 0.45$, a constant substraction of 200 J mol^{-1} from their data well reproduces (within 10 J mol^{-1}) our H^E values in this concentration range. Their H^E values[13] are also more exothermic than ours in the range $x_2 = 0.6$ to $x_2 = 0.9$—a constant addition of 120 J mol^{-1} to their data also reproduces well within 10 J mol^{-1} our H^E values in this concentration range. We are unaware of any data at 308.15 K with which to compare our results for 1,4-dioxane+bromoform.

The results were examined on the basis of Barker's theory which allows a molecule of type A occupying r_A sites on a Z-coordinated lattice to have $q_A^Z = r_A^Z - 2r_A + 2$ neighbouring contact sites; each site having an interaction energy with the neighbouring part of the surface of another molecule. The contact types are further sub-divided into classes; the number in the μth class of the molecule A denoted by $Q_{\mu A}$. As 1,4-dioxane has almost the same molar volume as that of the various solvents used here $r_A = r_S = 2$ and $Z = 4$ has been used throughout this paper. Further chloroform and bromoform are assumed to have 2 classes of contact sites, the hydrogen atom is assumed to have one contact Q_H of one class while the residual part

TABLE 1

MEASURED HEATS OF MIXING, H^E AND COMPARISON OF VALUES CALCULATED ACCORDING TO BARKER'S THEORY AT MOLE FRACTIONS x_1 OF COMPONENT 1

x_1	H^E ($J\ mol^{-1}$)		x_1	H^E ($J\ mol^{-1}$)	
	Exptl.	*Barker*		*Exptl.*	*Barker*
1,4-Dioxane (1)+chloroform (2)					
			(0.5000)	(−2080)	(−2084.74)
0.2069	−1438.47		0.5504	−2015.84	
0.2583	−1676.85		0.5975	−1911.71	
0.2976	−1823.86		0.6717	−1678.13	
(0.3000)	(−1850)	(−1830.56)	(0.7000)	(−1580)	(−1573.67)
0.3200	−1890.91		0.7141	−1504.80	
0.3693	−2010.67		0.7458	−1360.36	
0.4129	−2073.10		0.8087	−1050.91	
0.4326	−2086.37		0.8412	−876.01	
0.4894	−2082.99				
1,4-Dioxane+bromoform					
			(0.5000)	(−1830)	(−1839.78)
0.1608	−1052.37		0.5182	−1816.04	
0.2314	−1368.98		0.5549	−1782.02	
0.2829	−1551.05		0.6030	−1710.05	
(0.3000)	(−1590)	(−1609.20)			
0.3240	−1660.00		0.6697	−1550.10	
			(0.7000)	(−1345)	(−1422.93)
0.3823	−1769.88		0.7224	−1383.67	
0.4008	−1799.02		0.7761	−1178.89	
0.4536	−1834.13		0.8535	−826.72	
0.4987	−1829.60				

TABLE 2

PARAMETERS OF EQN (2) TOGETHER WITH THE STANDARD DEVIATIONS $\sigma(H^E)$ AND INTERACTION ENERGIES

	h_0	h_1	h_2	$\sigma(H^E)$ ($J\ mol^{-1}$)	U_1 ($J\ mol^{-1}$)	U_2 ($J\ mol^{-1}$)	U_3 ($J\ mol^{-1}$)
1,4-Dioxane+ chloroform	−8313.47	1588.31	1421.26	1.54	230.29	−4903.43	−5889.94
1,4-Dioxane+ bromoform	−7320.18	−848.41	213.29	2.19	230.29	−4617.98	−5319.15

has 5 contact point Q_X of another class. Again 1,4-dioxane is assumed to have two classes of contact sites, the two oxygen atoms having contacts of one class while the residual part having contact sites of another class. The interactions considered were a specific (O–H) interaction between the oxygen atoms of 1,4-dioxane and the proton of the haloforms and of strength U_2; all the non-specific interactions, for the sake of simplicity, are assumed to have the same strength U_1. Interactions between contact sites of the same class are taken to have zero interaction energy.

For 1,4-dioxane+chloroform, the two oxygen atoms of dioxane were first assumed to have 4 contact sites Q_{OA} of one class and the residual part R has 2 contact sites of another class. Excess energy of mixing at constant volume U_V^E values were then evaluated from the expression

$$U_V^E = -2RT[(x_O x_x + x_R x_H + x_R x_x)\eta_1 \ln \eta_1 + \eta_2 \ln \eta_2 (x_O x_H)] \tag{3}$$

where the various parameters x depend upon the number of interactions of various contact sites of different classes in molecules A and B of the binary mixture in the manner described in ref. 8. These parameters were evaluated by solving the following simultaneous quadratic eqns (4)–(7) with certain assumed values of U_1 and U_2.

$$x_O[x_O + \eta_1 x_R + \eta_2 x_H + \eta_1 x_x] = Q_{OA} x_{A/2} \tag{4}$$

$$x_R[\eta_1 x_O + x_R + \eta_1 x_H + \eta_1 x_x] = Q_{RA} x_{A/2} \tag{5}$$

$$x_H[\eta_2 x_O + \eta_1 x_R + x_H + \eta_1 x_x] = Q_{HB} x_{B/2} \tag{6}$$

$$x_x[\eta_1 x_O + \eta_1 x_R + \eta_1 x_H + x_x] = Q_{XB} x_{B/2} \tag{7}$$

where $\eta_i = \exp(-U_i/RT)$ $(i = 1$ or $2)$, U_1 and U_2 are the interaction energies (per mole), x_A is the mole fraction of A and R is the gas constant. It was found that no values of U_1 and U_2 gave U_V^E values in this case that came any close to the experimental H^E values for this mixture.

The two oxygen atoms of 1,4-dioxane in dioxane+chloroform were then assumed to have 2 contact sites Q_{OA} of one class and the residual part R has 4 contact sites Q_{RA} of another class. U_V^E values were then calculated from expression (3) in the manner described above. U_V^E values at $x_1 = 0.3$, 0.5 and 0.7 for the best U_1 and U_2 values of 230.29 and −5084.98 J mol^{-1} were −1546.27, −2058.14 and −1033.05 J mol^{-1}, respectively. Neglecting the contributions of volume change of mixing V^E, to U_V^E, we take $U_V^E \approx H^E$ and so that these U_V^E values at $x_1 = 0.3$, 0.5 and 0.7 now make a better reproduction of H^E data for 1,4-dioxane+chloroform. The theoretical reproduction of the experimental H^E data for this mixture is not good in either of these two cases, the latter being a better one. The failure in the latter case may be due to the assumption that the oxygen atoms of 1,4-dioxane have contacts of one type only.

We now suppose that the two oxygen atoms of 1,4-dioxane in dioxane+chloroform have 2 contact sites of the same class but of two different subclasses. Either one or both of these sites on the two oxygen atoms of dioxane may be involved in its interaction with chloroform. The interaction, when only one oxygen atom of 1,4-dioxane is involved with chloroform, i.e., $Q_{OA} = 1$, is assumed to have an interaction energy of U_2 while that when both of the contact sites on the two oxygen atoms of 1,4-dioxane are involved, i.e., $Q_{O'A} = 2$, is taken to have an interaction energy of U_3. The proton interacting with Q_{OA} is designated as H while that interacting with $Q_{O'A}$ is labelled at H^1. If 1,4-dioxane+chloroform contains both AB and AB_2 complex species in solution, U_V^E would be expressed by

$$U_V^E = -2RT[(x_O x_x + x_{O'} x_x + x_R x_H + x_R x_{H'} + x_R x_x)\eta_1 \ln \eta_1 + (x_O x_H)\eta_2 \ln \eta_2 + \\ + (x_{O'} x_{H'})\eta_3 \ln \eta_3] \tag{8}$$

where the various parameters were evaluated by solving the following simultaneous quadratic eqns (9)–(14) for certain assumed values of U_1, U_2 and U_3.

$$x_O[x_O + \eta_1 x_{O'} + \eta_1 x_R + \eta_2 x_H + \eta_2 x_{H'} + \eta_1 x_x] = Q_{OA} x_{A/2} \tag{9}$$

$$x_{O'}[\eta_1 x_O + x_{O'} + \eta_1 x_R + \eta_3 x_H + \eta_3 x_{H'} + \eta_1 x_x] = Q_{O'A} x_{A/2} \tag{10}$$

$$x_R[\eta_1 x_O + \eta_1 x_{O'} + x_R + \eta_1 x_H + \eta_1 x_{H'} + \eta_1 x_x] = Q_{RA} x_{A/2} \tag{11}$$

$$x_H[\eta_2 x_O + \eta_2 x_{O'} + \eta_1 x_R + x_H + \eta_1 x_{H'} + \eta_1 x_x] = Q_{HB} x_{B/2} \tag{12}$$

$$x_{H'}[\eta_3 x_O + \eta_3 x_{O'} + \eta_1 x_R + \eta_1 x_H + x_{H'} + \eta_1 x_x] = Q_{H'B} x_{B/2} \tag{13}$$

$$x_x[\eta_1 x_O + \eta_1 x_{O'} + \eta_1 x_R + \eta_1 x_H + \eta_1 x_{H'} + x_x] = Q_{XB} x_{B/2} \tag{14}$$

U_V^E values evaluated in this manner for $x_1 = 0.3$, 0.5 and 0.7 are recorded in Table 1 and they well reproduce the experimental H^E curve for this mixture. The analysis of H^E data for dioxane+chloroform in terms of the Barker's theory thus suggests that this mixture contains both AB and AB_2 molecular species in solution. These species would persist even to great dilution as Matsui et al.[14] have maintained in their analysis of their infinite dilution partial molar enthalpy of a binary solution containing dimethyl sulphoxide (A) and chloroform (B).

U_V^E values for 1,4-dioxane+bromoform were also analysed in the manner as described for 1,4-dioxane+chloroform. It was again observed that the assumption that this mixture also contains AB and AB_2 molecular species in solution yielded U^E values that reproduce pretty well H_V^E data for this mixture.

Examination of U_2 values for 1,4-dioxane+chloroform and 1,4-dioxane+bromoform shows that compared to bromoform, chloroform forms a stronger H-bond with 1,4-dioxane. The bromines in bromoform due to their size are not able to displace the charge on the C–H bond to such an extent as the chlorines in chloroform and consequently bromoform would form a weaker H-bond with dioxane. This should also be evident in H-bond formation in AB_2 species in these mixtures and the U_3 interaction energies support this conjecture.

ACKNOWLEDGMENTS

Author's sincere thanks are to Mr. R. C. Phutela and Mr. P.S. Arora for their help with the experimental work. It is a pleasure to record the help that the author received from the faculty at the P.A.U. Ludhiana.

REFERENCES

1 L. G. Hepler and D. V. Fenby, *J. Chem. Thermodyn.*, 5 (1973) 471.
2 D. V. Fenby and L. G. Hepler, *J. Chem. Thermodyn.*, 6 (1974) 185.
3 M. L. McGlashan and R. P. Rastogi, *Trans. Faraday Soc.*, 54 (1958) 496.
4 R. V. Orye and J. M. Prausnitz, *Trans. Faraday Soc.*, 61 (1965) 1338.
5 I. R. McKinnon and A. G. Williamson, *Austl. J. Chem.*, 17 (1964) 1374.
6 K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, 62 (1966) 2063.
7 J. R. Coates, J. B. Ott and D. E. Oyler, *Trans. Faraday Soc.*, 62 (1966) 1511.
8 J. A. Barker, *J. Chem. Phys.*, 30 (1952) 1526.
9 A. Vogel, *Practical Organic Chemistry*, Longmans-Green, London, 1968.
10 B. R. Sharma and P. P. Singh, *J. Chem. Thermodyn.*, 5 (1973) 361.
11 A. K. Adya, B. S. Mahl and P. P. Singh, *J. Chem. Thermodyn.*, 5 (1973) 393.
12 R. K. Nigam and B. S. Mahl, *J.C.S. Faraday I*, 68 (1972) 1508.
13 H. C. Van Ness and M. M. Abbott, *International Data Series*, No. 2, 1974, p. 93.
14 T. Matsui, L. G. Hepler and D. V. Fenby, *J. Phys. Chem.*, 77 (1973) 2397.