Communications

Molecular Interactions in Binary Mixtures of Chloroform with Benzene & Toluene*

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Chemical contribution to excess enthalpy for the binary mixture of chloroform with benzene and toluene have been calculated assuming 1 : 1 complex formation. The difference in the calorimetric and calculated excess enthalpy is attributed to physical (non-complexing) contribution.

WE reported[1] excess enthalpies of binary mixtures of chloroform with aromatic hydrocarbons and concluded qualitatively that hydrogen bonding were the predominant interactions in these mixtures without any mention of the physical (non-complexing) contribution. However, the observed excess enthalpy may conveniently be divided into physical (non-complexing) and chemical contributions, the latter being due to complex formation[2]. Chemical contribution to excess enthalpy can be calculated from equilibrium constant data obtianed from spectral studies. The difference between the calorimetric excess enthalpy and spectroscopically calculated excess enthalpy should be related to the physical contribution. In this note we have estimated the physical and chemical contributions to excess enthalpies for the binary mixtures of chloroform with benzene and toluene.

There is good evidence for association of chloroform (A) with aromatic hydrocarbons (B) to form 1 : 1 complex in the solid state[3] and in the liquid state[3-5], via hydrogen bonding. The association of chloroform with aromatics is represented by

$$A + B = AB \qquad ...(1)$$

The equilibrium constant of the association represented by Eq. (1) would be given by Eq. (2),

$$K = r(1-r)/(x_A x_B - r + r^2) \qquad ...(2)$$

where r represents the ratio of the amount of the complex AB formed at equilibrium to the sum of the stoichiometric amounts of A and B in the mixture; x_A and x_B are the stoichiometric mole fractions of A and B respectively.

The chemical contribution of excess enthalpy H_C^E of complex formation due to hydrogen bond inter-

action can be calculated from the relation (3),

$$H_C^E = r(\Delta H) \qquad ...(3)$$

where ΔH is the enthalpy of hydrogen bond association. Substituting the value of r from Eq. (2) in Eq. (3), we obtain an expression for H_C^E as a function of mole fractions of the two components A and B.

However, the calorimetric excess enthalpy H^E may be taken as the sum of physical and chemical contributions,

$$H^E = H_P^E + H_C^E \qquad ...(4)$$

where H_P^E and H_C^E represent the physical and chemical contributions respectively.

In Fig. (1) are compared the calorimetric[1] excess enthalpies with the chemical contributions arising from the formation of the $CHCl_3.C_6H_6$ and $CHCl_3.C_6H_5CH_3$ complexes. The equilibrium constant and ΔH values for both the systems are those reported in references (5) and (6) respectively.

The chemical contribution to excess enthalpy is greater than the calorimetric excess enthalpies for both of the binary mixtures. This clearly indicates that the physical contribution to excess enthalpy should be positive, which is obvious because the excess enthalpy for a mixture of carbon tetra-
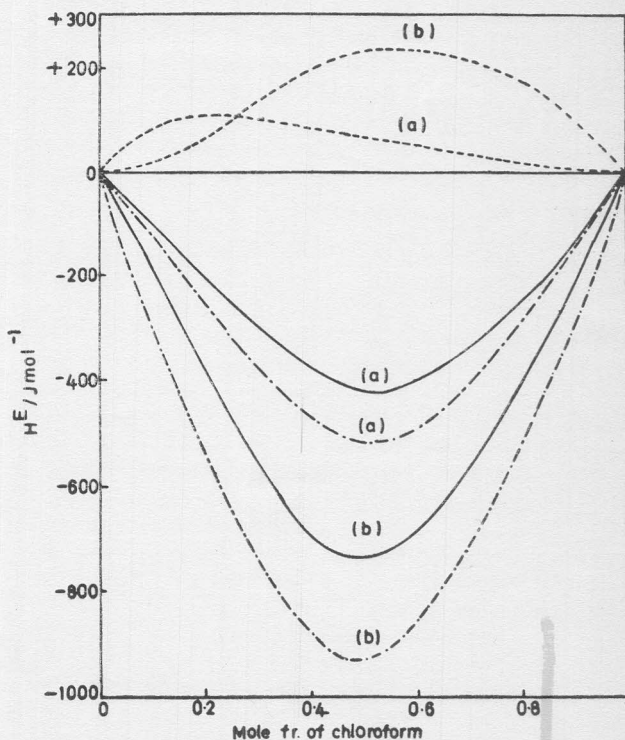

Fig. 1 — Comparison of excess enthalpies for (a) chloroform +benzene and (b) chloroform+toluene [(—) calorimeteric data (ref. 1); (—.—) spectroscopic data (Eq. 3); and (----) physical contribution (Eq. 4)]

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chloride+cyclohexane is positive[7] where a pure physical interaction would be expected.

The complex bonding between chloroform and aromatic hydrocarbons similar to other hydrogen bonds, is essentially electrostatic in character, but is considerably less stable than the more common hydrogen bond due to weak ionic character of the C-H bond. This is consistent with the lower value of chemical contribution to excess enthalpies of chloroform with benzene and toluene, which are —0·5 and —0·9 kJ mole^{-1} respectively for equimolar mixtures.

Reference

1. RASTOGI, R. P., NATH, J. & MISRA, R. R., *J. chem. Thermodynamics*, **3** (1971), 307.
2. McGLASHAN, M. L., *An. Rep. Chem. Soc.*, LIX (1962), 73.
3. REEVES, L. W. & SCHNEIDER, W. G., *Can. J. Chem.*, **35** (1957), 251.
4. PERRINS, N. C. & SIMONS, J. P., *Trans. Faraday Soc.*, **65** (1969), 390.
5. WEI-CHUWAN, LIN & SHYR-JIN, TSAY, *J. phys. Chem.*, **74** (1970), 1037.
6. JOHNSTON (Jr), M. D., GASPARRO, F. P. & KUNTZ (Jr), I. D., *J. Am. chem. Soc.*, **91** (1969), 5715.
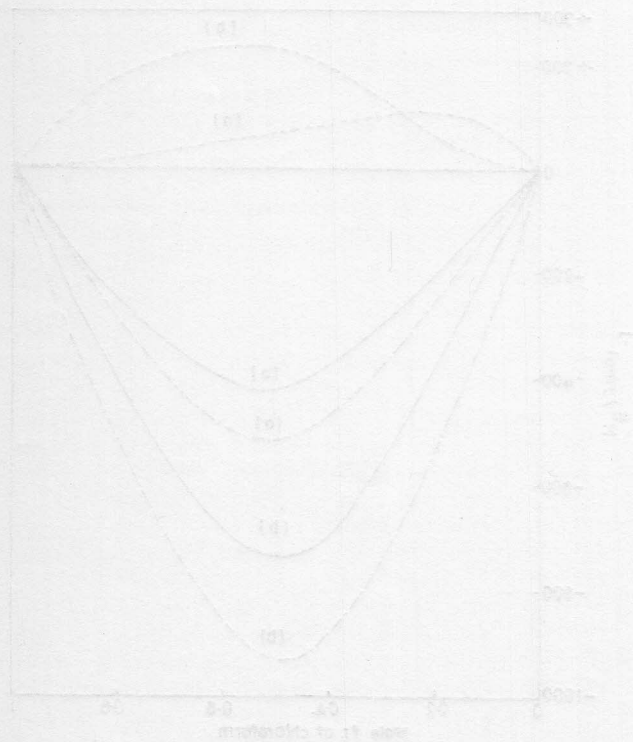7. ADCOCK, D. S. & McGLASHAN, M. L., *Proc. r. Soc., London*, **A226** (1954), 266.