Viscometric studies of hydrogen bonding

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Abstract. The viscometric method can be conveniently used for studying the interaction between weakly interacting systems. The systems studied are: methanol-acetone, ethanol-acetone, n-propanol-acetone and n-butanol-acetone in carbon tetrachloride. At 25°C, the equilibrium constants for the above ternary systems are 0·22, 0·30, 0·38 and 0·52 M^{-1} respectively. However, the heats of formation of complexes obtained by the viscometric method are high and decrease from methanol-acetone-CCl_4 to n-butanol-acetone-CCl_4.

Keywords. Hydrogen bonding; viscometry; equilibrium constants.

1. Introduction

Although the spectrophotometric method is probably the most common method used for determining association constants and other thermodynamic parameters of charge-transfer complexes, doubts have frequently been expressed as to the significance of the values, K_c, and ε, obtained by the spectral method alone (Childs *et al* 1971, 1972). It is surprising that even though, in principle, the formation of molecular complexes and hydrogen bonding can be detected and their composition established from a study of characteristic abrupt departures from ideal behaviour in some physical properties, *e.g.* vapour pressure, refractive index, surface tension and viscosity etc., many of these methods are hardly used (Vinogaradov and Linnel 1971). Recently we have begun the exploration of some non-spectral methods for studying the interaction between the molecules in solution and have demonstrated their applicabilities in obtaining the equilibrium constants directly (Singh and Bhat 1978; Singh *et al* 1980; Bhattacharjee and Bhat 1983). Even though the measurements of various thermodynamic excess functions of binary solutions (using viscometry) have been the subject of much research, there is hardly any report on using viscosity measurement method for ternary systems(Irving and Smith 1969). It was therefore felt that it was worthwhile to make an attempt to study the interaction between proton donors and proton acceptors (i.e., hydrogen bonding) viscometrically, in suitable media and to obtain equilibrium constants directly. The systems chosen for the studies are: methanol, ethanol, n-propanol and n-butanol as proton donors, acetone as proton acceptor, and carbon tetrachloride as solvent.

2. Materials and method

Acetone, carbon tetrachloride, methanol, ethanol, n-propanol and n-butanol were purified by standard procedures. The densitites and the corrected boiling points agreed well with literature data.

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The densities and viscosities of pure samples and those of 'binary mixtures' of known composition (mole fractions) of methanol, ethanol, n-propanol, n-butanol and acetone in carbon tetrachloride were determined at 25, 30, 35 and 40°C (± 0.1°C) by using a pyknometer and Ostwald's viscometer respectively and coefficients of viscosity were calculated. Similarly the densities and viscosities of ternary systems (of known composition) of alcohols-acetone-CCl_4 were determined. The experiments were repeated at least twice and the results were reproducible within the experimental error of $\pm 0.015 \times 10^{-3}$ poise.

The stoichiometry of the 'associated species (complex)' was determined by Job's continuous variation process (Job 1928).

The non-linear plot of any physical property of a 'mixed solution' against the concentration of the components, i.e. the deviation from ideal behaviour of the pure components in solution is an indication of the interaction between the two species, namely the donor D, and the acceptor A (after deducting the solvent contributions). If one can assume that the deviation is entirely due to the 'complex' alone, then the deviation should be proportional to the concentration of the complex. We have modified the procedure suggested by Yoshida and Osawa (1965) to obtain the equilibrium constant, K_c. The detailed procedure is given in Bhattacharjee and Bhat (1983).

3. Results and discussion

The viscosities of methanol, ethanol, n-propanol, n-butanol, acetone and carbon tetrachloride were determined at 25, 30, 35 and 40°C. The viscosity of methanol in carbon tetrachloride is higher than the expected value [i.e., $\Delta\eta = \eta_{obs} - \eta_{cal} = -\eta_{obs} - (x_1\eta_1 + x_2\eta_2)$] whereas in all other alcohols they are lower. The deviation in η value (i.e., $\Delta\eta$) shows that there is interaction between methanol and carbon tetrachloride and the maximum deviation is at 3:2 composition, which is temperature independent. As the observed values are higher than the expected values, it appears that due to 'complexation'/'association' between CH_3OH and CCl_4 molecules the viscosity has increased. Similar is the case for acetone-CCl_4 systems (2:3). It is known that acetone and carbon tetrachloride do interact to form a complex (Rao *et al* 1972; Rowlinson 1971). Singh and Rao (1967) studied the infrared spectra of methanol and showed that alcohols formed dimers or trimers in carbon tetrachloride solutions as dilute as 0.01 M. An NMR study by Dixon (1970) of methanol in CCl_4 showed the existence of trimers and octamers even in very dilute solutions. Therefore it is quite safe to assume that methanol etc. associate through hydrogen bonding in carbon tetrachloride solutions. So when carbon tetrachloride approaches alcohol molecules, there is a 'breaking' of the hydrogen bonding in associated alcohol molecules and formation of H-bonds with CCl_4 (Patterson and Hammaker 1967). Methanol is a small molecule (as compared to other alcohol molecules), the dimerization energy in methanol is maximum and it decreases from methanol to n-butanol (Vinogaradov 1971). As the dimerization energy is greater for methanol molecules, stability of 'associated' species is higher. Hence, breaking of the hydrogen bonds of methanol molecules (i.e. structure breaking effect) and then the formation of new hydrogen bonds (i.e. structure making effect) between MeOH and CCl_4 is less favoured as compared to the n-butanol-CCl_4 system which is what has been observed (Singh and Rao 1967). The deviation, $\Delta\eta$, increases in the order,
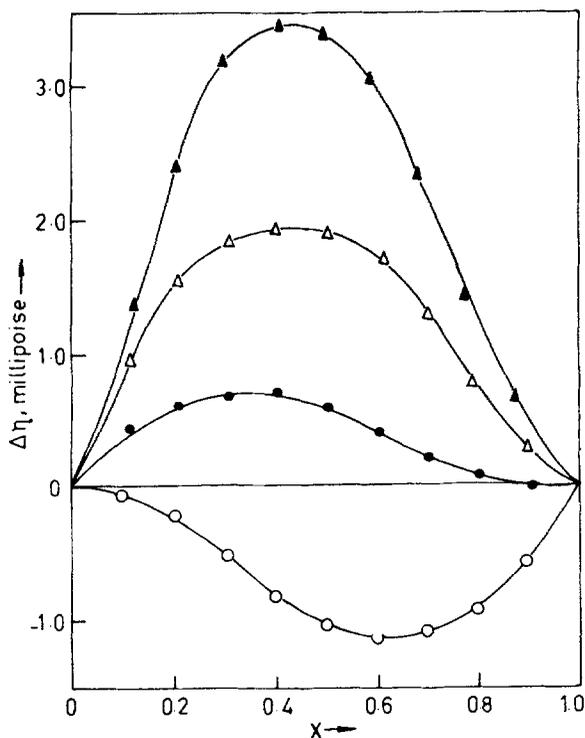
Figure 1. Variation of $\Delta\eta$, the difference between the η_{obs} and η_{cal} with the mole fraction of alcohols; (1) MeOH-carbon tetrachloride (O——O——O); (2) EtOH-carbon tetrachloride (●——●——●); (3) n-PrOH-carbon tetrachloride (△——△——△); (4) n-BuOH-carbon tetrachloride (▲——▲——▲).

MeOH-CCl$_4$ < EtOH-CCl$_4$ < n-PrOH-CCl$_4$ < n-BuOH-CCl$_4$, indicating that MeOH-CCl$_4$ interaction is less favoured as compared to n-BuOH-CCl$_4$ (figure 1). The stoichiometry is 2:3 in EtOH-CCl$_4$, n-PrOH-CCl$_4$ and n-BuOH-CCl$_4$. Similar observations are reported in literature for higher alcohols-dichloromethane mixtures (Choudhury and Naidu 1981; Reddy and Naidu 1977). The deviation decreases with increase in temperature. The energy of activation (for viscous flow) of pure components, namely, methanol, ethanol, n-propanol, n-butanol, acetone and carbon tetrachloride are 10·5, 16·9, 19·1, 21·0, 6·9 and 10·9 kJ mole^{-1} respectively and the corresponding values of the alcohols and acetone in CCl$_4$ are 10·5, 11·9, 12·7, 13·4 and 7·6 ($\pm$ 0·01) kJ mol^{-1} respectively. From these data it is clear that activation energy increases with the size of the molecules. Even though one would like to conclude that the viscosity and the energy of activation depend on the size of the molecule, one has to be cautious in cases like the present one, involving already 'associated' species and probably more than one H-bonded species between donor and acceptor molecules. It can be seen from the above data that the energies of activation of the 'mixtures' of alcohol-CCl$_4$ are lower than that of alcohol itself, which we are not in a position to explain, however, as we are dealing with 'complex'/'associated' molecules.

The viscosities of ternary systems, namely alcohol-acetone-carbon tetrachloride of different compositions, are determined at different temperatures (25, 30, 35 and 40°C).
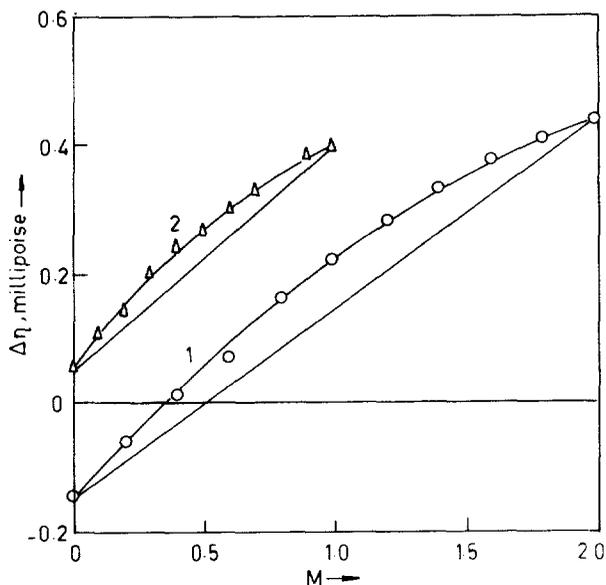
Figure 2. Variation of $\Delta\eta$, with molar concentration of acetone in MeOH-acetone-carbon tetrachloride, system at 25°C; (1) total concentration = 2 mole (○); (2) total concentration = 1 mole (△).

No maxima are found in the viscosity curves. But the non-linear plot of the difference in viscosities of the mixed solutions (i.e., $\eta_{cal} - \eta_{obs}$) against the concentration of acetone indicates the presence of a complex. A continuous variation plot of $\Delta\eta$, the difference in viscosity between the 'mixed solutions' and the calculated viscosities of the two solutions, shows the presence of a 1:1 complex in the experimental range of concentration (figure 2). From the figure it is clear that there is interaction between acetone and alcohol in CCl_4. The interaction (area under the curve in the plot) increases from MeOH-acetone-CCl_4 to n-BuOH-acetone-CCl_4 systems; this indicates the relative strength of the 'complexes', i.e., n-BuOH-acetone-CCl_4 > n-PrOH-acetone-CCl_4 > EtOH-acetone-CCl_4 > MeOH-acetone-CCl_4. The equilibrium constants were calculated (from the concentrations of the species rather than the activities) and at 25°C they are 0·22, 0·30, 0·38 and 0·52 M^{-1} for MeOH-acetone, EtOH-acetone, n-PrOH-acetone and n-BuOH-acetone in CCl_4 respectively. Here it is worth mentioning that Tamres and Strong (1979) have rightly pointed out that even contact charge-transfer complexes should have K values of the order of 0·11 M^{-1}. From the above data it is clear that the formation constant for the hydrogen bonded complex increases from MeOH-acetone to n-BuOH-acetone, assuming that the standard enthalpy of formation ΔH^0 of the hydrogen bond in a complex A-H-·-·-B and its standard entropy of formation ΔS^0 are independent of temperature. The heat of formation of these complexes were obtained from the plot of log K_c vs $1/T$ and these values are slightly higher than normal ($-\Delta H^0$ for MeOH-acetone, EtOH-acetone, n-PrOH-acetone and n-BuOH-acetone in CCl_4 are 63·4, 46·5, 40·7, 37·5 kJ/mole respectively). However, similar observations were made in literature for purine-H_2O-DMSO (Kanbour *et al* 1983), heterocyclic compounds-phenol (Sverdlover and Vatolina 1983), malamine

Table 1. Equilibrium constants and other thermodynamic parameters of *n*-alcohols-acetone in carbon tetrachloride.

System	K_c^* M^{-1}†				$-\Delta H^{0**}$ kJ/mole	$-\Delta G^0$ kJ/mole at 25°C	$-\Delta S^0$ kJ/mole
	25°C	30°C	35°C	40°C			
MeOH-acetone	0·22	0·16	0·09	0·07	63·5	−3·1	0·22
EtOH-acetone	0·30	0·22	0·17	0·12	46·5	−2·9	0·17
n-PrOH-acetone	0·38	0·25	0·21	0·17	40·7	−2·7	0·15
n-BuOH-acetone	0·52	0·41	0·31	0·27	37·5	−1·6	0·13

* K_c values were calculated from the K_x values, by using the equation, $K_x = \dfrac{K_c 1000 d_s}{M_s}$ where, d_s = density of the solvent in g/ml, M_s = Molecular weight of the solvent.
† Error limit = ±0·01; ** error limit = ±1·5.

cyanourate (Finkelshtein and Rukerich 1983). It may be recalled that the large enthalpies (≈ 60 kJ/mole) of formation of the complexes of nitrophenols with picric acid have been explained in terms of 1 : 1 proton transfer complexes in preference to the 1 : 1 H-bonded complexes (Vinogaradov 1971). However, in the present case we are not able to account for such high values of ΔH. Kohler (1984) has pointed out that it is difficult to compare the nonspectroscopic and spectroscopic evaluation of complexation equilibria (and other thermodynamic parameters) because nonspectroscopic—thermodynamic properties are determined by the activities of the species whereas spectroscopic properties are determined by their concentration. The values for the heats of complexation must be considered as presenting a composite result for alcohol-acetone-CCl$_4$ systems of different alcohol aggregation (Tse and Tamres 1977). The process of self association and preferential solvation results in a complex which seems to consist of acetone molecule interacting with an aggregate containing many alcohol molecules. The number of alcohol molecules in the aggregate is concentration dependent because of different degrees of self association and solvation. It is possible that the donor strength of the alcohol may change after association. Molecular orbital calculations on the association of water, of methanol and of other hydrogen bonded molecules show that the charge distribution of the polymeric molecule is different from that of the monomer (Hoyland and Kier 1969; Murthy *et al* 1969, 1970; Marita and Nagakura 1972). The negative charge on the oxygen atom in the molecule acting as the proton donor increases when the hydrogen bond is formed, and increases further if a trimer is formed, this in turn causes greater positive charge on the proton and the interaction between the proton and the oxygen of acetone is stronger. For an exothermic reaction, ΔG^0 is negative. However, in the present case ΔG^0 is positive ($K < 1$); and ΔS^0 is negative and this is possible because of the large negative ΔH^0.

As mentioned in our earlier communication, even though the usefulness of the viscometric method in the study of molecular complexes has already been established, the present procedure demands very careful measurements of viscosities involving long flow times in order to realise significant difference between solvent and dilute solutions. In addition to this, there are experimental difficulties such as making very accurate measurements of flow times, precise temperature control and keeping the system free

from dust, grease, etc. Moreover, the measurements are intrinsically time consuming. So even though the viscometric method can be used for studying the interaction between molecules in solution it may be more applicable where no alternative is available.

Acknowledgement

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