

## Viscometry in the study of molecular complexes

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**Abstract.** Viscometric method has been used to study the interaction between the weak interacting systems such as benzene-CCl<sub>4</sub>-cyclohexane, toluene-CCl<sub>4</sub>-cyclohexane and *o*-xylene-CCl<sub>4</sub>-cyclohexane. The equilibrium constants and other thermodynamic parameters have been reported and compared with literature data.

**Keywords.** Viscometry; molecular complexes; weak interacting systems.

### 1. Introduction

There has been an increasing interest in the study of molecular complexes and a number of different experimental procedures have been used to investigate the interaction between electron donors and electron acceptors with or without a third component. All the methods available to study the molecular structure and the nature of chemical bond also apply to molecular complexes. However, in spite of the fact that in principle, the interaction between molecules and the composition of the complex formed can be established from a study of the characteristic abrupt departure of some physical properties from ideal behaviour, like dielectric constant, refractive index, optical absorption, surface tension, viscosity etc, many of these methods are hardly used. Recently Bhat *et al* (1979); Bhat and Singh (1981, 1982) used non-spectral methods like surface tension, refractive index measurements, constant activity method etc., to study the interaction between the molecules in solutions, and demonstrated their applicabilities in obtaining the equilibrium constant directly. Although the measurements of various thermodynamic excess functions of binary solutions have been the subject of much research (from viscosity measurements) there is hardly any report on using viscosity measurement method for ternary systems except that of Irving and Smith (1969). It was therefore felt worthwhile to study the interaction of electron donors with electron acceptors in suitable media viscometrically and to obtain the equilibrium constant directly. The systems, chosen for the studies are benzene, alkyl benzenes-carbon tetrachloride-cyclohexane.

### 2. Material and method

Cyclohexane, carbon tetrachloride, benzene, toluene and *o*-xylene, were purified by standard procedures. The densities and the boiling points of the liquids agree with literature values.

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The densities and viscosities of pure samples and those of 'binary mixtures' of known compositions (mole fractions) of benzene, toluene, xylene, and carbon tetrachloride in cyclohexane were determined at 25, 30, 35 and 40°C ( $\pm 0.1^\circ\text{C}$ ) using Ostwald's viscometer and the coefficients of viscosities calculated. Similarly the densities and viscosities of ternary systems (of known compositions) of benzene- $\text{CCl}_4$ -cyclohexane etc, 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 'complex' was determined by Job's (1928) continuous variation method.

The nonlinear 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. Baur *et al* (1969) developed a procedure for obtaining equilibrium constant of a complex by studying the change in polarizability of the species. However, it is felt that the equilibrium constant  $K_c$  can be calculated by modifying the procedure of Yoshida and Osawa (1965) which is of more general nature.

For an equimolar mixture of  $D$  and  $A$  (with total concentration  $C$ ), the maximum deviation  $RS$  of any of the physical properties, (here  $\eta$ ) from the additivities can be written as

$$RS = \alpha x, \quad (1)$$

where  $\alpha$  is a proportionality constant and  $x$  is the concentration of the complex. When the total concentration is changed from  $C$  to  $C'$ , then

$$R'S' = \alpha x', \quad (2)$$

therefore

$$RS/R'S' = \alpha x/\alpha x' = x/x' = k \quad (3)$$

In the present case  $K_c$  is given by

$$K_c = x/[(C/2) - x]^2 = x'/[(C'/2) - x']^2. \quad (4)$$

Combining (3) and (4) and rearranging, we obtain

$$K_c = 2\sqrt{k} \{ \sqrt{k}(C + C') - (C + kC') \} / (C - kC')^2 \quad (5)$$

As the plot of  $\Delta\eta$  vs mole fraction is not always symmetrical,  $k$  is actually the ratio of the area under the curves.

### 3. Results and discussion

The viscosities of benzene, toluene, *o*-xylene and carbon tetrachloride in cyclohexane were determined at 25, 30, 35 and 40°C. The viscosities of benzene and alkylbenzenes in cyclohexane decrease with increase in concentration whereas that of carbon tetrachloride in cyclohexane increases with concentration. Here it can be recalled that benzene and alkylbenzenes are electron donors whereas carbon tetrachloride is an electron acceptor. Therefore the interaction between benzenes and cyclohexane and

carbon tetrachloride and cyclohexane is of different type. The viscosities of all the mixtures studied are lower than the expected values, *i.e.*

$$\Delta\eta^E = \eta_S - (\eta_A X_A + \eta_B X_B),$$

where  $\eta_S$  is the observed viscosity,  $\eta_A$  and  $\eta_B$  are the viscosities and  $X_A$  and  $X_B$  are the mole fractions of the components *A* and *B* respectively. The deviation of viscosity from the ideal behaviour with a maximum deviation of 0.4 and 0.5 molefraction of alkylbenzenes shows that there is an interaction between the systems. Our present data go in parallel with the data of heat of mixing. The maximum deviation of the plot of  $\Delta\eta$  against the molefraction of benzene in benzene-cyclohexane appears at 0.5 molefraction of benzene whereas for toluene and *o*-xylene the excess of viscosity maximum appears at 0.4 molefraction indicating the presence of 2:3 complex. Similar observations were made by Lorimer and Jones (1977) for chloroform-propionitrile and chloroform-butylonitrile and they are of the opinion that this is due to the resultant of specific and non-specific interactions. As the deviation from the ideal behaviour is due to the interaction between the two different types of molecules, the relative deviation should be an indication of the strength of interaction between the molecules. From the present data it is clear that the strength of interaction between cyclohexane and alkylbenzenes vary in the order, benzene-cyclohexane > toluene-cyclohexane > *o*-xylene-cyclohexane (figure 1). This trend is maintained at all the temperatures studied. This is an indication that the strength of the interaction depends on the substituent (steric effect) rather than on the polarizability of the molecule. This trend is in good agreement with the observations made by Nigam *et al* (1980) for aromatic hydrocarbons-nitromethanes. The activation energy for the viscosities of benzene, toluene, *o*-xylene, carbon tetrachloride and cyclohexane are 9.23, 9.25, 10.98, 11.43 and 13.58 kJ mol<sup>-1</sup>

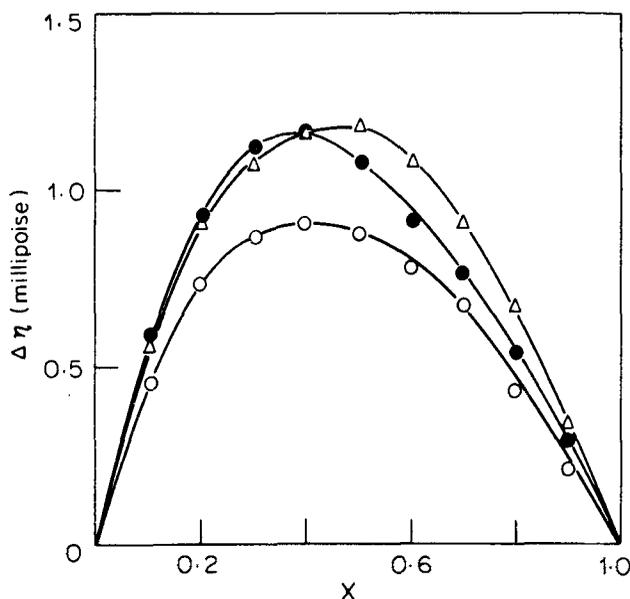


Figure 1. Variation of  $\Delta\eta$ , the difference between  $\eta_{cal}$  and  $\eta_{obs}$ , with the molefraction of alkylbenzenes at 25°C. ( $\Delta$ -benzene cyclohexane;  $\bullet$ -toluene cyclohexane and  $\circ$ -*o*-xylene cyclohexane).

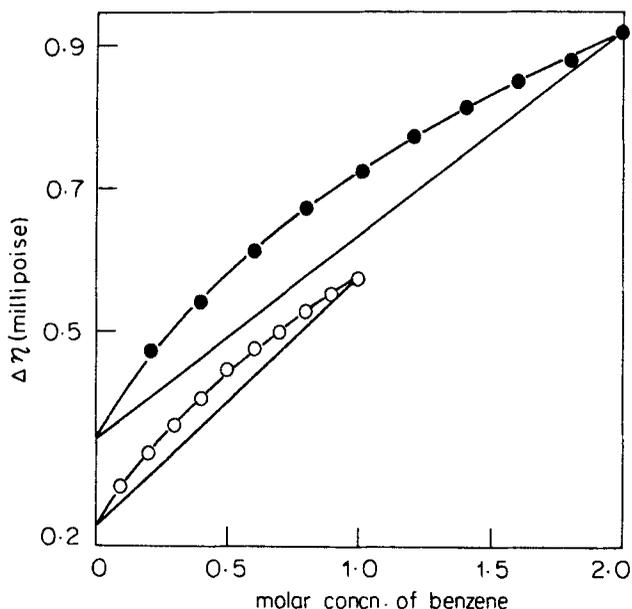
respectively. The increase in the activation energy with increase in size of the molecule (for alkyl benzenes) again confirm our earlier observations that the size and shape of the molecule is to be considered in determining the strength of interaction rather than the polarizability. The difference in the energy of activation (*i.e.*  $E_{\text{obs}}$  and  $E_{\text{cal}}$ ) varies in the order, *o*-xylene-cyclohexane > toluene-cyclohexane > benzene-cyclohexane. From these data we believe that the effect of *o*-xylene-cyclohexane complex on the energy of activation is much more than that of benzene-cyclohexane.

The viscosities of ternary systems, namely alkyl benzenes- $\text{CCl}_4$ -cyclohexane of different composition were determined at different temperatures (25, 30, 35 and 40°C). No maxima are found in the viscosity curves but the nonlinear plot of the difference in viscosities of the mixed solutions (*i.e.*  $\eta_{\text{cal}} - \eta_{\text{obs}}$ ) against the concentration of benzene indicates the presence of a complex. For brevity, only one such set of data is given in table 1. 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 only a 1:1 complex in the experimental range of concentrations. The deviation between the observed and calculated values is due to the interaction between the two species. From figure 2, it is clear that there is an interaction between the alkylbenzenes and carbon tetrachloride which increases with the electron-donating nature of the donor molecules, keeping the electron acceptor constant. The equilibrium constants and the free energies of formation of complexes (table 2) show that the equilibrium constants calculated from (5) are slightly higher than the literature data (obtained by different methods). However the values are increasing from benzene- $\text{CCl}_4$  to *o*-xylene- $\text{CCl}_4$ . The  $\Delta H^0$  values are also slightly higher and decrease from benzene- $\text{CCl}_4$  to *o*-xylene- $\text{CCl}_4$ . Our values of  $K_c$  cannot be compared with literature data as the latter make no mention about the solvent used. Secondly we have a higher concentration of solutions whereas in the literature the concentration range is very small. Our higher values may be due to the concentration effect since  $K_c$  depends on the concentration of the sample used. It is seen that although the equilibrium constants increase from benzene- $\text{CCl}_4$  to *o*-xylene- $\text{CCl}_4$  (which is expected on the strength of *n*-electron-donor

**Table 1.** Viscosities of mixed solutions of benzene-carbon tetrachloride in cyclohexane at 25°C.

Benzene (mol)	Carbon-tetra-chloride (mol)	Calculated viscosity (millipoise)	Observed viscosity (millipoise)	$\Delta\eta$ (millipoise)
0.0	1.0	8.4031	8.1792	0.2239
0.1	0.9	8.3649	8.0636	0.3013
0.2	0.8	8.3271	7.997	0.3301
0.3	0.7	8.2892	7.9304	0.3588
0.4	0.6	8.2514	7.8469	0.4045
0.5	0.5	8.2137	7.762	0.4520
0.6	0.4	8.1756	7.6921	0.4835
0.7	0.3	8.1313	7.6114	0.5199
0.8	0.2	8.0924	7.5614	0.5310
0.9	0.1	8.0538	7.5110	0.5430
1.0	0.0	8.0249	7.4491	0.5758

Error limit  $\pm 0.015$



**Figure 2.** Variation of  $\Delta\eta$  with the molar concentration of benzene in the benzene- $\text{CCl}_4$ -cyclohexane system at  $25^\circ\text{C}$ .

**Table 2.** Equilibrium constants and other thermodynamic parameters of alkylbenzenes-carbontetrachloride in cyclohexane.

System	$K_c^* 25^\circ\text{M}^{-1}$	$-\Delta H^\circ^\ddagger$ (kJ/mol)	$-\Delta F^\circ$ (kJ/mol)
Benzene- $\text{CCl}_4$	1.70 (0.21)	24.5 (25.4)	1.32
Toluene- $\text{CCl}_4$	3.20 (0.41)	17.7 (21.3)	2.88
<i>o</i> -xylene- $\text{CCl}_4$	4.07 (-)	12.2 (-)	3.47

Error limit: \* =  $\pm 0.05$ ; † =  $\pm 1.5$

The values in parentheses are taken from Glashan *et al* (1969)

ability) the enthalpies vary in the reverse order. Similar calorimetric observations were made by Glashan (1969). Irving and Smith (1969) are of the opinion that the viscometric method can be used satisfactorily in the case of strong complexes.

As it stands the present procedure demands very careful measurements of viscosities involving long flow times to realise significant differences between solvent and dilute solutions. In addition there are experimental difficulties such as accurate measurement of flow times, precise temperature control, dust-free grease materials etc. Moreover, the measurements are time-consuming. However, this method is useful where no alternative is available.

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