Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 89, Number 2, April 1980, pp. 139–144.

Surface tension measurements in the study of molecular complexes

RAM ADHAR SINGH, S P MISHRA and S N BHAT* India
Chemistry Department, Banaras Hindu University, Varanasi 221 005, India
* Chemistry Department, North-Eastern Hill University, Shillong 793 003,

MS received 4 June 1979 ; revised 27 August 1979

Abstract. Surface tension measurements can be used to investigate molecular complex formation in liquid solutions for strong and weak complexes. The association constant and epthalpy for triethylamine-iodine, hexamethylbenzene-tetracyanoethylene and ethanol-iodine in cyclohexane are $4{\cdot}55 \times 10^3$, 218 and $0.93\ M^{-1}$ at 25° C and 12·5, 7·7 and 5·1 kcal/mol respectively. These values compare well with those reported in the literature by other methods.

Keywords. Surface tension ; molecular complexes.

1. Introduction

Ever since Benesi-Hildebrand (1949) reported the interaction of iodine with aromatics, a variety of physical methods, such as optical spectroscopy, magnetic resonance spectroscopy, calorimetry, etc. have been employed to investigate molecular complexes. However, it is surprising that even though, in principle, the formation of molecular complexes can be indicated and their composition established from a study of characteristic abrupt departures from ideal behaviour in some physical properties, e.g., vapour pressure, surface tension, refractive index, dielectric constant, etc., many of these methods are hardly used. The only information available using the surface tension measurement method is from Nayar *et al* (1952) who pointed out that a correlation may exist between surface tension minima and complex formation. Ferroni and Gabrielli (1956) also reported the feasibility of determination of the equilibrium constant for iodine-ethanol in carbontetrachloride. It was therefore felt worthwhile to study the interaction of electron donors and acceptors in solutions by using the surface tension measurement method and compare the results with those obtained by spectroscopic methods. We have chosen (i) the triethylamine-iodine system where the interaction between triethylamine and iodine is very strong, (ii) the hexamethylbenzene-tetracyanoethylene system where the interaction is medium, and (iii) the ethanol-iodine system, a typical case of weak interaction.

2. Materials and methods

Cyclohexane, triethylamine, hexamethylbenzene, ethylalcohol and iodine were purified by using standard procedures. Tetracyanoethylene (DuPont) was recrystallised from chlorobenzene and purified by vacuum sublimation.

The surface tensions of pure components and of different solutions of different compositions (at constant total molar concentration) at different temperatures (25, 30, 35, 40 and 45° C) were measured in cyclohexane by the differential capillary rise method using a travelling microscope. The temperature of the solution was maintained constant ($\pm 0\cdot 1°$ C) by using a jacketed container through which water from a thermostat was circulated. The densities of the solutions at the same temperatures were measured by an Ostwald-Sprengel pyknometer. The experiments were repeated at least twice and the results were reproducible within the experimental error of 0·002 mN/m.

3. Results and discussion

3.1. *Triethylamine iodine*

The surface tensions of triethylamine in cyclohexane and iodine in cyclohexane decrease with increase in concentration of the solutes. The surface tension of the solvent is very much changed by the addition of a very small amount of solute in the initial stage. Up to 1·0 mM, the surface tension is a non-linear function of concentration, but then becomes a linear function between 1 and 50 mM. The range of concentrations of triethylamine and iodine is such that when they are mixed, they form neutral complexes ; this was confirmed spectroscopically. The non-linear plot of the surface tensions of the " mixed solution " against the concentration of triethylamine indicates the presence of a complex. For the sake of brevity, only one such set of data is given in table 1. A continuous variation plot of $\Delta\sigma$, the difference in surface tension between the " mixed solutions " and the calculated surface tensions of the two pure solutions, shows the presence of only 1 : 1 complex in the experimental range of concentration of 1 to 10 mM of amine (figure 1) ; similar observations were made earlier by Bist and Person (1969) for triethylamine-iodine by spectroscopy. As there is a linear relationship between $\Delta\sigma$ and the concentration of the complex, (i.e., similar to the test of Beer's law), we can conclude that if the two solutions show the same deviations of surface tensions, then they must have the same concentration of the complex (table 2) and the equilibrium constant for the system can be calculated by following the procedure adopted by Ferroni and Gabrielli (1956).

Consider the interaction of A with D,

$$A + D \rightleftharpoons AD.$$

Let C_A, C_A', C_D and C_D' be the initial concentrations of the acceptor and donor respectively for the two sets of solutions and C_{AD}, C_{AD}' be the concentration of the complexes. For the first set,

$$K = C_{AD}/[(C_D - C_{AD})(C_A - C_{AD})], \tag{1}$$

Table 1. Surface tensions of mixed solutions of triethylamine-iodine in cyclohexane at 25° C.

Triethylamine (millimoles)	Iodine (millimoles)	Observed surface tension (mN/m)	Calculated surface tension (mN/m)	$\Delta\sigma$ (mN/m)
0·5	9·5	23·366	23·266	0·100
1·0	9·0	23·376	23·260	0·116
1·5	8·5	23·395	23·255	0·140
2·0	8·0	23·401	23·250	0·151
2·5	7·5	23·423	23·246	0·177
3·0	7·0	23·430	23·234	0·196
3·5	6·5	23·435	23·231	0·204
4·0	6·0	23·448	23·221	0·227
4·5	5·5	23·452	23·222	0·230
5·0	5·0	23·458	23·220	0·238
5·5	4·5	23·443	23·217	0·226
6·0	4·0	23·365	23·212	0·153
6·5	3·5	23·328	23·206	0·122
7·0	3·0	23·277	23·205	0·072
7·5	2·5	23·253	23·188	0·065
8·0	2·0	23·239	23·185	0·054
8·5	1·5	23·229	23·177	0·052
9·0	1·0	23·209	23·173	0·036
9·5	0·5	23·191	23·148	0·043

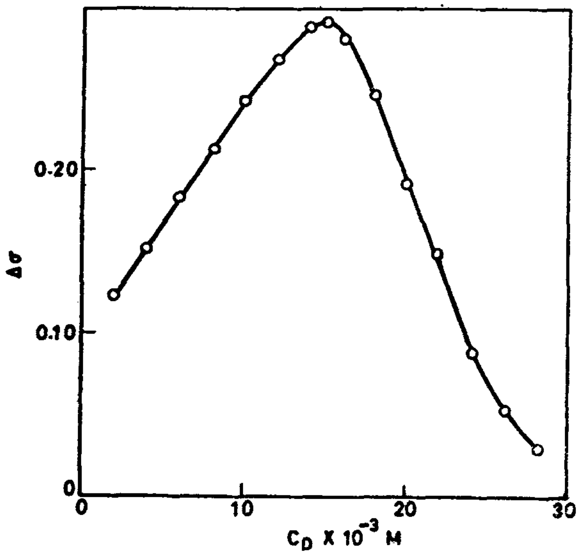

Figure 1. Plot of $\Delta\sigma$ *vs.* donor concentration of triethylamine at 25° C.

Table 2. Equilibrium constants from surface tension measurements for different sets of donors and acceptors in cyclohexane at 25° C.

System	1st set		2nd set		$\Delta\sigma$	K, M^{-1}	Average K, M^{-1}	— ΔH° kcal/mole
	Donor mM	Acceptor mM	Donor mM	Acceptor mM				
Triethylamine-iodine :	1·500	8·500	1·650	4·350	0·140	4·272 × 10^{3}		
	1·750	8·250	1·850	4·150	0·145	4·294 × ,,		
	2·005	7·995	2·150	3·850	0·150	4·785 × ,,	4·55 × 10$^{3\,(a)}$	12·5 (12·0)^{e}
	2·150	7·850	2·350	3·650	0·155	4·791 × ,,		
	2·250	7·750	2·550	3·450	0·160	4·293 × ,,	(4·71^{3} 10$^{3\,(d)}$)	
	2·400	7·600	3·000	3·000	0·165	4·857 × ,,		
Hexamethylbenzene-tetracyanoethylene	1·750	18·250	1·920	13·080	0·130	216	219$^{(b)}$	
	2·200	17·820	2·445	12·555	0·140	207		
	2·675	17·325	3·000	12·000	0·150	224	(222$^{(e)}$; 417$^{(f)}$)	7·7 (7·1)^{e}
	3·250	16·750	3·750	11·250	0·160	216		
	4·100	15·900	5·000	10·000	0·170	228		
Ethanol-iodine	2·250	27·750	2·750	22·250	0·130	0·91		
	3·000	27·000	3·750	21·250	0·140	0·92	0·93$^{(c)}$ (0·95$^{(g)}$	5·1
	3·800	26·200	4·940	20·060	0·150	0·95		(3,5,4,82^{g})
	4·175	25·825	5·505	19·495	0·160	0·92		
	5·400	24·600	7·600	17·400	0·170	0·93		

Error limit (a) ± 30; (b) ±5, (c) ±0·03.

The values in paranthesis are from the literature: (d) Nagakura (1956); (e) Singh and Bhat (1978); (f) Foster (1971); (g) Tse and Tamres (1977); (h) Rao *et al* (1972).

and for the second set,

$$K = C'_{AD}/[(C'_D - C'_{AD})(C'_A - C'_{AD})]. \tag{2}$$

Therefore

$$C_{AD}/[(C_D - C_{AD})(C_A - C_{AD})] = C'_{AD}/[(C'_D - C'_{AD})(C'_A - C'_{AD})]. \tag{3}$$

If $\triangle\sigma_1 = \triangle\sigma_2$, then $C_{AD} = C'_{AD}$.

From the above equations, we get a K value of

$$\frac{(C'_A C'_D - C_A C_D)[(C'_A + C'_D) - (C_A + C_D)]}{[(C'^2_A + C_A C_D) - C'_A (C_A + C_D)][(C'^2_D + C_A C_D) - C'_D (C_A + C_D)]}. \tag{4}$$

The K values thus obtained for different sets of data at 25° C are given in table 2, along with the enthalpies and it is clear that the equilibrium constants and enthalpies thus obtained are comparable to the values obtained by spectroscopic method by Rao *et al* (1972).

3.2. *Hexamethylbenzene-tetracyanoethylene*

The surface tensions of hexamethylbenzene and tetracyanoethylene in cyclohexane decrease with the increase in concentration of solutes and there is a linear relation between the surface tension and the concentrations of solutes in the experimental range ($1 \times 10^{-3} - 20 \times 10^{-3}$ M) of concentrations. Higher concentrations of hexamethylbenzene and tetracyanoethylene are used as the interaction between these two is not that strong. The deviation from the ideal behaviour of the pure components is due to the interaction of the two species (donor and acceptor) and the deviation is proportional to the concentration of the complex. The plot of $\triangle\sigma$ against the concentration of hexamethylbenzene shows only one maximum at half the donor concentration indicating that hexamethylbenzene forms only 1 : 1 complex with tetracyanoethylene in the experimental range of concentrations. The termolecular complexes, may be formed only when the concentration of either of the components is very high.

The value of K thus obtained for different sets of data are reported in table 2 along with the literature data. It is clear that the values of K and $-\triangle H°$ obtained by surface tension measurements are comparable to those obtained by Singh and Bhat (1978) by refractometry under similar conditions, but are quite low compared to the data reported by Foster and Kulevsky (1973). One of the possible reasons for this variation may be due to the different sets of experimental conditions. Tse and Tamres (1977) have also reported that the K value depends on the experimental conditions such as whether $A \gg D$, $D \gg A$ or $A \approx D$ and also on the nature of solvent.

3.3. *Ethanol-iodine*

The surface tensions of ethanol in cyclohexane and iodine in cyclohexane decrease with increase in concentration of the solutes and there is a good linear relationship between the surface tension and concentration in the range $1 \times 10^{-3} - 30 \times 10^{-3}$ M. Higher concentrations of ethanol and iodine (total conc. 30×10^{-3} M) are used as the interaction between ethanol and iodine is very weak. The small deviation from ideal behaviour of the pure components is due to the interaction of the two species (donor and acceptor) and the deviation is proportional to the concentration of the complex. The plot of $\Delta\sigma$ versus the concentration of ethanol shows only one maximum at half the donor concentration indicating that ethanol forms only 1 : 1 complex with iodine in the experimental range of concentrations.

The K values calculated by the procedure described above are given in table 2. The average value of K is $0{\cdot}931$ mole^{-1} at 25° C and the enthalpy, $-\Delta H^\circ$ is $5{\cdot}1$ kcal/mol. This value is comparable to the most recent reliable K value ($0{\cdot}95 \pm 0{\cdot}06$) reported by Tse and Tamres (1977). The higher value of K reported by the earlier workers may be due to the interaction of ethanol with the solvent, namely CCl_4 itself.

It therefore appears, that the method of surface tension measurements can be used not only to detect the formation of molecular complexes but also to determine the equilibrium constants and the thermodynamic properties of the complexes, even in the case of weak molecular complexes. However it may be interesting to examine closely related systems and then rationalise in terms of various effects.

Acknowledgements

The authors are thankful to Prof. M Tamres of University of Michigan, for providing capillary tubes, to Prof. O P Malhotra, Banaras Hindu University, to Prof. H Junjappa, Chemistry Department, for providing research facilities and to the University Grants Commission, New Delhi, for financial assistance.

References

Benesi H A and Hildebrand J H 1949 *J. Am. Chem. Soc.* **71** 2703

Bist H D and Person W B 1969 *J. Phys. Chem.* **73** 482

Ferroni E and Gabrielli G 1957 *J. Phys. Chem.* **60** 1258

Foster R and Kulevsky N 1973 *J.C.S.F. Trans. I* **69** 1427

Nayar M R, Srivastava L N and Nayar K V 1952 *J. Indian Chem. Soc.* **29** 241

Rao C N R, Bhat S N and Dwivedi P C 1972 *Appl. Spectrosc. Rev.* **5** 1

Singh R A and Bhat S N 1978 *J. Phys. Chem.* **82** 2322

Tse H C and Tamres M 1977 *J. Phys. Chem.* **81** 1367, 1376

Nagakura S 1957 *J. Am. Chem. Soc.* **80** 520

Foster R 1971 *J. Chem. Soc.* (*B*) 1283