Asian Journal of Chemistry Vol. 14, No. 2, (2002), 1077–1079

NOTE

Effect of Solvent Polarity on the Association Constant of the Charge Transfer Complex between 2,4-dinitrotoluene and Diphenylamine

S. MUZAFFAR ALI ANDRABI* and SAJJAD ATEHAR†
University Science Instrumentation Centre
University of Kashmir, Srinagar-190 006, India

In the present work, we describe the charge-transfer complexation of 2,4-dinitrotoluene, with diphenylamine in different solvents. A linear correlation was obtained between ln K and π* solvent polarity parameter of the solvents.

Key Words: Solvent, Polarity, Association, Constants, Charge transfer, Complex, 2,4-Dinitrotoluene, Diphenylamine.

The charge-transfer complexation of 2,4-dinitrotoluene and diphenylamine was studied in a number of solvents. As expected solvent polarity has shown a profound effect on the association constant of the complex. A linear correlation was obtained between ln K and π* solvent polarity parameter of the solvents.

2,4-Dinitrotoluene (DNT) and diphenylamine (DPA) were AR grade reagents from E. Merck (Darmstadt) and BDH (Poole, England) respectively, and were used as received. All the solvents were AR grade and used as received. The association constants were determined by optical spectroscopy using the Benesi-Hildebrand equation[1];

$$\frac{[A]_0}{A} = \frac{1}{K\varepsilon[D]_0} + \frac{1}{\varepsilon}$$

where $[A]_0$ is the initial concentration of the acceptor (DNT), $[D]_0$ the initial concentration of the donor (DPA) and K the association constant. A and ε are the absorbance and the molar absorptivity of the complex. Absorbance was measured at 400 nm and the absorbance of DNT was cancelled by taking an equal concentration of DNT in the reference cell—a method first developed by Mulliken[2]. $[A]_0$ was kept constant and $[D]_0$ varied and kept in excess over $[A]_0$. A plot of $[A]_0/A$ *vs.* $1/[D]_0$ is a straight line with intercept equal to 1/ε and slope equal to 1/Kε. K was obtained by dividing intercept by slope.

2,4-Dinitrotoluene-diphenylamine complex has been well characterized as a charge transfer complex[3] in CCl_4. Since the association constant is only 0.23 L mol^{-1} it implies that there is no likelihood of any ion formation even in polar solvents. Therefore, the position of equilibrium may be indicative of solvent polarity. The value of association constant K was measured in eleven solvents

---

†Department of Chemistry, University of Kashmir, Srinagar-190 006, India.

given in Table-1. The value of K increases with the solvent polarity of the solvents. A near exact linear relationship is obtained between ln K and π* solvent polarity parameter[4] of the solvents (Fig. 1). Effect of solvent polarity on the

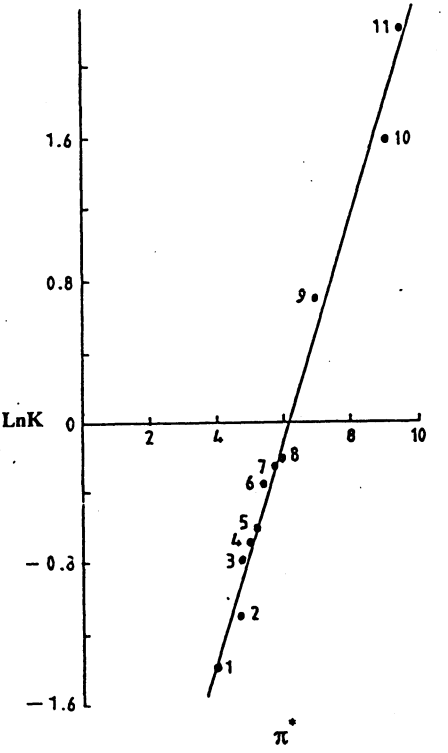

Fig. 1. A plot between ln K and π* for some solvents. The solvents are numbered according to Table-1.

TABLE-1
VALUE OF EQUILLIBRIUM CONSTANT K OF 2,4-DINITROTOLUENE DIPHENYLAMINE COMPLEX AND ln K IN DIFFERENT SOLVENTS

S. No.	Solvent	K (L mole^{-1})	ln K
1.	t-Butanol	0.25	−1.39
2.	1-Butanol	0.31	−1.14
3.	2-Propanol	0.45	−0.80
4.	Acetic acid	0.50	−0.70
5.	1-Propanol	0.54	−0.68
6.	Ethanol	0.69	−0.37
7.	Chloroform	0.76	−0.27
8.	Methanol	0.80	−0.22
9.	Acetone	0.00	0.69
10.	Ethylene glycol	0.82	1.57
11.	Formamide	8.88	2.18

association constants of charge-transfer complexes may have been studied before, but no such relationship has been obtained so far[5,6]. Such a linear relationship may be useful in predicting the solvent polarity of solvents or mixed solvents by measuring K of DNT-DPA complex in them.

REFERENCES

1. H.A. Benesi and J.H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
2. C. Reid and R.S. Mulliken, *J.Am. Chem. Soc.*, **76**, 3869 (1954).
3. M. Qureshi, S.A. Nabi, A. Mohammad and P.M. Qureshi, *J.Solid State Chem.*, **415**, 186 (1982).
4. H. Ratajczak and W.J. Orille-Thomas, Molecular Interactions, Vol. 3, John Wiley & Sons, New York.
5. J. Czekalle and K.O.Meyer, Z. *Phys. Chem.Frankf. Ausg.*, **27**, 185 (1961).
6. P. Verbiest, L. Verdonck and G.P. van der Keleu, *Spectrochim. Acta*, **49A**, 405 (1993).

(*Received*: 5 November 2001; *Accepted:* 15 February 2002) AJC-2642