

## DIELECTRIC AND DIPOLAR INTERACTION STUDIES OF A NON-POLAR SOLVENT INDUCED INFRA-RED FREQUENCY SHIFTS

Noor Ahmad and Nasim Rehana

*National Centre of Excellence in Physical Chemistry, University of Peshawar, Pakistan*

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### THEORY OF SOLVENT SHIFTS

In order to compare frequency shifts in different regions of the spectrum, the observed displacements are discussed by reference to the vapour frequency:

$$\Delta\nu/\nu = (\nu_{\text{vap}} - \nu_{\text{sol}})/\nu_{\text{vap}}$$

The theory considers a simple model of a diatomic oscillator in a continuous solvent medium of macroscopic dielectric constant  $\epsilon$  and the shift is assumed to result from instantaneously induced polarization of the surrounding non-polar solvent molecules by the solute dipole. Using classical electrostatics and equating the energy of the vibrating dipole to that of an anharmonic oscillator in its reaction field, the derived expression is:

$$\Delta\nu/\nu = C(\epsilon-1)/(2\epsilon+1)$$

This relationship is commonly referred to as the KBM [1] relationship.  $C$  is a constant depending upon the dimensions and electrical properties of the vibrating solute dipoles.

Buckingham [2] analysed the problem in a more general way and he expanded the above equation for a non-polar solvent as:

$$\Delta\nu/\nu = C + \frac{1}{2}(C_{\epsilon} + C_n) \left( \frac{\epsilon-1}{2\epsilon+1} \right)$$

Where  $\epsilon$  and  $n$  represent the dielectric constant and refractive index factor respectively. Plotting the observed relative shifts in non-polar solvents against the dielectric function  $\left( \frac{\epsilon-1}{2\epsilon+1} \right)$  yields values of  $C$  from the intercept and  $(C_{\epsilon} + C_n)$  from the slope.

### EXPERIMENTAL

The spectra of ethyl bromide in tetrachloro methane, benzene, cyclohexane and 1,4-dimethylbenzene is taken

on JASCO IR-I. The spectra is shown in Fig. 1 and Fig.2.

Dielectric constant of various solvents are measured on dipole meter type DMO1 [3] at 20°C. The relative shifts  $\Delta\nu/\nu$  are calculated and are given in Table 1. These values are plotted against the dielectric function  $(\epsilon - 1/2\epsilon + 1)$  which yields Fig. 3.

Dipole moment values of ethyle bromide in these non-polar solvents are calculated using dipole meter type DMO1 [3] and are tabulated in Table 2.

### RESULTS AND DISCUSSION

Considerable attention is focussed on the effect of non-polar solvent environment on IR frequencies. Table 1 shows that relative frequency shift is minimum in benzene while it is maximum in cyclohexane. This is comparable to the results given in Table 2, which shows minimum dipole moment in benzene and maximum in cyclohexane. We

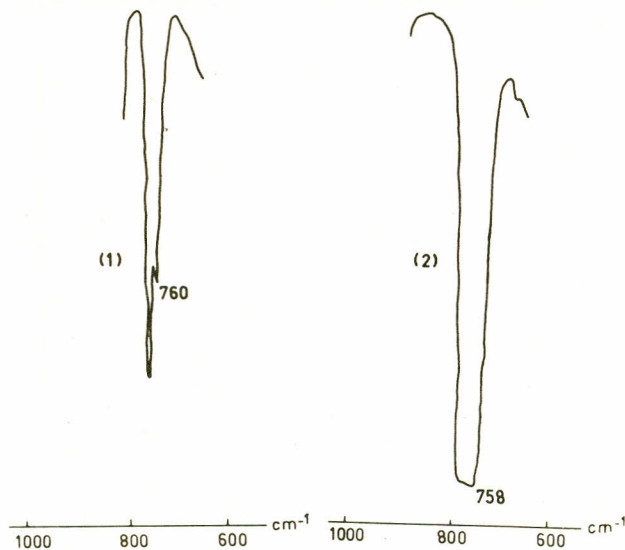


Fig 1. Spectra of ethyl bromide in (1) cyclohexane; (2) Tetra chloromethane (JASCO IR-I).

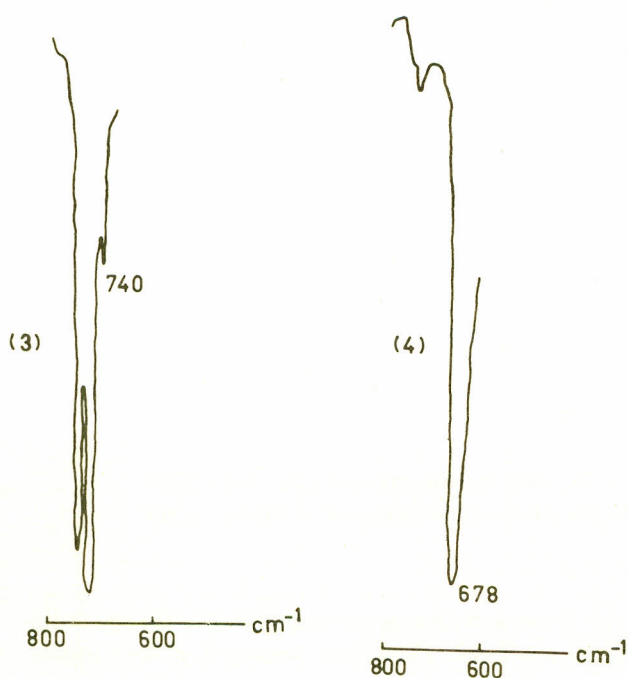


Fig. 2. Spectra of ethyl bromide in (3) 1,4-dimethyl benzene; (4) benzene (JASCO IR-1).

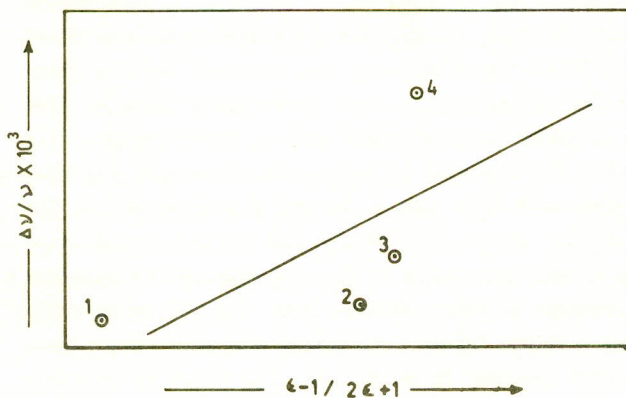


Fig. 3. Relative frequency shift of  $(C_2H_5Br)$  in various solvents as a function of the dielectric constant of the solvents. Solvents: (1) Cyclohexane. (2) Tetra chloromethane (3) 1,4-dimethyl benzene (*p*-xylene) (4) Benzene.

say that the shift can be fully accounted for in terms of solute solvent dipolar interaction and that the dielectric constant of the medium plays an insignificant part. Other factors must, however, have some influence on these dipoles, as the slopes of the BHW [4] plot obtained on plotting the relative shifts against a common standard [5] do not parallel other measure of the bond polarity as would

Table 1. Relative frequency shift of ethyl bromide in various solvents.

S.No.	Ethyle bromide in	$\nu$ $cm^{-1}$	$\Delta\nu/\nu 10^3$	$\frac{\epsilon-1}{2\epsilon+1}$
1.	Vapour state	770	—	—
2.	Cyclohexane	760	13.0	0.203
3.	Tetrachloromethane	758	16.0	0.226
4.	1,4-dimethyl benzene	740	39.0	0.229
5.	Benzene	675	123.0	0.231

Table 2. Dipolemoment of ethyl bromide in different solvents at 20<sup>0</sup>.

Solvent	Cyclohexane	Tetrachloromethane	1,4-dimethyl benzene	Benzene
Dipolemoment (Debyes)	1.93	1.86	1.79	1.69

be predicted on the basis of the dipolar association theory.

However, neither of the two major factors which contribute to the IR solvent shifts can be ignored and that their relative significance varies from case to case, being dependent as much on the particular dipolar absorber as on the solvent medium itself.

## REFERENCES

1. E. Bauer and M. Magat, *J. Phy. Radium*, **9**, 319 (1938).
2. (A). A.D. Buckingham, *Proc. Roy. Soc.*, **A248**, 169 (1958). (B). *Trans. Farad. Soc.*, **56**, 753 (1960).
3. Instruction Manual with Dipole Meter, Type DMOI of Wissenschaftlich-Technische Workstatten, G.M.B.H. Weilheim, West Germany.
4. L.J. Bellamy, R.L. Hallam and William, *Trans. Farad. Soc.*, **54**, 1120 (1958).
5. L.J. Bellamy and R.L. Hallam, *Trans. Farad. Soc.*, **55**, 14 (1959).