Dielectric Polarisation of Some Heterocyclic Compounds and Role of π-Electrons in Solution

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The dielectric moments at 35 °C of quinoline, pyridine and isoquinoline dissolved in four non-polar solvents viz. benzene, carbon tetrachloride, cyclohexane and dioxane are found to increase in this sequence in accordance with the molecular structure of these solutes. The surprisingly high moments of quinoline and pyridine in carbon tetrachloride indicate the formation of charge transfer complexes involving the π-electron systems of the solutes.

Introduction

The dipole moments reported in literature[1] for these compounds are not consistent[1]. We therefore have made new measurements and also discuss the role of the π-electrons in the interaction between the solutes and the solvents.

Experimental

The method and technique have been described elsewhere[2, 3].

Results an Discussion

Two values (i. e. 2.25 D and 2.15 D) for the moment of pyridine in the vapour state are reported[1]. To ascertain the correct value, the results have been discussed in the light of Higasi's theory[4–6].

The polarizabilities[7] of a pyridine molecule α_1, α_2 and α_3 along the three principal axes are 10.80×10^{-24} cm³, 11.88×10^{-24} cm³ and 5.7×10^{-24} cm³, respectively. Here α_1 lies in the axis of symmetry which bisects the nitrogen valence angle and both α_1 and α_2 lie in the plane of the molecule. These axes[8] of polarizability may be taken to be proportional to the geometrical axes of the molecule. Therefore in the case of pyridine

$$\frac{\alpha_2}{\alpha_1} = \frac{11.88 \times 10^{-24}}{10.80 \times 10^{-24}} = 1.10 = \frac{c}{a}$$

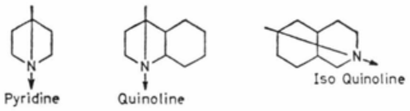
where c and a are the longer and shorter semi axes of pyridine, respectively. Since c/a is greater than unity, the theory predicts a positive solvent effect in case of pyridine. Our experimental data suggest that 2.15 D is the most convincing value. The views of Buckingham and LeFevre[9] also support this conclusion.

In an earlier communication[10] from this laboratory, it has been shown that in the case of a positive solvent effect, the induced moment in benzene will be 1.18 times greater than that in cyclohexane. Consequently the order of moments would be $\mu_{s(\text{benzene})} > \mu_{s(\text{cyclohexane})}$, as verified in Table 1.

Table 1. Apparent dipole moments (μ_s)* (in Debye).

Solvent	Solute		
	Pyridine $\mu_V = 2.15, 2.25$ $pK_a{}^{14} = 5.14$	Quinoline $\mu_V = 2.19, 2{,}31$ $pK_a{}^{14} = 4.85$	Isoquinoline $\mu_V = 2.75$ $pK_a{}^{14} = 5.40$
Benzene	2.33 2.11–2.28	2.25 2.16–2.27	3.05 2.49–2.63
Carbon tetrachloride	2.26 2.35	2.34 2.39	3.07 2.67
Dioxan	2.35 2.22 ± 0.02	2.27 –	2.49 –
Cyclohexane	2.20 2.22	2.19 –	2.41 –

Due to the fusion of the benzene rings in quinoline the acidic strength increases and this lowers the pK_a value which measures the availability of electrons on the nitrogen atom. The higher pK_a value of pyridine consequently suggests a higher moment value than that of quinoline. The order of observed moments in solution $\mu_{\text{isoquinoline}} > \mu_{\text{pyridine}} > \mu_{\text{quinoline}}$ is further supported on the basis of molecular diagrams[9] of these solutes.



In isoquinoline the resultant dipole vector passes through both rings and hence the availability of delocalized electrons for polarization by the hetero atom is much bigger than in the other two compounds. The higher pK_a value of isoquinoline is consistent with this fact.

The unexpectedly high values of μ_s in carbontetrachloride for pyridine and quinoline may be due to the specific interaction operating between solute and solvent. The nature of this interaction has been studied by the author[3, 12] in the light of the Earp and Glasstone[11] theory. Accordingly, we observe that in all the solvents the curves obtained by plotting $((\varepsilon_{12}-1)/(\varepsilon_{12}+2))^2$ vs P_{12} are linear and hence show the absence of chemical interaction in solution. Further the positive values of P^E (the excess polarization) eliminate the possibility of dipole association as well (Table 2). However the variations of P^E with $f_1 f_2$ (Fig. 1 and 2) for the systems pyridine + carbontetrachloride, quinoline + carbon-

Table 2.

(Pyridine + Carbontetrachloride)							
$f_1\,f_2$	0.0119	0.0184	0.0292	0.0422	0.0506	0.0599	
P^E	+0.654	+3.660	+2.300	+3.257	+3.739	+4.259	
(Quinoline + Carbontetrachloride)							
$f_1\,f_2$	0.0012	0.0042	0.0050	0.0064	0.0091	0.0123	0.0155
P^E	+0.113	+0.418	+0.505	+0.643	+0.960	+1.239	+1.556
(Quinoline + Benzene)							
$f_1\,f_2$	0.0087	0.0199	0.0309	0.0419	0.0507	0.0583	0.0653
P^E	+0.426	+1.155	+1.402	+2.004	+2.487	+2.887	+3.124

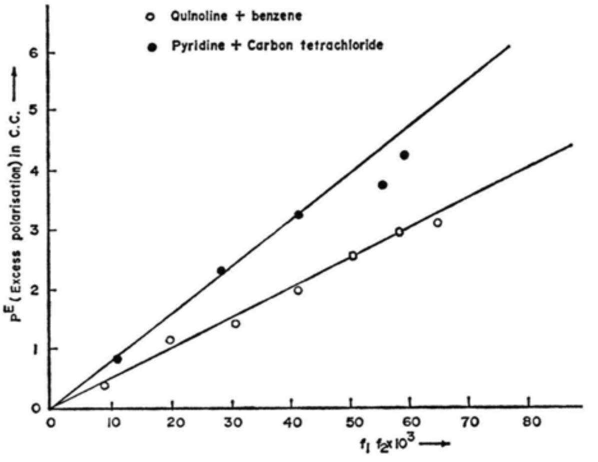


Fig. 1

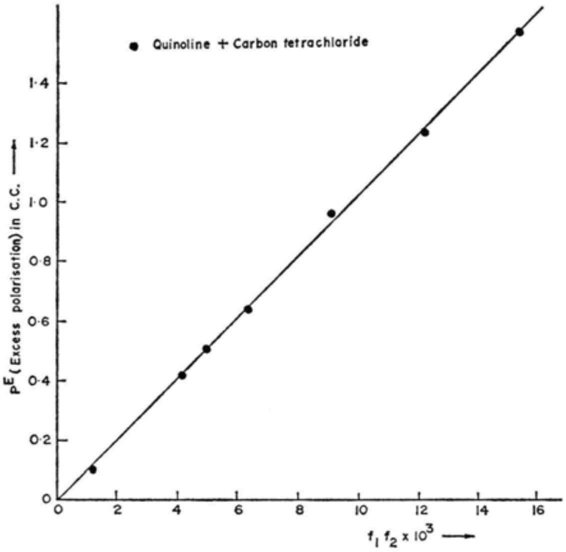


Fig. 2

tetrachloride, and quinoline + benzene show a linear relation and the curves pass through the origin. This suggests the formation of charge transfer complexes in these solvents. The specific interaction according to Goats, Sullivan and Ott [13] appears to be of the donor acceptor type. For the first two systems, it is expected that the nitrogen atom [14] of the pyridine ring donates π-electrons to the empty 3d level of the chlorine atom in carbontetrachloride. This is supported by the complex formation between benzene (donor) and carbontetrachloride (acceptor) reported recently [14]. For the system quinoline + benzene, solvent benzene appears to donate π-electrons to the second benzene ring in quinoline which contains no nitrogen atom and is comparatively deficient in π-electrons.

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