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Electric Dipole Moment of Pyrrole and Molecular Interaction in Solution

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Literature[1] reports two values for μ_s/μ_v namely 1.06 and 0.9 for pyrrole in benzene solution. Our orientation polarisation data on pyrrole discussed in terms of Higasi's theory favours the former. Further we observe that in benzene the solute forms donor-acceptor complexes, while in carbon tetrachloride it undergoes association through hydrogen bonding.

The moment values of pyrrole both in vapour and solution state cited earlier[2] are widely divergent. A survey of literature[1,3–7] shows that though Buckingham and others have carried much work on pyrrole, yet they have shown considerable variation in apparent moment. The discrepancy may be attributed to the specific interaction in solution. Consequently the purpose of the present investigation was to re-examine the apparent moment values and then to understand the interaction operating between solute and solvent from the data so obtained, with reference to theory of Earp and Glasstone.[8]

Experimental

The practical work essentially involves the measurements of dielectric constant and density of various solutions containing different mole fractions of the solute. The method and techniques have been described elsewhere.[9]

Pyrrole[12] (Fluke A.G., Buchs S. G., Switzerland) was distilled twice in a quickfit apparatus, where there was no possibility for the liquid to be in contact with atmospheric moisture and carbon dioxide. The fraction boiling at 128 °C was used.

The solution moment value μ_s has been determined by the method of Halverstadt and Kumler.[13] The constants α, β, ε_1 and V_1 in Halverstadt and Kumler equation have been evaluated by the method of least square. Electronic polarization P_e is the same as the molecular refraction for sodium D-line and has been taken from the literature.[14] Atomic polarization P_A has not been taken into consideratoin as suggested by Debye[15] namely that the electronic polarisation calculated from the sodium D-line partly compensates the neglect of atomic polarisation for which there is still no good method of evaluation.

The excess polarisation P^E needed for the present study, has been evaluated from the expression,

P^E = (Solution polarisation) − (Total polarisation)

The solution polarisation P_{12} is given by

$$P_{12} = \frac{\varepsilon_{12}-1}{\varepsilon_{12}+1}\cdot\frac{M_1f_1+M_2f_2}{d_{12}}$$

and total polarisation $= P_1f_1+P_2f_2$

where P_1 and P_2 are the molar polarisation of the solvent and the solute respectively and f_1 and f_2 are their respective mole fractions.

Results and Discussion

The values available in literature for μ_s/μ_v of pyrrole in benzene are 1.06 and 0.9. However we observe that the μ_s value of pyrrole in benzene is slightly greater than that in cyclohexane. This is in agreement with the positive solvent effect (*i.e.* $\mu_s > \mu_v$) as suggested by Higasi.[16–18] Consequently our observed data in benzene favours the value 1.06 for the ratio μ_s/μ_v. The experimental data has been shown in Table 2.

The molecular interaction in solution has been discussed in terms of the theory of Earp and Glasstone.[8]

Accordingly we observe that no chemical interaction takes place in the mixture since the variation of

TABLE 1. PYRROLE

Solvent	α	β	ε_1	V_1	$P_{2\infty}$
Benzene	6.8630	−0.1848	2.2514	1.1643	121.99
Carbon tetrachloride	3.5327	+0.6154	2.2062	0.6898	103.97
Cyclohexane	5.2857	−0.2808	1.9944	1.3157	104.71

TABLE 2.

Solvent	μ_s (apparent moment values) by present authors	μ_s (apparent moment values) by earlier workers[2]	μ_v^2 (moment in vapour state)
Benzene	2.26	2.2 , 1.74	1.55−1.65
Carbon tetrachloride	2.05	1.78, 1.76	1.84±0.08
Cyclohexane	2.06	1.75[3]	

TABLE 3.

	(Pyrrole + Benzene)						
f_1f_2	0.0005	0.0036	0.0042	0.0064	0.0073	0.0078	0.0116
P^E	+0.041	+0.267	+0.354	+0.450	+0.502	+0.556	+0.790
	(Pyrrole + Carbon tetrachloride)						
f_1f_2	0.0007	0.0012	0.0033	0.0051	0.0064	0.0066	0.0106
P^E	−0.641	−0.607	−0.511	−0.430	−0.388	−0.388	−0.170
	(Pyrrole + Cyclohexane)						
f_1f_2	0.0027	0.0034	0.0062	0.007	0.0087	0.0104	0.0127
P^E	−0.177	−0.148	+0.142	+0.251	+0.304	+0.451	+0.606

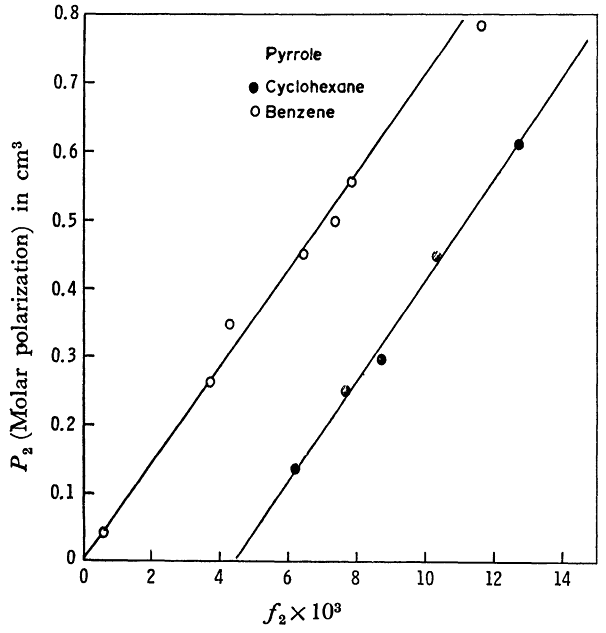


Fig. 1.

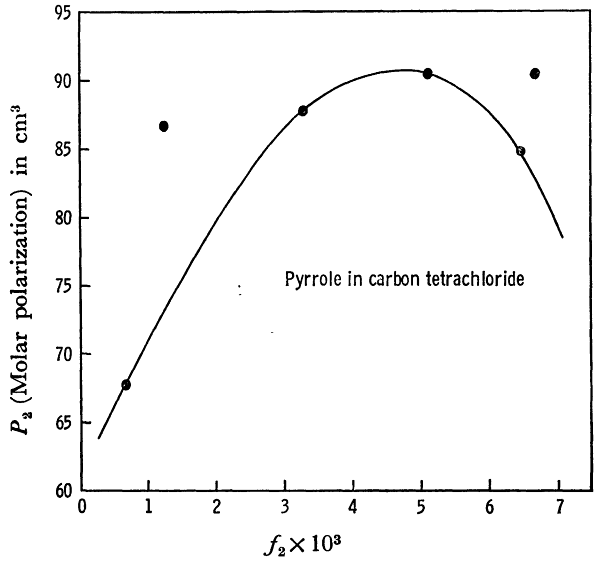
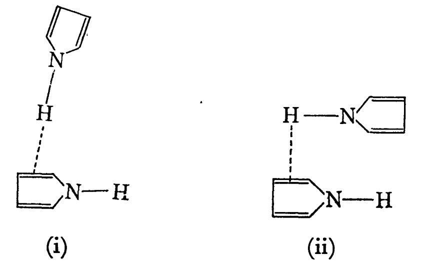


Fig. 2.

$\{(\varepsilon_{12}-1/\varepsilon_{12}+1)\}^2$ with P_{12} is linear. Further the values of P^E (the excess polarisation) in benzene and cyclohexane being positive (Table 3) eliminate the possibility of dipole association as well.

However the variation of P^E with $f_1 f_2$ (Fig. 1) for the system (pyrrole+benzene) is linear and passes through the origin. This shows the formation of charge-transfer complexes in solution. The specific interaction according to Goats and Sullivan[19)] in benzene appears to be of donor-acceptor type. Literature[20)] reports that pyrrole is practically non-basic and its hydrogen atom is acidic in nature. It seems probable therefore that pyrrole accepts the π electrons through its hydrogen atom from benzene. This is supported from the complex formation between benzene (donor) and carbon tetrachloride reported recently.[21)] The possibility of complex formation in cyclohexane does not arise as it has no π electrons. Our experimental data fully demonstrate this fact.

The negative values of P^E in carbon tetrachloride (Table 3) suggest that pyrrole undergoes association through hydrogen bonding in this solvent. To ascertain this view, the graph between P_2 and f_2 (Fig. 2) has been plotted, which shows a maxima.[9,22)] This observation is further supported from the study of infrared spectra[23,24)] of pyrrole in carbon tetrachloride. A lower value of pyrrole in carbon tetrachloride suggests head to head association. There seems to be the following two possibilities during association.



(i) (ii)

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