30. *Molecular Interaction: Polarisation Studies of Mixtures of Pyridine with Polyhalogenated Hydrocarbons.*

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The total molar polarisation at infinite dilution has been determined for pyridine in a number of solvents composed of mixtures of a non-polar halogenated hydrocarbon and benzene. The results are interpreted in terms of an interaction between pyridine and the halogenated hydrocarbon. The ability to interact increases in the series, *p*-dibromo- and *p*-dichloro-benzene, carbon tetrachloride, hexachloroethane, carbon tetrabromide.

PHYSICAL and chemical evidence has shown that amines can interact with polyhalogenated hydrocarbons.[1-5] Recent dipole-moment studies [1] have shown that the extent of interaction between amines and carbon tetrachloride, measured by the difference between the apparent dipole moment of the amine in carbon tetrachloride and benzene solutions ($\Delta\mu$), increases with increasing basicity of the amine but depends strongly on steric hindrance to the approach of carbon tetrachloride molecules to the amino-nitrogen atom. In the present work the interaction of pyridine with other non-polar halogenated hydrocarbons is investigated.

Most symmetrical halogenated hydrocarbons are solids, and it was necessary to carry out these polarisation measurements with the interacting components in a non-polar liquid, for which, because of the low solubility of the halogen compounds in the paraffins and cyclohexane, benzene was chosen.

EXPERIMENTAL

The heterodyne-beat apparatus, method of measurement, and calculation of results have already been described. Each polarisation measurement was carried out by making up six solutions of pyridine (wt. fraction range 0·001—0·01) in a solvent mixture composed of a known concentration of halogenated hydrocarbon in benzene. At least two sets of solutions, containing different mole fractions of halogenated hydrocarbon, were used, and the total polarisation of pyridine at infinite dilution was plotted against the mole fraction of halogenated hydrocarbon in the solvent mixture. Except for the polarity induced by weak interaction between the solvent components, which should be small, the solvent mixtures could be regarded as non-polar, and the equations normally used in calculating the total molar polarisation of the solute at infinite dilution are, therefore, still valid. The use of mixtures containing a high proportion of solid halogenated hydrocarbon dissolved in a volatile solvent introduced a number of experimental difficulties. Great care was taken to ensure that evaporation of benzene did not affect the specific volumes, and the total polarisation values quoted are considered to be accurate within ±0·05 c.c.

Preparation and Purification of Materials.—The purification of benzene and carbon tetrachloride has been previously described.[1] " AnalaR " pyridine was purified by crystallisation of the zinc chloride double salt and fractionated twice from phosphoric oxide in an efficient column with low hold-up. The best fraction was sealed into a large number of ampoules with a minimum of air space and stored in the dark; it had b. p. 116°/755 mm. (lit.,[6] 115·6°), and gave a picrate, m. p. 165°, n_D^{25} 1·5068 (lit.,[7] 165—166°, 1·5067).

The halogenated hydrocarbons were commercial samples, purified by steam distillation, recrystallisation from ethanol, and drying for two weeks in the dark under vacuum. These

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[1] Sharpe and Walker, *J.*, 1961, 2974.

[2] Davidson, VanderWerf, and Boatwright, *J. Amer. Chem. Soc.*, 1947, **69**, 3045; VanderWerf, Davidson, and Michaelis, *ibid.*, 1948, **70**, 908.

[3] Kinumaki and Aida, *Sci. Reports Res. Inst. Tôhoku Univ.*, 1954, *A*, **6**, 636.

[4] Collins, *Chem. and Ind.*, 1957, 704.

[5] Sharada and Murthy, *Current Sci.*, 1960, **5**, 179.

[6] Weissberger and Proskauer, " Organic Solvents, Physical Properties and Methods of Purification," Interscience, London, 1955.

[7] Rodd, " Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1957, Vol. IVa.

procedures gave hexachloroethane, m. p. 187° (lit.,[8] 187°), *p*-dichlorobenzene, m. p. 53° (lit.,[6] f. p. 53°), *p*-dibromobenzene, m. p. 87·5° (lit.,[9] 87·3°), carbon tetrabromide (first refluxed with dilute aqueous sodium carbonate to remove reactive bromide), m. p. 92·0° (lit.,[9] 91·0°).

Results.—These are tabulated.

Polarisation data for pyridine at 25°c.*

10^6w_2	ε_{12}	v_{12}	n^2_{12}	10^6w_2	ε_{12}	v_{12}	n^2_{12}
	Benzene				*Carbon tetrachloride*		
1411	2·2816	1·14424	2·24305	924	2·2393	0·63072	2·12392
4724	2·3044	1·14382	2·24346	2104	2·2548	0·63116	2·12422
5312	2·3074	1·14373	2·24355	3275	2·2706	0·63160	2·12460
7338	2·3210	1·14345	2·24373	4171	2·2831	0·63194	2·12489
8422	2·3285	1·14331	2·24394	5254	2·2979	0·63235	2·12536
1,0272	2·3413	1·14306	2·24406	5318	2·2984	0·63241	2·12541

$\varepsilon_{12} = 2\cdot2722 + 6\cdot697w_2$; $v_{12} = 1\cdot14444 - 0\cdot1342w_2$; $n^2_{12} = 2\cdot24290 + 0\cdot117w_2$; ${}_2P_\infty = 123\cdot43$ c.c.; $R_D = 25\cdot18$ c.c.; $\mu = 2\cdot19$ D (2·21,[10] 2·20,[11] 2·23,[12] 2·26,[13] 2·25 [14]).

$\varepsilon_{12} = 2\cdot2270 + 13\cdot404w_2$; $v_{12} = 0\cdot63038 + 0\cdot3754w_2$; $n^2_{12} = 2\cdot12354 + 0\cdot340w_2$; ${}_2P_\infty = 135\cdot33$ c.c.; $R_D = 24\cdot67$ c.c.; $\mu = 2\cdot33$ D (2·33,[13] 2·37 [14]).

10^6w_2	ε_{12}	v_{12}	10^6w_2	ε_{12}	v_{12}	10^6w_2	ε_{12}	v_{12}
Carbon tetrachloride, $f = 0\cdot32$			*Carbon tetrachloride*, $f = 0\cdot62$			*Carbon tetrachloride*, $f = 0\cdot79$		
1280	2·2778	0·97712	1239	2·2684	0·81961	1169	2·2570	0·71412
3293	2·2937	0·97722	2893	2·2848	0·81993	2221	2·2690	0·71442
5118	2·3082	0·97730	3727	2·2933	0·82008	3962	2·2890	0·71494
6931	2·3229	0·97738	4388	2·2997	0·82019	5222	2·3043	0·71530
7827	2·3305	0·97744	5660	2·3126	0·82044	5489	2·3074	0·71539
9483	2·3436	0·97752	6901	2·3252	0·82069	6315	2·3174	0·71562

$\varepsilon_{12} = 2\cdot2675 + 8\cdot043w_2$; $v_{12} = 0\cdot97706 + 0\cdot0477w_2$; ${}_2P_\infty = 126\cdot47$ c.c.

$\varepsilon_{12} = 2\cdot2560 + 9\cdot997w_2$; $v_{12} = 0\cdot81938 + 0\cdot1879w_2$; ${}_2P_\infty = 130\cdot83$ c.c.

$\varepsilon_{12} = 2\cdot2432 + 11\cdot687w_2$ $v_{12} = 0\cdot71382 + 0\cdot2818w_2$; ${}_2P_\infty = 133\cdot02$ c.c.

Hexachloroethane, $f = 0\cdot097$			*Hexachloroethane*, $f = 0\cdot152$			p-*Dichlorobenzene*, $f = 0\cdot209$		
1881	2·2920	1·00202	1655	2·3130	0·93910	1414	2·3283	1·02535
3724	2·3061	1·00191	3223	2·3268	0·93905	2960	2·3407	1·02534
5704	2·3215	1·00180	4667	2·3385	0·93906	4701	2·3543	1·02530
7367	2·3350	1·00180	6596	2·3555	0·93896	5645	2·3617	1·02530
8740	2·3450	1·00181	7381	2·3619	0·93901	7264	2·3740	1·02524
1,0344	2·3585	1·00173	1,0111	2·3865	0·93903	9708	2·3927	1·02522

$\varepsilon_{12} = 2\cdot2770 + 7\cdot842w_2$; $v_{12} = 1\cdot00208 - 0\cdot0373w_2$; ${}_2P_\infty = 124\cdot88$ c.c.

$\varepsilon_{12} = 2\cdot2990 + 8\cdot569w_2$; $v_{12} = 0\cdot93905 - 0\cdot0027w_2$; ${}_2P_\infty = 125\cdot69$ c.c.

$\varepsilon_{12} = 2\cdot3180 + 7\cdot690w_2$; $v_{12} = 1\cdot02538 - 0\cdot0167w_2$; ${}_2P_\infty = 124\cdot70$ c.c.

p-*Dichlorobenzene*, $f = 0\cdot335$			p-*Dibromobenzene*, $f = 0\cdot139$			p-*Dibromobenzene*, $f = 0\cdot196$		
757	2·3494	0·96792	1358	2·3385	0·96068	390	2·3662	0·87575
2562	2·3642	0·96802	3641	2·3563	0·96080	1473	2·3757	0·87589
4863	2·3829	0·96812	6905	2·3826	0·96101	2344	2·3833	0·87604
6338	2·3953	0·96821	7348	2·3874	0·96103	3952	2·3981	0·87625
8430	2·4122	0·96832	9825	2·4072	0·96122	5966	2·4158	0·87655
1,0660	2·4316	0·96839	1,1781	2·4228	0·96133	8065	2·4348	0·87680

$\varepsilon_{12} = 2\cdot3435 + 8\cdot170w_2$; $v_{12} = 0\cdot96790 + 0\cdot0470w_2$; ${}_2P_\infty = 124\cdot29$ c.c

$\varepsilon_{12} = 2\cdot3278 + 8\cdot028w_2$; $v_{12} = 0\cdot96060 + 0\cdot0605w_2$; ${}_2P_\infty = 123\cdot49$ c.c.

$\varepsilon_{12} = 2\cdot3625 + 8\cdot964w_2$; $v_{12} = 0\cdot87570 + 0\cdot1388w_2$; ${}_2P_\infty = 122\cdot90$ c.c.

* w_2 = wt. fraction of pyridine; f = mole fraction of halogenated hydrocarbon; ε_{12} and v_{12} = dielectric constant and specific volume, respectively, of the solution; ${}_2P_\infty$ = total molar polarisation of pyridine at infinite dilution; R_D = molecular refraction; μ = apparent dipole moment of pyridine.

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[8] Ref. 7, Vol. Ia.

[9] Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

[10] Cumper, Vogel, and Walker, *J.*, 1956, 3621.

[11] Leis and Curran, *J. Amer. Chem. Soc.*, 1945, **67**, 79.

[12] Goethals, *Rec. Trav. chim.*, 1935, **54**, 299.

[13] Middleton and Partington, *Nature*, 1938, **141**, 516.

[14] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405,

Polarisation data for pyridine at 25° c. (contd.)

Carbon tetrabromide, f = 0·056

10^6w_2	ε_{12}	v_{12}
767	2·3220	0·97729
1581	2·3292	0·97733
2449	2·3372	0·97735
3201	2·3439	0·97735
5632	2·3662	0·97740
6151	2·3712	0·97741

$\varepsilon_{12} = 2{\cdot}3150 + 9{\cdot}085w_2$;
$v_{12} = 0{\cdot}97730 + 0{\cdot}0162w_2$;
${}_2P_\infty = 137{\cdot}10$ c.c.

Carbon tetrabromide, f = 0·121

10^6w_2	ε_{12}	v_{12}
649	2·3714	0·83197
1327	2·3798	0·83215
2027	2·3876	0·83226
2696	2·3958	0·83238
5135	2·4243	0·83286
7098	2·4491	0·83321

$\varepsilon_{12} = 2{\cdot}3644 + 11{\cdot}705w_2$;
$v_{12} = 0{\cdot}83194 + 0{\cdot}1685w_2$;
${}_2P_\infty = 146{\cdot}05$ c.c.

Carbon tetrabromide, f = 0·162

10^6w_2	ε_{12}	v_{12}
392	2·3957	0·76887
1141	2·4055	0·76905
2716	2·4279	0·76941
3071	2·4327	0·76951
5917	2·4713	0·77015
8126	2·5019	0·77068

$\varepsilon_{12} = 2{\cdot}3903 + 13{\cdot}257w_2$;
$v_{12} = 0{\cdot}76878 + 0{\cdot}2336w_2$;
${}_2P_\infty = 150{\cdot}57$ c.c.

Carbon tetrabromide, f = 0·291

10^6w_2	ε_{12}	v_{12}
1159	2·4611	0·67023
2320	2·4806	0·67069
3516	2·5010	0·67111
4239	2·5129	0·67139
4669	2·5201	0·69155
5191	2·5298	0·69178

$\varepsilon_{12} = 2{\cdot}4416 + 16{\cdot}8721w_2$;
$v_{12} = 0{\cdot}66980 + 0{\cdot}3769w_2$;
${}_2P_\infty = 162{\cdot}79$ c.c.

Carbon tetrabromide in benzene

10^6w_2	ε_{12}	v_{12}	n^2_{12}
1563	2·2727	1·14316	2·24272
3247	2·2728	1·14175	2·24308
6106	2·2730	1·13941	2·24349
9787	2·2735	1·13624	2·24394
1,3677	2·2742	1·13305	2·24448
1,8473	2·2752	1·12900	2·24511
2,3517	2·2757	1·12487	2·24589

$\varepsilon_{12} = 2{\cdot}2724 + 0{\cdot}1349w_2$; $v_{12} = 1{\cdot}14445 - 0{\cdot}8337w_2$;
$n^2_{12} = 2{\cdot}24260 + 0{\cdot}138w_2$; ${}_2P_\infty = 39{\cdot}11$ c.c.;
$R_\text{D} = 38{\cdot}91$ c.c. $P_0 = 0{\cdot}20$ c.c.

DISCUSSION

The considerable steric effect of groups adjacent to the nitrogen atom suggests that the interaction is very weak.[1] For example, the $\Delta\mu$ value for pyridine (0·14 D) is reduced to 0·04 D by substitution of one phenyl group in the 2-position, and to —0·03 D by two phenyl groups as in 2,6-diphenylpyridine. The last value was also obtained for other amines where interaction could be expected to be negligible. Where the interaction is weak, so that a definite complex is not formed as a distinct entity, the increase in total polarisation of the amine should be proportional to the mole fraction of halogenated hydrocarbon in the solvent mixture.

The greater solubility of polyhalogenated hydrocarbons in benzene than in paraffins suggests that some interaction between the two components occurs. Solid " benzolates " (compounds of benzene with tetrahalogenomethanes) have, in fact, been reported.[15] However, the dipole moment data for carbon tetrabromide (which interacts strongly with pyridine) in benzene do not indicate the formation of a polar complex between such components, the orientation polarisation value (${}_2P_\infty - R_\text{D}$) of 0·2 c.c. being zero within the limits of experimental error. The polarisation measurements in these systems should, therefore, be a good guide to the extent of interaction between pyridine and the halogenated hydrocarbon.

The effect of benzene on the pyridine–carbon tetrachloride system is shown in Fig. 1, illustrating the linear relation between total molar polarisation of pyridine at infinite dilution and the mole fraction of carbon tetrachloride; this indicates weak interaction. The gradient of similar graphs for other halogenated hydrocarbons may be used as a measure of the extent of interaction (Fig. 2).

The slopes of the *p*-dibromo- and *p*-dichloro-benzene graphs (—1·1 and +4·3, respectively) indicate an extremely weak or no interaction. By comparison, the gradients of the carbon tetrachloride and hexachloroethane graphs (12 and 15, respectively) suggest significant interaction, and comparable values might be expected for these similar molecules.

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[15] Kapustinski, *Roczniki Chem.*, 1958, **32**, 121; Dutch P. 84,412 (*Chem. Abs.*, 1958, 2904e); Egan and Luthy, *Ind. Eng. Chem.*, 1955, **47**, 192.

A very much stronger interaction is indicated for carbon tetrabromide than for carbon tetrachloride. The non-linearity of the carbon tetrabromide graph suggests that a more stable complex may be formed and this may well be related to the greater polarisability of the bromine atoms.

Some preliminary calorimetric work has shown that a small amount of heat is usually absorbed when substituted pyridines are mixed with benzene, whereas with carbon tetrachloride an appreciable amount of heat is evolved (*e.g.*, the heat of mixing of 2,6-dimethylpyridine with carbon tetrachloride is about —450 *J*/mole), suggesting significant interaction. Polarisation work in progress has shown that the interaction is not restricted to amines but results also, for example, from molecules containing oxygen, sulphur, or phosphorus. This interaction appears fairly typical for molecules containing electronegative atoms with hybridised lone pairs, which in the absence of steric effects can interact with the halogen atoms.

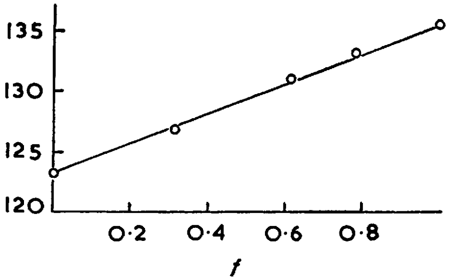


FIG. 1. Dependence of the total molar polarisation ($_2P_\infty$; c.c.) of pyridine at infinite dilution on the mole fraction (*f*) of carbon tetrachloride in a benzene–carbon tetrachloride mixture.

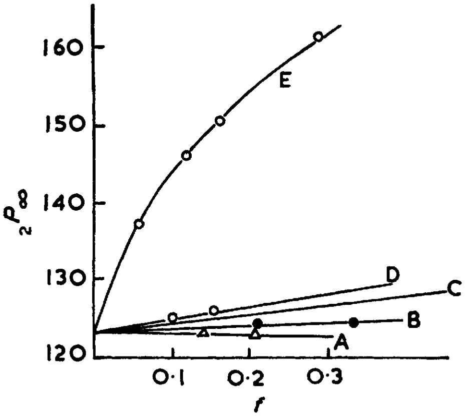
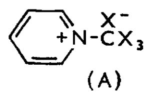


FIG. 2. Dependence of the total molar polarisation ($_2P_\infty$; c.c.) of pyridine at infinite dilution on the mole fraction (*f*) of halogenated hydrocarbon in a benzene–halogenated hydrocarbon mixture.

A, *p*-Dibromobenzene; B, *p*-dichlorobenzene; C, CCl_4; D, C_2Cl_6; E, CBr_4.

The quantum theory of the bonding in molecular complexes, as employed by Mulliken,[16] involves resonance between a no-bond structure (involving dipole–dipole and induced dipole forces) and an ionic form and appears to offer a possible mechanism for the interaction in at least some of these types of systems. If pyridine is the donor and an easily polarisable halogenated hydrocarbon (CX_4) the acceptor, the ionic form, which would offer only a very small contribution in the ground electronic state, would be (A).



(A)

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[16] Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.