

where k represents the Boltzmann constant and τ_∞ is the correlation time at the limit of infinite temperature. The results obtained are listed in Table IV.

The activation energies for the reorientations of the CH_3 and NH_3 groups in the β phase are larger than those determined for the groups in the δ phase. This confirms the preceding conclusion derived from the result of CW NMR that the β -phase salt forms rather more closely packed crystals than the δ -phase one. For β -phase methylammonium chloride, the activation energy values for the CH_3 and NH_3 reorientations have been reported¹⁰ to be 18.6 and 23.8 kJ mol^{-1} , respectively. These values are only slightly larger than the corresponding values of the bromide, indicating that the cations in each salt have very similar surroundings. The greater value of the activation energy for the NH_3 reorientation can be interpreted as the $\text{N-H}\cdots\text{Br}$ type hydrogen bonds being stronger than those of the $\text{C-H}\cdots\text{Br}$ type.

For the δ phase, almost the same activation energy value of ca. 8 kJ mol^{-1} has obtained for both the CH_3 and NH_3 reorientations. Previously, we studied the motion of methylammonium (MA) cation in $(\text{MA})_2\text{SnCl}_6$ and $(\text{MA})_2\text{PtCl}_6$ and found that the cation performs uncorrelated reorientation with an activation energy of ca. 8 kJ mol^{-1} ; i.e., both groups of the cation are activated to reorient individually over the internal barrier of reorientation. Accordingly, the present results indicate that the correlated reorientation of the cation in the δ phase of the bromide has approximately the same correlation time as the uncorrelated reorientation of the cation. Here, the correlated reorientation means the rotational reorientation of the cation as a whole about its C-N bond axis.

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Assessment of Intermolecular Association of Haloalkanes with *N,N*-Dibutyl-2-ethylhexanamide and Pyridine by Dielectric Permittivity and Polarization

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Notional stability constants K_1 for an *N,N*-disubstituted amide donor with chloroform additive (*n*-hexane and *n*-hexadecane solvents) are deduced from novel methods utilizing dielectric permittivity and are then contrasted with those found by dielectric polarization. Data arising from GLC, NMR, and IR for the same systems are presented for comparison. These range from 0.23 $\text{dm}^3 \text{mol}^{-1}$ (IR) to 2.34 $\text{dm}^3 \text{mol}^{-1}$ (NMR). The five permittivity methods are internally consistent and give on average 1.13 $\text{dm}^3 \text{mol}^{-1}$. The average dipole moment of the amide with media other than chloroform (4.32 D) is 3.70 D. Solvent effects and the permittivity methods are also examined with pyridine donor (benzene reference solvent) with carbon tetrachloride and carbon tetrabromide additives, where the former gives K_1 on average of 0.06 $\text{dm}^3 \text{mol}^{-1}$ while the latter exhibits K_1 of 0.20 $\text{dm}^3 \text{mol}^{-1}$. The dipole moment of pyridine is 2.19 D in benzene and 2.33 D in carbon tetrachloride; based upon the K_1 data it is expected to be 2.6–2.8 D in carbon tetrabromide.

Hypothesis of weak yet discrete donor (D)–additive (A) intermolecular association seemingly accounts for many of the thermodynamic and spectroscopic properties of a wide range of nonelectrolyte solutions. There remain nevertheless well-known and considerable discrepancies in measured stoichiometric equilibrium constants K_1 for the reaction $\text{D} + \text{A} \rightleftharpoons \text{DA}$ in supposed inert solvent S, whether assessed by chromatography, by spectroscopy, or by other techniques (e.g., ref 1 and 2). The situation has been compounded in recent years by Purnell and Vargas de Andrade³ and by Laub and Purnell,⁴ who found that a simple additive function described the infinite-dilution liquid–gas partition coefficients of a wide range of solutes with an equally diverse set of binary solvents without reference to terms in K_1 . Studies contemporary with these have cast some doubt upon the relations thereby derived, however, and, indeed, on the experimental evidence upon

which they were founded.⁵ Reassessment of the situation with systems comprising *n*-alkanes⁶ to those exhibiting consolute temperature⁷ has moreover failed to resolve the matter, since it has been demonstrated that multiple equilibria⁸ (particularly solvent self-association) might well mitigate the additivity hypothesis.

In the course of experimental study of systems wherein one or the other of the solvent components appears to dimerize,⁹ notional constants K_d have recently been de-

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- (1) Laub, R. J.; Pecsok, R. J. *J. Chromatogr.* **1975**, *113*, 47.
- (2) Laub, R. J.; Wellington, C. A. In "Molecular Association"; Foster, R., Ed.; Academic Press: London, 1979; Vol. 2, Chapter 3.
- (3) Purnell, J. H.; Vargas de Andrade, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 3585, 3590.
- (4) Laub, R. J.; Purnell, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 30, 35.
- (5) Harbison, M. W. P.; Laub, R. J.; Martire, D. E.; Purnell, J. H.; Williams, P. S. *J. Phys. Chem.* **1979**, *83*, 1262 and references therein.
- (6) Laub, R. J.; Martire, D. E.; Purnell, J. H. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1686; *J. Chem. Soc., Faraday Trans. 2*, **1978**, *74*, 213.
- (7) Laub, R. J.; Purnell, J. H.; Summers, D. M. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 362.
- (8) Williams, P. S. Ph.D. Thesis, University College of Swansea, Swansea, Wales, 1980. Laub, R. J.; Purnell, J. H., unpublished work. See ref 2.

duced from dielectric permittivity data for *N,N*-disubstituted amides in solution with supposed inert solvents.¹⁰ However, the small constants observed for *N,N*-dimethylacetamide (DMA) and *N,N*-dibutyl-2-ethylhexanamide (DBEHA) (ca 0.1–0.3 dm³ mol⁻¹; 288–298 K) and a value of zero for *N,N*-dimethylformamide (DMF) (*n*-hexane and carbon tetrachloride solvents) are just those expected on the basis of normal forces of dispersion¹¹ and must inevitably be regarded with some skepticism.^{12–14} It is therefore also unclear as to what significance should be lent the solvent dimerization hypothesis and subsequent expansion and apparent verification of the additivity relation detailed recently by Chien, Kopećni, Laub, and Smith.⁹ As a consequence, and in view of the continuing controversy surrounding the matter of weak interactions in nonaqueous media, we report here extension, to include dielectric polarization and permittivity, and GLC, IR, and NMR measurement of intermolecular association of the *N,N*-disubstituted amide DBEHA (which has been the subject of recent studies by us^{9,10}) with haloalkane and aromatic hydrocarbon additives in *n*-alkane solvents. The resultant data are intended in addition to provide means of assessment of the role of the additive species in random nonstoichiometric (albeit promiscuous) collision-induced pairing as well as the alternative seemingly indistinguishable view of weak interactions, namely, that such compounds when themselves employed as solvents can effect destabilization of discrete complex formation to the point of reduction of K_1 to zero.^{10,14}

Assessment of K_1 of Dielectrics

Dielectric Polarization. The dielectric properties of solutions have for many years been recognized as a potential means of assessment of intermolecular interactions.¹⁵ In the instance of stoichiometric 1:1 complex formation, the concentration-based equilibrium constant K_1 can be deduced from the solution polarization in accordance with the relation first derived by Few and Smith¹⁶

$$\frac{1}{(P_{D,\infty})_{A,S} - (P_{D,\infty})_S} = \left(\frac{1}{\Delta PK_1} \right) \left(\frac{M_D}{\rho_{D,S} w_D} \right) + \frac{1}{\Delta P} \quad (1)$$

where $(P_{D,\infty})_{A,S}$ is the limiting value of the molar polarization of component D at infinite dilution in solutions of A + S, $(P_{D,\infty})_S$ pertains to solvent S, and M , ρ , and w represent the molecular weight, the density, and the mass fraction of the subscripted species. ΔP is the change in total molar polarization of the system with complex formation

$$\Delta P = (P_{DA,\infty})_S - (P_{D,\infty})_S - (P_{A,\infty})_S \quad (2)$$

where $(P_{DA,\infty})_S$ and $(P_{A,\infty})_S$ are the limiting molar polarization of complex and species A, respectively, in S. The molar polarization of D at infinite dilution in pure S is

derived typically from the equation of Hedestrand¹⁷ and Halverstadt and Kumler¹⁸

$$(P_{D,\infty})_S = M_D \left[\frac{3\alpha v_S}{(\epsilon_S + 2)^2} + (v_S + \beta) \left(\frac{\epsilon_S - 1}{\epsilon_S + 2} \right) \right] \quad (3)$$

where v_S (eq 4a) and ϵ_S (eq 4b) are the specific volume

$$v_{D,S} = v_S + \alpha w_D \quad (4a)$$

$$\epsilon_{D,S} = \epsilon_S + \beta w_D \quad (4b)$$

intercept and the dielectric permittivity intercept and α and β are the respective slopes of plots of $v_{D,S}$ and of $\epsilon_{D,S}$ against w_D ($w_D \ll 0.1$). $(P_{D,\infty})_{A,S}$ is obtained via eq 3, where mixtures of constant composition of A + S are employed in place of S. Dipole moments μ are then deduced by assuming that the total molar polarization of D is the sum of the distortional (atomic and electronic) polarization $(P_{D,\infty}^d)_S$ and the orientational polarization $(P_{D,\infty}^o)_S$ and that^{19,20}

$$(P_{D,\infty}^d)_S = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \left(\frac{M_D}{\rho_D} \right) \quad (5a)$$

$$(P_{D,\infty}^o)_S = (P_{D,\infty})_S - (P_{D,\infty}^d)_S = \frac{4\pi}{3} N_0 \frac{\mu^2}{3kT} \quad (5b)$$

where n is the refractive index, N_0 is Avogadro's number, and k is Boltzmann's constant.²¹ The procedure is clearly somewhat cumbersome but has the advantage of providing ΔP and K_1 as well as the change in the dipole moment of D upon addition of A to the solution. This change $\Delta\mu$ can then be taken as evidence in favor of the formation (or absence) of discrete complexes (e.g. ref 13, 16, and 22).

Dielectric Permittivity. Although much less frequently employed than dielectric polarization, measurement of solution permittivity ϵ also provides means of assessment of intermolecular interaction.²³ We detail here novel and more convenient alternatives for interpretation of permittivity data which are based upon our previously reported method of study of dimerization of *N,N*-disubstituted amides.¹⁰ In the absence of donor-solvent, additive-solvent, or donor or additive self-association, ϵ may be written as a summation $\sum_{i=1}^n f_i C_i$, whence for solutions of D, A, and S

$$\epsilon = f_S C_S + f_A C_A + f_D C_D + f_{DA} C_{DA} \quad (6)$$

where the formation of a discrete 1:1 complex DA has been assumed and where f_i and C_i represent the intensity

(17) Hedestrand, G. *Z. Phys. Chem. Abt. B* 1929, 2, 428.

(18) Halverstadt, I. F.; Kumler, W. D. *J. Am. Chem. Soc.* 1942, 64, 2988. The relation has been questioned (Smith, J. W. *Trans. Faraday Soc.* 1952, 48, 802) but has been shown to have a firm theoretical basis (Taylor, W. J. *J. Phys. Chem.* 1975, 79, 1817). An alternative method has been derived by Guggenheim, but the results thereby obtained are virtually identical with those of the procedure described (Guggenheim, E. A. *Trans. Faraday Soc.* 1949, 45, 714).

(19) Lorentz, H. A. *Ann. Phys. (Leipzig)* 1880, 9, 641. Lorenz, L. V. *Ibid.* 1880, 11, 70.

(20) Clausius, R. "Die Mechanische Wärmttheorie"; Braunschweig, 1897; Vol. II 62. Mossotti, O. F. *Memorie Mat. Fis. Modena* 1850, 24, 49. See eg Hill, N. E.; Vaughan, W. E.; Price, A. H.; Davies, M. "Dielectric Properties and Molecular Behavior"; Van Nostrand Reinhold: London; 1969.

(21) Whence $\mu = 0.0128(P^o T)^{1/2}$ D.

(22) Bishop, R. J.; Sutton, L. E. *J. Chem. Soc.* 1964, 6100. Gowel, M.; Lumbruso, H. *Bull. Soc. Chim. Fr.* 1962, 2206, 2212. Waclawek, W. *Bull. Acad. Pol. Sci.* 1971, 29, 875.

(23) Rossotti, F. J. C.; Rossotti, H. "The Determination of Stability Constants"; McGraw-Hill: New York, 1961; pp 318–20. Maryott, A. A. *J. Res. Natl. Bur. Stand. (U.S.)* 1948, 41, 7.

(9) Chien, C.-F.; Kopećni, M. M.; Laub, R. J.; Smith, C. A. *J. Phys. Chem.* 1981, 85, 1864.

(10) Kopećni, M. M.; Laub, R. J.; Petkovic, Dj. M. *J. Phys. Chem.* 1981, 85, 1595.

(11) Prue, J. E. *J. Chem. Soc.* 1965, 7534.

(12) Scott, R. L. *J. Phys. Chem.* 1971, 75, 3843.

(13) Janini, G. M.; King, J. W.; Martire, D. E. *J. Am. Chem. Soc.* 1974, 96, 5368.

(14) See, for example; North, A. M.; Parker, T. G. *Trans. Faraday Soc.* 1971, 67, 2234. Guggenheim, E. A. *Ibid.* 1960, 56, 1159.

(15) Earp, D. P.; Glasstone, S. *J. Chem. Soc.* 1935, 1709, 1720. Ham-mick, D. L.; Norris, A.; Sutton, L. E. *Ibid.* 1938, 1755.

(16) Few, A. V.; Smith, J. W. *J. Chem. Soc.* 1949, 2781. See also: Cleverdon, B.; Collins, G. B.; Smith, J. W. *J. Chem. Soc.* 1956, 4499. Boud, A. H.; Smith, J. W. *Ibid.* 1956, 4507.

factor and the molar concentration of the subscripted species. Since D is at high dilution (as in the dielectric polarization method), dimerization of this species is unimportant, and the notional concentration C_D corresponds to the true concentration. We now seek to express ϵ in terms of K_1 . Conservation of mass $C_D^{\text{total}} = C_D^{\text{eq}} + C_{DA}$ with the equilibrium expression $K_1 = C_{DA}/(C_D^{\text{eq}}C_A)$ ($C_A \gg C_D$) provides

$$C_D^{\text{total}} = \left[\frac{1 + K_1 C_A}{K_1 C_A} \right] C_{DA} \quad (7)$$

Substitution of eq 7 for C_D and for C_{DA} in eq 6, followed by some rearrangement, produces

$$\epsilon = f_S C_S + f_A C_A + \left[f_D + (f_{DA} - f_D) \left(\frac{K_1 C_A}{1 + K_1 C_A} \right) \right] C_D^{\text{total}} \quad (8)$$

where, for constant C_S and C_A , ϵ will be linear in C_D^{total} of slope of the term in square brackets and of intercept of $f_S C_S + f_A C_A$. Designation, next, of the slope as $a = \{f_D + (f_{DA} - f_D)[K_1 C_A/(1 + K_1 C_A)]\}$ permits transformation of this quantity into the forms

$$\frac{C_A}{a - f_D} = \left[\frac{1}{(f_{DA} - f_D)} \right] \left(\frac{1}{K_1} \right) + \frac{C_A}{(f_{DA} - f_D)} \quad (9a)$$

$$\frac{1}{a - f_D} = \left[\frac{1}{(f_{DA} - f_D)} \right] \left(\frac{1}{K_1 C_A} \right) + \frac{1}{(f_{DA} - f_D)} \quad (9b)$$

where the former expression avoids the difficulty of extrapolation to regions of infinite dilution. Plots of $C_A/(a - f_D)$ against C_A or of $(a - f_D)^{-1}$ against C_A^{-1} then yield $(f_{DA} - f_D)^{-1}$ as the slope or intercept, respectively, where a is taken as the experimental slope of eq 8 at various concentrations of A. Finally, f_D is determined from permittivity measurement of highly dilute solutions of D in S, where $\epsilon = f_S C_S + f_D C_D$ and where f_D is the slope of plots of ϵ against C_D . K_1 and f_{DA} can then be calculated directly either from eq 9a or from eq 9b.

An alternative rearrangement of the slope of eq 8 produces

$$\frac{a - f_D}{C_A} = K_1 f_{DA} - a K_1 \quad (10)$$

where, in this instance, the left-hand side is plotted against a for various values of C_A to obtain K_1 and f_{DA} as the slope and intercept/slope quotient. The a term is again taken as the experimental slope of eq 8.

Experimental Section

The permittivity measurements were carried out with a Weihein Obermayern WTW DM-01 dipolmeter at 2 MHz. The refractive indices were determined with a Karl Zeiss Abbé type refractometer. The appropriate cells were in each case thermostated to $\pm 0.05^\circ\text{C}$ with a Lauda circulating water bath. A Karl Zeiss Model UR-10 infrared spectrophotometer with 0.0114-cm cells was used for the IR studies. The cell temperature was not controlled, but varied only between the limits of 21–23 $^\circ\text{C}$. The NMR studies employed a Varian 60 MHz Model EM360L spectrometer, where the experimental temperature was estimated from the chemical shifts of ethylene glycol to be 25–30 $^\circ\text{C}$. *N,N*-dibutyl-2-ethylhexanamide²⁴ (DBEHA)

TABLE I: Total Molar Polarization ($P_{D,\infty}$)_S,^a Distortion Polarization ($P_{D,\infty}^d$)_S,^b and Dipole Moment μ_D ^b for DBEHA in Indicated Solvents at 293 K

solvent	($P_{D,\infty}$) _S /cm ³	($P_{D,\infty}^d$) _S /cm ³	μ_D/D
<i>n</i> -hexane	363.70	83.44	3.67
cyclohexane	362.33	82.59	3.67
benzene	363.45	80.83	3.69
carbon tetrachloride	381.61	89.03	3.75

^a Equation 3. ^b Equation 5.

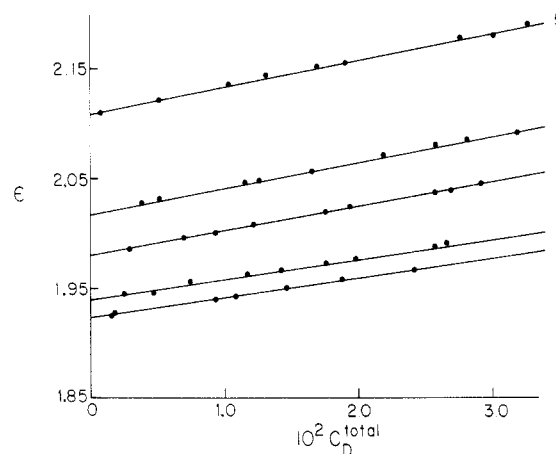


Figure 1. Plots of solution dielectric permittivity ϵ against DBEHA amide concentration C_D for fixed concentrations of chloroform C_A in *n*-hexane solvent. C_A : (1) 0.172, (2) 0.248, (3) 0.503, (4) 0.750, and (5) 1.24 M. Cf. text and eq 8.

was purified by molecular distillation (116–117 $^\circ\text{C}$ at 0.01 torr). Fresh quantities of chloroform were prepared by shaking several times with sulfuric acid, washing to neutrality, and drying over molecular sieves. All other compounds, also dried over molecular sieves, were the best available grades and were used as received. All mixtures were prepared by weight in a drybox.

Association constants K_1 were determined by IR by monitoring the absorbance of the carbonyl stretching band of the amide at 1600–1700 cm^{-1} . The DBEHA concentration was fixed at 0.1 mol dm^{-3} , while the additive/solvent ratio was varied over the range pure additive to pure solvent (*n*-hexane). The experimental data were reduced in accordance with the relations of Benesi and Hildebrand (B-H),²⁵ Scott,²⁶ and Scatchard.²⁷ For the NMR measurements, the chemical shifts of additives were determined relative to tetramethylsilane. The inert solvents were in this case *n*-hexane and *n*-hexadecane. The concentration of amide was varied from 0.2 mol dm^{-3} to pure amide, while the additive concentration was maintained at or below 0.02 mol dm^{-3} . Repeated spectra for the same solutions were in agreement to within 0.3 Hz. The experimental data were reduced according to the methods of Foster and his colleagues.²⁸ For the dielectric measurements the amide concentration was kept below $5 \times 10^{-3} \text{ mol dm}^{-3}$ while the additive/solvent ratio was varied as required (see later).

Results and Discussion

The total molar polarization ($P_{D,\infty}$)_S of DBEHA in various solvents is presented in Table I. Also shown are the distortion polarization ($P_{D,\infty}^d$)_S and the dipole moment μ_D .²⁹

(25) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

(26) Scott, R. L. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 787.

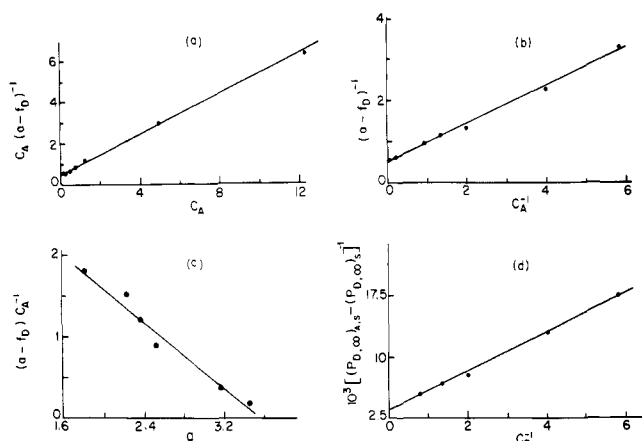
(27) Scatchard, G. *Ann. N. Y. Acad. Sci.* **1949**, *51*, 660.

(28) Foster, R.; Fyfe, C. A. *Trans. Faraday Soc.* **1965**, *61*, 1626. Foster, R.; Hammick, D. Ll.; Wardley, A. A. *J. Chem. Soc.* **1953**, 3817.

(24) We thank G. M. Gasparini, CNEN, Cassaccia, Rome, for supplying us with this material.

TABLE II: Additive Concentration Range, and Slopes and Intercepts of Plots of Eq 8 for DBEHA with *n*-Hexane Solvent at 293 K

$C_D/(\text{mol dm}^{-3})$	$f_D + (f_{DA} - f_D)K_1 C_A / (1 + K_1 C_A)$	$f_S C_S + f_A C_A$
Dichloromethane		
0.303	1.746	1.926
0.470	1.750	1.974
0.624	1.855	2.019
0.938	2.099	2.110
1.10	2.118	2.158
1.56	2.485	2.298
3.13	2.875	2.975
6.22	3.650	4.177
Chloroform		
0.172	1.784	1.924
0.248	1.925	1.941
0.503	2.238	1.978
0.750	2.376	2.019
1.24	2.523	2.109
Carbon Tetrachloride		
1.212	1.585	1.872
2.052	1.653	1.900
4.145	1.677	1.970
5.200	1.793	2.004
6.211	1.724	2.039
8.080	1.888	2.103
9.176	1.937	2.141
Benzene		
1.128	1.521	1.874
2.247	1.554	1.907
3.355	1.648	1.943
4.492	1.641	2.137
6.706	1.720	2.204
8.999	1.797	2.288
<i>n</i> -Hexane Solvent		
7.6518	1.4807	1.88777

Figure 2. Plots of (a) $C_A(a - f_D)^{-1}$ against C_A (eq 9a) and (b) $(a - f_D)^{-1}$ against C_A^{-1} for chloroform additive with DBEHA amide in *n*-hexane. Values of a taken as the slopes of plots typical of those shown in Figure 1. Plots of (c) $(a - f_D)C_A^{-1}$ against a (eq 10) and (d) $[(P_{D,\infty})_{A,S} - (P_{D,\infty})_S]^{-1}$ against C_D^{-1} (eq 1) for the same system.

We illustrate next the various methods of treatment of dielectric data (eq 9 and 10) with the system chloroform with DBEHA in *n*-hexane. Application of eq 8 is provided in Figure 1, where ϵ is plotted against C_D for DBEHA with various fixed concentrations of chloroform. The plots for all systems studied were as linear as that shown ($r > 0.9995$) and none gave evidence of ternary or higher com-

TABLE III: Association Constants K_1 and Complex Intensity Factors f_{DA} for DBEHA with Indicated Additives (*n*-Hexane Solvent) Derived from Dielectric Permittivity and Polarization, and IR, NMR, and GLC

additive	$K_1/(\text{dm}^3 \text{mol}^{-1})$	$f_{DA}/(\text{dm}^3 \text{mol}^{-1})$
dichloromethane	0.19 ± 0.08^a 0.04 ± 0.04^b	5.447^a 16.80^b
chloroform	0.94 ± 0.09^a 1.05 ± 0.09^b 1.22 ± 0.13^c 1.07 ± 0.08^d 1.39 ± 0.13^e 0.23 ± 0.09^f 2.36 ± 0.04^g 2.32 ± 0.04^h 2.31 ± 0.07^i	3.609^a 3.637^b 3.312^c 3.609^d
carbon tetrachloride	0.05 ± 0.05^a 0.15 ± 0.07^b	3.003^a 2.160^b
benzene	0.02 ± 0.06^a 0.01 ± 0.06^b	3.003^a 5.310^b

^a Equation 9a. ^b Equation 9b. ^c Equation 10. ^d Equation 8 and 11. ^e Equation 1. ^f IR. ^g NMR. ^h NMR (*n*-hexadecane solvent). ⁱ GLC (*n*-hexadecane solvent, 303 K; ref 9).

plex formation. The respective slopes a and intercepts ($f_S C_S + f_A C_A$) are given in Table II; the intercept for *n*-hexane, $\epsilon = 1.88777$, is in good agreement with that reported by Stokes,³⁰ $\epsilon = 1.88633$. Figure 2a,b and Table III provide illustration of the plots and resultant data obtained in accordance with eq 9a and 9b. The scatter is rather more substantial than that shown in Figure 1, and the use of Scatchard-type relations hence is recommended, here eq 10. Figure 2c illustrates the corresponding plot of $(a - f_D)C_A^{-1}$ against a for chloroform, the respective K_1 and f_{DA} data as before being listed in Table III.

Assumption of K_1 of ca. unity for chloroform with DBEHA indicates, for $C_D^{\text{total}} < 5 \times 10^{-2} \text{ mol dm}^{-3}$ and in the presence of moderate concentrations of additive, that 95–98% of the amide exists in the form of DA complex. In the absence of solvent, therefore, eq 6 can be written

$$\epsilon = f_A C_A + f_{DA} C_D \quad (11)$$

Plots of ϵ against C_D thereby yield f_{DA} from the slope. This value and those of f_S and f_D determined previously ($f_S = 0.2467 \text{ dm}^3 \text{mol}^{-1}$; $f_D = 1.4807 \text{ dm}^3 \text{mol}^{-1}$ in *n*-hexane; Table II) enable K_1 to be calculated directly from eq 8 for given C_A and C_D ; the result for chloroform is provided in Table III, where the agreement with eq 9a, 9b, and 10 is gratifying considering the diverse methods of data reduction employed.

In order to assess further the validity of the permittivity methods of measurement of K_1 , the procedure of Few and Smith (eq 1) was also employed for DBEHA with chloroform. The relevant plot is shown in Figure 2d, and the resultant K_1 ($1.39 \text{ dm}^3 \text{mol}^{-1}$; Table III) compares reasonably well with those obtained as described above. The permittivity and polarization techniques thus appear to offer some measure of internal consistency. However, the latter requires accurate measurement and extrapolation of density, permittivity, and refractive index of ternary mixtures (the latter if dipole moments are to be deduced) with one component in some instances at near-infinite dilution, which introduces the practical problem of compounding of error. The permittivity method, on the other hand, presents straightforward deduction of K_1 where, even

(29) The slight increase in μ_D for amide in benzene and in carbon tetrachloride weighs heavily against discrete interaction of these species. The high dipole moment of DBEHA even in *n*-hexane in contrast supports the likelihood of self-association of this compound even at moderate concentration.¹⁰

(30) Stokes, R. H. *J. Chem. Thermodyn.* 1973, 5, 379.

(31) Analogous discrepancies in the reduction of spectroscopic data have been discussed at length elsewhere (Deranleau, D. A. *J. Am. Chem. Soc.* 1969, 91, 4044, 4050). Equation 9a, for example, gives greater weight to solutions of high concentration of A.

though some graphical reduction of data is employed, the bulk of interpretation is placed upon slopes rather than upon the respective intercepts.

In efforts to evaluate further eq 1, 9, and 10, the IR spectroscopic K_1 for chloroform with DBEHA was determined as described in the Experimental Section; the result (Table III) represents the average of the three methods of data evaluation of Benesi and Hildebrand, Scott, and Scatchard where, not unexpectedly, some disagreement arose ($0.27 \text{ dm}^3 \text{ mol}^{-1}$ (B-H); $0.20 \text{ dm}^3 \text{ mol}^{-1}$ (Scott); $0.21 \text{ dm}^3 \text{ mol}^{-1}$ (Scatchard)). The proton NMR K_1 for chloroform additive with DBEHA is also presented in Table III, where the average of results of the two methods of data reduction of Foster et al. is reported. Good agreement is found for this and a previous study,⁹ and there is no apparent difference in K_1 for *n*-hexane and *n*-hexadecane solvents. Also shown as a matter of interest is the K_1 deduced from our previous GLC studies,⁹ where binary stationary phases comprising DBEHA + *n*-hexadecane (chloroform solute) were employed.

The data of Table III appear consistently to show *discrete* interaction of DBEHA with chloroform. However, the values of K_1 obtained by the various spectroscopic and chromatographic techniques employed in this and previous studies range over an order of magnitude (IR: $0.23 \text{ dm}^3 \text{ mol}^{-1}$; NMR: $2.34 \text{ dm}^3 \text{ mol}^{-1}$) with the dielectric data ($0.94\text{--}1.39 \text{ dm}^3 \text{ mol}^{-1}$) falling invariably with the average of the extrema.³² The situation is made still more complex since at moderate concentration the amide is presumed to self-associate.¹⁰ The GLC, IR, and NMR measurements were carried out with C_D at $0.1\text{--}0.2 \text{ mol dm}^{-3}$ (to pure amide in GLC and NMR), yet the differences in observed K_1 amount to a factor of 10. Highly dilute solutions of amide in contrast yield, from dielectric data, association constants with chloroform which are half those found by GLC and NMR. However, these data are just the opposite of what would be expected on the basis of diminished degree of association due to amide-amide interaction on the presumption that complex formation with dimerized DBEHA is less favored than that with monomer. We therefore cannot ascribe the differences in K_1 to the state of molecular aggregation of DBEHA.

In view of the K_1 data for all additives with DBEHA, we are led to reiterate the postulate (discussed by us at length previously¹⁰) that the variation of K_1 from one solvent to the next arises from complex destabilization by the solvent itself. The effects, further, may come about as a result either of competitive or of collisional forces but which, in any event, yield an energetically continuous spectrum of intermolecular encounters. Moreover, it does not seem entirely unreasonable to us to suppose that a particular solvent (e.g., benzene) will affect, in manner and magnitude, K_1 (IR) differently than K_1 (NMR) (due if nothing else to ring currents in the latter instance). In contrast, the permittivity method is transparent at 2 MHz to short-lived (10^{-11} s or so) contact pairing (which we equate with "solvent effects"), and the resultant K_1 data hence must be regarded as pertaining to persistent and long-lived complexes. The small increase in the dipole

moment of DBEHA in carbon tetrachloride ($\Delta\mu_D$ of 0.06 D; 3.69 D in benzene) coupled with K_1 values of 0.05 (eq 9a) and $0.15 \text{ dm}^3 \text{ mol}^{-1}$ (eq 9b) seem to indicate, for example, that there is little measurable interaction between these species other than that due to random collisional events. In contrast, the dipole moment of DBEHA with chloroform is 4.32 D,³³ i.e., $\Delta\mu_D = 0.65$ D, with $K_1 = 1.13 \text{ dm}^3 \text{ mol}^{-1}$ (the average of the dielectric data).³⁴

The data of Sharpe and Walker³⁴ for pyridine donor with carbon tetrachloride and carbon tetrabromide additives (benzene solvent) provide further illustration of the situation. The dipole moment of pyridine is 2.19 D in benzene and 2.33 D in carbon tetrachloride, and it may therefore be concluded that CCl_4 additive interacts only weakly with pyridine. Plots of the total molar polarization of pyridine against mole fraction of CCl_4 in fact give near-zero slope. Further recalculation and treatment of their data as required for eq 9a, 9b, and 10 provides values of K_1 of 0.04, 0.08, and $0.03 \text{ dm}^3 \text{ mol}^{-1}$, respectively. On the other hand, pyridine with carbon tetrabromide yields values of K_1 of 0.20, 0.18, and $0.15 \text{ dm}^3 \text{ mol}^{-1}$. We therefore expect a dipole moment of ca 2.6–2.8 D for pyridine with this additive.

We infer from these data, by way of summary, that the permittivity method of assessment of weak interactions offers a number of advantages over the conventional and more frequently employed techniques of GLC and spectroscopy. Each of the various data reduction relations (eq 9 and 10) yields association constants which are mutually consistent and which in particular can be said with little doubt to be unaffected by contact or other random interactions. Dipole moments in addition permit supplemental, although qualitative, conclusions to be drawn about the mode of interaction. Finally, assessment of solvent effects in principle becomes possible by measurement of K_1 for one or two donor-additive pairs with a large number of diluent media of varied type by IR, UV/vis, GLC, dielectric permittivity and polarization, and NMR. Since the "field" of solvent + additive (or of solvent + donor) which surrounds and presumably interacts with highly dilute donor (or additive) affects these various techniques through different mechanisms, K_1 will most likely vary with the same solvent from one technique to the next. An empirical scale of these effects can then be established. Detailed examination of the models from which K_1 is deduced with each method and correlation of these with the complexation constants arising from experiment must of course also be considered. The matter is one which we hope soon to explore by further and appropriate study.

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(33) Deduced from plots of μ against $(\epsilon - 1)^2$ for DBEHA with *n*-hexane, cyclohexane, carbon tetrachloride, and benzene solvents: Müller, H. *Phys. Z.* 1933, 34, 689; *Trans. Faraday Soc.* 1934, 30, 731.

(34) Sharpe, A. N.; Walker, S. J. *Chem. Soc.* 1961, 2974; 1962, 157; 1964, 2340. We agree, therefore, with the argument that small changes in dipole moments ($\Delta\mu$ of ca. 0.05 D) of this or that compound in one or another solvents are not sufficient to justify claims of discrete complex formation. On the basis of the present study, we in fact suggest that values of $\Delta\mu > 0.4$ D seem more reasonable as one criterion for judgement of stoichiometric association, for which *n*-hexane, cyclohexane, and benzene all appear to be appropriate reference solvents. Martire and co-workers,¹³ for example, rejected the notion of complexation of carbon tetrabromide with various simple aromatic hydrocarbons on the grounds that there was no discernible change in the dipole moment of the latter upon addition of the former (0.48 ± 0.07 D for toluene with $0.588 \text{ mol dm}^{-3}$ CBr_4 , *n*-decane solvent; 0.47 ± 0.09 D for toluene in *n*-decane).

(32) The distinction drawn, e.g., by Scott¹² between "thermodynamic" and "nonthermodynamic" methods of measurement of weak association therefore appears to us to be left open to question since, at least in this instance, the GLC and NMR formation constants agree closely while that from IR deviates substantially. In contrast, the GLC and IR data for alkynes with *N,N*-diethylamine are in close agreement (Queignec, R.; Wojtkowiak, B. *Bull. Soc. Chim. Fr.* 1970, 3829), while those derived by NMR and UV/vis techniques for aromatic hydrocarbons with 2,4,7-trinitrofluorenone range from positive through zero to negative (Purnell, J. H.; Srivastava, O. P. *Anal. Chem.* 1973, 45, 1111).