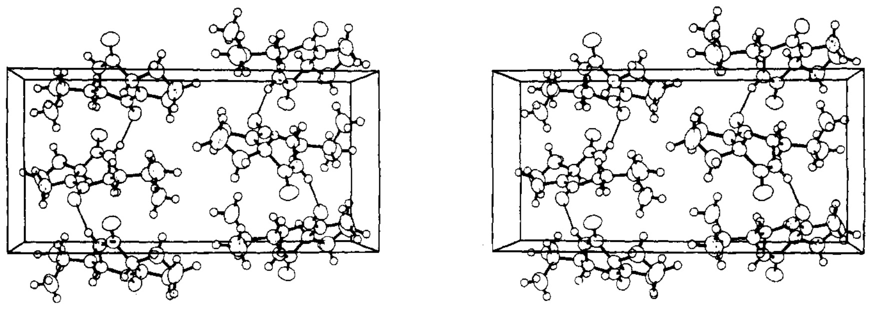

Figure 4. The molecular packing. Axial directions are *a*, ↓; *b*, →; and *c*, up from the plane of the paper. The light lines represent the NH···O hydrogen bonds.

jacent peptide unit containing C_1^{α}, N_1, C_2', O_2, and C_2^{α}. The intramolecular approaches $O_1 \cdots C_1^{\beta}$, $O_2 \cdots C_2^{\beta}$, and $O_2 \cdots C_1^{\delta}$ are 2.897, 2.830, and 2.838 Å, respectively, as compared to 2.820 and 2.822 Å for $O \cdots CH_3$ in III.

The leucyl chain is extended, with C_2^{α}, C_2^{β}, C_2^{γ}, and $C_2^{\delta_1}$ coplanar within 0.016 Å. All the H atoms, including those on $C_2^{\delta_2}$, are in the trans conformation with respect to each other. On the leucyl side of the molecule, the 14 nearest intramolecular $H \cdots H$ approaches range between 2.31 and 2.59 Å except for $H(C_2^{\gamma}) \cdots H(C_2^{\delta_2})$, which is ~2.14 Å. The $C_2^{\alpha}C_2^{\beta}C_2^{\gamma}$ angle is 114.6°, a value commonly found for the C^{β} angle in amino acids. The increase in this angle over a tetrahedral value is needed to separate sufficiently $H(N_2)$ from $H(C_2^{\gamma})$ and $H(C_2^{\alpha})$ from $H(C_2^{\delta_2})$.

The molecular packing is illustrated in Figure 4. The only possible hydrogen bond, $N_2H \cdots O_2'$ where O_2' is related to O_2 by the symmetry operation $-{}^1/_2 + x$, ${}^1/_2 - y$, $1 - z$, connects the molecules into infinite chains parallel to the *a* axis. The length of the $N_2H \cdots O_2'$ bond is 2.97 Å. Aside from the hydrogen bond, the closest intermolecular approaches are at normal van der Waals values. They are between the chains in the *c* direction, where $O_1 \cdots C_1^{\alpha}$, $O_1 \cdots C_2^{\alpha}$, and $O_2 \cdots C_1^{\beta}$ are 3.26, 3.35, and 3.36 Å, respectively, and between the chains in the *b* direction, where $C_1^{\gamma} \cdots C_1^{\delta}$ is 3.69 Å. Values for the thermal parameters are largest for the atoms at the periphery of the molecule, that is, for O_1, which is not involved in hydrogen bonding, and for C_1^{γ}, $C_2^{\delta_1}$, and $C_2^{\delta_2}$.

The Influence of Solvent on Ion Association. II. Proton Nuclear Magnetic Resonance of $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PCoBr_3]$

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Contribution from the W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois 61801. *Received January 13, 1971*

Abstract: The ion pairing interaction in $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PCoBr_3]$ has been studied by proton magnetic resonance spectroscopy in a series of different solvents. The observed paramagnetic resonance shifts of the *N*-methylene protons of the ammonium ion were determined for a 0.058 *M* solution in nine different solvents with the dielectric constant ranging from 4.65 to 64.2. By concentration *vs.* chemical shift studies, the concentration association constants and the isotropic resonance shifts of the *N*-methylene protons in the fully ion-paired species were determined in each of the following solvents: *o*- and *m*-nitrotoluenes, nitrobenzene, and propylene carbonate. The concentration association constants were found to be constant over a concentration range of 0.02–0.5 *M* in electrolyte and to increase with a decrease in dielectric constant of the solvent. This finding is used to challenge the common procedure of making activity corrections to spectrophotometric data. The *N*-methylene proton isotropic resonance shifts of the fully ion-paired species were the same within experimental error in the former three solvents and smaller in propylene carbonate. The smaller shift in propylene carbonate ($\epsilon = 63.0$) was interpreted to indicate a longer interionic distance for the ion pair in the higher dielectric solvent.

As part of our continued interest in solvent effects[2] and the application of nmr dipolar or "pseudocontact" shifts to the studies of ion pairing in solution,[3–5] we have examined the ion pairing interaction of $[(C_4H_9)_4N][(C_6H_5)_3PCoBr_3]$ as a function of solvent. In contrast to the earlier study[4] on $[(C_8H_{17})_3NCH_3]_3Fe(CN)_6$, the system we have chosen for the present study has the advantage that it is a simpler 1:1 electrolyte in polar solvents.

$$[(C_4H_9)_4N][(C_6H_5)_3PCoBr_3] \rightleftarrows [(C_4H_9)_4N]^+ + [(C_6H_5)_3PCoBr_3]^-$$

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[1] Abstracted in part from the Ph.D. Thesis of Y. Y. Lim, University of Illinois, Urbana, Ill., 1971.

[2] See, for example, R. S. Drago and K. F. Purcell, *Progr. Inorg. Chem.*, **6**, 271 (1964).

[3] I. M. Walker and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6951 (1968).

[4] J. C. Fanning and R. S. Drago, *ibid.*, **90**, 3987 (1968).

[5] D. G. Brown and R. S. Drago, *ibid.*, **92**, 1871 (1970).

By measuring the isotropic shift of a set of equivalent protons in the tetrabutylammonium ion which are rapidly exchanging between the free and paired forms, we are able to calculate the equilibrium constant and the paramagnetic isotropic shift of this set of protons in the fully ion-paired cation. The results from this study and others like it will lead to a better understanding of the factors involved in the association of ions in solution, a subject of considerable interest in recent years.[6,7] Isotropically shifted ion-pairing studies are particularly significant, because this method in effect counts only intimate ion pairs. Solvent-separated ion pairs are counted as dissociated, because the contact and pseudocontact shifts are expected to be insignificant. This particular complex was chosen for study because its solubility properties are such that a wide range of concentrations can be studied in a number of solvents.

Experimental Section

The nmr spectra were obtained on Jeolco C-60H and Varian A-60A spectrometers at 29° (±2°) for the 0.058 *M* solutions and at 34° (±2°) for the concentration *vs.* chemical shift studies. Tetramethylsilane was used as the internal reference. The visible spectra of the solutions were obtained with a Cary 14 recording spectrometer using a 1-mm quartz cell at room temperature (25°).

Preparation of Complexes. $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PCoBr_3]$ was prepared by the method reported by Rettig and Drago.[8] The crude product was recrystallized from 1-butanol and dried over anhydrous $CaSO_4$ under vacuum. The yield was 90%. The melting point (uncor) was 124°.

Anal. Calcd for $C_{34}H_{51}Br_3CoNP$: C, 50.83; H, 6.36; N, 1.75; Co, 7.34. Found: C, 51.09; H, 6.51; N, 1.71; Co, 7.32.

$[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PZnBr_3]$ was prepared in the same way as the Co(II) analog. The yield was 61%. The melting point (uncor) was 116.5–117°.

Anal. Calcd for $C_{34}H_{51}Br_3ZnNP$: C, 50.43; H, 6.30; Zn, 8.08. Found: C, 50.72; H, 6.38; Zn, 8.17.

Analyses were performed at the University of Illinois Microanalytical Laboratory under the supervision of Mr. Josef Nemeth.

Solvents. The chloroform used was of Baker Analyzed Reagent quality. It is necessary to remove all traces of ethanol (used as preservative) by a reported procedure[8] because ethanol was found to decompose the complex (as suggested by a change in visible spectrum). Bromobenzene was of Baker Analyzed Reagent grade; CH_2Cl_2 was of Mallinckrodt spectrophotometric grade. Both were dried over molecular sieves 4A for at least 6 hr prior to use. *o*-Dichlorobenzene (Eastman Organic Chemicals) was purified and dried as described.[8] Nitrobenzene (Mallinckrodt, Analytical Reagent) was fractionally distilled at reduced pressure and stored over molecular sieves 4A. *o*-Nitrotoluene (Matheson Coleman and Bell), 1,2-dichloroethane (Fisher Certified Reagent), and *m*-nitrotoluene (Eastman Organic Chemicals) were purified according to the methods described previously.[9] They were stored over molecular sieves 4A. Propylene carbonate (J. T. Baker Chemicals, practical grade) was dried over anhydrous $CaCl_2$ for 24 hr and distilled over 4A molecular sieves under reduced pressure twice [bp 123–124° (30 mm)]. The distillate was stored over 4A molecular sieves for at least 24 hr prior to use.

Treatment of Nmr Data. For the equilibrium $C + A \rightleftarrows CA$, where C represents the cation, A the anion, and CA the ion pair, the association constant K_{as} is defined as

$$K_{as} = [CA]/[C][A] \qquad (1)$$

where brackets denote concentration in terms of moles per liter of solution. No attempt is made to introduce the extended Debye-Hückel activity coefficients into the analysis because, as it turns out, the association constant in solvents with dielectric constant greater than 23 is quite constant in spite of a large variation in concentration.

When there is rapid exchange between protons in the paramagnetic and diamagnetic environments, the observed shift of the *i*th proton, ν_{oi}, is given by

$$\nu_{oi} = \nu_{di}N_d + \nu_{pi}N_p \qquad (2)$$

where N_p is the mole fraction of the cations in a paramagnetic environment and N_d is the mole fraction of the cations in the diamagnetic environment and

$$N_d + N_p = 1 \qquad (3)$$

From eq 1–3, it can be shown that

$$K_{as}^{-1} = \frac{[A_0]\Delta\nu_{pi}}{\nu_{oi} - \nu_{di}} - [A_0] - [C_0] + \frac{[C_0](\nu_{oi} - \nu_{di})}{\Delta\nu_{pi}} \qquad (4)$$

where $[A_0]$, $[C_0]$ denote the initial concentrations of anion and cation and $\Delta\nu_{pi} = \nu_{pi} - \nu_{di}$ is the observed isotropic shift of the *i*th set of protons.

In this paper, the set of equivalent protons used for the calculation is the methylene protons nearest to the nitrogen atom. Equation 4 has two unknowns, K_{as}^{-1} and $\Delta\nu_p$, which can simultaneously be determined by a modified version of a minimum-seeking computer program developed in this laboratory.[10,11]

Results

Electronic Spectra. In order to show that the complex anion remains intact in solution, the visible spectra of the various solutions were recorded and tabulated in Table I. The Co(II) is d^7 and the observed absorption is due to the ν_3 transition[12] which is $^4A_2 \rightarrow {}^4T_1$ (P) in pure T_d symmetry. This band is a complex multiplet[13] because of the effect of spin–orbit coupling in splitting up the $^4T_1$ (P) state and in coupling it to close-lying doublet states. The spread of the band is of the order of 10^3 wave numbers with contributions from the distortion of the ligand field from pure T_d

Table I. Visible Spectral Data of $[N(C_4H_9)_4][Co(PPh_3)Br_3]$ (All Spectra Were Run at 25°)

Solvent	λ_{max} (ε)
Mull (77°K)	566 (w),[a] 617 (sh), 634 (str), 646 (str), 673 (m), 687 (str), 715 (sh), 730 (str)
Chloroform	569 (29), 637.5 (894), 674 (554), 687 (655), 721.5 (821)
Methylene chloride	569 (29), 637.5 (920), 674 (534), 687.5 (655), 722 (829)
Bromobenzene	570 (34), 634 (977), 676 (507), 690 (671), 725 (855)
Nitrobenzene	570 (30), 634.5 (960), 675 (518), 689.5 (695), 724 (892)
m-Nitrotoluene	570 (30), 633 (950), 676 (470), 689 (655), 726 (850)
Ethylene dichloride	569, (30), 636 (902), 675 (512), 689 (648), 722 (842)
Propylene carbonate	567 (22), 635 (811), 673 (485), 686 (613), 722 (789)
o-Dichlorobenzene	570 (30), 634.5 (935), 675 (500), 689.5 (660), 724 (845)

[a] w = weak, sh = shoulder, str = strong, m = medium. All concentrations 1.0×10^{-2} *M*.

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(6) R. P. Taylor and I. D. Kuntz, Jr., *J. Amer. Chem. Soc.*, **91**, 4006 (1969).

(7) M. Szwarc, *Accounts Chem. Res.*, 2, 87 (1969).

(8) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 2966 (1966).

(9) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York, N. Y., 1966.

(10) N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, 81, 6138 (1959).

(11) T. F. Bolles and R. S. Drago, *ibid.*, **87**, 5015 (1965).

(12) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 258.

(13) F. A. Cotton and M. Goodgame, *J. Amer. Chem. Soc.*, **83**, 1777 (1961).

Table II. Nmr Spectral Data of 0.058 *M* Solution

No.	Solvent	ϵ (dielectric constant)[a]	$\nu_{oH(1)}$, Hz	$\nu_{dH(1)}$, Hz[b]	$\Delta\nu_{oH(1)}$ ($\nu_{oH(1)} - \nu_{dH(1)}$)
1	Chloroform	4.65	+311	−197	508
2	Bromobenzene	5.35	+396	−180	576
3	Methylene chloride	8.76	+168	−187	355
4	*o*-Dichlorobenzene	9.74	+270	−184	454
5	1,2-Dichloroethane	10.14	+25	−198	223
6	*m*-Nitrotoluene[c]	23.15	−26[d]	−210	184
7	*o*-Nitrotoluene	26.10	−50	−215	165
8	Nitrobenzene	33.70	−112	−210	98
9	Propylene carbonate	64.2[e]	−186	−193.5	7.5

[a] Data from "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, and corrected for temperature. [b] Chemical shift of the *N*-methylene protons of the reference compound $[(C_4H_9)_4N][(C_6H_5)_3PZnBr_3]$. [c] Measured at 34 ± 2°. [d] Estimated from the plot of $\Delta\nu_{oH(1)}$ *vs.* concentration (see Figure 1). [e] Y. Wu and H. L. Friedman, *J. Phys. Chem.*, **70**, 501 (1966), and corrected for temperature.

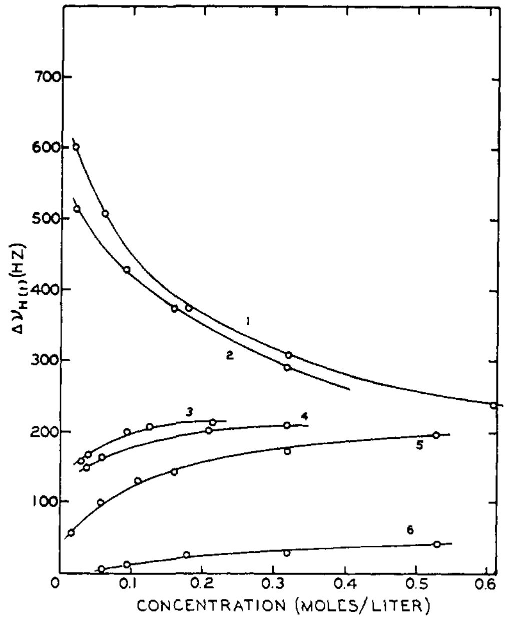

Figure 1. Concentration dependence of the chemical shift of $[n\text{-}(C_4H_9)_4N][(C_6H_5)_3PCoBr_3]$ in various solvents: 1, $CHCl_3$; 2, $o\text{-}C_6H_4Cl_2$; 3, *m*-nitrotoluene; 4, *o*-nitrotoluene; 5, $C_6H_5NO_2$; 6, propylene carbonate.

symmetry. A very broad band corresponding to the ν_2 transition was also observed in the ir region but was not reported because the absorption was so broad that the maximum could not be ascertained with any degree of certainty. The mull spectrum (at 77°K) has more bands than those in solution and since *o*-dichlorobenzene is expected to be inert with regard to substitution in the complex anion, the visible spectrum of $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3\text{-}PCoBr_3]$ in *o*-dichlorobenzene was used as reference with which the solution spectra of other solvents were compared. As can be seen from the results in Table I, the complex anion remains intact in all nine of the solvents listed. A point of caution is to be noted in the case of propylene carbonate. The spectrum of the 1×10^{-3} *M* solution contained an extra shoulder on the peak at 700 mμ and the extinction coefficient of the 635-mμ peak was smaller than that of the 722-mμ peak. This would indicate some sort of interaction between the complex anion and the solvent. However, on increasing the concentration of complex to 1×10^{-2} *M*, the 700-mμ peak disappeared and the extinction coefficient of the 635-mμ band became greater than that of the 722-mμ band. The extinction coefficient of the 635-mμ band in dilute solution also increased sharply on addition of $P(C_6H_5)_3$, suggesting the following reaction in dilute solution ($\leqslant 10^{-2}$ *M*)

$$\text{solvent} + (C_6H_5)_3PCoBr_3^- \rightleftharpoons Co(\text{solvent})Br_3^- + P(C_6H_5)_3$$

In more concentrated propylene carbonate solutions, the extent of replacement of the $P(C_6H_5)_3$ group by the solvent leads to a small percentage of solvated species and can be considered to have a negligible effect on our measurements which are mole fraction weighted shifts. Another point of interest is that in all the hydrogen-bonding solvents, *i.e.*, $CHCl_3$, CH_2Cl_2, and $C_2H_4Cl_2$, the difference between the intensities at 675- and 689-mμ bands is always smaller than those in nonhydrogen-bonding solvents, *e.g.*, bromobenzene, nitrobenzene, *o*-dichlorobenzene, etc., with the exception of propylene carbonate.

Nmr Studies. In order to determine whether a linear relationship exists between $\Delta\nu_{H(1)}$ and the dielectric constant, ϵ, similar to that found in trioctylmethylammonium hexacyanoferrate(III),[4] the nmr spectra of 0.058 *M* solutions in nine solvents were obtained and the *N*-methylene proton frequencies measured relative to tetramethylsilane. The results are presented in Table II. The numbering system used is

$$N{-}(\underset{1}{C}{-}\underset{2}{C}{-}\underset{3}{C}{-}\underset{4}{C})_4^+$$

and the assignments were made according to the methods previously described.[14,15] In low dielectric constant solvents, the resonance signals from H(1), H(2), H(3), and H(4) are well resolved. $\nu_{(H)1}$ is found at the highest field followed by $\nu_{(H)2}$, $\nu_{(H)3}$, and $\nu_{(H)4}$, respectively. As the dielectric constant of the solvent increases, the resonance frequency of H(1) begins to move downfield together with those of H(2), H(3), and H(4) and, since the resonance frequency of H(1) is shifted more than others, it begins to overlap with those from H(2) and H(3) in $C_2H_4Cl_2$ (ϵ = 10.4 at 29°) and in *m*-nitrotoluene (ϵ = 23.15). The signals from the four sets of protons are not resolved and the value given in Table II is estimated from the plot of $\Delta\nu_{H(1)}$ *vs.* concentration (see Figure 1). In *o*-nitrotoluene (ϵ = 26.10 at 29°), $\nu_{H(1)}$ is on the downfield side of the other three proton resonance signals (which are not resolved). The

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(14) D. W. Larsen, *Inorg. Chem.*, **5**, 1109 (1966); *J. Amer. Chem. Soc.*, **91**, 2920 (1969).

(15) G. N. La Mar, *J. Chem. Phys.*, **43**, 235 (1965).

Table III. Association of $[(C_4H_9)_4N][(C_6H_5)_3PCoBr_3]$ in Various Nonaqueous Solvents

No.	Solvent	Dielectric constant, ϵ (at 34°)	$\Delta\nu_p$, Hz[a]	K_{as}
1	Propylene carbonate	63.0	170 ± 25	0.85 ± 0.15
2	Nitrobenzene	33.3	265 ± 15	17.9 ± 1.4
3	*o*-Nitrotoluene	25.3	257 ± 15	82.4 ± 4.8
4	*m*-Nitrotoluene	23.1	262 ± 15	130 ± 19

[a] Error is estimated from the plot of $\Delta\nu_p$ *vs.* K_{as}^{-1}.

Table IV. Equilibrium Constant Data in Various Solvents

Solvent	Concn, mol/l.	$\Delta\nu_{H(1)}$ (obsd, ±2.0 Hz)	$\Delta\nu_{H(1)}$[a] (calcd)	Solvent	Concn, mol/l.	$\Delta\nu_{H(1)}$(obsd, ±2.0 Hz)	$\Delta\nu_{H(1)}$[a] (calcd)
Propylene carbonate	0.058	7.5	7.7	*o*-Nitrotoluene	0.0392	147	148
	0.094	12.0	11.8		0.0580	165	163
	0.178	20.7	20.1		0.210	203	202
	0.322	30.0	31.1		0.320	210	212
	0.532	43.5	43.1				
Nitrobenzene	0.02	59	58	Chloroform	0.02	601	449
	0.058	101	103		0.058	508	449
	0.111	131	132		0.178	375	449
	0.162	146	149		0.32	307	449
	0.320	175[b]	175		0.610	233	449
	0.531	197	192				
m-Nitrotoluene	0.0294	159	158	*o*-Dichlorobenzene	0.02	515	419
	0.0392	166.5	169		0.094	430	418
	0.0943	201.7	197		0.162	374	420
	0.1265	207	205		0.320	293	420
	0.2148	213	217				

[a] $\Delta\nu_H$ calculated from the K_{as} and $\Delta\nu_p$ that best fit the data. [b] Estimated from the plot of concentration *vs.* chemical shift.

same type of spectrum occurs in solvents of higher dielectric constants.

Concentration *vs.* chemical shift studies were made in chloroform, *o*-dichlorobenzene, *o*-nitrotoluene, *m*-nitrotoluene, nitrobenzene, and propylene carbonate solutions. In low dielectric constant solvents, *i.e.*, chloroform and *o*-dichlorobenzene, the isotropic shift decreases as concentration increases, whereas for the other solvents, the shift increases rather abruptly for concentration less than 0.1 *M* and then levels off as the concentration increases beyond this value (see Figure 1). Results of the calculation of K_{as} and $\Delta\nu_p$ are tabulated in Table III. An attempt was also made to evaluate both quantities in chloroform and *o*-dichlorobenzene, but the errors in K_{as} and $\Delta\nu_p$ are too large. The reason for this behavior will be explained later in the Discussion section. In the four solvents listed in Table III, K_{as} was found to increase with decrease in dielectric constant of the solvents. $\Delta\nu_p$ in propylene carbonate is smaller than those in the other three solvents where the value is the same within the limits of experimental error. The reliability of the $\Delta\nu_p$ and K_{as} values could be tested by comparing the observed values of $\Delta\nu_{H(1)}$ with those calculated from $\Delta\nu_p$ and K_{as}. The results are reasonably good in propylene carbonate and nitrobenzene as can be seen in Table IV. A plot of log K_{as} *vs* $1/\epsilon$ is shown in Figure 2.

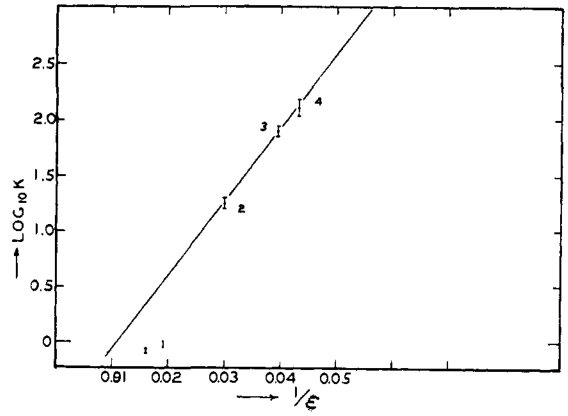
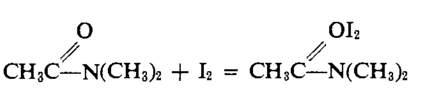


Figure 2. Plot of log *K* *vs.* $1/\epsilon$ for various solvents (numbering as in Table III).

Discussion

Implications of the K_{as} Determination. Much to our surprise, we were able to fit the data in nitrobenzene, *m*-nitrotoluene, *o*-nitrotoluene, and propylene carbonate to a 1:1 equilibrium concentration constant over a concentration range of 0.05–0.5 *M*. In these media (ϵ = 23–63), the data did not have to be corrected with activity coefficients to fit an equilibrium constant expression that was concentration independent up to 0.5 *M*. This fact prompts us to seriously question the validity of making activity coefficient corrections to equilibrium constant determinations when the system is studied by spectrophotometric procedures at comparable concentrations in polar solvents. In an earlier study from this laboratory,[16] we reported that the equilibrium constant for the system



$$CH_3C(=O)\text{—}N(CH_3)_2 + I_2 = CH_3C(OI_2)\text{—}N(CH_3)_2$$

in CCl_4 solvent was constant over ranges in which *N*,*N*-dimethylacetamide (DMA) was undergoing drastic changes in activity coefficient. We proposed that as-

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(16) R. S. Drago, R. L. Carlson, and N. J. Rose, *J. Amer. Chem. Soc.*, **83**, 3572 (1961).

sociation in the amide was retained in the product leading to a whole series of equilibria of the type

$$(DMA)_n + I_2 \longrightarrow (DMA)_nI_2$$

all with similar equilibrium constants. Alternatively, we could state that in excess DMA $\gamma_{\text{DMA-I}_2}/\gamma_{\text{DMA}}$ is a constant.

The ion-pairing system we have just completed could be similar in that

$$(CA)_nA^- + C^+ \longrightarrow (CA)_{n+1}$$

$$(CA)_mC^+ + A^- \longrightarrow (CA)_{m+1}$$

or

$$(CA)_mC^+ + (CA)_nA^- \rightleftharpoons (CA)_{m+n+1}$$

could all have comparable activity coefficient ratios for products and reactants leading to concentration-independent equilibrium constants. This would require that the ν_o values be similar for all the $(CA)_n$ species involved. We have recently reported a detailed evaluation of the effects of base and acid association on spectroscopically determined equilibrium constants.[17] It should be emphasized that fitting a set of data to a 1:1 equilibrium constant expression does not imply monomeric species.

If aggregation were to stabilize the product so that the equilibrium constants were not the same when n increases or if the equilibrium constant expression did not properly describe the equilibria in solution, *vide infra*, an activity correction to one or both reactants would enable one to improperly fit the data to the model imposed. It is possible that many activity corrections in the literature fall in this category. Clearly, the use of activity coefficients from any procedure that "counts" solvent-separated ion pairs as ion pairs (*e.g.*, conductivity) in correcting equilibrium data from a spectroscopic procedure which counts ion pairs differently is highly questionable. The fact that we have been able to calculate a constant concentration based equilibrium constant for ionic species in a solvent of low dielectric constant ($\epsilon \sim 23$) casts some doubt on many activity corrections in polar and aqueous media.

It is of interest to describe how an equilibrium situation which is expressed by the correct constant

$$K = \frac{[(CA)_{m+n+1}]}{[(CA)_mC^+][(CA)_nA^-]} \qquad (5)$$

can be fit by a 1:1 constant using a measurement that only counts C^+ when m is near zero. When m is large, the chemical shift of the cluster $(CA)_mC^+$ is expected to be similar to CA_{m+n+1}. Consequently, our nmr method only measures C^+ with m very small and constant or zero and does not count $(CA)_mC^+$. By a derivation similar to one shown previously[17]

$$[CA]_i = [\Sigma]\Delta\nu^0/\Delta\nu_{\text{obsd}} \qquad (6)$$

where $[\Sigma]$ is the sum of the concentration of all species which are aggregates, $\Delta\nu^0$ the shift of the fully clustered material relative to the free C^+, and $[CA]_i$ equal to the initial concentration of CA. This enables one to measure all of the material in the cluster and the free C^+ assuming all the species $(CA)_mC^+$, $(CA)_nA^-$, and $(CA)_{m+n+1}$ have the same shift. The reason we get a constant equilibrium constant when we use $[C^+]$ in expression 5 instead of $(CA)_mC^+$ is that $[(CA)_mC^+] = K'[C^+][CA_m]$ from $(CA)_m + C^+ \rightleftharpoons (CA)_mC^+$. Furthermore, the $\Sigma(CA)_nC^+ = \Sigma(CA)_mA^-$, so A^- is set equal to C^+ and another equilibrium constant relates $[(CA)_{m+n+1}]/[(CA)_m][(CA)_n]$. Thus, the constant we calculate is proportional to the true equilibrium constant and the data can be made to fit a 1:1 expression. As pointed out in our earlier paper,[17] meaningful enthalpies could be obtained from a temperature variation in K, but the entropies would be meaningless.

As can be seen from the discrepancy in $\Delta\nu_{\text{H(1)obsd}}$ and $\Delta\nu_{\text{H(1)calcd}}$ in Table IV for chloroform and *o*-dichlorobenzene, we were unable to fit the data in these solvents to a 1:1 expression. In these low dielectric constant solvents, very extensive ionic clustering occurs,[18] and the concentration of ionic species is expected to be very low. Extensive association was supported by molecular weight studies in these solvents. As can be seen in Figure 1, the value of $\Delta\nu_{\text{H(1)}}$ increases with decrease in concentration in these solvents, but $\Delta\nu_{\text{H(1)}}$ shows the opposite behavior in the other solvents studied. We attribute this behavior to the fact that the equilibrium in the nonpolar solvent upon dilution involves dissociation of the cluster to produce smaller clusters. Of these, the pseudocontact shift in the single ion pair AC (or a very small cluster) might be expected to be quite different from that in a cluster. (All the anionic neighbors in the cluster make a $(3\cos^2\theta - 1)/R_i^3$ contribution, which could in part cancel that found from one anion in the simple CA ion pair.) Thus, the nmr technique measures the fraction of singlet ion pairs dissociated in the chloroform and *o*-dichlorobenzene solvent. This would require that simple singlet ion pairs do not exist in the other solvents, because the chemical shift of all the ion pairs must be a constant.

These ideas require a major change in current practices used to treat data involving ionic equilibria. If correct, thermodynamic constants obtained in situations where activity corrections have been applied to one of the species would be worthless. An extreme analogy would involve trying to ascertain the meaning of data forced to fit a 1:1 equilibrium constant expression by correcting concentrations with activity coefficients for a system that was actually 2:1. Alternatively, changing chemical shifts or extinction coefficients could be easily masked with an activity coefficient correction producing a meaningless K.

Ion-Pair Distance as a Function of Solvent. In initial interpretations of the isotropic shift for ion-paired systems, $\Delta\nu_p$ was thought to arise solely from a nonzero dipolar interaction of the electron spin and electron orbit with the proton nuclear spin. For an axial system, the fractional isotropic dipolar shift is given by[19]

$$\left(\frac{\Delta\nu_p}{\nu_o}\right) = D\left(\frac{3\cos^2\theta_i - 1}{R_i^3}\right) \qquad (7)$$

where ν_o is the frequency of the alternating electromagnetic field, θ is the angle between the C_3 axis and the radius vector from the metal to the resonating proton, R_i is the length of this radius vector, and D is some function

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(17) F. L. Slejko, R. S. Drago, and D. G. Brown, submitted for publication.

(18) C. W. Davies, "Ion Association," Butterworth, Washington, D. C., 1962, Chapter 11.

(19) B. R. McGarvey, *J. Chem. Phys.*, 53, 86 (1970).

of the g tensor and of temperature and is a constant for all nuclei in a given molecule.

When eq 7 applies, the change in magnitude of the pseudocontact shift as one changes solvent should depend only upon the geometric factor $(3 \cos^2 \theta - 1)/R_i^3$. If the solvent does not undergo specific interactions with the complex, the g-tensor term is not expected to change appreciably as the solvent is varied. In ion-pairing systems, Walker, *et al.*,[20] have shown recently that the original La Mar equation[15] is in error and, for the H_1 proton

$$\left\langle \frac{3 \cos^2 \theta - 1}{R^3} \right\rangle_{av} = \frac{2}{a^3} \qquad (8)$$

where a is the distance between centers in the ion pair. Equation 8 is derived with the following assumptions. The cation approaches the paramagnetic anion along its C_3 axis opposite the metal–phosphorus bond, the cation tumbles freely about its center, and there are free rotations about the N–C, C_1–H_1, C_1–C_2, and C_2–H_2 axes.

Recently, it has been shown[5] by studying the ^{14}N isotropic resonance shifts of tetrabutylammonium cation ion paired to several paramagnetic anionic transition metal complexes that there is some type of weak covalent interaction between the cation and anion in the ion pair. This effect was also proposed[3] from earlier pmr spectra of tetrabutylammonium tetrahalometalates(II) which indicated that the H_1 proton is interacting with the halide ligands. It is very likely that in all cases the H_1 resonance position is at a higher field than might be expected from only "pseudocontact" interaction. The term, $\Delta\nu_p$, therefore, does not arise solely from "pseudocontact interaction" but rather is a combined contribution from the contact and pseudocontact interactions. The contact contribution coupled with the oversimplified assumptions of free rotation[20,21] and the very complicated nature of the equilibria described in the previous section invalidates the use of this method to produce quantitative values of distances.

In spite of the nonquantitative nature of these systems, the shortcomings described do not affect qualitative conclusions based on relative distances for the same ion pair in various solvents. The pseudocontact contribution should decrease with distance increase (eq 8), and the contact contribution is expected to fall off as the distance increases because the orbital overlap integrals should decrease. Slight deviations in this expected behavior of the contact term are not critical because the observed shift is dominated by the pseudocontact term. Using these arguments and since $\Delta\nu_p$ in propylene carbonate is greater than that in nitrobenzene, we are led to the conclusion that the interionic distance of the ion pair $[(C_4H_9)_4N][(C_6H_5)_3PCoBr_3]$ is larger in propylene carbonate than in nitrobenzene. Since the $\Delta\nu_p$ values are the same in the solvents nitrobenzene, *o*-nitrotoluene, and *m*-nitrotoluene within the limits of experimental error, we are not able to draw any conclusions about any changes in bond distance in this series. The change in dielectric constant in these three solvents is slight and, considering the magnitude of the change in going to propylene carbonate and the $1/R^3$ dependence of the shift, one might expect not to be able to detect a change in distance if it does occur. Referring to Figure 1, we see that $\Delta\nu_{H(1)}$ in $CHCl_3$ and $C_6H_4Cl_2$ is approaching the value for the nitrobenzenes as the concentration increases, suggesting similar anion–cation distances in these solvents.

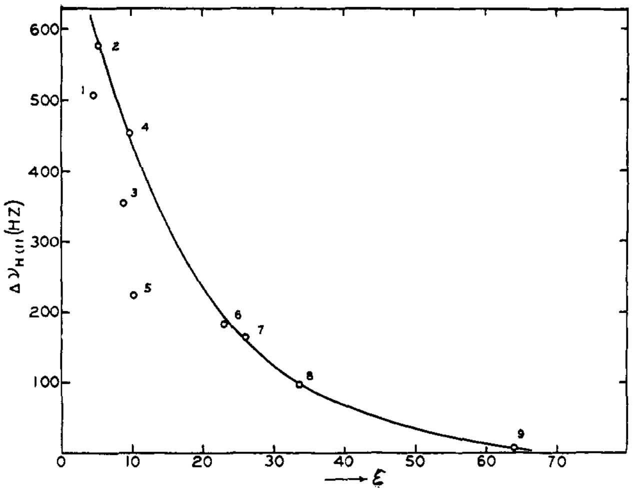

Figure 3. Chemical shift of the NCH_2 proton *vs.* ϵ (numbering as in Table II).

The sphere-in-continuum model of Fuoss,[22] Kraus, and Denison and Ramsey[23] predicts that the interionic distance should be independent of the dielectric constant of the solvent and that the plot of log K_{as} *vs.* $1/\epsilon$ should give a straight line. Our plot of log K_{as} *vs.* $1/\epsilon$ (Figure 2) shows clearly that propylene carbonate falls off the line in spite of the absence of any known specific solute–solvent interaction. The model may be applicable to the nonhydrogen-bonding solvents with dielectric constant ranging from 23 to 33 on the basis of only three pieces of data.

Our result is in conflict with a recent report[6] on the association of methyltributylammonium tetraphenylboride in various nonaqueous solvents (ϵ ranged from 19.3 to 34.3). The nmr results on this system were interpreted to indicate a decrease in ion-pairing distance with increase in dielectric constant. It was assumed in this[6] study that the chemical shift contribution from ring currents in the anion would decrease as the ion-pair distance increases. This is not necessarily true. A detailed knowledge of the geometry of the ion pair is required in order that the orientation of the protons relative to the various anisotropic regions of the ring is known as a function of ion-pair distance. The breakdown of the assumption that the anisotropic contribution will decrease with increasing distance in the tetraphenylboride ion pair could be the cause of the discrepancy. The assumption that the pseudocontact contribution will decrease with increasing distance is more firmly based with the analysis of the geometric factors discussed earlier.

As can be seen in Figure 3, our results do not fit the empirical straight line type of relationship previously reported[4] between $\Delta\nu_{H(1)}$ and ϵ. Even points 2, 4, 6, 7, and 8 which do not undergo specific interactions do

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(20) I. M. Walker, M. S. Quereshi, and L. Rosenthal, *Inorg. Chem.*, in press.

(21) J. A. Pople, W. G. Schneider, and W. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, pp 377–385.

(22) R. M. Fuoss, *J. Amer. Chem. Soc.*, 80, 5059 (1958).

(23) J. T. Denison and J. B. Ramsey, *ibid.*, 77, 2615 (1955).

not give a straight line. Since the anion is not shielded from the solvent as it was in the earlier study,[4] we anticipate that in the hydrogen-bonding solvents the ion pair would be more dissociated than in a nonhydrogen-bonding solvent with similar dielectric constant. As was shown in a previous report from this laboratory,[8] we would expect specific interaction of the hydrogen-bonding type to occur between chloroform and $(C_6H_5)_3PCoBr_3^-$. According to the relationship[4]

$$\Delta\nu_{H(1)} = \Delta\nu_p N_p$$

(where all the terms have the usual meaning[4]), the hydrogen-bonding solvents could either decrease the fraction of ions paired together or decrease $\Delta\nu_p$ as a result of an increase in interionic distance. Solvent-separated ion pairs would be counted as dissociated by this technique. In ethylene dichloride, another factor would favor a decrease in $\Delta\nu_{H(1)}$. Molecules of this solvent can exist in the gauche and trans forms. This equilibrium is disturbed by the electric field of the ion in favor of the gauche form[24] (polar form) with the resulting increase in the dielectric constant of the solvent medium in the vicinity of an ion in effect causing the bulk dielectric constant to poorly approximate this solvent's dielectric constant.

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A Procedure for Eliminating and Evaluating Solvent Effects on Thermodynamic Data for Donor–Acceptor Interactions

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Abstract: An elimination of solvation procedure (ESP) is reported which, under appropriate conditions, enables one to study donor–acceptor reactions in polar solvents and predict, from these data, an enthalpy of the adduct formation in the gas phase. The method is tested by predicting enthalpies in poorly solvating media from data in polar solvents. The predicted enthalpies are compared with those directly measured in the nonpolar solvent.

In a series of reports from this laboratory,[1,2] we have been concerned with the interpretation and evaluation of the magnitude of donor–acceptor interactions as manifested by the enthalpy of adduct formation. Enthalpies determined in poorly solvating media, or the gas phase, have been correlated by eq 1 where C_A, E_A

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

and C_B, E_B are empirically determined parameters referring to acceptor and donor, respectively.[1]

Ideally, gas-phase data free from solvation contributions to the enthalpy are desired for evaluation of donor and acceptor strength. However, the difficulty associated with present techniques for gas-phase measurements prevents accumulation of reasonably accurate or extensive amounts of data needed to test the validity of eq 1. Consequently, data obtained in the poorly solvating media (*i.e.*, solvents which do not undergo specific interactions greater than 0.2 kcal mol^{-1} and have dielectric constants equal to or lower than 2.3), carbon tetrachloride and cyclohexane, have been employed. It is well established that solution of gaseous materials in cyclohexane or CCl_4 is accompanied by an interaction between the solvent and solute, *e.g.*, at 21° the enthalpy of vaporization of diethyl ether is 9.39 kcal mol^{-1}, while the apparent molar enthalpy of solution of liquid diethyl ether in CCl_4 is -0.42 kcal mol^{-1}. Combining the above enthalpies leads to an enthalpy of solution of gaseous Et_2O in CCl_4 of -9.81 kcal mol^{-1}. Assuming $(C_2H_5)_2O$ to be monomeric in the gas and in dilute CCl_4 solution, this corresponds to a rather extensive nonspecific solvation energy of diethyl ether by CCl_4. Similar effects are to be expected for the Lewis acid as well as the adduct formed form the interaction of a Lewis acid with the donor diethyl ether. The same type of behavior is also noted in cyclohexane. The only way enthalpy data obtained in poorly solvating media can approach the gas phase is to have a cancellation of solvation terms for products and reactants. Such a cancellation may be possible when solvent–solute interactions are nonspecific and consist mainly of dispersion forces. Under these circumstances, the similarity of the products and reactants would lead one to anticipate a near cancellation of solvation terms. The product is often more polar, so dipole-induced dipole effects would be slightly larger. On the other hand, bond formation reduces the number of solvent molecules that can cluster around the adduct, compared to those around the free acid and base, slightly decreasing the solvation of the adduct compared to the reactants.

Previous reports from this laboratory illustrate the complications which can arise in polar solvents[3,4] or in

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[1] R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, **87**, 3571 (1965).

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