in the present and previous studies[3] and cannot be explained at present. One or more of the assumptions made in the determination of the hydration constants of the proton may be incorrect and thus will be subject to further study. Fortunately, the above discrepancy does not affect seriously the previously reported values of $Kt_{H(H_2O)_x^+}$, x varying from 1 to 4.[3,13]

The results in the present study are completely at variance with conclusions drawn by D'Aprano and Fuoss[8] from their experiments. They determined the conductance of picric acid solutions in mixtures of AN and water. Most of their measurements have been made at water concentrations much greater than 1 *M*. They concluded that the proton forms only a monohydrate $H \cdot H_2O^+$ and the picrate ion a trihydrate $Pi \cdot 3H_2O^-$. Even in perchloric acid solutions being only 1 *M* in water we have found previously that most of the protons are present in the form of tri- and tetrahydrates $H(H_2O)_3^+$ and $H(H_2O)_4^+$, and that the fraction present as the unhydrated proton is only of the order of 2×10^{-5} of $\Sigma[H_w^+]$. Furthermore, our previous data[3] and our present infrared studies indicate that the picrate ion forms only a monohydrate with the small formation constant of 0.3 ± 0.1. Finally, we have found no experimental evidence of formation of ion pairs, either $H_3O^+Pi_{1w}^-$ or $H_3O^+Pi_{3w}^-$. Like potassium picrate, such ion pairs should be relatively strong electrolytes and at the small hydrated proton and picrate ion concentrations be completely dissociated. If the H_3O^+ ion were less stable than the Pi_{3w}^-, the pa_{H_s} of a solution of picric acid in AN should decrease with increasing water concentration. In fact, the opposite effect was observed, suggesting that hydration of the proton is much more extensive than that of the picrate ion.

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Solvation Studies on *p*-Chloronitrobenzene Anion Radical in Acetonitrile–Alkyl Alcohol Solvent Mixtures at 25°

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Abstract: The variation of the nitrogen coupling constant of *p*-chloronitrobenzene anion radical in acetonitrile–alkyl alcohol solvent mixtures is interpreted on the basis of several solvent substitution steps. The variation of the *g* values and chlorine coupling constant is reported for the acetonitrile–methanol system.

The solvent dependence in electron spin resonance spectra (esr) of nitro aromatic compounds has received considerable attention in the past years. The increase in N^{14} hyperfine splitting (hfs) constants with progressive addition of polar solvent to less polar, aprotic solvents has been the subject of several qualitative and quantitative discussions.[2,3]

Gendell, Freed, and Fraenkel[3] suggested a model to account for mixed solvent effects in terms of rapidly exchanging radical-solvent complexes where each complex has a characteristic π-electron spin density distribution. A notably successful application of the theory was made by Stone and Maki[4] in their analysis of C^{13} hfs of *p*-benzosemiquinone anion radical in dimethyl sulfoxide–water mixtures. However, in several cases, difficulties have been encountered. The theory appeared inadequate for the analysis of the C^{13} hfs variation of *p*-benzosemiquinone in the water–acetonitrile (MeCN) system and for analysis of nitro aromatics in N,N-dimethylformamide (DMF)–water.[2h] It had limited success in an alcohol–DMF study of the fluorenone anion radical.[5] Gross and Symons[2h] suggested that the successful application of the GFF model may necessitate that solvents have similar characteristics and that there be no complicating features such as ion pairing or hydrogen bonding. Others[4] attributed failure to either an oversimplification of the solvation model or to inadequate activity data. In the fluorenone[5] study, the GFF model was applicable to solvent mixtures with a small amount of alcohol, but the continued increase in coupling with further addition of alcohol went beyond that expected by simple theory. It was proposed that the deviation could be interpreted by an additional "generalized" solvent effect.

The basic aim of this study was to analyze the effect of alcohol–MeCN mixed solvent systems on the esr spectrum of *p*-chloronitrobenzene (*p*-ClNB) anion radical. The alcohols include methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), and 1-butanol (1-BuOH). We wish to report a reasonable analysis of the N^{14}-coupling constant variation on the basis of the GFF theory of localized complexes. The entire range of data can be given an excellent fit in each system provided that the number of equilibria is

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extended. Activities of the binary solvents have been reported elsewhere.[6]

Though the main focus of this study was directed toward the interpretation of the nitrogen-coupling variations, the *g*-value shifts and chlorine-coupling variations noted in the MeOH–MeCN mixtures are included herein. Both measurements are most striking and the most easily obtained in the methanol system.

Experimental Section

Materials. MeOH, EtOH, and 1-PrOH were dried and purified according to the method for preparing "super-dry" ethanol.[7] Prior to distillation, 2-PrOH and 1-BuOH were dried over anhydrous K_2CO_3. MeCN was purified by successive distillation from NaH, P_2O_5, and CaH_2.[8] The indexes of refraction of these solvents at 25.0° were as follows: MeOH, 1.3266 (1.3266);[9] EtOH, 1.3594 (1.3594);[9] 1-PrOH, 1.3835 (1.3835);[9] 2-PrOH, 1.3753 (1.3747);[9] 1-BuOH, 1.3974 (1.3974 and 1.3970);[10] MeCN, 1.3416 (1.3416).[9]

Eastman reagent grade tetraethylammonium bromide (TEABr) was used as the supporting electrolyte. It was dried at 110° and stored over P_2O_5. Eastman reagent grade *p*-ClNB was stored over P_2O_5 and used without further purification.

The mixed solvent solutions were prepared by volume addition of MeCN, ROH, and stock solutions of TEABr and *p*-ClNB so that the solutions were 5×10^{-2} *M* in TEABr and $2\text{-}5 \times 10^{-3}$ *M* *p*-ClNB. The mole fractions of the solutions were independently determined with duplicate measurements varying by ≤ 0.001 mol fraction.

Electron Spin Resonance Spectra. Standard electrochemical techniques were employed for *in situ* generation of the radical anions.[11,12] Solutions were electrolyzed at −1.4 to −1.5 V *vs.* the saturated calomel electrode.

All spectra were taken with a Varian 4502 X-Band spectrometer equipped with a "Fieldial" magnetic field regulator and a multipurpose dual cavity. The spectra were recorded with a Hewlett-Packard X-Y recorder having a 17 × 11-in. bed. The field-scan ranges were calibrated with a tetracyanoethylene (TCNE) reference solution which has a nitrogen coupling constant of 1.574 G and a *g* value of 2.00270.[13]

Results and Discussion

Nitrogen Coupling Constant Variations and Interpretations. The solvent dependence of the *p*-ClNB anion radical nitrogen coupling constant is given in Figure 1. The effect of added alcohol shows the typical sharp increase in hfs as well as a smaller inflection around 0.6 mol fraction of ROH. Similarly, such a change in curvature may be noted in several solvent effect studies reported previously.[2i,4,5]

According to the GFF theory,[3] localized complexes between polar solvents and heteroatoms of organic free radicals cause π-electron spin density redistribution within the radical. In mixed solvents, therefore, various complexes may be present in solution simultaneously, with each complex having a characteristic spin density distribution and consequently a characteristic esr spectrum. Assuming that the fast-exchange approximation is applicable, the observed coupling represents the weighted average hfs of the individual species, *i.e.*

$$\bar{a} = \sum \rho_i a_i \tag{1}$$

where a_i is the coupling of the *i*th species (a radical-solvent complex) and ρ_i is the fraction of the same species.

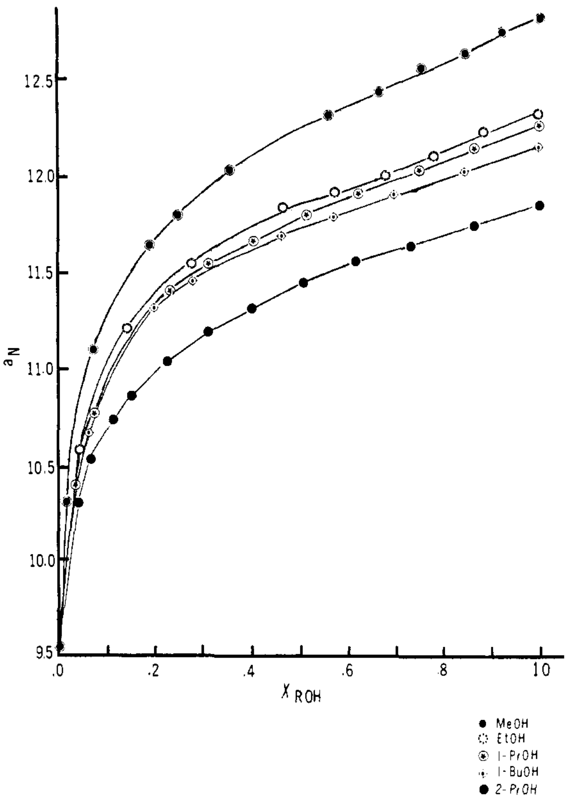

Figure 1. The variation of nitrogen coupling constants of *p*-ClNB anion radical as a function of mole fraction of alcohol.

We have considered that equilibrium processes involving the addition, substitution, or elimination of molecules in the solvent sheath may occur in mixed solvent systems. The postulated equilibrium types are then

S = substitution

$$\mathrm{RS_A + S_B \overset{K}{\rightleftharpoons} RS_B + S_A} \tag{2}$$

A = addition

$$\mathrm{R + S_B \overset{K}{\rightleftharpoons} RS_B} \tag{3}$$

E = elimination

$$\mathrm{RS_A \overset{K}{\rightleftharpoons} R + S_A} \tag{4}$$

R represents the nitro-aromatic compound and S_A and S_B represent the solvents MeCN and ROH, respectively. Expressions for ρ_i, derived in terms of the formation constants of individual species, are dependent on the particular sequence of equilibria assumed, *i.e.*, on the solvation model proposed. For example, if a series of three successive substitutions is proposed (an SSS model), then the solvation model includes four distinct complexes, $R(S_A)_3$, $R(S_A)_2S_B$, $RS_A(S_B)_2$, and $R(S_B)_3$. These shall be designated as species 1, 2, 3, and 4, respectively. The first equilibrium expression is given by

$$K_1 = \frac{[\mathrm{R(S_A)_2S_B}]}{[\mathrm{R(S_A)_3}]D} \tag{5}$$

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Table I. Input Data for Solvation Models[a]

Mol fraction of alcohol	Methanol		Ethanol		1-Propanol		2-Propanol		1-Butanol	
	D	a_N	D	a_N	D	a_N	D	a_N	D	a_N
0.01	0.032	10.09	0.033	9.98	0.040	9.94	0.031	9.95	0.070	10.00
0.02	0.068	10.40	0.069	10.24	0.076	10.28	0.064	10.11	0.134	10.20
0.03	0.100	10.61	0.103	10.39	0.112	10.35	0.100	10.23	0.193	10.37
0.04	0.131	10.76	0.141	10.52			0.135	10.33	0.248	10.50
0.05	0.160	10.89	0.173	10.63	0.184	10.62	0.171	10.42	0.289	10.60
0.075	0.229	11.12	0.252	10.84	0.263	10.85	0.255	10.59	0.388	10.79
0.10	0.292	11.28	0.321	11.01	0.337	10.99	0.329	10.71	0.466	10.95
0.15	0.400	11.52	0.440	11.25			0.464	10.88	0.586	11.19
0.20	0.498	11.68	0.537	11.41	0.578	11.33	0.575	11.00	0.675	11.34
0.25	0.582	11.82	0.626	11.53	0.676	11.43	0.673	11.10	0.747	11.43
0.30	0.664	11.93	0.700	11.63	0.758	11.52	0.755	11.19	0.807	11.52
0.35	0.744	12.03	0.768	11.71	0.835	11.59	0.827	11.26	0.857	11.59
0.40	0.824	12.11	0.828	11.77	0.907	11.66	0.896	11.32	0.903	11.65
0.45	0.909	12.19	0.888	11.82	0.970	11.72	0.958	11.38	0.948	11.70
0.50	1.002	12.25	0.960	11.87	1.035	11.78	1.027	11.44	0.996	11.75
0.55	1.114	12.30	1.038	11.91	1.092	11.84	1.099	11.49	1.042	11.80
0.60	1.239	12.36	1.134	11.95	1.158	11.90	1.187	11.54	1.100	11.84
0.65	1.392	12.41	1.237	11.98	1.242	11.95	1.288	11.58	1.169	11.88
0.70	1.576	12.47	1.374	12.02	1.348	12.00	1.403	11.62	1.252	11.92
0.75	1.829	12.53	1.547	12.07	1.488	12.05	1.550	11.66	1.369	11.96
0.80	2.152	12.59	1.797	12.12	1.673	12.09	1.757	11.71	1.550	12.00
0.85	2.691	12.64	2.200	12.17	1.989	12.14	2.065	11.75	1.844	12.04
0.90	3.690	12.70	2.971	12.23	2.550	12.18	2.629	11.79	2.381	12.08
0.95	6.432	12.75	5.289	12.28	3.906	12.22	4.589	11.83	4.056	12.12
1.00	∞	12.81	∞	12.32	∞	12.26	∞	11.87	∞	12.16

[a] D = activity of ROH/activity of MeCN.

wherein $D = a_{\mathrm{ROH}}/a_{\mathrm{MeCN}}$, the ratio of activities of the solvents.

Assuming that the equilibria are rapid, the nitrogen coupling constant for the SSS model can be expressed according to eq 1 as

$$\bar{a} = \frac{a_1 + a_2K_1D + a_3K_1K_2D^2 + a_4K_1K_2K_3D^3}{1 + K_1D + K_1K_2D^2 + K_1K_2K_3D^3} \tag{6}$$

The hyperfine coupling constants of complexes in pure MeCN and ROH (species 1 and 4) are a_1 and a_4, respectively. These, together with the average coupling constant, $\bar{a}$, and the ratio of the activities of the solvents, D, are all experimentally determined. The couplings of the mixed solvent complexes, a_2 and a_3, and the formation constants, K_1, K_2, and K_3, cannot be determined directly from the spectra. In order to solve equations such as (6), a nonlinear curve-fitting program was employed.[14]

Conceivably, a large number of solvation models involving variations of types and numbers of equilibria might be constructed. Hopefully, only one such model would satisfy the physical requirements of each system. Table I presents the input data which were interpolated from activity and a_N graphs for each mixed solvent system and used in the computer programs.

Efforts were first directed toward fitting the data with the simplest possible models, *i.e.*, those requiring only two or three species. It was assumed that at least one substitution equilibrium must occur since it is known that MeCN does solvate anions[15,16] and the alcohols have hydrogen-bonding capabilities. Nevertheless, the addition model, *A*, was attempted for MeOH–MeCN data but it resulted in a very poor fit of the data.

The solvation model, S, involves an equilibrium between two 1:1 complexes, $\mathrm{RS_{MeCN}}$ and $\mathrm{RS_{ROH}}$. Hydrogen-bond formation between solvent and nitro aromatic radicals has been demonstrated as a critical factor in determining $\mathrm{N^{14}}$ coupling constants,[2d] and Figure 2 illustrates our correlation between a_N and infrared data in pure alcohols. One might then predict that the principal species in alcohol solutions is the monomer complex, $\mathrm{RS_{ROH}}$. Indeed, the computer program converges with an S model for each of the mixed-solvent systems. However, the fit to the data is not sufficient to indicate the true level of structuring in the solutions. Figure 3 illustrates this fact with two representative graphs from the series. Table IIA includes the formation constants which result from the least-squares fit based on the S model.

Table IIA. S Solvation Model Output Data

Alcohol	K_1	SE[a]	Sum sq dev[b]
MeOH	4.45	0.13	0.136
EtOH	4.33	0.17	0.202
1-PrOH	4.09	0.19	0.288
2-PrOH	3.71	0.19	0.202
1-BuOH	3.58	0.29	0.748

[a] SE, standard error. [b] Sum sq dev = sum of squares of deviations, *i.e.*, $= \Sigma_i(Y_{i(\mathrm{obsd})} - Y_{i(\mathrm{calcd})})^2$. Between 22 and 25 points were used for each program.

Three-species models, substitution–substitution (SS) and substitution–addition (SA), proved inadequate in all cases. The former programs do not converge and the latter model results in an intermediate coupling for the mixed complex, $\mathrm{RS_{MeCN}S_{ROH}}$, which is larger than the coupling of the final complex, $\mathrm{R(S_{ROH})_2}$.

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(14) The least-squares curve fitting routine, available from the IBM 1620 library, was written by R. Vogel and adapted by G. Struble. For this study it was slightly modified and adapted for use with the Control Data Corporation 3300 Computer.

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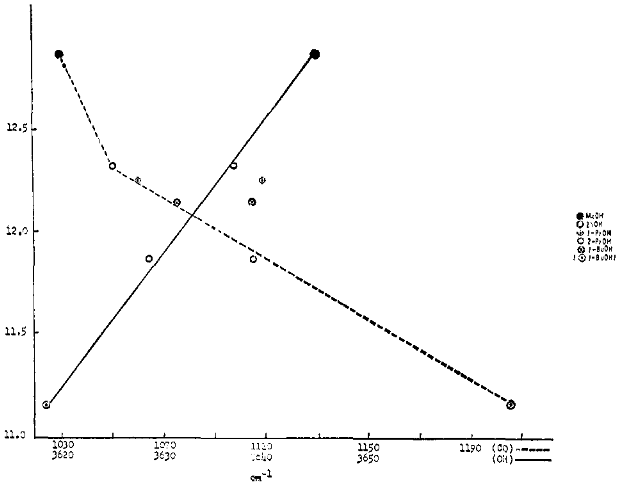

Figure 2. Relationships between a_N and ir data of pure alcohols: (- - - -) carbon-oxygen stretching frequencies from H. H. Zeiss and M. Tsutsui, *J. Amer. Chem. Soc.*, **75**, 897 (1953); (—) O-H stretching frequencies from T. P. Flynn, R. L. Werner, and B. M. Graham, *Aust. J. Chem.*, **12**, 575 (1959), and references therein.

We might note that the simpler models are adequate only when the data are severely restricted to low concentrations of alcohol. This observation concurs with the results of Luckhurst and Orgel[5] who fit the data on the fluorenone anion radical in DMF-alcohol when limiting the region to 0.16 mol fraction of alcohol. We chose to include all data to 0.95 mol fraction of alcohol in all our calculations.

Successful convergence was obtained with several four-species models for the MeOH-MeCN system, including SSS, SSA^2, SSA^3, and SAA^2 models. The A term with the exponent symbolized a simultaneous addition of two or three molecules of alcohol. Though each converged model provides an excellent fit to the data, only the triple substitution solvation model has output parameters which have reasonable values (Table IIB). Figure 3A shows the significant improvement when fitting the data with an SSS model. Similarly, the EtOH-MeCN mixed solvent system can be fit with the same series of models. However, as noted in Table IIB, the ordering of the coupling constants a_2 and a_3 is not satisfactory.

Table IIB. SSS Solvation Model Output Data

Methanol[a]		Ethanol[b]	
Parameter	SE	Parameter	SE
a_2 = 11.22	0.19	a_2 = 10.86	0.12
a_3 = 11.78	0.59	a_3 = 10.27	1.8
K_1 = 14.7	2.2	K_1 = 15.7	2.1
K_2 = 0.78	0.26	K_2 = 0.29	0.21
K_3 = 3.45	1.6	K_3 = 12.8	9.9
Sum sq dev = 2.2 × 10^{-3}		Sum sq dev = 1.7 × 10^{-3}	

[a] $a_1 = a_{\text{MeCN}}$ = 9.53; $a_4 = a_{\text{MeOH}}$ = 12.81. [b] $a_4 = a_{\text{EtOH}}$ = 12.32.

For the 1-PrOH, 2-PrOH, and 1-BuOH mixed solvents, an SSS^2 model was the only attempted four-species model which satisfied our computer. The output data in Table IIC shows the reasonable ordering of the coupling constants of intermediate species while Figure 3B illustrates the characteristically improved fit by extension from a two to a four-species model.

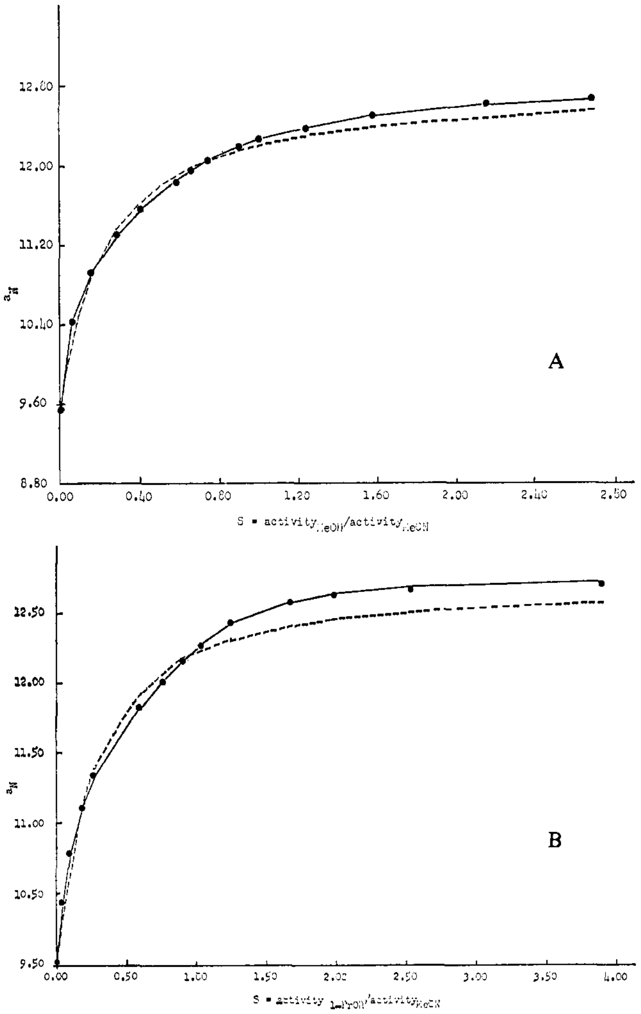

Figure 3. A. Calculated behavior of *p*-ClNB nitrogen coupling constants in MeOH-MeCN binary solutions based on an S (- - - -) model and on an SSS model (—). Points are experimental data. The plot was limited to D = 2.69 to better illustrate the fit of the data through the curvature. In the SSS model, the fit is equally good to the highest input datum of D = 6.432, *i.e.*, mol fraction of MeOH 0.95. B. Calculated behavior of *p*-ClNB nitrogen coupling constants in 1-PrOH-MeCN binary solutions based on an S model (- - - -) and on an SSS model (—).

Thus, we can conclude that the hfs trends in alcohol-MeCN mixed solvents can be best explained in terms of a series of equilibria involving four distinct species,

Table IIC. SSS^2 Solvation Model Output Data

1-Propanol[a]		2-Propanol[b]	
Parameter	SE	Parameter	SE
a_2 = 11.29	0.34	a_2 = 10.31	0.09
a_3 = 12.11	0.98	a_3 = 11.67	0.3
K_1 = 7.7	1.99	K_1 = 28.3	6.4
K_2 = 0.39	0.3	K_2 = 1.33	0.3
K_3 = 3.2	3.1	K_3 = 1.33	0.3
Sum sq dev = 1.4 × 10^{-3}		Sum sq dev = 4.2 × 10^{-3}	
1-Butanol[c]		1-Butanol	
Parameter	SE	Parameter	SE
a_2 = 10.93	0.4	K_1 = 6.56	2.6
a_3 = 11.20	1.4	K_2 = 0.44	0.26
		K_3 = 7.8	5.4
Sum sq dev = 5.3 × 10^{-3}			

[a] $a_4 = a_{\text{1-PrOH}}$ = 12.26. [b] $a_4 = a_{\text{2-PrOH}}$ = 11.87. [c] $a_4 = a_{\text{1-BuOH}}$ = 12.16.

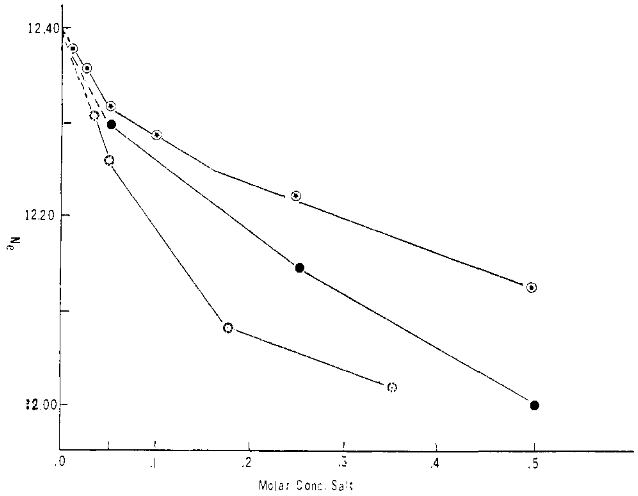

Figure 4. Dependence of a_N for *p*-ClNB anion radical on the molar concentration of supporting electrolyte.

thereby reducing the "generalized" solvent effects in alcohols to more specific models. However, three points should be raised for consideration.

First, there are obviously many other solvation models which could have been attempted so that these simplest solutions may not be the unique descriptions of the systems.

Secondly, the introduction of five parameters may provide for a series of converged models with questionable validity. Computer simulations must be accepted with care.[17]

Thirdly, an underlying assumption has been made that the presence of the supporting electrolyte does not affect the activities of the solvents; thus, the hfs trends are attributed solely to the solvents and the effects of the TEABr are considered to be constant throughout the concentration range. This widely accepted assumption is based on experimental evidence that couplings are independent of both the nature and concentration of tetraalkyl salts in most solvents.[18,19] It is quite valid in MeCN since we too observed no salt effect in the concentration range from 5×10^{-3} to 0.25 *M* TEABr and tetra-*n*-butylammonium bromide (TBABr). However, a recent report shows that there is a dependence of nitrogen hfs of *p*-dinitrobenzene on the concentration of TBABr and TBA-perchlorate salts in ethanol and methanol.[20] Nevertheless, at a concentration of 5×10^{-2} *M* salt, the study shows the coupling approaches the extrapolated value for the radical in the absence of the salt. Our observations in the case of the *p*-ClNB couplings in ethanol substantiate this study. The a_N splitting constants are truly dependent on both the salt and the concentration of the salt as illustrated in Figure 4. Yet the difference between the hfs at 5×10^{-2} *M* TEABr and the extrapolated value is only 0.08 G. Thus, the large variation in coupling reflects the changing solvent environment, and the "free-radical" N^{14} couplings would be expected to be only slightly larger than the experimental values obtained by electrochemical reduction.

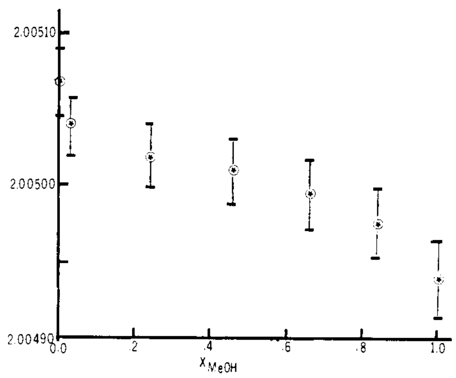

Figure 5. The variation of *g* values as a function of mol fraction of MeOH in of MeOH–MeCN binary solutions. Brackets indicate estimated experimental error.

g-Value Shifts. Little attention is generally given to *g*-value shifts of organic radicals because the shifts are small in relation to the free-spin value. We have measured small shifts in *g* values relative to the TCNE reference value of 2.00270 seen in the MeOH–MeCN system. The calculations are based on the following equation in which the main field, H_0, is 3400 G and ΔH is the difference in field between the centers of the TCNE and *p*-ClNB spectra.

$$g_{\text{unknown}} = g_{\text{TCNE}}\left(1 + \frac{\Delta H}{H_0}\right)$$

Figure 5 shows the variation of the *g* value with increasing MeOH. The total change in the *g* value is 0.00013. The decreasing values reported here concur with the study of solvent effects on *g* values of di-*t*-butyl nitric oxide.[21] Therein, measurements of the *g* value in various protic and aprotic solvents showed a shift toward higher values in the transition from the former to the latter type of solvent.

Chlorine Coupling Constant Variation in MeOH–MeCN. Accurate measurements of the chlorine coupling constants were difficult since only the two central lines of the quartet are sharp. Not only are the couplings small, but also there are two chlorine isotopes with nuclear moments giving rise to slightly different quartet splittings. Nonetheless, in solutions of high concentration (60% and greater), a series of coupling constants was obtained from the splitting superimposed on the nitrogen $m_I = +1$ and $m_I = 0$ lines. A small but systematic change of coupling was observed, as shown in Table III.

Table III. Variations of Chlorine Couplings and *g* Values in Methanol–Acetonitrile Mixed Solvent System

Mol fraction of methanol	a_{Cl}, G	*g* value, ±0.00002
0.000		2.00507
0.035		2.00504
0.244		2.00502
0.462		2.00501
0.663	0.16	2.00496
0.753	0.20	
0.839	0.21	2.00495
1.000	0.22	2.00494

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Arguing qualitatively, one can propose that, as the unpaired spin density becomes more localized at the nitro group due to solvation by the polar MeOH, the chlorine lone-pair electrons tend to back-bond into the π system. The net effect on the chlorine atom is greater unpaired electron density which is reflected in the larger hfs. Other literature values correlate with this view. Ayscough, *et al.*,[22] obtained a 0.24-G chlorine coupling in the photochemical reduction of *p*-ClNB in sodium ethoxide–ethanol solution. The increased coupling is reasonable if the sodium cations are seen as more effective in polarizing the spin density on the nitro group than MeOH. Further support for this hypothesis is given by Seo, *et al.*,[23] who reported couplings of 1.72 and 1.43 for Cl^{35} and Cl^{37}, respectively, in the electrochemical oxidation of tri-*p*-chlorotriphenylamine. This agrees with the above model since a full positive charge on the radical would be expected to cause a large increase in chlorine back-bonding. Nmr studies of *p*-fluoronitrobenzene also substantiate the model.[24]

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A Spectroscopic Study of the Ethanol–Iodine Complex

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Abstract: The spectroscopic properties of the charge-transfer band and the thermodynamic properties for the formation of the electron donor–acceptor complex between ethanol and iodine have been measured in solution in *n*-heptane and in methylene chloride. The measured absorbance of the complex in the ultraviolet region has been analyzed by the Liptay–Scott procedure to give K_f and ϵ_{ic}; measurements at different temperatures give $\Delta H_f°$ and $\Delta S_f°$. In this analysis there was a slight trend with wavelength; consideration of possible causes suggests that the most likely reason may be that the molar absorptivity of uncomplexed iodine changes as ethanol is added to the I_2 solution in *n*-heptane. The Liptay–Scott procedure is modified slightly to take this possibility into consideration and remove the trend in data, but the resulting values of K_f and ϵ_c are not changed drastically. The formation constant of the ethanol–I_2 complex in *n*-heptane is about twice as large as that found for the same complex in methylene chloride solution, but the stability (as measured by ΔH_f) is about the same in both solutions. The complex is found to be more stable ($\Delta H_f = -4.5$ kcal/mol in *n*-heptane) than had been previously reported. The maximum of the charge-transfer absorption is observed at 233 mμ (or about 0.3 eV to higher energies than previously reported), and the intensity is greater by about a factor of 2 than that previously reported. Reasons for these discrepancies are presented.

Properties of the ethanol–I_2 complex are of considerable importance for the understanding of electron donor–acceptor complexes, because it is a representative example of a complex between an alcohol acting as an n donor and the aσ acceptor, I_2. The ultraviolet and visible spectrum and the thermodynamic properties of this complex have been studied previously by de Maine[3] and by Amako,[4] with results summarized by Briegleb.[5]

The study by de Maine[3] was made in solution in CCl_4 as a solvent and included both the visible "blue-shifted" iodine absorption band and the ultraviolet charge-transfer band. That by Amako[4] was of the complex in solution in *n*-hexane and included only the "blue-shifted" visible iodine absorption band. Brandon, Tamres, and Searles had pointed out that the thermodynamic properties reported from these two studies were inconsistent with each other,[6] even allowing for the use of different solvents. Thus Amako[4] reported that the formation constant, K_x (296°K) = 6.99, and the enthalpy of formation, $\Delta H_f = -3.53$ kcal/mol, while de Maine[3] reported K_x (298°K) = 4.00, with $\Delta H_f = -2.10$ kcal/mol. Furthermore, de Maine reported that the maximum absorption for the ultraviolet band occurred at 243 mμ, with a very unusual shape for the band (falling off sharply on the high-frequency side; see curve III of our Figure 4), while Amako reported that the ultraviolet absorption band was broad with a maximum near 235 mμ, without giving further details.

Although the differences between these two studies were not excessive—especially the differences in K_x—further examination revealed additional inconsistencies. These include (1) comparison of the wavelength of maximum absorption reported by de Maine[3] with that found earlier by Ham[7] for the similar complex between

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