Quenching of the benzophenone-benzhydrol photoreduction was done in the conventional manner[35] with a photochemical merry-go-round.

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Effect of Water on the Dissociation and Dissociation Constant of Picric Acid in Acetonitrile[1]

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Abstract: Previously (ref 2) picrate buffers have been recommended to calibrate the glass electrode in acetonitrile. The dissociation constant, K^{d}_{HPi}, of picric acid used for the calculation of pa_H involved calculated pa_H values in other acid–base systems. In the present investigation the degree of dissociation of picric acid was increased by addition of various amounts (up to 1 *M*) of water, and the value of pK^{d}_{HPi} was found from the pa_H's measured with the glass electrode and the total picrate ion concentration determined spectrophotometrically. The latter type of determination does not involve any assumption. The pK^{d}_{HPi} found was equal to 10.9 as compared to the previous value of 11.0 ± 0.1. Formation of neither the ion pair $H_3O^+Pi^- \cdot 3H_2O$ nor of any other picric acid hydrate ion pair has been found. The predominant species of the proton in the presence of 1 *M* water are $H(H_2O)_3^+$ and $H(H_2O)_4^+$, while a small fraction of the picrate ions is present as $Pi^- \cdot H_2O$. From infrared measurements it could be concluded that picric acid is not hydrated in acetonitrile while $K^{f}_{Pi^- \cdot H_2O}$ was found equal to 0.3 ± 0.1.

In establishing a pa_H scale in acetonitrile (AN) we calculated the pa_H of mixtures of 2,5-dichlorobenzenesulfonic and methanesulfonic acids with their tetraalkylammonium salts and of *o*-nitroaniline (I) with its perchlorate, knowing pK^{d}_{HA} or $pK^{f}_{IH^+}$, and thus found at 25° $E°$ of the glass electrode *vs.* 0.01 *M* $AgNO_3$–Ag in AN.[2] The data covered a pa_H range between 4.0 and 8.0. A plot of the pa_H *vs.* potential had the theoretical slope. The plot was then extrapolated to potentials of the glass electrode measured in mixtures of picric acid with its tetrabutylammonium salt, and it was concluded that the pK^{d}_{HPi} of the picric acid was 11.0 ± 0.1. The picric acid–picrate mixtures in AN have the same buffer capacity as corresponding mixtures in water and therefore are ideally suitable for the calibration of the glass electrode in AN. Since the extrapolation was made from a pa_H range between 4 and 8 to values of the order of 11 and since the pa_H values of the mixtures used in the calibration were calculated, involving various assumptions, it appeared desirable to check in some independent way the value of 11.0 for the dissociation constant of picric acid, K^{d}_{HPi}. Picric acid is such a weak acid that the measurements of pa_H or picrate ion concentration in solutions of the acid in AN cannot provide reliable values of pK^{d}_{HPi} because of the almost unavoidable presence of traces (2×10^{-6}–2×10^{-5} *M*) of ammonia and possibly weaker basic impurities in the solvent.

The over-all dissociation constant of picric acid in AN is increased by addition of a base. In the present study we have used the weak base water to increase the dissociation of picric acid in AN, and we have measured a_{H^+} with the glass electrode and the total picrate ion concentration spectrophotometrically.

Previously, it was found that the proton is hydrated by one to four molecules of water,[3] the formation constants of $H(H_2O)_x^+$ being defined as

$$K^{f}_{H(H_2O)_x^+} = [H(H_2O)_x^+]/[H^+]_s[H_2O]^x \qquad (1)$$

the subscript s referring to the solvated species in the water-free solvent. The picrate ion is only slightly hydrated in AN upon addition of water. From solubility data of potassium picrate in presence of water, we have concluded that picrate can form at best a monohydrate[4]

$$Pi_s^- + H_2O \rightleftarrows Pi_w^- \qquad K^{f}_{Pi_w^-} = [Pi_w^-]/[Pi_s^-][H_2O] \qquad (2)$$

$K^{f}_{Pi_w^-}$ being of the order of 0.5. In the present paper the hydration constants of the picrate ion and of picric acid

$$HPi + H_2O \rightleftarrows HPi \cdot H_2O$$
$$K^{f}_{HPi \cdot H_2O} = [HPi \cdot H_2O]/[HPi][H_2O] \qquad (3)$$

were estimated from the first overtone of the –OH stretch of free water at 1410 mμ in mixtures of the acid or salt and water. We regarded the hydrogen bonded H···OH stretching band not to overlap with that of the free –OH band. A similar assumption was made by Coetzee[5] in his study of hydration of some amines.

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(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-1223-67.

(2) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **87**, 4428 (1965). $E°$ is the potential at unit hydrogen ion activity.

(3) I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **90**, 3320 (1968).

(4) M. K. Chantooni, Jr., and I. M. Kolthoff, *ibid.*, **89**, 1582 (1967).

Picric acid forms a week homoconjugate as deduced

$$\mathrm{HPi} + \mathrm{Pi_s^-} \rightleftarrows \mathrm{HPi_2^-} \qquad K^{\mathrm{f}}_{\mathrm{HPi_2^-}} = [\mathrm{HPi_2^-}]/[\mathrm{HPi}][\mathrm{Pi_s^-}] \quad (4)$$

from the solubility data of potassium picrate in presence of picric acid.[2] It is apparent that the reactions representing equilibria 1 and 2 result in increasing dissociation of picric acid in presence of water.

Our solvent did not contain any detectable amount of interfering acid impurity but did contain traces of basic impurities, mainly ammonia, a hydrolysis product. Picric acid reacts quantitatively with ammonia, even at concentration of this base of the order of 10^{-5} M or even less.

The concentration of basic impurities in the solvent, C_{B}, was determined in each set of measurements in absence of added water by adding an excess of picric acid and measuring the picrate ion concentration $[\mathrm{Pi^-}]_0$ spectrophotometrically, $[\mathrm{Pi^-}]_0$ being equal to $C_{\mathrm{BH^+}}$. In the presence of water we have calculated from the spectrophotometrically determined value of $[\mathrm{Pi^-}]_{\mathrm{t}}$, the total concentration of all picrate species, the concentration of unhydrated picrate ions, $[\mathrm{Pi}]_{\mathrm{s}}$, using eq 6 below. The values of $a_{\mathrm{H^+}}$ and $a_{\mathrm{Pi_s^-}}$ and the equilibrium concentration of unhydrated undissociated picric acid in picric acid solutions containing water yielded the value of $K^{\mathrm{d}}_{\mathrm{HPi}} = a_{\mathrm{H^+}}a_{\mathrm{Pi_s^-}}/[\mathrm{HPi}]_{\mathrm{s}}$. It is shown in the present study that under our experimental conditions no ion pair $\mathrm{H(H_2O)}_x^+\mathrm{Pi^-}$ is formed; therefore the analytical and equilibrium concentrations of picric acid could be taken equal, also taking into account that the over-all dissociation of picric acid never exceeded 2% of the total picric acid concentration at the highest water concentrations used.

In picric acid solutions containing water the total picrate concentration $[\mathrm{Pi^-}]_{\mathrm{t}}$ is

$$[\mathrm{Pi^-}]_{\mathrm{t}} = [\mathrm{Pi^-}]_{\mathrm{s}} + [\mathrm{Pi_w^-}] + [\mathrm{HPi_2^-}] = C_{\mathrm{BH^+}} + [\mathrm{H^+}]_{\mathrm{s}} + \sum_1^x [\mathrm{H(H_2O)}_x^+] \quad (5)$$

where $C_{\mathrm{BH^+}} = [\mathrm{Pi^-}]_0$. Defining[3]

$$y = 1 + \sum_1^x K^{\mathrm{f}}_{\mathrm{H(H_2O)}_x^+}[\mathrm{H_2O}]^x$$

$$V = 1 + K^{\mathrm{f}}_{\mathrm{Pi_w^-}}[\mathrm{H_2O}]$$

and substituting with eq 1, 2, and 4 into eq 5, eq 6 results.

$$[\mathrm{Pi^-}]_{\mathrm{t}} = [\mathrm{Pi^-}]_{\mathrm{s}}\{V + K^{\mathrm{f}}_{\mathrm{HPi_2^-}}[\mathrm{HPi}]\} = C_{\mathrm{BH^+}} + y[\mathrm{H^+}]_{\mathrm{s}} \quad (6)$$

In all experiments $[\mathrm{H^+}]_{\mathrm{s}} \ll [\mathrm{H(H_2O)}_x^+]$. All solutions had a small ionic strength, μ, equal to $[\mathrm{Pi^-}]_{\mathrm{t}}$. In the few instances where the activity coefficient, f, differed appreciably from unity, the limiting Debye–Hückel expression $-\log f = 1.53\sqrt{\mu}$ was used.

Experimental Section

Chemicals. Solvent. Eastman Kodak White Label acetonitrile was purified and dispensed as described previously.[2] The specific conductivity of the purified solvent was $2\text{–}7 \times 10^{-7}$ ohm^{-1} cm^{-1}. The water content of the solvent as determined by Karl Fischer titration was $1\text{–}2 \times 10^{-3}$ M, which was taken into consideration in the calculation of the equilibrium concentration of water in the picric acid solutions.

The concentration of basic impurities, C_{B}, was estimated to be $0.4\text{–}1.1 \times 10^{-5}$ M from the picrate ion concentration $[\mathrm{Pi^-}]_0$ in 0.02–0.2 M solutions of picric acid in the "anhydrous" solvent. $[\mathrm{Pi^-}]_0$ was found from the absorbance at 415 mμ (corrected for that of undissociated picric acid).

The dissociation in solutions of incompletely dissociated acids in AN increases with time of standing.[6,7] This has been interpreted by slow formation of a polymer of AN which is a considerably stronger base than AN.[6] The effect of time on the dissociation of picric acid has also been considered by Fuoss[8] and Moore and Johns.[9] In our experiments the effect of time of standing after preparation of the solutions was eliminated by extrapolation of the absorbance or $p a_{\mathrm{H}}$ to zero time. The time effect was found to be negligible in picric acid solutions being more than 0.1 M in water.

Picric acid was a product used previously.[2]

Hydrogen Chloride. In studies of the formation of an ion pair ($\mathrm{H_3O^+Pi^-}$) dry Matheson hydrogen chloride was passed directly into a 0.01 M picric acid solution in the spectrophotometer cell. The spectra were recorded immediately to obviate formation of imido hydrohalides.[10] The analytical concentration of hydrogen chloride was determined by acidimetric titration in water as described previously.[11]

Perchloric acid "monohydrate" was a G. F. Smith Co. product.

Instrumentation. Spectrophotometry. Absorbances in the visible region of the picrate ion in picric acid solutions containing water were measured in 1.00- and 1.90-cm stoppered silica cells using a Beckman DU spectrophotometer. Ultraviolet spectra of picric acid in presence of water and perchloric acid were run in a variable path-length silica cell set at 0.050 mm[12] in a Cary Model 16 recording spectrophotometer.

Near-infrared spectra in the range 1250–1600 mμ were run in a Beckman DK-2 recording spectrophotometer. Beckman 1-cm ir quartz cells were used. The reference cell was filled with AN. The following values of the absorbance index of water at 1410 mμ were found: 0.416, 0.398, 0.390, 0.384, and 0.373 at 0.30, 0.50, 0.82, 1.22, and 1.62 M water, respectively, which are in agreement with similar data reported by Coetzee.[5]

Potentiometric $p a_{\mathrm{H}}$ Measurements. The glass electrode, reference electrode, potentiometric cell, and pH meter were as those described elsewhere.[2]

Results

Hydration of Undissociated Picric Acid. Absorbance measurements of the first overtone of the –OH stretch of free water 1410 mμ in solutions of 0.366 and 0.63 M picric acid containing from 0.47 to 1.5 M water are tabulated in Table I. From the data in Table I it appears that picric acid is not hydrated. The absorb-

Table I. Effect of Picric Acid or Tetraethylammonium Picrate on Absorbance of Water at 1410 mμ

m_{MA}	$m_{\mathrm{H_2O}}$	A_{1410}	$[\mathrm{H_2O}]$	$[\mathrm{MA \cdot H_2O}]$	$[\mathrm{MA}]$	$K^{\mathrm{f}}_{\mathrm{MA \cdot H_2O}}$
MA = Picric Acid						
0.366	0.476	0.191	0.477	~0	0.36$_6$	~0
0.366	0.762	0.300	0.766	~0	0.36$_6$	~0
0.366	1.14	0.443	1.15	~0	0.36$_6$	~0
0.366	1.52	0.563	1.49	~0	0.36$_6$	~0
0.630	1.45	0.555	1.47	~0	0.63$_0$	~0
MA = Tetraethylammonium Picrate						
0.322	0.476	0.183	0.458	0.018	(0.304)	(0.12)
0.322	0.762	0.282	0.722	0.040	0.282	0.2$_0$
0.322	1.14	0.400	1.04	1.10	0.222	0.4$_3$
0.630	1.14	0.373	0.967	0.17$_3$	0.46	0.3$_9$
0.630	1.45	0.482	1.27	0.16	0.47	0.2$_7$
					Av	0.3 ± 0.10

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(5) W. S. Muney and J. F. Coetzee, *J. Phys. Chem.*, **66**, 89 (1962).

(6) M. K. Chantooni, Jr., Ph.D. Thesis, University of Minnesota, 1960.

(7) G. J. Janz and S. S. Danyluk, *J. Am. Chem. Soc.*, **81**, 3846 (1959).

(8) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **73**, 400 (1969).

(9) F. Moore and I. B. Johns, *J. Am. Chem. Soc.*, **63**, 3336 (1941).

(10) G. J. Janz and S. Danyluk, *ibid.*, **81**, 3850 (1959).

(11) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *ibid.*, **83**, 3927 (1961).

(12) M. K. Chantooni, Jr., and I. M. Kolthoff, *ibid.*, **90**, 3005 (1968).

Table II. Experimental Values of $a_{H^+\text{exptl}}$ and $[Pi^-]_t$ and Calculated Values of pK^d_{HPi} in Picric Acid Solutions Containing Water

m_{H_2O}	$pa_{H_s\text{exptl}}$[a]	$pa_{Pi_t^-\text{exptl}}$[b]	$pa_{H_s\text{exptl}} + pa_{Pi_t^-\text{exptl}} + \log C_{HPi}$	$pa_{H_s\text{exptl}} + pa_{Pi_s^-} + \log C_{HPi} = pK^d_{HPi}$	$pa_{H_s\text{calcd}} = pa_{Pi_t^-} + \log y$[c]	$pa_{H_s\text{calcd}} + pa_{Pi_s^-} + \log C_{HPi}$[d]
		$C_{HPi} = 0.027\ M$	$C_{BH^+} = 4 \times 10^{-6}$			
0.10	(7.50)	(4.75)	(10.68)	(10.7)	(6.7)	(10.0)
0.20	7.83	4.50	10.76	10.8	7.1	10.2
0.40	8.27	4.21	10.91	11.0	7.6	10.3
0.60	8.50	3.97	10.90	11.0	7.7	10.2
0.80	8.67	3.77	10.87	11.0	8.0	10.4
1.00	8.82	3.57	10.82	11.0	8.3	10.5
		$C_{HPi} = 0.176$	$C_{BH^+} = 1.3 \times 10^{-5}$			
0.10	6.97	4.30	10.52	10.7	(6.3)	(10.1)
0.20	7.32	4.15	10.72	10.9	6.7	10.3
0.40	7.80	3.77	10.82	11.0	7.1	10.4
0.60	8.04	3.49	10.78	11.0	7.3	10.3
0.80	8.20	3.23	10.68	10.9	7.5	10.3
1.00	8.30	3.01	10.56	10.9	7.8	10.4
			Av 10.75	Av 10.9		Av 10.4

[a] Potentiometric glass electrode value. [b] Spectrophotometric value. [c,d] From ref 3; see Discussion.

ance measurements were corrected for the absorbance of picric acid, its absorbance index being 0.055.

The absence of a hydronium picrate ion pair is deduced from the fact that the ultraviolet spectrum from 250 to 480 mμ of 0.0108 *M* picric acid in the presence of 0.1 *M* hydrogen chloride is identical with that in presence of 0.012 *M* perchloric acid and 0.59 *M* water. Even a solution 0.2 *M* in picric acid, 0.05 *M* in perchloric acid, and 0.5 *M* in water appears colorless to the naked eye. A hydronium picrate ion pair should have an ultraviolet spectrum which differs appreciably from that of undissociated picric acid.

Hydration of the Picrate Ion. From the near-infrared data in Table I, a value of $K^f_{Pi_w^-}$ equal to 0.3 ± 0.1 was found. The absorbance of tetraethylammonium picrate at 1410 mμ was taken into account, the absorbance index being only 0.03. From a study of the effect of water on the solubility of potassium picrate in AN a value of $K^f_{Pi_w^-} = 0.5$ was calculated.[4] Considering the assumptions made in the infrared measurements that the picrate salt is completely dissociated and that the tetraethylammonium ion is not hydrated, the above values of $K^f_{Pi_w^-}$ are in satisfactory agreement.

Effect of Water on Dissociation of Picric Acid. Potentiometric glass electrode pa_{H_s} data in 0.027 and 0.176 *M* picric acid solutions made 0.01 *M* in tetraethylammonium perchlorate (to increase electrolytic conductivity) and 0.1–1 *M* in water are presented in the second column in Table II. Values of $pa_{Pi^-_t\text{exptl}}$ derived from the spectrophotometrically determined picrate ion concentration in 0.027 and 0.176 *M* picric acid solutions in the presence of 0.1–1.0 *M* water are entered in the third column of Table II. The wavelengths used and the corresponding absorbance indices of the picrate ion were as follows: 415, 460, and 470 mμ; $\epsilon_{Pi^-} = 1.2 \times 10^4$, 1.6×10^3, and 4.4×10^2, respectively. Since the spectrum of 0.01 *M* tetrabutylammonium picrate was found to be identical with that in the presence of 1 *M* water or 0.05 *M* picric acid, the spectra of the unhydrated and monohydrated picrate and HPi_2^- ions appear to be the same. Under our experimental conditions it was necessary to correct for the absorption of *undissociated* picric acid only in 0.027 *M* picric acid solutions containing ≤0.01 *M* water, ϵ_{HPi} being 5.8 at 415 mμ. At higher water and/or picric acid concentrations longer wavelengths were used where the absorption of undissociated picric acid is negligible.

Values of $pa_{Pi_s^-}$ in columns 5 and 7 of Table II were calculated from the values of $pa_{Pi_t^-}$ using eq 6. Values of $pa_{H_s\text{calcd}}$ in columns 6 and 7 are referred to in the Discussion.

Discussion

In the present study the tacit assumptions have been made that the previously postulated value of $E°$ of the glass electrode, including the liquid junction potential, is correct and does not change in the presence of 1 *M* or less water. Moreover, it is assumed that the dissociation constant of picric acid is not affected at concentrations of water <1 *M*. The most important fact in the present paper is that the spectrophotometric determination of $[Pi^-]_t$ does not involve any assumption. If the assumptions involved in the calculation of pa_{H_s} from the glass electrode potentials were incorrect, no constant value of pK^d_{HPi} could have been found. Even if our previously determined values of $K^f_{HPi_2^-}$ and $K^f_{Pi_w^-}$ were slightly in error, the calculated pK^d_{HPi} values would be changed only slightly (see column 4, Table II). The dielectric constant of 1 *M* solution of water in AN has been found to be 36.8[8] as compared to a value of 36.0 in pure AN, the difference being so small that the electrostatic effect on pK^d_{HPi} can be neglected. It may also be added that C_{BH^+} became virtually negligibly small with respect to $\Sigma[H^+]$ when the water concentration is greater than 0.4 *M*. It is gratifying that our previously reported value of pK^d_{HPi} of 11.0 ± 0.1 is in excellent agreement with the average value of 10.9 in the present study.

In the sixth column of Table II are presented pa_{H_s} values calculated from the spectrophotometrically determined total picrate values (eq 6) and values of *y* previously determined in a study of the hydration constants of the proton in AN.[3] As an average, pa_{H_s} calculated is 0.5 unit smaller than $pa_{H_s\text{exptl}}$. This difference is greater than the experimental errors involved 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 $K^f{}_{H(H_2O)_x{}^+}$, 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.

[13] I. M. Kolthoff, S. Bhowmik, and M. K. Chantooni, Jr., *Proc. Natl. Acad. Sci. U. S.*, **56**, 1370 (1966).

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

[1] NASA Predoctoral Trainee, 1966–1969.

[2] (a) L. H. Piette, P. Ludwig, and R. N. Adams, *J. Amer. Chem. Soc.*, **83**, 3909 (1961); (b) L. H. Piette, P. Ludwig, and R. N. Adams, *ibid.*, **84**, 4212 (1962); (c) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963); (d) P. Ludwig, T. Layloff, and R. N. Adams, *J. Amer. Chem. Soc.*, **86**, 4568 (1964); (e) J. Q. Chambers, T. Layloff, and R. N. Adams, *J. Phys. Chem.*, **68**, 661 (1964); (f) J. Pannell, *Mol. Phys.*, **7**, 317 (1964); (g) W. M. Gulick, Jr., and D. H. Geske, *J. Amer. Chem. Soc.*, **87**, 4049 (1965); (h) J. M. Gross and M. C. R. Symons, *Trans. Faraday Soc.*, **63**, 2117 (1967); (i) W. M. Gulick, Jr., W. E. Geiger, Jr., and D. H. Geske, *J. Amer. Chem. Soc.*, **90**, 4218 (1968).

[3] J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

[4] A. W. Stone and A. H. Maki, *J. Amer. Chem. Soc.*, **87**, 454 (1965).

[5] G. R. Luckhurst and L. E. Orgel, *Mol. Phys.*, **8**, 117 (1964).