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the results for didecyl phthalate lie about 6% too low in F/F_{TRANS}, roughly consistent with the observation that its pressure coefficient of diffusion coefficient in the decane-based mobile phase is about 11% greater than those of anisole and benzyl acetate.

Pressure and Temperature Effects in Liquid Chromatography. The measured pressure effects on diffusion coefficient are large enough so that in modern high-speed liquid chromatography, where pressures near 20 MPa are common, diffusion coefficients of samples cannot be regarded as constant along the length of the column, especially in nonaqueous mobile phases. This certainly has an effect on correlations between the predictions of theoretical models and experimental results on peak spreading in packed columns. However, the large pressure gradients along the columns are generally accompanied by dissipative heating which has an even larger effect on both viscosity and diffusion coefficient which may be significantly different for different samples. The combined effects present a complex situation now under study.[9]

Registry No. EtAc, 141-78-6; BzAc, 140-11-4; HMB, 87-85-4; pentane, 109-66-0; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2; decane, 124-18-5; anisole, 100-66-3; didecyl phthalate, 84-77-5; *p*-xylene, 106-42-3; benzaldehyde, 100-52-7; diethyl phthalate, 84-66-2; dimethyl phthalate, 131-11-3; nitrobenzene, 98-95-3; acetophenone, 98-86-2; phenol, 108-95-2; benzophenone, 119-61-9; *o*-cresol, 95-48-7; benzil, 134-81-6; phenyltridecane, 123-02-4; dipropyl phthalate, 131-16-8; dibutyl phthalate, 84-74-2; dipentyl phthalate, 131-18-0; dioctyl phthalate, 117-84-0.

Protonation of Cationic Bases in Perchloric Acid: Establishment of the H_+ Scale in 0–11 M Perchloric Acid

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The protonation of several monocationic bases in perchloric acid was studied with UV–visible absorption spectroscopy. The H_+ scale in perchloric acid was established by using primary amine cationic bases as indicators. It was found that the H_+ scale in perchloric acid is more negative than in sulfuric acid. The acid-dissociation constants for compounds studied in both acids were found to be in reasonably good agreement with each other.

Introduction

The H_+ scale in concentrated sulfuric acid based upon primary amine indicators has recently been published[1] in order to supplant an older scale based in part upon quinoxaline derivatives.[2] In some cases, however, sulfuric acid is unsuitable for the study of protonation reactions because sulfonation of the substrate may occur. Furthermore, because of the presence of species such as $H_2S_2O_7$, concentrated sulfuric acid is a complex matrix. When such difficulties are encountered, perchloric acid is a suitable alternative medium for the study of the protonation of bases. The use of perchloric acid is also desirable in the study of the influence of water on prototropic reactivity since the activity of water in perchloric acid decreases more rapidly with increasing acid concentration than it does in sulfuric acid.[3–5]

Since a comprehensive study of the protonation of charged bases in perchloric acid has not been published, it was desired to establish the H_+ scale in perchloric acid by using a set of primary amine indicators. Furthermore, it was desired to investigate the relationship between the H_0 and H_+ acidity functions in perchloric acid. Finally, it was also desired to compare the H_+ functions in perchloric and sulfuric acids.

Experimental Section

3-Nitro-1,2-phenylenediamine, 2,6-diaminopyridine, and 4-aminopyridine (Aldrich, Milwaukee, WI) were used without further purification. 4-Bromo-6-nitro-1,2-phenylenediamine was synthesized from 2,6-dinitroaniline (Pfaltz and Bauer, Stanford, CT) by using published procedures.[6,7] 3-Aminopyridine, 4-nitro-1,2-phenylenediamine, and 1,2-phenylenediamine-4-carboxylic acid (Aldrich), 5-aminoquinoline (K & K Labs, Plainview, NY), and 8-aminoquinoline (Pfaltz and Bauer) were used without further purification. 4-Chloro-1,2-phenylenediamine (Pfaltz and Bauer) was recrystallized from petroleum ether. 6-Aminoquinoline (Pfaltz and Bauer) was purified by column chromatography on a silica column using methanol:chloroform (1:4) as eluent. 1,2-Phenylenediamine (Aldrich) was recrystallized from water. 5-Amino-8-hydroxyquinoline hydrochloride, a gift from Dr. Herman Gershon (Boyce Thompson Institute for Plant Research, Ithaca, NY), was purified by dissolving it in a minimum of methanol and then adding ethyl ether to initiate precipitation. The precipitate was then filtered and dried. 2-Nitro-*p*-phenylenediamine was synthesized from *p*-phenylenediamine (Aldrich) by the following procedure. Crude *p*-phenylenediamine crystals were first washed with ethanol to remove oxidized material. These crystals were then dissolved in acetic acid and the amine groups acetylated with acetic anhydride. The resulting precipitate was filtered and washed several times with hot water. Nitric acid (70%) was cooled in an ice bath and the precipitate slowly added to it while the mixture was stirred. This was poured onto ice and the resulting yellow precipitate filtered. To remove the acetyl groups, the precipitate was added to hydrochloric acid and heated. The solution was concentrated with a flash evaporator. The golden needles of 2-nitro-*p*-phenylenediamine hydrochloride were filtered and dried. The authenticity of the product was confirmed with NMR. 3-Amino-2,6-dibromopyridine was prepared by the method of Snyder and Spralding.[8]

Analytical reagent grade 70% perchloric acid (Mallinkrodt Chemical Works, St. Louis, MO) was diluted with deionized water

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TABLE I: Variation of the Absorbance at 252 nm and p*K* Calculation for 5.7 × 10^{-2} M Singly Protonated 5-Amino-8-hydroxyquinoline in Perchloric Acid at 25 °C[a]

					$pK' - [1.53\mu^{1/2}/(1 - aB\mu^{1/2})]$			
$[HClO_4]$	pH	A_{252}	log *I*	p*K*′	$aB = 1$	$aB = 2$	$aB = 3$	H_+
	4.10	1.162						
	4.00	1.210						
4.93×10^{-4}	3.20	1.246						
2.40×10^{-3}	2.60	1.082	0.75	1.85	1.78	1.78	1.78	2.57
3.14×10^{-3}	2.48	1.038	0.62	1.86	1.78	1.78	1.79	2.44
4.58×10^{-3}	2.30	0.942	0.41	1.89	1.79	1.80	1.80	2.23
5.98×10^{-3}	2.20	0.878	0.29	1.89	1.80	1.81	1.81	2.11
7.35×10^{-3}	2.10	0.820	0.19	1.91	1.79	1.80	1.81	2.01
8.67×10^{-3}	2.01	0.770	0.11	1.91	1.77	1.78	1.79	1.93
1.12×10^{-3}	1.95	0.678	−0.038	1.90	1.84	1.86	1.87	1.78
1.42×10^{-3}	1.85	0.610	−0.15	1.99	1.84	1.85	1.87	1.67
1.69×10^{-3}	1.75	0.560	−0.24	2.00	1.81	1.83	1.85	1.58
2.07×10^{-3}	1.70	0.502	−0.34	1.99	1.85	1.87	1.89	1.48
2.42×10^{-3}	1.61	0.478	−0.39	2.04	1.79	1.83	1.84	1.43
3.64×10^{-2}	1.45	0.370	−0.62	2.07	1.83	1.86	1.88	1.20
5.01×10^{-2}	1.35	0.322	−0.76	2.11	1.83	1.87	1.91	1.06
6.34×10^{-2}	1.25	0.300	−0.84	2.09	1.78	1.83	1.87	0.98
7.63×10^{-2}	1.15	0.282	−0.90	2.05	1.78	1.78	1.82	0.92
9.75×10^{-2}	1.05	0.256	−1.02	2.07				0.80
1.07×10^{-1}	1.00	0.240	−1.11					
1.77×10^{-1}		0.210	−1.33					
3.00×10^{-1}		0.196	−1.45					
9.75×10^{-1}		0.162						
av p*K* ± SD				1.98 ± 0.09	1.80 ± 0.03	1.82 ± 0.03	1.84 ± 0.04	

[a] Absorbance of the isolated conjugate base is 1.246 and that of the isolated acid is 0.162, $I = [BH^+]/[BH_2^{2+}]$.

TABLE II: Values of H_+ as a Function of the Molar Concentration of Perchloric Acid

$[HClO_4]$	H_+	$[HClO_4]$	H_+
2.40×10^{-3}	2.57	2.40	−1.44
4.00×10^{-3}	2.31	2.80	−1.62
6.00×10^{-3}	2.11	3.00	−1.70
1.00×10^{-2}	1.87	3.40	−1.86
1.50×10^{-2}	1.66	3.80	−2.02
2.00×10^{-2}	1.52	4.00	−2.10
4.00×10^{-2}	1.11	4.40	−2.27
6.00×10^{-2}	0.89	4.80	−2.46
8.00×10^{-2}	0.74	5.00	−2.69
1.00×10^{-1}	0.62	5.40	−2.74
1.20×10^{-1}	0.51	5.80	−2.95
1.40×10^{-1}	0.43	6.00	−3.06
1.60×10^{-1}	0.35	6.40	−3.30
1.80×10^{-1}	0.28	6.80	−3.46
2.00×10^{-1}	0.22	7.00	−3.55
2.40×10^{-1}	0.11	7.40	−3.76
2.80×10^{-1}	0.02	7.80	−4.00
3.20×10^{-1}	−0.05	8.00	−4.12
3.60×10^{-1}	−0.12	8.40	−4.38
4.00×10^{-1}	−0.18	8.80	−4.65
5.00×10^{-1}	−0.31	9.00	−4.80
6.00×10^{-1}	−0.41	9.40	−5.10
7.00×10^{-1}	−0.51	9.80	−5.41
8.00×10^{-1}	−0.60	10.00	−5.59
9.00×10^{-1}	−0.70	10.40	−5.93
1.00	−0.77	10.80	−6.30
1.20	−0.97		
1.60	−1.07		
1.80	−1.17		
2.00	−1.26		

to prepare solutions of varying acid concentration. These were standardized against standard sodium hydroxide which was standardized against potassium acid phthalate.

Stock solutions of each indicator were prepared with water or 1 M perchloric acid. To prepare working solutions, aliquots of the stock solutions were injected into 10-mL volumetric flasks and made up to volume with the appropriate standard perchloric acid solution. Absorption spectra of these solutions and of solutions of intermediate acid concentration were recorded at 25 °C on a Varian Cary 219 spectrophotometer. For those indicators whose protonation took place in dilute acid, the pH of the solution was monitored with a Markson Electromark pH meter fitted with a silver–silver chloride combination glass electrode. The pH of the solution was changed by adding aliquots of a solution higher in acid concentration but containing the same concentration of indicator. The molarity of the acid in the solution of each aliquot was calculated and used to determine the ionic strength of the medium, which was used in the correction of the apparent acid-dissociation constant (vide infra).

Results and Discussion

The ionization ratio, $I = [BH^+]/[BH_2^{2+}]$, of each indicator was obtained from the absorbance at a given wavelength, as in the previous work.[1] No medium effects on the spectra of the indicators were observed, and thus no corrections were necessary. In cases where several analytical wavelengths were used, there was good agreement between the dissociation constants calculated from each analytical wavelength.

Even though the pH meter was standardized with pH 1 buffer, the reliability of pH values at this extreme is uncertain. Therefore, 5-amino-8-hydroxyquinoline was chosen as the most basic indicator in the series since its dissociation constant could be determined accurately with the pH meter. In order to determine $pK_{BH_2^{2+}}$ (the thermodynamic dissociation constant of the indicator), the apparent dissociation constant, $pK'_{BH_2^{2+}}$, was corrected for changes in the ionic strength, μ, of the medium by using the extended Debye–Hückel law as shown in eq 1. Values of 1, 2, and 3 were

$$pK_{BH_2^{2+}} = pK'_{BH_2^{2+}} - \frac{1.53\mu^{1/2}}{1 + aB\mu^{1/2}} = pH - \log I - \frac{1.53\mu^{1/2}}{1 + aB\mu^{1/2}} \quad (1)$$

chosen for the *aB* term in eq 1. From Table I it can be seen that the value of the *aB* term did not affect the accuracy of $pK_{BH_2^{2+}}$ for 5-amino-8-hydroxyquinoline. In calculating values of H_+ (vide infra), the dissociation constant of this indicator was chosen to be 1.82 ± 0.03. This pK_a has not been reported previously. Values of log *I* between $pK_a \pm 1$ (corresponding to 10–90% protonation) were used in these calculations since values outside this range are less reliable. The same procedure was used to determine the dissociation constant of 6-aminoquinoline. A value of $aB = 1$ gave the best value of $pK_{BH_2^{2+}} = 0.90 \pm 0.03$ for this indicator. This value is in good agreement with that of 0.89 ± 0.03 which was subsequently calculated with the H_+ scale determined in this work,

TABLE III: Regression Coefficients for Plots of H_X vs. log I and Calculated and Literature pK's for Cationic Indictors in Perchloric Acid

	regression coeff							
	H_+ vs. log I			H_0 vs. log I			pK's	
compd	intercept ± SD	slope ± SD	cor	intercept ± SD	slope ± SD	cor	calcd ± SD	lit.
5-hydroxy-8-aminoquinoline							1.82 ± 0.03	
6-aminoquinoline	0.89 ± 0.01	0.98 ± 0.02	0.999				0.90 ± 0.03	1.19
5-aminoquinoline	0.12 ± 0.01	0.99 ± 0.01	0.999				0.17 ± 0.02	0.66
1,2-phenylenediamine	0.11 ± 0.01	1.02 ± 0.01	0.999	0.55 ± 0.01	0.90 ± 10.01	0.998	0.13 ± 0.01	1.67 (0.67)[a]
8-aminoquinoline	−0.73 ± 0.01	1.07 ± 0.01	0.998	−0.24 ± 0.01	1.02 ± 0.02	0.996	−0.72 ± 0.02	−0.13
4-chloro-*o*-phenylenediamine	−0.80 ± 0.01	0.99 ± 0.01	0.999	−0.31 ± 0.01	1.01 ± 0.01	0.999	−0.81 ± 0.02	−0.27 ± 0.03[a]
3-aminopyridine	−1.77 ± 0.01	0.98 ± 0.01	0.999	−1.34 ± 0.01	1.10 ± 0.01	0.999	−1.78 ± 0.03	−1.5
1,2-phenylenediamine-4-carboxylic acid	−1.70 ± 0.01	0.99 ± 0.01	0.999	−1.27 ± 0.01	1.10 ± 0.01	0.998	−1.71 ± 0.02	−1.26 ± 0.05[a]
2-nitro-*p*-phenylenediamine	−2.37 ± 0.01	0.99 ± 0.01	0.997	−2.02 ± 0.01	1.18 ± 0.01	0.999	−2.37 ± 0.01	
4-nitro-1,2-phenylenediamine	−3.16 ± 0.01	1.06 ± 0.02	0.995	−3.05 ± 0.01	1.42 ± 0.02	0.998	−3.17 ± 0.07	−2.75 ± 0.05[a]
2,6-diaminopyridine	−4.08 ± 0.01	1.01 ± 0.01	0.997	−4.23 ± 0.02	1.25 ± 0.03	0.990	−4.09 ± 0.02	
3-nitro-1,2-phenylenediamine								
A_{396}	−4.56 ± 0.01	0.98 ± 0.01	0.999	−4.84 ± 0.02	1.12 ± 0.03	0.993	−4.57 ± 0.094	−4.10 ± 0.06[a]
A_{222}	−4.61 ± 0.01	0.98 ± 0.01	0.999	−4.99 ± 0.04	1.33 ± 0.07	0.959	−4.62 ± 0.04	−4.10 ± 0.06[a]
2,3,6-triaminopyridine	−4.98 ± 0.01	0.99 ± 0.01	0.9997	−5.42 ± 0.02	1.36 ± 0.03	0.991	−4.98 ± 0.01	
4-bromo-6-nitro-1,2-phenylenediamine	−5.26 ± 0.02	0.99 ± 0.04	0.98	−5.64 ± 0.01	1.23 ± 0.01	0.997	−5.21 ± 0.05	
4-aminopyridine	−5.62 ± 0.01	0.72 ± 0.01	0.997	−6.22 ± 0.01	1.10 ± 0.02	0.996	−5.68 ± 0.14	−6.3[b]

[a] Dissociation constants determined in sulfuric acid.[2] [b] Dissociation constant determined in sulfuric acid.[15]

but it does not agree with the literature value of 1.19.[9] This is due to the fact that Brown and Plasz[9] calculated the dissociation constant of doubly protonated 6-aminoquinoline using the H_0 scale.

The H_+ scale was generated by using the overlap method of Hammett and Deyrup.[10] This method uses the equation

$$H_+ = \mathrm{p}K_{\mathrm{BH_2}^{2+}} + \log I \qquad (2)$$

where p$K_{\mathrm{BH_2}^{2+}}$ is the pK_a of the indicator as calculated with eq 1. Values of H_+ were thus calculated for solutions of high ionic strength ($\mu >> 0.1$) where eq 1 is not applicable but where log I = p$K_{\mathrm{BH_2}^{2+}}$ ± 1. The values of H_+ calculated in this way were then used in conjunction with eq 2 to calculate p$K_{\mathrm{BH_2}^{2+}}$ for a different indicator but which has an ionization overlapping that of the indicator used to determine H_+. The p$K_{\mathrm{BH_2}^{2+}}$ of this different indicator may then be used to generate values of H_+ in more concentrated acid, which may then be used to determine p$K_{\mathrm{BH_2}^{2+}}$ of yet another indicator, and so on. Generally, the agreement between H_+ values based on different indicators is quite good. Values of H_+ as a function of the molar concentrated of perchloric acid are presented in Table II. These values are plotted in Figure 1.

Equation 2 shows that a plot of H_+ vs. log I for a given indicator should be a straight line of unit slope and have an intercept of p$K_{\mathrm{BH_2}^{2+}}$. Plots of this sort were also used to determine the dissociation constants of the indicators used in this study. These plots were linear and had slopes of unity and correlation coefficients greater than 0.99. Table III lists the slopes, intercepts, and their standard deviations (SD) of the plots of H_+ vs. log I. The dissociation constant of 0.13 ± 0.01 for 5-aminoquinoline is somewhat more negative than the published value of 0.66.[9] This is explained by the fact that these authors used the H_0 scale in perchloric acid[11] for their determination. For the same reason 8-aminoquinoline, p$K_{\mathrm{BH_2}^{2+}}$ = −0.74 ± 0.04, and 3-aminopyridine, p$K_{\mathrm{BH_2}^{2+}}$ = −1.76 ± 0.02, appear to be more acidic than the previously reported values of −0.13[9] and −1.5[12] would suggest. Because of differences in activity coefficients, it is expected that, for a given concentration of a given mineral acid, $H_+ < H_0$. This expectation is realized in the above results.

It is more difficult to explain the difference between our value of p$K_{\mathrm{BH_2}^{2+}}$ = 0.08 ± 0.02 as opposed to the published valve of −1.67[13] for the dissociation constant of 1,2-phenylenediamine. These authors rationalized their valve of −1.67 as due to the mesomeric and inductive effects of and to steric inhibition of solvation by the ortho NH_3^+ group. Such a large deactivating effect by the NH_3^+ group is not supported by the consideration of the dissociation constants of substituted 1,2-phenylenediamines. For example, the dissociation constant of protonated 4-nitroaniline is 1.00[14], whereas that of doubly protonated 4-nitro-1,2-phenylenediamine in H_2SO_4 is −2.75.[1] This would suggest that the ortho NH_3^+ group has a deactivating effect of about 4 pK_a units. Similarly, 2-nitroaniline has a pK_{BH^+} of −0.25,[14] whereas as p$K_{\mathrm{BH_2}^{2+}}$ of 3-nitro-1,2-phenylenediamine in H_2SO_4 is −4.10,[1] again suggesting a deactivating effect of 4 log units. From the above approximations, the p$K_{\mathrm{BH_2}^{2+}}$ of 1,2-phenylenediamine in H_2SO_4 should be around 0.5. This is in good agreement with the valve of 0.67 which was previously published,[2] and we conclude that our valve of 0.08 ± 0.02 in $HClO_4$ is more reasonable than the value of −1.67.

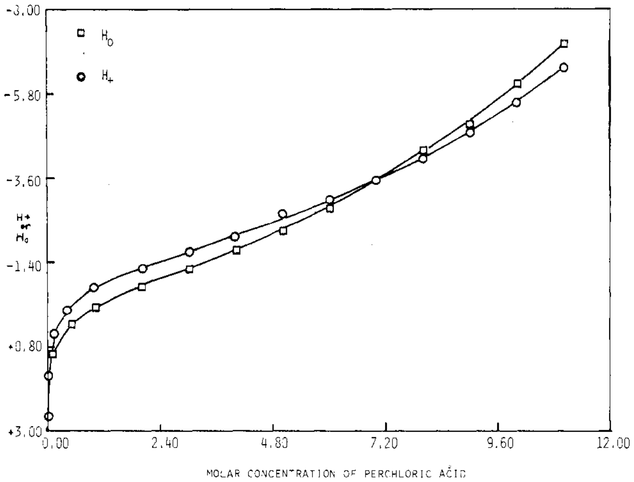

Figure 1. Plot of H_+ (○) and H_0 (□) as a function of the molar concentration of perchloric acid at 25 °C.

We observed that the H_+ scale in perchloric acid is more negative than the H_+ scale in sulfuric acid. This is in keeping with the observation that the H_0 scale in concentrated perchloric acid is more negative than the H_0 scale in concentrated sulfuric acid.[11]

A comparison of the H_0 scale in perchloric acid to the H_+ scale in the same acid shows that below 7 M acid the H_+ scale is more

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negative than the H_0 scale. Above this molarity, however, the H_+ scale becomes more positive than the H_0 scale. The reason for this change is unknown. That plots of H_+ vs. log I for all the indicators in this work (except for 4-aminopyridine) have unit slopes suggests that the prototropic behavior of these indicators is consistent and that the H_+ scale correctly describes their behavior. However, plots of H_0 vs. log I for the same indicators in concentrated perchloric acid have slopes greater than unity (except for two indicators). The H_0 scale, therefore, does not adequately describe the prototropic behavior of these compounds in concentrated perchloric acid. This finding is different from what was observed previously[1] in sulfuric acid, where in concentrated solutions of the acid the H_0 and H_+ scales are colinear. A comparison of the dissociation constants of those indicators that were studied in both perchloric and sulfuric acids shows that the dissociation constants in $HClO_4$ tend to be slightly more negative than they are in H_2SO_4, with the exception of 4-aminopyridine. This was also observed with the indicators used to establish the H_0 scales in concentrated perchloric and sulfuric acids.

The slope of the plot of H_+ vs. log I for 4-aminopyridine is 0.89 ± 0.01. This suggests that, as was the case of the H_+ scale in H_2SO_4, the H_+ scale in $HClO_4$ does not adequately describe the prototropic behavior of 4-aminopyridine. This compound appears to be more basic in $HClO_4$ than it is in H_2SO_4. This statement is supported by the following observations. In sulfuric acid, 4-aminopyridine is only 50% protonated when 4-bromo-6-nitro-1,2-phenylenediamine is 90% protonated. In perchloric acid, however, the former is 80% protonated when the latter is 90% protonated. Furthermore, the acid-dissociation constant of 4-bromo-6-nitro-1,2-phenylenediamine is the same in perchloric and sulfuric acids. These observations suggest that 4-aminopyridine is structurally different in perchloric acid than in sulfuric acid, perhaps by virtue of differences in solvation. This raises a legitimate question as to the suitability of 4-aminopyridine as an indicator to define part of the H_+ scale. However, the continuity of the curve in Figure 1 suggests that until a better indicator (i.e., a well-behaved arylamine) can be found, 4-aminopyridine will serve to establish the H_+ scale (at least approximately) for perchloric acid solutions up to ~11 M in concentration.

Registry No. $HClO_4$, 7601-90-3; 5-hydroxy-8-aminoquinoline, 89302-52-3; 6-aminoquinoline, 580-15-4; 5-aminoquinoline, 611-34-7; 1,2-phenylenediamine, 95-54-5; 8-aminoquinoline, 578-66-5; 4-chloro-*o*-phenylenediamine, 95-83-0; 3-aminopyridine, 462-08-8; 1,2-phenylenediamine-4-carboxylic acid, 619-05-6; 2-nitro-*p*-phenylenediamine, 5307-14-2; 4-nitro-1,2-phenylenediamine, 99-56-9; 2,6-diaminopyridine, 141-86-6; 3-nitro-1,2-phenylenediamine, 3694-52-8; 2,3,6-triaminopyridine, 4318-79-0; 4-bromo-6-nitro-1,2-phenylenediamine, 84752-20-5; 4-aminopyridine, 504-24-5.

Proton Conductivity in Supercooled Aqueous HCl Solutions

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Measurements of the electrical resistivity of 1, 0.1, and 0.01 M solutions of HCl and KCl in water to −32 °C are reported. Values of the proton conductivity λ_{H^+} in the HCl solutions are estimated. λ_{H^+} is a linear function of temperature in the range −32 to +45 °C, $\lambda_{H^+} = A(T/T_s - 1)$, and extrapolates to zero at $T_s = 227$ K. Implications concerning the structure of water at T_s are discussed.

Introduction

The unusual properties of supercooled water and aqueous solutions, recently reviewed by Angell[1] and by Lang and Lüdemann,[2] have generated much speculation[3-7] about the nature of the impending singularity[3] at $T_s \simeq -45$ °C and about the structural basis of the cooperative process in water that evidently generates long-range correlations as $T \rightarrow T_s$. Direct observations near T_s are not possible because even the smallest samples of water freeze[1] above −41 °C. Submicroliter samples are needed for studies below −20 °C. Thus, evidence about T_s is based on the extrapolation of results measured under difficult conditions.

A major motivation for conductivity studies on water is the fact that conductivity can be measured more precisely[7] than most other properties of small samples and can therefore provide a more stringent test of the power law type equations[3] that seem to describe the temperature dependence of the transport properties of water.

In this work we examine the proton conductance λ_{H^+} in supercooled HCl solutions. The previous measurements on KCl solutions[7] are extended to −32 °C and to 0.01 M and are used to estimate values of λ_{Cl^-}. Measurement of the resistivity of HCl solutions then yields λ_{H^+}.

The resistivities of the KCl and HCl solutions conform to power law equations of the form[3,7]

$$r = r_2(T/T_s - 1)^{-\gamma} \tag{1}$$

where r_2, T_s, and γ are constants. The values of γ are quite different for HCl and KCl. The derived values of λ_{H^+} are, however, linear in T

$$\lambda_{H^+} = A(T/T_s - 1) \tag{2}$$

and the parameters A and T_s vary in a simple way with concentration.

There is extensive literature[8-11] on the anomalous magnitude of the proton mobility in water, none of which predicts this simple temperature dependence.

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