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NMR OF HCl-DCl-WATER MIXTURES AND RELATED SALT SOLUTIONS

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March 1969

The molecular state of perchloric and nitric acids has been the subject of a number of recent publications.[1-4] Chemical shift measurements of HCl-DCl-water mixtures and a number of related salt solutions reported in the following support earlier conclusions.

Preparation of the various acid solutions involved the use of freshly distilled hydrochloric acid and water. The acid concentrations were determined by weight titration with a sodium hydroxide solution.[2] The constituents of the salt solutions were measured by weight before mixing.

Chemical shift measurements of the acid solutions, obtained by means of the standard sideband technique at 60 MHz, are given in Table I, together with the temperature t, the deuterium fraction r, the mole fraction x of HCl, the susceptibility correction g[2,5], and the ratio s/p of the shift with respect to Gutowsky's variable[6] $p = 3x/(2-x)$. The techniques used for the determination of r and t have been discussed previously.

Equations describing the dependence of the chemical shift on the isotopic composition and the acid concentration have been derived in detail by Redlich, Duerst and Merbach.[3] The limit of the ratio H/D at infinite dilution, expressed as a function of the mole fraction of deuterium r (= D/(D+H)), is

$$\lim \phi = (1-r)/r. \qquad (1)$$

A crude estimate for the degree of hydration of the hydrogen ion as a function of the temperature $t(^{o}C)$ is given by

$$q = 4.3 + 0.01\ t \quad . \tag{2}$$

The ratio of the limiting slopes for $r = 1$ and $r = 0$, s_{11} and s_{10} respectively, define the constant $k = s_{11}/s_{10}$. The specific shift of the undissociated molecule is called s_2. The degree of dissociation α can be expressed by means of a material balance and also as a function of the chemical shift s of the acid as

$$\alpha = 3(1+k\phi)(1-r-r\phi)/[pq\phi(k-1)] \tag{3}$$

and

$$\alpha = \frac{s(1-r)/p\phi - s_2/(1-\phi)}{ks_{10}/(1+k\phi) - s_2/(1+\phi)} \quad . \tag{4}$$

The behavior of s/p for $x \ll 1$ is of interest. For dilute solutions, ϕ may be represented as a linear function of x with the coefficient A as

$$\phi = (1-r)(1-Ax)/r \quad . \tag{5}$$

For dilute HCl solutions, α is equal to one. Substituting ϕ from (5) into (3) and solving for A, neglecting any terms higher than first order in x and p, we obtain

$$Ax = pq\ (k-1)/3 \quad . \tag{6}$$

From (4) and (6) we obtain for $\alpha = 1$ and $r = 1$ the approximation for dilute acid solutions

$$s/p = s_{11}[1-(k-1)qx/2] \quad . \tag{7}$$

The observed results for s/p are shown in Fig. 1. Empirical extrapolation to $x = 0$ furnishes the values of s_{10}, s_{11} and, therefore, the value of $k = s_{11}/s_{10}$ for any temperature. The slope of s/p against x can then be calculated from (7). The calculated slopes of s/p at the higher concentrations for 0° and $25^{\circ}C$ are in good agreement with the empirical results, but noticeable discrepancies exist between the empirical s/p values of $65^{\circ}C$ for $x = 0.36$ and the calculated straight lines. The discrepancies may be attributed to incomplete dissociation, although the experimental basis is, of course, narrow.

The specific shifts s_1 for light and heavy solutions of nitric, perchloric and hydrochloric acids are given in Table II for three temperatures. At a given temperature and deuterium ratio, variations in the specific shifts may be attributed to two anionic effects, rupture of hydrogen bonds and the formation of hydrated species whose hydration number is dependent upon the anion in question.[4] On the other hand, comparison of the data obtained at a given temperature for a given anion with different deuterium ratios reveals significant differences in the chemical shifts. Such differences in the chemical shifts and the corresponding specific shifts are primarily attributed to the preference of the hydrogen isotope to be in a solvated hydrogen ion aggregate rather than in bulk water.

Assessment of the influence of deuterium on the environment of the proton in strongly electrolytic solutions leads to information on the structure of various aqueous salt solutions in light and heavy water at $34^{\circ}C$. Hindman[8] and

Shoolery and Alder[9] have reported the chemical shifts of these salt solutions in light water. Our preliminary measurements are presented in Table III, which lists the temperature t, the deuterium fraction r, the mole fraction of the salt x, the observed chemical shift s(obs.) of the bulk solution, the chemical shift s' for light water solutions determined by linear extrapolation to the corresponding heavy water concentration, the estimated susceptibility correction g[5], and the susceptibility-corrected chemical shifts s.

The uncertainty in g for deuterium solutions suggests an examination of only the observed chemical shifts. The observed shifts s(obs.) of heavy water salt solutions are essentially the same within experimental error as the extrapolated chemical shifts s' of the corresponding light water solutions of the same salt. We must conclude, therefore, that the presence of deuterium does not exert an appreciable effect of its own on the relationship of the proton to a salt in its immediate environment under these conditions.

It is a pleasure to acknowledge the valuable suggestions of Professor Otto Redlich.

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Table I. Chemical Shifts in Parts per Million for HCl-DCl

t	r	x	g	s	s/p ratio
temp (°C)	deuterium fraction	mole fraction	suscep-tibility correction	shift (ppm)	
0.0	0.0	0.0183	-0.028	0.292	10.54
	0.0	0.0363	-0.056	0.574	10.34
	0.9924	0.0161	-0.023	0.372	15.32
	0.9817	0.0359	-0.050	0.826	15.07
25.0	0.0	0.0183	-0.026	0.320	11.55
	0.0	0.0363	-0.050	0.627	11.30
	0.9924	0.0161	-0.020	0.393	16.19
	0.9817	0.0359	-0.045	0.864	15.76
65.0	0.0	0.183	-0.019	0.358	12.92
	0.0	0.363	-0.048	0.689	12.41
	0.9924	0.161	-0.016	0.422	17.38
	0.9817	0.0359	-0.044	0.912	16.63

Table II. Specific Shifts of the Hydrogen Ions in Dilute Acids

t (°C)	HNO_3	$HClO_4$	HCl	DNO_3	$DClO_4$	DCl
0	10.070	8.666	10.74	15.594	13.940	15.53
25	11.073	9.184	11.81	16.348	14.161	16.53
65	12.150	10.102	13.43	17.026	14.515	17.98

Table III. Chemical Shifts in Parts per Million for the Salt Solutions

salt	t	r	x	s(obs.)	s'	g	s
	temp. (°C)	deuterium fraction	mole fraction	shift (ppm)	extrap-olated	suscep-tibility correction	shift (ppm)
$NaNO_3$	33.9	0.0	0.03244	-0.134	-0.155	-0.015	-0.149
$NaNO_3$	33.6	0.9985	0.03771	-0.157	-0.157	-0.018	-0.175
NaI	33.8	0.0	0.03296	-0.102	-0.099	-0.182	-0.284
NaI	34.0	0.9985	0.03180	-0.102	-0.102	-0.151	-0.253
$NaClO_4$	33.7	0.0	0.03481	-0.227	-0.236	-0.025	-0.252
$NaClO_4$	33.4	9.9985	0.03627	-0.237	-0.237	-0.028	-0.265
NaCl	34.0	0.0	0.03317	-0.058	-0.064	-0.090	-0.148
NaCl	33.8	0.9985	0.03661	-0.066	-0.066	-0.093	-0.159
NH_4Cl	33.6	0.0	0.03376	+0.023	+0.026	-0.068	-0.045
NH_4Cl	33.8	0.9260	0.03767	+0.026	+0.026	-0.068	-0.042

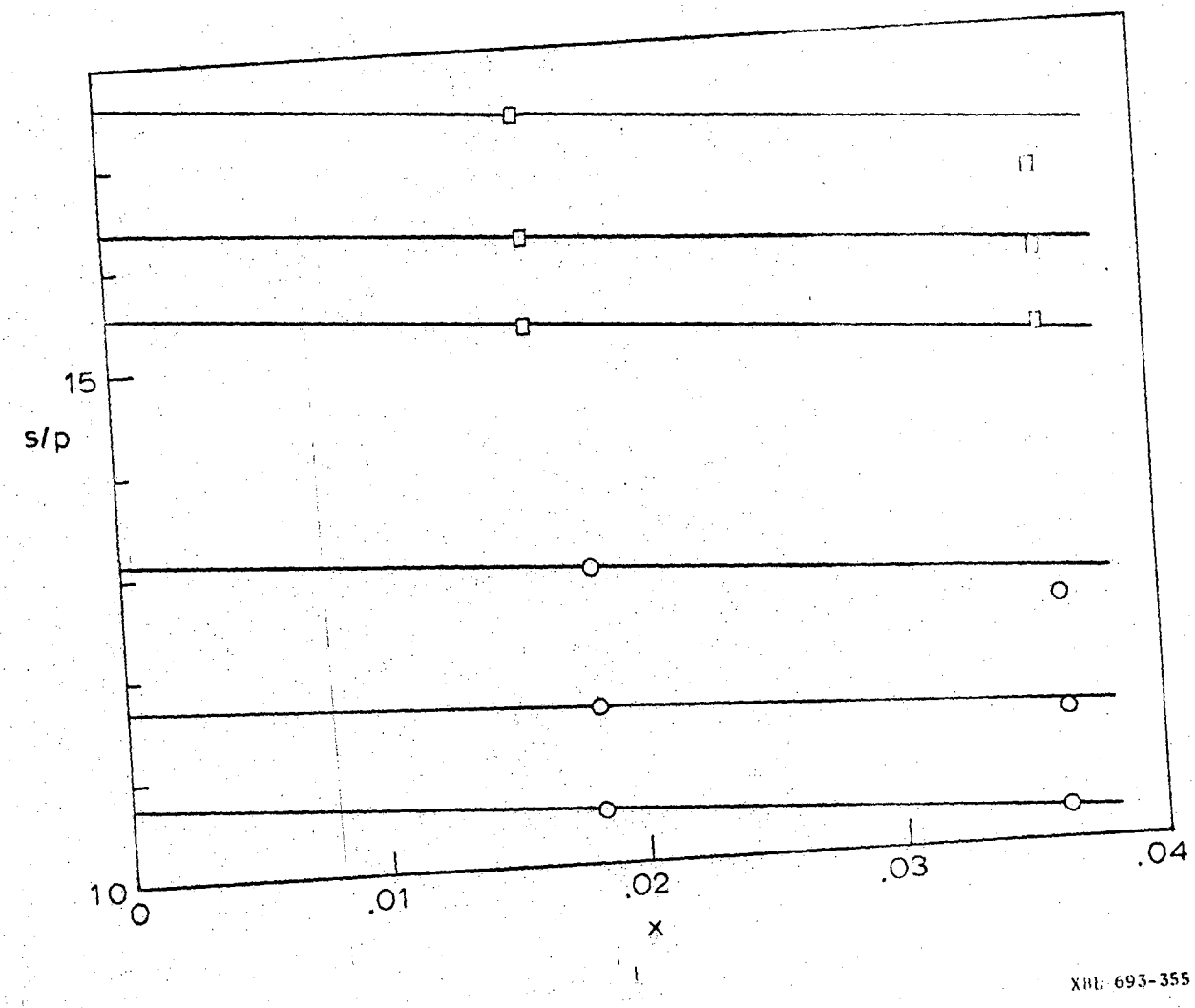

Fig. 1 s/p versus x. O, HCl; □, DCl. The lowest s/p curves correspond to 0°C, the intermediate to 25°C, and the highest to 65°C. The slopes are calculated.

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