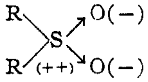
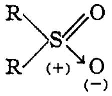
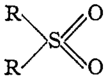
in addition to the sulfone function, and surprisingly enough we found the i value in this case to be considerably smaller than that of di-(p-nitrophenyl) sulfone.[13] In view of the behavior of the nitrobenzyl sulfone one can not attribute the sharp rise of the i values in the phenyl sulfone series to a simple accumulative effect of the basic groups. The sharply rising basicity of the nitrophenyl sulfones apparently is related to the existence of conjugation between the nitro and sulfone groups. The following explanation is offered for the purpose of correlating the experimental observations.

The electronic structures proposed for the sulfone group range from those in which both sulfur–oxygen bonds are doubly covalent to those in which both bonds are semipolar.[11,14] Presumably the actual structure of sulfones is a hybrid of several resonance structures, and the relative contribution of the individual forms III-V depends on the particular structural features present in a given molecule. If one examines the three contributing structures one notices a gradual decrease in the positive charge on the sulfur atom as we proceed from III to V. In sulfones in which nitro groups are conjugated with the sulfone function, the negative electromeric effect of the nitro group causes an electron deficiency near the sulfone group and this in turn would be expected to cause increasing contributions of structures IV and V to the ground state of the molecule. The benzyl sulfones, on the other hand, can be represented more accurately in terms of a structure such as III, and phenyl sulfone and sulfones containing electron-donating substituents are best represented by resonance structures such as VI. From the experimental i values of the sulfones investigated in this work it would seem that the relative basicities of sulfones increase as the electron distribution changes in the order: III < VI < IV < V. If this conclusion is correct, it follows that the basicity of the sulfone function depends more on the resonance stabilization of the protonated structure than on the fractional negative charge present initially on the oxygen atom.[15] We hope to investigate additional sulfones cryoscopically in order to ascertain the relationship between the basicities of sulfone groups and the structural features which could influence the relative contributions of the various sulfone resonance hybrids.[16]


III


IV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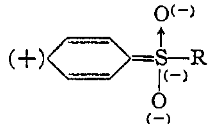
VI

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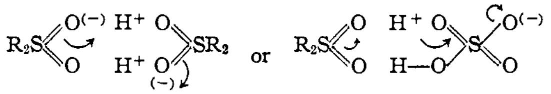
[13] Because of the critical significance of the i values of di-(p-nitrobenzyl) sulfone several careful experiments were carried out using fresh batches of sulfuric acid in each case. Within several hours upon the completion of the solution of each sample the experimental i factor had the value of nearly unity. As noted in Table I a slow oxidation side reaction then began which caused a noticeable evolution of sulfur dioxide and a gradual rise in the i values. Nearly quantitative recovery of the sulfone was possible after 12 hours: in an isolation experiment carried out with great care 0.681 g. of the initial 0.708 g. of sulfone was recovered. On the basis of these observations we believe the i value of di-(p-nitrobenzyl) sulfone to be nearly unity. In this connection we found the oxidation of benzyl sulfone to be too rapid for the determination of the i value of the simple ionization process, and this sulfone could not be recovered from the reaction mixture.

[14] (a) E. D. Amstutz, *et al.*, *Science*, **111**, 305 (1950); (b) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 234 (1949); *ibid.*, **72**, 1292 (1950); (c) H. P. Koch, *J. Chem. Soc.*, 408 (1949).

[15] A referee made the excellent suggestion that the protonated sulfone structure may be dimeric in line with the results of J. Walker (*ibid.*, 1996 (1949)) with amidinium complexes. Thus, the protonated sulfone may be best visualized as a resonating complex



[16] ADDED IN PROOF—Additional i values determined more recently support the above ideas: 4,4'-dichlorodiphenyl sulfone (i = 1.0); 3,3'-dinitro-4,4'-dichlorodiphenyl sulfone (i = 1.2).

PITTSBURGH, PENNA. RECEIVED FEBRUARY 5, 1951

[CONTRIBUTED FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Electromotive Force Studies in Aqueous Solutions of Hydrochloric Acid and *d*-Fructose at 25°

BY H. D. CROCKFORD AND ALEXANDER A. SAKHNOVSKY

The values of the electromotive force at 25° of cells of the type H_2 |HCl (m), d-fructose (x), H_2O (y) |AgCl, Ag were determined with acid concentrations to approximately 0.12 m and in 5 and 10% d-fructose solutions. From the data obtained the standard cell potentials were calculated. An ion size parameter of 6.6 Å. was found for hydrochloric acid in the solutions studied. The mean activity coefficients of hydrochloric acid in the two solvents were determined at rounded molalities. These were found to agree closely with those calculated by the Debye–Hückel equation.

The work reported on in this paper is a continuation of the studies being carried on in this Laboratory on the effect of mixed solvents on the thermodynamic properties of hydrochloric acid solutions. In this work electromotive force measurements were made on the cell

$$H_2 \mid \text{HCl } (m),\ d\text{-fructose } (x),\ H_2O\ (y) \mid \text{AgCl–Ag}$$

at 25° in solutions containing 5 and 10% of d-fructose by weight with acid concentrations ranging from approximately 0.005 to 0.12 m. From the data obtained have been calculated the activity coefficients, the standard cell potentials, and the value of the ion size parameter.

This work was undertaken for the purpose of studying ion size parameter values of hydrochloric acid in solutions of hydroxyorganic compounds. Work with d-glucose was reported by Williams, Knight and Crockford.[1] They found a value of 6.6 Å. for the ion size parameter, a value much higher than the 4.3 Å. value found by other investigators

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[1] Williams, Knight and Crockford, THIS JOURNAL, **72**, 1277 (1950).

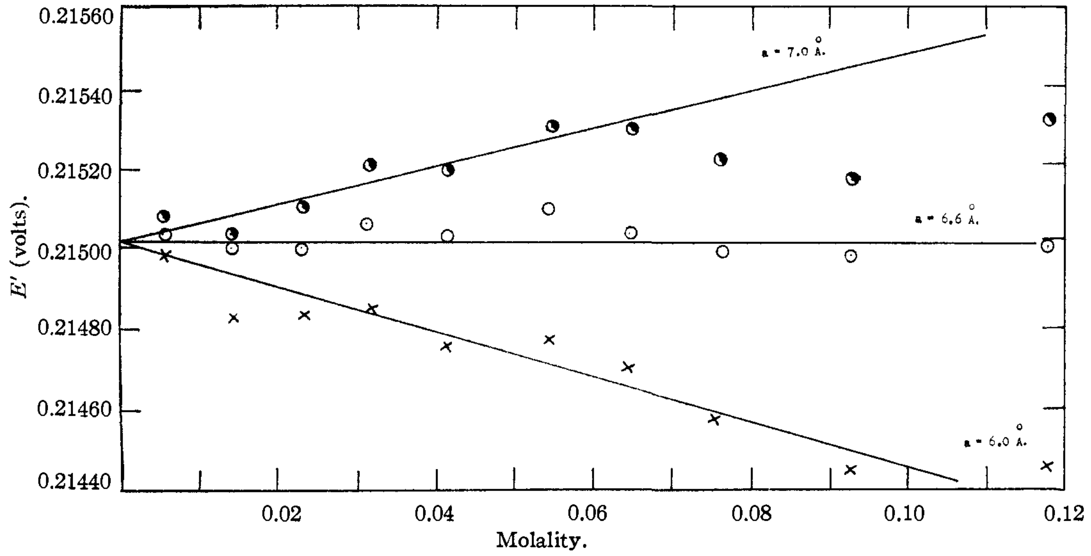

Fig. 1.—E' plots as function of the ion size parameter.

in mixed solvents and in pure water. A list of other investigations in the field of mixed solvents with hydrochloric acid is given in the paper of Williams, *et al.*[1]

Experimental

The methods of purification of chemicals (excluding *d*-fructose), the preparation of the electrodes, and the experimental procedures were essentially the same as those of Williams, *et al.*[1]

***d*-Fructose.**—Pfanstiehl crystalline *d*-fructose was used. It was purified by recrystallization from ethanol–water solution and protected from moisture in a tightly closed bottle.

Densities.—Density measurements were made at 25° in a pycnometer of about 25-ml. capacity.

Vapor Pressures.—The vapor pressures of the solvent mixtures were assumed to follow Raoult's law.

Dielectric Contents.—In the absence of accurate data on the dielectric constant of aqueous *d*-fructose solutions the corresponding *d*-glucose values employed by Williams, *et al.*,[1] were used. These values are 76.1 and 77.3 for the 10 and 5% solutions, respectively. Testing of the data with dielectric values slightly lower and slightly higher than these values showed that those used appeared to give the most consistent results.

The electromotive force measurements, corrected to 1 atm. of hydrogen, are averages of at least three cells usually agreeing within ±0.05 mv. The times necessary for equilibrium were substantially the same as those found by Williams, *et al.*,[1] in *d*-glucose solution. The results are expressed in international volts.

Calculations and Results

The standard electrode potentials were determined by use of the function E', defined by the equation

$$E' = E + 0.1183 \log m - \frac{0.1183\, A\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} - 0.1183 \log (1 + 0.002\, mM_{xy}) = E^0_{\mathrm{m}} + f(m) \quad (1)$$

in which E' is the apparent molal potential, E is the observed electromotive force corrected to 1 atm. of hydrogen, m is the molality, A and B are the Debye–Hückel constants, $\mathring{a}$ is the ion size parameter in Å., c is the concentration of the acid in moles per liter, and M_{xy} is the mean molecular weight of the solvent.

Table I gives the observed electromotive force, molality and E' (calculated for an ion size parameter of 6.6 Å.) for each of the solutions. Table II gives the values used for the constants in equation (1) in each of the two series of solutions.

Table I

10% *d*-fructose solutions			5% *d*-fructose solutions		
m	E	E'	m	E	E'
.0061133	0.48121	0.21504	0.0082450	0.47018	0.21895
.014161	.43975	.21495	.015140	.44033	.21905
.023319	.41548	.21499	.020112	.42651	.21906
.031242	.40134	.21507	.032910	.40252	.21901
.041616	.38745	.21503	.040342	.39261	.21895
.054141	.37487	.21509	.048296	38398	.21900
.064238	.36662	.21506	.067569	.36777	.21893
.076086	.35843	.21498	.090831	.35345	.21878
.092524	.34900	.21489	.11244	.34324	.21876
.11778	.33762	.21501			

Table II

Constants of Equation (1)

	A	B	M_{xy}	$\mathring{a}$, Å.	D
5% *d*-Fructose	0.52044	0.33105	18.86	6.6	77.3
10% *d*-Fructose	.53383	.33386	19.81	6.6	76.1

The usual procedure for determining the ion size parameter by plotting the right-hand side of Equation (1) for various values of a against the molality was followed. Three such plots are given in Fig. 1. It is seen that the best value of the ion size parameter is 6.6 Å., a value equal to that obtained by Williams and his co-workers.[1] This compares with the usual value of 4.3 Å. obtained by other investigators for various mixed solvents (other than hydroxy-organic compounds).

The value of E^0_{m} for each series of solutions was taken as that value of E' corresponding to the value of the ion size parameter which gave an $E' - m$ curve of zero slope. From the E^0_{m} values the E^0_{N} and E^0_{c} values were calculated by means of the relationships

$$E^0_{\mathrm{c}} = E^0_{\mathrm{m}} + 0.1183 \log d_0 \quad (2)$$

$$E^0_{\mathrm{N}} = E^0_{\mathrm{m}} - 0.1183 \log (1000/M_{xy}) \quad (3)$$

The values of these various standard cell potentials are given in Table III.

The density values for the various solutions were found to fit the empirical equations

$$d(5\%\ d\text{-fructose}) = 1.0168 + 0.0166m$$

$$d(10\%\ d\text{-fructose}) = 1.0369 + 0.0192m$$

TABLE III

	E^0_m	E^0_N	E^0_c
5% *d*-fructose	0.21900	0.01499	0.21985
10% *d*-fructose	.21502	.01352	.21689

The mean activity coefficients, $y_\pm$, of hydrochloric acid in the two *d*-fructose solutions were computed from the e.m.f. data by the equation

$$\log y_\pm = (E^0_m - E)/0.1183 - \log m \qquad (4)$$

The values so calculated were plotted against m on a large scale and the values at rounded molalities determined. These values are given in Table IV together with the values for pure water listed by Harned and Owen.[2]

The experimental values of the activity coefficients can be reproduced almost exactly by the Debye equation

$$\log y_\pm = -\frac{A\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} - \log (1 + 0.002mM_{xy}) + C'c \qquad (5)$$

in which C' is a constant introduced to account for the "salting out" effect. This constant was not found to be significant in these studies. In only two of the solutions was the deviation between the experimental and theoretical activity coefficients as much as 0.003. It is noted in Table IV that the activity coefficient increases from pure water to 5% *d*-fructose and then decreases for the 10% solution. The same increase and decrease was found for *d*-glucose by Williams, *et al.*[1]

TABLE IV

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN *d*-FRUCTOSE–WATER MIXTURES AT 25°

Molality	$X = 0$	$X = 5\%$	$X = 10\%$
0.005	0.9285	0.931	0.927
.01	.9048	.906	.903
.02	.8755	.877	.874
.03		.858	.853
.05	.8304	.835	.827
.07		.816	.810
.08		.809	.803
.10	.7964	.798	.791
.11		.793	.785

CHAPEL HILL, N. C. RECEIVED MARCH 7, 1951

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[2] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 340.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Anhydrous Niobium Tribromide and Trichloride. Preparation and Properties

BY CARL H. BRUBAKER, JR., AND RALPH C. YOUNG

Niobium tribromide has been prepared in a pure state by reduction of the pentabromide with hydrogen at 500°. The substance condensed as a black crust on the tube walls and as black rods on a cold finger-condenser. The rods were much more reactive than the crust. When the tribromide was sublimed *in vacuo* and collected upon a cool surface, the reactivity of the product depended on the temperature gradient. The tribromide decomposes to the metal and $NbBr_5$ at about 925°. Niobium trichloride, which was prepared in essentially the same way as the tribromide, is also obtained as crust and rods. It is more stable than the bromide and less reactive. X-Ray examinations indicated that both rods and crust had the same crystal structure and hence the difference in reactivity is probably a matter of surface. The behavior of both the trichloride and tribromide toward various reagents is given.

Niobium tribromide has not been previously reported but the preparation of anhydrous $NbCl_3$ was first accomplished by Roscoe,[1] in 1878, who led the vapor of $NbCl_5$ through a glass tube heated to redness. He described the trichloride as a black crust, composed of tiny plates "resembling sublimed iodine." Moreover, he reported that these plates were stable in the air, insoluble in water and inert to most aqueous acids and bases. They were oxidized by hot dilute nitric acid to Nb_2O_5. At red heat they reacted with CO_2 and formed $NbOCl_3$ and CO.

Süe[2] also prepared anhydrous $NbCl_3$ by reducing $NbCl_5$ vapor with H_2 at 400°. He too found the compound to be an inert black crust and found that it was attacked by oxygen and air only at temperatures above 270°, at which point it was converted to the pentoxide.

Emeléus and Gutman[3] reduced $NbCl_5$ by subliming it with hydrogen at 500° and obtained a gray-green product, the composition of which corresponded to no definite compound.

Since $TaBr_3$ had been found to be very reactive when prepared by the reduction of the tantalum pentabromide with hydrogen by a method employing the St. Claire–Deville "hot-cold" tube, it was decided to carry out the reduction of the pentabromide of niobium as well as the pentachloride in this same manner.[4,5]

Preparation of Anhydrous $NbBr_3$.—Niobium tribromide was prepared by bromination of 2 g. of granular niobium metal and subsequent reduction of the pentabromide in a continuous train (Fig. 1) to obviate the need of transferring the easily hydrolyzed pentabromide.

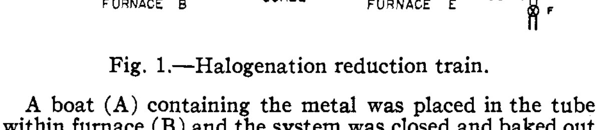

Fig. 1.—Halogenation reduction train.

A boat (A) containing the metal was placed in the tube within furnace (B) and the system was closed and baked out at 200° in a stream of dry nitrogen. When finally dry, furnace (B) was heated to 450° and dry bromine, with nitrogen-carrier, was led through the system at about 90 ml./min. (measured at 26°). When halogenation was complete, furnace (B) was cooled with dry nitrogen flowing through the system.

The $NbBr_5$ was then sublimed across the constriction (C) and through the glass wool plug (D). The constriction and

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[1] H. E. Roscoe, *Chem. News*, **37**, 26 (1878).

[2] P. Süe, *Bull. soc. chim.*, **6**, 830 (1939).

[3] H. J. Emeléus and V. Gutmann, *J. Chem. Soc.*, 2115 (1950).

[4] R. C. Young, *J. Chem. Ed.*, **20**, 378 (1943).

[5] R. C. Young and J. H. Hastings, Jr., THIS JOURNAL, **64**, 1740 (1942).