residues (see Fig. 3). Although the accuracy of the determinations is not sufficient to exclude the possibility of a linear increase with the first power, the apparent linear dependence upon the square root of the number of glycine residues is what one would expect from a statistical consideration of rigid molecules randomly distributed in all possible configurations resulting from potential minima symmetrically distributed about the valence bonds of the backbone chain. The triglycines appear to have approximately the same shapes, except for alanylleucylglycine which appears somewhat more spherical as would be expected since the large isobutyl group has been attached to the middle of the chain. Leucylglycine is more spherical than would be predicted. Perhaps in this case the Perrin equation fails since the assumed ellipsoid of revolution is a poor approximation for this molecule. The dipolar part of the molecule may undergo motion with very little change in the position of the hydrocarbon chain at one end of the molecule. Undoubtedly a more satisfactory picture would be obtained for these small irregular molecules if it were possible to discard the hydrodynamic view-point and the prolate spheroid model in favor of more accurate knowledge of the nature of the process of rotation.

Other complicating factors which have not been considered are the change in the volume of the rotating unit due to hydration resulting from hydrogen bonding of the dipolar molecule with water, and, second, hydrogen bonding within the peptide chain, which must occur to stabilize the structures of protein molecules. The second factor is probably of little importance since these peptide chains act as denatured proteins.

The writers wish to express their gratitude to Professor Eugene Pacsu for his helpful discussions relating to the polypeptides used in this investigation.

Summary

An apparatus has been constructed for the measurement of the dielectric constants of liquids at wave lengths from 40 to 80 cm. by the first Drude method. The dielectric constants of aqueous solutions of ten amino acid peptides in this region of anomalous dispersion have been measured, as have the viscosities of the solutions. The mechanism of dispersion has been discussed and the results have been combined with previous dielectric constant measurements at 10 meters in this Laboratory to calculate the relaxation times and shape factors for the solute molecules. Although the results are not inexplicable in terms of internal rotation around valence bonds in the molecules, the values and their trend are consistent with the simple picture of rotation of the molecule as a whole.

The Apparent Molal Volumes of Aqueous Solutions of Sulfuric Acid at 25°

BY IRVING M. KLOTZ AND CHARLES F. ECKERT

It has been known for some time that the apparent molal volume of a strong electrolyte may be expressed as a linear function of the square root of its volume concentration. For aqueous solutions of sulfuric acid, however, the apparent molal volumes show an unusual dependence on the concentration. In contrast to most electrolytes, the volumes rise very rapidly in the dilute range but approach a linear function of the square root of the concentration at high molarities. This behavior has been explained qualitatively as being due to the ionization of bisulfate ion.[1] With data on the dissociation constants of bisulfate ion a quantitative explanation of the observed volume changes in terms of the apparent molal volumes of the component ions is also possible. We have determined the densities of solutions of sulfuric acid from 0 to 3 molar, and have calculated, by a method of successive approximations, the apparent molal volumes of $H^+ + HSO_4^-$ ions.

Experimental.—The solutions were placed in Pyrex containers immersed in a thermostat at 25° ($\pm0.001°$). The density of each solution was measured by means of the sinker method described by Wirth.[2] The method was sensitive to differences of less than one part per million in the density.

(1) Geffcken and Price. Z. physik. Chem.. **26B**, 81 (1934).

(2) Wirth. THIS JOURNAL, **59**, 2549 (1937).

TABLE I[a]

APPARENT MOLAL VOLUMES OF $(H^+)_2(SO_4^=)$ and $(H^+)(HSO_4^-)$

Concn. H_2SO_4, moles/liter	$(d_s - d_0)$ 1000	ϕ_s, cc.	K_c	μ	ϕ_2	ϕ_1
0.01432	1.038	25.68	0.0185	0.0277	15.74	34.49
.02708	1.901	27.96	.0208	.0466	15.98	34.73
.04053	2.771	29.80	.0226	.0648	16.16	35.67
.05933	3.986	30.99	.0241	.0885	16.35	35.77
.0839	5.544	32.09	.0266	.1188	16.58	36.18
.0900	5.929	32.29	.0270	.1260	16.63	36.20
.1157	7.567	32.77	.0289	.1562	16.83	36.16
.3493	22.057	35.03	(.03)	.401	17.96	36.39
.6833	42.383	36.15	(.03)	.739	19.02	36.88
1.275	78.013	37.01	(.03)	1.332	20.43	37.40
2.030	122.214	37.99	(.03)	2.090	21.79	38.23
3.194	188.318	39.23	(.03)	3.244	23.45	39.35

[a] d_s is the density of the sulfuric acid solution and d_0 is that of pure water.

Concentrations were determined by titration against sodium hydroxide which had been standardized with potassium acid phthalate.

The Apparent Molal Volumes of (H^+) (HSO_4^-).—To interpret our data we have assumed that a solution of sulfuric acid may be considered as a mixture of two components, $(H^+)_2(SO_4^=)$ and $(H^+)(HSO_4^-)$. For a concentration of c_3 moles per liter of sulfuric acid we should have c_1 moles per liter of $(H^+)_2(SO_4^=)$ and $c_3 - c_1$ moles per liter of $(H^+)(HSO_4^-)$ where c_1 is determined by c_3 and by K_c, the classical ionization constant of bisulfate ion. If the volume change due to the addition of N_3 moles of sulfuric acid to the quantity of water necessary to give the concentration c_3 is ΔV, then

$$\phi_3 = \Delta V/N_3 = (c_1/c_3)\phi_2 + [(c_3 - c_1)/c_3]\phi_1 \qquad (1)$$

where ϕ_1 is the apparent molal volume of (H^+) (HSO_4^-), ϕ_2 that of $(H^+)_2(SO_4^=)$ and ϕ_3 the observed value. Consequently

$$\phi_1 = [\phi_3 - (c_1/c_3)\phi_2]/(1 - c_1/c_3) \qquad (2)$$

The classical ionization constant of bisulfate ion, K_c, is a function of the ionic strength, μ, and has been determined up to $\mu \sim 0.14$.[3] Since c_1 is a function of K_c and K_c is a function of μ, and consequently of c_1, it has been necessary to use a series of successive approximations to establish the value of c_1. For the dilute range the value of K_c for $\mu = 0$ was used to obtain the first provisional value of c_1. Then μ was estimated from this value of c_1, K_c interpolated from an appropriate graph, and a second value of c_1 determined. This process was continued until two successive evaluations of K_c agreed within the experimental error in the determination of this constant. At high concentrations no reliable data on K_c are

available. In this range, however, the correction due to the ionization of bisulfate ion is small and not very sensitive to the value chosen for K_c. We have computed this correction for three different values of K_c, 0.01, 0.03 and 0.09, and have found only small differences in the results obtained for ϕ_1. The constant of 0.03, however, gave the best agreement with the molal volumes in the dilute region.

An alternative procedure for calculating ϕ_1 in concentrated solutions of sulfuric acid is to compute values of K_c from the data given by Harned and Hamer[4] combined with the ionization constant of bisulfate ion at infinite dilution determined by Hamer[5] or by Klotz.[3] This method, however, involves extensive computations, and since a precise value of K_c is unnecessary in the concentrated region, this alternative procedure was not adopted.

The apparent molal volumes of $(H^+)_2(SO_4^=)$ were calculated from the appropriate data for potassium chloride, hydrochloric acid and potassium sulfate[2,6] with the added assumption that the respective volumes are linear functions of the square root of the total ionic strength. Such a behavior is not fulfilled by hydrochloric acid or potassium sulfate[2,6] but the errors so introduced occur mainly in concentrated solutions where the correction of ϕ_3 for the ionization of bisulfate ion is small.

Knowing c_1 and ϕ_2 we can calculate the apparent molal volumes of $(H^+)(HSO_4^-)$ by entering the appropriate quantities in equation (2). The significant steps in the calculation are outlined in Table I.

(3) Klotz, Ph.D. Dissertation, University of Chicago, 1940.

(4) Harned and Hamer, THIS JOURNAL, 57, 27 (1935).

(5) Hamer, ibid., 56, 860 (1934).

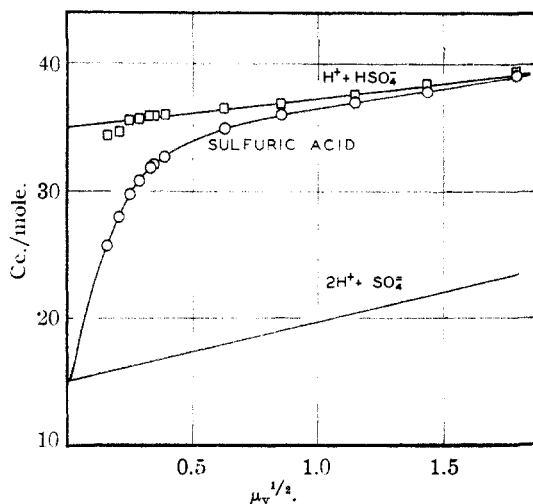(6) Wirth, ibid., 62, 1128 (1940).

Fig. 1.—Apparent molal volumes of sulfuric acid and its constituents: O, observed volumes; □; calculated volumes.

Figure 1 shows the results for the calculated volumes of the constituents of sulfuric acid solutions as well as the experimental data. The curve for sulfuric acid in the very dilute range (up to $\mu_v^{1/2} = 0.15$) was calculated from the volumes of the ionic components and shows a definite cusp just beyond $\mu_v^{1/2} = 0$. The observed apparent molal volume rises very rapidly as the concentration is further increased because more and more bisulfate ion is formed. As we reach concentrated solutions ($\mu_v^{1/2} > 0.5$) the proportion of sulfate ions becomes progressively smaller and the observed volumes

become, very nearly, those calculated for (H^+) (HSO_4^-). Thus the observed volumes of sulfuric acid from 0 to 3 molar can be interpreted quantitatively in terms of the respective contributions of the constituent ions.

The Volume Change on Ionization of Bisulfate Ion.—Extrapolation to infinite dilution yields a value of 35.1 cc./mole for $\bar{V}^0$ of $(H^+)(HSO_4^-)$. Combining this figure with that for $(H^+)_2(SO_4^-)$ we find the volume change upon ionization of bisulfate ion at infinite dilution to be -20.2 cc./mole:

$$HSO_4^- = H^+ + SO_4^- \qquad \Delta \bar{V}_2^0 = -20.2 \text{ cc./mole}$$

Summary

The densities of solutions of sulfuric acid have been determined over the concentration range of 0 to 3 molar and the apparent molal volumes interpreted in terms of the volumes of the hydrogen, sulfate and bisulfate ions.

The apparent molal volumes of hydrogen and bisulfate ions have been calculated by a series of successive approximations.

The Kinetics of the Thermal Reaction between Hydrogen and Cyanogen

BY N. C. ROBERTSON AND R. N. PEASE

Since the reactions of hydrogen with the various halogens have had such an important role in the development of chemical kinetics, it was thought that an investigation of the reaction with cyanogen might be profitable. The only reference to such a reaction is a report by Berthelot[1] that heating hydrogen and cyanogen in glass vessels in the neighborhood of 550° results in the formation of hydrogen cyanide together with a considerable amount of a polymer assumed to be paracyanogen.

The object of the present research was to establish the mechanism of this reaction in its relation to the other familiar reactions of hydrogen.

(1) M. Berthelot, Compt. rend., **89**, 63 (1878).

Experimental Procedure

The reaction was studied in a static system employing a silica vessel for most of the runs. This bulb, which was spherical and of some 550-cc. capacity, was placed at the center of a large electrically heated furnace which was provided with an auxiliary winding for the reaction chamber by means of which the temperature of the chamber was controlled to ±0.1° by a photoelectric potentiometer device connected to control thermocouples. The temperature was measured by means of two thermocouples immediately adjacent to the reaction vessel, heat losses and temperature gradient being minimized by packing the space for 10 inches above and below the reaction chamber with asbestos fiber. Apiezon was found to be satisfactory for stopcock lubrication.

Tank hydrogen was purified by passage over platinized