in equation (16) yields $a_2 = 3.82 \times 10^6$. The boundary displacement shown in Fig. 9 gave a value for $\Delta T = -0.1282$ and hence $a_1 = -2428$ from equation (12). With T for 0.1 N cadmium iodide taken as 0.3040, $a_0 = 0.5086$ from equation (11). The quadratic, $T = 0.5086 - 2428\, c + 3.82 \times 10^6\, c^2$, should thus touch the actual transference number function at three points in the interval from 0.1 N to 0.2 N. That it does is shown by the fact that a value for T computed for some intermediate concentration, say 0.15 N, falls accurately on the curve of Fig. 6, the computed value being indicated by the crossed circle in that figure.

From the relations derived above, together with the properties of the gradient curve through the boundary when the latter is moving as a steady state, it is thus possible to obtain quantitative information concerning the variation of the transference number over the concentration interval across the boundary. Unfortunately, a concentration boundary moving as a steady state is seldom realized in practice and a more general solution of equation (7) would, therefore, be desirable.

It is a pleasure, indeed, to acknowledge my indebtedness to Dr. D. A. MacInnes of these Laboratories for his interest in this work and for the care with which he reviewed the manuscript.

Summary

The motion, under the influence of an electric current, of boundaries between two different concentrations of the same electrolyte has been studied with the aid of the schlieren scanning method for recording refractive index gradients. The displacements of such boundaries have been shown to be proportional to the change of the transference number with the concentration. Experiments with several salts have shown that the method compares favorably in precision with the direct moving boundary method and is supplementary to the latter since it is applicable to salts, and at concentrations for which the direct method is not suitable.

The schlieren patterns obtained yield information concerning the manner in which the transference number varies with the concentration in the range included by the boundary. This is discussed with the aid of the differential equation for concentration boundaries. A solution of this equation is given for the case in which one of the boundaries moves as a steady state and is shown to be in agreement with the experiments.

NEW YORK, N. Y. RECEIVED MAY 5, 1943

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Values of the Constants in the Debye–Hückel Equation for Activity Coefficients[1]

BY GEORGE G. MANOV, ROGER G. BATES, WALTER J. HAMER AND S. F. ACREE

In the determination of ionization constants and the pH values of acids and bases in moderate concentrations, the activity coefficient of an ion is expressed in terms of certain natural and derived constants. The Debye-Hückel equation is most widely used for this purpose. As the National Bureau of Standards is engaged in establishing pH standards, the recent note of Stonehill and Berry[2] on this subject makes it desirable to record the constants used by the Bureau for this purpose.

Recent summaries[3,4] of the values of the general physical constants, together with values of the dielectric constant of water,[5] permit an accurate calculation of the constants A and B in the Debye-Hückel expression for the activity coefficient of electrolytes in aqueous solutions. The constants A and B may be evaluated for non-aqueous solutions if the dielectric constant of the solvent is known. In general, $A = (1.82455 \times 10^6)/(DT)^{3/2}$ and $B = (50.2904 \times 10^{-8})/(DT)^{1/2}$ for any solvent.

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[1] (Not copyrighted.) After this manuscript was submitted, the Editor kindly gave us an opportunity to examine the galley proofs of related notes by Van Rysselberghe and by Scatchard (THIS JOURNAL, **65**, 1249, 1249 (1943)).

[2] H. I. Stonehill and M. A. Berry, THIS JOURNAL, **64**, 2724 (1942).

[3] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

[4] H. T. Wensel, *J. Research Natl. Bur. Standards*, **22**, 375 (1939), RP 1189.

[5] J. Wyman and E. N. Ingalls, THIS JOURNAL, **60**, 1182 (1938).

With the use of the values[6] of Wensel, of Cragoe, and of Birge, calculations were made of the quantity 2.30259 RT/F, and of the constants A and B in the expression

$$-\log f = \frac{A z_1 z_2 \mu^{1/2}}{1 + B a_i \mu^{1/2}} + \text{higher terms}$$

where f and μ represent, respectively, the activity coefficient and ionic strength for either the molar or molal concentration scale. Values of 2.30259 RT/F, and of A and B expressed in terms of unit volume of solution and unit weight of solvent are given in Table I for the temperature range of 0 to 100°. The values for both A and B for unit weight of solvent agree with those calculated by Scatchard's[1] equation within 0.0001.

TABLE I

VALUES OF A, B AND 2.30259RT/F FROM 0 TO 100°

Temperature, °C.	A (abs. units) in terms of unit vol. of soln.	A' (abs. units) in terms of unit weight of solvent	B (cm.$^{-1}$ × 10^8) in terms of unit vol. of soln.	B' (cm.$^{-1}$ × 10^8) in terms of unit wt. of solvent	2.30259RT/F (int. volts)
0	0.4883	0.4883	0.3241	0.3241	0.054179
5	.4921	.4921	.3249	.3249	.055171
10	.4961	.4960	.3258	.3258	.056163
15	.5002	.5000	.3267	.3266	.057154
18	.5028	.5025	.3273	.3271	.057749
20	.5046	.5042	.3276	.3273	.058146
25	.5092	.5085	.3286	.3281	.059138
30	.5141	.5130	.3297	.3290	.060129
35	.5190	.5175	.3307	.3297	.061121
38	.5220	.5202	.3314	.3302	.061716
40	.5241	.5221	.3318	.3305	.062113
45	.5296	.5270	.3330	.3314	.063105
50	.5351	.5319	.3341	.3321	.064096
55	.5410	.5371	.3353	.3329	.065088
60	.5471	.5425	.3366	.3338	.066080
65	.5534	.5480	.3379	.3346	.067071
70	.5599	.5537	.3392	.3354	.068063
75	.5668	.5596	.3406	.3363	.069055
80	.5739	.5658	.3420	.3372	.070046
85	.5814	.5722	.3434	.3380	.071038
90	.5891	.5788	.3450	.3390	.072030
95	.5972	.5857	.3466	.3399	.073022
100	.6056	.5929	.3482	.3409	.074013

The uncertainties in the tabulated values of A and B at 0, 25, 50, 75, and 100°, computed from the uncertainties in the natural and derived constants are, respectively: 0.26, 0.16, 0.18, 0.19 and 0.41%; 0.09, 0.06, 0.06, 0.07 and 0.14%. The value of 2.30259RT/F has an uncertainty of 0.011% at all temperatures.

The values of the higher terms are determined empirically. For non-polar compounds the magnitude depends mainly upon the variation of the dielectric constant of the solvent with the concentration of the electrolyte. For polar and resonant compounds, however, data obtained by e. m. f., spectrophotometric, dipole moment, Raman and infrared measurements indicate that the magnitude of the interionic forces is partially dependent upon specific effects arising from the resonant and polar structure of the ions and moles of the solvent and of the various solutes, such as indicators, buffers and salts.

The values in Table I do not differ appreciably from those previously employed.[7] The differences in $-\log f$ (or in pK and pH) thus calculated at an ionic strength of 1.0 and a_i values of 3 Å. and 5 Å., respectively, are 0.0001 and 0.0002 for uni-univalent, and 0.0004 and 0.0007 for bi-bivalent electrolytes. Use of the older values, especially for the charge on the electron (4.770 × 10^{-10} abs. e. s. u.) and for Avogadro's number (6.064 × 10^{23}), lead to differences of 0.0018, 0.0013, 0.0070 and 0.0053 unit for the cases cited above. The sign and the magnitude of these differences depend upon the relation between the two sets of values for A and B. Measurements made at this Bureau on cells without liquid junctions indicate that a precision of about 0.001 unit in $-\log f$ (or pH or pK) is attainable. However, routine measurements of pH made by different practical methods and equipment may involve relatively large uncertainties.[8]

It should be noted that an uncertainty of ±0.1% in the value of the dielectric constant for water accounts for the major portion (approximately 80%) of the total uncertainties in the values of A and B at 25°. More accurate values of D for water in the pure state and containing various electrolytes from zero to high concentrations are evidently desirable for use in these functions as well as in the Onsager expression for electrical conductivities.

It should be pointed out that use of the various groups of "self-consistent" constants given by different authors in the extrapolation of e. m. f. data will yield nearly the same value for the nor-

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(6) The values of T_0, R, F, c and the conversion factors given by Wensel[4] and by Birge[3] are practically identical. These values are T_0 = 273.16 ± 0.02; R = 8.3144 ± 0.0006 absolute joules mole^{-1} deg.$^{-1}$ derived from the value obtained for RT_0 by C. S. Cragoe, *J. Research Natl. Bur. Standards*, **26**, 495 (1941), RP 1393; F = (9.650 ± 0.001) × 10^4 int. coulombs·g. equiv.$^{-1}$; c = (2.99776 ± 0.00004) × 10^{10} cm. sec.$^{-1}$; 1 int. joule = 1.00020 ± 0.00005 abs. joules; 1 int. volt = 1.00034 ± 0.00003 abs. volts; and 1 int. coulomb = 0.99986 ± 0.00002 abs. coulomb. The uncertainties, except for T_0 and R, are the probable errors quoted by Birge. The uncertainty of 0.02° in T_0 is that given by Wensel. Since RT_0 is known much more accurately than T_0, the percentage error in R is practically the same as that in T_0. The value of the electronic charge, e, is taken as (4.8025 ± 0.0010) × 10^{-10} abs. e. s. u. The values used for N_0 and k, (6.0230 ± 0.0012) × 10^{23} mole^{-1} and (1.38044 ± 0.00036) × 10^{-16} erg. deg.$^{-1}$, respectively, are consistent with the above units for F, c, e and R.

(7) W. J. Hamer, J. O. Burton and S. F. Acree, *J. Research Natl. Bur. Standards*, **24**, 269 (1940), RP 1189.

(8) R. G. Bates, W. J. Hamer, G. G. Manov and S. F. Acree, *ibid.*, **29**, 183 (1942), RP 1495.

mal potential of the cell[7] and for the limiting values of the ionization constant and the *p*H. However, each group of constants when used in the Debye–Hückel equation to fit observed activity coefficients will yield slightly different values for a_i and higher terms, depending upon the range of the concentration chosen.

Summary

Numerical values of A and B in the Debye–Hückel equation for activity coefficients in terms of unit volume of solution and unit weight of solvent, and of $2.30259RT/F$ for use in e. m. f. equations, are given at temperatures from 0 to 100°. The natural constants were chosen from the tabulations of Birge and of Wensel. Contributions of dielectric constant of the medium and of resonance of the ions to the higher terms of Debye–Hückel equations are discussed.

WASHINGTON, D. C. RECEIVED APRIL 28, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL]

Raman Spectra of Amino Acids and Related Compounds. VI. Sarcosine, Ethanolamine, Choline, Betaine and Betaine Derivatives[1]

BY JOHN T. EDSALL

In previous papers of this series[1,2] the effect of ionization of the carboxyl and amino groups, and of methylation of the amino group, has been systematically studied by observations of the Raman spectra of amines, carboxylic acids, and amino acids. Certain characteristic relations between variation of spectrum and variation of structure were observed. The present study, which deals with several compounds more complex in structure than those earlier reported, shows that many of the same correlations may be clearly traced even in the complicated spectra here reported. Closely related substances, such as choline and betaine, are also found to show striking and characteristic differences in Raman spectra. All the spectra here reported were obtained in aqueous solution.

The **experimental technique** has already been fully described.[1,2,3] The **materials** employed were as follows: (1) **Sarcosine** (Hoffman–La Roche) was used without further purification, in aqueous solution, 20% by weight. Sarcosine **hydrochloride** solution was prepared from sarcosine by adding an equivalent quantity of hydrochloric acid, plus excess hydrochloric acid, to a concentration of approximately 0.5 molar. This excess acid served to repress the ionization of the carboxyl group, so that the observed spectrum should arise only from the sarcosine cation, not from isoelectric sarcosine. Hydrochloric acid dissolved in water at this concentration gives rise to no Raman lines. The final solution of the hydrochloride contained about 20% of sarcosine by weight; it was shaken with norit and filtered several times through a no. 42 Whatman filter paper, directly into the Raman tube, to remove traces of suspended particles and give an optically clear solution. This procedure for clarification of solution has been generally employed in these studies.

(2) **Betaine hydrochloride** (m. p. 246–247°) (Eastman Kodak Co.) was used without further purification in 35% solution by weight, containing excess hydrochloric acid (1 molar). **Betaine** (m. p. 293–294°) was prepared from

TABLE I

RAMAN SPECTRA OF SARCOSINE AND SARCOSINE HYDROCHLORIDE IN AQUEOUS SOLUTION

$(CH_3)\,^+NH_2\cdot CH_2COOH$		$(CH_3)\,^+NH_2\cdot CH_2COO^-$	
Sannié and Poremski	Edsall	Sannié and Poremski	Edsall
369 (4)	368 (2)	369 (4)	370 (3)
486 (1b)	490 (2)	487 (2b)	490 (2)
516 (0)	...	...	...
585 (0b)	568 (2)	601 (2b)	596 (1b)
...	675 ($^1/_2$)	680 (vb?)	679 ($^1/_2$b)
843 (1)	841 (1)	867 (1b)	867 ($^1/_2$)
909 (5)	903 (3)	927 (6)	930 (4)
965 (3)	964 (2)	964 (3)	960 (1)
...	...	996 (1)	...
1059 (5)	1055 (2)	1054 (1)	1053 (4)
1116 (?)	...	1105 (5b)	...
1153–74 (1b)	1163 (1)	1151–68 (2d)	1167 (1)
1291 (1)	1254 (1)	...	...
...	1284 (1)	1292 (2)	...
...	...	1309 (5)	1320 (3b)
...	...	1408 (8b)	1408 (6b)
1425 (2)	1429 (2)	...	...
1469 (5)	1464 (3)	1467 (8)	1468 (4)
1602 (0vb)	1622 (1vb)	1610–15 (3)	1633 (2vb)
1737 (3b)	1732 (1b)	...	...
...	2840 (2)	2837 (1)	2833 ($^1/_2$)
2932 (?)	...	2922 (1)	...
2977 (3)	2979 (6)	2974 (10)	2969 (8)
3034 (?)	3049 (3)	3038 (4)	3044 (2)

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(1) The preceding paper of this series is by J. T. Edsall and H. Scheinberg, *J. Chem. Physics*, **8**, 520 (1940). Some of the data in the present communication were briefly discussed in *Proc. Am. Soc. Biol. Chem.* (1938); see *J. Biol. Chem.*, **123**, xxxiii (1938); also Table IV in reference 2c below.

(2) (a) J. T. Edsall, *J. Chem. Physics*, **4**, 1 (1936); (b) **5**, 225 (1937); (c) **5**, 508 (1937).

(3) J. T. Edsall and E. L. Sagall, THIS JOURNAL, **65**, 1312 (1943).