TABLE V

THE ACTIVITY COEFFICIENT FUNCTIONS OF GLYCINE AT INFINITE DILUTION IN SODIUM CHLORIDE SOLUTIONS AT 25°

M	log γ_1	log γ_{h_1}	log γ_2	log γ_{h_2}
0.1	0.003	−0.217	−0.174	−0.039
.3	.009	− .278	− .200	− .069

It is seen from Table V that sodium chloride has a much more pronounced effect on the two functions, log γ_{h_1}, and log γ_2, which involve a product of two ionic activity coefficients than on log γ_1 and log γ_{h_2} which involve a ratio of ionic activity coefficients. The effect of sodium chloride on log γ_{h_1} and log γ_2 is similar to that found for the activity coefficient functions of other weak acids.[22]

The data in Table II can also be used to calculate $[-\log m_H]_{0,M} \equiv pI$ for the isoelectric point of glycine at infinite dilution in water and salt solutions. From the relation $pI = -(^1/_2)\log(K_1K_2/\gamma_1\gamma_2) = (pk_1 + pk_2)/2$ values of pI at 25° in water and 0.1 and 0.3 molal sodium chloride solutions are, respectively, 6.065, 5.979 and 5.969.

Acknowledgment.—The author wishes to thank Professors B. B. Owen and H. S. Harned for their helpful advice.

Summary

The thermodynamic ionization constants, K_1 and K_2, of glycine have been redetermined at 5° intervals from 10 to 50°. Good agreement with the results of Owen is obtained at 25° but not at higher and lower temperatures.

The effect of sodium chloride upon the second ionization of glycine, $k_2 = [m_Hm_G/m_Z]_{0,M}$, has been determined from the electromotive forces of hydrogen–silver chloride cells containing glycine–sodium glycinate–sodium chloride buffers at 5° intervals from 5 to 55° and at constant ionic strengths of 0.1 and 0.3 molal.

Equations for computing $-\log K_1$, $-\log K_2$ and $-\log k_2$ as functions of the temperature are given. From them, the derived thermodynamic quantities ΔF^0, ΔH^0, ΔC_p^0, and ΔS^0 associated with the two ionization reactions as well as $[\log \gamma_H\gamma_G/\gamma_Z]_{0,M}$, $[\log \gamma_{OH}\gamma_Z/\gamma_G a_{H_2O}]_{0,M}$ and $[-\log m_H]_{0,M}$ at the isoelectric point have been calculated and discussed.

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[22] Reference 4, Fig. 4, or reference 13, p. 525.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Application of the Onsager Theory of Ionic Mobilities to Self-diffusion

BY LOUIS J. GOSTING[1] AND HERBERT S. HARNED

Recently, by the use of radioactive tracer techniques, the self-diffusion of a number of ions[2,3,4,5] has been studied. Since there has been some confusion in the interpretation of these data, it seems desirable to view the situation from the standpoint of an expression derived by Onsager[6] which reduces to a limiting law for self-diffusion of an ion as a special case. In this way a clear-cut and direct presentation of the problem can be effected and the experimental accuracy required in its solution estimated.

The phenomena involved are best visualized by considering two different types of diffusion:

1. **Diffusion of a Single Salt.**—When a salt diffuses, electrical neutrality requires that both the positive and negative ions move with the same velocity. Under this condition, the ionic atmospheres suffer no deformation and the "time-of-relaxation effect" vanishes.[6–9] Further, the electrolyte moves in one direction and the solvent by replacing it moves in the opposite direction. This "electrophoretic" effect is an important factor in single salt diffusion and its computation is necessary. Finally, since the activity coefficient of the electrolyte is not constant throughout the diffusing system, it appears in the theoretical equation for the diffusion coefficient as a thermodynamic term $(1 + c\partial \ln y_\pm/\partial c)$ where $y_\pm$ is the activity coefficient of the salt and c is in moles per liter. The theoretical computation of some examples of salt diffusion has been examined in detail in a number of recent contributions.[10–13]

2. **Diffusion in a Solution Containing Three or More Kinds of Ions.**—Since more than two ions are present in the solution, they need not move with the same velocity. While a general treatment of this case is very complicated, a simple limiting law has been derived by Onsager[6] for the diffusion coefficient of an ion at very low concentration compared to that of the other ions present whose concentrations are essentially constant throughout the solution. The activity coefficient of the ion in question is then sensibly constant, since the ionic strength of the solution containing it is kept constant, and the thermodynamic term given above is simply unity. Since, however, the migrating ion has a velocity relative to the other ions, its atmosphere is asymmetric and the time-of-relaxation effect is not zero, and its computation provides the necessary and sufficient basis for the calculation of the limiting law for the variation of the diffusion coefficient of the "trace" ion with the total ionic concentration. The electro-

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[1] du Pont Fellow, Yale University, 1949–1950.

[2] Adamson, *J. Chem. Phys.*, **15**, 762 (1947).

[3] Adamson, Cobble and Nielson, *ibid.*, **17**, 740 (1949).

[4] Whitway, MacLennan and Coffin, *ibid.*, **18**, 229 (1950).

[5] Wang and Kennedy, THIS JOURNAL, **72**, 2080 (1950).

[6] Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

[7] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[8] Harned, *Chem. Revs.*, **40**, 461 (1947).

[9] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950.

[10] Harned and Nuttall, THIS JOURNAL, **69**, 736 (1947); **71**, 1460 (1949).

[11] Harned and Levy, *ibid.*, **71**, 2781 (1949).

[12] Harned and Blake, *ibid.*, **72**, 2265 (1950).

[13] Gosting, *ibid.*, **72**, 4418 (1950).

phoretic effect is negligible because it depends on the concentration of the diffusing ion.

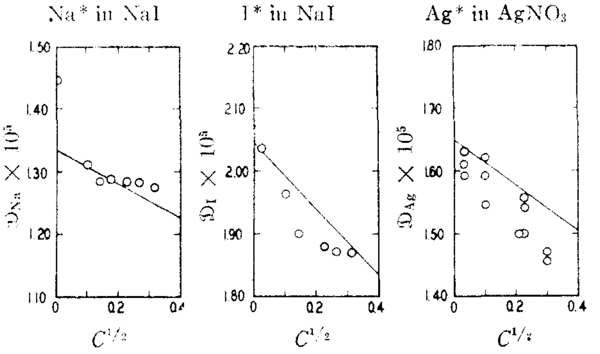

Fig. 1a. Fig. 1b. Fig. 1c.

Fig. 1.—Self-diffusion coefficients of radioactive sodium ion in sodium iodide (Fig. 1a), radioactive iodide ion in sodium iodide (Fig. 1b), and radioactive silver ion in silver nitrate (1c).

For this second type of diffusion, where one kind of ion is present in very small concentration in an electrolytic solution of otherwise nearly constant composition, Onsager's limiting law for the diffusion coefficient, $\mathfrak{D}_j$, of the j^{th} ion whose *transference number is very small* is

$$\mathfrak{D}_j = \omega_j\left[kT - \frac{\kappa e_j^2}{3D}\left(1 - \sqrt{d(\omega_j)}\right)\right] \tag{1}$$

where D is the dielectric constant, k the gas constant per molecule and T the absolute temperature. The equations

$$d(\omega_j) = \frac{\bar{\lambda}}{\bar{\Gamma}}\sum_i \frac{t_i}{(\omega_i + \omega_j)} \tag{2}$$

$$\bar{\lambda} = \sum_i n_i e_j^2 \omega_i \tag{3}$$

$$t_i = n_i e_i^2 \omega_i / \lambda \tag{4}$$

$$\kappa^2 = \frac{4\pi}{DkT}\Gamma \tag{5}$$

$$\bar{\Gamma} = \sum n_i e_i^2 \tag{6}$$

relate the function, $d(\omega_j)$, the conductance function, $\bar{\lambda}$, defined by equation (3), the inverse mean radius of the ionic atmosphere, κ, and the concentration function, $\bar{\Gamma}$, to the charge, e_i, the concentration, n_i, in molecules per unit volume, the transference number, t_i and the mobility, ω_i, of each ion in terms of summations over the i-ions present. The mobility, ω_i, is in cm. per sec. under a potential gradient of one dyne per cm. per molecule. By introducing the limiting ionic conductances, $\lambda_i^0 \propto \omega_i |z_i|$ in place of ω_i and the concentrations, c_i, in moles of ion per liter in place of n_i, equation (1) becomes

$$\mathfrak{D}_j = \frac{\lambda_j^0 RT}{|z_j| F^2} \times 10^{-7} - \frac{\lambda_j^0 |z_j| v^2 \epsilon}{3D} \times 10^{-9}\sqrt{\frac{4\pi}{1000DRT}}\left[1 - \sqrt{d(\omega_j)}\right]\sqrt{\Gamma} \tag{7}$$

where v is the velocity of light, ϵ is the electronic charge, R is the gas constant per mole, $|z_j|$ is the magnitude of the valence of the j^{th} ion and F is the Faraday. Equation (2) reduces to

$$d(\omega_j) = \frac{1}{\Gamma}\sum_i \frac{c_i |z_i| \lambda_i^0}{(\lambda^0/|z_j| + \lambda_i^0/|z_i|)} \tag{8}$$

and

$$\Gamma = \sum_i c_i z_i^2 \tag{9}$$

When only three kinds of ions are present, we let $j = 1$, and by equation (2) or (8)

$$d(\omega_1) = \left(\frac{|z_1|}{|z_2| + |z_3|}\right)\left(\frac{|z_2|\lambda_2^0}{|z_1|\lambda_2^0 + |z_2|\lambda_1^0} + \frac{|z_3|\lambda_3^0}{|z_1|\lambda_3^0 + |z_3|\lambda_1^0}\right) \tag{10}$$

since c_1 is negligibly small and $c_2|z_2| = c_3|z_3|$. For the case of self-diffusion, $|z_1| = |z_2|$ and $\lambda_1^0 = \lambda_2^0$, because the ionic conductances of the normal ion and the radioactive ion are practically identical. For the self-diffusion of 1–1 electrolytes where $|z_1| = |z_2| = |z_3| = 1$

$$d(\omega_1) = \frac{\lambda_2^0 + 3\lambda_3^0}{4(\lambda_2^0 + \lambda_3^0)} \tag{11}$$

in which 2 is the normal ion corresponding to the radioactive tracer and the ion of opposite charge is assigned the number 3.

Discussion

In Fig. 1 the Onsager limiting law, represented by the solid lines, is compared with recent experimental data for self-diffusion of the silver ion in silver nitrate,[4] and for the self-diffusion of both the sodium and iodide ions in sodium iodide solution.[5] The theoretical curves were computed by inserting the values,[14] $F = 96496$, $R = 8.3144 \times 10^7$, $T = 298.16$, $v = 2.9978 \times 10^{10}$, $\epsilon = 4.8024 \times 10^{-10}$, $D = 78.54^9$, $|z_1| = 1$ in equation (7) and the limiting ionic conductances,[15] $\lambda_{Na}^0 = 50.11$, $\lambda_I^0 = 76.8$, $\lambda_{Ag}^0 = 61.92$ and $\lambda_{NO_3}^0 = 71.44$, in equation (11). The resulting numerical equations for the diffusion coefficients in cm.^{2} sec.$^{-1}$ are

$$d(\omega_j) = 0.5526;\ \mathfrak{D}_{Na} \times 10^5 = 1.334 - 0.268\sqrt{c} \tag{12}$$

for radioactive ion in sodium iodide solution

$$d(\omega_j) = 0.4474;\ \mathfrak{D}_I \times 10^5 = 2.045 - 0.529\sqrt{c} \tag{13}$$

for radioactive iodide ion in sodium iodide solution and

$$d(\omega_j) = 0.5178;\ \mathfrak{D}_{Ag} \times 10^5 = 1.648 - 0.361\sqrt{c} \tag{14}$$

for radioactive silver ion in silver nitrate solution.

Although these results do not conform to the theory exactly, they are sufficiently close to the calculated values in the moderately dilute range of concentration to indicate that the theory is essentially correct. If this statement is true, then the experimental values at very dilute concentrations which fall considerably above the limiting law, such as the lowest concentration point (molality of the order of 10^{-4} to 10^{-5}) in Fig. 1a, are, for one reason or another, incorrect. In any case our procedure affords a logical method of approach to the problem. More accurate measurements will be required to prove the validity or invalidity of the limiting law. If this law ultimately proves to be exact, the deviations from it as the salt concentra-

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(14) Du Mond and Cohen, *Rev. Modern Phys.*, **20**, 82 (1948).

(15) MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 342.

tions increase will be a matter of considerable interest and importance. Another important test of the limiting law which must eventually be carried out is the diffusion of a trace ion in a salt solution whose ions are chemically different from the trace ion.

Summary

1. The Onsager equation for the diffusion coefficient of an ion at very low concentration in a salt solution of relatively high concentration has been adapted to the phenomenon of self-diffusion.

2. The limiting law of the theory has been derived and compared with experimental values of the self-diffusion of radioactive sodium ion and radioactive iodide ion in sodium iodide solutions, and of radioactive silver ion in silver nitrate solutions. The agreement between the theoretical predictions and experimental results is not exact but is reasonably satisfactory.

NEW HAVEN, CONN. RECEIVED JUNE 16, 1950

[CONTRIBUTION FROM DIVISION OF ANALYTICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Electrokinetics of Hydrogen Evolution.[1,2] II. Deuterium Overvoltage on Mercury

BY B. POST AND C. F. HISKEY

In a previous paper[3] measurements of hydrogen overvoltage on mercury cathodes were reported for a wide range of current densities and temperatures. Comparable measurements of deuterium overvoltage (*i.e.*, overvoltage in solutions of DCl in 99.8% D_2O) are described in this paper. From these measurements the value of the electrolytic separation factor of the hydrogen isotopes may be estimated and compared with the available experimental data.[4] It appears that these overvoltage and separation factor data enable us to exclude from consideration one mechanism which has been proposed as an explanation of hydrogen overvoltage.

Experimental

With the few exceptions to be noted below the apparatus and procedures employed in this investigation were identical with those described in ref. 3.

The use of deuterium and deuterium compounds necessitated the introduction of some minor changes in procedure. Dilution of the heavy water by light water had to be prevented. All equipment was dried carefully before use, and rinsed once by distilling several ml. of heavy water through the system. This water was then removed before the deuterium oxide which was to be used in the experiments was introduced.

Solutions of deuterium chloride in deuterium oxide were used as electrolytes. These were prepared by distilling heavy water onto anhydrous aluminum chloride and bubbling the evolved gas through the heavy water. This solution was subsequently distilled into the cathode compartment of the overvoltage cell.

In all runs the deuterium chloride concentration was 0.1 *M*. The acidity of the electrolyte solutions was determined by measuring the potential difference between a platinum black reference electrode in the cell and an external calomel electrode, as described in the previous paper.

Deuterium, purified in the gas train used for the hydrogen in the previous investigation, was used to flush the solutions and the overvoltage cells free of oxygen. All solutions were saturated with deuterium before use. The platinum black reference electrode within the cell served as a reversible deuterium electrode; overvoltages were measured between it and the working mercury cathode.

Experiments were made in duplicate in two cells differing only in cathode area (3.80 and 5.47 sq. cm.). About 50 ml. of deuterium oxide was used in each cell.

Results

Measurements were made at 4° (D_2O freezes at 3.8°), 11°, 20° and 10° intervals to 70°. Results of these measurements are listed in Table I.

TABLE I

DEUTERIUM OVERVOLTAGE ON MERCURY CATHODES

(0.1 *M* DCl)

Overvoltage (η) given in millivolts

i,				T, °C.				
amp./sq. cm.	4.0	11.0	20.0	30.0	40.0	50.0	60.0	70.0
1.0×10^{-6}	830	800	752	..	..	..	..	..
1.6×10^{-6}	850	824	780	..	..	..	..	..
2.5×10^{-6}	877	850	810	750	720	..	..	..
4.0×10^{-6}	902	873	842	790	750	710	..	..
6.3×10^{-6}	925	899	867	828	772	747	708	660
1.0×10^{-5}	949	919	890	850	810	770	738	706
1.6×10^{-5}	970	942	910	880	837	800	765	730
2.5×10^{-5}	990	969	932	900	860	829	792	762
4.0×10^{-5}	1012	995	958	927	880	850	822	788
6.3×10^{-5}	1039	1019	983	950	910	880	850	820
1.0×10^{-4}	1062	1040	1009	972	935	901	876	843
1.6×10^{-4}	1082	1063	1032	1000	960	931	902	870
2.5×10^{-4}	1109	1082	1052	1024	983	957	924	900
4.0×10^{-4}	1130	1110	1080	1050	1010	985	953	930
6.3×10^{-4}	1150	1132	1107	1074	1033	1009	984	957
1.0×10^{-3}	1175	1157	1128	1098	1060	1037	1008	982
1.6×10^{-3}	1200	1181	1150	1128	1087	1060	1038	1010
2.5×10^{-3}	1221	1204	1173	..	1110	..	1061	1040
4.0×10^{-3}	..	1230	1200	..	..	..	..	1070
6.3×10^{-3}	..	..	..	..	..	..	..	1100

Measurements made at current densities in excess of 10^{-5} amp./sq. cm. were reproducible to ±3 to 4 mv. in successive runs in one cell, and to ±6 mv. in separate cells using different batches of electrolyte and mercury.

As in the hydrogen investigation, it was found that measurements made at current densities less than 10^{-5} amp./cm.^{2}, above 20°, were generally unstable and showed marked deviations from a linear log i *vs.* η relation. In other regions investigated the relation between log i and η is linear.

Calculations of slopes of log i *vs.* η, and estimates of reproducibility are based on measurements made at current densities in excess of 10^{-5} amp./cm.^{2}.

Discussion of Experimental Results

Over the temperature and current density ranges investigated, deuterium overvoltages were from 50

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[1] This research was supported in part by a grant from the Office of Naval Research. That assistance is gratefully acknowledged.

[2] Some of this material was read before a meeting of the Metropolitan and Long Island Sections of the American Chemical Society, February, 1950, Brooklyn, N. Y.

[3] B. Post and C. F. Hiskey, THIS JOURNAL, **72**, 4203 (1950).

[4] See list of references in: A. H. Kimball, H. C. Urey and I. Kirschenbaum, "Bibliography of Research on Heavy Hydrogen Compounds," McGraw-Hill Book Co., New York, N. Y., 1949, pp. 285-286.