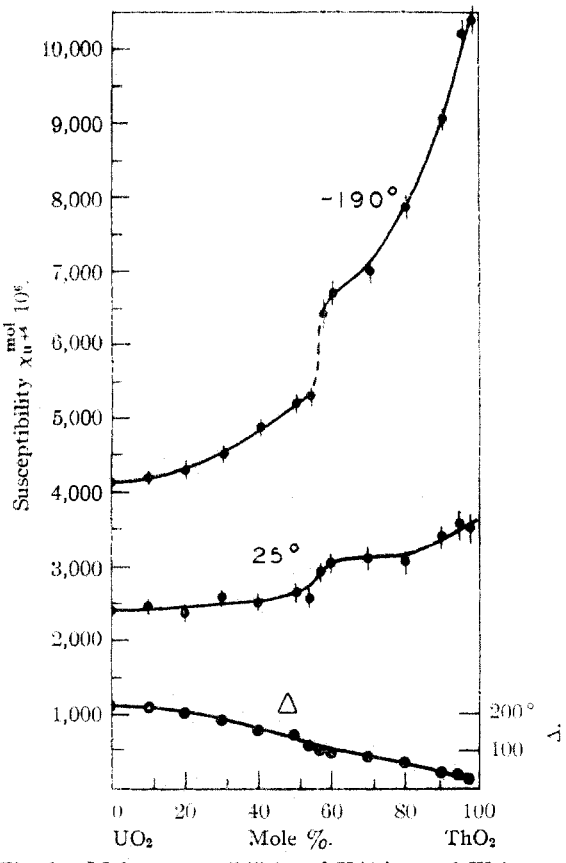

Fig. 1.—Molar susceptibilities of U^{+4} ion and Weiss constants of urania-thoria solid solutions.

108 to 290°, have all been reported.[6-9] These values, with the exception of that for UO_2, have been interpreted as proof for the $5f^2$ electron distribution in a $^3H_4$ state. The magnetic moment which may be derived for the gaseous U^{+4} ion in this state is 3.58 in LS coupling and 3.84 in jj coupling. By use of the $6d^2$ distribution with the $^3F_2$ state, analogous to the Ti^{+3} ion, there results a magnetic moment of 1.63 in LS coupling or 1.96 in jj coupling. For this reason, Hutchison and Elliott[8] rejected the $6d$ distribution.

A further possibility exists in the so-called "spin only" formula, which for two unpaired electrons gives a magnetic moment of 2.83 Bohr magnetons. The moment obtained from pure uranium dioxide is very close to this.[5] The present results with diluted solid solutions appear to confirm this result. If it is assumed that quenching of the orbital contribution occurs only for d electrons, then the results reported here must be interpreted as favoring the $6d^2$ distribution in tetravalent uranium.

Extrapolation of the susceptibility of U^{+4} to zero urania content permits a calculation of the magnetic moment for U^{+4} at infinite dilution. This procedure gives $\chi_{U^{+4}}^{mole} = 3600$ at 25° and 10600 ($\times 10^{-6}$) at −190°. This gives a moment for tetravalent uranium of 2.9 and 2.7, respectively, which shows even better agreement with the "spin only" formula.

Summary

The magnetic moment of tetravalent uranium has been determined in solid solutions of uranium dioxide with diamagnetic thorium dioxide in the concentration range 100 to 2% urania.

The molar susceptibility of the uranium rises sharply with increasing magnetic dilution, but this is due almost entirely to a diminution of the Weiss constant. The magnetic moment of the uranium shows little, if any, dependence on concentration. The moment at the greatest dilution is in agreement with the "spin only" formula for two unpaired electrons, and hence with the $6d$ rather than the $5f$ electron distribution.

EVANSTON, ILLINOIS RECEIVED MARCH 29, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Diffusion Studies on Dilute Aqueous Glycine Solutions at 1 and 25° with the Gouy Interference Method[1]

BY MARGARET S. LYONS AND JEAN V. THOMAS

The development of the Gouy interference method for diffusiometry[2-7] has provided a precise tool for the investigation of diffusion in solution. This method for the determination of diffusion coefficients makes use of the time-dependent refractive index gradient at the boundary between two solutions of different concentration. It is particularly useful in the study of non-electrolytes, since its expected accuracy of about 0.1% is much higher than that of other applicable methods.

Previous work[8] has shown that, even for systems which are nearly ideal in the thermodynamic

(1) This report is based upon theses submitted by Margaret S. Lyons and Jean V. Thomas to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degrees of Doctor of Philosophy and Bachelor of Science, respectively, in June, 1949.

(2) Gouy, *Compt. rend.*, **90**, 307 (1880).

(3) Longsworth, *Ann. N. Y. Acad. Sci.*, **46**, 211 (1945).

(4) Kegeles and Gosting, THIS JOURNAL, **69**, 2516 (1947).

(5) Longsworth, *ibid.*, **69**, 2510 (1947).

(6) Coulson, Cox, Ogston and Philpot, *Proc. Roy. Soc.* (*London*), **A192**, 382 (1948).

(7) Gosting, Hanson, Kegeles and Morris, *Rev. Sci. Instruments*, **20**, 209 (1949).

(8) Gosting and Morris, THIS JOURNAL, **71**, 1998 (1949).

sense, the measured diffusion coefficient is a function of concentration. For purposes of characterization, therefore, both the limiting value of the diffusion coefficient at infinite dilution and the concentration dependence of the coefficient may prove useful.

The present study of the diffusion of the dipolar ion, glycine, in aqueous solution was made by means of diffusion experiments at several concentrations of the solute (up to 4.8 g./100 ml.) and at the two temperatures, 1 and 25°. Such experiments yield specific refractive increment data in addition to the desired diffusion coefficients. The densities and viscosities of some glycine solutions were also measured so that the diffusion behavior of this amino acid could be related to some of its other physico-chemical properties.

Experimental Procedure and Calculations

Reagents.—Aminoacetic acid, C. P., from the Pfanstiehl Chemical Company, was used for the diffusion, viscosity, and density experiments. After being heated for 48–72 hours at 105°, duplicate samples of this reagent were found to have lost 0.068% in weight, and the loss was assumed to be the moisture content of the glycine. The ash content was determined as less than 0.02% noncombustible material. A high degree of purity was indicated also by conductance measurements at 0°. The data for 0.12 and 1.32 g. per 100 ml. solutions of glycine were consistent with the data of Mehl and Schmidt[9] well within the estimated experimental error of $\pm 5 \times 10^{-6}$ reciprocal ohms.

The glycine, whose weight *in vacuo* was corrected for moisture content, was dissolved and diluted to volume in flasks that had been calibrated to within 0.01%, using water saturated with air at the temperature of the experiment. All of the solutions used for diffusion experiments at 1 and 25° were within the *p*H range, 5.82–6.14, when the *p*H measurement was carried out at 25°. Solutions were not allowed to stand more than a few hours before use.

Diffusion Experiments.—The measurement of diffusion coefficients by the Gouy method has been described previously,[5,7,8] and in detail, but the essential features of the experiment, as performed in this Laboratory, may be outlined as follows:

A boundary between solutions of concentrations c_s and c_o was formed between the center and top sections of a Tiselius electrophoresis cell,[10-12] which had been aligned within the converging light from a single, long focal length lens. A capillary was inserted downward into the cell to the level of the optic axis, and through it liquid was withdrawn by siphoning until the boundary between solutions was centered on the optic axis and had been made as sharp as possible. During this procedure the fractional part of j_m, the number of wave lengths difference between the optical path through the solution of concentration, c_o, and that through the solution of concentration c_s, was determined. This was accomplished by employing the optical system as a double slit interferometer.[13] After formation of the sharp boundary, the capillary was withdrawn, and the double slits employed in the determination of the fractional part of j_m were removed from the optical path. The light from the horizontal slit source was then refracted by the diffusing boundary in the direction of increasing refractive index and formed a system of interference fringes, known as the Gouy phenomenon, at the focal plane of the optical system. Photographs of these fringes were taken after known times, t', had elapsed following the cessation of siphoning.

The distance, in the focal plane, between the undeviated slit image position and each zero of intensity in the Gouy fringe system, Y_j, is related to the experimental diffusion coefficient, D', by the equation[4]

$$Y_j = \{(j_m b\lambda)/(2\sqrt{\pi D't'})\}\, e^{-z_j^2} \equiv C_t e^{-z_j^2} \quad (1)$$

Here j is an integer corresponding to the given zero of intensity, b is the optical distance from the center of the diffusion cell to the focal plane (306.45 cm. at 1° and 305.56 cm. at 25°), and λ is the wave length of light used (5462.2 Å. *in vacuo*). The quantity, j_m, was determined by adding the fractional fringe displacement of Rayleigh interference bands measured during the boundary sharpening process to an integer one unit smaller than the number of bright fringes wholly or partly visible in the Gouy fringe system below the undeviated slit image position. The remaining factor, $e^{-z_j^2}$, relating j to the "reduced height" in the cell, z, was calculated for each fringe from the j for that fringe and j_m. It is a constant for a given fringe independent of the elapsed time of diffusion.

Since the term in braces in equation (1) should be a constant for all fringes at any given time of diffusion and may be denoted by the symbol C_t, this quantity was computed first from the most accurately known values of Y_j ($j = 1 - 10$). Then, employing the measured quantity, t', the average value of C_t for these fringes was used to calculate D'. In previous work[8] and in all the glycine diffusions studied D' was found to be a linear function of $1/t'$. This fact indicated that the diffusing boundary at $t' = 0$ was actually as blurred as though diffusion had taken place for the short time, Δt. The linearity of the plot permitted extrapolation of the function, D', to $1/t' = 0$, where Δt is negligible compared to t', and D' approaches D, the true diffusion coefficient for the system.[5] However, the extrapolation was susceptible to a consistent error which had to be avoided. The undeviated slit image position had been determined in effect before the diffusion experiment proper commenced,[8] and if the determination was in error by 2 microns, as it might have been, the consistent error in D' thus introduced would have increased non-linearly and become appreciable as $1/t'$ approached zero. The result of the error would have been that the plot of D' *vs.* $1/t'$ would have deviated slightly from linearity and that the extrapolation to infinite time no longer would have yielded the correct D. In all the experiments to be reported, this error was minimized by using only values of D' which would be affected by less than 0.04% by an error of 2 microns in the undeviated slit image position.

For the glycine diffusion experiments, a two-pronged stainless steel capillary siphon was substituted for the single capillary used before.[8]

The temperature of the diffusion thermostat was maintained at all times within 0.005° of the absolute temperature reported for the experiment.

Refractometric Measurements.—Specific refractive increments for the glycine have been calculated as before[8] from values of j_m, λ, and the cell thickness, a (2.4849 cm. at 1° and 2.4854 cm. at 25°). Following the previous procedure, these data were checked for a few cases, by studying the solutions used for the diffusion experiment in an auxiliary cell, with the aid of the double slit interferometer.

Density and Viscosity Determinations.—Specific gravities, determined from the loss in weight of a Pyrex bob suspended in the solutions and in water, were used to compute the densities, d, of six solutions of glycine at 1 ± 1° from the accepted density of water at that temperature. The concentrations of glycine ranged from 1 to 6 g. per 100 ml. solution. The flow times in an Ostwald viscometer at 1.00° of these same solutions were employed in the calculation of relative viscosities, η_r. A small kinetic energy term was found to be necessary in the calculations.

(9) Mehl and Schmidt, *J. Gen. Physiol.*, **18**, 467 (1935).

(10) Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

(11) Pappenheimer, Lundgren and Williams, *J. Exp. Med.*, **71**, 247 (1940).

(12) Longsworth, *Ann. N. Y. Acad. Sci.*, **41**, 267 (1941).

(13) Rayleigh, *Proc. Roy. Soc.* (*London*), **59**, 203 (1896).

Results

The data obtained from the diffusion experiments are summarized in Table I. Column 1 lists the average concentrations, $\bar{c}$, for each of the experiments. Since the diffusion coefficient obtained at a given $\bar{c}$ is not experimentally dependent on the concentration increment across the boundary (see reference (8) and the discussion of glycine experiments at $\bar{c} \cong 1.8$ and at 1.00° below), the diffusion coefficients reported are, within experimental error, differential coefficients corresponding to the stated concentrations.

TABLE I

SUMMARY OF DIFFUSION AND REFRACTOMETRIC DATA FOR AQUEOUS SOLUTIONS OF GLYCINE

1 $\bar{c}$[a]	2 Δc[b]	3 j_m	4 $10^3 \times \Delta n/\Delta c$	5 Δt, sec.	6 $D \times 10^5$, sq. cm./sec.	7 Av. dev., %
			1.00°			
0.25014	0.50028	43.47	1910.0 ± 1.7[c]	19.5	5.169	0.06
0.6001	1.2003	104.01	1904.9 ± 1.1[c]	7.1	5.107	.03
0.6002	1.2004	104.00	1904.5 ± 1.1	23.1[d]	5.097	.04
1.8008	1.2003	102.88	1884.2 ± 1.3	6.1	4.941	.04
1.8012	0.5029	43.10	1884.0 ± 1.9	15.6	4.942	.06
3.0015	1.2009	101.85	1864.3 ± 1.3[c]	9.9	4.793	.04
4.2003	1.1987	100.65	1845.8 ± 1.3	17.2	4.665	.02
			25.00°			
0.2503	0.5007	41.29	1812.4 ± 1.7	7.4	10.575	0.09
0.7203	1.2006	98.61	1805.1 ± 1.3	8.2	10.443	.02
1.1990	1.1987	98.14	1799.3 ± 1.3[c]	5.3	10.327	.03
1.7997	1.1999	97.92	1793.5 ± 1.3[c]	8.7	10.175	.03
2.9999	1.2016	97.30	1779.6 ± 1.3	10.5	9.885	.05
4.2017	1.2000	96.37	1765.0 ± 1.3[c]	7.6	9.547	.05

[a] $\bar{c} = (c_s + c_0)/2$, g./100 ml. solution. [b] $\Delta c = c_s - c_0$. [c] Checked by an independent refractometric measurement within 0.025%. [d] Boundary sharpened through a single capillary.

In column 2 are tabulated the concentration increments across the diffusion boundaries. It is estimated that the error introduced by volumetric preparation of each sample is about 0.01% in Δc. This error is combined with the estimated maximum errors of 0.02 in j_m and 0.03% in a[8] to obtain the errors listed in column 4 for the values of the specific refractive increment, $\Delta n/\Delta c$. As the footnote indicates, data from auxiliary refractometric determinations, referred to under "Experimental Procedure and Calculations," were used to confirm about half the specific refractive increments reported.

Columns 5, 6 and 7 record the results of applying the method of least squares to approximate D' as a linear function of $1/t'$. Eight to eleven values of D' at varying $1/t'$ were used for each calculation. The intercept of D' at $1/t' = 0$ is reported in column 6, and the "zero-time correction," Δt, derived from the slope of the linear function, appears in column 5. The "average deviation" of column 7 refers to the deviations of the experimental D' values from the straight line calculated for each experiment.

Since the diffusion coefficient of glycine is not independent of concentration, it is to be expected that the actual refractive index gradient across the boundary during a diffusion will differ to some extent from the ideal gradient assumed by the Kegeles and Gosting theory. The results of two diffusion experiments at 1.00° and at $\bar{c} \cong 1.8$ indicate that the error introduced by this experimental deviation from theory is negligible; for, if an appreciable error were caused by distortion of the ideal symmetrical refractive index gradient, its magnitude would be increased for the diffusion across the higher concentration increment, and the results of the two experiments would not agree. The present observation is in accord with previous findings.[8]

The marked consistency with the Kegeles and Gosting theory observed throughout the experiments is illustrated by the data of Table II. The theory predicts that the quantity $C_t\sqrt{t}$, where $t = t' + \Delta t$, should be the same constant for each fringe of the Gouy phenomenon at any time during a given diffusion experiment. Because a preliminary inspection of the data showed that $C_t\sqrt{t}$ for a given value of j did not vary with time except for the fringe, $j = 40$, of Experiment A, the average value of $C_t\sqrt{t}$ at each j, $\overline{C_t\sqrt{t}}$, is reported, and this quantity is seen to be practically independent of j. The variations observed at $j = 40$ of Experiment A may be accounted for

TABLE II

THE CONSTANCY OF $\overline{C_t\sqrt{t}}$ AS EVIDENCE OF THE CONSISTENCY OF DIFFUSION DATA WITH THEORY. GLYCINE DIFFUSIONS AT 1.00°

Minimum j	Experiment A $j_m = 43.10$ $\bar{c} = 1.8012$ $\Delta c = 0.5029$ Av. C_t for the 11 values of $t' = 1.491$ cm. $\overline{C_t\sqrt{t}}$	Experiment B $j_m = 102.88$ $\bar{c} = 1.8008$ $\Delta c = 1.2003$ Av. C_t for the 9 values of $t' = 2.544$ cm. $\overline{C_t\sqrt{t}}$
0	91.51 ± 0.03	218.49 ± 0.08
1	91.52 ± 0.04	218.48 ± 0.08
2	91.55 ± 0.04	218.58 ± 0.06
3	91.54 ± 0.03	218.57 ± 0.07
4	91.56 ± 0.02	218.52 ± 0.08
5	91.55 ± 0.04	218.52 ± 0.03
6	91.54 ± 0.04	218.53 ± 0.05
7	91.54 ± 0.04	218.53 ± 0.05
8	91.54 ± 0.04	218.56 ± 0.05
9	91.56 ± 0.04	218.56 ± 0.04
10	91.56 ± 0.04	218.57 ± 0.04
15	91.55 ± 0.05	
20	91.59 ± 0.09	218.49 ± 0.05
25	91.61 ± 0.11	
30	91.60 ± 0.15	218.50 ± 0.06
35	91.60 ± 0.26	
40	92.2 ± 1.7	218.58 ± 0.08
50		218.51 ± 0.10
60		218.54 ± 0.15
70		218.39 ± 0.20
80		218.58 ± 0.17
90		218.6 ± 0.7

by known optical errors of the diffusion equipment.

Three experimental factors, all related to the sharpness and stability of the initial boundary between the two solutions, appear to affect the magnitude of deviations from the constancy of $\overline{C_t\sqrt{t}}$ at varying j. These are: the sharpness of the initial boundary, as measured by Δt; the temperature of the solutions; and the concentration increment across the boundary. The lower temperature appears to favor a more ideal boundary, as does the greater difference in density between solutions. In the case of high concentration increments across the boundary, however, the consistency with theory may also reflect a reduction of relative error through the use of large Y_j values.

By the method of least squares, analytical expressions have been calculated for all the experimental results in terms of the glycine concentration. These are presented in Table III, together with the per cent. average deviation of the experimental data from the values calculated by means of the simple equations. The maximum concentration at which the expression is expected to hold also is given.

TABLE III

ANALYTICAL EXPRESSIONS FOR PHYSICAL CONSTANTS OF GLYCINE SOLUTIONS AS FUNCTIONS OF CONCENTRATION

Temperature = 1.00°

$D = 5.200\ (1 - 0.0303c + 0.0014c^2)\ 10^{-6}$ cm.²/sec. ± 0.08%; $c < 5$

$\Delta n/\Delta c = (1914.1 - 16.4c)\ 10^{-6}$ dl. soln./g. ± 0.02%; $c < 5$

$d = 0.99993 + 0.004584c - 0.00002 8c^2$ g./cc. ± 0.01%; $c < 6$

$\eta_r = 1 + 0.01364c + 0.00056c^2 \pm 0.03\%;\ c < 6$

Temperature = 25.00°

$D = 10.635\ (1 - 0.0241c)\ 10^{-6}$ cm.²/sec. ± 0.08%; $c < 5$

$\Delta n/\Delta c = (1813.5 - 11.4c)\ 10^{-6}$ dl. soln./g. ± 0.02%; $c < 5$

Discussion

It has been found[8] that the concentration dependence of the diffusion coefficient of sucrose in dilute aqueous solution is predicted with high accuracy by Gordon's[14] equation,

$$D = D_0\left[1 + c\frac{\mathrm{d}\ln f}{\mathrm{d}c}\right]/\eta_r \equiv D_0 q/\eta_r \qquad (2)$$

in which D_0 is the diffusion coefficient at infinite dilution, f represents the activity coefficient of the solute, and q is defined by the term in brackets. In deriving this equation, two assumptions were made: that the driving force for diffusion is the chemical potential gradient, and that the frictional coefficient for the diffusing particle is proportional to the macroscopic viscosity of the solution.

(14) Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

The results of applying Gordon's relationship to the data for glycine are shown in Table IV. Here column 2 lists the experimental diffusion coefficients for the mean concentrations tabulated in column 1. In column 3 will be found values for q, the thermodynamic correction factor defined by equation (2). For the determination of this factor ($[1 - 0.0283c + 0.00158c^2]$ at 1° and $[1 - 0.0209c + 0.00122c^2]$ at 25°), three sets of experimental data were employed. The isopiestic data of Smith and Smith[15] and of Richards[16] at 25° were recalculated on the basis of the Robinson and Stokes[17] values for the osmotic coefficients of their respective standards, sucrose and potassium chloride, and the results of the freezing point determinations of Scatchard and Prentiss[18] were made comparable by applying the thermal data of Gucker and co-workers.[19] A smoothed function for the osmotic coefficient of glycine at 25° was then found by averaging the results of the three experiments. In order to make use of this average osmotic coefficient at 1°, Gucker's thermal data were again applied. Densities determined in this laboratory at 1° and by Albright[20] at 25° were employed in the conversion of molal concentrations to our volume concentration units. The relative viscosities of column 4 were calculated at 1° from our analytical expression of Table III and at 25° from the linear function

$$\eta_r = 1' + 0.020_5 c \qquad (3)$$

interpolated between the 16 and 40° measurements of Bell and Madgin.[21]

TABLE IV

EXPERIMENTAL TESTS OF GORDON'S EQUATION

1	2	3	4	5	6
$\bar{c}$	$D \times 10^6$, sq. cm./sec.	q	η_r	$D \times 10^6/q$, sq. cm./sec.	$D\eta_r \times 10^6/q$, sq. cm./sec.
		1.00°			
0.25014	5.169	0.9930	1.0035	5.205	5.223
0.6001	5.107	.9836	1.0084	5.192	5.236
0.6002	5.097	.9836	1.0084	5.182	5.226
1.8008	4.941	.9541	1.0264	5.179	5.315
1.8012	4.942	.9541	1.0264	5.180	5.316
3.0015	4.793	.9292	1.0460	5.158	5.395
4.2003	4.665	.9089	1.0672	5.133	5.478
		25.00°			
0.2503	10.575	0.9949	1.0051	10.63	10.68
0.7203	10.443	.9856	1.0148	10.60	10.75
1.1990	10.327	.9767	1.0246	10.57	10.83
1.7997	10.175	.9663	1.0369	10.53	10.92
2.9999	9.885	.9483	1.0615	10.42	11.07
4.2017	9.547	.9337	1.0861	10.23	11.11

(15) Smith and Smith, *J. Biol. Chem.*, **117**, 209 (1937).
(16) Richards, *ibid.*, **122**, 727 (1938).
(17) Robinson and Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).
(18) Scatchard and Prentiss, THIS JOURNAL, **56**, 2314 (1934).
(19) (a) Gucker, Ford and Moser, *J. Phys. Chem.*, **43**, 153 (1939); (b) Gucker, Pickard and Ford, THIS JOURNAL, **62**, 2698 (1940).
(20) Albright, *ibid.*, **59**, 2098 (1937).
(21) Bell and Madgin, *J. Chem. Soc.*, 74 (1947).

If Gordon's equation is valid for the glycine–water system, column 6 of Table IV should contain constant values for the diffusion coefficient at infinite dilution, and these values should provide a check on the extrapolation of the experimental D to zero concentration. It is evident that the D_0 calculated by Gordon's equation deviates by more than experimental error from the experimental D_0, approaching it only as the concentration of glycine approaches zero. At 1° the deviation is directly proportional to the glycine concentration, but at 25° it approaches a maximum in the neighborhood of the highest mean concentration studied.

There is theoretical justification[22] for the employment of the thermodynamic factor, q, in equation (2), and an examination of the data used for its calculation indicates that it is in error by less than 0.5% even at the highest concentration. Therefore, the quantities $D \times 10^6/q$, shown in column 5, have been calculated in order to bring into evidence the magnitude of a frictional factor which, for this solute, should replace the relative viscosity in Gordon's equation. The required factor is found to increase linearly with the concentration at 1°, but at about one-fifth the rate at which the relative viscosity increases. At 25° the rate of increase of the frictional coefficient with concentration climbs from about one-fourth the rate of increase in relative viscosity to nearly three-fourths that rate at the highest concentration.

Since the observed behavior of sucrose is in accord with the assumption that the frictional coefficient of neutral particles in solution is proportional to the macroscopic viscosity of the solution, it is of interest to consider why glycine does not diffuse as though it were surrounded by a medium having the viscosity of the bulk solution. An explanation for this is provided by the suggestion of Robinson[23] that dipolar ions of glycine destroy the ice-like structure of the water solvent. Such a breakdown in structure would result in a lowered viscosity for those water molecules in the immediate vicinity of the glycine molecule which are most effective in hindering or facilitating diffusion. It would be expected that the viscosity of the solvent immediately surrounding the glycine molecule would be nearly independent of concentration and that the frictional coefficient of the solute would be affected only slightly by the relative viscosity of the bulk of the solution. As the amount of ice-like structure in the liquid water is much larger near the freezing point than at 25°,[24] the effect of the glycine should be and is especially noticeable at the lower temperature. At 25°, where the ice-like structure is not very extensive, the structure is largely broken down at the highest concentration studied; so that the rate of increase of the frictional factor is rapidly approaching the rate of increase of the relative viscosity.

The diffusion measurements are particularly sensitive to the loss of structure of liquid water in the presence of glycine because the diffusion rate is affected strongly by the conditions in the immediate neighborhood of the diffusing particle. However, other experimental data lend support to this qualitative explanation of the behavior of glycine solutions. Robinson[23] based his conclusions chiefly on calculations of the relative partial molal entropy of water in glycine solutions at 25°. From the data he presents, the differential entropy of dilution in excess of the ideally expected value is given in terms of the glycine molality, m, by

$$\bar{S}_1 - \bar{S}_1^0 = 0.0023m^2 \qquad (4)$$

The thermal and activity data cited in the present paper yield a corresponding equation for the system at 1°

$$\bar{S}_1 - \bar{S}_1^0 = 0.0141m^2 - 0.0040m^3 \qquad (5)$$

Robinson also points out that the relative viscosity of glycine solutions is low compared with that of solutions which do not exhibit a positive relative molal entropy for the solvent, *e. g.*, alanine solutions. The viscosity data presented herein constitute further evidence on this point. In addition, a decrease in volume of the solvent with increasing glycine concentration testifies to the collapse of the open, ice-like structure of the water in glycine solutions. At 25° the partial molal volume of the solvent is calculated from the density data to be

$$\bar{V}_1 = 18.016(1.0029 - 0.00001_8c^2) \qquad (6)$$

and at 1° it is

$$\bar{V}_1 = 18.016\ (1.0001 - 0.00002_8c^2) \qquad (7)$$

The entropy, viscosity and volume data all exhibit the temperature dependence which is expected from a consideration of the changing structure of liquid water.

An attempt has been made to correlate the diffusion results with the stepwise theory of viscosity and diffusion proposed by Eyring.[25] The theory is not applicable in its entirety to this system, but the basic concept of the replacement of one molecule by another through the formation of a hole in the liquid as the rate-determining step in diffusion may be employed. The glycine is about three times as large as the water molecule, and we will assume that the rate of diffusion is determined by the energy of activation required to move a water molecule from one equilibrium position in the liquid to the next. If the diffusion does progress by the shifting of water molecules in this manner, the energy of activation for diffusion of glycine should be the same as the energy of activation for viscous

(22) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).
(23) Robinson, *J. Chem. Phys.*, **14**, 588 (1946).
(24) Bernal and Fowler, *ibid.*, **1**, 515 (1933).
(25) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, N. Y., 1941, p. 477 ff.

flow of water. Applying the Arrhenius equation to the rates represented by the experimental quantities, D_0/T and $1/\eta$, at 1 and 25° (*cf.* Eyring's equations IX-28 and IX-112[25]), we find that the activation energy for diffusion at infinite dilution is 4275 cal./mole, while the activation energy for viscous flow of water is 4476 cal./mole. As it is unlikely that participation by the glycine molecule in the rate-determining step would decrease the activation energy for the process, it appears that the energy of activation may have been lowered by the breakdown of water structure in the vicinity of glycine molecules. It is of interest to note that the corresponding activation energy for the diffusion of sucrose[8] is 4641 cal./mole.

Thus the qualitative explanation of the observed concentration dependence of the diffusion coefficient of glycine in terms of the breakdown in structure of the water brought about by the presence of the solute is in accord with the interpretation of available results of entropy, viscosity, and volume determinations as well as with the conclusions to be drawn from the temperature dependence of the diffusion coefficient at infinite dilution.[26]

(26) The negative apparent molal compressibility reported for glycine by Gucker, Lamb, Marsh and Haag, THIS JOURNAL, **72**, 310 (1950), constitutes further evidence in support of Robinson's suggestion.

Acknowledgments.—The authors wish to express their appreciation of the interest and suggestions of Dr. J. W. Williams throughout the course of this research. They would also like to thank Dr. L. J. Gosting for permission to use the results of two diffusion experiments performed by him at 1°, and for his kindness in reading the manuscript of this paper. The research was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

Summary

The Gouy method for diffusiometry has been applied to the measurement of diffusion coefficients of glycine in aqueous solutions of concentrations up to 4.8 g. glycine per 100 ml. solution at 1 and 25°. Refractive index increments have been calculated from the results of the same experiments, and density and viscosity data were also obtained for glycine solutions at 1°.

The concentration dependence of the diffusion coefficients is not predicted correctly by Gordon's empirical equation, but the experimental behavior may be qualitatively explained by the suggestion of Robinson that glycine causes a breakdown in the ice-like structure of water.

MADISON, WISCONSIN RECEIVED MARCH 6, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Kinetics of the Base-catalyzed Methanolysis of Ortho, Meta and Para Substituted *l*-Menthyl Benzoates[1,2]

BY ROBERT W. TAFT, JR.,[3] MELVIN S. NEWMAN AND FRANK H. VERHOEK

Although the basic hydrolysis of esters has been the subject of numerous kinetic studies,[4] only one previous study of the kinetics and temperature coefficients of basic ester interchange[5a,b] has been made, and this involved a pseudo ester.[6] The present investigation was undertaken to provide quantitative data concerning the ester interchange reaction for esters of substituted benzoic acids. The kinetics of the reaction, the position of fission, and the effect of substituents in the acyl component of the ester on the rate were studied for the sodium methylate catalyzed reaction of a series of seventeen *ortho*, *meta* and *para* substituted *l*-menthyl benzoates with methanol. The rates of the ester interchange were measured at 30, 40 and 50°, enabling activation energies and $\log_{10} PZ$ factors to be calculated for each ester.

The *l*-menthyl esters were chosen in order that the rate of the reactions could be followed polarimetrically. Furthermore, by use of these esters it was possible to establish the position of fission in the methanolysis.

The effect on the reaction rates of the addition of water was also investigated.

(1) Taken from the dissertation submitted by Robert Wheaton Taft, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate school of the Ohio State University, 1949.

(2) Presented before the Organic Division of the American Chemical Society at Atlantic City, New Jersey, September 20, 1949.

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(4) For references see (a) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York and London, 1940, pp. 121, 184–197, 204, 211, 354–356 and 408–422; (b) Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, 2nd Ed., 1949, pp. 324, 408–422; also see Tomilla, *Ann. Acad. Sci. Fennicae*, Ser. A 57, No. 13, 3–24 (1941); No. 9, 3–12 (1941); No. 3, 3–34 (1942).

(5) (a) For equilibrium studies on alcoholysis of esters see Fehlandt and Adkins, THIS JOURNAL, **57**, 193 (1935); (b) kinetic studies of acid catalyzed ester interchange include the following: Dasannacharya, THIS JOURNAL, **46**, 1627 (1924); Patel and Watson, *J. Indian Inst. Sci.*, **16A**, 55–67 (1933); Rao, *J. Indian Chem. Soc.*, **20**, 69–75 (1943); Ducasse, *Bull. Soc. Chim.*, **12**, 918–920 (1945); Harfenist and Baltzly, THIS JOURNAL, **69**, 362 (1947); Farkas, Schachter and Vromen, *ibid.*, **71**, 1991 (1949).

(6) Schaefgen, Verhoek and Newman, *ibid.*, **67**, 253 (1945) (see also reference 13).