

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

A Study of the Diffusion of Glycolamide in Water at 25° with the Gouy Interference Method

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Using an improved Gouy diffusionmeter, the concentration dependence of the differential diffusion coefficient of glycolamide in water has been measured from 0 to 4 molar. Relative viscosity measurements are included to allow Gordon's equation to be tested for this system. Limiting values of the diffusion coefficient and refractive increment per mole for glycolamide are compared with corresponding values for its isomer, glycine, and the differences are discussed in terms of electrostriction.

In a recent publication¹ Longworth has reported diffusion coefficients for a series of amino acids, but diffusion data for the uncharged isomers of these compounds have not been available for comparison. The purpose of this paper is to present diffusion measurements as a function of concentration for glycolamide, the uncharged isomer of glycine, and thus provide additional information on the effect of molecular polarity. It has been shown² that polarity reduces the partial molal volume, \bar{V}_1 , of a solute because of electrostriction of the solvent by the charged solute molecules. Among relatively non-polar molecules a decrease in \bar{V}_1 correlates with a smaller molecular volume in solution and an increase in the diffusion rate, but as Longworth¹ points out dipole-dipole interaction between solvent and solute may increase the size of the diffusing aggregate thereby reducing the diffusion coefficient of a polar molecule. Electrostriction of the solvent by the solute should also cause glycine to have a greater specific refractive index increment than glycolamide. Both these hypotheses are borne out by the experimental data which follow.

As in earlier diffusion studies³⁻⁶ of two-component systems, relatively small concentration increments were used to ensure that differential values of the diffusion coefficient, D , are obtained, and it is believed that these values are correct to within 0.1%.

Experimental

Equipment.—The measurements reported in this study were made with equipment previously described,^{3,4,7} but for increased rigidity, precision and versatility the following modifications have been incorporated which will also allow the apparatus to be used for either the Gouy or integral fringe^{1,8,9} methods.

1. A new light source assembly consisting of a Gaertner L164 bilateral slit, filter holder, condenser lens and lamp house was constructed with these elements mounted in, or bolted on the ends of, a brass tube 2.5 inches in diameter. Bearings on the tube allowed rotation of the slit from a vertical to a horizontal position, and for focusing movement of the assembly along the optic axis was facilitated by mounting it on a lathe bed. The housing of the AH4 mercury lamp, used in conjunction with a 77A Wratten filter to isolate the green mercury line, was water cooled to prevent vertical movement of the slit due to heating of the slit mount. For

ease in alignment the mount was constructed to give adjustment in both vertical and horizontal planes.

2. To give greater reproducibility of the optical b distance and improved masking of the photographic plate a new camera was built and mounted, as was the source slit, on a lathe bed fixed between the I beams of the diffusion apparatus. The position of this bed relative to the I beams and the bath window mountings could be checked easily to better than 0.001 inch by means of stainless steel measuring rods fitting between contact points imbedded in the apparatus. The camera, photographic technique and plate-holder have been previously described.⁵

3. To obtain reproducible positioning of the diffusion cell, the cell-frame was kinematically suspended¹⁰ on $\frac{3}{4}$ -inch square brass bars which formed part of a rigid framework bolted directly to the I beams.

Diffusion reference corrections, δ , and the refractometer corrections, δ' , were obtained by averaging measurements of 6 and 3 sets of photographs, respectively. Two reference exposures were made for each diffusion or refractometer picture, with one taken before and one after the exposure through the cell. Values of δ employed in the calculation of D were obtained from a smooth graph of experimental δ values versus the glycolamide concentration. In no experiment was the maximum deviation from the mean greater than 3 microns. A graph of δ' versus concentration gave a straight line with an average deviation of one micron and in one instance the plot was used to obtain a value for δ' .

Previous papers^{5,6} have adequately described both the experimental technique and the method employed to calculate D . Measurements of the optical distance, b , during the course of these diffusion experiments yielded values from 307.85 to 307.88 cm., this small change with time being due to slight inelastic sagging of the cross bars supporting the cell frame. Ten diffusion pictures were taken during each experiment and values of D' were computed from either the first 6 or 8 minima using the Airy integral refinement¹ of the quarter wave approximation. It has been shown¹¹ that this refinement is adequate when more than fifty fringes are employed. Mean deviations of the experimental points from the least squared lines obtained by plotting D' against the reciprocal of t' ranged from ± 0.017 to $\pm 0.078\%$. The bath temperature, which at all times was within a hundredth of a degree of 25°, remained constant to $\pm 0.002^\circ$ during the course of each experiment. Observed diffusion coefficients, D , at each absolute temperature T , were corrected to 25.00° using the Stokes-Einstein relation $(D\eta/T)_{25.0} = (D\eta/T)_{\text{exp}}$ where η is the viscosity of water.

Solutions.—Glycolamide crystals prepared from ethyl glycolate¹² by the ammonolysis procedure of Gucker and Ford¹³ were recrystallized twice with centrifugal drainage from absolute ethanol, and then dried for six hours at 60° *in vacuo*. The total yield of purified material was 78%. On further heating under the same conditions a sample of this product gave a loss in weight of only 1 part in 10,000. A portion of the above sample was recrystallized a third time, and using a calibrated thermometer melting points of the second and third recrystallizations were both found to be in the range 115.7–115.9°, in agreement with the value of 115.8° obtained by Stokes.¹⁴ Refractive index measure-

- (1) L. G. Longworth, *THIS JOURNAL*, **74**, 4155 (1952).
- (2) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943, p. 159.
- (3) L. J. Gosting and M. S. Morris, *THIS JOURNAL*, **71**, 1998 (1949).
- (4) M. S. Lyons and J. V. Thomas, *ibid.*, **72**, 4506 (1950).
- (5) L. J. Gosting, *ibid.*, **72**, 4418 (1950).
- (6) L. J. Gosting and D. F. Akeley, *ibid.*, **74**, 2058 (1952).
- (7) L. J. Gosting, E. M. Hanson, G. Kegeles and M. S. Morris, *Rev. Sci. Instruments*, **20**, 209 (1949).
- (8) J. St. L. Philpot and G. H. Cook, *Research*, **1**, 234 (1948).
- (9) H. Svensson, *Acta Chem. Scand.*, **3**, 1170 (1949).

- (10) J. D. Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1938, p. 585.
- (11) L. J. Gosting and L. Onsager, *THIS JOURNAL*, **74**, 6066 (1952).
- (12) Obtained from the Matheson Co., Inc., East Rutherford, N. J.
- (13) F. T. Gucker and W. L. Ford, *J. Phys. Chem.*, **46**, 309 (1941).
- (14) R. H. Stokes, *Trans. Faraday Soc.* (in press).

ments relative to water on both the above samples gave values of $\Delta n/\Delta C$ equal to 9.308×10^{-3} in experiments where 0.2500 *N* glycolamide diffused into water.

Solutions of glycolamide, molecular weight 75.068, were prepared by weight with air-saturated, doubly-distilled water as solvent. Molarities, *C*, were calculated from the weight percentages *in vacuo* and the density data of Gucker and Ford¹³

$$d = 0.997074 + 0.019065C - 0.000129C^2 \quad C \leq 4.5 \quad (1)$$

Viscosity Measurements.—Using an Ubbelohde type viscometer with a water flow time of 283.2 sec., relative viscosities were determined on portions of the solutions made up for diffusion. In each case calculation of the relative viscosity required a small kinetic energy correction term.

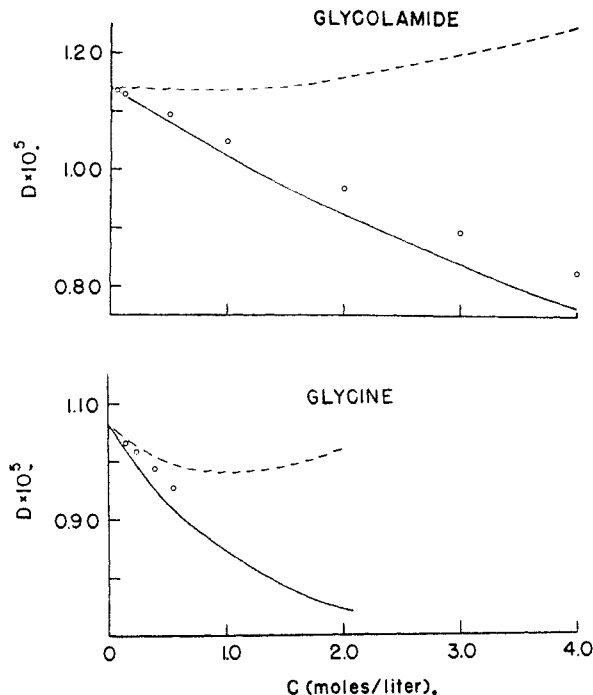


Fig. 1.—The concentration dependence of diffusion coefficients of glycolamide and glycine in water at 25°: O, experimental values; - - -, equation (7); —, equation (5).

Results

Values of the diffusion coefficients, *D*, obtained at mean concentrations $\bar{C} = (C_1 + C_2)/2$ and concentration increments $\Delta C = C_2 - C_1$ are tabulated in column 5 of Table I. To obtain suitable precision most of the experiments reported were designed to give approximately 100 fringes, but to assist in the evaluation of the limiting diffusion coefficient two experiments giving fewer fringes were made. To represent the experimental diffusion coefficients the method of least squares was used to obtain the quadratic expression

$$D \times 10^5 = 1.142_3 - 0.0956_4C + 0.00410_3C^2 \quad C \leq 4 \quad (2)$$

with an average deviation of $\pm 0.08\%$.

Refractive increments per mole were calculated using the relationship $\Delta n/\Delta C = \lambda j_m/(a\Delta C)$ where j_m is the total number of fringes, λ is the wave length, 5460.7 Å., of the green mercury line and *a* is the cell thickness, 2.486₂ cm. These refractive index increments of glycolamide, column 3, which are referred to the refractive index of air as unity, may be represented by the equation

$$(\Delta n/\Delta C) \times 10^3 = 9.312 - 0.056_4C + 0.0021_3C^2 \quad C \leq 4 \quad (3)$$

with an average deviation of $\pm 0.04\%$.

TABLE I

DIFFUSION COEFFICIENTS OF GLYCOLAMIDE IN WATER, *T* = 25.00°

1	2	3	4	5	6	7
\bar{C}	ΔC	$\frac{\Delta n/\Delta C}{\times 10^3}$	Δt	$\frac{D}{D_0} \times 10^5$ cm. ² sec. ⁻¹	$1 + C \frac{d \ln \gamma}{dC}$	$\frac{D_0}{D} \times 10^5$ cm. ² sec. ⁻¹
0.06004	0.12008	9.310	18.5 ^b	1.1366	0.9994	1.1444
.10000	.20000	9.306	3.8	1.1345	.9990	1.1476
.12490 ^a	.24980	9.308	7.0	1.1300	.9988	1.1463
.49951	.24902	9.282	91.9 ^c	1.0944	.9970	1.1575
.99983	.25018	9.255	9.4	1.0492	.9986	1.1707
2.00018	.24998	9.209	2.8	0.9688	1.0163	1.1948
2.99961	.25098	9.152	8.1	0.8925	1.0522	1.2088
3.99998	.24993	9.127	10.2	0.8251	1.0950	1.2340

^a The glycolamide for this experiment was part of the sample that had been three times recrystallized. ^b This starting time correction was obtained using a single pronged capillary. In all other experiments a double pronged capillary was used to sharpen the boundary. ^c This large value probably indicates a disturbance of the initial boundary while withdrawing the capillary from the cell. Since *D* from this experiment is consistent with values obtained in other experiments, it seems that unusually large values of Δt , while undesirable, do not necessarily invalidate an experiment.

The measured relative viscosity data are reproduced by the cubic equation

$$\eta_{rel} = 1 + 0.104_3C + 0.0084_5C^2 + 0.0013_2C^3 \quad C \leq 4.2 \quad (4)$$

with an average deviation of $\pm 0.06\%$.

Discussion

Diffusion coefficients of dilute sucrose solutions are represented³ accurately by the semi-empirical equation of Gordon¹⁵

$$D = D_0 \left[1 + C \frac{d \ln \gamma}{dC} \right] / \eta_{rel} \quad (5)$$

where *D*₀ is the limiting value of *D* as *C* → 0, γ is the activity coefficient of the solute on the molarity scale and η_{rel} is the macroscopic relative viscosity of the solution. This equation is similar to that proposed by Onsager and Fuoss¹⁶ except that the change in mobility, Ω/C , with concentration is approximated by the reciprocal of η_{rel} . If experimentally determined values of *D*, η_{rel} and $[1 + C d \ln \gamma/dC]$ are substituted into equation 5 the resulting values of *D*₀ will be constant if this equation is valid.

The extent of the deviations for glycolamide are shown in column 7. Similar deviations have been observed for urea, glycine and potassium chloride.⁴⁻⁶ In computing column 7, relative viscosities were obtained from equation 4, and the thermodynamic factor, $[1 + C d \ln \gamma/dC]$, column 6, for glycolamide was calculated from the isopiestic data of Stokes,¹⁴ by least squaring his experimental osmotic coefficients, ϕ , to obtain the analytical expression in terms of molality, *m*

$$\phi = 1 - 0.033_1m + 0.0040_7m^2 - 0.00025_1m^3 \quad m \leq 5.5 \quad (6)$$

with an average deviation of $\pm 0.06\%$. It is interesting to note that on the molarity scale glycol-

(15) A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

(16) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

amide is thermodynamically ideal up to one molar, *i.e.*, the factor $[1 + C d \ln y/dC]$ of the Onsager-Fuoss diffusion equation¹⁶ is approximately equal to one.

Relative contributions of the factors in Gordon's relation are seen for glycolamide in Fig. 1 where the experimental points, represented by circles, were extrapolated to $C = 0$ to obtain D_0 for computing predicted values of D (solid line) from equation 5. The contribution of the thermodynamic term alone (dashed line) was obtained from

$$D = D_0[1 + C d \ln y/dC] \quad (7)$$

For comparison Fig. 1 also presents corresponding data for glycine derived from previous isopiestic,¹⁷ density,¹⁸ viscosity¹⁹ and diffusion⁴ measurements. While for both compounds deviations from Gordon's equation are somewhat similar, the graph of D versus C for glycolamide has the smaller limiting slope, making for more ideal diffusion. Since the limiting diffusion coefficient for glycine is lower than that for glycolamide, it is evident that the moving aggregate is larger for the former compound, in agreement with the concept of electrostriction. The magnitude of the effects of dipole-

(17) E. R. Smith and P. K. Smith, *J. Biol. Chem.*, **117**, 209 (1937).

(18) F. T. Gucker, W. L. Ford and C. E. Moser, *J. Phys. Chem.*, **43**, 153 (1939).

(19) L. S. Mason, P. M. Kampmeyer and A. L. Robinson, *THIS JOURNAL*, **74**, 1287 (1952).

dipole interaction is better seen by comparing equations 2 and 3 with the equations of Lyons and Thomas⁴ for glycine at 25° in the form

$$D \times 10^6 = 1.063_5 - 0.192_4 C \quad (8)$$

and

$$(\Delta n/\Delta C) \times 10^3 = 13.61_4 - 0.64_2 C \quad (9)$$

Electrostriction, which makes the partial molal volume and partial molal heat capacity of glycine smaller than those of glycolamide,¹⁶ is seen to produce an inverse effect on the limiting values of $\Delta n/\Delta C$.

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The Chemical Thermodynamic Properties of 3-Methylthiophene from 0 to 1000°K.¹

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An experimental study has been made of various thermodynamic properties of 3-methylthiophene in the solid, liquid and vapor states (12 to 473°K.). The entropy of the liquid at 298.16°K., 52.18 ± 0.10 cal. deg.⁻¹ mole⁻¹, was computed from measured values of the heat capacity of the solid and liquid and the heat of fusion (2518 cal. mole⁻¹ at the triple point, 204.19 ± 0.05 °K.). Experimental results obtained for the heat capacity of the liquid [$C_{p,liq}$], the heat of vaporization [ΔH_v], the heat capacity in the ideal gaseous state [C_p°], and the second virial coefficient [$B = (PV - RT)/P$] are represented by the empirical equations: (1) $C_{p,liq}(\text{liq.}) = 46.074 - 0.17610 T + 6.8006 \times 10^{-4} T^2 - 6.8021 \times 10^{-7} T^3$, cal. deg.⁻¹ mole⁻¹ (207 to 337°K.); (2) $\Delta H_v = 13,593 - 13.913 T$, cal. mole⁻¹ (329 to 389°K.); (3) $C_p^\circ = -1.375 + 9.4508 \times 10^{-2} T - 4.2587 \times 10^{-5} T^2$, cal. deg.⁻¹ mole⁻¹ (375 to 473°K.); and (4) $B = 75 - 94.56 \exp(1000/T)$, cc. mole⁻¹ (329 to 473°K.). From determinations of the heat of combustion, the standard heat of formation [ΔH_f° (liq.)] of 3-methylthiophene from graphite, hydrogen and rhombic sulfur was found to be 10.49 ± 0.20 kcal. mole⁻¹ at 298.16°K. Calorimetric, spectroscopic and molecular structure data were used to compute the functions $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S° and C_p° at selected temperatures from 0 to 1000°K. The height of the potential barrier to internal rotation (*ca.* 600 cal. mole⁻¹) required for these calculations was evaluated from the experimental entropy and vapor heat capacity data. Values of ΔH_f° , ΔF_f° and $\log_{10} K_p$ for the formation of 3-methylthiophene in the ideal gaseous state from graphite, hydrogen and gaseous diatomic sulfur, were computed from the thermodynamic functions and appropriate calorimetric data.

An investigation of the chemical thermodynamic properties of thiophene³ initiated the experimental and computational program conducted in this Laboratory to obtain thermodynamic data for organic sulfur compounds that occur in crude petroleum or are produced in refining processes. The primary

(1) This investigation was performed as part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurements of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyoming.

(2) University of Lund, Lund, Sweden.

(3) G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, *THIS JOURNAL*, **71**, 797 (1949).

purpose of these investigations is to provide accurate data for key members of the important families of sulfur compounds. These data will then be used to construct, by approximate statistical mechanical methods,⁴ relatively complete tables of the chemical thermodynamic properties of organic sulfur compounds.⁵

This paper presents the results of detailed studies of the thermodynamic properties of 3-methylthio-

(4) *E.g.*, (a) K. S. Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39**, 435 (1946); (b) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

(5) The compilation and tabulation of selected values of the properties of organic sulfur compounds will be part of the program of American Petroleum Institute Research Project 44.