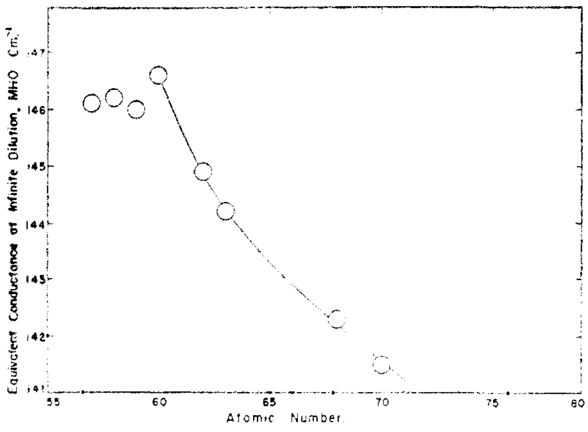

Fig. 3.—Variation of equivalent conductances at infinite dilution with atomic number for rare earth chloride solutions

$Nd_2(SO_4)_3 \cdot 8H_2O$ will show only one coördination number. At the present time there is insufficient evidence for conclusions to be made. Any speculations or deductions as to the causes of deviations from the Onsager law, etc., are being reserved for later papers after data for transference numbers, activity coefficients, partial molal volumes, heats of dilution and other properties have been obtained.

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

A Study of the Diffusion of Urea in Water at 25° with the Gouy Interference Method[1]

BY LOUIS J. GOSTING AND DAVID F. AKELEY

The variation with concentration of the diffusion coefficient, *D*, of urea in water has been measured in the concentration range from 0 to 4 molar. These values of *D* are self-consistent to within about 0.1%, and it was established that the results obtained are differential diffusion coefficients. As the Gouy interferometer measures the optical path difference between the two solutions forming each diffusion boundary, refractive index data for the system were also obtained.

Measurements with the Gouy interference method of the diffusion coefficients, *D*, of sucrose[2] and glycine[3] in water have shown the method to yield values which are self-consistent to within 0.1%, while a more recent investigation[4] of the diffusion of potassium chloride yielded data which were equally consistent with the results that Harned and Nuttall obtained with their conductance method.[5] At higher potassium chloride concentrations where the conductance method could not be used, the values of *D* obtained by Stokes[6] with an improved diaphragm cell are in good agreement with data from the Gouy method. Since the accuracy of the Gouy method thus appears to be well established, it may now be used with confidence to investigate the variation of *D* with concentration for different systems in order to test present theories and to provide a basis for future theoretical work on this transport process. This paper reports results of measurements on the urea–water system.

Experimental

Our measurements were made with the same equipment[2,3,7] used for the sucrose and glycine diffusion studies, except that a twin double-slit[4] was utilized to form an improved reference pattern for the diffusion pictures. The diffusion reference correction, δ, and the refractometer reference correction, δ', were each obtained by averaging measurements of 3 to 5 separate sets of photographs in each experiment, but the value of δ used for each experiment was taken from a smoothed plot of all δ values *versus* the concentration.

A Wratten 77A filter served to isolate the green line of an AH4 mercury lamp used to illuminate the source slit. The optical distance, *b*,[8] from the center of the diffusion cell to the emulsion of the photographic plate was found to be 304.5₂ cm.; while the cell thickness, *a*, along the optic axis, was shown to be 2.486₂ cm. by direct measurement with a traveling microscope and also with a special inside caliper.

In most experiments diffusion took place from a solution containing C_2 moles per liter into a more dilute solution of concentration C_1, rather than into water. All initial boundaries were sharpened by withdrawing from 90 to 140 ml. of liquid at a rate of about 4 ml. per minute from the cell through a two-pronged stainless steel capillary adjusted to the level of the optic axis. The second when sharpening was stopped was taken as the start of the diffusion; then the capillary was withdrawn from the cell. From 10 to 15 Gouy fringe photographs were taken over a period of about four hours in each experiment, and, using the Airy integral refinement[2] of the "quarter-wave approximation,"[9] apparent diffusion coefficients, D', were calculated from measurements of fringe minima numbered 1 through 8. To correct for slight but unavoidable imperfections in each initial boundary, D' was plotted against the reciprocal of the observed time for each experiment.[10] The intercept and slope of this line were determined by the method of least squares to give the correct diffusion coefficient, *D*, and the starting time correction, Δt. Values of Δt ranged from 3.4 to 7.7 seconds, while the mean deviation of points from the straight lines varied from 0.024 to 0.056%.

During all experiments the bath temperature was maintained constant to within ± 0.002°. Since the mean temperature of each experiment was always within 0.005° of

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[1] Presented before the Division of Physical and Inorganic Chemistry at the XIIth International Congress of Pure and Applied Chemistry, New York City, September, 1951.

[2] L. J. Gosting and M. S. Morris, THIS JOURNAL, **71**, 1998 (1949).

[3] M. S. Lyons and J. V. Thomas, *ibid.*, **72**, 4506 (1950).

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[5] H. S. Harned and R. L. Nuttall, *ibid.*, **71**, 1460 (1949).

[6] R. H. Stokes, *ibid.*, **72**, 2243 (1950); **73**, 3527 (1951).

[7] L. J. Gosting, E. M. Hanson, G. Kegeles and M. S. Morris, *Rev. Sci. Instruments*, **20**, 209 (1949).

[8] Here $b = \sum_i l_i/n_i$, where l_i is distance along the optic axis in each medium, *i*, of refractive index n_i, relative to air as unity.

[9] G. Kegeles and L. J. Gosting, THIS JOURNAL, **69**, 2516 (1947).

[10] L. G. Longsworth, *ibid.*, **69**, 2510 (1947).

25.000°, the small shift in correcting measured values of D to 25.000° was made with the equation

$$(D\eta/T)_{25^\circ} = (D\eta/T)_{\text{exp}} \qquad (1)$$

where T is absolute temperature, η is taken as the viscosity of water, and subscript exp denotes the experimental temperature.

Urea Solutions.—Following the procedure of Gucker and Ayres,[11] C.P. urea was recrystallized twice from conductance water using centrifugal drainage. The temperature was not allowed to exceed 60° and the final crystals were dried *in vacuo* at 55° for six hours after grinding in an agate mortar. The melting point of the urea was found to be 132.7–132.9° as read from a thermometer calibrated against a standard platinum resistance thermometer. This was in good agreement with the value of 132.6–132.8° reported by Gucker and Ayres.[11] Upon attempting to use the method of Glasgow, Streiff and Rossini[12] to obtain melting and cooling curves, noticeable decomposition of the urea occurred and the observed melting point was low (129.8–130.0°). Solutions were prepared by weight, using air-saturated double-distilled water as the solvent.[2] Taking the molecular weight of urea as 60.058, the weight per cent. of urea in vacuum was converted to moles per liter of solution, C, at 25° using the equation of Gucker, Gage and Moser[13] for the solution density, d.

$$d = 0.997074 + 0.0159686C - 1.3958 \times 10^{-4}C^2 + 2.593 \times 10^{-6}C^3 \qquad (2)$$

Urea purified in the above manner lost only 0.02% of its weight on drying *in vacuo* at room temperature for two weeks. Further drying for seven hours *in vacuo* at 65° resulted in an additional loss of about 0.03%, though a considerable amount of sublimation had occurred as indicated by crystals on the cooler parts of the desiccator. The difficulty of obtaining complete dryness may be a limit to the accuracy of the refractive index data given below.

Results

The experimental values of the diffusion coefficient, D, at different mean concentrations, $\bar{C} = (C_2 + C_1)/2$, are presented in column 4 of Table I. From the concentration increments, $\Delta C = C_2 - C_1$, and the total number, j_m, of fringes in each experiment, the refractive increments per mole, $\Delta n/\Delta C$, were computed from the values of the cell dimension, a, and the wave length, λ 5460.7 Å., of the mercury green line. Here $\Delta n = \lambda j_m/a$ and is referred to air as unity.

To show that these values of D are differential values, the data reported in Table II were obtained by keeping the mean concentration constant at 0.248 molar while varying the concentration increment across the boundary. Since there was no significant drift with ΔC in these values of D, it became possible to consider $\bar{C}$ as equivalent to C, and to use the relatively large value of 0.25 molar for ΔC in the experiments reported in Table I.

Determination of the constants in a quadratic equation by the method of least squares leads to the relation

$$D \times 10^5 = 1.381_7 - 0.0783_0C + 0.00464_6C^2 \quad C \leqslant 4 \qquad (3)$$

which expresses our values of D in Table I with an average deviation of 0.05%. Likewise, the following relation expresses the refractive index measurements in column 3 to 0.1% or better in $(n - n_0)$

$$n = n_0 + 8.613 \times 10^{-3}\,C - 4.4_3 \times 10^{-5}C^2 + 1.8_3 \times 10^{-6}\,C^3 \quad C \leqslant 3 \qquad (4)$$

where n is the refractive index of the solution and $n_0 = 1.3339771$ is the refractive index of water[14] for the green line of mercury.

TABLE I

DIFFUSION COEFFICIENT OF UREA IN WATER AS A FUNCTION OF THE CONCENTRATION, $\bar{C}$; $T = 25.00_0$°.

1 $\bar{C}$	2 ΔC	3 $(\Delta n/\Delta C) \times 10^3$	4 $D \times 10^5$, sq. cm./sec.	5 $[1 + C\,\partial \ln y/\partial C]$	6 $D_0 \times 10^5$ sq. cm./sec.
0.1250_1	0.2500_3	8.604	1.372_5	0.995_5	1.385_2
$.2475_0$	$.2499_8$	8.593	1.362_8	$.991_2$	1.387_8
$.5000_0$	$.2499_8$	8.569	1.343_3	$.983_2$	1.393_0
$.7500_1$	$.2500_4$	8.547	1.326_4	$.976_2$	1.399_8
$.9782_0$	$.2939_0$	8.534	1.308_6	$.970_6$	1.402_6
1.0000_3	$.2500_7$	8.524	1.307_4	$.970_1$	1.403_4
1.5000_4	$.2499_9$	8.487	1.274_0	$.960_6$	1.412_9
2.0000_5	$.2499_1$	8.458	1.244_8	$.954_9$	1.422_7
3.0001_6	$.2502_5$	8.400	1.189_0	$.954_4$	1.432_8
3.9999_4	$.2498_0$	8.329	1.142_5	$.968_7$	1.435_8

TABLE II

VALUES OF D AT A MEAN CONCENTRATION, $\bar{C}$, OF 0.248 FOR DIFFERENT CONCENTRATON INCREMENTS, ΔC; $T = 25.00_0$°

$\bar{C}$	ΔC	j_m	$(\Delta n/\Delta C) \times 10^3$	$D \times 10^5$ sq. cm./sec.
0.2491_2	0.1967_6	76.93	8.587	1.362_6
$.2475_0$	$.2499_8$	97.80	8.593	1.362_8
$.2475_3$	$.3499_2$	136.88	8.592	1.362_6
$.2475_0$	$.4949_9$	193.66	8.593	1.363_7

Discussion

Onsager and Fuoss[15] have shown that the variation of D with concentration for undissociated molecules may be expressed in terms of a mobility, Ω/C

$$D = RT\,(\Omega/C)\,[1 + C\,\partial \ln y/\partial C] \qquad (5)$$

where R is the gas constant, T is the absolute temperature and y is the activity coefficient of the solute on the C scale. Since the variation of Ω/C with C has not been calculated theoretically for non-electrolytes, it is of interest to compare our data with Gordon's equation[16,17]

$$D = D_0[1 + C\,\partial \ln y/\partial C]/\eta_{rel} \qquad (6)$$

in which D_0 is the limiting value of D as $C \rightarrow 0$, and the change of mobility with concentration has been approximated by the reciprocal of the macroscopic relative viscosity, η_{rel}, of the solution.

If equation (6) held for the diffusion of urea in water, D_0 computed from it at different concentrations would be constant. That this relation is only approximate for this case is seen from the drift in values of D_0 in column 6 of Table I which were computed by inserting the experimental values of D from column 4 into equation (6). For this calculation the equation

$$\ln y = -0.0373_0C + 0.00368_4C^2 \qquad (7)$$

was used to represent the isopiestic data of Scatchard, Hamer and Wood[18] in order to evaluate the thermodynamic term, $[1 + C\,\partial \ln y/\partial C]$, which is

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tabulated in column 5 to indicate its change with C, while the expression

$$\eta_{rel} = 1 + 0.037_0C + 0.0043_4C^2 \qquad (8)$$

was chosen to represent the data of several workers[19–22] for the relative viscosity of urea solutions. Since discrepancies exist between these viscosity data, equation (8) may be in error by a few parts per thousand. It will be noted, however, that the values of D_0 drift by more than this amount.

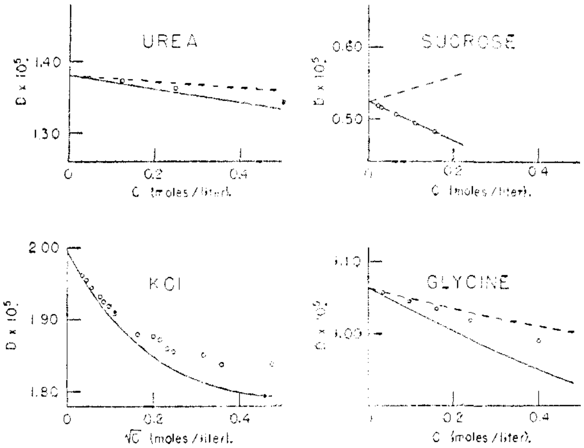

Fig. 1.—The variation with molarity, C, of diffusion coefficients of four compounds in aqueous solution at 25°: O, experimental values; - - - -, equation (9); ——, equation (6).

To demonstrate the manner in which each term of equation (6) varies with concentration, and to illustrate similarities in deviations from this equation, curves have been drawn, Fig. 1, for four systems whose diffusion coefficients have been determined with an accuracy of about 0.1%. Experimental values, represented by circles, are taken from the literature for potassium chloride,[4,5] glycine[3] and sucrose[2] while data for urea are from Table I. The solid lines represent variations in D with C predicted by equation (6) using values of D_0 determined by extrapolation of experimental data for the non-electrolytes, and from the Nernst limiting law for potassium chloride. Dashed lines were computed from the expression

$$D = D_0\,[1 + C\,\partial \ln y/\partial C] \qquad (9)$$

in which the mobility, (Ω/C), of equation (5) is held constant at its limiting value and the entire variation of D with C is attributed to the thermodynamic term.

It has been shown previously[5,23] that the data for potassium chloride are well represented up to 0.3 N by the complete Onsager–Fuoss theory[15] which predicts from the interionic attraction theory an appreciable variation of (Ω/C) with C. Since η_{rel} changes very little[21] over this concentration range, neither equation (6) nor equation (9) could be expected to hold for this salt. It is to be noted that the experimental points lie above the solid curve. This is also true of the other results except for the sucrose data which are well represented by equation (6) over the concentration range shown. While the data for both urea and glycine lie between the values predicted by equations (6) and (9), the less polar urea appears to conform more closely to equation (6). Additional experiments are planned on relatively non-polar solutes to see whether their diffusion coefficients, like those of sucrose, agree with equation (6) in relatively dilute solutions.

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