region, the rapid increase of the cross sections for all of the product ions with decreasing energy is best accounted for by assuming complex ion formation. The presence of atom transfer product ions in this region confirms this assumption. In the higher energy region, it is believed that the products arise as a result of an exchange of charge and kinetic energy during direct head-on collisions between the incident ions and the CCl_4 molecules.

One of the reasons for undertaking this investigation was to learn more about the role of ion–molecule reactions in chemical reactions of energetic species produced as a result of nuclear transformation. In the deuteron bombardment of compounds containing carbon, N^{13} is formed as a multiply charged positive ion. Recent work[6] on the deuteron bombardment of methanol, to which various rare gases were added, has indicated that the hot reactions involved ionic species, at least in part. Furthermore, the proposed mechanism involved CN ions and probably CN radicals as intermediates.

The ion–molecule reaction studied here which has the most direct bearing on such hot atom reactions is the one involving N^+ primary ions. The presence of significant amounts of $NCCl^+$ as a product of the N^+ reactions in the present experiment suggests an ionic mechanism to explain the NCCl obtained as a final product in the deuteron bombardment experiment mentioned above. The production of CN^+ in the N^+ reactions with CCl_4 is also compatible with the proposed mechanism in the case of deuteron-irradiated methanol. Of course the relative roles of ionic and neutral species in the over-all chemistry of reactions initiated by nuclear transformations cannot be evaluated without knowledge of the relative cross sections for reactions involving both species. However, it should be noted that, in Fig. 7, the cross sections are rising rapidly as the incident ion energy decreases in the 10-e.v. region. The flattening of the curves in the 5-e.v. region is believed to be largely instrumental since it is not observed in the case of the more intense N_2^+ primary beam. The probability of an ion–molecule reaction before the ion is neutralized depends on its cross section for reaction relative to that for neutralization and the steady-state concentrations of ions, electrons, and gas molecules. The behavior of the reaction cross section as the ion kinetic energy approaches bond energies suggests that the probability of reaction before the ion is neutralized may become significant under some conditions. For example, if the electron concentration is small relative to the ion concentration owing to the presence of gases with high electron attachment coefficients, ion–molecule reactions might be expected to play an important role in chemical effects of nuclear transformation.

Acknowledgment.—G. R. H. is indebted to the H. A. B. Dunning Foundation for a fellowship and to N.S.F. for a Summer National Science Foundation Fellowship.

[CONTRIBUTION FROM THE BIOPHYSICS DIVISION, SAHA INSTITUTE OF NUCLEAR PHYSICS, CALCUTTA-9, INDIA]

Measurement of the Diffusion Coefficients of Sucrose in Very Dilute Aqueous Solutions Using Jamin Interference Optics at 25°

BY AMALA CHATTERJEE

RECEIVED JUNE 24, 1963

Diffusion coefficients of sucrose in very dilute solutions have been measured at 25° as a function of concentration with the help of the Jamin interference optics and a microdiffusion cell. The details of the method have been described and the results compared with those obtained by Gosting and Morris with the help of the Gouy method at 25°. A very satisfactory agreement has been obtained.

Gosting and Morris[1] measured the diffusion coefficient of sucrose in aqueous solutions (25°) in the concentration range 0.75 to 5.25% (g./100 ml.) with the help of the Gouy method. On the other hand, English and Dole[2] performed the same experiments with supersaturated solutions of sucrose using a newly designed diffusion cell and observed that their data and those of Gosting and Morris fitted excellently on the same straight line when plotted in the same scale. The latter authors further observed that the schlieren method was far less consistent than the Gouy method in the measurement of the diffusion coefficient. The object of the present investigation is (1) to measure the diffusion coefficient of sucrose with the help of Jamin interference optics using a microdiffusion cell and to compare the results with those obtained by Gosting and Morris with the help of Gouy method, and (2) to extend the measurements to comparatively more dilute solutions of sucrose at 25°.

Experimental

Materials and Methods.—The diffusion experiments were carried out in a Tiselius type of microdiffusion cell (widths along and perpendicular to the light path are 5 and 1 mm., respectively) provided in the Antweiler microelectrophoresis diffusion equipment, where the quantity of the sample required was about 0.3 ml. A source of white light produced the interference fringes and the color sensitivity of the eye was used to detect the change in the solute concentration at any level of the cell occurring in the course of the diffusion process. A minimum concentration difference of about 10^{-5} g./ml. of sucrose can be easily detected with this system. The details of the optical arrangements and the sensitivity of the equipment have been described by Antweiler[3,4] elsewhere.

In the present method, different points along the height of the cell can be scanned in steps of 0.1 mm. The refractive increment Δn or the corresponding change in concentration ΔC compared to a reference channel is obtained directly as a function of x. This leads to a curve given by the well known diffusion equation

$$C_x = C_0/2\left[1 - 2/\sqrt{\pi}\int_0^{x/\sqrt{4Dt}} \exp(-x^2/4Dt)\, \mathrm{d}(x/\sqrt{4Dt})\right] \quad (1)$$

where C_x is the concentration at a distance x from the initial boundary at an instant after the formation of the boundary. Equation 1 may be written as

$$C_x/C_0 = {}^1/_2\int_{x/\sqrt{4Dt}}^{\infty} 2/\sqrt{\pi}\, \exp(-x^2/4Dt)\mathrm{d}(x/\sqrt{4Dt}) \quad (2)$$

Since the values of the probability integral

$$2/\sqrt{\pi}\int_{hx}^{\infty} \exp(-h^2x^2)\mathrm{d}(hx),\ h = 1\sqrt{4Dt}$$

are tabulated in standard texts for different hx one can prepare a table relating $x/2\sqrt{Dt}$ with any measured value of C_x/C_0 and this

(1) L. J. Gosting and M. S. Morris, *J. Am. Chem. Soc.*, **71**, 1998 (1949).
(2) A. C. English and M. Dole, *ibid.*, **72**, 3261 (1950).
(3) H. J. Antweiler, *Chem. Ing. Tech.*, **5**, 284 (1952).
(4) H. J. Antweiler, *Mikrochim. Acta*, **36**, 561 (1951).

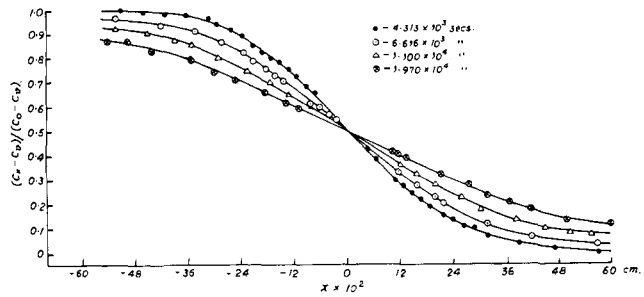

Fig. 1.—Solute concentration distribution in the diffusion cell at different times in the process of diffusion; $C = 2.07 \times 10^{-3}$ g./ml.

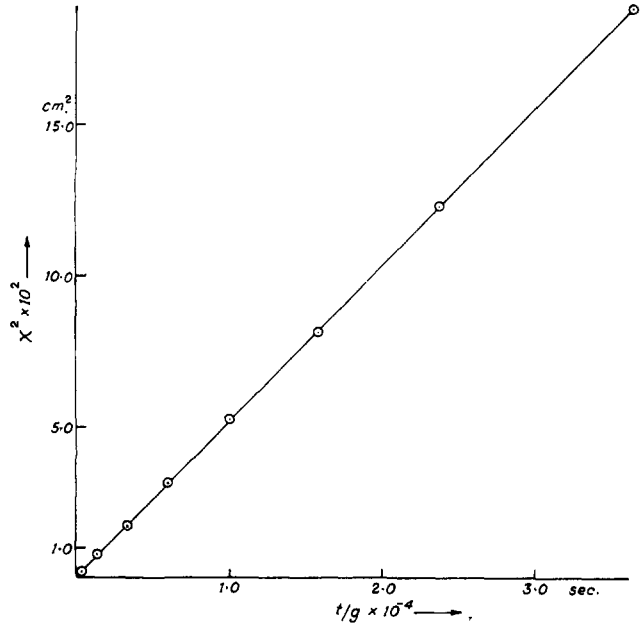

Fig. 2.—Determination of the average value of the diffusion coefficient, D', at $t = 1.100 \times 10^4$ sec. D' was obtained equal to 5.2096×10^{-6} cm.²/sec.

relation may be represented by

$$D = x^2/t \times g(C_x/C_0) \qquad (3)$$

With the help of such a previously prepared table the diffusion coefficient D may be obtained from the measured value of C_x/C_0 and t.

Often it is more practical to have the diffusion not between the concentration C_0 and 0 but between two solutions of concentrations C_0 and C_v ($C_0 > C_v$). In this case, eq. 3 becomes

$$D = x^2/t \times g(C_x - C_v/C_0 - C_v) \qquad (4)$$

With the help of the foregoing method, the diffusion coefficient of Merck reagent grade sucrose was measured. A small amount of sucrose was weighed in a semimicrobalance and dissolved in distilled water volumetrically. To determine the concentration of the solution a measured volume of this solution was taken in a weighing bottle, dried in a desiccator for weeks until the weight became constant, the weight of the empty bottle being known previously. The experiments were performed by allowing the sucrose solution of concentration C_0 to diffuse against the same solution of lower concentration C_v, the difference in concentration being always of the order of 2×10^{-3} g./ml. After filling, the cell should remain in the apparatus at least for 20 min. before the layering is done, in order that the temperature equilibration ensues. The layering is then done simply by sliding the lower half of the cell from the filling position to the measuring position. As the width of the measuring channel along the sliding direction is only 1 mm., the whole operation can be completed very smoothly within a few seconds with a little bit of practice. The whole process of layering can be viewed through an auxiliary optical system. At a time t after the layering of the two solutions, the whole cell covering a length of about 4 cm. was scanned. From the dial reading the fraction $C_x - C_v/C_0 - C_v$ was obtained directly and plotted against x. Large numbers of such individual measurements of $C_x - C_v/C_0 - C_v$ for different cell height positions were made in each time and a best fitting smooth curve was

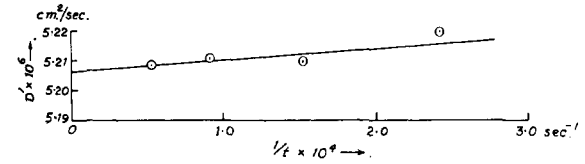

Fig. 3.—Illustration of a typical zero time correction for the data obtained from Fig. 1.

drawn through these points. Next, the intercept of the ordinate between the uppermost and lowermost positions of the curve was divided into twenty equal parts (which can be accurately done by simple adjustment of the ordinate scale), each division thus corresponding to $C_x - C_v/C_0 - C_v = 0.05$. Now, corresponding to any two symmetrical values of $C_x - C_v/C_0 - C_v$ (*e.g.*, 0.05 and 0.95, etc.), the corresponding cell height positions were noted, the distance between which gave the value of $2x$. Thus from one experimental curve a number of values (about 10) of the diffusion coefficient (eq. 4) were obtained and the average of these actually corresponded to the value of the diffusion coefficient D' at the time of measurement concerned. In order to take into account the time interval involved during the layering process, the values of the diffusion coefficient obtained for different times were plotted against the corresponding values of $1/t$ and extrapolated to $1/t = 0$. This gave the diffusion coefficient $D(\bar{C})$ at the mean concentration $\bar{C} = (C_0 + C_v)/2$. All the experiments were performed at a temperature 25 ± 0.01°. Freshly prepared solutions of sucrose were used in each experiment.

In respect to the present method of measurement a few additional points, however, need to be mentioned. The basic steps behind this method of measurement are similar to those of the Rayleigh fringe method. As the diffusion coefficient of sucrose is concentration dependent,[1] the first-order effects of this dependence in the measurement of D were eliminated following the theory established by Creeth[5]: (i) by measuring the distance between cell levels which correspond to symmetrical values of $C_x - C_v/C_0 - C_v$ (0.95 and 0.05, etc., as stated beforehand) and then using eq. 4 in calculating the value of D; and (ii) by keeping the value of ΔC very small.

For such small values of ΔC, the highest accuracy in the individual measurements of $C_x - C_v/C_0 - C_v$ is obviously of the order of 0.3%. These errors in the individual measurements are, however, not carried as such to the calculated value of D' corresponding to any particular time of measurements, as these errors are largely smoothed out by drawing the best fitting symmetrical curve and making subsequent deductions from the smooth curve and not from the individual experimental points, as described beforehand. Although the individual percentage errors of the measurements vary, the actual scatter of an experimental point about the smooth curve did not exceed a fixed value irrespective of the values of x (the maximum possible scatter depending on the minimum concentration difference measurable, *i.e.*, 10^{-5} g./ml. remains the same for all the measurements), and in a fairly expanded scale it was found not to exceed one small division (along the ordinate) of a millimeter graph. Thus from a large number of such experimental points (all not shown in Fig. 1 to avoid clumsiness) the best fitting curve can be drawn with considerable accuracy. If, in any case, the experimental scatters are wider or the two halves of the best fitting curve do not look symmetrical the corresponding data are at once rejected. As a further check, all the experimental curves obtained at different times of measurements for a particular run must cross at a single point, which is supposed to be the initial boundary position.

The measurements of the cell height (x) could be done by raising or lowering by every 0.1 mm. an optical table containing the interference system with the help of a crank. A full rotation of the crank, comprising ten discrete steps (accurately machined) at intervals of 36°, raises or lowers the table through a distance of 1 mm. A very high degree of accuracy is obtainable in this system[3] so that the contribution of the possible errors in the measurements of x to the scatter of the experimental points can be assumed to be negligible.

Further, the time t used in the calculation of D' was obtained by adding half of the time interval needed to scan the cell to the time at which the scanning was started. With some practice, the cell can be scanned in about 2 min. From the symmetry of the curve and from the pairing method adopted in the deduction of D', it can be reasonably assumed that the error that may thus be introduced is practically negligible.

Results and Discussion

A typical set of experimental curves describing the concentration distribution in the cell at different times from the initial layering is shown in Fig. 1.

(5) J. M. Creeth, *J. Am. Chem. Soc.*, **77**, 6428 (1955).

In Fig. 2 is shown a plot of x^2 against t/g, as obtained from one of the curves shown in Fig. 1. The slope of the least-square line drawn through these points gave the diffusion coefficient, D', corresponding to the particular time of measurement (see eq. 4). The closeness of the experimental points to the connecting straight line reveals the consistency of the present method of measurement. The maximum standard deviation in the different sets of data, obtained in the present series of experiments, from which the average values of D' were deduced, was about 0.3%. This may be compared with the corresponding value of 0.1% (from Table I of ref. 1, for $J_m \simeq 100$) obtainable by the Gouy method. A typical zero time correction has been illustrated in Fig. 3. From the intercept and slope of the least-square line the value of Δt was obtained as 8 sec., and the extrapolated value of D' to $1/t = 0$ or $D(\bar{C})$ was obtained equal to 5.206×10^{-6} cm.^{2}/sec., with an average deviation from the least-square line, ΔD equal to 0.035%. The values of the diffusion coefficient, $D(\bar{C})$, thus obtained for different mean solute concentrations $\bar{C}$ are shown in Table I.

TABLE I

THE DIFFUSION COEFFICIENT OF SUCROSE AT DIFFERENT CONCENTRATIONS (25°)

$\bar{C}$, 10^3 g./ml.	ΔC, 10^6 g./ml.	Δt, sec.	$D(\bar{C})$, 10^6 cm.^{2}/sec.	ΔD, %
1.06	2.12	0	5.219	0.031
2.07	2.20	8	5.206	.035
3.02	2.18	7	5.200	.038
4.07	2.10	15	5.190	.039
5.00	2.02	16	5.188	.019
10.60	2.80	4	5.145	.025

In this table column 3 gives the values of Δt and column 5 gives the values of ΔD as obtained for the respective cases. For the sake of comparison the values of $D(\bar{C})$ were plotted along with the data of Gosting and Morris (25°) and shown in Fig. 4. As the present set of measurements were carried out in a lower concentration range, a test experiment was performed with a mean solute concentration (1.06%) within the range used by Gosting and Morris. It can be seen from Fig. 4 that there is excellent agreement of the present data with those of Gosting and Morris both within and outside the concentration range used by them. The least-square line relating $D(\bar{C})$ with $\bar{C}$,

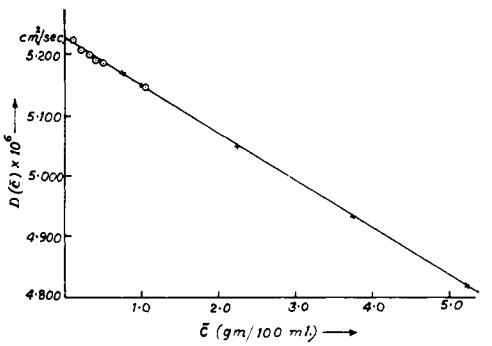

Fig. 4.—Plot of $D(\bar{C})$ against $\bar{C}$; × represents the data of Gosting and Morris, ⊙ the data of present work.

as obtained from the present data is given by

$$D(\bar{C}) = 5.224(1 - 0.0144\bar{C}) \times 10^{-6} \quad (5)$$

where $\bar{C}$ is given in g./100 cc. The average deviation of the experimental points from the above least-square line was 0.046%. This is to be compared with the corresponding equation obtained by Gosting and Morris

$$D(\bar{C}) = 5.226(1 - 0.0148\bar{C}) \times 10^{-6} \quad (6)$$

with an average deviation of 0.04%. The agreement is thus highly satisfactory and justifies the use of the present technique for the measurement of the diffusion properties of different solutes.

It should be noted, however, that the ΔC values used in the present experiments were appreciably different from those used by Gosting and Morris (25°). This merely points to the fact that the diffusion coefficient of sucrose is independent of the ΔC values.[1] Finally the present set of data when considered along with these of Gosting and Morris and English and Dole lead to the conclusion that the diffusion coefficient of sucrose obeys the same linear relation with the concentration of the solution irrespective of whether it is very dilute or supersaturated.

Acknowledgment.—The author wishes to express her indebtedness to Prof. N. N. Dasgupta for general guidance and to Dr. S. N. Chatterjee, School of Tropical Medicine, Calcutta, for valuable suggestions and discussions throughout the work. Financial assistance of the Ministry of Scientific Research and Cultural Affairs, Government of India, is also gratefully acknowledged.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISC., AND UNIVERSITY OF COLORADO, BOULDER, COLO.]

Equilibrium and Kinetic Studies on the Reaction of Chromium(III) Ion and Chloride Ion in Methanol–Water Solutions[1,2]

BY RICHARD J. BALTISBERGER AND EDWARD L. KING[3]

RECEIVED AUGUST 20, 1963

The formation of inner-sphere chlorochromium(III) ion was studied at 30.0, 43.6, and 60.0° in acidic aqueous methanol solutions from 0 to 70 mole % methanol. The binding of methanol in the first coordination shell of both chromium(III) ion and chlorochromium(III) ion was measured, and this was taken into account in arriving at the equilibrium quotient $Q_1 = [Cr(OH_2)_5Cl^{2+}]a_{H_2O}/[Cr(OH_2)_6^{3+}][Cl^-]$ which ranged at 30.0° from 0.107 in water to 6.2 in 70.6 mole % methanol; the ionic strength was 0.418 M. The value of ΔH was 7.4 kcal. mole^{-1} independent of the solvent composition, and the values of $\Delta S°$ ranged from 20.0 to 28.1 cal. mole^{-1} deg.$^{-1}$ over the range of solvents studied. The rate at which methanol replaces water in the first coordination shell of chromium(III) ion was determined and was found to be very similar to the rate of exchange of water between solvent and the first coordination shell of chromium(III) ion in aqueous solution. The rate at which chloride ion dissociates from chlorochromium(III) ion was found to be approximately 10-fold lower.

Experimental data pertinent to ion association in labile systems in mixed solvents generally yield composite equilibrium quotients in which concentrations of species with a particular charge but with different

(1) Based on the Ph.D. Thesis of Richard J. Baltisberger, University of Wisconsin, 1963.

(2) Supported in part under contract AT-(11-1)-1168 between the University of Wisconsin and the U. S. Atomic Energy Commission and in part by grant GP-680 to the University of Colorado from the National Science Foundation.

(3) Department of Chemistry, University of Colorado.