[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Measurement of Self-diffusion in Electrolyte Solutions[1,2]

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A study has been made of the sources of the discrepancies between values for the self-diffusion coefficients of ions in aqueous solutions as determined by various methods. Calibration of open-ended capillaries by comparing measured values with known differential diffusion data, has shown that the former values tend to be high, the effect being attributable in part to losses by mechanical convection. By direct calibration in dilute and concentrated solutions, it has also been shown that the value of the cell constant for a diaphragm cell does not change (within experimental error) over a concentration range. New measurements of the self-diffusion coefficients of sodium ion in sodium chloride solutions, with diaphragm cells calibrated in this manner, give values which agree with previous open-ended capillary measurements in concentrated solutions and approach them more closely in dilute solutions.

Papers from several laboratories have appeared in recent years reporting on self-diffusion measurements either for pure solvents or for solutes in aqueous solutions. Three different experimental techniques have been employed, namely, free diffusion in relatively wide tubes, diaphragm cells, and free diffusion from open-ended capillaries. In view of the fact that self-diffusion coefficients constitute an important and potentially very informative property of a solute, it is of serious concern that the three methods mentioned above have yielded results for ions in aqueous solution that do not agree well. This situation has been discussed briefly by Adamson[4] and by Mills and Kennedy,[5] and in the present paper are presented the results of the first section of a series of experiments designed to clarify the matter.

The following comparisons are available. The most serious example of disagreement between methods is afforded in the case of the coefficients reported for Na^+ and Cl^- in aqueous sodium chloride. In this instance Nielsen, Adamson and Cobble,[6] using the diaphragm cell method obtained values for both ions which in certain concentration regions differed widely from those of Wang and Miller[7] and Wang[8] who employed open-ended capillaries. In their paper, Nielsen, *et al.*, reported a few values for $\mathfrak{D}_{Na^+}$ in aqueous sodium iodide which agree well with those of Wang and Kennedy[9] using a free diffusion method. More recently, Burkell and Spinks,[10] using the opened-ended capillary method, reported a value of $\mathfrak{D}_{Na^+}$ in dilute sodium iodide agreeing well with the above values. These points are illustrated in Fig. 1 of this paper and more fully in Figs. 7 and 8 as given by Adamson.[4] In summary, it is seen that there are two distinct regions of disagreement. In dilute, *ca.* 0.5 *M* solutions, the open-ended capillary method tends to be high and to give in some cases a maximum, as compared to the other methods, and in very concentrated solutions, the results may be 10 to 15% lower than those with the other two methods.

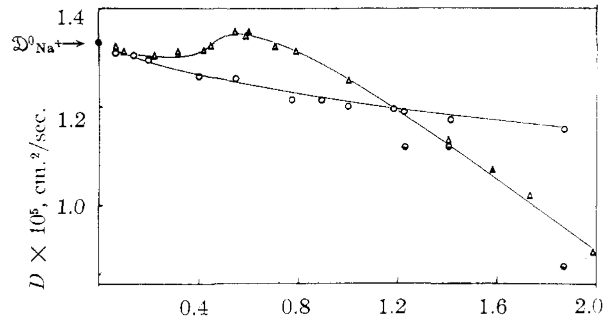

Fig. 1.—Self-diffusion coefficients of Na^+ in aqueous sodium chloride at 25°: △, values of Wang and Miller (open-ended capillary); ▲, this work (open-ended capillary); ○, Nielsen, Adamson and Cobble (diaphragm cell); ◒, Nielsen, Adamson and Cobble (diaphragm cell, 60 r.p.m. at concentrations > 1 *M*).

Analysis of Methods

In principle, all of the above methods should be equally valid and the sources of disagreement must lie in systematic errors arising from various aspects of the detailed procedures. The method employed by Wang and Kennedy,[9] free diffusion in relatively wide (*ca.* 0.1 cm.) tubes would seem to be the least complex in theory and the most free of hidden errors. Obvious difficulties, such as vibrational and thermal convection seem to have been minimized, and the results by this procedure, unfortunately available only for the ions of sodium iodide, should be reliable. On the other hand, Wang and Miller[7] have intimated that the grease employed may have led to errors and that the boundaries were not well formed.

The method employed by Nielsen, *et al.*,[6] the diaphragm cell, is a relative one since each cell is calibrated in terms of an empirical cell constant. There are accordingly more opportunities for systematic error, although the method is easy to handle experimentally and yields very precise results. Some form of stirring of the solutions in the two compartments on either side of the diaphragm is employed, and the cell constant, representing an effective pore area to length ratio, in general depends on the manner in which the stirring is ac-

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[2] This paper was presented at the September, 1954, Meeting of the American Chemical Society in New York.

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[4] A. W. Adamson, *J. Phys. Chem.*, **58**, 514 (1954).

[5] R. Mills and J. W. Kennedy, THIS JOURNAL, **75**, 6596 (1953).

[6] J. M. Nielsen, A. W. Adamson and J. W. Cobble, *ibid.*, **74**, 446 (1952).

[7] J. H. Wang and S. Miller, *ibid.*, **74**, 1610 (1952).

[8] J. H. Wang, *ibid.*, **74**, 1612 (1952).

[9] J. H. Wang and J. W. Kennedy, *ibid.*, **72**, 2080 (1950).

[10] J. E. Burkell and J. W. T. Spinks, *Can. J. Chem.*, **30**, 311 (1952).

complished. Means employed in the past include "gravity stirring," alternating rotation of the cell, end-over-end rotation, and sweeping of the diaphragm surfaces by magnetically-driven glass-encased iron rods. The calibration is made by carrying out a diffusion with an electrolyte of known diffusion coefficient, and hence rests ultimately on data obtained by optical or conductometric techniques employing a free diffusion system. Another detail is that in the calibration experiment an integral or average diffusion coefficient is obtained since a (near) stationary state diffusion is occurring between two reservoirs quite different in concentration, while the optical methods yield differential diffusion coefficients, *i.e.*, values for a particular concentration. These and other aspects of the calibration have been considered at considerable length by Stokes.[11] Briefly, a fairly standard procedure consists of employing sufficient stirring with magnetically-driven rods so as to be in the plateau region of the cell constant *vs.* stirring speed plot, and to determine the cell constant by diffusing 0.1 *M* potassium chloride into water. This cell constant is then assumed to hold for other solutions at this temperature.

There is a legitimate question, however, as to whether stirring adequate in the 0.1 *M* region will be precisely as adequate for very concentrated solutions. Nielsen, *et al.*,[6] found that with an increased rate of stirring, they obtained a significant increase in the diffusion coefficient, which remained constant after a certain critical speed was reached. They therefore assumed that the cell constant also changed with stirring speed or in other words that the lowest speed (60 r.p.m.) did not provide adequate mixing in the cell compartments. They were encouraged in this belief by finding that under these circumstances their values for $\mathfrak{D}_{Na^+}$ in sodium iodide agreed with those of Wang and Kennedy.[9]

The open-ended capillary method makes use of rather fine, thick-walled capillaries, (usually 3 to 6 cm. in length and *ca.* 0.06 cm. opening diameter) which are ground flat at the open end. The capillaries are filled with solution and immersed in a large reservoir of solution differing in concentration for differential diffusion and in radioactivity for self-diffusion measurements. After the diffusion period, the loss of material or activity from the capillaries is determined.

A possible source of error with this method is believed to be associated with the removal of solution from the top section of the capillary by mechanical convection. This convection may arise when a boundary is formed or broken between the two solutions (*i.e.*, when the capillary is immersed or withdrawn from the reservoir solution) and also from a scooping out effect caused by rapid or turbulent stirring of the reservoir solution. The first effect has been tested by Mills and Kennedy[5] and also by Krauss and Spinks[12] and has been assumed to have a negligible effect on the value of the self-diffusion coefficient. The second has been termed the "Δl" effect and has been discussed by Wang[13] and Mills and Kennedy.[5] Some difference of opinion exists as to the necessity of stirring the reservoir solution; Wang, *et al.*, and Mills and Kennedy have followed the practice of stirring this solution, while Anderson and Saddington,[14] Burkell and Spinks,[10] Haycock, *et al.*,[15] and Krauss and Spinks[12] did not stir. Other minor sources of error lie in the impeding or vibratory stirring effect of small air bubbles or foreign particulate matter that may lodge in the capillaries. These effects are minimized by degassing the solutions and filtering them through fine sinters. As used in an absolute method, such effects are not compensated by a calibration procedure as with the diaphragm cell, and must be evaluated absolutely. As a final comment, the open-ended capillary method has the advantage of being an absolute method, yet much easier to handle experimentally than free diffusion in larger bore tubes, and the disadvantage that precision is poor, being *ca.* ±2%.

The above presentation has been made in order to emphasize the fact that a considerable amount of examination of sources of error has been made already by the various investigators, and that each has felt his method to be reliable. In view of the discrepancies that none the less exist, however, it was considered desirable to make direct comparisons between the diaphragm and the open-ended capillary methods in the same laboratory and to make a renewed effort to locate the source of discord. It was felt that the cell constant determination might be the weak point in the diaphragm method, while with the open-ended capillary one, the difficulty in estimating errors absolutely made it desirable to calibrate the method against well-established reference points.

Experimental

Open-ended Capillary Method.—The same general procedure was employed as that of Anderson and Saddington,[14] as modified by Wang.[16] A new type diffusion flask or outer vessel was designed, however, in which stirring was accomplished magnetically. The magnetically-driven stirrer was pivoted on ground glass joints, and the openings in the outer vessel were equipped with ground glass stoppers. This arrangement provided a completely sealed system and eliminated transmission of motor vibration and also shocks given the flask by bumping of the mercury, which occurs when the usual mercury seal stirrer is employed. Moreover, the flask was cushioned by rubber mounts and supported on a separate framework from that of the stirring motor and thermostat equipment. Wang has stated that these fine capillaries are relatively insensitive to slight vibrations, but no exhaustive tests had been made and it seemed reasonable to take the above precautions.

The following partial reinvestigation of mechanical convection was made. The capillaries were filled with radioactive solution, about 3 *M* in sodium chloride, and immersed momentarily in a stirred bath at the same concentration. On removal, excess solution was carefully wiped off the faces of the capillaries and their contents centrifuged out and counted. The capillaries were cleaned, dried and refilled with the original solution, which was then centrifuged out and counted.

In order to obtain an absolute, although approximate, estimate of errors, differential diffusion runs were made with sodium chloride and potassium chloride solutions. The capillaries were filled with the more concentrated of the two solutions and the outer flask with a solution of about 25% lower concentration. The contents of each of the four capil-

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[11] R. H. Stokes, THIS JOURNAL, **72**, 2243 (1950).

[12] C. J. Krauss and J. W. T. Spinks, *Can. J. Chem.*, **32**, 71 (1954).

[13] J. H. Wang, THIS JOURNAL, **74**, 1182 (1952).

[14] J. A. Anderson and K. Saddington, *J. Chem. Soc.*, S381 (1949).

[15] W. Haycock, B. J. Alder and J. H. Hildebrand, *J. Chem. Phys.*, **21**, 1601 (1953).

[16] J. H. Wang, THIS JOURNAL, **73**, 510 (1951).

laries employed in a run were measured, both before and after diffusion, as separate determinations, by centrifuging the contents into small constricted tubes. The ejected solution was diluted with a measured volume of de-gassed water, and drawn into a pipet-type microconductance cell. The resistance of the cell and solution was then measured with a Jones–Dike bridge. Owing to the very small quantity of solution available, the cell could not be rinsed out in the usual manner, but instead was washed out with distilled water and dried with acetone before each measurement. As acetone would probably modify any platinization, the electrodes were of bright platinum. Polarization would not introduce error, however, as measurements at several frequencies allowed good linear extrapolations to infinite frequency to be made.

Self-diffusion data for sodium ion in sodium chloride solutions were also obtained, employing Na^{22} supplied by Oak Ridge National Laboratories. The contents of the capillary were centrifuged out as before and made up to a standard volume. This solution was then counted in a well-type scintillation counter. All differential and self-diffusion points were determined in quadruplicate, using four capillaries at a time.

Diaphragm Cell Measurements.—The diaphragm cells were of the type used by Stokes,[17] rather than the type with twin stopcocks on each end. Stokes' design has the advantage of minimizing any contamination by grease. For the runs based on calibration with sodium chloride solutions, the bottom compartment of the diaphragm cell was filled by drawing solution through the diaphragm by suction, then rinsing and filling the upper compartment with the less dense solution. For the runs based on potassium chloride calibrations, the diaphragm was filled with solution by inverting the cell and allowing lower compartment solution to drip through (the diaphragm being already filled with solution from the previous run) then proceeding as before. The solutions were deaerated, but it was felt that the second procedure was less apt to leave air bubbles trapped in the diaphragm. The usual pre-diffusion was allowed to take place, and both compartments were filled with fresh solution. After diffusion had occurred, the solutions were analyzed by the conductometric method. With the sodium chloride based runs, the entire contents of each compartment were allowed to drain out, while with the latter potassium chloride based runs, samples were pipetted out from each compartment to avoid any possible mixing of the compartments' contents by the surging that occurs during a draining procedure.

The cell contents were stirred by means of iron-cored glass rods which were made to sweep the upper and lower surfaces of the diaphragm by means of a rotating magnet. The pole pieces of the magnet were shimmed by iron cones to give a field such as to aid in maintaining the sweeps against the diaphragm. A speed of 60 r.p.m. was employed throughout.

The usual calibration procedure leads to a determination of the cell constant in the equation

$$\bar{\mathfrak{D}} = \frac{1}{Kt} \log \left[\frac{C_1 - C_2}{C_3 - C_4}\right] \tag{1}$$

where

$$K = \frac{1}{2.303(l/A)} \left[\frac{1}{V_1} + \frac{1}{V_2}\right] \tag{2}$$

C_1 and C_2 are the concentrations before, C_3 and C_4 the concentrations after diffusion and V the volume of the compartments, A and l the effective diaphragm area and thickness, and K the cell constant. Ordinarily, 0.1 M potassium chloride is allowed to diffuse into water and K calculated by using the appropriate value of the integral diffusion coefficient. In the present investigations, K was determined at various concentration levels by employing initial values of C_1 and C_2 differing by several tenths M and averaging up to 3.5 M and in some cases diffusing into pure water. In this manner, possible variations in cell constant with concentration, due presumably to variations in effectiveness of stirring, could be determined. In all cases the proper integral diffusion coefficients were inserted into equation 1, as calculated by Stokes' equation.[11]

Self-diffusion coefficients for Na^{22} in sodium chloride solutions were determined by following the same procedure as in the calibration experiments, the values of $\mathfrak{D}_{Na^+}$ being computed with the use of the cell constant determined for that region of concentration. In the sodium chloride calibrated series, it was assumed that the cell constants for 18.5° would be the same at 25°.

Results and Discussion

Open-ended Capillary Method.—Since several modifications had been made in the apparatus as designed by Wang,[16] the self-diffusion coefficient of sodium ion in sodium chloride solution was redetermined to see if the modifications had in any way affected the behavior of the apparatus. The values of $\mathfrak{D}_{Na^+}$ so determined were 1.342 ± 0.003 and 1.072 ± 0.017 ($\times$ 10^{-5} cm.^{2}/sec.) in 0.36 and 2.5 M sodium chloride, respectively, as compared to Wang and Miller's[7] values of 1.340 ± 0.035 and 1.075 ± 0.02. The comparison is shown in Fig. 1. The close agreement suggests that any findings with the modified apparatus should apply equally well to that used by the previous workers.

In Table I are shown the results of investigations into the loss of activity arising from immersion and withdrawal of the capillaries from a stirred bath.

TABLE I

Capillary no.	Counts/minute		Δ	Decrease, %
	Before immersion	After emersion		
1	3462 ± 36	3371 ± 41	91	2.65
2	3650 ± 31	3581 ± 22	69	1.9
3	3526 ± 44	3443 ± 40	83	2.4
4	3587 ± 68	3572 ± 41	15	0.5
5	3500 ± 31	3508 ± 40	−8	..
6	3361 ± 55	3274 ± 44	87	2.6
				1.7

It could not be determined whether the 1.7% loss occurred during immersion or withdrawal although the effect on a diffusion run would be somewhat different. The figure of 1.7% loss of activity can be compared with those of Mills and Kennedy[5] and Krauss and Spinks[12] who reported figures for a similar effect of 1.3% and <0.5%, respectively. These workers performed the test in still water, however, so that any difference could be attributable to superimposition of a scooping-out effect due to stirring. The absence of any marked discrepancy between the values suggests that the latter-named effect is not greater than that due to immersion of the capillaries.

A check was also made on the magnitude of the "Δl" effect by letting 3.9 M sodium chloride diffuse into 3 M and observing whether the integral diffusion coefficient so obtained varied with the length of the capillary used. For lengths varying between 4 and 5.8 cm. and a stirring rate of 100 r.p.m., the observed $\mathfrak{D}_{Na^+}$ values were constant within the usual ±2% error. This result emphasizes that until greater precision can be obtained with the capillary method, attempts to measure the "Δl" effect by using capillaries of different length is not very satisfactory.

Another avenue of attack on the problem was therefore adopted in which differential diffusion coefficients determined with the capillary method have been compared with those obtained with other methods. Three bases for comparison have been

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[17] R. H. Stokes, THIS JOURNAL, **72**, 762 (1950).

used. The first was based on Clack's[18] data for the differential diffusion coefficients of sodium chloride at 18.5°. Since his data had been corrected for solvent counterflow, they were recorrected to an apparatus frame of reference by the procedure of Hartley and Runnicles,[19] *i.e.*, each value was divided by the factor $(1 + c\bar{V})$ where $\bar{V}$ is the partial molal volume of the solute. In the second series, Stokes' data[11] for sodium chloride solutions at 25° have been used and in the third, values reported by Gosting[20] for differential diffusion in potassium chloride solutions. Reservations which must be borne in mind in making these comparisons, are that Clack's values have not been independently verified and that Stokes' values have been made with the diaphragm cell which, for the purpose of this inquiry, is subject to query in concentrated sodium chloride solutions.

The results of these differential diffusion experiments with open-ended capillaries are summarized in Table II.

TABLE II

DIFFERENTIAL DIFFUSION WITH OPEN-ENDED CAPILLARIES

c_1 moles/l.	c_2 moles/l.	$\mathfrak{D} \times 10^5$, cm.²/sec.		Diff., %
		Sodium chloride 18.5°		
		Clack	Capillary	
2.0	1.4	1.230	1.316 ± 0.026	7.0
			1.310 ± .020	6.5
3.5	2.5	1.280	1.329 ± .030	3.8
		Sodium chloride 25°		
		Stokes	Capillary	
0.7	0.2	1.474	1.513 ± 0.070	2.6
			1.514 ± .013	2.6
3.5	2.5	1.544	1.631 ± .060	5.6
			1.595 ± .024	3.3
		Potassium chloride 25°		
		Gosting	Capillary	
0.5	0.1	1.845	1.909 ± 0.038	3.5
			1.849 ± .040[a]	0.2
3.9	3.0	2.160	2.241 ± .040	3.7

[a] No stirring

It is seen that the differential diffusion coefficients obtained by the open-ended capillary method are consistently higher than the presumably correct values obtained by optical methods, the difference ranging from 2.5–7% and averaging about 4%. Since it was assumed that the capillary method would yield a mean diffusion coefficient corresponding to the differential coefficient for the mean of the two concentrations, it is possible that in some cases the discrepancy was due to a failure to properly compute the integral diffusion coefficient. However, the same difference of *ca.* 4% was obtained when 0.5 *M* potassium chloride was diffused into 0.1 *M* solution; since this range straddles the minimum in the plot of differential diffusion coefficient *vs.* concentration, very little change in diffusion coefficient could have occurred during the open-ended capillary diffusion and hence little error could have been introduced by assuming that the value of $\mathfrak{D}$ corresponding to the minimum should prevail. The evidence suggests that the capillary method does give high results and a close reinvestigation of the possibility of convectional losses is warranted. One of us (R.M.) has now begun a series of experiments in an attempt to further clarify the matter.

Diaphragm Cell Method.—Self-diffusion coefficients for sodium ion in sodium chloride solutions were determined by means of the diaphragm cell method, using cell constants determined separately for each concentration region, as discussed in the Experimental section. In Table III are presented the data for the series employing cell constants based on Clack's data[18] for sodium chloride at 18.5° (the self-diffusion data were obtained at 25°).

TABLE III

$\mathfrak{D}_{Na^+}$ BASED ON CALIBRATIONS WITH SODIUM CHLORIDE

Calibration at 18.5°

c_1 moles/l.	c_2 moles/l.	$\bar{\mathfrak{D}} \times 10^5$ cm.²/sec. Clack	K
4.25	3.75	1.325	0.0895
			.0921
		Av.	0.0908 ± 0.001
0.7	0.2	1.190	0.0957
			.0951
		Av.	0.0954 ± 0.0003

Self-diffusion of Na^{22} at 25°

c moles/l.	K	$\mathfrak{D}_{Na^+} \times 10^5$ (cm.²/sec.) Obsd.	Capillary	Nielsen, *et al.*
4.0	0.0908	0.850	0.910	1.140
0.6	.0954	1.214	1.310	1.216
0.3	.0954	1.230	1.350	1.260

The nearness of C_1 to C_2 in some of these calibrations made the determination of the cell constants relatively imprecise but is a necessary feature of this approach in the respect that conditions as close as possible to those prevailing in self-diffusion measurements are required. It is seen, however, that in 4 *M* sodium chloride $\mathfrak{D}_{Na^+}$ now agrees well with the open-ended capillary value (Wang and Miller[7]) rather than with the value of Nielsen, *et al.*[6] At the lower concentrations, however, the results agree well with those of Nielsen, *et al.*, while the capillary results were high by the expected several per cent.

The results of the second series, based on calibrations with potassium chloride solutions are summarized in Table IV.

Since the same cell was employed throughout, it is noteworthy that the cell constant for concentrated solutions was the same as determined by potassium chloride diffusion as by sodium chloride diffusion, while in dilute solutions, values differing by about 4% were obtained.

The reality of the 4% change in cell constant in the sodium chloride calibrations is questionable. In view of the data obtained from the potassium chloride calibrations which show essentially constant values over a wide range of concentrations (except for a 1% increase in dilute solutions) it seems reasonable to accept them as more nearly correct. As has been stated previously Clack's[18] data have not been checked, whereas Gosting's[20] curve coincides in

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[18] B. W. Clack, *Proc. Phys. Soc.*, **36**, 313 (1924).

[19] G. S. Hartley and D. F. Runnicles, *Proc. Roy. Soc.* (*London*), **A168**, 401 (1938).

[20] L. J. Gosting, THIS JOURNAL, **72**, 4418 (1950).

TABLE IV

$\mathfrak{D}_{\mathrm{Na}^+}$ BASED ON CALIBRATIONS WITH POTASSIUM CHLORIDE

Calibration at 25°

c_1 moles/l.	c_2	$\bar{\mathfrak{D}} \times 10^5$, cm.²/sec. Gosting	K
0.1	0	1.865	0.0915
			.0915[a]
0.7	0.2	1.847	.0921
			.0905
			.0907[a]
1.14	0	1.858	.0899
1.14	0.2	1.863	.0892
2.0	0.98	1.944	.0903[a]
3.9	3.0	2.160	.0907

Self-diffusion of Na^{22} at 25°

c moles/l.	K	$\mathfrak{D}_{\mathrm{Na}^+} \times 10^5$, cm.²/sec. Obsd.	Capillary	Nielsen, *et al.*
0.04	0.0915	1.290	1.300	1.300
		1.294		
.16	.0905	1.295	1.315	1.262
.30	.0905	1.289	1.350	1.258
.40	.0905	1.283	1.335	1.250
.60	.0905	1.283	1.315	1.215
1.44	.0905	1.202	1.205	1.198
2.56	.0905	1.088	1.07	1.17
4.00	.0905	0.929	0.904	

[a] Considered most reliable since the pipetting technique of sampling was employed.

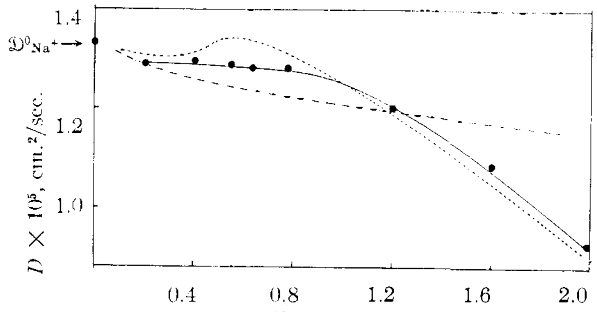

Fig. 2.—Self-diffusion coefficients of Na^+ in aqueous sodium chloride at 25°: ------, data of Wang and Miller; ·—·—, data of Nielsen, *et al.*; ●, this work (diaphragm cell calibrated KCl diffusion).

certain concentration ranges with the values of two other independent investigators.[21]

The evidence of these calibration and self-diffusion runs fails to show a maximum in $\mathfrak{D}_{\mathrm{Na}^+}$ such as reported by Wang and Miller[7] although a levelling off of the curve is observed in the same concentration region. At the same time if the potassium chloride calibration figures are used the self-diffusion values are several per cent. higher than the values of Nielsen, *et al.*[6] These points are illustrated in Fig. 2.

In summarizing the position in dilute solutions (below 1 *M*), the values are not yet unequivocal. In the interim, the diaphragm cell results (KCl calibration) can be taken as the most accurate but two salient points remain to be cleared up. The first of these is to discover under what conditions the open-ended capillary values agree with these diaphragm results and the second to explain why values measured by both methods agree in the more dilute region below 0.4 *M* where the 4% stirring effect should also be operative. Both of these points are under investigation by one of us (R.M.).

There seems little doubt however that the open-ended capillary method gives essentially correct values (possibly a few per cent. high) in concentrated solutions and the earlier values of Nielsen, *et al.*, are high. The source of error in this case is not easy to determine. The evidence suggest that these workers obtained bulk flow of some kind at stirring speeds >60 r.p.m. Further studies with increased stirring speeds are being made to substantiate this conclusion.

There remains the question of the agreement of Nielsen, *et al.*, with Wang and Kennedy[9] on the values of $\mathfrak{D}_{\mathrm{Na}^+}$ in concentrated sodium iodide solutions. It would seem likely from the present findings that the diaphragm results were incorrect and hence also Wang and Kennedy's values. In view of the fact that Wang and Miller,[7] in their paper, suggest that the capillary cell results may be in error and that one of the authors was associated with both projects, it seems reasonable to adopt this conclusion.

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(21) R. H. Stokes, THIS JOURNAL, **73**, 3527 (1951).