

Fig. 11.—Sedimentation diagram for the BPA in the same buffer used for diffusion experiment XIV: 60,000 r.p.m., 2580 sec., 0.91 g./100 ml. and 24°.

any contribution,  $\Omega_{\text{buffer}}$ , to this curve is probably less than  $1.5 \times 10^{-4}$  for which equation 23 and Table I indicate that any residual buffer gradient ( $r_{\text{buffer}} \approx 1/25$ ) is restricted to  $\alpha_{\text{buffer}} < 0.0006$ . According to equation 10 such a buffer gradient cannot influence  $D_A$  by more than 0.1%, so in this experiment the spacings of the Gouy fringes near the slit image have proved that any buffer gradient was too small to influence significantly the observed diffusion coefficient.

Assuming that only one impurity is present, we may attempt to determine  $D_1/D_2$  and  $\alpha_2$  by selecting the two values which enable equation 23 to fit best the crosses of the relative fringe deviation graph. To illustrate how this may be done, curves are shown in Fig. 10b representing three pairs of values of  $D_1/D_2$  and  $\alpha_2$  which yield the observed value of  $\Omega_{\text{max}} = 8.5 \times 10^{-4}$ . If each of these ratios, 4, 2 and 1.5, for  $D_1/D_2$  is assumed to be independent of buffer and temperature and is substituted with its corresponding value of  $\alpha_2$  into equation 10, together with  $(D_A)_{20,w} = 5.855 \times 10^{-7}$  cm.<sup>2</sup>/sec., the three values 5.892, 5.932 and 5.995,

respectively, are obtained for  $(D_1)_{20,w} \times 10^7$ , the diffusion coefficient of the albumin alone. While the best fit of the crosses, Fig. 10b, would be given by a ratio of  $D_1/D_2$  between 2 and 4, it is seen that each of the three ratios considered corresponds to the experimental points within their probable errors.

It should be emphasized that interpretation of protein diffusions by assuming only one impurity to be present may often be a gross oversimplification. In such cases quantitative interpretations appear to be limited to evaluation of different average diffusion coefficients with equation 39. The interpretation of the BPA experiment in terms of a single impurity was included to illustrate how, when this assumption is justified, the above theory for mixed solute diffusions is used to obtain  $D_1$ , and how much these values are influenced by experimental error.

Further experiments with BPA are contemplated to corroborate and extend the results from the single experiment reported above. The above data, however, when considered with those of Ogston,<sup>16,17</sup> Creeth<sup>53</sup> and Charlwood<sup>18,54</sup> indicate that the Gouy diffusimeter is both a sensitive and a very useful tool for the study of proteins.

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## The Self-diffusion Coefficients of Iodide, Potassium and Rubidium Ions in Aqueous Solutions<sup>1</sup>

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The self-diffusion coefficients of iodide, potassium and rubidium ions have been measured in a series of aqueous metal iodides of moderate to high concentration at 25°. The open-ended capillary method has been used throughout. In view of serious discrepancies that have arisen between self-diffusion coefficients measured by this capillary method and by the diaphragm cell method, an examination of possible sources of error has been made. The self-diffusion coefficients of large unhydrated ions as obtained by the improved method are found to exhibit a linear relationship up to comparatively high concentrations when their product with the specific viscosity is plotted against  $\sqrt{c}$ . A correlation of the slopes of the series of lines obtained in this way is attempted by taking into account the mean distance of approach of the ions and its effect on the potential energy of the ion in its ionic atmosphere. A simple picture of the mechanism of the self-diffusion process for unhydrated ions, based on this evidence, is suggested.

The increasing availability of artificially produced radioisotopes over the last decade has given impetus to the study of certain types of diffusion phenomena. In particular, the self-diffusion coefficients of ions in electrolytic solution have been measured by several methods, chief among which

are the diaphragm cell method and various forms of the single capillary method. In the results first reported, the two kinds of method gave fairly good agreement with one another. Thus Adamson<sup>2</sup> using a diaphragm cell and Wang and Kennedy<sup>3</sup> using a capillary cell obtained comparable values for the self-diffusion coefficients of Na<sup>+</sup> in aqueous

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(2) A. W. Adamson, *J. Chem. Phys.*, **15**, 760 (1947).

(3) J. H. Wang and J. W. Kennedy, *THIS JOURNAL*, **72**, 2080 (1950).

sodium iodide. Recently Burkell and Spinks,<sup>4</sup> using the open-ended capillary method originated by Anderson and Saddington,<sup>5</sup> were able to reproduce the self-diffusion coefficient of Na<sup>+</sup> in 0.1 M sodium iodide to give good agreement with Wang and Kennedy's value. However, Wang and Miller<sup>6</sup> have now measured the self-diffusion coefficients of Na<sup>+</sup> in aqueous sodium chloride by the open-ended capillary method and report values which differ radically from those obtained by Nielsen, Adamson and Cobble<sup>7</sup> with a diaphragm cell. A need for re-examination of both types of experimental method is therefore indicated, and we have included in this paper a report of our investigations into possible sources of error in the open-ended capillary method. The self-diffusion coefficients reported in this paper have all been obtained with the improved technique resulting from this preliminary investigation.

The theory of the open-ended capillary method and the procedure for obtaining the diffusion coefficient from the diffusion data are fully discussed by Wang.<sup>8</sup>

### Experimental Procedure

The apparatus in which diffusion took place was essentially the same as that described by Wang.<sup>9</sup> A three-necked flask of one-liter capacity was fitted with capillary holders and a mercury-seal stirrer. The shaft of the stirrer, which was connected through a gearbox to an electric motor, entered through the center neck and turned a plastic paddle at 100 r.p.m. The flask and contents were immersed in a large circulating bath which was kept by thermostatic control at  $25 \pm 0.02^\circ$ .

The capillaries were cut from lengths of precision bore tubing which had an inside diameter of 0.024". A glass seal was made on one end of each capillary and its length then measured by micrometer calipers with the aid of a steel plunger inserted into the bore. These lengths varied from 2 to 6 cm. The edges of the open end were ground to the shape of a truncated cone to provide a flat seating in the centrifuge tubes and also to reduce turbulence upon immersion.

Four radioisotopes were used, K<sup>42</sup>, Rb<sup>86</sup>, I<sup>131</sup> and Na<sup>22</sup>. The first three were obtained from the Isotope Division, U.S.A.E.C., Oak Ridge, Tennessee, and the last was produced in the Washington University cyclotron in the conventional manner.

Both the K<sup>42</sup> and Rb<sup>86</sup> isotopes were received in the form of their solid carbonates. Their respective tracer stock solutions were prepared in the following manner. After dissolution in water the carbonates were titrated with hydrogen iodide to a pH of 1. The solutions were then boiled for ten minutes to remove all remaining carbonate. Titration with the appropriate (potassium or rubidium) hydroxide then brought the solution to a pH of 7. This final pH point was determined by removal of a portion of the tracer solution for comparison with color standards which bracketed the pH to within 0.1 of a pH unit.

The I<sup>131</sup> was received "carrier-free" in weak basic sodium bisulfite solution. The bisulfite was removed by titration with hydrogen iodide to a pH of 7 and subsequent boiling. Any sulfate ions that may be present, due to air oxidation of the bisulfite, were reduced to a negligible fraction by adding solid lead iodide to the solution in slight excess. The solid lead iodide plus lead sulfate was centrifuged out of the

solution within 30 minutes to minimize exchange and consequent lowering of the specific activity.

The Na<sup>22</sup> activity was received as an impregnation in magnesium chips from a cyclotron target which had undergone deuteron bombardment. The chips were dissolved in nitric acid, and the solution heated to dryness and then ignited in a platinum crucible to convert the solid magnesium nitrate to the oxide. The Na<sup>22</sup> was extracted from this oxide residue with water, and the solution was put through an Amberlite IR-100 ion-exchange column. The adsorbed ions were eluted at a rate of 0.25 ml. per minute with 0.1 N hydrochloric acid. According to Bouchez and Kayas<sup>10</sup> this procedure gives a quantitative separation. The elution of the radioactive Na<sup>22</sup> was followed radiometrically in aliquots of the effluent and was stopped when the activity had dropped to a low value. At this point a test for magnesium species with *p*-nitrobenzene-azoresorcinol reagent gave negative results.

The procedure for a typical diffusion run is described. The capillaries were individually calibrated by filling them with radioactive solution as precisely as possible to the top of the tubes, by means of fine pipets drawn from glass tubing. We have found that a film of "Desicote"<sup>11</sup> on the face of the capillary prevents contamination with radioactivity and consequent error in calibration. The radioactive solution in each capillary was centrifuged into a numbered counting tube provided with a constriction to seat the capillary. Each capillary was twice filled with water and re-centrifuged. Tests showed that 99.9% of the activity was in this way transferred to the centrifuge tube. Finally the counting tubes were diluted up to the constriction mark with water, and their radioactivities measured. Multiple calibrations of the same capillary indicate that the probable error in the calibration is within the statistical counting error.

The capillaries were then washed consecutively with water and acetone, dried in an oven and refilled with tracer solutions. To ensure temperature equilibrium they were placed in the holders and lowered into the bath almost to their rims and held there for 30 minutes. After that time they were gently lowered into the bath. A drop of tracer solution covering the face of each capillary minimized extraction of the inner solution by turbulence upon immersion. At the end of a run, which usually required four or five days, the capillaries were taken out, and their contents centrifuged into the individual counting tubes in which their calibrations had been made.

The counting procedure was designed to take advantage of the  $\gamma$ -radiation emitted by the radioactive tracer isotopes. Two types of counters were used; a proportional gas counter and a scintillation counter. For geometrical consistency the same tubes were used for the original calibration and for the measurement of residual radioactivity after diffusion. In consequence the two measurements had to be made several hours apart. In order to correct for fluctuations in counter efficiency during this period, both a long-lived radiocobalt (Co<sup>60</sup>) standard and a standard prepared from the radioactivity being measured were counted before and after every sample. Corrections for radioactive decay were computed from these standards, by plotting the decay curve of the radioisotope. As a further check, samples were counted on both counters when the activity was sufficiently high.

The viscosities of hydrogen iodide and lithium iodide solutions were measured with a simple Ostwald viscosimeter. The apparatus was calibrated by measuring the viscosity of a 2.000 M potassium chloride solution, and comparing the value obtained with that reported in the literature. The results are shown in Tables I and II.

### Sources of Error

(1) **Stirring Rate.**—In a recent paper<sup>8</sup> Wang has discussed the effect of varying the stirring rate on the observed diffusion coefficients (the so-called  $\Delta l$  effect). A series of measurements of the apparent diffusion coefficient of Cl<sup>-</sup> in potassium chloride in which the stirring rate was varied continuously under the same experimental conditions was made by A. M. Friedman of this Laboratory. His results

(10) R. Bouchez and G. Kayas, *Compt. rend.*, **228**, 1222 (1949).

(11) "Desicote" is the trade-name for a trimethylsilicon chloride water-repellent which is manufactured by Beckman Instruments, Inc., South Pasadena, California.

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

(5) J. A. Anderson and K. Saddington, *J. Chem. Soc.*, S 381 (1949).

(6) J. H. Wang and Sara Miller, *THIS JOURNAL*, **74**, 1611 (1952).

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

(8) J. H. Wang, *ibid.*, **74**, 1182 (1952). See also A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, Chapter 4.

(9) J. H. Wang, *THIS JOURNAL*, **73**, 510 (1951).

TABLE I

RELATIVE VISCOSITIES OF AQUEOUS HI SOLUTIONS AT 25°

Concn. of HI solns. (form. wt./l.)	$\eta/\eta_0$	Concn. of HI solns. (form. wt./l.)	$\eta/\eta_0$
0.100	0.996	1.075	1.007
.200	0.995	2.210	1.034
.370	1.001	3.330	1.077
.440	1.001	4.430	1.135
.740	1.004		

TABLE II

RELATIVE VISCOSITIES OF AQUEOUS LiI SOLUTIONS AT 25°

Concn. of LiI solns. (form. wt./l.)	$\eta/\eta_0$	Concn. of LiI solns. (form. wt./l.)	$\eta/\eta_0$
0.010	1.010	1.134	1.120
.275	1.029	2.200	1.230
.550	1.058	3.300	1.398
.850	1.088	4.400	1.600

show that for our particular geometrical conditions approximately 100 r.p.m. is an optimum rate at which the  $\Delta t$  effect is approximately zero. This stirring rate was used in all the runs described in this work.

(2) **Mechanical Mixing on Immersion.**—The processes of immersion and withdrawal of capillaries from the bath probably produce turbulence and the formation of eddy currents over the upper surface, and there is a possibility that some of the radioactive solution in the capillary might be lost by mixing with the bath. The effect would be approximately equivalent to the effect produced by normal diffusion in a time  $\Delta t$ .

Estimates of the magnitude of this effect were made by filling six capillaries with radioactive solution and calibrating them twice. The capillaries were then refilled with tracer solution and large drops left on the face to simulate actual experimental conditions. They were then immersed and immediately withdrawn from a large bath of the same solution in the same manner as in a normal run. Excess solution was carefully removed from the top of the capillary with bibulous paper and the contents centrifuged out and counted. Results are given in Table III.

TABLE III

Capillary no.	Calibration (counts/min.)	Activity after immersion (counts/min.)	Decrease, %
1	6160	6124	0.6
2	6619	6447	2.7
3	6192	6021	2.8
4	6112	6092	0.3
5	6231	6186	.7
6	6183	6128	.9

It will be observed that the greatest decrease in counting rates was only 2.8% and the average decrease approximately 1.3%. These activity values were substituted in the equation<sup>3</sup>

$$\frac{c_{av}}{c_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp - (2n+1)^2 \pi^2 D t / 4l^2$$

where  $c_0$  is the activity before immersion and  $c_{av}$  that after immersion and withdrawal. The value of  $D$  was known from previous experiments so it was possible to solve for  $t$ . (In view of the high value of  $c_{av}/c_0$  four terms of the convergent series had to be taken into account in making this calculation.) The value of  $t$  so obtained, which we take as the equivalent diffusion time  $\Delta t$ , was of the order of 100 seconds. As the normal time of a diffusion run is of the order of 300,000 seconds, this would introduce an error in  $D$  of only 0.03% and so can be entirely neglected.

(3) **Density Differences.**—In ordinary diffusion experiments under conditions such that a concentration gradient is present, the gradient in specific gravity may be used to suppress convection and bulk mixing. This stabilizing effect is absent in tracer-diffusion experiments. It was thought that enrichment of the water in the tracer solutions

with deuterium oxide would provide a stabilizing density gradient. In preliminary experiments in which 10% of deuterium oxide was used, it was found that the measured diffusion coefficients were greater by a factor of approximately 3% than in normal runs. Enrichment with 2%  $D_2O$  did not affect the diffusion coefficient within experimental error, and in our experiments, with the exception of the hydrogen iodide runs, we have used as a solvent for the tracer inside the capillary, water that contained 2% deuterium oxide. Under these conditions the densities of the tracer solutions were always greater than those of the bath solutions by about 0.2%.

(4) **Ion Adsorption.**—In some experiments with  $Na^{22}$  it was observed that there was residual radioactivity left in the capillaries even after repeated washing. The effect became increasingly pronounced with solutions of high specific activity. We looked for but did not observe adsorption with any of the other ions used in this work. It is worth noting that this effect would probably be greatly magnified in other types of diffusion measurements in which a sintered glass diaphragm is used, owing to the enormous surface area of the glass.

(5) **Effect of pH Differences.**—Many tracer solutions are received in either acidic or basic solution. If not carefully neutralized before use, these may impart to the specific tagged solutions a pH different from that in the bath solution. In order to gain some knowledge of the effect of a pH difference a series of experiments was carried out in which tracer solutions of varying pH were allowed to diffuse into neutral bath solutions. The results obtained are shown in Table IV.

TABLE IV

SELF-DIFFUSION COEFFICIENTS OF  $Na^+$  IN  $NaCl$  AT 25°

Concn. (form. wt. per 1000 g. $H_2O$ )	pH of tracer	pH of bath	$D \times 10^5$ ( $cm.^2/sec.$ )
0.1	3.1	7.0	$1.330 \pm 0.005$
0.1	7.0	7.0	$1.325 \pm .010$
1.0	7.0	7.0	$1.301 \pm .020$
1.0	1.5	7.0	$1.567 \pm .050$
1.0	2.8	7.0	$1.788 \pm .020$
1.0	10.0	7.0	$1.463 \pm .004$
1.0	12.5	7.0	$1.444 \pm .030$
1.0	5.0	5.0	$1.290 \pm .020$

The evidence indicates that a pH difference between tracer and bath can cause a large error in the value of the diffusion coefficient. It might be suggested that the effect is related to the very high diffusion coefficients of both  $H^+$  and  $OH^-$  ions, but more work is necessary before any conclusion can be drawn.

Many solutions have normally a pH of about 5 due to the presence of dissolved carbon dioxide. If these solutions are degassed, it is essential therefore that both tracer and bath solutions undergo similar treatment. We have been unable to detect any difference between the diffusion coefficients of solutions both of which were at pH 5 and both at pH 7. Degassing has not therefore been incorporated in our procedure.

(6) **Concentration Gradients.**—In tracer-diffusion experiments it is necessary to make the concentrations of tracer and bath solutions as nearly the same as possible. At low concentrations and particularly where the tracer solution consists of 1 or 2 ml. of liquid, very great care is required to achieve precision concentration control, and it is possible that a concentration difference may exist which will amount to an appreciable percentage of the concentration. It seemed prudent therefore to investigate the effect of a given concentration difference at various total concentrations. Experiments have been carried out in which a 5% concentration gradient existed between tracer and bath at two concentrations. In all cases the tracer solution contained 2%  $D_2O$  to ensure that the density gradient was always in the same direction. The measurements at the lower concentration were made by A. M. Friedman; those at the higher concentration are a part of the present work. Both results are shown in Table V.

It appears that at very low concentrations the diffusion coefficient is not appreciably affected by a small relative concentration gradient between tracer and bath. At high

TABLE V

SELF-DIFFUSION COEFFICIENTS OF Na<sup>+</sup> IN NaCl AT 25°

Concn. of tracer (form. wt./l.)	Concn. of bath (form. wt./l.)	$D \times 10^6$ (cm. <sup>2</sup> /sec.)
0.950	1.000	1.285 ± 0.006
1.000	1.000	1.310 ± .010
1.050	1.000	1.348 ± .020
0.010	0.010	1.347 ± .010
0.0105	0.010	1.336 ± .010

concentrations, however, an effect is evidenced for the same relative concentration gradient. It is suggested that concentration gradient errors may be determined more by the absolute rather than the relative magnitude of the concentration difference.

Insofar as at high concentrations the solutions are not expected to have even a 1% concentration difference and at low concentrations a concentration difference greater than 5% is improbable, it would appear that the effect of diffusion potential resulting from solute concentration gradient is not a serious source of error, at least for solutions not containing H<sup>+</sup> or OH<sup>-</sup> ions as solute.

## Self-diffusion Coefficients

The ion self-diffusion coefficients that have been measured in this work are presented in Tables VI, VII, VIII and IX. Each coefficient is the mean of three or four measurements; the error listed is the root-mean-square deviation.

TABLE VI

SELF-DIFFUSION COEFFICIENTS OF I<sup>-</sup> IN HI (aq.) AT 25°

Concn. of HI soln. (form. wt./l.)	$D \times 10^6$ (cm. <sup>2</sup> /sec.)	Concn. of HI soln. (form. wt./l.)	$D \times 10^6$ (cm. <sup>2</sup> /sec.)
0.050	2.011 ± 0.010	1.075	1.877 ± 0.010
.100	2.013 ± .005	2.210	1.780 ± .020
.145	2.003 ± .015	3.320	1.705 ± .040
.290	1.970 ± .010	4.040	1.643 ± .025
.806	1.903 ± .035		

TABLE VII

SELF-DIFFUSION COEFFICIENTS OF I<sup>-</sup> IN LiI (aq.) AT 25°

Concn. of LiI soln. (form. wt./l.)	$D \times 10^6$ (cm. <sup>2</sup> /sec.)	Concn. of LiI soln. (form. wt./l.)	$D \times 10^6$ (cm. <sup>2</sup> /sec.)
0.061	2.004 ± 0.020	1.134	1.694 ± 0.030
.125	1.991 ± .050	2.000	1.540 ± .020
.237	1.910 ± .030	3.340	1.268 ± .010
.500	1.847 ± .040	4.100	1.220 ± .030
.760	1.795 ± .035		

TABLE VIII

SELF-DIFFUSION COEFFICIENTS OF Rb<sup>+</sup> AND I<sup>-</sup> IN RbI (aq.) AT 25°

Concn. of RbI soln. (form. wt./l.)	$D_{Rb^+} \times 10^6$ (cm. <sup>2</sup> /sec.)	$D_{I^-} \times 10^6$ (cm. <sup>2</sup> /sec.)
0.010	2.055 ± 0.025	2.035 ± 0.020
.038	2.047 ± .010	
.040		1.990 ± .020
.070	2.037 ± .020	
.100		1.990 ± .025
.110	2.017 ± .010	
.185	2.008 ± .015	
.250		1.976 ± .015
.370	2.004 ± .010	
.510		1.919 ± .015
.640	1.995 ± .010	
.850		1.860 ± .020
.927	1.993 ± .010	
1.255		1.840 ± .025
1.308		1.824 ± .025

TABLE IX

SELF-DIFFUSION COEFFICIENTS OF K<sup>+</sup> AND I<sup>-</sup> IN KI (aq.) AT 25°

Concn. of KI soln. (form. wt./l.)	$D_{K^+} \times 10^6$ (cm. <sup>2</sup> /sec.)	$D_{I^-} \times 10^6$ (cm. <sup>2</sup> /sec.)
0.010		2.020 ± 0.010
.048		2.001 ± .015
.050	1.970	
.100	2.005 ± 0.030	1.985 ± .020
.200		1.975 ± .020
.290	2.060 ± .040	
.300		1.965 ± .025
.500	2.030 ± .030	1.955 ± .015
.774	2.080 ± .050	
1.000	2.030 ± .040	1.941 ± .020
1.440		1.920 ± .010
1.960	1.910 ± .050	
2.000		1.891 ± .005
3.000		1.842 ± .005
3.062	1.850 ± .060	

## Discussion

**Diffusion Coefficients at Infinite Dilution.**—The Nernst equation, which expresses the diffusion coefficients of ions at infinite dilution in terms of their limiting conductances, may be adapted for self-diffusion

$$D_i^0 = \frac{RT}{ZF^2} \lambda_i^0 \quad (1)$$

where  $Z$  is the charge of the ion in electronic units,  $F$  the faraday,  $R$  the perfect gas constant and  $T$  the absolute temperature.

It is difficult to test this equation by extrapolation of our experimental curves because there are few points in the dilute concentration region. However, values for the limiting self-diffusion coefficients have been determined by calculation of the intercept on the  $D$  axis of the best straight line, as found by a least squaring procedure, passing through the lowest three or four points. A much more precise method for some ions that has become available as a result of a relationship found in this work, is to extrapolate the straight line which is obtained from a plot of  $D\eta/\eta_0$  against  $c^{1/2}$ . Limiting conductance values calculated from the Nernst equation are compared to those that were estimated by both the above methods in Table X. In most cases the agreement is very good.

TABLE X

Ion	Electrolyte	$D^0 \times 10^6$ Nernst eq. (cm. <sup>2</sup> /sec.)	$D^0 \times 10^6$ Least squaring data (cm. <sup>2</sup> /sec.)	$D^0 \times 10^6$ Extrap. of $D \times \eta/\eta_0$ (cm. <sup>2</sup> /sec.)
I <sup>-</sup>	LiI	2.045	2.040	2.044
I <sup>-</sup>	HI	2.045	2.015	2.045
I <sup>-</sup>	RbI	2.045	2.032	2.075
I <sup>-</sup>	KI	2.045	2.033	2.046
Rb <sup>+</sup>	RbI	2.072	2.057	2.077

**Cation Self-diffusion.**—The self-diffusion coefficient for K<sup>+</sup> ion diffusing in potassium iodide shows a maximum at a concentration of about 0.7  $M$ . The corresponding values for Rb<sup>+</sup> diffusing in rubidium iodide do not exhibit a maximum, at least in the concentration range studied. Similar maxima have been obtained by Wang<sup>8</sup> and by Wang and Miller<sup>9</sup> for Na<sup>+</sup> ion diffusing in potassium chloride

and in sodium chloride, respectively. Wang<sup>8</sup> interprets these maxima as resulting from two opposing effects acting upon the diffusion rate: with increasing salt concentration there is a tendency toward reduction of the activation energy for diffusion caused by the relative increase of distortion in the immediately surrounding water molecules, and at the same time there is a tendency toward increase of the activation energy caused by the increase in short-range interionic attraction. According to his postulates, the first effect should be greater the more hydrated the ion; for the same reason the effect is not observed with most anions. If our cation diffusion curves are examined in the light of Wang's postulates, no definite conclusion as to agreement or disagreement can be drawn. The rather sharp difference between the behavior of  $K^+$  and  $Rb^+$  ions is striking. However, speculation as to the cause of these maxima should perhaps be withheld until there is some explanation of their absence in all measurements so far reported by the diaphragm cell technique.

**Iodide Self-diffusion.**—It is possible to correlate the self-diffusion coefficients of  $I^-$  ion in the various iodide solutions with two particular solution vari-

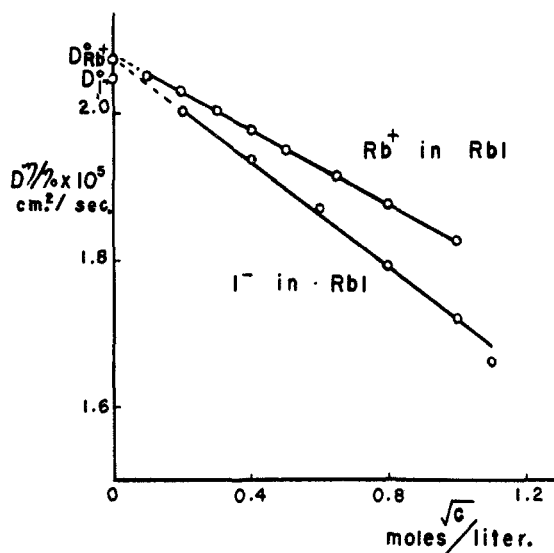


Fig. 1.—Diffusion-viscosity product vs.  $\sqrt{c}$  for  $Rb^+$  and  $I^-$  ions in  $RbI$  solutions.

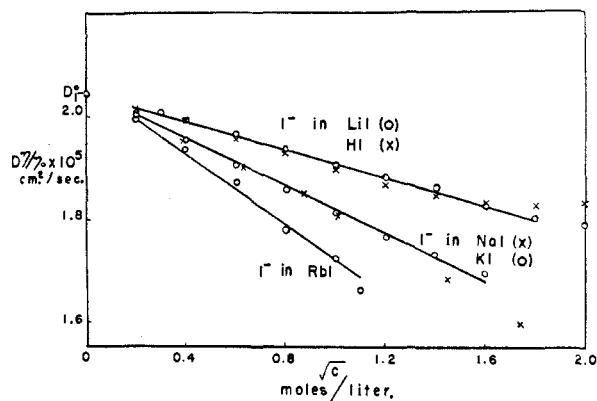


Fig. 2 Diffusion-viscosity product vs.  $\sqrt{c}$  for  $I^-$  ion in several iodide solutions.

ables: (a) the viscosity of the medium, and (b) a parameter related to the size of the cation. The theoretical justification for these comparisons is not well-established, but the data correlation obtained with them suggests that the treatment has some validity.

As a first approximation the diffusion coefficients of particles are assumed to be inversely proportional to the viscosity of the medium in which they diffuse. Both the Stokes-Einstein equation and the more recent treatment of Eyring contain a term of this form. In Fig. 1 are plotted  $D\eta/\eta_0$  vs.  $\sqrt{c}$  curves for the diffusion of  $Rb^+$  and  $I^-$  ions in  $RbI$  solutions, and in Fig. 2 are plotted similar curves for the diffusion of  $I^-$  ions in the several iodide solutions. It will be observed that although these products are not constant, there is a simple linear relationship with  $\sqrt{c}$  up to high concentrations. (As has been indicated in the first section of the Discussion, extrapolation of these straight lines gives the limiting diffusion coefficient as  $\sqrt{c}$  tends to 0 in good agreement with the Nernst equation values.) It is significant that the linear relationship just described holds only for large ions usually considered to be unhydrated. Other ions, such as  $Na^+$ ,  $K^+$ ,  $Cl^-$  and  $SO_4^{2-}$  ions, do not exhibit linearity in their  $D\eta/\eta_0$  vs.  $\sqrt{c}$  plots.

It will be observed in Fig. 2 that the  $I^-$  in  $LiI$  and  $HI$  lines fall very closely together, below them are the lines for  $I^-$  in  $NaI$  and  $KI$ , and below these the  $I^-$  in  $RbI$  line. The series of slopes follows an order that conforms with generally accepted size and hydration characteristics of the cations, in contrast to the anomalous order observed in plots of the diffusion coefficients uncorrected for viscosity. In attempting to offer a more quantitative explanation for the slopes obtained with the differing cations, we have assumed that the size of the hydrated cation affects the iodide ion diffusion rate by its effect on the charge distribution in the ionic atmosphere, which determines the potential imposed upon the central ion. In the Debye-Hückel ion atmosphere treatment as applied to activity coefficient theory in dilute solution, this size effect leads to the introduction of the  $\delta$  parameter, termed the mean distance of closest approach of the ions and evaluated from the fitting of experimental activity coefficient curves. If the diffusion rate is in some way related to the total potential imposed by the presence of the ion atmosphere, then a comparison of the curves in Fig. 2 after the introduction of a potential correction, ought to show this dependence. As a first step toward testing this idea, we have plotted in Fig. 3 our  $D\eta/\eta_0$  values against the function  $c^{1/2}/(1 + 0.3288\delta c^{1/2})$ . The  $\delta$  values used are those listed in Harned and Owen.<sup>12</sup> It is apparent that the curves for  $I^-$  ion diffusing in rubidium, potassium, sodium and hydrogen iodides do fall very closely together, and that for lithium iodide is only very slightly separated from the others. The practical coincidence of these curves with an over-all deviation of  $\pm 2\%$  is rather remarkable,

(12) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, Table 12-5-2 (parameters for equation 12-5-3).

particularly in view of the fact that the simple correction in the Debye-Hückel treatment is only meant to apply to dilute solutions and a similar correction for activity coefficient data is valid only up to concentrations of about 0.1 *M*. If the correlation is real, and if a more explicit relationship between these terms can be found, it may be possible to calculate the self-diffusion coefficients of large unhydrated ions from viscosity data and a knowledge of the mean distance of approach of the ions. Alternatively, a value for the  $\delta$  parameter might be determined from diffusion and viscosity data.

A very simple picture of the self-diffusion process for "unhydrated" ions is suggested by this treatment. We visualize a charged body moving through a viscous medium and having restraints imposed upon its passage from two sources acting essentially independently of one another. The first restraint is due to the necessity for the solvent molecules to move out of the ion's path and so is approximately proportional to the macroscopic viscosity. The second is imposed by the necessity of the ion to acquire enough energy to be displaced from its atmosphere; this is quantitatively related to its total potential due to the ion atmosphere. Thus the larger the hydrated counter ions, the further from the central ion will be the average charge of the ion atmosphere, and the smaller will be the binding potential at the central ion. Thus, if the diffusion rate is so related to the potential imposed upon the ion, then, after viscosity has been corrected for, the  $I^-$  ion in LiI should diffuse faster than in KI and NaI and faster

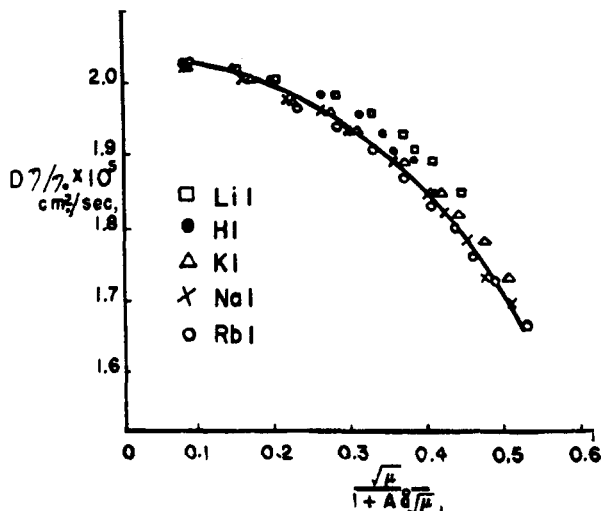


Fig. 3.—Diffusion-viscosity product vs. a function including the Debye-Hückel  $\delta$  parameter for iodide ion diffusing in aqueous iodides.

again than in RbI which is in complete accord with the experimental data.

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## The Effect of Some Salts on the Solubility of Potassium Bromide in Acetic Acid at 30°

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The solubility of potassium bromide in acetic acid at 30° is 0.01837 molal. Its solubility in the presence of various univalent added salts, in concentrations ranging from roughly 0.001 to 0.1 *m*, has been determined. Sodium acetate, sodium trichloroacetate, sodium formate, lithium acetate and lithium formate each produce a marked increase in solubility, which can be accounted for quantitatively by assuming that the salts exist almost completely undissociated in solution (probably as ion-pairs), and that exchange reactions of the type  $KBr + MX \rightleftharpoons MBr + KX$ , proceeding until equilibrium is established, are responsible for the increased solubility. Potassium acetate, potassium formate and sodium bromide, each having one ion in common with potassium bromide, produce only a slight effect on the solubility, a very small increase. This appears to be attributable to an association reaction of the type  $KBr + KX \rightleftharpoons A$ , occurring to a small extent.

Several investigations of salt effects on the solubilities of other salts in acetic acid have been reported.<sup>1</sup> The results of some of these studies have been compared with values calculated from the Debye-Hückel theory, assuming complete ionic dissociation of the salts in solution. In general, moderately good agreement was obtained provided rather large values of the ion diameter  $a$  were used, and especially if the Gronwall, LaMer

and Sandved<sup>2</sup> extension of the theory was employed. The work of Bjerrum<sup>3</sup> and of Fuoss and Kraus,<sup>4</sup> however, makes it appear probable that in acetic acid, as well as in other solvents of moderately low dielectric constant, dissolved salts exist largely as associated ion-pairs in equilibrium with relatively small concentrations of free ions. In the light of this view the application of the Debye-

(1) (a) R. P. Seward and C. H. Hamblet, *THIS JOURNAL*, **54**, 554 (1932); (b) A. W. Scholl, A. W. Hutchison and G. C. Chandlee, *ibid.*, **55**, 3081 (1933); (c) A. W. Davidson and H. Geer, *ibid.*, **60**, 1211 (1933); (d) E. Griswold, A. Ash and L. McReynolds, *ibid.*, **67**, 372 (1945).

(2) T. H. Gronwall, V. K. LaMer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

(3) N. Bjerrum, *Det. Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **7**, No. 9, 1 (1926).

(4) R. M. Fuoss and C. A. Kraus, *THIS JOURNAL*, **55**, 476, 1019 (1933).