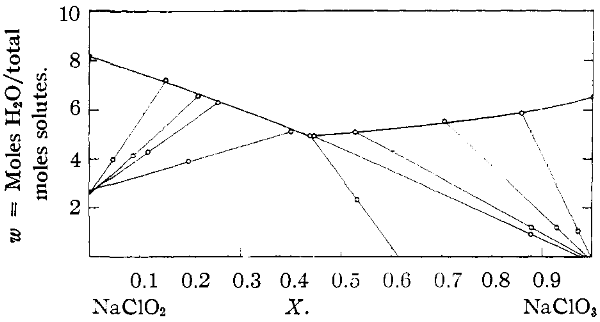

Fig. 1.—The system sodium chlorite–sodium chlorate–water at 15°.

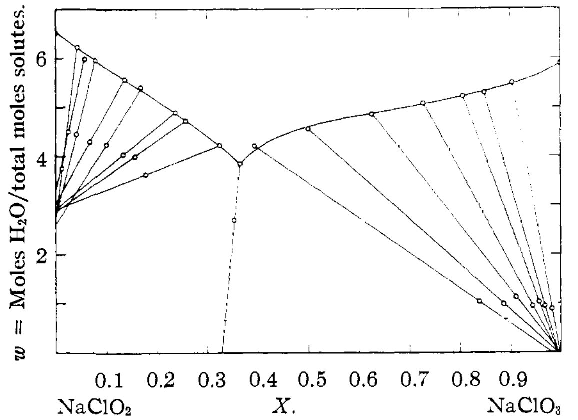

Fig. 2.—The system sodium chlorite–sodium chlorate–water at 25°.

ride, hypochlorite, chlorate and alkali have been described by White.[2]

The solutions and wet residues were analyzed for chlorite ion and chlorate ion. The water in the liquid phase and the wet residue solid were determined by difference.

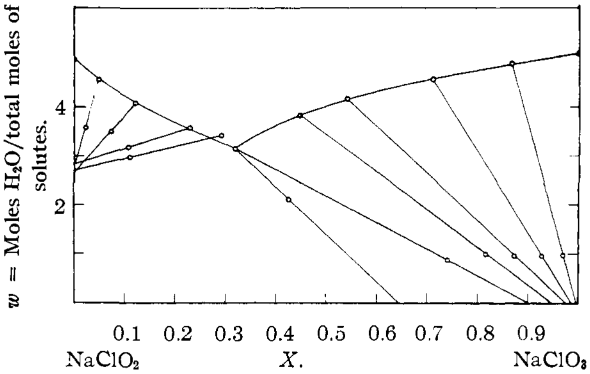

Fig. 3.—The system sodium chlorite–sodium chlorate–water at 35°.

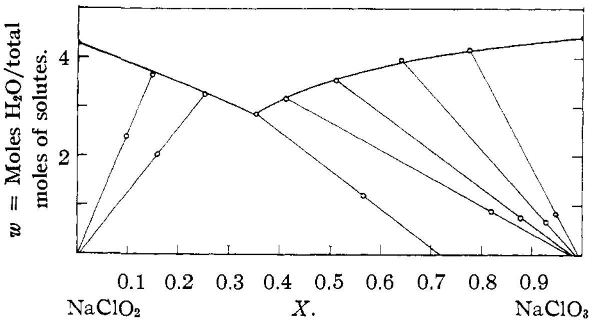

Fig. 4.—The system sodium chlorite–sodium chlorate–water at 45°.

The Ternary System Sodium Chlorite–Sodium Chlorate–Water.—In this system four isotherms have been worked out: 15, 25, 35 and 45°. The data are summarized in Table I and shown in Figs. 1, 2, 3 and 4. They show only the trihydrate of sodium chlorite already known, sodium chlorite and pure sodium chlorate.

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[2] J. F. White, *Am. Dyestuff Reporter*, **31**, 484 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Self-diffusion Coefficients of Potassium, Cesium, Iodide and Chloride Ions in Aqueous Solutions[1]

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The self-diffusion coefficients of potassium, cesium, iodide and chloride ions have been measured in a series of aqueous metal halides of moderate to high concentration at 25°. The open-ended capillary method has been used for all experiments. Investigation of the sources of error of the capillary method has been extended. The self-diffusion coefficients of large unhydrated ions are found to exhibit the same type of linear relationship as was reported by Mills and Kennedy.[2] A possible explanation of the maxima obtained for hydrated ions is suggested.

During the past ten years considerable interest has arisen in the measurement of self-diffusion coefficients of ionic solutions by the use of radioactive tracers. Measurements have been made with diaphragm cells, of the diffusion coefficients of sodium ion in aqueous sodium chloride,[3] of sodium ion in aqueous sodium iodide,[4] and of sodium ion and chloride ion in aqueous sodium chloride,[5] all at 25°. Diffusion tubes have been used to measure the self-diffusion coefficients of sodium ion and chloride ion in aqueous sodium chloride,[6] and modified diffusion tubes have been used to measure the coefficients of sodium ion and iodide ion in aqueous sodium iodide.[7] More recently measurements have

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[1] Submitted by A. M. Friedman as part fulfilment of the requirements for the Ph.D. degree at Washington University, St. Louis.

[2] R. Mills and J. W. Kennedy, THIS JOURNAL, **75**, 5696 (1953).

[3] A. P. Brady and D. J. Salley, *ibid.*, **70**, 914 (1948).

[4] A. W. Adamson, *J. Chem. Phys.*, **15**, 762 (1947).

[5] A. W. Adamson, THIS JOURNAL, **74**, 446 (1952).

[6] L. P. Jehle, Ph.D. Thesis, University of California, Berkeley, 1938.

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

been made by the capillary method introduced by Anderson and Saddington[8] and improved by Wang.[9] The self-diffusion coefficients of thallous ion in perchloric acid[10] at 25°, of potassium ion in potassium iodide, of rubidium ion in rubidium iodide, and of iodide ion in hydrogen iodide, lithium iodide, potassium iodide and rubidium iodide, all in aqueous solution[2] at 25°, of sodium ion in aqueous sodium chloride[11] and potassium chloride,[12] and of chloride ion in aqueous sodium chloride[13] at 25° have been measured by this method.

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.[12]

In all these investigations, except that of Mills and Kennedy, no quantitative generalization has been found for the variation of the self-diffusion coefficient with concentration in the moderately concentrated region. This present work was undertaken to obtain more information on the relationship of the self-diffusion coefficient to the concentration.

Experimental Procedure

The apparatus in which diffusion took place was essentially the same as that described in the literature.[2,9] The potassium chloride bath solutions were made by weighing the desired amount of dry salt of A.R. grade in a volumetric flask and diluting this to volume. The cesium iodide solutions were made from cesium iodide which had been prepared by the addition of cesium sulfate to a 1% excess of fresh barium iodide solution, filtering off the barium sulfate, and recrystallizing the resulting cesium iodide three times. To test the purity of the cesium iodide solution one milliliter was evaporated to dryness in a vacuum desiccator and the residue was weighed. The weight of the residue agreed within 1% with that expected from titration of the iodide in the solution. Because of the extreme ease of oxidation of concentrated cesium iodide solutions the bath solutions were not made from a weighed amount of the dry salt; rather they were made by approximate dilution and immediately placed under a nitrogen atmosphere in a stirred flask in the 25° bath. After a period of 24 hours aliquots were removed for potentiometric titrations,[14] and a sample was removed for viscosity measurements with an Ostwald viscosimeter.

The radioactive cesium and iodide tracers used were Cs^{134} and I^{131}. These were obtained essentially carrier-free from the Isotopes Division of the U.S.A.E.C., and the stock solutions were made by addition of enough carrier to make 10^{-5} molar tracer of the proper radioactivity to give convenient counting rates for the amount of solution contained in a capillary cell. For each diffusion experiment one milliliter of this stock solution was evaporated to about 0.1 ml. under a heat lamp and then evaporated to dryness in a vacuum desiccator; the desiccator was used because it had been found that the carrier-free tracers, especially the iodide, tended to form radiocolloids when evaporated entirely in air. The dry residues were then dissolved in about 1 ml. of the stock solutions to form the capillary solutions for diffusion. We found that a tenfold increase in either carrier or tracer concentration caused no effect on the measured diffusion coefficients.

The radiochlorine was obtained from the same source, as Cl^{36} in the form of 0.01 *N* hydrochloric acid. Brom thymol blue indicator was added, and the solution was titrated to *p*H 7 with carbonate-free potassium hydroxide. The neutral solution was then boiled with prewashed charcoal (to remove the indicator) and filtered.

The potassium isotope K^{42} was received as solid potassium carbonate. This was dissolved in water, and in the presence of an indicator sufficient hydrochloric acid was added to bring the solution to *p*H 3. The mixture was boiled for an hour, back titrated to *p*H 7 with potassium hydroxide, boiled with charcoal, filtered, and then treated in the same manner as the stock potassium chloride tracer made from the radiochlorine.

The capillaries were filled and emptied in the manner described by Mills and Kennedy,[2] except for the Cl^{36} samples. These capillaries were emptied and rinsed onto glass counting plates by means of fine pipets. The Cl^{36} samples were counted in a thin window argon–methane proportional counter with an over-all efficiency of 37%. The other samples were counted in a stilbene crystal scintillation counter. The counting rates of both types of samples were reproducible within 1%.

The over-all change in the diffusion coefficients is only about 10 or 20% for a three hundred-fold change in concentration. We wished to obtain values with experimental errors no greater than 1 or 2%. Systematic determinations of several possible sources of error were made as will be described briefly below. Mills and Kennedy[2] have presented evidence concerning other possible sources of error.

1. **Stirring Rate.**—If the bath solution is stirred rapidly some of the capillary solution will be swept out by the flow. The result would be diffusion from an effectively shortened capillary. If on the other hand the bath solution is insufficiently stirred, the concentration of the radioactive species will be appreciable at the mouth of the capillary and a short distance outside it, effectively increasing the length of the bore. The difference between the true and apparent diffusion coefficients can be related to this change, Δl, in the effective length of the capillary.[12] Diffusion runs in 0.05 *M* potassium chloride with a Cl^{36} tracer using capillaries 2 to 6 cm. long were made at various stirring rates. The results give $\Delta l = 0$ at 90 r.p.m.. $\Delta l = 1.5$ mm. at 0 r.p.m., and $\Delta l = -0.2$ mm. at 160 r.p.m. for our geometry. We adopted this geometry and the 90 r.p.m. stirring rate for all subsequent work. Synchronous motors geared down to 90 r.p.m. were used. That the effects of stirring were negligible at this stirring rate and under these conditions was confirmed for several systems at various concentrations.

2. **Temperature Fluctuations.**—Because rapid temperature fluctuations could cause convection currents in the capillaries, the heating and cooling of the water-baths was carefully controlled. The exterior thermostat temperature was found to vary 0.01°, and the inner flask temperature varied 0.001°, both with a 2-minute cycle. A trial diffusion run with the temperature variations artificially increased tenfold resulted in an apparent increase of only 0.05% in the diffusion coefficient. Because this was well within the experimental uncertainty we concluded that the usual temperature variation had no noticeable effect on the diffusion coefficients.

Values of the relative viscosity were taken from the literature.[15,16] In addition several determinations were made on each salt with a 1-ml. Ostwald viscosimeter. Agreement between literature and measured values was within 1%.

Self-diffusion Coefficients.—The results obtained in the measurements of the self-diffusion coefficients are tabulated in Tables I, II and III. Each coefficient is the mean of from three to six determinations. The error listed is the root-mean-square deviation; the average tabulated error in this work is 1.23%. The temperature was 25.00 ± 0.005° in all cases.

Discussion

Iodide Self-diffusion.—Mills and Kennedy[2] noticed that linear plots are obtained for the self-diffusion of I^- ions in various salt solutions when

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(8) J. A. Anderson and K. Saddington, *J. Chem. Soc.*, S381 (1949).

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

(10) C. Hargraves, A.M. Thesis, Washington University, St. Louis, Mo., 1952.

(11) J. H. Wang and S. Miller, THIS JOURNAL, **74**, 1611 (1952).

(12) J. H. Wang, *ibid.*, **74**, 1182 (1952).

(13) J. H. Wang, *ibid.*, **74**, 1612 (1952).

(14) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Ed. 1, The Macmillan Co., New York, N. Y., 1936, p. 485.

(15) "International Critical Tables," Vol. 5, Ed. 1, McGraw–Hill Book Co., New York, N. Y., 1925, p. 17.

(16) G. Jones and H. J. Fornwalt, THIS JOURNAL, **58**, 619 (1936).

TABLE I

SELF-DIFFUSION COEFFICIENTS OF K^+ AND Cl^- IN AQUEOUS KCl

Concn. of KCl (form. wt./l.)	$D \times 10^5$, K^+ (cm.²/sec.)	$D \times 10^5$, Cl^- (cm.²/sec.)
0.040	1.890 ± 0.01	1.982 ± 0.062
.100	1.870 ± .029	1.912 ± .005
.250	2.033 ± .034	1.989 ± .034
.500	2.135 ± .004	2.020 ± .030
1.000	2.113 ± .040	2.037 ± .035
2.000	2.013 ± .040	1.908 ± .040
3.000	1.903 ± .010	1.787 ± .047

TABLE II

SELF-DIFFUSION COEFFICIENTS OF Cs^+ AND I^- IN AQUEOUS KCl

Concn. of KCl (form. wt./l.)	$D \times 10^5$, Cs^- (cm.²/sec.)	$D \times 10^5$, I^- (cm.²/sec.)
0.050	2.055 ± 0.020	2.027 ± 0.010
.100	2.040 ± .010	....
.250	2.012 ± .070	2.016 ± .050
.500	1.990 ± .010	2.004 ± .010
1.000	1.988 ± .010	1.991 ± .020
2.250	1.964 ± .013	1.964 ± .040
3.700	1.841 ± .010	1.807 ± .030

TABLE III

SELF-DIFFUSION COEFFICIENTS OF Cs^+ AND I^- IN AQUEOUS CsI

Concn. of CsI (form. wt./l.)	$D \times 10^5$, Cs^+ (cm.²/sec.)	$D \times 10^5$, I^- (cm.²/sec.)
0.00141	2.091 ± 0.020	....
.04765	2.058 ± .015	2.002 ± 0.010
.1136	2.047 ± .011	1.959 ± .020
.5126	2.076 ± .037	1.958 ± .031
.6900	2.007 ± .001	1.977 ± .010
1.195	2.094 ± .025	1.976 ± .030

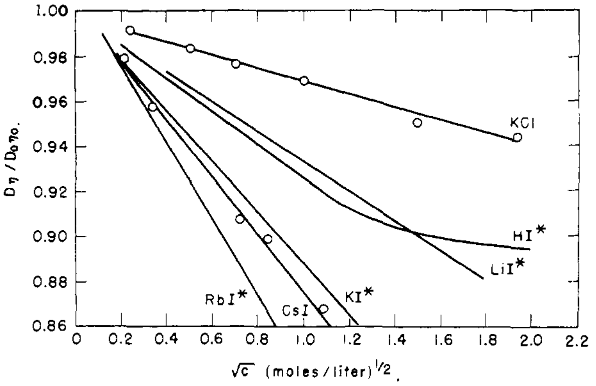

Fig. 1.—Diffusion coefficient–viscosity product for I^- ion in various solutions compared to the concentration: *, from the work of Mills and Kennedy.[2]

the product of the self-diffusion coefficient and relative viscosity of the solution is plotted against the square root of the concentration. In Fig. 1 are plotted the $D\eta/\eta_0$ *vs.* $\sqrt{c}$ curves for the iodide ions in CsI and in KCl solutions; the curves of Mills and Kennedy are included for comparison. It is noted that the order of increasing slopes of the linear portions is: KCl < HI, LiI < KI < CsI < RbI. At least for the alkali iodides this is in the order of the limiting conductances of the cations, and for the last five solutions corresponds to the order generally agreed upon as that of decreasing hydrated cation radii.

To correlate these results, Mills and Kennedy[2] suggested a simple picture of the self-diffusion process postulating restraints to diffusion from viscosity and from the electric potential of the counter-ion atmosphere. An additional factor[9] may result from the semi-crystalline nature of the solvent water. It may be expected that the diffusing ion has to move from one open lattice position to another. In this case any increase in the disorder of the solvent should result in an increase in the diffusion coefficient. Therefore, for solutions of the same ionic potential, we can expect the diffusion coefficients of a particular ionic species, corrected for viscosity, to be higher in the presence of surrounding ions which produce the larger amount of distortion in the solvent, that is, for the counter ion of higher hydration or of equal hydration but of larger size. This could explain the order of the slopes in Fig. 1. In the case of diffusion of I^- in KCl the surrounding ions are the more hydrated Cl^- ions and hydrated K^+ ions, and in this medium the iodide diffusion coefficient corrected for viscosity remains higher than in the other solutions.

Potassium and Chloride Ion Diffusion.—Here, as in the work reported by Wang[12] and by Mills and Kennedy,[2] a maximum appears in the self-diffusion coefficient. Wang[12] has explained this by ascribing the rise to disorder in the solvent and the decrease from the maximum to ion dipole interaction. Another possible explanation may be a change in the degree of hydration of the diffusing ion with concentration. This would cause an increase in *D* with increasing concentration until some "dehydrated" state is reached; thereafter *D* would decrease due to the increasing counter-ion potential. However, such maxima still have not been reported by workers using the diaphragm cell technique.

Cesium Ion Diffusion.—Presumably the cesium ion is not hydrated and would have the same type of behavior as the iodide ion. A plot (not shown) of the values of $D\eta/\eta_0$ for Cs^+ in CsI against $c^{1/2}$ is linear over the entire concentration range.

ST. LOUIS, MO.