635. *Diffusion Coefficients of the Chromate Ion in Concentrated Solutions.*

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Diffusion coefficients of the chromate ion have been measured for concentrations between 0·1M and 2·75M at pH 7 by using sodium chromate labelled with chromium-51, also for 2M-solutions between pH 2 and pH 10. The results obtained indicated that only chromate or hydrogen chromate ions are likely to exist over the range investigated.

THE rate of diffusion of an ion or molecule may be directly related to its size,[1] so that measurement of the diffusion coefficient gives an excellent indication of ionic or molecular dimensions. Until the introduction of the use of radioactive isotopes, measurements of the rates of diffusion of ions and molecules had to be made in the presence of a concentration gradient. Anderson and Saddington [2] developed a method of measurement employing radioactive tracers and obtained information concerning the variation of self-diffusion coefficient, and hence the composition, of aqueous tungstic acid solutions over a range of pH. Other workers [3] have investigated Anderson and Saddington's experimental method with particular reference to possible limitations in technique and have also produced more rigorous mathematical treatments of the theory of self-diffusion. Similar methods were subsequently employed by these workers to investigate the diffusion coefficients of ions in alkali-metal halide solutions at various concentrations.

The object of the present investigation was to estimate sizes of chromate ion over a range of pH and concentration in connexion with the possible existence of polychromate ions.

Preliminary work on the diffusion of chromate ions in dilute sodium chromate solutions

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[1] Robinson and Stokes, " Electrolyte Solutions," Butterworths Scientific Publns., London, 1955, p. 12.

[2] Anderson and Saddington, *J.*, 1949, S381.

[3] Wang, *J. Amer. Chem. Soc.*, 1952, **74**, 1182; Friedman and Kennedy, *ibid.*, 1955, **77**, 4499; Mills, *ibid.*, p. 6116.

indicated that there is little change in ion size over a wide range of pH. When more concentrated solutions were investigated anomalous results were often obtained and precise conclusions could not be drawn. Such anomalies were subsequently eliminated by boiling the solution under reduced pressure before use. The results, correlated with viscosity data, provided information on the nature of the chromate ion. In order to eliminate a further possible error, the influence of cell diameter on the accuracy of the results was also determined.

EXPERIMENTAL

Method.—A stock solution of sodium chromate (*ca.* 3M) was prepared, filtered, and standardised gravimetrically. It was heated to the b. p. under reduced pressure and then immediately cooled. Portions were diluted to the required molarity, the pH being adjusted by the addition of hydrochloric acid or sodium hydroxide solution.

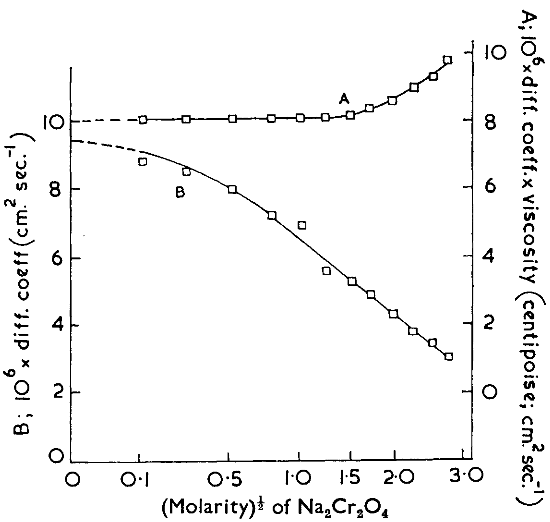

FIG. 1. Plots of (molarity)$^{\frac{1}{2}}$ against (A) diffusion coefficient × viscosity and (B) diffusion coefficient for sodium chromate solution at pH 7 and 25°. (The experimental points are each the average of at least 2 results.)

The apparatus was substantially the same as that used by Anderson and Saddington. The main container was a 250 ml. beaker closed with a rubber bung, through the centre of which passed a glass rod supporting a Perspex platform on which the diffusion cell was placed. The cells were made from 2 cm. lengths of precision-bore glass-capillary tubing closed at one end with ground-glass plates. The open ends were ground smooth and flat, and the average bore and volume of each cell were measured by using mercury.

Sodium chromate (120 ml.) of the required molarity and pH was added to the main container, and a further amount (20 ml.) was added to a small conical flask together with sodium chromate solution (0·1 ml.) containing 0·1 mc of chromium-51. Both solutions were placed in the thermostat-bath at 25° (±0·1°) and allowed to reach thermal equilibrium. Two cells were filled with the solution containing the tracer by means of a fine glass tube attached to a hypodermic syringe. One, the measurement cell, was filled until the meniscus was raised above the top of the bore so that " drag out " was avoided on its submergence into the bulk solution. The other, the reference cell, was filled level with the top of the bore. The measurement cell was placed in its holder and lowered into the bulk solution so that the level of the solution was just below the top of the cell. After 2 hr. in the thermostat-bath, the cell was gently submerged.

Diffusion was allowed to proceed for 40—60 hr., after which the measurement cell was raised from the bulk solution, removed from its holder, and dried with absorbent tissue. The contents of the measurement and the reference cell were withdrawn by the syringe and, together with washings, transferred to two matched 3 ml. test-tubes. The contents of the tubes were adjusted to a fixed volume with distilled water and their activities measured by means of a scintillation counter.

After correction of the recorded counts for background and the difference in volume between measurement and reference cells, the fraction of activity remaining in the cell after diffusion was determined. The diffusion coefficient was calculated by using the equation $D = \pi L^2(1 - \gamma)^2/4t$, where D = diffusion coefficient (cm.^{2} sec.$^{-1}$), L = length of diffusion cell (cm.), t = time of diffusion (sec.), and γ = fraction of radioactive isotope remaining in the cell after diffusion (see Appendix).

The viscosities of the chromate solutions used for diffusion coefficient measurements were determined at 25° in an Ostwald viscometer.

Results.—It is customary to correct diffusion measurements for viscosity changes as it has been shown that the product of these two variables is constant in solutions up to fairly high concentrations provided that there is no change in ionic size. Fig. 1 shows diffusion coefficients plotted against (molarity)$^{\frac{1}{2}}$ at pH 7, in the manner used by previous authors.[3] The product of diffusion coefficient and viscosity is also shown. Fig. 2 shows similar variations with pH for 2M-solutions. The Table shows the influence of cell diameter on diffusion coefficient for 2M-solutions at pH 7. Since there is no significant variation in the results between cell diameters from 0·11 cm. to 0·44 cm., this will not be discussed further.

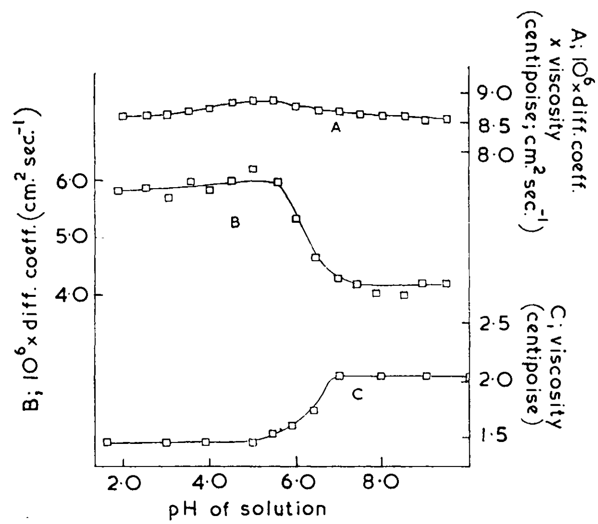

FIG. 2. Effect of pH on the diffusion coefficient, etc., for 2M-sodium chromate at 25°. (The experimental points are each the averages of at least 3 results.)

Cell diam. (cm.)	0·115	0·230	0·440
No. of determns. of D	7	6	6
10^6 Mean diff. coeff. (cm.^{2} sec.$^{-1}$)	4·57	4·69	4·72
10^6 Standard error (cm.^{2} sec.$^{-1}$)	0·13	0·13	0·10

CONCLUSIONS

Fig. 1 shows that the fall in the value of the diffusion coefficient, D, with increasing concentration is accompanied by a proportionate increase in solution viscosity, η, so that the product, $D\eta$, is constant from infinite dilution up to 1·5M-solutions. The deviation of $D\eta$ from constancy at higher molarities (7% at 2M to 15% at 2·5M) may be due to reduction of the amount of hydration of the chromate ions or to deviations from ideality. The variation of the diffusion coefficient of chromate ions with increasing molarity of the solution occurs in a uniform manner, similar to that described by several workers[3,4] investigating simple alkali halide solutions, and shows no evidence of polychromate formation over the entire concentration range investigated.

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[4] Berne and Weill, *J. Phys. Chem.*, 1960, **64**, 272.

The Einstein–Stokes relation:

$$D = kT/6\pi\eta r$$

(where k is the Boltzmann constant and T the absolute temperature) has been used to determine the " molecular radius " of diffusing particles. Although such determinations have not proved to be very precise, the product $D\eta$ is useful in indicating changes which may occur in molecular particle size. Fig. 1 shows that the diffusion coefficient, when corrected for the effect of viscosity, is reasonably constant from infinite dilution up to quite high molarities.

Consider the reaction:

$$2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

the diffusion of chromate ions in acid solutions should be considerably slower than in alkaline solutions if all other factors remain constant. Fig. 2 shows that the diffusion coefficient of chromate ions in 2M-solution is much smaller in alkaline than in acid solutions, results which are the exact converse of the situation expected from equation 1. However, it will be observed that there is a proportionate viscosity change between pH 5 and pH 7 and the product, $D\eta$, is constant (within 8%) over the entire pH range investigated. It may be concluded that the difference in diffusion coefficients in acid and alkaline solutions is solely a viscosity effect and that the species existing over the entire pH range have similar ionic size. It is unlikely that the reaction described in equation 1 is correct and a more likely reaction is:

$$CrO_4^{2-} + H^+ = HCrO_4^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The change in viscosity between pH 5 and pH 7 may be due to factors described by Harned and Owen.[5] They state that for electrolyte solutions viscosity results from the resistance to deformation of the atmosphere of oppositely charged ions surrounding the central ion. In the cases of CrO_4^{2-} and $HCrO_4^-$ ions it is suggested that the stronger ionic atmosphere would be associated with the former. Equimolar solutions containing CrO_4^{2-} ions would therefore have greater viscosities than those containing $HCrO_4^-$ ions.

APPENDIX

The concentration $c(x,t)$ of the radioactive species at time t and distance x from the closed end of the capillary tube is given by the diffusion equation

$$D \cdot \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \text{ where } t \geqslant 0 \text{ and } 0 \leqslant x \leqslant L \quad . \; . \; . \; . \; . \quad (3)$$

Initially $c = c_0$, and we have the boundary conditions

$$\frac{\partial c}{\partial x} = 0 \text{ at } x = 0$$

$$c = 0 \text{ at } x = L.$$

for all values of t greater than 0.

Introducing the Laplace transform we have:

$$\bar{c}\,(x,s) = \int_0^\infty c(x,t)e^{-st}\,dt.$$

Equation (3) transforms to:

$$D\,\frac{\partial^2 \bar{c}}{\partial x^2} = s\bar{c} - c_0.$$

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[5] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," 2nd edn., Reinhold Publ. Corp., New York, 1950, p. 68.

Subject to the boundary conditions,

$$\frac{\partial \bar{c}}{\partial x} = 0 \text{ at } x = 0$$

$$\bar{c} = 0 \text{ at } x = L.$$

The solution of the transformed equation is

$$\bar{c}(x,s) = \frac{c_0}{s}\left(1 - \frac{\cosh qx}{\cosh qL}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $q = \sqrt{(s/D)}$. On inversion this yields

$$c(x,t) = \frac{4c_0}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\frac{(2n+1)\pi x}{2}\exp\left[-\frac{D(2n+1)^2\pi^2 t}{4L^2}\right].$$

Hence the fraction of the active species remaining in the tube after diffusion is given by:

$$\gamma(t) = \frac{1}{L}\int_0^L \frac{c(x,t)}{c_0}\,\mathrm{d}x = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\mathrm{e}^{-(2n+1)^2\theta}, \quad . \quad . \quad . \quad . \quad (5)$$

where $\theta = \pi^2 Dt/4L^2$.

Now for moderate to large values of Dt, equation 5 converges very rapidly and is therefore very suitable for the computation of $\gamma(t)$ since only the first term need be retained. However, for small values of Dt this is not so and an alternative simple first-order approximation may be obtained by noting that an expansion for small values of t is produced by considering large values of the transform variable s. Thus from equation (4) it can be seen that the Laplace transform $\bar{\gamma}(s)$ of $\gamma(t)$ is given by:

$$\bar{\gamma}(s) = \frac{1}{L}\int_0^1 \frac{\bar{c}(x,s)}{c_0}\,\mathrm{d}x = \frac{1}{s} - \frac{1}{sqL}\tanh qL;$$

and for large values of s this gives

$$\bar{\gamma}(s) \simeq \frac{1}{s} - \frac{\sqrt{D}}{Ls^{\frac{3}{2}}}.$$

Inversion yields:

$$\gamma(t) \simeq 1 - \frac{\sqrt{D}}{L}\cdot\frac{2}{\sqrt{\pi}}\cdot t^{\frac{1}{2}},$$

which gives

$$D = \frac{\pi L^2}{4t}\cdot(1-\gamma)^2.$$

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