cipitation occurred after several minutes and the crystals were filtered after standing for one hour, washed with cold water, and air-dried at room temperature. The spectral measurements were made on relatively fresh samples, and the effects of any structure changes in the compound on standing for several months have not yet been studied.

[CONTRIBUTION FROM THE BOSTON UNIVERSITY DEPARTMENT OF CHEMISTRY, BOSTON, MASSACHUSETTS]

The Identical Diffusion Coefficients of Isostructural Heteropoly Anions. The Complete Independence of D from Ionic Weight

BY LOUIS C. W. BAKER AND MICHAEL T. POPE[1,2]

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The "self"-diffusion coefficients of $[SiMo_{12}O_{40}]^{-4}$ and its isomorph, $[SiW_{12}O_{40}]^{-4}$, were measured at 30° by the open capillary method. These ions are very stable, virtually unsolvated, and almost spherical. Their ionic weights differ greatly. The diffusion coefficients are identical, demonstrating the complete non-validity of "Riecke's Law." Diffusion and dialysis rates are independent of molecular weight *per se*. Similar measurements were made for the isomorphs: $[CoMo_6O_{21}]^{-3}$ and $[CrMo_6O_{21}]^{-3}$. The results also test recent postulates for relating diffusion rates of polyanions to the numbers of exterior oxygen atoms available for H-bonding to the solvent. The results discourage hopes for that correlation. For polyanions and coördination complexes, even the most approximate estimations of ionic weight from diffusion data are almost completely unreliable, and chemical interpretations which have been based on such evidence should be disregarded.

A great deal of effort, especially on the part of persons interested in the chemistry of heteropoly and isopoly electrolytes, has been expended upon determining diffusion coefficients, dialysis coefficients and coefficients of electrodialysis, for the purpose of estimating ionic weights of species in solution. The results of recent researches along these lines appear in leading journals. Further, several of the most authoritative recent inorganic texts and reference works expound relationships between ionic weights and diffusion or dialysis coefficients and describe various detailed chemical interpretations which derive ultimately from "ionic weights" so determined. Although supposed difficulties in successfully relating ionic weights to diffusion or dialysis data are commonly mentioned, these works hold that (1) the ionic weight *per se* of the diffusing species is the main factor in determining diffusion and dialysis coefficients and (2) rough estimates, at least, of ionic weight may be obtained from such data.

On the other hand, the most valuable modern theories of diffusion in liquids[3-8] predict that the molecular or ionic weights will play no role whatever[9] in determining rates of diffusion. These treatments take the view that, for a given solvent, only the size and shape of the diffusing species, plus the magnitude of its interactions with adjacent particles, will affect the diffusion coefficient.

One object of the present experiments was to provide an unambiguous test of the conflicting postulates in this regard. Heretofore all the ions studied have been sufficiently dissimilar that discrepancies between observed diffusion rates and those predicted on the basis of ionic weight variation could be ascribed to a number of other factors.

This paper reports diffusion coefficients, measured in exactly comparable manner, for two pairs of isomorphous polyanions. The first pair was 12-tungstosilicate, $[SiW_{12}O_{40}]^{-4}$ (ionic weight = 2875), and 12-molybdosilicate, $[SiMo_{12}O_{40}]^{-4}$ (ionic weight = 1820). These ions are very stable under the conditions used.[10-12] They are almost spherical and virtually identical in size, structure,[13] charge and negligible degree of solvation.[14]

The results show that for these two anions the diffusion coefficients at infinite dilution are identical, within the small experimental error, despite the large difference in ionic weight. The diffusion coefficients change very little with concentration, such changes being linear in the regions studied.

The diffusion coefficients of another pair of isostructural[15] unsolvated[16] anions, 6-molybdocobaltiate and 6-molybdochromiate, were also measured in an identical manner. The results for all four ions

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(3) R. H. Stokes, *Rev. Pure and Appl. Chem.*, **5**, 60 (1955).

(4) S. Glasstone, K. J. Laidler and H. Eyring,"The Theory of Rate Processes," McGraw–Hill Book Co., New York, N. Y., 1941.

(5) J. Frenkel, *Z. Physik*, **35**, 652 (1926).

(6) G. S. Hartley, *Phil. Mag.*, **12**, 473 (1931).

(7) A. E. Stearn, E. M. Irish and H. Eyring, *J. Phys. Chem.*, **44**, 981 (1940).

(8) B. Ottar, "Self-Diffusion and Fluidity in Liquids," Oslo University Press, Oslo, Norway, 1958.

(9) In the course of an excellent modern treatment, Ottar³ estimates (p. 74) that roughly 0.17×10^{-5} is the fraction of the activation energy used to accelerate the molecular mass during a molecular jump in aqueous diffusion.

(10) L. Malaprade, *Ann. Chim.*, [10], **11**, 159, 172 (1929).

(11) L. C. W. Baker, "Properties of Heteropoly Molybdates," Climax Molybdenum Co., Information Bulletin Cdb-12, New York, N. Y., 1956, p. 7.

(12) M. C. Baker, P. A. Lyons and S. J. Singer, THIS JOURNAL, **77**, 2011 (1955).

(13) R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 1076 (1934); J. F. Keggin, *Proc. Roy. Soc. (London)*, **A144**, 75 (1934); J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935); W. Hückel, "Structural Chemistry of Inorganic Compounds," Vol. 1, Elsevier Publishing Co., Inc., Amsterdam, the Netherlands, 1950, p. 192.

(14) T. Kurucsev, A. M. Sargeson and B. O. West, *J. Phys. Chem.*, **61**, 1569 (1957).

(15) G. A. Tsigdinos, M. T. Pope and L. C. W. Baker, THIS JOURNAL, **82**, in press (1960). See also Abstracts of Papers Presented before the Division of Inorganic Chemistry, Am. Chem. Soc. National Meeting, Boston, Massachusetts, 1959.

(16) M. T. Pope and L. C. W. Baker, *J. Phys. Chem.*, **63**, 2083 (1959).

provide a test of a recent proposal for correlating diffusion coefficients of polyanions on the basis of numbers of H-bonds which are plausible between the polyanions' exterior oxygen atoms and the solvent molecules. These new data do not support existing hopes for the success of that approach.

Experimental

Preparation of Compounds.—AR reagents were used throughout and all products were recrystallized several times. $(NH_4)_3[CoMo_6O_{21}]\cdot10H_2O$ and $(NH_4)_3[CrMo_6O_{21}]\cdot 10H_2O$ were prepared by standard methods.[17-19] $K_4[SiMo_{12}O_{40}]\cdot18H_2O$ was prepared by adding 30% KCl solution to a cold solution containing 60 g. of 12-molybdosilicic acid in 40 ml. of water. The acid was prepared by the method of Strickland.[20] $K_4[SiW_{12}O_{40}]\cdot18H_2O$ was prepared in a similar manner from 12-tungstosilicic acid, which itself had been obtained by a modification of North's method.[21] (AR $Na_2SiO_3\cdot9H_2O$ was substituted for the water-glass solution.) Samples of all four salts were also prepared on 1-2 g. scales using Mo-99 and W-185.

Diffusion Measurements.—The elegant radiotracer method of Anderson and Saddington[22] was used. For each compound a solution containing solute made with radioactive atoms was allowed to diffuse from capillaries into a chemically identical, non-radioactive solution. Diffusion was estimated by counting the radioactivity of the contents of the capillaries. For each compound, sets of such measurements were made at three concentrations. In this procedure, the possibility of shifts in chemical equilibrium is removed, as is the need for the presence of excess supporting foreign electrolyte. The capillaries were approximately 0.1 cm. in bore and their accurately measured lengths varied from 2.45 to 2.70 cm. Stirring was not used. All the solutions were made up to total ionic strengths of 1.0 with $NaClO_4$. The pH of each solution was adjusted to 4.0 with perchloric acid. In each experiment the solution in the capillaries was at exactly the same concentration (determined by analyses) as the surrounding solution with respect to each solute it contained.

The concentration ranges studied were 0.003 to 0.011 M for the 12-heteropoly anions and 0.008 to 0.021 M for the 6-heteropoly anions. The concentration ranges were limited on one hand by the solubilities of the salts and on the other by the activities of the radioactive samples. The experiments were carried out at 30.0°, the temperature being constant within 0.02°. Diffusion times ranged from 3 to 4 days. Beta and gamma activities were determined with standard proportional and scintillation counters. Each point was determined from the mean of 3 or 4 experiments, using capillaries of varying length. The spread of such data was in no case greater than that indicated by the diameters of the points shown in Fig. 1, and in most cases the spread was much less.

The results are plotted in Fig. 1. The values of the diffusion coefficients at infinite dilution were obtained by extrapolation. These are recorded in Table I.

TABLE I

	Ionic weight	"Self"-diffusion coef. × 10⁶ at infinite dilution[a] (30.0°), cm.²/sec.
$[CoMo_6O_{21}]^{-3}$	971	7.4 ± 0.2
$[CrMo_6O_{21}]^{-3}$	964	$7.4 \pm .2$
$[SiMo_{12}O_{40}]^{-4}$	1820	$6.2 \pm .2$
$[SiW_{12}O_{40}]^{-4}$	2875	$6.1 \pm .2$

[a] Open capillary method, unstirred.

Discussion

Most attempts to deduce ionic weights from diffusion or dialysis measurements in liquids have been

(17) L. C. W. Baker, et al., THIS JOURNAL, **77**, 2136 (1955).

(18) L. C. W. Baker, B. Loev and T. P. McCutcheon, ibid., **72**, 2374 (1950).

(19) R. D. Hall, ibid., **29**, 692 (1907).

(20) J. D. H. Strickland, ibid., **74**, 862 (1952).

(21) E. O. North, "Inorganic Syntheses," Vol. I, McGraw–Hill Book Co., Inc., New York, N. Y., 1939, p. 129.

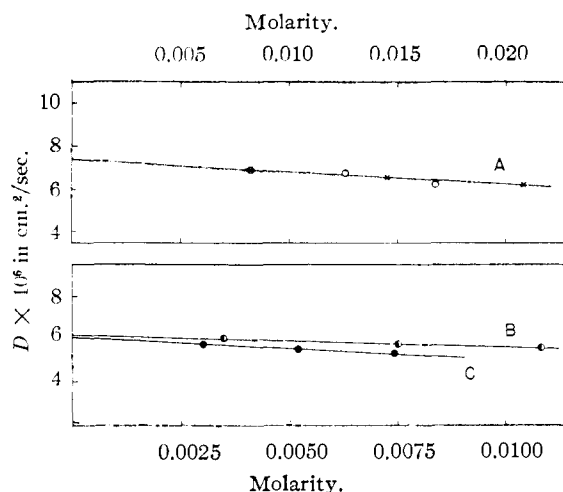(22) J. S. Anderson and K. Saddington, J. Chem. Soc., S381 (1949).

Fig. 1.—Diffusion coefficients at 30.0°, pH = 4.0, and ionic strength = 1.0: line A, O = $[CrMo_6O_{21}]^{-3}$ and X = $[CoMo_6O_{21}]^{-3}$; Line B, ◐ = $[SiMo_{12}O_{40}]^{-4}$; Line C, ● = $[SiW_{12}O_{40}]^{-4}$.

based upon a relationship known as "Riecke's Law"[23]

$$D\frac{\eta}{\eta_0}\sqrt{M} = \text{a constant.}$$

The present unambiguous test shows finally that this relationship is *wholly* invalid.

Although Riehl and Wirths[24] interpreted dialysis results for a number of simple ions on a basis which ignored their ionic weights, widespread use of the above expression continued. Some of the results and interpretations obtained from application of this and similar equations have been severely criticized by several workers on various grounds, including: precision of experimental techniques, choice of reference ions, degrees of solvation assumed, lack of chemical homogeneity of solutes, equilibrium shifts caused by concentration gradient, insufficiency of supporting electrolyte, non-uniformity of membrane pore-size, and neglect of variations in ionic shapes and charges. Most of these treatments and several current ones hold, however, to the central idea that molecular or ionic weights as such are related to diffusion or dialysis coefficients in liquids, and might be estimated if the complicating factors could be empirically incorporated into some relationship or made similar for the reference solution and the solution under investigation. The test reported herein demonstrates that such an approach cannot be rewarding.

The stepwise curves which numerous workers obtained by plotting diffusion coefficients against pH or other variables retain a certain value, of course, in that many of them indicate points where changes of solute species occur.

Current inorganic literature concerning polyanion chemistry contains numerous detailed chemical interpretations and formulations based directly or indirectly upon "ionic weights" deduced from dialysis or diffusion data. Often it is not obvious that such data were among the essential bases for given

(23) E. Riecke, Z. physik. Chem., **6**, 564 (1890); H. Euler, Wied. Ann., **63**, 273 (1897).

(24) N. Riehl and G. Wirths, Z. physik. Chem., **194**, 97 (1944).

interpretations. Therefore considerable care is indicated for readers in this field.

The data herein support the modern theories of liquid diffusion which envision that the rate-determining process for the diffusion of a large solute species is the movement of the solvent molecules around it, by means of a succession of jumps into holes of dimensions comparable to those of a solvent molecule.[25]

Valid theoretical and empirical relationships connecting molecular weight and diffusion rate can sometimes be devised for particular groups of large solute species.[26-28] These equations apply between solute particles having the same (1) shape, (2) interaction with solvent molecules and (3) internal density within the diffusing species. Such methods only introduce the molecular weight inasmuch as it depends upon the molecular volume and hence often involve an inverse proportion between diffusion coefficient and cube root of the molecular weight.

It was therefore tempting to compare the ratio of the diffusion coefficients reported above for the 12-molybdosilicate and the 6-molybdocobaltiate with the quotient of the cube roots of their ionic weights. Indeed the correspondence is close. That this and similar cases *can* be fortuitous results of compensating factors is emphasized by the fact that the ratio of the effective hydrodynamic radii, revealed by viscosity measurements,[14,16] is far from close. The structure of these 6-molybdates is unknown, although structural considerations indicate that it is probably a flattened spheroid, the shorter radius of which is below the limit for good applicability of the Einstein equation. These factors account for the poor fit of the ratio of equivalent hydrodynamic radii. It has been shown recently that these 6-molybdo anions are monomeric and very stable in solution.[15,29]

The identical diffusion coefficients prove that 12-molybdosilicate has the same hydrodynamic radius as 12-tungstosilicate, *viz.*, 5.6 Å., as recently determined for the latter ion by viscosity data.[14] This is in good agreement with the unsolvated ionic radii in crystals.[13] Similarly, the diffusion results show that the apparent hydrodynamic volume, obtained from viscosity,[16] for the 6-molybdocobaltiate ion must be identical with that of the 6-molybdochromiate. Viscosity measurements were not possible for the latter ion owing to decomposition of its concentrated acid.[16]

If the ionic radii of the spherical 12-heteropoly anions are calculated by means of the Stokes–Einstein equation, from the diffusion coefficients given in this paper, the results are decidedly smaller than the crystallographic radii. Although the radii of these ions are at the limit of the applicability of that equation, this calculation confirms[30] that, for

large polyanions as for smaller ions, the "unstirred" open-capillary method employed for measuring these diffusion coefficients probably gives results which are consistently slightly higher than "absolute" values. It has been shown recently that the method can be modified to compensate for this.[30] Nevertheless the conclusions of this paper are not altered. since all the data were obtained in exactly comparable fashion.

That the diffusion coefficients for 12-molybdosilicate are very slightly higher than those of 12-tungstosilicate in the more concentrated region (Fig. 1), may be ascribed to the very slightly lower stability of the first ion[12,31] or to slightly greater strength of the free acid of the tungsten complex. Both of these factors would operate in the same direction: the first by creating a trace concentration of smaller molybdate species and the latter by decreasing the relative availability of those exterior oxygens which can form H-bonds between the polymolybdate and water molecules. There may also be a very slight difference in the inherent H-bonding tendencies of tungstate groups as contrasted with isomorphous molybdate groups.

Ottar recently has contributed significant concepts to the modern theory of diffusion and fluidity in liquids.[8,32] Upon critical reëxamination of diffusion coefficients of simple oxyanions of the type $X^{+v}O_4^{-(8-v)}$, $X_2^{+v}O_7^{-(14-2v)}$, etc., he noted that, for anions containing the same central atom, the diffusion coefficients at constant temperature are related as

$$D_1\sqrt{w_1} = D_2\sqrt{w_2} \qquad (1)$$

where w_1 and w_2 are the numbers of "external" oxygen atoms in each ion, *i.e.*, $w = 4$ for XO_4, $w = 6$ for X_2O_7, etc. The equation appears to be valid for ions in which $X = Si$, Cr, P or V. Ottar proposed a theory wherein the diffusion coefficient is a function of (1) the number (n) of contacts between a solute particle and surrounding solvent molecules (practically, for oxyanions in water, the number of H-bonds between solute particle and solvent), (2) the mean free path (λ) of solvent molecules and (3) the probability of a molecular jump. Using Eyring's expression for the latter, Ottar showed that

$$D = \frac{\lambda^2}{6\sqrt{n}} \cdot \frac{kT}{h} \cdot e^{-\Delta F/RT} \qquad (2)$$

If diffusion coefficients are compared under conditions where both the λ's and the ΔF's can be assumed to be equal, equation 2 reduces to the observed empirical equation 1 (w directly proportional to n).

As a corollary to more important work, Ottar extended the above treatment to polyanions, using some original data and selections from the results of Jander and of Anderson and Saddington.[22] Thus, experimentally

$(D_{MoO_4}/D_{Mo_7O_{24}}^{-6})^2 = 4.0$ and $(D_{WO_4}/D_{paratungstate})^2 = 4.8$

For the simple tetrahedral MoO_4^{-2} and WO_4^{-2} ions it was assumed,[8,32] reasonably, that each oxygen

(25) R. E. Powell, W. E. Roseveare and H. Eyring, *Ind. Eng. Chem.*, 33, 431 (1941).

(26) A. Polson and D. van der Reyden, *Biochim. et Biophys. Acta*, 5, 358 (1950); A. Polson, *ibid.*, 21, 185 (1956).

(27) L. Friedman and P. G. Carpenter, THIS JOURNAL, 61, 1745 (1939).

(28) J. W. McBain, C. R. Dawson and H. A. Barker, *ibid.*, 56, 1021 (1934).

(29) E. Matljevic and M. Kerker, *ibid.*, 81, 5560 (1959).

(30) R. Mills, *ibid.*, 77, 6116 (1955); R. Mills and A. W. Adamson.

ibid., 77, 3454 (1955); R. Mills and J. W. Kennedy, *ibid.*, 75, 5696 (1953).

(31) P. Souchay and J. Faucherre, *Bull. soc. chim. France*, 18, 355 (1951).

(32) B. Ottar, *Acta Chem. Scand.*, 9, 344 (1955); B. Ottar, *Saert. av Tids. for Kjemi, Berg. Metal.*, 6, 92 (1955); B. Ottar, *J. Chim. Phys.*, 856 (1957).

atom can form three H-bonds with adjacent water molecules. In the condensed anions the oxygen atoms are at the vertices of MoO_6 and WO_6 octahedra which are sharing edges with one another. The possible number of H-bonds per oxygen atom in the polyanions is therefore much less. From the above ratios, equation 1, plus the crystal structures of $[Mo_7O_{24}]^{-6}$ (paramolybdate),[33] $[Mo_8O_{26}]^{-4}$ ("tetramolybdate")[33] and $[H_{10}W_{12}O_{46}]^{-10}$ (paratungstate),[34] Ottar concludes that an average of two H-bonds per oxygen atom is likely for polyanions.[35]

Although this is a plausible average value, it must be remembered that in most polyanion structures some oxygen atoms are completely shielded from contact with the solvent. Others are only slightly exposed, while a few project prominently. It is therefore to be expected that the average number of H-bonds per oxygen atom will vary considerably according to the structure of the anion.

Unfortunately, the various series of isopolyanions for which considerable diffusion data are available were not well-suited for testing Ottar's proposals. In most cases the structures of the species present in such solutions are unknown and in many instances even their formulas are as yet unclarified.

A major purpose of the present work, therefore, was to measure the diffusion coefficients for two 12-heteropoly anions of well-established formula, structure, and nearly spherical shape, in order to test the new proposals more rigorously.

(33) I. Lindqvist, Arkiv Kemi, 2, 349 (1950).

(34) I. Lindqvist, Acta Cryst., 5, 667 (1952).

(35) Unfortunately, the role of the ten constitutional hydrogen atoms in paratungstate is completely unknown[34] and was completely neglected in the calculation.

For the 6-heteropoly species used, the formulas are well-known,[16,17,29] although each of those anions might contain as many as three molecules of consitutional water. It is virtually certain that every oxygen atom in these 6-heteropoly species is exposed to the solvent.

Calculation on the basis outlined above, using any of the present results, reveals an "average value" of only one H-bond per oxygen atom for any of these four heteropoly species.

The reference diffusion coefficients for simple MoO_4^{-2} and WO_4^{-2} were obtained by extrapolating to 30° the same Jander and Anderson values which Ottar used. This was done by plotting[8] $\log D/T$ vs. $1/(RT)^2$.

Consideration of these results, especially in conjunction with the known structures of these ions and those used by Ottar, unfortunately greatly reduces any hope that diffusion coefficients of polyanions may be correlated, even approximately, on the bases discussed above. In several respects the discrepancies run too strongly in directions opposite to those predicted. Still less is it indicated that diffusion coefficients will be of value in revealing the status of unknown polyanions in solution. More good data on species of known structure and stability might reveal some basis for correlation.

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Influence of Structure on the Stability of Some Heterocyclic Amine Chelates[1,2]

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The acid dissociation constants of 2-aminomethyl benzimidazole and analogous compounds, as well as the stability constants of the Cu(II), Co(II), Ni(II) and Zn(II) chelates, have been determined by the potentiometric titration method. The ratio of $\log K_{AV}/\log K_{RH^+}$ was used as a criterion of steric effects in planar chelates. By this method it was found that the benzene portion of benzimidazole apparently exerts little or no steric effect in chelates of the aminoalkyl derivatives. The absence of steric effects in the aminoalkyl-benzimidazoles was used to explain the apparent lack of agreement between stability constants of the benzimidazole carboxylic acids and those found for similar compounds by previous authors.

Several studies have been made on the effect of sterically blocking groups on the stability of complexes.[3-5] Freiser and Johnston,[5] in studying the effect of methyl substitution in the 8-hydroxyquino-

(1) Presented in part before the Physical Chemistry Division of the 135th National Meeting of the A.C.S. at Boston, Mass., April, 1959.

(2) Based on a thesis submitted by John W. Thompson to the Graduate School of the University of Notre Dame in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) F. Basolo and R. K. Murmann, THIS JOURNAL, 74, 5243 (1952); 76, 211 (1954).

(4) F. Basolo, Y. T. Chen and R. K. Murmann, ibid., 75, 1478 (1953); 76, 956 (1954).

(5) H. Freiser and W. D. Johnston, Anal. Chim. Acta, 11, 201 (1954).

line molecule, found that chelates of the 2-methyl derivative were less stable than the corresponding chelates of the 4-methyl derivative and that the Ni(II) chelate of the 2-methyl compound was less stable than the corresponding Co(II) chelate. This inversion of the Ni–Co order, which Freiser attributed to steric effects, was also found with chelates of 2-(o-hydroxyphenyl)-benzimidazole and analogous compounds.[6] In these compounds the steric effects apparently were produced by the benzene portion of the benzimidazole molecule. Previous work on the carboxylic acid derivatives of benzimi-

(6) H. Freiser and W. D. Johnston, ibid., 11, 201 (1954).