60. *Estimation of Deviations from Stokes's Law for Small Molecules, and of the Shape of Some Organic Ions in Solution.*

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An empirical procedure for estimating deviations from Stokes's law for small molecules has been developed. Molecular volumes were determined from models, and used to calculate r, the molecular radius. The Stokes's law radius, r_s, was calculated from the limiting ionic conductance, by using small spherical ions as test systems. Some assumptions about the hydration of organic anions had to be made. The procedure used was checked by calculating the hydration numbers of inorganic ions, and values obtained agreed closely with those from activity coefficients.

The shapes of long-chain organic anions were calculated from the limiting ionic conductance by using the Stokes's law correction and Perrin's relationships. The long hydrocarbon chain in the anion was curled in solution. The nature of the polar head group affected the degree of contraction; the dicarboxylic acid anions being most extended, alkyltrimethylammonium derivatives less extended, and monocarboxylic acid anions and the dodecyl sulphate anion least extended.

As long-chain aliphatic ions appear to curl in solution, in order to minimise the high hydrocarbon–water interfacial energy, it would be interesting, with regard to the energy changes accompanying micelle formation by this type of ion, to gain some idea of the extent of contraction. In principle, the shape could be determined from the limiting ionic conductance, but this interpretation is very difficult. First, Stokes's law fails for small ions; secondly, the volumes of the ions must be assessed; thirdly, the shape must be related to the limiting ionic conductance; and fourthly, the extent of ionic hydration must be known.

By studying the conductance of organic anions which consisted of aromatic structures and so did not contract in solution, it was shown [1] that Perrin's relations between the frictional coefficient of an ellipsoid and its shape could be applied to small molecules. Providing that the volume of the molecule is known, the limiting ionic conductance can therefore be interpreted in terms of shape by using a suitable model.

In this paper an empirical procedure is developed for assessing deviations from Stokes's law; this is based on that suggested by Stokes and Robinson,[2] and involves certain assumptions about the hydration of organic ions; it can be checked by calculating the hydration numbers of inorganic ions, and comparing these numbers with those derived from activity coefficients.

Deviations from Stokes's Law.—Stokes and Robinson [2] made the valuable suggestion that the conductances of symmetrical unhydrated tetra-alkylammonium ions could be used to calculate the Stokes's law radius, r_s, while the true radius, r, could be determined from the molar volumes; a graph of deviation from Stokes's law of r/r_s against r_s was obtained. Use of these corrections resulted in rather a high set of hydration numbers (h) for inorganic ions.

The molecular volume obtained from the molar volume provides a measure in the state where the molecule in question is surrounded by other molecules of the same size. A molecule may have a different volume when surrounded by smaller molecules, as when a large organic ion is in aqueous solution. Examination of crystallographic data shows that there is considerable free space between hydrocarbon chains for most organic ions,

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[1] Elworthy, *J.*, 1962, 3718.

[2] Stokes and Robinson, " Electrolyte Solutions," 2nd edn., Butterworths Scientific Publns., London, 1959, p. 124.

and this space may be considerably diminished in solution in water as the surrounding molecules are then small. The use of molar volumes would make r rather large.

While the smaller symmetrical quaternary ammonium ions, such as tetramethyl- and tetraethyl-ammonium, are obviously spherical, it is possible that larger ones, such as tetrapropyl- and tetrabutyl-ammonium, are somewhat asymmetric. The hydrocarbon chains are long enough to become reasonably flexible, and it is possible that they may associate with one another; this process would help to diminish the high hydrocarbon–water interfacial energy, and would result in an asymmetric ion. Because of this doubt about sphericity, these ions were not used in the Stokes's law deviation graph presented here.

Difficulty was experienced in using the original deviation graph [2] in conjunction with the conductances of spherical mono- and di-carboxylate anions. To fit these into the graph, by using, for consistency with Stokes and Robinson's procedure, the molar volumes to assess r, a hydration of three water molecules per carboxyl group had to be assumed. This seemed an unreasonably large number when compared with two water molecules per sodium ion, and one per potassium ion, determined from activity coefficient data (see below).

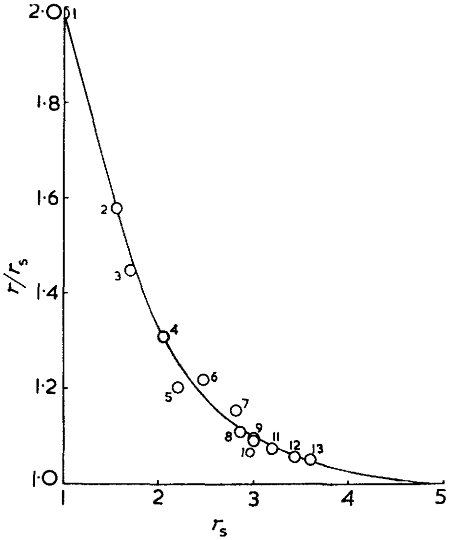

FIG. 1. Plot for Stokes's law deviations. For symbols see text.

1, H_2O.[3, 4] 2, Methylamine (Jones, Spuhler, and Felsing, *J. Amer. Chem. Soc.*, 1942, **64**, 965). 3, Formate (Soxton and Darken, *ibid.*, 1940, **62**, 846). 4, NMe_4^+ (Daggett, Bair, and Kraus, *ibid.*, 1951, **73**, 799). 5, Acetate (MacInnes and Shedlovsky, *ibid.*, 1932, **54**, 1429). 6, Oxalate (Darken, *ibid.*, 1941, **63**, 1007). 7, NEt_4^+ (Daggett *et al.*, *loc. cit.*). 8, Malonate (Jeffery and Vogel, *J.*, 1935, 21). 9, Succinate (*loc. cit.*). 10, Methylmalonate (*idem, J.*, 1936, 1756). 11, Dimethylmalonate (*loc. cit.*). 12, Diethylmalonate (*loc. cit.*). 13, Dipropylmalonate (*loc. cit.*).

The approach adopted here was to assess molecular volumes from the Catalin models, in a manner similar to that described before,[1] by determining the positions of the outside surfaces of, say, the methylene chain. This gave a cross-sectional area of 13·2 Å^2, and a volume for the CH_2 group of 16 Å^3. CH_3 had a volume of 19 Å^3 and $-CO_2^-$ 28 Å^3, while the volume of water had to be taken as 30 Å^3. This procedure is roughly similar to determining the closest distance of approach of the water molecules to the organic ions. If different volume equivalents are chosen, the deviation graph alters. It has been found, by repeating all the calculations on the organic ions, that an increase or decrease of volume equivalents has only a small effect on the final shape obtained for the ions.

Small spherical ions, such as formate, acetate, oxalate, malonate, malonate derivatives, methylamine, and tetraethyl- and tetramethyl-ammonium, were examined as test systems, being chosen so that any shape factors would be small. A prolate ellipsoid with an axial ratio of 1·4 : 1 has a frictional resistance only 1% greater than that of a sphere of the same volume. To bring these ions into line with tetra-alkylammonium ions, a hydration of one water molecule per charged head group had to be assumed. The Stokes's law deviation graph derived from the data on these ions (Fig. 1) is a reasonable plot.

To check the assumptions so far made, the hydration numbers of inorganic ions were calculated. The test systems used gave the smallest r_s at 1·55 Å, so the mean self-diffusion coefficient of water[3,4] was used to give an additional point at $r_s = 1$ Å, for a tentative extrapolation to small radii. The calculated hydration numbers were: Li^+, 3·3; Na^+, 2·2; K^+, 1·2; Rb^+, 1·0; Cs^+, 0·8; Mg^{++}, 6·9; Ca^{++}, 5·3; Ba^{++}, 4·4; La^{+++}, 9·3; F^-, 1·8; Cl^-, 0·7; Br^-, 0·4; and I^-, 0·1. Stokes and Robinson[5] showed that hydration numbers calculated from activity coefficients were: NaCl, 2·7 (2·9); KCl, 1·7 (1·9); $CaBr_2$, 6·2 (6·1); BaI_2, 5·5 (4·6); $LaCl_3$, 10·2 (11·4). Here values from the present correction procedure are given in parentheses. The agreement between the sets of hydration numbers is reasonable. From the diffusion coefficient of sucrose,[6] *h* was calculated to be 5, on the assumption of a spherical particle, in good agreement with the concept of a pentahydrated sucrose molecule in solution.[7] Any electrostriction of the water molecule was neglected in deriving the correction graph, and also in calculating *h* values for the ions.

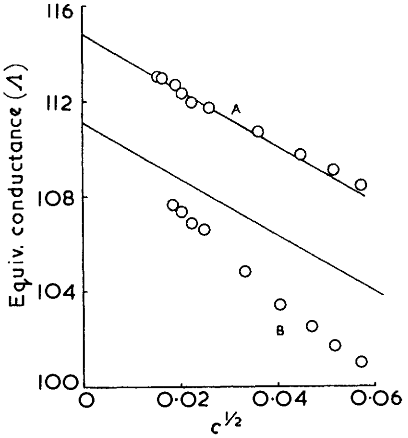

FIG. 2. Plot of equivalent conductance against $c^{\frac{1}{2}}$ for (A) dipotassium decane-1,10-dicarboxylate and (B) dipotassium thapsate.

EXPERIMENTAL AND RESULTS

Potassium decane-1,10-dicarboxylate and tetradecane-1,14-dicarboxylate were prepared by refluxing the free acid or the methyl ester with 20% " AnalaR " potassium hydroxide in 50% aqueous ethanol for 4 hr., cooling and filtering the mixture, washing the solid with alcohol, and recrystallising it three times from alcohol–water. Assays, involving a strong anion-exchanger to liberate potassium hydroxide, which was titrated with standard acid, gave purities of 99·8% in both cases. The conductance bridge and experimental methods used have been described.[1]

Plots of equivalent conductance against $(\text{normality})^{\frac{1}{2}}$ for potassium decanedioate and potassium thapsate are given in Fig. 2. The results have been corrected for hydrolysis by Jeffery and Vogel's method.[8] Conductance measurements on potassium sebacate and hexadecane-1,16-dicarboxylate have been made.[9] The limiting conductances (λ°) of the anions are: sebacate 43·9, decane-1,10-dioate 41·3, thrapsate 37·6; hexadecane-1,16-dioate 36·2.

Results for the conductances of short-chain dicarboxylates,[8] monocarboxylates,[10] alkyltrimethylammonium ions,[11] sodium dodecyl sulphate,[12] and dodecylamine chloride[13] are available, and are used for determining ionic shape.

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[3] Wang, *J. Amer. Chem. Soc.*, 1951, **73**, 510.
[4] Wang, Robinson, and Edelman, *J. Amer. Chem. Soc.*, 1953, **75**, 466.
[5] Ref. 2, p. 250.
[6] Gosting and Morris, *J. Amer. Chem. Soc.*, 1949, **71**, 1998.
[7] Ref. 2, p. 244.
[8] Jeffery and Vogel, *J.*, 1935, 21.
[9] Elworthy, *J. Pharm. Pharmacol.*, 1959, **11**, 557.
[10] Dippy, *J.*, 1938, 1222.
[11] McDowell and Kraus, *J. Amer. Chem. Soc.*, 1951, **73**, 2170; Baer and Kraus, *ibid.*, p. 1129.
[12] Muckerjee, Mysels, and Dolin, *J. Phys. Chem.*, 1958, **62**, 1390.
[13] Kuhn and Kraus, *J. Amer. Chem. Soc.*, 1950, **72**, 3676.

DISCUSSION

Conductance of Long-chain Organic Ions.—In previous work,[1] an ellipsoid with three unequal semi-axes (a, b, and c) was used as a model for aromatic anions in solution, the frictional coefficient being calculated from a knowledge of a, b, and c. Unfortunately, the reverse procedure is not possible, as there are a large number of alternative $a : b$ and $b : c$ ratios which would fit the observed frictional coefficient. The prolate ellipsoidal model ($b = c$) seems reasonable for use with the molecules under study. The frictional ratio, f/f_0 (frictional resistance of an ellipsoid that of a sphere of equal volume) was determined by successive approximations. As the presence of a shape factor decreases r_s, various f/f_0 values were applied to the r_s calculated from the observed limiting conductance, until the product of r_s and the Stokes's law deviation factor equalled the true radius of the molecule. *E.g.*, for $CH_3{\cdot}[CH_2]_7{\cdot}NMe_3^+$, if $f/f_0 = 1$, $r_s = 3{\cdot}515$, deviation $= 1{\cdot}058$, $r = 3{\cdot}722$, to be compared with 3·585 from volume equivalents. If $f/f_0 = 1{\cdot}050$, $r_s = 3{\cdot}348$, deviation $= 1{\cdot}071$, so $r = 3{\cdot}585$. When f/f_0 is found, the ratio $a : b$ can be obtained either from Perrin's equations [14] or from tables; [15] and, from the volume of the molecule, a and b can be obtained as $V = 4\pi ab_2/3$. As the limiting ionic conductance is used in these calculations, we are only considering ionic shapes at infinite dilution, and not the effect of concentration upon shape.

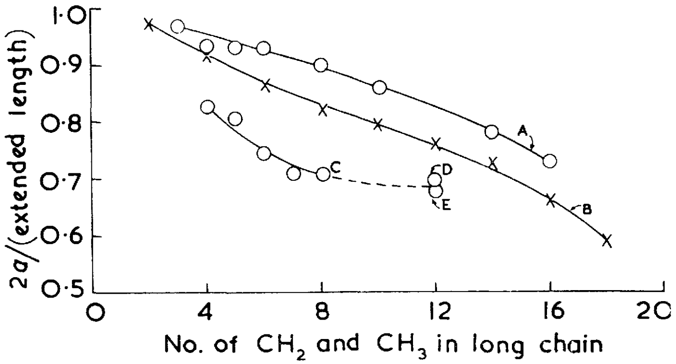

FIG. 3. Extension of various molecules in aqueous solution. (A) Dicarboxylates. (B) Alkyltrimethylammonium compounds. (C) Monocarboxylates. (D) Sodium dodecyl sulphate. (E) Dodecylamine.

In Fig. 3 the ratio $2a$/(total extended molecular length) is plotted against the number of CH_2 and CH_3 groups in the long chain. The extended length was measured from molecular models, and an allowance was made for the hydrating water in the case of the carboxylate anions, by letting the water molecule be present as a hemispherical cap next to the $-CO_2^-$ group in the line of the long chain. As the chain length increases, greater flexibility is bestowed by the presence of a larger number of C–C bonds, which permits a larger amount of curling.

The amount of extension of the molecule also depends on the nature of the polar head-group. Monocarboxylate anions have chains which are more curled than the other anions studied, possibly because the hydrated head-group helps to maintain water in close contact with the whole hydrocarbon surface, thus keeping the interfacial energy per unit area high. In contrast, the alkyltrimethylammonium compounds have part of the hydrocarbon chain shielded from the water by the presence of the unhydrated $^-NMe_3^+$ group, which

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[14] Perrin, *J. Phys. Rad.*, 1934, **5**, 497.

[15] Svedburg and Pedersen, " The Ultracentrifuge," Oxford Univ. Press, 1940, p. 41.

forms a hemispherical cap at the end of the ellipsoid. There is a smaller area of hydrocarbon chain in contact with water, and a greater extension of the chain is shown. When the chain is very long, it is very flexible and can be represented by an ellipsoid about 2·5 times as long as it is wide. The dicarboxylate anions, having two negatively charged polar groups, are more extended than the other molecules studied, presumably because the repulsive energies between the polar heads outweigh the effect of the water–hydrocarbon interfacial energy. A reasonable degree of contraction begins only with decane-1,10-dicarboxylic acid. Diffusion studies on dipotassium hexadecane-1,16-dioate[9] showed that while dimerisation occurred true micelle formation did not. This indicates that, for these $\alpha\omega$-dicarboxylates, the energy expended to force a large number of polar groups together when forming the micelle outweighs the energy saved by placing the hydrocarbon chains out of contact with the water.

The results for dodecylamine and sodium dodecyl sulphate are included in Fig. 3 and fit moderately the monocarboxylic acid series.

It is generally acknowledged (cf. ref. 16) that incorporation of monomers into micelles results in the loss of the high hydrocarbon–water interfacial energy, as the hydrocarbon chain is then in contact with other similar chains. This process decreases the energy of the system. A certain strain would be imposed, owing to curling of the monomer chains, while in the micelles the chains suffer no restraint and can extend themselves. There should, therefore, be a further decrease of energy due to this extension, rather like the energy provided by releasing a compressed spring. Little account has been taken of this effect. In general, the longer the chain, the greater will be the strain; so the decrease of energy on micelle formation will also be larger.

Perrin's Relationships.—In a previous paper,[1] a satisfactory test of Perrin's relationships was made by using the conductance of aromatic anions and fitting them with an ellipsoidal model having three unequal semi-axes. The many factors complicating the interpretation of the limiting ionic condutance required Stokes's law to be assumed over the molecular size range studied, and no hydration of the anions was assumed. The test was valid on these terms. It was an oversimplification, and the results have been recalculated by using the Stokes's law deviation graph and the degree of hydration used for the aliphatic carboxylate anions. A few of the results are here tabulated. The symbols have been defined before.[1] The agreement between calculated and observed frictional ratios is good. It is interesting that either the procedure given before or the present one may be used to give reasonable shape factors for hydrated molecules.

Observed and calculated frictional coefficients.

	$Ph{\cdot}CO_2^-$	p-$MeO{\cdot}C_6H_4{\cdot}CO_2^-$	p-$Bu^t{\cdot}C_6H_4{\cdot}CO_2^-$	$PhCH_2{\cdot}CO_2^-$
f_e/f_s (calc.)	1·066	1·105	1·063	1·070
(obs.)	1·071	1·120	1·050	1·079

	$({\cdot}C_6H_4{\cdot}SO_3^-{-}4)_2$	*cis*- $PhCH{:}CH{\cdot}CO_2^-$	*trans*- $PhCH{:}CH{\cdot}CO_2^-$	*trans*- p-$MeO{\cdot}C_6H_4{\cdot}CH{=}CH{\cdot}CO_2^-$
f_e/f_s (calc.)	1·081	1·013	1·093	1·133
(obs.)	1·075	1·011	1·084	1·150

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[16] Alexander and Johnson, "Colloid Science," Oxford Univ. Press, 1950, p. 671.