720. *A Test of Perrin's Relationships for Small Molecules.*

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Perrin's relationships between the frictional coefficients and shapes of non-spherical molecules have been extended to ellipsoidal models with three unequal axes. Data on the conductance of aromatic anions have been supplemented by measurements on sodium and potassium naphthalene-1,5-disulphonate, biphenyl-4,4'-disulphonate, and anthraquinone-2,6-disulphonate. A reasonable agreement has been obtained between calculated and observed limiting ionic conductances for the organic anions, indicating that Perrin's relationships apply over the range of molecular size studied.

INTEREST has recently been shown in " boloform " electrolytes, which contain two or more polar groups separated by a hydrocarbon moiety. Atkinson, Yokoi, and Hallada [1] have studied the conductances of benzene-1,3-disulphonates and naphthalene-1,3,6-trisulphonates, both of which are " boloform " electrolytes.

Organic ions are generally not spherical, and theoretical treatments of conductance data may involve the introduction of correction terms to account for the deviation from sphericity. Perrin [2] gives equations for calculating the frictional resistance to motion of ellipsoids, the results usually being expressed as a comparison with the frictional resistance of a sphere of the same volume as the ellipsoid. These relationships have been applied to macromolecules, but no systematic test has been made of them for small molecules.

In this work, systems have been chosen containing molecules which are reasonably rigid in the sense that they cannot easily expand or contract in solution, that is, molecules containing aromatic structures. Conductance measurements give a means of assessing the frictional resistance of a molecule, while its shape can be found from molecular models.

Frictional Coefficients and Molecular Asymmetry.—The balance between the driving force on an ion and the frictional resistance leads to [3a]

$$\lambda_0 = |z|F^2/Nf, \tag{1}$$

where λ_0 is the limiting equivalent ionic conductance, $|z|$ is the valency, and f is the frictional coefficient. For a spherical particle of radius r, where η is the viscosity of the medium,[4]

$$f_s = 6\pi\eta r, \tag{2}$$

in which it is assumed that the particles are unsolvated, and that Stokes's law holds; the latter assumption is also involved in the derivation of Perrin's relationships. We shall here confine ourselves to these cases.

In representing non-spherical molecules, ellipsoidal models are generally chosen, usually prolate and oblate ellipsoids of revolution. To allow greater flexibility in representing shape, ellipsoids with three unequal semi-axes (a, b, and c) are now considered. This type of particle has three frictional coefficients, f_1, f_2, and f_3, and the mean frictional coefficient, f_e, is

$$1/f_e = (1/f_1 + 1/f_2 + 1/f_3)/3. \tag{3}$$

In Perrin's 1936 paper, equations (96) and (97) are, respectively:

$$D = (D_1 + D_2 + D_3)/3 = kT(1/f_1 + 1/f_2 + 1/f_3)/3$$

and
$$D = kT(3S + a^2P + b^2Q + c^2R)/48\pi\eta = kTS/12\pi\eta$$

[1] Atkinson, Yokoi, and Hallada, *J. Amer. Chem. Soc.*, 1961, **83**, 1570.
[2] Perrin, *J. Phys. Radium*, 1936, **7**, 1; 1934, **5**, 497.
[3] Stokes and Robinson, " Electrolyte Solutions," 2nd edn., Butterworths, London, 1959, (a) p. 43; (b) p. 120.
[4] Alexander and Johnson, " Colloid Science," Oxford University Press, 1950, p. 211.

where D is the diffusion coefficient. (For the remaining symbols see the original paper.) From these equations and equation (3), we obtain

$$f_e = 12\pi\eta/S \tag{4}$$

where

$$S = \int_0^\infty \frac{ds}{\sqrt{(a^2 + s)(b^2 + s)(c^2 + s)}} \tag{5}$$

Perrin gives solutions for S as:

Prolate ellipsoid, $a > b = c$,

$$S = (2/\sqrt{a^2 - b^2}) \ln\left[(a + \sqrt{a^2 - b^2})/b\right], \tag{6a}$$

Oblate ellipsoid, $b > a = c$,

$$S = (2/\sqrt{b^2 - a^2}) \tan^{-1}(\sqrt{b^2 - a^2}/a). \tag{6b}$$

The elliptic integral (5) is soluble for the case where the three semi-axes are unequal,[5] and for $a > b > c$:

$$S = (2/a\sqrt{1 - c^2/a^2})F(\theta, \phi)$$

where

$$\theta = \sin^{-1}\sqrt{(a^2 - b^2)/(a^2 - c^2)} \text{ and } \phi = \sin^{-1}\sqrt{1 - c^2/a^2}. \tag{7}$$

$F(\theta, \phi)$ has been tabulated, *e.g.*, by Dale.[6]

Substitution of equation (4) for the frictional coefficient part of eqn. (1) affords

$$\lambda_e = |z|F^2S/12\pi\eta N, \tag{8}$$

which gives the required relationship between ellipsoidal shape and the limiting ionic conductance.

EXPERIMENTAL

The conductance bridge was constructed according to Shedlovsky's directions,[7] except that an amplifier of the type described by Allan, Gabriel, and Robinson [8] was used, together with a cathode-ray oscilloscope as an indicator of balance. The cell constant apparently varied with concentration (0·3% over a resistance range of 1000—20,000 ohms), and this effect was compensated for by calibrating the cell with various concentrations of potassium chloride solution. Determinations of the equivalent conductances of sodium chloride solutions gave values differing by $\pm 0.1\%$ from literature figures, and results on sodium sulphate solutions are given later. Solvent resistances were measured on the same day as the conductances of salt solutions, and all solutions were made up by weight. Measurements were made at $25° \pm 0.003°$.

" AnalaR " sodium and potassium chloride, and sodium sulphate were recrystallised three times from conductance water, and dried at 250°. Naphthalene-1,5-disulphonic acid was prepared by ion exchange from a commercial sample of its sodium salt. The free acid was neutralised with either " AnalaR " sodium or potassium hydroxide, and the salt precipitated with alcohol, filtered, recrystallised three times from conductance water, and dried at 120—130°. The material was assayed by converting a weighed amount into the free acid by passage down a strong cation-exchange column, and titration of the effluent with standard sodium hydroxide solution.

The sodium and potassium salts of anthraquinone-2,6-disulphonic acid, and of biphenyl-4,4'-disulphonic acid were prepared similarly from commercial samples. All assays gave a purity of 99·9% or higher.

[5] Crane, personal communication.
[6] Dale, " Five Figure Tables of Mathematical Functions," Arnold, London, 1949, p. 94.
[7] Shedlovsky, *J. Amer. Chem. Soc.*, 1930, **52**, 1793.
[8] Allan, Gabriel, and Robinson, *Electronic Eng.*, 1957, **29**, 597.

RESULTS

The conductance results are shown in Figs. 1 and 2 as plots of equivalent conductance (Λ) against (normality)$^{\frac{1}{2}}$, $c^{\frac{1}{2}}$. After a preliminary Λ_0 value had been found from these graphs, the results were fitted by the Fuoss–Onsager extended equation:

$$\Lambda = \Lambda_0 - Sc^{\frac{1}{2}} + Ec \log c + Jc$$

(the symbols are defined by Fuoss and Accascina [9]). Sodium sulphate solutions were used to test the apparatus, giving $\Lambda_0 = 132\cdot2$, agreeing well with $132\cdot1$ cm.^{2} ohm^{-1} equiv.$^{-1}$, found by
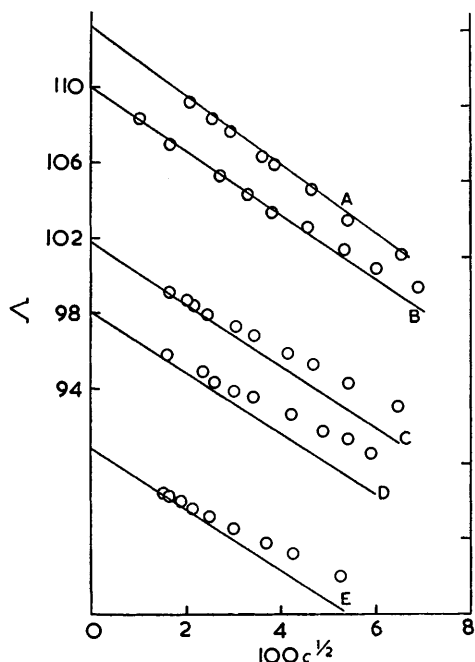

FIG. 1. Plot of equivalent conductance against $c^{\frac{1}{2}}$ for sodium salts. A, Sodium sulphate (right-hand scale). B, Benzene-1,3-disulphonate (from ref. 1). C, Naphthalene-1,5-disulphonate. D, Biphenyl-4,4'-disulphonate. E, Anthraquinone-2,6-disulphonate (right-hand scale).
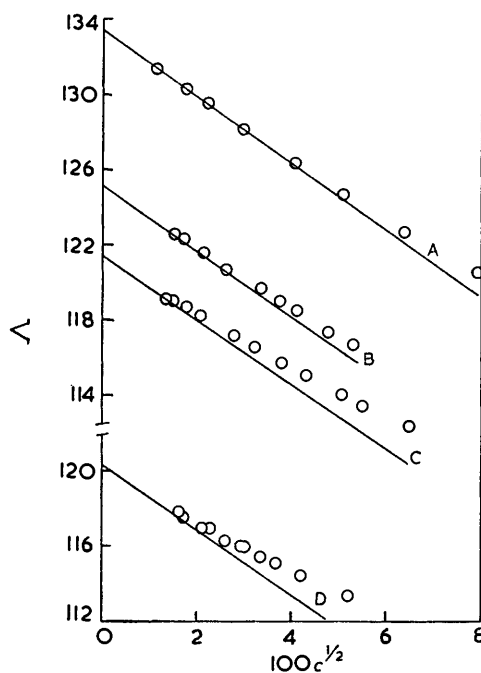
FIG. 2. Plot of equivalent conductance against c for potassium salts. A, Benzene-1,3-disulphonate (from ref. 1). B, Naphthalene-1,5-disulphonate. C, Biphenyl-4,4'-disulphonate. D, Anthraquinone-2,6-disulphonate.

Jenkins and Monk.[10] When $50\cdot1$ was used for $\lambda_0(Na^+)$, and $73\cdot5$ for $\lambda_0(K^+)$, the λ_0 values found for the anions were:

	λ_0 (from sodium salt)	λ_0 (from potassium salt)
Naphthalene-1,5-disulphonate	$51\cdot6$	$51\cdot6$
Biphenyl-4,4'-disulphonate	$47\cdot9$	$47\cdot9$
Anthraquinone-2,6-disulphonate	$46\cdot7$	$46\cdot8$

The Onsager limiting slope is shown in the Figures, and it is interesting to note that for 2 : 2 electrolytes, deviations from it appear to increase as the size of the anion increases.

Including those of Atkinson *et al.*,[1] data are available on five sulphonates. Conductance

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[9] Fuoss and Accascina, " Electrolyte Conductance," Interscience Publ. Inc., New York, 1959, ch. XV.

[10] Jenkins and Monk, *J. Amer. Chem. Soc.*, 1950, **72**, 2695.

studies on substituted benzoic, phenylacetic, and cinnamic acids have been made by Dippy and his co-workers,[11] and provide suitable data for testing Perrin's relationships.

DISCUSSION

It was necessary to choose suitable models from which the relative proportions and volumes of the molecules studied could be measured. The use of molar volumes was discarded, as it was considered that the packing of large molecules about one another, as in the solid state, would differ considerably from the packing of small water molecules around a larger organic molecule. The Catalin models were used, so that the dimensions of an asymmetric molecule measured from them would be in proportion to one another. The volumes of aromatic rings were found by measuring the areas of the models on graph paper and multiplying by their thickness; the volumes of substituent groups were determined by displacement in water. The sum of ring and substituent group volumes gave the total molecular volume.

It was straightforward to measure the length ($2a$) and breadth ($2b$) of the models, making the measurements at right angles to one another, choosing the longest dimension of the model to be $2a$, and keeping $a > b > c$, but there was some difficulty in determining the depth ($2c$), as the substituent groups in the aromatic rings differed in depth from them. The procedure adopted was to calculate the volume (V) of the molecule, measure a and b, and calculate c from $V = 4\pi abc/3$. Bulky substituent groups, with widths greater than 2·5 Å (the depth of the benzene ring), caused the calculated value of c to increase: *e.g.*, benzoate ion, $2c = 2·60$ Å; 4-ethylbenzoate ion, $2c = 2·78$ Å; 4-t-butylbenzoate ion, $2c = 3·30$ Å. This procedure provided a convenient method of averaging the molecular depth.

With the exception of naphthalene-1,3,6-trisulphonate, benzene-1,3-disulphonate, and 4-t-butyl-2,6-dimethylbenzoate, the molecules chosen for study corresponded roughly to rod-like form. However the use of the three-dimensional model, and equations (7) and (8), allowed the greatest flexibility for computing S. Most of the molecules fitted reasonably well into this ellipsoidal model.

The limiting ionic conductance of a sphere, λ_s, was calculated from the molecular volume by using equation (1), while that of an ellipsoidal molecule, λ_e, was found from equations (7) and (8). The results are also expressed as the ratio of these frictional coefficients, f_e/f_s. The measured limiting ionic conductance. $\lambda_{obs.}$, gave values for $f_{e\ obs.}$. By using the simpler prolate and oblate models, the ratios $f_e/f_{s\ prol.}$ and $f_e/f_{s\ obl.}$ were calculated for comparison; for the prolate model, b was found by averaging the two shortest molecular dimensions, while, for the oblate model, b was obtained by averaging the two longest dimensions [see equations (6a and b)]. Nearly all the molecules studied fell between the prolate and oblate cases, thus justifying the use of equation (7) in the calculations.

The limiting anion conductances of the benzoate ion [12] and the sulphonate ions were the most precise of the values given in Table 1, the precision being 0·2% or better. The remainder of the $\lambda_{obs.}$ values were obtained in the study of dissociation constants, and were often the mean of several runs on the sodium salts and free acids, *e.g.*, for *cis*-cinnamic acid the observed values were 32·4, 32·8, and 32·5. The precision of most of the $\lambda_{obs.}$ values was probably not more than $\pm 1\%$.

Comparison of the observed and calculated values of f_e/f_s showed that the agreement was generally better than 2% (average deviation, 1·7%). In view of the precision of $\lambda_{obs.}$ for most of the systems, this agreement seemed good, and for the sulphonates and the benzoate ion, which have the most precisely determined $\lambda_{obs.}$ values, the average deviation was 1·3%. The remaining discrepancy was probably due to the model chosen. The

[11] Dippy and Lewis, *J.*, 1936, 644; 1937, 1008, 1426; Dippy, Lewis, and Williams, *J.*, 1935, 343. Dippy and Williams, *J.*, 1934, 161, 1888; Dippy and Page, *J.*, 1938, 357; Baker, Dippy, and Page, *J.*, 1937, 1774; Dippy, Hughes, and Laxton, *J.*. 1954, 1470.
[12] Brockman and Kilpatrick, *J. Amer. Chem. Soc.*, 1934, **56**, 1483.

Observed and calculated ionic conductances and frictional coefficients.

	$\lambda_{obs.}$	λ_s	λ_e	f_e/f_s (obs.)	f_e/f_s (calc.)	f_e/f_s (prol.)	f_e/f_s (obl.)	Diff.*
Benzoates								
benzoate	$32\cdot3_4$	$35\cdot1_1$	$32\cdot3_5$	1·086	1·085	1·044	1·093	−0·1
p-chloro-	32·1	34·0	30·3	1·059	1·122	1·065	1·108	+5·8
p-methyl-	30·0	34·0	30·6	1·133	1·111	1·058	1·096	−2·0
p-bromo-	29·8	33·5	30·0	1·124	1·117	1·068	1·107	−0·6
p-methoxy-......................	29·0	33·3	29·4	1·148	1·133	1·053	1·113	−1·3
p-ethyl-	30·0	32·8	29·3	1·093	1·119	1·072	1·104	+2·4
p-isopropyl-	28·7	31·8	28·7	1·108	1·108	1·068	1·089	0
p-*t*-butyl-	28·4	30·9	28·3	1·088	1·092	1·063	1·074	+0·4
p-*t*-butyl-2,6-dimethyl-.........	26·7	29·6	25·8	1·109	1·147	1·039	1·142	+3·4
Phenylacetates								
phenylacetate	30·6	33·8	30·8	1·105	1·097	1·049	1·082	−0·7
p-methyl-	29·9	32·8	29·6	1·097	1·108	1·063	1·092	+1·0
p-nitro-	28·1	32·3	28·5	1·149	1·133	1·083	1·115	−1·4
p-methoxy-......................	28·7	32·2	28·4	1·122	1·134	1·082	1·113	+1·1
p-ethyl-	28·7	31·8	28·4	1·108	1·120	1·076	1·099	+1·1
p-isopropyl-	28·4	30·8	27·8	1·085	1·108	1·073	1·086	+2·1
p-*t*-butyl-	28·0	30·0	27·5	1·071	1·091	1·068	1·073	+1·9
Cinnamates								
cis-cinnamate	32·6	33·0	31·5	1·012	1·048	1·026	1·026	+3·5
trans-cinnamate	30·4	33·0	29·7	1·086	1·111	1·063	1·095	+2·3
p-chloro-*trans*-	28·4	32·1	28·1	1·130	1·142	1·088	1·120	+1·1
p-methyl-*trans*-	29·3	32·1	28·5	1·096	1·126	1·079	1·108	+2·7
p-nitro-*trans*-	28·3	31·7	27·4	1·120	1·157	1·100	1·132	+3·2
p-methoxy-*trans*-	26·8	31·6	27·2	1·179	1·162	1·100	1·130	−1·5
Sulphonates								
benzenedisulphonate	59·9	62·4	58·4	1·042	1·068	1·013	1·066	+2·5
naphthalenedisulphonate ...	51·6	56·7	51·0	1·099	1·112	1·023	1·112	+1·2
naphthalenetrisulphonate ...	71·5	81·1	70·2	1·134	1·155	1·061	1·148	+1·8
biphenyldisulphonate	47·9	54·3	48·2	1·134	1·127	1·101	1·092	−0·6
anthraquinonedisulphonate ...	46·7	52·2	46·1	1·118	1·133	1·083	1·114	+1·3

* Percentage difference about mean value between columns five and six.

procedure adopted here was to choose an " equivalent ellipsoid " of the same volume as the real molecule, and which fitted it as closely as possible. Although the fit was reasonable in the majority of cases, it was not exact. The calculated value of f_e/f_s based on prolate and oblate models generally gave poorer results than the three-dimensional model; the latter model also had the advantage that no choice was needed between prolate and oblate forms.

cis- and *trans*-Cinnamates provided an interesting example of isomers whose differing shapes were reflected in their $\lambda_{obs.}$ values; the *trans*-form was more extended and had a greater frictional resistance to motion than the *cis*-form. The limiting anion conductance of the *cis*-form was 1·072 times that of the *trans*-form, while $S_{cis}/S_{trans} = 1\cdot061$, in reasonable agreement.

Any deviations from Stokes's law would upset the agreement between $\lambda_{obs.}$ and λ_e; these deviations are likely to be greater for the smaller molecules, cf. Stokes and Robinson.[3b] The Table shows that the differences between $\lambda_{obs.}$ and $\lambda_{calc.}$ appear to be reasonably random, and independent of molecular size. If Stokes's law fails to apply, then the smallest anions, such as benzoate, 4-methyl- and 4-methoxy-benzoate, and phenylacetate, should have $\lambda_{obs.}$ values that are too high. As this does not appear to be the case, Stokes's law appears to hold over the range of molecular size studied.

Rossi, Bianchi, and Rossi[13] have studied the diffusion of some simple molecules in water. As these were flexible aliphatic molecules, no rigid model could be chosen to represent their shape. A comparison was made between the calculated radius of gyration for the molecules, and the observed Stokes's law radius. A reasonable proportionality

[13] Rossi, Bianchi, and Rossi, *J. Chim. phys.*, 1958, **55**, 91, 97.

was obtained. As the radius of gyration approach provides to some extent a measure of shape, it will be interesting to compare this approach with the ellipsoidal one for some flexible molecules.

Diffusion studies [14] on dipotassium 1,16-hexadecanedicarboxylate indicated that the aliphatic hydrocarbon chain connecting the two polar groups was considerably curled in solution. For this reason molecules with principally aromatic structure had to be chosen to test Perrin's relationships. Work is in progress on the application of these relationships to obtain the actual extended lengths in solution of aliphatic molecules of the dicarboxylic acid type.

[14] Elworthy, *J. Pharm. Pharmacol.*, 1959, **11**, 557.