W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon, Oxford, 1967, Vol. 3, pp 231–402.

(3) R. D. Bertrand, R. D. Compton, and J. G. Verkade, *J. Am. Chem. Soc.*, **92**, 2702 (1970).

(4) A. H. Cowley, M. C. Damasco, J. A. Mosbo, and J. G. Verkade, *J. Am. Chem. Soc.*, **94**, 6715 (1972).

(5) E. Farnworth and J. M. Miller, *Can. J. Spectrosc.*, **17**, 103 (1972).

(6) R. S. Armstrong, M. J. Aroney, R. K. Duffin, H. J. Stootman, and R. J. W. Le Fevre, *J. Chem. Soc., Perkin Trans. 2*, 1272, 1362 (1973).

(7) M. Barfield, D. M. Grant, and D. Ikenberry, *J. Am. Chem. Soc.*, **97**, 6956 (1975).

(8) "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, N.Y., 1975.

(9) J. Hrostowski, R. J. Myers, and G. C. Pimentel, *J. Chem. Phys.*, **20**, 518 (1952).

(10) R. S. Bottei and A. W. Laubengayer, *J. Chem. Phys.*, **66**, 1449 (1962).

(11) R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, **43**, 2166 (1965).

(12) D. S. Marynick and W. D. Lipscomb, *J. Am. Chem. Soc.*, **94**, 8699 (1972).

(13) I. R. Epstein, T. F. Koetzle, R. M. Stevens, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **92**, 7019 (1970).

(14) P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, **9**, 1430 (1970).

(15) G. M. Bodner and L. G. Sneddon, *Inorg. Chem.*, **9**, 1421 (1970).

(16) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

(17) J. F. Ditter, E. B. Klusmann, J. D. Oakes, and R. E. Williams, *Inorg. Chem.*, **9**, 889 (1970).

(18) T. Onak and E. Wan, *J. Chem. Soc. Dalton Trans.*, 665 (1974). In this reference the ^{1}H NMR values reported for H(5,6) and H(1,7) of 2,4-$C_2B_5H_7$ are in error and each should be lowered by ca. 0.7 ppm.

(19) T. Onak, *Inorg. Chem.*, **7**, 1043 (1968).

(20) T. Onak, G. B. Dunks, R. A. Beaudet, and R. L. Poynter, *J. Am. Chem. Soc.*, **88**, 4622 (1966).

(21) R. L. Williams, N. N. Greenwood, and J. H. Morris, *Spectrochim. Acta*, **21**, 1579 (1965).

(22) D. S. Marynick and W. N. Lipscomb, *J. Am. Chem. Soc.*, **94**, 8692 (1972).

(23) F. H. A. Rummens and R. H. Krystynak, *J. Am. Chem. Soc.*, **94**, 6914 (1972).

(24) J. F. Ditter, E. B. Klusmann, R. E. Williams, and T. Onak, *Inorg. Chem.*, **15**, 1063 (1976).

(25) H. D. Johnson, S. G. Shore, N. L. Mock, and J. C. Carter, *J. Am. Chem. Soc.*, **91**, 2131 (1969); S. G. Shore, Chapter 3 in "Boron Hydride Chemistry", E. Muetterties, Ed., Academic Press, New York, N.Y., 1975.

(26) T. Onak and G. B. Dunks, *Inorg. Chem.*, **5**, 439 (1966).

The Effect of Charge upon Mobility. A Critical Examination of the Zwanzig Equation

D. F. Evans,* C. Chan, and B. C. Lamartine

Contribution from the Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.

Received March 7, 1977

Abstract: The diffusion coefficients of a homologous series of tetraalkyltins (Me_4Sn, Et_4Sn, Pr_4Sn, Bu_4Sn), tetraethylmethane, and carbon tetrachloride in acetrontrile, ethanol, 2-propanol, and 1-butanol at 25 °C, and in acetone, methanol, and 1-octanol at 10 and 25 °C, have been determined using the Taylor dispersion technique and the Gouy interferometer. Deviations from the predictions of Stokes' law as large as a factor of 4 are observed in some cases. Comparison of the diffusion coefficient for tetraalkyltins with ionic mobilities for the tetraalkylammonium ions allows the dielectric friction coefficient of the Zwanzig equation to be determined directly. It is found that the theory overestimates this effect by as much as a factor of 10.

Traditionally, ionic mobilities have been discussed in terms of deviations from Stokes' law. Although there are a number of unresolved problems associated with using continuum theory to describe the hydrodynamic behavior of small ions, Stokes' law has nevertheless been widely applied in detecting solvent structural effects[1] and in calculating hydration numbers.[2]

In addition to the hydrodynamic frictional force implicit in Stokes' law, Born,[3] Fuoss,[4] and Zwanzig[5] have shown that a more complete description of ionic mobility also requires the inclusion of a dielectric frictional force. The Zwanzig theory provides reasonable qualitative agreement in the sense that it predicts curves similar in shape to those observed experimentally. However, the quantitative agreement is poor possibly because the Zwanzig equation is in essence a correction to Stokes' law.

The question of the validity of Stokes' law when applied to small solutes can be answered experimentally by diffusion measurements. To this end, we have measured the diffusion coefficients of a number of symmetrical tetraalkyltins in a variety of solvents. These data permit the hydrodynamic friction coefficient to be determined directly. Since these neutral compounds are similar in size and shape to tetraalkylammonium ions, a comparison of their transport behavior allows the effect of charge upon mobility to be directly ascertained. In addition, the diffusion data allow the dielectric friction coefficient to be determined experimentally and compared to that predicted by the Zwanzig equation.

Experimental Section

Apparatus. Except where noted, the diffusion data were obtained using the Taylor dispersion technique. In this method, a small sample (10 μL) of a dilute solution (~1–3% by weight) is injected into the solvent as it flows through a capillary tube. Taylor[6] has shown that provided that the flow is laminar, the combination of flow and diffusion results in a Gaussian distribution of the solute along the tube. For liquids, the diffusion coefficient can be determined from the expression[7]

$$D = \frac{0.2310 r^2 t_R}{(W_{1/2})^2} \qquad (1)$$

where D is the binary diffusion coefficient, r is the radius of the capillary tube, t_R is the residence time of the solute in the tube, and $W_{1/2}$ is the eluted peak width at half its height.

The solvent flow through the capillary is controlled by a Cheminert metering pump, Model CMP-2V. The pumping rate was adjusted so that the average volume flow was 0.5 cm/s or less. We have used two capillary tubes, a 200-ft long stainless steel tube of 0.02-in. diameter and a 300-ft long stainless steel tube of 0.03-in. diameter (Superior Tube Co.). An injection port located at the top of the capillary tube contained a silicone rubber septum coated with Teflon (Unimetric Corp.) which allowed the sample to be injected directly into the capillary with a microsyringe. At the other end of the capillary, the solute dispersion peak was detected with a Waters differential refractometer Model R401 and recorded with a chart recorder. The capillary tubing was placed in a constant temperature bath which was controlled to ±0.01 °C. The temperature of the differential refractometer cell was controlled by circulating water from the bath through it.

In our preliminary experiments, the fluid flow was controlled by

Table I. Comparison of Our Results with Those in the Literature

System (A/B)	$D_{AB}^0 \times 10^5$, cm²/s	Number of determinations	$D_{AB}^0 \times 10^5$, cm²/s[a] (lit. value)
Urea/methanol	1.60 ± 0.01	10	1.597
Glycerol/methanol	1.34 ± 0.02	5	1.305
Formamide/methanol	2.08 ± 0.03	5	2.070
Dextrose/methanol	0.949 ± 0.004	4	0.938
Urea/H_2O	1.38 ± 0.01	10	1.382
	1.377 ± 0.005[b]	5	1.382
Dextrose/H_2O	0.668	1	0.6765

[a] L. G. Longsworth, *J. Phys. Chem.*, **67**, 689 (1963); *J. Am. Chem. Soc.*, **75**, 5705 (1953). [b] Determined with a metering pump.

Table II. Diffusion Coefficients ($D_{AB}^0 \times 10^5$, cm²/s) at 25 and 10 °C

	25 °C							10 °C		
	Acetone	Acetonitrile	Methanol	Ethanol	2-Propanol	1-Butanol	1-Octanol	Acetone	Methanol	1-Octanol
CCl_4	3.63 ± 0.03[a]	3.32[b]	2.25 ± 0.02[c]	(1.50)[d]	0.936 ± 0.018	0.843 ± 0.004	0.381 ± 0.002 0.389[b]	2.81 ± 0.02	1.76 ± 0.02	0.237 ± 0.002
Et_4C	3.11 ± 0.02		1.87 ± 0.03		0.649 ± 0.002	0.586 ± 0.004		2.53 ± 0.09	1.42 ± 0.01	
Me_4Sn	3.38 ± 0.03	3.06[b]	2.06 ± 0.02 2.04[b]	1.25[b]	0.803 ± 0.006	0.700 ± 0.003	0.331 ± 0.002 0.326[b]	2.73 ± 0.03	1.62 ± 0.02	0.208 ± 0.003
Et_4Sn	2.92 ± 0.04	2.42[b]	1.66 ± 0.04	0.950[b]	0.577 ± 0.002	0.490 ± 0.003	0.240 ± 0.004 0.235[b]	2.36 ± 0.04	1.27 ± 0.02	0.156 ± 0.001
Pr_4Sn	2.36 ± 0.03	2.01[b]	1.38 ± 0.01		0.458 ± 0.006	0.391 ± 0.001	0.176 ± 0.002	1.93 ± 0.02	1.05 ± 0.01	0.106 ± 0.002
Bu_4Sn	2.00 ± 0.02		1.18 ± 0.01	0.604[b]	0.394 ± 0.001	0.324 ± 0.003	0.137 ± 0.001 0.132[b]	1.58 ± 0.01	0.89 ± 0.01	0.084 ± 0.001

[a] Compared with 3.54 and 3.59 at 25.15 °C and 0.9953 mole fraction of acetone by D. K. Anderson, J. R. Hall, and A. L. Babb, *J. Phys. Chem.*, 62, 404 (1958). [b] Determined by Gouy interferometry. [c] Compared with 2.248 at 25 °C and 0.998 average mole fraction of methanol in solution by D. K. Anderson and A. L. Babb, *J. Phys. Chem.*, 67, 1362 (1963). [d] Literature value, D. K. Anderson and A. L. Babb, *ibid.*, 67, 1362 (1963).

Table III. Hydrodynamic Frictional Coefficients ($f = kT/D\eta\pi r$) at 25 and 10 °C

		25 °C							10 °C		
	r, A	Acetone	Acetonitrile	Methanol	Ethanol	2-Propanol	1-Butanol	1-Octanol	Acetone	Methanol	1-Octanol
CCl_4	2.73	4.36	4.24	3.87	2.96	2.51	2.21	1.67	4.54	3.75	1.49
Et_4C	3.40	4.09		3.74		2.91	2.56		4.05	3.74	
Me_4Sn	3.06	4.18	4.11	3.77	3.16	2.61	2.38	1.72	4.17	3.64	1.52
Et_4Sn	3.55	4.17	4.47	4.03	3.59	3.13	2.93	2.04	4.16	4.00	1.74
Pr_4Sn	3.94	4.65	4.85	4.37		3.55	3.31	2.51	4.58	4.36	2.31
Bu_4Sn	4.26	5.08		4.73	4.70	3.82	3.69	2.98	5.18	4.76	2.70

regulating the pressure of nitrogen gas on a reservoir containing the solvent. When this was replaced by the metering pump, our accuracy and precision increased by a factor of 2. We found that the diffusion coefficient is independent of flow rate below a value of 1 cm/s.

We have also determined the diffusion coefficient in some of our systems using the Gouy interferometer. The apparatus and experimental procedures are discussed in detail elsewhere.[8] The diffusion cell was similar in design to that of Longsworth,[9] except that it was constructed from stainless steel instead of glass.

Materials. All of the solvents were reagent grade and were used without further purification. All of the solutes, which included tetraethylmethane (99.9%+, API Standard Reference Material, Carnegie-Mellon University), carbon tetrachloride (99%+, J. T. Baker), tetramethyltin (99%+, Aldrich), tetraethyltin (98%+, MCB), tetrapropyltin (98%+, Alfa Products), and tetrabutyltin (98%+, Aldrich) were used as received.

Results

In order to check the performance of our Taylor dispersion apparatus, the diffusion coefficients of solutes in water and methanol were measured and compared with published values (Table I). The agreement is quite good, the average deviation being 0.9%. The value for glycerol in methanol shows the largest discrepancy, i.e., 2.6%..The diffusion coefficients for the tetraalkyltins and other symmetrical solutes as determined with the Taylor dispersion apparatus are given in Table II. These are the averages resulting from four or more diffusion measurements. The values obtained from the Gouy interferometer are also given in Table II and in general are the result of a single determination.

Table III shows the values of the hydrodynamic frictional coefficient, f, calculated from Stokes' law. In its basic form, Stokes' law relates the velocity with which a sphere of radius r moves through a continuum of viscosity η under an applied force. Assuming that this equation is applicable when the sphere becomes comparable in size to the solvent materials, Stokes' law for diffusion can be expressed as

$$D^0\eta = kT/f\pi r_s \tag{2}$$

where k is the Boltzmann constant, T the temperature, and r_s the hydrodynamic radius. The analogous equation for ionic conductance at infinite dilution, λ^0, is

$$\lambda^0\eta = |z|\mathcal{F}^2/Nf\pi r_s \tag{3}$$

where $|z|$ is the absolute charge on the ion, $\mathcal{F}$ is the Faraday, and N is Avogadro's number. According to the Nernst postulate, the diffusion coefficient for a single species at infinite dilution can be related to the limiting ionic conductance by $\lambda^0 = D^0|z|\mathcal{F}^2/kT$.

In calculating the values of f from eq 2, r_s was set equal to the estimated value of the crystallographic radius r_x obtained using the procedure of Edwards[10] and Bondi.[11] The corre-

Table IV. Solvent Parameters[a]

	ϵ_0	ϵ_∞	$\tau \times 10^{-11}$,s	η, cP
Acetone	20.56[b]	1.9[c]	0.31[c]	0.303[b] (0.357)[d]
Acetonitrile	35.95[e]	2[f]	0.39[g]	0.3409[e]
Methanol	32.62[e] (35.75)[h]	5.6[h] (5.9)[h]	4.77[h] (6.69)[h]	0.5513[i] (0.690)[i]
Ethanol	24.33[j]	4.2[h]	12.8[h]	1.0826[i]
2-Propanol	19.41[k]	3.35[l]	36[l]	2.0436[i]
1-Butanol	17.1[h]	2.95[h]	47.7[h]	2.5710[i]
1-Octanol	9.8[h]	3.1[h]	136[h]	7.538[m] (12.88)[n]

[a] The values are at 25 °C except those in parentheses, at 10 °C. [b] Reference 15. [c] J. Calderwood and C. P. Smyth, *J. Am. Chem. Soc.*, **78,** 1295 (1956). [d] "CRC Handbook of Chemistry and Physics", 51st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970. [e] G. P. Cunningham, Q. A. Vidulich, and R. L. Kay, *J. Chem. Eng. Data,* **12,** 336 (1967). [f] Optical value. [g] R. Krishmaji and A. Morsingh, *J. Chem. Phys.*, **41,** 827 (1964). [h] F. Buckley and A. A. Maryott, *Natl. Bur. Stand. (U.S.), Circ.*, **No. 589** (1958). [i] "Selected Values of Properties of Chemical Compounds", Thermodynamics Research Center Data Project. [j] D. F. Evans and P. Gardam, *J. Phys. Chem.*, **72,** 3281 (1968). [k] W. Dannhauser and L. W. Bahe, *J. Chem. Phys.*, **40,** 3058 (1964). [l] T. Koshii, E. Arie, M. Nakamura, H. Takahashi, and K. Higasi, *Bull. Chem. Soc. Jpn.*, **47,** 623 (1974). [m] This work. [n] Calculated from M. K. Karapetyants and Y. Go-Sen, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **4,** 580 (1961).

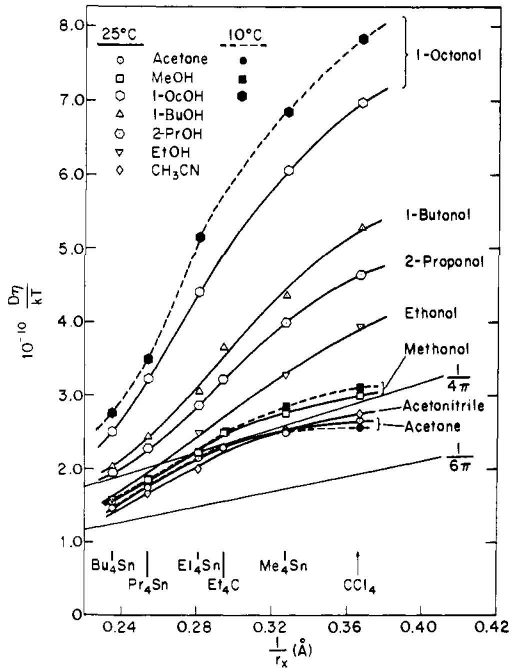


Figure 1. The diffusion-viscosity product for the tetraalkyltins, CCl_4, and CEt_4 as a function of estimated crystallographic size, temperature, and solvent. The predictions of Stokes' law are also shown.

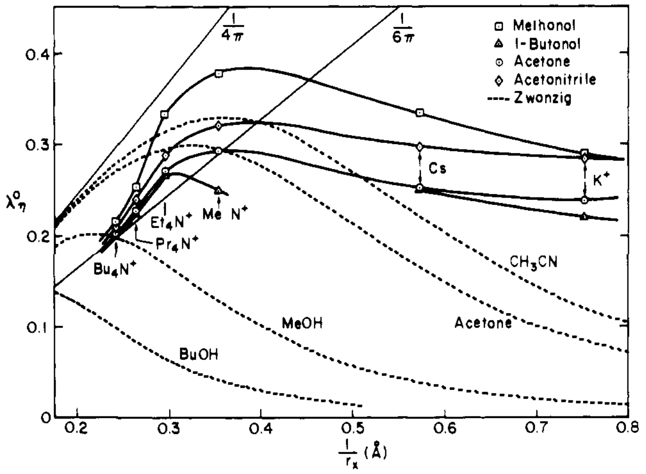


Figure 2. The limiting conductance-viscosity product for the alkali metal and tetraalkylammonium ions as a function of crystallographic size and solvent. The predictions of Stokes' law and the Zwanzig theory are also shown.

sponding values for the tetraalkylammonium ions were obtained in the same way. The viscosities employed in this calculation are given in Table IV.

Discussion

The diffusion data for tetraalkyltins and carbon tetrachloride in protic and aprotic solvents show that the transport behavior of small uncharged solutes is more complex than anticipated. Values of $D\eta/kT$ vs. $1/r_x$ are shown in Figure 1 along with the predictions of Stokes' law for perfect stick, $f = 6$, and perfect slip, $f = 4$. For the alcohols, the values of $D\eta/kT$ increase as the molecular size of the solvent increases. For the smallest solutes, CCl_4 and Me_4Sn, $D\eta/kT$ in octanol is four times larger than the value predicted by eq 2. In addition, a large negative temperature dependence is observed. Stokes' law predicts that $D\eta/kT$ should be invariant with temperature. In the aprotic solvents, acetone and acetonitrile, the deviations from Stokes' law are much smaller.

The corresponding data for the alkali metal ions and the tetraalkylammonium ions are shown in Figure 2, where $\lambda\eta$, the Walden product, is plotted vs. $1/r_x$. Comparison of Figures 1 and 2 for the tetraalkytins and the tetraalkylammonium ions, which are comparable in size and shape, shows that the departures from Stokesian behavior are larger for the nonelectrolytes than for the corresponding ions. This is surprising, since it has always been implicitly assumed that the uncharged solutes would show only small deviation from the Stokes' law, and the deviations observed for electrolytes could be attributed mainly to the ion-solvent interaction.

The diffusion data raise two main questions. First, why do the small uncharged solutes show such large deviations? Monte Carlo calculations for hard spheres[12] establish that for self-diffusion the correct value of f in eq 2 is 4. Thus, one has a well-established reference line. The most obvious explanation is that the long hydrocarbon chains of the higher alcohols are responsible for the observed behavior. In an effort to determine this, we presently are investigating the diffusion of tetraalkytins in the hydrocarbons hexane, decane, and tetradecane, and will pursue this question when we have these data. The second question is: How can one account for the effect of charge upon mobility? The explanation which has received the most attention in recent years is that given in terms of the Zwanzig equation and will be examined in detail below.

In 1920 Born[3] pointed out that an ion moving through so-

Table V. The Values of $\Gamma = (|z|\,^2/N_A)/\lambda^0\eta_0$, $\alpha = f\pi r$, and $B' = (\Gamma - \alpha)r^3$ for the Tetraalkylammonium Ions

		Acetone			Acetonitrile			Methanol						Ethanol			2-Propanol			1-Butanol		
		25 °C $B = 381$			25 °C $B = 256$			25 °C $B = 1870$			10 °C $B = 1930$			25 °C $B = 1930$			25 °C $B = 6340$			25 °C $B = 8060$		
	r, Å	Γ	α	B'	Γ	α	B'	Γ	α	B'	Γ	α	B'	Γ	α	B'	Γ	α	B'	Γ	α	B'
Me_4N^+	2.84	52.80	38.1	327	48.17	37.0	248	40.80	34.0	151	39.87	32.8	157	48.16	26.8	475	57.74	22.5	748	62.18	19.9	942
Et_4N^+	3.39	57.02	43.6	522	53.58	45.8	303	46.35	40.1	243	45.48	39.6	229	48.79	36.0	489	51.53	30.9	803	57.82	27.9	1165
Pr_4N^+	3.81	67.95	53.5	799	64.53	56.2	460	60.87	50.9	551	59.74	50.9	488	62.15	47.6	804	65.61	40.7	1377	68.33	38.1	1672
Bu_4N^+	4.15	76.84	64.4	889	73.91	66.6	522	72.03	60.4	831	71.27	60.6	762	72.60	57.9	1050	74.61	48.8	1844	76.70	46.6	2151

lution brings about reorientation of solvent dipoles in its immediate vicinity. Since the solvent dipoles require a finite time to relax after the ion passes, a retarding or dielectric frictional force is set up between the ion and the solvent dipoles. Born reasoned that the effect would be proportional to the cube of the radius but did not pursue the analysis any further. The effect was independently rediscovered by Fuoss[4] in 1967. Zwanzig[5] derived a numerical expression for this effect based on the continuum model and obtained

$$\lambda^0\eta = \frac{|z|\mathcal{F}^2}{fr + B/r^3} \tag{4}$$

where

$$B = Re^2(\epsilon_0 - \epsilon_\infty)\tau/\epsilon_0(2\epsilon_0 + 1) \tag{5}$$

The constant R is equal to $3/8$ and $3/4$ for the perfect sticking and perfect slipping boundary conditions, respectively. The values of f are the same as those for eq 2, i.e., 6 and 4. The values of ϵ_0, the dielectric constant at zero frequency, ϵ_∞, the dielectric constant at infinite frequency, τ, the dielectric relaxation time, and η required to calculate B for the solvents of interest are given in Table IV.

The Zwanzig equation has been discussed by a number of writers. The results can be summarized with the aid of Figure 2 where the predictions of the Zwanzig equation are compared with conductance data for ions in acetronitrile,[13,14] acetone,[15] methanol,[16,17] and butanol.[18,19] The theory predicts the correct general shape for the Walden product curves in that $\lambda^0\eta$ goes through a maximum and decreases as the ion size decreases. For acetonitrile and acetone, as for most aprotic solvents, the predicted maximum value of $\lambda\eta$ is in reasonable agreement with that observed experimentally.[20] However, the values for the alkali metal ions are too small, an effect that has been attributed to dielectric saturation. A careful examination of this effect has shown that such a correction makes the disagreement worse, not better.[21] For the alcohols, as for most hydrogen-bonding solvents, the maximum value of $\lambda^0\eta$ for monovalent ions predicted by the Zwanzig equation is too small by a factor of 2 or 3 and occurs at a value of r_x which is too small.[22] For di- and trivalent iors the agreement between the predicted and observed values for $(\lambda\eta)_{max}$ is somewhat better.[23]

Inspection of eq 4 shows that the Zwanzig equation is in essence a correction to Stokes' law. This suggests that the discrepancy between the predicted and experimentally observed values of $(\lambda\eta)_{max}$, particularly in the alcohols, may result from using a hydrodynamic frictional coefficient that is too large. The correct values of f for the tetraalkylammonium ions can be determined from the diffusion data for the R_4Sn compounds given in Table III, since the values of f are known as a function of solute size.

If one rearranges the Zwanzig equation into the form

$$(\mathcal{F}^2/N\lambda^0\eta - f\pi r)r^3 = B \tag{6}$$

the hydrodynamic and dielectric frictional forces can be separated. The left-hand side of eq 6 depends on limiting ionic conductances and the values of $D\eta/kT$ (eq 2); consequently values of B can be calculated directly. The values of $\mathcal{F}^2/(N\lambda^0\eta)$ for the tetraalkylammonium ions are given in Table V along with values of B calculated from eq 6. Since the conductances and diffusion coefficients are known to ~±0.5% and ±1%, respectively, the difference between these two quantities is much larger than the experimental uncertainty.

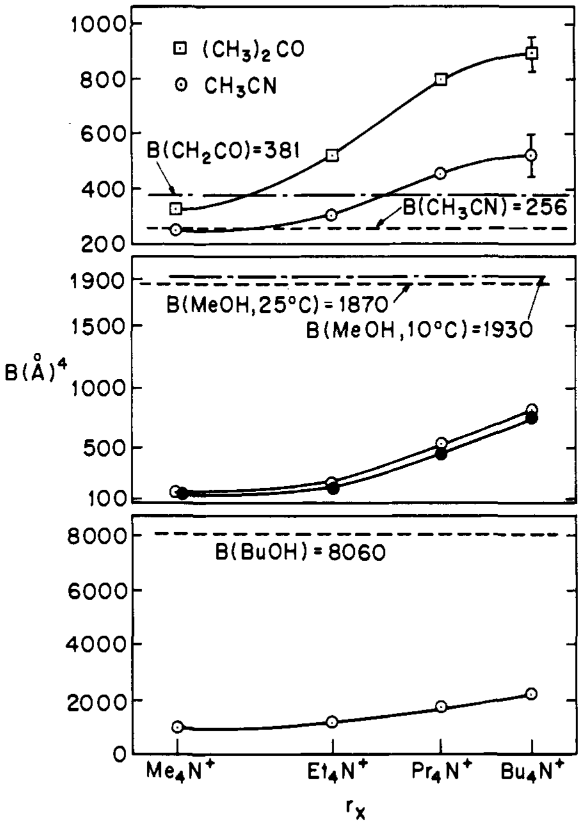


Figure 3. Comparison of the values of B predicted by the Zwanzig equation, eq 5, with those calculated from conductance and diffusion data, eq 6. The error bars are drawn assuming an uncertainty of ±0.5% in λ and of ±1% in D.

In Figure 3, the values of B for acetone, acetonitrile, methanol, and 1-butanol calculated from eq 5 and determined from eq 6 are compared by plotting B vs. r_x for the tetraalkylammonium ions. The Zwanzig theory, eq 5, predicts that for a given solvent B is constant independent of ionic size. The experimental data yield curves. This means that not only is the magnitude of B wrong, but also that the cubic dependence on r is incorrect.

In the alcohols, all of the data points lie below the predicted value of B. Thus, the dielectric frictional effect is overestimated by the Zwanzig equation by as much as a factor of 10. In acetone and acetonitrile, the agreement is better, but the best agreement is observed with the smaller ions. Comparison of the values of $f\pi\eta$ and B/r^3 shows that for the aprotic solvents the dielectric frictional term is always small compared to the hydrodynamic term. Thus, the reason that the Zwanzig equation appears to fit the data in aprotic solvents is simply that large errors in B will have relatively small effects.

This analysis of limiting ionic mobility demonstrates that a more refined equation is required. It suggests that the predicted values of B are grossly in error and that other effects besides dielectric and hydrodynamic frictional forces will probably have to be considered. However, the ability to unambiguously determine the numerical value of the hydrodynamic frictional coefficient as a function of solute size provides a better framework within which to evaluate the factors determining the mobility of ions.

Acknowledgments. This work was supported by National Science Foundation Grant ENG75-02029 A01. D.F.E. has an NIH Career Development Award 5K4-AM-12972.

References and Notes

(1) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, **70**, 2325 (1966).
(2) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", 2nd ed, Butterworths, London, 1959, p 126.
(3) M. Born, *Z. Phys.*, **1**, 221 (1920).
(4) R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.*, **45**, 807 (1959).
(5) R. Zwanzig, *J. Chem. Phys.*, **38**, 1603 (1963); **52**, 3625 (1970).
(6) G. I. Taylor, *Proc. R. Soc. London, Ser. A*, **219**, 186 (1953); **225**, 473 (1954).
(7) E. Grushka and J. Kikta, Jr., *J. Phys. Chem.*, **78**, 2297 (1974).
(8) B. C. Lamartine, Ph.D. Thesis, Case Western Reserve University, 1977.
(9) L. G. Longsworth, *Rev. Sci. Instrum*, **21**, 524 (1950).
(10) J. T. Edwards, *J. Chem. Educ.*, **47**, 261 (1970); *Chem. Ind.* (*London*), 774 (1956).
(11) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
(12) B. J. Alder, D. M. Gross, and T. E. Wainwright, *J. Chem. Phys.*, **53**, 3813 (1970).
(13) D. F. Evans, C. Zaqoyski, and R. L. Kay, *J. Phys. Chem.*, **69**, 3878 (1965).
(14) R. L. Kay, B. J. Hales, and C. P. Cunningham, *J. Phys. Chem.*, **71**, 3925 (1967).
(15) D. F. Evans, J. Thomas, J. A. Nadas, and M. A. Matesich, *J. Phys. Chem.*, **75**, 1714 (1971).
(16) R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **69**, 4208 (1965).
(17) J. P. Butler, H. I. Schiff, and A. R. Gordon, *J. Chem. Phys.*, **19**, 752 (1951); R. E. Jervis, D. R. Muir, J. P. Butler, and A. R. Gordon, *J. Am. Chem. Soc.*, **75**, 2855 (1953).
(18) D. F. Evans and P. Gardam, *J. Phys. Chem.*, **73**, 158 (1969).
(19) H. V. Frishaur, Ph.D. Thesis, Free University of Berlin, Berlin, West Germany, 1974.
(20) R. Fernández-Prini and G. Atkinson, *J. Phys. Chem.*, **75**, 239 (1971).
(21) R. Fernández-Prini, *J. Phys. Chem.*, **77**, 1314 (1973).
(22) H. S. Frank, "Chemical Physics of Ionic Solutions", B. E. Conway and R. G. Barradas, Ed., Wiley, New York, N.Y., 1966, p 61.
(23) T. L. Broadwater, T. J. Murphy, and D. F. Evans, *J. Phys. Chem.*, **80**, 753 (1976).

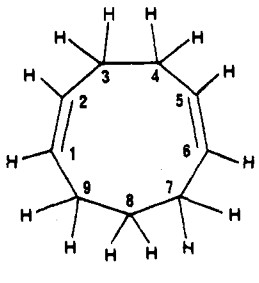
Conformational Properties of *cis,cis*-1,5-Cyclononadiene. Dynamic Nuclear Magnetic Resonance Spectroscopy and Iterative Force-Field Calculations

Frank A. L. Anet* and Issa Yavari

Contribution No. 3808 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received March 16, 1977*

Abstract: The 251-MHz ^{1}H and the 63.1-MHz ^{13}C NMR spectra of *cis,cis*-1,5-cyclononadiene (I) have been investigated over the temperature range from −5 to −170 °C. Unlike the ^{13}C spectrum, the ^{1}H spectrum of I shows a dynamic NMR effect in the vicinity of −60 °C. The NMR data are interpreted in terms of a pair of chiral chairlike conformations with C_2 symmetry. A free energy of activation ($\Delta G^{\ddagger}$) of 10.3 ± 0.3 kcal/mol is calculated from the ^{1}H NMR data for the conformational enantiomerization of I. Iterative force-field calculations on I give results consistent with the NMR findings.

cis,cis-1,5-Cyclononadiene (I) is the most stable member of the isomeric cyclononadienes and is readily available by reduction of 1,2,6-cyclononatriene[1] with diimide[2] or metal-ammonia,[3] or by base catalyzed isomerization[4] of 1,2-cyclononadiene.[5] Palladium catalyzed rearrangement of bicyclo[6.1.0]non-4-ene also gives I in high yield.[6] Several uses of I in organic[7] and organometallic[8] syntheses have been described.



I

Although there is presently no published experimental data on the structure or conformational properties of I itself, the temperature dependence of the ^{1}H NMR spectra of several heterocyclic analogues of dibenzo-1,5-cyclononadiene have recently been discussed by Ollis and Stoddart,[9] who have also carried out empirical force-field calculations on some of these molecules. The only published theoretical treatment of the conformations of I makes use of a simple procedure which does not minimize the energy by allowing the conformations to relax to their optimum geometries.[10]

The successful determination of the conformational features of *cis,cis*-1,5-cyclooctadiene (II) by ^{1}H and ^{13}C NMR spectroscopy[11] and iterative force-field calculations[12] prompted us to investigate the conformational properties of I, a molecule which can be considered as a higher homologue of II.

Experimental Section

cis,cis-1,5-Cyclononadiene was synthesized from 1,2-cyclononadiene[5] by base catalyzed isomerization,[4] and its ^{13}C NMR spectrum in $CDCl_3$ had bands at δ(ppm) 131.0 and 129.9 (olefinic ^{13}C), 28.7 (homoallylic ^{13}C), 26.7 and 24.4 (allylic ^{13}C).

All NMR spectra were measured on a superconducting solenoid spectrometer operating at 59 kG.[13,14] The proton noise-decoupled ^{13}C NMR spectra are Fourier transforms of accumulated free induction decays and were obtained under the following conditions: 45° pulse angle, 8K data points, 11 013 Hz spectrum width, and an exponential broadening function corresponding to 4 Hz broadening. For variable temperature ^{13}C NMR spectra a mixture of $CHFCl_2$:CHF_2Cl (1:1) was used as solvent and a fluorine line of the solvent was employed for lock purposes. The variable temperature proton NMR spectra were obtained in a frequency sweep mode with $CHFCl_2$ as the solvent.