

# Molecular Reorientation in Liquids. Experimental Test of Hydrodynamic Models

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**Abstract:** The experimental viscosity dependences of reorientation times of small molecules in liquids are compared to those predicted by the hydrodynamic slip model. It is found that the slip model successfully predicts the viscosity dependence for most small molecules in solution in the absence of strong solute-solvent interactions.

It has long been known that equations derived from hydrodynamics are successful in predicting rotational diffusion coefficients of large molecules.<sup>1</sup> In previous papers we have presented data which indicate that the reorientation of small molecules in solution may be hydrodynamic in character.<sup>2-5</sup> We have found that in the absence of strong solute-solvent interactions (e.g., H bonding) the reorientation time is a function of solution viscosity only and not the specific choice of solvent. In addition the reorientation times,  $\tau$ , fit the following equation

$$\tau = C\eta + \tau_0 \quad (1)$$

where  $\eta$  is the solution viscosity,  $C$  is the viscosity dependence (slope), and  $\tau_0$  is the zero viscosity intercept. This intercept has been found to be similar to the classical free rotor reorientation time,  $\tau_{FR}$ <sup>6</sup>

$$\tau_{FR} = (2\pi/9)(I/kT)^{1/2} \quad (2)$$

where  $I$  is the moment of inertia.

We have found that the viscosity dependence (slope),  $C$ , is less than that predicted by the Stokes-Einstein equation which is derived from hydrodynamics using "stick" boundary conditions.<sup>7</sup> Recently Hu and Zwanzig have made calculations of the rotational friction coefficients for ellipsoids with "slip" boundary conditions.<sup>8</sup> In this paper we compare experimentally determined viscosity dependences with viscosity dependences predicted by hydrodynamics with slip boundary conditions. We find good agreement between experimental and predicted viscosity dependences in organic solvents except for the smallest molecules studied. Reorientation times in aqueous solutions fall between those predicted by the slip and stick models and depend on the strength of the H bond between the solute and H<sub>2</sub>O.

## Measurement of Reorientation Times

Reorientation times in solution can be measured by a variety of techniques. We have found that depolarized

(1) See, for instance, C. Tanford, "Physical Chemistry of Macromolecules," Wiley, New York, N. Y., 1961, Chapter 6.

(2) G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **58**, 5570 (1973).

(3) G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **59**, 5310 (1973).

(4) G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **59**, 5321 (1973).

(5) D. R. Bauer, G. R. Alms, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, in press.

(6) F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, **56**, 404 (1972); **56**, 413 (1972).

(7) A. Einstein, "Investigations on the Theory of the Brownian Movement," Dover, New York, N. Y., 1956, pp 19-34.

(8) C. Hu and R. Zwanzig, *J. Chem. Phys.*, **60**, 4354 (1974).

Rayleigh scattering and <sup>13</sup>C nmr spin-lattice relaxation times are particularly useful techniques. Reorientation times can be determined conveniently and accurately ( $\pm 5-10\%$ ) without isotopic substitution (as is required by some other methods). Both techniques measure the relaxation of a second-order ( $l = 2$ ) Legendre polynomial so that reorientation times can be compared directly. For concentrated solutions, pair correlations can affect the light-scattering results, but these effects can be corrected for by extrapolation to infinite dilution.<sup>3</sup> For molecules with cylindrical symmetry, the reorientation time measured by light scattering is the reorientation time of the molecular symmetry axis (or, equivalently, the reorientation time about an axis perpendicular to the symmetry axis). For molecules with less symmetry, reorientation times about all axes contribute to the light-scattering reorientation time.<sup>9</sup>

The <sup>13</sup>C spin-lattice relaxation time is determined by reorientation of the C-H bond vectors. Huntress has related the reorientation time determined by nmr to the components of the rotational diffusion tensor for anisotropic rotational diffusion.<sup>10</sup> In general reorientation about all molecular axes contributes to the nmr reorientation time, and thus the reorientation times as measured by nmr and light scattering will usually be different. By combining reorientation time data from both techniques it is possible to extract information about anisotropic reorientation around the different molecular axes.<sup>5</sup> The fact that both methods are  $l = 2$  processes means that the reorientation time about a given axis as measured by these techniques is, in the rotational diffusion approximation, related to the rotational diffusion coefficient,  $\Theta$ , by  $\tau = 1/6\Theta$ . In the rotational diffusion approximation it is assumed that rotation proceeds by a large number of extremely small, independent steps. If reorientation in a particular liquid on the characteristic time scale of the experiment does not proceed by rotational diffusion, then the  $\tau$ 's measured by light scattering and nmr should no longer be simply related to  $1/6\Theta$ . This is expected to be the case for very small nearly spherical molecules.

## Calculation of Reorientation Times

The Stokes-Einstein equation relates the rotational diffusion coefficient to the friction coefficient,  $\zeta$ ,  $\Theta = kT/\zeta$  where  $\zeta = 8\pi a^3\eta$  for a spherical particle of radius  $a$  immersed in a medium of viscosity  $\eta$ .<sup>7</sup> If the rotational diffusion assumption is obeyed, the predicted reorienta-

(9) R. Pecora, *J. Chem. Phys.*, **49**, 1036 (1968).

(10) W. T. Huntress, Jr., *J. Chem. Phys.*, **48**, 3524 (1968).

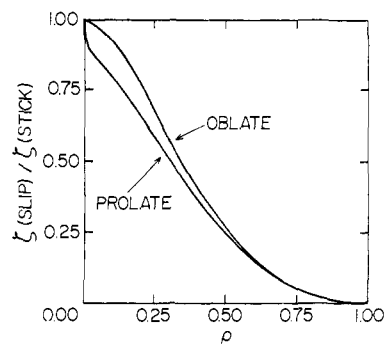
tion time,  $\tau$ , as determined by light scattering and nmr is given by

$$\tau = V\eta/kT \quad (3)$$

where  $V$  is the molecular volume. Thus  $C = V/kT$ . Perrin has calculated the friction coefficients for prolate and oblate ellipsoids.<sup>11</sup> The results are equations similar to eq 3 but multiplied by functions of the axial ratio.

These equations were derived using the hydrodynamic approximation. That is, hydrodynamic equations are used to calculate the friction coefficient of a large particle immersed in a "continuum" fluid. Also it is assumed that at the surface of the particle the fluid rotates with the particle. This is the "stick" boundary condition. Previous work indicates that the results of hydrodynamic theories may be valid for small molecules in solvents of similar size but that the stick boundary condition may not apply.<sup>2,5,12</sup> Molecular dynamics calculations indicate that the hydrodynamic approximation with a "nonstick" or "slip" boundary condition is successful in predicting the *translational* diffusion coefficient of hard sphere fluids.<sup>12</sup> Experimental measurements of translational diffusion coefficients of small rigid molecules in  $\text{CCl}_4$  are also consistent with the slip model (70% are within  $\pm 10\%$  of the value predicted by the slip model) except for the smallest molecules reported (e.g.,  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{CH}_4$ ) which diffuse faster than predicted.<sup>13</sup> A consequence of this model is that for a sphere rotating under slip conditions, the reorientation time would have no viscosity dependence and the sphere would reorient inertially.<sup>8</sup> The reorientation times of camphor and adamantane, two nearly spherical molecules, appear to be almost inertial in agreement with this prediction.<sup>14,15</sup> Hu and Zwanzig have calculated the ratio of friction coefficient with slip to the friction coefficient with stick boundary conditions for prolate and oblate ellipsoids.<sup>5</sup> These ratios are shown in Figure 1 as a function of  $\rho$ , the ratio of the shorter axis to the longer axis. The friction coefficient is calculated for reorientation of the symmetry axis. The friction coefficient for reorientation about the symmetry axis is zero since it displaces no solvent on rotation.

A calculation of the viscosity dependence,  $C$ , of the reorientation time based on the slip model requires knowledge of the molecular volume,  $V$ , and the axial ratio,  $\rho$ . Molecular volumes were calculated from van der Waals increments.<sup>13</sup> These volumes agreed well with volumes estimated from molecular models. In order to determine the ellipsoid which would best fit the molecular shape, the following procedures were used. First, dimensions of the different molecular axes were estimated using space filling models. For molecules with cylindrical symmetry (e.g., benzene), the value of  $\rho$  could be determined directly from these estimates. For molecules with less symmetry it was necessary to make further approximations. For molecules in which the reorientation times about the



**Figure 1.** The ratio of the friction coefficient,  $\zeta$ , calculated using slip boundary conditions to that calculated using stick boundary conditions for prolate ellipsoids and for oblate ellipsoids vs.  $\rho$ , the ratio of the shorter axis to the longer axis.

different axes were known (toluene and nitrobenzene)  $\rho$  was estimated for each axis by taking the ratio of the shortest and longest dimensions perpendicular to the axis about which the reorientation time is measured. For example, the value of  $\rho$  for reorientation about the  $x$  axis was determined by taking the ratio of the dimensions of the  $y$  and  $z$  axes. For molecules in which only one reorientation time is known (e.g., benzoic acid dimer), the molecule was considered to be a prolate or oblate ellipsoid. The value of  $\rho$  was determined by averaging the two most similar dimensions and taking the ratio of that average to the third dimension. Most of the error in these calculations stems from the problem of approximating real molecular shapes with ellipsoids of revolution.

#### Comparison of Experimental and Calculated Viscosity Dependences

A comparison of experimental viscosity dependence (slope) to that predicted by hydrodynamics with slip and stick boundary conditions is shown in Table I for organic solvents. The slope for the stick boundary condition was calculated using Perrin's modification of eq 3. Unless otherwise noted all data in Table I are from ref 2-5. Experimental slopes for samples 1-7 were determined by measuring the reorientation time at several viscosities and fitting the data to eq 1. The other slopes were estimated by measuring the reorientation time at one viscosity and calculating the slope by assuming that the intercept is given by eq 2. As long as the measured reorientation time is much greater than the calculated intercept, this method is nearly as accurate as doing the viscosity dependence study.

The reorientation times of the symmetric tops calculated by the slip model and measured by light scattering can be compared directly, since both methods measure reorientation of the symmetry axis. For molecules with less symmetry, the light-scattering spectrum consists of the sum of 2 to 5 Lorentzians whose line widths are determined by the reorientation times about all three axes. As discussed above for molecules for which only the light-scattering reorientation time is known (no. 8-15), the viscosity dependence as determined by the slip model was calculated by considering the molecule to be a prolate or oblate ellipsoid. Thus the calculated viscosity dependence is an average of the viscosity dependences about the two axes most similar in length.

(11) F. Perrin, *J. Phys. Radium*, **5**, 33 (1934); **7**, 1 (1936).

(12) B. J. Alder, D. M. Gass, and T. E. Wainwright, *J. Chem. Phys.*, **53**, 3813 (1970).

(13) J. T. Edward, *J. Chem. Educ.*, **47**, 261 (1970).

(14) M. Jauquet and P. Laszlo, *Chem. Phys. Lett.*, **15**, 600 (1972).

(15) K. F. Kuhlmann, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).

Table I. Viscosity Dependences in Organic Solvents

Molecule	Axis <sup>a</sup>	Volume, Å <sup>3</sup>	$\rho$	$C_{stick}$ , psec/cP	$C_{slip}$ , psec/cP	$C_{exptl}$ , psec/cP
1. Benzene		80	0.52 ± 0.01	22	5.0 ± 0.5	3.5 ± 0.1
		80	~1	26	~0	0.0 ± 0.1
2. Hexafluorobenzene <sup>b</sup>		108	0.44 ± 0.01	31	10.3 ± 0.5	9.5 ± 0.5
3. Mesitylene		133	0.46 ± 0.01	37	11.3 ± 0.5	10.6 ± 0.8
		133	<i>c</i>	48	<i>c</i>	1.0 ± 0.3
4. CH <sub>3</sub> I		55	0.62 ± 0.02	16	2.2 ± 0.3	1.3 ± 0.3
5. Toluene	<i>x</i>	80 <sup>d</sup>	0.54 ± 0.01	21.5	4.6 ± 0.4	3.2 ± 0.4
	<i>y</i>	97	0.43 ± 0.01	30	10.5 ± 1	12.5 ± 1.5
	<i>z</i>	97	0.87 ± 0.04	33	0.5 ± 0.3	0.0 ± 0.3
6. Nitrobenzene	<i>x</i>	103	0.54 ± 0.01	27	5.5 ± 1	2.5 ± 0.5
	<i>y</i>	103	0.38 ± 0.02	33	14.5 ± 2	26 ± 5
	<i>z</i>	103	0.8 ± 0.04	35	1 ± 0.5	0.6 ± 0.4
7. <i>p</i> -Xylene		115	0.47 ± 0.01	32	9.7 ± 1	10.5 ± 1
8. Methyl acetate		71	0.58 ± 0.03	22	3.9 ± 0.6	3.5 ± 0.8
9. Biphenyl <sup>e</sup>		150	0.41 ± 0.01	64	23 ± 2	24 ± 3
10. Fluorene <sup>e</sup>		157	0.42 ± 0.01	68	23 ± 2	27 ± 4
11. 1,4-Diphenyl-1,3-butadiyne <sup>e</sup>		204	0.26 ± 0.01	162 ± 10	91 ± 10	98 ± 6
		212	0.29 ± 0.01	143 ± 5	74 ± 5	76 ± 5
12. Benzoic acid <sup>f</sup>		107	0.43 ± 0.01	43	14 ± 2	15.7 ± 1.5
13. Acetic acid <sup>f</sup>		141	0.40 ± 0.02	62	22 ± 4	20 ± 2
14. Propanoic acid <sup>f</sup>		209	0.36 - 0.45	80-105	23-43	29 ± 5

<sup>a</sup> Unless otherwise stated reorientation is reorientation about an axis normal to the symmetry axis: ||, reorientation about symmetry axis; *x*, reorientation about axis in ring passing through substituent; *y*, reorientation about axis in ring  $\perp$  to *x*; *z*, reorientation about axis  $\perp$  to ring. <sup>b</sup> D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, submitted for publication. <sup>c</sup> See discussion. <sup>d</sup> Assumes methyl group rotates independently. <sup>e</sup> Unpublished work. <sup>f</sup> Dimer in CCl<sub>4</sub>.

Since the light-scattering reorientation time for these "low symmetry" molecules depends on reorientation about all three axes, in general the light-scattering viscosity dependence and the calculated viscosity dependence may not be directly comparable. However, as long as the molecule is approximately ellipsoidal for both polarizability and rotational diffusion coefficient tensors (that is,  $\alpha_{xx} \approx \alpha_{yy} \neq \alpha_{zz}$  and  $\theta_{xx} \approx \theta_{yy} \neq \theta_{zz}$ ), the light-scattering spectrum, to a good approximation, consists of one Lorentzian of half-width  $6\theta_s - 2\Delta$  where  $\theta_s = 1/3(\theta_{xx} + \theta_{yy} + \theta_{zz})$  and  $\Delta = [( \theta_{xx} - \theta_{yy} )^2 + ( \theta_{zz} - \theta_{xx} )( \theta_{zz} - \theta_{yy} )]^{1/2}$ . The quantity  $6\theta_s - 2\Delta$  is found to be very similar to the average of the two slower diffusion coefficients. The calculation of the viscosity dependence by the slip model also gives an average of the viscosity dependences of the two slower reorientation times, so that the results of the light scattering and slip model calculations should be roughly comparable. For example, *p*-xylene is one of the "least" ellipsoidal molecules studied. Considering the molecule to be an oblate ellipsoid gives a predicted slope,  $C = 9.7 \pm 1$  psec/cP. If we use the method described above for toluene and nitrobenzene to calculate the reorientation times about all three axes, we find that the viscosity dependence of the light-scattering reorientation time ( $6\theta_s - 2\Delta$ ) as calculated by the slip model is  $9.0 \pm 1$  psec/cP. Thus the light-scattering reorientation time is determined by nearly the same combination of reorientation times about the molecular axes as the calculation of the reorientation time by the slip model.

It can be seen that the slip model describes the viscosity dependence of the reorientation times very well except for benzene and methyl iodide, two of the smaller and more spherical molecules studied. The loss of accuracy of the slip model for very small molecules may come about for two reasons. First, as discussed above, the rotational diffusion assumption may no longer be valid for these molecules. Second, when the volume of the solute molecule becomes less than that of

the solvent molecules, we might expect that the use of the solvent continuum hypothesis would not be valid. For instance, the solute could reorient very rapidly in the "holes" of the solvent. This failure of the continuum approach may also explain the translational diffusion results for the very small molecules discussed above. In fact, considering the crudeness of the hydrodynamic approximation, it is surprising that the slip model works as well as it does.

A few of the molecules studied merit more discussion. Nitrobenzene is the only "large" molecule whose experimental viscosity dependences are not well predicted by the slip model. Nitrobenzene solutions exhibit strong pair correlation effects<sup>3</sup> and have been postulated to contain a weak dimer.<sup>16</sup> The reported viscosity dependences were determined from 50% (v/v) solutions in nitrobenzene which may account for the discrepancy.<sup>17</sup> The viscosity dependence of the reorientation about the symmetry axis in mesitylene is not zero. Models show that mesitylene appears almost triangular about this axis. Thus reorientation about this axis will displace some solvent molecules and we should expect some viscosity dependence in the reorientation time. The valeric acid dimer in CCl<sub>4</sub> is another interesting case. Even though the molecular volume is similar to those of the benzoic acid dimer and 1,4-diphenyl-1,3-butadiyne, the viscosity dependence is roughly  $1/3$  as much. The predicted slopes range from 43 psec/cP (all trans configuration) to 23 psec/cP (highly coiled configuration). The experimental value of 29 psec/cP indicates either that the molecule is on the average fairly

(16) (a) R. W. Taft, G. B. Klingsmith, and S. Ehrenson, *J. Amer. Chem. Soc.*, **87**, 3620 (1955); (b) K. Kimura and R. Fujishiro, *Bull. Chem. Soc. Jap.*, **35**, 85 (1962).

(17) The values of *f* and *g* for nitrobenzene found in ref 3 were used in eq 21 of ref 3 along with the light-scattering reorientation time for the 50% nitrobenzene solutions to calculate the "single particle" reorientation time. This single particle time was then combined with the <sup>13</sup>C nmr relaxation times for the 50% nitrobenzene solutions to obtain the results in Table I.

**Table II.** Viscosity Dependences in Aqueous Solutions<sup>a</sup>

Molecule	Volume, Å <sup>3</sup>	$\rho$	$C_{\text{stick}}$ , psec/cP	$C_{\text{slip}}$ , psec/cP	$C_{\text{exptl}}$ , psec/cP
1. HCOOH	38.5	$0.6 \pm 0.05$	10.1	$1.6 \pm 0.3$	$6.4 \pm 0.5$
2. HCOO <sup>-</sup>	35.2	$0.6 \pm 0.05$	9.5	$1.5 \pm 0.2$	$3.7 \pm 0.5$
	76.7 <sup>b</sup>	$0.55 \pm 0.05$	21	$4.2 \pm 0.5$	
3. CH <sub>3</sub> COOH	55.5	$0.6 \pm 0.05$	14.7	$2.4 \pm 0.3$	$9.9 \pm 0.6$
4. CH <sub>3</sub> COO <sup>-</sup>	52.2	$0.6 \pm 0.05$	14	$2.2 \pm 0.3$	$5.0 \pm 0.5$
	93.7 <sup>b</sup>	$0.55 \pm 0.05$	25.6	$5.1 \pm 0.5$	
5. CH <sub>3</sub> COOCH <sub>3</sub>	71	$0.58 \pm 0.03$	22	$3.9 \pm 0.6$	$4.5 \pm 1$
6. CH <sub>3</sub> CH <sub>2</sub> COOH	72.5	$0.55 \pm 0.05$	23	$4.5 \pm 0.5$	$12.9 \pm 2$

<sup>a</sup> All data are from ref 4. <sup>b</sup> Hydrated volume.

coiled or more likely that the flexibility allows for more rapid reorientation than an equivalent rigid structure.

The experimental viscosity dependences in aqueous solutions fall in between the predictions of the slip and stick models as shown in Table II. It is known that all of these molecules can form hydrogen bonds to the solvent, H<sub>2</sub>O. Edward has estimated the hydrated volume of the CO<sub>2</sub><sup>-</sup> group to be 41 Å<sup>3</sup> greater than the unhydrated volume.<sup>13</sup> Using these volumes, the predicted slip viscosity dependences agree very well with those measured for the two anions studied. Methyl acetate is the most weakly H bonded and has a viscosity dependence that is very nearly like that predicted by the slip model. Reorientation for the neutral acids has a considerably greater viscosity dependence than that of the corresponding anion. It is clear that it is more difficult to predict reorientation times in aqueous solutions because of the effects of H bonding on

reorientation. Reorientation in aqueous solutions may be described by hydrodynamics involving either some combination of stick and slip boundary conditions or by slip boundary conditions with an additional "hydration" volume.

In conclusion, hydrodynamics with slip boundary conditions can successfully predict the reorientation times of most small molecules in the absence of strong solute-solvent interactions. When these interactions are present, the reorientation time falls between the predictions of the slip and stick models.

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## Carbon-13 Chemical Shielding Tensors in Calcium Formate

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**Abstract:** The <sup>13</sup>C chemical shift tensors for the two crystallographically nonequivalent ions in calcium formate have been determined by high resolution solid state nmr in a single crystal, using a sensitivity enhancement technique. The eigenvectors of the tensors are found to be only approximately aligned with a coordinate system oriented along the symmetry directions of the OCO groups, indicating a strong perturbation of the ions by the crystal field and suggesting that the ions may not be planar. The principal values of the shift tensors in ppm with respect to liquid benzene (increasing toward high field), along with their approximate directions, are: -106 and -111 (along C-H), -61 are -57 (in OCO plane perpendicular to C-H), 24 and 24 (perpendicular to the OCO plane), for the first and second tensors, respectively. The equality of the isotropic shifts, -48 ppm for both, gives no hint of the observed differences between the ions.

Just as high resolution nmr in liquids has been enormously important to chemists in the study of molecular structure and dynamics in the liquid state, high resolution nmr in the solid state now promises to be an even richer source of information about molecules and their interactions with their environments. For instance, the chemical shift tensor of a nucleus in a molecule in the solid state may yield information about the local electronic environment of the nucleus and its local site symmetry. In the liquid state the directional character of these properties is lost through rapid mo-

lecular tumbling. Recent advances in experimental techniques have enabled high resolution nmr studies of dilute spins such as <sup>13</sup>C in solids, with great increases in signal sensitivity.<sup>1</sup>

### Experimental Section

With this in mind, we have undertaken the determination of the <sup>13</sup>C chemical shielding tensors in crystalline calcium formate. The pulse sequence used in this experiment is shown in Figure 1. It is

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