Friction Coefficients and Correlation Times for Anisotropic Rotational Diffusion of Molecules in Liquids Obtained from Hydrodynamic Models and ^{13}C Relaxation Data

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A hydrodynamic model is presented to describe fully anisotropic rotational dynamics of asymmetric ellipsoids in liquids. The model by Gierer and Wirtz is extended to deal with anisotropic rotations and combined with the model by Youngren and Acrivos for slip boundary conditions. The combined model is applied to obtain the reorientational correlation times for the hydrocarbon 5,6-dimethyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene in different solvents. The results from these calculations are compared to experimental values from ^{13}C nuclear relaxation data. Calculated and experimental results agree very well, and the new combined model is believed to represent an important contribution for describing rotational molecular dynamics in liquids.

Introduction

It is difficult to describe the dynamics of liquids on a molecular level. In particular, the relation between rotational correlation times τ_θ and macroscopic viscosity η is a topic of permanent interest, but until now without a satisfactory theoretical solution. It is well-known from a number of authors[1−7] that the experimentally determined rotational correlation times τ_θ are found to be a linear function of macroscopic viscosity η over temperature T:

$$\tau_\theta = \tau_0 + \tau_{\text{red}} \frac{\eta(T)}{T} \tag{1}$$

This relationship is verified by different experimental techniques, but a model to calculate τ_0 and τ_{red} properly is still lacking. Conventional hydrodynamics account for the linear dependence on η/T but are unable to accurately determine τ_{red}, which is normally at least by a factor of 5 too large. The constant τ_0 is generally not treated by hydrodynamic models.

Thus, various authors made attempts to extend the conventional macroscopic hydrodynamic view to a description on a more molecular level. The resulting quasi-hydrodynamic models could be distinguished by the considerations taken into account concerning the molecular shape, which might be based on spherical, symmetrical, or asymmetrical rotators, and concerning the used boundary conditions. The agreement with the experimentally determined rotational behavior varies significantly for these different hydrodynamic models. Comparative investigations by Dote, Kivelson, and Schwartz[3] and Harris and Newman[8] and also investigations of hydrocarbons by the present authors[9] show that none of the published models is able to reproduce the correlation times *and* the anisotropy of the molecular reorientational dynamics.

It is the aim of the present study to develop a new hydrodynamic model that is able to give correct results for the order of magnitude of the correlation times and to describe the anisotropy of rotational motions properly. Therefore, the spherical model by Gierer and Wirtz[10] (GW) is extended for fully anisotropic rotational dynamics. It is assumed, analogous to Gierer and Wirtz, that the surrounding fluid can be separated into different spherical shells. For rotations about each of the principal rotational diffusion axes these shells have radii determined by the asymmetry of the ellipsoid. Subsequently, this extension is combined with the anisotropic model by Youngren and Acrivos[11] (YA) with slip boundary conditions. First the hydrodynamic models by Stokes,[12] Einstein,[13,14] and Debye,[15] Gierer and Wirtz,[10] and Youngren and Acrivos[11] are presented, and then the extended model by the present authors is introduced. In the following section this new model is applied to describe the molecular rotational dynamics for molecules of the hydrocarbon 5,6-dimethyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene in different solvents. The calculated rotational friction coefficients from the GW and YA models and the new model are compared to experimental values determined from ^{13}C relaxation data.

Hydrodynamic Models for Molecular Reorientations

General Remarks. For an asymmetric ellipsoid with semiaxes a, b, c and Cartesian coordinates x, y, z parallel to the semiaxes the parameter equation is given by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \tag{2}$$

It is assumed that the ellipsoid is rotating with a small angular velocity $\boldsymbol{\omega}$ in an infinite mass of a viscous incompressible liquid ($\nabla\mathbf{v} = 0$) with the velocity field $\mathbf{v}$. The equation of motion for the surrounding fluid, referred to the principal axes $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$ of the ellipsoid, is given in the diffusive limit by the creeping-flow Navier−Stokes equation

$$\eta\nabla^2\mathbf{v} = \frac{1}{\rho}\nabla\rho \tag{3}$$

with viscosity η, density ρ, and pressure p. The type of solution for eq 3 depends on the assumed boundary conditions and is given by the velocity field. For that the hydrodynamic stress tensor $\boldsymbol{\sigma}$ is defined by

$$\sigma_{ij} = -p\delta_{ij} + \eta\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right), \quad i, j = x, y, z \tag{4}$$

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with $\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$. From the stress tensor the acting torque **T** is obtained with

$$\mathbf{T} = -\int_A \mathbf{r}\times(\boldsymbol{\sigma}\mathbf{n})\,\mathrm{d}A = \boldsymbol{\omega}\boldsymbol{\zeta} \tag{5}$$

Here, A denotes the surface of the fluid layer and **n** the normal vector on that surface. The fluid volume is limited on one side by the ellipsoid surface and on the other side by a supposed sphere of a very large radius having its center at the origin of the ellipsoid. The relationship between the torque and the angular velocity $\boldsymbol{\omega}$ is given by the symmetric friction tensor $\boldsymbol{\zeta}$. The friction tensor is diagonalized by choosing its coordinate system being equal to the principal axis system of the ellipsoid. Then $T_i = \zeta_{ii}\omega_i$ is the torque in the i direction for rotation about the axis i, and the resulting elements are the rotational friction coefficients $\zeta_i \equiv \zeta_{ii}$.

The correlation time $\tau_{\theta i}$ for rotational motion about axis i is then given by

$$\tau_{\theta i} = \frac{\zeta_i}{6kT} \tag{6}$$

with the Boltzmann constant k.

Stokes,[12] Einstein,[13,14] and Debye[15] (SED). The expression by Stokes[12] for the translational motion of a sphere in a fluid was used by Einstein in his studies on translational[13] and rotational[14] diffusion of small spherical particles in liquids. In order to describe dielectric relaxation, Debye[15] obtained for the isotropic rotational diffusion of a spherical molecule with radius a under stick boundary conditions for the surrounding fluid

$$\tau_{\mathrm{SED}} = \frac{8\pi\eta a^3}{6kT} \tag{7}$$

and thus for the friction coefficient

$$\zeta_{\mathrm{SED}} = 8\pi\eta a^3 \tag{8}$$

The surrounding medium was treated by Debye as a continuous fluid with no internal structure. However, this approach gives only a poor agreement between experimental and calculated molecular correlation times for molecules of small or medium sizes.

Gierer and Wirtz[10] (GW). The latter assumption of the SED model is a strong simplification and approximately valid only for describing rotational dynamics of spherical macromolecules, since their size is normally much larger than that of the solvent molecules. However, when the solvent molecules are of comparable size to the solute molecules or of the same size as in the case of neat liquids, the surrounding medium cannot be assumed to be continuous, and the discrete character of the medium has to be considered.

The fact that the diffusing molecules are embedded in a structured and noncontinuous fluid was taken into account by Gierer and Wirtz.[10] In their model it was assumed that the moving molecule has a spherical shape with radius r and that it is surrounded by onion-like shells consisting of spherical solvent molecules with radius r_{L}. The GW model appears to be a model with stick boundary conditions but considering the discrete nature of the surrounding fluid. The resulting friction coefficient ζ_{GW} for a rotating spherical molecule is then given by

$$\zeta_{\mathrm{GW}} = 8\pi\eta r^3 \frac{1}{6\dfrac{r_{\mathrm{L}}}{r} + \left(1 + \dfrac{2r_{\mathrm{L}}}{r}\right)^{-3}} \tag{9}$$

with the microviscosity factor f_{GW},

$$f_{\mathrm{GW}} = \left[6\frac{r_{\mathrm{L}}}{r} + \left(1 + \frac{2r_{\mathrm{L}}}{r}\right)^{-3}\right]^{-1} \tag{10}$$

In the macroscopic limit $r \gg r_{\mathrm{L}}$, the microviscosity factor becomes equal to unity, which reproduces the known SED result; for neat liquids f_{GW} is approximately 1/6. Our eq 10 is different from eq 2 in ref 10: Gierer and Wirtz did not quote the factor of 2 in the solution of the integral following their eq 18, which results also in a missing factor of 2 in their eq 21, giving a small error in calculated microviscosity factors.

For the rotational correlation time the following relation is valid:

$$\tau_{\mathrm{GW}} = \frac{8\pi\eta r^3}{6kT}\left[6\frac{r_{\mathrm{L}}}{r} + \left(1 + \frac{2r_{\mathrm{L}}}{r}\right)^{-3}\right]^{-1} = \tau_{\mathrm{SED}} f_{\mathrm{GW}} \tag{11}$$

Youngren and Acrivos[11] (YA). This model is an extension of the model by Hu and Zwanzig[16] for symmetrical ellipsoids to the general case of asymmetric ellipsoids. Youngren and Acrivos[11] solved the linearized Navier–Stokes equation with slip boundary conditions numerically for a number of surface elements of the observed ellipsoid and integrated over the whole surface. Friction results from the displacement of the surrounding medium when the nonspherical body rotates. They obtained for the friction coefficients of an asymmetric ellipsoid with semiaxes $a > b > c$ rotating about the three principal axes i

$$(\zeta_{\mathrm{YA}})_i = \frac{4}{3}\pi\eta abc\lambda_i, \quad i = x, y, z \tag{12}$$

with the dimensionless friction factor λ_i depending on the ratios $\alpha = b/a$ and $\beta = c/a$ of the semiaxes. After numerical solution of the Navier–Stokes equation Youngren and Acrivos listed values for friction coefficients in Table 1 of ref 11. This table, however, lists actually the values for $(4/3)\alpha\beta\lambda_i$[8,17] and not the λ_i values as stated. The correct values are given by Sension and Hochstrasser.[17]

The correlation times for rotations of the ellipsoid about the three principal axes are

$$(\tau_{\mathrm{YA}})_i = \frac{2\pi\eta abc}{9kT}\lambda_i, \quad i = x, y, z \tag{13}$$

Extended Gierer–Wirtz–Youngren–Acrivos Model (EGWYA). Some authors have shown, and further investigations of the present authors[9] will demonstrate, that by application of the GW model the best agreement between experimental and calculated isotropic rotational correlation times is obtained for a number of different molecules when compared to other hydrodynamic models. Thus, it appeared straightforward to develop an anisotropic extension of the GW model to the general case of asymmetric ellipsoids. First, we tried to adopt the procedure of Gierer and Wirtz and to solve the hydrodynamic equations for ellipsoids by employing the expressions $R_{mi} = a + ml$ with $i = x, y, z$ in the integration over the ellipsoidal surface and then summing up the resulting elliptic integrals over the surrounding shells. However, this led to very complex expressions. Since it was one aim of the present study to develop a simple model that is easily applied to different liquids, the procedure described in the following was applied.

It was assumed that the spherical shell model of Gierer and Wirtz is also applicable to asymmetric ellipsoids; that is the ellipsoidal shape of the rotating bodies was approximated by spheres with a different radius for rotation about each of the ellipsoidal semiaxes. To take the ellipsoidal shape into account, the corresponding radii are asymmetry-weighted averages over the semiaxes of the ellipsoid. This assumption seemed to be reasonable, because the real velocity field **v** around the ellipsoid appears to be more or less spherical at distances of 3 or 4 times the ellipsoidal diameter from the ellipsoid, and it seems to be difficult to identify whether there is a sphere or an ellipsoid rotating in the center.

The calculation of this mean radius $\bar{r}_i$ is demonstrated for the rotation of the ellipsoid described by eq 2 about the x direction. The mean radius is proportional to the geometrical average of the two semiaxes perpendicular to x: $\bar{r}_x \propto \sqrt{bc}$, which means making the ellipsoid symmetrical in the yz plane. To consider the asymmetry in the direction of the rotation axis x, into account, $\sqrt{bc}$ is weighted by the ratio of the ellipsoidal size $\sqrt{a\sqrt{bc}}$ in direction x and the average radius $\sqrt{bc}$ perpendicular to x:

$$\begin{aligned} \bar{r}_x &= \frac{\sqrt{a\sqrt{bc}}}{\sqrt{bc}}\sqrt{bc} \\ &= a^{1/2}(bc)^{1/4} \end{aligned} \tag{14}$$

Here, $\sqrt{a\sqrt{bc}}$ is the geometrical average of the semiaxis a in direction x and the average radius $\sqrt{bc}$ perpendicular to x. The other two mean radii for $i = y, z$ were obtained by cyclic permutation. The result is a conversion of the asymmetric ellipsoidal geometry to an averaged spherical geometry but with a different radius for rotation about each of the principal axes of the ellipsoid.

Now the friction coefficients can easily be calculated quite analogously to the procedure of Gierer and Wirtz by using the averaged radiius $\bar{r}_i$ in the expression for the radius of the mth shell around the ellipsoid:

$$R_{mi} = \bar{r}_i + ml, \quad m = 0, 1, 2, 3, ... \quad \text{and} \quad i = x, y, z \tag{15}$$

The surrounding solvent molecules were approximated to be spheres with thickness l. Then, the torque exerted by rotation of a neighboring shell is

$$T_i = \frac{2}{3}\frac{4\pi R_{mi}^{\ \ 4}}{l}\eta\omega_{mi} \tag{16}$$

with the angle velocity ω_{mi} of shell m relative to the neighboring shell.

To obtain the friction coefficients $(\zeta_{\mathrm{EGW}})_i$ for rotation of the ellipsoidal molecule in the first solvent shell, the total angle velocity ω_i resulting from the sum over the velocities of each shell $\omega_i = \sum_{m=0}^{\infty}\omega_{mi}$ has to be calculated:

$$(\zeta_{\mathrm{EGW}})_i = \frac{T_i}{\omega_i} = \frac{8\pi\eta}{3}\frac{1}{\sum_{m=0}^{\infty}\frac{l}{R_{mi}^{\ \ 4}}} \tag{17}$$

The sum can be separated into a dominant part for $m = 0$ and a remaining term:

$$\sum_{m=0}^{\infty}\frac{l}{R_{mi}^{\ \ 4}} = \frac{l}{\bar{r}_i^{\ 4}} + \sum_{m=1}^{\infty}\frac{l}{R_{mi}^{\ \ 4}} \tag{18}$$

The remaining sum may now be replaced by an integral over the shells:

$$\sum_{m=1}^{\infty}\frac{l}{R_{mi}^{\ \ 4}} \cong \int_1^{\infty}\frac{l}{(\bar{r}_i + ml)^4}\mathrm{d}m \tag{19}$$

The resulting friction coefficients $(\zeta_{\mathrm{EGW}})_i$ for rotation of the ellipsoidal molecule about the principal axes are then given by

$$\begin{aligned} (\zeta_{\mathrm{EGW}})_x &= 8\pi\eta abc\frac{1}{12\frac{r_{\mathrm{L}}}{a} + \frac{(bc)^{1/4}}{a^{1/2}\left(1 + \frac{4r_{\mathrm{L}}}{a^{1/2}(bc)^{1/4}}\right)^3}} \\ (\zeta_{\mathrm{EGW}})_y &= 8\pi\eta abc\frac{1}{12\frac{r_{\mathrm{L}}}{b} + \frac{(ac)^{1/4}}{b^{1/2}\left(1 + \frac{4r_{\mathrm{L}}}{b^{1/2}(ac)^{1/4}}\right)^3}} \\ (\zeta_{\mathrm{EGW}})_z &= 8\pi\eta abc\frac{1}{12\frac{r_{\mathrm{L}}}{c} + \frac{(ab)^{1/4}}{c^{1/2}\left(1 + \frac{4r_{\mathrm{L}}}{c^{1/2}(ab)^{1/4}}\right)^3}} \end{aligned} \tag{20}$$

For the thickness l of the surrounding shells a geometrically averaged radius $r_{\mathrm{L}} = 2(a_{\mathrm{L}}b_{\mathrm{L}}c_{\mathrm{L}})^{1/3}$ was used with $l = 2\ r_{\mathrm{L}}$. To emphasize the effect of the asymmetry of the surrounding particles, it was found necessary to take double of the geometrical average for r_{L}.

The corresponding rotational correlation times are

$$(\tau_{\mathrm{EGW}})_i = \frac{(\zeta_{\mathrm{EGW}})_i}{6kT} \quad \text{and} \quad i = x, y, z \tag{21}$$

Since the rotation of an asymmetric ellipsoid is considered, the displacement of the surrounding fluid also has to be taken into account, and thus the friction coefficients resulting from the Youngren−Acrivos model are added. The total friction is given just by the sum of these two frictional contributions:

$$(\zeta_{\mathrm{EGWYA}})_i = (\zeta_{\mathrm{EGW}})_i + (\zeta_{\mathrm{YA}})_i \tag{22}$$

and thus

$$(\tau_{\mathrm{EGWYA}})_i = \frac{(\zeta_{\mathrm{EGWYA}})_i}{6kT} = (\tau_{\mathrm{EGW}})_i + (\tau_{\mathrm{EGW}})_i \tag{23}$$

Results and Discussion

To demonstrate the quality of the applied models (GW, YA, and EGWYA), the experimental and calculated reorientational correlation times $\tau_{\theta i}$ for 5,6-dimethyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene (5,6-$\mathrm{Me_2}$-THMN, **1**) are compared in Table 1. The experimental correlation times were obtained from ^{13}C relaxation data for solutions of compound **1** (0.12 mol kg^{-1}) in the solvents [^{2}H$_2$]dichloromethane, [^{2}H$_6$]benzene, and [^{2}H$_2$]-tetrachloroethane at a temperature of 308 K. The values of $\tau_{\mathrm{red},i}$ in eq 1 were calculated from the models and equated to the $\tau_{\theta i}$ with the assumption that the τ_{0i} can be neglected. The orientation of the principal coordinate system parallel to the semiaxes of the ellipsoid is shown in Figure 1.

As can be seen from the experimentally determined rotational correlation times, the 5,6-$\mathrm{Me_2}$-THMN molecules rotate aniso-

TABLE 1: Experimental and Calculated Reorientational Correlation Times $\tau_{\theta i}$ and Relative Errors Δ for 0.12 mol kg^{-1} 5,6-Me$_2$-THMN in the Solvents [^{2}H$_2$]Dichloromethane, [^{2}H$_6$]Benzene, and [^{2}H$_2$]Tetrachloroethane at a Temperature of T = 308 K

solvent		$\tau_{\theta x}$/ps (Δ/%)		$\tau_{\theta y}$/ps (Δ/%)		$\tau_{\theta z}$/ps (Δ/%)	
[^{2}H$_2$]dichloromethane	experimental	7.37		12.5		5.67	
	GW	9.14	(24)	9.14	(−27)	9.14	(61)
	YA	1.04	(−86)	4.74	(−62)	1.48	(−74)
	EGWYA	7.05	(−4)	9.53	(−24)	5.38	(−5)
[^{2}H$_6$]benzene	experimental	7.01		13.2		5.99	
	GW	10.9	(55)	10.9	(−17)	10.9	(82)
	YA	1.35	(−81)	6.13	(−54)	1.92	(−68)
	EGWYA	8.44	(21)	11.8	(−11)	6.51	(9)
[^{2}H$_2$]tetrachloroethane	experimental	20.5		41.6		14.3	
	GW	23.3	(14)	23.3	(−44)	23.3	(63)
	YA	3.26	(−84)	14.9	(−64)	4.65	(−77)
	EGWYA	18.5	(−10)	27.0	(−45)	14.5	(1)

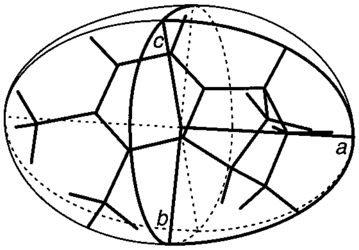

Figure 1. Molecular structure of 5,6-dimethyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene with respect to the orientation of the principal axis system of the inertial tensor and of the semiaxes *a*, *b*, and *c* of the ellipsoid.

tropically, and the anisotropy is approximately the same for all three solutions. When the experimental correlation times are compared to those calculated by the models GW, YA, and EGWYA, the following conclusions can be drawn.

(i) The calculated isotropic correlation times from the GW model have the correct order of magnitude but are of course unable to describe the anisotropy of the reorientational dynamics.

(ii) The YA model neither reproduces the magnitude of the correlation times nor describes the anisotropy correctly. All rotational correlation times are underestimated by the model; the relative difference Δ between model and experimental values ranges from −54 to −86%. Furthermore, the order of the model correlation times (*x*, *z*, *y*) is not the same as for the experimental ones (*z*, *x*, *y*).

(iii) The presented EGWYA model not only gives the correct order of magnitude for the correlation times but also reproduces the anisotropy. Only the rotation about the *y* axis is systematically calculated too small for all solutions (−11 to −45%), whereas the calculated values for rotations about the other two axes show positive as well as negative deviations (−10 to 21%). The deviations could result from the fact that the model is only dealing with idealized asymmetric ellipsoids. But the geometry of 5,6-Me$_2$-THMN is, as shown in Figure 1, different from an ellipsoidal one. Additionally, for the concentrations of **1** in the investigated solutions solute−solute interactions could not be excluded.

(iv) The three hydrodynamic models GW, YA, and EGWYA give an approximately correct description of reorientational dynamics. This illustrates the fact that the dynamics of liquids, in which the molecules interact mainly by van der Waals interactions, can be represented by hydrodynamic models that picture the fluid surrounding the moving molecules as being more or less homogeneous.

Conclusions

The presented model EGWYA, given as a combination of an anisotropic extension of the model by Gierer and Wirtz[10] to asymmetric ellipsoids and the anisotropic model of Youngren and Acrivos,[11] is a significant improvement compared to the semi-hydrodynamic models discussed in the literature. The EGWYA model is able to give the rotational correlation times in the correct order of magnitude *and* to reproduce the anisotropy of the rotational dynamics for the investigated hydrocarbon molecules interacting with the solvent mainly by van der Waals interactions. Further investigations are necessary to prove whether the new model is also valid for other types of solutions.

Methods

Densities were measured at 308 K with the digital densitometer DMA 10 by Heraeus and viscosities with the micro falling-sphere viscosimeter by Haake Mess−Technik. NMR measurements were performed on a Bruker AM 250 spectrometer (B_0 = 5.875 T, $\nu_0(^1\mathrm{H})$ = 250.13 MHz, $\nu_0(^{13}\mathrm{C})$ = 62.90 MHz, the deuterated solvents as internal lock). Dipolar ^{13}C relaxation times were obtained by measurement of the ^{13}C relaxation times and the corresponding nuclear Overhauser factors at a temperature of 308 K. The spin−lattice relaxation times were determined by the inversion−recovery pulse sequence under ^{1}H broad-band decoupling and repeated 5 times; those for the NOE factors 10 times. The spin−lattice relaxation times and NOE factors were extracted from signal heights; the relaxation times were calculated by a three-parameter exponential fit implemented in the spectrometer software. The mean standard deviations of the mean experimental data were below 3% for the relaxation times and less than 7% for the NOE factors. The error in the temperature was estimated to be ±1 K. The concentration of the 5,6-Me$_2$-THMN was 0.12 mol kg^{-1} in the investigated [^{2}H$_2$]dichloromethane, [^{2}H$_6$]benzene, and [^{2}H$_2$]tetrachloroethane solutions. Further details concerning experimental techniques and sample preparation are given in ref 20.

The experimental rotational correlation times were calculated from the dipolar ^{13}C relaxation times by use of the Woessner[18] formalism and application of the FORTRAN program MAIN.[19] It was assumed that the rotational diffusion principal axis system coincides with the principal axis system of inertia. The possible error resulting from this assumption is less than 10% in the determination of the correlation times.

The molecular geometry of **1** was obtained from a geometry optimization using the AM1 method[21] in the MOPAC program package.[22] To obtain the ellipsoidal semiaxes, the principal axes of the ellipsoid were chosen to be parallel to the principal axes of inertia. By considering the van der Waals radii of the atoms, the longest distances in these three directions determine the semiaxes. Thus, the whole van der Waals volume of the observed molecule is inside the so-defined asymmetric ellipsoid. The error in the rotational correlation times choosing the semiaxes in this way is supposed to be less than 10%. The molecular structure of the 5,6-Me_2-THMN and the surrounding ellipsoid is presented in Figure 1. The lengths of the semiaxes are $a = 518$ pm, $b = 412$ pm, and $c = 335$ pm. To calculate the rotational correlation times for the hydrodynamic models, the macroscopic viscosities of the investigated solutions were measured at a temperature of $T = 308$ K: η(5,6-Me_2-THMN in [$^2H_2$]dichloromethane) = 0.533 mPas, η(5,6-Me_2-THMN in [$^2H_6$]benzene) = 0.691 mPas, and η(5,6-Me_2-THMN in [$^2H_2$]-tetrachloroethane) = 1.685 mPas. The corresponding radii r_L used in the calculation of the friction coefficients were 537, 590, and 670 pm, respectively.

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