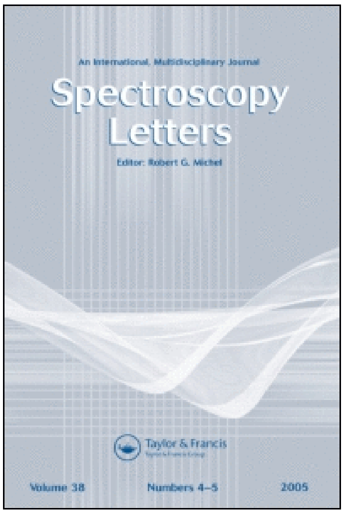

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TEMPERATURE DEPENDENCE OF ROTATIONAL DIFFUSION IN CH_2Cl_2

Key Words: Molecular Reorientation, Rotational Correlation Times

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ABSTRACT

Various *a priori* theoretical models have been utilized to predict the temperature dependence of reorientational correlation times of the C-H and C-Cl vectors in liquid CH_2Cl_2.

It was found that rotational times calculated by the Hu-Zwanzig slip model were a factor of two shorter than experimental values. Correlation times predicted via the Hynes-Kapral-Weinberg theory showed improved agreement with measured τ_c's, particularly τ_c(C-Cl). However the best results were obtained by using the Gierer-Wirtz microviscosity model to characterize the 'tumbling' motion, while assuming that 'spinning' about the unique axis is inertially controlled free rotation. With this model, the agreement between theoretical and experimental correlation times was quite satisfactory for both the C-H and C-Cl vectors at all temperatures.

INTRODUCTION

In a recent investigation of the temperature dependence of ^{13}C NMR relaxation in CH_2Cl_2,[1] it was found that the J-Extended

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Diffusion theory[2,3] provided a consistent explanation of the measured dipolar and spin-rotation relaxation times ($T_{1DD}(^{13}C\text{-}H)$ and T_{1SR}). Specifically, angular momentum correlation times, τ_J, calculated from reorientational times, τ_c, via the model predicted spin-rotation relaxation times that were in reasonable agreement with experimental values of T_{1SR}.

However, in a subsequent study of ^{13}C T_1's of dichloromethane in solution,[4] the Extended Diffusion model was not consistent with the experimental data. Therefore, several *a priori* theories of rotation[5] were utilized to calculate rotational correlation times which were compared with experimental τ_c's determined from $T_{1DD}(^{13}C\text{-}H)$. One of these models provided a consistent explanation of trends in τ_c, particularly in Lewis basic solvents.

In order to determine the applicability of these theories to molecular reorientation in dichloromethane, we have utilized the various models to calculate correlation times for rotation of both the C-H and C-Cl vectors in CH_2Cl_2 as a function of temperature. Below, the results are compared with experimental τ_c's determined from ^{13}C dipolar T_1's ($\tau_c(C\text{-}H)$)[1] and from ^{35}Cl quadrupolar T_1's ($\tau_c(C\text{-}Cl)$).[6]

RESULTS AND DISCUSSION

Although dichloromethane is an asymmetric top molecule, two of the components of its inertia tensor are quasi-degenerate[7] as are two of the semi-axes of its volume ellipsoid.[8] Therefore, its reorientation is often approximated as that of a prolate symmetric top, with a ratio of minor to major semi-axes, $\rho = b/a = 0.67$.[5] Within the stricture of this approximation, the unique axis is parallel to the Cl-Cl vector, and the C-H and C-Cl vectors lie at 90° and 34°, respectively, relative to the top axis.[8]

Presented in the first row of the Table are the experimental correlation times (interpolated to 25°C), $\tau_c(90°)=\tau_c(^{13}C\text{-}H)$[1] and $\tau_c(34°)=\tau_c(^{35}Cl)$,[6,9] and their respective activation energies.

TABLE

Experimental and Calculated Reorientational Correlation Times and Activation Energies in Dichloromethane

	$\tau_c(90°)$[b] [ps]	$\|E_a(90°)\|$[b] [kcal/mol]	$\tau_c(34°)$[c] [ps]	$\|E_a(34°)\|$[c] [kcal/mol]
Experimental[a]	0.59	1.91	1.03	1.94
Hu-Zwanzig/Free Rotor	0.33	1.39	0.48	1.65
Hynes-Kapral-Weinberg	0.89	1.40	1.11	1.59
Microvisc/Free Rotor	0.71	1.76	1.08	1.59

[a] Correlation times at 25°C

[b] From ^{13}C-H dipolar relaxation times (Ref. [1])

[c] From ^{35}Cl quadrupolar relaxation times (Ref. [6])

The temperature dependences of the experimental correlation times are also displayed in the Figure. As seen in the Table, the two activation energies are almost equal, but $\tau_c(34°)>\tau_c(90°)$, by approximately a factor of 1.7. It was noted in the earlier study[1] that this ratio lies within experimental error of the maximum calculated value, $\tau_c(34°)/\tau_c(90°) = 1.55$, which is obtained only if the reorientation is highly anisotropic, i.e. if $D_z/D_x>>1$; D_z and D_x are the two diffusion constants for rotation parallel and perpendicular to the unique axis.

The first theory of anisotropic rotation was formulated by Perrin,[10] who solved the Navier-Stokes hydrodynamic equation using the 'stick' boundary condition and obtained expressions for D_x and D_z in symmetric top molecules. Utilizing Eq. [2] of

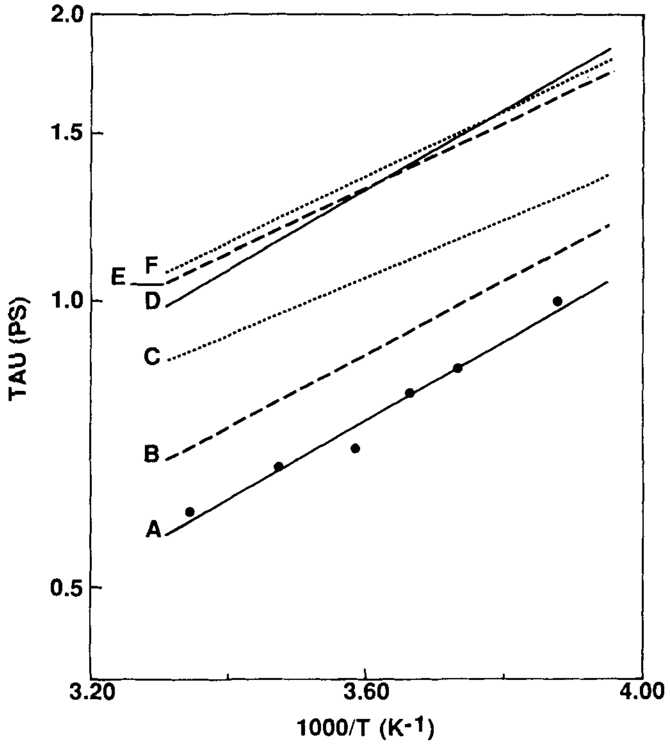

FIG. Temperature dependence of correlation times.

$\tau_c(90°)$: (A) experimental; (B) Microvisc/Free Rotor; (C) Hynes-Kapral-Weinberg

$\tau_c(34°)$: (D) experimental; (E) Microvisc/Free Rotor; (F) Hynes-Kapral-Weinberg

Ref. [4], one finds for CH_2Cl_2 at room temperature that $D_x=2.5\times10^{10}$ s^{-1} and $D_z=3.0\times10^{10}$ s^{-1}. Then, using the standard equation[11] relating τ_c to D_x, D_z and the angle, θ (e.g. Eq. [7] of Ref. [1]), the calculated correlation times are $\tau_c(90°)=6.1$ ps and $\tau_c(34°)=6.5$ ps. Clearly, these values are much longer than the experimental τ_c's by as much as an order of magnitude, as has been found in most reorientation studies of small to moderate size molecules.[5]

Hu and Zwanzig[12] commented that the failure of Perrin's model to describe adequately the reorientational dynamics of many systems probably results from application of the 'stick' boundary condition. They solved the Navier-Stokes equation numerically using the alternative 'slip' boundary condition (i.e. zero tangential stress) and obtained an expression for D_X of symmetric top molecules (e.g. Eq. [2] of Ref. [4]). In the 'slip' limit, there is no friction retarding rotation about the top axis. Therefore, this motion is inertially controlled, and D_Z can be calculated from the 'Free Rotor' correlation time (Eq. [4] of Ref. [4]) by $D_Z=6(\tau_Z)_{FR}^{-1}$.

Utilizing the combined Hu-Zwanzig/Free Rotor approach, we have calculated the diffusion constants, D_X and D_Z, and from them, the correlation times, $\tau_C(90°)$ and $\tau_C(34°)$, in CH_2Cl_2 as a function of temperature.

Although not shown in the Figure (to avoid congestion), the room temperature values and the activation energies are presented in the Table. The correlation times calculated via the 'slip' model are clearly an improvement over those determined from Perrin's 'stick' equations. However, the agreement with experiment is far from quantitative. One sees that both $\tau_C(90°)$ and $\tau_C(34°)$ are roughly a factor of two shorter than the experimentally measured times; the same inequality is found at all temperatures. This result suggests that although the 'slip' boundary condition is more realistic than the 'stick' limit, the molecular frictional forces actually lie somewhere between the two extremes.

Hynes, Kapral and Weinberg (HKW),[13] noting the failure of either of the above approaches to quantitatively characterize reorientation, formulated a model which incorporates a slip coefficient, β, into a modified boundary condition. They also presented a method by which β may be estimated from Enskog collision theory. Although originally developed for spherical particles, the HKW model has been extended in an intuitive fashion to symmetric top molecules by Tanabe.[14,15]

Using the equations and methodology of Refs. [4], [14] and [15], we have calculated the temperature dependence of rotational diffusion constants and correlation times in CH_2Cl_2.

As seen in the Table, the calculated room temperature correlation time for C-Cl vector, $\tau_c(34°)$, is fairly close to the experimental value. The calculated activation energy is somewhat lower than the measured E_a. However, from the Figure, one observes a reasonably close agreement between theory and experiment, within 3% to 8% at all temperatures. The agreement, though, is less satisfactory for rotation of the C-H vector, $\tau_c(90°)$. From both the Table and Figure, it is seen that τ_c's calculated from the modified HKW model range from 30% to 50% greater than the experimental times.

Another approach that lies between the purely 'slip' and 'stick' limiting cases has been suggested by Gillen[16] and Griffiths.[17] They have noted that in many symmetric top molecules, 1) the tumbling rotation of the top axis, D_x, is diffusionally controlled and well characterized by the microviscosity model of Gierer and Wirtz,[18] whereas 2) rotation about the axis, D_z, is basically that of a Free Rotor (*vide supra*).

The Gierer Wirtz expression for the rotational diffusion constant is:

$$D = \frac{1}{f_{GW}} \frac{kT}{8\pi a^3 \eta}$$

η is the solution viscosity. For neat liquids, $f_{GW}=(6.125)^{-1}$. The original development was for spherical molecules in which case 'a' is the molecular radius. However, in applying the model to the tumbling motion of a symmetric top, it is intuitively more reasonable to take 'a' to be half the length of the symmetry axis. For dichloromethane, assuming an average radius, $r=(ab^2)^{1/3} =2.375$ Å,[19] and an axial ratio, $\rho=b/a=0.67$,[5] one finds that a=3.10 Å.

Using the above equation for D_x and the Free Rotor expression for D_z,[20] we have calculated reorientation times of the

C-H and C-Cl vectors at various temperatures in the liquid phase. As seen from both the Table and the Figure, the combined Microviscosity/Free Rotor approach predicts values of $\tau_c(34°)$ that are surprisingly close both to those calculated with the HKW model and to the experimental results. However, one sees also that calculated reorientation times of the C-H vector, $\tau_c(90°)$, are in much better agreement with experiment than those predicted by the HKW approach.

We wish to comment also that even though the two models yield values of $\tau_c(34°)$ that are close to equal, their descriptions of the molecular reorientation of CH_2Cl_2 are actually quite different. Specifically, diffusion constants obtained from the HKW theory at room temperature are: $D_x=13.4\times10^{10}$ s^{-1} and $D_z=25.9\times10^{10}$ s^{-1}. On the other hand, the Microviscosity/ Free Rotor model yields: $D_x=8.3\times10^{10}$ s^{-1} and $D_z=92.5\times10^{10}$ s^{-1}. Thus, the latter approach predicts that the reorientation is highly anisotropic (i.e. $D_z>>D_x$) in agreement with experimental NMR results.[1,8]

In summary, it has been found that both the HKW and Microviscosity/Free Rotor theories provide a more realistic characterization of the temperature dependence of reorientational correlation times in CH_2Cl_2 than does the purely 'slip' model of Hu and Zwanzig.[12] In addition, the latter of the two models provides a better estimate of rotational times of the C-H vector, $\tau_c(90°)$. However, it would be inappropriate to conclude that the Microviscosity/Free Rotor approach is in all respects superior since, unlike the HKW theory,[13] it fails to adequately explain the solvent dependence of rotational times in dichloromethane.[4]

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REFERENCES

1. Rodriguez, A. A., and Schwartz, M., J. Magn. Reson. (Aug., 1987)

2. McClung, R. E. D., J. Chem. Phys. 1972; 57: 5478

3. McClung, R. E. D., Adv. Molec. Relax. and Interact. Processes 1977; 10: 83

4. Rodriguez, A. A., Chen, A. F. T., and Schwartz, M., Adv. Molec. Relax. and Interact. Processes (submitted)

5. Boere, R. T., and Kidd, R. G., Ann. Reports on NMR Spectrosc. 1982; 13: 319

6. O'Reilly, D. E., Peterson, E. M., and Yasaitis, E. L., J. Chem. Phys. 1972; 57: 890

7. Myers, R. J., and Gwin, W. D., J. Chem. Phys. 1952; 20: 1420

8. Brier, P. N., and Perry, A., Adv. Molec. Relax. and Interact. Processes 1978; 13: 1

9. The correlation time, $\tau_c(34°)$, in the table was obtained using the gas phase quadrupole coupling constant. As noted in Ref. (1), use of the solid state coupling constant yielded correlation times that were inconsistent with $\tau_c(90°)$

10. Perrin, E., J. Phys. Radium 1934; 5: 497

11. Woessner, D. E., J. Chem. Phys. 1962; 37: 647

12. Hu, C.-M., and Zwanzig, R., J. Chem. Phys. 1974; 60: 4354

13. Hynes, J. T., Kapral, R., and Weinberg, M., J. Chem. Phys. 1978; 69: 2725

14. Tanabe, K., Chem. Phys. 1978; 31: 319

15. Tanabe, K., Chem. Phys. 1979; 38: 125

16. Gillen, K. T., and Griffiths, J. E., Chem. Phys. Letters 1972; 17: 359

17. Griffiths, J. E., Chem. Phys. Letters 1973; 21: 354

18. Gierer, A., and Wirtz, K., Zeit. Naturforsch. 1953; A8: 532

19. Mourits, F. M., and Rummens, F. H. A., Can. J. Chem. 1977; 55: 3007

20. Bartoli, F. J., and Litovitz, T. A., J. Chem. Phys. 1972; 56: 413

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