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Rotational Microviscosity Factor from Intramolecular Dipole–Dipole Contribution and Deuteron Relaxation Time

Sir:

Assuming a model of central spherical solute molecule surrounded by shells of spherical solvent molecules, Gierer and Wirtz[1] have shown that the rotational microviscosity factor f_r is about $\frac{1}{6}$ for a pure liquid. Several authors[2-7] have separated the intramolecular dipole–dipole contribution, $(1/T_1)_{\text{dd-intra}}$, from the other contributions to relaxation by studying resonances of two or more nuclei of a given molecule. The experimental values of $(1/T_1)_{\text{dd-intra}}$ tend to disagree with the Bloembergen, Pound, and Purcell (BPP) theory[8] or the BPP theory modified to include the microviscosity factor $f_r = \frac{1}{6}$. Nevertheless, a comparison of the experimental values with the calculated values enables a direct determination of f_r.

Glasel[9] has shown that, instead of the commonly accepted value of $f_r = \frac{1}{6}$ for several liquids, $f_r = \frac{1}{12}$ gives a better agreement with the experimental deuteron relaxation results. The values of f_r for several liquids calculated using $(1/T_1)_{\text{dd-intra}}$ and deuteron relaxation data are presented in this note.

In the limit of extreme narrowing, the nuclear spin–lattice relaxation time, T_1, due to quadrupolar coupling is given by

Table I. Published Values of Density, Viscosity, and Deuteron Quadrupole Coupling Constant in the Perdeuterated Analog of the Given Liquid at 25°C

Liquid	Mol wt	Density d (g/cm^3)	Viscosity η (cP)	$(e^2qQ/h)_D$ (kHz)
CH_2I_2	267.87	3.307^a	2.590^a	176^e (CD_2I_2)
CH_2Br_2	173.86	2.4815^a	0.966^a	172^e (CD_2Br_2)
CH_2Cl_2	84.94	1.316^a	0.430^a	170^f (CD_2Cl_2)
C_6H_6	78.11	0.873^b	0.605^b	183^g (C_6D_6)
$C_6H_3D_3$	81.11	0.873^b	0.605^b	183^g (C_6D_6)
C_6H_5Br	157.02	1.485^c	1.075^c	175^h (C_6D_5Br)
CH_3CN	41.05	0.776^d	0.345^d	171^g (CD_3CN)

[a] V. Griffing, M. A. Cargyle, L. Corvese, and D. Eby, *J. Chem. Phys.*, 58, 1054 (1954). [b] See ref 12 pp 140, 141. [c] See ref 12, pp 173, 174. [d] See ref 13, Vol. 3, p 28, and ref 7, pp 117, 118. [e] Estimated. [f] See ref 14. [g] See ref 15. [h] See ref 2.

$$\left(\frac{1}{T_1}\right)_q = \frac{3}{10}\pi^2 \frac{2I+3}{I^2(2I-1)} \left(\frac{e^2qQ}{h}\right)^2 (\tau_c)_q \qquad (1)$$

where e^2qQ/h is the quadrupole coupling constant and $(\tau_c)_q$ is the reorientational correlation time.

Assuming that the contribution to $(1/T_1)_{\text{dd-intra}}$ arises from interactions between identical spins (I_j, I_j) on the same molecule and the interactions between non-identical spins (I_j, I_k) on the same molecule, then $(1/T_1)_{\text{dd-intra}}$ for spin $I_j = \frac{1}{2}$ nuclei is given by

$$\left(\frac{1}{T_1}\right)_{\text{dd-intra}} = \hbar^2\gamma^2{}_j \left[\frac{3}{2}\gamma^2{}_j \sum \langle r^{-6}{}_{jj}\rangle + \frac{4}{3}\sum I_k(I_k+1)\gamma^2{}_k\langle r^{-6}{}_{jk}\rangle\right] (\tau_c)_{\text{dd-intra}} \qquad (2)$$

where γ_j and γ_k are the gyromagnetic ratios of spins j and k, respectively, r_{jj} is the distance between two identical spins, r_{jk} is the distance between two nonidentical spins and $(\tau_c)_{dd}$ is the correlation time. It is assumed that $(\tau_c)_{\text{dd-intra}}$ is very much shorter than the Larmor period.

Since $(1/T_1)_q$ and $(1/T_1)_{\text{dd-intra}}$ are intramolecular effects which depend in the same way on molecular reorientation, $(\tau_c)_q$ can be assumed to be equal to $(\tau_c)_{\text{dd-intra}}$ and is given by[1,8]

$$(\tau_c)_q = (\tau_c)_{\text{dd-intra}} = \frac{4}{3}\pi f_r\, \eta \frac{a^3}{kT} \qquad (3)$$

for a rigid molecule of radius a· η is the coefficient of viscosity. Assuming hexagonal close-packed liquid structure, the radius a is given by

$$\frac{4}{3}\pi a^3 = 0.74\frac{M}{dN} \qquad (4)$$

where M = molecular weight, d = density, N = Avogadro's number, and 0.74 is the filling factor.

Combining eq 3 and 4

$$(\tau_c)_q = (\tau_c)_{\text{dd-intra}} = 0.74\frac{M\eta}{kTdN}f_r \qquad (5)$$

Measurements of deuteron T_1 in oxygen-free samples of CD_2I_2 and CD_2Br_2 were made at a frequency of 4 MHz using pulsed NMR techniques.[10] $(1/T_1)_{\text{dd-intra}}$ values for CH_2I_2 and CH_2Br_2 were obtained by measuring proton T_1 as a function of proton concentration in oxygen-free mixtures of CH_2I_2–CD_2I_2 and CH_2Br_2–CD_2Br_2. Oxygen was removed from the samples by the freeze–pump–thaw technique described in an earlier paper.[11] For all other liquids $(1/T_1)_q$ and $(1/T_1)_{\text{dd-intra}}$ values were taken from the published data.

The values of density, viscosity, and deuteron quadrupole coupling constant in the perdeuterated analog of each liquid are shown in Table I. The values of f_r calculated using eq 1,

Table II. $(1/T_1)_{\text{dd-intra}}$, $(1/T_1)_{\text{D}}$ of Deuterons Measured in the Perdeuterated Analog of the Given Liquid and f_r Calculated from eq 1, 2, and 5 at 25°C

Liquid	$(1/T_1)_{\text{D}}$, sec^{-1}	$(1/T_1)_{\text{dd-intra}}$, sec^{-1}	$1/f_r$	
			eq 1	eq 2
CH_2I_2	1.93	0.119	14.9	14.7
CH_2Br_2	0.74	0.052	10.8	11.9
CH_2Cl_2	0.312[a]	0.019[a]	11.4	11.8
C_6H_6	0.714[b]	0.009[c]	11.2	14.9
$C_6H_3D_3$	0.714[b]	0.00079[d]	11.2	14.6
C_6H_5Br	1.905[c]	0.027[d]	8.1	7.6
CH_3CN	0.154[f]	0.020[e]	15.3	12.8

[a] See ref 13. [b] See ref 2. [c] See ref 5 and 6. [d] See ref 6. [e] See ref 3. [f] See ref 4.

2, and 5 are shown in Table II. It can be seen from Table II that the values of f_r are of the order of $^1/_{12}$ for nearly all the liquids. It may be mentioned that Gierer and Wirtz[1] assume spherical rotation in their microviscosity model and acetonitrile[3,4] has nonspherical rotation because it rotates about ten times faster about the methyl group symmetry axis than it does about an axis perpendicular to the symmetry axis. However, taking into account the errors involved in the deuteron quadrupole coupling constant, and in reading the figures for T_1, it is quite reasonable to assume that $f_r \sim {}^1/_{12}$ instead of the commonly accepted value of $f_r = {}^1/_6$. Furthermore, the value of $f_r = {}^1/_{12}$ gives a better agreement between the experimental values of $(1/T_1)_{\text{dd-intra}}$ and the values calculated using the BPP theory modified to include the rotational microviscosity factor.

It can be seen from Table II that the values of f_r obtained from the deuteron T_1 data agree with the values obtained from $(1/T_1)_{\text{dd-intra}}$ values. This would indicate that the assumption $(\tau_c)_q = (\tau_c)_{\text{dd-intra}}$ is justified.

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Book Reviews[*]

Les Grandes Réactions de la Synthèse Organique. By J. MATHIEU, R. PANICO, and J. WEILL-RAYNAL (Ecole Nationale Superieure des Techniques Avancées). Hermann, Paris xv. 1975. 356 pp. 76.00 F (about $19.00).

This large paperback book is meant to serve as a review and quick reference for the well-established synthetic reactions that are the backbone of organic chemistry. They are arranged in five groups: Condensations; Dimerizations; Insertions; Cleavages; and Rearrangements. Each section has a short introduction which includes some comment on mechanism, and organized presentation of each reaction in brief form, often less than one page. Some representative examples are given in equation form, with a reference (many are to "Organic Syntheses", but most are to recent journal articles). Both classical reactions and those of recent introduction are included. References to review articles or chapters, or to other leading references, are also given. Some of these are unfortunately rather outdated, but this fact does not seriously detract.

Because so much of the information is in the form of equations and references, only a minimal knowledge of French is needed. There is both a subject index and an index of synthons. The book appears to be useful enough to warrant personal purchase by graduate students and professional organic chemists.

Geochemistry of Water. Edited by Y. KITANO (Nagoya University). Dowden, Hutchinson & Ross Inc., Stroudsburg, Pa. 1975; distributed by Halsted Press, John Wiley & Sons, New York. xv + 455 pp. $27.00.

This is another in the series "Benchmark Papers in Geology", the philosophy behind which is to collect and sift for key papers in a basic area, and to make them more easily available in a single volume. It is surprising to note that the editor has selected no paper earlier than 1953 for this volume, which is concerned with the chemical and isotopic composition of sea water, rain and river water, and deep subsurface (connate) waters. The subject of medicinal spring waters is essentially ignored, and neither Oscar Baudisch nor balneology is to be found in the important papers, many of which may be unfamiliar to chemists although of much significance to them. The papers themselves, reproduced from the original journals, are amplified with comments by the editor.

Synthesis of Life. Edited by CHARLES C. PRICE (University of Pennsylvania). Dowden, Hutchinson & Ross, Inc., Stroudsburg. Pa. 1974. xiii + 391 pp. $22.00.

This somewhat misleadingly titled book is a volume in the series "Benchmark Papers in Organic Chemistry". It is a collection of key papers reprinted by photoreproduction from the original journals: one of them is in German; the rest are in English. The selections are deployed in three groups: The Natural Synthesis of Biomonomers, concerned with chemical evolution and primordial generation of organic compounds; Synthesis of Biopolymers, concerned with natural and total laboratory synthesis of peptides, proteins, and nucleic acids; and Self-Organizing Systems of Biopolymers, concerned with ribosomes, enzymes, optical activity, and proliferation. As in previous volumes of the series, thoughtful, critical, and stimulating comments (actually, short essays) by the editor are included with each group of papers. The whole subject is one that should strike at least some chord of interest with any chemist.

Symmetry Principles in Solid State and Molecular Physics. By MELVIN LAX (City University of New York). John Wiley & Sons, Inc., New York, N.Y. 1974. xi + 499 pp. $19.50.

Melvin Lax is eminently qualified to author a book dealing with symmetry in solid state physics, having done extensive theoretical work in this field. In this book he has brought together most of the

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[*] Unsigned book reviews are by the Book Review Editor.