Physical Chemistry

S.-Kh. G. Kashaev, B. Le, M. Z. Zinyatov

1964

SovietRxiv

Abstract

Full Text

Physical Chemistry

S.-Kh. G. Kashaev, B. Le, M. Z. Zinyatov

Proton Spin-Lattice Relaxation, Viscosity, and Molecular Vibrations in a Series of *n*-Paraffins

(Presented by Academician B. A. Arbuzov on March 26, 1964)

This paper gives a joint discussion of results obtained by us from studies of proton spin-lattice relaxation in a series of *n*-paraffins, of the values of their viscosity, and of some characteristic parameters of combination spectra. A common character has been found in the experimental regularities of the quantities considered as functions of the number of carbon atoms in the molecule.

The times characterizing proton spin-lattice relaxation were obtained by the spin-echo method. The possibilities of this method and the parameters of the spin-echo spectrometer are described in paper (^1). The measurements were carried out at $295 \pm 1^\circ$ K; the accuracy of the measurements was of the order of $\pm 5\%$. A series of *n*-paraffins C_5–C_{18} was investigated, which at this temperature are liquids, with the exception of C_{18}, which at 295° K is in the solid state. The samples were first deoxygenated in order to exclude, as far as possible, the mechanism of spin-lattice relaxation due to paramagnetic contamination, and were checked for purity by the method of combination light scattering.

The results of the investigations and the values of the quantities considered are summarized in Table 1. Here n is the number of carbon atoms in the molecule, T_1 is the proton

Table 1

n	T_1, sec	η, cP	W, cm^{-1}	ν, cm^{-1}	$\beta = \frac{1}{T_1\eta}$, $cP^{-1}\,sec^{-1}$	n	T_1, sec	η, cP	W, cm^{-1}	ν, cm^{-1}	$\beta = \frac{1}{T_1\eta}$, $cP^{-1}\,sec^{-1}$
5	14.0	0.236	–	406	–	12	1.9	1.441	1046.6	194	0.365
6	8.9	0.300	541.0	373	0.375	13	1.5	1.809	1111.4	–	0.369
7	6.8	0.408	659.9	311	0.360	14	1.2	2.222	1205.7	–	0.375
8	4.9	0.532	717.3	283	0.384	15	1.0	2.720	1273.3	–	0.368
9	3.9	0.695	808.2	249	0.369	16	0.8	3.290	1332.4	150	0.380
10	3.0	0.881	876.3	231	0.378	17	0.7	3.980	1390.9	–	0.359
11	2.3	1.144	954.3	–	0.380	18	0.55	–	1416.2	–	–

n	T_1, sec	η, cP	W, cm^{-1}	ν, cm^{-1}	$\beta = \frac{1}{T_1\eta}$, $cP^{-1}\ sec^{-1}$	n	T_1, sec	η, cP	W, cm^{-1}	ν, cm^{-1}	$\beta = \frac{1}{T_1\eta}$, $cP^{-1}\ sec^{-1}$

spin-lattice relaxation time, η is the viscosity (their values are borrowed from tables (^2, ^3)), W is the activation energy, found from plots of $\ln\eta$, $1/T$ (T is the temperature in °K); the value of W for $n = 5$ is not given, since at the temperature of the investigation n-pentane is close to the critical evaporation temperature, and determination of W is difficult, and, for the same reason, n-pentane is not included in our subsequent quantitative considerations; ν are the frequencies of the lines of the combination spectra that are assigned to deformation skeletal vibrations of the molecules (^4). For convenience of discussion the values W and ν are given in identical units, cm^{-1}. The last column contains the calculated values of the relaxation parameter,

$$\beta = 1/T_1\eta.$$

Of the results of the investigations at the indicated constant temperature, the greatest interest is presented by the constancy, within the accuracy of the experiment, of the relaxation parameter $\beta = 0.372$ for the entire series of paraffins studied.

In studies involving dilution of organic liquids in nonmagnetic solvents, the constancy of β is a criterion of the smallness of intermolecular dipole-dipole interactions (^5). In our case, considering a successive series of paraffins as a kind of "dilution" of the CH_3 groups by CH_2 groups, but by groups incorporated into the structure of the molecule, we may assume that

The constancy of the relaxation parameter also indicates the smallness of intermolecular interactions. Indeed, if the intermolecular interaction were substantial, then the more than threefold increase in molecular size on going from C_5 to C_{14} should have caused a substantial change in the parameter β. Also in favor of this assumption is the well-known proposition that in crystalline n-paraffins the intermolecular interaction is, at least, one order of magnitude smaller than the intramolecular one ([6]). The foregoing leads to the opinion that, in the case of n-paraffins, the experimentally observed times T_1 are caused chiefly by intramolecular interactions; more specifically, the motion modulating the interaction between spins, which determines proton spin-lattice relaxation, is intramolecular motion. The relation between the spin-lattice relaxation rate $1/T_1$ and the viscosity η through a constant relaxation parameter by the relation $1/T_1 = \beta\eta$ creates the view that the viscosity of n-paraffins is also caused chiefly by intramolecular motion. This relation also indicates that clarification

of the nature of viscosity will make it possible to penetrate into the details of the mechanism of spin–lattice relaxation.

It is known that the temperature dependence of the viscosity of nonassociated liquids is well represented by the dependence ([7]): $\eta = Ae^{W/kT}$.

Here A and W are quantities which, in the first approximation, do not depend on temperature (W is called the activation energy).

The temperature dependence of viscosity is determined mainly by the factor $e^{W/kT}$, and hence by the value of the activation energy. According to ([7]), the value of W is determined by molecular motion, and the constancy of β makes it possible to assume that this motion is intramolecular. Therefore, taking into account that intramolecular interactions are well manifested in combination spectra, the activation energies were compared with the frequencies of combination lines. In doing so, our attention was focused on the low-frequency lines (up to 500 cm^{-1}), whose intensity in the Stokes region decreases as the temperature of the sample is increased, just as the viscosity of the sample decreases with increasing temperature.

It is characteristic that the combination spectra of n-paraffins in the solid state up to 500 cm^{-1} have only one line each, the frequencies of which are assigned to deformational vibrations of the carbon skeleton of paraffin molecules on the basis of the corresponding theoretical calculations of the longitudinal vibrations of models of continuous elastic rods ([4]). These frequencies of the combination lines were taken by us as the basis for comparison with the activation energy. The basis for the admissibility of comparing activation energies found for liquid paraffins with the frequencies of combination-scattering lines for solid states is the following. According to ([4]), the extended form of paraffin molecules, characteristic of the solid state, is one of the stable configurations of molecules in the liquid state, if the number of carbon atoms in the molecule is not too large. This explains the presence of the mentioned spectral lines in the solid and liquid states, and only starting with C_{16} are there no corresponding lines in the liquid state. Consequently, comparison of W for the liquid state with ν for the solid state is permissible up to C_{16}.

One could have limited oneself to members of the series up to C_{16} and proceeded to the final conclusion of our work. However, according to ([8]), the absence in the spectra of the liquid state of combination lines characteristic of the solid state and attributed to skeletal vibrations still does not mean that such vibrations do not exist in the liquid state, since these vibrations may prove inactive for large molecules in the sense of manifestation in the spectra. The reason for this is that, according to the theory, vibrations of skeletal frequencies are performed by each elementary ethylene cell, whereas in combination-scattering spectra only those fundamental types of vibrations can be active in which the corresponding atoms in all elementary cells move in phase ([10]). Owing to the slight deformation of a long molecule in the liq-

in the solid state the phase of the vibrations of the elementary cells may be

Fig. 1

Figure 1: Fig. 1

disrupted; thereby the activity will be disrupted, and the vibrations may not appear in the spectra. On this basis we also retained the frequency discussed for C_{16}. It is characteristic (Fig. 1) that the frequency for solid C_{16} fits well into the regularity we established for chains with a smaller number of carbon atoms. This, in turn, is possibly convincing evidence for the existence, in the liquid state, of vibrations of elementary cells with this frequency, but inactive for combination spectra.

Fig. 1

A comparison of the values of W and ν is made in Fig. 1. All quantities in units of cm^{-1} are plotted on a logarithmic scale as a simple function of the number n. Curve 1 gives the dependence of W, 2 the dependence of ν, 3 a straight line parallel to the n axis, which is an axis of symmetry for the dependences W and ν; it corresponds to the energy level $T_0 = 445$ cm^{-1}, constant for the whole series of paraffins. The energy T_0 is evidently associated with the boiling point, since the values of the boiling points tend toward this value with increasing n (see curve 4). From the symmetry of curves 1 and 2 with respect to the straight line 3 there follows the dependence: $W = T_0^2/\nu$.

Thus, we find that the activation energy is inversely proportional to the frequency of the deformation vibrations of the carbon skeleton of the paraffin molecules. The viscosity values, consequently, also depend on the frequency of the skeletal vibrations of the molecule. This result is in good agreement with the theory of viscosity ([9]), which states that, in the case of liquids with weak intermolecular interaction, "all the observed effects point to the necessity of introducing into the theory of liquid viscosity a term depending on intramolecular flexibility."

The relation $1/T_1 = \beta\eta$ at constant β leads to the conclusion that spin-lattice relaxation in the case of n-paraffins is also associated with skeletal vibrations of the molecules. In this connection, evidently, for the relaxation mechanism the relative motion of neighboring protons bound to different carbon atoms of the molecule is essential, since, in considering skeletal vibrations, the CH_2 groups are assumed to move as a whole. It is also possible that individual atoms of residual oxygen play an essential role in the relaxation mechanism ([11]).

Kazan State Pedagogical
Institute

Kazan Institute of Organic Chemistry
Academy of Sciences of the USSR

Received
4 III 1964

CITED LITERATURE

1. A. Sh. Agishev, M. Z. Zinyatov, S.-Kh. G. Kashaev, N. S. Kucheryavenko, F. M. Samigullin, *Instruments and Experimental Techniques*, **1**, 1963.

2. *Physicochemical Properties of Individual Hydrocarbons*, ed. V. M. Tatevskii, 1960.

3. *Handbook of the Chemist*, **1**, 1963.

4. S. Mizushima, *Molecular Structure and Internal Rotation*, IL, 1957.

5. F. A. Bovey, *J. Chem. Phys.*, **32**, 1877 (1960).

6. C. Liang, S. Krimm, G. Sutherland, *J. Chem. Phys.*, **25**, 543 (1956).

7. Ya. I. Frenkel, *Collected Selected Works*, **3**, Publishing House of the Academy of Sciences of the USSR, 1959.

8. I. Kellner, *Proc. Phys. Soc.*, A **64**, 521 (1951).

9. A. Bondi, *Viscosity Theory; Rheology, Theory and Applications*, ed. F. Eirich, IL, 1962.

10. S. Bhagavantam, T. Venkatarayudu, *Theory of Groups and Its Application to Physical Problems*, IL, 1959.

11. A. Abragam, *Nuclear Magnetism*, ed. G. V. Skrotskii, IL, 1963.

Note: Figure translations are in progress. See original paper for figures.