Viscosity, Raman Scattering Spectra, and Thermodynamic Parameters of the Homologous Series of Normal Paraffins C_5-C_{18}

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Viscosity, Raman Scattering Spectra, and Thermodynamic Parameters of the Homologous Series of Normal Paraffins C_5-C_{18}

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The true nature of a substance can be established only by jointly considering experimental results obtained by different physical methods. A critical review of the existing research results and their joint discussion have allowed us to obtain interesting experimental regularities for a series of normal paraffins. A preliminary examination of data for other homologous series showed that the regularities obtained are of a more general character.

The temperature dependence of the viscosity of nonassociated liquids at constant pressure, as is known, is well described by an expression of the type:

$$\eta = Ae^{W/kT}$$

Here A and W are quantities which, to a first approximation, do not depend on temperature; k is Boltzmann' s constant, and T is the absolute temperature.

A number of authors have dealt with the theoretical justification of this dependence. In particular, Ya. I. Frenkel, in order to justify this dependence, proceeded from the assumption that "at temperatures close to the melting temperature, thermal motion in liquids must have the same character as in solids, i.e., it is reduced mainly to harmonic vibrations of particles about certain mean equilibrium positions" (^{1}). However, in the liquid state a substantial contribution to thermal motion is also made by the translational motion of molecules—"jumps into a new equilibrium position."

In our work, the main attention is focused on the physical meaning of the quantity W, called the activation energy. In Ya. I. Frenkel' s theory, the energy W enters into the expression determining the "time of settled life of a molecule." Since during the period of settled life a molecule undergoes vibrations, then, in our opinion, the energy W must in some way be connected with the vibrational energy of the molecule. On the basis of experimental results, we set ourselves the task of determining with what kind of molecular vibrations W is associated and how this connection is quantitatively expressed. At the same

Fig. 1

Figure 1: Fig. 1

time, it is desirable to determine whether there is a definite connection with thermodynamic parameters.

To solve this problem, the activation energy W, found as usual from a plot of $\ln \eta$ versus $1/T$, was compared with the vibrational frequencies of the molecule supplied to us by Raman light-scattering spectra. In doing so, taking into account the dependence of viscosity on temperature, we paid attention only to that part of the Raman spectra (up to 500 cm^{-1}) where the intensity of the lines is also strongly affected by temperature. In this case, the temperature dependence of the ratio of the intensity I_a of the anti-Stokes line, characterizing the number of excited molecules, to the intensity I_c of the Stokes line, characterizing the number of unexcited—

of the molecules is given by expression (2):

$$\frac{I_a}{I_c} = \left(\frac{\nu + \nu_{\text{vib}}}{\nu - \nu_{\text{vib}}}\right)^4 e^{-h\nu_{\text{vib}}/kT}.$$

As is known, experiment splendidly confirms the validity of this relation: with increasing temperature, anti-Stokes lines appear. It is characteristic that anti-Stokes lines have so far been observed only for small vibrational energies, up to 600-700 cm^{-1}.

We supplemented the tabulated Raman spectra with spectra of higher members of the series of normal paraffins under consideration (^{3}); however, further consideration of the problem led to the necessity, in the discussion, of also having the spectra of these paraffins in the crystalline state. Therefore we limited ourselves to spectra available in the literature (^{4}).

In Fig. 1 all the quantities considered are plotted on a logarithmic scale, in the same units of energy (cm^{-1}), as a simple function of the number n of carbon atoms in the molecule. Curve 1 gives the dependence of the activation energies W, found from tabulated viscosity values (^{5,6}).

Fig. 1

Curves 2 and 3 show the dependences of the Raman frequencies ν_l and ν_c of n-paraffins in the liquid and crystalline states. It should be noted, however, that in the crystalline state, up to 500 cm^{-1}, the spectra have only one line each with frequencies ν_c (curve 2), whereas in the liquid state, in addition to these lines of lower intensity, there is also a whole series of other lines; curve 3 expresses the dependence of the frequencies ν_l of the more intense lines in the liquid state. The greater completeness of the spectrum in the liquid state is due to the appearance of lines of various rotational isomers, while the simplicity in the crystalline state is caused by the freezing of internal rotation (^{4}).

Curve 4 reproduces the dependence of the melting temperature T_{m} (the temperature has been converted from the °C scale to the °K scale with subsequent recalculation into units of cm^{-1}), and curve 5 gives the dependence of the entropy values $S^{\circ}_{298.16}$ of paraffins in the liquid state (^{5}).

Consideration of the character of the dependences makes it possible to draw a number of substantial conclusions.

1. As the number of carbon atoms increases, the change in all the dependences considered slows down. The greatest change occurs at small values of the number of carbon atoms. Molecular spectroscopy (^{7}), with respect to the frequencies of Raman lines, explains this mainly by the effect of the terminal methyl groups, whose contribution decreases with increasing number of carbon atoms. In the theory of viscosity (^{8}), increased mobility is ascribed to the terminal groups. On this basis one could state that the "end-group effect" also extends to the activation energy, entropy, and melting temperature considered by us (and also, one can be convinced, to the boiling temperature).

A more detailed consideration of the low-frequency part (up to 500 cm^{-1}) of the Raman spectra of n-paraffins made it possible to establish that the frequency lines ν_{c}, most clearly manifested in the crystalline states, are due to deformation vibrations of the carbon skeleton of the mo–

molecules [4]. The activation energies and entropies considered by us have, in magnitude, the same rate of change as the rate of change of the frequency ν_{k}. This gives grounds to suppose that the change in the quantities under consideration with increasing number of carbon atoms is due to a change in the frequency of the deformational vibrations of the carbon skeleton of the molecule, and not to the influence of the terminal methyl groups. The direct influence of the increased mobility of the terminal methyl groups is possibly reflected in the melting temperature, since the rates of change of T_{m} and of the frequencies ν are the same.

2. A general survey of the plots in Fig. 1 makes it possible to see that, in the indicated system of coordinates, the plots of the different functions are pairwise symmetric with respect to lines 6, 7, 8 parallel to the n axis, corresponding to energy levels: $T_1 \approx 250\ \mathrm{cm}^{-1}$, or ≈ 295°K, $T_2 \approx 445\ \mathrm{cm}^{-1}$, or ≈ 640°K, $T_3 \approx 88\ \mathrm{cm}^{-1}$, or ≈ 127°K. Thus, for example, plot 2 of the frequencies ν is symmetric to plot 4 of the melting temperatures (the axis of symmetry is line 6), plot 1 of the activation energies is symmetric to plot 3 of the frequencies ν_{k} (the axis of symmetry is line 7), and plot 3 is symmetric to plot 5 of the entropies (the axis of symmetry is line 8). This circumstance makes it possible to relate the physical quantities under consideration by simple relations:

$$T_{\mathrm{m}} = \frac{T_1^2}{\nu}; \qquad W = \frac{T_2^2}{\nu_{\mathrm{k}}}; \qquad S^{\circ}_{2\varepsilon 8,16} = \frac{T_3^2}{\nu_{\mathrm{k}}}.$$

Here T_1, T_2, T_3 are constants, respectively identical for all representatives of the homologous series of n-paraffins under consideration and, evidently, have a definite physical meaning characterizing the features of the entire homologous series. For example, it may be noted that T_1 is evidently related to the melting temperatures, since the values of T_{m} with increasing number of carbon atoms tend toward the value T_1. The plots of T_{m} and ν intersect at the value T_1. This leads to a special feature: representatives of the paraffins located to the left of the point of intersection are liquids at T_1, while those to the right are in the solid aggregate state. The quantity T_2 is connected with the evaporation temperatures. As in the preceding case, one may convince oneself that the values of the evaporation temperatures approach this value T_2. For paraffins with evaporation temperatures above T_2, there may be the special feature that the act of evaporation is impossible without preliminary decomposition into smaller molecules. On the other hand, one may expect that plots 1 and 3 intersect at T_2. In this case there is also a special feature: the lower paraffins, located to the left of the point of intersection, evaporate at temperatures below the value T_1. This suggests a possible mutual conditioning of the values T_1 and T_2. An analogous opinion may be expressed with regard to T_3. Evidently, T_3 is related to crystallization temperatures.

3. The obtained dependence $W = T_2^2/\nu_{\mathrm{k}}$ makes it possible to state that one of the important viscosity parameters—the activation energy—is inversely proportional to the frequency (energy) of the deformational vibrations of the carbon skeleton of the molecule, and the constancy of the value T_2 for the entire series of paraffins means that the change in the values of the activation energy from one representative of the paraffins to another is due only to a change in the frequency of the deformational vibrations of the carbon skeleton of the molecule.

4. The conditioning of the activation energy by deformational vibrations explains the independence of the activation energy from temperature, since the frequencies of the Raman spectrum lines, and consequently also the frequencies of the corresponding molecular vibrations, are practically not subject to the influence of temperature. A substantial change in frequency is possible only with a change in intermolecular interactions as a result of phase transitions, formation of chemical bonds, etc. [2]. In this case a change in the activation energy also takes place.

The absence of a dependence of viscosity on optical illumination permits the supposition that excitation of the deformational vibrations of the molecule is effected not by optical quanta, but by thermal quanta.

The indicated connection between the activation energy and the deformational vibration makes it possible to explain the temperature dependence of viscosity on the basis of the theory for the intensity of Stokes and anti-Stokes lines, and to assume that the decrease of viscosity with increasing temperature is due to an increase in the number of molecules in which the deformational vibration of the carbon skeleton is excited, and, correspondingly, to a decrease in the number of unexcited molecules.

Two other dependences, $T_{\mathrm{m}} = T_1^2/\nu_1$ and $S_{298.16} = T_3^2/\nu_{\mathrm{k}}$, indicate that the thermodynamic parameters are also connected with molecular motion; namely, the change in melting temperature from one representative of the paraffins to another is due to a change in the character of the internal rotation of the molecule, while the change in entropy, as in the case of the activation energy, is connected with a change in the frequency of the deformational vibrations. These two dependences may serve as a basis for clarifying the physical meaning of the heat of fusion.

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