APPLICATION OF THE FLORY MODEL TO SOUND VELOCITIES IN NORMAL PARAFFIN LIQUIDS

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Summary

On the basis of a known statistical-mechanical theory of normal paraffin liquids, an expression for sound velocity is derived. It is found that the variation of sound velocity among the members of the series is fairly well explained in terms of a factor denoting the number of elementary "cells" occupied by a molecule.

1. Introduction

A statistical mechanical treatment of normal paraffin liquids has been given by Kurata and Isida,[1] and relationships derived on this basis between certain physical constants and the number of carbon atoms. On the assumption that the number of segments in a molecule is proportional to $n^{2/3}$, theoretical foundations have been suggested for empirical relationships involving critical temperatures and pressures, and critical temperatures and boiling points.[2,3] This theory, having the same form as Flory's theory of polymer solutions,[4] appears to constitute a good approximation to normal paraffin liquids.

In the present paper, the same theory is applied to derive an expression for sound velocity, and this is compared with experimental values. Indeed, it has long been known that the sound velocity in paraffins, as in the case of a large number of series of organic compounds, increases with increasing chain length.[5]

2. Expression for Sound Velocity

In the theory, the entire system is divided into cells, the volume of the elementary cell (τ) being independent of the chain length, and one molecule of the paraffin, having n carbon atoms, is regarded as filling x consecutive cells. Thus, the system containing N molecules, and of total volume V, can be mathematically identified with a solution N rod-like polymers distributed among $(V/\tau - xN)$ single-site solvent molecules. On the basis of the treatment given by Flory,[4] the free energy is given below :

$$F = Nf + kT\left[\left(\frac{V}{\tau} - xN\right) ln.\left(1 - \frac{\tau x N}{V}\right) + N ln \frac{\tau x N}{V} + \frac{z\psi}{kT}(V - \tau x N)\frac{\tau x N}{V}\right]$$

where the first term refers to the internal degrees of freedom, z is the number of nearest neighbour cells, and ψ represents the increase in free energy arising from the translation of the chain through a cell, involving the rearrangement of

(Segment pair) + (Hole-pair) − 2 (Segment-Hole).

The pressure is then given by

$$P = -\left[\frac{\partial F}{\partial V}\right]_{T,N}$$

$$= \frac{kT}{\tau}\left[ln\left(1 + \frac{x\tau}{v}\right) - (x - 1)\frac{\tau}{v} + \frac{z\psi}{2kT}\cdot\frac{x^2\tau^2}{v^2}\right]$$

where $v = V/N$ = volume per molecule.

The sound velocity is now given by

$$C^2 = \left[\frac{\partial P}{\partial \rho}\right]_S = -\gamma\frac{M}{\rho^2}\cdot\left[\frac{\partial P}{\partial V}\right]_T$$

$$= \gamma\frac{RT}{M}\cdot\left[1 - \frac{x^2\,\tau/v}{1 + x\tau/v} + \frac{z\psi}{kT}\cdot\frac{x^2\tau}{V}\right]$$

where γ = ratio of the specific heats.

This can also be written,

$$\Delta = \left[\frac{Mc^2}{\gamma RT} - 1\right] = \frac{x^2\tau}{v}\left[\frac{1}{1 + x\tau/v} - a\right]$$

3. COMPARISON WITH EXPERIMENT

Values of sound velocity at 20° C. for normal paraffin liquids $n = 5$ to $n = 9$ have been given by Bergmann (the data being those of Schaffs[6]). Values of γ can be calculated from the values of sound velocities c, specific heats C_p and thermal expansion coefficients α with the aid of the well-known formula,

$$\gamma = 1 + \frac{T\alpha^2c^2}{JC_p}.$$

These values decrease from 1·3 to 1·2 for $n = 5$ to $n = 9$. (Values of C_p and α are taken from *International Cirtical Tables.*)

Regarding the value of x we can consider Egloff's[7] data on the molecular volume at the boiling point, which can be represented by means of the linear curve, and put

$$x = \frac{V_n}{V_1} = 0{\cdot}48 + 0{\cdot}52n.$$

(1) Now, from the equation for Δ, we can derive the following quadratic in τ,

$$ax^3\tau^2 + [x^2(1 - a) + x\Delta]\,v\tau - v^2\,.\,\Delta = 0\,.$$

Regarding the value of a, the value of $(z\epsilon/\kappa)$ obtained by Kurata and Isida from the curves representing the relation between critical temperature and the number of carbon atoms, can be taken, as these are in accordance with the values of the potential energy of intermolecular interaction obtained from data on the second virial coefficient $(2k/z\epsilon = 0{\cdot}002755)$. Taking $x = (a + bn)$ as before, values of τ can be obtained, and are found to have a more or less constant value for the members of the series, $n = 5$ to $n = 9$. (The actual values range from $\mathrm{N}\tau = 34{\cdot}4$ c.c. to $31{\cdot}8$ c.c.)

(2) Further, it is found that the quantity (Δ/x^2) remains practically constant throughout the series, varying from 2·7 to 2·8, as shown by the accompanying table, in which the values of x are those computed from the molecular volume data mentioned above. Now, since τ can be assumed constant, this amounts to the assumption that the quantity within brackets in the expression for Δ is a constant. Since here again, the major contribution is made by the first term, the expression $\mathrm{N}(v - x\tau)$, which, on the basis of the theory, represents the volume occupied by the vacant cells (in a volume V) the latter quantity can to a first approximation be regarded constant throughout the series. This can be roughly seen to be the case, by considering the values of the molecular volume $\mathrm{V} = (\mathrm{M}/\rho)$, and the values of τ computed above. The results are given in Table I.

TABLE I

Paraffin	x	$\Delta = \dfrac{\mathrm{M}c^2}{\gamma \mathrm{RT}} - 1$	$\dfrac{\Delta}{x^2}$	$\mathrm{N}\tau$
C_5H_{12}	3·08	25·9	2·72	34·4
C_6H_{14}	3·60	36·2	2·78	33·9
C_7H_{16}	4·12	47·8	2·81	33·1
C_8H_{18}	4·64	58·3	2·77	32·5
C_9H_{20}	5·16	71·8	2·71	31·8

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