THE DEPENDENCE ON PRESSURE OF THE VELOCITY OF ULTRASONIC WAVES IN LIQUIDS AND THE AVAILABLE VOLUME OF MOLECULES *)

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Using the Kittel formula for the pressure coefficient of the velocity of propagation of ultrasonic waves in liquids and the Kuczera formulae for the temperature coefficients of the velocity of ultrasound, a relation has been derived between the «available volume» of the liquid molecules and the repulsion exponent in the Lennard-Jones potential of the molecularinteraction. The values of the available volume» for a number of liquids have been determined. It has also been shown that the degree of space filling increases in a homologous series of saturated hydrocarbons with the increasing number of the homologue.

1. Introduction

An important quantity describing some acoustical properties of liquids, for instance in addition to the velocity of propagation, the attenuation of ultrasonic waves, and their dependence on temperature and pressure, is the so-called free available molar volume V_a of liquid molecules [3]. According to SCHAAFFS [8], p. 242, it can be defined as a difference between the molar volume V of the liquid and the specific volume B of the molecules per mole of the liquid:

$$V_a = V - B. \tag{1}$$

This volume should not be identified with the so-called «free volume» encountered in model theories of liquids, defined as the region in which the centre of mass of a molecule can move.

KITTEL [3] taking advantage of the Tonks equation of state

$$pV(1 - \theta^{1/3}) = RT, \tag{2}$$

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where p denotes the pressure, R is the gas constant, T — the absolute temperature, and $\theta = B/V$, has derived a relation between the velocity of propagation of ultrasonic waves in a liquid w and the «available volume»,

$$w = \frac{V}{V_a} \left(\frac{3\varkappa_c}{\varkappa_g} \right)^{1/2} w_g \tag{3}$$

where $\varkappa_c$ denotes the ratio of the specific heats of a liquid at constant pressure and constant volume, $\varkappa_g$ is the ratio of the specific heats at constant pressure and constant volume of the given substance in the gaseous state, while w_g is the velocity of ultrasound in the gas,

$$w_g = \left(\frac{\varkappa_g R T}{M} \right)^{1/2}, \tag{4}$$

where M denotes the molar mass.

2. The dependence of the velocity of propagation of ultrasound in a liquid on the pressure

For the pressure coefficient of the velocity of propagation of the ultrasonic waves in a liquid, Kittel derived from (3) the formula

$$\frac{1}{w} \left(\frac{\partial w}{\partial p} \right)_T = \left(\frac{V}{V_a} - 1 \right) \beta_T, \tag{5}$$

where β_T denotes the isothermal coefficient of compressibility of the liquid, and the remaining symbols are as previously.

The pressure coefficient of the velocity of ultrasound can be related to the temperature coefficients, at constant pressure and at constant volume, of the propagation velocity of ultrasonic waves in a liquid [9].

Writing $(\partial w/\partial T)_p$ in the form of a Jacobian $\partial(w, p)/\partial(T, p)$ (cf. [5], p.69) and using the transformation

$$\frac{\partial(w, p)}{\partial(T, p)} = \frac{\partial(w, p)}{\partial(T, V)} \frac{\partial(T, V)}{\partial(T, p)}, \tag{6}$$

we obtain

$$\left(\frac{\partial w}{\partial T} \right)_p = \left(\frac{\partial w}{\partial T} \right)_V - \left(\frac{\partial w}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V. \tag{7}$$

Since

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{\partial(p, V)}{\partial(p, T)} \frac{\partial(p, T)}{\partial(T, V)} = \frac{a}{\beta_T}, \tag{8}$$

where α denotes the cubic expansion coefficient of the liquid, from (7) and (8) we obtain

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T = \left[\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_V - \frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_p\right]\frac{\beta_T}{\alpha}. \tag{9}$$

3. The dependence between the available volume and the intermolecular potential

We assume that intermolecular action in the liquid is described by the generalized Lennard-Jones potential

$$\Phi(r) = -\frac{A}{r^6} + \frac{D}{r^n}, \tag{10}$$

where r denotes the intermolecular distance, n — the individual exponent for each liquid describing the magnitude of the repulsion forces of the molecules, and A and D are constants.

Using the Kuczera [4] relations for the temperature coefficients of the velocity of ultrasound:

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_p = -\frac{n}{6}\,\alpha, \tag{11}$$

and

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_V = \frac{7}{6}\,\alpha, \tag{12}$$

we obtain from formula (9) the following expression for the pressure coefficient of the velocity of ultrasonic waves:

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T = \frac{n+7}{6}\,\beta_T. \tag{13}$$

Comparing formulae (5) and (13) we see that there is a relation between the available volume of the liquid molecules and the exponent n of the repulsion in the intermolecular potential:

$$V_a = \frac{6}{n+13}\,V. \tag{14}$$

The values of the available molar volume V_a, evaluated from the above formula, are given in the Table, the data on the velocity of ultrasonic waves and the temperature coefficients of the velocity being taken from [1, 6], and the values of the cubic expansion coefficients α from [7]. The values of pressure coefficients of the velocity of propagation of ultrasonic waves $w^{-1}(\partial w/\partial p)_T$, evaluated from the Kittel formula (5) by substituting in it the ratios V_a/V determined in this paper, are in good agreement with the experimental values of these coefficients.

Table. Values of the available volume of the liquid molecules obtained from formula (14) for $T = 293$ K

Substance	$V \times 10^2 [\text{m}^3]$	$a \times 10^5$ [K^{-1}]	w [ms^{-1}]	$-\left(\dfrac{\partial w}{\partial T}\right)_p$	n	V_a/V	$V_a \times 10^6$ [m^3]
n-pentane	115.202	161	1008	4.2	15.5	0.210	24.19
n-hexane	130.770	135	1116	4.4	17.5	0.197	25.76
n-heptane	146.520	124	1154	4.0	16.8	0.201	29.45
n-octane	162.720	116	1192	3.9	16.9	0.200	32.54
n-nonane	173.440	107	1234	3.8	17.3	0.198	34.34
n-decane	194.670	101	1255	3.7	17.5	0.197	38.43
n-dodecane	226.760	96	1300	3.7	17.8	0.195	44.22
n-tetradecane	260.200	89	1331	3.6	18.2	0.192	49.96
n-hexadecane	291.930	80	1358	3.5	19.3	0.186	54.30
benzene	88.968	123	1324	4.8	17.5	0.197	17.53
bromoform	87.463	91	931	2.2	15.3	0.212	18.54
chloroform	80.281	127	1001	3.4	16.1	0.206	16.54
cyclohexane	108.161	119	1277	4.6	18.2	0.193	20.87
carbon tetra-chloride	96.567	123	938	3.0	16.1	0.206	19.89

4. Conclusions

The values of the admitted volume of the liquid molecules are determined by the values of the repulsion exponent in the intermolecular potential. The Table shows that in the case of a homologous series of saturated hadrocarbons the ratio V_a/V decreases with increasing length of the chain that forms a molecule of a given chemical compound.

This indicates that the degree of space filling increases with increasing number of the homologue and confirms the conclusions of SCHAAFFS [8], p. 254, and BONDI [2] on space filling in a homologous series of saturated hydrocarbons, derived by other means. The author of this paper has shown [10], p. 104, that the ratio of the free volume to the molar volume also decreases in the homologous series of saturated hydrocarbons with increasing number of the homologue.

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