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TEMPERATURE AND PRESSURE CHANGES OF THE "COLLISION FACTOR" IN SCHAAFFS' MOLECULAR-KINETIC THEORY OF WAVE PROPAGATION IN LIQUIDS

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Expressions have been derived which describe the pressure coefficient and temperature coefficient at constant pressure and volume of the "collision factor" s which determines, in Schaaffs' molecular-kinetic theory, the values of the velocity and attenuation coefficient of ultrasonic waves propagating in liquid. The values of the former coefficients have been determined for homologous series of saturated hydrocarbons, alkyl iodides, and benzene derivatives.

1. Introduction

According to Schaaffs' molecular–kinetic theory [4], p. 253, the velocity of ultrasonic waves in liquid is determined by the space filling and the elasticity of molecular collisions and is expressed by the formula

$$w = w_{\infty} s r, \tag{1}$$

where w is the propagation velocity of ultrasonic waves, w_{∞} – a constant coefficient equal to 1600 [m/s], s – collision factor (*Stossfaktor*) determining the elasticity of the collisions of the molecules of the liquid, $r = B/V$, B being the specific volume of a mol of molecules, and V – molar volume of the liquid.

The value of the collision factor s determines also the attenuation of ultrasonic waves in liquid. According to Schaaffs ([4], p.437) the attenuation coefficient of ultrasonic waves in non-relaxation region is expressed as

$$\frac{\alpha}{\nu^2} = C\frac{4-s}{s^4 r^3}, \tag{2}$$

where α – attenuation coefficient, ν – wave frequency, C – constant coefficient determined by Schaaffs and equal to 1.1×10^{-13} [s²/m]. Thus the temperature and pressure dependencies of the collision factor define the corresponding relations for the attenuation coefficient of ultrasonic waves.

2. Temperature dependence of the collision factor

Schaaffs, Kuhnkies and Woelk [5] have demonstrated that the temperature dependence of the collision factor in some liquids can be expressed by

$$s = 4\left(1-\frac{T}{962}\right), \tag{3}$$

where T is the absolute temperature.

Sette [6] (cf. also [1], p. 247) has shown, using Rao's rule expressed in the form

$$w^{1/3}V = \text{const.} \tag{4}$$

and the Sugden formula for the dependence of the density of liquid on temperature

$$\varrho-\bar{\varrho} = \varrho_0\left(1-\frac{T}{T_c}\right)^{0,3}, \tag{5}$$

where ϱ is the density of the liquid, $\bar{\varrho}$ – the density of saturated vapour, ϱ_0 – the density at absolute zero temperature, T_c – the critical temperature, that

$$s = K\left(1-\frac{T}{T_0}\right)^{0.6}, \tag{6}$$

where K is a constant characteristic for the given liquid and depends, among other, on ϱ_0.

In the present paper, temperature coefficients of the collision factor at constant pressure and volume have been determined using the generalized Rao's rule ([4], p. 281)

$$w^{6/n}\,V = \text{const.}, \tag{7}$$

where the exponent $6/n$ is individual for each liquid, and from the Kuczera [2] formula for temperature coefficient of ultrasound velocity at constant volume

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_V = \frac{7}{6}\gamma, \tag{8}$$

where γ is the bulk coefficient of expansion of liquid at constant pressure. It follows from (1) and (7), after simple calculations, that

$$\frac{1}{s}\left(\frac{\partial s}{\partial T}\right)_p = \left(1-\frac{n}{6}\right)\gamma, \tag{9}$$

and from (1) and (8)

$$\frac{1}{s}\left(\frac{\partial s}{\partial T}\right)_V = \frac{7}{6}\gamma. \tag{10}$$

Table 1 summarizes temperature coefficients $(1/s)(\partial s/\partial T)_p$ and $(1/s)(\partial s/\partial T)_V$ of the collision factor calculated from the above formulae for homologous series of saturated hydrocarbons, alkyl iodides and benzen derivatives. The exponents $6/n$ have been determined from the relation implied by Rao's rule (7)

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

and using the data from Landolt-Börnstein Tables [3] and the data of Bergmann ([1], p. 235).

Table 1. **The values of temperature coefficients of the collision factor $(1/s)(\partial s/\partial T)_p$ and $(1/s)(\partial s/\partial T)_V$ determined from equations (9) and (10)**

Substance	$\gamma\times 10^5\,[\mathrm{K}^{-1}]$	n	$-\frac{1}{s}\left(\frac{\partial s}{\partial T}\right)_p\times 10^5$	$\frac{1}{s}\left(\frac{s}{T}\right)_V\times 10^5$
n-pentane	161.00	19.20	354.20	187.80
n-hexane	135.00	16.86	244.30	157.50
n-heptane	124.40	17.30	234.30	145.10
n-octane	114.00	17.36	215.90	133.00
n-nonane	102.00	18.11	205.90	119.00
n-decane	101.50	17.43	193.30	118.40
n-dodecane	96.20	17.77	188.90	112.20
n-tetradecane	89.40	18.58	187.40	104.30
n-hexadecane	80.00	19.32	177.70	93.80
methyl iodide	125.00	17.28	234.90	145.80
ethyl iodide	116.90	17.10	216.80	136.40
propyl iodide	109.50	17.11	202.70	127.70
butyl iodide	102.00	15.65	164.10	119.00
benzene	123.00	19.12	269.00	143.50
fluorobenzene	116.00	18.14	234.70	135.30
chlorobenzene	98.00	17.57	188.90	114.30
bromobenzene	90.30	17.72	176.40	105.30
iodobenzene	83.00	17.40	157.70	96.80

3. Pressure dependence of the collision factor

It follows from thermodynamic considerations that the temperature coefficient of the ultrasound velocity at a constant pressure can be written in the form

$$\left(\frac{\partial w}{\partial T}\right)_p = \frac{\partial(w,p)}{\partial(T,p)} = \frac{\partial(w,p)}{\partial(T,V)}\,\frac{\partial(T,V)}{\partial(T,p)}, \tag{12}$$

where $\partial(w,p)/\partial(T,p)$, $\partial(w,p)/\partial(T,V)$, and $\partial(T,V)/\partial(T,p)$ are the respective jacobians.

By specifing relation (12) one obtains

$$\left(\frac{\partial w}{\partial T}\right)_p = \left(\frac{\partial w}{\partial T}\right)_V - \left(\frac{\partial w}{\partial p}\right)_T\cdot\frac{\gamma}{\beta_T}, \tag{13}$$

since $(\partial p/\partial T)_V = \gamma/\beta_T$, where β_T is the isothermal coefficient of the compressibility of liquid. By combining equations (1), (8), (11), and (13) one obtains an expression for the pressure coefficient of the collision factor:

$$\frac{1}{s}\left(\frac{\partial s}{\partial p}\right)_T = \frac{n+1}{6}\beta_T. \tag{14}$$

Table 2 presents the values of coefficients $(1/s)(\partial s/\partial p)_T$ calculated from equation (14). The values β_T refer to normal pressure and have been calculated from the formula

$$\beta_T = \frac{\varkappa}{\varrho w^2}, \tag{15}$$

where $\varkappa$ is the ratio of the specific heats at constant pressure and constant volume, calculated from (1) and (7),

$$\varkappa = 1 + \frac{T\gamma^2 w^2}{c_p}, \tag{16}$$

where c_p is the specific heat at constant pressure per unit mass of the liquid.

Table 2. The values of coefficients $(1/s)(\partial s/\partial p)_T$ at 293 K from equation (14)

Substance	$\beta_T \times 10^{11}\,[\mathrm{m^2/N}]$	$\frac{1}{s}\left(\frac{\partial s}{\partial p}\right)_T \times 10^{10}\,[\mathrm{m^2/N}]$
n-pentane	210.80	71.00
n-hexane	157.17	54.60
n-heptane	142.61	43.50
n-octane	124.10	38.00
n-nonane	112.50	35.80
n-decane	115.52	35.50
n-dodecane	95.46	29.90
n-tetradecane	88.04	28.70
n-hexadecane	84.77	28.70
benzene	94.86	31.80
fluorobenzene	94.54	30.20
chlorobenzene	80.44	24.90
bromobenzene	65.48	20.40
iodobenzene	59.51	18.30

4. Conclusions

It follows from an analysis of Tables 1 and 2 that:

(a) The collision factor decreases with temperature increase if heating is carried at a constant pressure since the derivative $(\partial s/\partial T)_p$ is negative. In the homologous series the values of $(1/s)(\partial s/\partial T)_p$ decrease as the number of the homologue grows.

(b) The collision factor increases with temperature increase if heating is carried at a constant volume since the derivative $(\partial s/\partial T)_V$ is positive. In the homologous series the values of $(1/s)(\partial s/\delta T)_V$ decrease as the number of the homologue grows.

(c) The collision factor grows with pressure increase and the values of coefficients in homologous series decrease as the number of the homologue grows.

Schaaffs formula (2) as well as relations (9) and (14) derived in this paper make it possible to calculate temperature and pressure coefficients of ultrasonic wave attenuation. In the case of benzene derivatives the calculated coefficients are only in qualitive agreement with experimental data. This problem was treated in detail elsewhere [8].

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