

**ON THE EVALUATION OF THE PRESSURE COEFFICIENT OF THE SURFACE TENSION
OF LIQUIDS BY MEASUREMENTS OF THE VELOCITY OF ULTRASONIC WAVES**

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A formula has been derived to evaluate the pressure coefficient $(\partial\sigma/\partial p)_T$ of the surface tension by measuring the velocity of propagation of ultrasonic waves. It was found that the calculated values of this coefficient are in good agreement with the experimental data obtained by other authors. The values of the coefficients $(\partial\sigma/\partial p)_T$ and $\sigma^{-1}(\partial\sigma/\partial p)_T$ have been calculated for a number of liquids. The results obtained permitted us to determine the density of the surface layer of a liquid at the interface with gas. For saturated hydrocarbons and alcohols both the value of the coefficient $\sigma^{-1}(\partial\sigma/\partial p)_T$ and the percentage reduction of the density, of the surface layer in relation to the liquid density decrease monotonically with the increasing length of the chains of molecules in a given chemical compound.

1. Introduction

The effect of pressure on the value of the surface tension of liquids depends on the kind of gas above the liquid surface. The solution of gas in the liquid leads to a reduction on its surface tension [3, 8-10]. RUSANOV [8], and also SAHLI [9] have found experimentally that the surface tension of liquids increases with increasing pressure, only when the gas above the liquid neither dissolves in it, nor is subject to absorption by the surface layer. In the papers cited the gas used to obtain the pressure [8] was helium or the pressure was produced by means of centrifugal forces [9] to avoid the solution of gas in the boundary layer. Further consideration concerns the effect of pressure on the surface tension of liquids, when the gas does not dissolve in the boundary layer.

2. Empirical relationships defining the pressure dependence of the surface tension of liquids

PARTINGTON, in his monograph [6], gives a number of empirical relations between the isothermal compressibility of a liquid and its surface tension. Thus, according to RICHARDS and PALITZSCH, the relation

$$\beta_T^4 \sigma^{4/3} = 2.53 \times 10^{-3} \left[\frac{\text{dynes}}{\text{cm} \times \text{atm}} \right] \quad (1)$$

holds true over a pressure range from 100 to 500 atm, where β_T is the isothermal compressibility of the liquid and σ is the surface tension of the liquid.

According to TYRER, the relation

$$\beta_T \sigma^{4/3} = 1.2 \times 10^{-3} T^{1/3} \left[\frac{\text{dynes}}{\text{cm} \times \text{atm} \times \text{deg}^{1/3}} \right] \quad (2)$$

is satisfied for pressures up to 1 atm, where T is absolute temperature. GOPALA RAO [2], using phenomenological considerations, has established the formula

$$\sigma = \left(\frac{A}{\beta_T} \right)^{1/\tau}, \quad (3)$$

in which A and τ are constants for a given liquid.

The above formulae indicate an increase in the surface tension of liquids with increasing pressure, since the isothermal compressibility decreases with increasing pressure.

3. Eötvös' rule and the dependence of the surface tension on the pressure

It will be shown that the formula describing the pressure coefficient of the surface tension can be derived using EÖTVÖS' rule [6]

$$\sigma V^{2/3} = K(T_c - T), \quad (4)$$

where V denotes the molar volume of the liquid, T_c is the critical temperature (in Kelvin degrees), K is a coefficient independent of the temperature, and the other symbols are as stated.

At the same time it should be proved that the coefficient K is independent of pressure variations. This can be done using BRILLOUIN'S [1] generalized analysis of the various types of packing structure of molecules in liquids. According to BRILLOUIN, thermal motions of the surface molecules propagate throughout the surface in the form of capillary waves, whose phase velocity w_1 , as can be easily proved are given by [4]

$$w_1 = \left(\frac{\sigma \omega}{\varrho_1} \right)^{1/3}, \quad (5)$$

where ϱ_1 is the surface density of the liquid layer and ω is the cyclic frequency of the molecular vibrations. From formula (5) we obtain

$$\omega^2 = \frac{\sigma \gamma^3}{\varrho_1}, \quad (6)$$

where γ is the wave number. For the group velocity w_2 of the capillary waves we have

$$w_2 = \frac{d\omega}{d\gamma} = \frac{3}{2} w_1. \quad (7)$$

BRILLOUIN has shown that the capillary waves apply, per unit length of the boundary of the surface, a force F which can be expressed by

$$F = \frac{w_2}{w_1} \frac{\varepsilon}{2}, \quad (8)$$

provided that the waves are completely diffused. The quantity ε in equation (8) denotes the energy of the thermal motions of molecules per unit surface area of the liquid. This energy can be expressed by

$$\varepsilon = \frac{3RT}{S_m}, \quad (9)$$

where R is the gas constant and S_m is the surface area of a monomolecular layer of a mole of the liquid. If the surface tension at an absolute temperature $T = 0$ K is denoted by σ_0 , then it follows from formulae (7)-(9) that at a temperature T we have

$$\sigma = \sigma_0 - \frac{3}{4} \varepsilon = \sigma_0 - \frac{9RT}{4S_m} \quad (10)$$

which implies that

$$-\left(\frac{\partial \sigma}{\partial T}\right)_p S_m = \frac{9}{4} R, \quad (11)$$

where the area S_m of the surface can be expressed in terms of the molar volume of the liquid. This, however, requires the knowledge of the packing structure of the molecules. It can be easily shown that for a cubic packing structure with an intermolecular distance d we have the following relations (where N is Avogadro's number) for the molar volume:

$$V = Nd^3 \quad (12a)$$

in the case of a simple cubic (S.C.) structure;

$$V = \frac{4}{3\sqrt{3}} Nd^3 \quad (12b)$$

for a body centred cubic packing structure (B.C.C.);

$$V = \frac{1}{\sqrt{2}} Nd^3 \quad (12c)$$

for a face centered cubic structure (F.C.C.).

According to BRILLOUIN the surface S_m can be expressed by the formula

$$S_m = Nd^2. \quad (13)$$

From formulae (12a)-(12c) and (13) we obtain in succession:

$$S_m = N^{1/3} V^{2/3} \quad (14a)$$

for S.C. molecular packing;

$$S_m = \left(\frac{3\sqrt{3}}{4} \right)^{2/3} N^{1/3} V^{2/3} \quad (14b)$$

for B.C.C. packing;

$$S_m = 2^{1/3} N^{1/3} V^{2/3} \quad (14c)$$

for the structure with the most dense packing (F.C.C.).

From formulae (11) and (14a)-(14c) Eötvös' coefficient K for the different packing structures can be easily evaluated. We obtain the following values: 2.21×10^{-7} [JK⁻¹] for S.C. structures, 1.86×10^{-7} [JK⁻¹] for B.C.C. structures, and 1.757×10^{-7} [JK⁻¹] for F.C.C. structures.

Experimental values of the coefficient for normal liquids with spherically-symmetrical molecules are typically about 2.2×10^{-7} [JK⁻¹], and this leads to the conclusion that the packing structure of these liquids is of the S.C. type.

It can thus be concluded that Eötvös' coefficient does not change with pressure variation, provided that the packing structure of the molecules does not change at the same time, i.e. provided that the pressure is not too large. A precise statement of the limiting pressure below which the value of Eötvös' coefficient remains constant would require knowledge of the temperature dependence of the surface tension of the liquids for various pressures. These data are not available from the literature. The limit can, however, be evaluated as is shown in section 5 of this paper, to within about 10^6 [Nm⁻²].

Since Eötvös' coefficient does not depend on the pressure, from equation (4), for pressures that are not too large, we obtain

$$\frac{1}{\sigma} \left(\frac{\partial \sigma}{\partial p} \right)_T + \frac{2}{3} \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = 0. \quad (15)$$

Use now the formula for the propagation velocity of ultrasonic waves,

$$w^2 = \frac{\kappa}{\rho \beta_T}, \quad (16)$$

where κ denotes the ratio of the specific heats of the liquid at constant pressure and constant volume, β_T is the isothermal compressibility of the liquid, ρ — the density, and w — the phase velocity of the ultrasonic waves. From (15) and (16) we obtain the following expression for the pressure coefficient of the surface tension of a liquid:

$$\left(\frac{\partial \sigma}{\partial p} \right)_T = \frac{2}{3} \frac{\sigma \kappa}{\rho w^2}. \quad (17)$$

The values of the coefficients $(\partial\sigma/\partial p)_T$ and $\sigma^{-1}(\partial\sigma/\partial p)_T$, evaluated from formula (17) for a number of liquids, are shown in Table 1. Experimental data concerning ρ were taken from tables by LANDOLT-BÖRNSTEIN [5], the values of the surface tension from [7], and the values of κ from [11]. The error of

Table 1. Values of the pressure coefficients of the surface tension of liquids $(\partial\sigma/\partial p)_T$ and $\sigma^{-1}(\partial\sigma/\partial p)_T$ obtained from formula (17) at temperature of 293 K

Substance	$(\partial\sigma/\partial p)_T \times 10^{11} [\text{m}]$	$\sigma^{-1}(\partial\sigma/\partial p)_T \times 10^{-9} [\text{m}^{-2} \text{N}^{-1}]$
bromoform	1.17	0.37
chloroform	1.82	0.67
carbon tetrachloride	1.85	0.69
carbon disulphide	2.00	0.62
bromoethane	1.64	0.68
iodoethane	1.85	0.63
<i>n</i> -pentane	2.33	1.40
isopentane	2.08	1.39
<i>n</i> -hexane	2.04	1.11
cyklohexane	1.76	0.69
<i>n</i> -heptane	1.93	0.95
<i>n</i> -octane	1.81	0.83
isooctane	1.82	0.97
<i>n</i> -nonane	1.67	0.73
<i>n</i> -decane	1.70	0.71
<i>n</i> -dodecane	1.61	0.63
<i>n</i> -tetradecane	1.57	0.59
<i>n</i> -hexadecane	1.55	0.56
<i>o</i> -xylene	1.59	0.53
<i>m</i> -xylene	1.62	0.56
<i>p</i> -xylene	1.62	0.57
toluene	1.71	0.60
benzene	1.82	0.63
nitrobenzene	1.36	0.31
methyl alcohol	1.83	0.81
ethyl alcohol	1.77	0.75
<i>n</i> -propyl alcohol	1.55	0.65
isopropyl alcohol	1.56	0.72
<i>n</i> -butyl alcohol	1.45	0.59
isobutyl alcohol	1.50	0.66

the calculated values of the pressure coefficient of the surface tension $(\partial\sigma/\partial p)_T$ does not exceed 0.3%. SAHLI [9] has experimentally obtained a value of $(\partial\sigma/\partial p)_T = 1.8 \times 10^{-11} [\text{m}]$ for alkanes and this coincides within experimental error with the mean value of the coefficient $(\partial\sigma/\partial p)_T$ calculated for these compounds in Table 1.

Furthermore, the pressure coefficients of the surface tension $\sigma^{-1}(\partial\sigma/\partial p)_T$ of a number of homological saturated hydrocarbons decrease with the increasing number of the homologue, i.e. with an increase in the length of the chain forming the molecule. A similar pattern is also observed for *n*-alcohols.

4. Computation of the density of the surface layer of a liquid from the dependence of the surface tension on pressure

RUSANOV, KOTCHUROVA and KHABAROV [8] state a relation between the pressure coefficient of the surface tension of a liquid and the relative change of density of the surface layer of the liquid,

$$\frac{\rho - \rho_1}{\rho} = \frac{1}{\delta} \left(\frac{\partial \sigma}{\partial p} \right)_T, \quad (18)$$

Table 2. Density ρ_1 of the surface layer of various liquids at 293 K, evaluated from formula (19)

Substance	$\left(\frac{V}{N}\right)^{1/3} \times 10^{10}$ [m]	ρ [kg m ⁻³]	ρ_1 [kg m ⁻³]	$\frac{\rho - \rho_1}{\rho} 100\%$
bromoform	5.26	2890	2826	2.23
chloroform	5.11	1487	1434	3.56
carbon tetrachloride	5.43	1594	1540	3.40
carbon disulphide	4.64	1264	1209	4.32
bromoethane	4.98	1461	1413	3.29
iodoethane	5.12	1936	1866	3.62
<i>n</i> -pentane	5.76	626	601	4.04
isopentane	5.78	620	598	3.61
<i>n</i> -hexane	6.01	659	637	3.39
cyclohexane	5.64	778	754	3.12
<i>n</i> -heptane	6.24	684	663	3.09
<i>n</i> -octane	6.46	702	682	2.84
isooctane	6.50	691	671	2.80
<i>n</i> -nonane	6.60	718	700	2.53
<i>n</i> -decane	6.86	731	713	2.47
<i>n</i> -dodecane	7.22	750	733	2.22
<i>n</i> -tetradecane	7.56	763	747	2.08
<i>n</i> -hexadecane	7.86	774	759	1.97
<i>o</i> -xylene	5.87	880	856	2.72
<i>m</i> -xylene	5.89	864	840	2.75
<i>p</i> -xylene	5.89	861	837	2.74
toluene	5.61	866	840	3.05
benzene	5.29	878	848	3.44
nitrobenzene	5.53	1206	1176	2.46
methyl alcohol	4.06	792	756	4.50
ethyl alcohol	4.59	790	760	3.86
<i>n</i> -propyl alcohol	4.99	804	779	3.09
isopropyl alcohol	5.03	786	762	3.05
<i>n</i> -butyl alcohol	5.34	810	788	2.72
isobutyl alcohol	5.35	802	780	2.74

where δ denotes the thickness of the surface layer, and the other symbols are as stated. Assuming — according to RUSANOV — that the thickness of the surface layer of the liquid is equal to the mean intermolecular distance d , calculated from formula (12a), we obtain the following expression for the density of the surface layer:

$$\rho_1 = \rho \left[1 - \left(\frac{V}{N} \right)^{-1/3} \left(\frac{\partial \sigma}{\partial p} \right)_T \right]. \quad (19)$$

Table 2 gives densities of the surface layer of various liquids. It can be seen that the density of the surface layer of a liquid is several percent lower than the density of the liquid itself. For a number of homological saturated hydrocarbons this reduction decreases with an increasing homologue number, from 4.04% for *n*-pentane to 1.97% for hexadecane. A reduction in the value of the expression $(\rho - \rho_1)/\rho$, with an increasing number of carbon atoms in the molecule, can also be observed for *n*-alcohols.

5. Conclusions

From the considerations presented in this paper the following conclusions can be drawn:

1. The coefficient K in Eötvös' formula, describing the dependence of the surface tension of a liquid on the temperature, is independent of the pressure unless the pressure is sufficiently high to change the packing structure of the molecules.

2. The formula derived in this paper, describing the pressure coefficient of the surface tension of a liquid, provides results which are in agreement with those obtained by other authors, e.g. SAHLI et al. [9]. SAHLI states that, in the case of carbon tetrachloride, the pressure coefficient of the surface tension begins to increase with increasing pressure no earlier than at a pressure of 2×10^6 [Nm^{-2}]. This implies an evaluation of the limiting pressure, at which the packing structure of the molecules remains unchanged, on about 10^6 [Nm^{-2}].

3. Formula (17) makes possible to evaluate the density of the surface layer of a liquid from the propagation velocity of ultrasonic waves in the liquid.

4. In a series of homological saturated hydrocarbons the value of the pressure coefficient of the surface tension $(\partial \sigma / \partial p)_T$ decreases with an increase of the homologue number. In the case of alcohols, it decreases with an increase in the number of carbon atoms in the molecule.

5. The density of the surface layer of a liquid is several percent lower than that of the liquid itself. In a homological series of saturated hydrocarbons, or of alcohols, the percentage reduction of the density of the surface layer, relative to the density of the liquid itself, decreases monotonically with an increase in the length of the chain which forms a molecule of a given compound.

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