

THE RELATION OF THE SPECIFIC ACOUSTIC IMPEDANCE OF LIQUIDS AND THE SURFACE TENSION

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Theorems for the dependence of the specific acoustic impedance (ρc) of organic liquids on the surface tension (σ) are proposed and substantiated. It was found that for a given liquid the quotient $N = \rho c / \sigma$ is constant at different temperatures. For liquids with similar chemical structure $N = \rho c / \delta \approx \text{const}$.

Formulae for the sound propagation velocity and its temperature coefficient which permit the evaluation of the said parameters from the density and surface tension of a liquid are given. An analysis of the accuracy of the values of sound velocities has been made and the temperature coefficients $\Delta c / \Delta t$, calculated for ten liquids, have been compared with the coefficients obtained by experiment. A reversal of the relationship for N permits calculation of the surface tension with an accuracy that is sufficient for practical purposes.

It has long been known that there exists an intimate relationship between the sound velocity in a liquid and the surface tension of this liquid, and attempts have been made to express this relationship in a mathematical form. K. ALTENBURG has calculated the velocity of elastic waves in a liquid to be equal to

$$c = 5.663\sqrt{\sigma} \sqrt[6]{\frac{6.024 \cdot 10^{23}}{\rho_l^2 M} \frac{\rho_l}{\rho_l - \rho_g}},$$

where σ denotes the surface tension in dynes/cm, ρ_l — the liquid density in g/cm³, ρ_g — the density of gas adjoining the liquid in g/cm³, and M — the molecular weight of the liquid.

Calculations made using this formula are, however, arduous, and the results are not always confirmed by experiment.

On the other hand, there is no information in the literature on attempts to relate the surface tension with the acoustic impedance although the establishment of such a dependence seems obvious. This problem, particularly for organic liquids, has been the subject of the investigations which are reported in the sequel.

On the basis of calculations made for over one hundred organic liquids (the initial data and the results for some of these liquids are given in the subsequent tables) we have come to the following conclusions:

1. The quotient of the specific acoustic impedance (ρc) and the surface tension (σ) for a given organic liquid have a constant value which is independent of temperature, i.e. $\rho c/\sigma = \text{const}$.

2. The quotient of the specific acoustic impedance and the surface tension for organic liquids of similar chemical structure, which do not contain in their molecules atoms other than C, H, O and N, are approximately constant, i.e. $\rho c/\sigma \approx \text{const}$.

3. The quotient of the specific acoustic impedance and the surface tension for organic liquids, which contain in their molecules, in addition to atoms of C and, eventually, H, O and N, other atoms but of the same element for all of these liquids, are functions of the weight content of this element in the molecule, i.e.

$$\frac{\rho c}{\sigma} = f\left(\frac{nm}{M}\right),$$

where n denotes the number of atoms of the element other than C, H, O and N in the molecule, m the atomic weight of this element, and M the molecular weight of the liquid.

Denoting by the letter N the value of the expression $\rho c/\sigma$, in which we will substitute values of c in m/s (for the sake of simplicity), ρ in g/cm³ and σ in dynes/cm, we obtain:

$N \approx 38.5$ for unbranched chain hydrocarbons (Table 1),

$N \approx 39.6$ for ketones,

$N \approx 40.0$ for cyclic substances and branched chain hydrocarbons (Table 2),

$N \approx 40.7$ for unbranched alcohols,

$N \approx 42.7$ for branched alcohols,

$N \approx 42.9$ for unbranched carboxylic acids,

$N \approx 43.7$ for esters (Table 3).

The presence of trivalent nitrogen or unsaturated bonds in a chain or ring in a liquid molecule in most cases reduces the numerical value N , while the presence of more than two atoms of oxygen in the molecule increases it.

The value of N for organic liquids, that contain in their molecules atoms of elements other than C, H, O and N, increases exponentially with the weight content of this element in the molecule. This is shown in Tables 4 and 5 and in Fig. 1. The constancy of the numerical value of N with changing temperature has been proved in a sample of twelve organic liquids in Fig. 2. Small and insignificant differences are probably caused by insufficient accuracy of values of parameters taken from the tables.

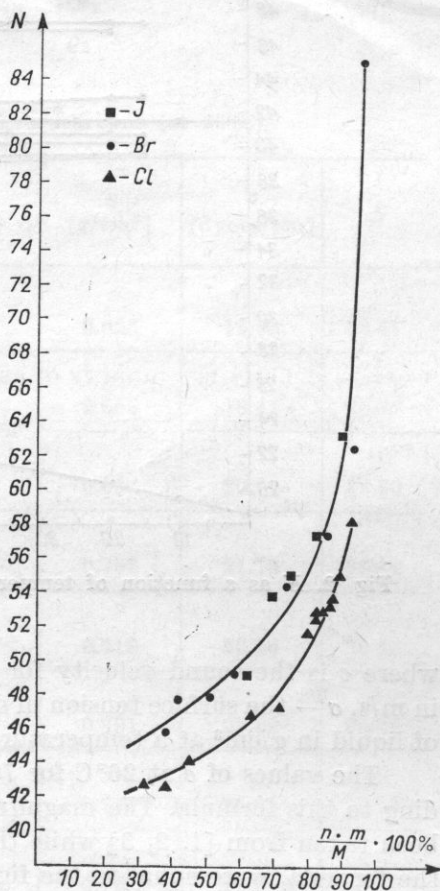
The values of the parameter N at various temperatures for water have also been calculated. The results are shown in Fig. 2. It was found that within

a range from 0 to 100°C the value of N for water increases from 18.55 to 25.13.

Liquid gases H_2 , O_2 and N_2 exhibit a similar dependence of N on the temperature. Lack of sufficient data does not permit the investigation of this problem in as many cases as would be needed to draw universal conclusions about the function $N = f(t)$ for inorganic liquids. However, it does not seem that all of them should behave in a similar manner to water and the liquid gases. For example, Table 6 gives the results of a calculation made for mercury. Within the temperature range from 0 to 200°C, the value of N for mercury is perfectly constant (the deviation from the mean does not exceed 0.08%). At temperatures no lower than about 250°C N shows a gradual which rise in the proximity of the boiling point (357°C) reaches about 5%. However, it is not clear if there is a real deviation of the value of N from a constant value or whether the values of sound velocity used for the calculation were already overstated. They were calculated on the basis of the coefficient $\Delta c/\Delta t = 0.464$ m/s·deg, cited after HUBBARD and LOOMIS by SCHAAFFS, and measured in the temperature range from 0 to 70°C. The extrapolation for the value of c above 200°C is thus risky.

The rules presented in this paper provide a simple method to evaluate

Fig. 1. N as a function of the percentage content of Br, Cl and J in molecules of organic liquids



any of the parameters involved in the formula $qc = N\sigma$ from the other parameters, if they are known for a given temperature. Furthermore, this relation can be useful in investigating the properties of various organic liquids, and also permits a new look at the essence of the acoustic impedance of a liquid.

On the basis of the relations presented we may write, at a temperature $t^\circ\text{C}$, the equality

$$c = \frac{N\sigma}{\rho}, \quad (1)$$

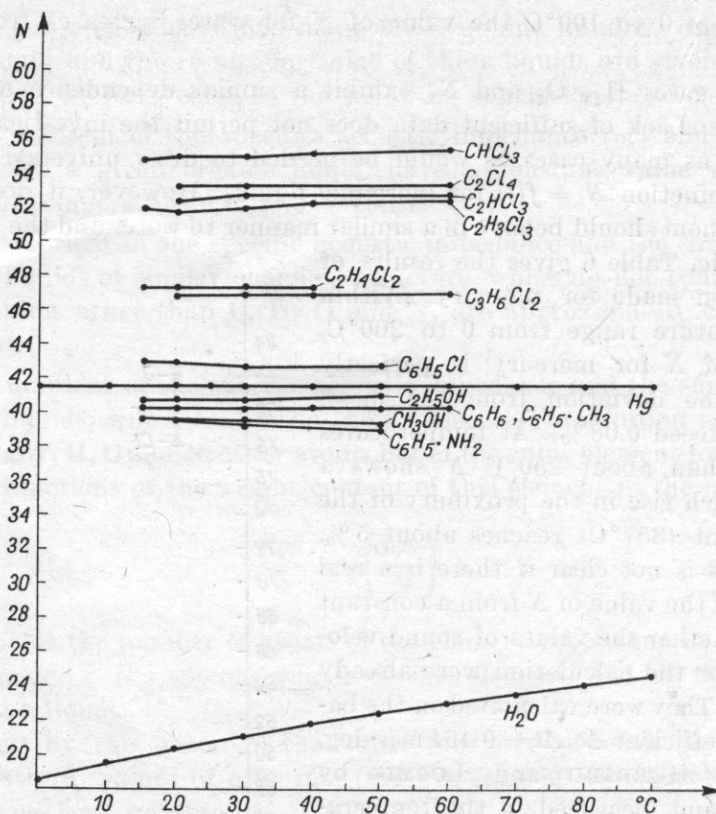


Fig. 2. N as a function of temperature for 12 organic liquids, mercury and water

where c is the sound velocity for a given organic liquid at a temperature $t^{\circ}\text{C}$ in m/s, σ — the surface tension in dynes/cm at temperature $t^{\circ}\text{C}$, ρ — the density of liquid in g/cm^3 at a temperature $t^{\circ}\text{C}$.

The values of c at 20°C for 70 organic liquids have been calculated according to this formula. The magnitudes of the surface tension and density have been taken from [1, 2, 3] while the values of the parameter N , substituted in the formula, were equal to the figures given above. The results obtained have been compared with sound velocities as stated in a standard reference book [4]. The differences between the calculated and measured values of c as follows:

Difference m/s	0-10	11-20	21-30	31-40	41-50	over 50
Number of liquids	36	17	9	5	2	1
%	51.4	24.3	12.9	7.1	2.9	1.4

The mean difference of the calculated and measured sound velocities for seventy organic liquids is 15 m/s and this corresponds to 1-2% of the mean sound velocity of these liquids.

The formula for the temperature coefficient $\Delta c/\Delta t$ of the sound velocity can be derived by simple transformations of formula (1) for the sound velocity.

For temperatures t_1 and t_2 :

$$c_1 = \frac{N\sigma_1}{\rho_1} \quad \text{and} \quad c_2 = \frac{N\sigma_2}{\rho_2}$$

Table 1. N for unbranched paraffin hydrocarbons (at 20°C)

Hydrocarbon	c [m/s]	ρ [g/cm ³]	σ [dynes/cm]	N
C ₅ H ₁₂ n-pentane	1030	0.626	16.63	38.77
C ₆ H ₁₄ n-hexane	1083	0.659	18.41	38.77
C ₇ H ₁₆ n-heptane	1154	0.684	20.29	38.90
C ₈ H ₁₈ n-octane	1192	0.702	21.78	38.42
C ₉ H ₂₀ n-nonane	1234	0.718	22.96	38.59
C ₁₀ H ₂₂ n-decane	1255	0.731	23.89	38.40
C ₁₂ H ₂₆ n-dodecane	1300	0.750	25.48	38.26
C ₁₄ H ₃₀ n-tetradecane	1331	0.763	26.66	38.09
C ₁₆ H ₃₄ n-hexadecane	1363	0.776	27.64	38.27

Mean N : 38.50 ± 0.4 ($0.4 \approx 1.0\%$)

Subtracting both sides of these formulae we obtain

$$c_1 - c_2 = N \left(\frac{\sigma_1}{\rho_1} - \frac{\sigma_2}{\rho_2} \right)$$

Table 2. N of branched hydrocarbons and cyclic substances (at 20°C)

Substance	c [m/s]	ρ [g/cm ³]	σ [dynes/cm]	N
1	2	3	4	5
C ₆ H ₁₀ cyclohexane	1305	0.811	26.55	39.9
C ₆ H ₁₂ cyclohexane	1277	0.779	24.95	39.9
C ₆ H ₆ benzene	1324	0.879	28.87	40.3
C ₇ H ₈ toluene	1328	0.867	28.53	40.4
C ₈ H ₁₀ m-xylene	1343	0.864	28.9	40.1
C ₈ H ₁₀ p-xylene	1334	0.861	28.37	40.5
C ₈ H ₁₀ o-xylene	1364	0.880	30.03	40.0
C ₈ H ₁₀ ethylbenzene	1338	0.868	29.2	39.8
C ₉ H ₁₂ propylbenzene	1342	0.878	29.10	40.5
C ₉ H ₁₂ 1,2,3-trimethylbenzene	1372	0.894	31.27	39.2
C ₁₀ H ₁₄ butylbenzene	1351	0.862	29.38	39.6
C ₆ H ₅ NO ₂ nitrobenzene	1475	1.206	43.9	40.5
C ₆ H ₇ N aniline	1659	1.022	42.9	39.5
C ₇ H ₉ N m-toluidine	1594	0.989	38.3	41.2
C ₇ H ₉ N c-toluidine	1618	0.999	40.8	39.6

Table 2, ctd.

1	2	3	4	5
C_7H_9N methylaniline	1586	0.984	39.6	39.4
$C_7H_7NO_2$ o-nitrotoluene	1473	1.163	41.67	41.1
$C_8H_{11}N$ dimethylaniline	1509	0.956	36.6	39.4
$C_5H_{11}N$ piperidine	1400	0.860	30.64	39.3
C_9H_7N chinoline	1600	1.098	45	39.0
$C_6H_{15}N$ triethylamine	1143	0.730	20.9	39.9
$C_{10}H_{18}$ trans-decaline	1403	0.873	29.89	41.0
$C_{10}H_{18}$ cis-decaline	1451	0.895	32.18	40.3
$C_{10}H_{12}$ tetraline	1484	0.969	36.2	39.7
C_7H_{16} 2,2,3-trimethylbutane	1101.5	0.6901	18.86	40.3
C_7H_{16} 3-methylhexane	1135.5	0.687	19.56	39.9
C_7H_{16} 2-methylhexane	1120	0.6789	19.21	39.6
C_7H_{16} 2,4-dimethylpentane	1083.5	0.6745	18.12	40.3
C_7H_{16} 2,3-dimethylpentane	1148.5	0.6942	19.82	40.2
C_7H_{16} 3-ethylpentane	1169.5	0.6982	20.46	39.9

Table 3. N of esters (at 20°C)

Ester	c [m/s]	ρ [g/cm ³]	σ [dynes/cm]	N
C ₃ H ₆ O ₂ ethyl formate	1160	0.917	23.84	44.6
C ₃ H ₆ O ₂ methyl acetate	1182	0.934	24.49	45.1
C ₄ H ₈ O ₂ propyl formate	1192	0.906	24.5	44.1
C ₄ H ₈ O ₂ ethyl acetate	1177	0.9005	23.9	44.3
C ₅ H ₁₀ O ₂ propyl acetate	1198	0.887	24.3	43.7
C ₅ H ₁₀ O ₂ ethyl propionate	1183	0.890	24.27	43.4
C ₆ H ₁₂ O ₂ ethyl butyrate	1197	0.879	24.58	42.8
C ₈ H ₈ O ₂ methyl benzoate	1472	1.088	37.6	42.6
C ₉ H ₁₀ O ₂ ethyl benzoate	1463	1.047	35.5	43.1

Table 4. N of organic liquids containing bromine in the molecule ($m = 79.9$) at 20°C

Substance	% by weight of bromine in the molecule	c [m/s]	ρ [g/cm ³]	σ [dynes/cm]	N
CHBr ₃ bromoform	94.8	931	2.890	31.68	84.9
C ₂ H ₂ Br ₄ 1,1,2,2-tetrabromomethane	92.5	1041	2.967	49.6	62.3
C ₂ H ₄ Br ₂ ethylene bromide	85.1	1009	2.178	38.37	57.3
C ₂ H ₅ Br ethyl bromide	73.3	900	1.461	24.15	54.4
C ₄ H ₉ Br n-butyl bromide	58.3	1019	1.274	26.33	49.3
C ₆ H ₅ Br bromobenzene	50.9	1170	1.495	36.5	47.9
C ₈ H ₁₇ Br n-octyl bromide	41.4	1182	1.166	28.89	47.7
C ₁₀ H ₇ Br bromonaphthalene	38.6	1372	1.487	44.64	45.7

Table 5. N of organic liquids containing chlorine in the molecule ($m = 35.4$) at 20°C

Substance	% by weight of chlorine in the molecule	c [m/s]	ρ [g/cm ³]	σ [dynes/cm]	N
CCl ₄ carbon tetrachloride	92.2	938	1.594	35.68	58.2
CHCl ₃ chloroform	89.1	1001	1.487	27.1	54.9
C ₂ HCl ₅ pentachloroethane	87.6	1113	1.672	34.6	53.8
C ₂ Cl ₄ tetrachloroethylene	85.5	1063*)	1.618*)	32.32	53.2
C ₂ H ₂ Cl ₄ tetrachloroethane	84.5	1170	1.595	35.2	53.0
CH ₂ Cl ₂ methylene chloride	83.5	1093	1.318	27.1	53.1
C ₂ HCl ₃ trichloroethylene	81.0	1055*)	1.464*)	29.5	52.4
C ₂ H ₃ Cl ₃ 1,1,1-trichloroethane	79.7	992*)	1.333*)	25.56	51.7
C ₂ H ₄ Cl ₂ 1,2-dichloroethane	71.5	1216	1.252	32.23	47.2
C ₃ H ₆ Cl ₂ 1,2-dichloropropane	62.8	1162	1.155	28.65	46.8
C ₃ H ₇ Cl 1-chloropropane	45.1	1091	0.890	22.0	44.1
C ₄ H ₉ Cl chlorobutane	38.3	1140	0.885	23.66	42.6
C ₆ H ₅ Cl chlorobenzene	31.5	1289	1.104	33.2	42.9

*) according to measurements made by the author

Table 6. N as function of temperature for mercury

$^{\circ}\text{C}$	c [m/s]	ρ [g/cm ³]	σ [dynes/cm]	N
0	1460.2	13.5955	479.5	41.40
10	1455.6	13.5708	477	41.41
20	1451.0	13.5462	475	41.38
25	1448.7	13.5340	473.5	41.41
30	1446.4	13.5212	472.5	41.39
40	1441.7	13.4967	470	41.40
50	1437.1	13.4729	467.5	41.42
100	1413.9	13.3522	456	41.40
150	1390.7	13.232	444	41.44
200	1367.5	13.1148	433	41.42
250	1344.3	12.994	416	41.99
300	1321.1	12.8806	400	42.54
350	1297.9	12.757	381	43.46

If both sides of this equation are divided by $\Delta t = t_2 - t_1$, we obtain a formula from which $\Delta c/\Delta t$ can be evaluated without any information about the sound velocity of a given liquid:

$$\frac{\Delta c}{\Delta t} = \frac{N}{t_2 - t_1} \left(\frac{\sigma_1}{\rho_1} - \frac{\sigma_2}{\rho_2} \right). \quad (2)$$

It is a common practice to quote the sound velocity in a given liquid at a certain temperature (most tables state values at 20°C). Thus only the coefficient $\Delta c/\Delta t$ is unknown, and different sources state different values. Substituting the value of $N = c_1 \rho_1 / \sigma_1$ into formula (2), we get

$$\frac{\Delta c}{\Delta t} = \frac{c_1}{t_2 - t_1} \left(1 - \frac{\rho_1 \sigma_2}{\rho_2 \sigma_1} \right). \quad (3)$$

Calculations have been made using formulae (2) and (3) for 10 typical organic liquids. The results of these calculations, and also the measured values of $\Delta c/\Delta t$ compiled by SCHAAFFS are given in Table 7.

On the basis of the analysis of the data contained in Table 7 and other data, not cited in this paper, it can be concluded that using the quoted formulae

it is possible to calculate, with good accuracy, the temperature coefficient of sound velocity in organic liquids, provided that:

— the numerical values from which the coefficient $\Delta c/\Delta t$ is evaluated must be extremely accurate (the accuracy of the surface tension in particular should be at least 0.01 dynes/cm),

— the temperature range Δt is as wide as possible.

Table 7. Comparison of calculated and measured values of $\Delta c/\Delta t$ for 10 organic liquids

Liquid	Data used for calculations				$\Delta c/\Delta t$ [m/s·deg] calculated ¹⁾	$\Delta c/\Delta t$ [m/s·deg] measured
	t [°C]	ρ [g/cm ³]	σ [dynes/cm]	c [m/s]		
1	2	3	4	5	6	7
Hexane C ₆ H ₁₄	20	0.6594	18.41	1083	4.74	4.4 ⁵⁰ ₁₀
	60	0.6221	14.33	—	4.72	
Heptane C ₇ H ₁₆	20	0.68276	20.29	1154	4.33	4.0 ⁹⁰ ₀
	90	0.6236	13.64	—	4.29	4.14 ⁵⁰ ₀
Octane C ₈ H ₁₈	20	0.7022	21.78	1192	4.04	3.95 ¹⁰⁰ ₂₀
	120	0.6168	12.64	—	—	4.22 ⁵⁰ ₀
Benzene C ₆ H ₆	20	0.8790	28.87	1324	4.55	4.48 ⁸⁰ ₁₀
	80	0.8145	21.24	—	4.51	4.60 ⁷⁰ ₁₀ 4.78 ⁵⁰ ₁₀
Toluene C ₆ H ₅ CH ₃	20	0.8669	28.53	1328	4.24	4.30 ⁵⁰ ₀ 4.30 ₁₀
	—	—	—	—	—	—
<i>o</i> -xylene C ₆ H ₄ (CH ₃) ₂	20	0.8801	30.03	1364	3.81	3.80 ¹⁰⁰ ₂₀
	100	0.8029	21.27	—	3.81	
Methanol CH ₃ OH	20	0.7915	22.55	1123	3.08	3.23 ⁶⁰ ₂₀
	50	0.7650	20.0	—	3.18	3.25 ⁵⁰ ₀ 3.26 ⁵⁰ ₀ 3.3 ³⁰ ₁₀
Ethanol C ₂ H ₅ OH	20	0.7894	22.55	1159	3.37	3.15 ⁷⁰ ₂₀
	50	0.76315	19.9	—	3.38	3.16 ⁷⁰ ₂₀ 3.4 ³⁰ ₁₀ 3.50 ⁵⁰ ₀
Methyl acetate CH ₃ COO·CH ₃	20	0.9338	24.49	1182	4.92	4.63 ³⁰ ₁₀
	30	0.92065	23.14	—	4.77	4.73 ⁵⁰ ₁₀
Ethyl acetate CH ₃ COO·C ₂ H ₅	20	0.9005	23.9	1177	4.65	4.5 ³⁰ ₁₀
	50	0.8635	20.2	—	4.58	4.88 ⁵⁰ ₁₀

¹⁾ the upper value has been calculated from formula (3), the lower value — from formula (2).

Table 8. Comparison of calculated and measured values of surface tension at various temperatures for fifteen organic liquids

Liquid	$\frac{\Delta c}{\Delta t}$ [m/s·deg] used for calculations	t [°C]	σ measured [dynes/cm]	σ calculated [dynes/cm]
1	2	3	4	5
Hexane C_6H_{14}	4.4^{50}_{10}	60	14.33	14.55
Heptane C_7H_{16}	4.14^{50}_0	90	13.64	13.86
Octane C_8H_{18}	3.95^{100}_{20}	120	12.64	12.79
Benzene C_6H_6	4.60^{70}_{10}	80	21.24	21.17
Toluene $C_6H_5 \cdot CH_3$	4.30^{50}_0	40	26.13	26.10
<i>o</i> -Xylene $C_6H_4 \cdot (CH_3)_2$	3.80^{100}_{20}	100	21.27	21.29
Methanol CH_3OH	3.25^{50}_0	50	20.0	19.90
Ethanol C_2H_5OH	3.50^{50}_{10}	50	19.9	19.82
Methyl acetate $CH_3COO \cdot CH_3$	4.73^{50}_{10}	30	23.14	23.18
Ethyl acetate $CH_3COO \cdot C_2H_5$	4.88^{50}_{10}	50	20.2	20.07
Carbon tetrachloride CCl_4	3.30^{50}_0	100	16.48	16.60
Chlorobenzene C_6H_5Cl	3.70^{50}_0	50	29.6	29.38
Dichloropropane $C_3H_6Cl_2$	3.80^{60}_0	60	23.8	23.80
Trichloroethylene C_2HCl_3	3.5^{30}_{20}	60	24.4	24.36
Tetrachloroethylene C_2Cl_4	3.3^{30}_{15}	60	26.9	26.99

Note. In the two last items $\Delta c/\Delta t$ according to the author's measurements

Attention should be drawn to the rather frequently occurring discrepancies in the numerical data for the surface tension from different sources. It would appear that formulae presented here can be used for the verification of these data. Furthermore, it is possible to calculate the surface tension of organic liquids for cases where the value of σ for a given temperature is unknown. For this purpose suitable transformations of formulae (1) and (3) are used:

$$\sigma = \frac{\rho c}{N}, \quad (4)$$

$$\sigma_2 = \frac{\sigma_1 \rho_2}{\rho_1} \left(1 - \frac{\Delta c}{\Delta t} \frac{t_2 - t_1}{c_1} \right). \quad (5)$$

The values obtained with the aid of these formulae do not in most cases differ by more than 0.3 dynes/cm from measured values of the surface tension. For practical purposes this accuracy is quite satisfactory. In Table 8 the results of calculations according to formula (5) are compared with values of the surface tension obtained by the direct measurement.

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