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Intermolecular Free Lengths in the Liquid State

II. Surface Tension

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Owing to the great biological and chemical importance of surface phenomena, the surface tension of liquids has been closely studied. A large number of relations has been demonstrated between surface tension and other properties (see Partington [1]). However no attention appears to have been devoted to the intermolecular free length. As this constitutes a simple and characteristic property of the liquid state, we shall in this work study the surface tension as a function of it.

The free length between the surfaces of the molecules in the bulk of the liquid, hereafter designated the free length (L), may be defined as

$$L = 2(V_T - V_0)/Y \tag{1}$$

where V_T and V_0 are the molar volumes at T°K and O°K respectively, and Y is the molecular surface of one mole. This definition, which involves an approximation, has been thoroughly discussed in a previous work [2].

PURE LIQUIDS

In Fig. 1 the surface tension (σ) for 53 non-associated organic liquids has been plotted as a function of the free length (L) at 20° C. All liquids have been included for which it was possible to obtain accurate values for surface tension and zero volume (V_0). The surface tension values have been taken from Timmermann *et al.*[3] Harkins *et al.*[4] and Landolt-Börnstein Tabellen. Where several divergent values for the same liquid were found, the average value has been used. The free lengths have been computed according to equation (1)

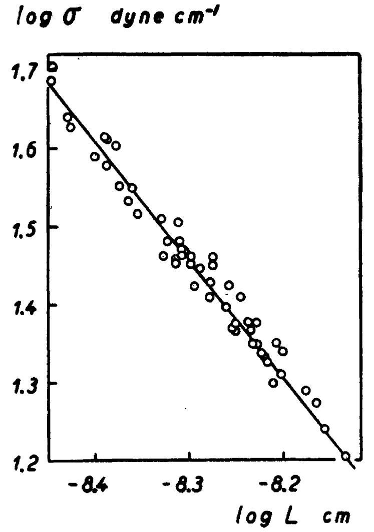

Fig. 1. Surface tensions (σ) plotted as a function of intermolecular free lengths (L) in 53 non-associated liquids at 20° C. L has been calculated from the definition (1).

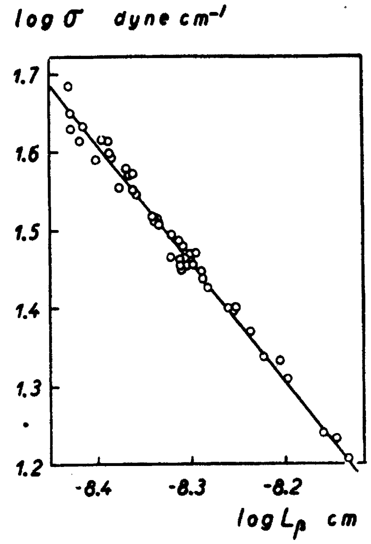

Fig. 2. Surface tensions (σ) plotted as a function of intermolecular free lengths (Lβ) in 46 nonassociated liquids at 20° C. Lβ has been calculated from the adiabatic compressibilities.

from molar volumes, and these have been given for most of the liquids in Table I : 1 (Jacobson[3]). Fig. 1 suggests a relation of the type

$$\sigma = kL^{-\frac{3}{2}} \tag{2}$$

where log $k = -10.986$ forcgs units at 20° C.

In order to test the validity of equation (2) free lengths have been computed from surface tension values according to this equation and compared with those computed from the definition (1). The average deviation in the values thus computed for L for 53 liquids amounts to 3.6 %. This deviation is due partly to errors in the values used for σ and V_0 and partly to equation (2) being approximate. The errors in V_0 can be surmounted, as the free lengths may be computed from the adiabatic compressibility (β) according to Jacobson[2]. In Fig. 2 the surface tension for 46 liquids has been plotted as a function of the free length (L_β) computed from compressibility values. As may be seen from the figure, there is better agreement between σ and L_β than between σ and L. It is probable, though not proved, that this better agreement is due to the error in V_0, and thus in free length, being eliminated when L_β is employed. The mean divergence between L_β and the free length computed

Table 1. Examples of intermolecular free lengths calculated from surface tension (σ), adiabatic compressibility (β) and molar volumes (V_O and V_T) at 20° C.

Substance	σ dyne/cm	Intermolecular free length, 10^{-8} cm		
		Calc. from σ Eq. (2)	Calc. from β	Calc. from V_O and V_T Eq. (1)
Pentane	16.0	0.75	0.74	0.74
Hexane	17.3	0.71	0.70	0.70
Heptane	20.4	0.64	0.64	0.64
Octane	21.5	0.61	0.61	0.60
Benzene	28.9	0.50	0.50	0.50
Toluene	28.9	0.50	0.50	0.49
Cyclohexane	26.5	0.53	0.55	0.55
Ethylbenzene	28.0	0.50	0.50	0.49
Ethyl ether	17.0	0.72	0.72	0.72
Ethyl acetate	23.8	0.57	0.55	0.59
Butyl acetate	24.8	0.56	0.56	0.60
Carbon tetrachloride	26.5	0.53	0.52	0.51
Chloroform	26.8	0.53	0.50	0.52
Chlorobenzene	32.7	0.46	0.46	0.44
Bromobenzene	37.2	0.43	0.44	0.41
Iodobenzene	39.2	0.41	0.41	0.41
Fluorobenzene	27.8	0.52	0.51	0.51
Aniline	43.4	0.38	0.37	0.37

according to (2) is 2.2 %. This divergence may be due in part to experimental errors, since the determinations of surface tension and compressibility were done on different samples of the liquids, so that different degrees of purity probably had an effect. Some examples of surface tension values employed are given in Table 1, as are also free lengths computed from molar volumes, from surface tension and from adiabatic compressibility.

A close study of equation (2) at different temperatures shows that k and the exponent vary somewhat between 0 and 50° C. The variation in the exponent, however, is small and for practical purposes it may be put equal to $-3/2$ within the temperature range stated. The constant k then assumes the values given in Table 2. *If definitions other than (1) for the free length are used, then*

Table 2. Values for the constant k at different temperatures.

Temp °C	log k
0	-11.032
10	-11.008
20	-10.986
25	-10.976
30	-10.966
40	-10.948
50	-10.932

the constant k and possibly also the exponent must be recalculated if equation (2) is to hold good.

Equation (2) also holds good for associated liquids, if account is taken of the degrees of association. This means that association factors can be calculated from surface tension values by means of the relation demonstrated.

SOLUTIONS AND GIBBS' ADSORPTION EQUATION

Equation (2) should also be valid for solutions and liquid mixtures. This is analogous to the situation for compressibility in which the corresponding equation derived from data for pure liquids also holds good for mixtures, with an accuracy of around one per cent [2]. In actual fact the relation demonstrated makes it possible in certain cases to compute surface concentrations from the surface tensions of the solutions *via* free lengths. For this, however, the dependence of the free length on the concentration must be known. For non-associated solutions this can be obtained from equation I : (6) [2]. For practical purposes it is then advisable to plot a curve for this, which can subsequently be employed for locating concentrations that correspond to free lengths, which are computed by means of (2) from the surface tensions of the solutions.

It is of interest to compare surface concentrations thus computed with the results obtained with Gibbs' adsorption equation. For dilute solutions this may be written

$$\Gamma = -\frac{c}{RT}\frac{\mathrm{d}\sigma}{\mathrm{d}c} \tag{3}$$

where Γ is the concentration of the solute at the surface, in moles per square centimetre, in excess of that in the bulk, c is the bulk molar concentration of the solute, R the gas constant and T the absolute temperature. Many attempts have been made to verify Gibbs' equation. Most of these, however, have failed, and the reason for this has been disscused by Michaud[5] and others. However excellent agreement was obtained by McBain and Humphrey[6] with their microtome technique, and their experiments constitute strong evidence for the validity of Gibbs' equation.

In our case, the comparison is rendered more difficult by the fact that Gibbs' equation gives the adsorption in number of moles per square centimetre of liquid surface, whereas the concentrations computed *via* free length are expressed as moles per litre or the like. In order to make the results comparable, the thickness of the surface layer in which the adsorption takes place must be estimated. The adsorption is greatest in the top monomolecular layer, rapidly approaching zero in the layers immediately below. In view of this, we have assumed a mean thickness equivalent to about two monomolecular layers. In this way the adsorption according to Gibbs' equation may be expressed in moles per litre.

Surface concentrations have been computed for a number of solutions of non-associated liquids, both from Gibbs' equation and from surface tensions *via* free lengths. The requisite surface tension values have been taken from smoothed curves plotted from values according to Taubmann[7]. Solutions of

Table 3. Surface concentrations of heptane and cyclohexane in nitrobenzene solutions calculated from surface tensions over the free lengths (c_L) *and from Gibb's adsorption equation* (c_G).

Bulc conc. mole/lit	Surface tension σ dyne/cm	Surface conc. c_L mole/lit	$-\frac{d\sigma}{dc}$	Surface conc. c_G mole/lit	$\frac{c_G}{c_L}$
Heptane					
0.1	41.7	0.62	19.4	0.77	1.24
0.2	39.7	1.12	16.8	1.35	1.21
0.3	38.0	1.59	14.8	1.83	1.15
0.5	35.2	2.32	12.3	2.61	1.13
0.7	32.9	2.95	10.1	3.61	1.22
1.0	30.3	3.60	7.4	3.54	0.98
Cyclohexane					
0.1	42.9	0.35	9.4	0.43	1.23
0.2	42.0	0.75	9.0	0.82	1.09
0.3	41.1	1.05	8.3	1.16	1.10
0.5	39.5	1.64	7.1	1.72	1.05
0.7	38.1	2.18	6.7	2.31	1.06
1.0	36.3	2.94	5.3	2.82	0.96

heptane, octane, cyclohexane and benzene, each in nitrobenzene, have been studied at bulk concentrations between 0.05 and 1.00 mole per litre. In all cases the thickness of the adsorption layer has been assumed to be 12 Å. To enable computation of surface concentrations from the equations (2) and I(6), the necessary density values for the solutions were determined with a pycnometer. Examples of the values employed and the results obtained for solutions of heptane and cyclohexane can be seen in Table 3. The last column shows the ratios between surface concentrations computed via Gibbs' equation (c_G) and via free lengths (c_L). The ratio has a value close to one, and similar values were obtained for other solutions studied. At low concentrations the computations are made uncertain by experimental errors and at high concentrations equation (3) does not hold good.

The fact that the values for c_G/c_L is close to one for different solutions and different concentrations supports the assumption that equation (2) is also applicable to solutions. Indirectly, the conclusion may also be drawn that the thickness of the adsorption layer was correctly estimated. Solutions of associated substances were not investigated, as the conditions with these become unsurveyable if their degree of association is not known.

DISCUSSION

It should be noted that the free length L in the empirical relation demonstrated refers to conditions inside the bulk of the liquid. Whether this bulk length in pure liquids is equal to the free length in the surface layer cannot be decided. Nevertheless, there must be a simple relation between these two entities, a relation which is included in equation (2). Therefore computation of surface concentrations in the study of solutions presented above was possible.

The compressibility (β) for a liquid is approximately proportional to the square of the free length[2]. If this is combined with the relation (2) given, we get

$$\beta\sigma^{\frac{4}{3}} = constant \tag{4}$$

which is a well known relation (*cf.* Partington[1], p. 139). It holds good, approximately, for both adiabatic and isothermal compressibility, but the constant assumes different values in the two cases.

SUMMARY

The empirical relation $\sigma = kL^{-\frac{3}{2}}$ is shown between the surface tension σ in normal and associated liquids and the free intermolecular length L in the bulk of the liquids. The constant k varies to some extent with the temperature

and log $k = -10.986$ holds good at 20° C for cgs units. The relation has been tested on 53 organic liquids and it has been found that L can be computed from the surface tension with an accuracy of a few per cent. The relation is also valid for solutions and in certain cases makes possible a computation of surface concentrations. Comparison has been made with Gibbs' adsorption equation and good agreement was obtained, on the assumption that the thickness of the layer within which adsorption takes place is equivalent to about two monomolecular layers.

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