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Abstract

Full Text

Physical Chemistry

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On the Interrelation of the Structure of the Surface Layer of a Pure Liquid with Its Surface and Bulk Properties

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The structure of the surface layer of a solution of a surface-active substance has been studied by using the Gibbs equation ([1]). Subsequently it was also shown ([2]) how this equation can be applied to the study of the structure of the surface layer of a pure solvent (water) in the case of a solution of a surface-inactive substance. The structure of monomolecular films of insoluble substances on the surface of water has been studied by investigating their compressibility ([3], [4]). Information on the structure of the surface layer of a pure liquid at the boundary with vapor, however, is extremely limited.

Fig. 1. Schematic of a liquid film b, stretched inside a frame K with a movable wall C; a is the surface layer.

Let us consider the conditions of equilibrium in each of the two surface layers of a film of pure liquid stretched inside a rigid frame with one movable edge. It is sufficient to examine the equilibrium of the forces acting on the area of the cross section of the surface layer and applied to the movable edge per 1 cm of its length (Fig. 1). Let A be the resultant of the molecular forces applied to the edge and directed into the film. These forces tend to draw molecules from the surface phase into the bulk phase. In the opposite direction, the movable edge is acted upon by the thermal pressure P_t, developed by the liquid inside the surface layer along the interface, and by the external force applied in order to keep the film in the stretched state, which by definition is equal to the surface tension σ with the opposite sign. For a surface-layer thickness δ cm, the equilibrium condition is

$$A - P_t\delta - \sigma = 0; \qquad (1)$$

this is an implicit form of the equation of state of the surface layer of a pure liquid. Comparison of (1) with the Helmholtz-Gibbs equation leads to the expression for the temperature coefficient of surface tension in the general form:

$$\partial\sigma/\partial T = -P_t\delta/T. \tag{2}$$

According to Ya. I. Frenkel, the thermal pressure in the surface layer of a pure liquid can be expressed by the relation

$$P_t \simeq RT/V_S, \tag{3}$$

where R is the gas constant, and V_S is the molecular volume of the liquid in the surface layer.

Substitution of (3) into (1) and (2) gives the expression for the surface tension and its temperature coefficient:

$$\sigma = A - \left(\frac{\varphi\gamma N}{V}\right)^{2/3}\frac{iR}{h}T; \tag{4}$$

$$\frac{d\sigma}{dT} = -\left(\frac{\varphi\gamma N}{V}\right)^{2/3}\frac{iR}{n}, \tag{5}$$

where V is the molecular volume of the liquid in the bulk phase; φ is the ratio of the densities of the liquid in the surface layer and in the bulk; $\chi = \varepsilon/S^{1/2}$ is the asymmetry factor of a molecule at the surface; ε is the length of the molecular axis in the surface layer normal to the surface; S is the area occupied by a molecule at the surface; N is Avogadro' s number; i is the number of monomolecular layers forming the surface layer of the liquid; n is the association factor (the number of molecules forming a complex in the surface phase).

It follows from (3) that

$$P_t\delta = i\varepsilon RT/V_s. \tag{6}$$

But

$$V = S\varepsilon nN, \tag{7}$$

therefore,

$$P_t\delta = ikT/nS, \tag{8}$$

which gives from (2)

Fig. 2

Figure 2: Fig. 2

$$d\sigma/dT = -ik/nS. \tag{9}$$

In the very important case when $i = 1$ and $n = 1$, we have

$$S = -\frac{k}{d\sigma/dT}. \tag{10}$$

Relations (9) and (10) make it possible to interpret the dependence of the temperature coefficient of surface tension for members of various homologous series of aliphatic compounds on the number of carbon atoms in the molecule (Fig. 2) ([6]): the molecules of the initial members of these series are oriented parallel to the surface, and therefore S increases with increasing length, which entails a decrease of $-d\sigma/dT$, determined by the ratio i/n. With further elongation of the chain, the cohesion of the hydrocarbon "tails" makes the vertical orientation energetically more and more favorable, and the decrease of $-d\sigma/dT$ becomes less sharp, since the effect of the increase in molecular length is compensated by a change in their angle of inclination. Finally, for the higher homologues, the orientation of the molecules at the greatest angle to the surface is realized, and $-d\sigma/dT$ asymptotically tends to the lower limit 0.07 erg/cm$^2\cdot$deg, common to many homologous series of aliphatic compounds.

Fig. 2. Graphs of the dependence of $-d\sigma/dT$ on the number of carbon atoms in homologous series: **1** $-n$-hydrocarbons; **2** $-n$-nitriles; **3** $-n$-fatty acids; **4** $-n$-amines.

The conclusion suggests itself that the molecules of the higher members of these series are oriented in the surface layer identically and, consequently, occupy the same area S_m.

Assuming that under conditions of complete orientation of the molecules association may be disregarded ($n = 1$), and also accepting that in the case of very long molecules of the higher homologues the layer is monomolecular ($i = 1$), we find from (10) the limiting value of the area S_m for $-d\sigma/dT = 0.07$. This gives

$$S_m = 19.71\ \text{Å}^2$$

in good agreement with the area per molecule in an insoluble condensed monomolecular film on the surface of water with dense packing of the chains or with rearrangement of densely packed head groups ([3]):

$$S'_m = 20.5\ \text{Å}^2.$$

This area is determined with an accuracy up to 1 $Å^2$, and thus the agreement should be regarded as very good, which confirms the similarity between the structure of insoluble condensed films on water and the structure of the surface layer of the pure liquids forming these films.

Table 1

Substance	a, $\frac{\text{erg}}{\text{cm}^2 \cdot \text{deg}}$	b, $\frac{\text{erg}}{\text{cm}^2 \cdot \text{deg}}$	$\frac{i}{n}$	l, Å	l_0, Å	Substance	a, $\frac{\text{erg}}{\text{cm}^2 \cdot \text{deg}}$	b, $\frac{\text{erg}}{\text{cm}^2 \cdot \text{deg}}$	$\frac{i}{n}$	l, Å	l_0, Å
Li	0,14	0,175	0,80	3,14	2,80	In	0,10	0,153	0,65	3,71	3,00
Na	0,10	0,116	0,86	3,71	3,45	Pb	0,12	0,136	0,88	3,39	3,19
K	0,06	0,075	0,79	4,80	4,28	Bi	0,13	0,130	1,00	3,26	3,26
Cu	0,2	0,255	0,79	2,63	2,33	Sb	0,025	0,140	0,18	7,43	3,14
Ag	0,13	0,192	0,68	3,23	2,68	Sn	0,18	0,150	1,22	2,77	3,05
Au	0,10	0,164	0,61	3,71	2,90	Sn	0,065	0,150	0,44	4,61	3,05
Zn	0,22	0,220	1,00	2,50	2,50	He	0,10	0,103	0,97	3,71	3,65
Hg	0,17	0,163	1,04	2,85	2,91	H_2O	0,142	0,143	0,99	3,02	3,11
Al	0,14	0,195	0,72	3,14	2,66	CH_3OH	0,085	0,087	0,98	4,03	3,98

In the case of symmetric molecules in equation (5) one may set $\gamma = 1$, $\varphi = 1$, and then

$$-\frac{d\sigma}{dT} = \frac{ik}{n} \left(\frac{N\rho}{M} \right)^{2/3}, \tag{11}$$

where ρ is the density of the liquid in the bulk; M is its stoichiometric molecular weight.

With the aid of (11) one can calculate the coefficient i/n, since all the other quantities are known. From the physical meaning of the quantity i it follows that $i \geqslant 1$. If the molecules do not dissociate, then for n there is also the restriction $n \geqslant 1$. Hence it follows that when $i/n > 1$ necessarily $i > 1$, while when $i/n < 1$ it necessarily follows that $n > 1$. Thus, the deviation of the quantity i/n from unity may serve as a criterion of the polymolecular character of the surface layer or of association in it.

Table 2

Substance	a, $\frac{\text{erg}}{\text{cm}^2 \cdot \text{deg}}$	b, $\frac{\text{erg}}{\text{cm}^2 \cdot \text{deg}}$	$\frac{i}{n}$
Ne	0,30	0,154	1,95
Ar	0,17	0,104	1,63
Mg	0,29	0,159	1,83
Fe	0,5	0,252	1,99
Ni	0,5	0,260	1,93

Substance	$a, \dfrac{\text{erg}}{\text{cm}^2 \cdot \text{deg}}$	$b, \dfrac{\text{erg}}{\text{cm}^2 \cdot \text{deg}}$	$\dfrac{i}{n}$
CCl_4	0,115	0,047	2,46
$CHCl_3$	0,113	0,053	2,45
CS_2	0,160	0,064	2,50

For molten metals, whose atoms are characterized by high symmetry, and also for certain other liquids consisting of not very asymmetric molecules, the values of i/n were calculated from (11).

Tables 1 and 2 give the quantities $a = -d\sigma/dT$, $b = (N\rho/M)^{2/3}k$, and also i/n, calculated as a/b.

In addition, Table 1 compares the linear dimensions of molecules obtained with the aid of (10)

$$l = S^{1/2} = \left(-\frac{k}{d\sigma/dT}\right)^{1/2} \tag{12}$$

with those calculated from the bulk density of the liquid

$$l_0 = (M/N\rho)^{1/3}. \tag{13}$$

As can be seen from the table, the linear dimensions of the molecules, found by two such different methods, are in satisfactory agreement with one another for most of the substances considered. The quantity i/n for most metals is close to unity.

Let us write (5) in the form

$$\frac{d\sigma}{dT} = -(\varphi\gamma)^{2/3}\frac{i}{n}\frac{k}{S_0}, \tag{14}$$

where $S_0 = (V/N)^{2/3}$ is the effective area occupied by a molecule at the surface –

of the liquid surface, averaged over all possible orientations. From (14) and (9),

$$(\varphi\gamma)^{2/3} = S_0/S, \tag{15}$$

where S is the real area per molecule. When the molecules are oriented in the form of a palisade, then $S_0 > S$ and, consequently, $(\varphi\gamma)^{2/3} > 1$, which by (5), for $i = 1$ and $n = 1$, gives

$$-\frac{1}{k}\left(\frac{M}{N\rho}\right)^{2/3}\frac{d\sigma}{dT} > 1. \tag{16a}$$

When the molecules lie flat in the surface layer, then $S_0 < S$,

$$(\varphi\gamma)^{2/3} < 1, \qquad -\frac{1}{k}\left(\frac{M}{N\rho}\right)^{2/3}\frac{d\sigma}{dT} < 1. \tag{16b}$$

In the case of molecular symmetry (or symmetric orientation), $S_0 = S$,

$$(\varphi\gamma)^{2/3} = 1, \qquad -\frac{1}{k}\left(\frac{M}{N\rho}\right)^{2/3}\frac{d\sigma}{dT} = 1. \tag{16c}$$

The quantities entering into these relations are known; therefore the proposed orientation criterion can easily be checked if the condition $i/n = 1$ is fulfilled.

Table 3

Substance	Temperature interval, °C	K_E, erg/mol · deg	c, erg/mol · deg	d, erg/mol · deg	$\frac{c}{K_E}\cdot 100, \%$
Diethyl ether	130–140	1.27	0.01	1.28	0.7
Ethyl formate	130–140	1.74	0.02	1.76	1.1
Ethyl acetate	130–140	1.48	0.02	1.50	1.4
Benzene	130–140	1.51	0.02	1.53	1.3
Chlorobenzene	150–160	1.42	0.02	1.44	1.4
Acetic acid	130–140	1.11	0.03	1.14	2.7
Methyl alcohol	130–140	1.34	0.02	1.36	1.5
Ethyl alcohol	130–140	1.36	0.02	1.38	1.5

Let us write (5) in the form

$$\frac{d(\sigma V^{2/3})}{dT} - \sigma\frac{dV^{2/3}}{dT} = -(\varphi\gamma N)^{2/3}\frac{i}{n}k. \tag{17}$$

In Table 3, which illustrates this relation of quantities, the values $K_E = -d(\sigma V^{2/3})/dT$, $c = \sigma dV^{2/3}/dT$, $d = V^{2/3}d\sigma/dT$, and $(c/K_E)\cdot 100$ are given for substances of different classes.

Neglecting the small second term on the left-hand side of equation (17), which amounts to 1–5% of the first, we have

$$K_E = \frac{d(\sigma V^{2/3})}{dT} \simeq -(\varphi\gamma N)^{2/3}\frac{i}{n}k.$$

Thus, the Eötvös coefficient is

$$K_E = 0.984(\varphi\gamma)^{2/3}\frac{i}{n}. \tag{18}$$

Hence, in particular, it is seen that K_E is inversely proportional to the first power of n, rather than to the power 2/3 according to Eötvös (7). This makes it possible to give a qualitative explanation for those deviations of K_E (8) from the normal value that are observed in many liquids.

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Note: Figure translations are in progress. See original paper for figures.