INTERMOLECULAR ENERGY AND SURFACE TENSION IN PURE NON AUTOASSOCIATED LIQUIDS

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RESUMEN

Se deduce una ecuación para calcular la energía libre en la superficie de un líquido, como una función de las densidades ortobáricas. Se considera la contribución molecular al área de la superficie de moléculas globulares, moléculas planas y parafinas normales y se calcula la tensión superficial para las especies anteriores.

Los valores calculados de la tensión superficial presentan excelente concordancia con los valores experimentales.

ABSTRACT

An equation is deduced to calculate the molecular free energy at the liquid surface, as a function of the orthobaric densities. The molecular contribution to the surface area of globular molecules, plane molecules and normal paraffins is considered and the surface tension is calculated; these values present an excellent agreement with the experimental ones.

INTRODUCTION

The model. At any temperature, for the liquid-vapor equilibrium, it is possible to consider the existence of M_S molecular sites at the interphase, visited by N_S molecules that come from the liquid and $(N_S)_V$ molecules that come from the vapor phase. The total number of molecules in the liquid phase is $N_L = N_i + N_S$ where N_i is the number of inner molecules. There is a dynamic equilibrium among N_S and N_i; all the molecules have access to all the liquid phase and the molecular partition functions (1) can be expressed by

$$f_i = (qeV_L / N_i)(f_{rve})_i e^{-C_i \varepsilon_p / KT}; \qquad (1)$$
$$f_S = (qeV_L / N_S)(f_{rve})_S e^{-C_S \varepsilon_p / KT}$$

where $q = \frac{(2\pi mKT)^{3/2}}{h^3}$, V_L the volume of the liquid, f_{rve} denotes the product of the rotational, vibrational and electronic partition functions, C is the average number of nearest neighbors around any central molecule (coordination number), ε_p is the pair molecular potential energy, K the Boltzmann constant, h the Planck constant and T the absolute temperature, (subscrits i for the interior and S for the surface). The partition function for the liquid ensemble can be formulated as

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$$F = f_i^{N_i} f_s^{N_s}$$

with $v = V_L / N_L$ the mean molecular volume,

$$F = \left(qev \tfrac{N_L}{N_i} [f_{rve}]_i e^{-C_i \varepsilon_p / KT} \right)^{N_i} * \left(qev \tfrac{N_L}{N_S} [f_{rve}]_S e^{-C_S \varepsilon_p / KT} \right)^{N_S} \qquad (2)$$

As the rotational, vibrational and electronic partition functions are equal at the interior and at the surface, the Helmholtz free energy A = – $KT \ln F$, is then

$$A = -KT \ln\left[\left[\tfrac{N_L}{N_i} \right]^{N_i} \left[\tfrac{N_L}{N_S} \right]^{N_S} \right] - N_L KT \ln[qevf_{rve}]_L + N_i C_i \varepsilon_p + N_S C_S \varepsilon_p \qquad (3)$$

By the thermodynamic equation for entropy

$$S = -\left[\frac{dA}{dT} \right]_v$$

and noting that if V_L is kept constant (as isolating the phases by a wall), this implicates that N_L is constant and N_i and N_S too, the effect is to have a faster or slower equilibrium among the N_i and the N_S positions due to the variation in the translational energy. We have then

$$S = K \ln\left[\left[\frac{N_L}{N_i} \right]^{N_i} \left[\frac{N_L}{N_S} \right]^{N_S} \right] + N_L K \frac{d}{dT}\left[T \ln\left[qev\left[f_{rve} \right] \right] \right] - \frac{d}{dT}\left[N_i C_i \varepsilon_p + N_S C_S \varepsilon_p \right] \qquad (4)$$

The second term in this equation is the contribution of the translational, vibrational and electronic entropies. The third term takes into account that the system always deviates more or less from the average state and a certain reversible work is done in returning to its equilibrium state; there is a relative frequency of volume fluctuations in a given small element of volume, therefore in intermolecular distances and in potential energy consequently (see also eq. (15)). The first term is the contribution to the entropy due to an higher disorder caused by the presence of two main groups N_S and N_i of molecules with energies quite distinguishable. This term can be properly taken as the entropic part (ΔS_S) of the work for the reversible process of transference of molecules from the interior to the surface and vice-versa.

$$\Delta S_S = K \ln\left[\left[\frac{N_L}{N_i} \right]^{N_i} \left[\frac{N_L}{N_S} \right]^{N_S} \right] \qquad (5a)$$

$$\Delta S_S = -N_L K \left[\left[\frac{N_i}{N_L} \right] \ln\left[\frac{N_i}{N_L} \right] + \left[\frac{N_S}{N_L} \right] \ln\left[\frac{N_S}{N_L} \right] \right] \qquad (5b)$$

As a function of the relation N_S/N_i, eq. (5b) can be written in the form:

$$\frac{\Delta S_S}{N_L} = -K \left[\frac{\frac{N_S}{N_i} \ln\left(\frac{N_S}{N_i} \right)}{1 + \frac{N_S}{N_i}} - \ln\left(1 + \frac{N_S}{N_i} \right) \right] \qquad (6)$$

The energy of one molecule at the surface is

$$\varepsilon_S = C_S \varepsilon_p + \left[\varepsilon_K \right]_S + \left[\varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{el} \right]_S$$

and the energy of one molecule inside the liquid is

$$\varepsilon_i = C_i \varepsilon_p + \left[\varepsilon_K \right]_i + \left[\varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{el} \right]_i$$

where ε_k is the kinetic energy (the subscrits are self explanatory). As the inner and surface rotational, vibrational and electronic energies are equal,

$$\Delta\varepsilon = \varepsilon_S - \varepsilon_i = \left[C_s - C_i\right]\varepsilon_p + \left[\varepsilon_K\right]_S - \left[\varepsilon_K\right]_i \qquad (7)$$

The coordination number at the surface can be defined as one half the interior coordinaion number, $C_S = 1/2C_i$; one interior molecule has three square components of velocity, while on the surface there are two square components of velocity and according to the energy equipartition theorem

$$\left[\varepsilon_K\right]_i - \left[\varepsilon_K\right]_s = \frac{1}{2}KT$$

and

$$\Delta\varepsilon = \varepsilon_S - \varepsilon_i = -\frac{1}{2}C_i\varepsilon_p - \frac{1}{2}KT \qquad (8)$$

The molecules are in thermodynamic equilibrium, so it is possible to use the Boltzmann exponential law to estimate the ratio N_S/N_i:

$$\frac{N_S}{N_i} = \frac{e^{-\varepsilon_s/KT}}{e^{-\varepsilon_i/KT}} = e^{-\Delta\varepsilon/KT} \qquad (9)$$

and eq. (6) becomes

$$\frac{\Delta S_S}{N_L} = K\left[\frac{\Delta\varepsilon / KT}{1 + e^{\Delta\varepsilon/KT}} + \ln\left[1 + e^{-\Delta\varepsilon/KT}\right]\right] \qquad (10)$$

The reversible work ($-W_m$, maximum) for the transference of one interior molecule (just under the surface) to the surface equals the free energy change (Δa) for the process.

$$-W_m = \Delta a = \Delta\varepsilon - T\frac{\Delta S_S}{N_L} \qquad (11)$$

On the other hand

$$\Delta a = \gamma_S a_S \qquad (12)$$

Where γ_S is the surface tension and a_S is the contribution of one molecule to the surface area. By means of eqs. (12), (11) and (10)

$$\gamma_S a_S = KT\left[\frac{\Delta\varepsilon / KT}{1 + e^{-\Delta\varepsilon/KT}} - \ln\left[1 + e^{-\Delta\varepsilon/KT}\right]\right] \qquad (13)$$

and with eq. (8)

$$\gamma_S a_S = KT\left[\frac{-\dfrac{C_i\varepsilon_p}{2KT} - \dfrac{1}{2}}{1 + e^{\frac{C_i\varepsilon_p}{2KT}}e^{\frac{1}{2}}} - \ln\left[1 + e^{\frac{C_i\varepsilon_p}{2KT}}e^{\frac{1}{2}}\right]\right] \qquad (14)$$

It has been shown (1) that for those zones of the liquid-vapor equilibrium where the vapor behaves ideally

$$C_i\varepsilon_p = KT\ln\left[\frac{d_V}{d_L}\right] \qquad (15)$$

where d_V and d_L are the orthobaric densities of vapor and liquid respectively ; if this is the case

$$\gamma_S a_S = KT\left[\frac{-\ln\left(\dfrac{d_V}{d_L}\right)^{1/2} - \dfrac{1}{2}}{1 + \left(\dfrac{d_V}{d_L}\right)^{1/2} e^{1/2}} - \ln\left[1 + \left(\dfrac{d_V}{d_L}\right)^{1/2} e^{1/2}\right]\right] \qquad (16)$$

MOLECULAR CONTRIBUTION TO THE SURFACE AREA AND THE SURFACE TENSION

Globular molecules

It can be shown (2), that if a liquid is formed by N_L spheres of radius r and it is uniformly dispersed as an unimolecular film, the variation of the total area (O) with respect to the total number of molecules is

$$\frac{dO}{dN_L} = \frac{2V_L}{r}$$

where V_L is the volume of the sphere. It is interpretated here that one half dO/dN_L is the contribution per molecule to the surface area when there are many molecules under the surface layer:

$$a_s = \frac{1}{2}\frac{dO}{dN_L} = \frac{V_L}{r} = \frac{1}{3}\left(4\pi r^2\right) \qquad (17)$$

In other words, the contribution of one molecule to the surface area is *1/3* the molecular area. As $r = r_e/2$, the middle point between molecular centers

$$a_s = \frac{1}{3}\left[4\pi\left(\frac{r_e}{2}\right)^2\right] = \frac{\pi}{3}r_e^2 \qquad (18)$$

(note: for this geometry, $\frac{\varphi_L}{N} = \frac{4}{3}\pi\left(\frac{r_e}{2}\right)^3$; $r_e = \left(\frac{6\varphi_L}{\pi N}\right)^{1/3}$; where φ_L is the molar volume).

Results obtained with globular molecules

In Tables 1, 2 and 3, for CCl_4, cyclohexane and cyclopentane, the density of the liquid and vapor (ideal), average intermolecular distance (r_e), surface molecular free energy (eq. (16)) and area (a_s eq. (18)), the surface tension calculated and experimental, are presented (vapor pressures from Antoine´s equation (4); for CCl_4 $\ln p = A_o - B_o/T - C_o/T^2$; $A_o = 15.384676$, $B_o = 2406.2521$, $C_o = 229284.52$.

n-Alkanes

In this work it has been possible to establish empirically, that the molecular contribution to the area of the surface can be expressed by

$$a_g = \frac{n_g + 4}{3}\frac{1}{3}\left[4\pi\left(\frac{r_{gg}}{2}\right)^2\right] = \frac{n_g + 4}{3}\frac{\pi}{3}r_{gg}^2 \qquad (19)$$

where n_g is the number of groups (equal to the number of carbon atoms) and r_{gg} is the distance between groups of neighbor molecules. Equation (19) means that 1/3 of the group area (as in eq. (18)) multiplied by the quantity $(n_g + 4)/3$ that is interpretated as the average number of groups that a molecule exhibits on the surface, makes the contribution to the area.

Results obtained with n-Alkanes

Equations (16) and (19) give good results in the zone of the liquid-vapor equilibrium where the vapor behaves ideally. To illustrate the results obtained only two temperatures in Table 4 have been selected for each n-alkane (the method to calculate r_{gg} is given in ref. (1)).

Plane molecules

The following liquids have been considered : benzene, toluene, xylenes and trimethyl benzenes. The average volume for these molecules can be well represented by an oblate spheroid.

$$\bar{v} = \frac{3}{4}\pi a^2 b \qquad (20)$$

where a is the major semi-axis and b the minor semi-axis of the generatrix ellipse of excentricity ε, $b/a = \sqrt{1-\varepsilon^2}$, and $\varepsilon = 0.56184$ (1). By elementary calculus it is shown that the surface area of the oblate spheroid is

$$A_o = 4\pi a^2 g(\varepsilon) \qquad (21)$$

where the function

Table 1. Carbon tetrachloride. Parameters to calculate the surface tension.

t °C	d_L g/cm^3	r_e 10^8 cm	d_V 10^4 g/cm^3	$\gamma_S a_S$ 10^{13} erg	A_S $10^{15} cm^2$	γ_S $dyne/cm$	γ_S obs (3)
10	1.6132	6.71141	4.8867	1.33813	4.71689	28.37	28.05
20	1.5939	6.73839	7.6403	1.28288	4.75489	26.98	26.70
30	1.5748	6.76552	11.5161	1.22773	4.79326	25.61	25.54
40	1.5557	6.79310	16.8026	1.17260	4.83241	24.27	24.41

Table 2. Cyclohexane. Parameters to calculate the surface tension.

t °C	d_L g/cm^3 (3)	r_e 10^8 cm	d_V 10^4 g/cm^3	$\gamma_S a_S$ 10^{13} erg	a_S $10^{15} cm^2$	γ_S $dyne/cm$	γ_S obs (3)	γ_S obs (4)
20	0.77842	6.99852	3.5694	1.29285	5.12910	25.21	25.20	24.98
30	0.76928	7.02613	5.4203	1.23649	5.16964	23.92	23.82	23.78
40	0.75975	7.05538	7.9616	1.18005	5.21278	22.64	-	22.62
50	0.74605	7.09831	11.3537	1.12218	5.27641	21.27	-	21.5

Table 3. Cyclopentane. Parameters to calculate the surface tension.

t °C	d_L g/cm^3 (4)	r_e 10^8 cm	d_V 10^4 g/cm^3	$\gamma_S a_S$ 10^{13} erg	a_S $10^{15} cm^2$	γ_S $dyne/cm$	γ_S obs (4)
10	0.7552	6.65268	6.7316	1.10299	4.63470	23.80	23.64
20	0.7454	6.68170	9.9618	1.04831	4.67523	22.42	22.42
30	0.7356	6.71125	14.2852	0.99352	4.71666	21.06	21.23
40	0.7258	6.74132	19.9200	0.93864	4.75903	19.72	20.05

Table 4. n-Alkanes. Parameters to calculate the surface tension.

Substance	*t* °C	d_L g/cm³ (4)	r_{gg} 10^8 cm	d_V 10^4 g/cm³	$\gamma_S a_S$ 10^{13} erg	a_S 10^{15}cm²	γ_S dyne/cm	γ_S obs (4)
C_5	-10	0.6546	4.14774	5.0084	1.05647	5.40471	19.55	19.35
	10	0.6357	4.20594	11.5940	0.94226	5.65747	16.95	17.15
C_6	20	0.6594	4.23343	5.7140	1.14847	6.2592	18.36	18.40
	40	0.6411	4.29170	12.2302	1.03078	6.42935	16.03	16.35
C_7	20	0.6838	4.23667	1.9421	1.39966	6.89206	20.31	20.30
	50	0.6583	4.31724	7.0412	1.21252	7.15671	16.94	17.20
C_8	20	0.7025	4.24224	0.6535	1.64317	7.53840	22.69	22.73
	50	0.6784	4.31759	2.8540	1.44646	7.80857	18.52	18.66
C_9	20	0.7176	4.24770	0.2158	1.88355	8.18762	23.00	22.92
	50	0.6944	4.31972	1.1492	1.67373	8.46764	19.77	20.25
C_{10}	30	0.7224	4.27614	0.1388	2.04510	8.93592	22.89	22.91
	60	0.6996	4.34765	0.7760	1.82424	9.23730	19.75	20.15
C_{11}	30	0.7328	4.28098	0.04804	2.27654	9.59589	23.72	23.76
	60	0.7106	4.35036	0.32588	2.03913	9.90945	20.58	21.05
C_{12}	30	0.7416	4.28559	0.01600	2.51330	10.2577	24.50	24.47
	60	0.7198	4.35356	0.13439	2.25433	10.5856	21.30	21.81
C_{13}	30	0.7492	4.28976	0.005297	2.74948	10.9200	25.18	25.11
	60	0.7277	4.35667	0.05519	2.46753	11.2633	21.91	22.50

$$g(\varepsilon) = \frac{\sqrt{1-\varepsilon^2}}{\varepsilon} arctg \frac{\varepsilon}{\sqrt{1-\varepsilon^2}} \tag{22}$$

It is assumed that the contribution of one molecule to the surface area of the liquid is proportional (β) to $A_o/3$

$$a_S = \beta \frac{A_o}{3}$$

and empirically it has been found in this work that $\beta = (1 + 1/25)^{(1+n_m)}$ where n_m is the number of methyl groups in the molecule, and

$$a_S = \frac{4}{3}\pi a^2 g(\varepsilon)[1 + 1/25]^{(1+n_m)} \tag{23}$$

Results obtained with plane molecules

In Table 5, for these substances, two temperatures have been selected to ilustrate the results (vapor pressures to calcu-

Table 5. Plane molecules. Parameters to calculate the surface tension.

Substance	*t* °C	d_L g/cm³ (4)	*a* 10^8 cm	d_V 10^4 g/cm³	$\gamma_S a_S$ 10^{13} erg	a_S 10^{15}cm²	γ_S dyne/cm	γ_S Obs (4)
benzene	10	0.8895	3.47796	2.0140	1.40023	4.62894	30.25	30.24
	50	0.8469	3.53532	10.5115	1.17447	4.78290	24.56	24.88
toluene	20	0.8669	3.70645	1.1005	1.57601	5.46742	28.83	28.53
	60	0.8300	3.76058	6.1621	1.34530	5.62829	23.90	23.94
o-xylene	10	0.8868	3.85643	0.1532	1.93170	6.15562	31.38	31.16
	50	0.8549	3.90382	1.3427	1.68630	6.30781	26.73	26.76
m-xylene	10	0.8726	3.87724	0.1960	1.87858	6.22222	30.19	29.78
	50	0.8384	3.92926	1.6402	1.63340	6.39030	25.56	25.36
p-xylene	30	0.8525	3.90748	0.6531	1.74234	6.31964	27.57	27.22
	70	0.8173	3.96279	3.9066	1.50243	6.49982	23.11	23.0
1,3,5,Me$_3$	20	0.8652	4.05247	0.1135	2.05730	7.06924	29.10	28.83
benzene	70	0.8237	4.11942	1.6201	1.73311	7.30474	23.73	23.8
1,2,3-Me$_3$	20	0.8944	4.00788	0.06906	2.16755	6.91453	31.35	31.27
benzene	40	0.8786	4.03176	0.2392	2.03443	6.99718	29.07	29.20
1,2,4-Me$_3$	20	0.8758	4.03605	0.09515	2.09665	7.01209	29.90	29.71
benzene	60	0.8434	4.08709	0.8872	1.83724	7.19054	25.55	25.60

late the ideal vapor density by Antoine´s equation (4)).

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