

RELATION BETWEEN SURFACE TENSION AND PARAMETERS OF THE LENNARD-JONES EQUATION FOR INTERMOLECULAR POTENTIAL*

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A relation has been derived between surface tension of pure substances and the parameters of the Lennard-Jones equation for intermolecular potential. The substitution for these parameters from empirical relations makes it possible to calculate the surface tension from critical temperature and critical volume of the substance considered. The derived relation has been verified by comparing the calculated values of surface tensions with the values measured for 22 pure substances.

In our previous papers¹⁻³, the expression for calculating the surface tension of pure substance γ was derived from the thermodynamic condition for equilibrium in a system in which a force field acts:

$$\gamma = \int_0^{\infty} \Phi \frac{\rho_s}{M} ds, \quad (1)$$

where Φ is the adsorption potential defined as the work necessary for transferring one mol of molecules considered from the bulk phase to a certain place in the surface layer, ρ_s is the density in the surface layer, M molecular mass and s is the distance from the phase boundary. The value of adsorption potential Φ is a function of the distance from the phase boundary. To be able to derive this function it is necessary to use some of the relations for the dependence of intermolecular potential φ on the distance of centres of two interacting molecules. In one of our foregoing works¹, the intermolecular potential was expressed by the equation $\varphi(r) = -A/r^6$ and on making use of some simplifying assumptions, the relation between surface tension of pure substances, their saturated vapour pressure and density was derived.

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THEORETICAL

The intermolecular potential between two identical particles will be expressed here by the equation⁴

$$\varphi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (2)$$

On the assumption that intermolecular forces are central and additive we get, for the intermolecular energy of one particle inside a system, the relation

$$\begin{aligned} E_\infty &= \int_d^\infty \varphi(r) N 4\pi r^2 dr = \\ &= -\frac{16}{3}\pi N\varepsilon\sigma^6(1/d^3) + \frac{16}{9}\pi N\varepsilon\sigma^{12}(1/d^9), \end{aligned} \quad (3)$$

where N is the number of particles in unit volume, ε and σ are the parameters of the Lennard-Jones equation (2), r is the distance of centres of interacting molecules and d is the distance of centres of two adjacent molecules.

Now we will consider a molecule which is close to the surface and which therefore is not surrounded by the other particles uniformly in all directions. The distance of the centre of molecule from the phase boundary will be denoted by s . The intermolecular energy of such a particle is then given by the relation:

$$\begin{aligned} E_s &= \int_d^\infty \varphi(r) N(2\pi r^2 + 2\pi rs) dr = -\frac{8}{3}\pi N\varepsilon\sigma^6(1/d^3) - \\ &- \frac{1}{2}\pi N\varepsilon\sigma^6(s/d^4) + \frac{8}{9}\pi N\varepsilon\sigma^{12}(1/d^9) + \frac{4}{3}\pi N\varepsilon\sigma^{12}(s/d^{10}) \end{aligned} \quad (4)$$

for the case that the centre of the molecule considered is nearer to the phase boundary than its diameter d ($s < d$) and by the relation

$$\begin{aligned} E_s &= \int_d^s \varphi(r) N 4\pi r^2 dr + \int_s^\infty \varphi(r) N(2\pi r^2 + 2\pi rs) dr = \\ &= -\frac{16}{3}\pi N\varepsilon\sigma^6(1/d^3) + \frac{4}{3}\pi N\varepsilon\sigma^6(1/s^3) + \\ &+ \frac{16}{9}\pi N\varepsilon\sigma^{12}(1/d^9) - \frac{4}{45}\pi N\varepsilon\sigma^{12}(1/d^9) \end{aligned} \quad (5)$$

for the molecules whose centre is at a larger distance from the surface than their diameter ($s > d$).

The adsorption potential Φ can be then calculated from the equation

$$\begin{aligned} \Phi &= \frac{4}{3}\pi N_A N\varepsilon\sigma^6(1/d^3) - \pi N_A N\varepsilon\sigma^6(s/d^4) - \\ &- \frac{4}{9}\pi N_A N\varepsilon\sigma^{12}(1/d^9) + \frac{4}{45}\pi N_A N\varepsilon\sigma^{12}(s/d^{10}) \quad \text{for } s < d \end{aligned} \quad (6)$$

and

$$\Phi = \frac{2}{6}\pi N_A N \varepsilon \sigma^6 (1/d^3) - \frac{2}{45}\pi N_A N \varepsilon \sigma^{12} (1/s^9) \quad \text{for } s > d, \quad (7)$$

where N_A is the Avogadro number.

If we substitute these relations for Φ into Eq. (1) and for ϱ_s we insert $\varrho_s = \varrho_\infty (E_s/E_\infty)$ where ϱ_∞ is the density in the bulk liquid phase¹ we will get the relation for the surface tension:

$$\begin{aligned} \gamma = 2\pi N_A^2 \left(\frac{\varrho_\infty}{M}\right)^2 \varepsilon \left[\int_0^d \left(\frac{2}{3} \frac{\sigma^6}{d^3} - \frac{1}{2} \frac{\sigma^6 s}{d^4} - \frac{2}{9} \frac{\sigma^{12}}{d^9} + \frac{1}{5} \frac{\sigma^{12} s}{d^{10}} \right) \cdot \right. \\ \left. \left(-\frac{2}{3} \frac{\sigma^6}{d^3} - \frac{1}{2} \frac{\sigma^6 s}{d^4} + \frac{2}{9} \frac{\sigma^{12}}{d^9} + \frac{1}{5} \frac{\sigma^{12} s}{d^{10}} \right)^2 \cdot \left(-\frac{4}{3} \frac{\sigma^6}{d^3} + \frac{4}{9} \frac{\sigma^{12}}{d^9} \right)^{-2} ds + \right. \\ \left. + \int_d^\infty \left(\frac{1}{6} \frac{\sigma^6}{s^3} - \frac{1}{45} \frac{\sigma^{12}}{s^9} \right) \left(-\frac{4}{3} \frac{\sigma^6}{d^3} + \frac{1}{6} \frac{\sigma^6}{s^3} + \frac{4}{9} \frac{\sigma^{12}}{d^9} - \frac{1}{45} \frac{\sigma^{12}}{s^9} \right) \cdot \right. \\ \left. \cdot \left(-\frac{4}{3} \frac{\sigma^6}{d^3} + \frac{4}{9} \frac{\sigma^{12}}{d^9} \right)^{-1} \right] ds. \quad (8) \end{aligned}$$

If the distance d to which the centres of two adjacent molecules can come up is put equal to σ we will get, by solving Eq. (8) for the calculation of the surface tension, the relation

$$\begin{aligned} \gamma = 0.40225 \cdot 10^4 \pi N_A^2 (\varrho_\infty/M)^2 \varepsilon \sigma^4 = \\ = 0.6325 \cdot 10^4 (\varrho_\infty/M)^2 (\varepsilon/k) \sigma^4, \quad (9) \end{aligned}$$

where k is the Boltzman constant, density ϱ_∞ is in units of g cm^{-3} , ε/k in K and σ in nm.

The values read from tables can be substituted for the parameters of the Lennard-Jones equation ε and σ or they can be calculated from critical quantities according to the empirical relations⁶

$$\varepsilon/k = 0.76 T_k, \quad \sigma = 0.0841 V_k^{1/3}, \quad (10)$$

where T_k is inserted in K and V_k in $\text{cm}^3 \text{mol}^{-1}$. By inserting these relations into Eq. (9) we get the relation which enables us to calculate the surface tension of pure substance from its density and critical quantities:

$$\gamma = 0.24047 (\varrho_\infty/M)^2 T_k V_k^{4/3}. \quad (11)$$

This relation has been verified by calculating surface tensions of 22 organic non-polar or weakly polar substances. These values are compared with experimental ones in Table I.

DISCUSSION

As we can find out from the table the mean error of surface tension calculated according to Eq. (11) is $\pm 6.08\%$. The maximum found error is for toluene, the lowest errors are for benzene, 2-methylhexane and methylcyclopentane.

TABLE I

Comparison of Experimental Surface Tensions γ_{exp} with Values Calculated from Eq. (10)^a

Substance	T_K	V_K	ϱ_{20°	γ_{exp}	γ_{calc}	Deviation %
n-Pentane	470.4	310.616	0.6238	16.00	17.60	+10.00
n-Hexane	508.0	316.141	0.6993	18.41	18.81	+ 2.17
n-Heptane	540.2	421.134	0.6836	19.65	19.06	- 2.98
Isopentane	461.0	308.024	0.6196	14.99	16.28	+ 8.58
3-Methylpentane	504.4	366.809	0.6642	18.12	18.91	+ 4.35
2-Methylhexane	531.1	432.30	0.6788	19.17	19.14	- 0.11
2,3,3-Trimethylbutane	531.5	395.54	0.6900	18.7	17.59	- 5.45
Benzene	561.7	256.636	0.8789	28.89	27.88	- 0.02
Toluene	593.9	319.801	0.8669	28.52	32.63	+14.40
<i>o</i> -Xylene	631.2	376.086	0.8800	30.1	27.27	- 9.45
<i>m</i> -Xylene	616.8	383.416	0.8641	28.63	26.35	- 7.97
<i>p</i> -Xylene	615.9	385.465	0.8610	28.36	26.31	- 7.24
Ethylbenzene	617.2	318.095	0.8671	29.20	26.49	- 9.28
Chlorobenzene	632.4	308.073	1.1062	32.65	30.53	- 6.49
Bromobenzene	670.2	323.513	1.4952	35.72	32.44	- 9.20
Tetrachloromethane	556.4	275.915	1.5940	26.76	25.80	- 3.60
Cyclopentane	511.8	259.815	0.5729	22.57	23.03	+ 2.04
Cyclohexane	553.9	309.713	0.5293	25.1	23.86	- 4.50
Methylcyclopentane	532.8	322.689	0.7486	22.18	21.90	- 1.27
Methylcyclohexane	553.9	372.168	0.7693	23.73	21.44	- 9.67
Diethyl ether	466.8	278.123	0.7135	17.06	18.88	+10.69
Ethyl acetate	523.2	286.318	0.9006	23.75	24.81	+ 4.46

^a Values of the quantities T_K , V_K , ϱ_{20° and γ_{exp} are taken over from the literature⁵.

The experimental values of surface tensions of 22 chosen pure substances would be best represented by the relation

$$\gamma = 0.24346(\rho_{\infty}/M)^2 T_k V_k^{4/3}. \quad (12)$$

The constant in this equation differs from the theoretically determined one only by 1.20%. This relatively very good agreement which, however, could be influenced by the choice of substances compared, despite the fact that this choice has been incidental, justifies us to assume that the model considerations used in deriving describe well the real behaviour of non-polar or slightly polar substances.

REFERENCES

1. Šišková M.: This Journal 35, 1641 (1970).
2. Šišková M., Erdős E.: This Journal 31, 2318 (1966).
3. Šišková M., Erdős E.: This Journal 31, 2327 (1966).
4. Hirschfelder J. O., Curtiss C. K. F., Bird R. B.: *Molecular Theory of Gases and Liquids*. Wiley, New York 1954.
5. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, Amsterdam 1950.

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