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Why are the values of the surface tension of most organic liquids similar?

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The values of the surface tension of most organic liquids are of the same order of magnitude. The explanation is that surface tension is governed by London dispersion forces, which are independent of the permanent dipole moment of the molecules. The surface tension of organic liquids (with the exception of polymers and polymer solutions) depends on the ionization potential and the diameter of the molecule only. These parameters vary slightly for organic liquids. © 2010 American Association of Physics Teachers.

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I. INTRODUCTION

Surface tension is one of the most fundamental properties of fluids.^{1–4} Surface tension governs many phenomena in plant biology and medicine. Capillary waves produced by a stone tossed into a lake, the cloud formation, the walking of water striders on the surface of water, and the formation of dew are examples that are at least partially governed by surface tension.^{2,3} The surface tension is related to the different energy of the surface molecules, which are missing about half their interactions (see Fig. 1). The similar values of the surface tensions of liquids that are very different physically and chemically are summarized in Table I.⁵ The values of the surface tension of most organic liquids are in the range of 20–65 mJ/m². This narrow range is in contrast to other mechanical properties of liquids, such as viscosity. For example, the surface tensions of alcohol and glycerol are of the same order of magnitude,⁵ in contrast to the viscosity of ethyl alcohol at ambient conditions, which is equal to 1.2×10^{-3} kg/m s, and the viscosity of glycerol, which is 1.5 kg/m s. A more striking example is honey, whose viscosity can be very high, but whose surface tension is 50–60 mJ/m².⁶ Why is the range of values of surface tension so narrow? I answer this question in the spirit of Weisskopf,⁷ who explained why materials are as dense and heavy as they are. The explanation will lead to an expression relating the surface tension to fundamental physical constants.

II. SURFACE TENSION AND INTERMOLECULAR FORCES

The energy states of molecules in the bulk and at the surface of a liquid are not the same due to the differences in the local environment of molecules. An important misinterpretation should be avoided: It is often supposed that there exists a force pulling a surface molecule into the liquid bulk. The resulting force on a molecule in the bulk and at the interface equals zero because both bulk and interface molecules are in mechanical equilibrium. This frequent misinterpretation was discussed and analyzed in Ref. 8. An increase in the liquid/vapor surface causes a rise in the number of interface molecules and consequent growth in the surface energy. Liquids tend to decrease the number of interface molecules to decrease the surface energy.

We can measure the surface tension by performing work to bring molecules from the interior to the surface. Surface tension can be defined in two equivalent ways: As the work necessary to increase the surface area or as a force along a

line of unit length, where the force is parallel to the surface but perpendicular to the line. Let the potential describing the pair intermolecular interaction in the liquid be $U(r)$. The surface tension γ can be determined as

$$\gamma = f_m \frac{1}{d_m} \cong \frac{N|U(d_m)|}{2} \frac{1}{d_m} = \frac{N|U(d_m)|}{2d_m^2}, \quad (1)$$

where f_m is the force necessary to bring a molecule to the surface, which can be roughly estimated as $f_m \cong (N/2)|U(d_m)|/d_m$, where d_m is the diameter of a molecule, N is the number of nearest neighbor molecules (the multiplier $\frac{1}{2}$ is due to the absence of molecules in the vapor phase), and $1/d_m$ is the number of molecules per unit length of the liquid surface.

There are three main kinds of intermolecular interactions $U(r)$. The attractive interaction between identical dipolar molecules is given by the Keesom formula,

$$U_K(r) = -\frac{p^4}{3(4\pi\epsilon_0)^2 kT} \frac{1}{r^6}, \quad (2)$$

where p is the dipole moment of the molecule, k is Boltzmann's constant, T is the temperature, and r is the distance between molecules.³ The Debye interaction between dipolar molecules and induced dipolar molecules is

$$U_D(r) = -\frac{2p^2\alpha}{(4\pi\epsilon_0)^2} \frac{1}{r^6}, \quad (3)$$

where α is the polarizability of the molecule.³ The quantum mechanical London dispersion force results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles. Its potential is given by

$$U_L(r) = -\frac{3\alpha^2 I}{4(4\pi\epsilon_0)^2} \frac{1}{r^6}, \quad (4)$$

where I is the ionization potential of the molecule.³

The London dispersion force in Eq. (4) governs intermolecular interactions in organic liquids.³ It is several orders of magnitudes larger than the dipole-dipole Keesom and Debye forces in Eqs. (2) and (3).³ In Appendix A we compare the dipole-dipole and London interactions for the acetone molecule, which has a dipole moment of as high as 2.9 D, where the unit of a dipole moment is a Debye given by $1 \text{ D} = 3.3 \times 10^{-30} \text{ C m}$. The dominance of London interactions explains why polar and nonpolar liquids have similar values of the surface tension.

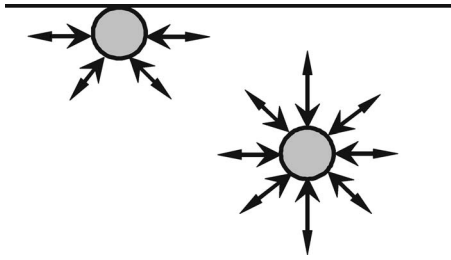


Fig. 1. A molecule at the surface misses about half its interactions.

CCl_4 is a nonpolar ($p=0$) liquid with a surface tension similar to that of strongly polar chloroform ($p=1.60$ D) and dichloromethane ($p=1.04$ D). Acetone is characterized by a large dipole moment and a small value of the surface tension ($p=2.9$ D, $\gamma=24$ mJ/m²). The data in Table I show that there is no correlation between surface tension and dipole moment. Thus, it can be inferred that the attraction between molecules is mostly given by Eq. (4), which is independent of the permanent dipole moment of a molecule. If we take into account that $\alpha \approx 4\pi\epsilon_0 r_m^3$ (where r_m is the radius of the molecule, see Appendix B) and substitute α into Eq. (4), we find

$$U_L(r) = -\frac{3}{4} I \frac{r_m^6}{r^6} = -\frac{3I}{2^8} \left(\frac{d_m}{r}\right)^6. \quad (5)$$

The corresponding Lennard-Jones potential is given by

$$U(r) = \frac{3I}{2^9} \left[\left(\frac{d_m}{r}\right)^{12} - 2\left(\frac{d_m}{r}\right)^6 \right]. \quad (6)$$

The minimum value of the potential in Eq. (6) equals

$$|U(d_m)| = \frac{3I}{2^9}. \quad (7)$$

We substitute Eq. (7) into Eq. (1) and obtain

$$\gamma \cong \frac{3N}{2^{10}} \frac{I}{d_m^2}. \quad (8)$$

Equation (8) shows why the surface tensions of organic liquids have similar values. We see that the surface tension of organic liquids depends only on the ionization potential I and the diameter of the molecule. These parameters vary slightly

Table I. Surface tension, enthalpy of vaporization, and dipole moment (in terms of D) of some organic molecules.

Liquid	Surface tension (mJ/m ²)	Enthalpy of vaporization (kJ/mol)	Dipole moment
Glycerol, C ₃ H ₈ O ₃	64.7	91.7	2.56
Formamide, CH ₃ ON	55.5	60.0	3.7
CCl_4	25.7	32.54	0
Chloroform, CHCl ₃	26.2	31.4	1.04
Dichloromethane, CH ₂ Cl ₂	31	28.6	1.60
Toluene, C ₇ H ₈	28.5	38.06	0.36
Ethyl alcohol, C ₂ H ₆ O	22	38.56	1.7
Acetone, C ₃ H ₆ O	24	31.3	2.9

for organic liquids. Moreover, Eq. (8) predicts that $\gamma \approx (\text{constant})/d_m^2$, which is the dependence found for n -alkanes.⁹

In the spirit of Ref. 7, natural dimensionless parameters can be introduced: $I = \beta R_y$ and $d_m = \lambda a_0$, where $a_0 = h^2/me^2$ is the Bohr radius, m and e are the mass and charge of the electron, and h is Planck's constant.⁷ The substitution of these parameters into Eq. (8) gives

$$\gamma \cong \frac{3N R_y \beta}{2^{10} a_0^2 \lambda^2}. \quad (9)$$

The potential of ionization for most organic liquids is close to 10 eV; thus, $\beta \approx 0.7$ and λ is in the range of $6 < \lambda < 12$.^{3,5,10} The substitution of $N=6$, $\beta=0.7$, and $\lambda=10$ into Eq. (9) leads to the realistic value for γ of 0.1 J/m².

The molar enthalpy of vaporization of liquids is also governed by the pair intermolecular interaction. Thus, it can be expected that it would vary slightly. The qualitative data in Table I support this suggestion. For the liquids that we have discussed, it varies in the range of 28.6–91.7 kJ/mol.

III. DISCUSSION

We have shown that surface tension is purely a quantum effect. London dispersion forces governing the surface tension originate in quantum mechanics. London dispersion forces are insensitive to the permanent dipole moment of the molecule and depend only on the ionization potential and diameter of the molecule. These parameters vary slightly for organic liquids (with the exception of polymers and polymer solutions, where the situation is extremely complicated). Thus, the similarity of surface tension values for organic liquids is clear.

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APPENDIX A: COMPARISON OF DIPOLE-DIPOLE AND LONDON ATTRACTIONS FOR ACETONE

We compare the magnitude of the dipole-dipole U_K and London U_L potentials for acetone, which has a very high dipole moment $p=2.9$ D and, hence, a high value of U_K is expected. Equations (2) and (4) yield

$$\frac{U_K}{U_L} = \frac{4p^4}{9kT\alpha^2 I}, \quad (A1)$$

where $\alpha = 4\pi\epsilon_0 r_m^3$. For acetone, $r_m = 3.15 \times 10^{-10}$ m (see Ref. 11) and $I = 9.7$ eV (see Ref. 12). For $T = 300$ K, we find that

$$\frac{U_K}{U_L} \cong 5 \times 10^{-2}. \quad (A2)$$

We see that even for the acetone molecule, which has an unusually high dipole moment, the dipole-dipole interaction is much weaker than the London interaction.

APPENDIX B: POLARIZABILITY OF SPHERICAL MOLECULES

Consider a spherical molecule consisting of a nucleus of charge $+q$ and an electron cloud of radius r_m and charge $-q$. A static electric field E induces a dipole moment p in the molecule

$$p = \alpha E, \quad (\text{B1})$$

where α is the polarizability of the molecule. Let us estimate how strong a field is needed to displace the electron cloud relative to the nucleus so that the nucleus is moved a distance r_m .^{3,7} The dipole moment of the molecule is $p = qr_m$. The Coulomb force F that would drive the nucleus to the center is $F = kq^2/r_m^2$. This force is compensated by the external force qE . Thus, we need an electric field $E = kq/r_m^2$ to hold the molecule in this unusual state. Substitution into Eq. (A2) yields

$$p = qr_m = \alpha k \frac{q}{r_m^2}, \quad (\text{B2})$$

and $\alpha = r_m^3/k = 4\pi\epsilon_0 r_m^3$. This result was exploited for the derivation of Eq. (5).

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