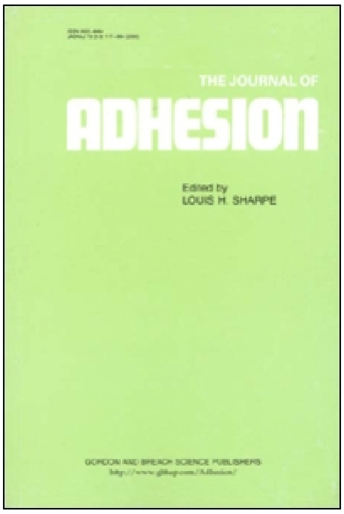

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Surface Tension in Relation to Cohesive Energy with Particular Reference to Hydrocarbon Polymers

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To cite this Article Hobin, T. P.(1972) 'Surface Tension in Relation to Cohesive Energy with Particular Reference to Hydrocarbon Polymers', The Journal of Adhesion, 3: 3, 237 — 247
To link to this Article: DOI: 10.1080/00218467208072195
URL: http://dx.doi.org/10.1080/00218467208072195

J. Adhesion, 1972, Vol. 3, pp. 237—247

Printed in Northern Ireland

Surface Tension in Relation to Cohesive Energy with Particular Reference to Hydrocarbon Polymers

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(*Received November* 9, 1970)

A known relationship between heat of vaporisation, surface tension and molar volume applicable to spherical non-polar molecules is modified to apply also to linear molecules; the treatment involves calculation of molar surface areas corresponding to the appropriate "fully-packing" molecular shapes.

A linear relationship between the ratio cohesive energy density/surface tension and the reciprocal of molar volume is predicted for members of homologous series and demonstrated, with data for the *n*-paraffins.

INTRODUCTION

Knowledge of the surface tensions and contact angles of the viscous polymers used to bind together the solid ingredients of some rocket propellants would be helpful for the better understanding of the physical behaviour of the propellants in terms of the energy interactions between the various phases present. Unfortunately, the direct measurement of the surface properties of viscous materials has proved to be difficult[1,2], and this has led in the present work to an indirect approach to the problem involving the assessment of surface properties from the more-readily-available cohesive energy data.

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PUBLISHED RELATIONSHIPS BETWEEN COHESIVE ENERGY AND SURFACE TENSION

References to relationships between heat of vaporisation and surface tension are numerous. Partington, for example[3], cites many examples of these. One of the more successful relationships is that of Hildebrand[4]:

$$\gamma = k\left(\frac{V}{N}\right)^{1/3} \cdot \frac{E_v}{V}, \tag{1}$$

where γ = surface tension, k = constant, V = molar volume, N = Avogadro's number, and E_v = energy of vaporisation = heat of vaporisation − expansion energy (i.e. $\Delta H_v - RT$).

This equation, which applies to non-polar or only slightly polar molecules of approximately spherical shape, is of empirical origin. Schonhorn[5], however, has claimed that an analogous equation may be rigorously derived from the rigid-sphere theory of liquids.

Eq. (1) is equivalent to a statement that

$(\Delta H_v - RT)/\gamma$ is proportional to A

where A, the molar surface area, is proportional to $N(V/N)^{2/3}$.

Attempts have been made to apply the Hildebrand relationship to polymer molecules, e.g. Lee[6], who treated the polymer repeat groups as unconstrained spherical molecules, and Wu[7], who attempted to evaluate the empirical relationship between A and V for polymer species. In the present work the changes in proportionality between A and V on passing from spherical monomer molecules to linear oligomers and thence to infinite polymer molecules are considered from first principles and are used to extend the Hildebrand relationship to these other types of molecules.

EVALUATION OF MOLAR SURFACE AREAS

Simple molecules

Molecular surface area is a somewhat ambiguous quantity being dependent on the shape and dimensions ascribed to the individual molecules. It is plausible to consider it as the surface area of the solid body formed when the liquid has been cleaved by imaginary planes or surfaces such that every molecule is separated from its neighbours by a cleavage plane. The solid formed by the planes around each molecule then gives a "fully-packing" shape for the molecule. This shape is considered to be more realistic for the purpose of calculation of surface areas or surface energies than that of a non-packing shape such as a sphere. The simplest fully-packing shape would be that of a cube, representing a molecule with six nearest neighbours. Simple molecules are more likely to have twelve nearest neighbours in the liquid state; for these the appropriate fully-packing molecular shape would be that of a dodecahedron.

In the case of a rhombic dodecahedron.

$$\text{Molecular surface area} = \frac{A}{N} = 3d^2\sqrt{2},$$

$$\text{Molecular volume} = \frac{V}{N} = \frac{d^3}{\sqrt{2}},$$

where A = molar surface area, V = molar volume, N = Avogadro's number, d = shortest diameter.

From this it follows that

$$A = 3N\sqrt{2}\left(\frac{V}{N}\sqrt{2}\right)^{2/3}.$$

The molar surface areas of a number of derivatives of methane, ethane and cyclic hydrocarbons, calculated from molar volume in this way, are listed in Table I, together with values $(\Delta H_v - RT)/\gamma$ for comparison.

Linear molecules

The simplest fully-packing shape for a linear molecule is that of a rod with square cross-section. A more realistic shape for molecular packing would be that of a rod of hexagonal cross-section; for such a rod of length l and smallest diameter d

$$\text{Area} = d^2\sqrt{3} + \frac{6}{\sqrt{3}}dl,$$

$$\text{Volume} = \frac{d^2 l}{2}\sqrt{3}.$$

In order to calculate molar surface area it is necessary to know the effective length and diameter, the term "effective" being used to denote the actual average dimensions occupied by the molecule as distinct from the van der

TABLE I

Surface areas and other data for simple liquids at 25°C

Liquid	Molar volume (cm^3)	10^{-9} × calculated molar surface area (cm^2)	10^{-9} × hard-core surface area (cm^2)	Surface tension, γ (dyn/cm) (20°C)	$\Delta H_v - RT$ (cal/mole)	10^{-9} × $(\Delta H_v - RT)/\gamma$ (cm^2/mole)
Carbon tetrachloride	97.1	9.53	7.28	27	7188	11.1
Chloroform	80.7	8.91	6.03	27.1	6928	10.7
Methylenechloride	64.5	7.26	4.95	26.5	6422	10.1
Ethylbromide	75.1	8.04	5.55	24.2	6207	10.8
Ethyliodide	81.1	8.45	5.95	29.4	7437	10.5
Bromoform	87.9	8.91	6.84	41.5	9803	9.9
Benzene	89.4	9.00	6.01	28.9	7508	10.9
Cyclohexane	108.7	10.2	7.53	25.5	7313	12.0
Toluene	106.9	10.1	7.45	28.5	8498	12.5
Chlorobenzene	102.1	9.88	7.13	33.6	9228	11.5
Pyridine	80.9	8.48	—	38.0	9074	10.0

References for data are as follows: Molar volumes, Ref. 8; hard-core surface areas, Ref. 9; surface tensions, Ref. 10; heats of vaporisation Ref. 8.

Surface areas in the second column were calculated from molar volumes using the formulae for a rhombic dodecahedron.

Waals or "hard-core" dimensions defined by bond lengths and angles. The effective dimensions should be the hard-core dimensions increased by a uniform amount all round. For the purpose of calculation it is assumed, initially, that the effective length is the same as the hard-core length in order to calculate an approximate effective diameter from molar volume. The amount by which the calculated diameter exceeds the hard-core diameter is then added to the hard-core length and the calculation repeated to give a more accurate value for the effective diameter.

The values obtained at this stage are sufficiently close to the absolutely self-consistent values obtainable by reiteration. The hard-core dimensions of the *n*-paraffins can be calculated as follows:

$$\text{Length} = [(n - 1)l_{C-C} + 2l_{C-H} + 2r_H] \cos\theta$$

$$\text{Diameter} = [l_{C-C} + 2l_{C-H} + 2r_H] \sin\theta,$$

where n = number of chain carbon atoms, l_{C-C} = carbon–carbon bond length, l_{C-H} = carbon–hydrogen bond length, r_H = radius of hydrogen atom, and $\theta = 35^\circ\ 16'$ (i.e. $[\frac{1}{2}\ 180^\circ - 109^\circ\ 28']$).

The bond lengths quoted in Ref. 10 were used to calculate the molar surfaceareas listed in Table II. The corresponding values of $(\Delta H_v - RT)/\gamma$ are also given.

Hard-core surface areas and volumes

Bondi[9] has drawn up a list of group contributions to van der Waals volumes and surface areas of hydrocarbons and substituted hydrocarbons. The areas calculated in this way (Tables I and II) are those of curved surfaces, hence they relate to shapes which are not fully-packing. There is in fact an approximately linear relationship between Bondi's surface areas and those calculated in the present work; this arises because each repeat group adds a constant amount to the surface area irrespective of the method of calculation.

ENERGY OF VAPORISATION/SURFACE TENSION IN RELATION TO MOLAR SURFACE AREA

A graph of $(\Delta H_v - RT)/\gamma$ vs. A is shown in Figure 1. It is seen to be a straight line embracing the data for both spherical and linear molecules.

TABLE II

Surface areas and other data for *n*-paraffins at 25°C

Liquid	Molar volume (cm³)	$10^{-9}\times$ calculated molar surface area (cm²)	$10^{-9}\times$ hard-core molar surface area (cm²)	Surface tension, γ (dyn/cm)	$\Delta H_v - RT$ (cal/mole)	$10^{-9}\times$ $(\Delta H_v - RT)/\gamma$ (cm²/mole)
Pentane	116	11.9	8.29	15.48	5.72	15.7
Hexane	132	13.5	9.64	17.90	6.95	16.4
Heptane	147	14.8	11.0	19.80	8.14	17.1
Octane	164	16.2	12.3	21.26	9.32	18.5
Decane	196	18.9	15.0	23.44	11.7	21.1
Dodecane	229	21.4	17.7	24.98	14.0	23.6
Tetradecane	261	23.9	20.4	26.2	16.3[a]	26.0
Hexadecane	294	26.4	23.1	27.1	18.5	28.7
Octadecane	327	28.9	25.8	28.0	21.4[a]	32.0
Eicosane	360	31.4	28.5	28.6	23.1[a]	33.8

[a] Estimated by extrapolation.

References for data are as follows: molar volumes, Ref. 10; hard-core surface areas, Ref. 9; surface tensions, Ref. 10; heats of vaporisation, Ref. 8.

Surface areas in the second column were calculated from molar volumes on the basis that the molecules had the shape of rods with hexagonal cross-section.

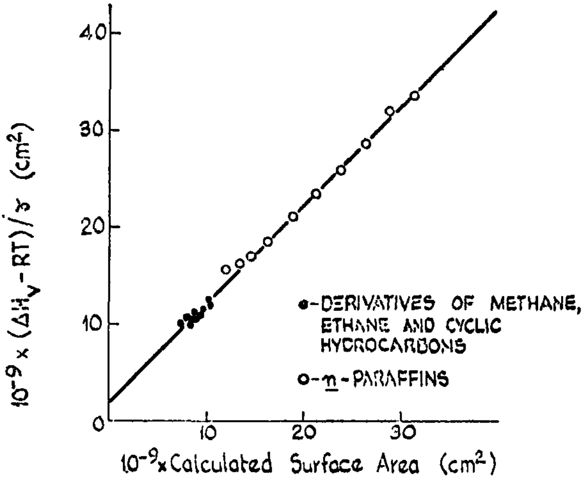

FIGURE 1 $(\Delta H_v - RT)/\gamma$ vs. surface area

As drawn the slope is unity and there is a slight intercept on the $(\Delta H_v - RT)/\gamma$ axis; the relationship can be expressed as follows:

$$(\Delta H_v - RT)/\gamma = A + 2.0 \times 10^9, \tag{2}$$

where $(\Delta H_v - RT)$ is in ergs/mole, γ is in ergs/cm², and A is in cm²/mole. Since $(\Delta H_v - RT)/V$ = cohesive energy density (c.e.d.), then

$$\text{c.e.d.}/\gamma = \frac{A}{V} + \frac{2.0 \times 10^9}{V}, \tag{3}$$

where V is the molar volume in cm³, and c.e.d. is in ergs/cm³.

Because of the connection between calculated surface areas and Bondi's hard-core surface areas referred to above, relationships similar to Eqs. (2) and (3) also exist in respect of hard-core areas, but the intercept in Eq. (2) becomes

$$5.5 \times 10^9 \text{ instead of } 2.0 \times 10^9 \text{ cm}^2/\text{mole}.$$

Any of the above relationships may be used to calculate the surface tension of a non-polar or slightly polar liquid from ΔH_v or from c.e.d.

RELATIONSHIPS FOR HIGH MOLECULAR WEIGHT POLYMERS

High molecular weight polymers are non-volatile and so direct estimates of heats of vaporisation are not possible. However, in many cases cohesive energy densities can be calculated by indirect methods[11].

For high polymers, molar volume, V, is very large and so Eq. (3) becomes

$$\begin{aligned} \text{c.e.d.}/\gamma &= \frac{\text{molar surface area}}{\text{molar volume}}, \\ &= \frac{\text{surface area of repeat group}}{\text{volume of repeat group}}. \end{aligned} \tag{4}$$

If the repeat group is considered as a section of rod of length l and of hexagonal cross section with shortest diameter d, then

$$\text{area} = \frac{6}{\sqrt{3}}\, dl \text{ and volume} = \frac{d^2 l}{2} \sqrt{3}.$$

Hence

$$\text{c.e.d.}/\gamma = \frac{\text{area}}{\text{volume}} = \frac{4}{d}$$

since volume of repeat group

$$= M_r/N\rho = \frac{d^2 l}{2}\sqrt{3},$$

where M_R = molecular weight of the repeat group, ρ = density of amorphous polymer, and N = Avogadro's number.

d can be calculated if l is known.

For polyethylene

$$l = l_{C-C} \cos 35° \, 16'.$$

The density of liquid polyethylene at 20°C has been estimated to be 0.855 g cm^{-3},[12]

hence $M_R/\rho = 16.4 \text{ cm}^3$,

and $d = 4.99 \times 10^{-8} \text{ cm}$,

so that $\text{c.e.d.}/\gamma = \frac{\text{area}}{\text{volume}} = \frac{4}{d} = 8.01 \times 10^{7} \text{ cm}^{-1}$

The c.e.d. of amorphous polyethylene has been reported to be 70 cal/cm^3 at 20°C[12]. The surface tension at 20°C has been estimated by extrapolation of results of measurements at higher temperatures. The values obtained range from 31.5 to 36 dyn/cm[13], depending on the quality and molecular weight of the polymer. Branch methyl groups lower surface tension, but the sample with the lowest methyl group content gave $\gamma = 36$ dyn/cm. Using this value, we obtain

$$\text{c.e.d.}/\gamma = \frac{70 \times 4.18 \times 10^7}{36} = 8.13 \times 10^7\,\text{cm}^{-1}.$$

This is very close to the calculated value.

The same level of agreement is not obtained when the treatment is applied to vinyl polymers—$(CH_2CHX)_n$; these, unlike polyethylene, have variable diameters along their chains which makes it difficult to envisage a realistic molecular shape that is capable of void-free packing. Consideration of the corresponding hard-core areas and volumes for a selection of vinyl repeat groups, however, reveals the significant fact that the ratio of hard-core area/volume is much the same for each of the various vinyl repeat groups. Thus the ratios calculated from Bondi's incremental values are (in units of $10^8 \times \text{cm}^{-1}$):

polyethylene	1.32
polyisobutylene	1.37
rubber	1.31
polyvinylchloride	1.30
polypropylene	1.32
polystyrene	1.15

Bearing in mind the observed relationship between calculated molar surface areas and the hard-core surface areas, it might be expected that the ratio

$$\text{molar surface area/molar volume}$$

would also be constant for the vinyl polymers, from which it would follow that

$$\text{c.e.d.}/\gamma = \text{constant}$$

In fact a correlation between c.e.d. and the critical surface tension for wetting, γ_c, for polymers has been observed by Gardon[14], who did not specify the nature of the correlation. More data has since become available[11,15] and a plot of c.e.d. vs. γ_c for various amorphous polymers is shown in Figure 2. (γ_c can only be considered analogous to actual surface tension for polymers with amorphous or liquid-like surfaces.)

This tendency for the vinyl polymer molecules to have similar area/volume ratios probably accounts for the encouraging results obtained in previous attempts at the application of the Hildebrand equation to polymers[5,6].

The c.e.d. of the propellant binder polyisobutylene is 65 cal/cm³[3,11]; this, from Figure 2, corresponds to a surface tension of 29.5 dyn/cm, which is in agreement with the values found experimentally in these laboratories, namely 26–33 dyn/cm depending on the molecular weight and source of the polymer[1].

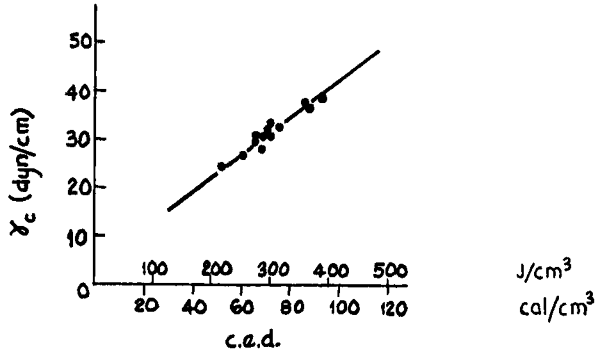

FIGURE 2 Surface tension vs. c.e.d. for vinyl polymers

OTHER RELATIONSHIPS

For members of an homologous series, except for a few of the lower members, each additional repeat group adds a constant amount to both the total molar surface area, A, and to the total molar volume, V, so it follows that V is proportional to A. Hence, since $(\Delta H_v - RT)/\gamma$ is also proportional to A, we can write

$$(\Delta H_v - RT)/\gamma = aV + b,$$

where a and b are constants. Hence, for members of homologous series

$$\text{c.e.d.}/\gamma = a + b/V.$$

Investigation of this relationship for the n-paraffins using the c.e.d. values of Bristow and Watson[8] indicates that c.e.d./γ is related linearly to $1/V$ as shown in Figure 3. Extrapolation to $1/V = 0$ yields a value of c.e.d./$\gamma = 1.88$ for the infinite polymer (polyethylene). The experimental value of c.e.d./γ is 70 cal/cm³/36 dyn/cm = 1.94, which compares favourably with the predicted value.

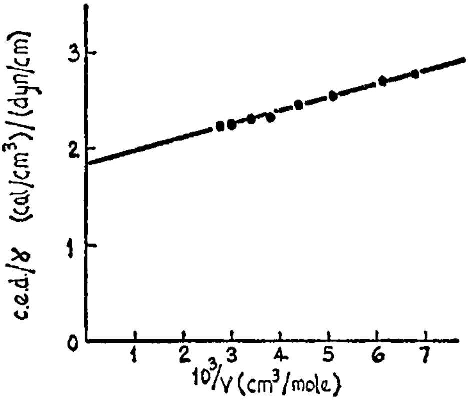

FIGURE 3 c.e.d./γ vs. $1/v$ for n-paraffins

CONCLUSIONS

The surface tension of any non-polar substance can be estimated from its heat of vaporisation or from its cohesive energy density. A relationship exists between c.e.d./γ and reciprocal of molar volume for members of homologous series.

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