

MOLECULAR ORIENTATION OF LIQUID ALIPHATIC HYDROCARBONS ON THE SURFACE AND AT THE INTERFACE WITH WATER

Jan KLOUBEK

*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 182 23 Prague 8*

Received February 15, 1989

Accepted April 17, 1989

The validity of the Fowkes theory for the interaction of dispersion forces at interfaces was inspected for the system water–aliphatic hydrocarbons with 5 to 16 C atoms. The obtained results lead to the conclusion that the hydrocarbon molecules cannot lie in a parallel position or be randomly arranged on the surface but that orientation of molecules increases there the ratio of CH_3 to CH_2 groups with respect to that in the bulk. This ratio is changed at the interface with water so that the surface free energy of the hydrocarbon, γ_{H} , rises to a higher value, $\gamma_{\text{H}}^{\text{d}}$, which is effective in the interaction with water molecules. Not only the orientation of molecules depends on the adjoining phase and on the temperature but also the density of hydrocarbons on the surface of the liquid phase changes. It is lower than in the bulk and at the interface with water. Moreover, the volume occupied by the CH_3 group increases on the surface more than that of the CH_2 group. The dispersion component of the surface free energy of water, $\gamma_{\text{W}}^{\text{d}} = 19.09 \text{ mJ/m}^2$, the non-dispersion component, $\gamma_{\text{W}}^{\text{n}} = 53.66 \text{ mJ/m}^2$, and the surface free energies of the CH_2 and CH_3 groups, $\gamma(\text{CH}_2) = 32.94 \text{ mJ/m}^2$ and $\gamma(\text{CH}_3) = 15.87 \text{ mJ/m}^2$, were determined at 20°C . The dependence of these values on the temperature in the range $15\text{--}40^\circ\text{C}$ was also evaluated.

A considerable amount of effort has been expended in evaluating the surface free energy of solids from the contact angles of liquids. Nonetheless, this subject cannot be considered completely clarified and continues to draw a great deal of attention. A recent paper¹ has been devoted to check the Fowkes theory on the system liquid–liquid and experimentally determined values of the corresponding surface and interfacial free energies, γ_i and γ_{ij} , respectively, of water, mercury, and various organic liquids have been used to this purpose. This work is aimed to determine precisely the dispersion component of the surface free energy of water, $\gamma_{\text{W}}^{\text{d}}$. To this purpose, the system water–aliphatic hydrocarbons is used and the orientation of the molecules on the surface and at the interface is considered. All the γ_i and γ_{ij} values, the work of adhesion, W_{A} , and spreading pressure, Π , are expressed in mJ/m^2 .

Fowkes² proposed the following relationship for the water (W)–liquid saturated hydrocarbon (H) interface:

$$W_{\text{A}} = \gamma_{\text{W}} + \gamma_{\text{H}} - \gamma_{\text{WH}} = 2(\gamma_{\text{H}}\gamma_{\text{W}}^{\text{d}})^{1/2} \quad (1)$$

from which he found $\gamma_{\text{W}}^{\text{d}} = 21.8 \pm 0.7$ at 20°C . This value continues to be used most frequently in the literature. Fowkes based his evaluation on the assumption that the interaction occurs at the interface between water and saturated hydrocarbons only through the dispersion components of the surface free energies because γ_{H} equals $\gamma_{\text{H}}^{\text{d}}$.

Johnson and Dettre³ expressed doubts about the validity of Eq. (1). They found from other γ_{H} and γ_{WH} data (at 24.5°C) that the $(\gamma_{\text{W}} - \gamma_{\text{WH}})/\gamma_{\text{H}}$ dependence on $1/\gamma_{\text{H}}^{1/2}$ is linear but that it does not pass through the point (0; -1) as would correspond to Eq. (1). They concluded that the interaction of water with higher hydrocarbons does not include the entire value of γ_{H} but only a part of it. For hexadecane with $\gamma_{\text{H}} = 27.3$ at 24.5°C , e.g., only $\gamma_{\text{H}}^{\text{d}} = 23.7$ interacts with $\gamma_{\text{W}}^{\text{d}}$.

Gillap et al.⁴ evaluated deviations from Eq. (1) differently. They found from their γ_{H} and γ_{WH} data (at 25°C) that, according to Eq. (1), the calculated $\gamma_{\text{W}}^{\text{d}}$ values decrease roughly linearly in dependence on $\log n$ (where n is the number of C atoms in the straight chain of the saturated hydrocarbon). The results of both these papers^{3,4} do not agree with the Fowkes theory.

Aveyard et al.^{5,6} considered more closely the fact that $\gamma_{\text{W}}^{\text{d}}$ depends on n using larger and more precise data set for γ_{H} and γ_{WH} (at 20°C) than Fowkes. These data are given in Table I and will be used here. Table I also contains the W_{A} values (for $\gamma_{\text{W}} = 72.75$), molecular weight, M , hydrocarbon density, ρ (g/cm^3), and the $\gamma_{\text{W}}^{\text{d}}$ values calculated from Eq. (1). A decrease of $\gamma_{\text{W}}^{\text{d}}$ in dependence on n can be clearly seen.

TABLE I

Basic and calculated data for the saturated normal aliphatic hydrocarbons-water interfaces at 20°C

n	M	ρ	γ_{H}	γ_{WH}	W_{A}	$\gamma_{\text{W}}^{\text{d}}$		γ_{H}'	γ_{W}^*
						Eq. (1)	Eq. (2)		
5	72	0.6263	15.98	50.23	38.50	23.19	24.20	19.44	66.21
6	86	0.6595	18.42	50.80	40.37	22.12	22.32	21.37	69.22
7	100	0.6836	20.20	51.23	41.72	21.54	21.56	22.82	71.05
8	114	0.7022	21.64	51.69	42.70	21.06	21.07	23.91	71.77
9	128	0.7174	22.86	51.96	43.65	20.84	20.88	24.98	72.11
10	142	0.7298	23.78	52.26	44.27	20.60	20.70	25.70	72.30
11	156	0.7402	24.60	52.51	44.84	20.43	20.59	26.36	72.41
12	170	0.7488	25.34	52.86	45.23	20.18	20.42	26.82	72.48
14	198	0.7624	26.58	53.32	46.01	19.91	20.28	27.76	72.56
16	226	0.7734	27.48	53.77	46.46	19.64	20.12	28.30	72.61

n Number of carbon atoms in the straight chain of the hydrocarbon; ρ density (in g/cm^3) from ref.⁸; γ_{H} , γ_{WH} and W_{A} (in mJ/m^2) from refs^{5,6}; $\gamma_{\text{W}}^{\text{d}}$, γ_{H}' and γ_{W}^* calculated values (see text).

Instead of the geometric mean used by Fowkes, Wu⁷ recommended the harmonic mean which for the interface water–hydrocarbon writes

$$W_A = \gamma_W + \gamma_H - \gamma_{WH} = 4\gamma_W^d\gamma_H/(\gamma_W^d + \gamma_H). \quad (2)$$

The γ_W^d values calculated from Eq. (2) are included in Table I and they show a similar decrease as those from Eq. (1).

Aveyard et al.^{5,6} based their studies on the assumption that the hydrocarbons lie in parallel position to the interface and that the work of adhesion between water and the CH₂ groups, $W(\text{CH}_2)$, is different from that between water and the CH₃ groups, $W(\text{CH}_3)$. The overall work (or the average work) of adhesion, W_A , then depends on the $A(\text{CH}_2)$ and $A(\text{CH}_3)$ areas occupied by the CH₂ and CH₃ groups at the interface. Accordingly, they proposed the following equations:

$$A_H = 2A(\text{CH}_3) + (n - 2) A(\text{CH}_2) \quad (3)$$

and

$$W_A A_H = W(\text{CH}_3) 2A(\text{CH}_3) + W(\text{CH}_2)(n - 2) A(\text{CH}_2). \quad (4)$$

After rearrangement of Eq. (4) to

$$W_A A_H/A(\text{CH}_2) = 2W(\text{CH}_3) A(\text{CH}_3)/A(\text{CH}_2) + (n - 2) W(\text{CH}_2) \quad (4a)$$

and substituting the corresponding W_A values (see Table I), $A(\text{CH}_2) = 0.05 \text{ nm}^2$ and $A(\text{CH}_3) = 0.11 \text{ nm}^2$, they obtained a linear dependence between the left-hand side of Eq. (4a) and $(n - 2)$ yielding $W(\text{CH}_2) = 52$ and $W(\text{CH}_3) = 30$. Aveyard⁶ then classified the dependence of γ_H on ϱ/M as “accurately” linear and used the equation

$$\gamma_H = \gamma(\text{CH}_2) + b\varrho/M, \quad (5)$$

where b is a constant, to determine the surface free energy corresponding to the CH₂ groups. Thus, he obtained $\gamma(\text{CH}_2) = 34.7$ at $\varrho/M = 0$. Substituting $\varrho = 0.339 \text{ g/cm}^3$ for liquid ethane at 20°C into Eq. (5), he determined $\gamma_H = \gamma(\text{CH}_3) = 10.8$. Substitution of these values and the above values for $W(\text{CH}_2)$ and $W(\text{CH}_3)$ in Eq. (1) yielded $\gamma_W^d = 19.5$ for the interaction of water with CH₂ groups and $\gamma_W^d = 20.8$ for the interaction with CH₃ groups. Aveyard concluded⁶ that these results confirmed the validity of the Fowkes theory. However, although the two values of γ_W^d obtained by Aveyard are similar, they indicate that γ_W^d is not constant and depends on the adjoining phase. Thus, either the Fowkes theory or the approach employed by Aveyard

cannot be correct. We try to clear the problem in this paper. The so-far neglected dependence of γ_w^d on the temperature will also be considered.

RESULTS AND DISCUSSION

The Concept of Random Arrangement of the Hydrocarbon Chains at the Interface

Table II summarizes the results obtained from evaluation of various linear dependences for hydrocarbons with straight unbranched chains with 5 to 16 carbon atoms. To judge the validity of Aveyard's results we will first consider the dependence of the hydrocarbon molar volume $V_M = M/\rho$ (at 20°C) on the number of carbons in the chain using the equation

$$M/\rho = 2V(\text{CH}_3) + (n - 2)V(\text{CH}_2). \quad (6)$$

The excellent linearity of this dependence is indicated by the coefficient of determination, r^2 (see Table II). The determined molar volumes of the CH_3 and CH_2 groups (b and $a/2$ in Table II) yield their cross-sectional areas within the liquid phase, $[V(\text{CH}_2)]^{2/3} = A(\text{CH}_2) = 6.388 \text{ cm}^2/\text{mol} = 0.08958 \text{ nm}^2/\text{group}$ and $[V(\text{CH}_3)]^{2/3} = A(\text{CH}_3) = 10.260 \text{ cm}^2/\text{mol} = 0.14385 \text{ nm}^2/\text{group}$. These values differ from those employed by Aveyard both in magnitude and in relative size. Substitution of these

TABLE II

Evaluation of the constants in the linear dependences $y = a + bx$

Eq.	y	x	a	b	r^2
(4a)	a	n	-14.3745	50.9886	0.99997
(5)	γ_H	q/M	34.8875	-2.158.0875	0.99966
(6)	M/ρ	$n - 2$	65.7245	16.1471	0.99995
(7)	γ_H	$n^{-0.625}$	38.2171	-60.7698	0.99994
(8a)	b	c	-1.2079	33.9585	0.99993
(9)	d	c	2.2360	5.9353	0.99999
(13)	e	f	35.9590	31.5004	0.99988
(14)	e	g	19.1453	19.0665	0.99997
(20)	$\log \pi$	$1/n$	-1.6385	13.4008	0.99993

$a) y = W_A(2A(\text{CH}_3)/A(\text{CH}_2) + n - 2); b) y = \gamma_H A_H / 2A(\text{CH}_3); c) x = (n - 2) A(\text{CH}_2) / 2A(\text{CH}_3); d) y = \gamma_H^{1/2} A_H / 2A(\text{CH}_3); e) y = n(2A(\text{CH}_3) + nA(\text{CH}_2) - 2A(\text{CH}_2)) / (A(\text{CH}_3) - A(\text{CH}_2)); f) x = n^2 A(\text{CH}_2) (1 + 0.063/n + 0.032a/n^2) / \gamma_H (A(\text{CH}_3) - A(\text{CH}_2)); g) x = (2n/W_A)^2 \gamma(\text{CH}_2) A(\text{CH}_2) (1 + 0.063/n + 0.032a/n^2) / (A(\text{CH}_3) - A(\text{CH}_2)).$

values in Eq. (4a) again yields excellent linearity, with $W(\text{CH}_2) = 50.99$ and $W(\text{CH}_3) = 27.27$ somewhat lower than given by Aveyard.

Equation (4) is based on the assumption that the carbon groups are present at the interface in the ratio $(n - 2) \text{CH}_2$ to 2CH_3 . It should be noted that this ratio need not be related with the idea that the molecules lie parallel to the surface or interfacial plane. It would be, in fact, far more acceptable to assume that the molecules are randomly oriented and, consequently, that the ratio of CH_2 to CH_3 groups on the surface is the same as that in the bulk of the liquid. This assumption leads to the same ratio of these groups as for a plane parallel arrangement of molecules.

Verification of the γ_w^d values for interaction of water with CH_2 and CH_3 groups according to Eq. (1) requires to determine the $\gamma(\text{CH}_2)$ and $\gamma(\text{CH}_3)$ values. First, recalculating the same dependence as Aveyard, i.e. Eq. (5), we obtain the $\gamma(\text{CH}_2)$ value with a relatively high coefficient of determination (see Table II). Nevertheless, a slight curvature is apparent in the plot of this dependence. Therefore, the linear extrapolation up to $\rho/M = 0$ according to the Eq. (5) cannot give the correct $\gamma(\text{CH}_2)$ value. It is also not clear whether the value of $\rho = 0.339 \text{ g/cm}^3$ can be used for ethane in Eq. (5) for the calculation of $\gamma(\text{CH}_3)$ because it relates to an increased pressure.

A linear dependence of γ_H on $\log n$ is mentioned in the literature⁴. The data used here do not confirm this linearity but rather clearly define a curve. In contrast, the relation

$$\gamma_H = \gamma(\text{CH}_2) + bn^{-0.625} \quad (7)$$

exhibits excellent linearity, yielding $\gamma(\text{CH}_2) = 38.22$, which is much higher than that obtained from Eq. (5). However, substitution of $n = 2$ in Eq. (7) yields the unrealistic value of $\gamma_H = \gamma(\text{CH}_3) = -1.19$. Thus, extrapolation according to Eq. (7), similar to Eq. (5), is only possible in a limited range and $\gamma(\text{CH}_3)$ cannot be found in this way.

Equation (3) will now be applied in combination with the respective surface free energies (in contrast to the work of adhesion used in Eq. (4) by Aveyard)

$$\gamma_H A_H = \gamma(\text{CH}_3) 2A(\text{CH}_3) + \gamma(\text{CH}_2) (n - 2) A(\text{CH}_2) \quad (8)$$

which rearranged to

$$\gamma_H A_H / 2A(\text{CH}_3) = \gamma(\text{CH}_3) + \gamma(\text{CH}_2) (n - 2) A(\text{CH}_2) / 2A(\text{CH}_3) \quad (8a)$$

yields $\gamma(\text{CH}_2) = 33.96$ and $\gamma(\text{CH}_3) = -1.21$. The negative value of $\gamma(\text{CH}_3)$ clearly indicates that the use of Eq. (8) is not justified.

Finally, $2(\gamma_H \gamma_w^d)^{1/2}$ from Eq. (1) will be substituted into Eq. (4) in place of W_A to apply the Aveyard method to the $\gamma(\text{CH}_2)$ and $\gamma(\text{CH}_3)$ evaluation. In agreement

with Eq. (1), $2(\gamma(\text{CH}_2) \gamma_w^d)^{1/2}$ will be used in place of $W(\text{CH}_2)$ and $2(\gamma(\text{CH}_3) \gamma_w^d)^{1/2}$ in place of $W(\text{CH}_3)$. The resulting equation

$$\gamma_H^{1/2} A_H / 2A(\text{CH}_3) = \gamma(\text{CH}_3)^{1/2} + \gamma(\text{CH}_2)^{1/2} (n - 2) A(\text{CH}_2) / 2A(\text{CH}_3) \quad (9)$$

yields $\gamma(\text{CH}_2) = 35.23$ and $\gamma(\text{CH}_3) = 5.00$.

The surface free energy cannot have a negative value and there is also no good reason why $\gamma(\text{CH}_2)$ should differ so greatly from $\gamma(\text{CH}_3)$. The surface free energy obtained from contact angles of liquids by using Eq. (1) in combination with the Young equation for paraffin wax and polyethylene² equals 25.5 and 35.0, respectively, and it should approach $\gamma(\text{CH}_2)$. The value of $\gamma(\text{CH}_3)$ can roughly be estimated from the maximum spreading pressure of oxyethylene dodecanols on water⁹ extrapolated to the value for dodecanol. At the respective condition, the close packed monolayer of the alcohol molecules is oriented perpendicular to the interfacial plane with the hydrophilic groups pointing toward water. If the hydrophilic group has the cross-sectional area not larger than that of the hydrocarbon chain, as it is the case of dodecanol, then only CH_3 groups are present on the surface and the extrapolated spreading pressure Π gives the value of $\gamma_w - \Pi = 16$ which should be close to $\gamma(\text{CH}_3)$. Thus, neither the negative values obtained for $\gamma(\text{CH}_3)$ from Eqs (7) and (8a) nor the results from Eqs (5) and (9) can be true and the concept of random arrangement of the hydrocarbon molecules on the surface of the liquid phase appears to be incorrect.

The Concept of Oriented Arrangement of the Hydrocarbon Chains at the Interface

Two opposing tendencies act on the hydrocarbon molecules. Thermal motion leading to random arrangement is counteracted by a tendency to attain a state with the minimal surface free energy by an oriented arrangement of molecules increasing the number of CH_3 groups on the surface owing to $\gamma(\text{CH}_3) < \gamma(\text{CH}_2)$. The increase of the number of CH_3 groups is assumed to be inversely proportional to the number of C atoms in the chain, n , because the longer is the molecule, the more difficult should be its orientation. Accordingly, we can write the equation

$$A_H = (2 + a/n) A(\text{CH}_3) + (n - 2 - a/n) A(\text{CH}_2) \quad (10)$$

in which a is a characteristic constant expressing the tendency of the molecules to be oriented on the surface. Similarly as for Eq. (8),

$$\gamma_H A_H = \gamma(\text{CH}_3) (2 + a/n) A(\text{CH}_3) + \gamma(\text{CH}_2) (n - 2 - a/n) A(\text{CH}_2). \quad (11)$$

Finally, it will be assumed that the surface free energies of liquids with $\gamma = \gamma^d$ differ

owing to the area they occupy on the surface (A) and to their molecular weight (or the weight of the molecule fraction) (M) according to the empirical formula

$$\gamma_1 A_1 / M_1^{0.45} = \gamma_2 A_2 / M_2^{0.45}. \quad (12)$$

The approximate validity of Eq. (12) follows from the data for the halogen compounds⁸ given in Table III. The mean of $\gamma A / M^{0.45}$ values for all halogen compounds and groups with one carbon atom from Table III is 0.866 ± 0.107 , which is in agreement with the respective value for the CH_2 group. Therefore, according to Eq. (12), we can write

$$\gamma(\text{CH}_3) = 1.0317\gamma(\text{CH}_2) A(\text{CH}_2)/A(\text{CH}_3). \quad (12a)$$

Substitution of Eqs (10) and (12) into Eq. (11) yields

$$\begin{aligned} & n(2A(\text{CH}_3) + nA(\text{CH}_2) - 2A(\text{CH}_2)) / (A(\text{CH}_3) - A(\text{CH}_2)) = \\ & = -a + \gamma(\text{CH}_2) n^2 A(\text{CH}_2) (1 + 0.063/n + 0.032a/n^2) / \gamma_H (A(\text{CH}_3) - A(\text{CH}_2)). \end{aligned} \quad (13)$$

In the first approximation, the term $(0.063/n + 0.032a/n^2)$ in Eq. (13) was neglected and from the linear regression the values of $a = 31.71$ and $\gamma(\text{CH}_2) = 31.47$ were obtained. Thereafter, this value of a was used in the term $0.032a/n^2$ for the second

TABLE III
Data at 20°C for the empirical relation (12)

Group	γ , mJ/m ²	ρ , g/cm ³	M	A , nm ²	$\gamma A / M^{0.45}$
CH_2Cl_2	28.12	1.3255	84.9	0.225	0.855
CHCl_3	27.28	1.4891	119.4	0.261	0.827
CCl_4	26.77	1.5940	153.8	0.295	0.819
$-\text{CH}_2\text{Cl}^a$	32.23	1.2529	49.5	0.163	0.906
$-\text{CHCl}_2^b$	36.04	1.5945	83.9	0.197	0.967
CH_2Br_2	38.7	2.4910	173.8	0.238	0.903
CHBr_3	31.68	2.8905	252.7	0.276	0.726
$-\text{CH}_2\text{Br}^c$	38.91	2.1804	93.9	0.172	0.868
CH_3I	30.14	2.2790	141.9	0.220	0.714
CH_2I_2	50.8	3.3212	267.8	0.262	1.074
$-\text{CH}_2-^d$	31.50	—	14.0	0.090	0.860

^a 1,2-Dichloroethane; ^b 1,1,2,2-tetrachloroethane; ^c 1,2-dibromoethane; ^d methylene in aliphatic hydrocarbons.

approximation giving $a = 35.59$ and $\gamma(\text{CH}_2) = 31.49$. The third approximation yielded already a sufficiently accurate result, $a = 35.96$ and $\gamma(\text{CH}_2) = 31.50$ (cf. Table II). The respective $\gamma(\text{CH}_3)$ according to Eq. (12a) is 20.24.

The constant a from Eq. (13) can be employed to determine the amount of CH_3 and CH_2 groups on the surface. The number of CH_3 groups is $2 + a/n$ (see Eq. (10)). Accordingly, e.g. for hexadecane, the CH_3/CH_2 ratio on the surface is 1/2.3, while this ratio would be 1/7 for plane parallel or random arrangement. However, unrealistic values of $(2 + a/n) > n$ appear up to heptane.

It can be expected that, at the interface between a hydrocarbon and water, the action of the water molecules will lead to a change in the ratio of the groups, CH_3/CH_2 , compared to that at the hydrocarbon-air interface. It is again assumed that Eq. (10) is valid. If $W_A^2/4\gamma_W^d$ from Eq. (1) and Eqs (10) and (12) are substituted into Eq. (11) then

$$\begin{aligned} n(2A(\text{CH}_3) + nA(\text{CH}_2) - 2A(\text{CH}_2))/(A(\text{CH}_3) - A(\text{CH}_2)) = & \quad (14) \\ = -a + \gamma_W^d(2n/W_A)^2 \gamma(\text{CH}_2) A(\text{CH}_2) (1 + 0.063/n + 0.032a/n^2)/ & \\ / (A(\text{CH}_3) - A(\text{CH}_2)). & \end{aligned}$$

In the first approximation, the linear dependence between the left-hand side of Eq. (14) and $(2n/W_A)^2 \gamma(\text{CH}_2) A(\text{CH}_2)/(A(\text{CH}_3) - A(\text{CH}_2))$ yields $\gamma_W^d = 19.09$ (for 20°C). The result of the third approximation is given in Table II, γ_W^d being equal to 19.07 at 20°C. In contrast to the value obtained by Aveyard, this value does not depend on the groups with which the water molecules are in contact and is in good agreement with that derived theoretically by Padday and Uffindel¹⁰, $\gamma_W^d = 19.2$.

According to the number of CH_3 groups determined as $2 + a/n$ for a from Eq. (14), the ratio CH_3/CH_2 of the groups at the interface with water is, e.g., for hexadecane 1/4.0. Compared to the interface with air, the hydrocarbon arrangement at the interface with water is such that the relative content of CH_2 groups is increased, which must lead to a change in the force acting across the interface. Thus, γ_H on the right-hand side of Eq. (1) must be replaced by its effective value, γ'_H . The values of γ'_H calculated from Eq. (1) for the experimental W_A and for $\gamma_W^d = 19.07$ are in agreement with those calculated from Eq. (11) by using the constant a from Eq. (14) and are listed in Table I. In contrast to the change of γ_H to γ'_H on the right-hand side of Eq. (1), γ_H in the Dupré equation (on the left-hand side of Eq. (1)) remains unchanged. The effect of the molecular rearrangement on the work of adhesion is here included in γ_{WH} .

The value of $\gamma(\text{CH}_2) = 31.50$ obtained by linear extrapolation using Eq. (13) is identical with both γ_H and γ'_H for a hypothetical hydrocarbon with an infinitely long carbon chain. Thus, $\gamma(\text{CH}_2)$ can be substituted in the right-hand side of Eq. (1) and yields $W(\text{CH}_2) = 49.02$ and $\gamma(W\text{CH}_2) = 55.23$. Similarly, $\gamma(\text{CH}_3) = 20.24$

yields $W(\text{CH}_3) = 39.29$ and $\gamma(\text{WCH}_3) = 53.70$. However, these values of $W(\text{CH}_3)$ and $\gamma(\text{WCH}_3)$ do not fit in the series of the measured W_A and γ_{WH} values in Table I, respectively.

It should be noted that there are other examples in the literature of a change in the orientation of molecules at various interfaces. Molecules in monolayers were found to be oriented differently at the interface with air and with liquids¹¹. Also surfaces of solid polymers are relatively mobile and can adopt different configurations depending on the polarity of the adjoining phase^{12,13}.

The concept of the oriented arrangement of the hydrocarbon molecules gives better results than the concept of the random arrangement. However, some unsatisfactory conclusions remain: the calculated $\gamma(\text{CH}_3)$ is higher than γ_{H} values of lower hydrocarbons, $\gamma(\text{WCH}_3)$ and $W(\text{CH}_3)$ deviate from the expected values, and the number of CH_3 groups on the surface calculated by using the constant a is unreal for lower hydrocarbons.

Density of CH_2 Groups and Interactions at Interfaces

A change in γ_{H} can result not only from a change in the ratio of CH_2 to CH_3 groups but also from a change in the densities of these groups (at constant temperature). It can be assumed, in agreement with the Eötvös equation, which we can write in the form

$$\gamma A = a + bT, \quad (15)$$

that, at constant temperature, a change of $A(\text{CH}_2)$ to $A'(\text{CH}_2)$ would lead to a change of $\gamma(\text{CH}_2)$ to $\gamma'(\text{CH}_2)$ according to the equation

$$\gamma(\text{CH}_2) A(\text{CH}_2) = \gamma'(\text{CH}_2) A'(\text{CH}_2) \quad (16)$$

which is basically in agreement with Eq. (12).

The cross-sectional area of a single CH_2 group in the liquid phase can be calculated for cyclopentane, for which $\gamma_{\text{H}} = 22.57$ and $\rho = 0.7454 \text{ g/cm}^3$ at 20°C (ref.⁸), yielding $A = [(M/\rho)/5N_{\text{AV}}]^{2/3} = 0.0992 \text{ nm}^2$. This is larger than $A(\text{CH}_2)$ calculated from Eq. (6) for aliphatic hydrocarbons and thus, γ_{H} for cyclopentane is smaller than $\gamma(\text{CH}_2)$. On the other hand, the area A of a single CH_2 group of cyclopentane is smaller than the average area of one carbon group in pentane (calculated from $3A(\text{CH}_2) + 2A(\text{CH}_3)$). In agreement with this, γ_{H} for cyclopentane is higher than for pentane. In spite of this qualitative agreement with Eq. (16), the values do not agree quantitatively. If $\gamma(\text{CH}_2) A(\text{CH}_2)$ is substituted on one side of Eq. (16) and γ_{H} for cyclopentane on the other side, a higher A value is obtained on the surface of the liquid phase than that derived from the bulk density. Thus, the arrangement of the cyclopentane molecules on the surface corresponds to a lower density of CH_2 groups than in the bulk.

It follows similarly for cyclohexane, for which $\gamma_H = 25.24$ (ref.¹⁴) and $\rho = 0.7785$ g/cm³ at 20°C (ref.⁸), that $A = 0.0964$ nm² for one CH₂ group in the bulk, while Eq. (16) gives $A = 0.1118$ nm² on the surface. Substitution of $W_A^2/4\gamma_W^d$ for γ_H according to Eq. (1) and a similar substitution of $[W(\text{CH}_2)]^2/4\gamma_W^d$ for $\gamma(\text{CH}_2)$ converts Eq. (16) to

$$[W(\text{CH}_2)]^2 A(\text{CH}_2) = W_A^2 A. \quad (17)$$

Substitution of the values determined for aliphatic hydrocarbons, i.e., $W(\text{CH}_2) = 49.02$ and $A(\text{CH}_2) = 0.0896$ nm² on the left-hand side of Eq. (17) and $W_A = 48.83$ for cyclohexane (from $\gamma_H = 25.24$ and $\gamma_{WH} = 49.16$, ref.¹⁴) on the right-hand side yields the area of the CH₂ group for cyclohexane at the interface with water, $A = 0.0899$ nm². This is smaller than found for the interface with air or in the bulk of the liquid. Thus, the cyclohexane molecules are more ordered at the interface with water showing an increased density of their CH₂ groups.

It follows from the above that the area of molecules or their groups on the surface or at the interface does not agree with the area calculated from the bulk density. However, $\gamma(\text{CH}_2)$ calculated from Eq. (13) and γ_W^d from Eq. (14) do not depend on the absolute value of $A(\text{CH}_2)$ for aliphatic hydrocarbons, but on the ratio of $A(\text{CH}_3)/A(\text{CH}_2)$. The calculated values remain valid provided that the ratio of $A(\text{CH}_3)/A(\text{CH}_2)$ is the same on the surface or at the interface as in the bulk of the liquid.

Other Theories for the Evaluation of Interactions at the Interface

Similarly as a decrease of γ_W^d with increasing n was found according to the Fowkes Eq. (1) (see Table I), the interaction parameter Φ in the Girifalco and Good equation¹⁵

$$W_A = \gamma_W + \gamma_H - \gamma_{WH} = 2\Phi(\gamma_W\gamma_H)^{1/2} \quad (18)$$

also decreases. If γ_H on the right-hand side of Eq. (18) is replaced by γ_H' from Table I, then constant $\Phi = 0.5120$ for interaction of all hydrocarbons results.

A question may arise whether the deviations of γ_W^d and Φ in Eqs (1) and (18), respectively, are not caused by neglecting the spreading pressure, Π , which changes γ_W to γ_W^* while γ_H remains unchanged. Johnson and Dettre³ found the values of Π from measurements on water in contact with the air saturated with hydrocarbon vapours. They further found that the Antonow rule,

$$\gamma_W^* = \gamma_W - \Pi = \gamma_H + \gamma_{WH}, \quad (19)$$

is valid when a hydrocarbon duplex film is formed on the water surface, i.e., of the given hydrocarbons, only for pentane and hexane. The Π data of Johnson and

Detre for hydrocarbons with $n = 6, 7, 8, 10,$ and 12 can be used to evaluate the equation (at 24.5°C)

$$\log \Pi = a + b/n, \quad (20)$$

which exhibits good linearity (see Table II), while pentane does not fit in. The values of γ_{H} and γ_{WH} in Table I and Eq. (19) can be employed to calculate $\Pi = 6.54$ and $\gamma_{\text{W}}^* = 66.21$ for pentane at 20°C . Similarly, $\Pi = 3.53$ and $\gamma_{\text{W}}^* = 69.22$ for hexane. According to Eq. (20), the dependence of $\log \Pi$ on n based on the values of Jones and Ottewill¹⁶ at 20°C has approximately the same slope, b , as that above found at 24.5°C . Accordingly, this b and Π from Eq. (19) for hexane were employed to recalculate the constant a in Eq. (20) at 20°C , $a = -1.6832$, and the Π values for other hydrocarbons (except for pentane) at 20°C were determined. The corresponding values of $\gamma_{\text{W}}^* = \gamma_{\text{W}} - \Pi$ are given in Table I.

The decrease of γ_{W} to γ_{W}^* also includes the effect of the solubility of hydrocarbons in water. On the other hand, it can be assumed that γ_{H} is not affected by water vapour. Substitution of $W_{\text{A}}^* = \gamma_{\text{W}}^* + \gamma_{\text{H}} - \gamma_{\text{WH}}$ for W_{A} in Eq. (1) does not yield constant $\gamma_{\text{W}}^{\text{d}}$. W_{A}^* and γ_{W}^* in Eq. (18) do not yield constant Φ either. These results show that neither Eq. (1) nor Eq. (18) can be adjusted by using the surface tension of water in equilibrium with the saturated hydrocarbon vapour, γ_{W}^* .

The Dependence of the Surface Free Energy and Its Components on the Temperature

The evaluation was carried out by using the ρ , γ_{H} and γ_{WH} data for hexane, heptane, octane, and nonane at $15-40^\circ\text{C}$ given in Table IV. The data at 20°C agree with those in Table I. For the other temperatures, the γ_{H} values calculated from the slopes $-\text{d}\gamma_{\text{H}}/\text{d}T$ given by Yuk and Jhon¹⁴ were used, the slopes being equal to 0.1022 for hexane, 0.0980 for heptane, and 0.0951 for octane. The average values of γ_{H} for nonane were taken from the literature⁸; they give $-\text{d}\gamma_{\text{H}}/\text{d}T = 0.0941$. The γ_{WH} values according to Aveyard et al.⁵ at some temperatures were completed by using the slope $-\text{d}\gamma_{\text{WH}}/\text{d}T = 0.0890$. The ρ values were taken from the literature⁸. Furthermore, the values of $W_{\text{A}} = \gamma_{\text{W}} + \gamma_{\text{H}} - \gamma_{\text{WH}}$ based on the data in Tables IV and VI were introduced into Eq. (14).

The ρ values were used to evaluate $V(\text{CH}_2)$ and $V(\text{CH}_3)$ from Eq. (6). In all cases, the coefficient of determination, r^2 , is 0.99999 or better. Nonetheless, the values at 20°C differ from those found for the above set of hydrocarbons with $n = 5$ to 16 . The $A(\text{CH}_3)$ and $A(\text{CH}_2)$ values (calculated from the bulk density) and their ratios are given in Table V. Not only do these values increase with the temperature, but also the ratio of $A(\text{CH}_3)/A(\text{CH}_2)$ increases. Table V also gives the ratio of $A(\text{CH}_2)$ at the temperature T to $A(\text{CH}_2)$ at 20°C calculated from Eq. (6) (for the cross sections of the CH_2 group in the bulk of the liquid) as well as from Eq. (16), where the ratio

TABLE IV

Basic values for calculation of the dependence of $\gamma(\text{CH}_2)$ and $\gamma_{\text{W}}^{\text{d}}$ on temperature (ρ in g/cm^3 , γ_{H} and γ_{WH} in mJ/m^2)

T $^{\circ}\text{C}$	Hexane			Heptane			Octane			Nonane		
	ρ	γ_{H}	γ_{WH}	ρ	γ_{H}	γ_{WH}	ρ	γ_{H}	γ_{WH}	ρ	γ_{H}	γ_{WH}
15	0.6639	18.93	51.27	0.6878	20.69	51.68	0.7062	22.12	52.16	0.7216	23.32	52.43
20	0.6595	18.42	50.80	0.6836	20.20	51.23	0.7022	21.64	51.69	0.7174	22.86	51.96
25	0.6550	17.91	50.41	0.6794	19.71	50.79	0.6982	21.16	51.28	0.7138	22.38	51.54
30	0.6505	17.39	49.92	0.6751	19.22	50.34	0.6942	20.69	50.83	0.7099	21.92	51.11
35	0.6459	16.88	49.49	0.6708	18.73	49.90	0.6901	20.21	50.37	0.7061	21.44	50.65
40	0.6412	16.37	49.05	0.6665	18.24	49.49	0.6860	19.74	49.93	0.7023	20.97	50.21

TABLE V

Calculated areas, A (nm^2), and surface free energies, γ (mJ/m^2), of the CH_2 and CH_3 groups in dependence on the temperature

T $^{\circ}\text{C}$	$A(\text{CH}_2)$	$A(\text{CH}_3)$	$A(\text{CH}_3)/$	$A(\text{CH}_2)(T)/A(\text{CH}_2)(20^{\circ})$		a	$\gamma(\text{CH}_2)$	r^2	$\gamma(\text{CH}_2)$ (cor.)	$\gamma(\text{CH}_3)$ (cor.)	a (cor.)
	Eq. (6)	Eq. (6)	$A(\text{CH}_2)$	Eq. (6)	Eq. (16)						
15	0.0889	0.1438	1.6178	0.9977	0.9910	32.53	31.18	0.99998	33.20	16.07	13.73
20	0.0891	0.1447	1.6243	1.0000	1.0000	34.16	30.90	0.99998	32.94	15.87	14.68
25	0.0891	0.1460	1.6385	1.0002	1.0100	35.07	30.59	0.99999	32.68	15.60	15.46
30	0.0892	0.1472	1.6501	1.0011	1.0170	36.74	30.38	1.00000	32.42	15.36	16.34
35	0.0892	0.1484	1.6638	1.0016	1.0266	37.95	30.10	1.00000	32.16	15.11	17.22
40	0.0892	0.1498	1.6789	1.0018	1.0343	39.38	29.87	0.99999	31.90	14.85	18.07

of the cross sections of the CH_2 groups on the surface equals the ratio of $\gamma(\text{CH}_2)$ (20°C)/ $\gamma(\text{CH}_2)$ (T). A comparison of the tabulated values of $A(\text{CH}_2)$ (T)/ $A(\text{CH}_2)$ (20°C) shows that the areas on the surface do not correspond to those in the bulk (as already found above for cyclic hydrocarbons) and increase more rapidly with the temperature than in the bulk. The $\gamma(\text{CH}_2)$ values together with the constants a and coefficients of determination calculated from Eq. (13) in the third approximation are also given in Table V. Table VI lists the results calculated for water as the third approximation according to Eq. (14). For completeness, the known γ_{W} values are appended.

The values of $\gamma_{\text{W}}^{\text{d}}$, $\gamma(\text{CH}_2)$, $A(\text{CH}_2)$, and $A(\text{CH}_3)$ calculated for hydrocarbons in the range of $n = 6-9$ at 20°C are somewhat different from those found for hydrocarbons in the range of $n = 5-16$, which we consider to be more precise even though the r^2 values are lower. However, there are some doubts about the correctness of these results because of the shortcomings mentioned at the end of the section on the oriented arrangement. Moreover, in the previous and in this sections, it has been shown that the area of $A(\text{CH}_2)$ on the surface or at the interface differs from that in the bulk. The results calculated from Eqs (13) and (14) do not depend on the actual values of $A(\text{CH}_3)$ and $A(\text{CH}_2)$ but they depend on their ratio, $A(\text{CH}_3)/A(\text{CH}_2)$. It can be assumed that not only $A(\text{CH}_2)$ on the surface is larger than in the bulk but that $A(\text{CH}_3)$ increases on the surface more than $A(\text{CH}_2)$. If we anticipate the ratio of $A(\text{CH}_3)/A(\text{CH}_2)$ to be $4/3$ times higher on the surface than in the bulk we obtain from Eq. (13) for the set of C_5-C_{16} hydrocarbons at 20°C $\gamma(\text{CH}_2) = 32.94$ and $a = 14.68$. We see that this change of the $A(\text{CH}_3)/A(\text{CH}_2)$ ratio causes a moderate increase of $\gamma(\text{CH}_2)$ but a significant decrease of a . Using this $\gamma(\text{CH}_2)$ and the increased ratio of $A(\text{CH}_3)/A(\text{CH}_2)$ in Eq. (12), we obtain $\gamma(\text{CH}_3) = 15.87$ which corresponds to the estimate from the spreading pressure given at the end of the section on the random arrangement. Furthermore, the latter $\gamma(\text{CH}_2)$ and $A(\text{CH}_3)/A(\text{CH}_2)$ values in Eq. (14) give $\gamma_{\text{W}}^{\text{d}} = 19.09$ and $a = 5.85$.

TABLE VI

Values calculated from Eq. (14) at various temperatures

$T, ^\circ\text{C}$	γ_{W}	a	$\gamma_{\text{W}}^{\text{d}}$	r^2	$a(\text{cor.})$	$\gamma_{\text{W}}^{\text{d}}(\text{cor.})$	$\gamma_{\text{W}}^{\text{n}}(\text{cor.})$
15	73.49	17.98	19.58	0.99987	5.57	19.50	53.99
20	72.75	18.90	19.24	0.99985	5.85	19.09	53.66
25	71.97	19.42	18.85	0.99985	6.23	18.68	52.39
30	71.18	19.69	18.36	0.99987	7.04	18.27	52.91
35	70.37	20.55	17.99	0.99990	7.18	17.86	52.51
40	69.56	21.31	17.56	0.99989	7.68	17.45	52.11

From the $\gamma(\text{CH}_2)$ data in Table V, the slope $-\text{d}\gamma(\text{CH}_2)/\text{d}T = 0.0522$ was determined and used with the above $\gamma(\text{CH}_2) = 32.94$ at 20°C to calculate the corrected values, $\gamma(\text{CH}_2)$ (cor.). The $\gamma(\text{CH}_3)$ (cor.) values corresponding to the $\gamma(\text{CH}_2)$ (cor.) were calculated from Eq. (12) with the increased ratio of $A(\text{CH}_3)/A(\text{CH}_2)$. Furthermore, a (cor.) values were determined from Eq. (13). All these values are given in Table V.

Similarly, the $\gamma_{\text{w}}^{\text{d}}$ (cor.) values in Table VI were calculated from the slope $-\text{d}\gamma_{\text{w}}^{\text{d}}/\text{d}T = 0.0820$. The respective non-dispersion component of the surface free energy, $\gamma_{\text{w}}^{\text{n}}$ (cor.) = $\gamma_{\text{w}} - \gamma_{\text{w}}^{\text{d}}$ (cor.), and a (cor.), are also given there.

It follows from Eq. (10) that the number of CH_3 groups and thus also their overall area on the surface of the liquid phase and at the interface with water increase more steeply with decreasing number of C atoms in the chain than in the case of their random arrangement. The smaller is the molecule, the more easily it can orient so that its CH_3 groups lie preferentially at the interface. Values of a from Eqs (13) and (14) (see Tables V and VI) indicate that the orientation of the CH_3 groups toward the interface is greater for the interface with air than with water. This is because the water molecules interact better with the CH_2 than with CH_3 groups, causing a change in the arrangement at the interface with water and a decrease in the number of CH_3 groups with respect to that on the surface. The magnitude of the interaction is reflected in the work of adhesion which equals $W(\text{CH}_2) = 50.15$ and $W(\text{CH}_3) = 34.81$ (at 20°C) according to Eq. (1).

As shown in Tables V and VI, the values of a in Eqs (13) and (14) increase with increasing temperature. It could be expected that a higher temperature would decrease the molecular orientation, but an opposite effect predominates. This effect may be caused by an easier orientation on the surface and by a steeper decrease of $W(\text{CH}_2)$ in comparison with $W(\text{CH}_3)$ at the interface with water. The relative areas of the surface and of the interface with water occupied by CH_3 groups according to equation

$$A(\text{CH}_3) \text{ (rel.)} = A'(\text{CH}_3)/(A'(\text{CH}_3) + A'(\text{CH}_2)), \quad (21)$$

in which

$$A'(\text{CH}_3) = (2 + a(\text{cor.})/n) (4/3) A(\text{CH}_3)$$

and

$$A'(\text{CH}_2) = (n - 2 - a(\text{cor.})/n) A(\text{CH}_2),$$

are given in Table VII. Although the actual increase of the ratio $A(\text{CH}_3)/A(\text{CH}_2)$ on the surface and at the hydrocarbon-water interface with respect to the bulk is not known, we may assume that the values in Table VII illustrate the changes in the orientation of molecules to a reasonable approximation. It should be noted that $(4/3) A(\text{CH}_3)/A(\text{CH}_2) = 2.14$ leads to a plausible value of $\gamma(\text{CH}_3)$ and it is similar to the ratio of the areas used by Aveyard⁶ (2.20).

TABLE VII

Relative areas occupied by CH_3 groups of hydrocarbon molecules oriented on the surface (OS) and at the interface (OI) and of randomly arranged hydrocarbon molecules (RA) at various temperatures

T °C	Hexane			Heptane			Octane			Nonane		
	OS	OI	RA	OS	OI	RA	OS	OI	RA	OS	OI	RA
15	0.844	0.673	0.519	0.738	0.589	0.463	0.652	0.523	0.418	0.581	0.470	0.381
20	0.861	0.680	0.520	0.753	0.596	0.464	0.666	0.529	0.419	0.594	0.475	0.382
25	0.875	0.691	0.522	0.767	0.606	0.466	0.679	0.538	0.421	0.606	0.483	0.384
30	0.891	0.712	0.524	0.782	0.623	0.468	0.692	0.553	0.423	0.618	0.496	0.386
35	0.905	0.717	0.526	0.796	0.628	0.470	0.705	0.557	0.425	0.631	0.500	0.388
40	0.919	0.730	0.528	0.809	0.640	0.472	0.718	0.568	0.427	0.642	0.510	0.390

REFERENCES

1. Kloubek J.: Collect. Czech. Chem. Commun. 52, 271 (1987).
2. Fowkes F. M.: Ind. Eng. Chem. 46, 40 (1964).
3. Johnson R. E. jr, Dettre R. H.: J. Colloid Interface Sci. 21, 610 (1966).
4. Gillap W. R., Weiner N. O., Gibaldi M.: J. Am. Oil Chem. Soc. 44, 71 (1967).
5. Aveyard R., Briscoe B. J., Chapman J.: J. Chem. Soc., Faraday Trans. 1, 68, 10 (1972).
6. Aveyard R.: J. Colloid Interface Sci. 52, 621 (1975).
7. Wu S.: J. Polym. Sci., C 34, 19 (1971).
8. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, New York, 1950.
9. Lange H.: Kolloid Z. 182, 123 (1962).
10. Padday J. F., Uffindell N. D.: J. Phys. Chem. 72, 1407 (1968).
11. Grubb S. G., Kim M. W., Rasing Th., Shan Y. R.: Langmuir 4, 452 (1988).
12. Ruckenstein E., Sang Hwan Lee: J. Colloid Interface Sci. 120, 153 (1987).
13. Sang Hwan Lee, Ruckenstein E.: J. Colloid Interface Sci. 120, 529 (1987).
14. Yuk S. H., Jhon M. S.: J. Colloid Interface Sci. 116, 25 (1987).
15. Girifalco L. A., Good R. J.: J. Phys. Chem. 61, 904 (1957).
16. Jones D. C., Ottewill R. H.: J. Chem. Soc. 1955, 4076.

Translated by the author.