Interfacial Properties of Hydrocarbons

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Abstract

The interfacial tension of aliphatic hydrocarbon-water systems has been found to increase in a linear fashion as a function of the log of hydrocarbon chain length. Contrary to the literature, values of ϕ and $\gamma\ H_2^dO$ were observed to be also dependent on hydrocarbon chain length. The relationship between hydrocarbon chain length and interfacial tension is actually opposite to that predicted by Antonow's rule. The results are discussed in terms of hydrocarbon-water interaction and water-structure at the interface.

Introduction

PRESENT KNOWLEDGE of the properties of the oil-water interface is meager by comparison with knowledge of the air-water surface. This situation has limited our understanding of a number of biological phenomena. Generally, studies on the adsorption properties of compounds at oil-water interfaces do not take into consideration possible differences in the interfacial tensions between water and the various oils employed. It has been widely accepted that the interfacial tensions of liquid aliphatic hydrocarbons against water approximate 50 dynes/cm. However, a review of the literature indicates that these values display a poor constancy but vary from 48 to 53 dyne/cm with no apparent relationship between chain length and interfacial tension (1–5). The possible inclusion of trace impurities in the oil phase, as well as the greater sensitivity to these impurities of interfacial tension values of liquid-liquid interfaces, by comparison to liquid-air surfaces, has doubtless contributed to the heterogeneity of data. Unforunately, different members of the aliphatic hydrocarbon series have been used in adsorption studies of given compounds by various workers (6–10), thereby creating difficulty in comparing their individual results.

Antonow (11), was the first to propose a specific relationship which allows one to calculate interfacial tension values in systems where the surface tensions of the individual liquids are known. Antonow's rule may be expressed as

$$\gamma_{12} = |\gamma_1 - \gamma_2|, \qquad [1]$$

where γ_{12} is the interfacial tension and γ_1 and γ_2 are the surface tensions of the mutually saturated liquids. This relation may be applied only when the spreading coefficient is zero, and its general use to obtain even approximate interfacial tension values may result in significant error.

Recently, Girifalco and Good (2), developed the following equation,

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\phi(\gamma_1\gamma_2)^{1/2}, \qquad [2]$$

where ϕ is a constant for each system. The value of ϕ may be calculated from molar volume data or from surface and interfacial tension values since,

$$\phi = \frac{4\ V_1^{1/3}V_2^{1/3}}{(V_1^{1/3} + V_2^{1/3})^2} = -\frac{\Delta\ F_{12}^{a}}{(\Delta F_1^{c}\Delta F_2^{c})^{1/2}} \qquad [3]$$

In Eq. 3, V is the molar volume, ΔF^a is the free energy of adhesion (corresponding to $\gamma_{12} - \gamma_1 - \gamma_2$), and ΔF^c is the free energy of cohesion for phase i (corresponding to $2\gamma_i$).

More recently, Fowkes (4), has suggested that interfacial tension can be resolved into two force components, d and h, corresponding respectively to van der Waal or dispersion attractive forces, and hydrogen bonding forces, i.e.,

$$\gamma = \gamma^d + \gamma^h \qquad [4]$$

Fowkes further suggested that the total surface energy of hydrocarbons, as well as the interactions between water and hydrocarbons, is primarily attributable to dispersion forces.

If the dispersion forces acting between the unlike molecules in the interfacial region can be predicted from the geometric mean of the dispersion force components of the hydrocarbon and water, the Girifalco-Good equation can be expressed as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d\gamma_2^d)^{1/2} \qquad [5]$$

From experimentally determined surface tension and interfacial tension values, Fowkes (4), calculated that γ^d of water was a constant equal to 21.8 dynes/cm. Interestingly, both Girifalco and Good (2), and Becher (3), utilizing Eq. 2, reported a value for ϕ of 0.55 for the hydrocarbon-water systems tested, with the exception of the tetradecane-water system reported by Girifalco and Good.

Data obtained in our laboratory, as well as those recently reported by Aveyard and Haydon (12), indicate that values of γH_2^dO and ϕ are not constant but vary in a regular manner with respect to the chain length of the hydrocarbon. In addition, we have found experimentally that the relationship between hydrocarbon chain length and interfacial tension values against water is opposite to that predicted by Antonow's rule. It is the purpose of this report to present these data and to consider the existing relationships between surface and interfacial tensions in the light of these new data.

TABLE I
Surface Tension and Interfacial Tension Values for Hydrocarbon-Water Systems

	Surface tension (dynes/cm)			Interfacial tension (dynes/cm)			
	Before purification	After purification	After equilibration	Before purification	After purification	After equilibration	Calculated by Eq. 1
Water	72.5	72.0	72.0	......	......	......	.....
Hexane	18.3	18.4	18.5	49.0	49.4	49.5	53.5
Octane	21.4	21.5	21.6	48.4	50.3	50.2	50.4
Decane	24.0	23.7	23.8	49.6	51.1	50.8	48.2
Dodecane	25.3	25.3	25.4	48.8	51.8	51.5	46.6
Tetradecane	26.4	26.5	26.6	50.3	52.2	51.9	45.4
Hexadecane	27.2	27.6	27.6	49.6	52.6	52.4	44.4

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TABLE II

Work of Cohesion, Work of Adhesion and Spreading Coefficients for the Various Hydrocarbons on Water

	W_c	W_a	S
Hexane	36.8	40.9	+4.1
Octane	43.0	43.3	+0.3
Decane	47.4	44.9	−2.5
Dodecane	50.6	45.8	−4.8
Tetradecane	53.0	46.6	−6.4
Hexadecane	55.2	47.2	−8.0

Experimental

Fractionally distilled, demineralized water was used in all experiments. The hydrocarbons, hexane, octane, decane, dodecane, tetradecane, and hexadecane, were purchased from Eastman Organic Chemicals. They were purified according to the method of Weiner et al. (13) and repeatedly passed through an alumina-silica gel column until constant interfacial tension values against water were obtained. The surface tension value of each hydrocarbon, after purification, agreed with reported data (14,15).

Interfacial tension measurements were made using mutually saturated liquids which were equilibrated about 72 hr after mixing. Interfacial tension was determined by the Wilhelmy plate method (11); a thin, roughened platinum plate was used to insure complete wetting of the plate. In order to compensate for buoyancy effects, the plate was routinely adjusted as close to the interface as possible before interfacial tension measurements were made. The buoyancy corrections were then found to be less than 0.02 dynes/cm as determined experimentally according to the method of Ruyssen (16). Measurements were also made by the drop volume method (13). In all cases, the interfacial tension values found by each method agreed to within 0.1 dyne/cm. All determinations were carried out at 25 ± 0.1C.

The ability of each of the hydrocarbons to spread on water was determined by carefully placing a drop of the hydrocarbon in the center of a pie plate filled with water at 25C. An overhead film projector was used to aid in the visualization of the extent of spreading.

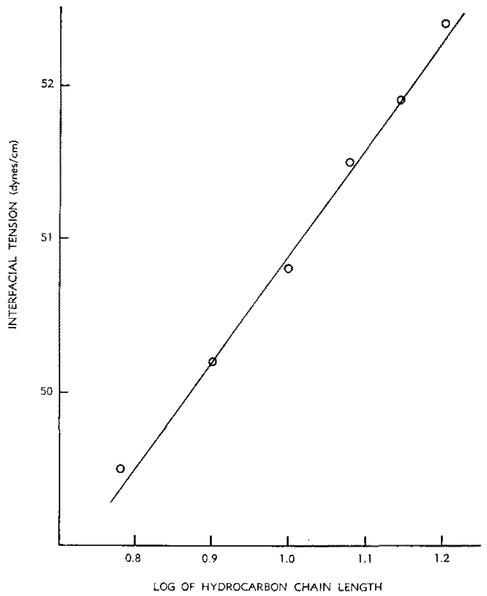

FIG. 1. Relationship between hydrocarbon chain length and interfacial tension.

Results

The data for the surface and interfacial tension measurements before and after purification are summarized in Table I. It should be noted that while surface tension values of the hydrocarbons vary only slightly before and after purification, the interfacial tension values are markedly affected. Comparison of columns 6 and 7 of Table I indicates the wide divergency between interfacial tension values calculated by means of Antonow's rule and those obtained experimentally. The relationship between chain length of the hydrocarbon and interfacial tension is demonstrated in Fig. 1. Aveyard and Haydon (12) reported interfacial tension values slightly higher than those obtained in our laboratory, but both sets of data gave identical slopes.

Table II shows the work of cohesion (W_c), work of adhesion (W_a) and the initial spreading coefficient (S), calculated for each of the hydrocarbons. These values were obtained using the following equations:

$$W_c = 2\gamma_1, \quad [6]$$

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12}, \quad [7]$$

$$\text{and } S = W_a - W_c, \quad [8]$$

where the subscripts 1 and 2 refer to the hydrocarbon and water, respectively. The relationship between W_a, W_c, and S, and hydrocarbon chain length is depicted in Fig. 2.

A positive value of S indicates that the oil should spread on the water surface. Experimentally, it was found that hexane spread rapidly, octane spread less rapidly and quickly retracted to form a lens, but the remainder of the hydrocarbons failed to spread.

By means of Eqs. 2 and 5 values of ϕ and γH_2^0O were calculated for each hydrocarbon. These data are plotted as a function of hydrocarbon chain length in Fig. 3. The significant dependence of both ϕ

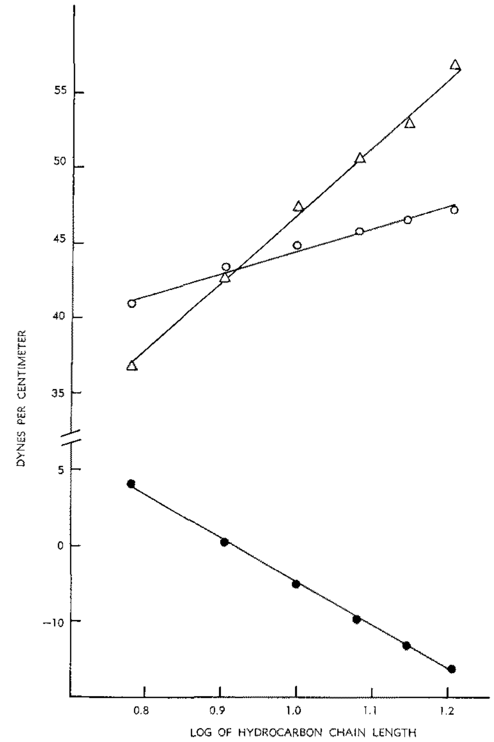

FIG. 2. Work of adhesion (○); work of cohesion (Δ) and spreading coefficient (●) plotted as a function of log hydrocarbon chain length.

and γH_2^dO on chain length is apparent. Recalculation of the Girilfalco and Good data to extend the values of ϕ to three decimal places also indicates a reduction of ϕ with increasing chain length, with the exception of the hexane value. It should be noted that the data suggest a similar trend of increasing interfacial tension values with increasing chain length, again with the exception of hexane.

Discussion

Various physical constants of hydrocarbons, such as surface tension and density, are proportional to the hydrocarbon chain lengths (17). Therefore, it seems surprising that interfacial tension values of hydrocarbons against water, as reported in the literature prior to this investigation, have shown no such relationship. The simplified models of the hydrocarbon-water interface (2,4), devised to explain the chain length independent interfacial properties of hydrocarbons, are hardly applicable. In order to explain the present results a more complex model of the interface must be proposed.

Fortunately, the investigations of Drost-Hansen (18) permitted examination of our data within the framework of a more realistic interfacial model. Drost-Hansen has proposed that the oil-water interface displays considerable structure consisting of clusters or "cages" of water molecules which may serve as "binding sites" for the molecules of oil (hydrocarbon) at the interface. The greater the extent of this interaction, the lower the interfacial tension.

Solubility studies of hydrocarbons in water suggest that hydrocarbon-water interactions involve two processes, hydrophobic hydration and hydrophobic bonding (19). When a hydrocarbon is placed in the bulk it will tend to be incorporated by clusters of water molecules and actually stabilize the cluster. This phenomenon is termed hydrophobic hydration. However, because of van der Waal's attractive forces there is also a strong attractive tendency between the hydrocarbon molecules. This latter process, hydrophobic bonding, is further favored by the large entropy gain in breaking water clusters. Hydrophobic bonding accounts for the very poor solubility of hydrocarbons in water and plays an important role in micelle formation by various compounds. Both hydrophobic hydration and hydrophobic bonding are enhanced by increasing chain length. However, the latter is far more sensitive to changes in chain length and, therefore, solubility decreases with increasing hydrocarbon chain length.

It is proposed that at the interface an analogous situation exists. The hydrocarbon molecules have a tendency to interact and stabilize the water clusters while at the same time tend toward self-interaction and disruption of water clusters. The latter effect becomes more and more significant at increasing chain length and accordingly interfacial tension increases as a function of chain length.

The apparent similarity of bulk and interfacial hydrocarbon-water interaction is further illustrated by considering the spreading coefficient data. As shown in Fig. 2, spreading coefficient decreases with increasing chain length. This decrease results from a cross-over of the work of adhesion (W_a) and work of cohesion (W_c) curves, also depicted in Fig. 2. Although both W_a and W_c increase with increasing chain length, the work of cohesion increases at a much faster rate than the work of adhesion. Since W_c is indicative of the cohesive forces of the hydrocarbons, whereas W_a is a function of the adhesive forces between the hydrocarbons and water, the data may be explained in the following manner. As the chain length of the hydrocarbon increases, hydrophobic bonding at the interface increases to such an extent that the ability of the hydrocarbon molecules to interact with interfacial water clusters diminishes in proportion to their chain length. This decreased interaction is reflected by the increased interfacial tension values.

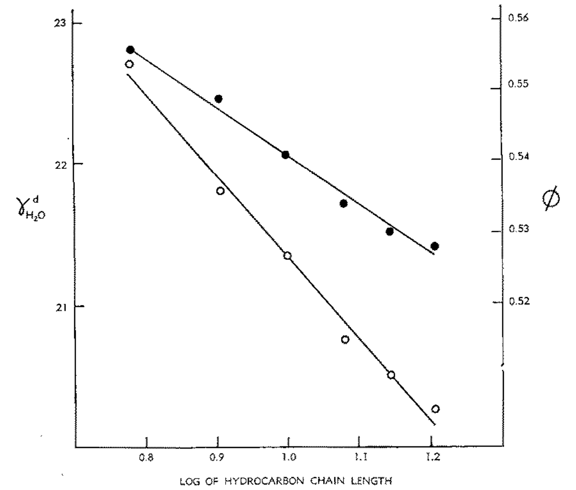

FIG. 3. Relationship between γH_2^dO (○, left scale) and Ø (●, right scale), and hydrocarbon chain length.

The existence of a complex interfacial region is further supported by the relation of ϕ and γH_2^dO to hydrocarbon chain length, shown in Fig. 3. Whereas the linearity may be merely fortuitous, the fact that both ϕ and γH_2^dO are dependent upon chain length denotes the lack of simplicity of the hydrocarbon-water interface.

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