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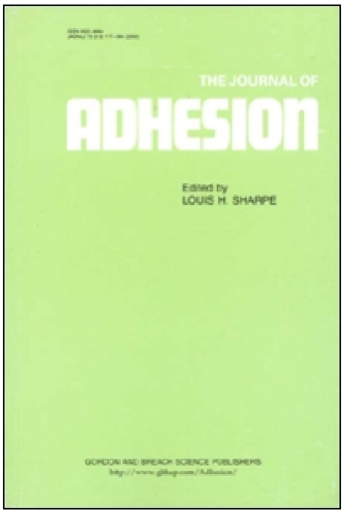

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On a Theory of Interfacial Tension

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The hypothesis, according to which the forces across the interface between a dipole liquid and a liquid free of permanent dipoles are determined only by the dispersion (London) components, contradicts a basic equation of electrodynamics and the present knowledge of molecular interactions, and is not supported by observations on interfacial tension.

The Journal of Adhesion published two papers[1,2] based on the concept (fashionable at present) that the interfacial tension γ_i between a dipole liquid and an immiscible liquid free of dipoles is determined by the dispersion component of the intermolecular forces only; in the following this assumption is denoted as segregation hypothesis. Lord Rayleigh[3] showed that, *if* the force F exerted by a molecule is a universal function of the distance r from the molecule, then

$$\gamma_i = \gamma_1 + \gamma_2 - 2(\gamma_1\gamma_2)^{0\cdot5} \qquad (1)$$

If the segregation hypothesis is accepted, equation

$$\gamma_i = \gamma_1 + \gamma_2 - 2(\gamma_1^d\gamma_2^d)^{0\cdot5} \qquad (2)$$

results[4]; γ_1^d is that part of the surface tension γ_1 of the first liquid which can be attributed to London dispersion forces and γ_2^d is the analogous component of the surface tension γ_2 of the second liquid.

The rationale of Eqs. (1) and (2) may be stated in qualitative terms. When the interface between the two liquids increases by unit area, molecules of liquid 1 have to move from the bulk to the boundary exactly as when the second phase is the vapor of 1 rather than liquid 2; thus γ_i has a term equal to γ_1. An analogous remark applies obviously to liquid 2, whence γ_2 appears in the equation. But the molecules of liquid 1, when they move toward the interface, are attracted by the molecules of liquid 2, and this attraction is stronger than that of the "rare" vapor; hence, the correction term $-2(\gamma_1\gamma_2)^{0\cdot5}$ is negative. Usually,[5] the attraction constant a_{12} in the van der Waals equation for a mixture of two gases is approximately equal to $(a_1a_2)^{0\cdot5}$, a_1 and a_2 being the van der Walls constants for the individual gases. By analogy, it was assumed that the attraction across the interface was proportional to $(\gamma_1\gamma_2)^{0\cdot5}$; as mentioned above, a stricter proof was given by Rayleigh for the systems in which the function f in the equation $F = f(r)$ was independent of the nature of the two liquids. However, if the dipoles (and ions) of liquid 1 have no effect on the molecules of liquid 2 (which carry no permanent dipole), then, it is argued, the product $\gamma_1^d\gamma_2^d$ should be substituted for $\gamma_1\gamma_2$. Since liquid 2 is nonpolar, γ_2^d may be set equal to γ_2; thus Eq. (2) has only one unknown (namely γ_1^d) and this thus can be calculated.

That the segregation hypothesis is incorrect, can be shown by at least two reasonings.

(a) All intermolecular forces known at present are of the electromagnetic nature. A fundamental equation of electricity is $F = Ee$; the force F on a charge e is equal to the product of e and the field intensity E. At a given moment at a given place, there is only one value of this intensity. An electron in liquid 2 (nonpolar) is at any time acted upon by a force proportional to the local E, and this E is the result of all charges (and their motions) within the "sphere of molecular action". The segregation hypothesis is equivalent to assuming that the above electron knows, what part of the real E is caused by permanent dipoles and can refuse to follow the corresponding fraction of the total force. In a field of 1 volt/cm, the electron would be affected by only 0.5 volt/cm if one half of the field intensity is a result of the permanent dipoles present in liquid 1. If this assumption were justified, the whole science of electricity would have to be scrapped.

(b) As mentioned above, the van der Waals constant a_{12} of a binary gas mixture is approximately equal to $(a_1a_2)^{0\cdot5}$. If the segregation hypothesis is adopted, then the a_{12} of a mixture of a polar (1) and a nonpolar (2) gas would be expected to be equal to $(a_1^d a_2)^{0\cdot5}$; a_1^d is the dispersion part of a_1. This conclusion is refuted by measurements. Thus, $a_{12} \approx (a_1a_2)^{0\cdot5}$ for the mixtures of polar sulfur dioxide (dipole moment 1.6×10^{-18} e.s.u.) with nonpolar hydrogen or nitrogen[6]. The accuracy of Berthelot's equation is approximately equal for the pair "carbon dioxide plus carbon disulfide" (both nonpolar) and the pair "carbon dioxide plus water".[7]

A semi-theoretical treatment of the forces between a permanent dipole and a nonpolar molecule was attempted by Stockmayer[8,9]. Represent the second virial coefficient B of the gas mixture as a function of temperature T in the form $B(T) = B_0 - (A/RT)\,e^{D/T}$, A and D being two constants. The theory shows that A can be formulated as $A = A_0 + A_p$ and D as

$D = D_0 + D_p$; A_0 and D_0 depend only on intermolecular forces common to all molecules, and A_p and D_p differ from zero only if the molecules are polar. It is seen here, how far the segregation is justifiable. The constants A and D may be represented as sums of polar and nonpolar terms, but the second virial coefficient itself depends on both and cannot be split.

It should be realized that "the distinction between the various types of forces is somewhat fictitious and actually leads to serious difficulties when we try to obtain the total force by combining the short-range and the long-range forces. . . ." (Ref. 9, p. 917). This simply means that an electron feels only the total field E and cannot analyze it in its component parts.

Two papers published when the first draft of this note had already been completed seem to be in agreement with the above criticism. In one[10], an attempt was made to calculate interfacial tension from the theories of molecular forces and the conclusion reached that "in principle we cannot obtain γ_2^d from experiments on surface and interfacial tensions only".

In the second paper the segregation concept was employed to calculate the polar term of the hypothetical surface tension of some solid polymers, and in several instances negative values have been obtained; this unexpected result also lends no support to the above concept.[11]

A hypothesis contradicting many cherished ideas still may be convincing if it accounts for experimental facts that cannot be explained by the older theories. No such fact exists as far as interfacial tension is concerned. Testing of the segregation hypothesis by means of experimental data is clearly unfavorable to it. For instance,[4] the γ_1^d of water was calculated from the interfacial tensions γ_i between water and eight hydrocarbons (for which γ_2^d was assumed to be equal to γ_2). The intention was to show that γ_1^d (a property of water only) remained constant when γ_i varied. In reality, the spread of the γ_1^d values is 0.087 of the mean γ_2^d and the spread of the γ_i values is 0.039 of the mean γ_i. Thus the experimental result is that, contrary to prediction, the dispersion component of the force exerted by water depends on the hydrocarbon, while the interfacial tension γ_i between hydrocarbons and water is *independent of the nature of the former*. It must be added, however, that γ_i in these systems is not suitable for testing the hypothesis because it depends above all on the miscibility between the two phases[12] which is not considered in the theory.

The miscibility probably is less important for the γ_i between mercury and many common liquids. The dipole moment of water is only by about 7% greater than that of lower aliphatic alcohols but the number of dipoles *in unit volume of water is about five times that in unit volume* of 2-methylpropanol. Thus, it would be predicted that Eq. (2) would not be applicable to the interface of water and mercury at all but would be less in error for the pair of mercury and 2-methylpropanol. The opposite behavior is found in the experimental data: the γ_i of the mercury–water boundary quantitatively agrees with Eq. (2) but the γ_i of Hg–C_4H_9OH is too small by 29 dyn/cm.

It is not worth while to start from a hypothesis which contradicts our fundamental knowledge of electricity and molecular forces and to reach, finally, a conclusion which is refuted by interfacial tension data.

No doubt, the interaction between permanent dipoles and ions in one phase and nonpolar molecules in another phase in many systems is smaller than the dispersion forces between the two liquids (see, for instance, Ref. 10); but it should be ascertained in every instance whether the difference is great enough for the former interaction to be neglected.

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