
COMMENTS ON THE ANTONOW AND INTERFACIAL INTERACTION RULES

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Results presented for the aliphatic hydrocarbon-water interface show that the recent hypothesis of the free energy minimization called interfacial interaction rule, which was suggested as a theoretical base of the Antonow rule, cannot be generally valid.

Basing on the idea of minimization of the free energy at the interfaces between two liquids, Lipatov and Feinerman¹ suggested the hypothesis that the work of adhesion, W_{12} , between the liquid phases 1 and 2, with the respective surface tensions $\gamma_1 > \gamma_2$, equals the work of cohesion of the phase with the lower value of the surface tension, i.e.,

$$W_{12} = W_{22} \quad (1a)$$

The thermodynamic work of adhesion is given by the Dupré equation

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \quad (2a)$$

and, for the work of cohesion of the phase 2, the relation

$$W_{22} = 2\gamma_2 \quad (3a)$$

is generally accepted. Substitution of Eqs (2a) and (3a) into Eq. (1a) yields the relation

$$\gamma_{12} = \gamma_1 - \gamma_2 \quad (4a)$$

which has been suggested by Young² and later mentioned by other authors³⁻⁶. Antonow then promoted the hypothesis⁷⁻⁹ that for partially soluble liquids, which are mutually saturated and have the surface tensions $\gamma_{1s} > \gamma_{2s}$, the equation

$$\gamma_{12} = \gamma_{1s} - \gamma_{2s} \quad (4b)$$

is valid. This is known as the Antonow rule and it is mentioned in most monographs and manuals on surface chemistry.

For a saturated liquid 2 with the surface tension γ_{2s} , it may be assumed that its work of cohesion is

$$W_{22s} = 2\gamma_{2s} \quad (3b)$$

and, in accord with Eq. (1a),

$$W_{12s} = W_{22s} \cdot \quad (1b)$$

Feinerman and Lipatov¹⁰ called Eqs (1b) and (4b) (together with Eqs (1a) and (4a) for mutually insoluble liquids) the interfacial interaction rule.

Some authors¹¹⁻¹³ tried to prove the validity of Eq. (4b), but others¹⁴⁻¹⁷ showed examples demonstrating its invalidity. Therefore, it could be considered only as an approximation with many exceptions¹⁸ and with no theoretical foundations¹⁹. However, the deviations from Eqs (4a) and (4b) were qualitatively elucidated^{10,15} by an orientation and a density change of molecules at the interface. The change in the arrangement of molecules should affect the attractive force with which one phase interacts with the other. Furthermore, the hypothesis of minimization^{1,10} according to Eqs (1a) and (1b) should be a theoretical base substantiating Eqs (4a) and (4b). Unfortunately, the authors did not support their hypothesis by an evaluation of the molecular orientation and its influence on the surface and interfacial tensions. Only recently, the data evaluating quantitatively the orientation of aliphatic hydrocarbons at the interfaces with air and water have been published²⁰ and they will be used in this paper to check the hypothesis of the energy minimization called the interfacial interaction rule. This is also important for judging whether the method for the surface free energy determination of solids, γ_s , based on the validity of the Antonow rule, is correct. Elton²¹ substituted the interfacial tension at the solid-liquid interface, γ_{SL} , from the equation

$$\gamma_{SL} = \gamma_L - \gamma_s \quad (4)$$

(for $\gamma_L > \gamma_s$) into the Young equation

$$\gamma_s = \gamma_L \cos \Theta + \gamma_{SL} \quad (5)$$

and thus he obtained the relation

$$\gamma_s = \gamma_L(1 + \cos \Theta)/2 \quad (6)$$

which makes it possible to calculate γ_s from the surface tension of liquids, γ_L , and from their contact angle on solids, Θ . The same method is recommended by Lipatov and Feinerman¹.

RESULTS AND DISCUSSION

The thermodynamic work of adhesion is given by the difference between the initial and final states of the free energies, Eq. (2a). If the liquids are mutually soluble we can distinguish two stages of the work of adhesion, namely

$$W_{12} = W_s + W_{12s}, \quad (7a)$$

where the free energy difference on the surfaces resulting from mutual saturation of both adjoining phases is

$$W_s = \gamma_1 + \gamma_2 - \gamma_{1s} - \gamma_{2s} \quad (8)$$

and the work of adhesion of the saturated phases is

$$W_{12s} = \gamma_{1s} + \gamma_{2s} - \gamma_{12}. \quad (2b)$$

While the sum of Eqs (2b) and (8) is identical with the Dupré equation (2a) we can also consider the work of adhesion as the second step (2b) alone.

If, in addition to the saturation, an orientation of molecules at the interface takes place we can write

$$W_{12} = W_s + W_o + W_{12o} \quad (7b)$$

where W_s is given by Eq. (8), the work of orientation is

$$W_o = \gamma_{1s} + \gamma_{2s} - \gamma_{1so} - \gamma_{2so} \quad (9)$$

and the net adhesion is

$$W_{12o} = \gamma_{1so} + \gamma_{2so} - \gamma_{12}. \quad (2c)$$

Joining Eqs (2c) and (9) we obtain Eq. (2b).

Thus, we have three equations to express the work of adhesion. Similarly, we have also three equations for the work of cohesion. In addition to Eqs (3a) and (3b), we should consider that the surface tension of the oriented layer, γ_{2o} , differs from the force in the bulk involving randomly arranged molecules, γ_{2b} , so that for oriented molecules we write

$$W_{22o} = 2\gamma_o \quad (3c)$$

which, however, is not the true work of cohesion but a term used to express the condition of the energy minimization only. Also, the measured values of γ_2 or γ_{2s} refer to the arrangement of molecules at the liquid-air interface and, therefore, neither Eq. (3a) nor Eq. (3b) are valid if orientation of surface molecules takes place. In such

a case, the actual work of cohesion equals^{22,23}

$$W_{22b} = 2\gamma_{2b} . \quad (3d)$$

Furthermore, Eq. (3b) need not give the actual work of cohesion even if no orientation takes place because the solute concentration in the bulk can be lower than in the surface layer (the solute is surface active). Nevertheless, even when W_{22s} is not the work of cohesion it may represent the condition of the energy minimization.

Finally, to complete the minimization hypothesis, we should add the equation

$$W_{12o} = W_{22o} \quad (1c)$$

in which W_{22o} need be identical neither with W_{22} according to equation (3a) nor with W_{22s} according to Eq. (3b) because the orientation of molecules at the liquid–liquid interace may differ from the interface liquid–air²⁰.

To apply the above ideas to the aliphatic hydrocarbons (H)–water (W) interfaces we should note that the surface tension of hydrocarbons, γ_H , is not changed by the influence of water solubility while the surface tension of water decreases to γ_{ws} due to the solubility of hydrocarbons. Furthermore, we assume that molecules of water do not take any oriented position while the reorientation of hydrocarbons changes their γ_H at the interface liquid–air to γ_{Ho} at the interface hydrocarbon–water²⁰. The cohesion forces in the bulk correspond to the term $2\gamma_{Hb}$ (refs^{22,23}). Accordingly, we can rewrite the above equations as

$$W_{WH} = \gamma_w + \gamma_H - \gamma_{WH} \quad (2a')$$

$$W_{WHs} = \gamma_{ws} + \gamma_H - \gamma_{WH} \quad (2b')$$

$$W_{WHo} = \gamma_{ws} + \gamma_{Ho} - \gamma_{WH} \quad (2c')$$

$$W_{WHb} = \gamma_{ws} + \gamma_{Hb} - \gamma_{WH} \quad (2d')$$

and

$$W_{HH} = 2\gamma_H \quad (3a') = (3b')$$

$$W_{HHo} = 2\gamma_{Ho} \quad (3c')$$

$$W_{HHb} = 2\gamma_{Hb} . \quad (3d')$$

Furthermore, to check the minimization hypothesis, we evaluate the following deviations Δ from Eqs (1a)–(1d).

$$\Delta_a = W_{WH} - W_{HH} = \gamma_w - \gamma_H - \gamma_{WH} \quad (10a)$$

$$\Delta_b = W_{WHs} - W_{HH} = \gamma_{ws} - \gamma_H - \gamma_{WH} \quad (10b)$$

$$\Delta_c = W_{\text{WHo}} - W_{\text{HHo}} = \gamma_{\text{Ws}} - \gamma_{\text{Ho}} - \gamma_{\text{WH}} \quad (10c)$$

$$\Delta_d = W_{\text{WHb}} - W_{\text{HHb}} = \gamma_{\text{Ws}} - \gamma_{\text{Hb}} - \gamma_{\text{WH}} \quad (10d)$$

The data at 20°C used for the evaluation were already published elsewhere^{20,22}; they are summarized in Table I ($\gamma_{\text{w}} = 72.75 \text{ mJ/m}^2$). The deviations obtained from

TABLE I

Values of the surface and interfacial tensions of aliphatic hydrocarbons; all values are in mJ/m^2

n^a	γ_{H}^b	γ_{Ho}^c	γ_{Hb}^d	γ_{Ws}^e	γ_{WH}^f
5	15.98	19.44	22.62	66.21	50.23
6	18.42	21.37	23.85	69.22	50.80
7	20.20	22.82	24.82	71.05	51.23
8	21.64	23.91	25.60	71.77	51.69
9	22.86	24.98	26.25	72.11	51.96
10	23.78	25.70	26.79	72.30	52.26
11	24.60	26.36	27.25	72.41	52.51
12	25.34	26.82	27.64	72.48	52.86
14	26.58	27.76	28.29	72.56	53.32
16	27.48	28.30	28.80	72.61	53.77

^a Number of C atoms in the aliphatic chain. Surface tension of hydrocarbons: ^b measured; ^c corresponding to the same orientation as at the interface with water; ^d for the random arrangement as in the bulk. ^e Surface tension of water saturated with the respective hydrocarbon. ^f The measured interfacial tension between water and hydrocarbons.

TABLE II

Deviations (in mJ/m^2) from the equality between the work of adhesion and the work of cohesion

n	Eq. (10a)	Eq. (10b)	Eq. (10c)	Eq. (10d)
5	6.54	0.00	-3.46	-6.64
6	3.53	0.00	-2.95	-5.43
7	1.32	-0.38	-3.00	-5.00
8	-0.58	-1.56	-3.83	-5.52
9	-2.07	-2.71	-4.83	-6.10
10	-3.29	-3.74	-5.66	-6.75
11	-4.36	-4.70	-6.46	-7.35
12	-5.45	-5.72	-7.20	-8.02
14	-7.15	-7.34	-8.52	-9.05
16	-8.50	-8.64	-9.46	-9.96

Eqs (10a)–(10d) are given in Table II. They clearly show that, for the system aliphatic hydrocarbons–water, the hypothesis of minimization is invalid regardless of whether it includes the total work of adhesion (Eq. (10a)), the work of adhesion after saturation (Eq. (10b)), and after molecular reorientation (Eq. (10c)), or the actual work of cohesion (Eq. (10d)). Hence, considering the orientation of molecules at the interface does not help to provide a theoretical base for the validity of the Antonow rule. Zero values of Δ according to Eq. (10b), in which the molecular reorientation is neglected, are only obtained if the Antonow rule is identical with the Young equation, i.e. when the contact angle of a hydrocarbon drop on water is zero and the drop spreads to form a duplex film (pentane and hexane). Thus, we conclude that the general use of the Antonow rule (Eq. (4b)) as well as of Eq. (6) for the solid–liquid system cannot be correct. The hypothesis of energy minimization at interfaces^{1,10} had the purpose to provide a theoretical background for the Antonow rule and for other relations based on it, but this hypothesis is shown to fail even when supplemented by the idea that a rearrangement of molecules changes the interaction forces at the interface.

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