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Thermodynamic Relation of Interfacial Tensions in Three Fluid Phases

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Synopsis. The thermodynamic relation was derived for the interfacial tensions at the three interfaces of two immiscible solutions and their vapor phase at a constant temperature. The relation obtained was experimentally tested by measuring each interfacial tension of systems which consisted of organic (alcohols(C_4—C_{10}), triolein, and hexadecane) and aqueous phases. The relation of the interfacial tensions was valid for the polar oil–water systems. but not for the hexadecane–water system unless a surfactant was added.

It is well known as the so-called Antonoff rule that the interfacial tension at two liquid phases can be expressed by the difference in each surface tension at the vapor–solution interfaces. The validity of Antonoff rule, introduced without any theoretical proof,[1] has been tested by many investigators. The crucial conclusion, however, has not yet been drawn.[2–6]

The present work attempts to establish the thermodynamic relation between each surface tension at the three interfaces (*e.g.*, vapor–water, vapor–oil, and oil–water) of the vapor and the two liquid phases, which are mutually saturated. The relation derived will be verified by experiments.

Theoretical

The system taken is that in which the two liquid phases, which are mutually saturated, are equilibrated with the vapor phase at a constant temperature and pressure. Let us consider what relation is established in these interfacial tensions when the system is altered in an isothermal and reversible change, as is shown in Fig. 1, at a constant total volume and mass. We assume that the internal energy for the whole system, U, is completely defined by the variables of the following function:

$$U = U(T,\ V,\ \sum_{\theta} A^{\theta},\ N) \tag{1}$$

where T is the absolute temperature; V, the total volume of the system; A^{θ}, the interfacial area at the interface, θ, and N, the total number of moles of the species in the system. The interfacial total excess volume, V^e, is defined and assumed by the Gibbs convention as follows:

$$V^e = V - \sum_{j} V^j = 0 \tag{2}$$

Therefore, N is related to:

$$N = \sum_{ij} n_i^j + \sum_{i\theta} \Gamma_i^{\theta} A^{\theta} \tag{3}$$

where n_i^j is the mole numbers of the component i in the homogeneous bulk phase, j; Γ_i^{θ}, the mole numbers of the component i per unit area at the interface, θ; the summations of j and θ are taken over the three bulk (k, l, and m) and interfacial (α, β, and γ) phases, and i is taken for the binary components (1 and 2). The total excess internal energy of the interface, U^e, is defined as:

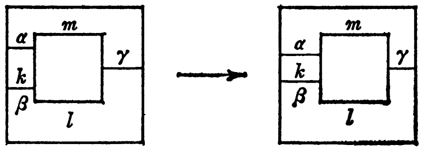

Fig. 1. Isothermal changes in interfacial area at constant total volume and mass. The phases, k, l, m show two immiscible solutions and their vapor, and α, β, γ three interfaces.

$$U^e = U - \sum_{j} U^j = \sum_{\theta} U^{\theta} \tag{4}$$

where U^j and U^{θ} denote the internal energies of the bulk phases, j, and the interfacial phase, θ, defined as follows:

$$\left.\begin{aligned} & U^j = U^j(T,\ V^j,\ \sum_{i} n_i^j) \\ \text{and:}\quad & U^{\theta} = U^{\theta}(T,\ A^{\theta},\ \sum_{i} \Gamma_i^{\theta}) \end{aligned}\right\} \tag{5}$$

Since, from the definition of Eq. 2, Γ_1^{θ} is equal to zero, for the infinitesimal changes of U^e we obtain:[7]

$$\mathrm{d}U^e = \sum_{\theta}\left[\left(\frac{\partial U^{\theta}}{\partial T}\right)_{\mathrm{A},\Gamma}\mathrm{d}T + \left(\frac{\partial U^{\theta}}{\partial A^{\theta}}\right)_{\mathrm{T},\Gamma}\mathrm{d}A^{\theta} + \left(\frac{\partial U^{\theta}}{\partial \Gamma_2^{\theta}}\right)_{\mathrm{T},\mathrm{A}}\mathrm{d}\Gamma_2^{\theta}\right] \tag{6}$$

and:

$$\left(\frac{\partial U^{\theta}}{\partial A^{\theta}}\right)_{\mathrm{T},\Gamma} = \sigma^{\theta} + b^{\theta}$$

where σ^{θ} is the interfacial tension at the interface, θ, and b^{θ} is the heat of expansion of the interface, θ. Usually this term can not be neglected in the adiabatic expansion for the thin film surfaces, but it is customarily considered to be approximately zero for the adsorbed films. If the variation in the surface area does not affect any thermodynamic stabilities of the system under the conditions considered, we obtain:

$$\mathrm{d}U^e = \sum_{\theta} (\sigma^{\theta} + b^{\theta})\mathrm{d}A \tag{7}$$

Furthermore, the changes in the surface area at each interface, according to the process shown in Fig. 1, are related to:

$$\mathrm{d}A^{\alpha} = \mathrm{d}A^{\beta} = -\mathrm{d}A^{\gamma} = \mathrm{d}A \neq 0 \tag{8}$$

This equiarea change at a constant total area establishes the trivial nature of the contribution of the b^{θ} term to the internal energy change of the system as a whole, because the dissipation of the surface at the γ interface and the creation of new surfaces at the α and β interfaces occur simultaneously. Thus, if the total b^{θ} terms are compensated for, the interfacial systems can be changed isothermally. Therefore, substituting Eq. 8 into 7, we obtain finally:

$$\sigma^{\alpha} + \sigma^{\beta} = \sigma^{\gamma} \tag{9}$$

Consequently, Eq. 9, the so-called Antonoff relation,

Table 1. Interfacial tensions in the vapor–oil–water interfaces

Substance	Temp / °C	$\sigma^{v/w}$ / mN m^{-1}	$\sigma^{v/o}$ / mN m^{-1}	$\sigma^{o/w}$ / mN m^{-1}	$\sigma^{o/w}_{cal}$ / mN m^{-1} from Eq. 9$^{a)}$
1-Butanol	25	26.7	24.8	2.0	1.9
1-Hexanol	25	30.0	25.5	4.8	4.5
1-Octanol	25	33.5	27.0	6.7	6.5
1-Decanol	25	36.5	28.0	9.0	8.5
Triolein	30	50.3	31.2	19.0	19.1
Hexadecane	30	71.0	27.5	51.4	43.5
Hexadecane + surfactant$^{b)}$	30	65.8	27.0	38.2	38.8

a) α = v/o, β = o/w, γ = v/w. b) *N*-Dodecyl-β-alanine was added as a surfactant.

is derived thermodynamically for a system which is composed of the vapor and two liquid phases, which are mutually saturated at a constant temperature and pressure. The validity of Eq. 9 can be tested experimentally.

Experimental

Normal alcohols with carbon atoms of 4, 6, 8, and 10, triolein and hexadecane were used as one liquid phase, while the other was water. The organic and aqueous phases were mutually saturated by letting stand them for 10 days with occasional shaking. The surface tensions of the three interfaces were measured by the Wilhelmy plate method. When the tension of the oil–water interface was measured, particular attention was paid to the wetting and the correction of buoyancy for the plate.[8] The interfacial tension was measured within an experimental error of ±0.3 mN m^{-1}. The temperature of the system was controlled by circulating the thermostatic water.

Results and Discussion

The results are shown in Table 1. It may be seen that Eq. 9 was valid for the alcohol–water and triolein–water systems, but not for the hexadecane–water system. The inconsistency of Eq. 9 with the experimental results for the hexadecane–water system was mainly considered to be the result of the incompleteness of the mutual solubilities.[9] The hexadecane–water system, however, to which a surfactant soluble in both liquid phases was added, obeyed the relation of Eq. 9. The use of such a surfactant is considered to promote the increasing mutual solubilities of the system and to favor the formation of stable films at each interface, as in the polar oil–water system.

In conclusion, if the system is allowed to reach the thermodynamic equilibrium, and if the equilibrium interfacial tensions are measured, Eq. 9 can be used to explain the correlation between the interfacial tensions of the three fluid phases, especially for the systems composed of the two polar liquid phases with high mutual solubilities.

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