Colloid Polym Sci (2007) 285:1505–1508
DOI 10.1007/s00396-007-1723-8

ORIGINAL CONTRIBUTION

Molar surface energy and Eötvös's law

An application of the parametric representation of capillarity theory

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Received: 13 March 2007 / Revised: 17 May 2007 / Accepted: 16 June 2007 / Published online: 14 August 2007

Abstract The apparatus of classical capillarity theory does not explicitly contain the general dimensional equation of its own scalar variables. Introduction of such an equation permits the interpretation of experimental physical quantities characterizing the bulk phases from the point of view of the capillary interaction. Eötvös's law is one of the basic empirical equations of capillarity relating to the molar-free energy of the free liquid surface. The extended theory also enables Eötvös's Law to be deduced in a relatively simple way, proving that the heuristic potential of this parametric method goes beyond the limits of traditional theory.

Keywords Capillary theory · General dimension equation

Although the classical theory of capillarity [1–3] has been outstandingly successful, its formulation does not explicitly contain the general dimension equation that is also valid for its own scalar variables. The inadequacy of this method is illustrated by the fact that the principal basis of the empirical Eötvös law [4, 5], for the liquid/vapour layers of relatively simple structures that can easily be examined, could be established only by invoking quantum-physical considerations of surface waves [6], although a number of molecular kinetics experiments were carried out [7–11]. The relationships for free surfaces are usually described by power functions containing critical state determinants, which can also be used to interpret a number of non-capillary effects [12, 13]. However, such functions are seldom employed in the basic formulation, in spite of the correlation between the correspondence principle and the surface tension [14].

The formulation of classical capillarity theory involves the general (material-independent) interactions in a more or less exact form: the Gibbs and Young equations, respectively, incorporate most adsorption and wetting effects. However, even the cardinal variables of the theory (such as solid surface tensions) cannot be determined within the traditional framework. In principle, the empirical rules for the free surface of fluids formed with their own vapour (e.g. the material equations of temperature or the density dependence) can be derived only with great difficulty. The theory is extended by the general dimension equation to form a coherent (algebraically compatible) system that can be unified. A capillarity theory based on the traditional formulation is thus constructed that is logically complete and also contains the empirical correlations. The formalism providing a scale-independent state description (parametric representation) is based on the resolution of collective variables, such as the surface tension, that are simultaneously dependent on the variables of adjoining bulk phases [15, 16].

This article is an application of the extended capillarity theory for the theoretical confirmation of Eötvös's law.

Dimension equation and the individual state parameters

The so-called *general dimension equation* involves scalar variables. The variable set of the traditional formulation is constructed from the same type of physical quantities (scalar or reducible to scalar components): consequently, the former is also valid for the latter.

According to the parametric representation, the values of the derived capillarity quantities of the interface $S_{\phi\psi}$ separating the adjacent phases ϕ, ψ is simultaneously determined by the independent partial interactions $\{...,i,...\}$ and their individual fundamental variables $\{...{}_{\phi}x_i;\ {}_{\psi}x_j...\}$

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[15]. Therefore, the surface tension $\gamma_{\phi\psi}$ can be expressed by quantities of the bulk phases which generate the interfacial layer. Thus, based on the general dimension equation for any material parameter [15]

$$\chi_\phi = \prod_{i=1}^{r} \left|{}_\phi x_i^{\nu_i}\right| \tag{1}$$

the surface tension can be given by the expression

$$\gamma_{\phi\psi} = \chi_\phi \chi_\psi \tag{2}$$

In Eq. 1, χ_ϕ is contributed by the fundamental variables of the bulk phase ϕ; the exponent ν_i depends only on the ith partial interactions. The traditional relationships of classical capillarity theory can be given in the so-called parametric representation by using the transformation formula 1. Thus, the instructions for the measurement of the individual quantities can also be interpreted. The material parameters for liquid phases can be deduced from surface tension data [15, 17].

The partial interactions of the basic quantities ${}_\phi x_i$ that determine the state of the neighbouring bulk phases are either different from each other (local state variables) or identical (pseudo-local quantities). The fundamental equilibrium variable of temperature variation is a single-valued, continuous and monotonic function of the canonical temperature T, ${}_\phi x_T = \tau(T)$. The tension parameter is the product of the variable ${}^0\chi_\phi$ containing the non-thermal fundamental quantities and the temperature factor $\tau(T)$:

$$\chi_\phi = {}^0\chi_\phi [\tau(T)]^{\nu_T} \tag{3}$$

Introducing $\left\{{}^0\chi_\phi\ {}^0\chi_\psi\right\} = {}^0\gamma_{\phi\psi}$, the surface tension of the interface $S_{\phi\psi}$ can be given by the following general expression:

$$\gamma_{\phi\psi} = {}^0\gamma_{\phi\psi} [\tau(T)]^{2\nu_T} \tag{4}$$

The actual values of the derived quantities also depend on the algebraic structure of $\tau(T)$. The function $\tau(T)$ can generally be expressed as a MacLaurin series. For simplicity, in this paper we neglect the higher terms. The values of the derivative $d\tau/dT$ are thus identical for each phase, owing to the pseudo-local behaviour, i.e.,

$$\tau(T) \cong c' + cT \tag{5}$$

c and c' are constants depending on the material. Therefore,

$$\left(\frac{\partial \gamma_{\phi\psi}}{\partial T}\right) = {}^0\gamma_{\phi\psi}\left\{2\nu_T [\tau(T)]^{2\nu_T - 1}\left(\frac{\partial \tau(T)}{\partial T}\right)\right\} = \gamma_{\phi\psi}\left(2\nu_T \frac{1}{T + (c'/c)}\right) \tag{6}$$

The exponent can be obtained by a simple algebraic transformation

$$\nu_T = \frac{1}{2}\frac{1}{\gamma_{\phi\psi}}\left(\frac{\partial \gamma_{\phi\psi}}{\partial T}\right)[T + (c'/c)] \tag{7}$$

From the Gibbs-Helmholtz equation

$$u_{\phi\psi} = \gamma_{\phi\psi} - T\left(\frac{\partial \gamma_{\phi\psi}}{\partial T}\right) = \gamma_{\phi\psi}\left(1 - 2\nu_T \frac{T}{T + (c'/c)}\right) \tag{8}$$

If c/c' is known, the exponent can be calculated:

$$\nu_T = \frac{1}{2}\left(1 - \frac{u_{\phi\psi}}{\gamma_{\phi\psi}}\right)\left(1 - \frac{(c'/c)}{T}\right) \tag{9}$$

Applying Eq. 4, the relationship between the actual and reference temperatures can be given by the following nonlinear expression:

$$\gamma_{\phi\psi}(T) = \gamma_{\phi\psi}^{\mathrm{ref}} + {}^0\gamma_{\phi\psi}\left[(cT + c')^{2\nu_T} - (cT_{\mathrm{ref}} + c')^{2\nu_T}\right] \tag{10}$$

Employing a Taylor series, the temperature factor can be expressed as a function of $(T_{\mathrm{ref}}\text{-}T)$. Therefore, introducing the value of $(1/\tau)(\partial\tau/\partial T)$ at T_{ref}, the temperature dependence of the $\{\phi;\ \psi\}$ phase pair can be given as

$$\gamma_{\phi\psi}(T) = \gamma_{\phi\psi}^{\mathrm{ref}} + \left[\gamma_{\phi\psi}^{\mathrm{ref}} \frac{2\nu_T}{T_{\mathrm{ref}} + (c'/c)}\right] \left\{(T - T_{\mathrm{ref}}) + \frac{1}{2\nu_T}\sum_{n=2}^{\infty}\left[\binom{2\nu_T}{n}\left(\frac{1}{T_{\mathrm{ref}} + (c'/c)}\right)^{n-1}\right](T_{\mathrm{ref}} - T)^n\right\} \tag{11}$$

This general expression can be directly applied to liquid/vapour—i.e., free—interfaces. The S_{LV} layer and, consequently, its interfacial tension, disappears at its critical temperature T_{crit}. From Eqs. 4 and 5 in the critical state

$$T_{\mathrm{crit}} = -(c'/c) \tag{12}$$

that is,

$$\gamma_{LV}(T) = -\left(\frac{\partial \gamma_{LV}}{\partial T}\right)_{ref} \left\{(T_{crit} - T) + \frac{1}{2\nu_T}\sum_{n=2}^{\infty}(-1)^n\binom{2\nu_T}{n}(T_{ref} - T_{crit})\left[1 - \left(\frac{T - T_{ref}}{T_{crit} - T_{ref}}\right)^n\right]\right\} \tag{13}$$

The γ_{LV}-dependent contribution of the temperature variation of the capillarity quantities can therefore be determined.

Table 1 Physico-chemical data and Eötvös constants of selected liquids [18–20]

Liquid	T °C	T_{crit} °C	γ_{LV} mN/m	$\frac{\partial\gamma_{LV}}{\partial T}$ mN/m K	V_M cm^3/mol	u_{LV} mN/m	ν_T	k_E $\frac{10^{-7}\text{J}}{\text{mol}^{2/3}\text{K}}$	k_E^{calc} $\frac{10^{-7}\text{J}}{\text{mol}^{2/3}\text{K}}$
Acetic acid	20	321.8	27.59	−0.099	57.2	56.73	0.543	1.3571	1.4756
Acetone	25	235	24.02	−0.112	73.3	57.41	0.489	2.0033	1.9616
Argon	−189	−122	13.30	−0.241	28.8	33.58	0.607	1.8651	2.2643
Benzene	20	290.5	28.8	−0.11	84.3	61.04	0.516	2.0469	2.1148
Bromobenzene	20	397	35.82	−0.116	104.7	69.82	0.610	2.1106	2.5768
Carbon monoxide	−192	−138.7	9.60	−0.207	36.7	26.42	0.575	1.9890	2.2893
Carbon tetrachloride	25	289.1	26.48	−0.122	96.4	62.85	0.608	2.1079	2.5649
Chlorine	−70	144	33.15	−0.189	47.0	71.54	0.610	2.0174	2.4614
Chlorobenzene	25	359.2	26.67	−0.129	101.7	65.13	0.808	1.7387	2.8106
Chloroform	25	263	26.67	−0.129	79.6	65.13	0.575	2.0735	2.3870
Cyclohexane	20	281	25.24	−0.118	180	59.83	0.610	3.0829	3.7618
n-Heptane	20	266.8	20.14	−0.098	146.7	48.86	0.611	2.3101	2.8266
n-Hexane	20	234.8	18.40	−0.102	130.5	48.30	0.595	2.2038	2.6242
Methylacetate	22	233.7	25.7	−0.11	79.9	58.16	0.453	2.2520	2.0406
Nitrogen	−195	−147.1	8.75	−0.226	17.3	26.41	0.618	1.2219	3.0214
n-Octane	20	298.2	21.6	−0.095	162.3	49.45	0.611	2.3101	2.8266
1-Octanol	20	358	27.5	−0.079	158	50.80	0.527	2.2019	2.3234
Oxygen	−203	−119	18.10	−0.256	14.0	36.06	0.594	1.2516	1.4870
Toluene	20	106.3	28.52	−0.118	106.3	63.11	0.622	2.1276	2.6479
Water	20	374	72.8	−0.147	18.0	115.89	0.357	1.4124	1.0096
Xenon	−109	37.3	18.46	−0.130	37.3	43.83	0.526	1.6381	1.7259

Molar surface energy and the Eötvös Law

The molar surface energy

$$E_M(T) = \gamma_{LV}(T)[V_M(T)]^{2/3} \tag{14}$$

contains the surface tension of the free liquid surface and the liquid phase molar volume, V_M. The basic variables collectively determine the temperature dependence of the derived physical quantity. In Eqs. 13 and 14

$$k_E = -\frac{1}{2\nu_T}\left(\frac{\partial\gamma_{LV}}{\partial T}\right)_{\text{ref}} V_M^{2/3} = \gamma_{LV}^{\text{ref}}\frac{1}{(T_{\text{crit}} - T_{\text{ref}})}V_M^{2/3} > 0 \tag{15}$$

can be introduced as the extension of the $(\partial\gamma_{LV}/\partial T)$ variable. The quantity k_E, defined by Eq. 15, depends only on the universal constant ν_T and on chemical properties. If the temperature of the reference state is identical with the actual temperature T of the system (i.e., $T_{ref}=T$), the derived $E_M(T)$ is determined as

$$\begin{aligned} E_M(T) &= k_E\left\{(T_{\text{crit}} - T) + \tfrac{1}{2\nu_T}\sum_{n=2}^{\infty}(-1)^n\binom{2\nu_T}{n}(T_{\text{ref}} - T_{\text{crit}})\right\} \\ &= k_E(T_{\text{crit}} - T)\left\{1 - \sum_{n=2}^{\infty}\tfrac{(-1)^n}{2\nu_T}\binom{2\nu_T}{n}\right\} \end{aligned} \tag{16}$$

The term with the summation sign is an alternating series of decreasing elements with sum A. Thus, formally, neglecting the quantity A compared to unity, the expression reduces to a (quasi-) linear function of the temperature.

The molar surface energy is expressed in a quasi-linear approximation by Eötvös's empirical law [4, 5],

$$\gamma_{LV}V_M^{2/3} \cong k_E(T_{\text{crit}} - T) \tag{17}$$

where the factor k_E is the Eötvös constant.

In reality, the molar surface energy is a complicated function of temperature, and moreover, it is not true that $A\approx 0$. By introducing the quantity $A(T_{\text{crit}} - T) = T^{\bullet}$, the relation

$$\gamma_{LV}V_M^{2/3} \cong k_E(T_{\text{crit}} - T - T^*) \tag{18}$$

may be derived from the general expression, which corresponds to the revised Ramsay–Shields formula [21, 22] for liquids in the range of $T^{\bullet}$ values 277–279 K.

According to the Gibbs phase rule, the temperature T and pressure p exert identical effects. The pressure dependence can therefore be described by formulae that are formally identical to the temperature variation. It follows that the pressure-dependent analogy of Eötvös's Law is

$$\gamma_{LV}V_M^{2/3} \cong k_E(p_{\text{crit}} - p - p*) \tag{19}$$

The verification of this expression is very difficult due to the lack of necessary data.

Table 1 contains values determined from the individual parameters of the components. Calculated Eötvös constants are also compared to reference data. The average of the k_E

values is slightly different from that obtained from the surface wave approach, namely, 2.45. It must be kept in mind that errors in the measured data are propagated into this calculation. The discrepancy may exceed ±14% when $T-T_{crit}$ is either too narrow or too large. In these cases, the simplifications adopted in the derivation, e.g. using only the first term of the MacLaurin series, is certainly a poor approximation.

The Eötvös (and the modified Ramsay–Shields) law and their generalizations can be directly determined on the basis of the extended capillarity theory with the individual representation.

Acknowledgement We extend our warm thanks to György Bosznai for his invaluable assistance. KL thanks Erik Geissler for fruitful discussions.

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