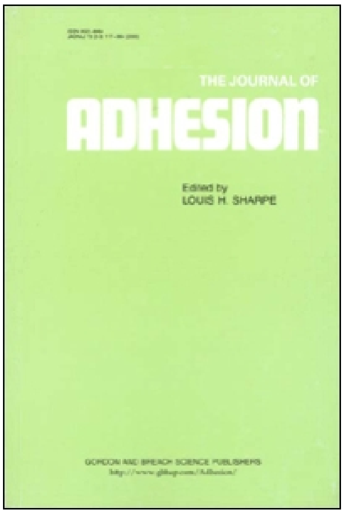

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Entropic Effects Involved in the Formation of an Interface: Assessment of Acid-Base Interactions by Wetting*

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The temperature dependence of different thermodynamic quantities-surface and interfacial tensions, $\gamma_i(T)$ and $\gamma_{ij}(T)$, reversible work of adhesion, $W_{ij}(T)$, and related enthalpic and entropic components, ΔH and ΔS-are studied for both van der Waals and acid-base bonding interfaces. The importance of entropic effects involved in the wetting process is assessed and discussed depending on the nature of interfacial interactions. According to these results, the contribution of entropic effects to the reversible work of adhesion appears to be an effective quantity in describing interfacial phenomena, especially those involving acid-base interactions.

KEY WORDS Surface-interface tension; wetting; temperature dependence; entropic effects; acid-base interactions.

INTRODUCTION

Many aspects of contact angle and wetting measurements are governed or highly influenced by the temperature-dependent properties of the interacting phases.[1–6] The effect of temperature in analysing wetting quantities has often been assumed to be negligible, if not completely ignored. Despite the recent effort to understand these temperature-dependent behaviors, especially those related to thermodynamic quantities-free energy, energy and entropy of interface formation-, some problems still remain concerning the reproducibility of the results[1–4] and their physical meaning. Some problems are due to the diversity of experimental methods but others arise from the particular way in which materials (polymers), which often contain additives, are altered by their processing conditions.

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The primary objective of this work is to establish, through a simple thermodynamic treatment of temperature-dependent wetting measurements, both the physical relevance and numerical importance of the entropic effects involved in the formation of an interface. From experimental results and a thermodynamic derivation of the different entropic contributions to the free energy, we will show how these entropic effects can account for the structure of an interface. More specifically, for acid-base bonding interfaces, we will discuss the importance and incidence of neglecting these entropic terms on the determination of the acid-base energy of interactions, following the approach of Fowkes and co-workers.

To address this problem, liquid-liquid systems for which interfacial phenomena are enhanced due to the intrinsic molecular mobility have been used, instead of usual polymer-liquid interfaces. These systems include both van der Waals type interfaces represented by water-dodecane and dimethylformamide-dodecane, and acid-base bonding interfaces represented by water-ether and water-chloroform. The choice of these acid-base bonding systems was straight-forward: among liquids non-miscible with water, chloroform and ether can exchange acid-base interactions as they present opposite acid-base characters. In this respect, and based on the asymmetry of the electrons donor-acceptor sites across the interface, their interactions *versus* water can constitute a model system.

For clarity, we will adopt the following nomenclature for the liquid-vapor and the corresponding liquid-liquid interfaces: n-dodecane (H, for hydrocarbon), water (W), dimethylformamide (DMF), chloroform ($CHCl_3$), ether (Et_2O).

THEORETICAL APPROACH AND METHOD

When two phases are brought into contact, the overall energetic balance, expressed by the variation of the Gibbs free energy, ΔGij, contains at least two contributions: the enthalpy, ΔHij, and the entropy, $T\Delta S$ij, associated with the intermolecular interactions. For non-miscible and reversible interacting phases, a simple thermodynamic approach of temperature-dependent wetting measurements should allow us to determine the variation of the Gibbs free energy, as well as the related enthalpy and entropy of wetting. The final objective of this work is to determine these thermodynamic quantities, showing thereby the numerical and phenomenological importance of the entropic effects involved in the formation of the interface. The free energy of adhesion between non-miscible liquids *i* and *j* is expressed according to the relation of Dupré as

$$Wij = -\Delta Gij = \gamma_i + \gamma_j - \gamma_{ij} \qquad (1)$$

where γ_i and γ_{ij} are, respectively, the surface and interfacial tensions of the liquids.

When only van der Waals forces are operative (for instance W-H and DMF-H), the corresponding free energy of adhesion at such an interface is obtaind according to Fowkes as

$$W_{i-H} = W^d = 2(\gamma_i^d, \gamma_H)^{1/2} \qquad (2)$$

where γ_i^d is the dispersive component of the surface tension of water (or DMF), and γ_H the surface tension of n-dodecane. This relation is quite a good approximation for these interfaces, since the rigorous application requires the similarity of both the molecular dimensions and interactions through the interface.

In relations (1) and (2) the temperature dependence of the surface and interfacial tensions $\gamma_i(T)$ and $\gamma_{ij}(T)$ is determined from independent measurements, using the Wilhelmy plate method as described in the experimental section. Equating (1) and (2) for W-H and DMF-H interfaces leads to the following dispersive component γ^d expression for either water or DMF

$$\gamma^d(T) = [(\gamma_H + \gamma_i - \gamma_{iH})^2/4\gamma_H]_T. \tag{3}$$

Relation (3) is used to determine the temperature dependence of the dispersive component, γ^d, of water and DMF. Subsequently, the combining rule, (2), is used, in a similar fashion, for the contribution of the dispersive forces to the reversible work of adhesion at acid-base bonding interfaces (W-$CHCl_3$, W-Et_2O) observing that for $CHCl_3$ and Et_2O, we have $\gamma_{\text{total}} \approx \gamma^d$. The contribution of entropy to the reversible work of adhesion is derived using the Gibbs-Helmholtz equation which applies at equilibrium, irrespective of the nature of the interfacial interactions

$$-\Delta H_{ij} = T^2 \frac{\partial\left(\Delta \frac{G_{ij}}{T}\right)}{\partial T} = W_{ij} - T\frac{\partial W_{ij}}{\partial T} \tag{4}$$

where $T(\partial W/\partial T) = T\Delta S$ represents the entropic contribution of intermolecular interactions to W_{ij}.

These entropic effects, associated with the wetting process, can be derived from reversible thermodynamic relations by considering either the energy[7] or the enthalpy[8] as the relevant state function. Starting from the common and general definition of the enthalpy as $H = U + pV$, it follows that for a heterogeneous system containing an interface, $dH = TdS + Vd_p + \gamma dA + \mu dn$. The excess free energy per unit area at constant (n, p) is then related to the enthalpy through the temperature and the entropy component according to

$$\gamma_i = \Delta H_i - T\Delta S_i \tag{4.1}$$

where ΔH_i is the excess surface enthalpy per unit area involved when the surface is reversibly extended and $-\Delta S_i = -[S_i(\text{surface}) - S_i(\text{bulk})] = d\gamma_i/dT$ is < 0

When creating an interface *ij* from surfaces *i* and *j*, the corresponding final excess free energy per unit area at equilibrium (γ_{ij}) is defined in the same way as

$$\gamma_{ij} + H_{ij}(\text{interface}) - [(H_i(\text{bulk}) + H_j(\text{bulk})] - T[S_{ij} - (S_i(\text{bulk}) + S_j(\text{bulk}) \tag{4.2}$$

where the enthalpy and entropy terms represent, respectively, the interfacial excesses over the bulk when bulk molecules are brought at the interface if the interface is reversibly extended. From relation (4.2), the first derivative of γ_{ij} with temperature is

$$(d\gamma_{ij}/dT) = [S_i(\text{bulk}) + S_j(\text{bulk})] - S_{ij}(\text{interface}) \tag{4.3}$$

Using the equation of Dupré given in relation (1), the temperature dependence of the reversible work of adhesion W_{ij} is obtained as

$$\partial W_{ij}/\partial T = [(\gamma_i + \gamma_j) - d\gamma_{ij}]/dT = S_{ij}(\text{interface}) - [S_i(\text{surface}) + S_j(\text{surface})] \tag{4.4}$$

Regardless of the specific nature of ΔS (molecular translation, rotation, vibration or conformation), relation (4.4) allows a phenomenological interpretation of the entropic contribution to the reversible work of adhesion.

When acid-base interactions at the interfaces are considered (W-Et_2O; W-$CHCl_3$), relation (4) applies as well. The corresponding specific enthalpy and entropy (ΔH^{ab}, ΔS^{ab}) are then expressed through the acid-base component W^{ab} of the reversible work of adhesion according to Fowkes as

$$W_{ij}^{ab} = W_{ij} - 2(\gamma_i^d \cdot \gamma_j^d)^{1/2} \tag{5}$$

In the following, our experimental results will be presented and discussed using these basic relations (1–5).

MATERIALS AND EXPERIMENTAL METHOD

With the exception of water, all liquids used in this study, n-dodecane (*H*), dimethylformamide (DMF) diethyl-ether (Et_2O) and chloroform ($CHCl_3$) were from Fluka, had a minimum purity of 99.5% and were used without further purification. Freshly deionized and distilled water was used. The wetting measurements were made using the Wilhelmy plate method on a dynamic tensiometer (DCA-322 from Cahn) using a platinum plate. The wetting liquids and the platinum plate were placed in a double-walled environmental chamber connected with a thermostat. The liquids were introduced using glass pipettes previously washed with the liquid. The system was allowed to equilibrate before each experiment. Equilibration was checked out at both liquid-air and liquid-liquid interfaces using a thermocouple needle which was previously cleaned with absolute ethanol and dried under nitrogen. The equilibration time depends on which temperature is considered but about 15 minutes was required. The equilibrium temperature was stable within a range of 0.2°C. For each temperature, a minimum of five runs were made and the roughened platinum plate was cleaned and flamed before each experiment. Unless otherwise specified, the wetting (dewetting) rate was 5 μm/s with investigated temperatures ranging from 5 to 50°C. The non-miscibility of liquids for interfacial tension measurements has been checked in the investigated temperature range from the Handbook of Chemistry and Physics (6th edition, 1988–89). Despite this assumed non-miscibility, some local interdiffusion or preferential adsorption can occur at the interface, affecting somewhat the experimental values as mentioned in earlier works.[9]

The total surface tension of water, DMF, $CHCl_3$ and Et_2O was first determined in a one-phase measurement, while the surface tension of the n-dodecane and its interfacial tension against water and DMF were drawn from the two-phase measurements (Figs. 1 and 2).

The general equilibrium condition describing the dynamic wetting is written according to Figure 1 as

$$F = mg_{(Pt)} - \rho_L \cdot gAd + l.\gamma_L \cos\theta_{L/Pt} \tag{6}$$

where A and l represent, respectively, the cross sectional area of the plate and its perimeter, d is the immersion depth of the plate in the liquid and g is the gravitational force constant.

Practically, the system is zeroed before the experiment so that the force exerted on the plate at zero immersion depth ($\rho_L gAd = 0$) reduces actually to surface forces $l.\gamma_L \cos\theta_{L/Pt}$.

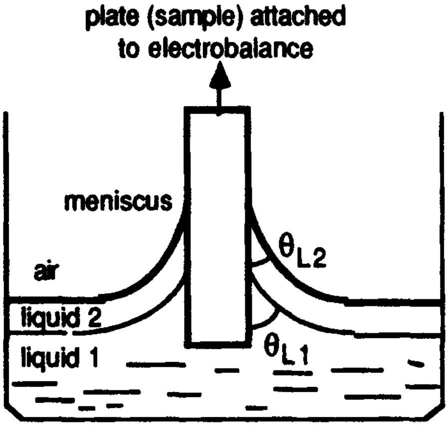

FIGURE 1 Principle of the experimental (Wilhelmy) method: general case of a "two-phase" measurement with an ordinary wetting probe (sample).

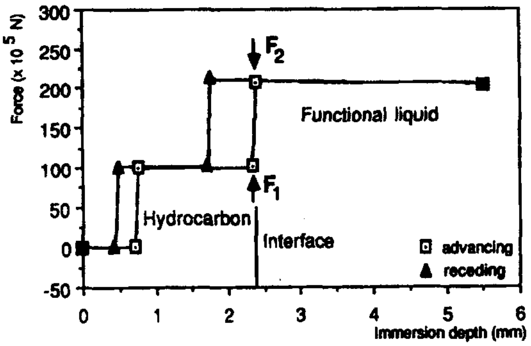

FIGURE 2 A typical experimental wetting curve-(H/W) system at 10° C.

Surface tension of the different liquids are obtained from F in a single-phase measurement, assuming a complete wetting of the platinium plate by the liquid ($\cos\theta_{L/Pt} = 1$).

For W-H, DMF-H, W-CHCl$_3$ and W-Et$_2$O interfaces, the equilibrium equation is derived as follows, considering total wetting of the plate by the interface as shown in Figure 1

$$F_2 = l.(\gamma_{L1} + \gamma_{L1L2}) - (\rho_{L1}\cdot d_{L1} + \rho_{L2}\cdot d_{L2})\cdot gA \tag{7}$$

when the plate is at the interface in the receeding or advancing mode, the interfacial force is then given by

$$(F_2 - F_1) = F_{12} = l\cdot\gamma_{L1L2} \tag{8}$$

Considering this relation (8) and the expression of the dispersive component given in relation (3) where H is the L_1 phase, the following equation is found for the temperature dependence of the dispersive component of water and DMF surface tension $\gamma_L(T)$.

$$\gamma_L^d(T) = \left[\frac{\left(\gamma_L + \gamma_H - \frac{F_{L-H}}{l}\right)^2}{4\gamma_H}\right]_T \tag{9}$$

These experimental values of surface tensions, interfacial tensions and dispersive components, as determined from the previous equations, have been used for the thermodynamic analysis according to the relations of Dupré, Fowkes and Gibbs-Helmholtz (relations (1), (2) and (4)).

RESULTS AND DISCUSSION

Temperature Dependence of Surface Tensions

The general temperature-dependent behavior corresponding to the experimental data is given by relation (10):

$$\gamma_L(T) = \gamma_L^0 + \frac{d\gamma_L}{dT}(T - 293\,\mathrm{K}) \tag{10}$$

The temperature coefficients as well as the absolute values of the surface tensions are in excellent agreement with those reported by different authors,[10–12] with a typical correlation coefficient, $r \geqslant 99.5\%$, see Table I.

The physical meaning of these results is straightforward, following relation (4.1), since surface molecules have a higher entropy compared with bulk molecules.

TABLE I
Surface tension of liquids at 293 K and their temperature coefficients

Liquids	γ_L^0 (mJ/m^2)	$d\gamma_L/dT \pm \sigma$ (mJ/m^{2}K)
water	73.6	-0.144 ± 0.020
DMF	37.7	-0.122 ± 0.021
Et_2O	17.9	-0.090 ± 0.010
$CHCl_3$	27.6	-0.120 ± 0.011
H	25.8	-0.088 ± 0.013

Liquid-liquid Interfacial Tensions

As for surface tensions, a linear temperature-dependent behavior is observed for liquid-liquid interfacial tensions according to

$$\gamma_{L1L2}(T) = \gamma^0_{L1L2} + \frac{d\gamma_{L1L2}}{dT}(T - 293\,\mathrm{K}) \tag{11}$$

where γ^0_{L1L2} is the interfacial tension at $T_0 = 293$ K as shown in Table II.

The typical correlation coefficient of the regression lines represented by relation (11) is better than 99%. It is noteworthy that the temperature coefficients of interfacial tensions are notably smaller than those measured for surface tensions. Unlike surface tensions, the physical meaning of the entropic variation ($d\gamma_{L1L2}/dT$) associated with interfacial tensions is less obvious based on equation (4.3). For instance, we would expect to have S_{12} (interface) $\leqslant$ [S_1 (bulk) + S_2 (bulk)] for (W-Et_2O) and (W-$CHCl_3$) systems since interfacial molecules are somewhat pinned by acid-base bonds, whereas only very weak acid-base auto-association can take place within Et_2O and $CHCl_3$ bulk molecules. Therefore, it seems that for non-miscible liquid-liquid systems and whatever the nature of interfacial forces (van der Waals or acid-base), the bulk molecules are more constrained (higher order) than those involved in the interfacial phase.

The temperature dependence of the dispesive component of water and DMF surface tension has been determined from relations (3), (10) and (11) and, respectively, given by

$$\gamma^d_W(T) = 24.4 - 0.11\,(T - 293\,\mathrm{K}); \quad \gamma^d_{\mathrm{DMF}}(T) = 34.1 - 0.09\,(T - 293\,\mathrm{K}) \tag{12}$$

TABLE II
Liquid/liquid interfacial tensions at 293 K and their temperature coefficients

liquid/liquid interface	γ^0_{L1L2} (mJ/m^2)	$d\gamma_{L1L2}/dT \pm \sigma$ (mJ/m^{2}K)
H/W	49.5	-0.030 ± 0.015
H/DMF	4.2	-0.040 ± 0.010
Et_2O/W	6.9	-0.070 ± 0.012
$CHCl_3$/W	29.1	-0.050 ± 0.011

Except for very sparse and controversial values reported in the literature,[1,4] and determined using polyethylene or eicosane, there is a real lack of reference data for the temperature dependence of the dispersive component of the surface tension of functional (polar) liquids. For instance, values reported for water, glycerol and hydrazine hydrate[4] ($N_2H_4.H_2O$) do not show any simple or general feature with temperature. This work is necessary for temperature-dependent wetting measurements, but also for the understanding on how the different interaction potentials contributing to the cohesion vary with each other.

Reversible Energy of Adhesion and Related Thermodynamic Components

The variation of the reversible energy of adhesion has been calculated using the relation of Dupré and the linearised surface and interface tensions (relations (10) and (11). Accordingly, $W_{L1L2}(T)$ is found to vary linearly for both van der Waals and acid-base bonding interfaces as shown in relation (13) and Table III.

$$W_{L1L2}(T) = W^0_{L1L2} + \frac{dW_{L1L2}}{dT}(T - 293\,\mathrm{K}) \qquad (13)$$

The mean temperature coefficient of these reversible works ($dW_{L1L2}/dT \approx -0.18$) is significantly higher than those measured for surface (interface) tensions and their respective components.

A quite interesting point about these results concerns the respective values of the free energy of adhesion for Et_2O/W and $CHCl_3$/W interfaces. As shown in Table III, $W_{L1L2}(Et_2O/W)$ is notably higher than $W_{L1L2}(CHCl_3/W)$ while for total surface tensions, $\gamma_{Et_2O} < \gamma_{CHCL_3}$. In fact, ether is a non acid-base associated liquid presenting a strong electron-donor ability. Therefore, there is a potential capacity of this liquid to establish acid-base bonds when interacting with an electron-acceptor species which does not appear in its total surface tension. This demonstrates the usefulness of the acid-base concept, as it raises the more basic question of whether the total surface tension (as usually measured) is relevant in predicting the interfacial interactions, at least for a class of materials.

The respective contribution of the total enthalpy (ΔH_{L1L2}) and entropy (ΔS_{L1L2}) to the free energy of adhesion is calculated at room temperature according to the Gibbs-Helmholtz equation (relation (4)) and reported in Table IV. The negative values

TABLE III
Free energy of adhesion for liquid/liquid interfaces at 293 K and their temperature coefficients

Liquid/liquid interface	W^0_{L1L2} (mJ/m^2)	$dW_{L1L2}/dT \pm \sigma$ (mJ/m^{2}K)
H/W	50.5	−0.20
H/DMF	61.0	−0.17
Et_2O/W	85.0	−0.16
$CHCl_3$/W	72.5	−0.21

TABLE IV
Contribution of enthalpy and entropy terms to the free energy of adhesion ($T = 293$ K)

Liquid/liquid interface	ΔH^0_{L1L2} (mJ/m^2)	$T\Delta S_{L1L2}$ (mJ/m^2)
H/W	−109.0	−58.6
H/DMF	−111.0	−49.8
Et_2O/W	−132.0	−46.9
$CHCl_3$/W	−134.0	−61.5

of ΔS_{L1L2} are associated with a general loss of entropy (freedom) for interfacial molecules, compared with surface molecules of the separate phases (see relation (4.4)). Since W_{L1L2} is positive, this general entropy reduction is balanced by the enthalpy term to minimise the free energy of wetting.

The Gibbs free energy of adhesion is rearranged so that the entropy effects appear as a weighing factor to ΔH_{L1L2}.

$$-\Delta G_{\text{adh.}} = W_{\text{adh.}} = -\Delta H_{\text{adh.}} \cdot \left(1 - \frac{T\Delta S_{\text{adh.}}}{\Delta H_{\text{adh.}}}\right).$$

Because $\Delta H_{\text{adh.}}$ is expressed in cal/mole, the interfacial density of interacting pair sites (n^{ab} in mole/m^2) is introduced in the previous equation as proposed by Fowkes for the acid-base contribution to the work of adhesion ($W^{ab} = -\text{f} \cdot n^{ab} \cdot \Delta H^{ab}$). The factor, f, which contains the entropic effects through $(1 - T\Delta S_{\text{adh.}}/\Delta H_{\text{adh.}})$ has been generally supposed to be equal to unity since $T\Delta S_{\text{adh.}}/\Delta H_{\text{adh.}}$ was assumed negligible.[13]

In the more general cases studied here, including both van der Waals and acid-base interactions, it appears that the mean value of the entropy factor $(1 - T\Delta S_{\text{adh.}}/\Delta H_{\text{adh.}})$ is about 0.55 which is quite different from unity. This demonstrates that the entropy term involved in wetting (adhesion) processes is important and should be considered for reliable analyses.

In the case of acid-base bonding interfaces, the specific components ΔH^{ab} and ΔS^{ab} can be derived based on the additivity of the different intermolecular interactions to the reversible energy. The Gibbs-Helmholtz relation (4) for W/Et_2O and W/$CHCl_3$ interfaces is then

$$\Delta H^{ab} = -W^{ab}(T) + T\partial W^{ab}/\partial T$$

where

$$W^{ab}_{L1L2}(T) = W_{L1L2}(T) \; - 2(\gamma^d_{L1} \cdot \gamma^d_{L2})^{\frac{1}{2}}_T$$

Unlike water or formamide, Et_2O and $CHCl_3$ are not auto-associated by hydrogen bonds. As a consequence, the surface tension of Et_2O and $CHCl_3$ as measured by conventional methods using either platinum plate or reference apolar polymer (PTFE),

TABLE V
Acid-base contribution to the total energy and entropy of interface formation ($T = 293$ K)

Liquid/liquid interface	W^{ab} (mJ/m^2)	$T\Delta S^{ab} = T(\partial W^{ab}/\partial T)$ (mJ/m^2)	ΔH^{ab} (mJ/m^2)
Et_2O/W	40.8	8.8	−32.0
$CHCl_3$/W	19.9	5.9	−14.0

exhibits mainly dispersive forces, so that $\gamma_L(T) \approx \gamma_L^d(T)$. Since the temperature dependence of the different terms shown in the above relation was previously established, the specific acid-base contributions have been calculated and summarized in Table V.

The respective acid-base enthalpy of interface formation is in good agreement with the molecular structure of the interacting species: $\Delta H^{ab}(Et_2O\text{-}W) \approx 2 \cdot \Delta H^{ab}(CHCl_3\text{-}W)$. In most of the usual acid-base approaches (Gutmann, Drago, Pearson),[14–16] the hard-hard "—H...O—" interaction in (W-Et_2O) is expected to be stronger than the H_2O...$HCCl_3$ in (W-$CHCl_3$) as shown by the electron donor-acceptor numbers (DN, AN) of these liquids.[14]

	water	Et_2O	$CHCl_3$
DN(kcal/mole)	18.0	19.3	0.0
AN	54.8	3.9	23.1

The second interesting feature of these results is that the entropy contribution due to acid-base interactions is positive ($\partial W^{ab}/\partial T > 0$), especially for the stronger acid-base bonding interface (W-Et_2O). This gives rise to a negative term ($-T\Delta S^{ab}$) which adds to the exothermic enthalpy ΔH^{ab} to minimize further the Gibbs free energy of interface formation. This specific gain of entropy is associated with the upset of a new entropy component at the interface-the acid-base one. This new component, initially absent at least for surface molecules of Et_2O and $CHCl_3$ which are free from acid-base auto-association should then appear in relation (4.4). Accordingly, the interfacial entropy term in relation (4.4) is specified as $S_{ij} = S^d + S^{ab}$, whereas the surface terms S_i(surface) is only dispersive in nature, at least for Et_2O and $CHCl_3$.

CONCLUSION

The first objective of this work was to establish, through temperature-dependent wetting measurements, the respective contributions of the enthalpy and entropy effects involved in the reversible formation of an interface. The numerical importance and, tentatively, the physical meaning, have been shown using model liquid/liquid systems with van der Waals and acid-base bonding interfaces. For acid-base interactions, a single measurement at a given temperature is not sufficient to determine the acid-base enthalpy (ΔH^{ab}), since the entropy correction, represented by ($1 - T\Delta S_{adh.}/\Delta H_{adh.}$), can be significantly different from unity. This approach is being developed to study the temperature-dependent wetting of model surfaces such as self-assembled monolayers.

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