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Short Communication

Identification of the interfacial energies determined by the Gibbs adsorption integral in solid-liquid-vapour systems

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ABSTRACT

It is shown that the Gibbs adsorption integral yields differences of certain interfacial energies in solid-liquid-vapour systems, namely $(\gamma_S - \gamma_{SV})$, $(\gamma_S - \gamma_{SL})$ and $(\gamma_{SV} - \gamma_{SL})$, where γ_S, γ_{SV} and γ_{SL} are the solid surface energy at zero vapour pressure, the solid-vapour interfacial energy at monolayer coverage and the solid-liquid interfacial energy respectively. It is also shown that the liquid-solid contact angle could be obtained by evaluating the integral in the range of vapour pressures between saturation and monolayer coverage.   © 2010 Trade Science Inc. - INDIA

INTRODUCTION

What interfacial energies are determined in a solid-liquid–vapour system through the use of the Gibbs adsorption integral was first proposed by Bangham[1] who considered that the Gibbs integral evaluates surface pressures over all the range of pressures i.e. P/P_0 from 0-1. Subsequent authors ([2-6] to mention a few) either followed Bangham or suggested other interpretations[7-10].

In order to identify the interfacial energies under consideration, we shall follow a short road to the objective. We will be interested in the values of the integral for two vapour pressure ranges which appear in the integral limits. These are $(0-P_m)$ and $(0-P_S)$, where P_m is the vapour pressure at monolayer coverage (as determined previously from an adsorption isotherm) and P_S is the vapour pressure of the pure liquid. These two pressure ranges are sufficient for the identification of all

the interface energies found in the solid-liquid-vapour systems.

In the first pressure range the integral reads,

$$-\int_0^{P_m} d\gamma = \int_0^{P_m} \Gamma \, RT \, d \ln P \qquad (1)$$

and in the second pressure range the integral is,

$$-\int_0^{P_S} d\gamma = \int_0^{P_S} \Gamma \, RT \, d \ln P \qquad (2)$$

where Γ is the adsorption density, usually expressed in mol per unit surface area.

In order to identify the quantities in the left hand side of eq. (1), we proceed to describe the experimental set up used to obtain the required data.

In short we fix our attention in a solid sample and an electrolyte solution having a vapour pressure P_m in separate crucibles placed inside a vacuum desiccator for the time necessary to obtain the thermodynamic equilibrium between the solid and the liquid vapour. In this system the surface energies in the final state (at equi-

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librium) are the solid-vapour interface energy at mono-layer coverage γ_{SV} and the surface tension of the electrolyte solution γ_E, hence the total surface energy in the final state is $(\gamma_{SV} + \gamma_E)$.

In the initial state the total surface energies is $(\gamma_S + \gamma_E)$, where γ_S is the surface energy of the solid at vapour pressure zero.

The difference between the final and initial states is,

$$\Delta = \gamma_{SV}\text{-}\gamma_S \qquad (3)$$

Eq. (3) represents the result of the integration of the term in the LHS of eq. (1) which can now be written as,

$$\gamma_S - \gamma_{SV} = \int_0^{P_m} \Gamma\, RT\, d\ln P = \pi \qquad (4)$$

where π is known as the surface pressure and γ_{SV} is the solid-vapour interfacial energy at monolayer coverage.

Repeating the above experiment but with pure liquid (vapour pressure, P_S) the surface energies are $(\gamma_S + \gamma_L)$ in the initial state and $(\gamma_{SL} + \gamma_L)$ in the final state[8], where γ_{SL} is the solid–liquid interfacial energy and γ_L is that of the water-vapour interface. That the final state is given as $(\gamma_{SL} + \gamma_L)$ is worth comment. In both the initial and final states may be present in the desiccator two or more liquid (or solid) surfaces (samples), but only one should be taken into account in the thermodynamic calculations. Such situation usually occurs when a thick liquid film is formed on the solid surface, as is the case under consideration at $P_S = 1$[3,5,8,10].

Thus the difference in surface energies between the final and the initial states is therefore,

$$\Delta = \gamma_{SL}\text{-}\gamma_S \qquad (5)$$

Eq. (5) represents the LHS term in eq. (2), thus,

$$\gamma_S - \gamma_{SL} = \int_0^{P_S} \Gamma\, RT\, d\ln P \qquad (6)$$

Now the difference between eq. (6) and (4) gives,

$$\gamma_{SV} - \gamma_{SL} = \int_{P_m}^{P_S} \Gamma\, RT\, d\ln P \qquad (7)$$

In view of the Young equation,

$$\gamma_{SV} - \gamma_{SL} = \gamma_L\, \cos\theta \qquad (8)$$

It is hence possible to obtain the contact angle using adsorption isotherm data.

Recollecting, eq. (4) and (6) define what the Gibbs adsorption integral determines in a solid-liquid-vapour system i.e. differences between certain interfacial energies. The individual values of each energy remain unknown, since there are 3 variables and only two equations[10].

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