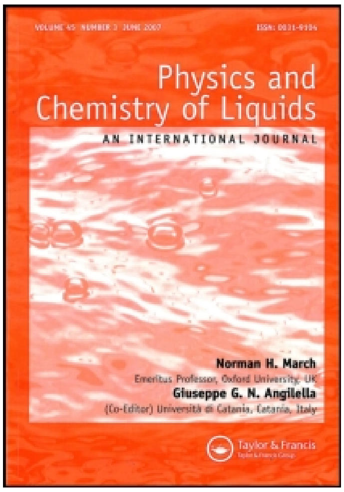

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Letter

Some Properties of the Gibbs–Guggenheim Relations

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The Gibbs adsorption formula for a binary mixture of liquids, $\Gamma_2 = \Gamma_1(x/(1-x)) - (x/RT)\,\partial\gamma/\partial x$, and Guggenheim's formula, $A_1\Gamma_1 + A_2\Gamma_2 = 1$, are examined in a practical case, the surface of a liquid mixture of adiponitrile and tris(dioxa-3,6-heptyl)amine (Γ_1 and Γ_2 are the surface concentrations of the two components, x is the bulk mole fraction of component 2, R is the gas constant, T is the temperature, A_1 and A_2 are the area of the components per monolayer of unit surface area and γ is the surface tension). Loci of constant values of $E = (\Gamma_2/\Gamma_1)/(x/(1-x))$ are plotted in the plane A_1, A_2. Such loci (1) are linear (2) pass through the point A_1^*, $A_2^* = RT/(\partial\gamma/\partial x(1-x))$, $-RT/(x(\partial\gamma/\partial x))$ and (3) possess a linear scale parallel to the A_1 axis. Measurements of Γ_1 and Γ_2 carried out by He(I) photoelectron spectroscopy support the above better if it is assumed that not one but N monolayers are sampled by the technique, with $A_1\Gamma_1 + A_2\Gamma_2 = N$. The value of N is found to be between 1 and 2.

Guggenheim[1] gives the Gibbs adsorption relation for a binary liquid in the form

$$\Gamma_2 = \Gamma_1(x/(1-x)) - (x/RT)\,\partial\gamma/\partial x \tag{1}$$

Alternatively Eq. (1) can be written

$$E = 1 - \frac{(1-x)}{RT\Gamma_1}\,\partial\gamma/\partial x \tag{2}$$

In Eq. (2) E is given by

$$E = (\Gamma_2/\Gamma_1)/(x/(1-x)) \tag{3}$$

As Guggenheim points out, the above expressions are as far as pure thermodynamics can take us and he adds by way of assumption

$$A_1\Gamma_1 + A_2\Gamma_2 = 1 \tag{4}$$

In Eq. (4), A_1 and A_2 have the dimensions of unit surface area per mole, Γ_1 and Γ_2 have dimensions the inverse of these (mole per unit surface area) and the equation implies the formation of one superficial monolayer by adsorption of one component over the other. From Eq. (4), the slope of a plot of A_2 against A_1 is

$$\left(\frac{\partial A_1}{\partial A_2}\right)_{\Gamma_1,\Gamma_2} = -Ex/(1-x) \tag{5}$$

and hence the loci of constant values of E in the plane A_1, A_2 are linear (see Figure 1). It is also easily shown that all such loci pass through the point given by

$$A_1^* = \frac{RT}{\partial\gamma/\partial x(1-x)} \tag{6}$$

$$A_2^* = \frac{-RT}{x(\partial\gamma/\partial x)} \tag{7}$$

As can be easily proved, there exists a linear scale of E in the A_1, A_2 plane, horizontal to the A_1 axis and with its origin on the vertical line $A_1 = A_1^*$.

By measuring the He(I) photoelectron spectra of pure adiponitrile, $NC(CH_2)_4CN$, and tris(dioxa-3,6-heptyl)amine,

$$N(CH_2CH_2OCH_2CH_2OCH_3)_3,$$

we were able to resolve the spectrum of a mixture containing $x = 0.0825$ of the amine into its components[2] and hence to determine $E = 4.5$; by the stalagmometer method[3] we determined $\partial\gamma/\partial x = -28.9$ at $x = 0.0825$. These values enabled the plotting of the loci of constant values of E in Figure 1.

From the molar volumes of the pure liquids it can be estimated, assuming spherical molecules, that $A_1 = 0.24 \times 10^{10}$ and $A_2 = 0.483 \times 10^{10}$ cm^2 mole^{-1} (adiponitrile being component 1) and the corresponding point lies on the $E = 6.5$ locus in Figure 1, rather than on the $E = 4.5$ locus. The discrepancy lies outside experimental error and appears to be connected with the question of the depth of sampling of photoelectron spectroscopy; it might be expected[4] that the electrons excited by He(I) irradiation would escape through at least two, possibly three monolayers. The sampling depth has always been a problem in such measurements, McBain[5] for example used a method of skimming the surface which sampled a depth of

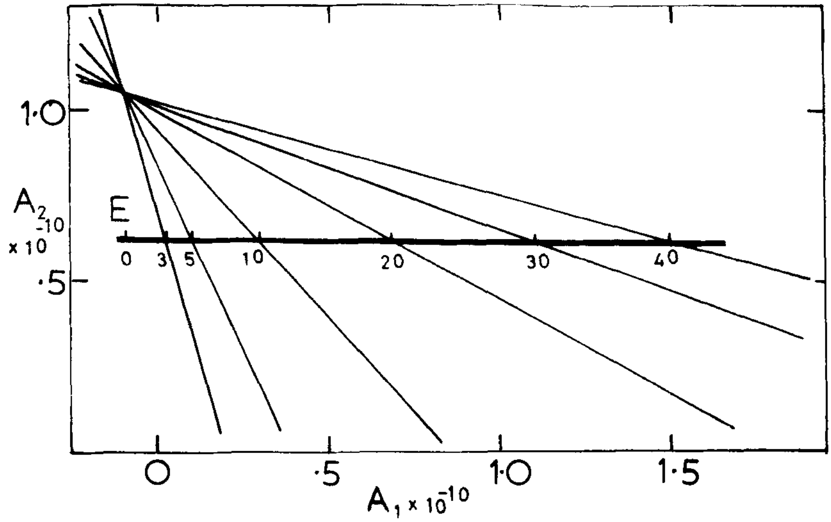

FIGURE 1 Plots of constant values of E = (ratio of surface concentrations)/(ratio of bulk concentrations) for a liquid mixture of adiponitrile (component 1) and tris(dioxa-3,6-heptyl)-amine (component 2) having a mole fraction x for component 1 of 0.0825. Values computed from Eqs (1) and (4). The slope of the surface tension against x curve was determined to be -28.9 ergs cm^{-2}. A focus is found (Eqs 6 and 7) and a linear scale of E horizontal to the A_1 axis. The value of E determined independently by photoelectron spectroscopy was 4.5, in poor agreement with the value of 6.5 derived from molecular areas, A_1 and A_2, calculated from the densities of the liquids ($A_1 = 0.24 \times 10^{10}$, $A_2 = 0.483 \times 10^{20}$ cm^2 mole^{-2}). The implication is that the depth of sampling lies between 1 and 2 monolayers.

no less than 0.05 mm; he assumed that Γ_1 is unchanged from the bulk value which seems to be illogical if Γ_2 is to vary. Nevertheless near perfect agreement between theory and experiment was claimed.[5]

If, instead of Eq. (4), Eq. (8) is used with the number of monolayers, N, included

$$A_1\Gamma_1 + A_2\Gamma_2 = N \tag{8}$$

the focus of loci now lie at the point NA_1^*, NA_2^* instead of A_1^*, A_2^*. Another relationship is

$$E = 1 - \frac{1}{A_1^*\Gamma_1} \tag{9}$$

Using Eq. (8) it can be derived that the value $N = 1.23$ brings the experimental and the theoretical values of E into coincidence. Most of the error lies in determination of $\partial\gamma/\partial x(\pm 20\%)$ and therefore no more is claimed than that N lies between 1 and 2.

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