logically explained in terms of the physical model proposed, but neither of them is covered by the simple mathematics used.

CONCLUSIONS

1. Bubbles of diameter of 1 to 2 cm. formed serially at spacings of 3 to 4 cm. at a single circular 0.406 in. in diameter orifice rise in a chainlike fashion in stagnant glycerine or water, and frequently coalesce within 60 cm. of the orifice. In distilled water the bubbles frequently collide without coalescing: a small amount of sodium ethyl xanthate added to the water causes them to coalesce when they collide.
2. This coalescence can be described reasonably well by a wake-coalescence model, which assumes that the only significant forces acting on the lower bubble are its buoyant force and the inertia drag force, which decreases as it enters the wake of the preceding bubble.
3. The experimental results seem to agree about equally well with the predictions of the model, based on two different assumed wake geometries. This indicates that the assumed shape of the wake is not particularly significant.
4. The model incorrectly predicts a greater rate of increase in relative velocity in the last stages of the coalescence process than is experimentally observed.

ACKNOWLEDGMENT

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NOTATION

A_p = projected area, sq. ft.
C_D = drag coefficient
F_d = drag force, lb.$_f$
g = acceleration of gravity, ft./sec.^{2}
h = geometric quantity as defined in Figure 2, ft.
$h^* = h/R$
k = exponential decay constant, Equation (17), 1/ft.
L_c = cone height as defined in Figure 2, ft.
$L_c^* = L_c/R$
R = bubble radius, ft.
t = time, sec.
$t^* = tV_t/R$
$t_c^* = t^*$ at coalescence
V = velocity, ft./sec.
V_r = relative velocity between two coalescing bubbles, ft./sec.
V_t = terminal velocity of a single bubble in a stagnant fluid calculated according to reference *4*, ft./sec.
x = vertical distance between bubbles, ft.
$x^* = x/R$

Greek Letters

α = geometrical quantity as defined in Figure 2, ft.
$\alpha^* = \alpha/R$
ρ = liquid density, lb.$_m$/cu. ft.

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A Thermodynamic Consistency Test for Adsorption from Binary Liquid Mixtures on Solids

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A thermodynamic consistency test for adsorption from binary liquid mixtures is derived using the Gibbs equation for adsorption. Adsorption data for the liquid mixture pairs *A-B*, *A-C*, and *B-C* on the same adsorbent must be thermodynamically consistent. The consistency test is applied to experimental data for adsorption from the binary liquid mixtures benzene-cyclohexane, benzene-*n*-heptane and cyclohexane-*n*-heptane on silica gel at 30°C.

The recent monograph by Kipling (*6*) provides a review of research on adsorption at the liquid-solid interface. Kipling points out that "The fundamental investigation of adsorption proceeded only slowly, in spite of its technological importance." There are at least two reasons for slow progress in the field of adsorption from liquids. First, there is a basic difference in the treatment of adsorption at the liquid-solid interface and adsorption at the gas-solid interface. A thorough explanation of the problem is given in Chapter II of the book by Defay, Prigogine, Bellemans, and Everett (*3*). Second, the application of the principles of thermodynamics to the variables measured for adsorption at the liquid-solid interface has been neglected.

The objective of this work is to examine the role of thermodynamic consistency in adsorption from liquids on solids.

THE THERMODYNAMIC SYSTEM

The system consists of a liquid phase, called the adsorbate, in contact with a solid phase, called the adsorbent. The portion of the liquid phase close to the adsorbent, where the liquid molecules interact with the solid, is called the adsorbed phase. Variables pertaining to the adsorbed phase will be identified by the prime symbol. The remainder of the liquid phase, which consists of molecules far removed from the surface so that liquid-solid molecular interactions are negligible, is called the bulk liquid. The adsorbate and the adsorbent are assumed to be mutually insoluble.

THE DIFFERENCE BETWEEN ADSORPTION FROM GASES AND ADSORPTION FROM LIQUIDS

The thermodynamic equations governing adsorption from gases and their mixtures have been discussed previously (*8*). Here it is explained why the same equations cannot be applied to adsorption from liquids.

A plot of the concentration of the i^{th} component of the adsorbate, as a function of the distance from the adsorbent surface, is given in Figure 1. The origin ($z = 0$) is located at an arbitrarily chosen position within the adsorbent. If the adsorbed phase is defined to include all molecules whose centers are located within the distance z_0 from the surface, the number of moles of component i adsorbed (n_i') is given by

$$n_i' = \int_{z=0}^{z_0} A c_i(z)\, dz \tag{1}$$

A is the specific surface area of the adsorbent and n_i' is therefore the number of moles of component i adsorbed per unit mass of adsorbent. Equation (1) shows that n_i' is a function of the value of z_0. Differentiation of Equation (1) yields

$$\frac{dn_i'}{dz_0} = A c_i(z_0) \tag{2}$$

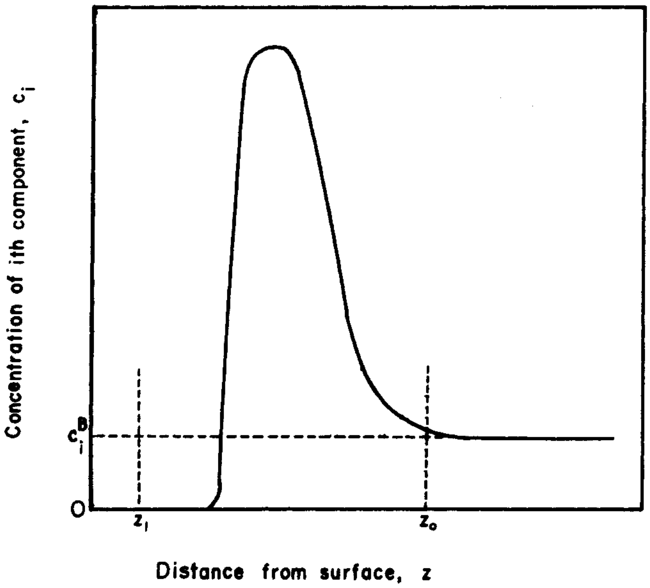

Fig. 1. Concentration profile for adsorption from a fluid on a solid.

If, as in Figure 1, z_0 is chosen so that the concentration at z_0 is approximately equal to that in the bulk phase, or

$$c_i(z_0) \cong c_i^B \tag{3}$$

then Equations (2) and (3) may be combined to give

$$\Delta n_i' \cong A c_i^B \Delta z_0 \tag{4}$$

In order to be a meaningful experimental variable, n_i' should be insensitive to the choice for the position of z_0, or

$$\frac{\Delta n_i'}{n_i'} << 1 \tag{5}$$

The fraction of the surface covered (θ) is defined by

$$\theta = \frac{a N_A n_i'}{A} \tag{6}$$

Equations (4) to (6) may be combined to get

$$\frac{c_i^B N_A\, a \Delta z_0}{\theta} << 1 \tag{7}$$

as a necessary criterion for the measurement of the number of moles in the adsorbed phase. The thickness of the adsorbed phase is of the order of several molecular diameters. The value of Δz_0 is therefore of the order of a molecular diameter.

If the bulk phase is a gas at low pressure, typical values of the variables in Equation (7), at half coverage of the surface, are $c_i^B = 10^{-6}$ mole/cc.; $a = 30$ Å.^{2}, $\Delta z_0 = 5$ Å., and $\theta = 0.5$, so that

$$\frac{c_i^B N_A\, a \Delta z_0}{\theta} \cong 10^{-4}$$

which shows that there is no serious ambiguity involved in measuring the amount adsorbed from gases at low pressure.

If the bulk phase is a liquid, on the other hand, the bulk concentration is of the order of 10^{-2} mole/cc. This value for the concentration, used with the values of the other variables given previously, yields

$$\frac{c_i^B N_A\, a \Delta z_0}{\theta} \cong 1 \ .$$

It may therefore be concluded that the amount adsorbed is not generally a meaningful experimental variable in the case of adsorption from liquids.

The same conclusion applies to adsorption from gases at high pressure. Measurements under these conditions have shown apparent anomalies such as a decrease in the total amount adsorbed with increasing pressure (*7*). In fact, these seemingly anomalous results are only a reflection of the fact that the total amount adsorbed is not a meaningful experimental variable.

Models intended to circumvent this difficulty have been proposed. A monomolecular layer assumption has been widely used to define the thickness of the adsorbed layer. If the liquid is a mixture, this assumption determines not only the total amount adsorbed but the composition of the adsorbed phase as well (*6*). But the monomolecular layer assumption is not subject to experimental verification for the reasons already stated.

THE SURFACE EXCESS

It has been shown that the amount adsorbed is not generally a meaningful experimental variable for the adsorption of liquid mixtures on solids. The pertinent experimental variable is the surface excess (5). The surface excess is defined as the difference between the amount adsorbed and the hypothetical amount adsorbed if the composition of the adsorbed phase were unperturbed (that is, equal to the composition of the bulk liquid) by the surface of the adsorbent, or

$$n_i^E = n'(x_i' - x_i) \tag{8}$$

Summation of both sides of Equation (8) over all the components of the adsorbate gives

$$\sum_i n_i^E = 0 \tag{9}$$

The following development deals with binary liquid mixtures on solids. Variables (x_i, n_i) without superscripts refer to the bulk liquid phase. An overall material balance for component number 1 and number 2 yields

$$n^t = (n_1 + n_2) + (n_1' + n_2') \tag{10}$$

The material balance for component 1 is

$$n^t x_1^t = (n_1 + n_2)x_1 + n_1' \tag{11}$$

x_1^t is defined by

$$x_1^t \equiv \frac{n_1 + n_1'}{n^t} \tag{12}$$

Substitution of $(n_1 + n_2)$ from (10) into (11) gives

$$n^t x_1^t = n^t x_1 + n_1' - (n_1' + n_2')x_1 \tag{13}$$

For a binary mixture, Equation (8) reduces to

$$n_1^E = n_1' - (n_1' + n_2')x_1 \tag{14}$$

Combination of (13) and (14) gives the result

$$n_1^E = n^t(x_1^t - x_1) \tag{15}$$

The quantities n^t and x_1^t, which refer to the adsorbed phase plus the bulk liquid phase, can be measured before contacting the adsorbent with the liquid mixture. x_1, the composition of the bulk liquid, can be measured after the attainment of adsorption equilibrium. Thus the surface excess can be measured experimentally.

THE GIBBS EQUATION

The Gibbs adsorption equation (see Equation 6.8 of reference *3*) is

$$A d\sigma = -S' dT - \sum_i n_i' d\mu_i \tag{16}$$

For a binary adsorbate along an isotherm, (16) reduces to

$$A d\sigma = -n_1' d\mu_1 - n_2' d\mu_2 - n_S' d\mu_S \tag{17}$$

At constant temperature and pressure for the insoluble adsorbent

$$d\mu_S = 0 \tag{18}$$

The Gibbs-Duhem equation for the bulk liquid phase, for fixed temperature and pressure, is

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \tag{19}$$

Substitution of $d\mu_S$ from (18) and $d\mu_2$ from (19) into (17) yields

$$A d\sigma = -\frac{n_1' - (n_1' + n_2')x_1}{x_2} d\mu_1 \tag{20}$$

Combination of (14) and (20) gives

$$A d\sigma = -\frac{n_1^E}{x_2} d\mu_1 \tag{21}$$

The liquid-phase activity coefficient for component 1 is defined by

$$\mu_1(T, P, x_1) = \mu_1^*(T, P) + RT \ln(\gamma_1 x_1) \tag{22}$$

$\mu_1^*(T, P)$ is the chemical potential of pure liquid 1 at the temperature and pressure of the system. At constant temperature and pressure, differentiation of (22) gives

$$d\mu_1 = RT\, d \ln(\gamma_1 x_1) \tag{23}$$

Substitution of $d\mu_1$ from (23) into (21) gives the useful expression

$$A d\sigma = -\frac{RT n_1^E}{x_1(1 - x_1)\gamma_1} d(\gamma_1 x_1) \tag{24}$$

The product

$$\varphi \equiv A\sigma \tag{25}$$

is the appropriate variable for adsorption in microporous solids such as molecular sieves. φ has the units of energy per unit mass of adsorbent. Substitution of (25) into (24) gives

$$d\varphi = -\frac{RT n_1^E}{x_1(1 - x_1)\gamma_1} d(\gamma_1 x_1) \tag{26}$$

Equation (26) may be integrated at constant temperature and pressure:

$$\varphi_1 - \varphi_2 = -RT \int_{x_1=0}^{1} \frac{n_1^E}{x_1(1 - x_1)\gamma_1} d(\gamma_1 x_1) \tag{27}$$

The integrand in (27) approaches finite limits at $x_1 = 0$ and $x_1 = 1$. φ_1 is the surface tension (multiplied by A) for the adsorption of pure component 1 and φ_2 is the surface tension (multiplied by A) for the adsorption of pure component 2. It has been shown previously (*11*) that Equation (27) may be used for the calculation of the difference in surface tensions. Here the objective is to devise a thermodynamic consistency test.

DEGREES OF FREEDOM

For the adsorption system defined previously there are four thermodynamic degrees of freedom for adsorption from a binary liquid mixture. A convenient set of independent variables is T, P, x_1 and the specific surface area of the adsorbent. For a particular adsorbent in a fixed state of aggregration

$$n_1^E = n_1^E(x_1) \quad \text{(fixed } T, P\text{)} \tag{28}$$

A THERMODYNAMIC CONSISTENCY TEST

The consistency test is the integration of Equation (26) through a closed loop. The most convenient path is the adsorption of the three binary liquid mixtures which can be formed from any set of three liquids. Ternary adsorption data are not needed. Application of Equation (27) to the path of binary adsorption for any set of three liquids adsorbed on the same solid leads to a set of three integrals:

Step 1 (1-2 binary adsorbate):

$$\varphi_1 - \varphi_2 = -RT \int_{x_1=0}^{1} \frac{n_1^E}{x_1(1 - x_1)\gamma_1} d(\gamma_1 x_1) \tag{29}$$

Step 2 (1-3 binary adsorbate):

$$\varphi_3 - \varphi_1 = -RT \int_{x_3=0}^{1} \frac{n_3^E}{x_3(1 - x_3)\gamma_3} d(\gamma_3 x_3) \tag{30}$$

Step 3 (2-3 binary adsorbate):

$$\varphi_2 - \varphi_3 = -RT \int_{x_2=0}^{1} \frac{n_2^E}{x_2(1-x_2)\gamma_2}\, d(\gamma_2 x_2) \qquad (31)$$

The sum for the three steps in this closed-path integration must be zero:

$$(\varphi_1 - \varphi_2) + (\varphi_3 - \varphi_1) + (\varphi_2 - \varphi_3) = 0 \qquad (32)$$

The consistency test, Equation (32), uses binary adsorbate data. Of course other consistency tests based upon integration paths through the region of ternary adsorption could be devised.

EXPERIMENT

Chemicals

The adsorbent was silica gel, 8-12 mesh, furnished by the Davison Chemical Company, Baltimore, Md. (Davison designation PA400). The surface area of this gel is 740 sq. m./g (*9*). The silica gel was reactivated by heating to 430°C. for 6 to 8 hr. under vacuum. The properties of the reagents, obtained from Matheson, Coleman and Bell Company, are recorded in Table 1.

TABLE 1. REFRACTIVE INDICES OF REAGENTS

Material	Refractive index, n_D^{25} Experimental	Literature
Benzene	1.4978	1.4979 (4)
Cyclohexane	1.4236	1.42358 (12)
n-heptane	1.3850	1.38511 (1)

Procedure

The objective is the measurement of the function in Equation (28) for each binary mixture. A binary mixture was prepared for each experimental point. The mass of the mixture was determined gravimetrically and the concentration was analyzed refractometrically. A weighed amount of adsorbent was then added to the binary mixture. The system consisting of the binary mixture and the adsorbent was shaken for 10 to 12 hr. in a screw-capped Erlenmeyer flask placed in a reciprocating shaker. The temperature was thermostatically controlled to 30 ±0.1 °C. The equilibrium composition of the bulk liquid (x_1) was then analyzed refractometrically; the calibration curves needed for the refractometric analyses were prepared by us. Finally, the surface excess was calculated by means of Equation (15).

Results

The surface excess as a function of the equilibrium composition of the bulk liquid phase is given in Tables 2, 3, and 4 and plotted in Figures 2, 3, and 4. For the mixture cyclohexane-*n*-heptane, Figure 4 shows that the silica gel exhibited no preference for one compound or the other.

TABLE 2. ADSORPTION OF LIQUID MIXTURES OF BENZENE (1)-CYCLOHEXANE (2) ON SILICA GEL AT 30°C.

mmoles/g. n_1^e	x_1	mmoles/g. n_1^e	x_1
0.674	0.011	1.096	0.549
1.008	0.030	0.908	0.630
0.986	0.033	0.900	0.652
1.274	0.074	0.785	0.703
1.361	0.078	0.802	0.708
1.425	0.107	0.683	0.740
1.454	0.145	0.680	0.755
1.579	0.202	0.488	0.810
1.552	0.240	0.460	0.811
1.555	0.344	0.451	0.844
1.410	0.398	0.261	0.906
1.415	0.434	0.191	0.927
1.362	0.443	0.130	0.930
1.240	0.508	0.173	0.945
1.192	0.536		

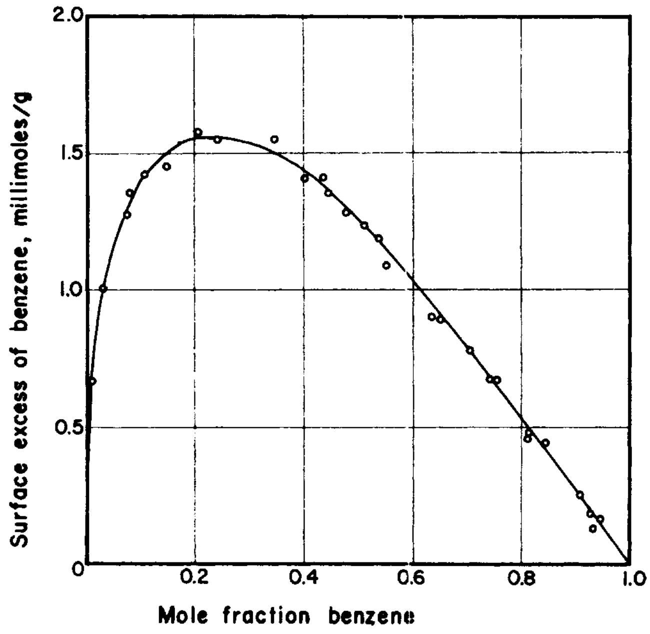

Fig. 2. Adsorption of benzene-cyclohexane mixtures on silica gel at 30°C.

TABLE 3. ADSORPTION OF LIQUID MIXTURES OF BENZENE (1)-*n*-HEPTANE (2) ON SILICA GEL AT 30°C.

mmoles/g. n_1^e	x_1	mmoles/g. n_1^e	x_1
0.466	0.006	1.464	0.396
0.695	0.022	1.429	0.405
1.005	0.044	1.352	0.480
1.273	0.071	1.230	0.542
1.180	0.076	1.122	0.596
1.440	0.126	0.915	0.675
1.608	0.153	0.963	0.693
1.572	0.169	0.836	0.709
1.546	0.174	0.703	0.769
1.641	0.224	0.560	0.806
1.615	0.278	0.563	0.819
1.672	0.295	0.333	0.866
1.624	0.340	0.124	0.955

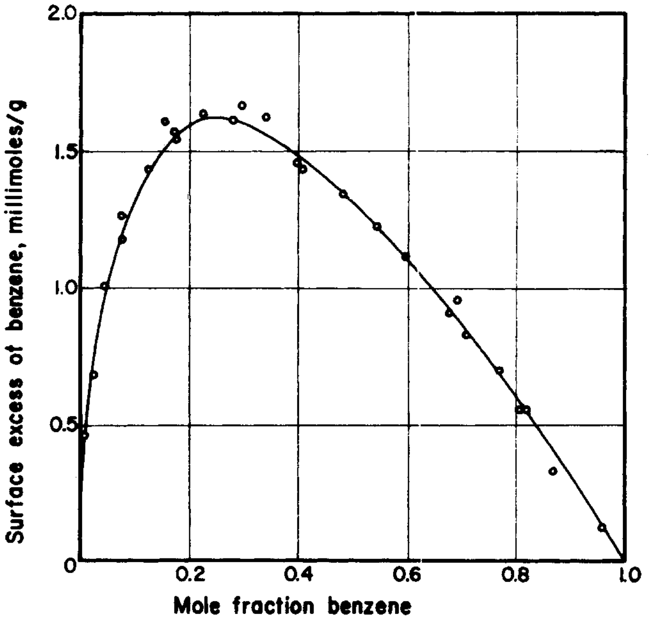

Fig. 3. Adsorption of benzene-*n*-heptane mixtures on silica gel at 30°C.

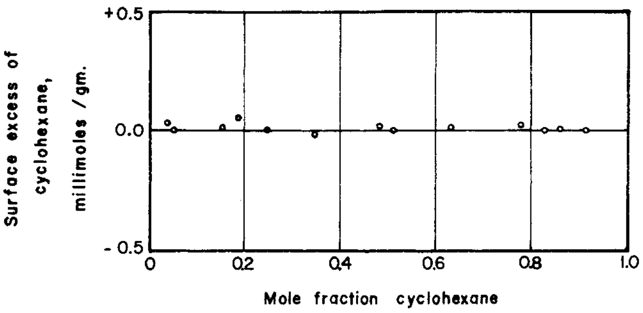

Fig. 4. Adsorption of cyclohexane-*n*-heptane mixtures on silica gel at 30°C.

TABLE 4. ADSORPTION OF LIQUID MIXTURES OF CYCLOHEXANE (1)-*n*-HEPTANE (2) ON SILICA GEL AT 30°C.

mmoles/g. n_1^e	x_1
0.036	0.041
0.000	0.055
0.014	0.157
0.054	0.190
0.000	0.250
0.021	0.349
0.021	0.484
0.000	0.513
0.020	0.633
0.020	0.780
0.000	0.831
0.000	0.862
0.000	0.911

Analysis of Results

The integrals in Equations (29), (30), and (31) were evaluated using graphical methods. The activity coefficients for the bulk liquids were needed. For the mixture benzene–cyclohexane, the activity coefficients for the mixture were available in the literature (*10*) at 40° and 70°C. The values at 30°C. were estimated by assuming that the enthalpy of mixing is independent of temperature or, equivalently, that the logarithm of the activity coefficient varies linearly with the reciprocal of the absolute temperature. Similarly for the mixture *n*-heptane–benzene, the experimental activity coefficients at 60° and 80°C. (*2*) were used to estimate the values at 30°C. For the mixture *n*-heptane–cyclohexane, the activity coefficients were not needed for the integration because the surface excess is zero.

The results of the integration of the Gibbs equation are given in Table 5. The differences in surface tension for the pure liquids on silica gel were calculated using Equation (25) with $A = 740$ sq. m./g. (*9*). Table 5 shows that the sum of the integrals is zero as required by the test, Equation (32). Therefore these data are thermodynamically consistent.

Recently we measured the surface excess for the mixtures benzene–ethyl alcohol, cyclohexane–ethyl alcohol, and benzene–cyclohexane adsorbed on silica gel at 30°C. The data are not thermodynamically consistent, in spite of the fact that data for the same mixtures adsorbed on activated carbon exhibit thermodynamic consistency. Further investigation is needed, but the implication is that the data are inconsistent because one of the components, ethyl alcohol, is chemisorbed on the silica gel. If chemisorption occurs, Equations (8) and (15) do not account for the amount of alcohol consumed in the chemical reaction and therefore cannot be used to determine the surface excess.

TABLE 5. CALCULATION OF DIFFERENCES IN SURFACE TENSION USING THE GIBBS EQUATION. THE NOTATION IS BENZENE (1), CYCLOHEXANE (2), AND *n*-HEPTANE (3)

Binary mixture	J/g Differences in φ	dyne/cm. Differences in σ
1-2	$\varphi_1 - \varphi_2 = -18.1$	$\sigma_1 - \sigma_2 = -24.5$
1-3	$\varphi_3 - \varphi_1 = 18.1$	$\sigma_3 - \sigma_1 = 24.5$
2-3	$\varphi_2 - \varphi_3 = 0$	$\sigma_2 - \sigma_3 = 0$
	Sum = 0	Sum = 0

CONCLUSIONS

The procedure proposed and applied here may be used to test the thermodynamic consistency of experimental data for the adsorption of liquid mixtures on solids. A more important application is that the consistency relationship imposes a constraint on the parameters of any model for adsorption from liquid mixtures.

ACKNOWLEDGMENT

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NOTATION

a = surface area occupied by adsorbate molecule
A = specific surface area of adsorbent
c_i = concentration of i^{th} component
n = number of moles per unit mass of adsorbent
N_A = Avogadro's number
R = gas constant
S = entropy
T = absolute temperature
x = mole fraction
z = distance measured perpendicular to adsorbent surface
z_0 = location of dividing surface

Greek Letters

γ = activity coefficient
μ = chemical potential
σ = surface tension
θ = fraction of surface covered
φ = defined by Equation (25)

Subscripts

i = component i
1 = component 1
2 = component 2
S = adsorbent

Superscripts

= adsorbed phase
E = surface excess
t = adsorbed phase plus bulk phase
$*$ = pure liquid
B = bulk fluid phase

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