A Note on the Thermodynamics of Surface Tension of Binary Solution

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In the prediction of the surface tension of vapor-liquid interface (2) and of the interfacial tension of liquid-liquid interface of the binary solution (5), the interfacial layer may be treated as a regular solution. Another assumption usually made is that partial molal surface areas, $\overline{\Omega}_i$, of the components are independent of composition (2, 5). The validity of this assumption cannot be proven directly because there are no experimental data on the variation of $\overline{\Omega}_i$ with composition.

The systems of benzene–carbon disulfide, water-ethanol, and diethyl ether–benzene are studied in detail. Some thermodynamic relationships which are needed in the derivation of the integral test listed in this section can also be found in Hildebrand and Scott (2).

At constant temperature and pressure the Gibbs' adsorption formula for the vapor-liquid interface of a binary system is:

$$\Omega d\sigma + x_1^s \, d\mu_1 + x_2^s \, d\mu_2 = 0 \qquad (1)$$

with the equilibrium criterion:

$$\mu_i = \overline{G}_i = \overline{G}_i^s; \quad i = 1, 2 \qquad (2)$$

The Gibbs-Duhem relation for the liquid phase of a binary system at constant temperature and pressure is:

$$x_1 \, d\mu_1 + x_2 \, d\mu_2 = 0 \qquad (3)$$

The combination of Equations (1) and (3) gives

$$\Omega d\sigma + \frac{x_1^s - x_1}{x_2} d\mu_1 = 0 \qquad (4)$$

The total free energy of the interface, G, is defined as the sum of the Gibbs free energy and surface energy, that is

$$G = x_1^s \, (\overline{G}_1^s + \overline{\Omega}_1\sigma) + x_2^s \, (\overline{G}_2^s + \overline{\Omega}_2\sigma)$$

x_1^s moles of pure component 1 have a total free energy of x_1^s $(G_1^o + \Omega_1\sigma_1)$, and x_2 moles of pure component 2 have a total free energy of x_2^s $(G_2^o + \Omega_2\sigma_2)$. Therefore, molal total free energy of mixing of the interface, ΔG_m^s, becomes

$$\Delta G_m^s = x_1^s(\overline{G}_1^s + \overline{\Omega}_1\sigma) + x_2^s(\overline{G}_2^s + \overline{\Omega}_2\sigma) - x_1^s(G_1^o + \Omega_1\sigma_1) - x_2^s(G_2^o + \Omega_2\sigma_2) \qquad (5)$$

The surface activities for components 1 and 2 are defined with pure components chosen as standard state.

$$(\overline{G}_i^s + \overline{\Omega}_i\sigma) - (G_i^o + \Omega_i\sigma_i) = RT \ln a_i^s; \quad i = 1, 2 \qquad (6)$$

If we assume that the partial molal surface areas $\overline{\Omega}_1$ and $\overline{\Omega}_2$ are independent of composition, then

$$\overline{\Omega}_i = \Omega_i; \quad i = 1, 2 \qquad (7)$$

This assumption is often made in the prediction of surface tension or liquid-liquid interfacial tension of solutions. Then Equation (6) becomes

$$\overline{G}_i^s - G_i^o = RT \ln a_i^s - \Omega_i \, (\sigma - \sigma_i); \quad i = 1, 2 \qquad (8)$$

INTEGRAL TEST

The integral test (area test) and the differential test for the consistency of vapor-liquid equilibrium data have been derived and extensively used. No analogous work has been done for the interfacial zone. In this section, by using the assumption of constant partial molal surface area $\overline{\Omega}_i$, an analogous formula for area test can be derived. Therefore, the formula may be useful in testing the validity of the assumption of constant $\overline{\Omega}_i$.

The substitution of Equations (7) and (8) into Equation (5) yields

$$\Delta G_m^s = RT \, (x_1^s \ln a_1^s + x_2^s \ln a_2^s) \qquad (9)$$

The activity coefficient of the interface is defined as

$$a_i^s = \gamma_i^s \, x_i^s; \quad i = 1, 2 \qquad (10)$$

For an ideal solution, $\gamma_i^s = 1$, therefore, the total free energy of mixing for an ideal interfacial solution becomes:

$$\Delta G_{m\ \mathrm{;\ ideal}}^s = RT \, (x_1^s \ln x_1^s + x_2^s \ln x_2^s) \qquad (11)$$

The molal excess total free energy of mixing of the interface, ΔG_{ex}^s, equal to $(\Delta G_m^s - \Delta G_{m\ \mathrm{;\ ideal}}^s)$, or

$$\Delta G_{ex}^s = RT \ln \, (x_1^s \ln \gamma_1^s + x_2^s \ln \gamma_2^s) \qquad (12)$$

By differentiating Equation (12) at constant temperature and pressure, we obtain

$$d(\Delta G_{ex}^s) = RT \left(x_1^s \, d \ln \gamma_1^s + x_2^s \, d \ln \gamma_2^s + \ln \frac{\gamma_1^s}{\gamma_2^s} d \, x_1^s \right) \qquad (13)$$

The assumption that molal surface areas are independent of composition leads to

$$\Omega = x_1^s \, \Omega_1 + x_2^s \, \Omega_2 \qquad (14)$$

Differentiation of Equation (6) at constant temperature and pressure yields

$$d \, \overline{G}_i^s = d\mu_i = RT d\ln \, a_i^s - \Omega_i d\sigma \qquad (15)$$

where the equilibrium criterion given by Equation (2) has been used. Combining Equations (10), (14), and (15) with the Gibbs' adsorption equation, Equation (1), we have

$$x_1^s \, d \ln \gamma_1^s + x_2^s \, d \ln \gamma_2^s = 0 \qquad (16)$$

or

$$\frac{x_1^s}{x_2^s} = - \frac{d \ln \gamma_1^s}{d \ln \gamma_2^s} \qquad (17)$$

where the identity, $x_1 \, d \ln x_1 + x_2 \, d \ln x_2 = d \, x_1 + d \, x_2 = 0$, has been used.

Another useful relationship can be derived by the substitution of Equation (16) into Equation (13), then

$$d(\Delta G_{ex}^s) = R \ T \ln \frac{\gamma_1^s}{\gamma_2^s} d \, x_1^s \qquad (18)$$

Since ΔG_{ex}^s equals zero for a pure component, integration of the above equation from $x_1^s = 0$ to $x_1^s = 1$ gives

$$\int_0^1 \ln \frac{\gamma_1^s}{\gamma_2^s} d \, x_1^s = 0 \qquad (19)$$

Equations (17) and (19) are derived by using a strictly thermodynamic method with the assumption of constant molal surface area. Therefore, these two equations can be used to test the validity of this assumption, provided interface concentrations and interface activity coefficients can be evaluated. Equation (17) is a differential test and Equation (19) is an integral test. The latter is more convenient to use, hence Equation (19) will be used in the following discussions.

CALCULATION OF Ω, x^s AND γ^s

x^s and γ^s are difficult to determine. However, they can be evaluated from surface tension data, vapor-liquid equilibrium data, and molal surface area of pure components. No experimental data for molal surface area has been published. For nonpolar substances the molal surface area may be estimated from the following equation (*2*), provided they do not depart seriously from spherical symmetry.

$$\Omega = N\left(\frac{V}{N}\right)^{2/3} = N^{1/3}\,V^{2/3} \tag{20}$$

where V is the molal volume of liquid and N is the Avogadro number.

The substitution of Equation (15) into Equation (1) yields

$$x_1{}^s = \frac{x_1 - x_2\,\Omega_2\,\dfrac{d\sigma}{d\mu_1}}{1 + x_2(\Omega_1 - \Omega_2)\,\dfrac{d\sigma}{d\mu_2}} = 1 - x_2{}^s \tag{21}$$

Since

$$d\mu_i = R\ T\ d\ \ln\ \gamma_i\ x_i;\quad i = 1, 2$$

for the liquid phase, then we have

$$\frac{d\sigma}{d\mu_i} = \frac{1}{RT}\ \frac{d\sigma}{d\ \ln\ \gamma_i\ x_i};\quad i = 1, 2 \tag{22}$$

Equations (21) and (22) can be used to calculate $x_1{}^s$ and $x_2{}^s$ from experimental $\gamma - x$ and $\sigma - x$ relations.

For the liquid phase

$$\mu_i - \mu_i{}^o = R\ T\ \ln\ a_i = R\ T\ \ln\ \gamma_i\ x_i;\ 1, 2 \tag{23}$$

By substituting Equation (23) into Equation (8), we have

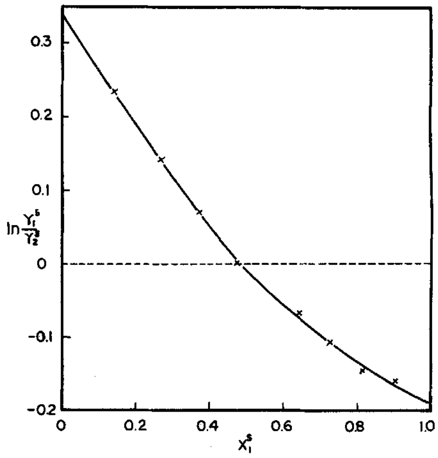

Fig. 1. Integral test for benzene-carbon disulfide system.

$$a_i{}^s = \gamma_i{}^s\ x_i{}^s = \gamma_i\ x_i\ e^{\frac{(\sigma-\sigma_i)\Omega_i}{RT}};\quad i = 1, 2 \tag{24}$$

The above equation has been obtained by Hildebrand and Scott (*2*). It can be used to calculate the interface activity coefficients, $\gamma_i{}^s$, because the interface concentrations have been obtained from Equations (21) and (22).

Benzene-Carbon Disulfide System

Surface tension data for the benzene-carbon disulfide system are available at 18°C. (*3*), vapor-liquid equilibrium data are available at 20°C. (*4*). Since activity coefficients of liquid solution vary only slightly with temperature, and temperature difference is rather small, the activity coefficients at 20°C. are used for 18°C. Table 1 shows the calculation result. Figure 1 shows that the ratio of the areas above and below the line of $\ln\ \gamma_1{}^s/\gamma_2{}^s = 0$ is about 10:7. Therefore, the assumption of constant molal surface area may be acceptable for this system.

TABLE 1. INTERFACE ACTIVITY COEFFICIENTS OF BENZENE–CARBON DISULFIDE SYSTEM AT 18°C.

Mole fraction of benzene x_1	Surface tension σ, dyne./cm.	Activity coeff. γ_1	γ_2	Interface conc. $x_1{}^s$	Interface activity coeff. $\gamma_1{}^s$	$\gamma_2{}^s$	$\ln\frac{\gamma_1{}^s}{\gamma_2{}^s}$
0.0	32.24	——	1.000	0	——	1.000	——
0.1	31.35	1.587	1.005	0.146	1.279	1.012	0.233
0.2	30.73	1.422	1.018	0.270	1.189	1.030	0.142
0.3	30.25	1.290	1.038	0.373	1.132	1.054	0.071
0.4	29.88	1.192	1.069	0.472	1.074	1.072	0.001
0.5	29.64	1.125	1.110	0.558	1.055	1.096	—0.038
0.6	29.37	1.080	1.162	0.640	1.039	1.110	—0.066
0.7	29.22	1.046	1.227	0.725	1.024	1.140	—0.106
0.8	29.11	1.024	1.302	0.812	1.017	1.176	—0.145
0.9	29.04	1.009	1.385	0.904	1.010	1.218	—0.156
1.0	29.98	1.000	——	1.000	1.000	——	——

density of C_6H_6 at 18°C. = 0.882 g. ml., $\Omega_{1/N}$ = 28 A.^{2}, Equation (20).
density of CS_2 at 18°C. = 1.265 g. ml., $\Omega_{2/N}$ = 21 A.^{2}, Equation (20).

Water-Ethanol System

Surface tension and vapor liquid equilibrium data are available at 25°C. (*1, 7*). The surface areas per molecules of ethanol and water are chosen as 21.2 A.^{2}, and 9.64 A.^{2}, respectively (*2, 8*). These values are calculated from Equation (20). Table 2 and Figure 2 illustrate the results. Therefore, this test indicates that either Equation (20) does not hold for polar solutions or the assumption of constant $\overline{\Omega}_i$ is not valid, or both.

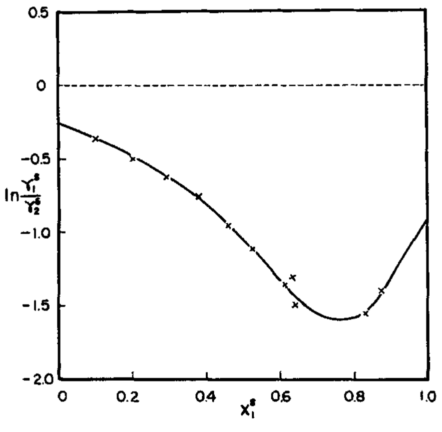

Fig. 2. Integral test for water-ethanol system.

TABLE 2. INTERFACE ACTIVITY COEFFICIENTS OF WATER–ETHANOL SYSTEM

Mole fraction of water x_1	Surface tension σ, dyne./cm.	Activity coeff. γ_1	γ_2	Interface conc. x_1^s	Interface activity coeff. γ_1^s	γ_2^s	$\ln \frac{\gamma_1^s}{\gamma_2^s}$
0.0	22.0	—	1.00	0	—	1.000	—
0.1	22.6	2.32	1.00	0.101	0.722	1.037	—0.361
0.2	23.2	2.10	1.02	0.202	0.664	1.088	—0.494
0.3	23.85	1.87	1.06	0.293	0.621	1.156	—0.620
0.4	24.6	1.66	1.13	0.380	0.575	1.250	—0.755
0.5	25.4	1.46	1.25	0.458	0.535	1.384	—0.951
0.6	26.35	1.29	1.45	0.525	0.506	1.528	—1.110
0.7	27.6	1.17	1.76	0.612	0.474	1.816	—1.343
0.8	29.7	1.08	2.77	0.631	0.505	1.830	—1.287
0.9	36.6	1.02	3.02	0.640	0.624	2.761	—1.487
0.96	47.86	1.00	3.42	0.832	0.654	3.08	—1.551
0.98	55.57	1.00	3.39	0.872	0.762	2.99	—1.371
1.0	72.2	1.00	—	1.000	1.000	—	—

Diethyl Ether-Benzene System

Table 3 shows the interesting result of the ether-benzene system at 18°C. The vapor-liquid equilibrium follows Raoult's Law at this temperature (*6*). Incidentally, the activity coefficients of the interface are nearly equal to unity.

TABLE 3. INTERFACE ACTIVITY COEFFICIENTS OF ETHER-BENZENE SYSTEM AT 18°C.†

Mole fraction of ether x_1	Surface§ tension σ, dyne./cm.	Interface conc. x_1^s	Interface activity conc. γ_1^s	γ_2^s
0.000	28.94‡	0.00	—	1.000
0.2085	25.43	0.374	1.020	0.995
0.4130	22.82	0.627	0.995	1.028
0.5121	21.72	0.717	0.994	1.024
0.6110	20.67	0.785	0.997	1.018
0.8090	18.99	0.907	1.003	1.027
1.0000	17.44	1.000	1.000	—

† Density of ether at 18°C. = 0.716 g./ml., $\Omega_{1/N}$ = 30.9 A.^{2}.
‡ The surface tension is slightly different from that given in Table 1.
§ Reference 5.

DISCUSSION

We have thus shown that the molal surface area may be consider independent of composition for such nonpolar systems as ether–benzene or benzene–carbon disulfide. However, we do not claim this as a general rule. Incidentally, the ether-benzene system, in which vapor pressure follows Raoult's Law, shows that the interface is an ideal solution. The deviation from Equation (19) is so great for the polar system of water–ethanol, that we cannot conclude that $\overline{\Omega}_i$ is independent of concentration. We can only conclude that either the $\overline{\Omega}_i$ values for the pure components cannot be determined from Equation (20), or that $\overline{\Omega}_i$ is not independent of composition, or both.

The effect of air on the surface tension has been neglected in the calculation. The extension of this method to liquid-liquid interface is of interest.

NOTATION

a = activity
G = Gibbs free energy
N = Avogadro number
R = gas constant
T = absolute temperature
V = molal volume
x = mole fraction

Greek Symbols

γ = activity coefficient
σ = surface tension
Ω = molal surface area
μ = chemical potential

Superscripts

s = interface
o = pure component as standard state
— = partial quantities

Subscripts

i = component i, $i = 1, 2$
m = change due to mixing
ex = excess quantities
ideal = ideal solution

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