

On the Necessity of Using Activities in the Gibbs Equation

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We show that using mole fractions x_s instead of activities a_s in the Gibbs equation for analyzing surface tension curves for onset of amphiphilic association may be open for discussion. First, we determined the activity coefficients for the simple binary water–ethanol and water–*n*-propanol systems from vapor pressure measurements. The activity coefficients are neither unity nor are they constant in the range where the surface tensions σ of the binary systems decrease from the water value down to the value of the pure alcohols. Second, a break in the σ vs $\ln x_s$ curves disappears when proper σ vs $\ln a_s$ curves are constructed. The implication for determining critical micelle concentrations and headgroup areas of surfactants from surface tension curves is addressed.

Introduction

The concept of surface tension is central for the field of surface science. In the subfield of surfactant science the measurement of surface tension is employed as a tool used to determine the ability of a surfactant to display surface activity and to form micellar association structures. The surface tensions of mixtures of surfactants with water typically show a decrease from around 72 mN/m for the surface tension of pure water to values around 30 mN/m with increasing surfactant concentration. Above the critical micelle concentration (cmc), the surface tension remains nearly constant. At constant pressure the Gibbs equation reads (see e.g., ref 1)

$$d\sigma = -S^\sigma dT - \sum_i \Gamma_i^\sigma d\mu_i \quad (1)$$

It reduces at constant temperature for a single surfactant in water to

$$d\sigma = -\Gamma_s^w d\mu_s \quad (2)$$

where the superscript *w* means that we have chosen the dividing surface so that the water excess $\Gamma_w^\sigma = 0$. The variation of the surfactant chemical potential

$$\mu_s = \mu_s^o + RT \ln a_s \quad (3)$$

is

$$d\mu_s = RT d \ln a_s = RT \frac{da_s}{a_s} \quad (4)$$

where the activity a_s is

$$a_s = \gamma_s x_s \quad (5)$$

with the rational activity coefficient γ_s and mole fraction x_s of the surfactant. From eqs 4 and 5 it is obvious that a replacement of a_s by x_s is only permissible if $\gamma_s = 1$ (in eq 5) or at least a constant, i.e., $d\gamma_s/dx_s = 0$, which would suffice to reformulate eq 4

$$d\mu_s = RT \frac{dx_s}{x_s} = RT d \ln x_s \quad (6)$$

The lack of knowledge of γ_s has frequently led to the (unwarrented) assumption that instead of eq 2 and therein eq 4

$$d\sigma = -\Gamma_s^w RT d \ln a_s \quad (7)$$

one might use

$$d\sigma = -\Gamma_s^w RT d \ln x_s \quad (8)$$

We demonstrate that this assumption is not correct, even for systems as simple as binary water–alcohol systems.

Determination of the Activity Coefficients for Water–Alcohol Mixtures

There are various ways to measure and to empirically describe activity coefficients. We use vapor pressure measurements to

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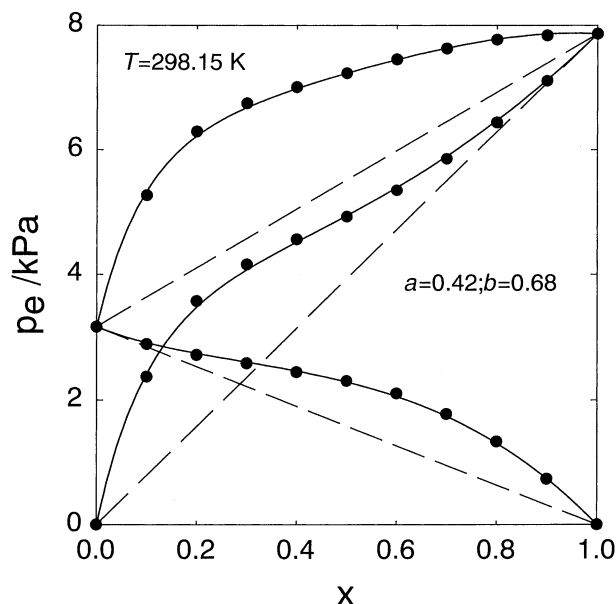


Figure 1. Equilibrium vapor pressures of water–ethanol at 25 °C. x : Mole fraction of ethanol; dashed lines: ideal case (Raoult's law); full lines: nonideal case (van Laar description, see eqs 9–13).

demonstrate the nonideality and describe the nonideality by the van Laar equations for the activity coefficients.² According to the van Laar treatment the activity coefficients are interrelated

$$\log \gamma_w = \frac{a}{\left(1 + \frac{a(1-x_s)}{bx_s}\right)^2} \quad (9)$$

$$\log \gamma_s = \frac{b}{\left(1 + \frac{bx_s}{a(1-x_s)}\right)^2} \quad (10)$$

and are determined by only two additional parameters, a and b . The equilibrium vapor pressure is

$$p = p_w + p_s \quad (11)$$

with the partial vapor pressures

$$p_w = p_{w,0} \gamma_w x_w \quad (12)$$

and

$$p_s = p_{s,0} \gamma_s x_s \quad (13)$$

where the $p_{i,0}$ values are the vapor pressures of pure water and pure surfactant, respectively.

In Figure 1 we analyze the same vapor pressure data for water–ethanol as previously studied by Guggenheim.³ The deviations from ideality are quite substantial. Water forms the left system, ethanol forms the right system. Accordingly, $x = x_s$. The van Laar equations describe the experimental vapor pressures very well using $a = 0.42$ and $b = 0.68$.

In Figure 2 we apply the same procedure to the water–*n*-propanol systems recently measured by Viisanen and Strey.⁴ Here the van Laar constants are $a = 0.56$ and $b = 1.14$. The van Laar treatment permits a sufficient analytical description of the activities.

Analysis of Surface Tensions of Water–Alcohol Mixtures

Recently, the surface tensions of water–ethanol previously studied by Teitelbaum et al.⁵ (as reviewed and compiled by

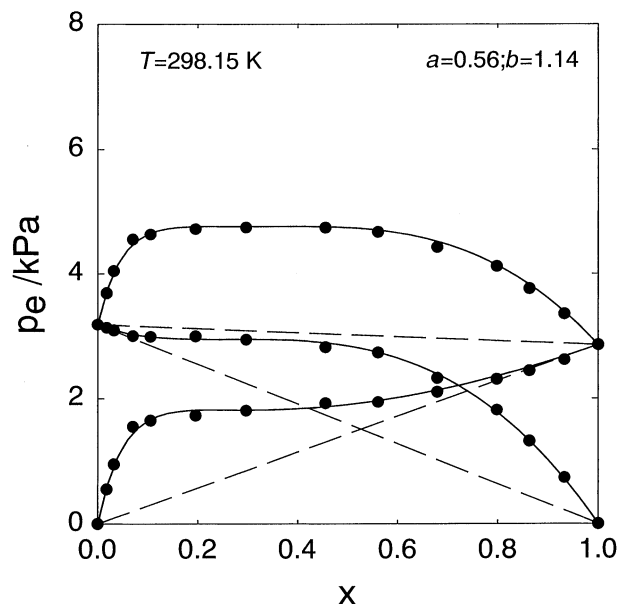


Figure 2. Same as Figure 1 for water–*n*-propanol.

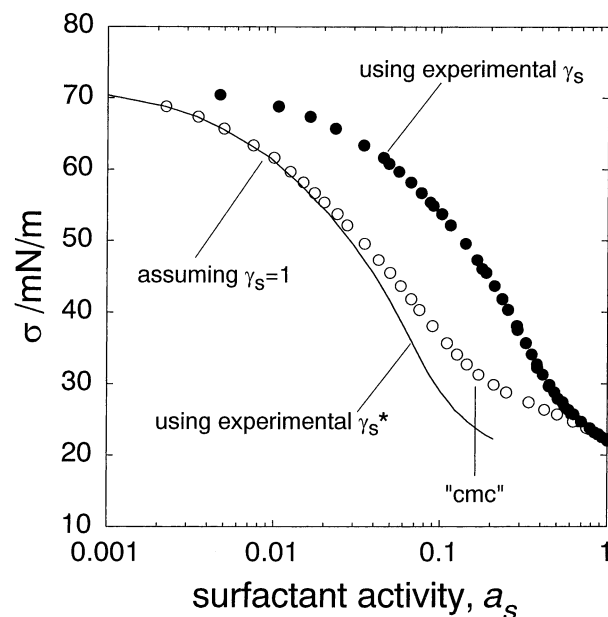


Figure 3. Surface tensions of water–ethanol at 25 °C. a_s : Activity of ethanol. Hollow symbols: surface tension vs mole fractions x_s (assuming $\gamma_s = 1$); full symbols, surface tension vs activities a_s (using activity coefficients γ_s determined from Figure 1); full line, using practical activity coefficients γ_s^* forcing agreement at high (ideal) dilution.

Timmermans⁶) were reproduced and substantially extended by Aratono et al.⁷ We compared the various data sets. They superimpose within the experimental error. In Figure 3 we consider for clarity only the data of Aratono et al.⁷ The hollow symbols refer to the assumption $\gamma_s = 1$. With some imagination one is able to construct an intersection of two straight lines⁸ which are denoted in Figure 3 by “cmc”. The full symbols are obtained if one uses the experimental activities. These are at hand because we determined the activity coefficients ourselves. As an immediate observation, we note that the break in the sequence of hollow points disappears, if plotted against the activity; a necessity, if $\gamma_s \neq 1$. This is the case, as one can see from Table 1, where the activity coefficients, the activities, and the mole fractions are given. Therefore, the “cmc”, as the break has been referred to by Kahlweit et al.,⁸ is in fact unsupported.

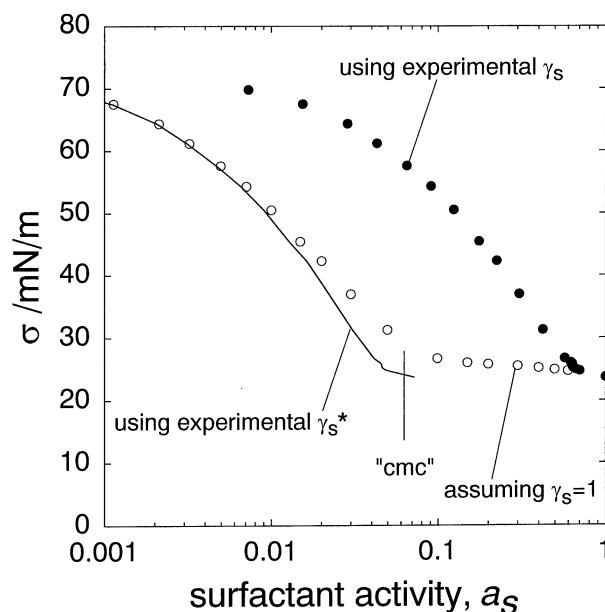
TABLE 1: Surface Tension of Binary Water–Alcohol Systems, Included Are Also Activities and Activity Coefficients^a

Water–Ethanol				
x_s	σ/mNm^{-1}	a_s	γ_w	γ_s
0	71.94	0.0000	1.000	4.786
0.000999	70.37	4.715e-3	1.000	4.762
0.002241	68.72	0.0106	1.000	4.732
0.003496	67.30	0.0164	1.000	4.703
0.004997	65.67	0.0233	1.000	4.667
0.007495	63.33	0.0345	1.000	4.610
0.009986	61.55	0.0455	1.000	4.553
0.0125	59.60	0.0562	1.000	4.497
0.01498	58.13	0.0666	1.001	4.443
0.0175	56.60	0.0768	1.001	4.390
0.02003	55.39	0.0869	1.001	4.336
0.024	53.67	0.1021	1.001	4.255
0.02752	52.19	0.1152	1.002	4.185
0.03508	49.52	0.1418	1.003	4.041
0.0425	47.33	0.1661	1.004	3.907
0.04993	45.49	0.1888	1.006	3.780
0.05788	43.59	0.2114	1.008	3.652
0.06698	41.82	0.2353	1.011	3.514
0.07505	40.31	0.2551	1.013	3.398
0.09011	38.11	0.2883	1.019	3.199
0.1102	35.67	0.3266	1.027	2.964
0.1263	34.16	0.3531	1.035	2.796
0.145	32.71	0.3801	1.046	2.622
0.1702	31.29	0.4113	1.062	2.417
0.2098	29.79	0.4512	1.091	2.151
0.2499	28.76	0.4839	1.126	1.936
0.3402	27.32	0.5417	1.222	1.592
0.4208	26.34	0.5857	1.326	1.392
0.5029	25.70	0.6298	1.452	1.252
0.6252	24.63	0.7009	1.674	1.121
0.7512	23.84	0.7859	1.947	1.046
0.8772	22.86	0.8859	2.269	1.010
1	22.22	1.0000	2.630	1.000

Water– <i>n</i> -Propanol				
x_s	σ/mNm^{-1}	a_s	γ_w	γ_s
0.0000	71.97	0.0000	1.000	13.80
5.300e-4	69.79	7.275e-3	1.000	13.73
1.130e-3	67.50	0.0154	1.000	13.64
2.120e-3	64.35	0.0286	1.000	13.50
3.230e-3	61.20	0.0431	1.000	13.34
4.960e-3	57.60	0.0650	1.000	13.10
7.090e-3	54.29	0.0908	1.000	12.81
0.0100	50.53	0.1243	1.001	12.43
0.0149	45.45	0.1762	1.001	11.83
0.0200	42.27	0.2249	1.002	11.24
0.0300	36.96	0.3062	1.005	10.21
0.0497	31.25	0.4242	1.012	8.534
0.0992	26.67	0.5718	1.044	5.764
0.1500	26.00	0.6211	1.094	4.140
0.2000	25.77	0.6335	1.158	3.167
0.3000	25.48	0.6343	1.323	2.114
0.4000	25.18	0.6416	1.533	1.604
0.4984	24.88	0.6643	1.781	1.333
0.5970	24.67	0.7025	2.069	1.177
1.0000	23.66	1.0000	3.631	1.000

The same conclusion was reached in a related communication by Friberg et al.⁹

The analogous result for water–*n*-propanol is shown in Figure 4. The surface tension data recently measured,¹⁰ which are more coherent than previous data sets,^{5,6} seem to show a sharp break, if the hollow symbols referring to the assumption $\gamma_s = 1$ are considered. The full symbols show again that the correct use of activities changes the findings dramatically. As can be seen, the break in the sequence of hollow points is changed into a smooth sigmoidal variation, if activities are used. Furthermore, those data located above the apparent “cmc” are pushed together.

**Figure 4.** Same as Figure 3 for water–*n*-propanol.

This is a consequence of the activity becoming nearly constant and close to unity above the “cmc”.

In surfactant science, because of the use of solid surfactants and/or long chain molecules of low volatility, a practical system of activity coefficients is occasionally in use. Then the surfactant activity coefficient is defined as

$$\gamma_s^* = \gamma_s / \lim_{x_s \rightarrow 0} \gamma_s \quad (14)$$

and the surfactant solution is conceived as an ideal solution at infinite dilution. In effect this leads to a lateral shift of the previously calculated surface tension–activity curves (the full points in Figures 3 and 4). The results obtained using γ_s^* are shown as full lines which now coincide with the surface tension versus x_s at the dilute end. Although the choice of the reference point for the chemical potential is obviously a matter of convenience, the use of γ_s^* in Figures 3 and 4 enables us to see immediately the difference in limiting slope of the surface tension curve as the “cmc” is approached, which will express itself in disparate values of the area of per surfactant molecule. One should note that the actual definition of the activity coefficients does not affect the slope of the curves. Therefore, we will continue to use the rational activity coefficient γ_s in the following. From Table 1 one can see that (i) the numerical value of γ_s is far from unity and this even more so the larger the alcohol molecule and (ii) γ_s varies considerably in the range of surface tensions before they level off at the “cmc”. In fact γ_s decreases by a factor of 2. Therefore, calculating Γ_s^w using eq 8 in the form

$$\Gamma_s^w = -RT \frac{d\sigma}{d \ln x_s} \quad (15)$$

must lead to erroneous results, which then directly affects values for the area per surfactant molecule which are usually calculated from

$$a_h = (\Gamma_s^w N_A)^{-1} \quad (16)$$

The high density of data points of the water–ethanol data by Aratono et al.⁷ permits a further analysis. In Figure 5 the

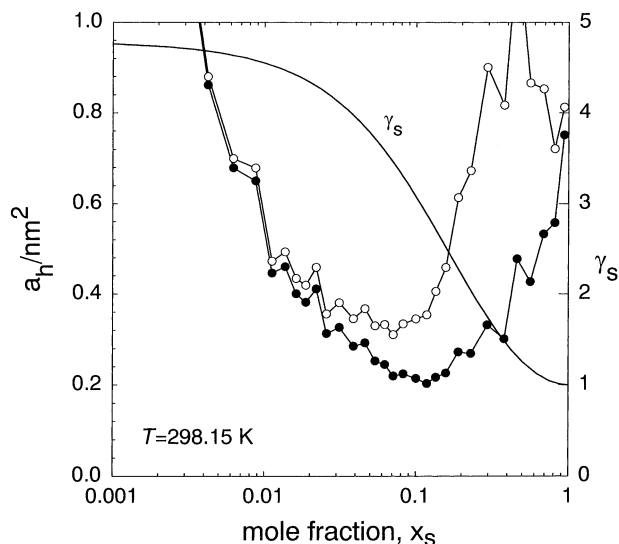


Figure 5. Areas per molecule of water–ethanol evaluated using eq 15 (hollow) and 17 (full symbols). The activity coefficient is also shown. Note the strong variation of γ_s in the vicinity of the “cmc” (cf. Figure 3).

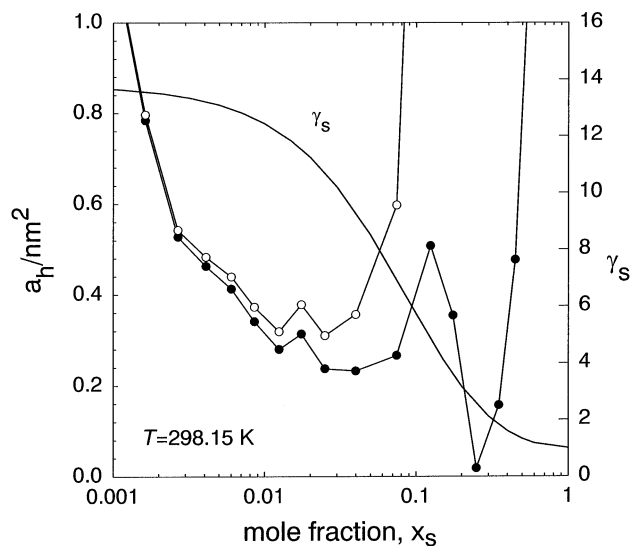


Figure 6. Same as Figure 5 for water–*n*-propanol.

surface tension data are first evaluated using eqs 15 and 16 (hollow symbols). This is the typical procedure performed numerous times in the literature. The full symbols demonstrate the quantitative changes by using more correctly

$$\Gamma_s^w = -RT \frac{d\sigma}{d \ln a_s} \quad (17)$$

instead of eq 15. Included in Figure 5 is also the activity coefficient γ_s of ethanol. As can be seen at very low and very high alcohol fractions, where γ_s is constant, but different from unity, the difference between a_h calculated using eq 15 or 17 is marginal. But in the intermediate range, where γ_s varies and where the “cmc” is located, the use of activities is mandatory. The value of minimum area changes by as much as 50%. As an aside, note that the actual value of the minimum value of $a_h = 0.20 \text{ nm}^2$ of the correct evaluation is close to that used by Guggenheim in his model description of the water–ethanol surface.³

In Figure 6 the analogue procedure is carried through for water–*n*-propanol. Also here the area per molecule in the

vicinity of the “cmc” is affected dramatically. The minimum value drops from a much too large 0.32 nm^2 to a more reasonable 0.23 nm^2 . We believe it is obvious that the minimum at $x_s = 0.25$ is an artifact arising from the piling up of the data in this region making the derivative very sensitive to finite experimental accuracy.

Implications for Solutions of Micelle-Forming Surfactants

One may wonder which of the observations made above are going to carry over to mixtures of genuine surfactants with water? The answer is in principle, all of them; in practice, some of them. Recalling that γ_s values for *n*-propanol are larger than those for ethanol (cf. Table 1) and considering only the length of the alkyl chain, it can be expected that γ_s for long-chain surfactants at concentrations below the cmc takes even larger values than for the alcohols. Because for concentrations above the cmc the surfactant resides mostly in micelles, the activity remains nearly constant and, because the activity is exactly unity at $x_s = 1$, it will have to become near unity at the cmc. Therefore, dramatic changes in γ_s in a region below the cmc for solutes of increasing molecular size are to be expected where eq 15 is usually applied.

However, in addition to molecular size, γ_s is affected by other factors related to molecular structures, such as the nature of hydrophilic groups including ionizable groups, or conformation. Consequently, extension of observations for short-chain alcohols may not be so obvious. In addition, because the cmc values for genuine surfactants are low, even if $\gamma_s > 1$ it is reasonable to expect that the values are practically constant. For ionic surfactants, there is evidence from electromotive force measurements that the mean-ionic (practical) activity coefficient at concentrations below the cmc is close to unity or nearly invariant with concentration (see for example refs 11–15). Therefore, for such systems use of eq 15 appeared to be justified. For shorter-chain surfactants of relatively high cmc, as suggested by Friberg et al.,⁹ the problem outlined above may be significant.

The following question is justified: Why, with the exception of electromotive force measurements for a limited number of ionic surfactants, have there been no attempts to measure activity coefficients of genuine surfactants? The answer lies presumably in the fact that the determination of activity coefficients of such molecules is rather difficult. The vapor pressure is low and the direct determination by vapor pressure measurements becomes imprecise. At low concentrations other techniques such as freezing point depression and osmotic pressure are, in general, insensitive. Therefore precise measurements of activity coefficients of surfactants are urgently needed. For shorter-chain surfactants, techniques based on colligative properties as well as evaluation of activities from light-scattering intensities should be practical.¹⁶

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