R&D NOTES

Activity Coefficients on Different Concentration Scales and Reference States

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The activity coefficient measures the degree of departure of a substance's behavior from ideal or ideally dilute behavior and is a very important thermodynamic parameter. Its numerical values depend on concentration scales and reference states at fixed temperature and pressure. However, its dependency on reference states chosen have not been considered fully. Some activity coefficients using different definitions have been obtained by various experimental and/or theoretical methods. Therefore, the conversions of activity coefficients from one concentration scale and/or from one reference state to another are very significant, not only in theoretical researches but also in applications. However, these conversions are tricky and confusing. Here we report the relationship between activity coefficients and some methods for their conversions.

Consider a ternary system, as an example: electrolyte (E)–nonelectrolyte (N)–water (W). Generally, there are two molality scales: one in which the electrolyte is regarded as the solute, whereas the N–W mixture as the mixed solvent, and thus the molality of E (m_E^M), is defined as the number of moles of E per kilogram (kg) of mixed solvent; the other in which the electrolyte and nonelectrolyte are regarded as two solutes and pure water as the solvent, molalities of E (m_E^W) and N (m_N^W) are defined as the number of moles of E and N per kg of pure water, respectively. They are called "the water-molality" and are denoted usually by m_E and m_N in the following. When $m_N = 0$, that is, for the binary E–W system, a superscript "0 " will be used (m_E^0). It is easy to deduce[1]

$$m_E^W = m_E^M(1 + 0.001 m_N M_N) = m_E^M/(1 - w_N) \qquad (1)$$

where M_N and w_N denote the molar mass of N and the mass fraction of N in the mixed solvent (N–W), respectively.

With respect to m_E^M, the molality-scale mean activity coefficient of E is denoted by $\gamma_\pm^{m(M)}$, which is referred to unity at infinite dilution in a given mixed solvent (the subscript " $\pm$" denotes the mean ionic quantity and will be omitted in the following). Similarly, $\gamma^{m(W)}$denotes the water-molality-scale mean activity coefficient of E with respect to m_E^W, which is referred to unity at infinite dilution in pure water. Based on the thermodynamic theory, the following relationship was derived:

$$\gamma^{m(W)} = \gamma_\infty^{m(W)} \gamma^{m(M)} \qquad (2)$$

where $\gamma_\infty^{m(W)}$ is the limiting mean activity coefficient of E at a given m_N at infinite dilution of E. Experimentally, its value can be obtained from measured values of $\gamma^{m(W)}$ and $\gamma^{m(M)}$. Plots of $\gamma^{m(M)}$ vs. $\gamma^{m(W)}$ for the sucrose–NaCl–water system are presented in Figure 1, indicating that Eq. 2 can work well. Obviously, if one obtains values of $\gamma_\infty^{m(W)}$, then the conversion can easily be made between $\gamma^{m(W)}$ and $\gamma^{m(M)}$. We suggest several methods for evaluating $\gamma_\infty^{m(W)}$ as follows.

Method 1. Based on the Debye–Hückel extended equation,[2] the following relation was derived from Eq. 2:

$$\log \gamma^{m(W)} = \log \gamma_\infty^{m(W)} + \frac{-AI^{1/2}}{(1 + Ba^\circ I^{1/2})} + Cm_E^M - \log(1 + 0.001 \nu m_E^M M_{NW}) \qquad (3)$$

where A and B are the Debye–Hückel constants, a° is the ion size parameter, C is the ion-interaction parameter, and M_{NW} is the mean molar mass of the mixed solvent (N–W).

Method 2. Based on the Pitzer equation[3] and Eq. 2, we have

$$\log \gamma^{m(W)} = \log \gamma_\infty^{m(W)} + f_\gamma + B_\gamma m_E^M + C_\gamma (m_E^M)^2 \qquad (4)$$

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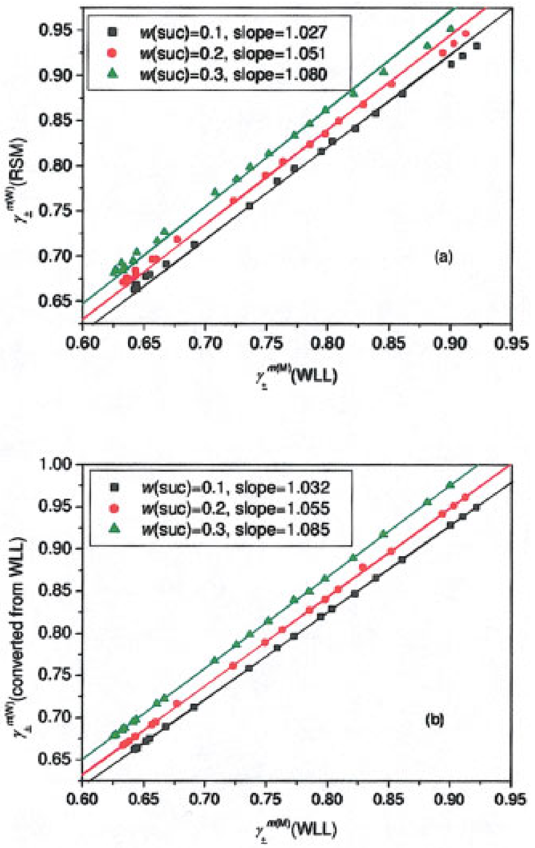

Figure 1. Plots of $\gamma^{m(W)}$ vs. $\gamma^{m(M)}$ for the sucrose (suc)–NaCl–water system.

$\gamma^{m(M)}$ was taken from data in Wang et al.,[8]; $\gamma^{m(W)}$ (a) was taken from data in Robinson et al.[7a] and Stokes[7b] and (b) was obtained from the conversion of $\gamma^{m(M)}$ in Wang et al.[8] by Stokes.[7b] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

where f_γ, B_γ, and C_γ are the parameters defined by Pitzer.

Method 3. Based on the Sen–Johnson–Roy equation[4] and Eq. 2, we have

$$\log \gamma^{m(W)} = \log \gamma_\infty^{m(W)} + A_1(m_E^M)^{1/2} + A_2(m_E^M) + A_3(m_E^M)^{3/2} + \cdots \quad (5)$$

where A_i represents the empirical parameters.

Method 4. From the values of standard Gibbs free energies of transfer, $\gamma_\infty^{m(W)}$ can been calculated by

$$\Delta_t G^{\circ m(M)} = \nu RT \ln[\gamma_\infty^{m(W)}(1 + 0.001 m_N M_N)] \quad (6a)$$

where $\Delta_t G^{\circ m(M)}$ is the standard Gibbs energy of transfer of E from water to the W–N mixture and the infinite dilution of E in the given N–W mixed solvent is taken as the reference state on the m_E^M scale. If we choose the infinite dilution of E in the water solvent containing N at m_N as the reference state on the m_E^W scale, then the following equation should be used:

$$\Delta_t G^{\circ m(W)} = \nu RT \ln \gamma_\infty^{m(W)} \quad (6b)$$

given that these two standard Gibbs free energies of transfer meet the relation[1]

$$\Delta_t G^{\circ m(M)} = \Delta_t G^{\circ m(W)} + \nu RT \ln(1 + 0.001 m_N M_N) \quad (6c)$$

Method 5. Based on the Scatchard theory,[5] one obtains the following equation[6]:

$$\log[\gamma^{m(W)}/\gamma^0] = C_1 m_N + C_2 m_N m_E + C_3 m_N^2 + C_4 m_E^2 m_N + C_5 m_E m_N^2 + C_6 m_N^3 + \cdots \quad (7)$$

where C_i are the parameters indicating the interactions between E and N, which can be obtained from the fits of experimental data (such as cell potentials). When $m_E \rightarrow 0$, Eq. 7 reduces to

$$\log[\gamma_\infty^{m(W)}/\gamma_\infty^0] = C_1 m_N + C_3 m_N^2 + C_6 m_N^3 + \cdots \quad (8)$$

where $\gamma_\infty^0 = 1$.

Method 6. According to cross-differential relation, it can be derived when m_N is not high that

$$\ln \gamma_\infty^{m(W)} = 1/2 k_S m_N \quad (9)$$

where k_S is the salting constant on the natural logarithm.

Using the literature values of $\gamma^{m(W)}$ for the sucrose–NaCl–W system,[7-9] the $\gamma_\infty^{m(W)}$ values were obtained least-squares by methods 1 to 3, respectively, and are listed in Table 1, indicating that these values are in good agreement with those evaluated experimentally except for method 3. In methods 1 and 2, the Debye–Hückel parameters *A* and *B* are needed, whereas in method 3 these parameters are not needed in the fit. Values of $\Delta_t G^{\circ m(M)}$ can be applied directly to the calculation of $\gamma_\infty^{m(W)}$ from Eq. 6a. On the other hand, if the values of $\gamma^{m(W)}$ were determined at different molalities, then methods 5 and 6 can also be selected to evaluate the $\gamma_\infty^{m(W)}$ because, when these determinations are made, C_i and/or k_S can be obtained at the same time. Values of $\gamma_\infty^{m(W)}$ were also evaluated by methods 5 and 6 and are included in Table 1. The agreement is also good. Relative error is not greater than 2%.

It is necessary to point out that in the use of activity coefficients and their conversions, the following points should be noted:

(1) Because the activity coefficient is a correcting factor for the concentration, its value corresponds to a concentration scale, such as water-molality,[7,11] mixed solvent-molality,[8,12] molarity, and mole faction.

(2) The activity coefficient depends on the reference state chosen. Generally, the infinite dilution of the solute is taken as its reference state, in which $\gamma \rightarrow 1$. However, on the water-molality scale, two reference states can be chosen. One is the infinite dilution of the solute in pure water (that is, $m_N = 0$)[7,11] and another is in a given m_N ($m_N \neq 0$).[13]

(3) Log$[\gamma_\infty^{m(W)}/\gamma_\infty^0]$ is called the primary medium effect.[14] However, the medium effect is also defined as $\log(\gamma_\infty^c/\gamma_\infty^0)$, where $\gamma_\infty^c/\gamma_\infty^0$ is the so-called transfer activity coefficient.[15]

(4) For a fixed-composition E–N–W solution, the numerical values of both concentrations and corresponding activity coefficients depend on their scales. For example, for a given su-

Table 1. Comparison of the Limiting Activity Coefficients ($\gamma_{\infty}^{m(\mathrm{W})}$) of NaCl at Various m_{N} Obtained from Experimental Data with Those Evaluated from Different Methods for the Sucrose–NaCl–Water System at 298.15 K[a]

	w(suc) = 0.1			w(suc) = 0.2			w(suc) = 0.3		
Methods	RSM[b]	ZHUO[c]	WLL[d]	RSM[b]	ZHUO[c]	WLL[d]	RSM[b]	ZHUO[c]	WLL[d]
Experimental[e]	1.027(2)	1.030(2)	1.032(0)	1.051(2)	1.057(2)	1.055(0)	1.080(3)	1.087(0)	1.085(0)
Method 1[f]	1.017(1)	1.021(1)	1.030(2)	1.031(1)	1.037(1)	1.045(2)	1.066(1)	1.074(1)	1.085(2)
Method 2[g]	1.017(0)	1.021(0)	1.033(2)	1.038(0)	1.044(0)	1.054(1)	1.065(1)	1.074(1)	1.088(2)
Method 3[h]	1.011(1)	1.012(1)	1.038(5)	1.030(1)	1.032(1)	1.055(4)	1.051(2)	1.058(4)	1.093(6)
Method 4[i]			1.019			1.059			1.085
Method 5[j]		1.020(7)			1.042(7)			1.068(7)	
Method 6[k]			1.019			1.043			1.075

[a] Numbers in parentheses give the standard deviation in the final digit. Values of $\gamma^{m(\mathrm{M})}$ were taken from ref 8.
[b] Values of $\gamma^{m(\mathrm{W})}$ were taken from ref 7.
[c] Values of $\gamma^{m(\mathrm{W})}$ were taken from ref 9.
[d] Values of $\gamma^{m(\mathrm{W})}$ were obtained from the conversation of $\gamma^{m(\mathrm{M})}$ in ref 8 by Stokes (see ref 7b).
[e] Obtained from plots of $\gamma^{m(\mathrm{W})}$ vs $\gamma^{m(\mathrm{M})}$ through zero.
[f] Obtained from method 1.
[g] Obtained from method 2.
[h] Obtained from method 3.
[i] Obtained from method 4. $\Delta_t G^{\circ m(\mathrm{M})}$ was taken from ref 10.
[j] Obtained from method 5.
[k] Obtained from method 6. The salting constant $k_{\mathrm{S}} = 0.116$ kg mol^{-1} was taken from ref 10.

crose–NaCl–water solution at $m_{\mathrm{S}} = 0.730$ mol kg^{-1} (20 wt %) at 298.15 K, $m_{\mathrm{E}}^{\mathrm{M}} = 0.1000$ mol kg^{-1} and $\gamma^{m(\mathrm{M})} = 0.749$,[8] whereas $m_{\mathrm{E}}^{\mathrm{W}} = 0.125$ mol kg^{-1} and $\gamma^{m(\mathrm{W})} = 0.790$.[7]

In conclusion, the relationship between activity coefficients is derived from different concentration scales. Some methods are given for converting activity coefficients. A comparison is made between the activity coefficients converted by different methods, indicating that these values are in good agreement with each other and these methods can be successfully applied to the conversions of activity coefficients based on different definitions.

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