Supporting Information

Improvement of the Zdanovskii-Stokes-Robinson Model for Mixtures Containing Solutes of Different Charge Types

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This document describes, first, the complete derivation of eq 30 for $\ln(\gamma_R)$. This is also relevant to the other activity coefficient equations. Second, the derivation of the "mixture" contributions to solute activity coefficients (eq 32) is also given, as only the final equations have been presented elsewhere.

1. Equation 30 for the Activity Coefficient of Solute R

The expression for $\ln(\gamma_R)$ is obtained from the McKay-Perring equation (eq 10 or eq 11), based upon using eq 20 for the total water content of the solution (W_{total}). Recall that, for this derivation, we assume that the solution mixture contains four solutes r_1, r_2, q_1 and q_2 and that the selected species R is r_1. The first step is to determine expressions for the three terms within the integral in eq 11.

Beginning with eq 21 for $1/m$:

$$\frac{1}{m}=\frac{x_r}{m_r^o}+\frac{x_{q_1}}{m_{q_1}^o}+\frac{x_{q_2}}{m_{q_2}^o} + \frac{M_w}{\ln(a_w)}\left[\left(x_r\nu_r+x_{q_1}\nu_{q_1}+x_{q_2}\nu_{q_2}\right)\phi' - x_r\nu_r\phi_r^{o}{}' - x_{q_1}\nu_{q_1}\phi_{q_1}^{o}{}' - x_{q_2}\nu_{q_2}\phi_{q_2}^{o}{}'\right] \tag{S1}$$

the first three terms are converted to osmotic coefficients, yielding

$$\frac{1}{m}=\frac{-M_w}{\ln(a_w)}\left[x_r\nu_r\phi_r^o+x_{q_1}\nu_{q_1}\phi_{q_1}^o+x_{q_2}\nu_{q_2}\phi_{q_2}^o+\left(x_r\nu_r+x_{q_1}\nu_{q_1}+x_{q_2}\nu_{q_2}\right)\phi' - x_r\nu_r\phi_r^{o}{}' - x_{q_1}\nu_{q_1}\phi_{q_1}^{o}{}' - x_{q_2}\nu_{q_2}\phi_{q_2}^{o}{}'\right] \tag{S2}$$

For a mixture in which solute group r contains the two solutes r_1 and r_2, then $\mathbf{r}_r = \mathbf{r}_{r_1} + \mathbf{r}_{r_2}$. Multiplying eq S2 by m/m^* (equivalent to $(\Sigma_s n_s)/(\Sigma_s n_s\nu_s)$) gives:

$$\frac{1}{m^*}=\frac{-M_w}{\ln(a_w)}\left[\left(\mathbf{r}_{r_1}+\mathbf{r}_{r_2}\right)\phi_r^o+\mathbf{r}_{q_1}\phi_{q_1}^o+\mathbf{r}_{q_2}\phi_{q_2}^o+\phi' - \left(\mathbf{r}_{r_1}+\mathbf{r}_{r_2}\right)\phi_r^{o}{}' - \mathbf{r}_{q_1}\phi_{q_1}^{o}{}' - \mathbf{r}_{q_2}\phi_{q_2}^{o}{}'\right] \tag{S3}$$

Equation S3 is one of the terms in the McKay-Perring integral. Next, this must be differentiated and multiplied by $\mathbf{r}_c$ (which is equal to $\mathbf{r}_{r_2} + \mathbf{r}_{q_1} + \mathbf{r}_{q_2}$, or $1 - \mathbf{r}_{r_R}$). The osmotic coefficients ϕ', ϕ_r^o, and $\phi_r^{o\prime}$ in eq S3 all have non-zero differentials, and the differentials of the various ratios **r** have the following values: $d\mathbf{r}_{r_1}/d\mathbf{r}_c = -1$, $d\mathbf{r}_{r_2}/d\mathbf{r}_c = \mathbf{r}_{r_2}/\mathbf{r}_c$, $d\mathbf{r}_{q_1}/d\mathbf{r}_c = \mathbf{r}_{q_1}/\mathbf{r}_c$ and $d\mathbf{r}_{q_2}/d\mathbf{r}_c = \mathbf{r}_{q_2}/\mathbf{r}_c$. Using these substitutions yields:

$$\mathbf{r}_c\left(\frac{\partial 1/m^*}{\partial \mathbf{r}_c}\right)_{a_w} = \frac{-M_w}{\ln(a_w)}\Bigg[-\mathbf{r}_c\phi_r^o + \mathbf{r}_{r_2}\phi_r^o + \mathbf{r}_{q_1}\phi_{q_1}^o + \mathbf{r}_{q_2}\phi_{q_2}^o + \mathbf{r}_c\left(\frac{\partial\phi'}{\partial \mathbf{r}_c}\right)_{a_w} + \mathbf{r}_c\phi_r^{o\prime} - \mathbf{r}_{r_2}\phi_r^{o\prime} - \mathbf{r}_{q_1}\phi_{q_1}^{o\prime}$$
$$- \mathbf{r}_{q_2}\phi_{q_2}^{o\prime} - \mathbf{r}_c(\mathbf{r}_{r_1} + \mathbf{r}_{r_2})\left(\frac{\partial\phi_r^o}{\partial \mathbf{r}_r}\right)_{a_w} - \mathbf{r}_c(\mathbf{r}_{r_1} + \mathbf{r}_{r_2})\left(\frac{\partial\phi_r^{o\prime}}{\partial \mathbf{r}_r}\right)_{a_w}\Bigg] \quad \text{(S4)}$$

The final term in the McKay-Perring integral involves the molality of solute R and is given by:

$$\frac{1}{k_R m_R^o} = \frac{-M_w}{\ln(a_w)}\phi_R^o \quad \text{(S5)}$$

The complete McKay-Perring expression for $\ln(\gamma_R)$ is obtained by substituting eqs S3, S4 and S5 into eq 11 of the paper:

$$\ln(\gamma_R) = \ln(\gamma_R^o) + \ln(\nu_R m_R^o/m^*)$$
$$+ \frac{1}{M_w}\left(\frac{k_R}{\nu_R}\right)\int_o^{\ln(a_w)}\Bigg\{\frac{-M_w}{\ln(a_w)}\Bigg[-\mathbf{r}_c\phi_r^o + \mathbf{r}_{r_2}\phi_r^o + \mathbf{r}_{q_1}\phi_{q_1}^o + \mathbf{r}_{q_2}\phi_{q_2}^o + \mathbf{r}_c\left(\frac{\partial\phi'}{\partial \mathbf{r}_c}\right)_{a_w} + \mathbf{r}_c\phi_r^{o\prime} - \mathbf{r}_{r_2}\phi_r^{o\prime}$$
$$- \mathbf{r}_{q_1}\phi_{q_1}^{o\prime} + \mathbf{r}_c(\mathbf{r}_{r_1} + \mathbf{r}_{r_2})\left(\frac{\partial\phi_r^o}{\partial \mathbf{r}_c}\right)_{a_w} - \mathbf{r}_c(\mathbf{r}_{r_1} + \mathbf{r}_{r_2})\left(\frac{\partial\phi_r^{o\prime}}{\partial \mathbf{r}_c}\right)_{a_w} - \mathbf{r}_{q_2}\phi_{q_2}^{o\prime}\Bigg]$$
$$+ \frac{M_w}{\ln(a_w)}\left[(\mathbf{r}_{r_1} + \mathbf{r}_{r_2})\phi_r^o + \mathbf{r}_{q_1}\phi_{q_1}^o + \mathbf{r}_{q_2}\phi_{q_2}^o + \phi' - (\mathbf{r}_{r_1} + \mathbf{r}_{r_2})\phi_r^{o\prime} - \mathbf{r}_{q_1}\phi_{q_1}^{o\prime} - \mathbf{r}_{q_2}\phi_{q_2}^{o\prime}\right]$$
$$- \frac{M_w}{\ln(a_w)}\phi_R^o\Bigg\}\, d\ln(a_w) \quad \text{(S6)}$$

where γ_R^o is the activity coefficient of solute R in a solution of pure aqueous R (of molality m_R^o) at the water activity of the mixture. Equation S6 simplifies to:

$$\ln(\gamma_R) = \ln(\gamma_R^o) + \ln(\nu_R m_R^o/m^*)$$
$$+ \left(\frac{k_R}{\nu_R}\right)\int_o^{\ln(a_w)}\Bigg\{\phi_r^o - \phi_R^o - \mathbf{r}_c(\mathbf{r}_{r_1} + \mathbf{r}_{r_2})\left(\frac{\partial\phi_r^o}{\partial \mathbf{r}_c}\right)_{a_w} - \mathbf{r}_c\left(\frac{\partial\phi'}{\partial \mathbf{r}_c}\right)_{a_w} + \mathbf{r}_c(\mathbf{r}_{r_1} + \mathbf{r}_{r_2})\left(\frac{\partial\phi_r^{o\prime}}{\partial \mathbf{r}_c}\right)_{a_w}$$

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$$-\phi_r^{o}{}' + \phi'\Bigg\}\frac{\mathrm{d}\ln(a_\mathrm{w})}{\ln(a_\mathrm{w})} \qquad \text{(S7)}$$

The integral in eq S7 contains, first of all, three terms that are unrelated to the extension developed in this paper. It is also true that, for the model without extension:

$$\ln(\gamma_\mathrm{R}) = \ln(\gamma_\mathrm{R}^{o,r}) + \ln\left(\left(\nu_\mathrm{R} m_\mathrm{R}^{o,r} + \nu_{r_2} m_{r_2}^{o,r}\right)/m^*\right)$$

$$\equiv \ln(\gamma_\mathrm{R}^{o,r}) + \ln(W_\mathrm{total}/w^{o,r}) + \ln\left(\left(\nu_\mathrm{R} n_\mathrm{R} + \nu_{r_2} n_{r_2}\right)/\sum_s \nu_s n_s\right) \qquad \text{(S8)}$$

(see eq 15 of Clegg, Seinfeld, and Edney: *J. Aerosol Sci.* **2003**, *34*, 667-690). Evidently the first three terms in the integral in eq S7 are equal to

$$\ln(\gamma_\mathrm{R}^{o,r}/\gamma_\mathrm{R}^{o}) + \ln\left(\left(\nu_\mathrm{R} m_\mathrm{R}^{o,r} + \nu_{r_2} m_{r_2}^{o,r}\right)/\nu_\mathrm{R} m_\mathrm{R}^{o}\right) \qquad \text{(S9)}$$

where $m_\mathrm{R}^{o,r}$ and $m_{r_2}^{o,r}$ in eq S9 are the molalities of the solutes R and r_2 in a solution containing those solutes only, at the water activity of the mixture. Thus we can transform eq S7 to

$$\ln(\gamma_\mathrm{R}) = \ln(\gamma_\mathrm{R}^{o,r}) + \ln\left(\left(\nu_\mathrm{R} m_R^{o,r} + \nu_{r_2} m_{r_2}^{o,r}\right)/m^*\right)$$

$$+\left(\frac{k_\mathrm{R}}{\nu_\mathrm{R}}\right)\int_o^{\ln(a_\mathrm{w})}\left\{-\mathrm{r_c}\left(\frac{\partial\phi'}{\partial \mathrm{r_c}}\right)_{a_\mathrm{w}} + \phi' - \phi_r^{o}{}' + \mathbf{r}_\mathrm{c}\left(\mathbf{r}_{r_1} + \mathbf{r}_{r_2}\right)\left(\frac{\partial\phi_r^{o}{}'}{\partial \mathbf{r}_\mathrm{c}}\right)_{a_\mathrm{w}}\right\}\frac{\mathrm{d}\ln(a_\mathrm{w})}{\ln(a_\mathrm{w})} \qquad \text{(S10)}$$

By considering the case of a solution whose osmotic coefficient is described by eq 7 in the paper, and carrying out a similar procedure to that described in section 2.2 (eqs 16 and 17), the value of the integral in eq S10 is found to be

$$\ln(\gamma_\mathrm{R}') - \ln(\gamma_\mathrm{R}^{o,r}{}') - \ln\left(\left(\nu_\mathrm{R} m_R^{o,r}{}' + \nu_{r_2} m_{r_2}^{o,r}{}'\right)/m^*{}'\right) \qquad \text{(S11)}$$

Substituting expression S11 into eq S10 an analytical equation for $\ln(\gamma_\mathrm{R})$ is obtained:

$$\ln(\gamma_\mathrm{R}) = \ln(\gamma_\mathrm{R}^{o,r}) + \ln(\gamma_\mathrm{R}'/\gamma_\mathrm{R}^{o,r}{}') + \ln\left(\left(\nu_\mathrm{R} m_\mathrm{R}^{o,r} + \nu_{r_2} m_{r_2}^{o,r}\right)/m^*\right)$$

$$-\ln\left(\left(\nu_\mathrm{R} m_\mathrm{R}^{o,r}{}' + \nu_{r_2} m_{r_2}^{o,r}{}'\right)/m^*{}'\right) \qquad \text{(S12)}$$

or

$$\ln(\gamma_\mathrm{R}) = \ln(\gamma_\mathrm{R}^{o,r}) + \ln(\gamma_\mathrm{R}'/\gamma_\mathrm{R}^{o,r}{}') + \ln\left(\frac{W_\mathrm{total}\, w^{o,r}{}'}{W_\mathrm{total}{}'\, w^{o,r}}\right) \qquad \text{(S13)}$$

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It is clear that eq S12 is analogous to eq 29 for $\ln(\gamma_Q)$ except that the activity coefficients γ^o, and water masses w^o, are for solutions containing both solutes r_1 and r_2 and not just the solute whose activity coefficient is being calculated.

2. Mixture Contributions to the Activity Coefficients

Consider, first, a mixture containing two solutes, 1 and 2, which dissociate into ν_1 and ν_2 ions, respectively, in solution. (One or both solutes may also be non-dissociating, in which case ν is equal to unity.) Equation (6) of McKay and Perring (1953) yields the mean molal activity coefficient of solute 1 (γ_1) in the mixture, and can be written:

$$\ln(\gamma_1) = \ln(\gamma_1^o) + \ln(k_1 m_1^o/m^*)$$

$$+\left(\frac{1}{M_w}\right)\left(\frac{k_1}{\nu_1}\right)\int_0^{\ln a_w}\left\{-\left(\frac{1}{m^{*2}}\right)\left(\frac{\partial m^*}{\partial \ln \mathbf{r}_2}\right)_{a_w} - \frac{1}{m^*} + \frac{1}{k_1 m_1^o}\right\} d\ln a_w \qquad \text{(S14)}$$

where γ_1^o and m_1^o are the activity coefficient and molality, respectively, of solute 1 in a pure aqueous solution at water activity a_w. The quantity m^* can be any linear combination of the molalities m_1 and m_2 in the mixture at the specified water activity. Hence, $m^* = k_1 m_1 + k_2 m_2$ (see equations 3 and 4 of McKay and Perring, 1953). Symbol M_w (kg) is the molar mass of the solvent, water. The ratio $\mathbf{r}_2$ is equal to $k_2 m_2/m^*$.

Expressions for the terms $(1/(k_1 m_1^o) - 1/m^*)$ and $-(1/m^{*2})(\partial m^*/\partial \ln \mathbf{r}_2)_{a_w}$ are needed in order to evaluate the integral in the above equation, and so provide an analytical expression for the activity coefficient γ_1. These terms are derived below, first for the two solute case, and then for three solutes and (by extension) a multicomponent solution.

Activity Coefficient Equations for a Two Solute Mixture

We begin with:

$$W_{total} = w_1^{o} + w_2^{o} + (n_1 + n_2)x_1x_2(A^0 + A^1y_{1,2} + Ba_w) \qquad \text{(S15)}$$

where W_{total} (and each w_i^{o}) are kg of solvent, water. Subscripts (1,2) for the mixture parameters (which are specific to the interaction of this pair of solutes) are omitted here for simplicity. The total molality of the solutes m in the mixture is equal to $m_1 + m_2$, and in this solution $y_{1,2} = x_2 = n_2/(n_1 + n_2) = m_2/(m_1 + m_2)$. Dividing both sides of equation (S15) by $(n_1 + n_2)$ we obtain:

$$1/m = x_1/m_1^{o} + x_2/m_2^{o} + x_1x_2(A^0 + A^1x_2 + Ba_w) \qquad \text{(S16)}$$

Defining $b = (A^0 + A^1x_2 + Ba_w)$, and multiplying by m/m^* gives

$$1/m^* = m_1/(m^*m_1^{o}) + m_2/(m^*m_2^{o}) + bm_1m_2/(m\,m^*) \qquad \text{(S17)}$$

We then substitute $\mathbf{r}_2/k_2$ for m_2/m^*, and $(1 - \mathbf{r}_2)/k_1$ for m_1/m^*, yielding:

$$\frac{1}{m^*} = \frac{1}{k_1m_1^o} + \mathbf{r}_2\left(\frac{1}{k_2m_2^o} - \frac{1}{k_1m_1^o}\right) + bm_2\left(\frac{1-\mathbf{r}_2}{k_1m}\right) \qquad \text{(S18)}$$

Equation (S18) can be rearranged to give an expression for the second set of terms in the integral in equation (S14):

$$\frac{1}{k_1m_1^o} - \frac{1}{m^*} = \mathbf{r}_2\left(\frac{1}{k_1m_1^o} - \frac{1}{k_2m_2^o}\right) - bm_2\left(\frac{1-\mathbf{r}_2}{k_1m}\right) \qquad \text{(S19)}$$

The differential in equation (S14) can be evaluated using the definition of $1/m^*$ in equation (S18) by recognizing that $-(1/m^{*2})(\partial m^*/\partial \ln \mathbf{r}_2)_{a_w}$ is equal to $+\mathbf{r}_2(\partial(1/m^*)/\partial \mathbf{r}_2)_{a_w}$. The problem is further simplified by the fact that all terms *not* involving b in the integral in equation (S14) ultimately cancel, and are henceforth ignored. It is because of this cancellation that solute activity coefficients in solutions obeying the standard ZSR relationship (i.e., without b) are given by the first two terms in equation (S14) only (Stokes and Robinson, *J. Phys. Chem.* **70**, 2126-2130, 1966). However, for the more general case we have:

$$\ln(\gamma_1) = \ln(\gamma_1^{\circ}) + \ln(k_1 m_1^{\circ}/m^*)$$

$$+\left(\frac{1}{M_w}\right)\left(\frac{k_1}{\nu_1}\right)\int_0^{\ln a_w}\left\{\mathbf{r}_2\left(\frac{\partial(bm_2(1-\mathbf{r}_2)/k_1 m)}{\partial \mathbf{r}_2}\right)_{a_w} - bm_2\left(\frac{1-\mathbf{r}_2}{k_1 m}\right)\right\} d\ln a_w \qquad \text{(S20)}$$

Next, using $m_1 = \mathbf{r}_1 m^*/k_1$, and $m_2 = \mathbf{r}_2 m^*/k_2$, we determine that:

$$\frac{m_2}{m} = x_2 = \frac{\mathbf{r}_2}{k_2/k_1 + (1-k_2/k_1)\mathbf{r}_2} \qquad \text{(S21a)}$$

$$= \mathbf{r}_2/K \qquad \text{(S21b)}$$

where K is the denominator in equation (S21a), and x_2 is the solvent free mole fraction of solute 2. Substituting for the two occurrences of m_2/m in equation (S20) so that the integral is expressed in terms of the ratio $\mathbf{r}_2$ (which is invariant with respect to $\ln a_w$), the terms in the integral in equation (S20) can be evaluated to yield:

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$$\frac{b\mathbf{r}_2}{k_1 K}\left[\frac{\mathrm{d}b}{\mathrm{d}\mathbf{r}_2}\frac{(1-\mathbf{r}_2)\mathbf{r}_2}{b}-\frac{\mathbf{r}_2}{K}\right] \tag{S22}$$

Only the A^1 term in b varies with respect to $\mathbf{r}_2$, and $\mathrm{d}b/\mathrm{d}\mathbf{r}_2$ is given by:

$$\frac{\mathrm{d}b}{\mathrm{d}\mathbf{r}_2}=\frac{A^1}{K}\left[1-\frac{\mathbf{r}_2(1-k_2/k_1)}{K}\right] \tag{S23}$$

Some further simplification allows equation (S20) to be written as:

$$\ln(\gamma_1) = \ln(\gamma_1^{\circ}) + \ln(k_1 m_1^{\circ}/m^*) + \left(\frac{1}{M_\mathrm{w}}\right)\left(\frac{k_1}{\nu_1}\right)\int_0^{\ln a_\mathrm{w}}\left\{-(1/k_1)x_2^2(b-x_1A^1)\right\}\mathrm{d}\ln a_\mathrm{w} \tag{S24}$$

$$= \ln(\gamma_1^{\circ}) + \ln(k_1 m_1^{\circ}/m^*) - \left(\frac{1}{M_\mathrm{w}}\right)\left(\frac{k_1}{\nu_1}\right)\left(\frac{x_2^2}{k_1}\right)\int_0^{\ln a_\mathrm{w}}\left\{A^0+A^1(x_2-x_1)+Ba_\mathrm{w}\right\}\mathrm{d}\ln a_\mathrm{w} \tag{S25}$$

Finally, we substitute $\nu_1 = k_1$, $\nu_2 = k_2$, and evaluate the integral to obtain:

$$\ln(\gamma_1) = \ln(\gamma_1^{\circ}) + \ln(\nu_1 m_1^{\circ}/m^*) - \left(\frac{x_2^2}{\nu_1 M_\mathrm{w}}\right)\left\{[A^0+A^1(x_2-x_1)](\ln a_\mathrm{w}) - B(1-a_\mathrm{w})\right\} \tag{S26}$$

The corresponding expression for the activity coefficient of solute 2 is the same as equation (S26), but with subscripts 1 and 2 transposed.

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Activity Coefficient Equations for a Multicomponent Mixture

Next, we extend the treatment above to an indefinite number of components by first deriving the equations for a three solute mixture. The equation for the water content is:

$$1/m = x_1/m_1^{\mathrm{o}} + x_2/m_2^{\mathrm{o}} + x_3/m_3^{\mathrm{o}} + x_1x_2(A^0_{1,2} + A^1_{1,2}y_{1,2} + B_{1,2}a_w)$$

$$+ x_1x_3(A^0_{1,3} + A^1_{1,3}y_{1,3} + B_{1,3}a_w) + x_2x_3(A^0_{2,3} + A^1_{2,3}y_{2,3} + B_{2,3}a_w) \qquad \text{(S27)}$$

Defining $b_{i,j} = (A^0_{i,j} + A^1_{i,j}y_{i,j} + B_{i,j}a_w)$, $m^* = k_1m_1 + k_2m_2 + k_3m_3$, $m = m_1 + m_2 + m_3$, $y_{i,j} = n_j/(n_i + n_j)$, and multiplying equation (S27) by m/m^* we obtain:

$$1/m^* = m_1/(m^*m_1^{\mathrm{o}}) + m_2/(m^*m_2^{\mathrm{o}}) + m_3/(m^*m_3^{\mathrm{o}}) + b_{1,2}m_1m_2/(m\,m^*)$$

$$+ b_{1,3}m_1m_3/(mm^*) + b_{2,3}m_2m_3/(m\,m^*) \qquad \text{(S28)}$$

The McKay-Perring equation for the activity coefficient of solute 1 applies to the two solute system, and in order to use it here solutes 2 and 3 (which are present in a constant ratio) are treated as a single combined solute, c. Thus equation (S28) is equivalent to:

$$1/m^* = m_1/(m^*m_1^{\mathrm{o}}) + m_c/(m^*m_c^{\mathrm{o}}) + b_{1,c}m_1m_c/(m\,m^*)$$

$$+ b_{2,3}m_2m_3/(m\,m^*) \qquad \text{(S29)}$$

where $m_c = m_2 + m_3$, and $m^* = k_1m_1 + k_cm_c$, and $m = m_1 + m_c$. The quantity m_c^{o} is the molality of combined solute c in a solution containing c only, at the water activity of the system. The mixture term $b_{1,c}$ is defined by:

$$b_{1,c} = b_{1,2}n_2/n_c + b_{1,3}n_3/n_c = b_{1,2}m_2/m_c + b_{1,3}m_3/m_c \qquad \text{(S30)}$$

Equation (S29) is next expressed in terms of the variable $\mathbf{r}_c$, which is equal to $(k_2m_2 + k_3m_3)/m^*$ (or k_cm_c/m^*):

$$\frac{1}{m^*} = \frac{1-\mathbf{r}_c}{k_1m_1^o} + \frac{\mathbf{r}_c}{k_cm_c^o} + \frac{b_{1,c}(1-\mathbf{r}_c)m_c}{k_1m} + \frac{b_{2,3}m_2m_3}{m^*m} \qquad \text{(S31)}$$

In order to substitute for molalities m_2 and m_3 in equation (S31) we note that solutes 2 and 3 are present in the mixture in a constant ratio. Therefore we define $m_3 = Dm_2$ (where D is a constant) and hence $m_c = m_2(1 + D)$. It also follows that $k_c = (k_2 + Dk_3)/(1 + D)$. Using these relationships, the last term in equation (S31) can be written $b_{2,3}\mathbf{r}_cm_c(D/(1 + D)^2)/(k_cm)$. Finally, using one further substitution, $m_c/m = \mathbf{r}_c/(k_c/k_1 + (1 - k_c/k_1)\mathbf{r}_c)$, or $\mathbf{r}_c/K$, we write:

$$\frac{1}{m^*} = \frac{1}{k_1m_1^o} + \mathbf{r}_c\left(\frac{1}{k_cm_c^o} - \frac{1}{k_1m_1^o}\right) + \frac{b_{1,c}(1-\mathbf{r}_c)\mathbf{r}_c}{k_1K} + \frac{b_{2,3}\mathbf{r}_c^2D}{k_cK(1+D)^2} \qquad \text{(S32)}$$

This expression is equivalent to equation (S18) for the two solute case, and must be differentiated to give $\mathbf{r}_c(\partial(1/m^*)/\partial\mathbf{r}_c)_{a_w}$ in the McKay-Perring integral. The other term in the integral is obtained by rearranging equation (S32):

$$\frac{1}{k_1m_1^o} - \frac{1}{m^*} = \mathbf{r}_c\left(\frac{1}{k_1m_1^o} - \frac{1}{k_cm_c^o}\right) - \frac{b_{1,c}(1-\mathbf{r}_c)\mathbf{r}_c}{k_1K} - \frac{b_{2,3}\mathbf{r}_c^2D}{k_cK(1+D)^2} \qquad \text{(S33)}$$

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All elements of equations (S32) and (S33) not involving $b_{1,c}$ or $b_{2,3}$ can be ignored, as for the two solute case, as they sum to zero in the integral. The expression for the activity coefficient of solute 1 in the three solute mixture then becomes:

$$\ln(\gamma_1) = \ln(\gamma_1^{o}) + \ln(k_1 m_1^{o}/m^{*})$$

$$+\left(\frac{1}{M_w}\right)\left(\frac{k_1}{\nu_1}\right)\int_0^{\ln a_w}\left\{\mathbf{r}_c\left(\frac{\partial E}{\partial \mathbf{r}_c}\right)_{a_w} - \frac{b_{1,c}(1-\mathbf{r}_c)\mathbf{r}_c}{k_1 K} - \frac{b_{2,3}\mathbf{r}_c^2 D}{k_c K(1+D)^2}\right\} d\ln a_w \qquad \text{(S34)}$$

where the expression E to be differentiated is given by:

$$E = \frac{b_{1,c}(1-\mathbf{r}_c)\mathbf{r}_c}{k_1 K} + \frac{b_{2,3}\mathbf{r}_c^2 D}{k_c K(1+D)^2} \qquad \text{(S35)}$$

Of the quantities in equation (S35), k_1, K, and D are constants. The only term within $b_{1,c}$ that is differentiable is $((m_2/m_c)A^1{}_{1,2}y_{1,2} + (m_3/m_c)A^1{}_{1,3}y_{2,3})$. The parameter $A^1{}_{2,3}$ in $b_{2,3}$ is multiplied by factors involving m_2 and m_3, which are both components of c, hence $db_{2,3}/d\mathbf{r}_c = 0$. Differentiating equation (S35):

$$\mathbf{r}_c\left(\frac{\partial E}{\partial \mathbf{r}_c}\right)_{a_w} = \frac{\mathbf{r}_c b_{1,c}(1-2\mathbf{r}_c)}{K} - \frac{b_{1,c}\mathbf{r}_c(1-\mathbf{r}_c)(1-k_c/k_1)}{k_1 K^2}$$

$$+\left(\frac{db_{1,c}}{d\mathbf{r}_c}\right)\frac{\mathbf{r}_c(1-\mathbf{r}_c)}{k_1 K} + \frac{2b_{2,3}\mathbf{r}_c D}{k_c K(1+D)^2}$$

$$-\frac{b_{2,3}\mathbf{r}_c^2 D(1-k_c/k_1)}{k_c K^2(1+D)^2} \qquad \text{(S36)}$$

and noting that $-\mathbf{r}_c(1 - \mathbf{r}_c)(1 - k_c/k_1)/K = \mathbf{r}_c(1 - 1/K)$, and $-\mathbf{r}_c^2(1 - k_c/k_1)/K = -\mathbf{r}_c(1 - (k_c/k_1)/K)$, equation (S36) simplifies to:

$$\mathbf{r}_c\left(\frac{\partial E}{\partial \mathbf{r}_c}\right)_{a_w} = \left(\frac{\mathbf{r}_c b_{1,c}}{k_1 K}\right)\left\{\left(\frac{db_{1,c}}{d\mathbf{r}_c}\right)\frac{(1-\mathbf{r}_c)\mathbf{r}_c}{b_{1,c}} + \frac{1-\mathbf{r}_c}{K} - \frac{\mathbf{r}_c}{K}\right\}$$

$$+\left(\frac{\mathbf{r}_c b_{2,3} D}{k_c K(1+D)^2}\right)\left(\mathbf{r}_c + \frac{\mathbf{r}_c k_c}{k_1 K}\right) \qquad \text{(S37)}$$

Combining equation (S37) with the other two terms in the integral in equation (S34) we obtain the following expression for integration:

$$+\left(\frac{\mathbf{r}_c b_{1,c}}{k_1 K}\right)\left\{\left(\frac{db_{1,c}}{d\mathbf{r}_c}\right)\frac{(1-\mathbf{r}_c)\mathbf{r}_c}{b_{1,c}} - \frac{\mathbf{r}_c}{K}\right\} + \frac{\mathbf{r}_c b_{2,3} D}{k_c K(1+D)^2}\left(\frac{\mathbf{r}_c k_c}{k_1 K}\right) \qquad \text{(S38)}$$

This can be further simplified: the term in $b_{1,c}$ is equivalent to $-b_{1,c}(m_c/m)^2/k_1$, and that in $b_{2,3}$ to $+b_{2,3}(m_c/m)^2 m_2 m_3/(k_1 m_c^2)$. The element of $b_{1,c}$ that is differentiable with respect to $\mathbf{r}_c$ is $(m_2/m_c)A^1_{1,2}y_{1,2} + (m_3/m_c)A^1_{1,3}y_{1,3}$, and the value of $db_{1,c}/d\mathbf{r}_c$ can be obtained by first expressing $\mathbf{r}_c$ in terms of m_2 ($\mathbf{r}_c = m_2(1 + D)k_c/(k_1 m_1 + m_2(1 + D)k_c)$) and then using the formula $db_{1,c}/d\mathbf{r}_c = (db_{1,c}/dm_2)/(d\mathbf{r}_c/dm_2)$. The value of this differential, when substituted into (S38), yields the term $((m_2/m_c)A^1_{1,2}m_1m_2/(m_1 + m_2)^2)(m_c/m)/k_1$. Finally, combining the three terms in the integral, and writing out $b_{1,c}$ and $b_{2,3}$ in full, we obtain:

$$\begin{aligned}
&(-1/k_1)(m_c/m)^2[(m_2/m_c)A^0_{1,2} + (m_3/m_c)A^0_{1,3} \\
&+ (m_2/m_c)A^1_{1,2}(y_{1,2} - (m/m_c)m_1m_2/(m_1 + m_2)^2) \\
&+ (m_3/m_c)A^1_{1,3}(y_{1,3} - (m/m_c)m_1m_3/(m_1 + m_3)^2) \\
&+ ((m_2/m_c)B_{1,2} + (m_3/m_c)B_{1,3})a_w \\
&- (m_2m_3A^0_{2,3}/m_c^2 + m_2m_3A^1_{2,3}y_{2,3}/m_c^2) \\
&- (m_2m_3B_{2,3}/m_c^2)a_w]
\end{aligned} \qquad \text{(S39)}$$

Grouping terms together, and simplifying, the following interaction functions can be defined:

$$\mathbf{A}_{1,c} = (n_2/n_c)A^0_{1,2} + (n_3/n_c)A^0_{1,3} + (n_2/n_c)A^1_{1,2}y_{1,2}(1 - y_{2,1}/x_c)$$
$$+ (n_3/n_c)A^1_{1,3}y_{1,3}(1 - y_{3,1}/x_c) \qquad \text{(S40)}$$

where $x_c = (n_2 + n_3)/(n_1 + n_2 + n_3)$. Note also that $y_{3,1} = n_1/(n_1 + n_3)$, and is different from $y_{1,3}$ which is equal to $n_1/(n_1 + n_3)$. There is also:

$$\mathbf{B}_{1,c} = (n_2/n_c)B_{1,2} + (n_3/n_c)B_{1,3} \qquad \text{(S41)}$$

$$\mathbf{A}_{2,3} = n_2n_3A^0_{2,3}/n_c^2 + n_2n_3A^1_{2,3}y_{2,3}/n_c^2 \qquad \text{(S42)}$$

$$\mathbf{B}_{2,3} = n_2n_3B_{2,3}/n_c^2 \qquad \text{(S43)}$$

Using the above terms in expression (S39) allows equation (S34) for the activity coefficient of solute 1 to be written:

$$\ln(\gamma_1) = \ln(\gamma_1^\circ) + \ln(k_1m_1^\circ/m^*)$$
$$+\left(\frac{1}{M_w}\right)\left(-\frac{1}{\nu_1}\right)\left(\frac{m_c}{m}\right)^2 \int_0^{\ln a_w} \{\mathbf{A}_{1,c} - \mathbf{A}_{2,3} + (\mathbf{B}_{1,c} - \mathbf{B}_{2,3})a_w\} \mathrm{d}\ln a_w \qquad \text{(S44)}$$

Each of the interaction functions in the above equation involves only mole ratios of solutes, which are invariant with respect to $\ln a_w$. The integral in equation (S44) is easily solved to give:

$$\ln(\gamma_1) = \ln(\gamma_1^\circ) + \ln(k_1m_1^\circ/m^*)$$
$$+\left(\frac{1}{M_w}\right)\left(-\frac{1}{\nu_1}\right)\left(\frac{m_c}{m}\right)^2 \{(\mathbf{A}_{1,c} - \mathbf{A}_{2,3})(\ln a_w) - (\mathbf{B}_{1,c} - \mathbf{B}_{2,3})(1 - a_w)\} \qquad \text{(S45)}$$

Noting that $(m_c/m)^2 = x_c^2 = (1 - x_1)^2$, it is clear that equation (S45) is of the same form as equation (A13) for the two solute case, except with the additional interaction functions $\mathbf{A}_{2,3}$ and $\mathbf{B}_{2,3}$.

Finally, we consider the extension of equation (S45) to an indefinite number of solutes. In this case the combined solute c, and the quantities n_c, m_c, and x_c, include all solutes except 1 (whose activity coefficient is being calculated). Also, the definitions of functions $\mathbf{A}_{2,3}$ and $\mathbf{B}_{2,3}$ are expanded to include all possible pairs of individual solutes excluding 1. For example, in a four solute system these pairs would be (2,3), (2,4) and (3,4). The complete definition of the activity coefficient equation for the general case is given in Section 2 of Clegg, Seinfeld and Edney (*J. Aerosol Sci.* **2003**, *34*, 667-690).