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The Free Energy of Transfer from a Binary to a Ternary Solution by the Isopiestic Measurements

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A new method of calculating the free energy of transfer of a solute from a binary to a ternary solution on the mole fraction scale from isopiestic measurements is reported. It was proved that only the new method is consistent.

A knoledge of thermodynamic properties of aqueous ternary solutions is necessary for clear understanding of the interactions in many aqueous ternary systems containing two electrolytes, an electrolyte and a nonelectrolyte, and two nonelectrolytes. The knowledge is also fundamental to a comprehension of the mechanism of the denaturation of proteins and the interactions in complex biological systems.

It is shown that the chemical potential of each component in ternary solution can be calculated at various concentrations by the isopiestic vapor pressure method. The free energy of transfer of a solute from a binary to a ternary solution is obtained at various concentrations from the chemical potentials in these solutions.

In actual biological systems, the concentrations of some solutes are very low, while, for instance, the average local concentrations of amino acids and peptides within the protein molecule are very high.[1] Further, the free energy of transfer is found to alter even its sign at some concentration range.[2] Consequently, not only the interactions at the standard state but also the concentration dependence of the interactions are very important.

Unfortunately, contradiction is found in the calculation of the transfer free energy on the mole fraction scale in recent papers.[3,4]

Here we report a new consistent expression for the free energy of transfer from isopiestic measurements.

The Free Energy of Transfer on Molality Scale

Since the concentration of the solute is measured on molality scale in the isopiestic method, we start with the free energy of transfer on the molality scale. The chemical potentials of solute 1 in a binary and in a ternary (solute 2 and water) solution on the molality scale, μ_{10} (m) and μ_1 (m), are expressed as follows,

$$\mu_{10}(m) = \mu_{10}^0(m) + \nu_1 RT \ln m_{10}\gamma_{10} \tag{1}$$

$$\mu_1(m) = \mu_1^0(m) + \nu_1 RT \ln m_1\gamma_1 \tag{2}$$

where $\mu_{10}{}^0(m)$ and $\mu_1{}^0(m)$ are the standard states in a binary and in a ternary solution, respectively. m_{10} and γ_{10} are the molality and the activity coefficient of solute 1 in a binary solution, and m_1 and γ_1 are the corresponding quantities in a ternary solution. γ_1 is the number of moles of ions formed from 1 mole of solute 1.

The immediate result of isopiestic vapor pressure measurements is the chemical potential of the volatile solvent (water) in the ternary solution. The chemical potentials of the solutes are calculated by Gibbs-Duhem equation,

$$n_w d\mu_w = -n_1 d\mu_1 - n_2 d\mu_2 \tag{3}$$

where

$$d\mu_i = \nu_i RT \, d\ln m_i\gamma_i \quad (i = 1 \text{ or } 2) \tag{4}$$

Equation (4) implies the assumption that d $\mu_j{}^0 = 0$. In other words, the activity coefficient of solute 1 is unity in the standard state in water and not in the standard state in a water-solute 2 solvent,[5]

$$\mu_{10}^0(m) = \mu_1^0(m) \tag{4a}$$

Consequently, the free energy of transfer of solute 1 from a given molality in water to the same molality in water-solute 2 solution is given by,

$$\Delta G_t(m) = \mu_1 - \mu_{10} = \nu_1 RT \ln (\gamma_1/\gamma_{10}) \tag{5}$$

The $\Delta G_t(m)$ in Eq. (5) has the same value as that of $\Delta G_t(m)$ which is defined by the change in excess free energy,

$$\Delta G_t(m) = \mu_1^{ex} - \mu_{10}^{ex}$$

where μ_1^{ex} and $\mu_{10}^{ex}$are the excess free energy (or nonideal free energy) defined by Friedman.[6]

The values of $\Delta G_t(m)$ of glycylglycine (solute 1) from water to urea-water solutions at various concentrations of glycylglycine (m_1) and urea (m_2) are shown in Table 1.

TABLE 1. FREE ENERGY OF TRANSFER ON MOLALITY SCALE (in J/mol) OF GLYCYLGLYCINE FROM WATER TO UREA SOLUTIONS

m_1	m_2					
	1.0	2.0	3.0	4.0	5.0	6.0
0	−232	−430	−587	−705	−793	−865
0.5	−147	−280	−391	−478	−546	−606
1.0	−102	−202	−289	−358	−411	−455
1.5	−82.8	−167	−238	−288	−317	−327

The Free Energy of Transfer on Mole Fraction Scale

The Examination of Previous Experessions.[4] When solute 2 is treated as a component of the mixed solvent, the appropriate concentration scale for solute 1 is the mole fraction. According to the definition in the previous paper,[4]

$$\Delta G_t(N) = \nu_1 RT \ln (f_1/f_{10}) \tag{6}$$

where $\Delta G_t(N)$ is the free energy of transfer of solute 1 from water to water-species 2 solution at constant mole fraction. f_{10} and f_1 are the activity coefficients of solute 1 in mole fraction scale in a binary and in a ternary solution, respectively. The activity coefficient of the solute in molality scale is converted into the rational activity coefficient as usual by

$$f_{10} = \gamma_{10}(1+0.001\,W_{\mathrm{A0}}\nu_1 m_{10}) \tag{7}$$

where W_{A0} is the molecular weight of pure solvent. Let m_1' denote the molality of solute 1 in the ternary solution when the mole fraction of solute 1 in the ternary solution is the same as in a binary solution, then we have,

$$m_1' = (1+0.001\,W_{\mathrm{A0}}\nu_2 m_2)m_{10} \tag{8}$$

In the ternary solution, f_1 is related to γ_1' by

$$f_1 = \gamma_1'(1+0.001\,W_{\mathrm{A}}\nu_1 m_1') \tag{9}$$

where γ_1' is the activity coefficient of solute 1 at m_1' and W_{A} is the molecular weight of mixed solvent (water-species 2) defined by[3,4]

$$W_{\mathrm{A}} = \frac{55.51\,W_{\mathrm{A0}} + W_2 m_2}{55.51 + m_2} \tag{10}$$

where W_2 and m_2 are the molecular weight and molality of species 2 in the mixed solvent, respectively.

To examine whether these definitions are consistent or not, we subtract $\Delta G_{\mathrm{t}}(m)$ from $\Delta G_{\mathrm{t}}(N)$. Then, at any concentration, using Eqs. (5) to (10), we obtain

$$\frac{\Delta G_{\mathrm{t}}(N) - \Delta G_{\mathrm{t}}(m)}{\nu_1 RT} = \ln\left\{\frac{1+0.001\,W_{\mathrm{A}}\nu_1 m_1'}{1+0.001\,W_{\mathrm{A0}}\nu_1 m_{10}}\right\} + \ln(\gamma_1'/\gamma_1) \tag{11}$$

At infinite dilution, $\gamma'_1 = \gamma_1$, then,

$$\frac{\Delta G_{\mathrm{t}}(N) - \Delta G_{\mathrm{t}}(m)}{\gamma_1 RT} = 0 \tag{12}$$

On the other hand, since the chemical potential of solute 1 in a binary solution on mole fraction scale is,

$$\mu_{10}(N) = \mu_{10}^0(N) + \nu_1 RT \ln N_{10} f_{10} \tag{13}$$

Combining Eqs. (1) and (13), in a binary solution we have,

$$\ln f_{10} = \ln \gamma_{10} + \ln(m_{10}/N_{10}) + \frac{\mu_{10}^0(m) - \mu_{10}^0(N)}{\nu_1 RT} \tag{14}$$

Similarly in a ternary solution,

$$\ln f_1 = \ln \gamma_1' + \ln(m_1'/N_1) + \frac{\mu_1^0(m) - \mu_1^0(N)}{\nu_1 RT} \tag{15}$$

Substituting Eqs. (14) and (15) into Eq. (6) and combining Eqs. (5) and (6), we obtain

$$\frac{\Delta G_{\mathrm{t}}(N) - \Delta G_{\mathrm{t}}(m)}{\nu_1 RT} = \frac{\mu_1^0(m) - \mu_{10}^0(m)}{\nu_1 RT} - \frac{\mu_1^0(N) - \mu_{10}^0(N)}{\nu_1 RT} + \ln(m_1' N_{10}/N_1 m_{10}) + \ln(\gamma_1'/\gamma_1) \tag{16}$$

where $N_1 = N_{10}$. Substituting Eqs. (4a) and (8) into (16), we have

$$\frac{\Delta G_{\mathrm{t}}(N) - \Delta G_{\mathrm{t}}(m)}{\nu_1 RT} = -\frac{\mu_1^0(N) - \mu_{10}^0(N)}{\nu_1 RT} + \ln(1+0.001\,W_{\mathrm{A0}}\nu_2 m_2) + \ln(\gamma_1'/\gamma_1) \tag{16a}$$

Combining Eqs. (11) and (16a), we obtain,

$$\frac{\mu_1^0(N) - \mu_{10}^0(N)}{\nu_1 RT} = \ln(1+0.001\,W_{\mathrm{A0}}\nu_2 m_2) - \ln\left\{\frac{1+0.001\,W_{\mathrm{A}}\nu_1 m_1'}{1+0.001\,W_{\mathrm{A0}}\nu_1 m_{10}}\right\}$$

which becomes at infinite dilution of solute 1,

$$\frac{\mu_1^0(N) - \mu_{10}^0(N)}{\nu_1 RT} = \ln(1+0.001\,W_{\mathrm{A0}}\nu_2 m_2) \tag{17}$$

Equation (17) shows that the difference between standard states on mole fraction scale in a binary and in a ternary solution depends on the concentration of solute 2. The free energy of transfer, defined by Eqs. (6), (7), (9), and (10) does not mean the difference in chemical potentials in the two states, but it means,

$$\Delta G_{\mathrm{t}}(N) = \mu_1(N) - \mu_{10}(N) - \nu_1 RT \ln(1+0.001\,W_{\mathrm{A0}}\nu_2 m_2) \tag{17a}$$

Furthermore, using Eq. (17), we can examine Eq. (9). The usual relation between $\mu_{10}^0(m)$ and $\mu_{10}^0(N)$ is obtained from Eq. (14),

$$\frac{\mu_{10}^0(m) - \mu_{10}^0(N)}{\nu_1 RT} = -\ln\left(\frac{1000}{W_{\mathrm{A0}}}\right) \tag{14a}$$

Then, using Eqs. (4a), (14a), and (17),

$$\frac{\mu_1^0(m) - \mu_1^0(N)}{\nu_1 RT} = \frac{\mu_1^0(m) - \mu_{10}^0(m)}{\nu_1 RT} - \frac{\mu_1^0(N) - \mu_{10}^0(N)}{\nu_1 RT} - \frac{\mu_{10}^0(N) - \mu_{10}^0(m)}{\nu_1 RT} = -\ln\left(\frac{1000}{W_{\mathrm{A0}}} + \nu_2 m_2\right) \tag{18}$$

Equation (18) is substituted in Eq. (15), we obtain

$$f_1 = \gamma_1'\left(1 + \frac{\nu_1 m_1'}{\dfrac{1000}{W_{\mathrm{A0}}} + \nu_2 m_2}\right) = \gamma_1'\left(1 + 0.001\frac{1000}{\dfrac{1000}{W_{\mathrm{A0}}} + \nu_2 m_2}\nu_1 m_1'\right) \tag{19}$$

Equation (19) differs from Eq. (9). For consistency, 1000 in the numerator in the second term in parenthesis of Eq. (19) should be $(1000 + W_2 m_2)$. That is, the definition of f_1 by Eqs. (9) and (10) is not right.

The Consistent Expression for ΔG_{t}(N). Here $\Delta G_{\mathrm{t}}(N)$ is defined by Eq. (6), and Eqs. (7) and (8) hold too. The difference between this and previous section is only in the definition of f_1. f_1 is defined by

$$f_1 = \gamma_1'\{1+0.001\,W_{\mathrm{A0}}(\nu_1 m_1' + \nu_2 m_2)\} \tag{20}$$

Now, at any concentration, from Eqs. (5), (6), (7), (8), and (20), we obtain

$$\frac{\Delta G_{\mathrm{t}}(N) - \Delta G_{\mathrm{t}}(m)}{\nu_1 RT} = \ln\left\{\frac{1+0.001\,W_{\mathrm{A0}}(\nu_1 m_1' + \nu_2 m_2)}{1+0.001\,W_{\mathrm{A0}}\nu_1 m_{10}}\right\} + \ln(\gamma_1'/\gamma_1) \tag{21}$$

At infinite dilution of solute 1, $\gamma'_1 = \gamma_1$, so, Eq. (21) gives

$$\frac{\Delta G_{\mathrm{t}}(N) - \Delta G_{\mathrm{t}}(m)}{\nu_1 RT} = \ln(1+0.001\,W_{\mathrm{A0}}\nu_2 m_2) \tag{22}$$

which differs from Eq. (12) in previous section.

On the other hand, Eq. (16a) also holds here, consequently, combining Eqs. (16a) and (21), we obtain

$$\frac{\mu_1^0(N) - \mu_{10}^0(N)}{\nu_1 RT} = \ln(1+0.001\,W_{\mathrm{A0}}\nu_2 m_2) - \ln\left\{\frac{1+0.001\,W_{\mathrm{A0}}(\nu_1 m_1' + \nu_2 m_2)}{1+0{,}001\,W_{\mathrm{A0}}\nu_1 m_{10}}\right\}$$

which becomes at infinite dilution of solute 1,

TABLE 2. FREE ENERGY OF TRANSFER ON MOLE FRACTION SCALE (in J/mol) OF GLYCYLGLYCINE FROM WATER TO UREA SOLUTIONS

m_{10}	N_1	m_2					
		1.0	2.0	3.0	4.0	5.0	6.0
0	0	−189	−342	−456	−533	−579	−611
0.5	0.008927	−108	−201	−272	−319	−348	−369
1.0	0.017696	−64.0	−126	−174	−204	−216	−218
1.5	0.026311	−44.8	−90.4	−122	−129	−110	−82.4

$$\frac{\mu_1^0(N)-\mu_{10}^0(N)}{\nu_1 RT}=0 \qquad (23)$$

That is, the standard states in a binary and in a ternary solution are the same on mole fraction scale too, and $\Delta G_t(N)$ means the difference in chemical potentials of the solute in a ternary and binary solution, as in the case of $\Delta G_t(m)$. The difference between the standard states in the ternary solution on molality and on mole fraction scale is obtained by combining Eqs. (4a), (14a), and (23),

$$\frac{\mu_1^0(m)-\mu_1^0(N)}{\nu_1 RT}=-\ln(1000/W_{A0}) \qquad (24)$$

By substituting Eq. (24) into Eq. (15), we obtain the same equation for f_1 as Eq. (20). Consequently, the definition of $\Delta G_t(N)$ by Eq. (6) and f_1 by Eq. (20), results in the consistent relation.

The value of $\Delta G_t(N)$ at infinite dilution which is expressed by Eq. (22) has the same value as the quantity defined by Bower and Robinson as a measure of the medium effect.[7]

The values of $\Delta G_t(N)$ of glycylglycine from water to urea-water mixture are tabulated in Table 2. $\Delta G_t(N)$ has less negative values than $\Delta G_t(m)$.

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