Bull. Chem. Soc. Jpn., **74**, 47–52 (2001)

New Predictive Equations for the Specific and Apparent Molar Heat Capacities of Multicomponent Aqueous Solutions Conforming to the Linear Isopiestic Relation

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(Received April 5, 2000)

The linear isopiestic relation has been used together with well-known thermodynamic equations to establish new simple predictive equations for the specific and apparent molar heat capacities. These equations can provide predictions for multicomponent solutions conforming to the linear isopiestic relation using only information on the corresponding binary subsystems. No additional empirical parameters are involved. The predictive capabilities of the equations have been tested by comparing with the experimental specific or apparent molar heat capacities for the ternary systems ($NaCl–NaNO_3–H_2O$, $NaCl–NaClO_4–H_2O$, $NaCl–KBr–H_2O$, $NaCl–CaCl_2–H_2O$, $NaCl–MgCl_2–H_2O$, and $CaCl_2–MgCl_2–H_2O$) at 298.15 K and the reciprocal system ($K–Na–Cl–SO_4–H_2O$) at 373.15 K. The agreement is excellent over the entire experimental composition ranges.

Zdanovskii[1] in 1936 discovered empirically a linear isopiestic relation for ternary aqueous electrolyte solutions. Later, Stokes and Robinson[2] derived the same relation for multicomponent aqueous non-electrolyte solutions in their semi-ideal hydration model. This relation can be written as

$$\sum_j \frac{m_j}{m_j^0} = 1$$
$$(a_w = \text{constant and } 0 \le \frac{m_j}{m_j^0} \le 1), \quad (1)$$

where a and m denote the activity and molality (mol kg^{-1}), respectively; subscript w denotes water, and superscript 0 together with subscript j represent the quantity of j in the j-th binary solution. Since then, Eq. 1 has been extended to such systems as aqueous non-electrolyte–electrolyte mixtures (include ternary systems of poly-electrolytes and water-soluble polymers[3,4]);[5–8] also, the results for 51 aqueous systems have been tabulated by Chen et al.[4] Recently, we have in previous papers of this series[9] experimentally extended this linear relation to quaternary aqueous electrolyte solutions and quaternary aqueous non-electrolyte solutions. More recently, we have presented new linear isopiestic relations for saturated solutions whose unsaturated sub-systems obey Eq. 1.[10]

Systematic studies of Eq. 1 have resulted in many novel findings. It has been found to be a versatile tool predicting the water activity of ternary aqueous solutions,[4] evaluating the Pitzer ternary parameters (θ_{ij} and Ψ_{ijk}),[11] and predicting the activity coefficient of either solute in the ternary and quaternary electrolyte or non-electrolyte solutions[2,9,12] by using the Mckay and Perring equation[13] and data of the corresponding binary sub-systems of equal water activity (recently, we have successfully extended this approach to four aqueous non-electrolyte–electrolyte mixtures[14]). Since the other thermodynamic properties of multicomponent solutions also play an important role in such areas as chemistry and chemical engineering,[15,16] oceanography,[17] steam power,[18] water treatment,[19] and oil recovery,[20] and extensive data for the properties of binary aqueous solutions have been reported and evaluated in the literature, we have recently started a series of studies focusing on developing new predictive approaches that can make use of this available information and provide accurate predictions for multicomponent solutions. In the first paper of this series,[21] a new predictive equation for the densities of multicomponent solutions was established by using Eq. 1 and well-known thermodynamic equations, which has been shown to be able to provide very accurate predictions of density data for seven ternary solutions by using only information concerning the binary sub-systems.

The heat capacities are useful, or even essential, for various important thermodynamic calculations, and recently the heat-capacity data of binary solutions of a large number of electrolytes have been evaluated and modeled by using the Pitzer equations.[22,23] Therefore, in this paper the author attempts to establish new predictive equations for specific and apparent molar heat capacities for multicomponent solutions in terms of their binary sub-systems of equal water activity. The specific or apparent molar heat capacities have been well established[24–29] for the following systems and their binary sub-systems: $NaCl–NaNO_3–H_2O$, $NaCl–NaClO_4–H_2O$, $NaCl–KBr–H_2O$, $NaCl–CaCl_2–H_2O$, $NaCl–MgCl_2–H_2O$ and $CaCl_2–MgCl_2–H_2O$ at 298.15 K and the reciprocal system $Na–K–Cl–SO_4–H_2O$ at 373.15 K. Thus, the accuracy of the newly established equations has been tested by comparisons with these experimental data.

New Predictive Equations for the Specific and Apparent Molar Heat Capacities

In the following section, Eq. 1 coupled with the well-known thermodynamic equations is applied to derive new simple predictive equations for the specific and apparent molar heat capacity. In these derivations, variables with the superscript 0 and the subscript *j* denote the quantities of *j* in the binary solutions of equal water activity, and those without the superscript 0 denote the corresponding quantities in the multicomponent solutions.

The excess enthalpy, $\Delta_{\text{mix}}H$, accompanying the dissolution of solutes in 1 kg water can be expressed as

$$\Delta_{\text{mix}}H = (\overline{H}_{\text{w}} - H_{\text{w}})/M_{\text{w}} + \sum_j m_j(\overline{H}_j - \overline{H}_j^{\,I}) + \sum_j m_j(\overline{H}_j^{\,I} - H_j), \tag{2}$$

where H_w and H_j denote the molar enthalpy of water and solute *j*, respectively. $\overline{H}_w$ and $\overline{H}_j$ represent the partial molar enthalpy of water and solute *j* in solution, respectively. $\overline{H}_j^I$ denotes the partial molar enthalpy of solute *j* at infinite dilution. Using the temperature derivatives of activities, we obtain

$$\Delta_{\text{mix}}H = -\frac{RT^2}{M_{\text{w}}}\left(\frac{\partial \ln a_{\text{w}}}{\partial T}\right)_{P,N} - RT^2\sum_j m_j\left(\frac{\partial \ln a_j}{\partial T}\right)_{P,N} + \sum_j m_j\left(\overline{H}_j^{\,I} - H_j\right), \tag{3}$$

where *a* and *M* denote the activity and the molar mass, respectively.

Similarly, if we prepare a binary solution of the *j*-th solute at the same water activity as the mixed solution, we obtain

$$\Delta_{\text{mix}}H_j^0 = -\frac{RT^2}{M_{\text{w}}}\left(\frac{\partial \ln a_{w,j}^0}{\partial T}\right)_{P,N} - RT^2 m_j^0\left(\frac{\partial \ln a_{\text{j}}^0}{\partial T}\right)_{P,N} + m_j^0\left(\overline{H}_j^{\,I} - H_j\right). \tag{4}$$

Since m_j and a_j in a mixture are related to their values, m_j^0 and a_j^0, in the *j*-th binary sub-systems of equal water activity by Eq. 1 [2,9,12] and Eq. 5,[21]

$$a_j = \frac{\nu_j m_j}{\sum_j \nu_j m_j} a_j^0, \tag{5}$$

where ν_j ($j = B$ and C) is the salt stoichiometric coefficient, we can then reach

$$\Delta_{\text{mix}}H = \sum_j \frac{m_j}{m_j^0}\Delta_{\text{mix}}H_j^0. \tag{6}$$

Differentiation of Eq. 6 with respective to temperature gives the following linear relation:

$$c_P = \sum_j \frac{m_j}{m_j^0} c_{P,j}^0, \tag{7}$$

where c_p and $c_{p,j}^0$ are the specific-heat capacities of the multicomponent systems and their binary sub-systems of equal water activity, respectively.

The apparent molar heat capacity, $C_{p,\phi}$, is defined by[28,29]

$$C_{P,\phi} = \left[c_P(1 + \sum_j m_j M_j) - c_{P,\text{w}}^*\right] \Big/ \sum_j m_j\ , \tag{8}$$

where $C_{p,\phi}$ and c_p are the apparent molar heat capacity and the specific-heat capacity of the multicomponent solution. $c_{p,w}{}^*$ is the specific-heat capacity of water. M_j is the molar mass of solute *j*. Using Eq. 7 and rearranging, we obtain

$$C_{P,\phi} = \left\{\left(1 + \sum_j m_j M_j\right)\left[\sum_j \frac{m_j}{1 + m_j^0 M_j} C_{P,\phi(j)}^0 + c_{P,w}^* \sum_j \frac{m_j}{m_j^0(1 + m_j^0 M_j)}\right] - c_{P,w}^*\right\} \Big/ \sum_j m_j. \tag{9}$$

Equation 9 can provide predictions for the apparent molar heat capacities of the multicomponent systems from the data of the binary sub-systems of equal water activity.

Comparison with Literature Data

In this study, the derived predictive equations were tested by comparing with the following experimental data. (1) The experimental specific-heat capacities of the ternary systems ($NaCl–NaNO_3–H_2O$ and $NaCl–NaClO_4–H_2O$ at 298.15 K) and the reciprocal system ($Na–K–Cl–SO_4–H_2O$ at 373.15 K), and (2) the apparent molar heat capacities of the ternary systems ($NaCl–KBr–H_2O$, $NaCl–CaCl_2–H_2O$, $NaCl–MgCl_2–H_2O$, and $CaCl_2–MgCl_2–H_2O$ at 298.15 K). The test procedure is briefly described as follows:

(1) Determine the compositions of the ternary and quaternary systems (m_j) and their binary sub-systems ($m_j{}^0$) of equal water activity by the following procedure:[8,11] (a) The values of $m_j{}^0$ ($j = B, C, D,...$) are calculated from the osmotic data (φ_j) in binary solutions[30–32] and the relation $\nu_B m_B^0 \varphi_B^o = \nu_C m_C^0 \varphi_C^o = \nu_D m_D^0 \varphi_D^o = ...$; (b) the compositions of the ternary solutions of equal water activity are determined by choosing the values of m_B and then calculating the values of m_C from Eq. 1; (c) determine the compositions of the quaternary systems by choosing the values of m_B and m_C and then calculating the values of m_D from Eq. 1.

(2) Represent the experimental data for the binary sub-systems ($Q^0{}_{P,\phi(j)}$, where Q denotes the specific or apparent molar heat capacities) and the multicomponent systems ($Q^0{}_{P,\phi(\text{Exp})}$) by the polynomial fits.

(3) Calculate the data for the multicomponent systems by using the $Q^0{}_{P,\phi(j)}$ values of the binary sub-systems and Eq. 7 or Eq. 9.

(4) Compare the predictions with the experimental data obtained from the polynomial fits. In this paper, the average absolute difference between the predicted and measured data over the entire experimental composition range of the multicomponent systems, δ_n, is defined by

$$\delta_n = \sum_i^n \left|Q_i^{Exp} - Q_{i,n}^{Cal}\right| \Big/ N, \tag{10}$$

where Q^{Exp} is the experimental quantity, and $Q_{i,n}^{Cal}$ is the corresponding values calculated from Eps. 7 and 9, respectively. N is the number of experimental data points.

Because the ternary system NaCl(B)–NaNO$_3$(C)–H$_2$O(A) obeys Eq. 1,[4] the experimental specific-heat capacities of this system and its binary sub-systems[24] have been used to test the predictive capability of Eq. 7. The experimental mole ratio of B/C is 1/1 and the experimental composition ranges of the ternary system and the binary sub-systems are I < 6.0 mol kg^{-1}. Therefore, the comparison is confined to the corresponding composition range. The thus-obtained results are shown in Fig. 1. The δ_n value is 0.0004. The isopiestic data are not available in the literature that we have collected for the system NaCl(B)–NaClO$_4$(C)–H$_2$O(A). We assume here that it conforms to Eq. 1, and then use the measured specific-capacities of this system and its binary sub-systems[24] to test Eq. 7. The results, Fig. 1, show that δ_n = 0.0011.

The specific-heat capacities of the reciprocal system,[25] Na–K–Cl–SO$_4$–H$_2$O, at 373.15 K were measured at the fixed ionic ratios $\frac{m_{Na^+}}{m_{Na^+} + m_{K^+}} = 0.761$ and $\frac{m_{Cl^-}}{m_{Cl^-} + m_{SO_4^{2-}}} = 0.594$. Since the ternary systems (NaCl(B)–KCl(C)–H$_2$O(A) and NaCl(B)–Na$_2$SO$_4$(D)–H$_2$O(A)) conform to Eq. 1,[4] we may assume that the quaternary system (NaCl(B)–KCl(C)–Na$_2$SO$_4$(D)–H$_2$O(A)) obeys Eq. 1 and then follow Conti et al.[25] to characterize the reciprocal system by the mole ratio $x_B : x_C : x_D = 0.446 : 0.300 : 0.254$. In the third step, the predictions for the reciprocal system are obtained from Eq. 7 using the data of the corresponding three binary sub-systems at 373.15 K.[26,27] The results are compared in Fig. 2 to the experimental data. The agreement is excellent over the experimental composition

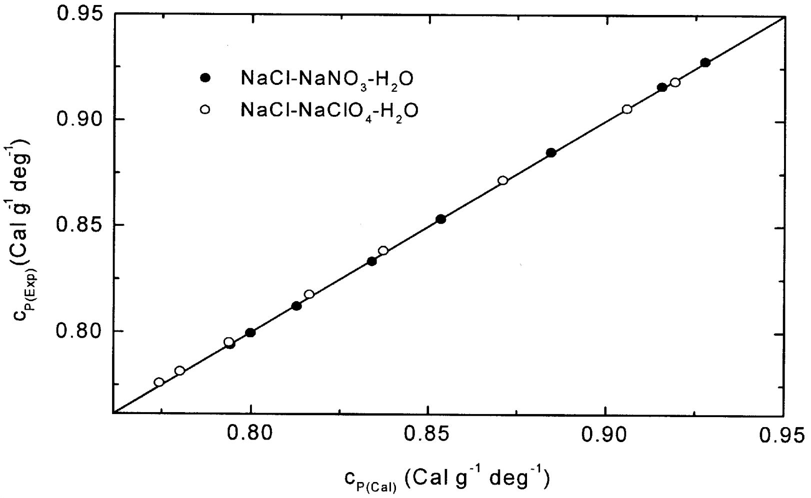

Fig. 1. Experimental[24] (solid line) and predicted (symbols) specific-heat capacity of the ternary systems NaCl–NaNO$_3$–H$_2$O and NaCl–NaClO$_4$–H$_2$O at 298.15 K.

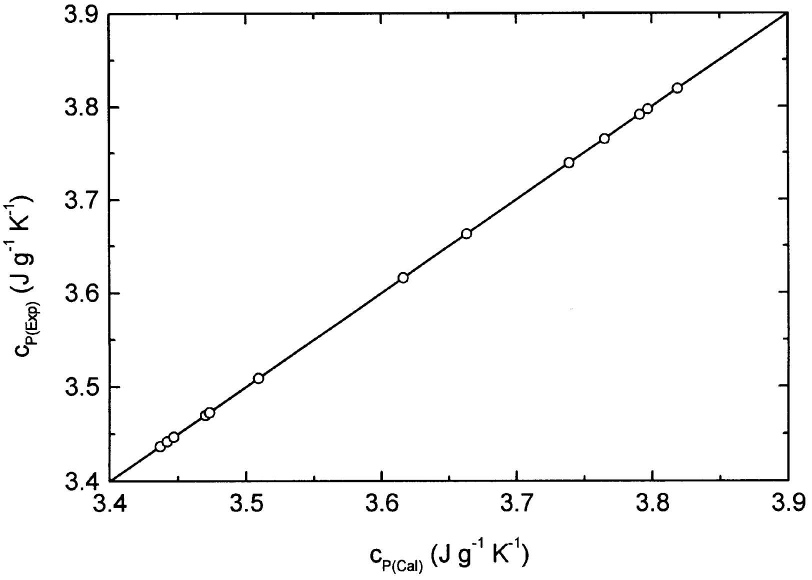

Fig. 2. Experimental[25] and predicted the specific-heat capacity of the reciprocal system Na–K–Cl–SO$_4$–H$_2$O (characterized[25] by the quaternary system NaCl–KCl–Na$_2$SO$_4$–H$_2$O) at 373.15 K.

range, with $\delta_n = 0.003$ J g^{-1} K^{-1} (the experimental uncertainty is ± 0.02 J g^{-1} K^{-1}).[25]

Because the ternary systems (NaCl(*B*)–KBr(*C*)–H_2O(*A*), NaCl(*B*)–$CaCl_2$(*C*)–H_2O(*A*), NaCl(*B*)–$MgCl_2$(*C*)–H_2O(*A*), and $CaCl_2$(*B*)–$MgCl_2$(*C*)–H_2O(*A*)) conform to Eq. 1,[4] the apparent molar heat capacities for these systems and their binary sub-systems measured by Lemire et al. (*LCSL*)[28] and Saluja et al. (*SJLL*)[29] were used for a data comparison. Young's rule[33] has frequently been used to estimate the apparent molar heat capacities of multicomponent systems, and has thus also been used to calculate the apparent molar heat capacities of the above ternary systems from the values of the binary sub-systems. This rule can be written as

$$C_{p,\phi,Y} = \sum_j \frac{m_j}{\sum_j m_j} C_{P,\phi,j}, \qquad (11)$$

where $C_{P,\phi,Y}$ and $C_{P,\phi,j}$ represent the apparent molar heat capacities of the multicomponent solution and the binary system of the *j*-th solute at the ionic strength of the multicomponent solution. The average absolute difference between the predicted ($C_{P,\phi,Y}$) and measured data over the entire experimental composition range of the ternary systems ($2.9 \le I$ (mol kg^{-1}) ≤ 5.2), δ_Y, is defined by

$$\sigma_Y = \sum_i^n \left| Q_i^{Exp} - Q^{Cal}{}_{i,Y} \right| / N, \qquad (12)$$

where Q^{Exp}, $Q^{Cal}_{i,Y}$ and N have the means specified above.

The thus-obtained results for the system NaCl(*B*)–$CaCl_2$(*C*)–H_2O(*A*) are shown in Fig. 3. The predictions using the new equation are in excellent agreement with the experimental values, with $\delta_n = 0.4$. The predictions using Young's rule also agree well the measured data, with $\delta_Y = 2.6$. The tests using the data of the ternary systems (NaCl(*B*)–$MgCl_2$(*C*)–H_2O(*A*) and $CaCl_2$(*B*)–$MgCl_2$(*C*)–H_2O(*A*)) and their binary sub-systems[29] have been deposited in Figs. S1 and S2 (supporting materials). The results are $\delta_n = 1.2$ and $\delta_Y = 3.4$ for the former system and $\delta_n = 2.1$ and $\delta_Y = 2.3$ for the latter system, respectively. These results indicate that the agreement between the predicted ($C_{P,\phi,(Cal)}$) and measured ($C_{P,\phi,(Exp)}$) values is also good over the entire experimental composition ranges for both systems because the uncertainty in the *SJLL* experimental data[29] is ≤ ± 4 J K^{-1} mol^{-1}. Note that, for the latter case, the absolute deviations of Young's rule from the measured data, $C_{P,\phi,(Y,cal)} - C_{P,\phi,(exp)}$, are in some cases outside the range of the experimental uncertainties. It has been shown[28] that Young's rule holds within the experimental uncertainties for the system NaCl(*B*)–KBr(*C*)–H_2O(*A*) at an ionic strength of 0.5 mol kg^{-1}. Therefore, Eq. 9 has also been checked by a comparison with the data reproduced by using Young's rule and the data of the binary sub-systems.[28,29] As can be seen from Fig. S3, the agreement is excellent.

Discussion

It has been found that,[2,4,9,10] if the molecules of the solutes are alike in size and shape and the solute-solute interactions (interchange energies) are negligible compared to the solute-solvent interactions (hydration energies), the mixed solutions conforms to Eq. 1 under isopiestic equilibrium (i.e. constant water activity). For example, the molten salt mixture NaCl–$BaCl_2$ conforms to Raoult's law;[34] the ternary solution NaCl–$BaCl_2$–H_2O(*A*) at constant a_A obeys Eq. 1 very well.[35] In this section, we discuss the thermodynamic behavior of the mixed solution *B*–*C*–...–*A* obeying Eq. 1 at constant a_A.

Let $\Delta_{mix}G^0{}_j$, $\Delta_{mix}S^0{}_j$, $\Delta_{mix}H^0{}_j$, and $\Delta_{mix}V^0{}_j$ denote the free-energy change, entropy change, enthalpy change and volume change accompanying the dissolution of the *j*-th solute in 1 kg of water. Let $\Delta_{mix}G$, $\Delta_{mix}S$, $\Delta_{mix}H$, and $\Delta_{mix}V$ represent the cor-

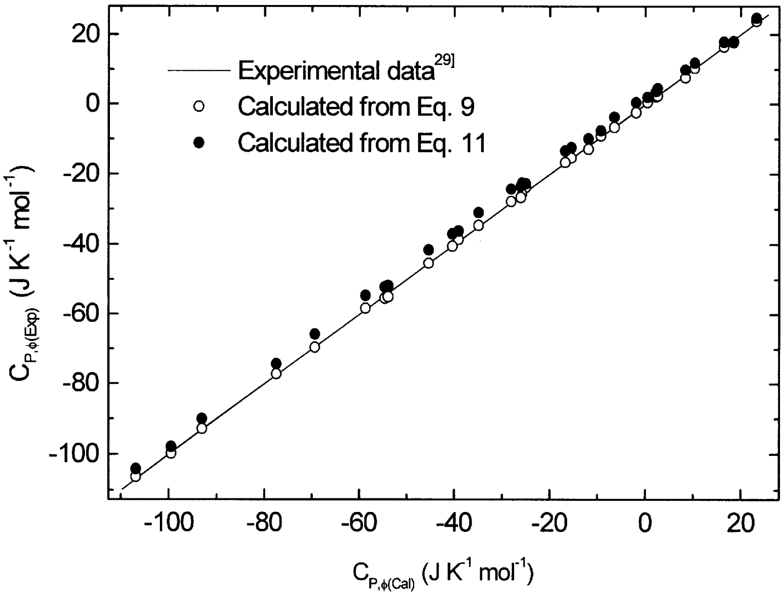

Fig. 3. Experimental[29] and predicted the apparent molar heat capacity of the ternary system NaCl–$CaCl_2$–H_2O at 298.15 K.

responding properties accompanying preparing a mixed solution of the same water activity as that of its binary solutions. Then, $\Delta_{\rm mix}G^0_j$ and $\Delta_{\rm mix}G$ can be expressed as

$$\Delta_{\rm mix}G^0_j = \frac{1}{M_A}RT\ln a^0_{A,j} + RTm^0_j\ln a^0_j, \tag{13}$$

$$\Delta_{\rm mix}G = \frac{1}{M_A}RT\ln a_A + RT\sum_j m_j\ln a_j, \tag{14}$$

where M_A is the molar mass of A(kg mol^{-1}), $1/M_A$, $m^0{}_j$, and m_j is equal to the amount (mol) of A and solute j in binary and mixed solutions, respectively. Using Eq. 13 and the fact that $a_w = a^0{}_{w,j}$, we obtain

$$\sum_j \frac{m_j}{m^0_j}\Delta_{\rm mix}G^0_j = \frac{1}{M_A}RT\ln a_A\sum_j\frac{m_j}{m^0_j} + RT\sum_j m_j\ln a^0_j. \tag{15}$$

If we define $Y_j = \nu_j m_j/\sum_j \nu_j m_j$, Eq. 5 can be rewritten as

$$\frac{a_j}{a^0_j} = Y_j. \tag{16}$$

If the mixed solution B–C–...–A conforms to Eq. 1, the combination of Eqs. 1, 14, 15, and 16 yields

$$\Delta_{\rm mix}G - \sum_j\frac{m_j}{m^0_j}\Delta_{\rm mix}G^0_j = RT\sum_j m_j\ln Y_j. \tag{17}$$

As noted above, for a solution obeying Eq. 1, $\Delta_{\rm mix}H$ is related to $\Delta_{\rm mix}H^0{}_j$ by Eq. 6, namely

$$\Delta_{\rm mix}H - \sum_j\frac{m_j}{m^0_j}\Delta_{\rm mix}H^0_j = 0. \tag{18}$$

Combining Eqs. 17 and 18 yields

$$\begin{aligned}
&\Delta_{\rm mix}S - \sum_j\frac{m_j}{m^0_j}\Delta_{\rm mix}S^0_j \\
&= \sum_j\frac{m_j}{m^0_j}\left[(\Delta_{\rm mix}H - \Delta_{\rm mix}G) - (\Delta_{\rm mix}H^0_j - \Delta_{\rm mix}G^0_j)\right]/T \\
&= -R\sum_j m_j\ln Y_j.
\end{aligned} \tag{19}$$

In a previous paper[21] the author showed that, if the mixed solution obeys Eq. 1, $\Delta_{\rm mix}V$ is linked to the values of $\Delta_{\rm mix}V^0{}_j$ by

$$\Delta_{\rm mix}V - \sum_j\frac{m_j}{m^0_j}\Delta_{\rm mix}V^0_j = 0. \tag{20}$$

Equations 1, 17, 18, 19, and 20 may be called *iso*–a_A relations for the thermodynamic properties between the mixed solution B–C–...–A and its binary solutions, j–A ($j = B$, C, ...), of equal a_A. In concision, we call them here *iso*–a_A relations.

We now consider the case where the multicomponent solution B'–C'–...–A' and its binary solutions i–A' ($i = B'$, C', ...) are all ideal solutions. In this case, it can be shown that the thermodynamic properties of this multicomponent solution are related to those of its binary solutions of equal $a_{A'}$ (i.e. the mole fraction of A', $x_{A'}$) by equations that are similar to Eqs. 1, 17, 18, 19, and 20. The derivations of these equations are given in Appendix 1 (supporting materials). Here, we call these equations the *iso*–$a_{A'}$ relations for the thermodynamic properties between the ideal solution B'–C'–...–A' and its binary ideal solutions i–A' ($i = B'$, C', ...) of equal $a_{A'}$, namely *iso*–$a_{A'}$ relations.

The above comparisons show that, if the molecules of solutes (B, C, ..., j) are sufficiently alike in size, shape and have negligible interchange energy, the *iso*–a_A relations are as simple as the *iso*–$a_{A'}$ relations. Since the terms on the right-hand of the *iso*–a_A relations may indicate the contributions from mixing of the binary solutions, j–A ($j = B$, C, ...), of equal a_A, these relations may suggest that the non-ideality of a mixed solution obeying Eq. 1 can be adequately accounted for in terms of that of its binary solutions of equal a_A. This may be the basis for accurate predictions of the thermodynamic properties of mixed solutions (B–C–...–A) obeying Eq. 1 in terms of those of the corresponding binary solutions (j–A ($j = B$, C, ...)) of equal a_A.

Conclusion

In this paper, the author has presented new predictive equations for the specific and apparent molar heat capacities. These equations relate these properties at isopiestic equilibrium between solutions of the single solute and the multicomponent solutes. The most important feature of these equations is that they require only knowledge about properties of the corresponding binary sub-systems, but involve no extra empirical parameters. The tests presented here have shown that these equations can provide accurate predictions of the specific and apparent molar heat capacities in the present seven systems. For the present latter four systems studied, the new equation is better than Young's rule for predicting the apparent molar heat capacities of the ternary solutions from data of the binary subsystems.

Supporting Materials

Figures S1–S3, showing plots of $C_{P,\phi,(Exp)}$ vs $C_{P,\phi,(Cal)}$ for the ternary systems ($NaCl$–$MgCl_2$–H_2O, $CaCl_2$–$MgCl_2$–H_2O, and $NaCl$–KBr–H_2O) at 298.15 K, and Appendix 1, giving the derivation of the *iso*–$a_{A'}$ relations for the thermodynamic properties between the ideal solution (B'–C'–...–A') and its binary ideal solutions (i–A' ($i = B'$, C', ...)) of equal $a_{A'}$ (in total 5 pages), are deposited as Document No. 74006 at the Office of the Editor of Bull. Chem. Soc. Jpn.

The present research was supported by the Science Foundation of University of Petroleum (No. ZX9903), by the National Natural Science Foundation of China (No. 20006010), and by the Open Science Foundation of the State Key Laboratory of Heavy Oil Processing (No. 200005).

References

1 A. B. Zdanovskii, *Tr. Solyanoi Lab. Akad. Nauk SSSR*, **No. 6** (1936).

2 R. H. Stokes and R. A. Robinson, *J. Phys. Chem.*, **70**, 2126 (1966).

3 T. Okubo and N. Ise, *J. Phys. Chem.*, **74**, 4284 (1970).

4 H. Chen, J. Sangster, T. T. Teng, and F. Lenzi, *Can. J. Chem. Eng.*, **51**, 234 (1973).

5 R. A. Robinson and R. H. Stokes, *J. Phys. Chem.*, **66**, 506

(1962).

6 F. J. Kelly, R. A. Robinson, and R. H. Stokes, *J. Phys. Chem.*, **65**, 1958 (1961).

7 V. E. Bower and R. A. Robinson, *J. Res. Nat. Bur. Stand. A*, **69**, 131 (1965).

8 H. Uedaira and H. Uedaira, *J. Phys. Chem.*, **74**, 1932 (1970).

9 Y. F. Hu and Z. C. Wang, *J. Chem. Thermodyn.*, **26**, 429 (1994); Z. C. Wang, H. L. Yu, and Y. F. Hu, *J. Chem. Thermodyn.*, **26**, 171 (1994); Y. F. Hu and Z. C. Wang, *J. Chem. Thermodyn.*, **29**, 879 (1997); Y. F. Hu, *J. Solution Chem.*, **27**, 457 (1998); Y. F. Hu and T. M. Guo, *Phys. Chem. Chem. Phys.*, **1**, 3303 (1999).

10 Y. F. Hu and Z. C. Wang, *J. Chem. Soc., Faraday Trans.*, **94**, 3251 (1998).

11 V. K. Filippov and Y. A. Fedorov, *J. Solution Chem.*, **15**, 611 (1986).

12 H. Majima and Y. Awakura, *Metal. Trans., B*, **17**, 621 (1986); **19**, 349 (1988).

13 H. A. C. Mckay and J. K. Perring, *Trans. Faraday Soc.*, **49**, 163 (1953).

14 Y. F. Hu, *J. Chem. Soc., Faraday Trans.*, **94**, 913 (1998).

15 D. J. Turner, "Thermodynamics of Aqueous Systems with Industrial Applications," ed by S. A. Newman, Am. Chem. Soc., Washing, D. C. (1980).

16 I. K. Iskander and H. M. Selim, "Engineering Aspects of Metal Waste Management," Lewis Publisher (1992).

17 F. P. Millero, *J. Pure Applied Chem.*, **57**, 1015 (1985).

18 E. B. Woodruff and H. B. Lammers, "Steam Plant Operation," McGraw Hill Inc. (1950).

19 J. M. Montgomery, "Water Treatment Principles and Design," John Wiley and Sons, Inc. (1985).

20 A. M. Rowe and J. C. S. Chou, *J. Chem. Eng. Data*, **15**, 61 (1970).

21 Y. F. Hu, *Phys. Chem. Chem. Phys.*, **2**, 2379 (2000).

22 C. M. Criss and F. J. Millero, *J. Phys. Chem.*, **100**, 1288 (1996).

23 C. M. Criss and F. J. Millero, *J. Solution Chem.*, **28**, 849 (1999).

24 Yu A. Epikhin and M. S. Stakhanova, *Russian J. Phys. Chem.*, **41**, 1157 (1967).

25 G. Conti, P. Gianni, and M. R. Tine, *Thermochim. Acta*, **85**, 159 (1985).

26 G. Conti, P. Gianni, and M. R. Tine, *Thermochim. Acta*, **145**, 61 (1989).

27 S. Likke and L. A. Bromley, *J. Chem. Eng. Data*, **18**, 189 (1973).

28 R. J. Lemire, A. B. Campbell, P. P. S. Saluja, and J. C. LeBlanc, *J. Nucl. Mater.*, **201**, 165 (1993).

29 P. P. S. Saluja, D. J. Jobe, J. C. LeBlanc, and R. J. Lemire, *J. Chem. Eng. Data*, **40**, 398 (1995).

30 R. A. Robinson and R. H. Stoke, "Electrolyte Solutions," Butterworths, London (1965).

31 R. T. Pabalan and K. S. Pitzer, *Thermochim. Acta*, **33**, 354 (1988).

32 R. T. Pabalan and K. S. Pitzer, *J. Chem. Eng. Data*, **15**, 61 (1970).

33 T. F. Young and M. B. Smith, *J. Phys. Chem.*, **58**, 716 (1954).

34 J. J. Egan and J. Bracker, *J. Chem. Thermodyn.*, **6**, 9 (1974).

35 R. A. Robinson and V. E. Bower, *J. Res. Nat. Bur. Stand. A*, **69**, 19 (1965).