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Relationship Among the Raoult Law, Zdanovskii−Stokes−Robinson Rule, and Two Extended Zdanovskii−Stokes−Robinson Rules of Wang[†]

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In this paper, the Raoult law (*C. R. Acad. Sci. Ser. C* **1887**, *104*, 1430), the Zdanovskii−Stokes−Robinson (ZSR) rule (*Trudy Solyanoi Laboratorii Akad. Nauk SSSR* **1936**, No. *6*, 5; *J. Phys. Chem.* **1966**, *70*, 2126), and two extended ZSR rules of Wang (*Acta Metall. Sinica* **1980**, *16*, 195; *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1045) are presented in a unified way. Similar to the Raoult law, which was first noted empirically in pyridine solutions, the ZSR rule for isopiestic mixed electrolyte and nonelectrolyte aqueous solutions can be extended to every kind of liquid and solid solutions such as organic mixtures, aqueous and nonaqueous electrolyte and nonelectrolyte solutions, liquid and solid alloys, molten salt mixtures, slags, and nonstoichiometric solid solutions, resulting in two extended ZSR rules of Wang. Although the solutions obeying the Raoult law (or the related classically ideal solution model) are very few as compared with the classically nonideal solutions, one classically ideal solution {B+C+...+Z} may mix with many pure components A to form the classically nonideal solutions {A+B+C+...+Z} following the first extended ZSR rule (or the related partial ideal solution model) or mix with much more nonideal solutions {A1+A2+...+Aq} to form the classically nonideal solutions {A1+A2+...+Aq+B+C+...+Z} obeying the second extended ZSR rule (or the related ideal-like solution model). This would indicate that the ZSR rule and its extended forms are as important as the Raoult law for multicomponent systems.

Introduction

One of the primary goals of physical chemistry is to understand the variety of chemical phenomena in a unified way. There are many types of liquid and solid solutions in nature such as organic mixtures, aqueous and nonaqueous electrolyte and nonelectrolyte solutions, alloys, molten salt mixtures, slags, and nonstoichiometric solid solutions, which are important for chemistry, biology, geology, materials science, and engineering. Scientists working with different types of solutions often use not only different experimental methods and equipments but also different concentration units, equations, and formalisms, the latter of which make it difficult for scientists in one field to understand or benefit from advances in other fields.

The Raoult law and the related classically ideal solution model are fundamentally important in solution thermodynamics. In this study, we discuss the thermodynamic and statistical relationships among the Raoult law, Zdanovskii−Stokes−Robinson (ZSR) rule,[1−3] and two extended ZSR rules of Wang,[4−10] which all hold good at constant temperature and pressure.

Raoult Law and the Model

The Raoult law was first proposed empirically for vapor pressure measurements of pyridine solutions and may be expressed as

$$p_i = p_i^\circ x_i \tag{1}$$

where $i \in (B, C, ..., Z)$ denotes components in the solution {B+C+...+Z}; p_i and x_i are pressure and mole fraction of component i; and the superscript ° denotes pure substance so that p_i° is pressure of pure component i. Although scientists often have different opinions on solution models, particularly at the liquid state, one of the first successes for understanding different kinds of solutions in a unified way would be the development of the classically ideal solution model, which is based on the Raoult law and derived from a quasilattice treatment.[11] The Raoult law is now normally rewritten as

$$a_i = x_i \tag{2}$$

for every kind of solution {B+C+...+Z} with zero interchange energies among B,C, ..., Z, where a_i is the activity of component i. Since the classically ideal solution model may also be followed by the solutions with dissociation or polymerization, such as the molten salt mixtures {NaCl + BaCl$_2$} and {AgBr + PbBr$_2$}, the classically ideal solution model equations may generally be given by

$$V_m = \sum_i x_i V_{m,i}^\circ \tag{3a}$$

$$S_m = \sum_i x_i S_{m,i}^\circ - R\sum_i x_i \ln z_i \tag{3b}$$

$$H_m = \sum_i x_i H_{m,i}^\circ \tag{3c}$$

$$G_m = \sum_i x_i G_{m,i}^\circ + RT\sum_i x_i \ln z_i \tag{3d}$$

$$\mu_i = \mu_i^\circ + RT \ln z_i \tag{3e}$$

$$a_i = z_i \tag{3f}$$

within $0 \le x_i \le 1$, which connect the properties of the solution {B+C+...+Z} with those of its pure components B, C, ..., Z, where V_m is molar volume; S_m is molar entropy; H_m is molar enthalpy; G_m is molar Gibbs energy; μ_i is chemical potential of component i; $V_{m,i}^\circ$, $S_{m,i}^\circ$, $H_{m,i}^\circ$, and $G_{m,i}^\circ$ are molar quantities

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of pure component i; μ_i° is chemical potential of pure component i; R is gas constant; T is temperature; and z_i is a composition variable of component i, such as $z_i = [\nu_i^+ n_i/(\nu_B^+ n_B + \nu_C^+ n_C)]^{\nu_i^+} \cdot [\nu_i^- n_i/(\nu_B^- n_B + \nu_C^- n_C)]^{\nu_i^-}$ for a molten salt mixture {B+C} with no common ion; $z_i = [\nu_i^- n_i/(\nu_B^- n_B + \nu_C^- n_C)]^{\nu_i^-}$ for a molten salt mixture {B+C} with the same cation; $z_i = [\nu_i^+ n_i/(\nu_B^+ n_B + \nu_C^+ n_C)]^{\nu_i^+}$ for a molten salt mixture {B+C} with the same anion; and $z_i = [n_i/(n_B + n_C)] = x_i$ for a nondissociation and nonpolymerization system {B+C}. Here, n_i is mole number of component i, and ν_i^+ and ν_i^- are stoichiometric coefficients for cation and anion of component i in ionization reactions.

As pointed out by Stokes,[12] one can probably say that no real solution is known that conforms exactly to the classically ideal solution model, but mixtures of substances differing only in isotopic composition come very close to it. In addition, a classically ideal solution or classically near−ideal solution may also be formed by mixing closely similar components, such as isomers, homologues, and rare earths or actinides, at the same oxidation state. However, pairs of closely similar components are very few as compared with the pairs of dissimilar components. More importantly, the closely similar components often coexist with one or more other components in nature to form classically nonideal solutions (or real solutions). Moreover, one classically ideal solution {B+C+...+Z} may mix with various pure components A or various solutions {A1+A2+...+Aq} to form numbers of the classically nonideal solutions {A+B+C+...+Z} or {A1+A2+...+Aq+B+C+...+Z}, which are very interesting for both theorists and experimentalists.

ZSR Rule and the Model

Many theoretical models have been developed for nonideal solutions to describe their deviations from Raoult law and the related classically ideal solution model. These nonideal solution models often contain more or less interaction terms, for example, the well-known Pitzer ion-interaction model for pure and mixed aqueous solutions.[13] Recently, we[14,15] presented a new modified form of the Pitzer model for pure and mixed rare earth electrolyte aqueous solutions to very high concentrations, which contains five parameters for {water + NH_4NO_3},[14] six parameters for {water + $RE(NO_3)_3$},[14] and an additional six parameters for {water + NH_4NO_3 + $RE(NO_3)_3$},[15] where RE = rare earths.

Unlike the commonly used models, the ZSR rule is a linear concentration relation[1−4]

$$\sum_i (m_i/m_i^{1\circ}) = 1 \tag{4}$$

within $0 \le (m_i/\sum_k m_k) \le 1$ $\{k \in (B, C, \cdots, Z)\}$ for the isopiestic mixed electrolyte and nonelectrolyte aqueous solutions {water (A) + solute (B) + solute (C) +...+ solute (Z)} with mutually self-canceled or negligible solute−solute interactions as compared to solute−solvent interactions[2] (or with zero interchange energies among B, C, ..., Z),[14] which indicates the identity of the isopiestic line, along which water activity is fixed, and the mixing line, where m_i is molality of component i and the superscript 1° combined with the subscript i denotes binary subsystem {A+i}, so that $m_i^{1\circ}$ is molality of component i in the binary subsystem {water (A) + solute (i)}. Stokes and Robinson[2] theoretically derived eq 4 for isopiestic mixed nonelectrolyte aqueous solutions from a hydration treatment. Moreover, by using very precise isopiestic measurements for mixed nonelectrolyte aqueous solutions and mixed electrolyte aqueous solutions, they have quantitatively verified eq 4 or its equal[16]

$$\{\nu_B m_B^{1\circ}/(\nu_B m_B + \nu_C m_C)\} = 1 - b\{\nu_C m_C/(\nu_B m_B + \nu_C m_C)\}$$

with the parameter $b = \{1 - (\nu_B m_B^{1\circ}/\nu_C m_C^{1\circ})\}$, where the stoichiometric coefficient $\nu_i = \nu_i^+ + \nu_i^-$. For example, they reported the isopiestic data for the ternary systems {water (A) + mannitol (B) + sucrose (C)},[2] {water (A) + sorbitol (B) + sucrose (C)},[2] and {water (A) + NaCl (B) + $BaCl_2$ (C)}[16] at 298.15 K, for which the experimental deviations from eq 4 defined by

$$\Delta_m = \sum_i (m_i/m_i^{1\circ}) - 1$$

are all within $|\Delta_m| \le 0.002$ in the whole concentrations, which is within the experimental uncertainties.[17] In addition, they also made isopiestic measurements for the aqueous solutions containing both nonelectrolyte and electrolyte solutes at 298.15 K. Comparison of their measurements with eq 4 shows $|\Delta_m| \le 0.002$ at the concentrations of $(\nu_B m_B + \nu_C m_C) \approx 1.1\ \text{mol}\cdot\text{kg}^{-1}$ and $|\Delta_m| \le 0.005$ at $(\nu_B m_B + \nu_C m_C) \approx 1.6\ \text{mol}\cdot\text{kg}^{-1}$ for {water (A) + glycine (B) + KCl (C)}[18] and $|\Delta_m| \le 0.005$ at $(\nu_B m_B + \nu_C m_C) \approx 1.4\ \text{mol}\cdot\text{kg}^{-1}$ for {water (A) + mannitol (B) + KCl (C)}.[19,20] Here, $|\Delta_m| \le 0.002$ for {water (A) + NaCl (B) + $BaCl_2$ (C)} in the whole concentrations, and for {water (A) + glycine (B) + KCl (C)} at $(\nu_B m_B + \nu_C m_C) \approx 1.1\ \text{mol}\cdot\text{kg}^{-1}$ would indicate that the ZSR rule is not limited for mixtures of nonelectrolytes or for mixtures of electrolytes of the same charge type. Later, we experimentally found that eq 4 fits the isopiestic behavior of the quaternary systems {water (A) + mannitol (B) + sorbitol (C) + sucrose (D)}[21] and {water (A) + NaCl (B) + NH_4Cl (C) + $BaCl_2$ (D)}[22] as well as the mixed rare earth nitrate aqueous solutions {water (A) + $Y(NO_3)_3$ (B) + $La(NO_3)_3$ (C)},[14] {water (A) + $Y(NO_3)_3$ (B) + $Pr(NO_3)_3$ (C)},[14] {water (A) + $Y(NO_3)_3$ (B) + $Nd(NO_3)_3$ (C)},[14] {water (A) + $La(NO_3)_3$ (B) + $Pr(NO_3)_3$ (C)},[14] {water (A) + $La(NO_3)_3$ (B) + $Nd(NO_3)_3$ (C)},[14] {water (A) + $Pr(NO_3)_3$ (B) + $Nd(NO_3)_3$ (C)},[14] {water (A) + $Y(NO_3)_3$ (B) + $La(NO_3)_3$ (C) + $Pr(NO_3)_3$ (D)},[23] {water (A) + $Y(NO_3)_3$ (B) + $La(NO_3)_3$ (C) + $Nd(NO_3)_3$ (D)},[23] {water (A) + $Y(NO_3)_3$ (B) + $Pr(NO_3)_3$ (C) + $Nd(NO_3)_3$ (D)},[23] and {water (A) + $Y(NO_3)_3$ (B) + $La(NO_3)_3$ (C) + $Pr(NO_3)_3$ (D) + $Nd(NO_3)_3$ (E)}[24] within $|\Delta_m| \le 0.002$ in the whole concentrations at 298.15 K. In all these cases, the aqueous solutions are unsaturated. Some of the results are summarized in Figure 1.

First Extended ZSR Rule of Wang and the Model

Many extended ZSR rules have been developed for modeling various mixed aqueous solutions, which either contain interaction parameters[3,25,26] or incorpotate Debye−Hückel terms.[27] Unlike these extended ZSR rules for aqueous solutions, Wang[4−9] found that eq 4 can be rewritten as

$$\sum_i (\tau_i/\tau_i^{1\circ}) = 1 \tag{5a}$$

within $0 \le (\tau_i/\sum_k \tau_k) \le 1$ or

$$\omega = \sum_i (x_i/\sum_k x_k)\omega^{1\circ,i} \tag{5b}$$

within $0 \le (x_i/\sum_k x_k) \le 1$ and can be extended to every kind of solution {A+B+C+...+Z} with zero interchange energies among B, C, ..., Z at constant activity (or chemical potential or partial Gibbs free energy) of A, which indicates the identity of the isoactivity line of A and the mixing line, where τ_i may denote either molality, or mole fraction, or mass fraction of component i; ω may denote either total vapor pressure of the system if the pressure is not too high, or the solubility of solute A in one mole of the mixed solvent (B+C+...+Z), or the oxygen-to-metal ratio (O/M) for nonstoichiometric solid mixed-oxide solutions {oxygen (A)+B+C+...+Z}; $\tau_i^{1\circ}$ is the concentration of component i in the binary subsystem {A+i}; and $\omega^{1\circ,i}$ is the property of the binary subsystem {A+i}. Moreover, eq

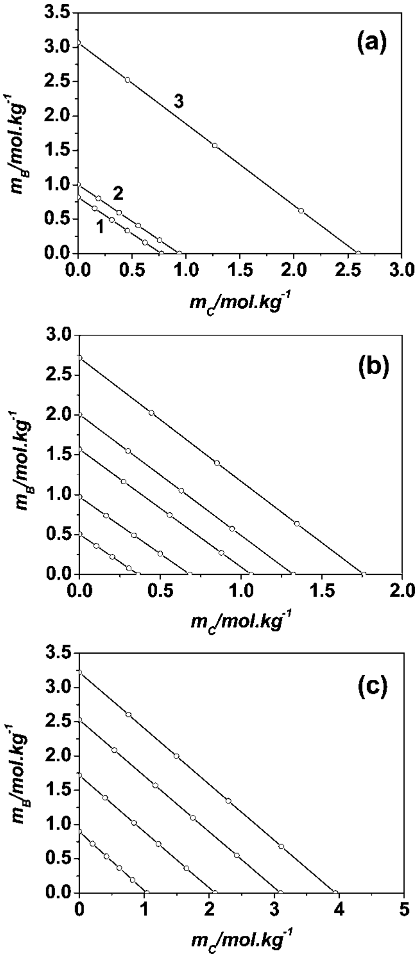

Figure 1. Isopiestic concentrations for the mixed electrolyte and nonelectrolyte aqueous solutions at 298.15 K: (a) lines 1 and 2 for {water (A) + mannitol (B) + sucrose(C)}[2] and line 3 for {water (A) + sorbitol (B) + sucrose(C)},[2] (b) {water (A) + NaCl (B) + $BaCl_2$ (C)},[16] and (c) {water (A) + $Y(NO_3)_3$ (B) + $La(NO_3)_3$ (C)}.[14] The solid lines are given by eq 4, the ZSR rule. For these systems, the experimental deviations are all within $|\Delta_m| \le 0.002$ in the whole concentrations.

5a may be valid at a constant other than partial molar quantity,[4,5] for example, the {water (A) + KCl (B) + KBr (C)} system at constant partial molar volume of water. It would be therefore that eq 5 may be called the first extended ZSR rule of Wang.

On the basis of eq 5a, Wang[4−9] developed a partial ideal solution model from a modified quasilattice treatment for every kind of solution {A+B+C+...+Z} with zero interchange energies among B, C, ..., Z with the main model eqs 5 and 6

$$V_m = \sum_i (x_i/x_i^{1°}) V_{m,i}^{1°} \qquad (6a)$$

$$S_m = \sum_i (x_i/x_i^{1°}) S_{m,i}^{1°} - R \sum_i x_i \ln z_i \qquad (6b)$$

$$H_m = \sum_i (x_i/x_i^{1°}) H_{m,i}^{1°} \qquad (6c)$$

$$G_m = \sum_i (x_i/x_i^{1°}) G_{m,i}^{1°} + RT \sum_i x_i \ln z_i \qquad (6d)$$

$$\mu_i = \mu_i^{1°} + RT \ln z_i \qquad (6e)$$

$$(a_i/a_i^{1°}) = z_i \qquad (6f)$$

within $0 \le (x_i/\sum_k x_k) \le 1$, which connect the properties of the solution {A+B +C+...+Z} with those of its binary subsystems {A+i} at constant activity of A, where $V_{m,i}^{1°}$, $S_{m,i}^{1°}$, $H_{m,i}^{1°}$, and $G_{m,i}^{1°}$ are molar quantities of the binary subsystem {A+i} and $\mu_i^{1°}$, $a_i^{1°}$, and $x_i^{1°}$ are chemical potential, activity, and mole fraction of component i in the binary subsystem {A+i}. Here, the composition variable z_i of component i is given by $z_i = [n_i/(n_B + n_C)]$ for a nondissociation and nonpolymerization system {A+B+C} but by different formulas for different kinds of ionic solutions {A+B+C}; for example, $z_i = [\nu_i^+ n_i/(\nu_B^+ n_B + \nu_C^+ n_C)]^{\nu_{i+}}$ for a molten salt mixture {$PbCl_2$ (A) + NaCl (B) + $BaCl_2$ (C)},[10] but $z_i = [\nu_i n_i/(\nu_B n_B + \nu_C n_C)]^{\nu_i}/[\nu_i^- n_i/(\nu_B^- n_B + \nu_C^- n_C)]^{\nu_{i-}}$ for aqueous solution {water (A) + NaCl (B) + $BaCl_2$ (C)},[10] though both containing NaCl (B) and $BaCl_2$ (C). Comparison of eq 6 with eq 3 shows that the partial ideal solution model may reduce to the classically ideal solution model at $x_A = 0$ and that a pure component A + a classically ideal solution {B+C+...+Z} = a partial ideal solution {A+B+C+...+Z}.[9] The Raoult law or classically ideal solution model for {B+C+...+Z} may be derived when the first extended ZSR rule of Wang or the partial ideal solution model for {A+B+C+...+Z} holds good from infinite of B, C, ..., Z, where $a_A = 1$ and all $a_i = 0$, to infinite of A, where $a_A = 0$.

Toluene and xylenes are homologues so that the classically ideal solution model may be closely obeyed by the binary organic mixtures {toluene (B) + *o*-xylene (C)} and {toluene (B) + *p*-xylene (C)}. On the other hand, the classically ideal solution model is slightly deviated by the binary melts {Bi (B) + Sn (C)} and {NaCl (B) + RbCl (C)} as well as by the binary organic mixture {acetone (B) + acetonitrile (C)}. Therefore, eq 5a was verified by using the literature cell voltage data of the ternary melts {Cd (A) + Bi (B) + Sn (C)}[28,29] and {AgCl (A) + NaCl (B) + RbCl (C)},[30] while eq 5b was checked by using the literature total vapor pressure data of {methyl acetate (A) + acetone (B) + acetonitrile(C)}[31] and the literature solubility data of iodine in {iodine (A) + toluene (B) + *o*-xylene (C)}[32] and {iodine (A) + toluene (B) + *p*-xylene(C)}.[32] Furthermore, isopiestic measurements of the nonaqueous solution {methanol (A) + NaBr (B) + NH_4Br (C)}[33] and the ternary melt {Hg (A) + Bi (B) + Sn (C)}[8] have been made and compared with eq 5a. The deviation defined by

$$\Delta_\tau = \sum_i (\tau_i/\tau_i^{1°}) - 1$$

$$\Delta\omega = \omega - \sum_i (x_i/\sum_k x_k)\omega^{1°,i}$$

is $|\Delta_\tau| \le 0.003$ for {methanol (A) + NaBr (B) + NH_4Br (C)}, $|(\Delta\omega/\omega)| \le 0.001$ for {iodine (A) + toluene (B) + *o*-xylene (C)}, as well as $|(\Delta\omega/\omega)| \le 0.005$ for {iodine (A) + toluene (B) + *p*-xylene (C)} and {methyl acetate (A) + acetone (B) + acetonitrile (C)}. Some of the results are summarized in Figure 2, which shows that eq 5a can fit the isoactivity lines of methanol in {methanol (A) + NaBr (B) + NH_4Br (C)} at 298.15 K very well and can approximately fit the isoactivity lines of Cd in {Cd (A) + Bi (B) + Sn(C)} at 773 K and of AgCl in {AgCl (A) + NaCl (B) + RbCl (C)} at 1073 K. Figures 3 and 4 show the activities of Bi and Sn along the isoactivity lines of Cd in {Cd (A) + Bi (B) + Sn (C)} and the activities of NaCl and RbCl along the isoactivity lines of AgCl in {AgCl (A) + NaCl (B) + RbCl (C)}, respectively, which approximately fit eq 6f.

Second Extended ZSR Rule of Wang and the Model

In the case that closely similar components (B, C, ..., Z) coexist with more than one other component (A1, A2, ..., Aq) to form classically nonideal solutions {A1+A2+...+Aq+B+C+...+Z}, Wang[10] developed an ideal-like model from another modified quasilattice treatment for every kind of the solution {A1+A2+...+Aq+B+C+...+Z} with zero interchange energies among B, C, ..., Z with the main model equations being

$$\sum_i (\tau_i/\tau_i^{q\circ}) = 1 \tag{7a}$$

$$\sum_i \{(m_i/m_\beta)/(m_i^{q\circ}/m_\beta^{q\circ,i})\} = 1 \tag{7b}$$

$$s_\beta = \sum_i (x_i/\sum_k x_k) s_\beta^{q\circ,i} \tag{7c}$$

$$V_\mathrm{m} = \sum_i (x_i/x_i^{q\circ}) V_{\mathrm{m},i}^{q\circ} \tag{8a}$$

$$S_\mathrm{m} = \sum_i (x_i/x_i^{q\circ}) S_{\mathrm{m},i}^{q\circ} - R\sum_i x_i \ln z_i \tag{8b}$$

$$H_\mathrm{m} = \sum_i (x_i/x_i^{q\circ}) H_{\mathrm{m},i}^{q\circ} \tag{8c}$$

$$G_\mathrm{m} = \sum_i (x_i/x_i^{q\circ}) G_{\mathrm{m},i}^{q\circ} + RT\sum_i x_i \ln z_i \tag{8d}$$

$$\mu_i = \mu_i^{q\circ} + RT \ln z_i \tag{8e}$$

$$(a_i/a_i^{q\circ}) = z_i \tag{8f}$$

within $0 \le (x_i/\sum_k x_k) \le 1$, which connect the properties of the solution {A1+A2+...+Aq+B+C+...+Z} with those of its (q+1)-component subsystems {A1+A2+...+Aq+i} at constant activities of A1, A2, ..., Aq, where eq 7a indicates the identity of the common isoactivity line of A1, A2, ..., Aq and the mixing line, $\beta \in (A1, A2, \cdots, Aq)$ denotes components having constant activities in the solution {A1+A2+...+Aq+B+C+...+Z} and its (q+1)-component subsystem {A1+A2+...+Aq+i}, $s_\beta[= n_\beta/(n_\mathrm{B} + n_\mathrm{C} + \cdots + n_\mathrm{Z})]$ denotes the solubility of solute β in the solution {A1+A2+...+Aq+B+C+...+Z} formed from a solute mixture [A1+A2+...+Aq] and a solvent mixture [B+C+...+Z]; and the superscript $q°,i$ (or the superscript $q°$ combined with the subscript i) denotes a property of the (q+1)-component subsystem {A1+A2+...+Aq+i}, so that $V_{\mathrm{m},i}^{q\circ}$, $S_{\mathrm{m},i}^{q\circ}$, $H_{\mathrm{m},i}^{q\circ}$, and $G_{\mathrm{m},i}^{q\circ}$ are molar quantities of the subsystem {A1+A2+...+Aq+i}; $\mu_i^{q\circ}$, $a_i^{q\circ}$, $x_i^{q\circ}$, and $m_i^{q\circ}$ are chemical potential, activity, mole fraction, and molality of component i in the subsystem {A1+A2+...+Aq+i}; $\tau_i^{q\circ}$ is the concentration of component i in the subsystem {A1+A2+...+Aq+i}; $m_\beta^{q\circ,i}$ is the molality of component β in the subsystem {A1+A2+...+Aq+i}, and $s_\beta^{q\circ,i}$ denotes the solubility of solute β in the subsystem {A1+A2+...+Aq+i}. In the special case that τ denotes molality and β = water, eq 7b reduces to eq 7a due to

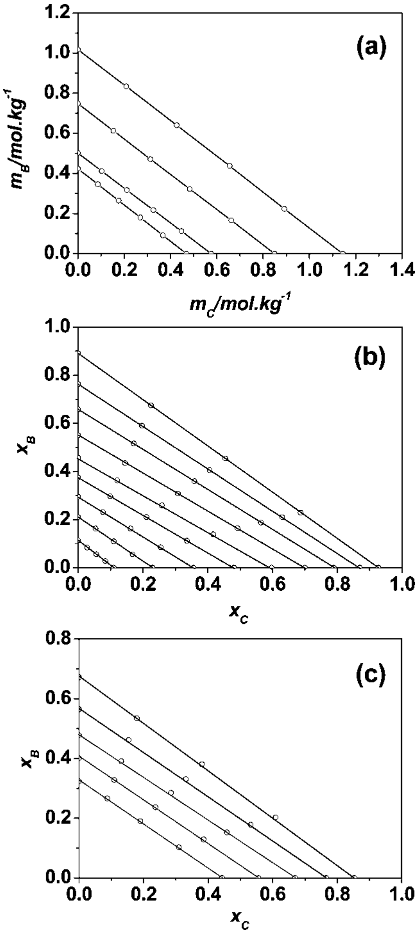

Figure 2. Isopiestic concentrations for (a) {methanol (A) + NaBr (B) + NH_4Br (C)} at 298.15 K,[33] (b) {Cd (A) + Bi (B) + Sn (C)} at 773 K,[28,29] and (c) {AgCl (A) + NaCl (B) + RbCl (C)} at 1073 K.[30] The solid lines are given by eq 5a, the first extended ZSR rule of Wang.

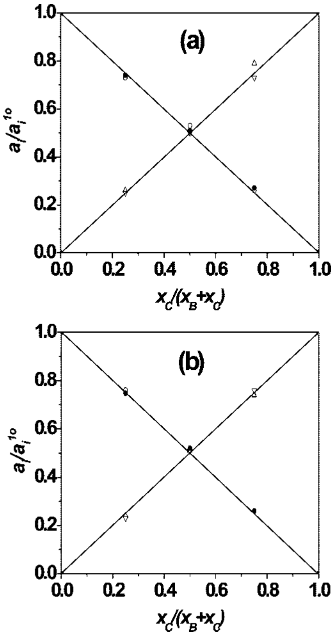

Figure 3. Activities of Bi and Sn in {Cd (A) + Bi (B) + Sn (C)} at 773 K[28,29] along the isoactivity lines of Cd: (a) $a_\mathrm{A} = 0.6$ and 0.5 and (b) $a_\mathrm{A} = 0.3$ and 0.2. The solid lines are given by eq 6f, the partial ideal solution model.

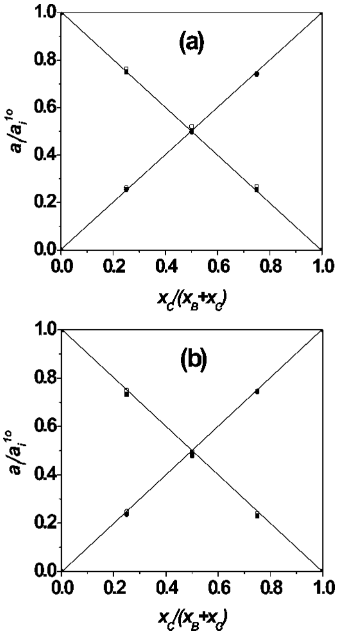

Figure 4. Activities of NaCl and RbCl in {AgCl (A) + NaCl (B) + RbCl (C)} at 1073 K[30] along the isoactivity lines of AgCl: (a) $a_\mathrm{A} = 0.6$ and 0.5 and (b) $a_\mathrm{A} = 0.3$ and 0.2. The solid lines are given by eq 6f, the partial ideal solution model.

$m_\beta = m_\beta^{q\circ,i} = 55.506\ \text{mol}\cdot\text{kg}^{-1}$. It would be therefore that eq 7 may be called the second extended ZSR rule of Wang.

Comparison of eqs 7 and 8 with eqs 5 and 6 and with eq 3 shows that the ideal-like solution model reduces to the partial ideal solution model at $q = 1$ (i.e., A1 = A and $x_{A2} = x_{A3} = \cdots = x_{Aq} = 0$) and to the classically ideal solution model at $q = 0$ (i.e., $x_{A1} = x_{A2} = \cdots = x_{Aq} = 0$) and that a classically nonideal solution {A1+A2+...+Aq} + a classically ideal solution {B+C+...+Z} = an ideal-like solution {A1+A2+...+Aq+B+C+...+Z}. The Raoult law or classically ideal solution model for {B+C+...+Z} may be derived when the second extended ZSR rule of Wang or the ideal-like solution model holds good from infinite of B, C, ..., Z, where all $a_i = 0$, to infinite of A1, A2, ..., Aq, where all $a_\beta = 0$, for {A1+A2+...+Aq+B+C+...+Z}.

Equation 7c has been verified[10,34] by the joint solubility measurements of a solute mixture [iodine (A1) + anthracene (A2)] in {iodine (A1) + anthracene (A2) + toluene (B) + benzene (C)}, {iodine (A1) + anthracene (A2) + toluene (B) + *m*-xylene (C)}, {iodine (A1) + anthracene (A2) + toluene (B) + *o*-xylene (C)}, {iodine (A1) + anthracene (A2) + toluene (B) + *p*-xylene (C)}, {iodine (A1) + anthracene (A2) + *m*-xylene (B) + *o*-xylene (C)}, {iodine (A1) + anthracene (A2) + *m*-xylene (B) + *p*-xylene (C)}, {iodine (A1) + anthracene (A2) + *o*-xylene (B) + *p*-xylene (C)}, and {iodine (A1) + anthracene (A2) + toluene (B) + *m*-xylene (C) + *p*-xylene (D)} at 298.15 K, where the concentration of iodine was determined directly by titrimetric measurements but that of anthracene was calculated by deducting the iodine concentration from the total absorption spectrophotometric measurements for the mixture of iodine and anthracene so that the experimental precision for anthracene was limited by the uncertainty of the two methods. The deviations defined by

$$\Delta s_\beta = s_\beta - \sum_i \left\{x_i \Big/ \sum_k x_k\right\} s_\beta^{q\circ,i}$$

for all these systems are $|\Delta s_{A1}| \le 0.001$ and $|\Delta s_{A2}| \le 0.0001$, which are within the experimental uncertainties of the titrimetric and spectrophotometric measurements. Equations 7a and 7b have also been checked[10,35−40] by the isopiestic measurements for a number of the mixed aqueous solutions {water (A1)+A2+...+Aq+B+C+...+Z} with one or two saturated solutes or alcohols denoted by A2 and A3 and with two or three unsaturated solutes denoted by B, C, ..., Z at 298.15 K.

It would be very difficult to experimentally determine the activities of B, C, ..., Z in the solution {A1+A2+...+Aq+B+C+...+Z} related to its subsystems {A1+A2+...+Aq+*i*} at constant activities of A1, A2, ..., Aq to directly verify eq 8f. Recently, we[15] developed an indirect method, which combines the isopiestic measurements with Pitzer model calculation for NH_4NO_3-saturated quaternary systems {water (A1) + NH_4NO_3 (A2) + $Y(NO_3)_3$ (B) + $Pr(NO_3)_3$ (C)} and {water (A1) + NH_4NO_3 (A2) + $Pr(NO_3)_3$ (B) + $Nd(NO_3)_3$ (C)}. The results fit eq 8f very well.

Discussion

The Raoult law was first discovered empirically for vapor pressure measurements of pyridine solutions, while the ZSR rule was discovered empirically and theoretically derived for isopiestic mixed electrolyte and nonelectrolyte aqueous solutions. The classically ideal solution model derived from a quasilattice treatment makes the Raoult law valid for every kind of liquid and solid solution {B+C+...+Z} such as organic mixtures, aqueous and nonaqueous electrolyte and nonelectrolyte solutions, alloys, molten salt mixtures, slags, and nonstoichiometric solid solutions. The partial ideal solution model and ideal-like solution model derived from modified quasilattice treatments result in two extended ZSR rules of Wang, which are valid for every kind of liquid and solid solution {A+B+C+...+Z} at constant activity of A and for {A1+A2+...+Aq+B+C+...+Z} at constant activities of A1, A2, ..., Aq, respectively. The classically ideal solution model, partial ideal solution model, and ideal-like solution model are all valid within $0 \le (x_i/\sum_k x_k) \le 1$ for the systems with zero interchange energies among B, C, ..., Z. The relationship among the three models might be given by "a pure component A + a classically ideal solution {B+C+...+Z} = a partial ideal solution {A+B+C+...+Z}" and "a classically nonideal solution {A1+A2+...+Aq} + a classically ideal solution {B+C+...+Z} = an ideal-like solution {A1+A2+...+Aq+B+C+...+Z}". In other words, in the case that {B+C+...+Z} follows the classically ideal solution model, the partial ideal solution model is valid over the whole range of the activity of A for a classically nonideal solution {A+B+C+...+Z} and the ideal-like solution model, over the whole range of the activities of A1, A2, ..., Aq, for a classically nonideal solution {A1+A2+...+Aq+B+C+...+Z}. Therefore, after extension, the ZSR rule would be as important as the Raoult law in multicomponent systems. These rules and models might be used to predict thermodynamic properties of a solution {A+B+C+...+Z} or {A1+A2+...+Aq+B+C+...+Z} based on the chemical nature of pure components *i* (= B, C, ..., Z) and the themodynamic properties of binary subsystems {A+*i*} or (q+1)-component subsystems {A1+A2+...+Aq+*i*}.

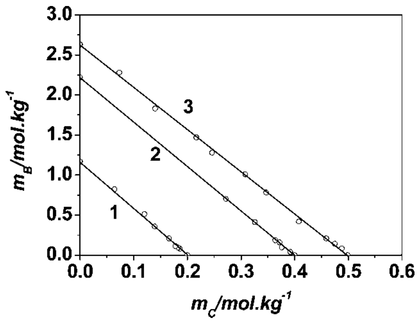

Figure 5. Isopiestic concentrations for the {water (A) + NaPAA (B) + NaCl (C)} solution[41] at 298.15 K: line 1 at $m_C^{1\circ} = 0.200\ \text{mol}\cdot\text{kg}^{-1}$, line 2 at $m_C^{1\circ} = 0.400\ \text{mol}\cdot\text{kg}^{-1}$, and line 3 at $m_C^{1\circ} = 0.499\ \text{mol}\cdot\text{kg}^{-1}$. The solid lines are given by eq 4, the ZSR rule. The experimental deviations are within $|\Delta_m| \le 0.04$ at $m_C^{1\circ} = 0.200\ \text{mol}\cdot\text{kg}^{-1}$ and $|\Delta_m| \le 0.02$ at $m_C^{1\circ} = (0.400 \text{ and } 0.499)\ \text{mol}\cdot\text{kg}^{-1}$.

In addition, in the case that {B+C+...+Z} deviates from the classically ideal solution model, the two extended ZSR rules of Wang, partial ideal solution model and ideal-like solution model, may also be valid for {A+B+C+...+Z} and {A1+A2+...+Aq+B+C+...+Z}, respectively, in the B, C, ..., Z poor ranges because the interchange energies among B, C, ..., Z decrease with the addition of A and of A1, A2, ..., Aq, particularly at infinite of B, C, ..., Z.

Rard and Platford[17] have pointed out that isopiestic standards have successfully been established for aqueous solutions at 298.15 K, and under favorable conditions, an individual isopiestic molality at equilibrium can be determined to (± 0.05 to ± 0.1) %·m and molality ratio of the reference standard to the test solution determined to (± 0.1 to ± 0.2) %. Therefore, precise isopiestic measurements of unsaturated nonelectrolyte and electrolyte aqueous solutions at 298.15 K have widely been used to verify the ZSR rule. However, the precision of isopiestic molality may decrease obviously for polymer solutions, for which the polymer molecular mass was determined by additional measurements with relatively low precision. For example, Ise and co-workers[41] reported the standard isopiestic measurements for the {water (A) + NaPAA (B) + NaCl (C)} solution at 298.15 K. Figure 5 shows that their isopiestic data fit eq 4 well at $m_{\mathrm{C}}^{1^\circ} \leq 0.499\ \mathrm{mol\cdot kg^{-1}}$, but their isopiestic molality was determined only to ± 1 %·m due to the polymerization degree measurements by viscometry. In this case, mass fraction would be more suitable to be chosen as the isopiestic composition variable instead of molality, and the isopiestic precision could be determined to (± 0.05 to ± 0.1) %·τ (where τ = mass fraction), on which the uncertainty of polymerization degree measurements has no effect, so that eq 5a (where τ = mass fraction) instead of eq 4 might be chosen as the model equation to precisely compare the isopiestic measurements.

Literature Cited

(1) Zdanovskii, A. B. Regularities in the Property Variations of Mixed Solutions. *Trudy Solyanoi Laboratorii Akad. Nauk SSSR* **1936**, *No. 6*, 5–70.

(2) Stokes, R. H.; Robinson, R. A. Interactions in Aqueous Nonelectrolyte Solutions. I. Solute-Solvent Equilibria. *J. Phys. Chem.* **1966**, *70*, 2126–2131.

(3) Chen, H.; Sangster, J.; Teng, T. T.; Lenzi, F. A General Method of Predicting the Water Activity of Ternary Aqueous Solutions from Binary Data. *Can. J. Chem. Eng.* **1973**, *51*, 234–241.

(4) Wang, Z.-C. The Linear Concentration Rules at Constant Partial Molar Quantity $\bar{\Psi}_0$— Extension of Turkdogan's Rule and Zdanovskii's Rule. *Acta Metall. Sinica* **1980**, *16*, 195–206.

(5) Wang, Z.-C. Thermodynamics of Multicomponent Systems at Constant Partial Molar Quantity $\bar{\Psi}_0$ − Thermodynamical Aspect of Iso-$\bar{\Psi}_0$ Rules of Zdanovskii-Type and Turkdogan-Type. *Acta Metall. Sinica* **1981**, *17*, 168–176.

(6) Wang, Z.-C. *The Theory of Partial Simple Solutions for Multicomponent Systems in First China-USA Bilateral Metallurgical Conference*; The Metall. Ind. Press: Beijing, 1981; p 121.

(7) Wang, Z.-C. The Theory of Partial Simple Solutions for Multicomponent Systems. *Acta Metall. Sinica* **1982**, *18*, 141–152.

(8) Wang, Z.-C.; Zhang, X.-H.; He, Y.-Z.; Bao, Y.-H. High-Temperature Isopiestic Studies on {(1-y)Hg + y(1-t)Bi + ytSn}(1) at 600 K. Comparison with the Partial Ideal Solution Model. *J. Chem. Thermodyn.* **1989**, *21*, 653–665.

(9) Wang, Z.-C.; Lück, R.; Predel, B. Pure Component A + Classically Ideal Solution (B + C +. .) = ? *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3641–3646.

(10) Wang, Z.-C. Novel General Linear Concentration Rules and Their Theoretical Aspects for Multicomponent Systems at Constant Chemical Potentials − Ideal-Like Solution Model and Dilute-Like Solution Model. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1045–1058.

(11) Guggenheim, E. A. *Mixtures*; Oxford University Press: Oxford, 1952.

(12) Stokes, R. H. *Thermodynamics of Solutions in Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 1.

(13) Pitzer, K. S. *Ion Interaction Approach: Theory and Data Correlation in Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 3.

(14) Wang, Z.-C.; He, M.; Wang, J.; Li, J.-L. Modeling of Aqueous 3−1 Rare Earth Electrolytes and Their Mixtures to Very High Concentrations. *J. Solution Chem.* **2006**, *35*, 1137–1156.

(15) Wang, Z.-C.; He, M.; Gong, L.-D. Thermodynamics of Aqueous Complex Solutions Containing 3/1 Rare Earth Electrolyte Pairs and Salting-Out Agents to Very High Concentrations. *J. Phys. Chem. B* **2007**, *111*, 3704–3715.

(16) Robinson, R. A.; Bower, V. E. Thermodynamics of the Ternary System:Water-Sodium Chloride-Barium Chloride at 25 °C. *J. Res. NBS. A (Phys. and Chem.)* **1965**, *69*, 19–27.

(17) Rard, J. A.; Platford, R. F. *Experimental Methods: Isopiestic in Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 5.

(18) Bower, V. E.; Robinson, R. A. Thermodynamics of the Ternary System: Water-Glycine-Potassium Chloride at 25°c from Vapor Pressure Measurements. *J. Res. NBS. A (Phys. and Chem.)* **1965**, *69*, 131–135.

(19) Robinson, R. A.; Stokes, R. H. Activity Coefficients of Mannitol and Potassium Chloride in Mixed Aqueous Solutions at 25 °C. *J. Phys. Chem.* **1962**, *66*, 506–507.

(20) Robinson, R. A.; Stokes, R. H. Activity Coefficients in Aqueous Solutions of Sucrose, Mannitol and Their Mixtures at 25 °C. *J. Phys. Chem.* **1961**, *65*, 1954–1958.

(21) Wang, Z.-C.; Yu, H.-L.; Hu, Y.-F. Isopiestic Studies on {Mannitol + Sorbitol + Sucrose}(aq) at the Temperature 298.15 K. Comparison with the Partial Ideal Solution Model. *J. Chem. Thermodyn.* **1994**, *26*, 171–176.

(22) Hu, Y.-F.; Wang, Z.-C. Isopiestic Studies on {NaCl(m_{B}) + NH_4Cl(m_{C}) + $BaCl_2$(m_{D})}(aq) at the Temperature 298.15 K. A Quaternary System Obeying Zdanovskii's Rule. *J. Chem. Thermodyn.* **1994**, *26*, 429–433.

(23) He, M.; Wang, Z.-C. Interactions in the Quaternary Systems H_2O-$Y(NO_3)_3$- $La(NO_3)_3$-$Pr(NO_3)_3$, H_2O-$Y(NO_3)_3$-$La(NO_3)_3$-$Nd(NO_3)_3$ and H_2O-$Y(NO_3)_3$- $Pr(NO_3)_3$-$Nd(NO_3)_3$ to Very High Concentrations. *J. Solution Chem.* **2006**, *35*, 1607–1619.

(24) He, M.; Wang, Z.-C. Interactions in the Quinary System H_2O-Y-$(NO_3)_3$ -$La(NO_3)_3$-$Pr(NO_3)_3$-$Nd(NO_3)_3$ to Very High Concentrations. *J. Solution Chem.* **2007**, *36*, 1547–1558.

(25) Kirgintsev, A.; Luk'yanov, A. V. Isopiestic Investigations of Ternary Solutions. VIII. General Treatment of the Results for 34 Ternary Aqueous Salt Solutions. *Russ. J. Phys. Chem.* **1966**, *40*, 953–956.

(26) Clegg, S. L.; Seifeld, J. H.; Edney, E. O. Thermodynamic Modelling of Aqueous Aerosols Containing Electrolytes and Dissolved Organic Compounds. II. An Extended Zdanovskii-Stokes-Robinson Approach. *J. Aerosol. Sci.* **2003**, *34*, 667–690.

(27) Clegg, S. L.; Seifeld, J. H. Improvement of the Zdanovskii-Stokes-Robinson Model for Mixtures Containing Solutes of Different Charge Types. *J. Phys. Chem. A* **2004**, *108*, 1008–1017.

(28) Mellgren, S. Thermodynamic Properties of the Liquid Ternary System Bismuth-Cadmium-Tin. *J. Am. Chem. Soc.* **1952**, *74*, 5037–5040.

(29) Pelton, A. D.; Flengas, S. N. An Analytical Method of Calculating Thermodynamic Data in Ternary Systems. *Can. J. Chem.* **1969**, *47*, 2283–2292.

(30) Pelton, A. D.; Flengas, S. N. Thermodynamics of the Molten AgCl-RbCl-NaCl System by Electromotive Force Measurements. *J. Electrochem. Soc.* **1971**, *118*, 1307–1315.

(31) DiElsi, D. P.; Patel, R. B.; Abbott, M. M.; Van Ness, H. C. Excess Thermodynamic Functions for Ternary Systems. 3. Total Pressure Data and GE for Acetone-Acetonitrile-Methyl Acetate at 50 °C. *J. Chem. Eng. Data* **1978**, *23*, 242–245.

(32) Jiang, C.-Z.; Birbaum, C. S.; Fried, V. Solubility of Iodium in Mixed Solvents. *J. Chem. Eng. Data* **1983**, *28*, 78–81.

(33) Wang, Z.-C.; Li, X.-Y.; Liu, Y.-H. Isopiestic Studies on (Methanol + NaBr + NH_4Br) at the Temperature 298.15 K. Comparison with the Partial Ideal Solution Model. *J. Chem. Thermodyn.* **1998**, *30*, 709–712.

(34) Jin, X.-W.; Wang, Z.-C. Solubility of A Solute Mixture (Iodine + Anthracene) in Binary and Ternary Solvent Mixtures of Xylenes with or without Toluene, Comparison with the Ideal-Like Solution Model. *J. Chem. Thermodyn.* **2000**, *32*, 349–355.

(35) Wang, M.; Yang, D.-M.; Sun, S.-P.; Wang, Z.-C. Isopiestic Studies on the Quaternary System (Water + Methanol + Sodium Bromide + Ammonium Bromide) at the Temperature 298.15 K: Comparison with the Ideal-Like Solution Model. *J. Chem. Thermodyn.* **2000**, *32*, 389–392.

(36) Wang, M.; Zhang, H.; Yang, D.-M.; Wang, Z.-C. Isopiestic Studies on the Saturated Quinary Systems (Water + Sodium Chloride$_{\mathrm{(sat)}}$ + Glycine$_{\mathrm{(sat)}}$ + Sorbitol + Sucrose) and (Water + Sodium Chloride$_{\mathrm{(sat)}}$ + Barium Chloride$_{\mathrm{(sat)}}$ + Sorbitol + Sucrose) at the Temperature 298.15 K: Comparison with the Ideal-Like Solution Model. *J. Chem. Thermodyn.* **2001**, *33*, 711–717.

(37) Wang, M.; Wang, Z.-C.; Yang, D.-M.; Wang, J. Isopiestic Studies on the Quinary System (Water + Methanol + Ethanol + Sodium Bromide + Ammonium Bromide) at the Temperature 298.15 K: Comparison with the Ideal-Like Solution Model. *J. Chem. Thermodyn.* **2002**, *34*, 1575–1580.

(38) Wang, J.; Wang, Z.-C. An Ideal-Like Quaternary Aqueous Solution Equilibrated with A Solid Cadmium-Containing Complex. *Z. Phys. Chem.* **2004**, *218*, 881–885.

(39) Wang, J.; Wang, Z.-C.; Li, J.-L.; Yang, D.-M.; Gong, L.-D. Isopiestic Study of Water + Mannitol(sat) + Sodium Chloride + Ammonium Chloride + Barium Chloride at T = 298.15 K and Comparison with the Ideal-Like Solution Model. *J. Solution Chem.* **2005**, *34*, 369–373.

(40) Wang, M.; Zhang, H.; Wang, J.; Wang, Z.-C. Isopiestic Studies on the Saturated Systems {H_2O + $BaCl_2$(sat) + NaCl + NH_4Cl} and {H_2O + $BaCl_2$(sat) + Mannitol(sat) + NaCl + NH_4Cl} at the Temperature 298.15 K: Comparison with the Ideal-Like Solution Model. *J. Chem. Thermodyn.* **2007**, *39*, 316–321.

(41) Okubo, T.; Ise, N.; Matsui, F. Mean Activity Coefficient of Polyelectrolytes in the Ternary System Water-Sodium Polyacrylate-Sodium Chloride. *J. Am. Chem. Soc.* **1967**, *89*, 3697–3703.

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