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Isopiestic Determination of the Osmotic and Activity Coefficients of NaCl + SrCl₂ + H₂O at 298.15 K, and Representation with an Extended Ion-Interaction Model

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Isopiestic vapor-pressure measurements were made at 298.15 K for aqueous NaCl + SrCl₂ solutions, using NaCl(aq) as the reference standard. The measurements for these ternary solutions were made at NaCl ionic strength fractions of $y_1 = 0.17066, 0.47366,$ and 0.82682 for the water activity range $0.9835 \geq a_w \geq 0.8710$. Our results, and those from two previous isopiestic studies, were combined and used with previously determined parameters for NaCl(aq) and those for SrCl₂(aq) determined here to evaluate the mixing parameters ${}^S\theta_{\text{Na,Sr}} = (0.0562 \pm 0.0007) \text{ kg}\cdot\text{mol}^{-1}$ and $\psi_{\text{Na,Sr,Cl}} = -(0.00705 \pm 0.00017) \text{ kg}^2\cdot\text{mol}^{-2}$ for an extended form of Pitzer's ion-interaction model. These model parameters are valid for ionic strengths of $I \leq 7.0 \text{ mol}\cdot\text{kg}^{-1}$, where higher-order electrostatic effects have been included in the mixture model. If the fitting range is extended to the saturated solution molalities, then ${}^S\theta_{\text{Na,Sr}} = (0.07885 \pm 0.00195) \text{ kg}\cdot\text{mol}^{-1}$ and $\psi_{\text{Na,Sr,Cl}} = -(0.01230 \pm 0.00033) \text{ kg}^2\cdot\text{mol}^{-2}$. The extended ion-interaction model parameters obtained from available isopiestic data for SrCl₂(aq) at 298.15 K yield recommended values of the water activities and osmotic and activity coefficients.

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Introduction

In 1978 Macaskill et al.¹ reported the results from isopiestic measurements for the aqueous NaCl + SrCl₂ system at 298.15 K for water activities in the range $0.980 \geq a_w \geq 0.851$, using NaCl(aq) as the reference standard. Their measurements were made at five different constant ionic strength fractions of NaCl. Rard and Miller² subsequently reported isopiestic measurements at nearly the same five NaCl ionic strength fractions for solutions with $(0.862 \text{ to } 0.866) \geq a_w \geq 0.658$, using CaCl₂(aq) as the isopiestic reference standard. These isopiestic data extend the earlier results to the NaCl(cr) and SrCl₂·6H₂O(cr) crystallization limits (which probably extend slightly into the supersaturated molality range for SrCl₂ rich solutions). Activity coefficients of NaCl in the ternary solution mixtures, at constant ionic strengths of $I = (1.0, 3.0, 6.0) \text{ mol}\cdot\text{kg}^{-1}$, were reported by Lanier,³ based on emf measurements with an electrochemical cell containing a sodium “ion-selective” glass electrode. Filippov et al.⁴ reported solubilities for NaCl + SrCl₂ + H₂O and a thermodynamic analysis, but they did not report any new solvent or solute activity measurements. All of these studies were done at 298.15 K. We are not aware of any water activity or emf measurements for the aqueous NaCl + SrCl₂ system at other temperatures.

Rard and Miller^{5,6} have reported extensive mutual diffusion and density/apparent molar volume measurements for the aqueous NaCl + SrCl₂ system at 298.15 K. Reliable values of the four second derivatives of the excess Gibbs free energy with respect to molarities of the two solutes are required for a detailed analysis of these diffusion results within the framework of the thermodynamics of irreversible processes. The derivatives

are evaluated by first calculating the corresponding excess Gibbs energy derivatives with respect to the solute molalities. These derivatives are then combined with the appropriate derivatives of the molalities with respect to the molarities, which are calculated using the reported density data. The required molality derivatives of the excess Gibbs energy are $(1/RT)(\partial^2 G^{\text{ex}}/\partial m_1^2)_{T,p}$, $(1/RT)(\partial^2 G^{\text{ex}}/\partial m_1 \partial m_2)_{T,p}$, $(1/RT)(\partial^2 G^{\text{ex}}/\partial m_2^2)_{T,p}$, and $(1/RT)(\partial^2 G^{\text{ex}}/\partial m_2 \partial m_1)_{T,p}$, where G^{ex} is the excess Gibbs free energy per kilogram of solvent, R the gas constant, T the absolute temperature, 1 denotes NaCl and 2 denotes SrCl₂, and m_1 and m_2 , respectively, are the molalities of components 1 and 2 in the mixed electrolyte solutions.

Examination of the experimental diffusion data and tests of the Onsager Reciprocal Relations⁶ suggested that the values of the excess Gibbs energy derivatives calculated with the thermodynamic activity model parameters of Rard and Miller² are significantly more accurate at higher molalities than at lower molalities. Although Rard and Miller analyzed the isopiestic data for aqueous NaCl + SrCl₂ solutions both with Pitzer's ion interaction model and Scatchard's neutral electrolyte model, the latter model was recommended because it gave a more accurate representation of the experimental data.

It is now possible to refine the values of the osmotic and activity coefficients of the aqueous NaCl + SrCl₂ system at 298.15 K and thus improve the excess Gibbs energy derivative calculations.

First, the osmotic coefficients of the NaCl(aq) and CaCl₂(aq) isopiestic reference standards have been revised and refined^{7,8} since the original isopiestic results^{1,2} were published for aqueous NaCl + SrCl₂ solutions at 298.15 K. These revisions of the

reference standards should allow more accurate osmotic coefficients to be calculated from the published isopiestic molalities.^{1,2}

Second, Pitzer's original ion-interaction model⁹ was used to represent the aqueous NaCl + SrCl₂ activity data in the earlier studies.^{1,2} Archer⁷ subsequently introduced an ionic-strength dependence to the third virial coefficient of the ion-interaction model for binary electrolyte solutions, which allows thermodynamic data for the more soluble electrolytes to be represented more accurately. Clegg et al.¹⁰ extended Archer's approach to mixed electrolyte solutions, and their modified ion-interaction equations should better represent the osmotic and activity coefficients of aqueous NaCl + SrCl₂ solutions more accurately than the standard ion-interaction model.

Third, we have made additional isopiestic measurements for aqueous NaCl + SrCl₂ solutions at low and moderate molalities for the water activity range $0.9835 \geq a_w \geq 0.8710$, at three fixed ionic strength fractions, to better constrain the ion-interaction model fits. In this paper we report these new results, and combine them with those from the two previous isopiestic studies to evaluate the mixing parameters of the extended ion-interaction model for this system.

Experimental Section

The isopiestic experiments were performed during 1991 and 1992 at Lawrence Livermore National Laboratory (LLNL), at the temperature (298.15 ± 0.005) K (IPTS-68), using the apparatus described by Rard.¹¹ This apparatus, its operation, and the experimental conditions and techniques are essentially identical to those described in the earlier isopiestic investigation of aqueous NaCl + SrCl₂ solutions.² Rard and Platford¹²

give a very detailed general description of the isopiestic method with an emphasis on experimental aspects.

Three aqueous NaCl + SrCl₂ stock solutions were prepared by combining appropriate masses of an analyzed SrCl₂(aq) stock solution, of oven-dried Mallinckrodt analytical reagent NaCl(s), and of purified H₂O. The water was purified by deionization followed by distillation in a Barnstead still. The ionic strength fractions of NaCl and SrCl₂ in these stock solutions are close to three of those investigated by Macaskill et al.¹ and by Rard and Miller.² A primary NaCl(aq) isopiestic reference standard stock solution with a molality of 1.9962₃ mol·kg⁻¹ was also prepared by combining appropriate masses of oven-dried NaCl(s) and purified H₂O. A secondary, lower molality, NaCl(aq) stock solution with a molality of 0.86930₂ mol·kg⁻¹ was prepared from this concentrated stock solution and purified H₂O by mass dilution.

The SrCl₂(aq) stock solution was prepared by dissolving Baker Analyzed “low in magnesium” SrCl₂·6H₂O(cr) in purified water, followed by filtration to remove any insoluble material. The molality of this stock solution was first determined by thermal dehydration at (498 to 523) K of three mass aliquots, each acidified with one drop of concentrated HCl before the heating began, thereby yielding a molality of (3.3416₃ ± 0.0008₄) mol·kg⁻¹. After the dehydration analysis was complete, excess H₂SO₄(aq) was added to each crucible, the solutions were evaporated to dryness on a hot plate, and the crucibles transferred to a muffle furnace where they were heated to 773 K to convert the samples quantitatively to anhydrous SrSO₄(s). This gravimetric sulfate analysis yielded a molality of (3.3387₁ ± 0.0006₀) mol·kg⁻¹. A second dehydration analysis yielded (3.3413₇ ± 0.0005₅) mol·kg⁻¹. The average molality for these three analyses, 3.3404₃ mol·kg⁻¹, obtained by weighting the individual analysis results by the inverse square of the uncertainties, was accepted for calculation of isopiestic molalities. This weighted average is insignificantly different from the unweighted average of (3.3405₇ ± 0.0016₂) mol·kg⁻¹.

The assumed molar masses for molality calculations are 58.443 g·mol⁻¹ for NaCl, 158.526 g·mol⁻¹ for SrCl₂, 183.678 g·mol⁻¹ for SrSO₄, and 18.0153 g·mol⁻¹ for H₂O. All apparent masses were converted to masses using buoyancy corrections.

The NaCl(s) samples used for preparation of the binary and ternary solutions had been dried in an oven at ≈ 473 K. However, subsequent very detailed dehydration experiments^{13,14} demonstrate that commercial samples of NaCl(s) dried at this temperature contain around 0.13 % residual water. All stock solution molalities were corrected for the presence of this assumed amount of residual water in the NaCl(s) used.

The source SrCl₂·6H₂O(cr) was examined for impurities using direct current arc optical emission spectroscopy, and the results were reported previously.² This analysis indicated that the SrCl₂·6H₂O(cr) contained ≤ 0.011 mass-% of impurities, which were predominantly Ca and Ba.

Table 1 lists the isopiestic results for four experiments yielding the osmotic coefficients of SrCl₂(aq), where $m(\text{SrCl}_2)$ is the equilibrium molality of SrCl₂(aq) and $m^*(\text{NaCl})$ the equilibrium molality of the NaCl(aq) reference standard. The isopiestic results for the ternary solutions are given in Table 2 as the molalities of the NaCl(aq) isopiestic reference standard and the total molalities m_T of the aqueous NaCl + SrCl₂ solutions

$$m_T = m_1 + m_2 \quad (1)$$

where m_1 and m_2 are, respectively, the molalities of NaCl and SrCl₂ in the mixed electrolyte solutions. Also reported in Table 2 are the ionic strength fractions of NaCl, y_1 , in the mixtures given by

$$y_1 = m_1/I = m_1/(m_1 + 3m_2) \quad (2)$$

Each molality reported in Tables 1 and 2 is the average of a pair of samples used in the isopiestic equilibrations.

Samples of the $1.9962_3 \text{ mol}\cdot\text{kg}^{-1}$ NaCl(aq) stock solution were used as the reference standard for the experiments reported in Table 1 and the Series 1 experiments of Table 2, whereas the $0.86930_2 \text{ mol}\cdot\text{kg}^{-1}$ NaCl(aq) stock solution was used for the Series 3 experiments of Table 2.

The laboratory notebooks used for the experiments of Table 2 imply that the $1.9962_3 \text{ mol}\cdot\text{kg}^{-1}$ NaCl(aq) stock solution was also used for the Series 2 experiments of Table 2. However, the isopiestic ratios of the ionic molalities of the aqueous NaCl + SrCl₂ solutions to those of the corresponding NaCl(aq) reference solution ionic molalities were systematically displaced from the ratios for the Series 1 and Series 3 experiments. In addition, the ionic molality ratios for the Series 1 and 3 experiments were consistent with those reported by Macaskill et al.¹ The isopiestic ionic molality ratios for the Series 1 and 3 experiments at each of the three solute ratios were plotted as a function of the corresponding ionic molality ratios of the aqueous NaCl + SrCl₂ solutions, i.e., values of $\{(2m_1 + 3m_2)/2m^*\}$ were plotted against $(2m_1 + 3m_2)$. These ratios, together with the initial masses of each sample and their masses at isopiestic equilibrium, were used to back calculate the NaCl(aq) stock solution molality that would bring the Series 2 experiments into consistency with the Series 1 and 3 experiments. These calculated NaCl(aq) stock solution molalities were found to be consistent for the three equilibrations and the three solute ratios, yielding an average and standard deviation of $(2.0096_0 \pm 0.0015_3) \text{ mol}\cdot\text{kg}^{-1}$, and the NaCl(aq) molalities for the Series 2 experiments were adjusted accordingly. Another NaCl(aq) isopiestic reference stock solution with a molality of $(2.0110 \pm 0.0007) \text{ mol}\cdot\text{kg}^{-1}$ was in use when these isopiestic experiments were performed, which agrees with the back-calculated value within its experimental uncertainty. It is thus likely that this was the NaCl(aq) stock solution actually used for these experiments.

Tables 1 and 2 also report the molality-based osmotic coefficients of the NaCl(aq) reference standard, ϕ^* , which are needed for the calculation of the osmotic coefficients ϕ of the SrCl₂(aq) and aqueous NaCl + SrCl₂ solutions. Values of ϕ^* at 298.15 K were calculated using the equations and parameters of Archer,⁷ and the ϕ values using the fundamental equation for isopiestic equilibrium

$$\phi = \nu^* m^* \phi^* / \sum_i \nu_i m_i \quad (3)$$

Because NaCl(aq) was used as the isopiestic reference standard for all of our experiments, $\nu^* = 2$. For SrCl₂(aq) and other electrolytes of this charge type, eq 3 then has the very simple form

$$\phi = 2m^* \phi^* / 3m \quad (4)$$

where m denotes the equilibrium molality of SrCl₂(aq). For aqueous NaCl + SrCl₂ solutions, the corresponding equation is

$$\phi = 2m^* \phi^* / \sum_i \nu_i m_i \quad (5)$$

The values of $\sum_i \nu_i m_i$ may be calculated from the reported m_T and y_1 values of Table 2 using

$$\sum_i \nu_i m_i = (2m_1 + 3m_2) = \{3(1 + y_1)/(1 + 2y_1)\}m_T = (1 + y_1)I \quad (6)$$

Results

Evaluation of Parameters of Extended Pitzer Models for SrCl₂(aq) at 298.15 K.

Analysis of the osmotic and activity coefficients for aqueous NaCl + SrCl₂ solutions, using the extended form of Pitzer's ion-interaction model,¹⁰ first requires the

corresponding parameters for the two limiting binary solutions NaCl(aq) and SrCl₂(aq). Parameter values for NaCl(aq) at 298.15 K and 0.1 MPa were calculated from the temperature/pressure coefficients and equations reported by Archer⁷ in his critical analysis of the thermodynamic properties of this system. Values of the parameters of the standard Pitzer model are available for SrCl₂(aq) at 298.15 K,^{9,15} but they have not previously been determined for the extended ion-interaction models that generally represent the thermodynamic data more accurately. We therefore evaluated the parameters of these extended models for SrCl₂(aq).

An extended form of Archer's extended ion-interaction equation⁷ for the molality-based osmotic coefficient of a binary solution of an electrolyte, with one additional term, may be written as

$$\phi = 1 - |z_M z_X| A_\phi I^{1/2} / (1 + bI^{1/2}) + (2 \nu_M \nu_X / \nu) m \cdot B_{M,X}^\phi + (4 \nu_M^2 \nu_X z_M / \nu) m^2 \cdot C_{M,X}^{T\phi} + 4m^3 \cdot D_{M,X}^{(0)} \quad (7)$$

where $b = 1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$; A_ϕ is the Debye-Hückel limiting-law slope for ϕ ; M denotes the cation and X the anion; z_M and z_X are the valence (with sign) of the cation and the anion, respectively; ν_M and ν_X are the number of M and X ions formed by the complete dissociation of one molecule of the solute, respectively; and $\nu = \nu_M + \nu_X$. The $4m^3 \cdot D_{M,X}^{(0)}$ term was not used by Archer, but we include it to more accurately represent the isopiestic data at high molalities. The factor of 4 arises because this term formally represents the interaction between two chloride ions and one strontium ion: $m(\text{Cl}^-)^2 \cdot m(\text{Sr}^{2+}) = 4m^3$. The functions $B_{M,X}^\phi$ and $C_{M,X}^{T\phi}$ are defined by eqs 8 and 9:

$$B_{M,X}^\phi = \beta_{M,X}^{(0)} + \beta_{M,X}^{(1)} \cdot \exp(-\alpha_{M,X} I^{1/2}) \quad (8)$$

$$C_{M,X}^{T\phi} = C_{M,X}^{(0)} + C_{M,X}^{(1)} \cdot \exp(-\omega_{M,X} I^{1/2}) \quad (9)$$

In eqs 7 to 9, the ion-interaction parameters $\beta_{M,X}^{(0)}$, $\beta_{M,X}^{(1)}$, $C_{M,X}^{(0)}$, $C_{M,X}^{(1)}$, and $D_{M,X}^{(0)}$ are evaluated using experimental data. The corresponding extended ion-interaction model equation for the natural logarithm of the mean molal activity coefficient, γ_{\pm} , of the solute is

$$\begin{aligned} \ln \gamma_{\pm} = & -|z_M z_X| A_{\phi} \{ I^{1/2} / (1 + bI^{1/2}) + (2/b) \ln(1 + bI^{1/2}) \} + (2\nu_M \nu_X / \nu) m [2\beta_{M,X}^{(0)} + \\ & 2(\beta_{M,X}^{(1)} / \alpha_{M,X}^2 I) \{ 1 - (1 + \alpha_{M,X} I^{1/2} - \alpha_{M,X}^2 I / 2) \exp(-\alpha_{M,X} I^{1/2}) \}] + \\ & (2\nu_M^2 \nu_X z_M / \nu) m^2 [3C_{M,X}^{(0)} + 4(C_{M,X}^{(1)} / \omega_{M,X}^4 I^2) \{ 6 - (6 + 6\omega_{M,X} I^{1/2} + 3\omega_{M,X}^2 I + \\ & \omega_{M,X}^3 I^{3/2} - \omega_{M,X}^4 I^2 / 2) \exp(-\omega_{M,X} I^{1/2}) \}] + (16/3) m^3 \cdot D_{M,X}^{(0)} \end{aligned} \quad (10)$$

The accepted value of $A_{\phi} = 0.3915 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ for water at 298.15 K was taken from the critical evaluation of Archer and Wang,¹⁶ which is partially based on Hill's equation of state for water.¹⁷

Rard and Miller¹⁵ critically compared the experimental osmotic coefficient values for $\text{SrCl}_2(\text{aq})$ at 298.15 K, and concluded that three previous sets of isopiestic data^{1,18,19} were both consistent with each other and were in agreement with their own isopiestic measurements. As indicated by figure 4 in the 1981 paper by Holmes and Mesmer,²⁰ published emfs from supposedly reversible electrochemical cells containing $\text{SrCl}_2(\text{aq})$ are systematically and seriously in error. High-temperature isopiestic measurements are available from 382.96 to 524.12 K,^{20,21} but there is a lack of published isopiestic data between 298.15 K and 382.96 K. Furthermore, the available calorimetric data at intermediate temperatures, summarized by Holmes and Mesmer,²¹ are insufficient to adequately characterize the thermodynamic behavior between these two temperature regions, especially at higher molalities. Because of this gap between the higher- and lower-temperature isopiestic measurements, we restrict our analysis of the $\text{SrCl}_2(\text{aq})$ binary system to 298.15 K.

For the evaluation of the $\beta_{M,X}^{(0)}$, $\beta_{M,X}^{(1)}$, $C_{M,X}^{(0)}$, $C_{M,X}^{(1)}$, and $D_{M,X}^{(0)}$ parameters of the extended ion-interaction model at 298.15 K, unit weight was given to each osmotic coefficient calculated from the equilibrium molalities reported in three of the four consistent isopiestic studies^{1,15,19} and to the four new values given in Table 1, and a lower weight of 0.5 to the more scattered results from the other study.¹⁸ All of the osmotic coefficients of SrCl₂(aq) from the earlier studies^{1,15,18,19} were first recalculated using the equations and parameters reported in the more recent critical reviews of the thermodynamic properties of the isopiestic standards NaCl(aq),⁷ KCl(aq),²² and CaCl₂(aq).⁸ Robinson's older set of isopiestic data²³ was rejected because, as noted in several publications,^{1,15,19} the resulting osmotic coefficients are systematically lower than those from all of the subsequent isopiestic measurements by $\Delta\phi \approx 0.01$ at low molalities to $\Delta\phi \approx 0.04$ at higher molalities. Three outlying osmotic coefficients from the other studies were also given zero weight as described in footnote b of Table 3.

Our evaluated ion-interaction model parameters for SrCl₂(aq) are reported in Table 3 along with their standard errors, as are Archer's parameters for NaCl(aq).⁷ The SrCl₂(aq) fit to Archer's model (eq 7 without the $D_{M,X}^{(0)}$ term) has an unweighted standard deviation of $\sigma(\phi) = 0.00353$ with significant systematic deviations at low and at high molalities. Including the $D_{M,X}^{(0)}$ term reduced the standard deviation to $\sigma(\phi) = 0.00159$, and essentially eliminated the systematic differences between the experimental ϕ values and the model. We recommend the extended model fit with the $D_{M,X}^{(0)}$ term.

The osmotic coefficients of SrCl₂(aq) are plotted in Figure 1a as a function of the square root of the molality, and Figure 1b shows the differences $\Delta\phi$ between the experimental and fitted model values of the osmotic coefficients for this extended ion-interaction model fit that includes the $D_{M,X}^{(0)}$ term. The short-dashed curve in Figure 1b compares the osmotic coefficients calculated with the four-parameter model (no $D_{M,X}^{(0)}$ term) to the more accurate extended model. The differences between the two models are largest at high molalities. Results from the various isopiestic studies are in general agreement, with most of the differences falling within the 0.2% to 0.4% uncertainties of the osmotic coefficients of the NaCl(aq), KCl(aq), and CaCl₂(aq)

isopiestic reference standards used.^{7,8,22} The ϕ values from Macaskill et al.¹ and those reported in Table 1, both of which are based on use of NaCl(aq) as reference standard, show differences of about 0.3% with the Macaskill ϕ values being higher. Macaskill et al. dried their re-precipitated NaCl at 573 K; drying NaCl at this temperature has been shown to yield a residue containing about 0.1% residual water^{13,14} rather than anhydrous NaCl. About half of the difference between the osmotic coefficients of Macaskill et al.,¹ and those reported in Table 1, results from the neglect of this residual water when the NaCl(aq) reference standard molalities were calculated in the earlier study.

Table 4 gives our recommended values of ϕ , a_w , and γ_{\pm} at selected molalities for SrCl₂(aq) at 298.15 K, calculated with the last set of parameters of Table 3, using the extended ion-interaction model that includes the $D_{M,X}^{(0)}$ term.

Representation of the Thermodynamic Properties of Aqueous NaCl + SrCl₂ at 298.15

K with an Extended Pitzer Model. General expressions for Archer's extended form of Pitzer's ion-interaction model for mixed electrolyte solutions are given in appendix I of Clegg et al.¹⁰ For aqueous NaCl + SrCl₂ solutions these equations may be written in the following form for ϕ :

$$\phi = 1 + \{2/(2m_1 + 3m_2)\} [-A_{\phi} I^{3/2}/(1 + bI^{1/2}) + m_1(m_1 + 2m_2) \{ B_{Na,Cl}^{\phi} + Z \cdot C_{Na,Cl}^{T\phi} \} + m_2(m_1 + 2m_2) \{ B_{Sr,Cl}^{\phi} + Z \cdot C_{Sr,Cl}^{T\phi} \} + m_1 m_2 \{ \Phi_{Na,Sr}^{\phi} + (m_1 + 2m_2) \psi_{Na,Sr,Cl} \}] \quad (11)$$

where

$$Z = \sum_i (m_i |z_i|) = 2m_1 + 4m_2 = 2E \quad (12)$$

where E is the mass-equivalent concentration and z_i is the valence of the ion i . For the three ionic activity coefficients the corresponding relations are:

$$\ln\gamma(\text{Na}^+) = F + (m_1 + 2m_2)\{2B_{\text{Na,Cl}} + Z \cdot C_{\text{Na,Cl}}^T\} + m_1(m_1 + 2m_2)C_{\text{Na,Cl}}^T + m_2(m_1 + 2m_2)C_{\text{Sr,Cl}}^T + m_2\{2\Phi_{\text{Na,Sr}} + (m_1 + 2m_2)\psi_{\text{Na,Sr,Cl}}\} \quad (13)$$

$$\ln\gamma(\text{Sr}^{2+}) = 4F + (m_1 + 2m_2)\{2B_{\text{Sr,Cl}} + Z \cdot C_{\text{Sr,Cl}}^T\} + 2m_1(m_1 + 2m_2)C_{\text{Na,Cl}}^T + 2m_2(m_1 + 2m_2)C_{\text{Sr,Cl}}^T + m_1\{2\Phi_{\text{Na,Sr}} + (m_1 + 2m_2)\psi_{\text{Na,Sr,Cl}}\} \quad (14)$$

$$\ln\gamma(\text{Cl}^-) = F + m_1\{2B_{\text{Na,Cl}} + Z \cdot C_{\text{Na,Cl}}^T\} + m_2\{2B_{\text{Sr,Cl}} + Z \cdot C_{\text{Sr,Cl}}^T\} + m_1(m_1 + 2m_2)C_{\text{Na,Cl}}^T + m_2(m_1 + 2m_2)C_{\text{Sr,Cl}}^T + m_1m_2\psi_{\text{Na,Sr,Cl}} \quad (15)$$

where

$$F = -A_\phi\{I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})\} + m_1(m_1 + 2m_2)\{B_{\text{Na,Cl}} + Z \cdot C_{\text{Na,Cl}}^T/2\} + m_2(m_1 + 2m_2)\{B_{\text{Sr,Cl}} + Z \cdot C_{\text{Sr,Cl}}^T/2\} + m_1m_2\Phi_{\text{Na,Sr}} \quad (16)$$

The $\Phi_{\text{Na,Sr}}$, $\Phi_{\text{Na,Sr}}^\phi$, and $\Phi_{\text{Na,Sr}}^i$ terms in eqs 11, 13, 14, and 16 implicitly contain functions for the mixing of two distinct kinds of ions of like sign but unequal valence, ${}^E\alpha(I)$ and ${}^E\theta'(I)$,⁹ and the empirical mixing parameter ${}^S\theta_{\text{Na,Sr}}$:

$$\Phi_{\text{Na,Sr}} = {}^S\theta_{\text{Na,Sr}} + {}^E\alpha(I) \quad (17)$$

$$\Phi_{\text{Na,Sr}}^i = \{\partial\Phi_{\text{Na,Sr}}/\partial I\}_{T,p} = {}^E\theta'(I) \quad (18)$$

and

$$\Phi_{\text{Na,Sr}}^{\phi} = {}^{\text{S}}\theta_{\text{Na,Sr}} + {}^{\text{E}}\theta(I) + I \cdot {}^{\text{E}}\theta'(I) \quad (19)$$

where the superscript E applied to a function identifies it as an electrostatic contribution that does not depend on a specific characteristic of the pair of ions other than their electrical charges, and the superscript S denotes that the parameter represents the combined effect of electrolyte-specific short range forces.

The quantity ${}^{\text{E}}\theta(I)$ and its ionic strength derivative ${}^{\text{E}}\theta'(I) = \{\partial {}^{\text{E}}\theta(I)/\partial I\}_{\text{T,p}}$ can be calculated theoretically,⁹ and their values depend only the total ionic strength I and the valences of the ions of like sign, in this case $z(\text{Na}) = +1$ and $z(\text{Sr}) = +2$. The ${}^{\text{E}}\theta(I)$ and ${}^{\text{E}}\theta'(I)$ functions are equal to zero except for the mixing of ions of the same sign but difference valence. The equations used here to approximate ${}^{\text{E}}\theta(I)$ and ${}^{\text{E}}\theta'(I)$ are given in appendix I of Clegg et al.¹⁰ The only parameters of eq 11 and eqs 13 to 16 that are to be determined from the mixed electrolyte thermodynamic data are ${}^{\text{S}}\theta_{\text{Na,Sr}}$ and $\psi_{\text{Na,Sr,Cl}}$. If the theoretical electrostatic contributions to mixing, ${}^{\text{E}}\theta(I)$ and ${}^{\text{E}}\theta'(I)$, are neglected as is sometimes done, then $\Phi_{\text{Na,Sr}}$ is replaced with the constant parameter $\theta_{\text{Na,Sr}}$.

The other primed quantities of eq 16 are the following derivatives:

$$\dot{B}_{\text{M,X}} = \{\partial B_{\text{M,X}}/\partial I\}_{\text{T,p}}, \quad (20)$$

$$C_{\text{MX}}^{\text{T}'} = \{\partial C_{\text{M,X}}^{\text{T}}/\partial I\}_{\text{T,p}}. \quad (21)$$

where

$$B_{\text{M,X}} = \beta_{\text{M,X}}^{(0)} + 2\beta_{\text{M,X}}^{(1)} [\{1 - (1 + \alpha_{\text{M,X}}I^{1/2})\exp(-\alpha_{\text{M,X}}I^{1/2})\}/(\alpha_{\text{M,X}}^2I)] \quad (22)$$

$$C_{\text{M,X}}^{\text{T}} = C_{\text{M,X}}^{(0)} + 4C_{\text{M,X}}^{(1)} [\{6 - (6 + 6\alpha_{\text{M,X}}I^{1/2} + 3\alpha_{\text{M,X}}^2I +$$

$$\omega_{M,X}^3 I^{3/2} \} \exp(-\omega_{M,X} I^{1/2}) / (\omega_{M,X}^4 I^2)] \quad (23)$$

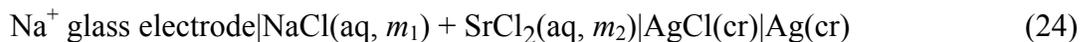
Explicit functional relations for $\dot{B}_{M,X}$ and $C_{M,X}^{T'}$ are given by Clegg et al.¹⁰

Test calculations indicated that there is no improvement gained from including the $D_{M,X}^{(0)}$ term in the $\text{SrCl}_2(\text{aq})$ model when representing the osmotic coefficients of aqueous $\text{NaCl} + \text{SrCl}_2$ mixtures. Thus we used the Archer model parameters for $\text{SrCl}_2(\text{aq})$, third column of Table 3, for the mixture calculations.

The osmotic coefficients from the earlier studies^{1,2} were first recalculated using the equations and parameters reported in the more recent critical reviews of the reference standards $\text{NaCl}(\text{aq})$ and $\text{CaCl}_2(\text{aq})$.^{7,8} For the evaluation of the $^S\theta_{\text{Na,Sr}}$ and $\psi_{\text{Na,Sr,Cl}}$ parameters, equal weight was given to each osmotic coefficient from the isopiestic studies of Macaskill et al.,¹ Rard and Miller,² and the new results reported in Table 2.

Figure 2a shows the dependence of the osmotic coefficient ϕ for aqueous $\text{NaCl} + \text{SrCl}_2$ solutions on the total solution molality m_T . Figure 2b gives an expanded view of the lower molality region, and Figure 3b the results for higher molalities. The crossovers observed in Figure 2 are a feature typical of the osmotic coefficients for mixtures of electrolytes of different charge types.

Electromotive force (emf) measurements have also been reported by Lanier³ for aqueous $\text{NaCl} + \text{SrCl}_2$ solutions at $I = 1.0, 3.0,$ and $6.0 \text{ mol}\cdot\text{kg}^{-1}$ at the temperature 298.15 K , using the following electrochemical cell:



Lanier referenced the measured emfs to those of the same cell filled with a saturated solution of $\text{NaCl}(\text{aq})$. If the emf of this cell is assumed to respond to the activity of NaCl in the binary and ternary solutions in an exactly Nernstian manner, then the difference

between the emf of the cell filled with an aqueous NaCl + SrCl₂ solution and the emf of the cell filled with a saturated NaCl(aq) solution will be given by

$$\Delta E = (RT/F)\ln[m_1 \cdot \gamma(\text{Na}^+) \cdot (m_1 + 2m_2) \cdot \gamma(\text{Cl}^-) / \{m_{1,0}(\text{sat}) \cdot \gamma_{\pm,1,0}(\text{sat})\}^2] \quad (25)$$

where $m_{1,0}(\text{sat})$ and $\gamma_{\pm,1,0}(\text{sat})$ are the molality and mean molal activity coefficient, respectively, of a saturated solution of NaCl(aq).

Rard et al.²⁴ discussed some of the problems of analyzing emfs to extract activity coefficients when the electrochemical cell contains a sodium ion responsive glass electrode or some other type of ion-selective electrode (ISE). The most important of these problems are: 1) an ISE generally does not exhibit an ideal Nernstian response to changes in the activity of the solute; 2) ISEs are usually not completely selective to the ion of interest and may respond to some extent to other ions present in the mixtures; and 3) glass electrodes and other liquid-filled ISEs can yield emfs that slowly drift with time especially when concentrated electrolyte solutions are being studied. However, Rard et al.²⁴ also noted that many of these systematic errors for ISEs partially canceled for aqueous NaCl + Na₂SO₄ solutions when the emfs of such cells were referenced to those of the same cell containing a NaCl(aq) solution at some “comparable concentration”, i.e., when the binary and ternary solutions have the same total ionic strengths or the same NaCl(aq) molality. A similar partial compensation of errors might be expected for cells filled with aqueous NaCl + SrCl₂ solutions and with NaCl(aq) solutions, if the binary and ternary solutions have the same total ionic strengths or the same NaCl(aq) molality. However, Lanier³ referenced all of the measured emfs for the aqueous NaCl + SrCl₂ system to those of the same cell filled with a saturated solution of NaCl(aq). Consequently a significant degree of compensation of errors might be expected only for the measurements made at the highest ionic strength of 6.0 mol·kg⁻¹.

Lanier³ made the emf measurements at the same six different ionic strength fractions y_1 , at total ionic strengths $I = (1.0, 3.0, \text{ and } 6.0) \text{ mol}\cdot\text{kg}^{-1}$. At $I = 6.0 \text{ mol}\cdot\text{kg}^{-1}$, Lanier also studied an additional six compositions with slightly different y_1 values. At $I = (1.0 \text{ and } 3.0) \text{ mol}\cdot\text{kg}^{-1}$ the reported values of the activity coefficient of NaCl in the aqueous NaCl + SrCl₂ solutions, $\gamma(\text{Na}^+) \cdot \gamma(\text{Cl}^-)$, are nearly independent of y_1 . However, at $I = 6.0 \text{ mol}\cdot\text{kg}^{-1}$ there is a significantly larger dependence of $\gamma(\text{Na}^+) \cdot \gamma(\text{Cl}^-)$ on the value of y_1 .

Lanier³ did not report the experimental emfs or ΔE values, so a complete reanalysis of the activity coefficients is not possible. Lanier's analysis was based on assumed values of $\gamma_{\pm,0}(\text{sat}) = 1.007$ and $m_{1,0}(\text{sat}) = 6.144 \text{ mol}\cdot\text{kg}^{-1}$. Archer's NaCl(aq) model⁷ yields $\gamma_{\pm,0}(\text{sat}) = 1.0066$ at this molality, and we therefore multiplied Lanier's reported $\{\gamma(\text{Na}^+) \cdot \gamma(\text{Cl}^-)\}^{1/2}$ values by a factor of $(1.0066/1.007) = 0.99960$.

Using the isopiestic data of Table 2, the results of Macaskill et al.,¹ and those of Rard and Miller² with ionic strengths $I \leq 7.0 \text{ mol}\cdot\text{kg}^{-1}$, the least-squares fits yield mixing parameter values of ${}^S\theta_{\text{Na,Sr}} = (0.0562 \pm 0.0007) \text{ kg}\cdot\text{mol}^{-1}$ and $\psi_{\text{Na,Sr,Cl}} = -(0.00705 \pm 0.00017) \text{ kg}^2\cdot\text{mol}^{-2}$ with $\sigma(\phi) = 0.00116$ when the higher-order electrostatic functions ${}^E\theta(I)$ and ${}^E\theta'(I)$ are included. As can be seen from Figure 3, this fit gives a very accurate representation of the available osmotic coefficients. For comparison, when the higher-order electrostatic functions ${}^E\theta(I)$ and ${}^E\theta'(I)$ are not included, $\theta_{\text{Na,Sr}} = (0.0036 \pm 0.0011) \text{ kg}\cdot\text{mol}^{-1}$ and $\psi_{\text{Na,Sr,Cl}} = -(0.0026 \pm 0.0003) \text{ kg}^2\cdot\text{mol}^{-2}$ with $\sigma(\phi) = 0.00175$. A total of 156 values of ϕ were given equal weight for the evaluation of these parameters. The fit that includes the ${}^E\theta(I)$ and ${}^E\theta'(I)$ functions gives a more accurate representation at lower ionic strengths and is therefore preferred. The osmotic coefficients of Rard and Miller² for solutions with $y_1 = 0.47397$ were not included in these fits because they are slightly displaced by about $\Delta\phi \approx 0.002$ from the results for other compositions of this system. However, this difference of about 0.17 % is well within the accuracy reported by Rard and Miller.

If the fitting range is extended to include the isopiestic results of Rard and Miller² that extend to the crystallization molalities ($I \leq 11.228 \text{ mol}\cdot\text{kg}^{-1}$) of these solutions, in addition to the data from Table 2 and of Macaskill et al.,¹ then ${}^S\theta_{\text{Na,Sr}} = (0.07885 \pm 0.00195) \text{ kg}\cdot\text{mol}^{-1}$ and $\psi_{\text{Na,Sr,Cl}} = -(0.01230 \pm 0.00033) \text{ kg}^2\cdot\text{mol}^{-2}$ with $\sigma(\phi) = 0.00409$. A total of 200 values of ϕ were given equal weight for the evaluation of these parameters. The standard deviation for this fit is larger by only a factor of 3.5 than that for the corresponding fit to the range $I \leq 7.0 \text{ mol}\cdot\text{kg}^{-1}$. However, there are significant systematic deviations between the experimental results and model values in some composition regions for the expanded range model that are as large as $\Delta\phi = 0.026$ for concentrated solutions with large ionic strength fractions of SrCl_2 . We recommend the parameters from the more accurate fits to osmotic coefficients in the range $I \leq 7.0 \text{ mol}\cdot\text{kg}^{-1}$, unless the mixing parameters are needed at very high molalities for a particular application.

Because of concern about the reliability of the emf measurements using ISEs as described five paragraphs above, the $\{\gamma(\text{Na}^+) \cdot \gamma(\text{Cl}^-)\}^{1/2}$ values from Lanier's study³ were not included in the model parameter evaluation. However, in Figure 4 we compare Lanier's values of $\ln\{\gamma(\text{Na}^+) \cdot \gamma(\text{Cl}^-)\}^{1/2}$ to those that were calculated with our model parameters ${}^S\theta_{\text{Na,Sr}} = (0.0562 \pm 0.0007) \text{ kg}\cdot\text{mol}^{-1}$ and $\psi_{\text{Na,Sr,Cl}} = -(0.00705 \pm 0.00017) \text{ kg}^2\cdot\text{mol}^{-2}$ that were constrained for the range $I \leq 7.0 \text{ mol}\cdot\text{kg}^{-1}$. The predicted values of $\ln\{\gamma(\text{Na}^+) \cdot \gamma(\text{Cl}^-)\}^{1/2}$ agree well with the experimental results of Lanier at $I = 1.0 \text{ mol}\cdot\text{kg}^{-1}$, are in reasonable agreement at $I = 3.0 \text{ mol}\cdot\text{kg}^{-1}$, but show significant systematic differences at $I = 6.0 \text{ mol}\cdot\text{kg}^{-1}$. These deviations are probably the result of failure of the Na^+ ISE to yield reliable results at high ionic strengths.

Evaluation of the Standard (Thermodynamic) Solubility Product for $\text{SrCl}_2\cdot 6\text{H}_2\text{O}(\text{cr})$ at 298.15 K

The standard (thermodynamic) solubility product K_s for $\text{SrCl}_2\cdot 6\text{H}_2\text{O}(\text{cr})$ in the absence of other solutes is given by the following equation

$$\begin{aligned}
K_s &= \{m(\text{Sr}^{2+}, \text{sat})m(\text{Cl}^-, \text{sat})^2/(m^\circ)^3\} \gamma(\text{Sr}^{2+}, \text{sat})\gamma(\text{Cl}^-, \text{sat})^2 a_w(\text{sat})^6 \\
&= 4 \{m(\text{sat})/m^\circ\}^3 \gamma_{\pm}(\text{sat})^3 a_w(\text{sat})^6
\end{aligned} \tag{26}$$

where “sat” denotes that the property refers to a saturated solution of $\text{SrCl}_2(\text{aq})$ and $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. Once a value of $m(\text{sat})$ at 298.15 K has been selected, values of $\gamma_{\pm}(\text{sat})$ and $a_w(\text{sat})$ can be calculated from the last set of parameters of Table 3.

Stokes¹⁸ reported $m(\text{sat}) = 3.520 \text{ mol}\cdot\text{kg}^{-1}$ determined by the isopiestic method, and Phillipov et al. reported $m(\text{sat}) = 3.52 \text{ mol}\cdot\text{kg}^{-1}$ from isothermal saturation and analysis of the solution molality. Linke²⁵ recommended a value for the mass fraction of SrCl_2 in the saturated solution, based on several consistent studies, that yields $m(\text{sat}) = 3.520 \text{ mol}\cdot\text{kg}^{-1}$, but also reported a slightly lower value of $m(\text{sat}) = 3.50 \text{ mol}\cdot\text{kg}^{-1}$ determined by the synthetic method. Rard and Miller¹⁵ reported $m(\text{sat}) = 3.5195 \text{ mol}\cdot\text{kg}^{-1}$ as the average from three isopiestic determinations, and Rard¹¹ reported the individual results from these three experiments along with the average and its uncertainty, $m(\text{sat}) = (3.5195 \pm 0.0026) \text{ mol}\cdot\text{kg}^{-1}$.

We select $m(\text{sat}) = (3.520 \pm 0.003) \text{ mol}\cdot\text{kg}^{-1}$ for the calculation of K_s . At this saturation molality, $\phi(\text{sat}) = 1.8045 \pm 0.0016$ (where this uncertainty is the standard deviation of the model fit) and thus $a_w(\text{sat}) = 0.70943 \pm 0.00030$, and $\gamma_{\pm}(\text{sat}) = 1.5042$. The uncertainty of the $\gamma_{\pm}(\text{sat})$ value is mainly the result of the larger uncertainty in the values of ϕ used to constrain the model parameters below $0.5 \text{ mol}\cdot\text{kg}^{-1}$, and we conservatively estimate this uncertainty as $0.01 \gamma_{\pm}(\text{sat})$. These values yield $K_s = (75.9 \pm 2.3)$.

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Table 1. Isopiestic Molalities of SrCl₂(aq) with a NaCl(aq) Reference Standard at 298.15 K ^a

$m(\text{SrCl}_2)$	$m^*(\text{NaCl})$	$\phi^*(\text{NaCl})$	$\phi(\text{SrCl}_2)$	t
mol·kg ⁻¹	mol·kg ⁻¹			d
1.7111 ₁ ± 0.0001 ₆	2.9492 ₂ ± 0.0006 ₄	1.0453 ₅	1.2011 ₆	10
1.8273 ₉ ± 0.0003 ₄	3.1934 ₆ ± 0.0004 ₃	1.0615 ₈	1.2367 ₈	14
1.9523 ₉ ± 0.0001 ₄	3.4584 ₉ ± 0.0006 ₃	1.0796 ₃	1.2749 ₈	12
2.1034 ₁ ± 0.0002 ₇	3.7845 ₆ ± 0.0000 ₂	1.1024 ₀	1.3223 ₃	19

^a Values of the osmotic coefficients of the NaCl(aq) reference standard solutions, ϕ^* , were calculated using the equation and parameters of Archer,⁷ which are reported in Table 3. The values of “ t ” are the isopiestic equilibration times in days.

Table 2. Isopiestic Molalities and Osmotic Coefficients of Aqueous NaCl + SrCl₂**Solutions with a NaCl(aq) Reference Standard at 298.15 K^a**

$m_{\text{T}}(y_1 = 0.17066)$	$m_{\text{T}}(y_1 = 0.47366)$	$m_{\text{T}}(y_1 = 0.82682)$	$m^*(\text{NaCl})$	$\phi^*(\text{NaCl})$	t
mol·kg ⁻¹	mol·kg ⁻¹	mol·kg ⁻¹	mol·kg ⁻¹		d
Series 1					
	2.7028 ₂ ± 0.0006 ₁		3.2502 ₁ ± 0.0003 ₆	1.0654 ₁	16 ^b
2.3214 ₇ ± 0.0001 ₆	2.8389 ₀ ± 0.0000 ₄		3.4242 ₀ ± 0.0004 ₃	1.0772 ₇	18
2.3478 ₃ ± 0.0003 ₄	2.8719 ₃ ± 0.0008 ₈		3.4677 ₈ ± 0.0002 ₄	1.0802 ₇	19
2.3800 ₁ ± 0.0001 ₅	2.9138 ₇ ± 0.0009 ₀		3.5225 ₄ ± 0.0000 ₃	1.0840 ₆	23
2.3863 ₃ ± 0.0008 ₉	2.9211 ₀ ± 0.0006 ₈	3.3666 ₃ ± 0.0005 ₁	3.5324 ₅ ± 0.0002 ₄	1.0847 ₄	21
2.2236 ₈ ± 0.0000 ₂	2.7092 ₀ ± 0.0002 ₄	3.1104 ₄ ± 0.0000 ₆	3.2584 ₂ ± 0.0000 ₂	1.0659 ₆	30
2.1305 ₅ ± 0.0000 ₄	2.5892 ₃ ± 0.0002 ₃	2.9666 ₃ ± 0.0003 ₅	3.1037 ₄ ± 0.0003 ₉	1.0555 ₇	20
1.9185 ₄ ± 0.0004 ₂	2.3167 ₀ ± 0.0007 ₅	2.6395 ₉ ± 0.0002 ₁	2.7573 ₁ ± 0.0002 ₈	1.0329 ₀	21
1.7234 ₃ ± 0.0016 ₃	2.0668 ₀ ± 0.0010 ₇	2.3427 ₇ ± 0.0014 ₁	2.4406 ₁ ± 0.0015 ₉	1.0129 ₉	21
1.5579 ₃ ± 0.0002 ₃	1.8556 ₁ ± 0.0000 ₈	2.0919 ₁ ± 0.0004 ₄	2.1763 ₃ ± 0.0002 ₉	0.9970 ₈	15 ^b
1.4137 ₀ ± 0.0005 ₁	1.6740 ₈ ± 0.0003 ₁	1.8790 ₀ ± 0.0001 ₂	1.9519 ₉ ± 0.0007 ₃	0.9841 ₃	39
Series 2 ^c					
1.1996 ₆ ± 0.0005 ₁	1.4079 ₃ ± 0.0001 ₅	1.5693 ₁ ± 0.0001 ₂	1.6256 ₅ ± 0.0011 ₉	0.9663 ₉	42
0.98105 ± 0.00022	1.1399 ₂ ± 0.0002 ₁	1.2613 ₉ ± 0.0000 ₂	1.3031 ₅ ± 0.0007 ₇	0.9503 ₉	9 ^b
0.88266 ± 0.00016	1.0210 ₀ ± 0.0001 ₅	1.1254 ₅ ± 0.0000 ₆	1.1618 ₄ ± 0.0007 ₃	0.9439 ₇	12
Series 3					
0.79906 ± 0.00025	0.92046 ± 0.0005 ₁	1.0107 ₅ ± 0.0002 ₂	1.0427 ₇ ± 0.0003 ₂	0.9389 ₁	58
0.66731 ± 0.00006	0.76356 ± 0.0004 ₂	0.83458 ± 0.0001 ₈	0.85986 ± 0.0003 ₀	0.9318 ₅	24 ^b
0.57322 ± 0.00029	0.65262 ± 0.0001 ₅	0.71069 ± 0.0001 ₅	0.73128 ± 0.0001 ₁	0.9275 ₄	47 ^b
0.39920 ± 0.00001	0.45082 ± 0.0002 ₅	0.48824 ± 0.0000 ₀	0.50136 ± 0.0001 ₄	0.9218 ₅	21 ^b

^a Values of the osmotic coefficients of the NaCl(aq) reference standard solutions, ϕ^* , were calculated using the equation and parameters of Archer,⁷ which are reported in

Table 3. The total molalities m_T are equal to $m_T = m_1 + m_2$, y_1 is the ionic strength fraction of NaCl in the mixtures, and “ t ” is the isopiestic equilibration time in days.

^b The constant temperature water bath used for the isopiestic equilibrations was controlled at the temperature 298.15 ± 0.005 K (IPTS-68) during these experiments. As part of the thermostat system, a refrigerator/circulator was used to pump cooled water through a copper heat-exchange coil to remove excess heat. This refrigerator/circulator malfunctioned several times while the experimental results reported in this table were being measured. The reported times for these six indicated experiments refer to the equilibration time after proper temperature control was re-established.

^c The three NaCl(aq) reference molalities were corrected as described in the text.

Table 3. Parameters for Extended Ion-Interaction Models for NaCl(aq) and SrCl₂(aq) at 298.15 K

	NaCl(aq)	SrCl ₂ (aq)	SrCl ₂ (aq)
parameter	parameter value ^a	parameter value ^b	parameter value ^b
$\beta_{M,X}^{(0)} \cdot (m^\circ)^c$	0.080634	0.28267 (0.0022)	-4.98121×10^{-2} (0.1244)
$\beta_{M,X}^{(1)} \cdot (m^\circ)$	0.263098	1.56251 (0.0103)	2.09159 (0.0043)
$C_{M,X}^{(0)} \cdot (m^\circ)^2$	0.0002624	-2.2499×10^{-4} (0.1900)	3.13089×10^{-2} (0.0186)
$C_{M,X}^{(1)} \cdot (m^\circ)^2$	-0.010052	9.2137×10^{-2} (0.1982)	0.840720 (0.0187)
$D_{M,X}^{(0)} \cdot (m^\circ)^3$			-4.77377×10^{-3} (0.0182)
$\alpha_{M,X} \cdot (m^\circ)^{1/2}$	2.0	2.0	2.0
$\omega_{M,X} \cdot (m^\circ)^{1/2}$	2.5	2.5	1.6
$A_\phi \cdot (m^\circ)^{1/2}$	0.3915	0.3915	0.3915
$\sigma(\phi)^d$		0.00353	0.00159

^a Parameters for NaCl(aq) at 298.15 K were calculated from the coefficients of Archer.⁷

^b Parameters for SrCl₂(aq) at 298.15 K were evaluated in this study without (first set) and with (second set) the $D_{M,X}^{(0)}$ term. In these fits, unit weights were given to the osmotic coefficients from Table 1 and to the recalculated results from Macaskill et al.,¹ Rard and Miller,¹⁵ and Downes,¹⁹ and a weight of 0.5 was given to the results of Stokes.¹⁸ Three discrepant points were given zero weight in these fits: $m = 0.7416 \text{ mol} \cdot \text{kg}^{-1}$ from reference 19 and $m = (0.3518 \text{ and } 4.038) \text{ mol} \cdot \text{kg}^{-1}$ from reference 18, the last molality being for a supersaturated solution. The number in parentheses following each parameter value for SrCl₂(aq) is the standard error of that parameter divided by the parameter value.

^c $m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$.

^d Unweighted standard deviation for the model fits to SrCl₂(aq) osmotic coefficients for $m \leq 3.8426 \text{ mol} \cdot \text{kg}^{-1}$ ($I \leq 11.528 \text{ mol} \cdot \text{kg}^{-1}$) with 97 ϕ values given non-zero weights.

Table 4. Smoothed Values of ϕ , a_w , and γ_{\pm} for SrCl₂(aq) at 298.15 K and at Selected Molalities, Using the Parameters of Table 3 for the Five Parameter Extended Pitzer Model^a

m (mol·kg ⁻¹)	ϕ	a_w ^b	γ_{\pm}
0.001	0.9622		0.8884
0.002	0.9492		0.8505
0.005	0.9271		0.7864
0.01	0.9071		0.7279
0.02	0.8859	0.999043	0.6633
0.05	0.8604	0.997678	0.5753
0.1	0.8482	0.995426	0.5135
0.2	0.8493	0.990862	0.4624
0.3	0.8611	0.98613 ₅	0.4411
0.4	0.8774	0.98121	0.4317
0.5	0.8962	0.97607	0.4288
0.6	0.9167	0.97071	0.4303
0.7	0.9383	0.96512 ₅	0.4348
0.8	0.9610	0.95930	0.4417
0.9	0.9845	0.95324	0.4508
1.0	1.0088	0.94694	0.4617
1.2	1.0598	0.93358	0.4888
1.4	1.1138	0.91918	0.5228
1.6	1.1708	0.90371	0.5640
1.8	1.2307	0.88716	0.6131
2.0	1.2932	0.86955	0.6709
2.2	1.3580	0.85089	0.7383
2.4	1.4246	0.83128	0.8164
2.6	1.4926	0.81080	0.9065
2.8	1.5613	0.78957	1.010
3.0	1.6302	0.76773	1.127
3.2	1.6984	0.74548	1.259
3.4	1.7653	0.72297	1.408
3.520 ^c	1.8045	0.70943	1.504
3.6	1.8301	0.70042	1.572

3.8	1.8919	0.67804	1.752
4.0 ^d	1.9499	0.65604	1.946

^a With the $\beta_{M,X}^{(0)}$, $\beta_{M,X}^{(1)}$, $C_{M,X}^{(0)}$, $C_{M,X}^{(1)}$, and $D_{M,X}^{(0)}$ parameters from the last column of Table 3.

^b The values of a_w are reported to the minimum number of figures required to reproduce the tabulated values of ϕ to 1 part in the last reported figure. Below $m = 0.02 \text{ mol}\cdot\text{kg}^{-1}$, ϕ is a more precise measure of non-ideal behavior than a_w .

^c Molality of saturated solution in equilibrium with $\text{SrCl}_2\cdot 6\text{H}_2\text{O}(\text{cr})$.

^d This concentration involves a short extrapolation beyond the maximum molality to which the model parameters were fitted, $3.8426 \text{ mol}\cdot\text{kg}^{-1}$.

Figure Captions

Figure 1. (a) Osmotic coefficients ϕ of $\text{SrCl}_2(\text{aq})$ at 298.15 K plotted against the square root of the $\text{SrCl}_2(\text{aq})$ molality (m). Symbols: open circles, measured values; line, fitted curve calculated with eq 7 and the parameters for five parameter extended model from the last column of Table 3. (b) Deviations (measured minus fitted) from the extended model (long-dashed horizontal line given by $\Delta\phi = 0$): filled circles, Downes¹⁹ with $\text{KCl}(\text{aq})$ as reference standard(aq); open circles, Stokes¹⁸ with $\text{CaCl}_2(\text{aq})$ as reference standard; crosses, Macaskill et al.¹ with $\text{NaCl}(\text{aq})$ as reference standard; asterisks, this work with $\text{NaCl}(\text{aq})$ as reference standard; squares, Rard and Miller¹⁵ with $\text{CaCl}_2(\text{aq})$ as reference standard. The short-dashed line shows the deviation of the four parameter Archer model from the five parameter extended model.

Figure 2. Measured and fitted osmotic coefficients (ϕ) of aqueous $\text{NaCl} + \text{SrCl}_2$ mixtures at 298.15 K, plotted against the total molality $m_T = m_1 + m_2$. Results are shown for the following approximate ionic strength fractions of NaCl ($y_1 = m_1/(m_1 + 3m_2)$): A, $y_1 = 0.171$; B, $y_1 = 0.328$; C, $y_1 = 0.474$; D, $y_1 = 0.647$; and E, $y_1 = 0.827$. (a) Lower and intermediate molality data: filled circles, filled triangles, and filled squares, this work (curves A, C, and E); all other symbols, Macaskill et al.¹ (all five curves). (b) Detail at low molality. (c) Higher molality data of Rard and Miller.² Values for ionic strength fraction C, and for all measurements at total ionic strengths $> 7.0 \text{ mol}\cdot\text{kg}^{-1}$, were not fitted. The cutoff limits are indicated with slanted bars. Dotted extensions to the solid lines show model predictions in this region.

Figure 3. Deviations (measured minus fitted) from the aqueous NaCl + SrCl₂ model, equation 11 using the fit with ${}^S\theta_{\text{Na,Sr}} = (0.0562 \pm 0.0007) \text{ kg}\cdot\text{mol}^{-1}$ and $\psi_{\text{Na,Sr,Cl}} = -(0.00705 \pm 0.00017) \text{ kg}^2\cdot\text{mol}^{-1}$. Symbols: small filled circles, this work; larger filled circles, Rard and Miller;² open circles, Macaskill et al.¹

Figure 4. Measured and predicted logarithms of the mean activity coefficient of NaCl, $\ln\gamma_{\pm}(\text{NaCl}) = \ln\{\gamma(\text{Na}^+) \cdot \gamma(\text{Cl}^-)\}^{1/2}$, in aqueous NaCl + SrCl₂ solutions at 298.15 K plotted against the ionic strength fraction of NaCl, y_1 , in the mixtures. Symbols: data of Lanier for ionic strengths $I = (1.0, 3.0, \text{ and } 6.0) \text{ mol}\cdot\text{kg}^{-1}$; lines, model predictions.

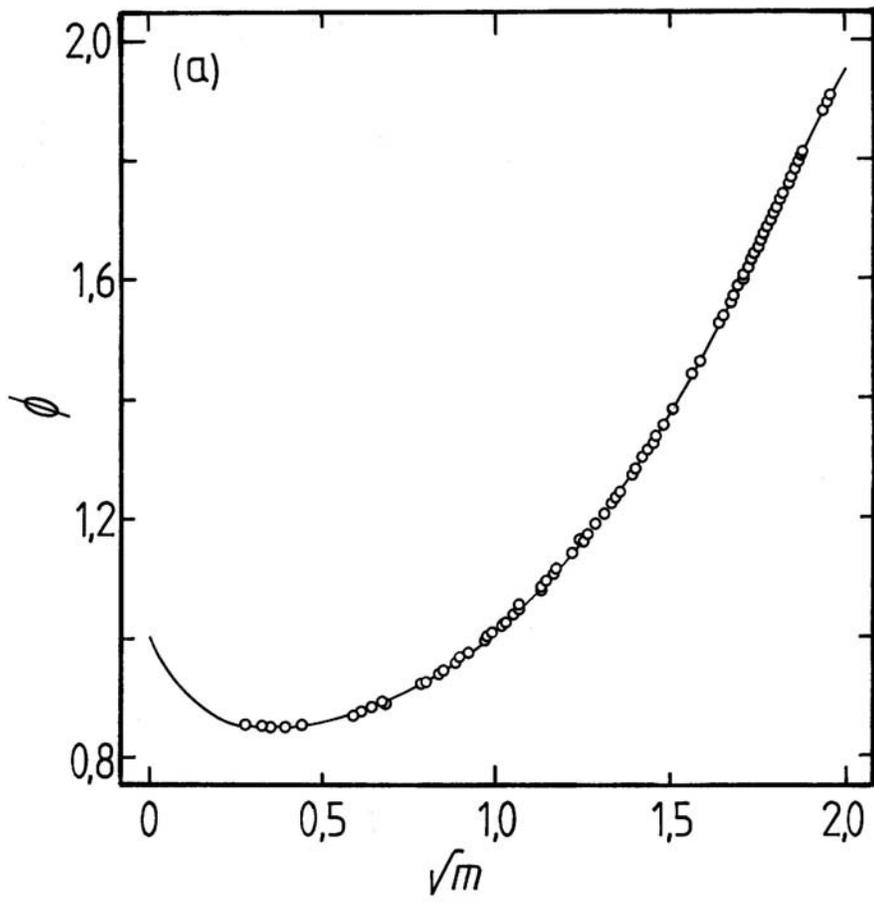


Figure 1 (a)

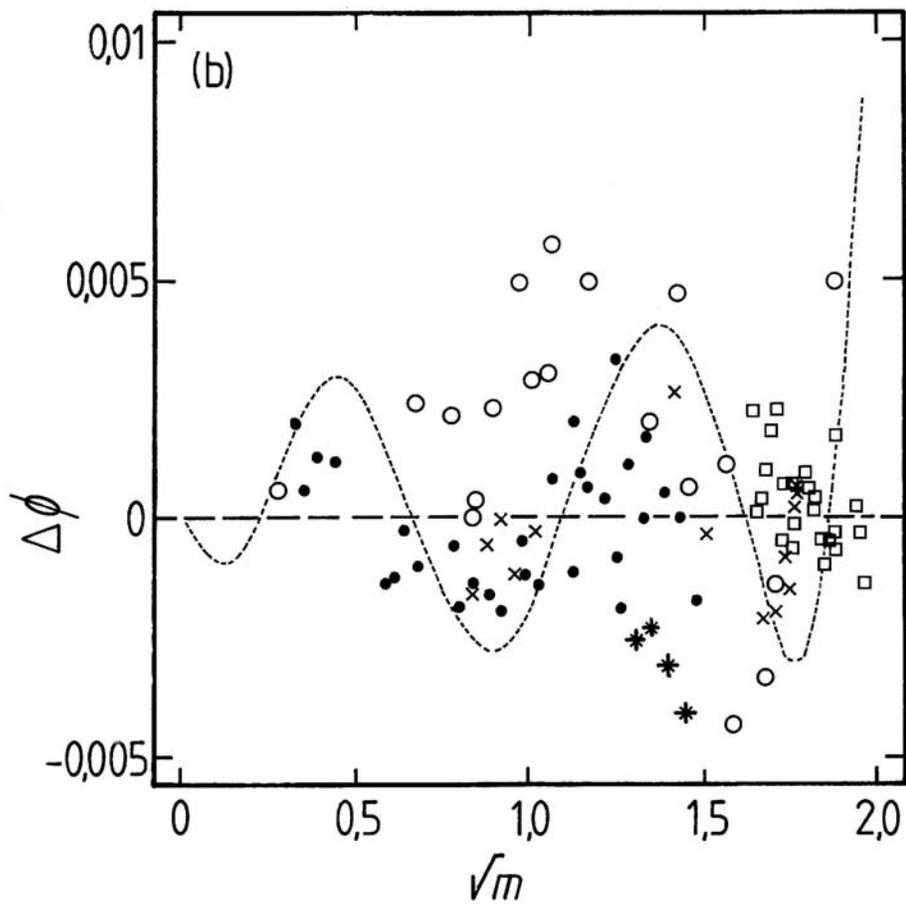


Figure 1 (b)

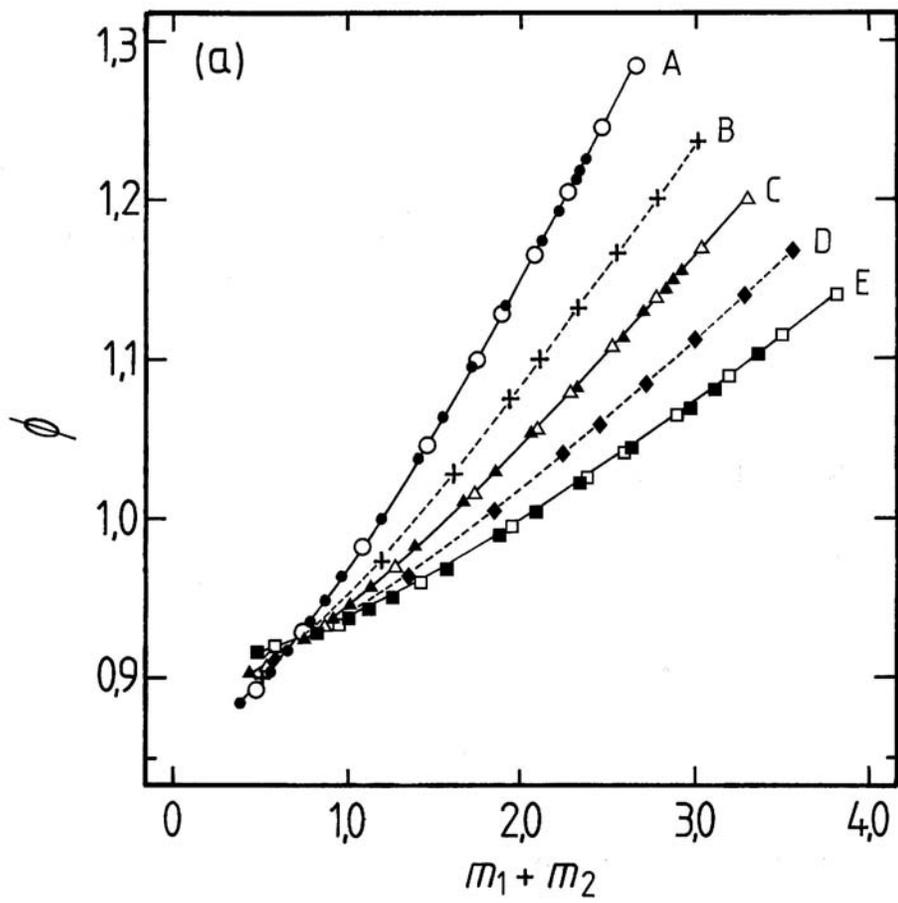


Figure 2 (a)

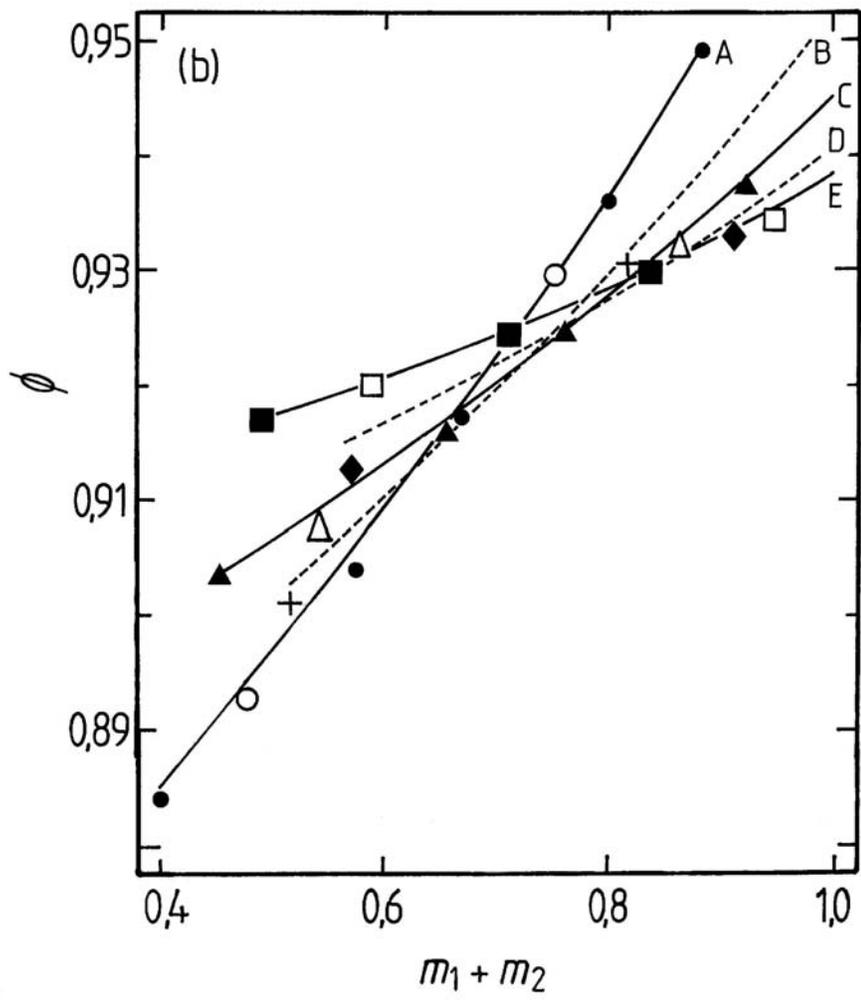


Figure 2 (b)

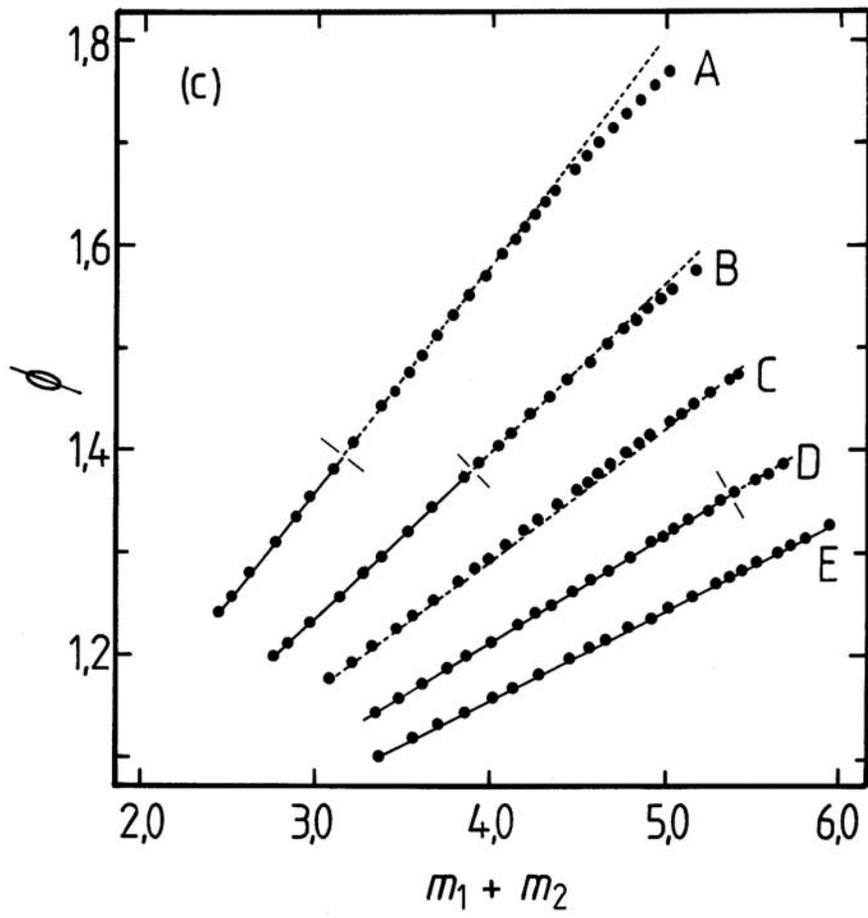


Figure 2 (c)

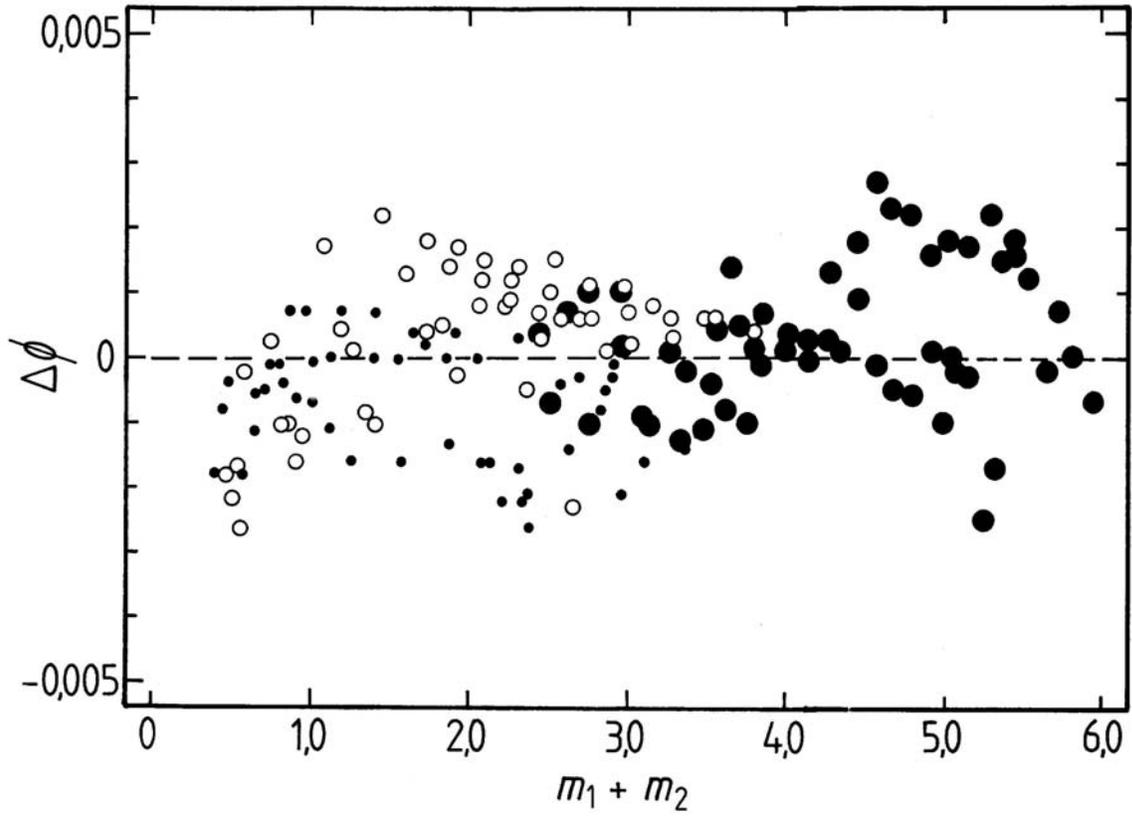


Figure 3

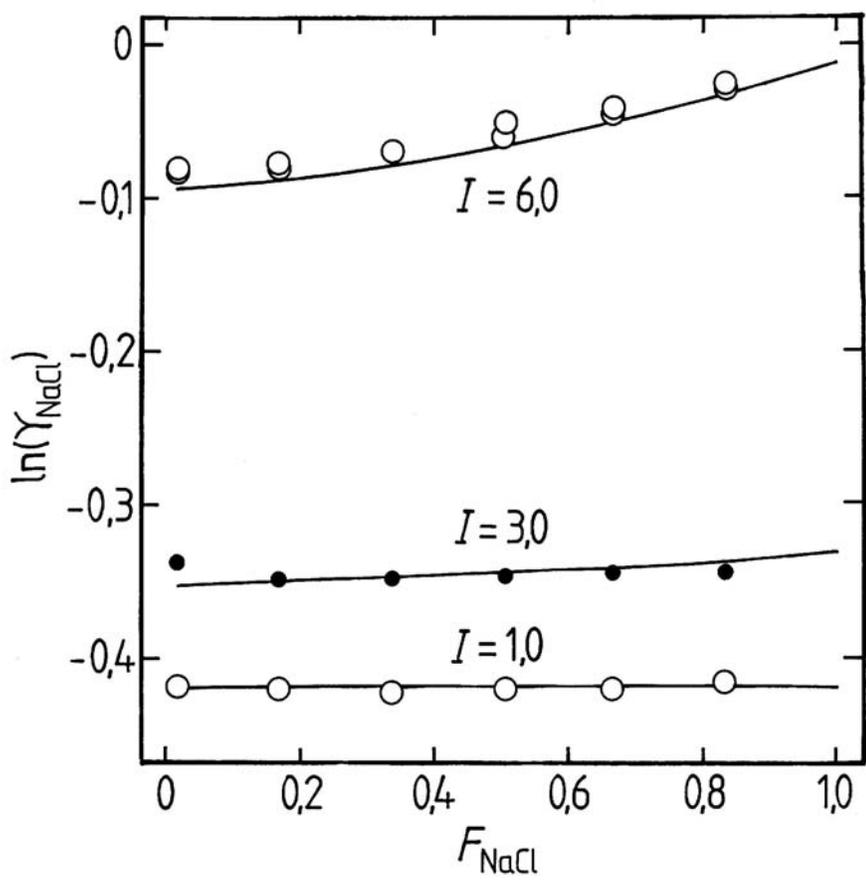


Figure 4