

# Reassessment of the Binary, Ternary, and Quaternary Interactions in Mixed Electrolytes from Thermodynamic Quantities: The Systems with Uncommon Ions Containing Hydrophobic Character<sup>‡</sup>

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Accurate estimates of the binary, ternary, and quaternary interactions in aqueous ionic mixtures with uncommon ions with hydrophobic character are presented. For this purpose, the values of the excess Gibbs free energy of mixing,  $\Delta_m G^E$ , obtained from our earlier isopiestic osmotic coefficients (Kumar, A. *J. Phys. Chem. B* 2003, 107, 2808) for the mixtures of NaCl with four guanidinium ( $\text{Gn}^+$ ) salts— $\text{CH}_3\text{COOGn}$ ,  $\text{GnNO}_3$ ,  $\text{GnClO}_4$ , and  $\text{Gn}_2\text{SO}_4$ —are analyzed with the help of the method developed by Leifer and Wigent. The methodology of Leifer and Wigent is based on the equations of Scatchard–Rush–Johnson and Friedman’s cluster integral expansion theory. The Scatchard–Rush–Johnson theory explicitly considers the quaternary and higher-order ionic interactions in the mixtures as compared to the specific ion interaction theory of Pitzer, which accounts for binary and ternary interactions only. The contributions due to binary, ternary, and quaternary interaction terms to total  $\Delta_m G^E$  are estimated and discussed critically. Also, the interaction between the same two cations, for example,  $\text{Gn}^+ - \text{Gn}^+$ , is estimated and found significant, which otherwise cannot be obtained by the use of Pitzer’s theory. The information obtained from the analysis of  $\Delta_m G^E$  is also supported by the newly measured excess volumes of mixing,  $\Delta_m V^E$ , at 298.15 K. The individual contributions of the binary, ternary, and quaternary interaction terms to total  $\Delta_m V^E$  are described. The binary, ternary, and quaternary interaction terms for both  $\Delta_m G^E$  and  $\Delta_m V^E$  are analyzed in terms of Friedman’s cluster integral expansion theory.

## Introduction

The modeling of the thermodynamic properties of mixed electrolyte solutions requires accurate knowledge of the excess Gibbs free energy of mixing. As such, the mixed electrolyte systems have numerous potential applications including many in chemical engineering, sea brines, geochemical, atmospheric aerosol chemistry, and biological systems such as proteins, amino acids, and nucleic acids. After the pioneering contribution of Debye and Huckel<sup>1</sup> in estimating the thermodynamic properties of extremely dilute electrolyte solutions, many empirical models have been proposed with the sole objective to predict the vapor pressures, activity coefficients, and thermal and volumetric properties of aqueous single and mixed electrolyte solutions up to high concentrations.<sup>2</sup> Though these models have been employed to predict the vapor pressures and activity coefficients of these solutions, no information can be obtained from these models on ion–water and ion–ion interactions. On the other hand, major developments in understanding these ionic interactions have been made in terms of Mayer’s ionic solution theory (MIST)<sup>3</sup> and Friedman’s cluster integral expansion theory (FCIET).<sup>4</sup> These theories later became the foundation for the development of the very useful semiempirical theory of Scatchard, Rush, and Johnson (SRJT)<sup>5</sup> and Pitzer’s specific ion interaction theory (PSIIT).<sup>6</sup> PSIIT, based on a combination of long-range interaction forces by the Debye–Huckel equation and short-range interaction forces by virial coefficients, has been used as a powerful tool to analyze the thermodynamic properties of single and mixed electrolyte solutions up to saturation and

under high temperatures and pressures. The equations developed in PSIIT are easy to use and also offer quantitative information on ion–water and ion–ion interactions. In general, three Pitzer coefficients— $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^\varphi$ —are required to describe the thermodynamic properties of a large number of single electrolyte solutions with an additional  $\beta^{(2)}$  for 2–2 electrolytes. These Pitzer coefficients indicate interactions between a cation and an anion of an electrolyte. When two electrolytes with or without a common ion are mixed together, interactions between two cations and anions of two different electrolytes also emerge together with those present between a cation and an anion of the same electrolyte. For example, in a mixture of two electrolytes, MX and NY (M and N are cations, and X and Y are anions), the interactions between M and N and X and Y species assume importance in addition to those present in the pairs of M and X and N and Y. Similarly, the interactions due to MNX, MNY, MXY, and NXY species can be significant at higher ionic concentrations. In PSIIT, the mixtures of electrolytes are analyzed by incorporating the Pitzer coefficients of pure electrolytes and then fitting the residuals in terms of binary mixing,  $\theta_{ik}$ , and ternary,  $\psi_{ijk}$ , interaction parameters. Efforts have been made to incorporate electrical terms for unsymmetrical mixing (for example, between  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ). These developments have been described elsewhere.<sup>6c</sup>

Two important points should be made with respect to PSIIT. As discussed above, first, the theory does not account for quaternary and higher-order multiplet interactions that are important in the mixtures containing hydrophobic ionic species such as guanidinium ( $\text{Gn}^+$ ) and the clathrate-forming and strong hydrophobic quaternary ammonium electrolytes. In these mixtures, the quaternary interactions have been recognized in several reports.<sup>7–13</sup> These interactions are absent in the mixtures of

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simple strong electrolytes. The evidence obtained from the ultrasonic absorption spectra of the clathrate-forming quaternary ammonium salts and  $\text{GnCl}$  indicates the formation of large clusters owing to the association of ions.<sup>14,15</sup> The effect of these clusters has also been observed in many solution properties such as viscosity, activity coefficient, and density.<sup>9</sup> An important criterion to probe the quaternary interactions in such mixtures has been due to complete violation of Harned's rule<sup>16</sup> when applied to correlate activity coefficients of one electrolyte with the composition of another electrolyte characterized by the clathrate formation. On the other hand, two Harned coefficients for each electrolyte can be sufficient to describe the activity coefficients of strong electrolytes in their mixtures. Higher-order terms, however, are required for the analysis of mixtures, which possess at least one clathrate-forming or hydrophobic species. In general, it is assumed that the main contribution to the total  $\Delta_m G^E$  of a mixture of strong electrolytes is due to binary and ternary interactions. The contribution of ternary interactions is much less as compared to the binary ones.<sup>17</sup> It is, therefore, important to emphasize here that though three or four Pitzer coefficients are sufficient to correlate the property-concentration data, the parameters are not the true indicators of the types of interactions in the mixtures containing clathrate-forming or hydrophobic species.<sup>18</sup> Second, PSIIT completely neglects interactions between the same ions. For example, the interactions between  $\text{M}-\text{M}$ ,  $\text{N}-\text{N}$ ,  $\text{X}-\text{X}$ , and  $\text{Y}-\text{Y}$  are assumed negligible. In the mixtures of simple electrolytes such as  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{MgCl}_2$ , and  $\text{CaCl}_2$ , these interactions (for example,  $\text{Na}^+-\text{Na}^+$ ,  $\text{K}^+-\text{K}^+$ ,  $\text{Mg}^{2+}-\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}-\text{Ca}^{2+}$ ) are thus assumed negligible within the framework of PSIIT. Such interactions, however, can be very significant in the mixtures containing hydrophobic cations, like  $\text{Gn}^+$ , and quaternary ammonium cations.<sup>8,17</sup> The importance of these interactions between two hydrophobic ions is highlighted on the basis of  $\Delta_m G^E$  calculated from the experimental osmotic coefficients.<sup>8</sup> In a true sense, PSIIT oversimplifies description of the thermodynamic behavior of the mixtures with such ionic species.

The SRJT, which is based on the combination of Debye-Huckel function and other adjustable parameters, has been employed to analyze the excess Gibbs free energy of mixing,  $\Delta_m G^E$ , of electrolyte solutions.<sup>5</sup> In this theory, though the number of adjustable parameters is larger than that in PSIIT, it offers a greater advantage in terms of the examination of contributions from different mixing terms to total  $\Delta_m G^E$ . The SRJT incorporates the contributions of the binary, ternary, quaternary, and higher-order interactions to total  $\Delta_m G^E$ . A simple and rigorous procedure was developed by Leifer and Wigent<sup>19</sup> to determine and separate the contributions of binary, ternary, quaternary, and higher-order interactions to  $\Delta_m G^E$ . For this purpose, these authors used a combination of FCIET and the SRJT.

Recently, we have quantified the ionic interactions as a result of mixing of strong hydrophobic and hydrophilic cations in a common anion environment.<sup>20,21</sup> We also examined these interactions between two hydrophobic cations. In such systems, the contributions to  $\Delta_m G^E$ , excess volumes of mixing,  $\Delta_m V^E$ , and excess compressibilities of mixing,  $\Delta_m K^E$ , were estimated in terms of binary and ternary interactions as determined by FCIET and PSIIT. In a very recent contribution from this laboratory, we compared the roles of different interactions in determining the  $\Delta_m G^E$  values for several mixed electrolytes with uncommon ions, in which one strong hydrophobic and hydrophilic cation or anion were present.<sup>22</sup> The mixtures studied included  $\text{NaCl}$ ,  $\text{CH}_3\text{COOGn}$  (henceforth abbreviated as  $\text{GnAc}$ ),

$\text{GnNO}_3$ ,  $\text{GnClO}_4$ , and  $\text{Gn}_2\text{SO}_4$  in full composition range up to high ionic strengths.

The purpose of this investigation is twofold: (1) The first purpose is to separate and accurately quantify the contribution of binary, ternary, quaternary, and higher-order interaction terms to mixing of  $\text{NaCl}$  with  $\text{GnAc}$ ,  $\text{GnNO}_3$ ,  $\text{GnClO}_4$ , and  $\text{Gn}_2\text{SO}_4$  using the method developed by Leifer and Wigent (LW).<sup>19a</sup> Though we had estimated the relative contributions of different interaction terms, a thoughtful suggestion from an anonymous reviewer<sup>7</sup> that the LW method<sup>19a</sup> is superior to the one given by PSIIT in delineating the quaternary and higher-order interactions in such mixtures inspired us to examine our data and analysis in detail. This, we present here, and (2) we then extend support to our findings obtained from the analysis of  $\Delta_m G^E$  by estimating these interactions from the newly measured  $\Delta_m V^E$  data and attempt to present a unified picture of ionic interactions in these systems. The ionic interactions in the above mixtures as delineated from the volumetric properties have not been addressed before in the literature. This work is organized as follows. After describing the experimental methods used for the measurement of volumes of the above-mentioned mixtures, we briefly outline the relevant equations to estimate the contribution due to various interaction terms to total  $\Delta_m G^E$  as described by Leifer and Wigent.<sup>19</sup> We then present new expressions for  $\Delta_m V^E$  and separate and quantify the contributions of binary, ternary, quaternary, and higher-order mixing terms to  $\Delta_m V^E$  in the above ionic solutions. The ionic strength of the mixtures investigated herein varied from 0.2 to 6 mol  $\text{kg}^{-1}$  of water.

## Experimental Section

The experimental details are described in our earlier work.<sup>22</sup> A.R. grade  $\text{NaCl}$ ,  $\text{GnNO}_3$ , and  $\text{Gn}_2\text{SO}_4$  procured commercially (Aldrich Chem. Co.) were recrystallized from water and dried under vacuum.  $\text{GnAc}$  and  $\text{GnClO}_4$  were prepared as reported in the literature.<sup>23</sup> All the solutions were prepared by weight in deionized water (specific conductivity of water  $<0.18 \text{ M}\Omega \text{ m}$ ). The molalities were accurate to  $2 \times 10^{-4}$ . The purity and concentration of the aqueous guanidinium salts were determined by the method of Nozaki.<sup>24</sup>

The excess volumes on mixing at constant ionic strength were measured by a continuous dilatometer.<sup>25</sup> A detailed description of the instrument and the methodology is given elsewhere.<sup>26</sup> The instrument was calibrated using directly measured volume changes on mixing for aqueous mixtures of  $\text{KBr}$  with tetra-*n*-butylammonium bromide.<sup>26</sup> The calibration was also checked against the volume changes on mixing data calculated from precise density data for aqueous mixtures of  $\text{KCl}$  with  $\text{GnCl}$ .<sup>20,21</sup> The  $\Delta_m V^E$  data were accurate to  $0.007 \text{ m}^3 \text{ mol}^{-1}$ . The precision of the  $\Delta_m V^E$  data measurements (based on triplicate readings) increased with the ionic strength of the mixtures. It was noted as  $\pm 0.005 \text{ m}^3 \text{ mol}^{-1}$  at low ionic strength, say  $I = 0.2 \text{ mol kg}^{-1}$ , and  $\pm 0.002 \text{ m}^3 \text{ mol}^{-1}$  at high ionic strength, say  $I = 6 \text{ mol kg}^{-1}$ . The measured  $\Delta_m V^E$  values were measured in  $\text{m}^3 \text{ mol}^{-1}$ , which were converted to  $\text{m}^3 \text{ kg}^{-1}$  of  $\text{H}_2\text{O}$  by multiplying it by the total molality of the mixture. Thus, both  $\Delta_m G^E$  and  $\Delta_m V^E$  have units as  $\text{J kg}^{-1}$  of  $\text{H}_2\text{O}$  and  $\text{m}^3 \text{ kg}^{-1}$  of  $\text{H}_2\text{O}$ , respectively.

The measurements were made at a constant temperature of 298.15 K. The temperature of a constant-temperature water bath (Julabo) was maintained to within 0.005 K. Throughout the paper,  $\text{NaCl}$  is denoted by A and the guanidinium salt by B.

## Equations

Earlier, our calculations of  $\Delta_m G^E$  for these mixtures at 298.15 K were based on PSIIT, which did not include the quaternary and higher-order interactions. We, therefore, first recalculated  $\Delta_m G^E$  by using the SRJT as applied to the single and mixed electrolyte solutions. We adapted the following procedure in this regard:

(1) The SRJ equations for correlating the osmotic coefficients,  $\varphi$ , with the molality,  $m$  (in mol kg<sup>-1</sup> of water), of aqueous single electrolytes (NaCl or any guanidinium salts) were applied to obtain SRJ parameters as

$$\varphi - 1 = (1/\nu m)[(2S/a^3 I)(1 + aI^{1/2} - 1/(1 + aI^{1/2})) + a^{(1)}I + a^{(2)}I^2 + a^{(3)}I^3 + \dots] \quad (1)$$

where  $\nu$  is the number of moles of ions per mole of electrolyte and defined by  $\nu = \nu_c + \nu_a$ , with  $\nu_c$  and  $\nu_a$  being the number of cations and anions, respectively. The parameter  $a$  is the distance-of-closest-approach parameter and  $a^{(1)}, a^{(2)}, a^{(3)}, \dots$  are known as the SRJ parameters and are evaluated from the least-squares analysis of experimental quantities.  $I$  is the ionic strength defined as  $I = 0.5 \sum m_i z_i^2$ , with  $z$  being ionic charge.  $S$  is the Debye–Huckel limiting slope with a value of  $-1.17582$  (mol kg)<sup>-1/2</sup> at 298.15 K.

We used eq 1 in our calculations, as the measured quantity was the osmotic coefficient,  $\varphi$ , rather than the activity coefficient,  $\gamma_{\pm}$ , of an electrolyte.

(2) Once the SRJ parameters for individual electrolytes are determined by eq 1, the  $\varphi$  values of mixtures were fitted to eq 2 to extract the SRJ mixing parameters. For convenience, we denote NaCl by A and any guanidinium salt by B.

$$\varphi - 1 = (I/(\nu_A m_A + \nu_B m_B))[\gamma_A \alpha_A + \gamma_B \alpha_B + y_A y_B (\beta_{AB}^{(0)} + \beta_{AB}^{(1)}(y_A - y_B) + \beta_{AB}^{(2)}(y_A - y_B)^2 + \dots)] \quad (2)$$

where  $y_A$  is the ionic strength fraction of A given by  $y_A = I_A/I$ , with an analogous definition for B, remembering  $y_A + y_B = 1$ . In eq 2,  $\beta_{AB}^{(0)}, \beta_{AB}^{(1)}, \beta_{AB}^{(2)},$  and so forth, are the SRJ mixing parameters.

(3) The activity coefficient of the electrolyte A in the mixture can then be computed by

$$\ln \gamma_{\pm A} = (I_A/\nu_A m_A)[(A_A + \alpha_A) + (\alpha_B - \alpha_A)y_B + y_B[B_{AB}^{(0)} + B_{AB}^{(1)}((y_A - y_B) + y_A) +$$

$$B_{AB}^{(2)}((y_A - y_B)^2 + 2y_A(y_A - y_B)) + \dots +$$

$$B_{AB}^{(n)}((y_A - y_B)^n + ny_A(y_A - y_B)^{n-1})] +$$

$$y_A y_B [(\beta_{AB}^{(0)} - B_{AB}^{(0)}) + (\beta_{AB}^{(1)} - 2B_{AB}^{(1)})(y_A - y_B) + \dots +$$

$$(\beta_{AB}^{(n)} - (n+1)B_{AB}^{(n)})(y_A - y_B)^n] \quad (3)$$

with an analogous expression for the activity coefficient of B in the mixtures of A and B.

In eq 3,

$$\alpha_A = (2S/a_A I)[1 + a_A I^{1/2} - 1/(1 + a_A I^{1/2}) - 2 \ln(1 + a_A I^{1/2})] + a_A^{(1)} I + a_A^{(2)} I^2 + a_A^{(3)} I^3 + \dots \quad (4a)$$

$$(A_A + \alpha_A) = (2S I^{1/2}/(1 + a_A I^{1/2})) + 2a_A^{(1)} I + 3a_A^{(2)} I^2/2 + 4a_A^{(3)} I^3/3 + \dots \quad (4b)$$

The above terms can also be written for B by substituting A by B.

The definitions of  $\beta_{AB}^{(n)}$  and  $B_{AB}^{(n)}$  are

$$\beta_{AB}^{(n)} = \sum_{k=n+1}^k I^k b_{AB}^{(n,k)} \quad (5)$$

$$B_{AB}^{(n)} = \sum_{k=n+1}^k (I^k/k) b_{AB}^{(n,k)} \quad (6)$$

In eqs 5 and 6,  $k = 1$  for pairs,  $k = 2$  for triplets,  $k = 3$  for quadruplets, and so on. The highest order of multiplets required to accurately fit the  $\varphi$ - $m$  data is denoted by  $k'$ .

(4) Now that the SRJ mixing parameters for each mixture are obtained, it is possible to write an expression for  $\Delta_m G^E$ . From the discussion given below, it will be clear that the contribution of binary, ternary, quaternary, and higher-order terms to total  $\Delta_m G^E$  can be accurately estimated.

In terms of the SRJT,  $\Delta_m G^E$  of the mixtures is given by

$$\Delta_m G^E = RT I y_A y_B [B_{AB}^{(0)} + B_{AB}^{(1)}(y_A - y_B) + \dots + B_{AB}^{(n)}(y_A - y_B)^n] \quad (7)$$

where  $B_{AB}^{(0)}, B_{AB}^{(1)},$  and  $B_{AB}^{(n)}$  are the Scatchard parameters. These parameters are obtained from the least-squares analysis of osmotic coefficient data as shown above. The LW method combines FCIET and the SRJT to estimate and separate the roles of binary, ternary, quaternary, and higher-order interaction terms to total  $\Delta_m G^E$  in terms of the Scatchard parameters as

$$\Delta_m G_p^E = RT I^2 y_A y_B b_{AB}^{(0,1)} \quad (8)$$

$$\Delta_m G_t^E = 0.5 RT I^3 y_A y_B [b_{AB}^{(0,2)} + b_{AB}^{(1,2)}(y_A - y_B)] \quad (9)$$

$$\Delta_m G_q^E = 0.3334 RT I^4 y_A y_B [b_{AB}^{(0,3)} + b_{AB}^{(1,3)}(y_A - y_B) + b_{AB}^{(2,3)}(y_A - y_B)^2] \quad (10)$$

$$\Delta_m G_{hoi}^E = (I^{n+2}/n + 1) RT y_A y_B [b_{AB}^{(0,(n+1))} + b_{AB}^{(1,(n+1))}(y_A - y_B) + \dots + b_{AB}^{(n,(n+1))}(y_A - y_B)^n] \quad (11)$$

Total  $\Delta_m G^E$  is therefore a combination of eqs 8–11 as

$$\Delta_m G^E = \Delta_m G_p^E + \Delta_m G_t^E + \Delta_m G_q^E + \dots + \Delta_m G_{hoi}^E \quad (12)$$

The subscripts p, t, q, and hoi refer to the binary, ternary, quaternary, and higher-order interactions, respectively.

The binary interactions are expressed by  $b^{(0,1)}$ , while the contribution due to ternary interactions is expressed by the parameters  $b^{(0,2)}$  and  $b^{(1,2)}$ . The parameters  $b^{(0,3)}, b^{(1,3)},$  and  $b^{(2,3)}$  are involved in characterizing the quaternary interactions. LW also illustrated the Scatchard parameters,  $b_{AB}$ , required for various types of interactions by using a type of Pascal triangle.<sup>27</sup>

The  $\Delta_m G^E$  values of an electrolyte mixture can be expressed in terms of FCIET, derived from MIST. Accordingly,



$$\Delta_m G^E = RTI^2 y_A y_B [g_0 + g_1(y_A - y_B) + g_2(y_A - y_B)^2 + \dots + g_n(y_A - y_B)^n] \quad (13)$$

where  $g_0$ ,  $g_1$ ,  $g_2$ , and  $g_n$  are known as the Friedman interaction parameters. As will be seen below, we shall focus on the binary, ternary, and quaternary interactions during the course of our work. Conventionally,  $g_0$  has been attributed to only binary interactions. In a similar fashion,  $g_1$  has been attributed to ternary interactions and so on. According to the LW method, however, at  $y_B = 0.5$ , where  $g_1$ ,  $g_2$ , and so forth, are absent and  $g_0$  is determined, other interactions are also present in addition to the binary ones. The ternary interactions are reflected by both the parameters  $g_0$  and  $g_1$  as

$$g_0 = g_{0p} + Ig_{0t} + I^2 g_{0q} \quad (14a)$$

$$g_1 = Ig_{1t} + I^2 g_{1q} \quad (14b)$$

$$g_2 = I^2 g_{2q} \quad (14c)$$

The relationship between the Friedman and SRJ parameters can be obtained from eqs 7 and 13 as

$$g_n = B_{AB}^{(n)} / I \quad (15)$$

which in turn are related to interaction parameters by

$$g_n = \sum_{k=n+1}^K (I^{k-1}/k) b_{AB}^{(n,k)} \quad n \geq 0 \quad (16)$$

Wigent and Leifer have described the relationship between the Scatchard interaction parameters and the Friedman interaction parameters for each interaction as given below:

$$g_{np} = b_{AB}^{(n,1)}, \text{ where } n = 0 \quad (17a)$$

$$g_{nt} = b_{AB}^{(n,2)} / 2, \text{ where } n = 0 \text{ and } 1 \quad (17b)$$

$$g_{nq} = b_{AB}^{(n,3)} / 3, \text{ where } n = 0, 1, \text{ and } 2 \quad (17c)$$

Thus,  $\Delta_m G^E$  can be decomposed into the contributions made by binary, ternary, and quaternary interactions in terms of FCIET as

$$\Delta_m G_p^E = RTI^2 y_A y_B g_{0p} \quad (18)$$

$$\Delta_m G_t^E = RTI^3 y_A y_B [g_{0t} + g_{1t}(y_A - y_B)] \quad (19)$$

$$\Delta_m G_q^E = RTI^4 y_A y_B [g_{0q} + g_{1q}(y_A - y_B) + g_{2q}(y_A - y_B)^2] \quad (20)$$

The above method has not been used earlier to analyze the  $\Delta_m V^E$  data. The  $\Delta_m V^E$  values of an electrolyte mixture can be expressed in terms of FCIET as

$$\Delta_m V^E = I^2 y_A y_B [v_0 + v_1(y_A - y_B) + v_2(y_A - y_B)^2 + \dots + v_n(y_A - y_B)^n] \quad (21)$$

The Friedman parameters for volume— $v_0$ ,  $v_1$ ,  $v_2$ , ...,  $v_n$ —can be correlated to the SRJ parameters for volume, for example,  $b_{AB}^{(0,1)V}$ ,  $b_{AB}^{(0,2)V}$ ,  $b_{AB}^{(1,2)V}$ ,  $b_{AB}^{(0,3)V}$ ,  $b_{AB}^{(1,3)V}$ , and  $b_{AB}^{(2,3)V}$ , by the expressions analogous to one given by eq 17. The appropriate expressions for estimating contributions due to binary, ternary, quaternary, and higher-order interactions to  $\Delta_m V^E$  are

$$\Delta_m V_p^E = I^2 y_A y_B b_{AB}^{(0,1)V} \quad (22)$$

$$\Delta_m V_t^E = 0.5 I^3 y_A y_B [b_{AB}^{(0,2)V} + b_{AB}^{(1,2)V}(y_A - y_B)] \quad (23)$$

$$\Delta_m V_q^E = 0.3334 I^4 y_A y_B [b_{AB}^{(0,3)V} + b_{AB}^{(1,3)V}(y_A - y_B) + b_{AB}^{(2,3)V}(y_A - y_B)^2] \quad (24)$$

$$\Delta_m V_{hoi}^E = (I^{n+2}/n + 1) y_A y_B [b_{AB}^{(0,(n+1)V} + b_{AB}^{(1,(n+1)V}(y_A - y_B) + \dots + b_{AB}^{(n,(n+1)V}(y_A - y_B)^n] \quad (25)$$

Total  $\Delta_m V^E$  is therefore a combination of eqs 22–25 as

$$\Delta_m V^E = \Delta_m V_p^E + \Delta_m V_t^E + \Delta_m V_q^E + \Delta_m V_{hoi}^E \quad (26)$$

The parameter  $b_{AB}^{(0,1)V}$  is thermodynamically related to  $b_{AB}^{(0,1)}$  on the lines suggested earlier<sup>6,28</sup>

$$b_{AB}^{(0,1)V} = \partial b_{AB}^{(0,1)} / \partial P \quad (27)$$

with analogous definitions for other parameters. It may be noted the expressions valid for  $\Delta_m V^E$  are analogous to those applicable to  $\Delta_m G^E$ .

## Results and Discussion

Since the measured quantity for the systems was  $\varphi$  and not  $\gamma_{\pm}$ , we used the SRJ equations for analyzing the  $\varphi$  values of both single and mixed electrolytes. The SRJ parameters of pure NaCl and guanidinium salts and their mixtures at 298.15 K are listed in Tables 1 and 2, respectively.

As mentioned above, there is no provision in PSIIT to account for the quaternary interactions, while in SRJT these interactions are given by the parameters  $b_{AB}^{(0,3)}$ ,  $b_{AB}^{(1,3)}$ , and  $b_{AB}^{(2,3)}$ . First, we fitted the  $\varphi$  data of these mixtures by setting  $b_{AB}^{(0,3)} = b_{AB}^{(1,3)} = 0$ ; the correlated  $\varphi$  values showed large deviations from the experimental ones. Then, we treated  $b_{AB}^{(0,3)}$  and  $b_{AB}^{(1,3)}$  as adjustable parameters and evaluated the importance of the parameter  $b_{AB}^{(2,3)}$  in correlating the osmotic coefficients of the mixtures containing guanidinium salts without and with  $b_{AB}^{(2,3)}$ . In the case of NaCl–GnAc, the deviations,  $\Delta\varphi$  ( $\Delta\varphi = \text{experimental } \varphi - \text{calculated } \varphi$  with and without  $b_{AB}^{(2,3)}$ ), are significant in the NaCl-rich region at lower ionic strength. These deviations, however, become high at higher ionic strength in the  $\text{GnNO}_3$ -rich mixtures of NaCl– $\text{GnNO}_3$ . The  $\Delta\varphi$  values are also important in the NaCl-rich mixture with  $\text{GnClO}_4$  at lower ionic strength. At moderate ionic strength, say 1.5 mol kg<sup>-1</sup>, the systematic deviations are noted in the case of NaCl– $\text{Gn}_2\text{SO}_4$  independent of the mixture composition. These observations as demonstrated in Figure 1 point out the importance of the quaternary interaction parameter  $b_{AB}^{(2,3)}$  in representing the  $\varphi$  data within experimental accuracy. No further parameters were required to fit the data, indicating the absence of higher-order mixing terms in these systems. The importance of the type of interactions in such mixtures expressed in the form of a Pascal triangle can be analyzed and understood by the method proposed by Leifer and Wigent.<sup>19a</sup> These authors also suggested the method to employ a minimum number of such parameters in fitting the data (see Figure 1 of ref 19a).

It is important to point out here that the  $\Delta_m G^E$  values computed by PSIIT differ from those obtained by the use of the SRJT. The SRJT parameters were then used in eq 7 to compute the  $\Delta_m G^E$  values. The revised  $\Delta_m G^E$  values for the NaCl–guanidinium salts at  $y_B$  values but at the highest ionic strengths of the mixtures are shown in Supporting Information

**TABLE 1: SRJ Parameters Together with Their Standard Errors for Pure Electrolytes**

parameter	NaCl	GnAc	GnNO <sub>3</sub>	GnClO <sub>4</sub>	Gn <sub>2</sub> SO <sub>4</sub>
$A$	$1.474\,07 \pm 0.000\,07$	$0.672\,31 \pm 0.000\,04$	$0.854\,35 \pm 0.000\,08$	$1.053\,24 \pm 0.000\,09$	$0.925\,41 \pm 0.000\,07$
$a^{(1)}$	$0.042\,06 \pm 0.000\,11$	$0.852\,11 \pm 0.000\,21$	$0.342\,34 \pm 0.000\,07$	$0.434\,34 \pm 0.000\,14$	$0.034\,22 \pm 0.000\,05$
$a^{(2)}$	$0.019\,55 \pm 0.000\,18$	$-0.123\,65 \pm 0.000\,19$	$-0.024\,50 \pm 0.000\,04$	$-0.045\,41 \pm 0.000\,05$	$0.014\,95 \pm 0.000\,09$
$a^{(3)}$	$-0.011\,31 \pm 0.000\,20$	$0.033\,41 \pm 0.000\,22$	$0.004\,52 \pm 0.000\,02$	$-0.001\,05 \pm 0.000\,01$	$-0.005\,43 \pm 0.000\,11$
$a^{(4)}$	0	$-0.000\,92 \pm 0.000\,07$	$-0.000\,75 \pm 0.000\,10$	$0.000\,19 \pm 0.000\,02$	$0.001\,01 \pm 0.000\,10$
$10^4\text{rmsd}$	5	5	5	6	6

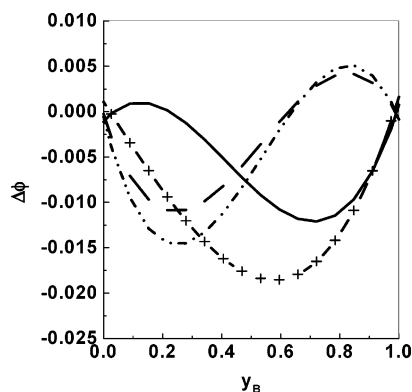
**TABLE 2: Best SRJ Mixing Parameters for Different Systems**

parameter	NaCl–GnAc	NaCl–GnNO <sub>3</sub>	NaCl–GnClO <sub>4</sub>	NaCl–Gn <sub>2</sub> SO <sub>4</sub>
$b^{(0,1)}$	$0.017\,47 \pm 0.000\,11$	$-0.892\,44 \pm 0.000\,26$	$-0.759\,52 \pm 0.000\,32$	$-0.934\,13 \pm 0.000\,28$
$b^{(0,2)}$	$-0.013\,84 \pm 0.000\,14$	$0.454\,77 \pm 0.000\,67$	$0.492\,43 \pm 0.000\,65$	$0.453\,43 \pm 0.00060$
$b^{(0,3)}$	$0.001\,86 \pm 0.000\,06$	$-0.101\,41 \pm 0.000\,18$	$-0.095\,432 \pm 0.000\,14$	$-0.113\,451 \pm 0.000\,20$
$b^{(1,2)}$	$-0.019\,561 \pm 0.000\,11$	$-0.594\,21 \pm 0.000\,34$	$-0.443\,13 \pm 0.000\,34$	$-0.693\,93 \pm 0.000\,45$
$b^{(1,3)}$	$0.001\,01 \pm 0.000\,09$	$0.005\,32 \pm 0.000\,13$	$0.004\,10 \pm 0.000\,11$	$0.007\,21 \pm 0.000\,09$
$b^{(2,3)}$	$0.000\,95 \pm 0.000\,02$	$0.003\,43 \pm 0.000\,10$	$0.001\,25 \pm 0.000\,09$	$0.005\,94 \pm 0.000\,22$
$10^4\text{rmsd}$	5	5	4	6

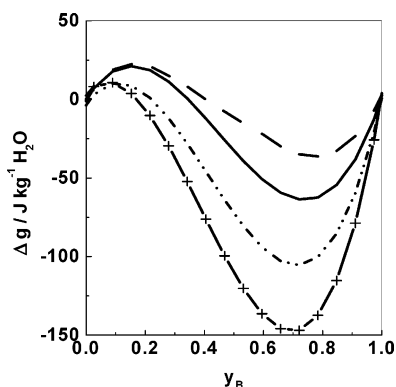
Figure S1. The maximum difference in the  $\Delta_m G^E$  values is seen in the NaCl-poor region of the mixtures. The shape of the  $\Delta_m G^E$ – $y_B$  plots obtained from both PSIIT and the SRJT is almost similar except in the low NaCl concentration region. In Figure 2 are plotted the differences,  $\Delta g$ , between  $\Delta_m G^E$  obtained from the SRJT and PSIIT as a function of  $y_B$  at the highest ionic strengths of all four systems. The  $\Delta g$  values are slightly positive in the NaCl-rich mixtures but become highly negative upon the addition of the guanidinium salts in aqueous NaCl. In the high concentrations of the guanidinium salts, PSIIT offers an overestimation of  $\Delta_m G^E$ . Note that the sign before  $\Delta_m G^E$  is

to be kept in mind during the discussions. A difference of  $-150\text{ J kg}^{-1}$  of  $\text{H}_2\text{O}$  in the NaCl mixture containing about 70%  $\text{Gn}_2\text{SO}_4$  at  $I = 6\text{ mol kg}^{-1}$  is about 18% of the  $\Delta_m G^E$  value obtained from the use of PSIIT. This difference is quite significant and can result in substantial change in the parameters, indicating the significance of the reevaluated ionic interactions. This behavior is common in all of the systems. The differences,  $\Delta g$ , are proportional to the ionic strengths of the mixtures at a given composition of mixtures.

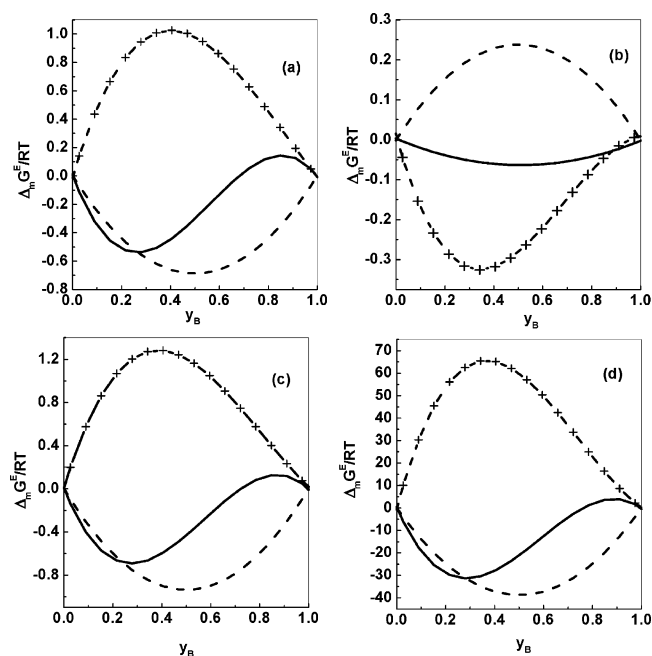
The contribution of binary, ternary, and quaternary mixing terms toward total  $\Delta_m G^E$  was calculated by eqs 8, 9, and 10, respectively. The contribution of different interaction terms toward total  $\Delta_m G^E$  for different systems as a function of  $y_B$  at the highest ionic strengths is demonstrated in Figure 3. Ionic strength dependence of the contribution of the binary, ternary, and quaternary interaction terms to  $\Delta_m G^E$  of different mixtures at the representative fixed  $y_B$  values of 0.2, 0.5, and 0.8 is demonstrated in Supporting Information Figures S2–S5.



**Figure 1.** Differences,  $\Delta\phi$  ( $\Delta\phi = \text{experimental } \phi - \text{calculated } \Delta\phi$  without  $b^{(2,3)}_{AB}$ ), as a function of  $y_B$  for the mixtures of NaCl with (---) GnAc at  $I = 1\text{ mol kg}^{-1}$ , (—) GnNO<sub>3</sub> at  $I = 1.4\text{ mol kg}^{-1}$ , (····) GnClO<sub>4</sub> at  $I = 0.5\text{ mol kg}^{-1}$ , (–+–) Gn<sub>2</sub>SO<sub>4</sub> at  $I = 1.5\text{ mol kg}^{-1}$ .



**Figure 2.** Differences,  $\Delta g$ , between the  $\Delta_m G^E$  values obtained from the SRJT and PSIIT for the mixtures of NaCl with the guanidinium salts; the symbols are the same as those in Figure 1.



**Figure 3.** Contribution of (---) binary  $\Delta_m G_p^E/RT$ , (—) ternary  $\Delta_m G_t^E/RT$ , and (–+–) quaternary  $\Delta_m G_q^E/RT$  interaction terms to total  $\Delta_m G^E/RT$  for the mixtures of NaCl with (a) GnAc at  $I = 2.5\text{ mol kg}^{-1}$ , (b) GnNO<sub>3</sub> at  $I = 1.4\text{ mol kg}^{-1}$ , (c) GnClO<sub>4</sub> at  $I = 2.6\text{ mol kg}^{-1}$ , and (d) Gn<sub>2</sub>SO<sub>4</sub> at  $I = 6\text{ mol kg}^{-1}$ .

From an examination of the  $\Delta G$  values, it is clear that the contributions to total  $\Delta_m G^E$  by the binary, ternary, and quaternary interaction terms are substantially changed after the use of the SRJT. Since the SRJT accounts for the interactions between two like-charged hydrophobic cations, for example,  $\text{Gn}^+-\text{Gn}^+$ , and quaternary interactions apart from binary and ternary ones, the revised contributions are more accurate and reliable.

In the NaCl–GnAc system, the binary interactions are negligible at low ionic strengths, say at  $I = 0.5 \text{ mol kg}^{-1}$ . The binary interactions, however, gradually become important with increasing ionic strength and are maximized in  $\sim 50\%$  mixtures of NaCl in GnAc at the highest ionic strength  $I = 2.5 \text{ mol kg}^{-1}$ . The ternary interactions become significant with increasing ionic strength. Interestingly, the ternary interactions are significant in the NaCl-rich region with a maximum enhancement in  $\sim 80\%$  NaCl. With the decreasing NaCl concentration at constant ionic strength, the ternary interactions decrease and are minimized at  $\sim 35\%$  NaCl. The ternary interactions are not favored in the mixtures rich in GnAc. This effect is also seen at low ionic strength, say  $0.5 \text{ mol kg}^{-1}$ . In the GnAc-poor mixtures, the ternary interactions are enhanced sharply with increasing ionic strength. This enhancement is poor in the NaCl-rich mixtures at constant ionic strength. On the other hand, the quaternary interactions are found to be significant at lower ionic strength, particularly in the GnAc-poor mixtures, and are absent in the mixture of  $I > 1 \text{ mol kg}^{-1}$ . In the NaCl with GnAc mixtures ( $I < 1 \text{ mol kg}^{-1}$ ) rich in NaCl, the quaternary interactions are maximized in  $\sim 80\%$  NaCl (see Figure 3a and Supporting Information Figure S2).

With the increasing concentration of GnAc, the quaternary interactions decrease significantly. In a nutshell, at  $y_B = 0.5$  and  $I = 0.5 \text{ mol kg}^{-1}$ , 53% of pairs, 16% of triplets, and 31% of quaternary interactions contribute to  $\Delta_m G^E$  in the NaCl–GnAc mixture. On the other hand, at  $I = 2.5 \text{ mol kg}^{-1}$ ,  $y_B = 0.5$ , the contributions of the binary, ternary, and quaternary interactions to  $\Delta_m G^E$  are estimated to be 35, 15, and 50%, respectively.

In terms of total  $\Delta_m G^E$ , the minimum occurs in about 20% of GnAc in the NaCl–GnAc mixtures, indicating that the water molecules are ordered in this region. However, since GnAc is a structure breaker, a higher concentration of GnAc at constant ionic strength decreases the orderliness of water molecules. The ternary and quaternary ionic interactions emerge into the picture with an increasing concentration of GnAc at the expense of binary interactions.

The newly arrived  $\Delta_m G^E$  values are minimized at  $\sim 25\%$   $\text{GnNO}_3$  and become zero at  $\sim 70\%$   $\text{GnNO}_3$  in its mixtures with NaCl, showing neutralization of hydrophilic forces ( $\text{Na}^+$ ) and hydrophobic forces ( $\text{Gn}^+$ ). In the NaCl-poor mixtures, the effect of  $\text{GnNO}_3$  on  $\Delta_m G^E$  is less than that of GnAc. The pairwise interactions do not contribute to  $\Delta_m G^E$  in the case of NaCl and  $\text{GnNO}_3$  at all compositions and ionic strengths. The ternary interactions in this system are present and are weaker in strength as compared to the quaternary interactions. One notes the asymmetry in the  $\Delta_m G^E - y_B$  curve in the low NaCl mixture, indicating maximum quaternary interactions. The ternary interactions reduce with increasing ionic strength in the  $\text{GnNO}_3$ -poor mixtures. This reduction in the ternary interactions is compensated by the quaternary interactions that are progressively present with the increase in ionic strength. This situation becomes opposite in the  $\text{GnNO}_3$ -rich mixtures with NaCl. For example, in the 20%  $\text{GnNO}_3$  mixture, the quaternary interactions contribute  $\sim 22\%$  at  $I = 0.5 \text{ mol kg}^{-1}$ , which is enhanced to

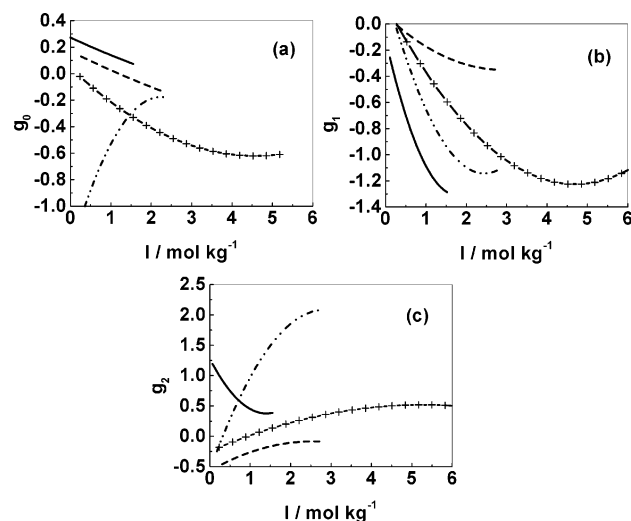
$\sim 57\%$  at  $I = 1.4 \text{ mol kg}^{-1}$ . This trend is balanced by the ternary interactions that are lowered from 37% at  $I = 0.5 \text{ mol kg}^{-1}$  to 8% at  $I = 1.4 \text{ mol kg}^{-1}$ . However, in the  $\text{GnNO}_3$ -rich mixture, say  $y_B = 0.8$ , the quaternary interactions are inhibited from  $\sim 35$  to 19% while going from  $I = 0.5$  to  $1.4 \text{ mol kg}^{-1}$ . The triplets are enhanced up to 19% at  $I = 1.4 \text{ mol kg}^{-1}$  as compared to those at  $I = 0.5 \text{ mol kg}^{-1}$  (Figure 3b and Supporting Information Figure S3).

When  $\text{GnClO}_4$  is mixed with NaCl, the binary interactions become important both at low and at high ionic strengths. These binary interactions are maximized in about 50% mixture at all studied ionic strengths. Lower ionic strengths of the mixtures are not characterized by the ternary interactions. The ternary interactions are enhanced with the ionic strength of the mixture. At  $I = 2.4 \text{ mol kg}^{-1}$ , the ternary interactions are dominant in the NaCl-rich region and decrease upon the addition of  $\text{GnClO}_4$ . The ternary interactions are not favored in these mixtures containing more than 70%  $\text{GnClO}_4$ . The quaternary interactions are not favored in this system at higher ionic strengths. However, at  $I = 0.5$  and  $1 \text{ mol kg}^{-1}$ , the  $\text{GnClO}_4$ -poor mixture is enriched with quadruplets. When higher concentrations of  $\text{GnClO}_4$  are added to NaCl at constant  $I = 0.5$  or  $1 \text{ mol kg}^{-1}$ , the quaternary interactions are not favored. For example, in a 20% mixture of  $\text{GnClO}_4$  at  $I = 0.5 \text{ mol kg}^{-1}$ , the binary interactions increase with increasing ionic strength, while the quaternary interactions follow an inverse rule (Figure 3c and Supporting Information Figure S4).

Upon mixing with  $\text{Gn}_2\text{SO}_4$  in NaCl at high ionic strength, the binary interactions are favored and are enhanced with ionic strength at all the mixture compositions. At a lower ionic strength, the binary interactions are not favored. The ternary interactions occur at all of the ionic strengths and are maximized in an  $\sim 20\%$  mixture of  $\text{Gn}_2\text{SO}_4$  in NaCl. The ternary interactions are reduced with increasing concentration of  $\text{Gn}_2\text{SO}_4$  (i.e., the mixture containing above 80%  $\text{Gn}_2\text{SO}_4$ ) at higher ionic strengths. On the other hand, these mixtures with  $y_B \leq 0.5$  and up to  $I = 1.5 \text{ mol kg}^{-1}$  are enriched with quadruplets, which are absent at  $I = 3$  and  $6 \text{ mol kg}^{-1}$ . The quaternary interactions are significant in the middle compositions of NaCl– $\text{Gn}_2\text{SO}_4$  mixtures at low ionic strengths. In the  $\text{Gn}_2\text{SO}_4$ -rich mixtures at the highest ionic strength  $I = 6 \text{ mol kg}^{-1}$ , the enhanced contribution of the binary interactions is compensated by the reduced ternary and quaternary interactions (Figure 3d and Supporting Information Figure S5).

The ions with the same structure breaking or making effect on water attract each other and consequently lower the free energy of ions. Accordingly, two hydrophobic ions attract each other, while there will be repulsion between two hydrophilic ions of the same charge. Also, the hydrophilic ions of the opposite charge attract each other. There is repulsion between a hydrophilic and hydrophobic ion. Thus, the negative contribution to the excess free energy indicates an attraction, while the positive one a repulsion.<sup>19b,29,30</sup>

The  $\Delta_m G^E$  values obtained from the revised method were fitted to FCIET (eq 13) to give the modified Friedman parameters— $g_0$ ,  $g_1$ , and  $g_2$ . These parameters are listed in Supporting Information Table S1. In parts a, b, and c of Figure 4 is shown the ionic strength dependence of the parameters  $g_0$ ,  $g_1$ , and  $g_2$ , respectively, for all four systems. The ionic strength dependence of these parameters is quite different from the trends obtained by the use of PSIIT.<sup>22</sup> In the conventional manner,  $g_0$ ,  $g_1$ , and  $g_2$  are related to the binary, ternary, and quaternary interactions, respectively. However, as shown later, the binary interactions are represented partially by  $g_0$ , while the ternary



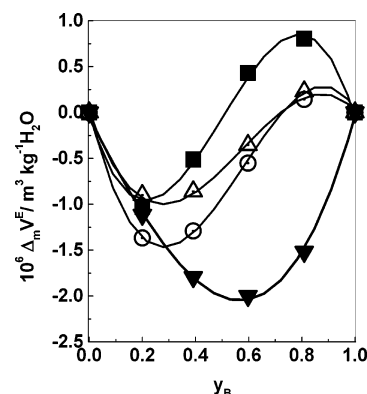
**Figure 4.** Ionic strength dependence of the Friedman parameters: (a)  $g_0$ ; (b)  $g_1$ ; (c)  $g_2$ . For symbols, see Figure 1.

interactions, by both  $g_0$  and  $g_1$ . These Friedman parameters can also be obtained from the SRJ parameters by the relationships shown earlier in the paper.

In the mixtures of NaCl with GnAc,  $g_0$  is positive at lower ionic strengths,  $I < 1 \text{ mol kg}^{-1}$ . The  $g_0$  parameter decreases with an increase in the ionic strength of the mixtures. It suggests that common ion pairing, for example,  $\text{Na}^+ - \text{Na}^+$ ,  $\text{Gn}^+ - \text{Gn}^+$ ,  $\text{Cl}^- - \text{Cl}^-$ , and  $\text{Ac}^- - \text{Ac}^-$ , is more preferred in the region of low ionic strengths as compared with the mixed ion pairs, such as  $\text{Na}^+ - \text{Gn}^+$  and  $\text{Cl}^- - \text{Ac}^-$ . In the region of lower ionic strengths, the common pairwise interactions are caused by strong hydrophobic interactions between two  $\text{Gn}^+$  species. The relative mutual interactions between two  $\text{Gn}^+$  ions are an example of hydrophobic bonding possibly due to a large entropy change of water, which accompanies the formation of pairs, triplets, and quadruplets. In the mixtures of higher ionic strengths,  $I > 1 \text{ mol kg}^{-1}$ , the picture, however, is reversed as the sign of  $g_0$  changes from positive to negative. In this range, the mixed ion pairs dominate over those made up of common ions. The decreased  $g_1$  values with ionic strength indicate the presence of the ternary interactions, which dominate at higher ionic strengths. The quaternary interactions are, however, inhibited when one proceeds from lower to higher ionic strength.

During the mixing of NaCl with  $\text{GnNO}_3$ , the sign of  $g_0$  is positive throughout the ionic strengths studied, indicating the preference of  $\text{Na}^+ - \text{Na}^+$  and  $\text{Gn}^+ - \text{Gn}^+$  interactions. In this case, unlike NaCl–GnAc mixtures,  $g_0$  does not change its sign with ionic strength. The ternary interactions are weak but contribute throughout the ionic strength. These interactions are maximized at the highest ionic strength. The quaternary interactions are inhibited in this system at all of the ionic strengths.

In the mixtures of NaCl with  $\text{GnNO}_3$  and with  $\text{Gn}_2\text{SO}_4$ ,  $g_0$  is negative throughout the ionic strengths investigated. This suggests that the  $\text{Na}^+ - \text{Gn}^+$  interactions in the presence of  $\text{ClO}_4^-$  and  $\text{SO}_4^{2-}$  anions are more preferred over the interactions occurring between common ions, such as  $\text{Na}^+ - \text{Na}^+$  and  $\text{Gn}^+ - \text{Gn}^+$ . From Figure 4a, it is clear that the nature of the anion plays an important role in deciding whether mixed cations will be preferred over common cations. This is also true in the case of anion mixing. However, in the NaCl– $\text{GnClO}_4$  mixtures,  $g_0$ , which is negative, increases sharply up to  $I = 2 \text{ mol kg}^{-1}$ , indicating the decreased role of mixed cation pairs, such as  $\text{Na}^+ - \text{Gn}^+$ , in the mixtures. The ternary interactions are favored



**Figure 5.**  $\Delta_m V^E$  versus  $y_B$  plots for the mixtures of NaCl with (■) GnAc at  $I = 2.5 \text{ mol kg}^{-1}$ , (△)  $\text{GnNO}_3$  at  $I = 1.4 \text{ mol kg}^{-1}$ , (○)  $\text{GnClO}_4$  at  $I = 2.6 \text{ mol kg}^{-1}$ , and (▼)  $\text{Gn}_2\text{SO}_4$  at  $I = 6 \text{ mol kg}^{-1}$ ; points are experimental.

with the increasing ionic strength, while the quaternary interactions are inhibited in the mixtures of NaCl– $\text{GnClO}_4$ . In the NaCl– $\text{Gn}_2\text{SO}_4$  mixtures, the variation of mixed ions,  $\text{Na}^+ - \text{Gn}^+$  and  $\text{Cl}^- - \text{SO}_4^{2-}$ , does not change with  $I > 3 \text{ mol kg}^{-1}$ . A sharp decrease in  $g_1$  with ionic strength up to  $3 \text{ mol kg}^{-1}$  for the mixing of NaCl and  $\text{Gn}_2\text{SO}_4$  denotes the presence of ternary interactions. In the  $\text{Gn}_2\text{SO}_4$  mixtures, the quaternary interactions are favored at low ionic strengths only and are unfavored at  $I > 1 \text{ mol kg}^{-1}$ . Thus, the quaternary interactions contribute to total  $\Delta_m G^E$  at very low ionic strengths.

To obtain support for the above-mentioned explanation on  $\Delta_m G^E$ , we now examine the excess volumes on mixing,  $\Delta_m V^E$  (recorded in Supporting Information Table S2), for the mixtures of NaCl with GnAc,  $\text{GnNO}_3$ ,  $\text{GnClO}_4$ , and  $\text{Gn}_2\text{SO}_4$  at different ionic strengths. The  $\Delta_m V^E - y_B$  plots of these systems at their highest ionic strengths are shown in Figure 5. The SRJ mixing parameters for  $\Delta_m V^E$  of aqueous mixtures of the guanidinium salts with NaCl are listed in Table 3. We do not list the SRJ parameters for pure electrolytes here, as we made direct measurements of  $\Delta_m V^E$  rather than calculating them from density data via the apparent molar volumes, as shown in our earlier work.<sup>20</sup> Upon mixing GnAc,  $\text{GnNO}_3$ , and  $\text{GnClO}_4$  with NaCl, the  $\Delta_m V^E$  values become negative, showing that the water molecules are ordered in the NaCl-rich mixtures.

The  $y_B$  values at which these minima in  $\Delta_m V^E$  are noted are independent of the ionic strengths of the mixtures. The  $\Delta_m V^E$  values after passing through zero become positive in the mixtures rich in the above guanidinium salts. Again, the  $y_B$  values (the NaCl-rich mixtures with low  $y_B$ , say 0.2) at which maxima in  $\Delta_m V^E$  are observed are seen to be independent of ionic strength. The water molecules are disordered in the mixtures rich in GnAc,  $\text{GnNO}_3$ , and  $\text{GnClO}_4$ . This effect is expected, as the hydrophobic effect caused by these guanidinium salts (except  $\text{Gn}_2\text{SO}_4$ ) overcomes the hydrophobic effect of  $\text{Na}^+$ . The  $y_B$  values at which  $\Delta_m V^E$  becomes zero are 0.51, 0.73, and 0.72 for the mixtures of NaCl with GnAc,  $\text{GnNO}_3$ , and  $\text{GnClO}_4$ , respectively. The mixing of NaCl with  $\text{Gn}_2\text{SO}_4$ , however, does not show a similar behavior. In this case, the  $\Delta_m V^E$  values are negative throughout irrespective of the compositions of the mixtures and ionic strengths. The  $\Delta_m V^E - y_B$  plots depict an asymmetric parabola at all of the ionic strengths.

A notable feature of this work is that  $\Delta_m V^E$  data support the information obtained from the analysis of  $\Delta_m G^E$  for all four mixtures.

Let us now examine the contributions of the binary, ternary, and quaternary interaction terms in the case of  $\Delta_m V^E$ . To compute the contributions of the mixing terms, the experimental



**TABLE 3: Best SRJ Mixing Parameters Together with Their Standard Errors for  $\Delta_m V^E$  of the NaCl–Guanidinium Salt Systems at 298.15 K**

$10^6 \times \text{parameter}$	NaCl–GnAc	NaCl–GnNO <sub>3</sub>	NaCl–GnClO <sub>4</sub>	NaCl–Gn <sub>2</sub> SO <sub>4</sub>
$b^{(0.1)V}/(\text{m}^3 \text{ mol}^{-2} \text{ kg})$	$0.1439 \pm 0.0004$	$-0.9711 \pm 0.0007$	$-1.3405 \pm 0.0009$	$-0.7535 \pm 0.0008$
$b^{(0.2)V}/(\text{m}^3 \text{ mol}^{-3} \text{ kg}^2)$	$-0.1124 \pm 0.0008$	$0.6853 \pm 0.0011$	$0.7224 \pm 0.0014$	$0.6538 \pm 0.0012$
$b^{(0.3)V}/(\text{m}^3 \text{ mol}^{-4} \text{ kg}^3)$	$0.0157 \pm 0.0004$	$-0.1615 \pm 0.0008$	$-0.0983 \pm 0.0009$	$-0.1955 \pm 0.0011$
$b^{(1.2)V}/(\text{m}^3 \text{ mol}^{-3} \text{ kg}^2)$	$-0.1726 \pm 0.0007$	$-0.7821 \pm 0.0013$	$-0.8522 \pm 0.0020$	$-0.9430 \pm 0.0022$
$b^{(1.3)V}/(\text{m}^3 \text{ mol}^{-4} \text{ kg}^3)$	$0.0138 \pm 0.0009$	$0.0252 \pm 0.0007$	$0.0199 \pm 0.0008$	$0.0385 \pm 0.0011$
$b^{(2.3)V}/(\text{m}^3 \text{ mol}^{-4} \text{ kg}^3)$	$0.0099 \pm 0.0014$	$0.0158 \pm 0.0015$	$0.0158 \pm 0.0017$	$0.0343 \pm 0.0026$
$10^6 \text{rmsd}/(\text{m}^3 \text{ kg}^{-1})$	0.006	0.007	0.006	0.008

$\Delta_m V^E$  values were fitted to eq 21 to yield the Friedman parameters— $v_0$ ,  $v_1$ , and  $v_2$ —for volume. These Friedman parameters were then employed to calculate the SRJ parameters for volume by using eq 16. The SRJ parameters for volume were substituted in eqs 22–24 to give the contribution of each term ( $\Delta_m V_P^E$ ,  $\Delta_m V_t^E$ , and  $\Delta_m V_q^E$ ) to  $\Delta_m V^E$  of the mixtures (Figure 6) as a function of  $y_B$  at the highest ionic strengths. The ionic strength dependence of the contribution made by the binary, ternary, and quaternary interactions to the total  $\Delta_m V^E$  values of the mixtures at different  $y_B$  values is demonstrated in Supporting Information Figures S6–S9.

In the NaCl–GnAc system (Figure 6a), the binary interactions are dominant except at the low ionic strengths studied. These binary interactions were enhanced with an increase in the ionic strength. The ternary interactions are maximized in ~20% GnAc, which decreases upon the addition of GnAc at constant ionic strength. In the mixture containing GnAc > 60%, the ternary interactions are inhibited and are minimized in the mixtures containing about ~60% GnAc. In the low GnAc region, the ternary interactions are enhanced with increasing ionic strength. The quaternary interactions are favored in the mixtures rich in NaCl at low ionic strengths only. The binary, ternary, and quaternary interactions contribute ~41, 24, and

35%, respectively, in the NaCl–GnAc mixtures at  $I = 2.5 \text{ mol kg}^{-1}$  and  $y_B = 0.5$ . The effect of various terms on  $\Delta_m V^E$  of NaCl–GnAc mixtures can be understood in a fashion similar to  $\Delta_m G^E$ .

In the mixtures of NaCl with GnNO<sub>3</sub> (Figure 6b), the binary interactions are unfavored throughout the ionic strengths. Also noted are the ternary interactions showing a weak independence of the ionic strength of the mixtures. The mixtures are characterized by both the ternary and quaternary interactions, with the former exhibiting a weaker dependence on ionic strength than the latter. The variations in the ternary and quaternary interactions in both GnNO<sub>3</sub>-poor and -rich mixtures with NaCl as obtained from the analysis of the  $\Delta_m V^E$  data are similar to those obtained for  $\Delta_m G^E$  as discussed above.

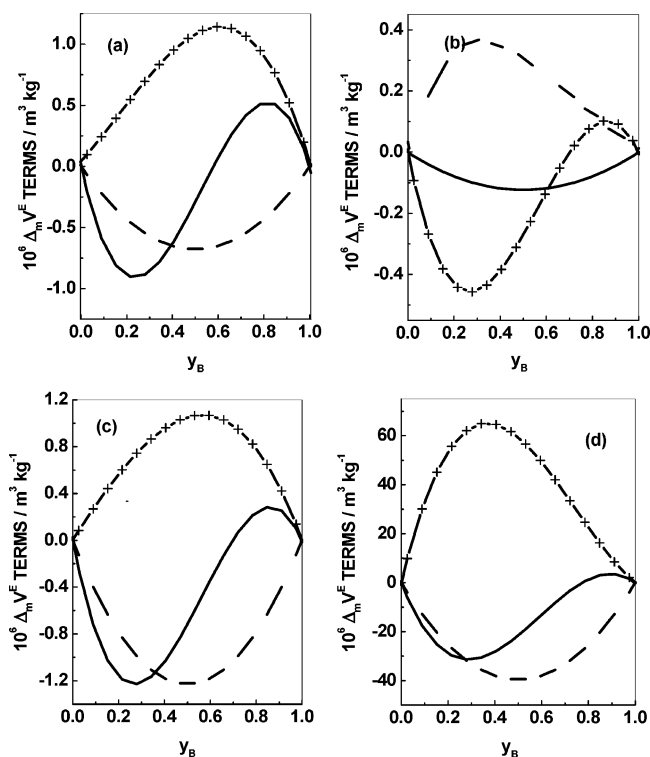
The mixing of NaCl and GnClO<sub>4</sub> (Figure 6c) is favored by the binary interaction terms that are enhanced with an increase in the ionic strength. The ternary interactions are enhanced in the NaCl-rich mixtures with GnClO<sub>4</sub>. The addition of GnClO<sub>4</sub> in NaCl decreases the ternary interactions in the mixtures containing above 70% GnClO<sub>4</sub>. These mixtures are not characterized by the quaternary interactions except at very low ionic strength with NaCl-rich mixtures, in which the binary interactions become significant.

The mixing of NaCl with Gn<sub>2</sub>SO<sub>4</sub> (Figure 6d) is enriched with the binary interactions that increase with an increase in the ionic strengths of the mixtures. On the other hand, the ternary interactions are favored in the NaCl-poor mixtures. These interactions are inhibited in the Gn<sub>2</sub>SO<sub>4</sub>-rich mixtures at high ionic strengths. An analysis of the mixtures of the lower ionic strengths shows the presence of the quaternary interactions, which are inhibited in the mixtures of higher ionic strengths.

Ionic strength dependence of the Friedman parameters for volume— $v_0$ ,  $v_1$ , and  $v_2$ —for aqueous mixtures of the guanidinium salts with NaCl, listed in Supporting Information Table S3, is depicted in Figure 7. In the case of the GnAc system, the  $v_0$  values, which are positive up to  $I = 1.4 \text{ mol kg}^{-1}$ , indicate the dominance of  $\text{Gn}^+ - \text{Gn}^+$  interaction over  $\text{Na}^+ - \text{Gn}^+$ . As shown in the case of  $\Delta_m G^E$ , the  $\text{Gn}^+ - \text{Gn}^+$  type of interactions are the result of strong hydrophobic interactions. However, in the mixtures of higher ionic strengths, at which the sign of  $g_0$  is changed, the  $\text{Na}^+ - \text{Gn}^+$  interactions are preferred over  $\text{Gn}^+ - \text{Gn}^+$ . The quaternary interactions ( $g_2$ ) are inhibited with increasing ionic strength, while the ternary interactions are enhanced under similar conditions.

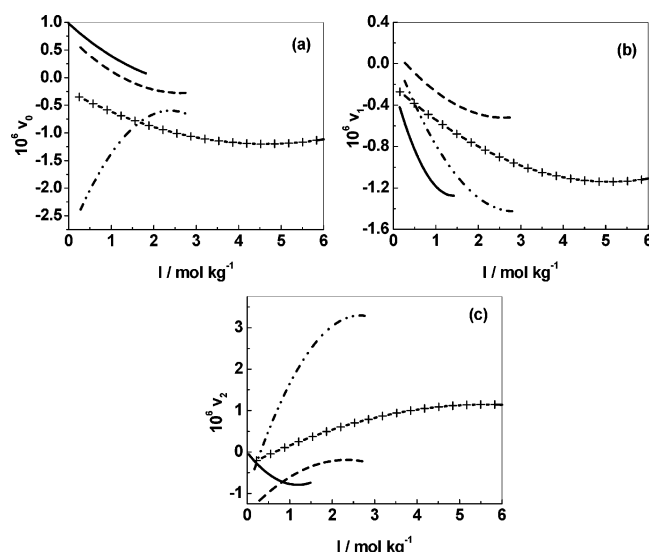
The positive  $v_0$  throughout the ionic strengths suggests the preference of  $\text{Gn}^+ - \text{Gn}^+$  over  $\text{Na}^+ - \text{Gn}^+$  interactions in the mixture of NaCl with GnNO<sub>3</sub>. However, this preference seems to reduce with increasing ionic strength and the ternary interactions come into play. The quaternary ( $v_2$ ) interactions play a significant role in determining  $\Delta_m V^E$  in terms of Friedman's theory.

The mixed  $\text{Na}^+ - \text{Gn}^+$  pairs dominate over the common cation  $\text{Na}^+ - \text{Na}^+$  and  $\text{Gn}^+ - \text{Gn}^+$  pairs during the mixing of NaCl with GnClO<sub>4</sub>. This preference becomes weaker at higher



**Figure 6.** Contribution of (---) binary  $\Delta_m V_P^E$ , (—) ternary  $\Delta_m V_t^E$ , and (— + —) quaternary  $\Delta_m V_q^E$  interaction terms to total  $\Delta_m V^E$  values for the mixtures of NaCl with (a) GnAc at  $I = 2.5 \text{ mol kg}^{-1}$ , (b) GnNO<sub>3</sub> at  $I = 1.4 \text{ mol kg}^{-1}$ , (c) GnClO<sub>4</sub> at  $I = 2.6 \text{ mol kg}^{-1}$ , and (d) Gn<sub>2</sub>SO<sub>4</sub> at  $I = 6 \text{ mol kg}^{-1}$ .





**Figure 7.** Ionic strength dependence of Friedman parameters for  $\Delta_m V^E$ : (a)  $v_0$ ; (b)  $v_1$ ; (c)  $v_2$ . For symbols, see Figure 1.

ionic strengths. The decreasing  $v_1$  with ionic strength suggests the enhanced role of the ternary interactions in this system at the expense of the quaternary interactions. Upon mixing NaCl and  $\text{Gn}_2\text{SO}_4$ , the binary interactions as shown by  $v_0$  are not greatly varied with ionic strength. The mixed  $\text{Na}^+ - \text{Gn}^+$  type of interactions are found to be important, but a steady increase in the ternary interactions with ionic strength is seen. The  $\text{Na}^+ - \text{Gn}^+$  pairs are preferred over the  $\text{Gn}^+ - \text{Gn}^+$  pairs. At very low ionic strength, the quaternary interaction terms play role. These interactions ( $v_2$ ) become unfavorable in the mixtures of higher ionic strengths.

A thorough investigation has shown that we have obtained a consistent picture of ionic interactions analyzed by both the  $\Delta_m G^E$  and  $\Delta_m V^E$  values. For example, in the case of the NaCl–GnAc system, a dominance of the binary interactions except at very low ionic strength is seen in both of the properties. Similarly, the ternary interactions are available in the NaCl-rich region, a situation supported by both  $\Delta_m G^E$  and  $\Delta_m V^E$  data. One can obtain similar consistent information on the quaternary interactions in the NaCl-rich regions at low ionic strengths. In short, the nature, type, and estimates of the interactions present in aqueous mixtures of the guanidinium salts with NaCl are fully consistent, as seen from both the  $\Delta_m G^E$  and  $\Delta_m V^E$  values of the mixtures.

As seen above, the approach developed by Wigent and Leifer provides a powerful tool for separating the binary, ternary, and quaternary interactions by the use of the Scatchard parameters, which is otherwise not possible by Friedman's interaction parameters alone. It is possible to interpret the behavior of these systems with the help of both the Friedman interaction and Scatchard parameters.

## Conclusions

In conclusion, the method developed by Wigent and Leifer, who used the Scatchard–Rush–Johnson and Friedman's cluster integration expansion theories, can account for a more complete description of ionic interactions in aqueous ionic solutions with hydrophobic species. As such, there is no provision in Pitzer's specific ion interaction theory to consider explicitly the effects due to quaternary and higher-order interactions. As shown earlier during the analysis of osmotic coefficient data,<sup>11</sup> it was not the correct way to calculate quaternary interactions from the residuals of the thermodynamic property obtained after incor-

poration of the binary and ternary interactions. The interactions higher than ternary in the systems discussed above should be evaluated within the framework of the method of Wigent and Leifer. Further, the interactions between two guanidinium cations are significant and should not be ignored. Another important conclusion of this work is that, though the Pitzer equations can be used with confidence to analyze the thermodynamic properties of strong electrolytes in general, the use of the above methodology is recommended when the systems contain hydrophobic and/or clathrate-forming ionic solutes. We are now incorporating the above LW method for quantifying the role of various interaction terms in the case of denaturation of protein by  $\text{GnCl}$ . These results will be communicated in due course. It is hoped that the method discussed above will help us in understanding the ionic interactions in more complex aqueous systems, involving biological molecules, as they possess hydrophobic species in their structures.

At last, we state that several other approaches, such as molecular theories and computer simulation methods, could also be useful in understanding the ionic interactions in these mixtures.<sup>31</sup> However, since such methodologies are cumbersome in highly concentrated electrolyte mixtures, those too with a hydrophobic component, the present investigation describes various interactions using experimental data and a semiempirical method with greater ease.

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**Supporting Information Available:** Tables listing the values of Friedman parameters and the experimental values of  $\Delta_m V^E$  and Figures showing a typical plot of the re-estimated values of  $\Delta_m G^E$  against  $y_B$ , the contributions of various interaction terms to  $\Delta_m G^E$ , and the contributions of various interaction terms to  $\Delta_m V^E$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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