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Thermodynamic Quantities of Surface Formation of Aqueous Electrolyte Solutions

II. Mixed Aqueous Solutions of NaCl and MgCl$_2$

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The surface tensions of binary salt mixtures made up from NaCl and MgCl$_2$ in aqueous solution were measured as a function of concentration and temperature. By analyzing the results, the thermodynamic quantities of surface formation such as entropy (Δs), Helmholtz free energy (Δf), and energy of surface formation (Δu) were evaluated. The Δf of the mixtures positively deviates from the straight line connecting those of NaCl and MgCl$_2$ aqueous solutions. On the other hand, Δs shows negative deviation from the linear relation. © 1999 Academic Press

Key Words: **surface tension; electrolytes; salts; mixture of salts; sodium chloride; magnesium chloride.**

INTRODUCTION

The surface tension-versus-concentration relations of aqueous solutions of simple salts have been measured by many researchers in order to elucidate the structure of the surface region. The early investigations were reviewed by Randels (1) and the following works were reviewed briefly in the introduction section of Weissenborn and Pugh's recent work (2). Notably the ion free layer model has been figured and has been used to explore properties of the surface region of aqueous salt solution (3–5). Johansson and Erikkson (3) explained the detailed profile of the surface zone based on the two Gibbs dividing surfaces, for which the excess number of moles of water and salts are, respectively, set equal to zero. Further studies have been made to elucidate properties and structures of the ion free layer defined by the two dividing surfaces (4, 5). Although it is probably true that the top layer of an aqueous salt solution is composed of only water molecules, several authors are reluctant about using the model to explore properties of the surface region of aqueous salt solution (2, 6). It stands to reason from a thermodynamic point of view that the surface region is a solution composed by water, air, and salt. If salt adsorbs at the air–water surface and interacts with surface water molecules, we expect that thermodynamic quantities of surface formations of mixed aqueous salt solution would reflect the interaction between two different salts in the surface region.

The temperature effect on the variation of surface tension of aqueous salt solutions has not attracted much investigation thus far. For mixtures of inorganic salts, it is very hard to find literature that considers the temperature effect on surface tension. In part I of this series (7), we demonstrated the significance of the temperature effect on surface tension which enables the evaluation of thermodynamic quantities such as entropy and energy of surface formation. By estimation of such a quantity defined as a change of thermodynamic quantity associated with the formation of the surface (8, 9), it is possible to obtain information of the surface region by means of which the interactions between components may be discussed. In the present study, we intend to evaluate the thermodynamic quantities of surface formation of binary salt mixtures made up from NaCl and MgCl$_2$ in aqueous solution by measuring the surface tension as a function of temperature and concentration.

MATERIALS AND METHOD

NaCl was of standard regent of 99.98% (Manakku Co.). MgCl2 was of high grade at >99.99% (Aldrich). Water was doubly distilled from a dilute alkaline permanganate solution. Surface tension was measured by means of the drop volume method described previously (10).

RESULTS AND DISCUSSION

Surface tension (γ) of the mixed solutions was measured in the concentration range of 0 to 1 mol kg^{-1} and temperature (T) range of 15 to 35°C at 2.5°C intervals. The thermodynamic formulation for the adsorbed films of binary surfactant mixtures was given by Motomura (8). This formulation can be applicable to the aqueous solution of salt mixtures. For the purpose of analysis of the binary mixture of NaCl and MgCl$_2$, which have a common anion but have cations with different valence, it is convenient to write the equations and thermody-

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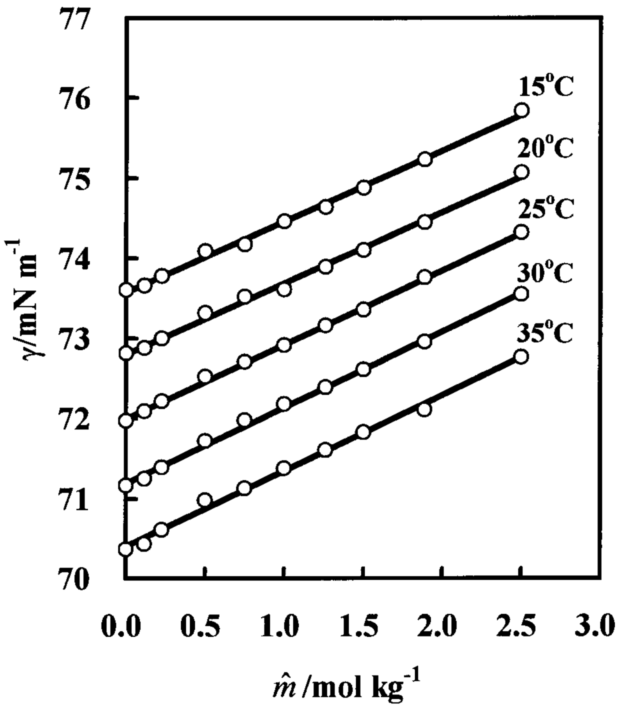

FIG. 1. Surface tension-versus-total molality relations of the mixture of $\hat{X}_2 = 0.60$ at constant temperatures.

namic quantities applicable to this specific case. We may write for the total molality of salts ($\hat{m}$) and the mole fraction of $MgCl_2$ ($\hat{X}_2$) the following expressions,

$$\hat{m} = m_{Na^+} + m_{Mg^{2+}} + m_{Cl^-} = 2m_1 + 3m_2 \qquad [1]$$

and

$$\hat{X}_2 = \frac{3m_2}{\hat{m}}, \qquad [2]$$

where m_1 and m_2 are the molality of NaCl and $MgCl_2$, respectively. For the adsorbed film of salts, the total excess number of moles of salts ($\hat{\Gamma}^{H}$) and the corresponding mole fraction of $MgCl_2$ ($\hat{X}_2^{H}$) are given as

$$\hat{\Gamma}^{H} = \Gamma^{H}_{Na^+} + \Gamma^{H}_{Mg^+} + \Gamma^{H}_{Cl^-} \qquad [3]$$

and

$$\hat{X}_2^{H} = \frac{3\Gamma_2^{H}}{\hat{\Gamma}^{H}}, \qquad [4]$$

in which $\Gamma^{H}_{Na^+}$, $\Gamma^{H}_{Mg^{2+}}$, $\Gamma^{H}_{Cl^-}$, and Γ_2^{H} are the excess number of moles of Na^+, Mg^{2+}, Cl^-, and $MgCl_2$ at the surface, respectively. Since $\hat{\Gamma}^{H}$ shows negative values for the aqueous salt solution, it must be noted that the physical significance of the $\hat{X}_2^{H}$ differs essentially from that for the adsorbed film of surfactant mixtures. The variation of γ as a function of T, pressure (p), $\hat{m}$, and $\hat{X}_2$ is then given by (8).

$$\begin{aligned} d\gamma = {} & -\Delta s dT + \Delta \nu dp \\ & - \frac{RT}{\hat{m}}\hat{\Gamma}^{H}\left[1 + \hat{X}_1^{H}\frac{\partial \ln f_1}{\partial \ln \hat{m}} + \hat{X}_2^{H}\frac{\partial \ln f_2}{\partial \ln \hat{m}}\right]d\hat{m} \\ & + RT\hat{\Gamma}^{H}\left[\frac{(\hat{X}_2 - X_2^{H})(3\hat{X}_1 + 4\hat{X}_2 - 2)}{\hat{X}_1\hat{X}_2(3\hat{X}_1 + 4\hat{X}_2)} \right. \\ & \left. - X_1^{H}\frac{\partial \ln f_1}{\partial \hat{X}_2} - X_2^{H}\frac{\partial \ln f_2}{\partial \hat{X}_2}\right]d\hat{X}_2, \end{aligned} \qquad [5]$$

where R is the gas constant, Δs and $\Delta \nu$ are the entropy and volume of surface formation, and f_1 and f_2 are mean activity coefficients of NaCl and $MgCl_2$, respectively.

As an example of the variation of γ of salt mixtures, the γ-versus-$\hat{m}$ relations at fixed T and γ-versus-T relationships at fixed $\hat{m}$ of the mixture of $\hat{X}_2 = 0.60$ are shown in Figs. 1 and 2, respectively. Within the observed ranges of $\hat{m}$ and T, the γ-versus-$\hat{m}$ relationships are almost linear, similar to those observed for single salt solutions, and the slope of the linear regression line obtained by least squares increases with increasing T. The γ-versus-T relationships of the mixture also

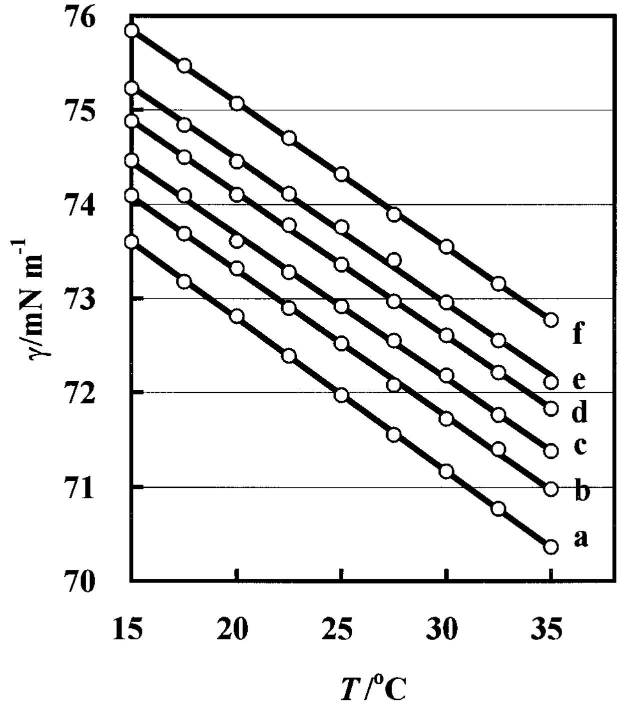

FIG. 2. Surface tension-versus-temperature relations of the mixture of $\hat{X}_2 = 0.60$ at fixed concentrations: (a) $\hat{m} = 0.00$ mol kg^{-1}; (b) 0.50; (c) 1.00; (d) 1.50; (e) 1.89; (f) 2.50.

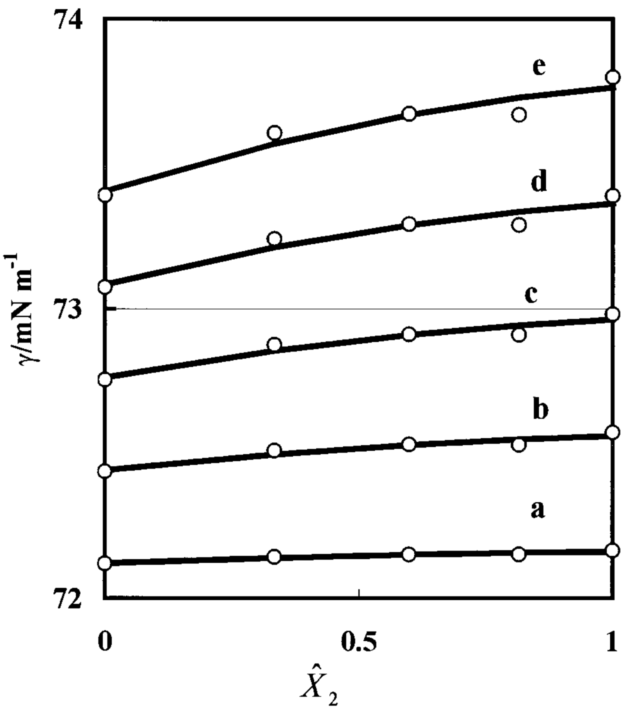

FIG. 3. Surface tension-versus-composition relations of the mixtures at constant concentrations: (a) $\hat{m} = 0.2$ mol kg^{-1}; (b) 0.6; (c) 1.0; (d) 1.4; (e) 1.8.

show a linear relation as for those observed for a single salt solution. The results observed for mixed salt solutions of different $\hat{X}_2$ also show similar behavior. Figure 3 shows the γ-versus-$\hat{X}_2$ relations at a given $\hat{m}$. Since the numerical value of γ is the same as the Helmfoltz free energy of surface formation (Δf) (9), this figure also shows the variation of Δf with $\hat{X}_2$ at each $\hat{m}$. The difference in Δf between NaCl and $MgCl_2$ becomes appreciable at higher $\hat{m}$. The larger increase in Δf caused by the addition of $MgCl_2$ is attributable to the larger number of charges on $MgCl_2$. For the mixtures, the deviations from the linear variation of Δf are clearly seen.

According to the thermodynamic formulation, the increase in γ due to the addition of salts causes negative adsorption of salt. The calculation of the negative adsorption of the mixture depends upon Eq. [5] and requires knowledge of the activity coefficients of salts and $\hat{X}_2^{\rm H}$. However, the calculation of $\hat{X}_2^{\rm H}$ also requires knowledge of activity coefficients of salts and the value of $\hat{X}_2^{\rm H}$. So we estimated $\hat{X}_2^{\rm H}$ values in the following manner. First, we applied Eq. [5] to $\hat{m}$-versus-$\hat{X}_2$ curves at constant T, p, and γ, assuming that the contribution of the activity coefficients can be negligible, and evaluated the temporary $\hat{X}_2^{\rm H}$ values. We then evaluated the contribution of the activity coefficients using these $\hat{X}_2^{\rm H}$ values and recalculated approximate $\hat{X}_2^{\rm H}$ values using Eq. [5]. The numerical values of the activity coefficients of the mixtures were taken from the work of Wu *et al.* (11). Figure 4 shows the contribution of the activity coefficient on the evaluated $\hat{X}_2^{\rm H}$ values. It is seen that the magnitude is insignificant compared with the difference between the values of $\hat{X}_2^{\rm H}$ and $\hat{X}_2$ values. Using these $\hat{X}_2^{\rm H}$ values and activity coefficients of salts in the mixtures, we then evaluated $\hat{\Gamma}^{\rm H}$ of the mixtures from the slope of γ-versus-$\hat{m}$ curves. The evaluated $\hat{\Gamma}^{\rm H}$ have negative values and the magnitude of the negative adsorption increases with increases in $\hat{m}$. In order to exhibit the effect of mixing on negative adsorption

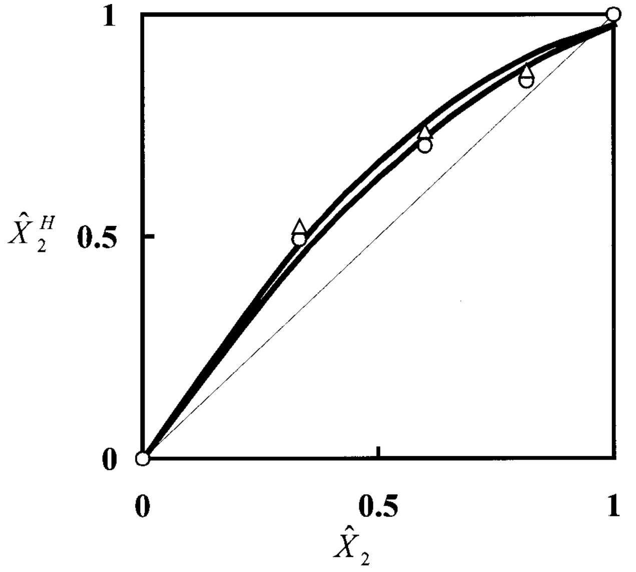

FIG. 4. Composition of $MgCl_2$ defined by the negative adsorption of salts.

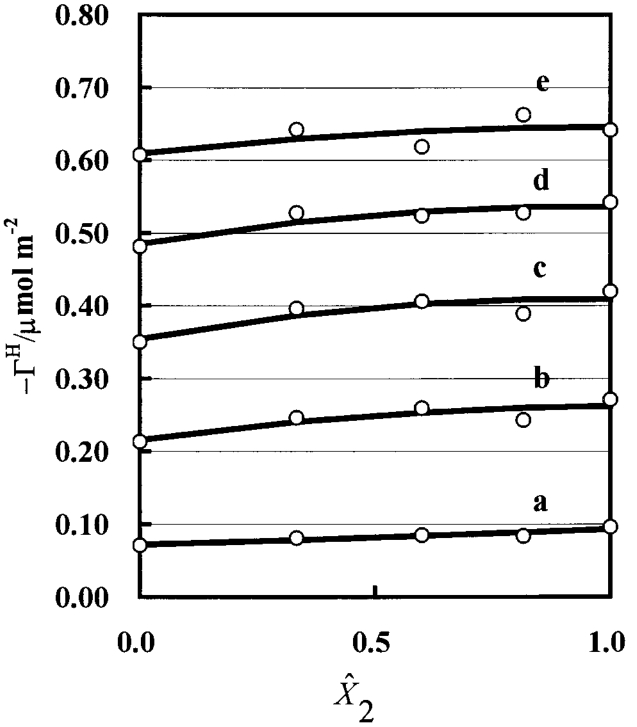

FIG. 5. Total negative adsorption-versus-composition relations at constant total concentrations: (a) $\hat{m} = 0.2$ mol kg^{-1}; (b) 0.6; (c) 1.0; (d) 1.4; (e) 1.8.

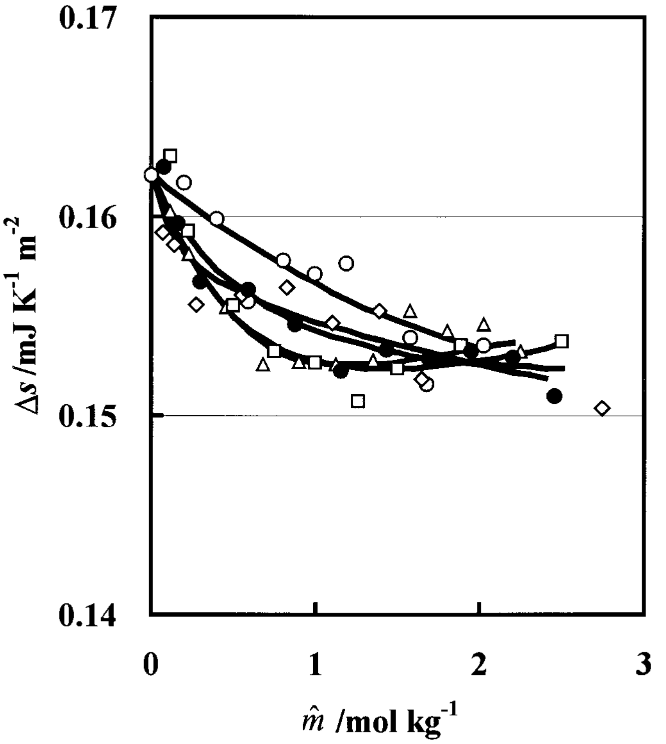

FIG. 6. Entropy of surface formation-versus-total concentration curves of the mixtures at constant composition: (○) $\hat{X}_2 = 0.00$; (△) 0.33; (□) 0.60; (◇) 0.82; (●) 1.00.

we graphed the $\hat{\Gamma}^{\mathrm{H}}$-versus-$\hat{X}_2$ relation at fixed $\hat{m}$ as shown in Fig. 5. The curves are convex upward, indicating that the mixing of NaCl and $MgCl_2$ enhances the negative adsorption. Although the deviation from the linear relation is small, this observation indicates that Na^+ and Mg^{2+} interact with each other in the surface.

Figure 6 and 7 show Δs-versus-$\hat{m}$ and Δs-versus-$\hat{X}_2$ relations derived from the slopes of the γ-versus-T relations. It is seen that Δs of the mixture decreases steadily with increasing $\hat{m}$ similar in shape to that of $MgCl_2$ and the variation becomes steady in the higher concentration region. It seems likely that the Δs values of NaCl, $MgCl_2$, and mixtures meet at almost the same value, as the concentration becomes higher. The detailed form of these curves at higher concentrations could not be determined because of the relatively large experimental error of 0.002; however, it is obvious that Δs is smaller for mixtures than for the pure salt solutions when compared at fixed $\hat{m}$ at a lower concentration region (Fig. 7). Figure 8 compares the energy of the surface formation (Δu) of mixtures with that of a pure salt solution. The numerical values are calculated from the relation (9),

$$\Delta u = T\Delta s + \gamma, \qquad [6]$$

in which we assumed that the volume of surface formation is negligible (12). The variations of Δu with concentration are slight; however, the deviations from the linear relation of the mixtures are obvious.

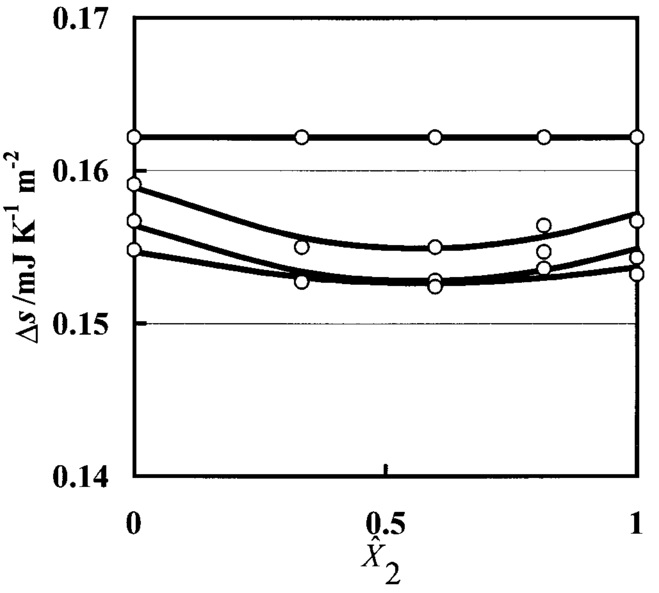

FIG. 7. Entropy of surface formation-versus-composition of the mixtures at constant total concentrations. The total concentration of the curves are 0.0, 0.5, 1.0, 1.5 mol kg^{-1} from top to bottom.

The variation of surface tension of mixtures is insensitive to the change of composition of salts to allow a determination of functional dependence of thermodynamic quantity on composition, but the tendency presented here is at least qualitatively

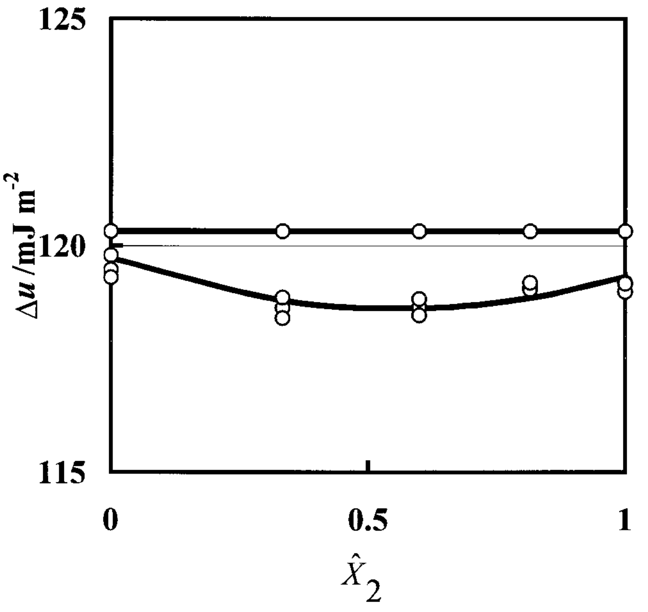

FIG. 8. Entropy of surface formation-versus-composition of the mixtures at constant total concentrations. The total concentration of the curves are 0.0, 0.5, 1.0, 1.5 mol kg^{-1} from top to bottom.

obvious. Surface tension, i.e., Δf, of the mixtures positively deviates from the straight line connecting those of NaCl and $MgCl_2$ aqueous solutions. This deviation corresponds to the findings of the hump on the $\hat{\Gamma}^H$-versus-$\hat{X}_2$ relation (Fig. 5). These results show the extremely complicated nature of the mixed salt solution system, when we consider this behavior with the distinct salt free layer model (3). Weissenborn and Pugh (2) cast doubt on whether the ion free layer model explains the figure of the surface region. They suggested that the concentration gradient of dissolved gas near the macroscopic bubble surface has some influence on surface tension. If we consider the surface region as a continuous two-dimensional isotropic solution (9), their suggestion is easily acceptable. We have shown that the adsorption of surfactants from oil phase at the oil–water interface depends on the interactions in the adsorbed film and the affinity between surfactants and water molecules. The adsorption of salts would occur in the same manner of surfactants. $MgCl_2$ characterized by stronger hydration ability is adsorbed less at air–water surface than NaCl. The deviation of the Δf-versus-$\hat{X}$ curve from the linear relation indicates that there are small interactions between Na^+ and Mg^{2+} in the surface region.

Recalling the definition of the thermodynamic quantity of surface formation, the Δs for the NaCl and $MgCl_2$ mixture can be presented as

$$\Delta s = \Gamma^{\mathrm{I}}_{\mathrm{w}}(s^{\mathrm{I}}_{\mathrm{w}} - s^{\mathrm{w}}_{\mathrm{w}}) + \Gamma^{\mathrm{I}}_{\mathrm{a}}(s^{\mathrm{I}}_{\mathrm{a}} - s^{\mathrm{A}}_{\mathrm{a}}) + \sum_i \Gamma^{\mathrm{I}}_i(s^{\mathrm{I}}_i - s^{\mathrm{W}}_i), \quad i = \mathrm{Na}^+, \mathrm{Mg}^{2+}, \mathrm{Cl}^-, \qquad [6]$$

where $\Gamma^{\mathrm{I}}_{\mathrm{w}}$, $\Gamma^{\mathrm{I}}_{\mathrm{a}}$, Γ^{I}_i, and $(s^{\mathrm{I}}_{\mathrm{w}} - s^{\mathrm{w}}_{\mathrm{w}})$, $(s^{\mathrm{I}}_{\mathrm{a}} - s^{\mathrm{A}}_{\mathrm{a}})$, $(s^{\mathrm{I}}_i - s^{\mathrm{W}}_i)$ are the number of moles in the surface region per unit area and the partial molar entropy change of adsorption of water, air, and ions, respectively. If we assume that Γ^{I}_i s are negligibly small and air is hardly soluble with water as the salt free layer model, the contribution of $(s^{\mathrm{I}}_{\mathrm{w}} - s^{\mathrm{w}}_{\mathrm{w}})$ will determine the variation of Δs. However, only the first term is insufficient to explain the minimum observed on Δs-versus-$\hat{X}_2$ curves. It seems likely that the dent would be due to the interaction between Na^+ and Mg^{2+} in the surface region. Similar arguments would be true for the Δu-versus-$\hat{X}_2$ relation (Fig. 8). The dent observed on the Δu-versus-$\hat{X}_2$ relation suggests that we should be concerned about specific interactions between Na^+ and Mg^{2+} in the surface region.

CONCLUSIONS

In part I of this series (7), we examined the effect of cation charge on the thermodynamic quantities of surface formation and showed that these quantities are helpful for understanding the effect of inorganic salts on water. In accordance with the experimental results of part I, we have examined here the change in these quantities for a mixed aqueous solution of NaCl and $MgCl_2$. For the mixtures Δs and Δu show smaller values than those for a pure aqueous solution when compared at fixed $\hat{m}$, while Δf of the mixtures positively deviates from the straight line connecting those of NaCl and $MgCl_2$. This observation indicates that electrical effects may take place between Na^+ and Mg^{2+}. Though thermodynamic quantities presented here do not provide a detailed structure of the surface region, we believe that an ion free layer model or the thickness of the ion free layer is insignificant to explain our experimental results.

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