Quantitative Analysis of Water Activity Related to Hydration Structure in Highly Concentrated Aqueous Electrolyte Solutions

Hideshi MAKI, a, b, *, Ren SOGAWA, b Masaharu FUKUI, b Shigehito DEKI, b, † and Minoru MIZUHATA b

a Center for Environmental Management, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan
b Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University,
1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan

* Corresponding author: maki@kobe-u.ac.jp

ABSTRACT

The measurements on the activity and solvation of H2O in hydrate melts and aqueous electrolyte solutions containing various metal chlorides were carried out by a vapor pressure measurement using a transpiration method and 1H quantitative NMR (1H qNMR). The electrolyte concentration dependence of the detection rate of H2O by the vapor pressure measurement clearly showed the change of the network structure of water including the second hydration spheres. The correlation between the enthalpy and entropy of vaporization showed the existence of different kinds of water-cation interactions.

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1. Introduction

Recently, the secondary batteries using aqueous electrolyte as an electrolytic solution have been extensively studied.1–6 In the study of the secondary batteries using aqueous electrolyte, the attempts are made to ease desolvation, the extend of potential window from the viewpoint of equilibrium and reaction rate, and increase the electromotive force of the secondary batteries by reducing the activity of water using a concentrated electrolyte solution.1,6,7 In this case, unlike the hydration structure of ordinary electrolytes, it is necessary to investigate the dynamic behavior of the solvent in a state which a sufficient hydration sphere is not constructed, however the information about it is still not sufficient. Therefore, in this study, the quantitative 1H NMR (1H qNMR)8–11 method and the vapor pressure measurement were carried out using highly concentrated aqueous electrolyte solution and hydrate melts, and the activity of water, the ion hydration structure, the water-water and water-cation interactions were evaluated.

2. Experimental

2.1 Vapor pressure measurement using a transpiration method

Samples were prepared in various concentration compositions from the reagent grade CaCl2, MnCl2, ZnCl2, and double-distilled water. Vapor pressure of sample solutions was measured at various temperatures by using the transpiration method12–14 with a Karl-Fischer automatic titrator.

From the equilibrium vapor pressure, \( P_{\text{H}_2\text{O}} \), obtained by the above measurement, the activity of water, \( \alpha_{\text{H}_2\text{O}} \), can be determined using the following equation:

\[
\alpha_{\text{H}_2\text{O}} = \gamma_{\text{H}_2\text{O}} \cdot X_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}} / P^o
\]

where \( \gamma_{\text{H}_2\text{O}} \) and \( X_{\text{H}_2\text{O}} \) is the activity coefficient, of H2O, the mole fraction of H2O, and the vapor pressure of pure water, \( P^o \), respectively. Furthermore, given that \( P^o \) is the standard pressure, the standard Gibbs evaporation energy, \( \Delta G^o \), is

\[
\Delta G^o = RT \ln P^o - RT \ln P_{\text{H}_2\text{O}} = -RT \ln (P_{\text{H}_2\text{O}} / P^o) = \Delta H^o - T \Delta S^o
\]

where \( R \), \( T \), \( \Delta H^o \) and \( \Delta S^o \) is the gas constant and the temperature of sample solution, the standard vapor enthalpy, and the standard vapor entropy, respectively.

2.2 Quantitation of H2O using 1H qNMR

Samples were prepared in various concentration compositions from the reagent grade LiCl, NaCl, KCl, MgCl2, CaCl2, and double-distilled water. 1H qNMR spectra were observed on an INOVA 400 pulse FT-NMR spectrometer (Varian Inc., USA) at 20 ± 0.5°C. 1H qNMR analysis was carried out using the integrated intensities of 1H NMR signals due to H2O molecules. 1H NMR signal intensities of 20 sample solutions which have different mixing ratios of H2O and D2O (i.e., \( 0 < [\text{H}_2\text{O}] / ([\text{H}_2\text{O}] + [\text{D}_2\text{O}]) < 1 \)) were measured as a calibration curve, and the calibration curve showed a high linearity with a correlation coefficient of 0.9992 or more.

3. Results and Discussion

The dependences of the activity coefficient of H2O on the concentration compositions at various temperatures are shown in Fig. 1. For all sample solutions, \( \gamma_{\text{H}_2\text{O}} \) decreased with decreasing molar ratio of H2O to electrolyte, \( r \) (i.e., \( [\text{H}_2\text{O}] / [\text{C}_X] \) (X = CaCl2, MnCl2, and ZnCl2)), however the decreases of \( \gamma_{\text{H}_2\text{O}} \) are not monotonous. In the CaCl2-H2O system, the decrease of \( \gamma_{\text{H}_2\text{O}} \) becomes remarkable around \( r = 5.5 \), and it is nearly constant in \( r < 5 \). In the MnCl2-H2O system, the decrease of \( \gamma_{\text{H}_2\text{O}} \) was remarkable in \( r < 10 \). In the ZnCl2-H2O system, the decrease of \( \gamma_{\text{H}_2\text{O}} \) becomes remarkable around \( r = 3 \), and it is nearly constant in \( r < 2.5 \). These suggest that the water-water and water-cation interactions becomes strong in the concentration region, and the network structure in solution changes. Furthermore, it should be noted that the previously reported electrical conductivity and its
and ZnCl2-H2O systems.

Discontinuous points are good agreement with those at the above inflection points in Fig. 1. It is obvious that the interaction between molecules in the solution changes markedly at these inflection points. Based on the r dependence of the Barclay-Butler correlation, three types of regions, namely RI, RII and RIII, were defined. The Barclay-Butler plots, namely ΔSf° vs. ΔHf° plots, are shown in Fig. 2. For the CaCl2-, and ZnCl2-H2O systems, these plots show clear discontinuous point, and the r values at the discontinuous points are good agreement with those at the above inflection points.

Figure 1. Dependence of the activity coefficient of H2O on the concentration compositions at various temperatures in the CaCl2- , MnCl2-, and ZnCl2-H2O systems.

Figure 2. Barclay-Butler relationships for the vaporization of CaCl2-, MnCl2-, and ZnCl2-H2O systems.

Figure 3. Determination of hydration number of ions from the slopes of the plots. The dashed line in Fig. 3 shows the extrapolation of the activity coefficient concentration dependence of the detected H2O ratios by 1H qNMR in the dilute electrolyte concentration region of 0.5 mol L−1 or less. Assuming that water molecules are not oriented to isolated ions and weakly interact to contact ion pair.

The dependence of the detected H2O ratios by 1H qNMR in LiCl-, NaCl-, KCl-, MgCl2-, and CaCl2-H2O systems on the r value are shown in Fig. 3. Remarkably, it is obvious that the detected H2O ratios by 1H qNMR (filled circles in Fig. 3) is smaller than the H2O amount (open circles in Fig. 3) calculated from the density measurement of sample solution. The dashed line in Fig. 3 shows the extrapolation of the electrolyte concentration dependence of the detected H2O ratios by 1H qNMR in the dilute electrolyte concentration region of 0.5 mol L−1 or less. Assuming that water molecules in the first hydrated shell of cations cannot be detected by 1H qNMR, the hydration number calculated from the slope of this dashed line tended to agree with the literature value23,24 (Table 1).

This obviously suggests that the mobility of the water molecules bound in the first hydration shell of cations are extremely restricted and thus cannot be detected by 1H NMR. This is in contrast to the activity measurement from vapor pressure which reflects the water-water and water-cation interactions, that is, the network structure of water including the first and second hydration spheres. On the other hand, in the electrolyte concentration of 0.5 mol L−1 or more, the detected H2O ratios by 1H qNMR shows an extraordinary change with increasing electrolyte concentration, namely, they show the local minimum value and increase, then turn to decrease again (LiCl- and NaCl-H2O systems) or the decrease once becomes mildly (MgCl2- and CaCl2-H2O systems). These reversal and mitigation of the decrease in the detected H2O ratios with the increase in the electrolyte concentration (C NaCl = 3 mol L−1, C CaCl2 = 1.5 mol L−1, C MgCl2 = 1 mol L−1) is considered to be owing to the release of H2O which hydrated to the cation and the anion at the initial stage of the formation of contact ion pair. Such a phenomenon is thought to be remarkable in the case of “structure-making ion” which strongly attract water in the hydration shell. Indeed, in the system containing K+ ion which is “structure-breaking ion”, the decrease of the detected H2O ratios by 1H qNMR is monotonous. Furthermore, the hydration structure in the intermediate electrolyte concentration region (i.e., 0.5 < CNaCl < 3 mol L−1, 0.5 < CNaCl < 2 mol L−1, 0.5 < CMgCl2 < 2.5 mol L−1, 0.5 < CCaCl2 < 1.5 mol L−1) may be more destabilized than that in...
the Debye-Hückel region. The water release owing to the formation of contact ion pairs which observed by $^1$H qNMR occurred in the much lower concentration region than the region where the g value reaches the inflection point. This study suggested that the formation behavior of contact ion pairs in highly concentrated aqueous electrolyte solution complicatedly may be changed with increase of the electrolyte concentration. Furthermore, it is shown that the possibility which the NMR signal intensity depends on the physicochemical environment of atoms and molecules. This suggests that quantitative NMR can be used as a novel tool to estimate the activity of observation chemical species. The findings obtained in this study are useful for elucidating of the enlargement of potential window of high concentration aqueous electrolyte solutions and the development of high voltage aqueous secondary batteries.

4. Conclusions

In the measurements of $\gamma$, $\Delta H^0$ and $\Delta S^0$ of H$_2$O by vapor pressure measurement, the changes of the hydration structure in the hydration shell and the interaction between molecules as the increase of the electrolyte concentration was shown. The activity measurement from vapor pressure reflected the change of the network structure of water including the first and second hydration spheres. In the $^1$H qNMR measurement, it was confirmed that a remarkable decrease in the detection rate of H$_2$O molecules as the increase of the electrolyte concentration. It can be regarded as a result of a significant decrease of the H$_2$O mobility in the hydration shell, and this suggests the possibility that the activity of various solvent molecules can be determined by $^1$H qNMR method. Furthermore, the decrease in the detection rate of water molecules was not monotonous with the increase in electrolyte concentration, and showed the inflection point peculiar to ions. It can be considered that the solvation structure of water in the first hydration zone changed by the formation of contact ion pair.

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**Table 1.** Hydration number of cations which calculated from the slope of the dashed line in Fig. 3 and the literature value.$^{22,23}$

|        | Li$^+$ | Na$^+$ | K$^+$ | Mg$^{2+}$ | Ca$^{2+}$ |
|--------|--------|--------|-------|-----------|-----------|
| This study | 5.4    | 6.5    | 7.8   | 7.5       | 8.8       |
| Literature | 4.2$^{23}$ | 5.4$^{23}$ | 6.3$^{23}$ | 6.0$^{24}$ | 7.6$^{23}$ |

**Figure 3.** Detected ratios of H$_2$O by $^1$H qNMR in LiCl-, NaCl-, KCl-, MgCl$_2$-, and CaCl$_2$-H$_2$O systems. (○) Detected H$_2$O amount by $^1$H qNMR; (○) calculated H$_2$O amount from density measurements of sample solutions.