Activity and Activity Coefficient of Water in Aqueous Solutions and Their Relationships with Solution Structure Parameters

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The water activity and the activity coefficient of water (γw) were calculated from the freezing point depression by using the Hildebrand and Scott’s equation for various solutions of electrolytes, sugars, alcohols, amide, and urea. The water activity measured from the freezing point depression was very close to that at room temperature, showing that the effect of temperature on the water activity is negligible. The activity coefficient of water was described well as a function of the solute mole fraction (Xs) by the following equation.

\[ \gamma_w = \exp(\alpha X_s^2 + \beta X_s^3) \]

The parameter α in this equation correlated well with the B-coefficient of viscosity for single-valent electrolytes, with the hydration parameter for nonelectrolytes, and with the number of equatorial-OH groups for sugars suggesting that the solution structure was reflected in this parameter.

Key words: water activity; activity coefficient of water; solution structure; hydration; viscosity

Water activity reflects the macroscopic state of water in food and affects various rate processes such as browning, oxidation, degradation of nutrients, enzyme reaction, and especially the growth rate of microorganisms.† Therefore, the concept of water activity is very important in relation to food preservation.

Although the water activity is very important as described above, there is a criticism that points out that the water activity cannot be a sole credible measure of food safety because the molecular specificity of the solute materials affects the state of water in a different manner.‡

In this paper, the activity coefficient of water, as well as water activity, is analyzed for various aqueous single-component systems. The difference in the concentration dependency was analyzed for activity and activity coefficient of water, and the molecular specificity of the solute is discussed in relation to the aqueous solution structure parameters.

Materials and Methods

Materials: Deoxyribose, ribose, and formamide were purchased from Tokyo Kasei Organic Chemicals. tert-Butyl alcohol was obtained from Wako Chemical Industries. Sodium chloride (superpure) was obtained from Merck KGaA. All of these chemicals were of reagent grade and used without further purification.

Measurement of freezing point depression. For aqueous solutions of sodium chloride, deoxyribose, ribose, formamide, and tert-butyl alcohol, freezing point depression was measured from the melting curve. The sample (5 mL) in a plastic tube (16 mm in diameter), equipped inside with a thermister (0.01°C in accuracy), was frozen completely at −20°C and then warmed in the atmosphere at room temperature. The sample tube was stirred with a Vortex mixer and the change in the temperature of the sample was recorded. For deoxyribose and ribose, the water content was analyzed by drying in a vacuum oven at 70°C for 3 h. For the solutions with other materials, the freezing point data from the literature were used.

Measurement of activity and activity coefficient of water. Water activity, \( \alpha_w \), was calculated from the freezing point depression using Hildebrand and Scott’s equation† as follows:

\[ \ln \alpha_w = -\frac{\Delta H_f (T_f - T)}{RT} + \frac{\Delta C_p}{R} \left( \frac{(T_f - T)}{T} \ln \left( \frac{T_f}{T} \right) \right) \]

where \( T \) is the freezing point of solution (K); \( T_f \) is the freezing point of water (K); \( \Delta H_f \) is the latent heat of water (= 6008 J/K/mol); \( \Delta C_p \) is the change of specific heat of water (≈ 38.7 J/mol·°C); \( R \) is the gas constant.

The activity coefficient of water, \( \gamma_w \), was calculated from the following equation:

\[ \gamma_w = \frac{\alpha_w}{X_w} \]

where \( X_w \) is molar fraction of water in the solution.

Results and Discussion

Freezing point depression

To verify the accuracy in the measurement of the freezing point, sodium chloride solution was used as a test sample. The observed freezing point was within 0.05°C as compared with the data in the literature.§

Activity and activity coefficient of water

As the water activity was calculated from the freezing point in this paper, the effect of temperature on the water activity was checked first because the water activity at the freezing point might be different from that at room temperature. Figure 1 compares the water activities of sucrose and urea solution from the freezing point and those§ measured at 25°C. The difference seems almost negligible for both solutions in a wide concentration range, showing the effectiveness of the estimation of water activity from the freezing point depression.

In the literature, Ferro Fontan and Chirife§ also used Eq. (1) and compared \( \alpha_w \) values at the freezing point and room temperature for various nonelectrolyte and electrolyte solutions and reported that the difference between the two is not likely to be larger than 0.01 \( \alpha_w \) units. Leric
Fig. 1. Comparison of Water Activities Measured at Freezing Point and at 25°C.

\( a_w \) from FPD\textsuperscript{39} (smoothed); \( \bigcirc \), sucrose\textsuperscript{99} at 25 C; \( \bullet \), urea\textsuperscript{90} at 25°C.

Fig. 2. Water Activity and Its Concentration Dependence for Various Aqueous Single-component Systems.

\( \bullet \), urea; \( \bigcirc \), sucrose; \( \triangle \), NaCl. ---, fitted by Eq. (4).

et al.\textsuperscript{11} also used Eq. (1) to calculate \( a_w \) for various single-component solutions and foods such as skim milk, coffee beverage, and fruit juices. They compared their results with \( a_w \) measured by an electric hygrometer and also concluded that the difference between the two methods differed by less than 0.01 \( a_w \) units. Chen\textsuperscript{12} obtained a simplified empirical equation to relate the freezing point with \( a_w \).

Concentration dependence of the activity and activity coefficient of water

Figure 2 shows the effects of concentration, as expressed by molar fraction, on water activity for aqueous solutions of urea, sodium chloride, and sucrose. For sodium chloride solution, the solute was assumed to be completely dissociated into sodium and chloride ions as a strong electrolyte.

When the solution is ideal, the water activity is equal to the molar fraction of water, \( X_w \), in the solution according to Raoult’s law.

\[
a_w = X_w = 1 - X_S
\]

where \( X_S \) is the molar fraction of solute.

For a non-ideal solution, \( a_w \) was approximated by the following equation:

\[
a_w = (1 - X_S)\exp(\alpha X_S^2 + \beta X_S^3)
\]

The solid lines in Fig. 2 are the results calculated by Eq. (4), which showed a good agreement with the experimental results with correlation coefficients higher than 0.999.

Equation (4) was applied to various solutions of electrolytes and nonelectrolytes. Table I summarizes the parameters \( \alpha \) and \( \beta \) in Eq. (4) for electrolyte solutions, which can describe the concentration dependence of water activity with correlation coefficients higher than 0.999.

Table II summarizes the parameters \( \alpha \) and \( \beta \) for various nonelectrolyte solutions. In this case, \( \gamma_w \)'s for most of solutions except formamide were described well by a single parameter equation assuming \( \beta = 0 \) in Eq. (4). The correlation coefficients were higher than 0.999 except for \( t \)-butyl alcohol.

Equation (4) apparently has the same form with the two-parameter Margules equation\textsuperscript{13} as long as water is concerned when the symmetric reference system \( (X_S = 0, \gamma_w = 1; X_w = 0, \gamma_S = 1) \) is used. As for the solute, however, we assume the asymmetric reference system \( (X_S = 0, \gamma_w = 1; \gamma_S = 1) \) so that Eq. (4) cannot be called the Margules equation. There are also many other theoretical equations such as the Wilson, UNIQUAC, and UNIFAC equations\textsuperscript{13} but there is no reason to replace Eq. (4) with those equations because Eq. (4) describes the concentration dependence of \( a_w \) very well. In addition, the aim of this paper is to investigate the physicochemical meaning of the parameter \( \alpha \) in Eq. (4) as described later.

In the literature, Norrish\textsuperscript{14} used the following simple assumption for the excess free energy of a binary mixture \( (\Delta G_e) \).

\[
\Delta G_e = CX_w X_S
\]

where \( C \) is a parameter representing the solute-solvent interaction.
interaction. This corresponds to the single-parameter Margules equation\(^1\) and also a single-parameter model of Eq. (4) as follows.

\[ a_w = (1 - X_3) \exp(\alpha X_3^2) \]  

(6)

Chirife et al.\(^{15,16}\) applied Eq. (6) to solutions of sugars, polyols, amino acids, organic acids, etc. Although they didn’t show the correlation coefficient, Eq. (6) was effective to describe the concentration dependence of \(a_w\) and the reported values of the parameter \(\alpha\) in Eq. (6) are not much different from those obtained here. A single-parameter equation like Eq. (6) is simple and convenient. In some cases, however, a second parameter is necessary to increase accuracy so that the two-parameter equation like Eq. (4) is useful for general applicability.

As for the concentration dependence of water activity, Favetto and Chirife\(^17\) proposed the following simple equation with a single parameter and applied it to various non-electrolyte and electrolyte solutions.

\[ a_w = 1 - Km \]  

(7)

where \(m\) is the molality and \(K\) is an experimental constant. This equation is simple and convenient but less satisfactory in accuracy in some cases. On the contrary, Chen\(^9\) proposed a three-parameter equation for the concentration dependence of \(a_w\) based on an extention of Raoult’s law as follows:

\[ a_w = 1/[1 - 0.0018(\beta + Bm^n)m] \]  

(8)

where \(\beta\), \(B\), and \(n\) are experimental fitting parameters. Although this equation was applicable to various sugars, salts, and acids with a good accuracy to \(\pm 0.001\) \(a_w\) unit, the equation with three parameters seems too complicated.

**Solution structure and activity coefficient of water**

From Eqs. (3) and (4), the activity coefficient of water, \(\gamma_w\), is expressed by the following equation.

\[ \gamma_w = \exp(\alpha X_3^2 + \beta X_3^3) \]  

(9)

The concentration dependence of the activity coefficient of water, described by this equation, is shown in Fig. 3 for urea, sucrose, sodium chloride, and ethanol solutions. The water structure-breaking material\(^{18,19}\) seems to give a \(\gamma_w\) larger than 1 (\(\alpha > 0\)) while the water structure-forming material\(^{18,19}\) seems to give a \(\gamma_w\) smaller than 1 (\(\alpha < 0\)).

The relationship between the parameter \(\alpha\) in Eq. (4) and the solution structure was explored more. For electrolytes, the water structure has been described by the \(B\)-coefficient of viscosity.\(^{18}\) Therefore, the \(\alpha\) value was compared with \(B\)-coefficient of viscosity for single-valent electrolyte solutions. The result in Fig. 4 shows a good correlation between the two parameters \((r = 0.979)\). The electrolytes in Fig. 4 were strong electrolytes so that the complete dissociation could be assumed while the same assumption was not applicable for multivalent electrolytes.

For nonelectrolyte solutions, the concept of the hydration parameter was proposed.\(^{19}\) This parameter describes the extent of hydration of solute in aqueous solutions by the deviation of the relative viscosity from Einstein’s equation of viscosity which assumes no solute-solvent interaction. Figure 5 compares the \(\alpha\) value and the hydration parameter for nonelectrolyte solutions. A good negative correlation is observed between the two parameters \((R = 0.914)\).

For sugar solutions, Ueda et al.\(^{10,21}\) reported that the number of equatorial OH-groups (e-OH) is an effective parameter to represent the solvent-solute interaction to describe the water structure from their NMR measurement on the spin-lattice relaxation time of \(H_2^{17}O\). Figure 6 compares the \(\alpha\) value for sugar solutions and the number of e-OH. A good negative correlation \((R = 0.844)\) was obtained again between the two parameters.

- Fig. 3. Activity Coefficient of Water for Various Aqueous Single-component Systems.
- Fig. 4. Correlation between the Parameter \(\alpha\) in Eq. (4) and the \(B\)-Coefficient of Viscosity for Single Valent Electrolyte Solutions \((R = 0.979)\).
- Fig. 5. Correlation between the Parameter \(\alpha\) in Eq. (4) and the Hydration Parameter for Aqueous Nonelectrolyte Solutions \((R = 0.914)\).
invert sugar, sorbitol, and sucrose. The interaction of solute with water, however, is strongly dependent on the number of e-OH instead of total OH groups in the molecule.\textsuperscript{20,21} Chirife and Ferro Fontan\textsuperscript{180} compared the parameter $z$ in Eq. (6) with the number of carboxyl groups of organic acids. A good correlation was reported between the two parameters for aqueous solutions of lactic acid, malic acid, tartaric acid, and citric acid. In this case, however, the number of molecules might be different through the difference in the dissociation constants among the solute at the same concentration. The parameter $z$ in Eq. (6) as well as Eq. (4) seems to reflect the state of the water in the solution so that the state of the solute in the solution should be considered before discussing the relationship between the parameter $z$ and the molecular structure of the solute.

In conclusion, the activity and the activity coefficient of water were well described by a two-parameter equation, Eq. (4). The parameter $z$ in this equation had a good correlation with the aqueous solution parameters such as the $B$-coefficient of viscosity for electrolytes, the hydration parameter for nonelectrolytes, and the number of e-OH groups for sugars, showing that the solution structure was reflected in the parameter $z$.

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References