

## Empirical formula of the surface tension of a water-1,4-dioxane mixture and the liquid structure of water in the solution

Koryo KOJIMA, Keiji KAWABATA\*, Susumu TAKAHASHI\*\*,  
Masanari KUDO\*\*\* and Sankichi TAKAHASHI\*

Department of Mechanical Systems on Information Technology,  
Hachinohe Institute of Technology, 88-1, Myo Oobiraki, Hachinohe, 031-8501, Japan

\*Mechanical Engineering Systems, Graduate School of Engineering, Hachinohe Institute of Technology,

\*\*Department of System and Information Engineering, Hachinohe Institute of Technology,

\*\*\*Department of Information Systems, The First High School Attached to Hachinohe Institute of Technology

### 1. Introduction

In a study<sup>1)2)</sup> using the <sup>17</sup>O-NMR chemical shift method, the authors have demonstrated that although the liquid structure of water in a water-1,4-dioxane mixture varies in a complex manner depending on the mixture mole fraction  $X_C$ , there is no binding between the components, which are independent of each other. With a view toward applying this feature in engineering fields, the authors have also identified empirical formulae<sup>5)6)</sup> for various physical properties of water-1,4-dioxane mixtures, such as density and viscosity, that are useful<sup>3)4)</sup> for the design of high-performance absorption-type freezers using an LiBr aqueous solution as the refrigerant.

Density<sup>5)</sup> could be estimated from the empirical formulae developed from the mean shrinkage rate based on the volume of the simple mixture model<sup>6)</sup> and the density of water in the solution could be estimated accurately from nondimensional values for density calculated as the mole fraction means of both components in the simple mixture model.

Viscosity<sup>6)</sup> could be estimated from nondimensional forms of empirical formulae derived from measured kinematic viscosity, and the viscosity of water in the solution could be estimated by utilizing dimensional analysis used for an equation representing a physical law.

Jaspar reported on the surface tension with respect to pure-component liquids and presented a table of surface tension values for about 2,200 substances, giving them as the primary function of temperature. The surface tension of a non-aqueous mixture is generally somewhat lower than an average surface tension obtained as the sum of the surface tensions of the pure components each multiplied by the relevant mole fraction, but the relation between the surface tension and concentration of an aqueous solution is complex. The relation in aqueous solutions of surface surfactant is extremely complex because organic matter is concentrated in the surface phase. These results suggest that the complex dependency of the physical properties of a solution, such as density, viscosity and surface tension, on the concentration results from changes in the liquid structure of water in the solution that are associated with changes in the solute concentration.

In this study of surface tension which changes in a complex manner according to the  $X_C$  and has significant effects on the fluidity and thermal transmissibility of the evaporative condensation component, or the water-1,4-dioxane mixture, the mole fraction and temperature-dependency of surface tension were determined under atmospheric pressure to consider the following.

- 1) The empirical formula of the surface tension of a water-1,4-dioxane mixture
- 2) The method for estimation of the surface tension of water in a water-1,4-dioxane mixture
- 3) Surface tension and the liquid structure of water in a solution

## 2. Experimental equipment and methods

### 2.1 Materials used

Deionized water made with a purifier and analytical grade 1,4-dioxane were used. The deionized water had pH = 5.518, conductivity =  $0.7715 \mu\text{S} \cdot \text{cm}^{-1}$  (298 K) and the concentrations of dissolved inorganic salts such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  were below the lower detection limits. The water-1,4-dioxane mixture used had water as its primary component and the mole fraction  $X_C$  in the range of 0.0 to 1.0 was determined to the nearest 0.1.

### 2.2 Determination of surface tension

Water from a digital low-temperature water bath set and stabilized at a given temperature with an external temperature sensor was circulated in an automated surface tensiometer, the water to be measured in the vessel was stabilized at a given temperature, and then the surface tension was measured to a precision

of  $0.01 \text{ mN} \cdot \text{m}^{-1}$ . The measured values of surface tension for both water ( $X_C = 1.0$ ) and 1,4-dioxane ( $X_C = 0.0$ ) were within  $\pm 1.0\%$  of the reference values.

### 3. Mole fraction dependency of the surface tension of a water-1,4-dioxane mixture

#### 3.1 Mole fraction dependency of surface tension and empirical formulae

##### (1) Mole fraction dependency

Figure 1 indicates the mole fraction dependency of the measured surface tension  $\sigma_m(X_C, T)$  (solid line) of a water-1,4-dioxane mixture and shows a tendency different in shape from that of density<sup>5)</sup> and viscosity<sup>6)</sup>, which show a maximum when  $X_C$  is about 0.8. It is independent of temperature and has a maximum, or the surface tension of water ( $X_C = 1.0$ ), that rapidly decreases as 1,4-dioxane is added until  $X_C$  is about 0.8, and slowly decreases afterwards to the surface tension of 1,4-dioxane ( $X_C = 0.0$ ). The  $X_C$  value of the branching point of these tendencies is virtually identical to the transition point ( $X_C = 0.83$ ) reported by Geddes. The reasons for the different mole fraction dependency from density<sup>5)</sup> and viscosity<sup>6)</sup> include the following.

- ① Surface tension of pure-component water is significantly different from that of 1,4-dioxane.
- ② Density<sup>5)</sup> and viscosity<sup>6)</sup> are physical phenomena occurring in a bulk liquid but surface tension is a phenomena occurring on a gas-liquid interface.

The latter (surface tension) varies to a lesser degree at or below the branching  $X_C$  value, irrespective of temperature. This is probably because the liquid composition is different between the surface and inside of a solution, or because a solution has a heterogeneous structure. This structure may explain why while the azeotropic composition of a water-1,4-dioxane mixture has an  $X_C$  of 0.650, the water-1,4-dioxane mixture exhibits a peculiar evaporation characteristic in that even if the liquid phase composition changes within the  $X_C$  value range of 0.625 to 0.825, the gas phase composition is virtually identical to the azeotropic composition ( $Y_C = 0.639\text{-}0.655$ ).

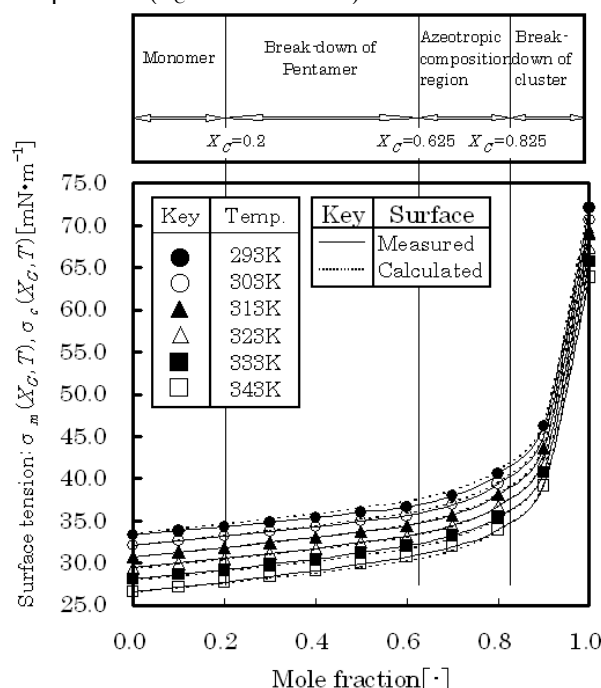


Fig.1 Measured surface tension and calculated tension of 1,4-dioxane aqueous solution

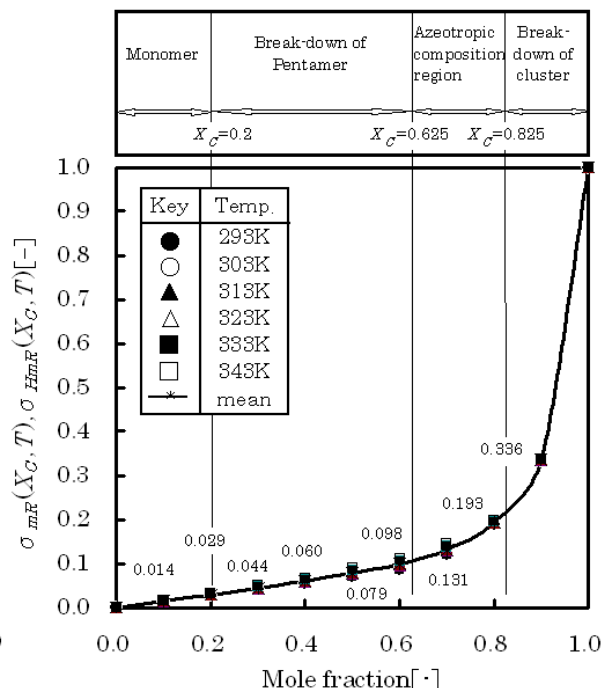


Fig.2 Non-dimensional measured surface tension of 1,4-dioxane aqueous solution

##### (2) Empirical formulae

As with density<sup>5)</sup> and viscosity<sup>6)</sup>, the mole fraction dependency of surface tension is similar in shape at each temperature so the surface tension of a solution at an optional temperature and  $X_C$  can be estimated by expressing them in an integrated manner.

Thus, empirical formulae were considered according to equation (1) based on  $X_C = 1.0$  in which  $\sigma_m(X_C, T)$  showed a maximum.

$$\sigma_{mR}(X_C, T) = \frac{\sigma_m(X_C, T) - \sigma_m(0.0, T)}{\sigma_m(1.0, T) - \sigma_m(0.0, T)} \dots \dots (1)$$

Figure 2 indicates the mole fraction dependency of  $\sigma_{mR}(X_C, T)$  (marked), and the mean  $\sigma_{HmR}(X_C, T)$  of  $\sigma_{mR}(X_C, T)$  at each  $X_C$  as expressed by equation (2) is also shown in the figure.

$$\sigma_{HmR}(X_C, T) = \frac{1}{6} \sum \sigma_{mR}(X_C, T) \dots \dots \dots (2)$$

The difference between  $\sigma_{mR}(X_C, T)$  and  $\sigma_{HmR}(X_C, T)$  at each temperature is 0.0184 (283 K,  $X_C = 0.6$ ) at the largest and 0.0063 on average, so  $\sigma_{HmR}(X_C, T)$  can represent them regardless of temperature.

If  $\sigma_{mR}(X_C, T)$  in equation (1) is substituted with  $\sigma_{HmR}(X_C, T)$ , then the surface tension of solution  $\sigma_c(X_C, T)$  can be calculated from equation (1').

$$\sigma_c(X_C, T) = \sigma_{HmR}(X_C, T) \times \{\sigma_m(1.0, T) - \sigma_m(0.0, T)\} + \sigma_m(0.0, T) \dots \dots \dots (1')$$

Reference values can be used for the surface tension of water  $\sigma_m(1.0, T)$  and that of 1,4-dioxane  $\sigma_m(0.0, T)$ , so the surface tension of a solution at an optional temperature and  $X_C$  can be calculated from equation (1') using the constant and reference values.

$\sigma_c(X_C, T)$  (broken line) was compared with  $\sigma_m(X_C, T)$  (solid line) in Figure 1. The difference between them was 2.257% (343 K,  $X_C = 0.6$ ) at the largest and 0.579% on average.

### 3.2 Estimation of surface tension by dimensional analysis

Estimation of the surface tension of water in a solution was attempted using dimensional analysis used in an equation representing a physical law.

Because surface tension represents the force to shrink a surface area per unit length, the dimensional equation of surface tension is given as equation (3).

$$\sigma = \left[ \frac{F}{L} \right] = \left[ \frac{F \cdot H}{L^2} \right] \left[ \frac{L}{H} \right] = \eta U \dots \dots \dots (3)$$

Thus, surface tension is the product of viscosity and rate.

The surface tension of a solution  $\sigma_c(X_C, T)$  can be calculated from equation (4) representing the product of viscosity  $\eta^6$ , which is an average viscosity estimated as the sum of the viscosity of the components of the simple mixture model each multiplied by the relevant mole fraction, and rate U.

$$\begin{aligned} \sigma_\beta(X_C, T) &= \eta_\beta(X_C, T) \cdot U = \frac{\{\eta_W(X_C, T)V_W(X_C, T)X_C + \eta_D(T)V_D(T)(1 - X_C)\}U}{V_W(X_C, T)X_C + V_D(T)(1 - X_C)} \\ &= \frac{\eta_W(X_C, T)U \cdot V_W(X_C, T)X_C + \eta_D(T)U \cdot V_D(T)(1 - X_C)}{V_W(X_C, T)X_C + V_D(T)(1 - X_C)} \\ &= \frac{\sigma_W(X_C, T)V_W(X_C, T)X_C + \sigma_D(T)V_D(T)(1 - X_C)}{V_W(X_C, T)X_C + V_D(T)(1 - X_C)} \dots \dots \dots (4) \end{aligned}$$

## 4. Method for estimation of the surface tension of water in a water-1,4-dioxane mixture

The surface tension of water  $\sigma_w(X_C, T)$  in a solution can be calculated from equation (4) as in equation (4').

$$\sigma_w(X_C, T) = \frac{\sigma_m(X_C, T)\{V_W(X_C, T)X_C + V_D(T)(1 - X_C)\} - \sigma_D(T)V_D(T)(1 - X_C)}{V_W(X_C, T)X_C} \dots \dots \dots (4')$$

Figure 3 shows a comparison of the mole fraction dependency of the surface tension of water  $\sigma_w(X_C, T)$  (solid line) in a solution as estimated from equation (4') and the measured surface tension of the solution  $\sigma_m(X_C, T)$  (broken line).

The surface tension of water in a solution rapidly decreased at each temperature until  $X_C$  was about 0.7 like the measured surface tension of the solution, but turned to an increase afterwards while showing some complex fluctuations. It showed great variation depending on the temperature when  $X_C$  was 0.1.

These findings suggest the strong effect of the solution composition on the gas-liquid interface where water is divided into single molecules.

## 5. Conclusion

The mole fraction dependency of the surface tension of a water-1,4-dioxane mixture was measured to study the empirical formulae for the surface tension of a solution, methods for estimation of the surface tension of water in the solution and the liquid structure of water. The following are the conclusions obtained:

- 1) The surface tension of a solution at an optional  $X_C$  and temperature can be estimated from empirical formulae obtained from nondimensional values for optional measured surface tension against the measured surface tension of water based on the measured surface tension of 1,4-dioxane.
- 2) The difference between the values obtained from empirical formula (1') deduced from the above idea and measured values was 2.257% (343 K,  $X_C = 0.6$ ) at the largest and 0.579% on average.
- 3) The surface tension of a solution at an optional  $X_C$  and temperature can be estimated by using dimensional analysis.
- 4) The surface tension of water in a solution at an optional  $X_C$  and temperature can be estimated from equation (4') deduced from the above idea.

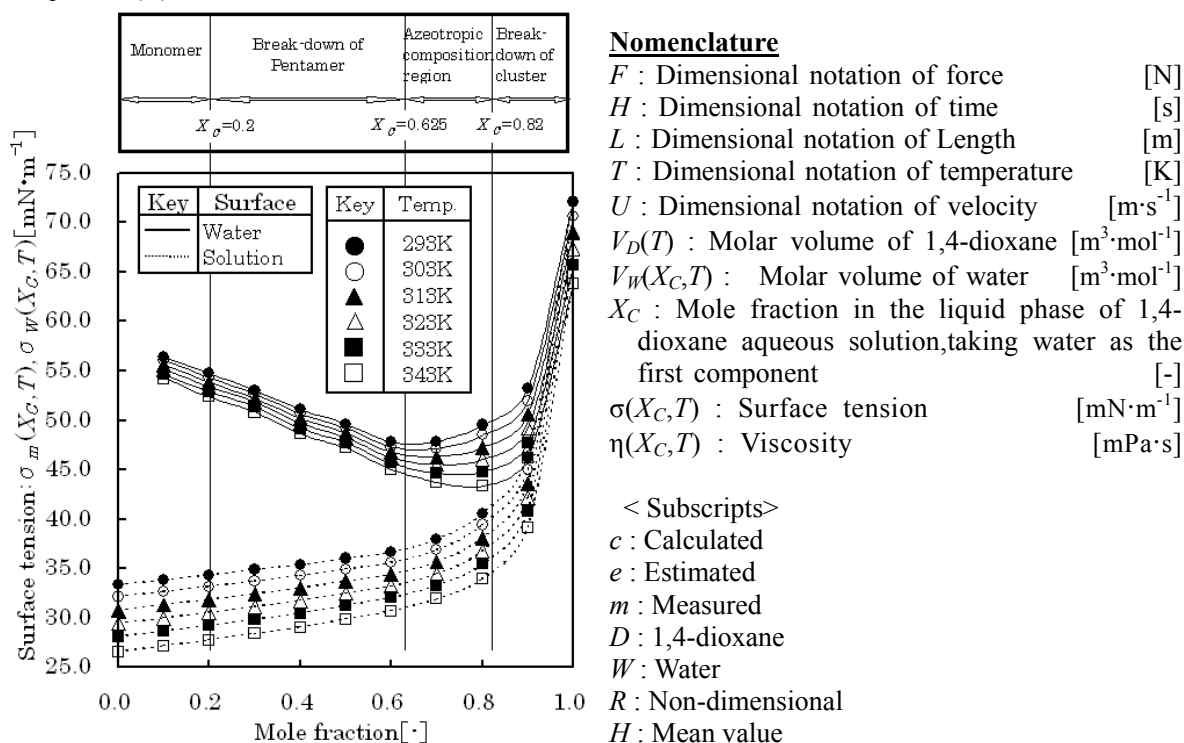


Fig.3 Measured surface tension of 1,4-dioxane aqueous solution and estimated surface tension of water in 1,4-dioxane aqueous solution

### Literature Cited

- 1) Su.Takahashi,K.Kojima,Sa.Takahashi: Liquid Structure of Aqueous 1,4-dioxane Solution Using the Chemical Shift of  $^{17}\text{O}$ -NMR, Kagaku Kogaku Ronbunshu of The Society of Chemical Engineers, Japan, Vol.25, No.4, pp.608-612(1999)
- 2) Su.Takahashi,K.Kojima,M.Kudo,Sa.Takahashi: Analysis of the Liquid Structure of Water Using the  $^{17}\text{O}$ -NMR Chemical Shift Method, Kagaku Kogaku Ronbunshu of The Society of Chemical Engineers, Japan, Vol.26, No.1, pp.40-44(2000)
- 3) M.Kudo,K.Kojima,Su.Takahashi,Sa.Takahashi : Influence of Liquid Structure of Water on Dehydration Reaction of  $\text{LiBr}\cdot 2\text{H}_2\text{O}$  in Aqueous LiBr Solution, Transactions of the Society of Heating, Air-Conditioning and Sanitary Engineers of Japan, No.79, (2000-10), pp.45-51
- 4) M.Kudo,K.Kojima,Su.Takahashi,D.Sakamoto,Sa.Takahashi : Solubility of LiBr in Water and Improvement by Addition of 1,4-dioxane, Transactions of the Society of Heating, Air-Conditioning and Sanitary Engineers of Japan, No.85, (2002-4), pp.1-9
- 5) K.Kojima,K.Kawabata,Su.Takahashi,M.Kudo,Sa.Takahashi : Simple Method for Estimating Various Physical Property of 1,4-dioxane Aqueous Solution and Liquid Structure of the Water in the Solution (part 1)—Density—, Proceeding of the 36<sup>th</sup> Japanese Joint Conference on Air-conditioning and Refrigeration(Tokyo), (2002-4), pp.101-104
- 6) K.Kojima,K.Kawabata,Su.Takahashi,M.Kudo,Sa.Takahashi : Simple Method for Estimating Various Physical Property of 1,4-dioxane Aqueous Solution and Liquid Structure of the Water in the Solution(part 2)—Viscosity—, Proceeding of the 36<sup>th</sup> Japanese Joint Conference on Air-conditioning and Refrigeration, (2002-4), pp.105-108