

Behavior of solutes in water + ethanol mixed solvent.
Part 1. Partial molar volumes, enthalpies of solution and
chemical shift of ^1H NMR for sucrose, urea and
1-phenyl-2-thiourea solutes \star

Hideo Ogawa a,\star , Norio Murase a , Sachio Murakami b

a Chemistry Laboratory, Faculty of Science and Engineering, Tokyo Denki University, Hatoyama,
Hiki-gun, Saitama 350-03, Japan

b Department of Chemistry, Faculty of Science, Osaka City University, 3-3-138 Sugimoto Sumiyoshi-ku,
Osaka 558, Japan

Received 1 September 1994; accepted 6 September 1994

Abstract

In order to explain the behavior of solutes in water + ethanol mixtures, the thermodynamic and NMR spectroscopic properties of the ternary solutions containing urea, sucrose and 1-phenyl-2-thiourea solutes in water + ethanol mixtures were investigated. The density, enthalpy of solution $\Delta_{\text{sol}}H$ and ^1H -NMR spectral measurements were carried out at 298.15 K, and the partial molar volumes of the solutes V_3^{r} and chemical shift δ were estimated. The V_3^{r} values for sucrose and 1-phenyl-2-thiourea are almost independent of the mole fraction of water in the water + ethanol mixture x_1 , although that for urea shows a complicated concentration dependence at higher x_1 values. The $\Delta_{\text{sol}}H$ values were endothermic for all systems. The absolute values of $\Delta_{\text{sol}}H$ for sucrose and 1-phenyl-2-thiourea increased rapidly on increasing the concentration of poor pure solvent, but that for urea showed a maximum at $x_1 = 0.9$. The δ values for water and ethanol were not affected by adding a small amount of solute. The δ values for the solute depend on x_1 in the same manner as that of the $-\text{CH}_2-$ proton of ethanol. These results suggest that sucrose and 1-phenyl-2-thiourea are distributed

\star Corresponding author.

\star Presented at the International and III Sino-Japanese Symposium on Thermal Measurements, Xi'an, 4–6 June 1994.

selectively in water or ethanol aggregates in the water + ethanol mixture, respectively, and, however, that urea is distributed in the mixed solvent with a fluctuated structure.

Keywords: Ethanol; Heat of solution; Mixed solvent; Partial molar volume; Water

1. Introduction

Investigations into liquid water and alcohols and their mixtures are very important, not only scientifically but also industrially, because water, alcohol and their mixtures are high-performance solvents, low in cost and safe to the environment. In general, the concentration dependence of an excess thermodynamic function and the partial molar quantities of water + alcohol mixtures are very complicated [1–7]. Thus, the behavior of solute molecules in water + alcohol mixed solvent has not been explained clearly.

In order to explain the behavior of solutes in water + ethanol mixed solvent, the thermodynamic and spectroscopic properties of some ternary solutions containing solutes (3) in the water (1) + ethanol (2) mixed solvent have been evaluated from their density, enthalpies of solution, and proton NMR spectral measurements at 298.15 K. Urea (U), sucrose (S) and 1-phenyl-2-thiourea (PU) were selected as the solutes to determine the differences in thermodynamic properties due to the differences in solubility in the component liquids of the mixed solvent: U is soluble in water and slightly soluble in ethanol; S is soluble in water and barely soluble in ethanol; and PU is barely soluble in water and soluble in ethanol.

2. Experimental

2.1. Materials

Water was deionized and twice distilled with $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ solution. Special grade ethanol (Wako Pure Chemical Ind., Ltd.) was shaken with 3 Å molecular sieves for more than 2 days and fractionally distilled with a 1-m column under dried air. No impurities were detected by GLC without water, and the water content was estimated to be less than 0.02 mol%.

Urea and sucrose were ultra-pure reagents (Schwarz/Mann). 1-Phenyl-2-thiourea was reagent-grade from Wako Pure Chemical Ind., Ltd. All solutes were dried under reduced pressure at 70°C for more than 5 h before use.

Sample solutions were prepared by mass. A large number of water + ethanol mixtures were first prepared, as mixed solvents for the entire composition range. For each solvent, several low concentration solutions were prepared containing less than 2 mass% of solute.

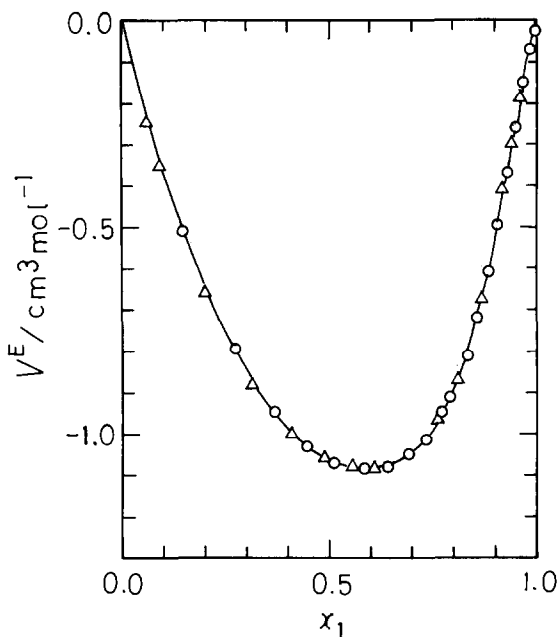


Fig. 1. Excess molar volumes V^E of water(1) + ethanol(2) mixture at 298.15 K. \circ , this work; Δ , Benson and Kiyohara [1].

2.2. Density measurement

The density measuring system used was recently constructed in our laboratory, as described in our earlier work [8]. The system consists of a vibrating tube densimeter (Anton Paar, DMA-602HW), a thermostated water bath controlled within ± 0.0004 K, a quartz thermometer (Hewlett Packard, 2804A) and a frequency counter (Iwatsu, SC7102) with stability less than 5×10^{-8} of a quartz oscillator. The imprecision of this apparatus was estimated to be less than 5×10^{-6} g cm $^{-3}$.

In this type of density measurement, two standard liquids are required to determine the two apparatus constants. Densities of water + ethanol mixed solvents of various concentrations were determined using the values for the two pure component liquids: $d_1 = 0.9970474$ g cm $^{-3}$ [9] and $d_2 = 0.785089$ g cm $^{-3}$ (observed) at 298.15 K. Densities of solutions of different concentrations of the solutes were determined using the values of the two mixed solvents as secondary standards. Molar excess volumes estimated from the densities of water + ethanol mixed solvent agreed well with those reported by Benson and Kiyohara [1] as seen in Fig. 1.

2.3. NMR measurement

$^1\text{H-NMR}$ spectra were measured using a 400 MHz FT-NMR spectrometer (JEOL, EX-400). Sample solutions containing 1 mass% solute were contained in an

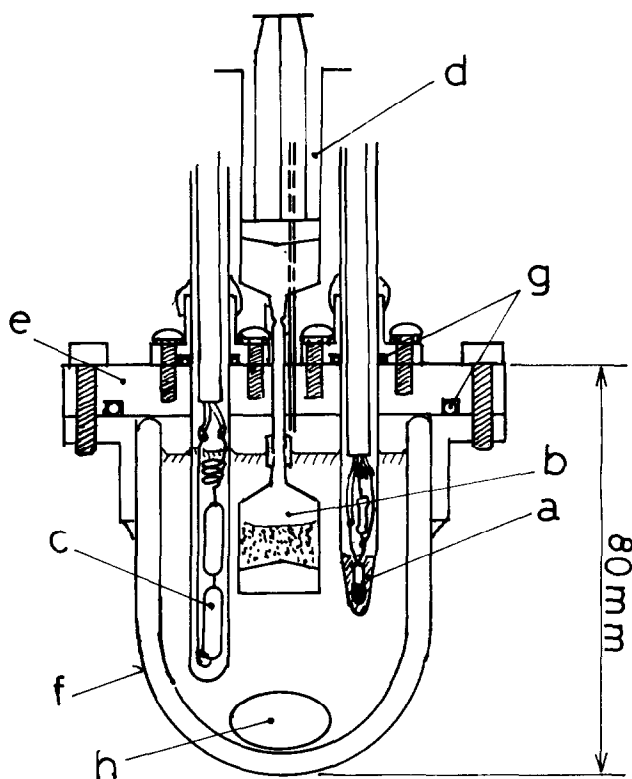


Fig. 2. Schematic diagram of constructed isoperibol calorimeter for measuring enthalpy of solution: a, thermistor; b, sample container; c, calibration heater (100 Ω metal-coated resistor); d, syringe for air pump; e, brass lid; f, 100 cm³ glass Dewar vessel; g, viton O-ring; h, stirrer bar (football shape).

NMR tube (5 mm i.d.). The CDCl₃ needed to lock the magnetic field and 1% TMS standard material were contained in another tube (3 mm i.d.), located at the center of a sample tube supported by two teflon rings. NMR spectral measurements of PU solution were not carried out.

2.4. Calorimetry

A simple isoperibol calorimeter was constructed for enthalpies of solution measurement in this study. A diagram of the calorimetric unit is shown in Fig. 2. The calorimetric unit is immersed in a thermostated water bath. A stirring bar rotates slowly using a magnetic stirrer. A thermistor used as the temperature-detecting device and a metal-coated resistor for electrical calibration were positioned in a glass tube, respectively, with silicone oil. Detection and calibration circuits were also constructed.

Less than 0.5 g of solute sample were contained in a short-cut polypropylene syringe. By pumping air from the outer syringe, a rubber lid was pushed out and

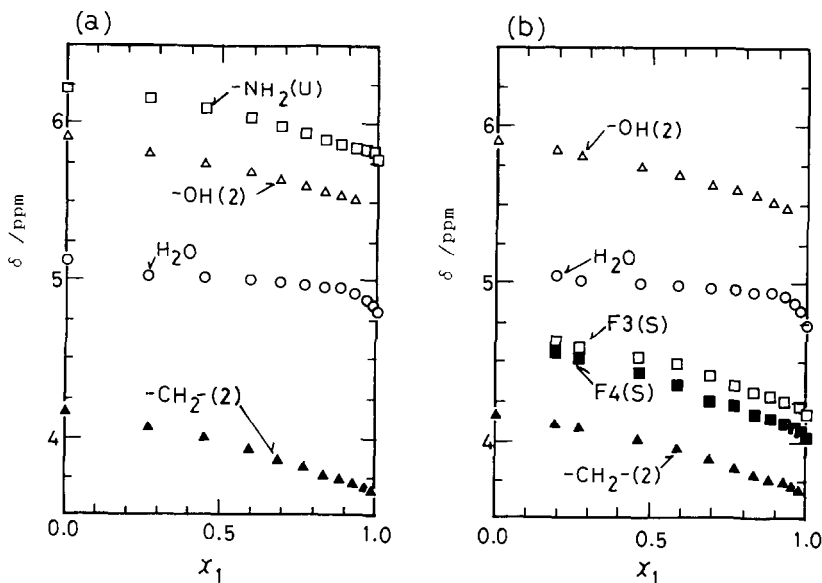


Fig. 3. Plots of chemical shift δ of ^1H -NMR signals relative to TMS for water(1) + ethanol(2) + 1% solute mixtures at 298.15 K. (a) Urea (U); (b) sucrose (S): F3 and F4, signal of ^1H bonded to the 3rd and 4th carbon atom on the fructose ring in sucrose, respectively.

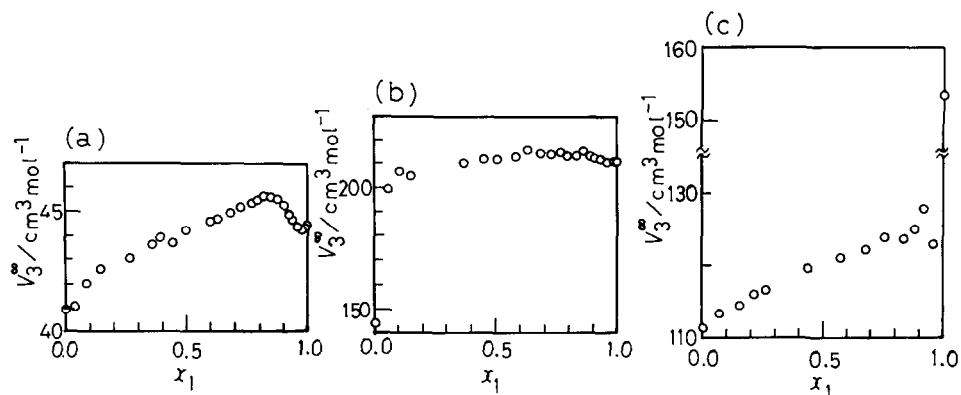


Fig. 4. Partial molar volumes at infinite solution V_3^∞ of urea (a), sucrose (b) and 1-phenyl-2-thiourea (c) in water(1) + ethanol(2) mixed solvent at 298.15 K.

the sample was dispersed in 95 cm³ of mixed solvent. Some silicone grease was coated on the lower inside of the syringe to ensure this operation. We call this procedure the “air-remote” method.

The enthalpies of solution of 99.9% KCl determined using this calorimeter were reproducible to within 0.3% and agreed with the recommended IUPAC value [10] to within 0.5%. However, the reproducibilities of the enthalpies of solution for the S and PU systems were fairly poor, especially for the volatile ethanol-rich region, because of the small heat change and large heat of evaporation.

3. Results and discussion

Partial molar volumes at low concentrations of the solutes, V_3^x , were calculated using the following equations and density data

$$V_3^x = \lim_{c_3 \rightarrow 0} \frac{\partial V}{\partial n_3} \approx \left\{ \frac{\Delta[V/(m_1 + m_2)]}{\Delta c_3} \right\}_{\text{av. at low } c_3}$$

where c_i and m_i are the molality and mass of component i , respectively. The molar enthalpies of solution with low concentration of solute, $\Delta_{\text{sol}}H$, were determined using the normal method. The chemical shift of the proton signal of 1% solution relative to that of TMS, δ , was determined using the computer system of the NMR spectrometer. All the determined properties were plotted against the mole fraction of water x_1 in the water + ethanol mixed solvent.

The chemical shifts of a representative proton in the component molecule of the solution are shown in Fig. 3. As seen in this figure, the signal of water is most instructive. This signal shifts notably to low magnetic field on adding ethanol at $x_1 > 0.8$, while the other signals increase monotonously. This indicates a strengthening of the hydrogen bonding of water as a result of the hydrophobic effect of the added ethanol. We have discussed and reported the NMR spectra for the binary mixtures of water + ethanol in detail elsewhere [11].

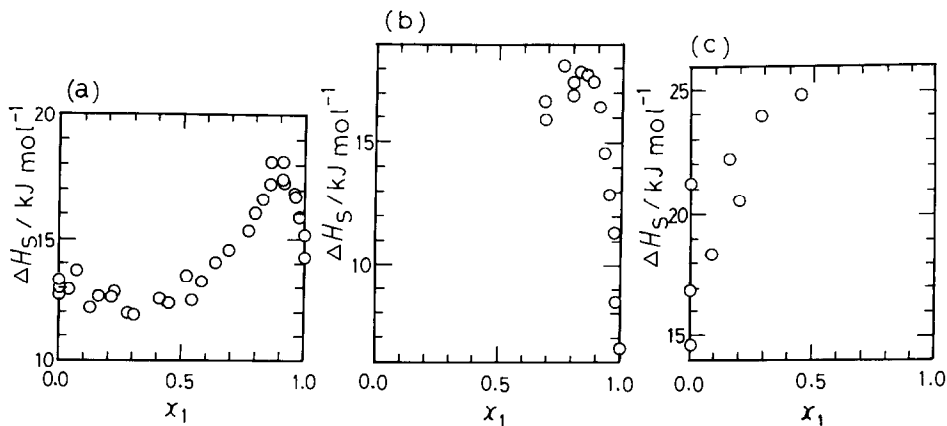


Fig. 5. Enthalpies of solution $\Delta_{\text{sol}}H$ of 0.2–0.5 g of (a) urea, (b) sucrose and (c) 1-phenyl-2-thiourea in 95 cm³ of water(1) + ethanol(2) mixed solvent at 298.15 K.

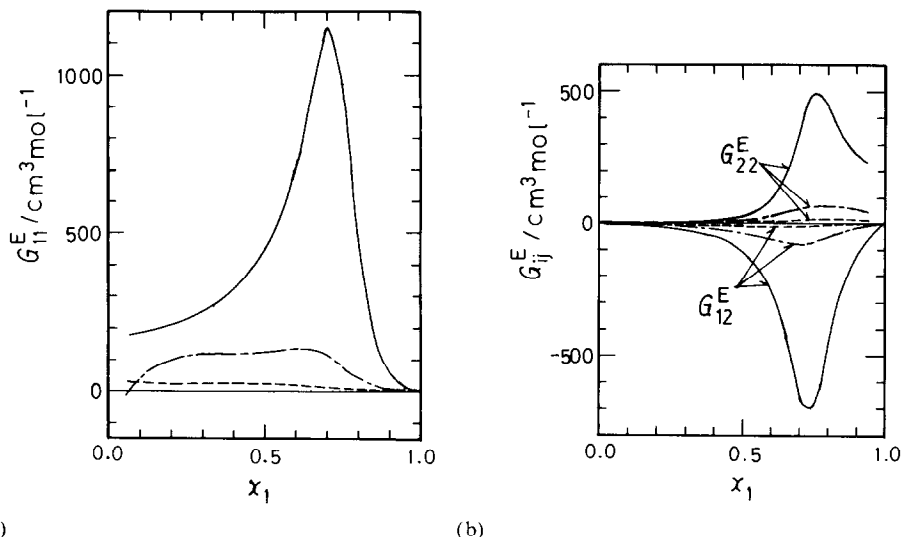


Fig. 6. Excess Kirkwood–Buff parameters G_{ij}^E for water(1) + alkanol(2) mixtures at 298.15 K, calculated from excess thermodynamic function data [1–6]. (a) G_{11}^E ; (b) G_{12}^E and G_{22}^E . Curves: ---, methanol; - · - ·, ethanol; —, propanol.

However, the δ values for water and ethanol were not affected by adding small amounts of solute. This means that a small amount of solute does not significantly change the molecular aggregates and solution structure in the water + ethanol mixture. In addition, the δ values for the solute depend on x_1 in almost the same manner as that of the $-\text{CH}_2-$ (ethylene) proton of ethanol. Therefore, the behavior of the solute is not explained clearly from these NMR data.

The partial molar volumes of the solutes in the low concentration range are shown in Fig. 4. The values for S and PU do not significantly depend on the composition of the mixed solvent except for the poor solvent component rich region. In this region, the precision of measurement was poor due to the very small density change resulting from the very low concentration of the solute. If such a solute is distributed in a good solvent, almost the same magnitude of volume will be generated with no relation to the composition of mixed solvent.

However, the partial molar volumes of urea depend on x_1 in a very complex manner, showing a maximum and a minimum in the water-rich region. We consider that a solute soluble in both water and ethanol is likely to show a minimum in partial molar volume, because the solvation and behavior of such a solute must resemble that of alcohol. It is well known that the concentration dependence of the partial molar volumes of alcohol in aqueous solution show a minimum in the water-rich region [1]. However, this phenomenon is not well explained. Ben-Naim treated the behavior of this solution theoretically and represented a similar minimum in entropy [12]. This problem may be explained clearly by the molecular dynamics method.

The enthalpies of solution are shown in Fig. 5. The results are endothermic for all systems; therefore the solutions are stabilized entropically. The absolute values of $\Delta_{\text{sol}}H$ for S and PU increase with increasing concentration of poor solvent component in the mixed solvent. $\Delta_{\text{sol}}H$ for U shows a maximum at $x_1 = 0.9$. The concentration dependence of $\Delta_{\text{sol}}H$ is the inverse of that of the partial molar volume.

To discuss the behavior of the solute in the mixed solvent, the binary solution of water and ethanol must be understood. In Fig. 6, excess Kirkwood–Buff parameters G_{ij}^E for water + normal alcohol mixtures are shown. These parameters represent the volume corresponding to the excess gathering between component molecules i and j over that of the ideal mixture, and are calculated using

$$G_{ij}^E = G_{ij} - G_{ij}^{\text{id}}$$

where G_{ij}^E is estimated from excess thermodynamic functions by the Ben-Naim method [13]. As seen in this figure, there is a local concentration fluctuation. The aggregation of water takes place extensively in the mole fraction range between 0.4 and 0.85.

The mixed solvent is distinguished into three composition regions: (a) the region of water aggregation; (b) the region of ethanol aggregation; (c) an intermediate region between (a) and (b).

Because the addition of a small amount of solute does not change the solvent structure, the solute should be distributed in the three regions described above by interaction with the component molecules of the mixed solvent. S or PU are distributed selectively in the region of water or ethanol aggregation in the water + ethanol mixed solvent, respectively. U is resolved in the region of (a) and (c).

4. Conclusions

A solute soluble in both water and ethanol is distributed in all the regions in the water + ethanol mixed solvent, and then the thermodynamic properties of such a solute show complicated concentration dependence similar to that of ethanol.

A solute soluble only in water or in ethanol is distributed selectively in the region of aggregation of water or ethanol in the mixed solvent, respectively, and then the concentration dependence of the thermodynamic properties of such a solute are simple.

Acknowledgments

The authors are grateful to the Research Institute for Technology of Tokyo Denki University for financial support. We also thank J. Takezawa, H. Murakami and F. Ikeda for experimental assistance.

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