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Molecular Association and Hydration Behavior
of 2-*n*-Butoxyethanol in Aqueous SolutionYuichi SATOKAWA^{*, **, †} and Toshiyuki SHIKATA^{**, ***}^{*}Central Research Laboratories, DIC Corporation, 631 Sakado, Sakura, Chiba 285-8668, Japan^{**}United Graduate School of Agricultural Science, Tokyo University of Agriculture and Technology,
3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan^{***}Graduate School of Agriculture, Tokyo University of Agriculture and Technology,
3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan

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Broadband dielectric spectrum measurements up to 50 GHz have been conducted for aqueous solution of 2-*n*-butoxyethanol (2BE) over a wide concentration range to investigate the state of molecular association of 2BE in aqueous solution. All the obtained dielectric relaxation spectra can be well decomposed into multiple Debye-type relaxation functions. The number of necessary relaxation modes clearly depended on the concentration of 2BE and was reasonably correlated with the molecular association state change of 2BE in aqueous solution. The concentration dependence of hydration number per 2BE molecule slightly decreased above a critical concentration for molecular association formation like micelles due to intermolecular hydrogen bonds formation between 2BE molecules.

Key Words: Dielectric relaxation / Aqueous solution / Hydration / Molecular association

1. INTRODUCTION

In response to the adoption of the 17 Sustainable Development Goals (SDGs)¹⁾ by the United Nations in 2015, many companies have decided their development policies in line with the SDGs. For example, the reduction of the release of hazardous chemicals to the environment through clean and environmentally sound technologies and industrial processes is targeted in the Goals 9 and 11. Due to the enhancement of such environmental awareness, chemical companies have been making efforts to shift their products to be environmentally friendly. Particularly in the field of coating materials such as paints, printing inks, and adhesives, one solution to implement such green products is to substitute organic liquids with water as the solvents²⁾. However, the complete replacement of organic solvents makes it difficult to maintain required characteristics such as dispersibility, driability, storage stability, etc. Therefore, it is significantly important to understand the physico-chemical properties of the mixture of organic solvents and water to control and improve the performance of the products.

2-*n*-butoxyethanol (2BE) have been commonly used in solvent-containing paint systems³⁾. 2BE is known to form aggregates or intermolecular associations in aqueous solutions above a kind of critical concentration, which is similar to the critical micelle concentration (CMC) usually observed in aqueous solution for surfactant molecules, and the structure and size of intermolecular associations formed by 2BE molecules in aqueous media have been studied in various ways. For example, Koga⁴⁾ claimed that the dissolving state of 2BE molecules in water changes depending on the concentration of 2BE based on the precise analysis of the derivatives of thermodynamic quantities. D'Angelo *et al.*⁵⁾ also reported that 2BE molecules possess different dissolving states in aqueous solution with increasing the mole fraction of 2BE from compressibility and infrared absorption measurements. Besides, many other studies were published so far, which examined aqueous 2BE systems using various kinds of techniques such as surface tensiometry⁶⁾, calorimetry⁷⁾, viscometry⁸⁾, ultrasound relaxation⁹⁾, dynamic light scattering^{10, 11)}, Taylor dispersion measurement¹²⁾, fluorescent spectroscopy¹³⁾, molecular dynamics simulation¹⁴⁾, X-ray scattering¹⁵⁾, neutron scattering¹⁶⁻¹⁸⁾, neutron spin echo¹⁸⁾, and so on. In many studies listed above, most authors found maxima or inflection points in the measured physical quantities at certain

[†] Corresponding author.

E-mail : yuichi-satokawa@ma.dic.co.jp

Tel: +81-43-498-4101; Fax: +81-43-498-2403

concentrations, and they discussed the points of similarity between the characteristics of the concentrations and CMC in aqueous surfactant solutions.

Several groups have reported the dielectric relaxation (DR) behavior of aqueous 2BE solutions. Kaatz *et al.*^{19, 20} and Joshi and Kumbharkhane²¹ adopted single Havriliak–Negami and/or Davidson–Cole type functions to describe the DR spectra for aqueous 2BE solutions, and the broadness of the distribution of relaxation times was discussed. Fioretto *et al.*²² claimed that the relaxation spectra for aqueous 2BE systems can be described with a single Debye-type relaxation function and the inflection point of the relaxation time–concentration curve corresponds to the critical point at which the 2BE molecules begin to form intermolecular associations in aqueous solution. Arikawa *et al.*²³ measured the complex permittivity of aqueous solution of 2BE in a terahertz frequency region and determined the hydration number of 2BE molecules. However, the relationship among molecular motions or dynamics, the hydration state, and the formation of intermolecular association of 2BE molecules in aqueous systems are not well understood so far.

Our group has been investigating the rotational motions of water and solute molecules, and the hydration/dehydration behavior of solute molecules in aqueous media using DR spectroscopic techniques^{24–28}. In this study, we adopted the DR spectroscopic techniques to investigate aqueous 2BE solution, and clearly detected the formation of intermolecular associations and a change of hydration state of 2BE molecules from the isolated monomeric state to associative one via the dynamical aspects determined dielectrically.

2. EXPERIMENTAL

2.1 Materials

2-*n*-butoxyethanol (2BE) was purchased from Wako pure chemicals (Osaka), and used without further purification. Highly de-ionized water was obtained by an Elix-5 system (Millipore-Japan, Tokyo) with a specific resistance higher than 15 MΩcm and was used as a solvent. Aqueous 2BE solution was prepared over the molar concentration of 2BE of $c = 0$ to 7.58 M (1.0 in mole fraction) for DR spectrum measurements.

2.2 Methods

Dielectric relaxation measurements were conducted using two different measuring systems. A dielectric probe kit 8507E, equipped with a network analyzer N5230C, ECal module N4693A, and performance probe 05 (Agilent

Technologies, Santa Clara, CA), was used for DR measurements over a frequency range from 50 MHz to 50 GHz ($3.14 \times 10^8 - 3.14 \times 10^{11} \text{ s}^{-1}$ in angular frequency (ω)). Real and imaginary parts (ϵ' and ϵ'') of electric permittivity were automatically calculated from reflection coefficients measured by the network analyzer via a program supplied by Agilent Technologies. The equipment was calibrated by a three-point calibration procedure prior to all the dielectric measurements. *n*-hexane, 3-pentanone and water were used as the standard materials. Details of the calibration procedure have been described elsewhere²⁹.

In the lower frequency range from 1 MHz to 3 GHz ($\omega = 6.28 \times 10^6 - 1.88 \times 10^{10} \text{ s}^{-1}$), DR measurements were conducted using an RF LCR meter 4287A (Agilent) equipped with a homemade electrode cell with a vacant electric capacity of $C_0 = 0.23 \text{ pF}$. The values of ϵ' and ϵ'' were calculated using the relationships $\epsilon' = CC_0^{-1}$ and $\epsilon'' = (G - G_{DC})(C_0\omega)^{-1}$, where C , G and G_{DC} represent measured electric capacitance, conductance and direct current conductance of the sample liquid, respectively. Details of the structure and the calibration procedure of the electrode cell used in this study have also been described elsewhere³⁰.

The partial molar volumes of the solute 2BE were determined from the results of density measurements performed using a digital density meter, DMA4500M (Anton Paar, Graz).

All the measurements have been performed at 25 °C.

3. RESULTS AND DISCUSSION

3.1 Dielectric Behavior

Dielectric spectra (ϵ' and ϵ'' vs ω) for aqueous 2BE solution at $c = 1.40 \text{ M}$ (and the mole fraction, $x_{2BE} = 0.03$), 2.11 M ($x_{2BE} = 0.05$) and 7.00 M ($x_{2BE} = 0.6$) are shown in Fig. 1 as typical examples. The dependencies of ϵ' and ϵ'' on ω were well described with the summation of a plural number of Debye-type relaxations as follows,

$$\epsilon' = \sum_{j=1}^n \frac{\epsilon_j}{1 + \omega^2 \tau_j^2} + \epsilon_\infty, \quad \epsilon'' = \sum_{j=1}^n \frac{\epsilon_j \omega \tau_j}{1 + \omega^2 \tau_j^2} \quad (1)$$

where ϵ_j , τ_j and ϵ_∞ represent the relaxation strength and time of mode j and the optical dielectric constant, respectively ($j = 1$ to n from a mode with the shortest relaxation time). The broken lines drawn in the figure represent the constituent Debye-type relaxation mode, ϵ'_j and ϵ''_j ($j = 1$ to n and the n value varied from 2 to 4 depending on c (or x_{2BE})). We have attempted to decompose the dielectric spectra into the minimum number of constituents to clarify the assignment and

physical meaning of each relaxation process. To confirm the validity of decomposition into multiple Debye-type relaxation modes for the spectra, the residuals of $\varepsilon' - \varepsilon'_1 - \varepsilon_\infty$ and $\varepsilon'' - \varepsilon''_1$ are also plotted in the same figure with closed symbols, which clearly demonstrate the presence of modes slower than mode $j = 1$. Although the number of constituent relaxation modes altered as a function of c (or $x_{2\text{BE}}$), the obtained relaxation spectra can be decomposed into 2 to 4 Debye-type relaxation functions for the aqueous 2BE system over a whole c (or $x_{2\text{BE}}$) range examined in this study, as will be discussed in the next paragraph.

The dependencies of τ_j and ε_j on c or $x_{2\text{BE}}$ for the aqueous 2BE system are shown in Figs. 2(a) and (b), respectively. As mentioned above, the number of constituent relaxation modes required to describe the experimental ε' and ε'' altered depending on c or $x_{2\text{BE}}$ as follows; 2 in a range of $c \leq 0.96$ M (or $x_{2\text{BE}} \leq 0.02$), 4 in a range of $0.96 < c < 7.00$ ($0.02 < x_{2\text{BE}} < 0.6$), and 3 in a range of $7.00 \leq c$ ($0.6 \leq x_{2\text{BE}}$). Based on the thermodynamical consideration⁴⁾, it has been reported that the dissolving state of 2BE in aqueous solution changes depending on the concentration, c , and there exists boundaries of dissociation states at $x_{2\text{BE}} = 0.0175$ and 0.46 . Most of the studies investigating physicochemical behavior or properties of aqueous 2BE systems reported a critical concentration of aggregate formation in the system, which was determined to be *ca.* 0.96 M ($x_{2\text{BE}} = 0.02$)^{4, 6, 7, 9, 10, 12-14, 16)}. The value of $c \sim 0.96$ M ($x_{2\text{BE}} \sim 0.02$) is reasonably agrees with the value at which the number of constituent dielectric relaxation modes changes from 2 to 4 in this study using DR spectroscopic techniques. These observations strongly suggest that the change of the number of relaxation modes reflects the change of molecular associating state of 2BE molecules in aqueous solution. In the concentration range below $c = 0.96$ M ($x_{2\text{BE}} = 0.02$), 2BE molecules are monomerically isolated in the aqueous continuous phase. In the concentration range of $0.96 < c < 7.00$ M ($0.02 < x_{2\text{BE}} < 0.6$), they form intermolecular associations. In the concentration range above $c = 7.00$ M ($x_{2\text{BE}} = 0.6$) they form continuous phase. The concentration dependent associating states of 2BE molecules in aqueous solution are schematically depicted in Fig. 3.

In the concentration range of $c \leq 0.96$ ($x_{2\text{BE}} \leq 0.02$), we found two relaxation modes $j = 1$ and 2. The mode $j = 1$ has the shortest relaxation time, τ_1 , and the τ_1 value is very close to the relaxation time of pure water at 25 °C, 8.3 ps. Besides, the ε_1 approximately linearly decreased with increasing the concentration in this range. Then, we conclude that the mode $j = 1$ is attributed to the rotational relaxation mode of free water molecules in the systems. The relaxation time of the

Fig. 1 Frequency, ω , dependencies of real and imaginary parts of electric permittivity, ε' and ε'' , for the aqueous 2BE solution at $c = 1.40$ M (or $x_{2\text{BE}} = 0.03$) (a), 2.11 M ($x_{2\text{BE}} = 0.05$) (b) and 7.00 M ($x_{2\text{BE}} = 0.6$) (c). Closed symbols represent the relaxation spectra after the subtraction of the contribution of free water in the system. Broken lines represent constituent Debye-type relaxation functions necessary for the best decomposition.

mode $j = 2$, τ_2 , is 2 to 3 times longer than the τ_1 value. Because the hydrated water molecules reside in hydration sites on solute molecules for a short period, the hydration lifetime, the rates of rotational molecular motions of hydrated water molecules are substantially reduced than that of free water molecules. This reduction would be related to a ratio of τ_2 to τ_1 , and then we attributed the relaxation mode $j = 2$ to the exchange process for hydrated water molecules by free water molecules. Because 2BE molecules have ether and hydroxy groups bearing finite dipole moments, the rotation of the molecules or these groups likely demonstrates the DR process even if an intramolecular hydrogen bond is formed in aqueous solution. However, such a DR process was not recognized in the obtained DR spectra in the concentration range. The reason for the disappearance of the DR would be that small 2BE molecules rotate at a high rate close to τ_2^{-1} in aqueous solution and the rotational process was not separately detected from the exchange mode of hydrated water molecules. The fact that the values of ε_2 were obviously greater than that estimated from the hydration number, n_{H} , which will be determined in a later section from the quantities of ε_1 assuming the identical relaxation strength for the hydrated water to that of free water molecules, supports this section.

Fig. 2 Dependencies of relaxation time, τ_j (a), and relaxation strength, ε_j (b), on c for aqueous 2BE solution.

Above $c = 0.96$ M ($x_{2\text{BE}} = 0.02$), we observed additional relaxation modes $j = 3$ and 4 as seen in Fig. 2. In this second concentration regime, 2BE molecules form intermolecular associations in water, and rotational molecular events of ether and hydroxy groups of 2BE molecules in the formed associations are expected to be much slower than that of free water molecules (τ_1^{-1}) and also the exchange process (τ_2^{-1}). Then, the additional relaxation modes, $j = 3$ and 4, can be attributed to substantially retarded rotational molecular motions of ether and hydroxy groups of 2BE molecules in the formed associations. The hydroxy group of 2BE can be three kinds of counterparts for hydrogen bonds: an intramolecular

$c \leq 0.96$

$0.96 < c < 7.00$

$7.00 \leq c$

• : water
• : 2BE

Fig. 3 Schematic depiction of concentration dependent molecular association states of 2BE molecules in aqueous solution.

hydrogen bond to the ether group of the same 2BE molecule, an intermolecular hydrogen bond to the ether group of another neighbor 2BE molecule, and that to the hydroxy group of another 2BE molecule as schematically depicted in Fig. 4. Dissociation of hydrogen bonds after their lifetimes always causes rotations of hydroxy and ether groups and leads to detectable dielectric relaxation processes. The number of intramolecular hydrogen bonds is greater than that of intermolecular ones for 2BE molecules forming intermolecular associations in the second concentration regime, because a chance for a hydroxy group proton to meet an ether group oxygen atom belonging to the same 2BE molecule is always more frequent than that to meet an ether group oxygen atom (or a hydroxy group proton) belonging to a different 2BE molecule quickly moving in aqueous solution. Then, the modes $j = 3$ and 4 would be assigned to the dissociation of intramolecular hydrogen bonds and that of intermolecular hydrogen bonds, respectively.

The relaxation times of modes $j = 3$ and 4 are $\tau_3 \sim 1 \times 10^{-10}$ s and $\tau_4 \sim 4 \times 10^{-9}$ s, respectively, as shown in Fig. 2(a). These values are approximately comparable to the rotational relaxation times of fluorescent probe molecules dissolved in aqueous 2BE solutions in the second concentration regime determined by using time-resolved fluorescence spectroscopic techniques¹³⁾. These findings obtained by the earlier studies support our assignment of relaxation modes 3 and 4.

It is worth writing that the ε_2 value clearly exhibits the maximum at *ca.* $c = 3.44$ M ($x_{2BE} = 0.1$) and is followed by decreasing above the concentration, while the ε_1 meaning the contents of free water molecules in the system demonstrates an obvious decreasing trend. These observations reveal that the exchange process for hydrated water molecules by free water ones is not fully performed for lack of free water molecule contents above $c = 3.44$ M ($x_{2BE} = 0.1$).

Some X-ray and neutron scattering studies have evaluated so-called correlation length (ζ) in aqueous 2BE solutions¹⁵⁻¹⁸⁾ assuming the Ornstein–Zernike equation. The values of ζ are ranged from several to several tens angstroms, reflecting the size of concentration fluctuation caused by the presence of intermolecular associations of 2BE molecules in aqueous solution. Moreover, in some studies such as light scattering³¹⁾, neutron scattering¹⁸⁾ and MD simulations¹⁴⁾, the size of the intermolecular associations was also estimated to be some tens of angstroms postulating the shape of the associations to be spheres with the average radius. Although the structure of intermolecular associations formed by 2BE in aqueous solution has not been clearly depicted so far, a hydrophilic portion including ether and hydroxy groups is

Fig. 4 Schematic diagram of three kinds of hydrogen bonds involving hydroxy groups of 2BE molecules in aqueous solution.

presumably located near the surface of intermolecular associations.

In the third concentration range, $0.6 < c < 7.58$ M ($0.6 < x_{2BE} < 1$), three dielectric relaxation modes were observed. Because the contribution of a continuous phase formed by 2BE is dominant in this concentration regime, we attributed the relaxation mode $j = 1$ mainly to the rotational relaxation mode of the ether group free from hydrogen bonding in the continuous phase formed by 2BE molecules. The reason for this assignment is that dibutyl ether bearing only an ether group with a finite dipole moment shows a dielectric relaxation mode at a relaxation time of *ca.* 8×10^{-12} s in pure liquid state at 25 °C, which is close to the τ_1 value in the third regime³²⁾. Because the rotational motion of free hydroxy groups of 2BE from hydrogen bonding in pure liquid state, $c = 7.58$ M ($x_{2BE} = 1.0$), is observed in a terahertz range³³⁾, it is observable in a frequency range beyond that of the experimental set up used in this study.

According to a previous nuclear magnetic resonance (NMR) study, methoxyethanol ($C(3)H_3OC(2)H_2C(1)H_2OH$), one of low mass analogues of 2BE, possesses a gauche conformation for the chemical bond of $C(1) - C(2)$ at a high population of *ca.* 85 %³⁴⁾. Such a high gauche content for the chemical bond proposes the formation of intramolecular hydrogen bonding at a substantially high fraction. Then, the contribution of intramolecular hydrogen bond formation should be greater than that of the intermolecular one for hydroxy groups of 2BE in the third regime. Consequently, the

Fig. 5 Relationship between the values of $\varepsilon_1\varepsilon_w^{-1}$ and the molar concentration, c , for the aqueous 2BE solution. Lines represent the theoretical prediction of c dependencies of $\varepsilon_1\varepsilon_w^{-1}$ with varying n_H in eq 2.

mode $j = 3$ with $\varepsilon_3 (> \varepsilon_2)$ can be assigned to the dissociation of intramolecular hydrogen bonds, and the other mode $j = 2$ to the dissociation of intermolecular hydrogen bonds, respectively.

3.2 Hydration Number

The depression observed in ε_1 with increasing c as seen in Fig. 2(b) in a relatively low concentration region, is explained by two factors: a volumetric effect of solute molecules and a hydration effect⁽²⁴⁾. The ratio of ε_1 to the dielectric relaxation strength of pure water, ε_w , can be given by eq 2⁽²⁴⁾

$$\frac{\varepsilon_1}{\varepsilon_w} = \frac{1 - 10^{-3}V_m c}{1 + 10^{-3}V_m c/2} - 10^{-3}V_w c n_H \quad (2)$$

where V_m and V_w , both in the units of $\text{cm}^3 \text{mol}^{-1}$, are the partial molar volumes of a solute 2BE molecule and that of water molecule, c is the molar concentration of the solute in the unit of M, and n_H is the hydration number per 2BE molecule, respectively. The first term of eq 2 represents the contribution of the volume fraction, $10^{-3}V_m c$, excluded by the presence of solute molecules. On the other hand, the second one represents the effect of water molecules hydrated to the solute molecules.

Figure 5 shows the relationship between the values of $\varepsilon_1\varepsilon_w^{-1}$ and the molar concentration, c , for aqueous solution of 2BE. The experimental $\varepsilon_1\varepsilon_w^{-1}$ values are far from the theoretically predicted line assuming $n_H = 0$. In a concentration range below $c \sim 1.5$ M, which corresponds to the critical concentration of intermolecular association formation of 2BE, the experimental $\varepsilon_1\varepsilon_w^{-1}$ data are on a line obtained assuming $n_H = 6$. Thus, we conclude that the hydration number, n_H , for 2BE in the isolated state is 6.

In the previous studies, hydration numbers of isolated hydroxy group and ethylene oxide unit (n_O and n_{OH}) are

evaluated to be 5 and 4, respectively, by using dielectric relaxation measurements.^(24, 27, 28) The determined value of $n_H = 6$ is smaller than 9, the sum of 5 and 4, suggesting the presence of intramolecular hydrogen bonds formed between ether oxygen and hydroxy group in 2BE molecules. When 2BE molecules form intramolecular hydrogen bonds, their hydroxy groups donate protons to the ether oxygen atoms and keep a couple of lone pairs with the ability accepting protons of water molecules leading to hydration. The hydration number of such a hydroxy group is estimated to be 4⁽²⁴⁾. On the contrary, the hydration number of ether oxygen atoms of 2BE molecules accepting protons from hydroxy groups will be reduced to unity because one of the lone pairs of the ether oxygen atoms is occupied with the hydrogen bond with the adjacent OH group and no longer form bridge-like hydration structure proposed in the previous study⁽²⁸⁾. Consequently, the hydration number of 2BE molecules forming intramolecular hydrogen bond (n_{HB}) is expected to be reduced down to *ca.* 5. If we assume that 2BE molecules possess only two dissolving states, *i.e.*, forming the intramolecular hydrogen bonding and free from it, the average hydration number can be described with a fraction of 2BE molecules forming intramolecular hydrogen bond (f) as in the following manner.

$$n_H = n_{HB}f + (n_O + n_{OH})(1 - f) \quad (3)$$

By substituting parameters, n_H , n_{HB} , n_O and n_{OH} , the value of $f = 0.75$ is obtained. The f value is comparable with the population of a gauche conformation in the methoxyethanol system⁽³⁴⁾. Intramolecular hydrogen bonding has also been identified using some spectroscopic techniques for 2BE and its analogues⁽³⁵⁻³⁷⁾.

In the second concentration regime, especially $c > 1.5$ M, the value of n_H seems to decrease as recognized in Fig 5. In this concentration regime, 2BE molecules begin to form intermolecular associations as described above. In intermolecular associations, 2BE molecules would share hydration water molecules with adjacent 2BE molecules. Then, the n_H value is reduced in comparison with the isolated state. The reduction of hydration number of 2BE molecules forming intermolecular associations in aqueous solution was also reported by Arikawa *et al.*⁽²³⁾, using terahertz reflectometric technique.

4. CONCLUSION

We studied the hydration state and dynamics of 2BE molecules in aqueous solutions over a wide concentration

range by means of dielectric spectroscopic techniques.

The number of constituent relaxation modes altered in accordance with the 2BE concentration, reflecting a change in molecular associating state of 2BE molecules in aqueous solution: isolatedly dissolved state, intermolecular association formation, and the continuous phase formation. The lifetimes of intramolecular and intermolecular hydrogen bonds were clearly detected as dielectric relaxation modes, because hydroxy and ether groups bearing finite dipole moments rotate after the lifetimes of hydrogen bond formation.

Hydration number per 2BE molecule was determined to be 6 for the isolated state in a dilute regime, and the depression of hydration number due to the formation of intermolecular associations was observed.

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