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SAXS Curve Shape Analysis of 2-Butoxyethanol Aqueous Solutions

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Synopsis. Small-angle X-ray scattering (SAXS) of 2-butoxyethanol aqueous solutions was measured over wide concentration and temperature ranges, and analyzed with polynomial expansion by taking up to the 4-th order term into consideration. It was shown that the mixing state was sensitively reflected in the higher order coefficient of the SAXS curve.

Aqueous solutions of small organic molecules often show anomalous behaviors in various transport and thermal properties due to peculiar mixing states.[1)] Small angle X-ray scattering (SAXS) is one of the most direct methods to understand the mixing state of liquids. In the analysis, the SAXS intensity curve $I(s)$ is expanded as follows: [2)]

$$I(s)=r_0-r_2s^2+r_4s^4-r_6s^6+\cdots, \qquad (1)$$

where

$$r_{2i}=(1/(2i+1)!)\int<\Delta\rho_e(0)\Delta\rho_e(r)>r^{2i}4\pi r^2\mathrm{d}r. \qquad (2)$$

Here s is the scattering parameter ($s=4\pi \sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of the X-rays), $\Delta\rho_e(r)$ is the difference of the electron density from the average at the position r, and $<\cdots>$ denotes the ensemble average.

Concentration fluctuations[3)] and Kirkwood–Buff parameters[4)] can be obtained from r_0, and the so-called correlation length ξ[5)] is calculated as $(r_2/r_0)^{0.5}$.[6)] These two (r_0 and r_2) have been the chief concern in the previous studies by SAXS.[6—8)] The same parameters can be obtained from light scattering studies,[5)] which have the advantage that the evaluation of $I(0)$ $(=r_0)$ is more accurate because of the small value of s. On the other hand, SAXS can cover a much wider s range, having the possibility of examining the shape of the scattering intensity curve in terms of higher order coefficients in Eq. 1 as long as accurate enough data can be accumulated.

We have developed a new SAXS diffractometer with a doubly bent crystal to improve accuracy,[9)] and applied it to the study of the mixing state of 1-propanol (abbreviated as NPA) aqueous solution.[10)] We have proposed a dimensionless parameter χ, which reflects the shape of the SAXS curve, defined as follows:

$$\chi=r_0\cdot r_4/r_2^2. \qquad (3)$$

In this study, the SAXS curve shape of 2-butoxyethanol (BE) aqueous solutions under various conditions was analyzed by the use of χ as well as ξ. Because BE aqueous solution has a lower critical solution temperature (LCST) near room temperature,[11,12)] and the correlation length and fluctuation parameters show very large variation with temperature and concentration,[11,13)] it is an ideal system to examine whether or not an analysis in terms of χ is meaningful in understanding the mixing state.

Experimental

BE aqueous solutions for SAXS measurements were prepared by weighing the components. Each sample was kept in a cell with about 0.1 mm-thick mica windows, and its SAXS was measured by a diffractometer with a doubly bent LiF crystal monochromator.[9)]

The data were corrected for background scattering, multiple scattering, Compton scattering, and absorption.[9)] The correlation length ξ was determined from an Ornstein–Zernike plot.[14)] Then each $I(s)$ in the region $\xi\cdot s<0.8$ was approximated by Eq. 1, and the coefficients were determined by a least-squares calculation. From these coefficients, χ was calculated according to Eq. 3.

Results and Discussion

Figure 1 shows a part of the miscibility curve of BE aqueous solution[11)] as well as the measured points of the present SAXS study. The LCST is ca. 49 °C.[11,12)] Somewhat different values have been reported as the critical composition; 5.98[12)] and 7 mol%.[11)]

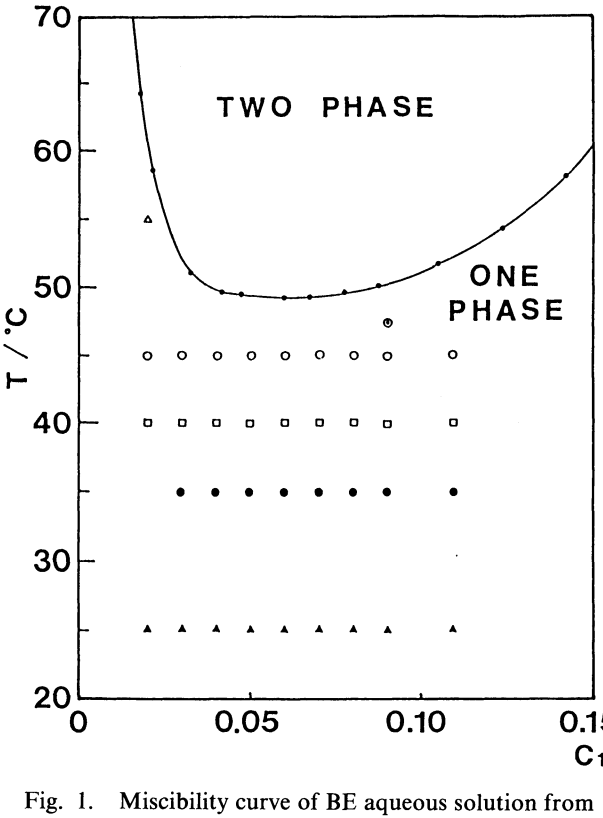

Fig. 1. Miscibility curve of BE aqueous solution from Ref. 11 and the measured points in the present work.

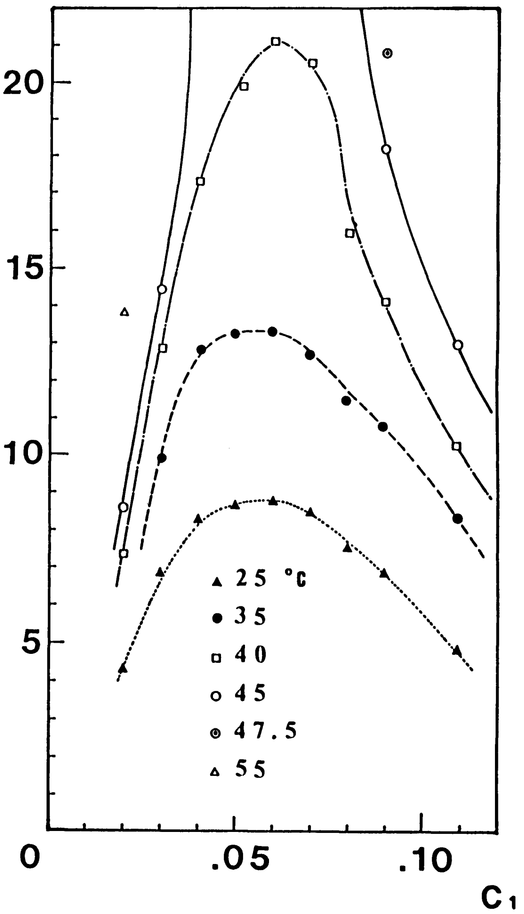

Fig. 2. ξ's plotted vs. BE mole fraction C_1 at various temperatures.

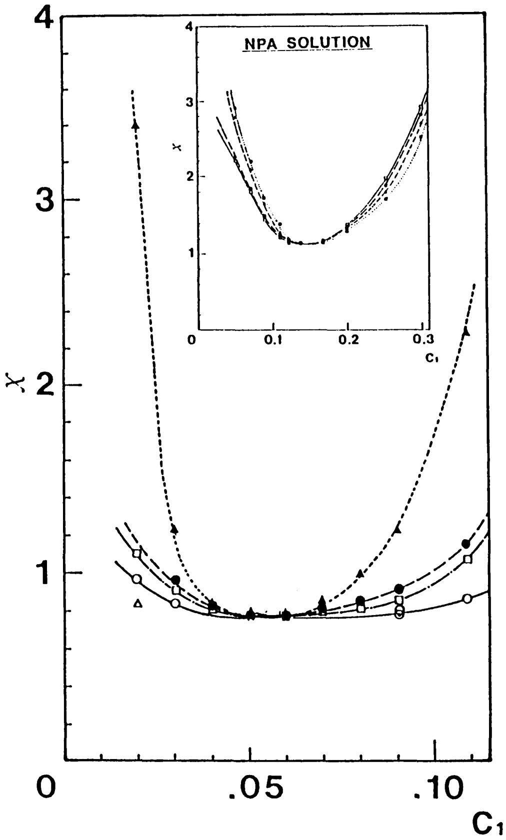

Fig. 3. χ's plotted vs. BE mole fraction C_1 at various temperatures. Inserted is a similar plot for NPA aqueous solution.[10] The temperatures are indicated by the following symbols; ■: 15, ▲: 25, ●: 35, □: 40, ○: 45, ⊙: 47.5, and △: 55 °C.

The ξ's determined by this study are plotted vs. BE mole fraction C_1 in Fig. 2. The value of ξ was largest near the critical composition (BE 5—7 mol%) and showed a marked increase with temperature rise at all the concentrations studied. In particular, under conditions very close to the LCST, ξ became too large to be evaluated accurately with the present SAXS diffractometer (the minimum s value measured was 0.03 Å^{-1}).

χ's are plotted vs. C_1 in Fig. 3. Contrary to ξ, χ was smallest (about 0.8) near the critical composition at all the temperatures studied. At off-critical compositions, χ was much larger, but decreased sharply with temperature rise and became almost 0.8 near the miscibility curve in Fig. 1.

Several studies have been performed concerning the mixing state of BE aqueous solution. It has been concluded from Rayleigh and Raman scattering that two types of clusters are formed in BE aqueous solution depending on the concentration; clathrate hydrate-like $g[(H_2O)_{50}BE]$ clusters and aggregate $h[(H_2O)_4BE]$ clusters.[11] The numbers g and h increase with temperature rise, eventually leading to phase separation. In accordance with this, an increase of ξ at higher temperatures has been observed from dynamic light scattering studies at 23 and 42 °C.[13] The temperature dependence of ξ shown in Fig. 2 more decisively illustrates cluster growth with temperature rise, although the form of the clusters can not be specified.

In addition to ξ, an analysis in terms of χ provides another piece of information about the clusters formed. This parameter has been interpreted to represent the size dispersion of fluctuating clusters formed in solution;[10] large/small χ corresponds to large/small size dispersion. Hence, the results shown in Fig. 3 show that, near critical composition (around 5 mol%), clusters having a fairly well-defined size are formed at all the temperatures studied, because χ is always small and is about 0.8. The size depends on temperature and becomes larger with temperature rise as is indicated by ξ.

On the other hand, at higher or lower concentrations, χ is much larger at room temperature and ξ is only about 5 Å, meaning that clusters, if they exist at all, are not well-defined. With temperature rise, however, χ becomes smaller, accompanied by an increase of ξ. That is, well-defined size clusters are becoming dominant and they grow with temperature rise.

It is well-known that the $I(s)$ near the critical condition is expressed by the Ornstein–Zernike (OZ) equation.[5] In that case, χ is calculated to be 0.8.[15] Experimentally, χ is observed to be 0.8 not only near the critical condition (LCST) but also near the miscibility curve and below the LCST. This suggests that $I(s)$ of off-critical solutions may also be approximated by the

OZ equation, if some conditions are satisfied. Indeed, the OZ equation has been found adequate to express $I(s)$ of t-butyl alcohol aqueous solutions for some concentration ranges[8] and employed to analyze $I(s)$ of SANS (small-angle neutron scattering) near the miscibility curve of K/KBr molten solutions.[14]

It is noteworthy to point out that the behavior of χ of BE aqueous solution is very peculiar. For comparison, a χ vs. C_1 plot for NPA aqueous solution is inserted in Fig. 3, where χ changes smoothly with concentration but varies little with temperature. NPA mixes with water at any concentration and at any temperature, and ξ changes gradually with concentration but shows almost no change with temperature;[10] modest/immodest local structure changes with temperature and concentration of NPA/BE are reflected by χ.

Improving accuracy in SAXS experiments has made it possible to determine higher order coefficients in Eq. 1 and they might be a clue to understanding the mixing state. In this study, it was shown experimentally that χ, which reflects the SAXS curve shape, is very sensitive to the mixing state and accordingly may be employed as a useful parameter. More work should be done, however, to fully extract the information contained in χ.

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15) In the case of a Lorentzian, χ must be equal to 1. Owing to the truncation effect, however, χ is calculated to be 0.8 if expanded between $0.03 < s < (0.8/\xi)$.