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How aggregation in aqueous 2-butoxyethanol solutions is influenced by temperature

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ABSTRACT

Aggregation and microheterogeneity in dilute aqueous solutions of 2-butoxyethanol (BE) are investigated employing molecular dynamic simulations. Solutions ranging in concentration from infinite dilution to the BE mole fraction, $X_{BE}=0.06$, are considered, over the temperature range 300–338.13 K. This range includes temperatures both below and above the lower critical solution temperature (LCST) of BE-water solutions. At all temperatures considered, BE association begins at a very low concentration and proceeds very rapidly up to $X_{BE}\approx 0.02$, then continues more slowly with the BE aggregates increasing in size with increasing concentration. Physically, the aggregates are loosely formed structures with significant amounts of water remaining in the BE-rich regions. The aggregation appears mainly driven by association of the hydrophobic tails of BE. As is characteristic of entropy driven hydrophobic association, BE aggregation occurs more rapidly and the aggregates increase in size with increasing temperature. Both the aggregate size and their growth with increasing temperature are in qualitative with size estimates from small angle neutron scattering (SANS) experiments. At temperatures above the experimental LCST, we observe demixing at a value of X_{BE} that lies within the two phase region. At higher temperatures and concentrations, the aggregate size approaches the length of the simulation cell, even when 64,000 molecules (water plus BE) are included in the sample. Finite-size effects come into play when the length scales associated with aggregation and microheterogeneity become comparable with the length of the simulation cell, and this important simulation issue is discussed.

1. Introduction

The physical properties of dilute aqueous solutions of short-chain alcohols, alkoxy alcohols, and amines, as well as of other small amphiphilic solutes often show anomalous behavior, which is attributed to some form of solute aggregation [1–17]. Such solutions are sometimes termed microheterogeneous because they have compositional inhomogeneities on length scales that exceed the granularity associated with molecular size. However, the microscopic nature of the aggregation and microheterogeneity is unclear in many solutions, and remains the subject of much active research.

In the present paper we consider dilute aqueous 2-butoxyethanol (BE, $CH_3-(CH_2)_3-O-(CH_2)_2-OH$) solutions, which exhibit features characteristic of microheterogeneity, in this case brought on by BE aggregation. Many physical properties of BE-water solutions undergo rather dramatic changes as functions of concentration and temperature [18–33]. For example, at 298 K many experimental studies [1,18,20–25,31,32] have reported sharp changes in different physical properties at $X_{BE}\approx 0.02$, where X_{BE} is the mole fraction of BE. This behavior is attributed to BE aggregation of some sort, although experiments do not reveal the precise microscopic nature of the BE aggregates. The phase diagram of BE-water is also unusual. At a pressure of 1 atm BE-water solutions can separate into BE-rich and water-rich phases, described by a closed loop coexistence curve [27,28,33–36], with a lower critical point (322.2 K, $X_{BE}=0.052$) and an upper critical point (403 K, $X_{BE}=0.07$). The structure of BE-water solutions has been investigated by means of light scattering [27,28,31–33,36–41] and small-angle neutron scattering (SANS) [42–44] experiments at different temperatures, and over the concentration range, $0.015<X_{BE}\leq 0.09$. These studies directly establish the presence of aggregates in BE-water solutions, and show that the aggregate size increases with increasing temperature. Many other physical properties, such as density [19], enthalpy [22], heat capacities [20,25], viscosity [27–29], diffusion [30] and ultrasound propagation [36], also suggest increasing inhomogeneity in BE-water solutions as the temperature is increased towards the lower critical solution temperature (LCST).

Recently, we reported [45] an exploratory, large-scale molecular dynamic (MD) investigation of model BE-water solutions at 298 K. We did observe the formation of relatively large BE aggregates at $X_{BE}\approx 0.02$ in qualitative agreement with experiment. The main purpose of the present paper is to determine the influence of temperature on the formation and structure of aggregated species in BE-water solutions of varying concentration. We also investigate the existence of an LCST. We find BE aggregates that grow in size with increasing temperature, and clear demixing is observed at a temperature above the experimental LCST. These observations are in qualitative accord with experiment, but we do note finite-size effects that require consideration. In our

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simulations 64,000 molecules (water plus BE) are used, but still at some concentrations and temperatures, the length scales associated with microheterogeneity approach the length of the simulation cell. This can distort the results obtained and introduce ambiguities into their physical interpretation. This issue is pertinent to the simulation of any system that has significant microheterogeneity, and is discussed in some detail.

The remainder of this paper is organized as follows. The model and simulation details are described in Section 2, results are presented and discussed in Section 3, and our conclusions are summarized in Section 4.

2. Models and simulation method

In all simulations, we employ the SPC/E water model [46] with the GROMOS 53A6 [47] model for BE. In earlier work [45], we demonstrated that the qualitative behavior of BE-water solutions does not appear to be strongly dependent on model parameters. In the GROMOS 53A6 model for BE, all alkyl groups are represented in the united atom (UA) approximation. In our simulations, all molecular bond lengths and angles are held fixed. All atom–atom interactions are described by Lennard–Jones (LJ) and Coulombic potentials, and the potential parameters are summarized in Table 1. The LJ cross interactions are obtained following the usual Lorentz–Berthelot combining rules.

All molecular dynamic (MD) simulations employ GROMACS [48,49] version 4.5.4 in double precision. The equations of motion are integrated using the leapfrog algorithm with a timestep of 1 fs. The LJ interactions are spherically truncated at 0.9 nm. The particle mesh Ewald (PME) method [50,51] is used to treat the Coulombic interactions. The real space interactions are evaluated using a 0.9 nm cutoff, and the reciprocal space interactions are calculated on a 0.12 nm grid with fourth order cubic spline interpolation. We report *NPT* simulation results for five different temperatures, 300, 316.15, 323.15, 328.15, and 338.13 K at a pressure of 1 atm. The temperature is controlled using a velocity rescaling algorithm [52] ($\tau_t = 0.1$ ps), and the pressure by applying the Berendsen coupling scheme [53] ($\tau_p = 1$ ps). The molecules are kept rigid by applying constraints to the interatomic distances within a molecule using the LINCS algorithm [54]. Initial configurations for the simulations are obtained by minimizing the energy of water and BE molecules placed in a cubical box, with the initial box sizes determined from experimental densities [19]. All systems were equilibrated for 2 ns, which was then followed by production runs of 26 ns. The results presented are averages over configurations sampled during the production runs.

In the present paper we consider solutions with BE mole fractions ranging from $X_{BE} = 0$ to 0.06. Even at these low BE concentrations, it is necessary to use relatively large samples in order to accommodate the BE aggregation and the resulting microheterogeneity. Therefore, we perform simulations with totals (water plus BE) of 32,000 and 64,000 molecules, with 64,000 being minimally adequate at the higher temperatures, where BE aggregation is more pronounced. Most simulations were carried out with initial configurations obtained as described above. However, to be certain that the aggregation observed is not influenced by the initial conditions, some test simulations at $X_{BE} = 0.06$ were performed in the following manner. First *NVT* simulations at an appropriate density were converged at 600 K, which is above the upper critical solution temperature of BE-water mixtures. At this temperature the BE and water molecules are thoroughly mixed. The system was then cooled to the desired temperature and equilibrated for 2–4 ns, followed by a production run of 25 ns. The results obtained in this way were in good agreement with those obtained from the other starting point, confirming that our results are independent of the initial conditions.

Table 1
Lennard–Jones parameters and partial charges for the models considered. The methylene carbon atoms are denoted C1–C5, with the location labels as shown: $CH_3-CH_2(1)-CH_2(2)-CH_2(3)-O-CH_2(4)-CH_2(5)-OH$.

Atom	σ (Å)	ϵ(kJ/mol)	Charge (e)
Water (SPC/E)			
O	3.166	0.6501	−0.8476
H	0.0	0.0	0.4238
BE (GROMOS G53A6 UNITED-ATOM)			
Methyl group	3.7479	0.86715	−0.108
$CH_2(1)$	4.0704	0.41054	0.194
$CH_2(2)$	4.0704	0.41054	0.143
$CH_2(3)$	4.0704	0.41054	−0.035
$CH_2(4)$	4.0704	0.41054	0.151
$CH_2(5)$	4.0704	0.41054	0.231
O (ether)	2.8492	1.05711	−0.345
O (hydroxyl)	2.9548	0.84961	−0.617
H (hydroxyl)	0.0	0.0	0.386

3. Results and discussion

To obtain a qualitative overview of our findings, it is useful to begin with configurational snapshots of different mixtures at different temperatures. Snapshots obtained with 64,000 molecules at temperatures of 300 and 338.13 K are shown in Figs. 1 and 2, respectively. Pictures are included for $X_{BE} = 0.02$, 0.04, and 0.06. At both temperatures, BE aggregation is clearly visible at $X_{BE} = 0.02$, and the aggregates clearly grow in size as the BE concentration is increased. An expanded view of a BE aggregate for $X_{BE} = 0.04$ at 338.13 K is shown in Fig. 3, with only those water molecules within 10 Å of a BE molecule included in the snapshot. One can see that the BE aggregates are rather loose in nature, and that significant numbers of water molecules remain within the BE-rich region.

Comparing Figs. 1 and 2, one notices that the aggregates appear to be larger and denser in BE at the higher temperature. It is also obvious that at 338.13 K the $X_{BE} = 0.06$ system has demixed into distinct BE-rich and water-rich phases. This phase separation is consistent with experiment. As noted earlier, BE-water solutions have a lower critical point at 322.2 K and $X_{BE} = 0.052$, and an upper critical point at 403 K and $X_{BE} = 0.07$, thus the point (338.13 K, $X_{BE} = 0.06$) lies in the region where two coexisting phases are expected. However, at 300 K the BE aggregates also appear nearly comparable in size to the length of the simulation cell. This suggests that the present molecular models may be tending towards demixing at 300 K, contrary to the situation for real BE-water solutions, which are miscible in all proportions at this temperature. An alternative explanation is that at 300 K and $X_{BE} = 0.06$, the BE aggregates are simply too large to properly fit into the simulation cell. This issue is further discussed below.

A more quantitative analysis is provided by radial distribution functions (rdfs) and related quantities. We have obtained atom–atom rdfs for all solute–solute, solute–solvent and solvent–solvent pairs, and here we consider a subset that is sufficient to describe the solution structure and BE aggregation. In the figures and in our discussion, particular atoms are designated as follows: H_{BE}, the hydroxyl hydrogen of BE; O_{HBE}, the hydroxyl oxygen of BE; O_{EBE}, the ether oxygen of BE; CH_3, the methyl group of BE; H_W, the hydrogen of water; and O_W, the oxygen of water. Unless otherwise stated, all results shown in the figures discussed below are those obtained with 64,000 molecules.

BE-water and BE-BE rdfs at $X_{BE} = 0.04$ are shown in Figs. 4 and 5, respectively, with results included for 300 and 338.13 K. From Fig. 4, we see that the peaks in the $H_{BE}-O_W$ and $O_{HBE}-H_W$ rdfs decrease significantly in height as the temperature is increased from 300 to 338.13 K, suggesting that hydrogen bonding between water and BE molecules is reduced at higher temperatures. The longer ranged part of the BE-water rdfs also decreases with increasing temperature, indicating increasing exclusion of water from BE aggregates as the temperature is increased. From Fig. 5, we note that the peak heights of the CH_3-CH_3, $O_{HBE}-H_{BE}$, and $O_{EBE}-H_{BE}$ rdfs, show a small increase