Nonionic Surfactant Mixtures in an Imidazolium-Type Room-Temperature Ionic Liquid

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Abstract: The physicochemical properties of nonionic surfactant mixtures in an aprotic, imidazolium-type room-temperature ionic liquid (RT-IL) have been studied using a combination of static surface tensiometry, dynamic light scattering (DLS), and cryogenic transmission electron microscopy (cryo-TEM). The surfactants used in this study are phytosterol ethoxylates (BPS-n, where n is an oxyethylene chain length of either 5 or 30) and the selected RT-IL is 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆). The shorter chain oxyethylene surfactant (BPS-5) exhibits greater surface activity in BmimPF₆ than BPS-30; hence, BPS-5 is a major component in driving the interfacial adsorption and molecular aggregation of the mixed system. The surface tension data demonstrate that an increased mole fraction of BPS-5 results in a decreased critical aggregation concentration (cac) and negatively increased Gibbs free energies estimated for molecular aggregation (ΔG°agg) and interfacial adsorption (ΔG°ads). Indeed, the compositions of the monolayer adsorbed at the air/solution interface and the molecular aggregate formed in the bulk solution are enriched with BPS-5. The combination of the DLS and cryo-TEM results demonstrates the spontaneous formation of multi-lamellar vesicles resulting from the BPS-5-rich composition of the molecular aggregates.

Key words: room-temperature ionic liquid, surfactant mixture, phytosterol ethoxylate, aprotic ionic liquid

1 INTRODUCTION

Room-temperature ionic liquids (RT-ILs) are a relatively new class of organic solvents. Their unique physicochemical properties such as excellent thermal stability up to 300°C or more, negligible volatility, and non-flammability make them ideal “green solvents” for many reactions of industrial importance. In the field of colloid and interface chemistry, RT-ILs have also received much attention¹,². For example, a wide range of research papers on RT-ILs were reviewed and categorized by Inoue from the perspective of surfactant chemistry³. These categories comprised the following: (i) RT-ILs as a new type of surfactant, (ii) the effects of RT-ILs on the aqueous solution properties of surfactants, (iii) the formation of microemulsions using RT-ILs as polar solvents, and (iv) the self-assembly of surfactants in RT-ILs. Our interest lies in the fourth category⁴,⁵. One of the key findings we reported in a previous paper⁶ is that phytosterol ethoxylates (BPS-n, where n is an oxyethylene chain length of 5, 10, 20, and 30) exhibit excellent surface activity in an aprotic, imidazolium-type RT-IL (1-butyl-3-methylimidazolium hexafluorophosphate, BmimPF₆). The resultant surface tension data suggest that the hydrophobic phytosterol groups are normally oriented toward the air phase and the polyoxyethylene chains are present in the RT-IL as an anchor. This molecular orientation is similar to that reported for nonionic polyoxyethylene alkyl ether surfactants in aqueous media.

Our current study addresses the physicochemical properties of binary surfactants in BmimPF₆. As mentioned earlier, the interfacial adsorption and aggregation properties of single surfactants from RT-ILs have attracted much attention. To the best of our knowledge, however, surfactant mixtures in RT-ILs have not yet been studied/report-ed. This is surprising considering that the physicochemical understanding of surfactant mixtures in aqueous media is of great interest in surfactant chemistry⁷. The surfactants employed in our current study are BPS-5 and BPS-30, which are the same surfactants used in our previous work⁸. Herein, we characterize the nonionic surfactant mixtures in BmimPF₆ on the basis of static surface tension,
dynamic light scattering (DLS), and cryogenic transmission electron microscopy (cryo-TEM) data.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

BmimPF<sub>6</sub> was kindly supplied by the Japan Synthetic Chemical Industry (Nippon Gohsei) and used as received. On the basis of the information provided by the supplier, the purity of the RT-IL sample is greater than 98%. The nonionic surfactants, BPS-5 and BPS-30, were obtained from Nikko Chemicals and used without purification. We note that the hydrophobic portion of the BPS-n surfactants comprises β-sitosterol, campesterol, and stigmasterol in a 2:1:1 ratio and the surfactants also contain less than 3 wt% of polyoxyethylene as a solvophilic impurity<sup>7</sup>. The chemical structures of BmimPF<sub>6</sub> and BPS-n are shown in Fig. 1.

2.2 Methods

The nonionic surfactants were first dissolved in BmimPF<sub>6</sub> at 80°C after which the solution was cooled to room temperature. To minimize any possible effects induced by the hygroscopic nature of BmimPF<sub>6</sub>, sample preparation was carried out under a nitrogen atmosphere with magnetic stirring.

The static surface tension was measured using a Kyowa Drop Master 700 based on the pendant drop method. This measurement was performed in a glove box under a nitrogen atmosphere at 25°C.

The apparent diameter of the surfactant aggregates in BmimPF<sub>6</sub> was estimated using an IBC NICOMP 380ZLS particle size analyzer equipped with a 5 mW He-Ne laser at a constant detector angle of 90°. The obtained scattering data were fitted using intensity-weighted cumulative analysis to estimate the diffusion coefficients of the surfactant assemblies in the solution. The apparent diameter was obtained from the diffusion coefficient using the Stokes-Einstein equation. These measurements were performed at a constant temperature of 25°C. At this temperature, the viscosity of BmimPF<sub>6</sub> was measured as 272.1 mPa s<sup>4</sup>; this value was used for the Stokes-Einstein analysis.

For the cryo-TEM measurements, the sample grid was prepared as follows: (i) a small amount of sample solution was mounted on a TEM copper grid coated with a holey carbon film, (ii) the grid was mounted using a pair of self-locking tweezers, (iii) the excess sample solution was removed from the grid using a filter paper, and (iv) the grid was introduced into liquid ethane cooled by liquid nitrogen. The prepared grid was then set on the cryo-specimen holder under liquid nitrogen cooling. Cryo-TEM measurements were made using a Hitachi H-7650 at an accelerating voltage of 120 kV under a low electron dose.

3 RESULTS AND DISCUSSION

Figure 2 shows the static surface tension of the BPS-5/BPS-30 mixtures in BmimPF<sub>6</sub> as a function of the total surfactant concentration. Mixtures prepared at mole fractions, α, of BPS-5 of 0.25, 0.5, and 0.75 were examined in this study. The surface tension data obtained for the single BPS-5 and BPS-30 systems are also given in Fig. 2. For all the single and mixed systems examined in this study, at low surfactant concentrations, the surface tension decreased gradually with increasing concentration until it attained a break point. The surfactant concentration attained at this point is assumed to be the critical aggregation concentration (cac) of each surfactant mixture in

![Fig. 1](image1.png)

**Fig. 1** Chemical structures of BmimPF<sub>6</sub> and β-sitosterol ethoxylates as a typical example of BPS-n (n = 5 and 30).

<sup>7</sup>In this study, the molecular weight of each BPS-n sample was calculated under the assumptions that the solvophobic (hydrophobic) part consists of the three components in a 2:1:1 molar ratio and the oxyethylene chain length is fixed at n. The solvophilic impurity included in the surfactant sample was ignored in this calculation. The calculation results are as follows: 631 g mol<sup>-1</sup> (BPS-5) and 1732 g mol<sup>-1</sup> (BPS-30).

![Fig. 2](image2.png)

**Fig. 2** Static surface tensions of the mixtures of BPS-5 and BPS-30 in BmimPF<sub>6</sub> as a function of the total surfactant concentration. The mole fraction of BPS-5 (α) is varied as follows: α = 0 (BPS-30), 0.25, 0.5, 0.75, and 1 (BPS-5).
BmimPF$_6$. The surface tension remains constant at concentrations above the cac, except in the BPS-30 single system. We assume that the increased surface tension observed for the BPS-30 single system primarily results from the increased viscosity of the solutions and subsequent gel formation$^{[9]}$.

The surface tension data shown in Fig. 2 allowed us to calculate some physicochemical parameters (Table 1), including the surface excess concentration estimated at the cac($\Gamma_{\text{ cac}}$), the occupied area per molecule at the cac ($A_{\text{ cac}}$), the standard Gibbs free energy of molecular aggregation in bulk solution ($\Delta G_{\text{ agg}}^{\text{0}}$), and the standard Gibbs free energy of adsorption at the air/solution interface ($\Delta G_{\text{ ads}}^{\text{0}}$)$^{[7]}$ as per the following equations:

$$\Gamma_{\text{ cac}} = -\frac{1}{RT} \frac{d\gamma}{d \ln C}$$  \hspace{1cm} (1)

$$A_{\text{ cac}} = \frac{1}{N_A \Gamma_{\text{ cac}}}$$ \hspace{1cm} (2)

$$\Delta G_{\text{ agg}}^{\text{0}} = RT \ln \left( \frac{\text{cac}}{\omega} \right)$$  \hspace{1cm} (3)

$$\Delta G_{\text{ ads}}^{\text{0}} = \Delta G_{\text{ agg}}^{\text{0}} - \frac{2h - \gamma_{\text{ cac}}}{\Gamma_{\text{ cac}}}$$ \hspace{1cm} (4)

where $\gamma$ is the equilibrium surface tension measured at the surfactant concentration of $C$, $\gamma_0$ is the surface tension of pure BmimPF$_6$ (45.5 mN m$^{-1}$)$^{[4]}$, $\omega$ is the molarity of BmimPF$_6$ (4.82 mol dm$^{-3}$), which was calculated on the basis of the density (1.37 g cm$^{-3}$) and molecular weight (284 g mol$^{-1}$) of BmimPF$_6$ reported in a previous paper$^{[8]}$, $T$ is the absolute temperature, $N_A$ is Avogadro’s number, and $R$ is the gas constant. We note that the $\Gamma_{\text{ cac}}$ and $A_{\text{ cac}}$ values estimated here indicate the degree of molecular packing at the air/solution interface under the assumption that no phase separation occurs between the two components when the adsorbed monolayer is formed. It is evident from Table 1 that increased $\alpha$ results in a decreased cac, an increased $\Gamma_{\text{ cac}}$ (and hence decreased $A_{\text{ cac}}$), and negatively increased $\Delta G_{\text{ agg}}^{\text{0}}$ and $\Delta G_{\text{ ads}}^{\text{0}}$ values. These results suggest that an increased mole fraction of BPS-5 induces greater adsorption and molecular aggregation capabilities as a result of the greater active surface nature of BPS-5 in BmimPF$_6$.

Additional physicochemical analyses on the basis of the surface tension data were carried out as follows. The first approach is based on the Clint analysis$^{[9]}$. Figure 3 shows the resultant cac data as a function of $\alpha$ and the cac curve computed using the Clint equation (assuming no significant interaction between the two surfactants):

$$\frac{1}{\text{cac}_{12}} = \frac{\alpha}{\text{cac}_1} + \frac{1-\alpha}{\text{cac}_2}$$ \hspace{1cm} (5)

where cac$_1$ and cac$_2$ are the cac values for the surfactant components 1 (BPS-5) and 2 (BPS-30), respectively, and cac$_{12}$ is the mixed cac value at $\alpha$. Clearly, the experimental cac data are slightly lower than the computed values. However, the deviation from the ideal mixing curve is rather small and the mixed cac data lie between those of the single surfactants.

The second analysis is based on the regular solution theory$^{[10]}$. The following equations give the mole fractions of the surfactant component 1 (BPS-5) in the monolayer adsorbed at the air/solution interface ($X_1$) and in the molecular aggregates formed in the bulk solution ($X_1^*$), and the interaction parameters estimated for the adsorbed monolayer ($\beta$) and molecular aggregates ($\beta^*$).

$$X_1 = \frac{X_1^*}{(1-X_1)^2 \ln[(1-\alpha)\text{cac}_2/(1-X_1)\text{cac}_1]} = 1$$ \hspace{1cm} (6)

$$\beta = \frac{\ln(\alpha C_{12}^* X_1^{*2})}{(1-X_1)^2 \ln[(1-\alpha)\text{cac}_2/(1-X_1)\text{cac}_1]} = 1$$ \hspace{1cm} (7)

$$X_1^* = \frac{X_1^{*2} \ln(\text{cac}_1/\text{cac}_2)}{(1-X_1)^2 \ln[(1-\alpha)\text{cac}_1/(1-X_1)\text{cac}_2]} = 1$$ \hspace{1cm} (8)
Table 2  Physicochemical parameters calculated from surface tension data.

<table>
<thead>
<tr>
<th>α</th>
<th>Adsorbed monolayer</th>
<th>Molecular aggregates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(X_1)</td>
<td>(β)</td>
</tr>
<tr>
<td>0.25</td>
<td>0.67</td>
<td>-2.7</td>
</tr>
<tr>
<td>0.50</td>
<td>0.80</td>
<td>-2.3</td>
</tr>
<tr>
<td>0.75</td>
<td>0.94</td>
<td>-1.4</td>
</tr>
</tbody>
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\[
β' = \frac{\ln(acac_{12} / (X_1 / cac))}{(1 - X_1)^2}
\]

where \(C_{1*}\), \(C_{2*}\), and \(C_{12*}\) are the surfactant concentrations of the single components 1 (BPS-5) and 2 (BPS-30) and their mixtures, which were estimated at a surface tension of \(γ^* = 31\) mN m\(^{-1}\). The calculation results are summarized in Table 2. One of the key results is that both the \(X_1\) and \(X'_1\) values are significantly larger than the \(α\) value in each mixed system. This indicates that both the monolayer and the aggregate are substantially enriched with BPS-5. This is consistent with the fact that both the \(ΔG^0_{agd}\) and \(ΔG^0_{ads}\) values negatively increase with increasing \(α\) and the lowest \(ΔG^0_{agd}\) and \(ΔG^0_{ads}\) values are seen in the single BPS-5 system. The deviation from ideal mixing between the two surfactant species is quantitatively supported by the calculated \(β\) and \(β'\) values, i.e., these values are always negative for all the mixtures and the deviation from 0 (ideal mixing) increases with decreasing \(α\). Therefore, it is suggested that BPS-5 is a major component that drives the overall surfactant adsorption and molecular aggregation in the mixed systems and this effect is more significant at lower mole fractions of BPS-5.

Nonionic surfactant mixtures in aqueous solutions have been widely investigated and the key findings of these studies were recently reviewed by Dong and Hao\(^6\). Regular solution analysis on the basis of experimental surface tension data has suggested that the mixing of polyoxyethylene alkyl ether surfactants in aqueous solutions yields an ideal mixture, although negative interaction parameters are usually obtained in such systems\(^{11}\). For example, in earlier work by Rosen and Hua\(^{11}\), the mixtures of trioxyethylene dodecyl ether (C\(_{12}\)EO\(_3\)) and octaoxyethylene dodecyl ether (C\(_{12}\)EO\(_8\)) give the interaction parameter (\(β\)) > -0.39, which is negatively smaller than the \(β\) values calculated for our systems. Nonideal mixtures of nonionic surfactants in aqueous media have also been reported, but such systems are only seen when surfactants with significantly different molecular cross-sectional areas and volumes of hydrophobic (solvophobic) moieties are mixed\(^{60}\). In addition, it is noteworthy that the composition of the monolayer adsorbed at the air/aqueous solution interface under ideal mixing is generally enriched with the more surface active component\(^{11–13}\). This is consistent with our current results, as mentioned earlier.

Fig. 4  DLS data obtained for the mixtures of BPS-5 and BPS-30 in BmimPF\(_6\). The surfactant concentration is fixed at 2 × cac for each mixture and three mole fractions of BPS-5 are examined: \(α = 0.25, 0.5, \) and 0.75.

Fig. 5  Cryo-TEM images obtained for the mixtures of BPS-5 and BPS-30 in BmimPF\(_6\). The surfactant concentration is fixed at 4 × cac for each mixture and three mole fractions of BPS-5 are examined: \(α = 0.25, 0.5, \) and 0.75.

To characterize the molecular aggregates in bulk solutions, DLS and cryo-TEM measurements were performed. Figure 4 shows the DLS data obtained for the BPS-5 and BPS-30 mixtures in BmimPF\(_6\) at \(α\) of 0.25, 0.5, and 0.75. The total surfactant concentrations are set at 2 × cac for each mixture. The DLS data demonstrate the presence of
molecular aggregates with diameters in the range of 100-400 nm. This is supported by the cryo-TEM data in Fig. 5, which shows circular assemblies whose diameter is broadly consistent with the diameter estimated by DLS. The cryo-TEM images also demonstrate that the observed aggregates are multi-lamellar vesicles encapsulating the ionic liquid in the core. Since the electron density of the ionic liquid is greater than that of the surfactant films, the contrast is reversed in the cryo-TEM image (i.e., the surfactant bilayer is present in the bright region).

The combination of DLS and cryo-TEM data confirms the spontaneous formation of multi-lamellar vesicles of the surfactant mixtures in BmimPF$_6$. It should be recalled here that an increased oxyethylene chain length of BPS-$n$ results in a decreased assembly size, e.g., in BmimPF$_6$, BPS-10 forms vesicles with diameters in the range of 350-1150 nm, whereas BPS-30 yields spherical micelles with diameters in the range of 2-8 nm. This indicates that the shape (and size) of the molecular aggregates is determined by the critical packing parameter (CPP) of the BPS-$n$ surfactants: an increased CPP results in lesser curved assemblies such as vesicles, whereas a decreased CPP results in greater curved assemblies such as spherical micelles. In our current surfactant mixtures, regular solution analysis suggests that BPS-5 is the major component that forms the molecular aggregates. Hence, a multi-lamellar vesicle is a possible structure, although the vesicle size is not dependent on $\alpha$ within our experimental resolution.

4 CONCLUSIONS

The interfacial adsorption and molecular aggregation properties have been characterized for nonionic surfactant mixtures (BPS-5 and BPS-30) in the RT-IL (BmimPF$_6$). The surfactant with a shorter oxyethylene chain (BPS-5) exhibits greater surface activity in BmimPF$_6$ than the longer chain analogue (BPS-30); hence, the interfacial properties are predominantly influenced by BPS-5. For example, our current experimental data demonstrate that an increased mole fraction of BPS-5 results in a decreased cac and negatively increased $\Delta G^d_{\text{ads}}$ and $\Delta G^p_{\text{ads}}$ values. The compositions of the monolayer adsorbed at the air/solution interface and the molecular aggregate formed in the bulk solution were estimated to be enriched in BPS-5. The BPS-5-rich composition induces multi-lamellar vesicle formation, which is reflective of the larger packing parameter of BPS-5. Our current study only focuses on the dilute solution region of the surfactant mixtures in BmimPF$_6$, but the active control of surfactant assemblies may be possible by manipulating the concentration, mixing ratio, temperature, and so on.

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