Phase Behavior of Phytosterol Ethoxylates in an Imidazolium-Type Room-Temperature Ionic Liquid

Hideki Sakai^{1*}, Takanori Saitoh¹, Takeshi Misono¹, Koji Tsuchiya², Kenichi Sakai^{1*} and Masahiko Abe¹

¹ Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science (2641 Yamazaki, Noda, Chiba 278-8510, JAPAN)

² Department of Applied Chemistry, Faculty of Science, Tokyo University of Science (1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, JAPAN)

Abstract: The temperature-concentration phase behavior of nonionic surfactants in an aprotic imidazolium-type room-temperature ionic liquid (RT-IL) was evaluated on the basis of a combination of visual appearance, polarized optical microscopy, and small angle X-ray scattering data. Phytosterol ethoxylates (BPS-*n*, where *n* denotes oxyethylene chain lengths of 5, 10, 20, and 30) were used as surfactants in the RT-IL, 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆). The two component mixtures yielded various phases such as discontinuous cubic, hexagonal, and lamellar phases. An increased tendency toward formation of lesser-curved molecular assemblies was observed at higher BPS-*n* concentrations, at lower temperatures, and for shorter oxyethylene chain surfactants. These trends are similar to those observed in aqueous BPS-*n* systems; however, notable differences in the phase states of the aqueous system versus the BmimPF₆ system were evident. Comparison with the water system showed that the BmimPF₆ system yielded fewer phases and generally required higher BPS-*n* concentrations to induce phase transitions. Evaluation of the effects of addition of a third component (e.g., 1-dodecanol and dodecane) to the binary system on the phase behavior showed that at a given composition ratio of BPS-20 to BmimPF₆, the addition of 1-dodecanol generally results in the phase transition to lesser-curved assemblies whereas dodecane generated no significant effects. The observed phase change is satisfactorily rationalized by localized solubilization of the third component into the binary surfactant assemblies.

Key words: room-temperature ionic liquid, nonionic surfactant, phase behavior, BmimPF₆; phytosterol ethoxylates, solubilization

1 INTRODUCTION

Room-temperature ionic liquids (RT-ILs), a relatively new class of organic solvents, exhibit unique physicochemical properties such as excellent thermal stability up to 300°C or more, negligible volatility, and non-flammability, etc., making them "ideal green solvents" in many industrially important reactions. RT-ILs have also gained importance in the fields of colloid and interface chemistry^{1,2}. In a recent review presented by Inoue, prior studies on RT-ILs were classified into four main categories from the standpoint of surfactant chemistry³. These categories include (i) RT-ILs as a new type of surfactant, (ii) 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 current interest lies in the fourth category⁴⁻⁶. One

of the key findings of our previous work is that phytosterol ethoxylates (BPS-*n*, where *n* denotes oxyethylene chain lengths of 5, 10, 20, and 30) exhibit excellent surface activity in an aprotic, imidazolium-type RT-IL (1-butyl-3-methylimidazolium hexafluorophosphate, BmimPF₆)⁴. Surface tension data presented in that study suggest that the hydrophobic phytosterol groups of BPS-*n* are preferentially oriented toward the air phase and the polyoxyethylene chains are anchored in the RT-IL. In other words, the imidazolium-type RT-IL is a good solvent for the polar oxyethylene unit and a poor solvent for the apolar phytosterol unit, comparable to the reported case of nonionic polyoxyethylene alkyl ether surfactants in aqueous media. It was also found in the mentioned study, that the BPS-*n* surfactants spontaneously form molecular assemblies, exhibiting oxyethylene-chain-length- and concentration-dependent

*Correspondence to: Kenichi Sakai and Hideki Sakai, Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, JAPAN

E-mail: k-sakai@rs.noda.tus.ac.jp and hisakai@rs.noda.tus.ac.jp

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sizes and shapes⁴⁾. For example, structural transformation of the assemblies formed by BPS-20 in BmimPF₆ from micellar to various phases such as discontinuous cubic, hexagonal, and lamellar structures at 25°C occurred with increased concentration of BPS-20.

The interest in the phase behavior of surfactants in RT-ILs as it relates to colloid and interface chemistry is reflected in the reviews presented by Hao-Zemb¹⁾, Greaves-Drummond²⁾, Inoue³⁾, and Dong-Hao⁷⁾. The primary focus of these earlier studies has been on the self-assembly of surfactants in *protic* RT-ILs such as ethylammonium nitrate (EAN)^{8–11)}. The study by Araos and Warr⁸⁾ on the phase behavior of nonionic polyoxyethylene alkyl ether surfactants in EAN demonstrated that the overall phase behavior in EAN is very similar to that in water, although longer hydrocarbon chains are required in EAN to obtain the same phases as those obtained in water, due to the higher solubility of the surfactants in EAN than in water. In comparison to the phase studies using *protic* RT-ILs, there have been fewer systematic studies focusing on the phase behavior that occurs in *aprotic* RT-ILs^{12–14)}. In addition, no mesophases have been observed for nonionic polyoxyethylene alkyl ether surfactants in *aprotic*, imidazolium-type RT-ILs at any temperature and concentration⁷⁾. In order to fill the lacunae of data and deepen the understanding of the phase behavior of surfactants in *aprotic* RT-ILs, the current article presents the temperature-concentration phase diagram of BPS-*n* surfactants in BmimPF₆. The effects of addition of a third component (such as alkane and alcohol compounds) to the two-component mixtures on the phase states are also explored.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

BmimPF₆ 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-*n* (*n* denotes oxyethylene chain

lengths of 5, 10, 20, and 30), were obtained from Nikko Chemicals and used without purification. Note that the hydrophobic portion of the BPS-*n* surfactants consists of 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. The chemical structures of BmimPF₆ and BPS-*n* are shown in Fig. 1. The following chemicals were purchased from Tokyo Chemical Industry and used as received: 1-dodecanol (C₁₂OH), 1-hexadecanol (C₁₆OH), 1-octadecanol (C₁₈OH), and dodecane (C₁₂).

2.2 Sample preparation

Binary mixtures comprising BPS-*n* with BmimPF₆ were prepared as follows. The two components (at a fixed total weight of 1.37 g) were sealed into a 5 cm³ test tube under a nitrogen atmosphere in order to minimize any possible effects induced by the hygroscopic nature of BmimPF₆. The system was heated up to 120°C (using an oil bath) in the cases of BPS-5 and BPS-10, and up to 80°C (using a water bath) in the cases of BPS-20 and BPS-30. The system was then mixed for 1 min using a Vortex mixer, and finally, centrifuged at a constant rotation speed of 3,500 rpm using a Kokusan H11-NB centrifuge. This heating-mixing-centrifugation cycle was repeated three times, after which the system was equilibrated for 2 weeks in an incubator set at a constant temperature of 25°C. It is to be noted that the phase state was examined after this equilibration period, nevertheless, no significant change in the phase state was observed even after an additional equilibration period of 1 week.

Ternary mixtures consisting of BPS-*n* with BmimPF₆ and oil were prepared as follows. The three components (at a fixed total weight of 1 g) were sealed into a 5 cm³ test tube under a nitrogen atmosphere. The three components were added into the test tube in the following order: BPS-*n*, BmimPF₆, and oil. The system was heated up to either 120°C (using an oil bath) or 80°C (using a water bath), depending on the miscibility of the components. The system was then mixed for 1 min using a Vortex mixer, and finally, centrifuged at a constant rotation speed of 3,500 rpm using

Fig. 1 Chemical structures of BmimPF₆ and β -sitosterol ethoxylates as a typical example of BPS-*n* (*n* = 5, 10, 20, and 30).

a Kokusan H11-NB centrifuge. This heating-mixing-centrifugation cycle was repeated three times, following which the system was equilibrated for 3 weeks in an incubator set at a constant temperature of 25°C. The phase state was examined after this equilibration; no significant change in the phase state was observed even after an additional equilibration period of 1 week.

2.3 Characterization

Polarized optical microscope observations were performed in the temperature range of 25–120°C using an Olympus IMF-2 microscope.

Small angle X-ray scattering (SAXS) measurements were performed using an Anton Paar PW3830 system equipped with an in-situ cell and a humidity generator. The apparatus was operated at 40 kV and 50 mA using Cu-K α X-rays. The X-ray irradiation time was fixed at 10 min. A blue imaging plate was used to collect the X-ray scattered intensities. Owing to the translucent beam stop, the raw scattering data consistently include a reduced primary intensity at a scattering vector $q = 0$. All of the data were

normalized to the same incident primary-beam intensity for the transmission calibration and were corrected for background scattering from the capillary. SAXS measurements were carried out in the temperature range of 0–80°C.

3 RESULTS AND DISCUSSION

3.1 Binary mixtures (BPS-*n* + BmimPF₆)

The phase state of the binary mixtures comprising BPS-*n* + BmimPF₆ was examined on the basis of a combination of visual appearance, polarized optical microscopy, and SAXS measurements. As typical examples, SAXS spectra of the BPS-20 in BmimPF₆ system as a function of the BPS-20 concentration can be found in our earlier paper⁴. Figure 2 shows the resultant temperature-concentration phase diagram of BPS-*n* ($n = 5, 10, 20$, and 30) with BmimPF₆. Several phase states including a micellar phase (L_1), discontinuous cubic phase (I_1), hexagonal phase (H_1), lamellar phase (L_α), lamellar-gel phase (L_β), and reverse micellar phase (L_2) are observed along with coexistence

Fig. 2 The temperature-concentration phase diagrams of BPS-*n* ($n = 5, 10, 20$, and 30) with BmimPF₆: micellar phase (L_1), discontinuous cubic phase (I_1), hexagonal phase (H_1), lamellar phase (L_α), lamellar-gel phase (L_β), reverse micellar phase (L_2), ionic liquid phase (IL), and two-phase separation (II).

these phases in certain regions. In the ensuing segment, the phase behavior is discussed as a function of (a) concentration, (b) temperature, and (c) oxyethylene chain length.

(a) Evaluation of the phase behavior of the binary mixture as a function of the BPS-*n* concentration (at a given temperature) shows that in the cases of BPS-5 and BPS-10, the change in the surfactant concentration induces little change in the phase state. In contrast, the observed phase state is largely dependent on the surfactant concentration in the cases of BPS-20 and BPS-30; the increased surfactant concentration results in phase changes as L_1 - I_1 - H_1 - L_β for BPS-20, and as L_1 - I_1 - L_β for BPS-30. For these two analogs, it is clear that an increased surfactant concentration yields lesser-curved molecular assemblies. It should be recalled here, that in the mixed system comprising BPS-*n* in BmimPF₆, the oxyethylene unit of BPS-*n* acts as a solvophilic group and the phytosterol unit acts as a solvophobic group⁴⁾. This situation is similar to the aqueous BPS-*n* system¹⁵⁾, and hence, it is possible to understand the observed phase change using the concept of critical packing parameter (CPP)¹⁶⁾; the increased surfactant concentration results in an increased CPP, and hence, lesser-curved molecular assemblies tend to be formed, as observed in Fig. 2.

(b) Subsequent investigation of the effects of temperature on the phase behavior shows that the mixtures of BPS-5 and BPS-10 with BmimPF₆ yield a two-phase coexistence region at high temperatures. The region consists of an immiscible (or non-dissolved) BPS-*n* phase and a BmimPF₆ phase. It appears plausible that the two-phase separation results from the cloud point phenomenon. It is postulated that in a manner similar to the cloud point phenomenon generally observed in aqueous polyoxyethylene-type nonionic surfactant systems, increased temperature results in decreased solvophilicity of the oxyethylene unit with BmimPF₆. In the mixed systems of BPS-20 and BPS-30 with BmimPF₆, an increased temperature induces a phase transition from the I_1 , H_1 , and L_β phases to the L_1 phase. This indicates that the increased temperature results in increased thermal motion of the surfactant molecules in the systems, leading to the destabilization of the well-defined molecular assemblies.

(c) In the third evaluation, the phase diagrams obtained for the four surfactant samples were compared with each other to illustrate the effects of the oxyethylene chain length. As mentioned earlier, the shorter chain analogs (BPS-5 and BPS-10) yield a two-phase coexistence region at high temperatures, whereas no corresponding two-phase region appears for the longer chain analogs (BPS-20 and BPS-30). This reflects the greater solvophilicity of the longer chain analogs with BmimPF₆ (in other words, the cloud point temperature increases with increasing oxyethylene chain length). The molecular assemblies observed for the mixed systems are predicted using the CPP concept: the shorter chain analogs (i.e., smaller solvophilic

headgroup and hence larger CPP) tend to form lesser-curved assemblies (L_α), whereas the longer chain analogs tend to form greater-curved assemblies such as L_1 , I_1 , and H_1 .

In summary, lesser-curved molecular assemblies tend to be formed (a) at higher surfactant concentrations, (b) at lower temperatures, and (c) for shorter oxyethylene chain analogs. These trends are similar to those observed in the BPS-*n* + water systems¹⁵⁾, and hence, the data suggest that the overall phase behavior in the BPS-*n* + BmimPF₆ systems is largely similar to that in the BPS-*n* + water systems. However, notable differences in the phase states are observed in each of the two liquid systems. First, fewer phases are observed in the BmimPF₆ system than in the water system. For example, the H_1 phase is observed in the BPS-10 + water and BPS-30 + water systems¹⁵⁾, whereas this phase does not appear in the corresponding BmimPF₆ systems. Similarly, the L_2 phase is observed in the BPS-10, BPS-20, and BPS-30 aqueous systems (but the observed region is limited at high temperatures and at high surfactant concentrations)¹⁵⁾, whereas the L_2 phase is not identified in the corresponding BmimPF₆ systems within the investigated temperature-concentration range. Second, the temperature-concentration region in which a phase that is common to both systems is observed is somewhat different for the BmimPF₆ versus the aqueous system. This is exemplified by the experimental observation that at the fixed temperature of 25°C, the I_1 - L_1 phase transition occurs at a BPS-20 concentration of 34–35 wt% in the BPS-20 + BmimPF₆ system, whereas this transition occurs at a BPS-20 concentration of ca. 26 wt% in the BPS-20 + water system¹⁵⁾. The occurrence of the phase transition at higher BPS-20 concentrations in the BmimPF₆ system relative to the water system presumably results from the greater solvophilic nature of BPS-*n* with BmimPF₆ than with water, as was similarly suggested for the polyoxyethylene alkyl ether surfactants + EAN/water systems⁸⁾.

3.2 Ternary mixtures (BPS-20 + BmimPF₆ + Oil)

The ternary mixtures constituting BPS-20 with BmimPF₆ and oil were examined on the basis of a combination of visual appearance, polarized optical microscopy, and SAXS data. Before examining the ternary phase diagrams in detail, preliminary measurements were performed to determine the combination of the three components exhibiting the widest variety of phases for further study. In these measurements, phase transitions induced by addition of oils to the binary mixtures of BPS-20 and BmimPF₆ were investigated using five compositions of the binary mixtures and a fixed 5 wt% composition of the oils ($C_{12}OH$, $C_{16}OH$, $C_{18}OH$, and C_{12}). The results are summarized in Table 1. The addition of alcohols results in a phase transition to lesser-curved molecular assemblies. For example, transitions from the I_1 phase to the H_1 phase were observed in

Table 1 Effects of addition of oils into the binary mixtures of BPS-20 + BmimPF₆.

BPS-20 (wt%)	BmimPF ₆ (wt%)	Oil (wt%)	BPS-20 + BmimPF ₆	+ C ₁₂ OH	+ C ₁₆ OH	+ C ₁₈ OH	+ C ₁₂
29	66	5	L ₁	L ₁	L ₁	L _β	L ₁
43	52	5	I ₁	H ₁	H ₁ + L _β	L _β	I ₁
52	43	5	H ₁	H ₁	H ₁ + L _β	L _β	H ₁
62	33	5	H ₁	H ₁	H ₁ + L _β	L _β	H ₁
76	19	5	H ₁ + L _β	H ₁ + L _β	H ₁ + L _β	L _β	H ₁ + L _β

Fig. 3 The ternary phase diagrams of (a) BPS-20 + BmimPF₆ + C₁₂OH and (b) BPS-20 + BmimPF₆ + C₁₂ at 25°C: micellar phase (L₁), discontinuous cubic phase (I₁), hexagonal phase (H₁), lamellar phase (L_α), lamellar-gel phase (L_β), and bicontinuous microemulsion phase (D).

the C₁₂OH mixed system, and transitions from the H₁ phase to the L_β phase were observed in the C₁₆OH and C₁₈OH mixed systems. On the basis of the variety of observed phases, the ternary phase diagram of BPS-20 + BmimPF₆ + C₁₂OH was determined to be most suitable for more de-

tailed analysis. For comparison, the ternary phase diagram of BPS-20 + BmimPF₆ + C₁₂ was also studied.

Figure 3 shows the ternary phase diagrams of (a) BPS-20 + BmimPF₆ + C₁₂OH and (b) BPS-20 + BmimPF₆ + C₁₂. The addition of C₁₂OH into the binary mixtures of BPS-20 + BmimPF₆ produced a more significant impact on the phase state than addition of C₁₂. For example, the I₁-H₁-D (bicontinuous microemulsion phase) transition was observed with increasing C₁₂OH concentration at a given composition ratio of BPS-20/BmimPF₆ of 50/50 (in wt%). This indicates that the addition of increasing concentrations of C₁₂OH tends to generate lesser-curved assemblies. Notably, both the D phase and the L_α phase appear in the ternary system comprising BPS-20 + BmimPF₆ + C₁₂OH, whereas these two phases are not observed in the temperature-concentration phase diagram of the binary BPS-20 + BmimPF₆ system. In contrast, the addition of C₁₂ into the binary mixtures of BPS-20 + BmimPF₆ does not influence the phase state to a significant extent. At a given composition ratio of BPS-20/BmimPF₆ of 50/50 (in wt%), the I₁ phase observed in the binary system is still present after addition of C₁₂, and a further increase in the C₁₂ concentration only results in the separation of the C₁₂ phase from the I₁ phase.

The observed difference in the ternary phase diagrams of the C₁₂OH and C₁₂ systems is rationalized by the difference in the localization of the oil molecules solubilized into the surfactant assemblies. It is well known that in aqueous solubilization systems, apolar molecules such as alkanes tend to be solubilized into the core region of surfactant micelles whereas polar molecules including alcohols are solubilized into the palisade region of the micelles. The palisade-type solubilization facilitates an increased CPP of the surfactant molecules forming the assemblies, leading to the structural transition to the lesser-curved assemblies. This is consistent with the I₁-H₁-D phase transition observed in the present C₁₂OH system at a given composition ratio of BPS-20/BmimPF₆ of 50/50. In the case of the core-type solubilization observed with C₁₂, no drastic changes in the phase state are observed (**Fig. 3b**). However, SAXS measurements demonstrated that the increased C₁₂ concentration results in an increased *d*₁₁₀-spacing in the I₁ phase region whereas an almost constant *d*₁₁₀-spacing is present in the I₁ + C₁₂ coexistence region (**Fig. 4**). This suggests

Fig. 4 d_{110} -spacing measured for the BPS-20 + BmimPF₆ + C₁₂ system. The composition ratio of BPS-20 against BmimPF₆ is fixed at 50/50 in wt% and the C₁₂ concentration is varied (I₁: discontinuous cubic phase).

that the core-type solubilization with C₁₂ induces swelling of the surfactant assemblies forming the I₁ phase, and the non-solubilized C₁₂ molecules are separated from the I₁ phase in the two-phase coexistence region. This phase separation results from the saturation of the solubilization of C₁₂ into the surfactant assemblies.

Finally, a description of the I₁-L₁-I₁ phase transition observed at a given composition ratio of BPS-20/BmimPF₆ of 40/60 (in wt%) is presented (Fig. 3a). The I₁-L₁-I₁ phase transition occurs when C₁₂OH is added to the binary mixture of BPS-20 and BmimPF₆. It is postulated that in the C₁₂OH concentration range of 2-6 wt%, C₁₂OH acts as a cosolvent, leading to the increased solubility of BPS-20 in the mixed solvent (BmimPF₆ + C₁₂OH). Hence, the greater-curved assembly (L₁) is observed in this C₁₂OH concentration region. Further increase in the C₁₂OH concentration causes the reappearance of the I₁ phase as a result of solubilization of the excess C₁₂OH into the palisade region of the L₁ phase. The latter transition occurs by the same mechanism discussed above at a fixed composition ratio of BPS-20/BmimPF₆ of 50/50.

4 CONCLUSION

Phase diagrams of the temperature-concentration phase transitions of the two component mixtures comprising BPS-*n* (*n* = 5, 10, 20, and 30) with BmimPF₆ showed the existence of several phases including L₁, I₁, H₁, L_α, L_β, and L₂ phases, as a function of surfactant concentration, temperature, and the oxyethylene chain length. Increased tendency toward formation of lesser-curved molecular assemblies was observed at higher BPS-*n* concentrations, at lower temperatures, and for shorter oxyethylene chain analogs.

These trends are largely similar to the trends previously reported for the corresponding aqueous systems. It was also found, however, that there are notable differences in the phase states of the BmimPF₆ system versus the water system. The BmimPF₆ system yields fewer phases relative to the water system, and generally requires higher BPS-*n* concentrations to induce phase transitions. Evaluation of the effects of addition of a third component (e.g., C₁₂OH and C₁₂) to the binary system on the phase behavior showed that the addition of C₁₂OH results in the I₁-H₁-D phase transition at a given composition ratio of BPS-20/BmimPF₆ of 50/50 (in wt%). The observed phase change is satisfactorily rationalized by localized solubilization of the third material into the surfactant assemblies. It is anticipated that a wide variety of the phase states demonstrated in the aprotic RT-IL system may prove potentially useful as reaction fields for fabrication of inorganic-organic hybrid materials.

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