Thermodynamics of Aggregation of Ammonium/Tetraalkylammonium Perfluorooctanoates: Effect of Counterions[†]

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Ammonium/tetraalkylammonium perfluorooctanoates [$C_7F_{15}COON(C_nH_{2n+1})_4$, $n = 0, 1, 2, 3, 4$; abbreviated as APFO, TMAPFO, TEAPFO, TPAPFO, and TBAPFO, respectively] were investigated by electrical conductivity measurements at different temperatures T. The critical micelle concentration (cmc) as a function of T showed a typical U-shaped relationship for APFO, TMAPFO, TEAPFO, and TPAPFO, similar to that for ordinary ionic surfactants. However, TBAPFO presented behavior more like that of nonionic surfactants. APFO exhibited a complicated dependence of the degree of counterion association of aggregates (β) on T, probably because of its hydrolysis in solution. Both the cmc and standard Gibbs energy of aggregation ($\Delta_{\mathrm{aggr}}G°$) decreased with increasing counterion size, while the degree of counterion association (β) was found to increase with the counterion size. There was a linear relationship between ln(cmc) and the chain length of the counterions (n), suggesting that the hydrophobic chains of counterions made contributions to aggregation. APFO, TMAPFO, TEAPFO, and TPAPFO all exhibited the enthalpy−entropy compensation phenomenon. TBA^+ showed its own specialty in comparison with the other counterions and induced significant deviation from normal thermodynamic cases of surfactants. The β value for TBAPFO was very large and increased with increasing T, whereas β for the other surfactants decreased with increasing T.

Introduction

The effect of counterions on the properties of surfactants is an important aspect of both practical and theoretical significance. Among those various counterions, bulky counterions with hydrophobicity are of particular interest. For example, the effects of tetraalkylammonium counterions on the properties of dodecyl sulfates reported by Zana et al.[1−4] are essentially different from those of small counterions on anionic hydrogenated surfactants.[5−7] Fluorinated surfactants have a special structure in which the hydrogen atoms in common surfactants are totally or partially displaced by fluorines.[8] When hydrogenated counterions accompany the fluorinated surfactive ions, special properties of aggregation usually occur. For example, tetraethylammonium prevailed over lithium in adsorption on perfluorooctylsulfonate micelles and was responsible for bridging a threadlike structure;[9,10] tetrabutylammonium perfluorooctanoate even abnormally exhibited two cloud-point phenomena.[11,12] The salts of perfluorononanoic acid with ammonium and tetramethylammonium counterions were studied by Hoffmann et al. to investigate the shape of micelles.[13] In our previous work, the properties of ammonium/tetraalkylammonium perfluorooctanoates were studied using surface tension[14] and conductivity[15] measurements and NMR spectroscopy.[16] In the present work, we have studied the effects of counterions on the thermodynamic properties of aggregation of fluorinated surfactants. Conductivity curves for ammonium, tetramethylammonium, tetraethylammonium, tetrapropylammonium, and tetrabutylammonium perfluorooctanoates at different temperatures in aqueous solutions were measured. To the best of our knowledge, to date there has been no report on the thermodynamics of these fluorinated surfactants. This work is expected to contribute to a further understanding of the effect of counterions on fluorinated surfactants and give theoretical thermodynamic support for adjusting the relationship between structure and properties of fluorinated surfactants.

Experimental Section

Perfluorooctanoic acid monohydrate ($C_7F_{15}COOH \cdot H_2O$, 96 %, bp 192 °C) and tetraalkylammonium hydroxides [$N(C_nH_{2n+1})_4OH$, $n = 1$ to 4; 25 % solution in water for $n = 1$ to 3, 40 % solution in water for $n = 4$] were purchased from Acros. Ammonium perfluorooctanoate ($C_7F_{15}COONH_4$, APFO, ≥ 98.0 %) was purchased from Sigma. Tetraalkylammonium perfluorooctanoates [$C_7F_{15}COON(C_nH_{2n+1})_4$, TAAPFOs: TMAPFO, TEAPFO, TPAPFO, and TBAPFO for $n = 1$ to 4, respectively] were prepared by neutralizing perfluorooctanoic acid with the corresponding tetraalkylammonium hydroxides. No minima were observed in plots of surface tension (γ) versus ln(c) for these surfactants,[14] indicating no surface-active impurities.[17] Distilled water with conductivity less than 1.4 $\mu S \cdot cm^{-1}$ was used in all of the experiments.

The conductivities of aqueous solutions of the surfactants were measured using an Advanced Conductivity Orion 162A conductivity meter (Thermo) with a resolution of 0.01 $\mu S \cdot cm^{-1}$ and accuracy of ± 0.5 %. The measurements were made in a water bath maintained within ± 0.01 K of the desired temperature. The uncertainty in the critical micelle concentration (cmc) determined in this work was within 1 %, the details of which are shown in the Supporting Information.

Results and Discussion

Critical Micelle Concentrations of APFO and the TAAPFOs at Different Temperatures. The conductivity curves of aqueous solutions of APFO, TMAPFO, TEAPFO, and TPAPFO over the temperature range (15 to 45) °C are shown

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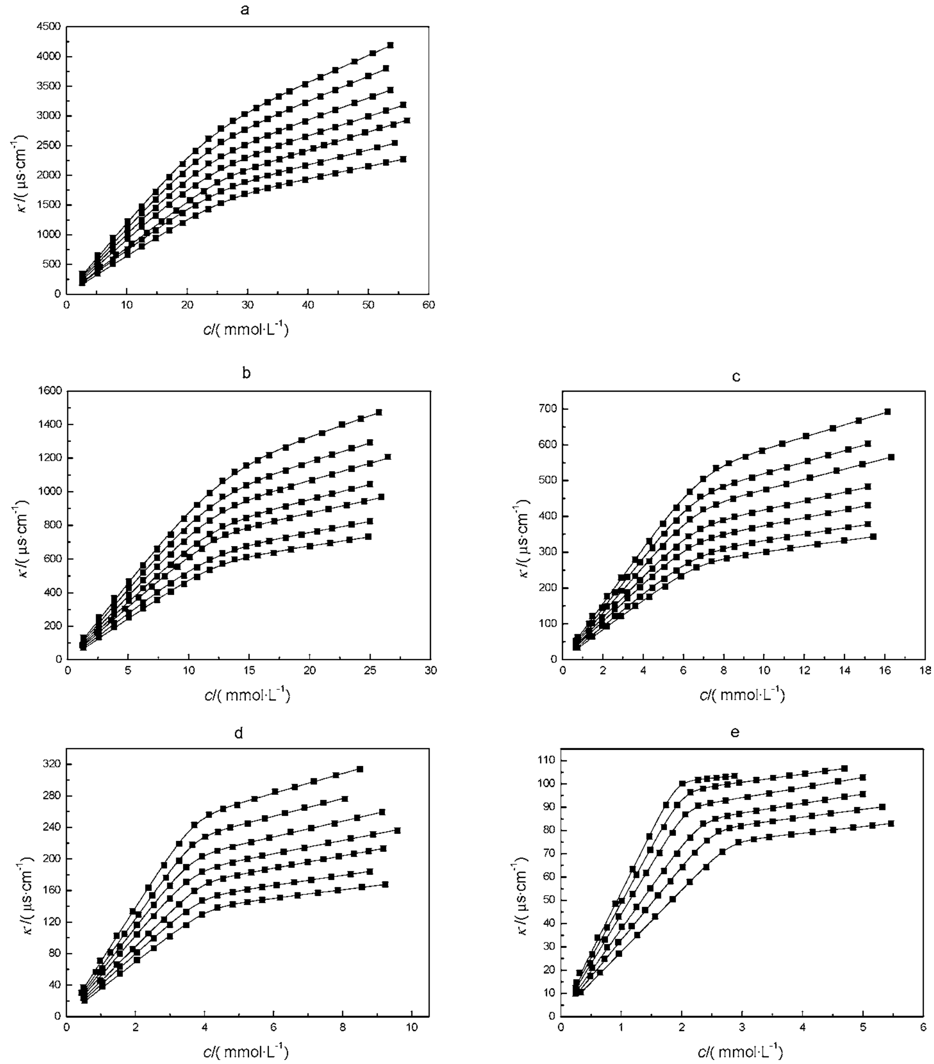

Figure 1. Plots of specific conductivity (*κ*) vs surfactant concentration (*c*) for solutions of (a) APFO, (b) TMAPFO, (c) TEAPFO, and (d) TPAPFO at temperatures (bottom to top) of (15, 20, 25, 30, 35, 40, 45) °C. (e) Plots of *κ* vs *c* for TBAPFO at (10, 15, 20, 25, 30, 35) °C (bottom to top). The dotted lines are fits to eq 1. For TBAPFO [panel (e)], the solution became turbid at relatively high concentration at 35 °C.

in Figure 1. When the counterion was tetrabutylammonium (TBA^+), phase separation occurred for the solution of TBAPFO at a relatively higher temperature similar to those of nonionic surfactants.[11] Therefore, we could measure the conductivity of TBAPFO only at relatively low temperatures of (10 to 35) °C (Figure 1). The experimental conductivity data are included in the Supporting Information.

All of the conductivity plots in Figure 1 showed a shape of two straight lines intersecting at the break point, which corresponds to the formation of aggregates. The conductivity data were fitted according to the integral form of the Boltzmann sigmoidal function proposed for the analysis of specific conductivity (*κ*) versus concentration (*c*) data for solutions of ionic surfactants:[18]

$$\kappa = a_0 + a_1 c + a_3(a_2 - a_1)\ln\left(\frac{1 + \exp[(c - a_4)/a_3]}{1 + \exp(-a_4/a_3)}\right) \tag{1}$$

The parameters a_0, a_1, a_2, a_3, and a_4 represent the value of κ in pure water, the slopes in the pre- and postmicellar regions, the width of transition between the two regions, and the central point of this transition region, respectively. The value of a_4 corresponds to the cmc of the surfactant. Figure 2 shows cmc values for solutions of APFO, TMAPFO, TEAPFO, TPAPFO, and TBAPFO at different temperatures *T*. It can be seen that over the whole temperature range investigated, the cmc values of perfluorooctanoates decreased with increasing counterion size (Figure 2), which is consistent with our previous work at 25 °C.[14−16] This could be attributed to the increasing binding ability of counterions on aggregate surfaces as the counterion size increases, that is, the increasing degree of counterion association (β) with increasing counterion size, as discussed later. The binding counterion could shield the electrostatic repulsion between surfactant headgroups, thus favoring the formation of aggregates. Moreover, for the tetraalkylammonium counterions, the hydrophobicity increases with the length of the alkyl chains, which also promotes the aggregation of surfactant molecules.

Additionally, we found that the relationship between ln(cmc) and the chain length of the counterions is linear (Figure 3), consistent with that between cmc and hydrophobic chain length for ordinary surfactants.[19] This also suggests that the hydrocarbon chains of the counterions made a contribution to the formation of aggregates.

In Figure 2, for APFO, TMAPFO, TEAPFO, and TPAPFO, the curves of cmc versus temperature are typically U-shaped, which is consistent with the relationship between cmc and

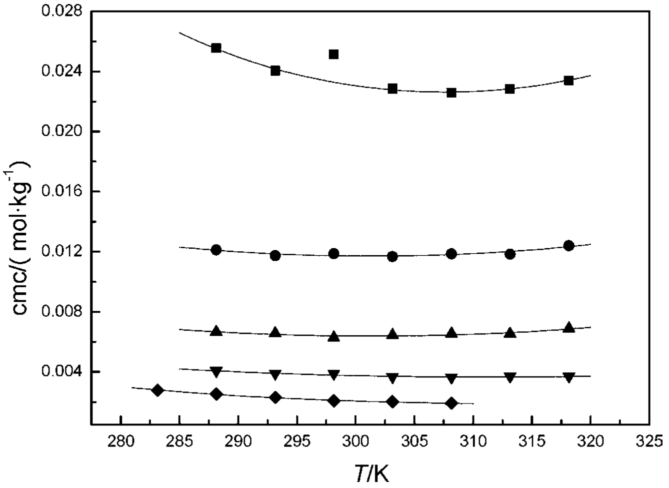

Figure 2. Variation of cmc with temperature (T) for the surfactants: ■, APFO; ●, TMAPFO; ▲, TEAPFO; ▼, TPAPFO; ◆, TBAPFO. The lines are fits based on the description of ln(cmc) vs T given by eq 7.

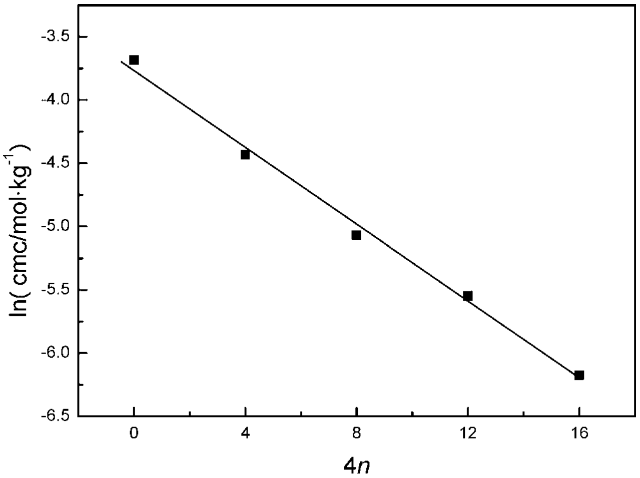

Figure 3. ln(cmc) as a function of the total number of carbons (4n) in the counterion at 25 °C.

temperature for ordinary ionic surfactants.[20,21] It is known that for ionic surfactants, the solubility becomes larger with increasing temperature, but for the TBAPFO system, the curve was interrupted by phase separation when temperature was increased. The performance of TBAPFO in which the cmc kept on decreasing with increasing temperature and then reached turbidity was similar to the variation of cmc with temperature for nonionic surfactants.[22] Figure 2 shows that the minima of the cmc versus T curves ($T_{\min}$) for APFO, TMAPFO, TEAPFO, and TPAPFO were approximately at the temperatures (307.7, 300.7, 301.3, and 311.6) K, respectively. It is known that $T_{\min}$ is a consequence of two opposing effects upon heating: (1) a decrease in the hydration of the ionic headgroup (and presumably of the counterion), which induces growth of hydrophobicity of the surfactant and hence to a decrease in the cmc, and (2) the breakdown of the structure of water unfavorable for hydrophobic interactions and hence to growth of the cmc.[23] The relationship between $T_{\min}$ and the hydrophobic chain length of surfactants is complicated. For cationic surfactants of quaternary ammonium salts, $T_{\min}$ decreases as the hydrophobic chain length increases;[21,24] however, complex dependences of $T_{\min}$ on the hydrophobic chain length have been found: $T_{\min}$ first increases and then decreases with increasing chain length for sodium perfluoroalkyl carboxylates,[25] while for sodium alkyl carboxylates, $T_{\min}$ first decreases and then increases.[26] Counterions could also show different effects on $T_{\min}$.[27,28] For APFO, TMAPFO, TEAPFO, and TPAPFO, the increase in the hydrocarbon chain length of the counterion induced a trend similar to that for the dependence of $T_{\min}$ on the chain length for sodium alkyl carboxylates,[26] i.e., the temperature of the minimum of U-shaped curve ($T_{\min}$) first decreased and then increased with the increase in the hydrophobic chain length of the counterion [the “minimum” of TBAPFO, if there had been one, would have appeared at a temperature (316.5 K) higher than that of TPAPFO (311.6 K), but TBAPFO clouded instead.). This also implies a contribution of the hydrocarbon chains of these counterions to aggregation. These results provide an explorative insight that a quantitative change of overall hydrophobicity might make the qualitative difference between those ionic and nonionic surfactants with the same hydrophobic chain length. With the increase of the counterion hydrophobicity, TBAPFO resembled a transition state for an ionic surfactant with some properties of nonionic ones. It might also probe into the role played by the headgroups in the term of hydrophobicity for nonionic surfactants.

For APFO, the minimum of the cmc versus T curve was at a relatively high temperature (307.7 K) (Figure 2). It is known that the $T_{\min}$ for the cmc versus T curve for sodium perfluorooctanoate is 316 K[25,26] and that for lithium perfluorooctanoate is 314 K.[28] APFO also showed a relatively large $T_{\min}$ in this work.

Degree of Counterion Association (β) and Gibbs Energy of Aggregation ($\Delta_{aggr}G°$) for APFO and the TAAPFOs. To further understand the effect of counterion size on the aggregation of perfluorooctanoates, the standard Gibbs energy of aggregation ($\Delta_{\text{aggr}}G°$) was estimated using the mass-action model:[29]

$$\Delta_{\text{aggr}}G° = (1 + \beta)RT\ln(\text{cmc}) \tag{2}$$

where the cmc is given in molality units (mol·kg^{-1}) and β is the degree of counterion association for the aggregate, which can be determined using:

$$\beta = 1 - \frac{a_2}{a_1} \tag{3}$$

where a_1 and a_2 are the slopes of the straight lines before and after the cmc in the conductivity plots, respectively (see eq 1).[30] The values of β for APFO and the TAAPFOs determined from conductivity using eq 3 at different temperatures are shown in Figure 4. The data were fitted by the second-order polynomial

$$\beta = a' + b'T + c'T^2 \tag{4}$$

where a', b', and c' are fitting parameters whose values are shown in the Supporting Information.

The β versus T curve for APFO in Figure 4 exhibits a variation without obvious rules. This relatively random variation could be explained by hydrolysis of APFO. It is known that APFO is the salt of a weak base and a strong acid that in solution becomes slightly acidic (pH 6) as a result of hydrolysis.[31] The possibility that the slight hydrolysis of APFO showed a relatively random influence on the degree of counterion association of aggregates versus temperature could be reasonable because no buffer was added.

For ordinary ionic surfactants, raising the temperature would accelerate the motion of particles in the solution, and thus, the degree of counterion association (β) would decrease.[32] In the present systems of TMAPFO, TEAPFO, and TPAPFO (Figure 4), β obeyed this rule for ordinary ionic surfactants. However, β increased with increasing temperature for TBAPFO and was quite large (Figure 4). This special behavior could be directly related to the special clouding phenomenon of TBAPFO in which TBA^+ counterions play the important role of bridging.[11] It should be emphasized that although it is known that there is immiscibility between fluorocarbon chains and hydrocarbon ones, in the present systems investigated, because of the electrostatic interaction, the counterions composed of hydrocarbon chains still bind to the surface of aggregates formed by fluorocarbon chains. The increasing β for longer hydrocarbon chains of counterions suggests that a hydrophobic interaction is one of the most important interactions between counterions and aggregates.

The standard Gibbs energy of aggregation ($\Delta_{aggr}G°$) estimated using eq 2 is shown in Figure 5. It was noted that $\Delta_{aggr}G°$ decreased approximately linearly with temperature. Comparison of the $\Delta_{aggr}G°$ values from APFO to TBAPFO at the same temperature also indicated that the bigger (i.e., the more hydrophobic) the counterion was, the greater contribution to aggregation it could make. The $\Delta_{aggr}G°$ of TBAPFO was found to decrease with increasing temperature at a faster rate than for the other surfactants, which is consistent with the behavior of its β value with temperature as discussed above.

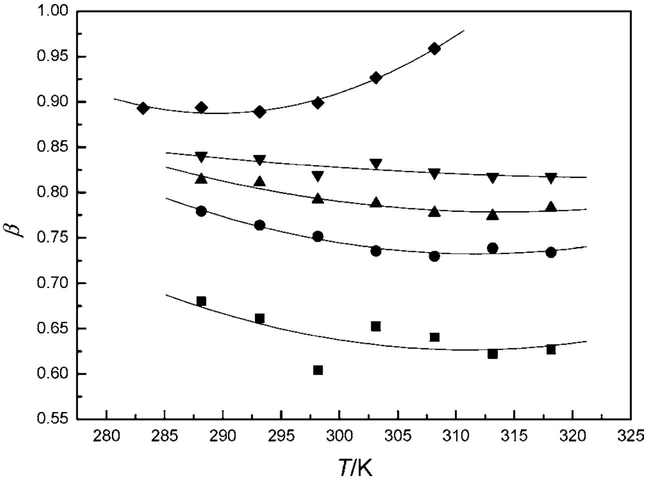

Figure 4. Degree of counterion association (β) of the surfactant aggregates vs temperature (T): ■, APFO; ●, TMAPFO; ▲, TEAPFO; ▼, TPAPFO; ◆, TBAPFO. The lines are fits to eq 4.

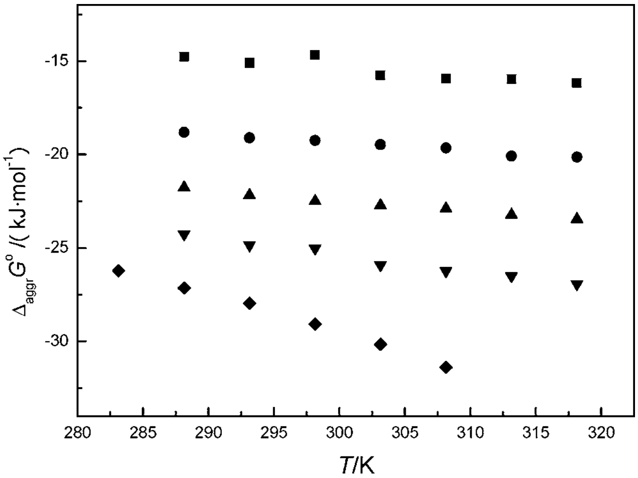

Figure 5. Relationship between $\Delta_{aggr}G°$ of the surfactants and temperature (T): ■, APFO; ●, TMAPFO; ▲, TEAPFO; ▼, TPAPFO; ◆, TBAPFO.

Enthalpy ($\Delta_{aggr}H°$) and Entropy of Aggregation ($\Delta_{aggr}S°$) for APFO and the TAAPFOs. The thermodynamic parameters of aggregation, such as the standard enthalpy ($\Delta_{aggr}H°$) and standard entropy ($\Delta_{aggr}S°$), can be obtained according to the following relations:[29]

$$\Delta_{aggr}H° = \left[\frac{\partial(\Delta_{aggr}G°/T)}{\partial(1/T)}\right] \tag{5}$$

$$\Delta_{aggr}S° = \frac{\Delta_{aggr}H° - \Delta_{aggr}G°}{T} \tag{6}$$

In eq 2, the ln(cmc) term in $\Delta_{aggr}G°$ can be fitted by the following second-order polynomial:[33−36]

$$\ln(\text{cmc}) = a + bT + cT^2 \tag{7}$$

where a, b, and c are fitting constants. The value of these parameters used for calculations are given in the Supporting Information. The fitting curves obtained using the relationship between ln(cmc) and T in eq 7 are shown in Figure 2. Thus, combining eqs 2, 4, 5, and 7 gives the following expression for $\Delta_{aggr}H°$:[33]

$$\begin{aligned}\Delta_{aggr}H° &= -RT^2\left[(1 + \beta)\frac{\partial \ln(\text{cmc})}{\partial T} + \frac{\partial \beta}{\partial T}\ln(\text{cmc})\right] \\ &= -RT^2[(1 + \beta)(b + 2cT) + (b' + 2c'T)\ln(\text{cmc})]\end{aligned} \tag{8}$$

The standard enthalpy ($\Delta_{aggr}H°$) and standard entropy ($\Delta_{aggr}S°$) of aggregation estimated using eqs 8 and 6, respectively, and their comparisons with $\Delta_{aggr}G°$ are shown in Figure 6, where it can be seen that $\Delta_{aggr}G°$, $\Delta_{aggr}H°$, and $\Delta_{aggr}S°$ depend linearly on temperature for APFO and the TAAPFOs. Enthalpy−entropy compensation was observed for APFO, TMAPFO, TEAPFO, and TPAPFO, causing the change in $\Delta_{aggr}G°$ to be very small. For APFO, TMAPFO, TEAPFO, and TPAPFO, $\Delta_{aggr}S°$ decreased with increasing temperature, which could be expected on the basis of "melting" of the "iceberg structure" of water molecules surrounding hydrophobic moieties.[37] This is a common fact of $\Delta_{aggr}S°$ for micellization of ordinary surfactants. The extensive hydrogen bonding in water gradually breaks down with increasing temperature, causing the importance of the entropic term of hydrophobic hydration to decrease and the dispersion interactions to become increasingly dominant.[38,39] For TBAPFO, abnormal thermodynamic behavior was observed: $\Delta_{aggr}H°$ remained positive and still increased with temperature. Thus, the increase of $\Delta_{aggr}S°$ was responsible for the negative value of $\Delta_{aggr}G°$ of aggregation (Figure 6). The aggregation of

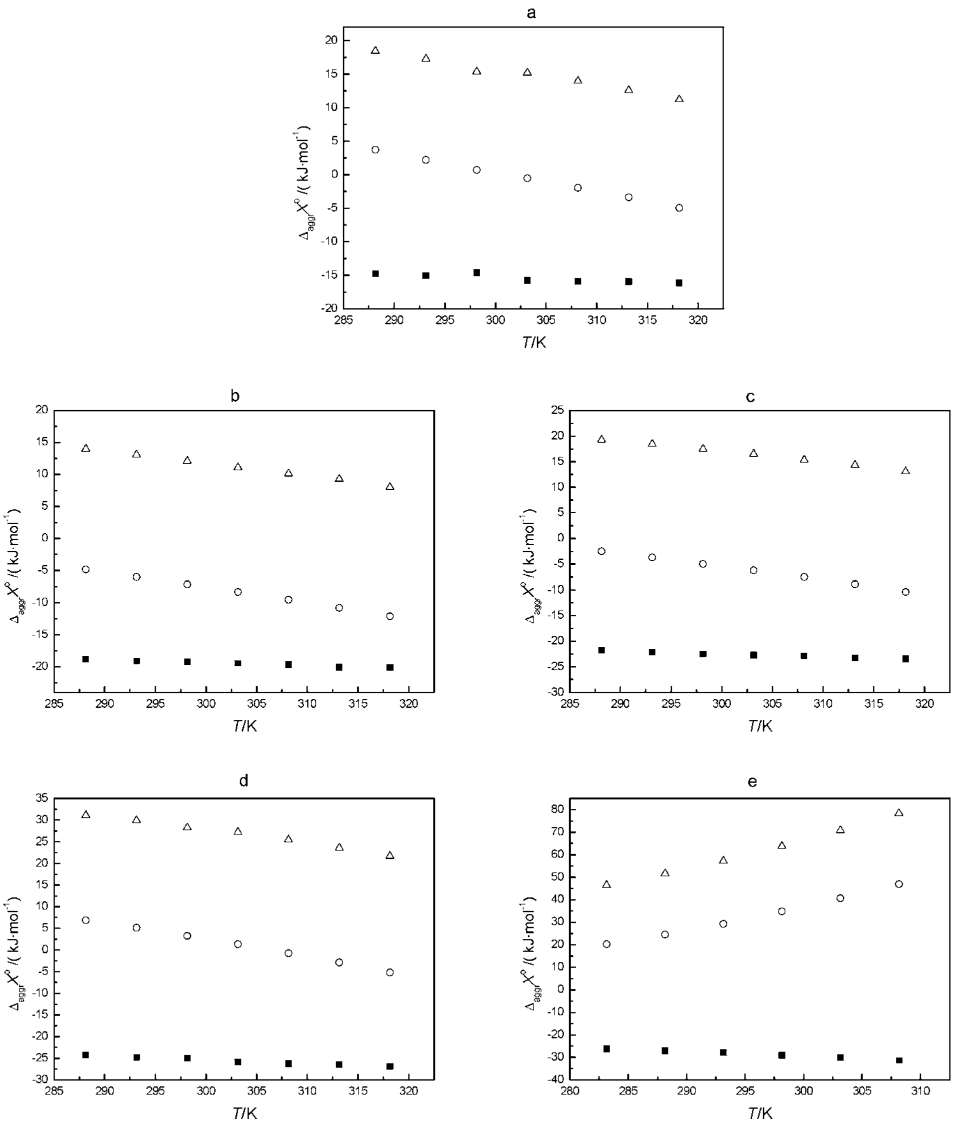

Figure 6. Dependence of the standard Gibbs energy $\Delta_{aggr}G°$, standard enthalpy $\Delta_{aggr}H°$, and standard entropy $\Delta_{aggr}S°$ of aggregation on temperature (T) for (a) APFO, (b) TMAPFO, (c) TEAPFO, (d) TPAPFO, and (e) TBAPFO: ■, $\Delta_{aggr}G°$; ○, $\Delta_{aggr}H°$; △, $T\Delta_{aggr}S°$.

TBAPFO was estimated as an entropy-driven process. The large $\Delta_{aggr}S°$ could be attributed to the strong binding of TBA$^+$ counterions, which destroys the structure of water surrounding the TBA$^+$ ions and induces disorder during association. $\Delta_{aggr}S°$ increased with temperature for TBAPFO, which is consistent with the result that the degree of counterion association β was observed to increase with temperature for TBAPFO (Figure 4). However, it does not seem reliable to believe that this is the only reason for this abnormal behavior. Maybe the tendency of phase separation for TBAPFO makes the application of the mass-action model inappropriate. At least on the basis of the extremely low level of specific conductivity of TBAPFO (Figure 1), the nonionic properties could be expected. Thus, the estimation results of TBAPFO in Figure 6 might be artificial and far away from the fact. In any event, TBAPFO truly behaved very specially in comparison with other the TAAPFO surfactants on the basis of this thermodynamic analysis.

It has been reported for sodium perfluorooctanoate[40] and tetraethylammonium perfluorooctylsulfonate[41] that the growth of micelles or transition between different forms of aggregates influences the degree of ionization. Thus, the values of the thermodynamic properties in the present work should also be a function of surfactant concentration for each specific system because of the possible change in aggregates. Therefore, the estimation of the values of thermodynamic properties is limited by the model and the complicated nature of the APFO, TMAPFO, TEAPFO, TPAPFO, and TBAPFO systems.

Summary

Fluorinated surfactants with various counterion sizes (APFO, TMAPFO, TEAPFO, TPAPFO, and TBAPFO) were studied by conductivity at different temperatures to evaluate their thermodynamic parameters. Hydrophobic interactions between counterions and aggregates showed a great contribution for aggregation, which was proved from several points of view. APFO, TMAPFO, TEAPFO, and TPAPFO all exhibited the enthalpy−entropy compensation phenomenon. TBAPFO was found to be special compared with other surfactants on the basis of the abnormal behavior of the cmc and β values versus T. This work could extend a thermodynamic insight for the special phase behavior of TBAPFO and give a further understanding of the effect of counterions on aggregation.

Supporting Information Available:

Experimental conductivity data for the APFO, TMAPFO, TEAPFO, TPAPFO, and TBAPFO systems at different temperatures, uncertainties in all of the variables determined for the surfactant systems (cmc, β, $\Delta_{aggr}G°$, $\Delta_{aggr}H°$, $\Delta_{aggr}S°$), and values of the parameters in eqs 4 and 7 used in the calculation of $\Delta_{aggr}H°$ for the surfactants. This material is available free of charge via the Internet at http://pubs.acs.org.

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