

Synthesis and Properties of a Novel Branched Polyether Surfactant

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Abstract A novel branched polyether surfactant (TPE) was prepared by anion polymerization with different proportions of propylene oxide (PO) and ethylene oxide (EO) using 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane as a core. The structures and average molecular weight (M_n) of the TPE were characterized by ¹H NMR and GPC. The cloud point was determined by turbidimetry in the presence of inorganic salts. Inorganic salts decreased the cloud point of TPE polyether in the following order: Na₂CO₃ > Na₂SO₄ > NaCl > CaCl₂ > MgCl₂. The effects of inorganic salts (NaCl, MgCl₂, CaCl₂, and NaSCN) and temperature on the surface activity of TPE in aqueous solution were investigated by surface tension measurements. The surface activity parameters and the thermodynamic parameters were calculated from surface tension data. Similar to the effect of increasing temperature, the salting-out inorganic salts such as NaCl, MgCl₂, and CaCl₂ favor the micellization and increase the maximum surface excess concentration, while the salting-in NaSCN has the opposite effect. The influence of NaCl on the morphology of micelles was investigated by TEM. The micellization is

entropy-driven at low temperature and enthalpy-driven at higher temperature. The TPE polyether has large surface activity and can be used as a demulsifier to break up crude oil emulsions.

Keywords Non-ionic surfactant · Branched polyether · Synthesis · Surface activity · Aggregation behavior

Introduction

Owing to the flexible design of the branches, different ratios of hydrophobic groups to hydrophilic groups, and the molecular weight of polypropylene oxide (PPO), polyethers comprising PPO–polyethylene oxide (PEO) are studied extensively with various methods and widely used in biomacromolecule separation, drug delivery, hydrogel, controlled release, and nanoparticle preparation [1–5]. In crude oil demulsification, branched polyethers can separate water from crude oil emulsions more effectively [6–9].

Bicyclic aromatic polyethers exceed their monocyclic counterparts in separating water from crude oil emulsions owing to the improved interaction between the bicyclic demulsifiers and the asphaltene molecules located at the oil–water interface, which are polynuclear aromatic compounds [10]. Moreover, the increased number of PPO–PEO chains and sequential polyether (R–PPO–PEO) can also improve the demulsification performance [9–13]. Here we develop a novel polyether based on the above conclusion with four aromatic rings and four number of PPO–PEO chains in sequential structure.

It is well known that crude oil from underground has plenty of inorganic salts [14–17], and the salts greatly influence the surface activity of polyethers [18–22]. Therefore, it is necessary to study the surface activity of

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polyethers at different temperature and inorganic salts because of the high temperature needed to break up crude oil emulsions.

Experimental Section

Materials

Propylene oxide (PO) 98 %, ethylene oxide (EO) 98 %, Na_2CO_3 , Na_2SO_4 , NaCl , CaCl_2 , MgCl_2 , KOH , and NaSCN were purchased from Sinopharm Chemical Reagent Corporation and used as received. 1,1,2,2-Tetrakis(*p*-hydroxyphenyl)ethane was synthesized in our laboratory according to Ref. [23]. Ultrapure water ($18 \text{ M}\Omega \text{ cm}^{-1}$) was used in the experiments.

Synthesis and Characterization of TPE

TPE polyether was synthesized by anionic polymerization with PO and EO using 1,1,2,2-tetrakis(*p*-hydroxyphenyl)ethane as precursor in the presence of potassium hydroxide (Scheme 1). The precursor was first dissolved in PO, and then the reaction was kept at 120–140 °C and pressure of 0.2–0.4 MPa in a pressure steel kettle with a magnetic drive stirrer, an electric heating mantle with a thermocouple inserted in the reactor body, and circulating water.

The structure of TPE was characterized by ^1H NMR (Bruker AV-400 spectrometer operating at 400 MHz). ^1H NMR (CDCl_3), δ : 1.13 (m, CH_3 , 3H), 3.4–3.8 (m, CHCH_2 and CH_2CH_2), 6.64 (d, ArH, 4H), 7.32 (d, C-ArH, 4H).

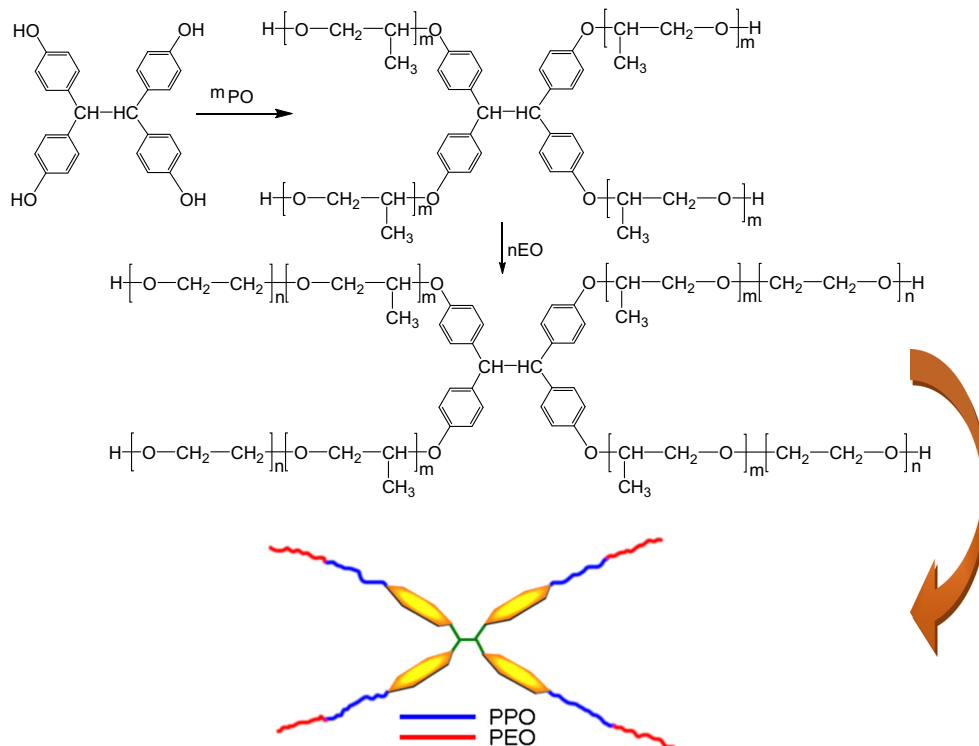
Gel Permeation Chromatography (GPC)

The average molecular weight was measured by GPC (Waters binary HPLC pump 1525 and a Waters 2414 refractive index detector) with standard polystyrenes and tetrahydrofuran as eluent.

Cloud Point Measurement

Cloud point measurement is usually performed by visual observation and taken as the temperature for the first appearance of turbidity [24–27]. To eliminate the visual error, a HACH 2100Q turbidimeter was employed to measure the turbidity of TPE polyether at various concentrations. A refrigerated circulator HD120-RT8 (Prima Instrument, UK) was used to control the sample temperature from 4 to 18 °C at a step of 0.5 °C. The turbidity of the sample is a function of nephelometric turbidity units (NTU) and temperature. The cloud point is defined as the temperature at the intersection of the two lines resulting from the fitting of the turbidity curve as a function of temperature before and after the inflection.

Scheme 1 Preparation of four-armed polyether TPE



Surface Tension Measurements

The surface tension measurements were performed on a K100 processor tensiometer (Germany, Krüss Corporation, precision 0.01 mN m^{-1}) at temperature from 25 to 65 °C within a step of 5 °C.

TEM Observation

The micelles formed in aqueous solutions were observed by transmission electron microscopy (TEM) using a JEM-2010 electron microscope. The sample was dropped onto copper grids followed by a drop of phosphotungstic acid (1 wt% aqueous solution) for staining.

Results and Discussion

Characterization of TPE

The structures of monomer and polymer were confirmed by the ^1H NMR spectrum shown in Fig. 1. The weight ratio of PO/EO validated by ^1H NMR according to the two signals at 0.9–1.3 and 3.4–3.8 ppm [10, 28, 29] is 2.66. The molecular weight (M_n) and distribution (M_w/M_n) of TPE obtained by GPC were 2250 and 1.21, respectively.

Cloud Point

Figure 2 shows the turbidity of TPE polyether at different concentrations as a function of temperature in aqueous solution. The intersection marked in the fittings to the turbidity curve is defined as the cloud point. It is obvious that the cloud point decreased remarkably with the increase in concentration below 20 g L^{-1} and changed slightly with concentration up to $20\text{--}50 \text{ g L}^{-1}$. This behavior indicates that the cloud point tends to keep constant with increasing concentration [30, 31]. The decrease in cloud point is ascribed to the increased micelle–micelle interaction with the increase in micelle concentration [32]. The interactions between micelles, which are influenced by the size and number of micelles, increase rapidly, then become almost constant, and finally affect the cloud point. The change in size and number of micelles with increasing concentration is confirmed by TEM as discussed below.

The cloud point at 50 g L^{-1} is 8 °C, lower than that reported for $\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$ or L64 (55 °C) at the same concentration [33]. Besides the very hydrophobic 1,2,2-tetrakis(*p*-hydroxyphenyl)ethane and large ratio of PO/EO, the branching, and greater symmetry may contribute to the lower cloud point of TPE polyether [34].

The turbidity curves and effect of several inorganic salts on the cloud points of TPE polyether at 5 g L^{-1} are

presented in Fig. 3. It suggests that the higher the concentration of inorganic salt is, the earlier the turbidity appears. As shown in Fig. 3f, a slight linear decrease in cloud point is seen with increasing concentration of aqueous salt solution. It is clear that the effect of inorganic salts on decreasing cloud point is in the following order: $\text{Na}_2\text{CO}_3 > \text{Na}_2\text{SO}_4 > \text{NaCl}$ and $\text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2$. Salts containing divalent anions such as SO_4^{2-} are known to be more effective at salting out the PEO chains than those containing monovalent anions like Cl^- [35–37]. The decrease in cloud point with different anion salts is more rapid than that of different cation salts, indicating that the cloud point of a surfactant solution depends on its cation group and anion group. The anion group has greater influence than the cation group, especially with large polyatomic anions [36].

Effect of Inorganic Salts on Surface Activity

Figure 4 displays the surface tension isotherms of TPE aqueous salt (NaCl , MgCl_2 , CaCl_2 , and NaSCN) solutions at the same anionic concentration of 1 mol L^{-1} . A steady decrease in surface tension with concentration was observed. Two intersections that appeared at higher concentration were as marked A and B. The surface tension initially decreases sharply before point A and thereafter decreases at a slower rate. This transition has been noted for PPO–PEO polyethers [38–40]. Before point A, the decrease in surface tension indicates the formation of polyether monolayer absorbed at the air–water interface, while point B corresponds to the formation of multimolecular micelles at the critical micelle concentration (cmc) [40]. The intermediate region between A and B is often attributed to the polydispersity of PPO–PEO polyethers or the formation of unimolecular micelles [38]. The addition of NaCl , MgCl_2 , and CaCl_2 known as salting-out salts promotes surface activity by reducing the surface tension, while salting-in salt such as NaSCN decrease surface activity.

The surface-active parameters such as maximum surface excess concentration (Γ_{max}), minimum surface area per molecule (A_{min}), effectiveness of surface tension reduction or surface pressure (π_{cmc}), and the efficiency of surface tension reduction and adsorption ($\text{p}C_{20}$) can be obtained by the following equations [41, 42]:

$$\Gamma_{\text{max}} = \frac{-1}{2.303 RT} \frac{\partial \gamma}{\partial (\log C)} \quad (1)$$

$$A_{\text{min}} = \frac{10^{18}}{N \Gamma_{\text{max}}} \quad (2)$$

$$\pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad (3)$$

$$\text{p}C_{20} = -\log C_{20} \quad (4)$$

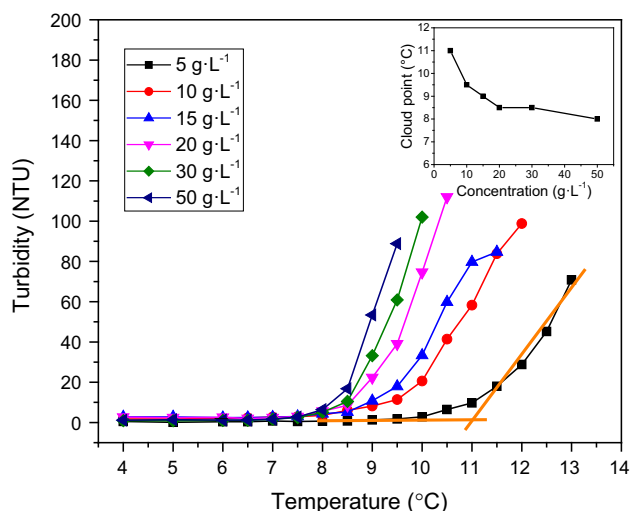


Fig. 2 Turbidity of TPE polyether at various concentrations as a function of temperature in aqueous solution. *Inset* is the cloud point of TPE polyether as a function of concentration

the performance in reducing surface tension of bulk phase concentration by 20 mN m^{-1} , whereas the effectiveness means the minimum surface tension that surfactant can reach. The increasing values of pC_{20} on the addition of NaCl, MgCl_2 , and CaCl_2 suggest that the salting-out salts promote the efficiency of surface tension reduction and adsorption, while the NaSCN reflects the opposite effect [35]. The Γ_{max} is a useful measure of the effectiveness of adsorption at the water–air interface [43]. The small increase of Γ_{max} indicates that the salting-out salts slightly favor the adsorption, whereas the salting-in NaSCN slightly inhibits the adsorption. The π_{cmc} has a similar result with Γ_{max} . It can be concluded that the salting-out salts promote both efficiency and effectiveness of surface tension reduction and adsorption.

The other useful parameter to evaluate the effect on micellization and adsorption processes is cmc/C_{20} . An increase in the cmc/C_{20} means that adsorption is facilitated more than micellization [43]. Both the larger pC_{20} and smaller cmc/C_{20} on the addition of salting-out salts suggest that these salts facilitate the micellization; on the contrary, the salting-in NaSCN favors the adsorption in accordance with the conclusion made by Zhai [20].

The salting-out salts decrease the cmc in the following order: $\text{NaCl} > \text{MgCl}_2 > \text{CaCl}_2$. The monovalent cation is more effective at salting out the polyether molecules than divalent cations such as Ca^{2+} and Mg^{2+} . It has been reported that anions have a more pronounced effect than cations [44]. For common monovalent anions, the typical order for their effect on the physical behavior of aqueous processes is known as the Hofmeister series [22, 44–47]: $\text{F}^- > \text{Cl}^- > \text{Br}^- \sim \text{NO}_3^- > \text{I}^- > \text{SCN}^-$. The Cl^- has a strong hydration effect compared with SCN^- which is

classified into poorly hydrated anions. It was originally believed that the Cl^- enhanced the water structure by disrupting the hydrogen-bonding network between polyether molecules and water, lowering the solubility of polyether molecules; whereas the poorly hydrated SCN^- interferes with the water structure. Deyerle and Zhang [45] proposed the interaction between these ions and polyether molecules. Well-hydrated Cl^- interacts with the hydrophilic PEO groups by changing the entropy of hydration water around the polyether, making these water molecules less available to the polyether and therefore decreasing the cmc. In contrast, poorly hydrated SCN^- enhances the polyether hydration by binding to hydrophobic PPO groups leading to the increase in cmc.

In accordance with the above results and research from Zhai and Chen [20, 39], the salting-in effect and salting-out effect are illustrated in Fig. 5. The conformation of polyether is strongly affected by inorganic salts. The salting-out salts compress the polyether molecules while the salting-in salts expand these molecules [18, 33].

The standard Gibbs free energy of micellization (ΔG_m^o) and Gibbs free energy of adsorption (ΔG_{ads}^o) are determined by [48, 49]

$$\Delta G_m^o = RT \ln X_{\text{cmc}} \quad (5)$$

$$\Delta G_{\text{ads}}^o = \Delta G_m^o - 0.6023 \times \pi_{\text{cmc}} \times A_{\text{min}} \quad (6)$$

where X_{cmc} is the mole fraction unit of the cmc value. According to the literature [43, 50], for nonionic surfactant, the ΔG_m^o can be given as

$$\Delta G_m^o = RT \ln \frac{\text{cmc}}{\omega} \quad (7)$$

where cmc is expressed in molar unit and ω is the number of moles of water per liter.

As would be expected, both micellization and adsorption are spontaneous whether with or without salts as reflected by the negative values of ΔG_m^o and ΔG_{ads}^o respectively. These more negative values and the increased cmc/C_{20} in the addition of salting-out salts facilitate the micellization more than adsorption. The more negative values of ΔG_{ads}^o than the corresponding values of ΔG_m^o indicate that adsorption is more spontaneous than micellization [51, 52], in accordance with the fact that when polyether molecules dissolve in water, these molecules are always adsorbed onto the air–water interface, and then aggregate to form micelles only when the concentration exceeds the cmc.

Morphology of Copolymer Aggregate

TEM micrographs were used to validate the morphology of TPE polyether micelles and the influence of NaCl on these micelles (Fig. 6). The micelles in aqueous solution are

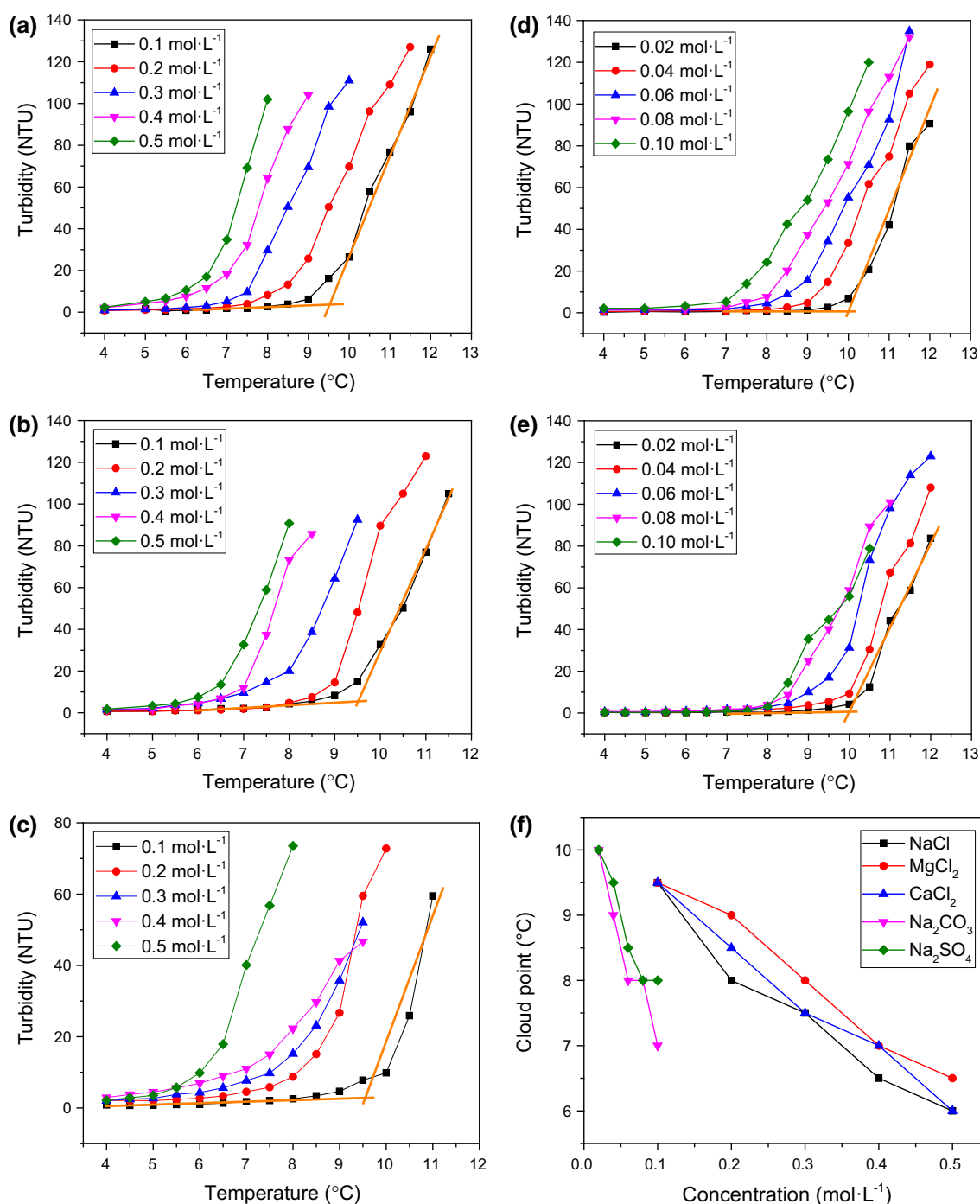


Fig. 3 Turbidity curves of TPE polyether in the presence of **a** NaCl, **b** MgCl₂, **c** CaCl₂, **d** Na₂CO₃, **e** Na₂SO₄ and the effect of salts (**f**) on the cloud point at 5 g L⁻¹

spherical, and the size and number of these micelles increase with increasing concentration of TPE polyether. The mean size of the micelles increase rapidly from 40 to 121 nm with concentrations from 10 to 30 g L⁻¹, and change slightly to 159 nm when the concentration reaches 50 g L⁻¹. This behavior affects the interaction between micelles, and finally affects the cloud point. The

tendency of the particle size of micelles to increase with concentration of polyether is in accordance with Ref. [53].

It was observed that little inorganic salts like NaCl have no influence on the mean size of micelles. With further increase in concentration of NaCl, the mean size of micelles increases continuously. The phenomenon that the particle size of micelles increases with increasing

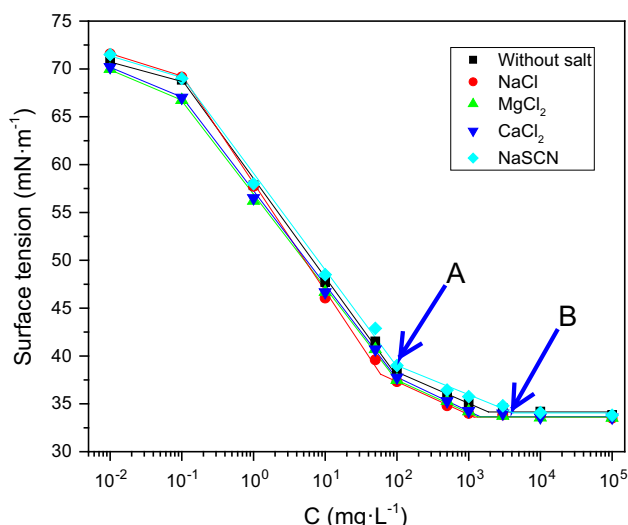


Fig. 4 Surface tension isotherms of the TPE aqueous solution in absence and presence of different inorganic salts at 25 °C

concentration of TPE polyether or inorganic salt indicates that the micelles are easy to grow and easy to separate into two phase [32]. When the concentration of NaCl is high, the image of NaCl can be seen clearly from TEM as shown in Fig. 6f.

Effect of Temperature on Surface Activity

Figure 7 demonstrates clearly the decrease in surface tension with increasing temperature of TPE polyether with and without NaCl at various temperatures. Table 2 shows surface-active parameters calculated from Eqs. (1), (2), (3), and (4). The effect of temperature on cmc is complex, the value appearing first to decrease and then to increase with further increase in temperature. Temperature increase causes decreased hydration of the hydrophilic PEO groups, resulting in the increase in hydrophobicity which favors micellization. When surfactant molecules dissolve in water, the degree of structured water is increased. However, the structured water surrounding the hydrophobic groups would be lost as the temperature increases, an effect that disfavors micellization. The two opposite effects

determine whether the cmc increases or decreases over a particular temperature range [43]. For TPE polyether, as the temperature increases further, the effect of the hydrophobic groups exerts a predominant influence as the cmc reaches a minimum value leading to the increase in cmc [54].

It is obvious that for both TPE solutions the γ_{cmc} decreases continuously as the temperature increases, and the presence of salting-out NaCl promotes the surface activity over the whole temperature range. π_{cmc} also decreases with increased temperature indicating the lower effectiveness in surface tension reduction, which is consistent with previous reports [43, 54].

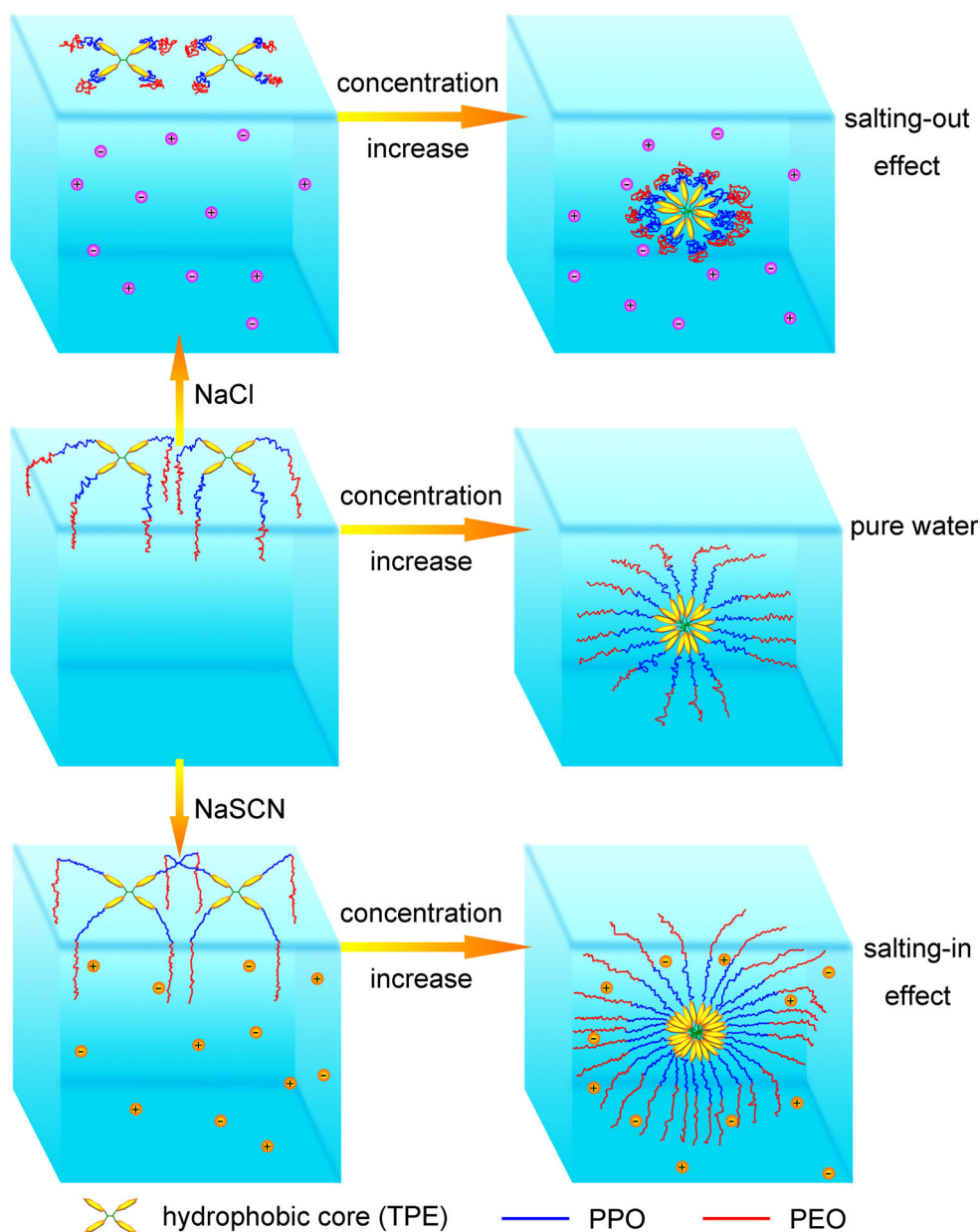
A_{min} is found to increase with increasing temperature whether in the absence or presence of NaCl in agreement with the previous reports [27, 52]. As reported [43], the A_{min} is mainly determined by PEO groups of polyether. At low temperature, the PEO groups protrude into the aqueous solution. The PEO chains become spread at the air–water interface at an elevated temperature, resulting in larger area of molecules. The presence of salting-out NaCl reduces the number of free water molecules in the bulk solution leading to the compression of the TPE molecules, therefore reducing the area. In addition, increased molecule motion and chain flexibility at elevated temperature resulting in expanding of polyether molecules contribute to the increase in A_{min} [55]. On the other hand, the increased dehydration of the PEO groups as the temperature increases improves the adsorption of polyether molecules as seen from increased pC_{20} .

The conformational transition of polymer at different temperature with the increase in concentration is illustrated in Fig. 8. With the increase in temperature, the hydrophobicity of the PPO chains increases leading to formation of a more compact hydrophobic core and polyether molecules form micelles more easily [39, 45]. However the PEO chains expand continuously as the temperature increases; as a result the micellar size increases at higher temperature as confirmed by small angle neutron scattering [33]. The conformational transition is also sensitive to salts.

Table 1 Surface activity parameters and the free energy of micellization of TPE aqueous solution in absence and presence of different inorganic salts at 25 °C

	cmc (mg L ⁻¹)	γ_{cmc} (mN m ⁻¹)	$\Gamma_{max} \times 10^6$ (mol m ⁻²)	A_{min} (nm ²)	π_{cmc} (mN m ⁻¹)	pC ₂₀	cmc/C ₂₀	ΔG_m^o (kJ mol ⁻¹)	ΔG_{ads}^o (kJ mol ⁻¹)
Without salt	1884	34.15	0.56	2.96	38.35	5.77	494	-27.5	-34.4
CaCl ₂	1448	33.65	0.63	2.66	38.85	5.87	474	-28.2	-34.4
MgCl ₂	1340	33.63	0.60	2.77	38.87	5.90	475	-28.4	-34.9
NaCl	1263	33.61	0.59	2.83	38.89	5.87	390	-28.7	-35.3
NaSCN	4214	34.05	0.53	3.12	38.45	5.70	936	-25.5	-32.8

Fig. 5 Schematic illustration of salting-in effect and salting-out effect on polyether molecules at the air/water surface



Thermodynamic Parameters of Micellization

The thermodynamic parameters such as enthalpy, entropy, and energy of surface formation can be evaluated from the temperature effect on surface activity. The enthalpy (ΔH_m^o) can be obtained by applying the well-known relations

$$\Delta H_m^o = -T^2 \frac{\partial(\Delta G_m^o/T)}{\partial T} = -RT^2 \frac{\partial \ln X_{\text{cmc}}}{\partial T} \quad (8)$$

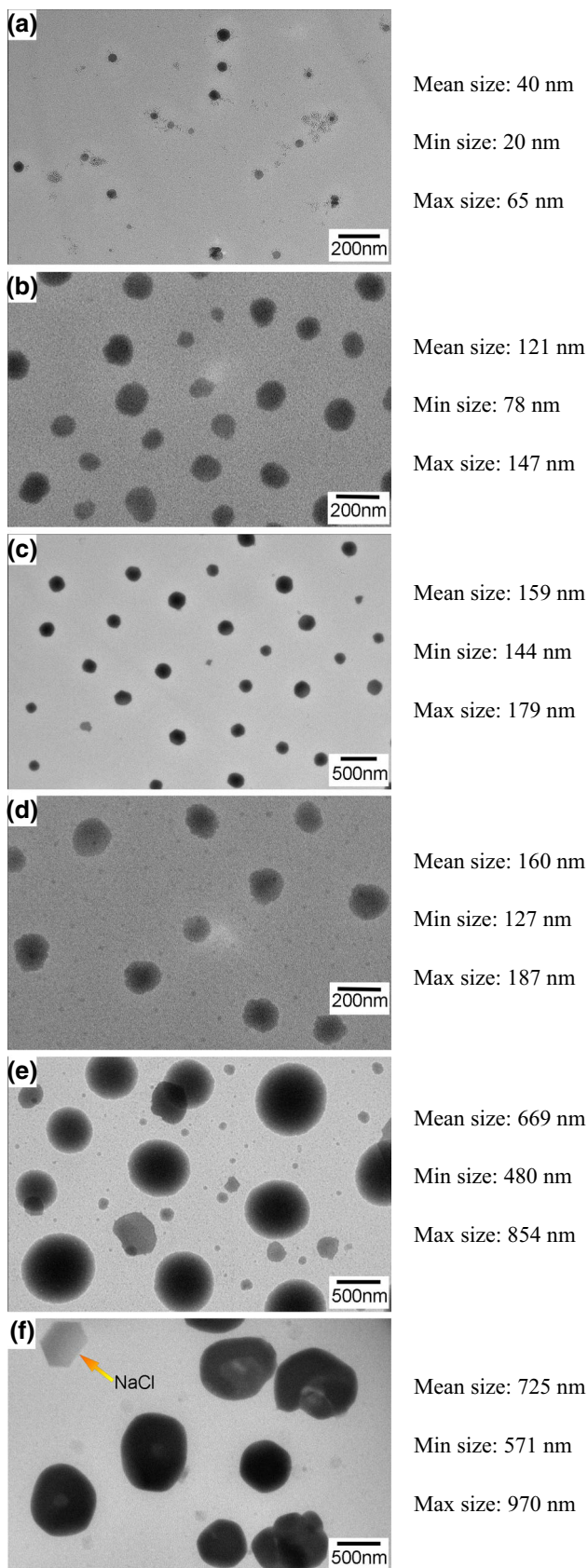
where the $\ln X_{\text{cmc}}$ is a 2nd-order polynomial function of temperature [54, 56]. It was reported that a new equation can fit the point excellently by the relation [57]

$$\ln X_{\text{cmc}}(T) = a + bT + \frac{c}{T} \quad (9)$$

where a , b , and c are determined by least-squared regression analysis. Once the Gibbs free energy and the enthalpy are obtained, obviously, the entropy can be determined by

$$\Delta S_m^o = \frac{\Delta H_m^o - \Delta G_m^o}{T} \quad (10)$$

Table 2 displays the thermodynamic parameters of TPE at different temperatures with or without NaCl. It is found that all the thermodynamic parameters decrease monotonically as the temperature increases over the whole temperature range from 25 to 65 °C. It is clear that



◀**Fig. 6** TEM micrographs and particle sizes of TPE polyether at **a** 10 g L⁻¹, **b** 30 g L⁻¹, **c** 50 g L⁻¹, **d** 50 g L⁻¹ with 1000 mg L⁻¹ NaCl, **e** 50 g L⁻¹ with 1000 mg L⁻¹ NaCl, and **f** 50 g L⁻¹ with 2000 mg L⁻¹ NaCl

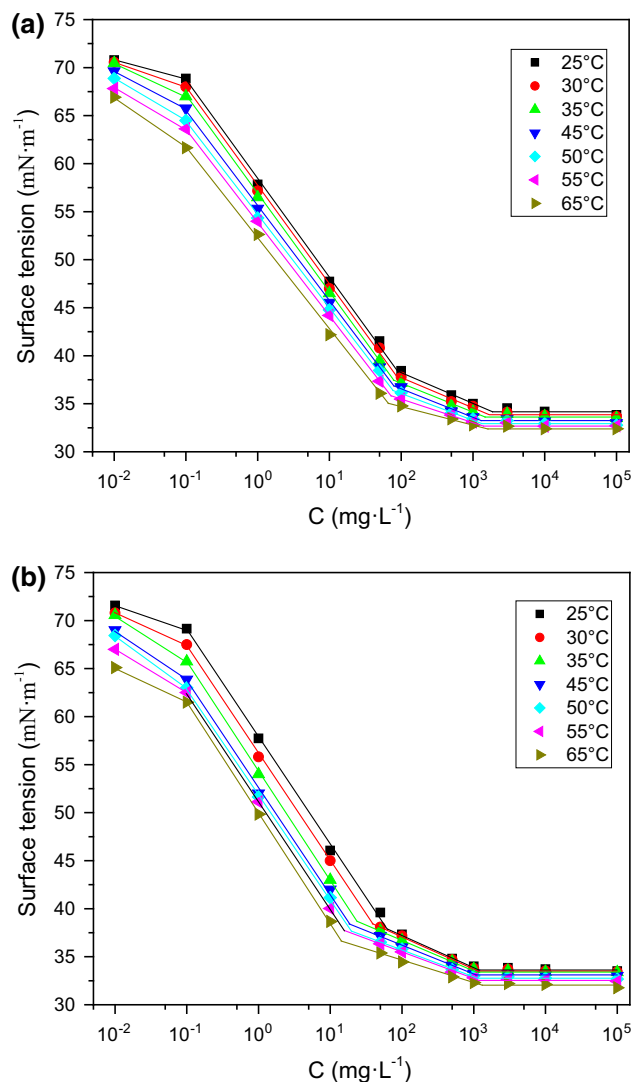


Fig. 7 Surface tension isotherms of the TPE aqueous solution at different temperature: **a** without salt, **b** with 1 mol L⁻¹ NaCl. Lines are only visual guides

the values of ΔH_m^o and ΔS_m^o are quite sensitive to temperature. The positive values of ΔH_m^o when the temperature is below 45 °C indicate that the transfer of unimers from solution to micelle is an endothermic process at low temperature, whereas the process transforms into exothermic at higher temperature. The thermal transformation of micellization is in accordance with Refs. [58, 59]. The smaller ΔS_m^o in aqueous NaCl solution than the corresponding value in aqueous solution indicates that

Table 2 Surface activity and thermodynamic parameters of TPE at different temperature without salt and with NaCl

Temperature (°C)	cmc (mg L ⁻¹)	γ_{cmc} (mN m ⁻¹)	$\Gamma_{\text{max}} \times 10^6$ (mol m ⁻²)	A_{min} (nm ²)	π_{cmc} (mN m ⁻¹)	pC ₂₀	ΔG_m^o (kJ mol ⁻¹)	ΔG_{ads}^o (kJ mol ⁻¹)	ΔH_m^o (kJ mol ⁻¹)	ΔS_m^o (kJ mol ⁻¹ k ⁻¹)
Without salt										
25	1884	34.15	0.56	2.96	38.35	5.77	-27.5	-34.4	25.6	0.18
30	1682	33.86	0.54	3.07	37.93	5.77	-28.3	-35.3	20.0	0.16
35	1483	33.62	0.51	3.25	37.59	5.79	-29.1	-36.4	14.3	0.14
45	1298	33.25	0.49	3.42	36.32	5.78	-30.4	-37.8	2.6	0.10
50	1324	32.93	0.45	3.71	36.01	5.79	-30.8	-38.8	-3.4	0.08
55	1398	32.66	0.39	4.28	35.33	5.81	-31.1	-40.2	-9.5	0.07
65	1630	32.39	0.29	5.65	35.12	5.85	-31.6	-43.6	-21.9	0.03
With NaCl										
25	1191	33.61	0.59	2.83	38.89	5.87	-28.7	-35.3	9.4	0.13
30	1140	33.50	0.58	2.87	38.29	5.95	-29.3	-35.9	6.4	0.12
35	1092	33.41	0.54	3.09	37.8	6.08	-29.8	-36.9	3.4	0.11
45	1071	33.10	0.49	3.39	36.53	6.11	-30.9	-38.3	-2.7	0.09
50	1131	32.76	0.45	3.7	36.16	6.12	-31.2	-39.3	-5.8	0.08
55	1176	32.53	0.44	3.8	35.48	6.13	-31.6	-39.7	-9.0	0.07
65	1323	32.06	0.36	4.62	35.45	6.14	-32.2	-42.1	-15.5	0.05

well-hydrated Cl⁻ interacts with PEO groups, disrupting the hydrogen bonds between TPE polyether molecules and water, decreasing the order of structured water and resulting in the increase in entropy.

Figure 9 shows the plot of these thermodynamic parameters as a function of temperature. In order to make the entropic contribution to ΔG_m^o clear, $-T\Delta S_m^o$ is employed instead of ΔS_m^o . The ΔG_m^o is the sum of the enthalpic (ΔH_m^o) and entropic ($-T\Delta S_m^o$) contributions. It is clear that with the increase in temperature ΔH_m^o decreases from positive to negative, whereas $-T\Delta S_m^o$ increased from negative toward positive in both samples leading to the weak effect of temperature on ΔG_m^o . The behavior of these thermodynamic parameters is in agreement with previous reports [58–60]. It means that in the low temperature region, the entropic contribution predominates the micellization process; whereas, at higher temperature the enthalpic contribution plays a significant role to keep the change of free energy small [60].

It is noted that as temperature increases, the ΔH_m^o becomes smaller. The enthalpy gain from the interaction of hydrocarbon chains will overcome the enthalpy loss due to the release of water molecules at low temperature, and the enthalpy loss becomes dominant gradually leading to the negative ΔH_m^o at elevated temperature. The interaction between polyether molecules and water induces the formation of an iceberg-like ordered structure of water molecules causing a significant decrease in entropy. This structure of water would be lost at elevated temperature leading to the increase in entropy. Finally, the entropy loss

will exceed the entropy gain, and thus, $-T\Delta S_m^o$ goes toward positive with increasing temperature.

It is observed that the entropy change is always positive over the whole temperature range. The increase in entropy has been attributed to the rupture of structured water molecules surrounding the polyether molecules and increased configurational entropy of hydrophobic chains transformed from the aqueous solution to micelle [54].

Enthalpy–Entropy Compensation

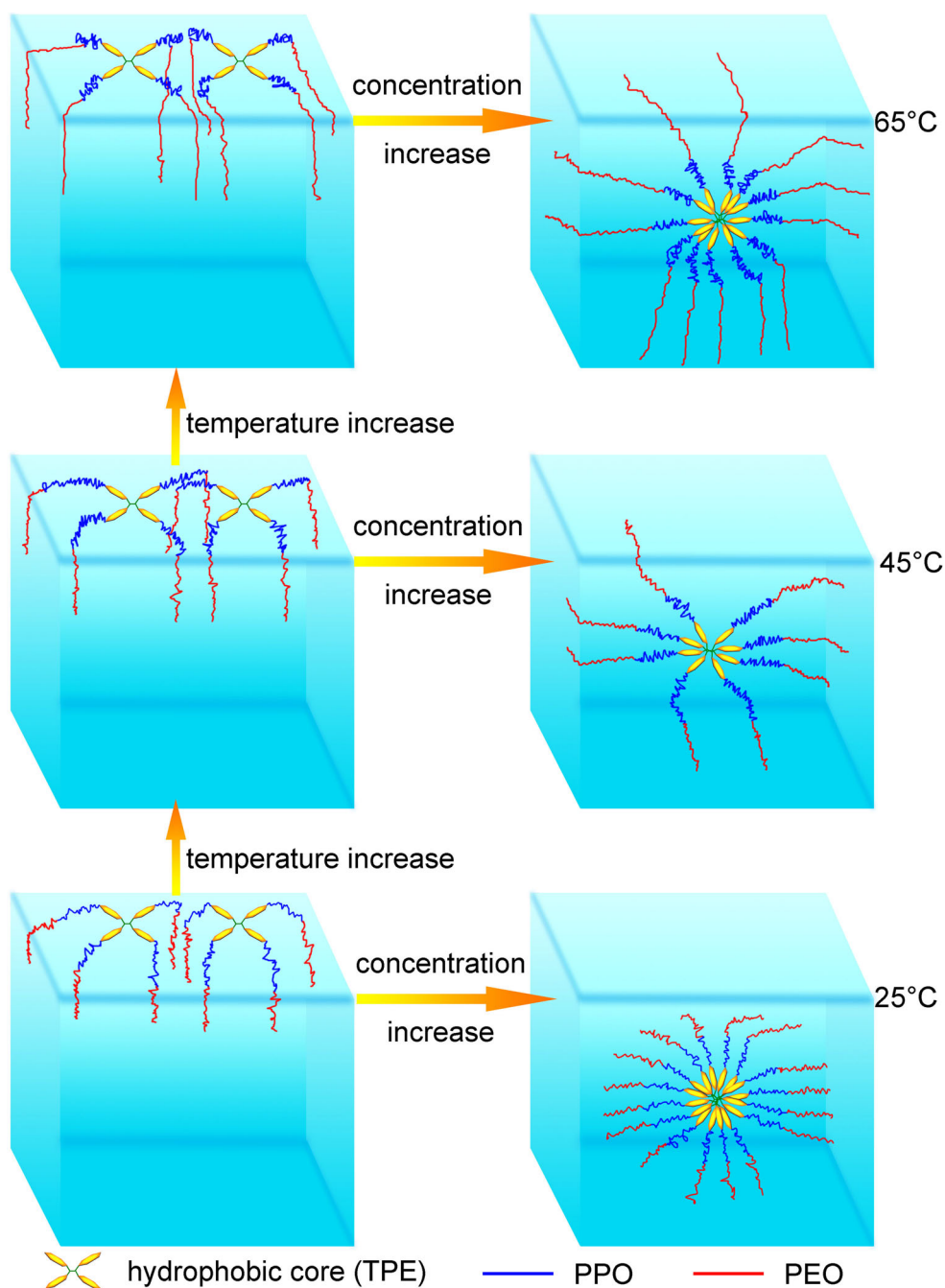
The phenomenon of a linear relation between the enthalpy changes and entropy changes in surfactant solution is observed in many studies and is known as enthalpy–entropy compensation [25, 26, 61, 62].

Figure 10 demonstrates that the enthalpy change varies linearly with entropy change and compensates each other, and the two lines almost having the same slope and intercepts. These linear changes are expressed in the form

$$\Delta H_{\text{mic}}^o = \Delta H_{\text{mic}}^* + T_c \Delta S_{\text{mic}}^o \quad (11)$$

The slope of these plots corresponds to the compensation temperature (T_c) representing the interaction between solvent–solvent and solvent–solute. The larger the value of T_c is, the greater the interaction is [25, 58]. The intercept, ΔH_{mic}^* , provides information on the solute–solute interactions and is considered as a measurement of the stability of micelle under the condition $\Delta S_m^o = 0$. The smaller the value of ΔH_{mic}^* is, the more stable the micelle is. Sugihara and Hisatomi [63] attributed the intercept to the

Fig. 8 Conformational transition of polyether as a function of temperature in aqueous solution



aggregation number of polyether depending on the polyether species. The T_c values in both samples are 317.5 K which is in agreement with the range of 300–325 K for nonionic surfactants [19, 39, 54, 60]. These values are larger than those reported for structurally similar linear Tetronics polyether (280–298 K) and branched Tetronics polyether (307.9 and 309.3 K).

The similar values of slope and intercept in the absence and presence of NaCl indicate that the salt has little influence on the enthalpy-entropy compensation of TPE polyether.

Conclusions

We prepared a novel PPO–PEO polyether with four aromatic rings and four branches. Inorganic salts can decrease the cloud point of the polyether as a result of the salting-out effect, especially on the addition of salts containing divalent anions such as SO_4^{2-} and CO_3^{2-} . As a surfactant, the polyether has high surface activity at room temperature and the activity is promoted by the increase in temperature as well as the addition of salting-out salts such as NaCl, MgCl_2 , and CaCl_2 . Not only the activity but also micellization is

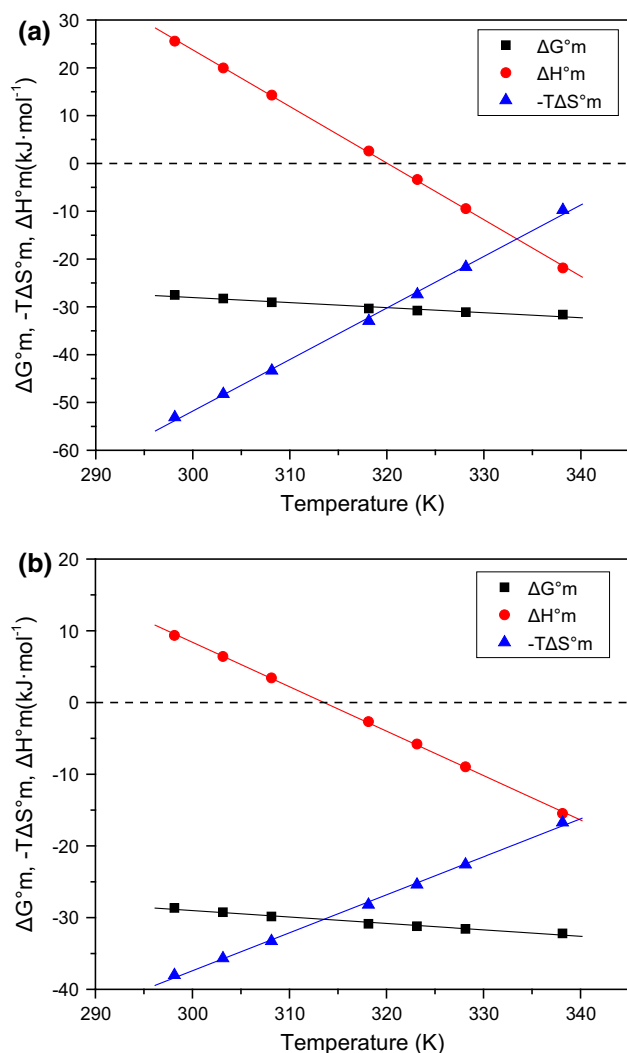


Fig. 9 Temperature dependence of thermodynamic parameters, ΔG_m° , ΔH_m° , and $-T\Delta S_m^\circ$ **a** in the absence of NaCl, **b** in the presence of NaCl

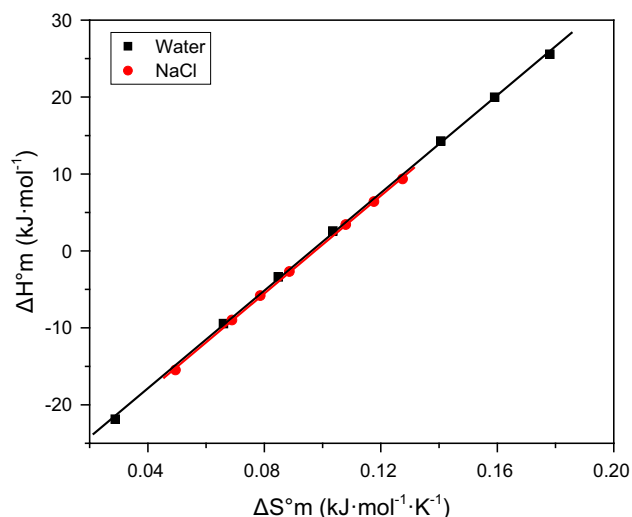


Fig. 10 Plot of enthalpy–entropy compensation relation in the absence and presence of NaCl

inhibited by the addition of salting-in NaSCN. The addition of inorganic salts causes great changes in the efficiency of surface tension reduction and adsorption, small changes in effectiveness of surface tension, but has little influence on the effectiveness of adsorption. The mean size and the number of micelles increase with increasing concentration as observed from TEM micrographs. Low concentrations of NaCl have no influence on the mean size of micelles, but the mean size of micelles increase with further increase in the concentration of NaCl. The cmc decreases first and then increases as temperature increases, indicating an increased dehydration of hydrophilic PEO groups with water at low temperature which favors the micellization and the increasing breakdown of ordered water surrounding the hydrophobic groups which disfavors micellization at higher temperature. The micellization is confirmed to be endothermic at low temperature and exothermic at higher temperature indicating that the micellization is entropy-driven and enthalpy-driven, respectively. The correlation between enthalpy and entropy change in micellization exhibits an excellent linearity. In addition, it is helpful for predicting the properties of polyether in breaking up crude oil emulsions or other uses.

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