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Effect of cationic structure on the micellization of surface active ionic liquids: A thermodynamic study

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Abstract

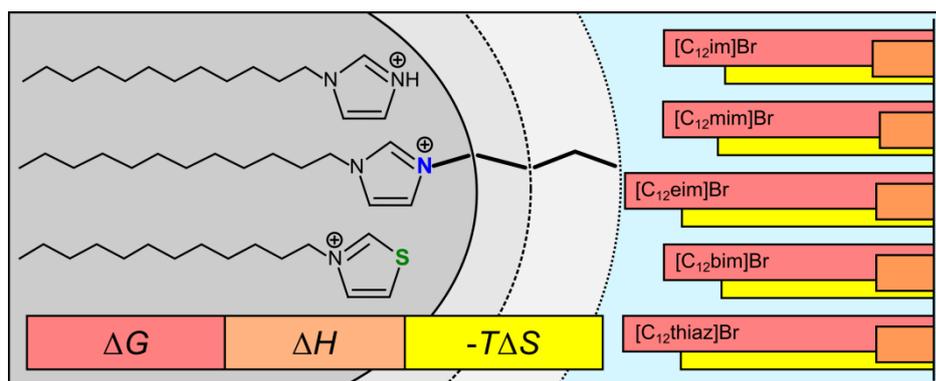
In this work the influence of cation structure on the micellization process at surface active ionic liquids (SAILs) in water is investigated by isothermal titration calorimetry (ITC) at temperatures between 298.15 and 318.15 K. First, 1-dodecylimidazolium bromide ($[C_{12}im]Br$) was studied, and then the length of alkyl chain on the N3 position is varied from methyl- (1-dodecyl-3-methylimidazolium bromide ($[C_{12}mim]Br$)), ethyl- (1-dodecyl-3-ethylimidazolium bromide, $[C_{12}eim]Br$), to butyl- (1-dodecyl-3-butylimidazolium bromide, $[C_{12}bim]Br$). In next step, the N3 was replaced by S atom in 3-dodecylthiazolium bromide ($[C_{12}thiaz]Br$) as an analogue of $[C_{12}im]Br$. Due to problems at synthesis and low solubility of other thiazolium analogues no further experiments on these systems were possible.

ITC experimental data were analyzed by the help of an improved model, yielding simultaneously the values of critical micelle concentration, cmc and enthalpy, $\Delta_M H^\theta$ by the fitting procedure together with the degree of counter ion binding, β , aggregation number, n , standard heat capacity, $\Delta_M c_p^\theta$ and Gibbs free energy, $\Delta_M G^\theta$ of micellization. It was found that the investigated systems behave mainly like common ionic surfactants and already investigated SAILs: the micellization process of investigated systems was detected as endothermic at low temperatures and exothermic at high temperatures; the values of cmc are decreasing with the increasing length of alkyl chain on N3 position. Between $[C_{12}thiaz]^+$ and Br^- weaker interactions were found in comparison to those between $[C_{12}im]^+$ and Br^- what can be ascribed to more expressed aromaticity of thiazolium ring.

$\Delta_M c_p^\theta$ values were further discussed, regarding the removal of water molecules from contact with nonpolar surface area upon micelle formation. It can be concluded, that the ethyl- and butyl-chain on N3 position are folded during the micellization process and thus they are (at least) partially removed from contact with water.

Key words: surface active ionic liquids, micellization, thermodynamics, isothermal titration calorimetry

Graphical abstract

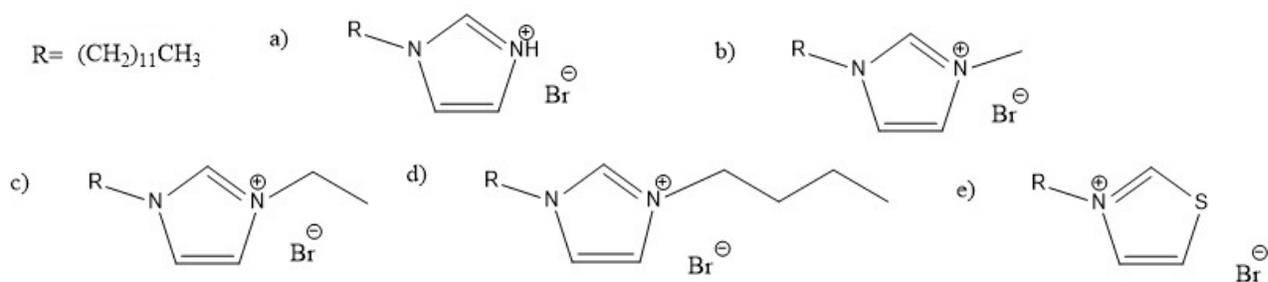


1. Introduction

Thermodynamic and transport properties of ionic liquids (ILs) solutions are highly influenced by their structure, e.g. from the alkyl chain length on the cation [1]. In our recent work also the great potential of surface active ionic liquids (SAILs) at the investigation of thermodynamic of micellization process in solutions due to possible variations in the structure of chain length and counter ions was showed [2]. It turned out that in many ways their behavior is identical to those observed by “usual” cationic surfactants: a) the critical micelle concentration is decreasing with the length of hydrophobic chain expressing a minimum in the temperature dependence and b) the micellization process is endothermic at low temperatures and exothermic at high temperatures. However, it was confirmed that the influence of counter ions plays an extremely important role and that the hydrophobicity of counter ions evidently contributes to the heat capacity change and the water accessible surface area removal upon the burial of non-polar group from the contact with water at micellization process. It was assumed that hydrophobic anions are partially incorporated in the micelle [2].

In this work, our research on micellization properties of SAILs in water is extended to the investigation of the influence of the structure of cations on this process. Four imidazolium-based SAILs with different alkyl chain on N3 position were studied: 1-dodecylimidazolium bromide ($[C_{12}im]Br$), 1-dodecyl-3-methylimidazolium bromide ($[C_{12}mim]Br$), 1-dodecyl-3-ethylimidazolium bromide ($[C_{12}eim]Br$), 1-dodecyl-3-butylimidazolium bromide ($[C_{12}bim]Br$) together with 3-dodecylthiazolium bromide ($[C_{12}thiaz]Br$) as analogue of $[C_{12}im]Br$. The synthesis of other thiazolium analogues turned out as unsuccessful, or the products were not soluble enough in the water to carry out the experiments. The structures of investigated SAILs are presented in Scheme 1.

The micellization was studied by isothermal titration calorimetry (ITC) as one of the most valuable techniques for thermodynamic analysis. The experiments were performed within the temperature range of 278.15 to 318.15 K in step of 10 K. The corresponding standard thermodynamic parameters of micellization (enthalpy, $\Delta_M H^\ominus$; Gibbs free energy, $\Delta_M G^\ominus$; entropy, $\Delta_M S^\ominus$; heat capacity change, $\Delta_M c_p^\ominus$) were estimated by fitting of the model equation based on the mass-action model to the experimental data [3]. In addition, $\Delta_M c_p^\ominus$ was further correlated to the changes in solvent accessible surface upon micelle formation.



Scheme 1. Structures of investigated systems: a) [C₁₂im]Br, b) [C₁₂mim]Br, c) [C₁₂eim]Br, d) [C₁₂bim]Br, e) [C₁₂thiaz]Br

2. Experimental section

2.2. Materials

All chemicals for preparation of ionic liquids were used as received without purification. Millipore ultrapure water for preparation of solution is applied. The summary of the provenance and purity of the chemicals is given in Table S1 in Supplementary data.

2.3. Synthetic procedures

2.3.1. Synthesis of 1-dodecylimidazolium bromide ($[C_{12}im]Br$)

A mixture of 6.81 g (0.1 mol) of imidazole and 6.73 g (0.12 mol) potassium hydroxide are mixed in 100 cm³ 30 min in anhydrous acetone at room temperature. 20 g (0.08 mol) 1-bromododecane 14.4 ml (0.06 mol) was added in small portions, and the mixture was heated for 24 h under reflux at 333 K. The solution was filtered to remove solid phase, and acetone was evaporated on a rotary evaporator. The obtained product is dissolved in 200 cm³ water, and 1-dodecylimidazole was extracted with diethyl ether. Diethyl ether was evaporated and obtained 1-dodecylimidazole dissolved in methanol (20 cm³). An equimolar amount of water solution of HBr was added by potentiometric titration. After evaporation of solvents obtained 1-dodecylimidazolium bromide was washed with ethyl acetate. The final, powdery products are gently heated under vacuum ($p = 10$ Pa) until constant mass was achieved and stored with P₂O₅ under the vacuum for the next 72 h. Structure of 1-dodecylimidazolium bromide used in this work was confirmed by NMR spectroscopy (Spectra in Supplementary data).

2.3.2. 1-dodecyl-3-methylimidazolium bromide ($[C_{12}mim]Br$),

Detailed procedure, as well as NMR spectra, are published in previous work [4].

2.3.3. 1-dodecyl-3-ethylimidazolium bromide ($[C_{12}eim]Br$) and 1-dodecyl-3-butylimidazolium bromide ($[C_{12}bim]Br$),

Detailed procedure, as well as NMR and IR spectra of these ILs, are published in our previous work [5].

1.3.1. Synthesis of 3-dodecylthiazolium bromide ($[C_{12}thiaz]Br$).

The equimolar amounts of 1-bromododecane and thiazole were dissolved in ethyl acetate, and the mixture was stirred at $T = 353.15$ K for 18 days without the formation of the reaction product. The same synthesis was also conducted in a single mode microwave reactor (Discover BenchMate, purchased from CEM Corporation) where equimolar amounts of thiazole and 1-bromododecane were mixed without solvent and transferred to microwave reactor. The final compounds were obtained by irradiation at 240 W and heating at $T = 353.15$ K in a quartz vessel for 30 min. Time of the irradiation and reaction temperature was the same for the synthesis of both compounds. After completion of the reaction, the pale yellow mixtures were purified by liquid-liquid extraction using ethyl acetate. After extraction, the solvent was removed using a vacuum. The final, powdery products, $[C_{12}thiaz]Br$ are gently heated under vacuum ($p = 10$ Pa) until constant mass was achieved and stored with P_2O_5 under the vacuum for the next 72 h. After that, chemicals were kept in the dry box under a nitrogen atmosphere.

When achieving a constant mass, yield was 24 % for $[C_{12}thiaz]Br$ and longer reaction time did not increase final yield. Structure of 3-dodecylthiazolium bromide used in this work was confirmed by NMR spectroscopy (Spectra in Supplementary data).

1.4. Isothermal titration calorimetry (ITC)

The heat changes associated with (de)micellization were measured using a VP-ITC microcalorimeter (MicroCal Inc., Malvern, UK). 1.00 g of triple distilled and degassed water was titrated with the surfactant solution added by a 300 μ L syringe in temperature intervals between 278.15 and 318.15 K. Successive aliquots of 3 μ L of surfactant solution were injected at 10-15 min intervals by a motor-driven syringe into the calorimeter cell under constant stirring at 300 rpm. The concentrations of surfactant in the stock solutions were 10-15 times higher than their cmc (Table S2 in Supplementary data). The area under the peak following each injection of the surfactant solution is proportional to the heat effect expressed per mole of added surfactant, obtained by integration of the raw signal. The concentration after each addition was calculated first in a mole of surfactant per kg of solution (applied in the thermodynamic analysis) from the known starting mass of the water in the cell, the concentration of the stock solution in the syringe and the density. We assumed the density of solution was equal to the density of pure water.

3. Thermodynamics of Micellization

Micellization is a well-known process where monomers form spherical structures due to the polar duality of molecules or ions which form monomers. The experimental ITC data in this work were fitted with the one-step model. In fact, micellization should be regarded as a multistep process or stepwise association with a series of equilibria with aggregation numbers starting from 2 to infinity and each with its own thermodynamic parameter. However, first, most of the formulations are unfavorable and therefore irrelevant for thermodynamic studies, and second, defining thermodynamic parameters for every aggregation number is highly impractical due to the requirement of too many parameters at fitting the experimental data. Furthermore, the fitting of the one-step model was sufficient to describe the micellization of studied systems.

Calculating amounts of species at given total concentration of surfactant

The simplest micellization model of a cationic surfactant can be represented with equilibria:



where C^+ represents the monomeric state of surfactant, A^- the corresponding counterions, β is the degree of counterion binding, n aggregation number and the micellar aggregate (M) with $C_n A_{\beta n}^{(1-\beta)n+}$ an effective charge $(1-\beta)n+$. The equilibrium between species can be expressed by the apparent equilibrium constant, K_M ,

$$K_M = \frac{x_M}{x_C^n x_A^{\beta n}} \quad (2)$$

where activities are approximated to be equal to a molar fraction of species.

K_M determines the composition of each species at given total concentration of surfactant, c , and can be obtained from standard Gibbs free energy of micellization, $\Delta_M G^0$,

$$\Delta_M G^0 = -\frac{RT}{n} \ln K_M \quad (3)$$

Applying the approximation of the activities being equal to a molar fraction of species the amounts of free counterions, n_c , free monomers, n_A and micelles, n_M can be calculated having the

information on concentration and density of the solution, total mass and molar masses of solvent and surfactant (see Supplementary data).

Enthalpy of solution

From known amounts of species in added titrant and cell before and after its addition theoretical enthalpy of solution can be calculated in two ways.

with enthalpies of ions

$$H = n_{\text{sol}} \overline{H}_{\text{sol}} + n_{\text{C}} \overline{H}_{\text{C}} + n_{\text{A}} \overline{H}_{\text{A}} + n_{\text{M}} \overline{H}_{\text{M}} \quad (4)$$

and enthalpies of ion pairs

$$H = n_{\text{sol}} \overline{H}_{\text{sol}} + n_{\text{CA}} \overline{H}_{\text{CA}} + n_{\text{M}} \overline{H}_{\text{CM}} \quad (5)$$

where indexes “sol”, “CA” and “MA” represents solvent, surfactant monomers in the form of ion pairs (an amount equal to free anions) and micelle/counterion pairs (an amount equal to micelles), respectively.

For ion pairs, simplified Guggenheim approximation is used to calculate standard enthalpies

$$\overline{H}_{\text{CA}} = \overline{H}_{\text{CA}}^0 + 2RT^2 B'_{\text{CA}} b_{\text{CA}} \quad (6)$$

$$\overline{H}_{\text{MA}} = \overline{H}_{\text{MA}}^0 + (1 + (1 - \beta)n) RT^2 B'_{\text{MA}} b_{\text{MA}} \quad (7)$$

where B_{CA}' , and B_{MA}' are the temperature derivatives of Guggenheim's coefficients B_{CA} , and B_{MA} . By combining standard enthalpy of micellization, $\Delta_{\text{M}}H^0$,

$$\Delta_{\text{M}}H^0 = \frac{1}{n} \overline{H}_{\text{MA}}^0 - \overline{H}_{\text{CA}}^0 \quad (8)$$

with eqs 5-7, the enthalpy of solution is obtained

$$H = n_{\text{sol}} \overline{H}_{\text{sol}} + n_{\text{S}} \overline{H}_{\text{CA}}^0 + n_{\text{M}} n \Delta_{\text{M},1} H^0 + 2RT^2 B'_{\text{CA}} b_{\text{A}} n_{\text{A}} + RT^2 (1 + (1 - \beta)n) B'_{\text{MA}} b_{\text{M}} n_{\text{M}} \quad (9)$$

which applies to any experimental method.

By the ITC experiment, measured heat changes are contributions of three enthalpies, divided by total surfactant amount added, $n_{\text{S,stock}}$;

$$\Delta H = \frac{q}{n_{\text{S,stock}}} = \frac{H - H_0 - H_{\text{stock}}}{n_{\text{S,stock}}} \quad (10)$$

enthalpy of stock solution, H_{stock} , and enthalpies of the solution in a cell before, H_0 , and after addition, H . By combining the equations (9) and (10), replacing the molalities and defining the change in the amount of micelles, $\Delta n_M/\Delta n$, as

$$\frac{\Delta n_M}{\Delta n} = n \frac{n_M - n_{M,0} - n_{M,\text{stock}}}{n_{S,\text{stock}}} \quad (11)$$

the final form of the model equation is given as:

$$\Delta H = \frac{\Delta n_M}{\Delta n} \Delta_M H^\theta + \frac{RT^2}{n_{S,\text{stock}}} 2B'_{CA} \left(\frac{n_C^2}{m_{\text{sol}}} - \frac{n_{C,0}^2}{m_{\text{sol},0}} - \frac{n_{C,\text{stock}}^2}{m_{\text{sol},\text{stock}}} \right) + \frac{RT^2}{n_{S,\text{stock}}} B'_{MA} (1 + (1 - \beta)n) \left(\frac{n_M^2}{m_{\text{sol}}} - \frac{n_{M,0}^2}{m_{\text{sol},0}} - \frac{n_{M,\text{stock}}^2}{m_{\text{sol},\text{stock}}} \right) \quad (12)$$

The enthalpy change in eq (12) is dependent on amounts of micelles and free surfactant before and after the addition of stock solution, the amounts of the stock solution itself, and the mass of solvent in all three. A detailed derivation is given in the Supplementary data, pages S5-S7.

The cmc for each of investigated system at a given temperature was estimated numerically from the inflection point of the line representing the dependence of $\Delta n_M/\Delta n$ on concentration.

In this work, a global fitting of the model equation to the corresponding experimental curves at all examined temperatures (see the Supplementary data) reduces their correlations significantly. However, some parameters (n , β , $\Delta_M G^\theta$) tend to have a greater error due to the fact that they are determined by the shape of the enthalpograms and not by absolute values of ΔH .

4. Results and Discussion

The dependence of experimental heat of dilution, ΔH , on surfactant concentration (enthalpogram) for titration of $[C_{12}\text{thiaz}]\text{Br}$ in water in the investigated temperature range is shown in Fig. 1 a). Similar enthalpy patterns were also obtained for other investigated systems at the same temperatures (Fig. S1 in the Supplementary data). In Fig. 1 b) the comparison of enthalpograms for all investigated systems is presented. As can be seen in Fig. 1 a), the heat effect at 298.15 K is relatively weak and therefore the effect at 308.15 K is compared in Fig. 1 b).

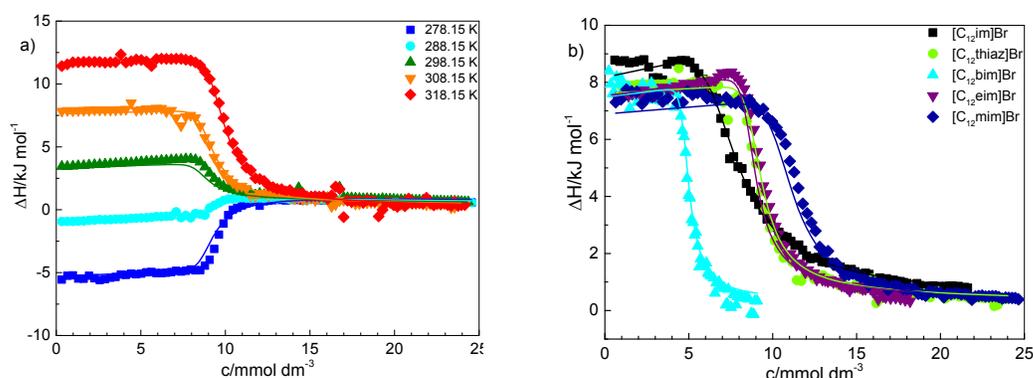


Fig. 1: a) Temperature-dependent enthalpograms for $[C_{12}\text{thiaz}]\text{Br}$; b) enthalpograms for $[C_{12}\text{im}]\text{Br}$, $[C_{12}\text{mim}]\text{Br}$, $[C_{12}\text{eim}]\text{Br}$, $[C_{12}\text{bim}]\text{Br}$, $[C_{12}\text{thiaz}]\text{Br}$ at 308.15 K in water. Solid lines represent the fits according to the model function (Eq. (14)).

As it can be seen from Figs. 1 and S1 in Supplementary data, the experiment can be described as follows: the surfactant in solution initially undergoes full demicellization, followed by monomer dilution resulting in linear dependence of enthalpy change vs. surfactant concentration in the calorimetric cell below the cmc. Thus, at the beginning of the experiment, the heat changes measured result from demicellization of surfactant micelles, dilution of monomers, corresponding counterions and their mutual interactions. In the linear region after the inflection point, which corresponds to cmc, solution undergoes mainly micellar dilution (and for the studied systems the micellization contribution is negligible) therefore the change in enthalpy remains nearly constant with increasing surfactant concentration.

Evidently, investigated systems, in general, obey the same pattern as it has been observed for classical surfactants [6,7] and already studied SAILs [2]. The values of cmc and $\Delta_M H^0$ were simultaneously determined by the fitting procedure together with the degree of the counter ion binding, β , and aggregation number, n , standard heat capacity, $\Delta_M c_p^0$, and Gibbs free energy, $\Delta_M G^0$ of micellization. In Table 1 the values for all studied systems at 298.15 K are listed together with the entropy contributions, whereas in Table S2 in Supplementary data cmc and all thermodynamic functions are presented at all investigated temperatures together with coefficients B_{CA}' and B_{MA}' (eq. 6) for all systems at all investigated temperatures. For [C₁₂mim]Br available literature data are added [2,4,8], whereas no comparison for other investigated systems is possible.

Table 1. Aggregation numbers for micelles, n , degree of counter ion binding, β , critical micelle concentration, cmc, Gibbs free energy, $\Delta_M G^\theta$, standard enthalpy $\Delta_M H^\theta$, entropy contributions, $T\Delta_M S^\theta$, standard heat capacity change upon micelle formation, $\Delta_M c_p^\theta$, for the investigated systems at the temperature of 298.15 K; the temperature $T^*(\text{cmc})$, at the minimum critical micelle concentration, cmc* and T_0 at $\Delta_M H^\theta = 0$. Where possible, the comparison with the literature data is added.^a

	n	β	cmc	$\Delta_M G^\theta$	$\Delta_M H^\theta$	$T\Delta_M S^\theta$	$\Delta_M c_p^\theta$	$T^*(\text{cmc})$	cmc*	T_0
[C ₁₂ im]Br	5 ± 1	0.7 ± 0.1	6.79 ± 0.30	-31.3 ± 4	-3.1 ± 0.1	28.22	-440 ± 15	293.2	6.72	290.5±0.1
[C ₁₂ mim]Br	12 ± 1 16.82 ± 0.01 ^b	0.62 ± 0.06 0.70 ± 0.01 ^c	10.39 ± 0.30 10.7 ± 0.5 ^b 10.29 ^d 9.68 ± 0.05 ^e	-31.3 ± 0.8 -32.91 ± 0.02 ^b	-2.18 ± 0.15 -2.53 ± 0.06 ^b	29.15 30.4 ± 0.1 ^b	-441 ± 10 -398 ± 3 ^b	295.7 291.9 ^b	10.18 10.5 ± 0.5 ^b	293.0±0.1 291.8 ^b
[C ₁₂ eim]Br	16.3 ± 1.5	0.74 ± 0.05	8.44 ± 0.20	-35.7 ± 1.0	-2.0 ± 0.2	33.66	-504 ± 20	294.0	8.44	294.0±0.1
[C ₁₂ bim]Br	17.9 ± 1.5	0.42 ± 0.01	4.69 ± 0.10	-31.1 ± 1.5	-1.21 ± 0.06	29.87	-582 ± 20	297.3	4.54	296.0±0.1
[C ₁₂ thiaz]Br	14 ± 2	0.8 ± 0.1	8.62 ± 0.30	-35.9 ± 1	-2.6 ± 0.2	33.32	-455 ± 20	294.8	8.45	292.2±0.1

^aUnits: $\Delta_M G^\theta$, $\Delta_M H^\theta$, $T\Delta_M S^\theta$, kJ mol⁻¹; $\Delta_M c_p^\theta$, J K⁻¹ mol⁻¹; T^* , T_0 , K; cmc, mmol dm⁻³

^bref [2] from ITC, the literature data for $\Delta_M G^\theta$ (and $\Delta_M S^\theta$) were recalculated to the rational scale, used in this paper.

^cref [2] from conductivity

^dref [4] from conductivity

^eref [8] from ITC

The temperature dependence of cmc shows typical U-shaped form (Fig. 2) reaching the minimum value cmc^* at the temperature T^* . These values, obtained from the corresponding derivative of the polynomial $\text{cmc}=A+BT+CT^2$, are listed in Table 1, whereas the coefficients of the polynomial are given in Table S3 in Supplementary data. As it is evident from Table 1, T^* is close to temperature T_0 , where $\Delta_M H^0 = 0$. Values of cmc, cmc^* , T^* and T_0 for $[\text{C}_{12}\text{mim}]\text{Br}$ are in reasonable agreement with the literature data [2,4,8] as well as the value of the degree of counter ion binding, β .

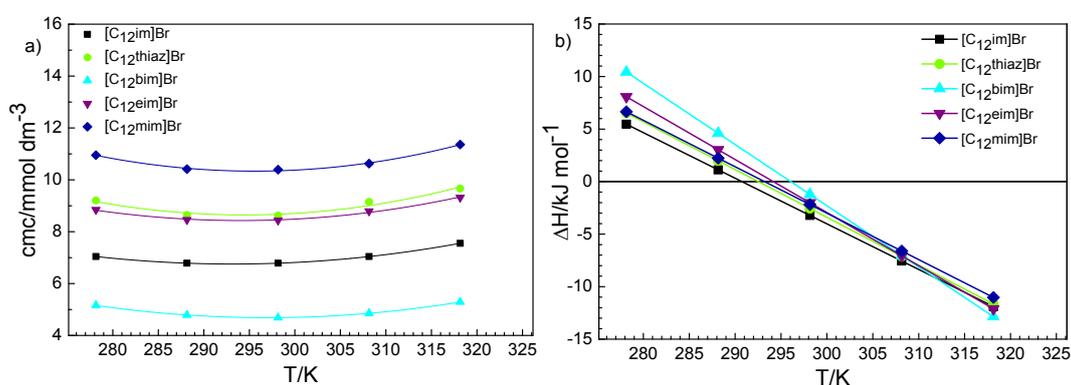


Fig. 2. Temperature dependence of a) cmc for investigated SAILs in water. Solid lines represent the corresponding polynomial fits, $\text{cmc}=A+BT+CT^2$. Coefficients are given in Table S3 in Supplementary data. b) $\Delta_M H^0$. Solid lines represent linear fit.

The comparison of thermodynamic functions at 308.15 K is given in Fig. 3. The reported errors in Table S2 in Supplementary data correspond to the precision of the experimental data and the fitting procedure assuming the proposed model is correct.

The micellization process of studied systems is endothermic at low temperatures and becomes exothermic at high temperatures, as it is evident from Table S2 in Supplementary data and Fig. S1 in Supplementary data. Such behaviour could be ascribed to the delicate balance between hydrophobic hydration of nonpolar parts (endothermic) and counter ion binding (exothermic) upon micellization, where former effect diminishes with temperature [9]. Here, temperature T_0 at which $\Delta_M H^0 = 0$ is in the range of room temperature ($T_0 = 293 \pm 3$ K) for all systems (Table 1, Figure 2b). In Fig. 3 (and Table S2 in Supporting data) an

interplay between enthalpy and entropy resulting in the negative values of Gibbs free energy, characteristic of spontaneous processes at constant p and T , is evident.

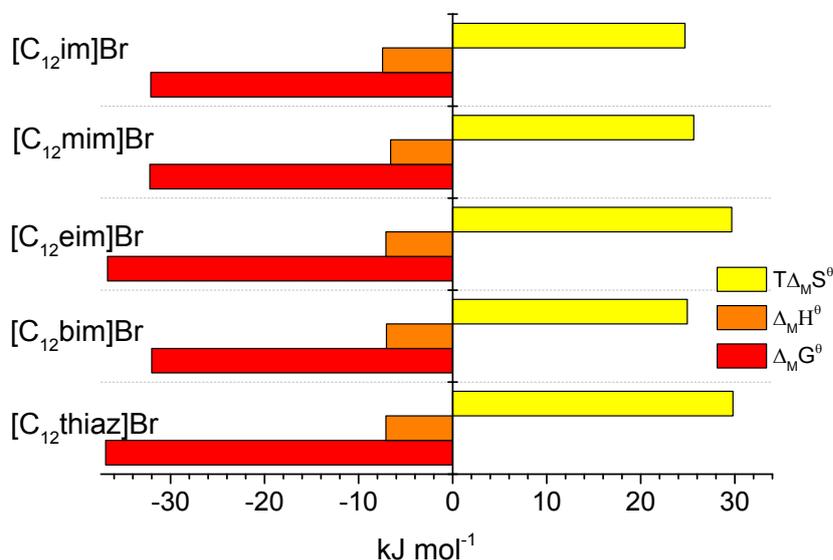


Fig. 3. Thermodynamic parameters of micellization for investigated systems in water at 308.15 K: standard enthalpy, $\Delta_M H^\theta$, Gibbs free energy, $\Delta_M G^\theta$, and entropy contributions, $T\Delta_M S^\theta$, for micellization at investigated systems in water as obtained by the fitting procedure.

From Table 1 and Figure 2a) it can be concluded, that the alkyl chain on the N3 position of imidazolium ring affect cmc crucially: cmc (298.15 K) decreases from 10.39 $\text{mmol}\cdot\text{dm}^{-3}$ for [C₁₂mim]Br to 4.69 at [C₁₂bim]Br. On the other hand, cmc (298.15 K) for [C₁₂im]Br is relatively low (6.79 $\text{mmol}\cdot\text{dm}^{-3}$) and lies between values of [C₁₂eim]Br and [C₁₂bim]Br. Obviously, the CH₃- group on N3 at [C₁₂mim]Br acts as a steric hindrance for Br⁻ binding and thus charge screening of polar headgroups is less efficient resulting in higher cmc as at [C₁₂im]Br. However, the ethyl- and butyl- chains seem to be less rigid with more expressed hydrophobic character and thus the cmc is decreasing with increasing length of alkyl chain on N3 position. It can be even assumed, that ethyl- and butyl- chains are partially incorporated in the micelles, what is in agreement with the values of $\Delta_M C_p^\theta$ (Table 1). The main driving force for the formation of micelles is namely the apparent disaffinity of water and the nonpolar (interacting) surfaces known as hydrophobic effect. This effect is reflecting in the value of $\Delta_M C_p^\theta$, which for micellization is always highly negative and can be ascribed to the removal

of water molecules from contact with nonpolar surface area upon micelle formation [10]. In our recent work we showed, that values of $\Delta_{MC_p}^{\theta}$ are dependent on the counter ions, especially if they can incorporate into the micelles [2].

By modeling the micellization processes as a transfer of surfactant molecules into the micellar phase, the heat capacity can be expressed in terms of the change of water accessible nonpolar and polar surface areas, derived by Spolar et al. [11] from protein folding

$$\Delta_{MC_p}^{\theta}(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -1.34(\pm 0.33) \cdot \Delta A_{np}(\text{\AA}^2) + 0.59(\pm 0.17) \cdot \Delta A_p(\text{\AA}^2) \quad (13)$$

where ΔA_p stand for the loss of water accessible polar and ΔA_{np} for nonpolar surface area upon protein folding. Because the hydrophilic head groups of non-ionic surfactants remain hydrated upon micelle formation, the “theoretical” contribution of water accessible nonpolar surface area change to the heat capacity change upon micelle formation, $\Delta_{MC_p}^{\theta}(\text{th}_{np})$, can be assumed to reflect only the change in exposure of the hydrophobic tails to water.

Consequently, the Eq. (13) is reduced to

$$\Delta_{MC_p}^{\theta}(\text{th}_{np})(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -1.34(\pm 0.33) \cdot \Delta A_{np}(\text{\AA}^2) \quad (14)$$

This approach turned out as useful for a series of non-ionic surfactants [12, 13].

According to Richards [14, 15, 16], water accessible surface area of a methylene group is 30 \AA^2 and 88 \AA^2 for a methyl group. Thus ΔA_{np} of the hydrophobic C_{12} alkyl chain is 478 \AA^2 , giving the value of $\Delta_{MC_p}^{\theta}(\text{th}_{np}) = 560 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Comparison of $\Delta_{MC_p}^{\theta}(\text{th}_{np})$, estimated by Eq. (14) with $\Delta_{MC_p}^{\theta}$ from Table 1 reveals that there is an evident discrepancy between theoretical and experimental values, what can be ascribed to the fact, that some methylene group of alkyl chain are still in contact with water upon micellization. On the other hand, bigger values of $\Delta_{MC_p}^{\theta}$ for $[C_{12}\text{eim}]\text{Br}$ and $[C_{12}\text{bim}]\text{Br}$ confirm the upper assumption that the ethyl- and butyl- chain can be folded during the micellization process and thus they are (at least) partially removed from contact with water enlarging consequently $\Delta_{MC_p}^{\theta}$ values.

This statement is also in agreement with the estimated aggregation numbers (Table 1), increasing in the order $[C_{12}im]Br < [C_{12}mim]Br < [C_{12}eim]Br < [C_{12}bim]Br$. Thus, alkyl chain on N3 position promotes the micellizations-bigger micelles are formed at lower cmc.

However, $[C_{12}im]Br$ with very low aggregation numbers (~ 5) and relatively low cmc (~ 7 mmol-dm⁻³) seems to be quite outstanding with its ability to form smaller aggregates at low cmc. Its properties also did not meet our expectation about similar properties of $[C_{12}im]Br$ and $[C_{12}thiaz]Br$. On the contrary, $[C_{12}thiaz]Br$ exhibits similar values of cmc as $[C_{12}eim]Br$ (Figure 2a) and $\Delta_M H^0$ as $[C_{12}mim]Br$ (Figure 2b) with an aggregation number (~ 14) between those of $[C_{12}mim]Br$ and $[C_{12}eim]Br$ (12 and 16, respectively).

The inclusion of sulphur atom in the five-membered heterocycle increases namely the aromaticity of thiazolium ring in comparison to imidazolium [17] and thus it is less reactive. In addition, it has been reported that H-bond interaction energy between water (or ligands) and S atom is much smaller than between water and N3 in imidazolium ring [18] confirming more hydrophobic character of thiazolium ring.

5. Conclusions

In present work the great potential of surface active ionic liquids (SAILs) for investigation of thermodynamics of micellization process in solutions was demonstrated again. This time, the structure of cations was varied-from increasing the length of alkyl chain on N3 position to replace of N3 with S atom. It turned out that the investigated systems obey similar rules as it has been reported for classical surfactants [5,6] and other SAILs [2]. First, the micellization process of investigated systems was detected as endothermic at low temperatures and exothermic at high temperatures which could be referred to the delicate balance between hydrophobic hydration of nonpolar parts (endothermic) and counter ion binding (exothermic) during the micellization process. Second, values of cmc are decreasing with the increasing length of alkyl chain on N3 position showing the typical U shape dependence on temperature. Nevertheless, the (relatively) small differences in cation structure make observable distinctions among studied SAILs: CH₃- group on N3 at $[C_{12}mim]Br$ is acting as a steric barrier and therefore micellization process occurs at higher cmc, compared to the $[C_{12}im]Br$ system; the ethyl- and butyl- chains with more hydrophobic character promote the

micellization. They also seem to be less rigid, accordingly, they can be folded, and micellization process will occur at lower cmc.

This assumption is in agreement with the values of $\Delta_{Mc_p}^0$. It could be noted that the values of $\Delta_{Mc_p}^0$ for investigated systems increase in the following order $[C_{12}im]Br \approx [C_{12}mim]Br < [C_{12}eim]Br < [C_{12}bim]Br$, which could be due to the fact that the methyl group (and also some methylene group of alkyl chain) are still in contact with water during the micellization process whereas ethyl- and butyl- chain can be folded and thus (at least) partially removed from contact with water.

This hypothesis is in accordance with the estimated aggregation numbers as well. In the observed order of increasing estimated aggregation numbers $[C_{12}im]Br < [C_{12}mim]Br < [C_{12}eim]Br < [C_{12}bim]Br$ it could be assumed that the alkyl chain promotes the micellization- bigger micelles are formed at lower cmc.

Nevertheless, an outstanding system seems to be $[C_{12}im]Br$ with its ability to form smaller aggregates at low cmc. Also, its properties did not meet our expectation about similar properties with the $[C_{12}thiaz]Br$. Obviously, the inclusion of S atom in a five-membered heterocycle increases the aromaticity (and consequently the hydrophobicity) of the thiazolium ring reducing also its reactivity [17]. Moreover, it has been reported that the H-bond interaction energy between water (or ligands) and S atom is much smaller than between water and N3 in imidazolium ring [1814]. Thus, the micellization properties of $[C_{12}thiaz]Br$ are more in line with $[C_{12}eim]Br$ due to the hydrophobic character of ethyl- group.

6. Acknowledgements

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7.. Supplementary data

NMR spectra, Thermodynamics of micellization, additional figures and data tables. Supplementary data associated with this article can be found in the online version

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Effect of cationic structure on the micellization of surface active ionic liquids: A thermodynamic study

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SUPPLEMENTARY DATA

Table S1. Provenance and purity of the samples.

Chemical name	Provenance	CAS Number	Purification method	Final mass fraction as stated by the supplier
Thiazole	Sigma Aldrich	288-47-1	Vacuum drying	$\omega \geq 0.99$
Imidazole	Sigma Aldrich	288-32-4	Vacuum drying	$\omega \geq 0.99$
1-bromododecane	Sigma Aldrich	143-15-7	Vacuum drying	$\omega \geq 0.99$
Potassium hydroxide	Sigma Aldrich	1310-58-3	-	$\omega \geq 0.85$
Acetone	Lachner	67-64-1	-	$\omega \geq 0.99$
Diethyl ether	Aldrich	60-29-7	-	$\omega \geq 0.99$
Methanol	Lachner	67-56-1	-	$\omega \geq 0.998$
Hydrobromic acid	Sigma Aldrich	10035-10-6	-	$\omega \geq 0.48$
Ethyl acetate	Sigma Aldrich	141-78-6	-	$\omega \geq 0.998$
1-dodecylimidazolium bromide	Synthesis in this work	-	SLE ^a , Rotary evaporation followed by drying	$\omega \geq 0.99^b$
1-dodecyl-3-methylimidazolium bromide ^c				$\omega \geq 0.99^c$
1-dodecyl-3-ethylimidazolium bromide ^d				$\omega \geq 0.99^d$
1-dodecyl-3-butylimidazolium bromide ^d				$\omega \geq 0.99^d$
3-dodecylthiazolium bromide	Synthesis in this work	-	SLE ^a , Rotary evaporation followed by drying	$\omega \geq 0.98^b$

^a SLE = solid-liquid extraction

^b determined by NMR

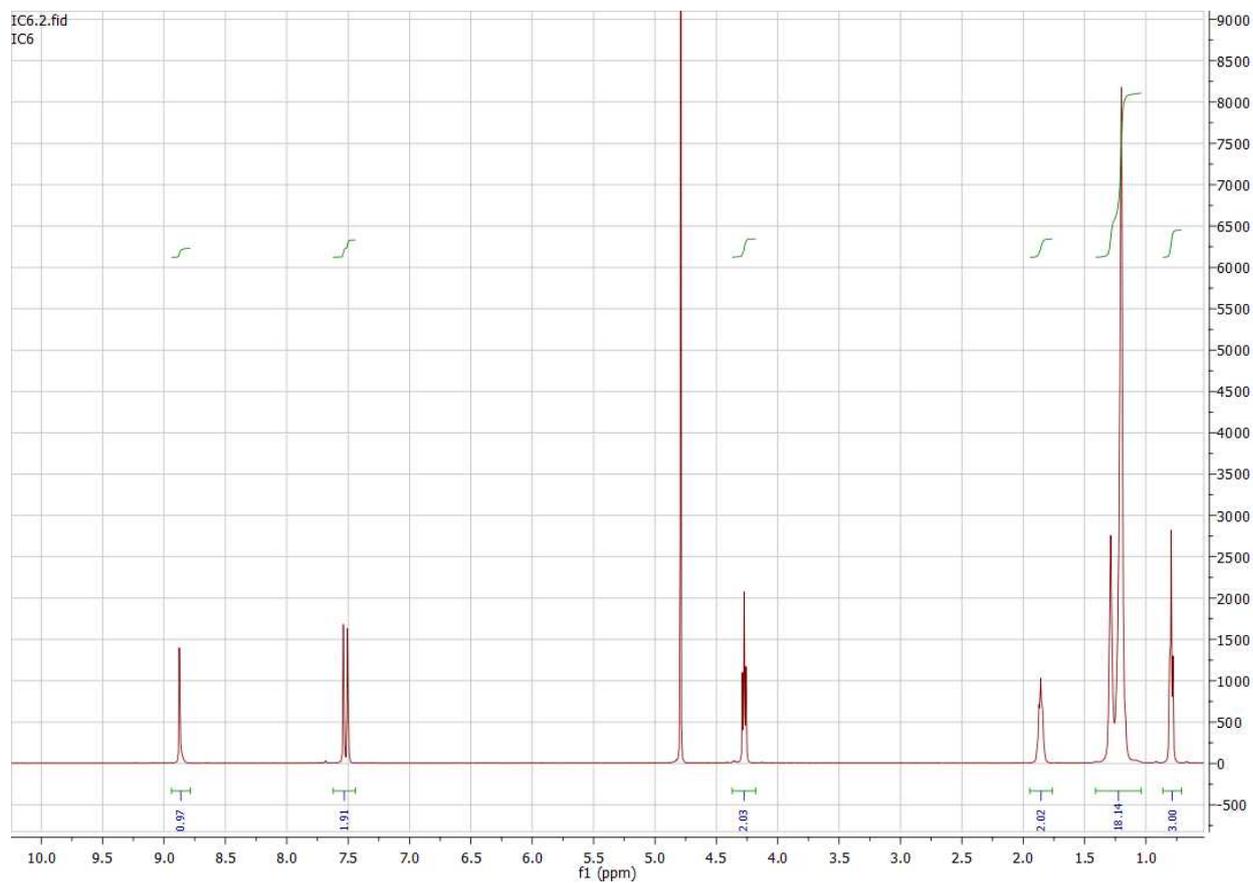
^cref [1]

^dref [2]

NMR spectra

[C₁₂im]Br

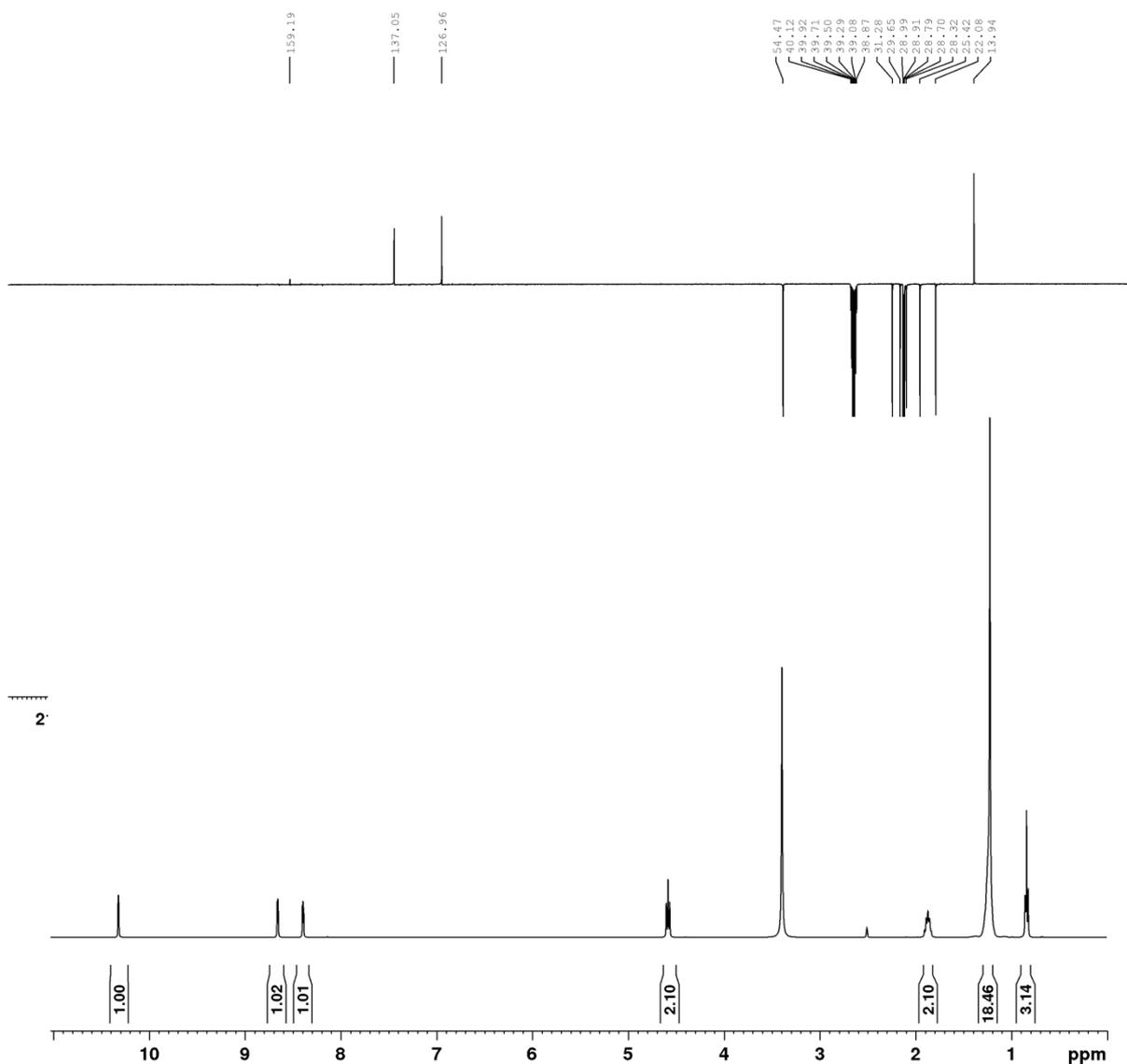
¹H NMR (500 MHz, D₂O) δ 8.87 (s, 1H), 7.54 (s, 1H), 7.51 (s, 1H), 4.27 (t, *J* = 7.2 Hz, 2H), 1.94 – 1.77 (m, 2H), 1.40 – 0.99 (m, *J* = 44.0 Hz, 18H), 0.79 (t, *J* = 6.5 Hz, 3H).



[C₁₂thiaz]Br

¹H NMR spectrum (DMSO-d₆): 0.84 (*t*, 3H, $J_{\text{CH}_2, \text{CH}_3}$ =7.0 Hz, CH₃ from alkyl side chain); 1.18-1.28 (*m*, 18H, 9CH₂); 1.87 (*m*, 2H, NCH₂CH₂C₁₀H₂₁); 4.58 (*t*, 2H, $J_{\text{CH}_2, \text{CH}_2}$ =7.3 Hz, NCH₂C₁₁H₂₃); 8.40 (*dd*, 1H, $J_{4,5}$ =3.7 Hz, $J_{2,4}$ =2.4 Hz, H-4); 8.66 (*dd*, 1H, $J_{4,5}$ =3.7 Hz, $J_{2,5}$ =1.3 Hz, H-5); 10.32 (*s*, 1H, H-2).

¹³C NMR spectrum (DMSO-d₆): 13.94 (C₁₁H₂₂CH₃); 22.08, 25.42, 28.32, 28.70, 28.79, 28.91, 28.99, 29.65, 31.28 (10 CH₂), 54.47 (NCH₂C₁₁H₂₃); 126.96 (C-4); 137.96 (C-4); 159.19 (C-2).



Thermodynamics of micellization

Calculating amounts of species at given total concentration of surfactant

The simplest micellization model of a cationic surfactant can be represented with equilibria



where C^+ represents the monomeric state of surfactant, A^- the corresponding counterions, β is the degree of counterion binding, n aggregation number and the micellar aggregate (M) with $C_n A_{\beta n}^{(1-\beta)n+}$ an effective charge $(1-\beta)n+$. The equilibrium between species can be expressed by apparent equilibrium constant, K_M ,

$$K_M = \frac{x_M}{x_C^n x_A^{\beta n}} \quad (ii)$$

where activities are approximated to be equal to molar fraction of species.

K_M determines composition of each species at given total concentration of surfactant, c , and can be obtained from standard Gibbs free energy of micellization, $\Delta_M G^\theta$,

$$\Delta_M G^\theta = -\frac{RT}{n} \ln K_M \quad (iii)$$

On the assumption that the density of the solution is always approximately 1 g mL^{-1} the total mass of solution, m , is approximated and by taking into account the molar mass of solvent and surfactant, the amount of solvent, n_{sol} , and the total amount of surfactant, n_S , are calculated. Introducing the sum of amounts of species, $\sum n_i$,

$$\sum n_i = n_{\text{sol}} + 2 n_S + (1 - (1 + \beta)n) n_M \quad (iv)$$

the amounts of free monomers, n_C ,

$$n_C = n_S - n_M n \quad (v)$$

and free counterion, n_A ,

$$n_A = n_S - \beta n_M n \quad (vi)$$

enables the transformation of eq ii into expression

$$K_M = \frac{n_M (n_{\text{sol}} + 2n_S + (1 - (1 + \beta)n) n_M)^{(1+\beta)n-1}}{(n_S - n_M n)^n (n_S - \beta n_M n)^{\beta n}} \quad (vii)$$

with only one unknown variable, the amount of micelles, n_M . This equation cannot be solved analytically therefore tangent method is used to find solution numerically.

Enthalpy of solution

Knowing all the amounts of species in added titrant and cell before and after its addition theoretical enthalpy of solution is calculated. Enthalpy of solution can be defined in two ways: with enthalpies of ions

$$H = n_{\text{sol}} \overline{H}_{\text{sol}} + n_{\text{C}} \overline{H}_{\text{C}} + n_{\text{A}} \overline{H}_{\text{A}} + n_{\text{M}} \overline{H}_{\text{M}} \quad (\text{viii})$$

and enthalpies of ion pairs

$$H = n_{\text{sol}} \overline{H}_{\text{sol}} + n_{\text{CA}} \overline{H}_{\text{CA}} + n_{\text{M}} \overline{H}_{\text{CM}} \quad (\text{ix})$$

where indexes “sol”, “CA” and “MA” represents solvent, surfactant monomers in form of ion pairs (amount equal to free cations) and micelle/counterion pairs (amount equal to micelles), respectively. For ion pairs simplified Guggenheim approximation³ is used to calculate standard enthalpies

$$\overline{H}_{\text{CA}} = \overline{H}_{\text{CA}}^0 + 2RT^2 B'_{\text{CA}} b_{\text{CA}} \quad (\text{x})$$

$$\overline{H}_{\text{MA}} = \overline{H}_{\text{MA}}^0 + (1 + (1 - \beta)n) RT^2 B'_{\text{MA}} b_{\text{MA}} \quad (\text{xi})$$

where B'_{CA} , and B'_{MA} are the temperature derivatives of Guggenheim's coefficients B_{CA} , and B_{MA} . By combining standard enthalpy of micellization, $\Delta_{\text{M}}H^0$,

$$\Delta_{\text{M}}H^0 = \frac{1}{n} \overline{H}_{\text{MA}}^0 - \overline{H}_{\text{CA}}^0 \quad (\text{xii})$$

with eqs ix-xi, the enthalpy of solution is obtained

$$H = n_{\text{sol}} \overline{H}_{\text{sol}} + n_{\text{S}} \overline{H}_{\text{CA}}^0 + n_{\text{M}} n \Delta_{\text{M},1} H^0 + 2RT^2 B'_{\text{CA}} b_{\text{A}} n_{\text{A}} + RT^2 (1 + (1 - \beta)n) B'_{\text{MA}} b_{\text{M}} n_{\text{M}} \quad (\text{xiii})$$

which applies to any experimental method.

ITC enthalpy change

Heat changes measured with ITC are contributions of three enthalpies, divided by total surfactant amount added, $n_{\text{S,stock}}$:

$$\Delta H = \frac{q}{n_{\text{S,stock}}} = \frac{H - H_0 - H_{\text{stock}}}{n_{\text{S,stock}}} \quad (\text{xiv})$$

enthalpy of stock solution, H_{stock} , and enthalpies of solution in cell before, H_0 , and after addition, H . By using eq xiii for each enthalpy and combining it with eq xiv, heat change after an addition of stock solution can be expressed as

$$\Delta H = \frac{n_{\text{sol}} - n_{\text{sol},0} - n_{\text{sol,stock}}}{n_{\text{S,stock}}} \overline{H}_{\text{sol}}^0 + \frac{n_{\text{S}} - n_{\text{S},0} - n_{\text{S,stock}}}{n_{\text{S,stock}}} \overline{H}_{\text{CA}}^0 + n \frac{n_{\text{M}} - n_{\text{M},0} - n_{\text{M,stock}}}{n_{\text{S,stock}}} \Delta_{\text{M}}H^0 + RT^2 \left(2B'_{\text{CA}} \frac{b_{\text{C}} n_{\text{C}} - b_{\text{C},0} n_{\text{C},0} - b_{\text{C,stock}} n_{\text{C,stock}}}{n_{\text{S,stock}}} + (1 + (1 - \beta)n) B'_{\text{MA}} \frac{b_{\text{M}} n_{\text{M}} - b_{\text{M},0} n_{\text{M},0} - b_{\text{M,stock}} n_{\text{M,stock}}}{n_{\text{S,stock}}} \right) \quad (\text{xv})$$

First two terms in eq xx are equal to zero because total amount of solvent and surfactant in the titration cell after the addition is the same as sum of amounts before the addition and the addition itself. Replacing molalities, b_i , by

$$b_i = \frac{n_i}{m_{\text{sol}}} \quad (\text{xvi})$$

and defining the change in amount of micelles, $\Delta n_M / \Delta n$, as

$$\frac{\Delta n_M}{\Delta n} = n \frac{n_M - n_{M,0} - n_{M,\text{stock}}}{n_{S,\text{stock}}} \quad (\text{xvii})$$

eq xv reduces into its final form

$$\Delta H = \frac{\Delta n_M}{\Delta n} \Delta_M H^\theta + \frac{RT^2}{n_{S,\text{stock}}} 2B'_{CA} \left(\frac{n_C^2}{m_{\text{sol}}} - \frac{n_{C,0}^2}{m_{\text{sol},0}} - \frac{n_{C,\text{stock}}^2}{m_{\text{sol},\text{stock}}} \right) + \frac{RT^2}{n_{S,\text{stock}}} B'_{MA} (1 + (1 - \beta)n) \left(\frac{n_M^2}{m_{\text{sol}}} - \frac{n_{M,0}^2}{m_{\text{sol},0}} - \frac{n_{M,\text{stock}}^2}{m_{\text{sol},\text{stock}}} \right) \quad (\text{xviii})$$

From the eqs iii, and xviii it is evident, that the ITC model equation for a given temperature may be described in terms of n , β , $\Delta_M G^\theta$, $\Delta_M H^\theta$, and the coefficients B'_{CA} and B'_{MA} at any surfactant concentration, c .

Global analysis

In the global analysis of ITC experimental data the Kirchoff's law

$$\Delta_M H^\theta = \Delta_M H_{T_r}^\theta + \Delta_M c_p^\theta (T - T_r) \quad (\text{xix})$$

and the integrated Gibbs-Helmholtz equation

$$\Delta_M G^\theta = T \left[\Delta_M G_{T_r}^\theta / T_r + \Delta_M H_{T_r}^\theta (1/T - 1/T_r) + \Delta_M c_p^\theta (1 - T_r/T - \ln(T/T_r)) \right] \quad (\text{xx})$$

are used, where $\Delta_M G_{T_r}^\theta$ is the standard Gibbs free energy and $\Delta_M H_{T_r}^\theta$ is the standard enthalpy of micellization at reference temperature T_r . Heat capacity of micellization, $\Delta_M c_p^\theta$, was taken as temperature independent in the examined temperature range. Moreover, B'_{CA} and B'_{MA} were assumed to be linearly depended with temperature introducing

$$B'_{CA,T} = B'_{CA,T_r} + B''_{CA} (T - T_r) \quad (\text{xxi})$$

$$B'_{MA,T} = B'_{MA,T_r} + B''_{MA} (T - T_r) \quad (\text{xxii})$$

B_{CA}'' and B_{MA}'' as the slopes and $B_{CA,T}'$ and $B_{MA,T}'$ values at reference temperature T_r .

From the eqs iii and xviii-xxii it is evident that the ITC model equations may be described in terms of n , β , $\Delta_M G_T^\theta$, $\Delta_M H_T^\theta$, $\Delta_M c_p^\theta$, and the coefficients $B_{CA,T}'$, $B_{MA,T}'$, B_{CA}'' and B_{MA}'' at any surfactant concentration, c , and temperature, T .

Fitting procedure

The values of the fitting parameters, either at one temperature or in global analysis at multiple temperatures, were obtained by fitting of the model equation to the experimental data points in the following manner. The model equation was compared to the experimental curves via the χ^2 function defined as:

$$\chi^2 = \sum_T f_T \sum_i (\Delta H_i - \Delta H_i^{\text{mod}})^2 \quad (\text{xxiii})$$

where ΔH_i and ΔH_i^{mod} represent the experimental and the model enthalpy, whereas f_T represents the correction factor which differs from 1 if error of experimental points at temperature T is significantly greater. By minimization of χ^2 function best-fit values of the above-mentioned global parameters were calculated using modified Simplex method which was ran at least 100 times each time from randomly generated starting set of parameters. Values of global parameters were further used to calculate corresponding parameters for each temperature. The entropy of micellization, $\Delta_M S^\theta$, associated with the examined process was obtained from the Gibbs-Helmholtz equation.

$$\Delta_M S^\theta = \frac{\Delta_M H^\theta - \Delta_M G^\theta}{T} \quad (\text{xxiv})$$

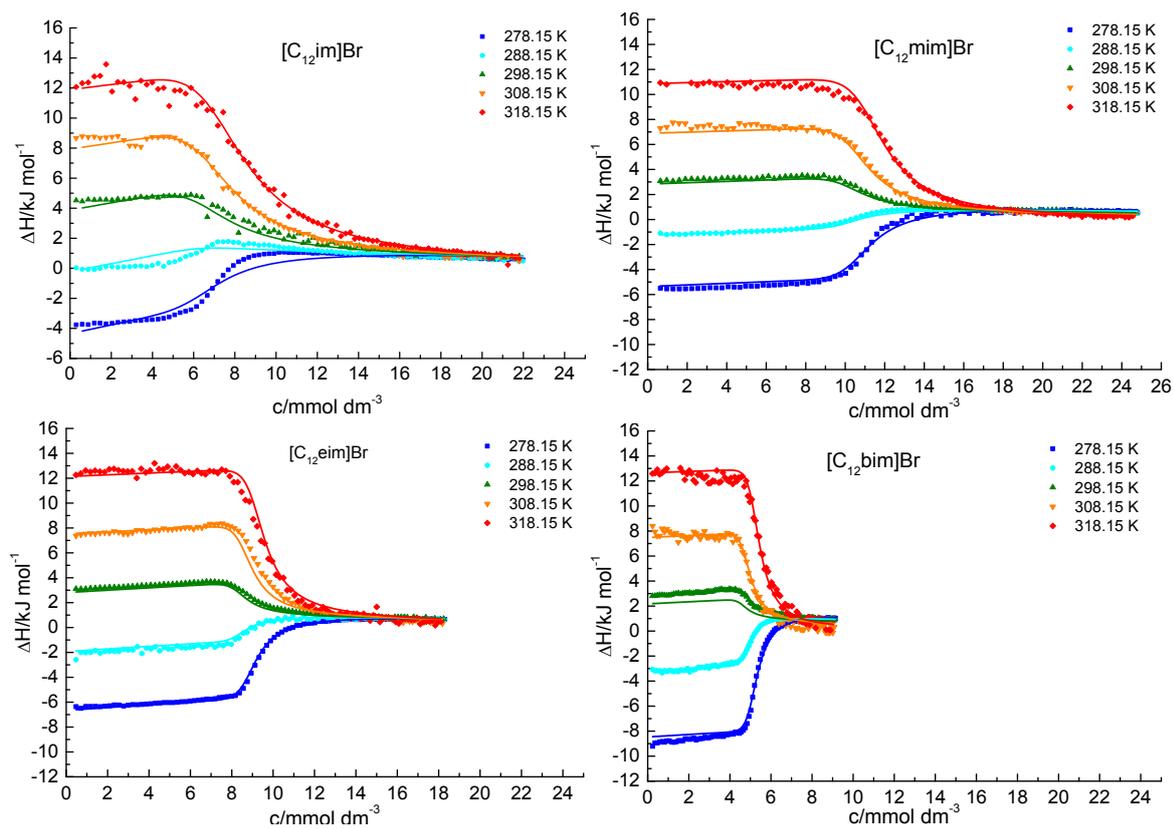


Figure S1. Temperature dependent enthalpograms for investigated systems, where solid lines represent the fit according to the one-step micellization model (equation xviii).

Table S2. Molar masses, M , of investigated systems, concentrations, m of stock solutions, critical micelle concentration, cmc, thermodynamic parameters of micellization for investigated C_{12} systems in water at all investigated temperatures: Gibbs free energies $\Delta_M G^0$, enthalpies $\Delta_M H^0$ and entropies of micellization $\Delta_M S^0$, and coefficients B_{CA}' and B_{MA}' for investigated systems water^a.

	M	m	T	cmc	$\Delta_M G^0$	$\Delta_M H^0$	$\Delta_M S^0$	B_{CA}'	B_{MA}'
[C ₁₂ im]Br	317.36	0.1001	278.15	7.04 ± 0.30	-29.1 ± 0.6	5.75 ± 0.04	128.5	0.11 ± 0.02	-0.205 ± 0.01
			288.15	6.79 ± 0.30	-30.2 ± 0.6	1.35 ± 0.04	112.9	0.10 ± 0.02	-0.183 ± 0.01
			298.15	6.79 ± 0.30	-31.3 ± 0.6	-3.05 ± 0.04	97.8	0.08 ± 0.02	-0.161 ± 0.01
			308.15	7.04 ± 0.30	-32.1 ± 0.6	-7.45 ± 0.04	83.2	0.07 ± 0.02	-0.140 ± 0.01
			318.15	7.55 ± 0.30	-32.9 ± 0.6	-11.85 ± 0.04	69.1	0.05 ± 0.02	-0.118 ± 0.01
[C ₁₂ mim]Br	331.34	0.1083	278.15	10.95 ± 0.30 11.0 ± 0.5 ^b	-29.1 ± 0.2 -30.60 ± 0.02 ^b	6.6 ± 0.1 5.4 ± 0.1 ^b	147.9 129.4 ± 0.7 ^b	0.025 ± 0.002	-0.351 ± 0.01
			288.15	10.41 ± 0.30 10.5 ± 0.5 ^b	-30.3 ± 0.2 -31.82 ± 0.02 ^b	2.2 ± 0.1 1.45 ± 0.08 ^b	130.1 115.6 ± 0.7 ^b	0.022 ± 0.002	-0.307 ± 0.01
			298.15	10.39 ± 0.30 10.7 ± 0.5 ^b	-31.3 ± 0.2 -32.91 ± 0.02 ^b	-2.2 ± 0.1 -2.53 ± 0.06 ^b	112.9 102.0 ± 0.3 ^b	0.019 ± 0.002	-0.264 ± 0.01
			308.15	10.62 ± 0.30 11.1 ± 0.5 ^b	-32.2 ± 0.2 -33.86 ± 0.02 ^b	-6.6 ± 0.1 -6.51 ± 0.08 ^b	96.3 88.9 ± 0.6 ^b	0.016 ± 0.002	-0.220 ± 0.01
			318.15	11.36 ± 0.30 12.0 ± 0.6 ^b	-33.0 ± 0.2 -34.69 ± 0.02 ^b	-11.0 ± 0.1 -10.5 ± 0.1 ^b	80.2 76.1 ± 0.6 ^b	0.012 ± 0.002	-0.177 ± 0.01
[C ₁₂ eim]Br	345.40	0.0799	278.15	8.85 ± 0.20	-33.1 ± 0.2	8.1 ± 0.2	140.6	0.044 ± 0.004	-0.99 ± 0.11
			288.15	8.46 ± 0.20	-34.5 ± 0.2	3.0 ± 0.2	120.0	0.039 ± 0.004	-0.95 ± 0.11
			298.15	8.44 ± 0.20	-35.7 ± 0.2	-2.0 ± 0.2	100.2	0.033 ± 0.004	-0.91 ± 0.11
			308.15	8.79 ± 0.20	-36.7 ± 0.2	-7.1 ± 0.2	81.0	0.027 ± 0.004	-0.87 ± 0.11
			318.15	9.32 ± 0.20	-37.6 ± 0.2	-12.1 ± 0.2	62.4	0.021 ± 0.004	-0.82 ± 0.11
[C ₁₂ bim]Br	373.41	0.0399	278.15	5.16 ± 0.10	-28.7 ± 0.7	10.43 ± 0.2	125.2	0.040 ± 0.004	-1.40 ± 0.11
			288.15	4.79 ± 0.10	-30.0 ± 0.7	4.60 ± 0.02	109.7	0.034 ± 0.004	-1.29 ± 0.11
			298.15	4.69 ± 0.10	-31.1 ± 0.7	-1.22 ± 0.02	94.7	0.029 ± 0.004	-1.19 ± 0.11
			308.15	4.86 ± 0.10	-32.0 ± 0.7	-7.04 ± 0.02	80.2	0.023 ± 0.004	-1.08 ± 0.11
			318.15	5.29 ± 0.10	-32.7 ± 0.7	-12.86 ± 0.02	66.1	0.017 ± 0.004	-0.98 ± 0.11
[C ₁₂ thiaz]Br	335.36	0.1098	278.15	9.21 ± 0.30	-33.3 ± 0.3	6.5 ± 0.2	143.3	0.017 ± 0.001	-0.70 ± 0.02
			288.15	8.64 ± 0.30	-34.7 ± 0.3	1.9 ± 0.2	127.3	0.015 ± 0.001	-0.63 ± 0.02
			298.15	8.62 ± 0.30	-35.9 ± 0.3	-2.6 ± 0.2	111.8	0.013 ± 0.001	-0.56 ± 0.02
			308.15	9.15 ± 0.30	-36.9 ± 0.3	-7.1 ± 0.2	96.7	0.011 ± 0.001	-0.49 ± 0.02
			318.15	9.66 ± 0.30	-37.8 ± 0.3	-11.7 ± 0.2	82.2	0.008 ± 0.001	-0.42 ± 0.02

^aUnits: M , g mol⁻¹; m , mol kg⁻¹ of solution; T , K; cmc, mmol dm⁻³; $\Delta_M G^0$, $\Delta_M H^0$, kJ mol⁻¹; $\Delta_M S^0$, J K⁻¹ mol⁻¹; B_{CA}' , B_{MA}' , kg K⁻¹ mol⁻¹

^bThe values were taken from [4]; the literature data for $\Delta_M G^0$ (and $\Delta_M S^0$) were recalculated to the rational scale, used in this paper.

Table S3. Coefficients A, B, C of polynomial $cmc=A+BT+CT^2$ ^a.

	A	B	C
[C ₁₂ im]Br	116.79 ± 0.24	-0.751 ± 0.002	0.0013 ± 0.0001
[C ₁₂ mim]Br	185.11 ± 10.32	-1.183 ± 0.069	0.0020 ± 0.0002
[C ₁₂ eim]Br	144.17 ± 11.31	-0.323 ± 0.076	0.0016 ± 0.0001
[C ₁₂ bim]Br	122.98 ± 0.45	-0.797 ± 0.003	0.0013 ± 0.0001
[C ₁₂ thiaz]Br	175.31 ± 31.92	-1.132 ± 0.214	0.0019 ± 0.0001

^aUnits: A/mm³·dm⁻³; B/ mmol·dm⁻³·K⁻¹; C/ mmol·dm⁻³·K⁻²

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