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What makes the solubilization of water in reversed micelles exothermic or endothermic? A titration calorimetry investigation

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Thermal effects of the solubilization of water in reversed micelles based on sodium (or potassium, ammonium) bis(2-ethylhexyl)phosphate (**1a**, **1b**, **1c**), potassium 2-ethylhexyl mono(2-ethylhexyl)phosphate (**2a**), and sodium bis(2-ethylhexyl)sulfosuccinate (AOT) have been investigated by titration calorimetry. It was found that the overall reaction is exothermic for the reversed micelles of **1a**, **1b**, and **2a**, while it is endothermic for the reversed micelle of **1c**. The influences of Ni^{2+} and urea on the molar enthalpy (ΔH_m) of the solubilization of water have also been studied. The ΔH_m value is reduced significantly by the presence of 0.1 M Ni^{2+}, while it increases again on going from 0.1 to 0.2 M Ni^{2+}. The ΔH_m value decreases with increasing urea concentration in the reversed micelles of both **2a** and AOT. Using a method in which the total molar enthalpy [ΔH_m(T)] is correlated to the molar ratio of water to surfactant (R), the molar enthalpies of bound (ΔH_B) and free (ΔH_F) water, and the maximum number of water molecules that can bond to a surfactant molecule (N_B) have been obtained. Both the qualitative and quantitative results reveal that the following three thermal effects are involved in the solubilization of water in reversed micelles: (1) an endothermic effect due to the breaking of the hydrogen-bonded network in bulk water (effect 1); (2) an exothermic effect arising from the interactions of water with the counterion and other head groups of the surfactant (effect 2) and (3) an endothermic effect due to the expansion or the dismantling of the quasi-lattice between the counterion and the anion of the surfactant (effect 3). For the AOT-based reversed micelle, effects 1–3 cannot totally explain its overall endothermicity. Thus, some special reasons have also been proposed to account for the "unusual" thermal behaviour of the AOT system.

1 Introduction

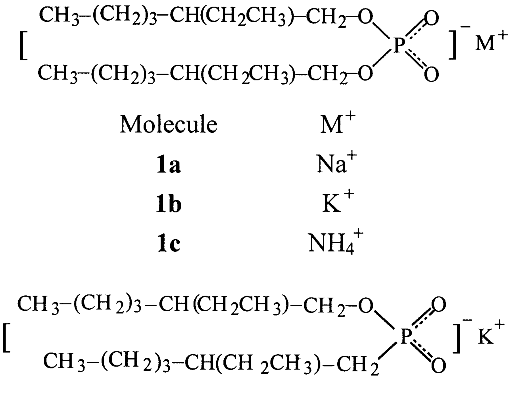
Studies on water-in-oil (w/o) microemulsions have received increasing interest. Besides their applications in tertiary oil recovery,[1,2] reversed micelles or w/o microemulsions have been successfully used as size-controlling microreactors for a variety of aqueous chemical reactions,[3] as vehicles for drug delivery,[4] as membrane mimetic systems,[5] and in separation and extraction processes of both metal ions and proteins.[6,7] Recently, w/o microemulsions have also been employed in effective nanoscale compartmentalization of nanoparticles and polymer syntheses.[8]

For all these applications, it is important to understand first the structures of the microemulsions. The interactions of water with polar head groups of surfactants are closely related to the rigidity and curvature of the interface,[9] and consequently, to it is noted that there was already a small amount of water present ($R = 0.26$) and, consequently, most AOT molecules had existed as the trimer in the reversed micellar solution of AOT in isooctane before the experiment was performed.[23]

On the basis of the above results, one can conclude that the solubilization of water in the AOT-based reverse micelle is undoubtedly associated with an overall endothermic effect. However, there may exist very complex endothermic and exothermic processes, which contribute simultaneously to the overall thermal effect. As far as the gain in entropy is concerned, a controversy still exists, whether the entropy gain results from the breaking of the water network or not. Thus, to shed some light on this problem, it is necessary to ascertain whether all the effects, 1–3, do appear and, if they do, whether they are more significant than the fluctuation of the microemulsion particle shape and the increased mobility of surfactant molecules. Gu *et al.*[27] reported that the solubilization of water in the reversed micelle of sodium dodecylbenzenesulfonate (SDBS) is slighly endothermic at very low R and then becomes exothermic, which is exactly opposite to the situation in the AOT-based system. The $-SO_3Na$ group exists in both SDBS and AOT molecules, but the thermal effects of the solubilization of water in SDBS-based and AOT-based reversed micelles are very different. What is the reason for this difference and can effects 1–3 totally account for the overall endothermic effect of the AOT system? Gu *et al.*[27] suggested that, for the AOT-based reversed micelle, the radius of the inner core of anhydrous reversed micelle (R_0) is smaller than the circumscribed radius of a "tetrahedron" (R_s) formed by five water molecules, leading to the overall endothermic effect. The opposite situation, *i.e.* $R_0 > R_s$ was suggested to occur for the SDBS-based reversed micelle, such that the overall effect is exothermic.[27] However, this explanation seems not well grounded because: (1) the "tetrahedron" formed by five water molecules is not the isolated structural unit existing in bulk water; (2) whether R_0 is larger than R_s or not could only govern the thermal effects for the initial addition of water, even if it was a reasonable explanation; (3) no quantitative data for R_0 and R_s were presented.[27]

In principle, microcalorimetry cannot provide information at the molecular level as the enthalpy refers essentially to macroscopic not microscopic characteristics. Therefore, it does not seem easy to distinguish a specific endothermic or exothermic effect from the overall thermal effect. For this reason, and also based on the fact that calorimetric studies on systems other than AOT are surprisingly scarce in the literature,[23] our strategy is to study first some new reversed micellar systems to find out the common features regarding the thermal effects of water solubilization, and then to examine the case of the AOT-based reversed micelle for comparison. We also think that changing the counterion of the surfactant, or putting additives, which can alter the structure of water and/or interact with the head groups of the surfactants, into water might provide more insight into the thermal effects of the solubilization of water in reversed micelles.

The reversed micellar systems studied here are mainly based on **1a**, **1b**, **1c**, and **2a** (see Scheme 1). These surfactants are commonly used as solvent extractants in hydrometallurgy and investigations on the structures and varying physicochemical properties of the reversed micelles or microemulsions based on these surfactants have also been carried out.[28–32] The strength of the interaction of water with the ammonium ion is much weaker than with sodium or potassium ions. Thus, it was observed in our previous work that the thermal effect of the solubilization of water in the reversed micelle of **1c** is different from those of **1a** and **1b**.[33] A similar phenomenon was found between ammonium 2-ethylhexylmono(2-ethylhexyl) phosphate and **2a**, or lithium (sodium) 2-ethylhexylmono(2-ethylhexyl)phosphate.[34] However, the reasons for these differences have not yet been ascertained.



Molecule	M^+
1a	Na^+
1b	K^+
1c	NH_4^+

2a

Scheme 1 Molecular structures of **1a**, **1b**, **1c**, and **2a**. After saponification, the P=O bond in **1** and **2** is not present due to the electron-cloud delocalization.[29a]

Except for the lithium ion, all the metal ions break the structure of water, due to their solvation effects in aqueous solutions.[35] Metal ions also interact electrostatically with the anions of the surfactants. Therefore, we have used aqueous solutions of $NiCl_2$ instead of pure water as titrant to examine how the overall thermal effect is changed, which will help decide whether the different endothermic and exothermic effects exist.

Urea is often used as a denaturing agent for proteins, but the mechanism is not well established. For this reason, it is important to study the effect of urea on organized assemblies, such as micelles,[36–39] reversed micelles,[40,41] vesicles,[36] and cyclodextrins.[42–45] Very recently, we reported the results of a quantitative investigation of the hydrophobic interaction mechanism between urea and molecular probes used in sensing microheterogeneous media, *i.e.* micelles and β-cyclodextrin.[43–45] Here, we will study the effect of urea on the thermal effect accompanying the solubilization of water in reversed micelles. This might provide some evidence for the existence of various thermal effects, since urea interacts with the head groups of the surfactants in reversed micelles,[40,41] and thus can alter, to some extent, the water solubilization process.

2 Experimental

2.1 Materials

Analytical reagents *sec*-octyl alcohol, *n*-heptane, urea, $NiCl_2$ (Beijing Chemical Plant, P. R. China), and AOT (Sigma) with purity >99% were used without further purification. AOT was dried in an oven and stored in a desiccator. Bis(2-ethylhexyl)phosphoric acid (**1**) and 2-ethylhexylmono(2-ethylhexyl) phosphoric acid (**2**) were purified by copper salt crystalization.[46] Water was bidistilled. *Sec*-octyl alcohol and *n*-heptane were stored over molecular sieves.

2.2 Preparation of surfactants

Known amounts of **1** or **2** were dissolved in known amounts of *n*-heptane, to which sodium, potassium or ammonia were gradually added in the presence of nitrogen. The mixtures were heated and allowed to react for at least three days, until all **1** and **2** were saponified, as confirmed by acid–base titration in a solution of ethanol. The products were diluted with mixtures of *n*-heptane and *sec*-octyl alcohol when they were used as titrands.

2.3 Instrument and methods

The measurements were performed with a Tronac Model 1250 titration calorimeter with its isoperibol system using a 25 ml reaction vessel. The volumes of the titrand solutions were 20 or 25 ml. The burette rates were 0.09974 or 0.3295 ml min^{-1}, while the times for each burette run were 15 and 6 s, respectively. The time interval between two successive increments (the stabilizing time) was 2–3 min. Before calorimetic measurements, the titration experiments in the flask were performed to ensure that the time intervals were long enough for the transparent microemulsions to be formed. The temperature in the reaction vessel was maintained at 25.000 ± 0.001 °C. The heat of solution of water was calculated by multiplying the effective thermal capacity and the temperature displacement by a small correction for the difference in temperature between the titrand solution and the bath. The errors in the measured enthalpies were estimated to be *ca.* ±5%.

3 Results

3.1 Thermal effects of the solubilization of water in reversed micelles of 1a, 1b, and 1c

The molar enthalpies of solubilization of water, *i.e.* ΔH_m as a function of R, for the reversed micelles based on **1a**, **1b**, and **1c**, are shown in Fig. 1A, 2A, and 3A, respectively. The ΔH_m values corresponding to the data points in the figures were obtained after each increment.

It is quite interesting to note that two types of thermal curves occur. One, for the reversed micelles of **1a** and **1b**, in which the solubilization of water is mainly associated with an overall exothermic effect (negative ΔH_m) and a slightly endothermic effect can also be seen at relatively higher R values. The other, for the reversed micelle of **1c**, in which an overall endothermic effect (positive ΔH_m) appears over the whole range of R values.

The structures of **1a**, **1b** and **1c** are similar, as shown in Scheme 1. Thus, it is clear that the difference in the two types of thermal curves arises essentially from the difference in the interactions of water with the counterions, *i.e.* Na^+, K^+, and NH_4^+. The hydration energy of K^+ in the gas phase is *ca.* −75 kJ (mol $H_2O)^{-1}$,[24] while that of Na^+ is *ca.* −100 kJ (mol of $H_2O)^{-1}$. Provided that the strength of the hydrogen bond between water and NH_4^+ is close to that of a hydrogen bond in bulk water, *i.e.* 17 kJ mol^{-1}, the exothermic effect (effect 2) accompanying the interaction of water with the counterion NH_4^+ in **1c** should be much smaller than those with Na^+ in **1a** and K^+ in **1b**. On the other hand, since at lower R values most water molecules added are bound to the head groups of the surfactants, the hydrogen-bonded network in bulk water has to be broken to a great extent in the solubilization of water in reversed micelles, which is associated with an endothermic effect (effect 1).

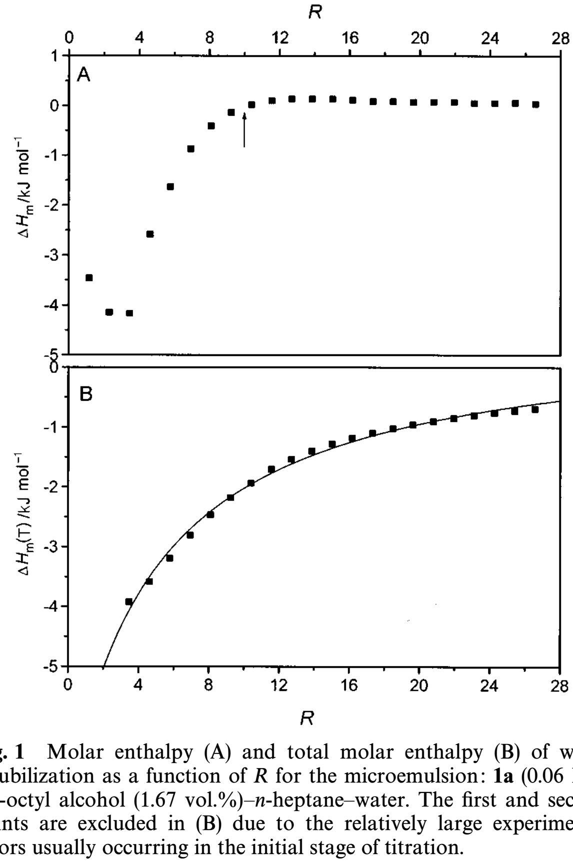


Fig. 1 Molar enthalpy (A) and total molar enthalpy (B) of water solubilization as a function of R for the microemulsion: **1a** (0.06 M)–*sec*-octyl alcohol (1.67 vol.%)–*n*-heptane–water. The first and second points are excluded in (B) due to the relatively large experimental errors usually occurring in the initial stage of titration.

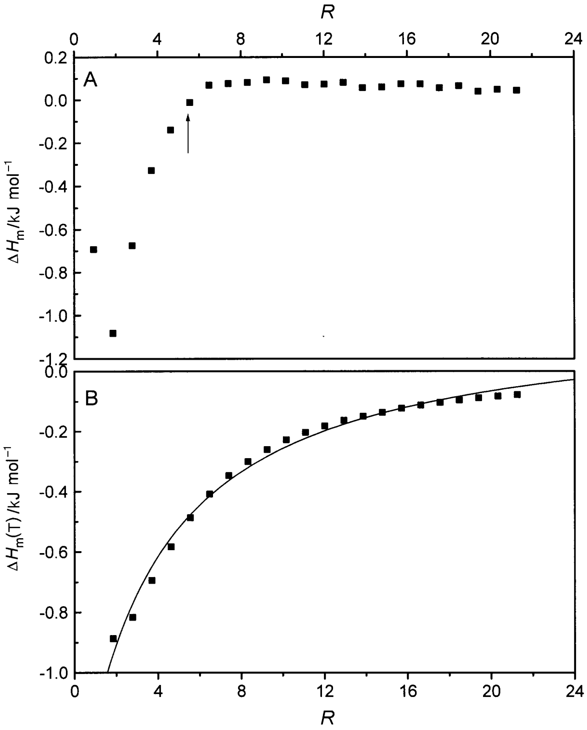


Fig. 2 Molar enthalpy (A) and total molar enthalpy (B) of water solubilization as a function of R for the microemulsion: **1b** (0.06 M)–*sec*-octyl alcohol (1.67 vol.%)–*n*-heptane–water. The first point is excluded in (B) due to the relatively large experimental error.

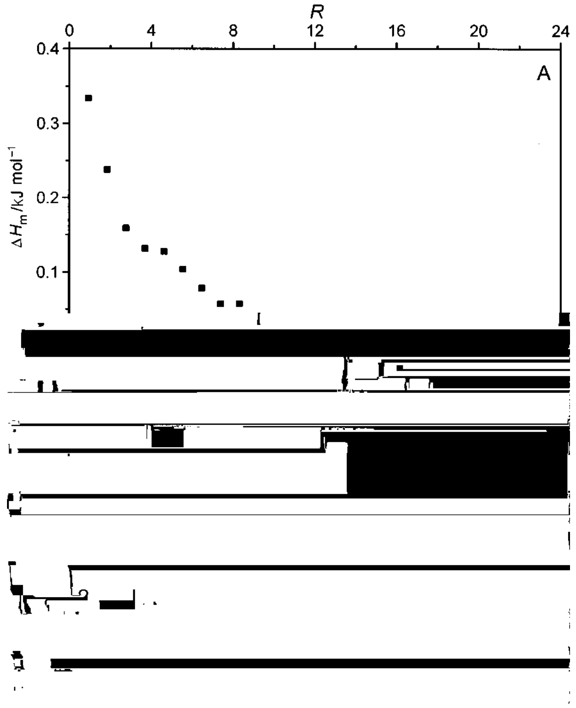


Fig. 3 Molar enthalpy (A) and total molar enthalpy (B) of water solubilization as a function of R for the microemulsion: **1c** (0.06 M)–*sec*-octyl alcohol (1.67 vol.%)–*n*-heptane–water.

For reversed micelles based on **1a** and **1b**, effect 2 should be larger than the endothermic effects, such that the overall effects are exothermic at $R \leq 10$ and 5.5 (Fig. 1A, 2A), respectively. However, when the R values exceed 10 and 5.5 for the microemulsions of **1a** and **1b**, respectively, the overall reaction becomes slightly endothermic. This indicates that the bound water layer is almost saturated. At this time, most water molecules added do not interact with the head groups of the surfactant and the structure of water is no longer broken. Thus, the slightly endothermic effect can only be ascribed to the swelling of microemulsion particles.[23] For the reversed micelle based on **1c**, the overall effect is endothermic. This is surely due to much weaker interaction between water and NH_4^+ relative to those of water with Na^+ or K^+. Actually, the total number of hydrogen bonds formed by water with NH_4^+ and other head groups in **1c** might be less than that in bulk water, where each water molecule in the hydrogen-bonded network forms four hydrogen bonds with the adjacent water molecules.[35]

3.2 Effect of Ni^{2+} on ΔH_m in the reversed micelle of 2a

In an aqueous solution of $NiCl_2$, the hydrogen-bonded network of water is partly broken. Thus, if an aqueous solution of $NiCl_2$ is used as titrant instead of pure water, effect 1 will be reduced substantially. On the other hand, the electrostatic interactions of Ni^{2+} with the anions of the surfactants might lead to an exothermic effect.

Fig. 4A shows ΔH_m as a function of R for the reversed micelle of **2a** in the absence and presence of Ni^{2+}. It can be seen that, over the whole range of R values studied, the ΔH_m value is negative, showing that the overall effect is exothermic. The presence of 0.1 M Ni^{2+} reduces markedly the ΔH_m value, which strongly supports the hypothesis that Ni^{2+} can break the water structure. It seems unexpected that, when the concentration of Ni^{2+} is further increased to 0.2 M, the ΔH_m

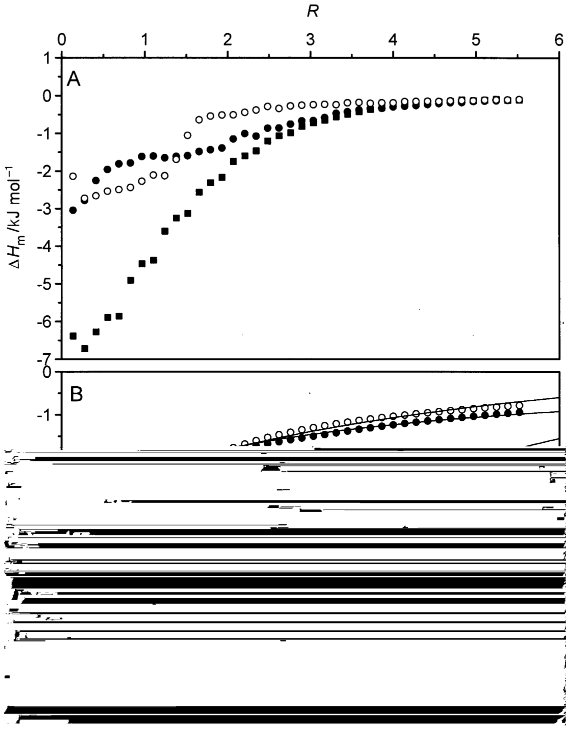
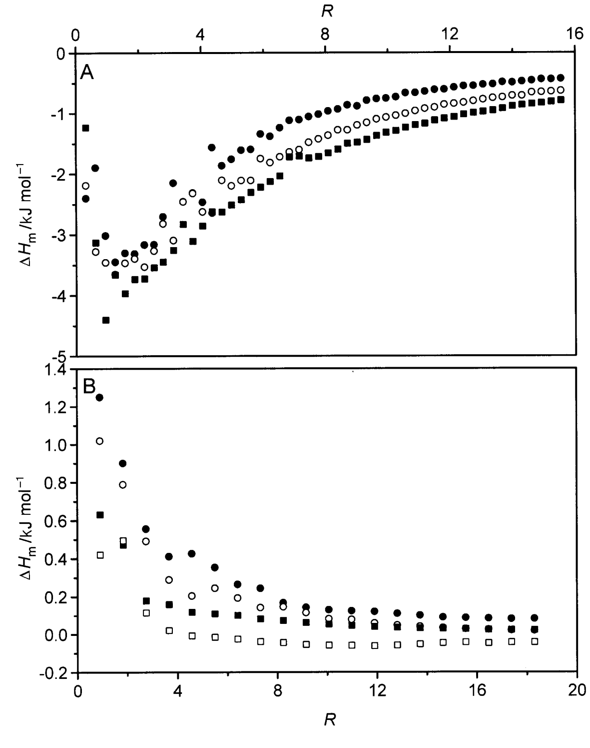


Fig. 4 Molar enthalpy (A) and total molar enthalpy (B) of water solubilization as a function of R for the microemulsion: **2a** (0.666 M)–*sec*-octyl alcohol (15 vol.%)–*n*-heptane–



replaced by urea.[40] Although there is no evidence to show whether all the water molecules bound to the surfactant are replaced by urea, it is quite safe to say that, even at lower R values, the hydrogen-bonded network in bulk water is not broken completely, which is very different from the situation in the absence of urea, where most hydrogen bonds in bulk water are broken in order for it to interact with the counterion and head groups of the surfactant. Thus, the endothermic effect accompanying the breaking of the water structure will be reduced remarkably. This should be the main reason why the ΔH_m value decreases in reversed micelles of both **2a** and AOT.

Now, it is quite clear that, although both Ni^{2+} and urea lead to smaller ΔH_m values, the mechanisms are very different. In the case of Ni^{2+}, the structure of water was broken to some extent before the water was added to the reversed micelles so that this part of the endothermic effect is excluded in the measured ΔH_m value. In the case of urea, however, the smaller ΔH_m value results from less hydrogen bonds in the added water being broken. On the basis of the above discussion, one can conclude that the calorimetric study of the urea effect on reversed micelles is in good agreement with the results based on some microscopic methods in the literature.[40,41] It also appears that the urea effect study can provide a good method of understanding the thermal effects associated with the solubilization of water in reversed micelles.

4 Discussion

To analyse quantitatively the results presented above, we estimate next the molar enthalpies for bound water (ΔH_B) and free water (ΔH_F), and the maximum number of water molecules that can bond to a surfactant molecule (N_B).

According to D'Aprano *et al.*, the molar fraction of bound water (X_B), the N_B value, and the total molar enthalpy [ΔH_m(T)], obtained from the total enthalpy averaged by the total amount of water added, are given by[15]

$$X_B = 1/[1 + (B/A)R] \quad (1)$$

$$N = A/B \quad (2)$$

$$\Delta H_m(T) = [\Delta H_B + \Delta H_F(B/A)R]/[1 + (B/A)R] \quad (3)$$

where A and B are constants. Provided that ΔH_F is approximately zero, eqn. (3) becomes

$$\Delta H_m(\mathrm{T}) = \Delta H_B/[1 + (B/A)R] \quad (4)$$

It should be pointed out that eqn. (1)–(4) are based on the assumptions that a continuous equilibrium exists between bound and free water and that the radius of the water pool (r_w) is linearly correlated to R through the following equation[15]

$$r_w = A + BR \quad (5)$$

Note, also, that eqn. (1)–(4) apply both in the absence and presence of cosurfactant, according to the method of D'Aprano *et al.*[15] Fig. 1B, 2B, and 3B depict the total molar enthalpy as a function of R for the microemulsions of **1a**, **1b**, and **1c**, respectively, while Fig. 4B is for the microemulsion of **2a** at $[Ni^{2+}] = 0$, 0.1, and 0.2 M, respectively.

Non-linear regression analyses (NLR) following eqn. (3) and (4) have been tried.[50] All the ΔH_B, ΔH_F, and B/A values obtained by the NLR method, as well as the N_B values, are listed in Table 1. It should be mentioned that the NLR analyses were not carried out for the microemulsions of **2a** and AOT with varying concentrations of urea, due to the fact that urea replaces some water molecules in the solvation layer.

It can be seen from Table 1 that the ΔH_B values are negative for microemulsions of **1a**, **1b**, and **2a** at $[Ni^{2+}] = 0$, 0.1, and 0.2 M, strongly supporting the fact that effect 2 is dominant over the sum of effects 1 and 3 in these systems. It is the ΔH_F value that can reflect the enthalpy of the fluctuation of the microemulsion particle shape and the increased mobility of surfactant molecules, including counterions, as suggested by Haandrikaman *et al.*[23] Since ΔH_F values are much smaller than the ΔH_B values for the microemulsions of **1a**, **1b**, and **2a** without Ni^{2+}, and also based on the fact that the ΔH_B value is actually the result of effect 2 compensated by effects 1 and 3, one can conclude that the thermal effect resulting from the fluctuation of the microemulsion particle shape and the increased mobility of surfactant molecules is not significant relative to effects 1–3 in the present study.

Table 1 Molar enthalpies of bound water (ΔH_B) and free water (ΔH_F), the B/A values, and the maximum number of bound water molecules per surfactant molecule (N_B) for various microemulsions (MEs)

System	ΔH_B/ kJ mol^{-1}	ΔH_F/ kJ mol^{-1}	B/A	N_B
ME (**1a**)	−7.26	0.677	0.194	5.2
ME (**1b**)	−1.53	0.194	0.282	3.5
ME (**1c**)	0.396	0	0.209	4.8
ME (**2a**)	−3.07	0.159	0.330	3.0
ME (**2a**, 0.1 M Ni^{2+})	−7.42	3.18	0.207	4.8
ME (**2a**, 0.2 M Ni^{2+})	−3.09	1.61	0.188	5.3

For the microemulsion of **1c**, the ΔH_B value is positive, indicating that effect 2 is smaller than the sum of effects 1 and 3. Thus, the different behaviour between **1c** and **1a**, **1b** is an indication that effect 2 is playing an important role. One can see, from Table 1, that the ΔH_F value is zero for the microemulsion of **1c**, which further supports that the thermal effect related to the fluctuation of the microemulsion particle shape and the increased mobility of surfactant molecules[23] is negligible. It has also been observed that the ΔH_F value is zero for the AOT-based microemulsion.[15] Thus, it is safe to say that the gain in entropy for the microemulsions of both **1c** and AOT mainly results from the breaking of the network in bulk water.

The quantitative data of ΔH_B values for the microemulsion of **2a**, both in the absence and presence of Ni^{2+} (Table 1), further confirm that Ni^{2+} acts as a water-structure breaker and that electrostatic interactions exist between Ni^{2+} and the anion of **2a**. It is interesting to note that ΔH_F values for the microemulsion of **2a** with Ni^{2+} are larger than that without Ni^{2+}. This can be interpreted in terms of the fact that more potassium ions are dissociated, owing to the competetive effect of Ni^{2+} interacting with the anion of **2a**, such that the total mobility of potassium ions in the water pool becomes larger.

Discussion of the N_B values summarized in Table 1 is helpful. It is noted that the N_B value increases in the order ME (**1b**) < ME (**1c**) < ME (**1a**) (where ME stands for microemulsion), which is exactly the order of increasing hydrated radius of the ions or decreasing ionic crystal radius for Na^+, NH_4^+, and K^+.[51] In the case of the reversed micelle of **1a**, it was found from FTIR measurements that the most significant variation in the phosphate stretching frequency occurs when the R value changes from 0 to 5.[29a] This shows that hydration of the head groups, as well as the counterion of **1a**, mainly takes place for $R = 0$–5, which agrees qualitatively with the N_B value of the **1a** system. For the AOT-based microemulsion, the hydrated number reported lies between 6 and 12.[13,16,21,23] Using differential scanning calorimetry (DSC) it has been shown that six water molecules are unfreezable and two of them interact more strongly with the head group of AOT than the remaining four water molecules.[13] It seems that calorimetry can only distinguish water molecules having relatively stronger interactions with counterions and other head groups of the surfactants, as compared with other methods. For the microemulsion of **2a**, the N_B value is increased by the presence of Ni^{2+}. This can be explained by the fact that a part of the potassium ions in the hydrated layer are replaced by Ni^{2+}, whose hydrated radius is larger than that of the potassium ion because of the larger electrostatic interaction of the former with water.

Evidence presented above strongly supports the hypothesis that effects 1–3 are involved in the solubilization of water in the reversed micelles studied. It can be inferred that these three effects should appear for all the reversed micelles of anionic surfactants including **1a**, **1b**, **1c**, **2a**, AOT and SDBS, because of the similar water solubilization processes. For some reversed micelles such as those of **1a**, **1b**, **2a**, and SDBS, effect 2 is dominent over the sum of effects 1 and 3, leading to the overall effect being exothermic. For some other reversed micelles, *e.g.* **1c**, the sum of effects 1 and 3 is larger than effect 2, which makes the overall effect endothermic. However, in the case of AOT, the overall endothermic effect cannot be described only by the above three effects, since the siutation of effect for the interactions of water with the counterion and other head groups, and an endothermic effect for the expansion or the dismantling of the quasi-lattice between the counterion and the anion of surfactant. For the AOT-based reversed micelle, the above three effects also exist, but they cannot totally explain the overall endothermic effect. The possible destruction of AOT trimers, the existence of trapped water molecules, the smaller molar fraction of the Na^+-bound water as compared with that of the sulfonate-bound water, and the water-induced change in the head group conformation might also play important roles.

The estimated maximum number of bound water molecules per surfactant molecule for the microemulsions of **1a**, **1b**, **1c**, and **2a** at $[Ni^{2+}] = 0$, 0.1, and 0.2 M, are consistent with the order of the decreasing hydrated radii of the ions.

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50 For the microemulsions of **1a**, **1b**, and **2a**, the fits according to eqn. (3) converge well (see Fig. 1B, 2B, and 4B), while those based on eqn. (4) do not. In the case of **1c**, however, reasonable NLR results can be obtained when eqn. (4) applies, which are reflected by the good fit in Fig. 3B. On the other hand, the NLR analysis following eqn. (3) has also been tried for the microemulsion of **1c** and the ΔH_F value was estimated to be -3.57×10^{-3} kJ mol^{-1} with larger standard error. This ΔH_F value is also negative and very small as compared with the ΔH_B value (0.392 kJ mol^{-1}). In addition, the ΔH_B and B/A values obtained following eqn. (3) and (4) are quite similar. Thus, we believe that for the microemulsion of **1c** the molar enthalpy of free water is practically zero.
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