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Calorimetric investigation of temperature effect on the interaction between poly(ethylene oxide) and sodium dodecylsulfate in water

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Abstract

The interaction of four poly(ethylene oxides), with molar masses of 1500, 3350, 10 000 and 100 000 g mol^{-1} with sodium dodecylsulfate, at 15, 25, 35 and 65 °C was investigated by isothermal titration calorimetry. No significant change of the critical aggregation concentration values or of the amount of surfactant bound was observed within this temperature range. The profiles for the variation of the observed enthalpies with surfactant concentration, however, are quite different for the four studied temperatures, what has been interpreted as a consequence of a change in the mode of poly(ethylene oxide) (PEO) interaction with sodium dodecylsulfate (SDS) micelles within this temperature range.

Keywords: Polymer–surfactant interaction; Isothermal calorimetry; Poly(ethylene oxide); Sodium dodecylsulfate

1. Introduction

Polymers and surfactants are present in a variety of products, displaying special properties that may differ from those of their individual solutions, due to the formation of complex structures as a consequence of their interaction. This interaction displays features that depend on the polymer and surfactant electrical charges, hydrophobicity and other characteristics, extensively described in textbooks and reviews (see, for instance, references [1–4]). With respect to ionic surfactants interacting with non-ionic polymers, the system sodium dodecylsulfate (SDS) + poly(ethyleneoxide) (PEO), is the most studied one. The general picture for this interaction proposes the formation of SDS aggregates surrounded by PEO chains, in a configuration referred to as "necklace". These aggregates start to form at concentrations lower than that required to form micelles in water, and are typically smaller than the normal SDS micelles. This interaction and the produced complex have been investigated by a variety of techniques like conductivity [5] or surface tension [6] measurements, fluorescence spectroscopy [7], NMR [8] or small angle scattering techniques [9].

Calorimetry has also been extensively applied to the investigation of SDS–PEO interactions, providing important information on the energetics of the interaction, besides revealing itself a sensitive tool for the determination of interaction parameters, such as the critical aggregation concentration (c.a.c.) [10]. A good example is a recent calorimetric investigation reported by Dai and Tam [11] on the interaction of SDS with PEO of varying molar masses, revealing different enthalpy profiles as a function of molecular weight, and identifying 1500 g mol^{-1} as the minimum molar mass for the interaction to proceed to the formation of SDS–PEO complexes.

Temperature is an important parameter for this interaction. Regarding SDS micelles, at temperatures close to ambient, no significant changes have been observed on c.m.c. values or aggregation numbers. As temperature is raised, SDS micelles are known to reduce their aggregation numbers, for instance, by 30% from 20 to 40 °C [12]. PEO aqueous solutions are much more intensely affected by temperature. These solutions exhibit a lower critical solution temperature (LCST) type behaviour, with a critical solution temperature that depends on PEO molar mass, all above 100 °C. This behaviour has been ascribed to changes of configuration of the PEO chain, resulting in a less polar conformer, and to less efficient hydrogen bonding with water, as temperature rises.

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This work aims at applying the well-established technique of isothermal titration calorimetry (ITC) to investigate changes caused by temperature variation on the interaction of SDS with PEO. For this purpose, the enthalpy changes accompanying the addition of SDS to aqueous solutions of PEO with molar masses of 1500, 3350, 10 000 and 100 000 g mol^{-1} were investigated at 15, 25, 35 and 65 °C, over a wide concentration range.

2. Experimental

The four samples of poly(ethylene oxide) used, with nominal molar masses of 1500, 3350, 10 000 and 100 000 g mol^{-1}, were purchased from Sigma. SDS used was also from Sigma, with 99% purity. All of these chemicals were used without further treatment.

Solutions were prepared by weight (accuracy within 0.1 mg), with water of Mili-Q Plus grade, from a Milipore ultrafiltration system.

The isothermal titration measurements were performed using a VP-ITC instrument, from MicroCal. The experiments consisted of consecutive injections of a concentrated surfactant solution (10 wt.% of SDS) into the calorimeter cell that initially contained 1.44 ml of water or of a 0.1 wt.% polymer solution. The samples were added from a gastight syringe controlled by the instrument, using an interval of 10 min between injections. Injection volumes varied between 3 and 15 μl. As the surfactant solution is added, the cell volume is kept constant by an overflow of solution, which is taken into account during calculations of actual concentrations of both surfactant and polymer in the cell. The system was calibrated by measuring the enthalpy of dilution of 10 wt.% propanol solutions in water producing values that agree, within less than 2%, with the proposed reference value [13]. Experiments were performed at 15, 25, 35 and 65 °C. At the lowest temperature, there were no signs of SDS precipitation. In control bench experiments no precipitation was observed above 13 °C at the used SDS concentrations.

3. Results

A typical result from an ITC investigation of surfactant addition to an aqueous solution of non-ionic polymer is represented in Fig. 1, showing the surfactant dilution curves in water and into polymer solution. These enthalpy values represent differential enthalpies, calculated dividing the energy exchanged at each injection by the number of moles of surfactant added in each step. For all these experiments, the initial surfactant solution (kept in the syringe) is well above its c.m.c., being then considered as composed almost entirely of micelles. As this solution is injected into the cell, these micelles are disrupted, and the surfactant molecules diluted, a process that, for the temperature at which the data of Fig. 1 were taken (17 °C), is exothermic, but that becomes endothermic as temperature is raised (see further results).

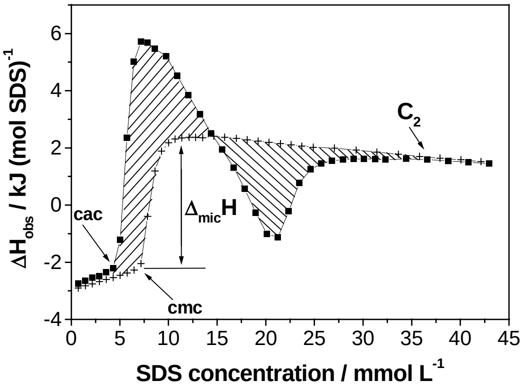

Fig. 1. Calorimetric results for the dilution of SDS in (+) water and in (■) 0.1 wt.% solutions of PEO 3350 g mol^{-1}, at 15 °C, indicating the parameters used to characterise this interaction (see text for definitions).

When this dilution process occurs in the presence of polymer, part of the surfactant molecules added interact with the polymer, causing the observed enthalpy to be slightly larger, as a consequence of a weak endothermic surfactant interaction with the polymer. As more surfactant is added, its concentration reaches a limit, called critical aggregation concentration (c.a.c.), above which a co-operative surfactant aggregation starts to occur, forming mixed aggregates containing some of the EO units of the polymer. These aggregates contain fewer surfactant molecules than their free micelles, for instance, ca. 30 SDS molecules, as reported by van Stam et al. [12]. This process is endothermic, due to the resultant dehydration of the EO units, and its co-operativity is revealed by the sudden increase in differential enthalpy as the process proceeds. The observed enthalpy goes through a maximum and then starts to decrease, becoming exothermic at higher surfactant concentrations. This change reflects the growth of the SDS aggregates, causing the release of part of the incorporated EO units, which are then rehydrated, an exothermic process. This process continues until reaching the so-called saturation concentration, C_2, at which the formation of free SDS micelles becomes thermodynamically favoured with respect to SDS interaction with the polymer, hence, the two dilution curves merge.

The overall polymer–surfactant energy of interaction, represented by the shaded area in Fig. 1, between the two dilution curves, can be calculated by subtracting the integral enthalpy of SDS dilution in the presence of polymer from the integral enthalpy of SDS dilution in water. Integral enthalpies were obtained by summing up the differential dilution enthalpies up to C_2.

The parameters related to the formation of SDS micelles in water, their critical micelle concentrations, c.m.c., and enthalpy of micelle formation, $\Delta_{mic}H$, can be also derived from the ITC experiments, as shown in Fig. 1. These results, obtained at the four studied temperatures, are listed in Table 1. They are all in close agreement with published data

Table 1
Calorimetrically determined values of critical micelle concentration, c.m.c., and enthalpy of micelle formation for SDS in water, at different temperatures

Temperature (°C)	c.m.c.[a] (mmol l^{-1})	$\Delta_{\mathrm{mic}}H$[b] (kJ mol^{-1})
15	6.9	4.8
25	7.0	0.4
35	7.2	−5.4
65	9.1	−16.7

[a] Uncertainty of c.m.c. values estimated to be smaller than ±0.5 mmol l^{-1}.

[b] Uncertainty of $\Delta_{\mathrm{mic}}H$ values smaller than 2% (except for value determined at 25 °C).

[14,15], confirming the small temperature effect on SDS c.m.c. values, but a significant variation in the enthalpies of micelle formation, which are positive at 15 °C, almost zero at 25 °C and become negative at higher temperatures, with an estimated $\Delta_{\mathrm{mic}}C_p$ of −430 J mol^{-1} K^{-1}.

The ITC results obtained on the interaction between SDS and three PEO (3350, 10 000 and 100 000), at the four temperatures are summarized in Fig. 2. At 15 and 25 °C, the curves representing the change in the observed enthalpies with SDS concentration display similar profiles, composed by a region where the enthalpy values for dilution of SDS into polymer solutions are higher (more endothermic) than those for dilution of SDS in pure water, followed by a region were these values are lower (less endothermic), until both curves merge. The position of the upper and lower peaks, as well as the maximum and minimum enthalpy values, are slightly different for PEO 3350, 10 000 and 100 000: the maximum occurs at closely the same concentrations for the three polymers, but with a lower enthalpy value for PEO 100 000; the position of the minimum is similar for the two largest PEO samples, with a less negative enthalpy value for PEO 100 000. The concentration at which the two dilution curves merge is larger for PEO 3350.

At higher temperatures, these profiles change notably. In part, this occurs because the process of forming SDS micelles becomes more exothermic as temperature is increased. In addition, the enthalpy changes due to polymer–surfactant interaction become less pronounced as the temperature increases. At 35 °C a slightly endothermic peak is observed at low SDS concentration, with a small exothermic peak close to saturation. At 65 °C the SDS dilution curve in polymer solution shows more positive enthalpies below c.a.c., and does not go under the curve for dilution in water, as occurred at lower temperatures. Interestingly, the c.a.c. values do not change significantly either with temperature or with the PEO molar mass, within this range, but are always significantly lower than the c.m.c. values measured in pure water.

At all the temperatures studied, the dilution curves for SDS into 0.1% PEO 1500 solutions differ significantly from

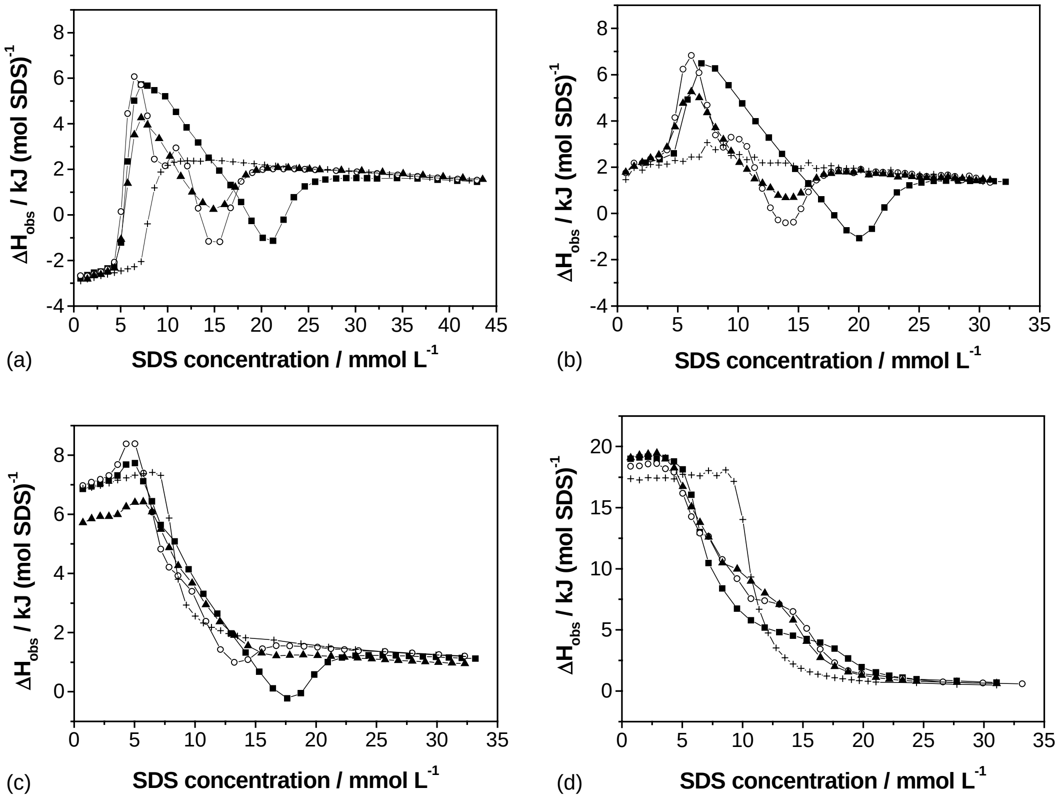

Fig. 2. Calorimetric titration curves from addition of 10 wt.% SDS to 0.1 wt.% solutions of (■) PEO 3350 g mol^{-1}, (○) PEO 10 000 g mol^{-1}, (▲) PEO 100 000 g mol^{-1}, and to water (+) (a) at 15 °C, (b) at 25 °C, (c) at 35 °C and (d) at 65 °C.

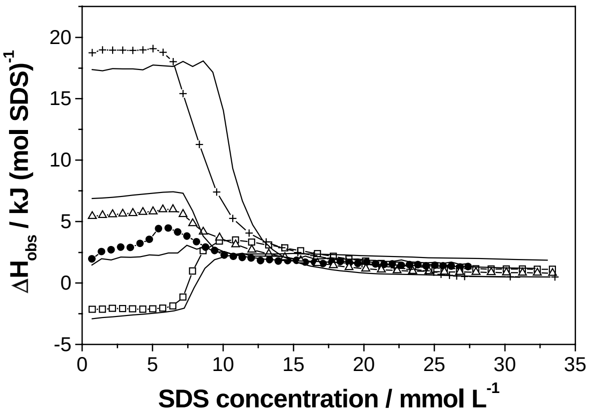

Fig. 3. Calorimetric titration curves from addition of 10 wt.% SDS to 0.1 wt.% solutions of PEO 1500 g mol^{-1} at: (□) 15 °C, (●) 25 °C, (△) 35 °C, (+) 65 °C. Full-drawn lines (—) represent the dilution of SDS in water for all temperatures.

those in water, but do not show the same features of those with larger PEO, as shown in Fig. 3. Enthalpy changes associated with the beginning of aggregation occur at slightly lower concentration in the presence of PEO 1500 than in water, indicating an effect due to the oligomer but, at higher SDS concentrations, the two curves coincide.

4. Discussion

The parameters for the interaction between SDS and PEO derived from calorimetric data are summarised in Table 2. From these data, one verifies that, within the studied temperature range, values of c.a.c. and C_2 do not change significantly with temperature. As a consequence, the number of SDS molecules per ethylene oxide unit at saturation, which is calculated by subtracting C_2 from the surfactant c.m.c. in water, and dividing by the actual amount of EO at C_2 (remembering that a small fraction of PEO, less than 6%, is lost due to cell overflow—see Section 2), is also unaltered within this temperature range. These ratios are slightly lower than 1, in agreement with other values reported for the interaction of SDS with the water-soluble non-ionic polymers PEO, PPO and PVP [16] and poly(*N*-isopropylacrylamide), PNIPAM [17].

PEO is known to become more poorly solvated by water as temperature increases, giving rise to its LCST behaviour. Interestingly, however, such changes in PEO hydration, do not result in a more intense interaction with SDS, as measured by the c.a.c. values [16], which are constant, as well as the amount of SDS bound. This may indicate that, within the present temperature range, these changes are not so profound as to affect the intensity of the interaction of PEO with SDS. However, in all studied temperatures, values of c.a.c. are always significantly lower than the corresponding c.m.c. values, which confirms that PEO is capable of interacting with SDS, inducing the formation of SDS aggregates. A different behaviour was recently observed for the interaction of SDS with PNIPAM [17], where changes of temperature between 17 and 29 °C, caused a 50% decrease in c.a.c. values. Such a difference may be attributed to the lower critical solution temperature of PNIPAM in water (ca. 32 °C) [17], again reinforcing that the present studies with PEO were conducted markedly below its LSCT (which is above 100 °C [18]).

The overall change in enthalpy due to SDS–PEO interaction can be estimated by subtracting the integral heats of dilution of SDS in polymer solution from those in water. It is suggested by the shape of the curves that the endothermic

Table 2
Parameters derived from calorimetric curves to characterise the interaction between SDS and PEO of different molar mass, at different temperatures

Polymer	c.a.c. (mmol l^{-1})	C_2 (mmol l^{-1})	*n* (SDS/EO)[a]	Δ*H*[b] (J mol^{-1})
15 °C (c.m.c. SDS = 6.9 mmol l^{-1})				
PEO 3350	4.9 ± 0.2	36 ± 2	1.31 ± 0.08	340
PEO 10 000	4.4 ± 0.2	25 ± 2	0.80 ± 0.09	350
PEO 100 000	3.9 ± 0.2	25 ± 2	0.80 ± 0.10	100
25 °C (c.m.c. SDS = 7.0 mmol l^{-1})				
PEO 3350	4.5 ± 0.3	28 ± 2	0.90 ± 0.10	−540
PEO 10 000	4.1 ± 0.2	20 ± 2	0.53 ± 0.10	170
PEO 100 000	3.9 ± 0.2	23 ± 2	0.66 ± 0.10	30
35 °C (c.m.c. SDS = 7.2 mmol l^{-1})				
PEO 3350	4.1 ± 0.2	27 ± 2	0.87 ± 0.09	−430
PEO 10 000	4.5 ± 0.2	20 ± 2	0.57 ± 0.10	−100
PEO 100 000	3.0 ± 0.2	23 ± 2	0.65 ± 0.05	−450
65 °C (c.m.c. SDS = 9.1 mmol l^{-1})				
PEO 3350	4.8 ± 0.2	29 ± 2	0.88 ± 0.10	−620
PEO 10 000	4.4 ± 0.2	25 ± 2	0.70 ± 0.10	−150
PEO 100 000	3.4 ± 0.2	25 ± 2	0.70 ± 0.09	−710

[a] Ratio between number of moles of SDS bound and moles of EO (calculated on a monomer basis).
[b] Values for the overall enthalpy of interaction, expressed per mole of bound SDS.

and exothermic peaks observed at 15 and 25 °C, represented by the dashed areas of Fig. 1, somehow cancel each other. This is confirmed by the small enthalpy values reported in the last column of Table 2. The compensation of both effects suggests that they are related to inverse processes. At lower SDS concentration, its aggregates formed around the PEO chains are known to be small [12]. That should cause a significant exposition of alkyl groups to water due to formation of these imperfect micelles. It has been proposed that PEO chains are incorporated into SDS micelles at this stage, a process that has been related to the solubilisation of small polar molecules as pentanol [15], which is also driven by the tendency to hide the SDS alkyl chains from water. The incorporation of EO groups into SDS micelles is expected to be an endothermic process, due to significant dehydration of PEO [4], in agreement with the calorimetry results pictured in Fig. 1. Being endothermic, such incorporation may only occur due to a favourable entropic contribution, which has been ascribed to the entropy increase associated with the release of water molecules from the solvation shell of PEO, a feature already reported as important in other processes involving PEO in aqueous solutions [19,20]. As the SDS concentration increases, its aggregates around PEO chain start to grow, reaching larger aggregation numbers, closer to the values observed for SDS micelles in water. Hence, more compact aggregates are formed, allowing the PEO chains to be released to a more hydrated environment, in the outer region of the aggregates. The corresponding dehydration of EO units gives rise to the exothermic contribution observed at higher SDS concentration in the calorimetric results of Figs. 1 and 2.

Another feature that arises from the analysis of the curves of Fig. 2 is that both the endothermic and exothermic peaks observed at 15 and 25 °C start to decrease as the temperature is raised to 35 °C, and vanish at 65 °C. In a calorimetric experiment such as the present one, the observed enthalpy is always a consequence of the product between the extent of interaction, represented by the amount of SDS molecules that actually bind to PEO, and the enthalpy of interaction expressed per mole of bound SDS. According to the model outlined above, this decrease in the observed enthalpy at higher temperatures may be ascribed to either a decrease in the extent of interaction, or to a decrease in the enthalpy change associated with this interaction. The first hypothesis opposes the observation that c.a.c. is lowered to the same extent at all the studied temperatures. Hence, it follows that the enthalpy of interaction will decrease as the temperature increases. As previously described, this enthalpy change is mainly ascribed to changes of PEO hydration due to displacement of water owing to the interaction with SDS aggregates. The enthalpy of hydration of PEO is known to decrease with the increase in temperature and, based on literature data [21,22] one can estimate a change from 7.4 to 5.5 kJ mol^{-1}, representing a 26% decrease, from 15 to 65 °C. Such a decrease cannot explain the differences shown in Fig. 2. One possible explanation to account for such difference is that the mode of PEO interaction with the SDS aggregates changes with temperature. Possibly, the extent of PEO incorporation decreases as the temperature rises until, at high temperatures (represented by the results at 65 °C in the present investigation) no significant PEO dehydration is observed. This means that the favourable effect of the incorporation of PEO units in covering the SDS alkyl chains and hiding them from water at the surface of the smaller aggregates formed at lower surfactant concentrations becomes less important as the temperature rises.

The interaction of PEO 1500 with SDS shows a different pattern, as shown in Figs. 2 and 3. For PEO 1500, the observed enthalpy changes do not differ significantly from the dilution of SDS in water, except that aggregation of SDS starts at a lower concentration. The existence of a minimum PEO molar mass of 900 g mol^{-1} for the interaction with ionic surfactants to proceed according to the model described above was recently proposed by Dai and Tam [11], suggesting that PEO of lower molar masses are not capable of inducing the formation of SDS aggregates, but interact with the micelles in a manner similar to smaller solutes. The difference in position for this minimum in molar mass may be ascribed to the fact that Dai and Tam based their statement on measurements performed at 25 °C, whereas the present investigation covers a wider temperature range. This behaviour would explain the observed decrease in SDS c.m.c., consistent with the stabilisation of micelles due to decrease of electrostatic repulsion between SDS headgroups, and to an entropic gain due to mixing [15], which occur associated with the incorporation of smaller solutes into ionic micelles. The similar enthalpy values observed for SDS dilution in water and in PEO 1500 solution suggest that such an interaction does not cause significant dehydration of the EO units, except, perhaps, at 25 °C.

For the other PEO studied in this work, 3350, 10 000 and 100 000 g mol^{-1}, the calorimetric results suggest a similar process of interaction, although with PEO 3350 the minimum of these curves always occur at higher SDS concentrations, associated with a slightly larger C_2 value. It has been already proposed [16] that the number of aggregates possible of being accommodated on a PEO chain varies with its molar mass. The range of 8000–10 000 g mol^{-1} has been proposed as the minimum size to accommodate more than one SDS aggregate per chain. The inflection shown in their enthalpy curves (more evident in the results at 15 and 25 °C shown in Fig. 2a and b), has been suggested to reflect of some kind of rearrangement or repulsion due to formation of a second SDS aggregate on the same PEO chain. Hence, as only one aggregate can be accommodated, the interaction of SDS with PEO 3350 would not be affected by the electrostatic repulsion likely to occur with larger PEO and, therefore, would present a higher amount of SDS molecules bound per PEO chain. Another difference observed for the larger PEO refers to the enthalpy values of the maxima and minima observed with PEO 10 000 and 100 000, being always less intense for the latter. As the energy released upon this interaction is ascribed to dehydration/hydration of EO units as they are incorporated/released from micelles, the different results for these PEO suggest that the interaction of PEO 10 000 with SDS aggregates causes a larger extent of hydration changes than that observed with PEO 100 000, possibly due to a different position of the EO units inside the aggregates.

In summary, the present calorimetric investigation, conducted between 15 and 65 °C, revealed that the tendency of SDS molecules to interact with PEO does not change with temperature. The variation of observed enthalpies with SDS concentration is consistent with an initial incorporation of EO units into the small SDS aggregates, an endothermic process due to PEO dehydration, followed by the moving of EO chains to an outer position as SDS aggregates grow, giving rise to an exothermic contribution, at higher surfactant concentration. These profiles are significantly changed as temperature is raised to 35 and 65 °C, suggesting that at 65 °C EO units are not incorporated into the SDS aggregates. There is no significant change in hydration and, hence, no change in enthalpy is observed.

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