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ELECTROSTATIC CONTRIBUTION TO THE INTERACTION OF α, β POLY(N-HYDROXYETHYL)-*DL*-ASPARTAMIDE WITH SODIUM DODECYLSULFATE MICELLES

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Abstract

The enthalpic effect due to the interaction between α, β poly(N-hydroxyethyl)-*DL*-aspartamide (PHEA) and sodium dodecylsulfate (SDS) in aqueous solutions as a function of the surfactant concentration was measured by the calorimetric technique at various NaCl concentrations. A marked influence of the added electrolyte on the PHEA–SDS interaction was observed. An analysis of the experimental enthalpies allows to estimate the electrostatic and the hydrophobic contributions to the enthalpy of interaction between PHEA and SDS micelles. The results were rationalized in terms of effects due to the screening of the charges residing on PHEA and SDS micelles.

Keywords: electrostatic contribution, α, β poly(N-hydroxyethyl)-*DL*-aspartamide, sodium dodecylsulfate micelles

Introduction

Interactions between polymers and surfactants in aqueous solutions have been the subject of many recent investigations [1–3]. The interest on this matter arises because some advantages are obtained when polymers and surfactants are both present in many industrial, biological and pharmaceutical products [4]. These advantages are a consequence of the marked changes in the properties of polymers and surfactants observed when these components are in the same aqueous solution.

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Surfactants strongly enhance solubility and chemical stability in water of many polymers [5, 6], whereas at the same time polymers modify surface activity and critical micellar concentration of surfactants [7, 8].

Besides, considering the ability of surfactant molecules to form spontaneously dynamical aggregates (micelles), the study of the interactions between some polymers of biological or pharmaceutical interest and surfactants is of utmost importance to estimate the binding ability of these polymers to biomembranes [9, 10]. In fact, micelles mimic some essential features of cell membranes without the complications arising from the cellular metabolic processes which generally make the interpretation of the experimental data a hard task.

According to the above reported considerations, we have recently investigated the interactions between a promising drug carrier, the α, β poly(N-hydroxyethyl)-*DL*-aspartamide (PHEA), and the micellar aggregates of some surfactants [3, 10]. It was noted that PHEA interacts more strongly with anionic surfactants than with cationic or non-ionic surfactants suggesting that electrostatic forces significantly contribute to the PHEA-micelles interaction.

To evidence the role of the electrostatic contribution to this interaction, we have studied the effect of a simple electrolyte (NaCl) on the formation of PHEA-micelles complex by calorimetry. In this paper we report and discuss the calorimetric measurements of the interaction between PHEA and sodium dodecylsulfate (SDS) in aqueous solutions as a function of the surfactant concentration at various NaCl concentrations. SDS was chosen since its negatively charged micelles carry the same charge found in many cell surfaces at physiological *pH* [11].

Experimental

Synthesis and purification of PHEA were performed using the methods reported in the literature [10, 12]. The viscosimetric average molecular weight of PHEA was $51\cdot10^3$. The structural features of PHEA are shown in Fig. 1.

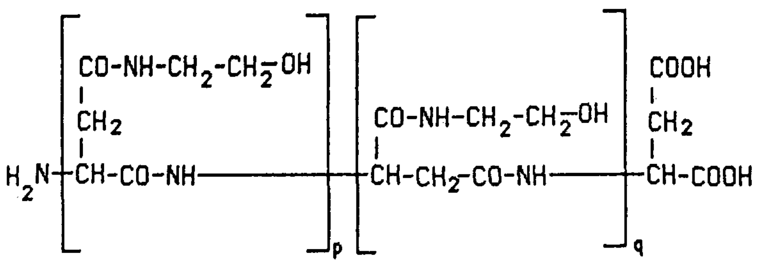

Fig. 1 Structure of PHEA (*p* and *q* are the number of repetitive units constituting the polymeric backbone). The values of *p* and *q* are nearly the same [13]

Sodium dodecylsulfate (SDS, Sigma product with 99% of stated purity) and sodium chloride (Merck product with 99.5% of stated purity) were used without further purification. Water was deionized and double distilled.

Calorimetric measurements were preformed at 25°C with an LKB Thermal Activity Monitor (TAM) equipped with a flow-mix cylinder (LKB, 2277-204). The solutions were driven by a peristaltic pump (Gilson, Minipuls 2) and the flow rates (nearly 0.004 $g \cdot s^{-1}$) were determined by mass. Each calorimetric measurement was carried out by mixing inside the calorimetric cell an aqueous solution at fixed PHEA molonity (moles of solute per kg of solution, $5 \cdot 10^{-5}$ $mol \cdot kg^{-1}$) with an aqueous solution containing the surfactant and NaCl. The thermal effect due to the dilution of the SDS plus NaCl aqueous solution was cancelled taking as baseline the signal obtained by mixing into the calorimeter this solution with water. No thermal effect due to the mixing of the PHEA solution with water was observed. The experimental molar enthalpy (ΔH_{exp}) was calculated per mole of polymer.

The estimated uncertainty in the ΔH_{exp} values is ±0.5 $kJ \cdot mol^{-1}$.

Table 1 Molar enthalpy (ΔH_{exp} / $kJ \cdot mol^{-1}$) of interaction between PHEA and SDS as a function of SDS concentration at various NaCl concentrations

[NaCl] = 0.0489		[NaCl] = 0.1060		[NaCl] = 0.1439	
[SDS]	$-\Delta H_{exp}$	[SDS]	$-\Delta H_{exp}$	[SDS]	$-\Delta H_{exp}$
0.00278	13.5	0.00152	26.9	0.00198	45.8
0.00496	28.6	0.00299	32.5	0.00567	50.2
0.0145	51.1	0.00860	40.1	0.0102	53.6
0.0281	83.7	0.0313	55.5	0.0204	59.9
0.0511	97.6	0.0337	52.7	0.0311	60.4
0.1058	138.0	0.0467	63.4	0.0394	68.0
0.1562	152.4	0.0592	66.7	0.0492	71.5
0.2687	204.6	0.0692	77.5	0.0593	78.1
		0.0887	85.8	0.0698	81.9
		0.1201	92.0	0.0801	90.0
		0.1531	102.7		
		0.1767	108.8		
		0.1940	113.7		
		0.2884	135.9		

Results and discussion

The experimental molar enthalpies (ΔH_{exp}) due to the interaction between PHEA and SDS in aqueous solutions as a function of the surfactant molonity, [SDS], at various NaCl molonity ([NaCl]) are reported in Table 1 and graphically depicted in Fig. 2. The ΔH_{exp} at [NaCl] = 0.1439 are reported within the SDS concentration range 0<[SDS]<0.08 since at [SDS]>0.08 the system becomes opalescent. For comparison, in Fig. 2 is also reported the trend of ΔH_{exp} at [NaCl] = 0 (dashed line) [14].

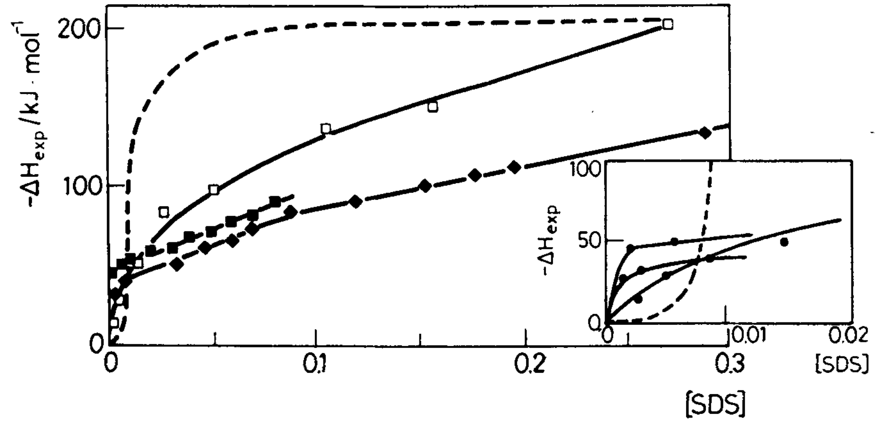

Fig. 2 Molar enthalpy (ΔH_{exp}/kJ·mol^{-1}) of interaction between PHEA and SDS as a function of [SDS] at various NaCl concentrations □, 0.0489; ◆, 0.1060; ■, 0.1439). The dashed line represents the trend of ΔH_{exp} at [NaCl] = 0

As can be seen, the enthalpic effect of the interaction between PHEA and SDS is strongly influenced by NaCl.

At [NaCl] = 0, the small enthalpic effect observed at [SDS]<0.005 (see insert in Fig. 2) was previously taken as an indication of negligible interaction between PHEA and SDS monomers whereas the rapid increase of ΔH_{exp} followed by a plateau region was interpreted in terms of a progressive binding of SDS micelles to the polymeric backbone [3]. In presence of NaCl, ΔH_{exp} starts to increase at lower [SDS] whereas at [SDS]>CMC it shows less exothermic values without reaching a plateau region.

All these features can be qualitatively explained considering that, when the electrolyte is present, micellar radius increases [15], whereas CMC, micellar dissociation degree [16] and charge density on the polymer decrease. Accordingly, micelles appear at lower [SDS] and the electrostatic interaction between PHEA and SDS micelles decreases. It follows that the total enthalpic effect (ΔH_{exp}) can be considered the sum of the following contributions

$$\Delta H_{\mathrm{exp}} = \Delta H_{\mathrm{PHEA\text{-}NaCl}} + \Delta H_{\mathrm{PHEA\text{-}SDS(e)}} + \Delta H_{\mathrm{PHEA\text{-}SDS(h)}} \tag{1}$$

where $\Delta H_{\mathrm{PHEA\text{-}SDS(e)}}$ and $\Delta H_{\mathrm{PHEA\text{-}SDS(h)}}$ are the contributions arising from the electrostatic and hydrophobic interactions between PHEA and SDS micelles, respectively, and $\Delta H_{\mathrm{PHEA\text{-}NaCl}}$ is the contribution due to the PHEA–NaCl interaction.

Table 2 Molar enthalpy ($\Delta H_{\mathrm{PHEA\text{-}NaCl}}$ / kJ·mol^{-1}) of interaction between PHEA and NaCl as a function of NaCl concentration

[NaCl]	$-\Delta H_{\mathrm{PHEA\text{-}NaCl}}$
0.00239	1.9
0.00817	3.2
0.0212	6.5
0.0678	23.0
0.1154	37.0
0.1572	48.2
0.2087	67.4

In order to evaluate $\Delta H_{\mathrm{PHEA\text{-}NaCl}}$ we have directly measured this contribution by mixing the aqueous solution of PHEA with aqueous solutions of NaCl at various [NaCl]. The results of these experiments are reported in Table 2 and graphically depicted in Fig. 3.

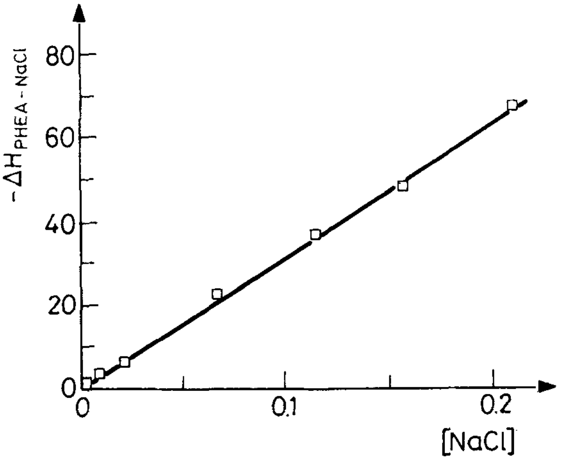

Fig. 3 Molar enthalpy ($\Delta H_{\mathrm{PHEA\text{-}NaCl}}$/kJ·mol^{-1}) of interaction between PHEA and NaCl as a function of [NaCl]

As shown in Fig. 3, $\Delta H_{\mathrm{PHEA\text{-}NaCl}}$ is exothermic and increases linearly by increasing the electrolyte concentration. According to Eq. (1), by subtracting $\Delta H_{\mathrm{PHEA\text{-}NaCl}}$ from ΔH_{exp}, the quantity $\Delta H_{\mathrm{PHEA\text{-}SDS(e+h)}}$, (i.e., the sum of the electrostatic and hydrophobic contributions) was obtained. $\Delta H_{\mathrm{PHEA\text{-}SDS(e+h)}}$ values for three selected [SDS] as a function of [NaCl] are shown in Fig. 4.

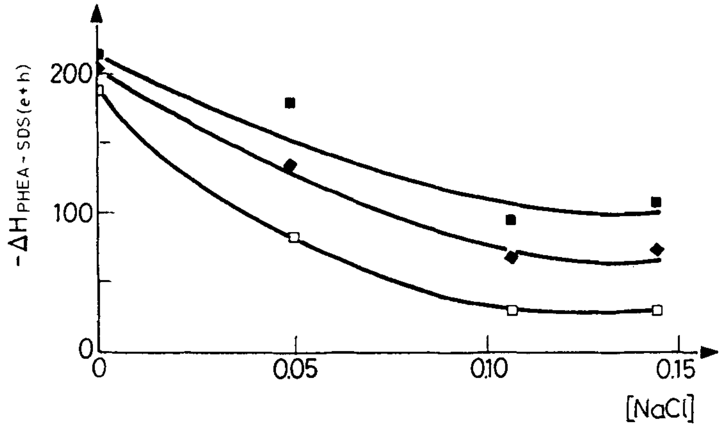

Fig. 4 Trend of $\Delta H_{\mathrm{PHEA\text{-}SDS(e+h)}}$ (kJ·mol^{-1}) as a function of NaCl concentration for three selected [SDS] (□, 0.05; ◆, 0.15; ■, 0.25). The $\Delta H_{\mathrm{PHEA\text{-}SDS(e+h)}}$ values at [SDS] = 0.15 and at [SDS] = 0.25 for the system at [NaCl] = 0.1439 were obtained by extrapolation of the pertinent experimental data

As can be seen, $\Delta H_{\mathrm{PHEA\text{-}SDS(e+h)}}$ decreases by increasing [NaCl] reaching a plateau region at [NaCl]>0.1. Since the electrolyte reduces progressively the electrostatic contribution, it seems reasonable to assume that the enthalpic effect at the plateau is an estimate of $\Delta H_{\mathrm{PHEA\text{-}SDS(h)}}$. It follows that $\Delta H_{\mathrm{PHEA\text{-}SDS(e)}}$ can be obtained by subtracting the value at the plateau from that at [NaCl] = 0. The resulting quantities are reported in Table 3.

Table 3 Values of $\Delta H_{\mathrm{PHEA\text{-}SDS(e)}}$ (kJ·mol^{-1}) and $\Delta H_{\mathrm{PHEA\text{-}SDS(h)}}$ (kJ·mol^{-1}) at three selected [SDS]

[SDS]	$-\Delta H_{\mathrm{PHEA\text{-}SDS(e)}}$	$-\Delta H_{\mathrm{PHEA\text{-}SDS(h)}}$
0.05	160	30
0.15	130	70
0.25	110	100

A perusal of Table 3 shows that, by increasing [SDS], $\Delta_{\mathrm{HPHEA\text{-}SDS(e)}}$ decreases (because the micellar dissociation degree decreases) whereas $\Delta_{\mathrm{HPHEA\text{-}SDS(h)}}$ increases (because the micellar radius increases).

It must be stressed that the above reported analysis may be considered only a semiquantitative evaluation of $\Delta H_{\text{PHEA-SDS(e)}}$ and $\Delta H_{\text{PHEA-SDS(h)}}$ since long range interactions between polymer and micelles were neglected. Moreover, it must be also evidenced that the observed marked effect on an electrolyte on PHEA–SDS micelles interaction suggests that a similar behavior can be expected on the binding ability of PHEA on cellular surfaces.

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Zusammenfassung — Mittels einer kalorimetrischen Methode wurde bei verschiedenen NaCl-Konzentrationen der Enthalpieeffekt der Wechselwirkung zwischen α, β Poly(N-Hydroxyethyl)-*DL*-Aspartamid (PHEA) und Natriumdodecylsulfat (SDS) in wäßriger Lösung als eine Funktion der Konzentration des oberflächenaktiven Stoffes gemessen. Dabei wurde ein deutlicher Einfluß des Elektrolytzusatzes auf die PHEA-SDS-Wechselwirkung festgestellt. Eine Analyse der experimentell ermittelten Enthalpiewerte gestattet eine Schätzung des elektrostatischen und hydrophobischen Beitrages zu den Enthalpien der Wechselwirkung zwischen PHEA- und SDS-Mizellen.