Surface Excess Enthalpy of PEO + Salt +Water and L35 + Salt + Water Aqueous Two-Phase Systems[†]

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Surface excess enthalpy, ΔH^{σ}, associated with the interfacial formation process was determined at 298.15 K for five different aqueous two-phase systems (ATPS): L35 + Li_2SO_4 + H_2O, PEO1500 + Na_2SO_4 + H_2O, PEO1500 + Li_2SO_4 + H_2O, PEO1500 + citrate + H_2O, and PEO4000 + Na_2SO_4 + H_2O. Where L35 is one triblock copolymer denominated poly(oxide ethylene)-block-poly(oxide propylene)-block-poly(oxide ethylene) with molar mass 1900 $mol \cdot g^{-1}$ and 50 % EO, PEO1500 is poly(oxide ethylene) with molar mass 1500 $mol \cdot g^{-1}$ and PEO4000 is poly(oxide ethylene) with molar mass 4000 $mol \cdot g^{-1}$. The results show that the interface formation process could be exothermic or endothermic depending on the aqueous two-phase systems and/or tie line length (TLL), and its value is in the range of (−21.00 to 5.00) mJ. The ΔH^{σ} measured was attributed a specific PEO−ion interaction associated with a polymer conformation change, both processes occurring at the interface phase. A significant effect of the electrolyte nature on the surface excess enthalpy was verified. Increasing the polymer size has an effect to release more energy for the ATPS interface formation process, while the substitution of PEO by L35, i.e, a hydrophobic increase on the top phase, makes more exothermic ATPS interface formation.

Introduction

The aqueous two-phase extraction technique for the purification of biomaterials and others strategic solutes has received increasing attention during the past three decades.[1−3] The extraction process relies on the unequal partitioning of species, such as proteins, nucleic acids, ions, and organic compounds, between the two phases and the interface of aqueous two-phase systems (ATPS). To understand the thermodynamics of this partitioning, it is of great interest to know the properties of the liquid−liquid interface. The interfacial tension (surface excess Gibbs energy) and the surface excess enthalpy per unit area are very important properties in any mass transfer model for an extraction process[4] or in the kinetics studies of the coagulation of droplets and phase separation.[5] Unfortunately, although the physics of interfacial phenomena is rapidly progressing, it still lacks a model which is able to predict interfacial properties in multicomponent mixtures from pure component or binary data alone. Therefore, in chemical engineering, empirical correlations based on experimental results must be developed.[6]

All studies[7−10] have measured the surface excess Gibbs energy per unit surface area, σ, and analyzed the dependence between the interfacial tension with other ATPS properties, such as polymer molar mass, electrolyte nature, pH, tie line length (TLL), and temperature. Interfacial tensions in aqueous polymer + polymer or polymer + salt ATPS have been found to be in the range (0.5 to 15) $mJ \cdot m^{-2}$. As is well-known,[11] the surface excess enthalpy per unit area can be calculated by the relationship between σ and temperature, as is shown by eq 1.

$$\Delta H_{\mathrm{A}}^{\sigma} = \sigma + \left(\frac{\partial \sigma}{\partial T}\right)_P \tag{1}$$

where $\Delta H_{\mathrm{A}}^{\sigma}$ and σ are the surface excess enthalpy and the surface excess Gibb energy, respectively, and $(\partial\sigma/\partial T)_P$ is the surface excess entropy. All properties are expressed per unit area, and T is the absolute temperature.

However, this approach (eq 1) is not very appropriate for an aqueous two-phase systems due to the strong dependence between phase composition and temperature.[12] So a change of the temperature promotes a change of the interfacial entropy, as calculated by eq 1, but also causes a modification of the interface composition. It is not an easy task to separate both contributions.[13] Hence it is necessary to measure directly the surface excess enthalpy associated with ATPS systems. Knowledge of these interfacial thermodynamic properties is helpful for understanding and interpreting the nature of interactions between the molecules on the interface and for modeling the mass and heat transfer at the interface generally present in liquid−liquid extraction, gas absorption, and condensation.[14]

To our best knowledge, calorimetric surface excess enthalpy has never been determined before for any aqueous two-phase systems. Microcalorimetry is a very sensitive (0.02 μW) and powerful technique for measuring energy change arising due to ATPS molecular interaction processes.[15]

In this work, the surface excess enthalpy, ΔH^{σ}, associated with ATPS interface formation was determined for the following systems L35 + Li_2SO_4 + H_2O, PEO1500 + Na_2SO_4 + H_2O, PEO1500 + Li_2SO_4 + H_2O, PEO1500 + citrate + H_2O, and PEO4000 + Na_2SO_4 + H_2O, at 298.15 K. Where L35 is one triblock copolymer denominated poly(oxide ethylene)-block-poly(oxide propylene)-block-poly(oxide ethylene) with molar mass 1900 $mol \cdot g^{-1}$ and 50 % EO, PEO1500 is poly(oxide ethylene) with molar mass 1500 $mol \cdot g^{-1}$ and PEO4000 is

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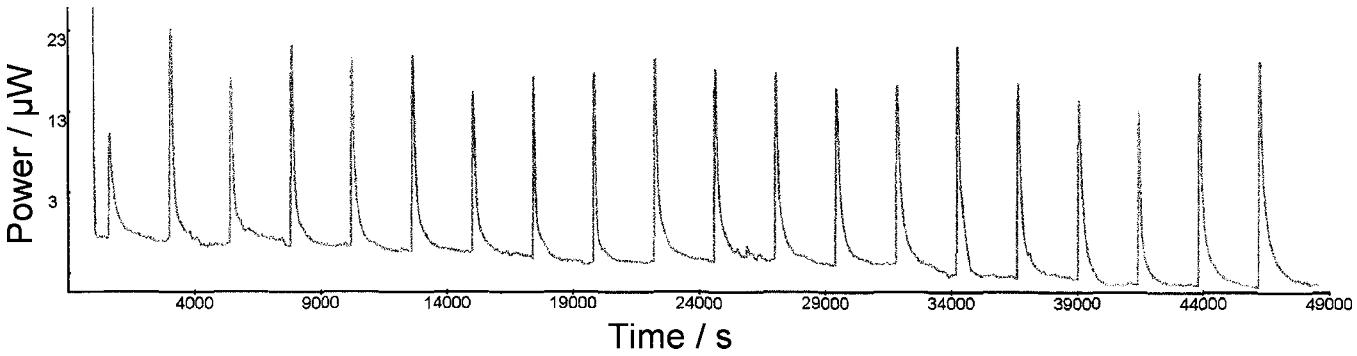

Figure 1. Isothermal titration microcalorimetric thermogram (power vs time).

Table 1. Surface Excess Enthalpy Values for PEO1500 + Citrate + H_2O ATPS as a Function of Volume Fraction (Φ) of the Top or Bottom Phase for Differences in Tie Line Length (TLL)

	ΔH^{σ}/mJ					
volumetric fraction	TLL 1 top phase added	TLL 2 top phase added	TLL 3 top phase added	TLL 1 bottom phase added	TLL 2 bottom phase added	TLL 3 bottom phase added
0.00476	−0.97	−2.85	−5.44	−0.95	−3.05	−5.13
0.00948	−1.00	−2.87	−5.50	−0.97	−3.03	−5.12
0.0142	−0.99	−2.86	−5.42	−0.92	−3.04	−5.17
0.0188	−0.99	−2.87	−5.54	−1.04	−3.04	−5.17
0.0234	−0.99	−2.83	−5.53	−1.23	−3.06	−5.16
0.0279	−0.88	−2.80	−5.47	−1.15	−3.05	−5.01
0.0324	−0.98	−2.80	−5.43	−1.13	−3.04	−5.15
0.0369	−0.99	−2.83	−5.40	−1.12	−3.02	−5.09
0.0413	−0.99	−2.74	−5.40	−1.03	−3.05	−5.06
0.0457	−0.98	−2.76	−5.49	−1.09	−3.06	−5.12
0.0500	−0.99	−2.88	−5.41	−1.07	−3.05	−5.09
0.0543	−0.98	−2.84	−5.30	−1.09	−3.06	−4.95
0.0586	−0.98	−2.83	−5.43	−1.16	−3.18	−5.08
0.0628	−0.98	−2.87	−5.41	−1.19	−3.17	−5.08
0.0670	−0.99	−2.82	−5.45	−1.18	−3.12	−5.16
0.0711	−0.98	−2.85	−5.43	−1.12	−3.10	−5.13
0.0752	−0.98	−2.86	−5.49	−1.06	−3.10	−5.08
0.0793	−1.00	−2.89	−5.43	−1.03	−3.06	−5.14
0.0833	−0.98	−2.82	−5.42	−0.96	−3.05	−5.08
0.0873	−0.98	−2.85	−5.36	−0.93	−3.11	−5.09

poly(oxide ethylene) with molar mass 4000 mol·g^{-1}. The election of the systems was to study the influence of polymer molar mass, electrolyte nature, and hydrophilic/hydrophobic balance on the surface excess enthalpy.

Experimental

Materials. The analytical grade reagents triblock copolymer L35 (M_w = 1945 g·mol^{-1}, 50 % ethylene oxide, M_w/M_n = 1.14, $(PEO)_{11}(PPO)_{16}(PEO)_{11}$), poly(ethylene oxide) (M_w = 1500 g·mol^{-1} (PEO1500)), and poly(ethylene oxide) (M_w = 4000 g·mol^{-1} (PEO4000)) were obtained from Aldrich Co. (USA). Na_2SO_4, Li_2SO_4, and sodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) were analytical reagent grade purchased from Vetec (Brazil).

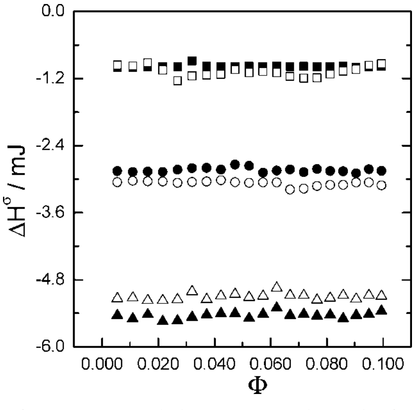

Figure 2. Surface excess enthalpy versus volumetric fraction (Φ) of PEO1500 + citrate + H_2O ATPS. Top phase added into the bottom phase (full symbols) and bottom phase added into the top phase (open symbols). ■,□ 1ª TLL; ●,○, 2ª TLL; and ▲,Δ, 3ª TLL.

Table 2. Surface Excess Enthalpy Values for PEO1500 + Li_2SO_4 + H_2O ATPS as a Function of Volume Fraction (Φ) of the Top or Bottom Phase for Differences of Tie Line Length (TLL)

	ΔH^{σ}/mJ			
volumetric fraction	TLL 1 top phase added	TLL 2 top phase added	TLL 1 bottom phase added	TLL 2 bottom phase added
0.00476	−2.94	−10.15	−3.48	−10.61
0.00948	−3.14	−10.26	−3.38	−10.26
0.0142	−3.07	−10.11	−3.38	−10.16
0.0188	−3.35	−11.07	−3.38	−10.62
0.0234	−3.23	−10.99	−3.35	−10.16
0.0279	−3.28	−10.53	−3.33	−10.14
0.0324	−3.24	−10.56	−3.47	−11.01
0.0369	−3.16	−10.05	−3.33	−11.04
0.0413	−2.82	−10.05	−3.23	−10.38
0.0457	−2.92	−10.69	−3.16	−10.16
0.0500	−2.88	−11.00	−3.38	−10.40
0.0543	−2.80	−10.69	−3.22	−10.20
0.0586	−2.84	−10.90	−2.94	−10.28
0.0628	−2.80	−10.26	−2.88	−10.17
0.0670	−2.79	−11.00	−2.80	−11.17
0.0711	−2.78	−10.68	−2.71	−10.10
0.0752	−2.74	−11.00	−2.59	−10.74
0.0793	−2.75	−10.70	−2.43	−10.55
0.0833	−2.76	−10.97	−3.30	−11.00
0.0873	−2.71	−10.37	−3.36	−10.35

Table 3. Surface Excess Enthalpy Values for PEO+Na_2SO_4+H_2O ATPS as a Function of Volume Fraction (Φ) of the Top or Bottom Phase for Differences Tie Line Length (TLL)

	ΔH^{σ}/mJ			ΔH_{σ}/mJ		
	PEO1500 + Na_2SO_4 + H_2O ATPS			PEO4000 + Na_2SO_4 + H_2O ATPS		
volumetric fraction	TLL 1 top phase added	TLL 2 top phase added	TLL 3 top phase added	TLL 1 top phase added	TLL 2 top phase added	TLL 3 top phase added
0.00476	0.16	−2.09	−5.32	−1.03	0.5	1.57
0.00948	0.16	−2.10	−5.21	−1.02	0.38	1.55
0.0142	0.16	−2.09	−5.04	−1.13	0.39	1.53
0.0188	0.16	−2.06	−5.41	−1.05	0.45	1.51
0.0234	0.21	−2.10	−5.45	−1.05	0.36	1.61
0.0279	0.15	−2.01	−5.42	−1.03	0.47	1.53
0.0324	0.15	−2.06	−5.31	−1.07	0.34	1.31
0.0369	0.16	−2.08	−5.40	−1.07	0.35	1.59
0.0413	0.15	−2.00	−5.34	−1.09	0.39	1.43
0.0457	0.13	−2.05	−5.32	−1.01	0.39	1.52
0.0500	0.09	−2.03	−5.24	−1.02	0.36	1.53
0.0543	0.16	−2.05	−5.22	−1.08	0.38	1.64
0.0586	0.16	−2.10	−5.32	−1.06	0.47	1.46
0.0628	0.09	−2.08	−5.37	−1.05	0.32	1.43
0.0670	0.15	−2.03	−5.40	−1.00	0.41	1.60
0.0711	0.16	−2.02	−5.58	−1.08	0.29	1.54
0.0752	0.17	−2.02	−5.42	−1.09	0.43	1.56
0.0793	0.22	−2.10	−5.41	−1.08	0.34	1.60
0.0833	0.16	−2.09	−5.37	−1.08	0.43	1.66
0.0873	0.16	−2.07	−5.47	−1.06	0.36	1.57

Deionized water (Millipore, Bedford, MA, USA) was used in all experiments.

Aqueous Two-Phase Systems. The biphasic systems were prepared by weighting appropriate quantities of the ATPS former compounds and water on an analytical balance (Gehaka, AG200, Brazil), with an uncertainty of ± 0.0001 g. The phase diagram of the following ATPS was obtained from literature data: L35 + Li_2SO_4 + H_2O,[16] PEO1500 + Na_2SO_4 + H_2O,[17] PEO1500 + Li_2SO_4 + H_2O,[17] PEO1500 + citrate + H_2O,[18] PEO4000 + Na_2SO_4 + H_2O.[19] Typically 6 g was prepared in liquid−liquid equilibrium cells. After vigorously stirring until it became turbid, the mixture was placed in a temperature-controlled bath (Microquimica, MQBTC 99-20, Brazil with an uncertainty of ± 0.1 K) for 72 h at 298.15 K. For calorimetry measurement, the top and bottom phases were collected carefully to avoid mutual contamination.

Surface Excess Enthalpy Determination. The calorimeter used to determine the enthalpy change associated with ATPS interfacial formation was an isothermal titration microcalorimeter, model CSC 4200 (calorimeter Science Corporation, USA), controlled by ITCRun software. The microreaction system was a titration mode with a 1.82 mL stainless steel vessel (sample and reference). Continuous heat leakage measurements were taken in an isothermal system. The energy associated with interfacial formation flowed through high-sensitivity thermopiles surrounded by a heat sink, which was stabilized at $\pm 1.8 \cdot 10^{-4}$ K. As the magnitude of heat exchange of a thermopile with

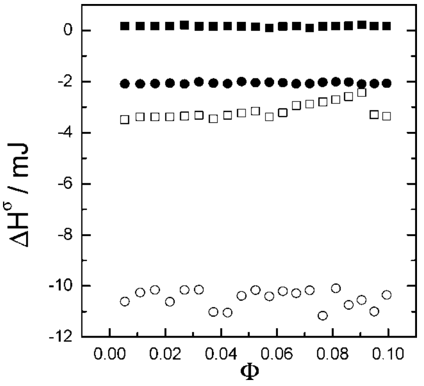

Figure 3. Surface excess enthalpy versus volumetric fraction (Φ) of PEO1500 + Na_2SO_4 + H_2O (full symbols) and PEO1500 + Li_2SO_4 + H_2O (open symbols) ATPS. ■, □, 1^{a} TLL; and ●, ○, 2^{a} TLL.

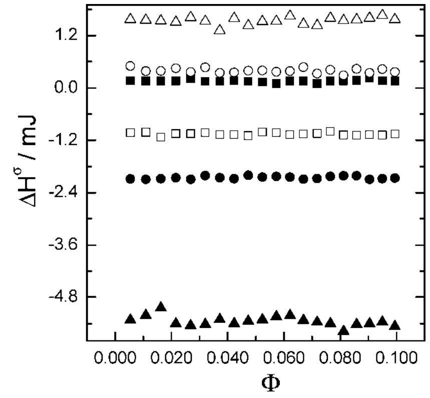

Figure 4. Surface excess enthalpy versus volumetric fraction (Φ) of PEO1500 + Na_2SO_4 + H_2O (full symbols) and PEO4000 + Na_2SO_4 + H_2O (open symbols) ATPS. ■,□, 1^{a} TLL; ●,○, 2^{a} TLL; and ▲,Δ, 3^{a} TLL.

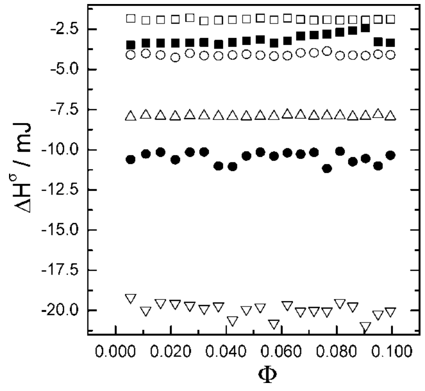

Figure 5. Surface excess enthalpy versus volumetric fraction (Φ) of PEO1500 + Li_2SO_4 + H_2O (full symbols) and L35 + Li_2SO_4 + H_2O (open symbols) ATPS. ■,□, 1^{a} TLL; ●,○, 2^{a} TLL; Δ, 3^{a} TLL; and ∇, 4^{a} TLL.

Table 4. Surface Excess Enthalpy Values for L35 + Li_2SO_4 + H_2O ATPS as a Function of Volume Fraction (Φ) of the Top or Bottom Phase for Differences in Tie Line Length (TLL)

	ΔH^σ/mJ			
volumetric fraction	TLL 1 top phase added	TLL 2 top phase added	TLL 3 top phase added	TLL 4 top phase added
0.00476	−19.19	−7.95	−4.10	−1.85
0.00948	−19.97	−7.86	−4.02	−1.97
0.0142	−19.51	−7.90	−4.12	−1.93
0.0188	−19.57	−7.94	−4.27	−1.90
0.0234	−19.68	−7.87	−4.00	−1.81
0.0279	−19.86	−7.90	−4.16	−1.99
0.0324	−19.71	−7.93	−4.17	−1.96
0.0369	−20.58	−7.93	−4.11	−1.93
0.0413	−19.93	−7.94	−4.07	−1.88
0.0457	−19.78	−7.91	−4.13	−1.82
0.0500	−20.77	−7.93	−4.19	−1.93
0.0543	−19.62	−7.84	−4.16	−1.82
0.0586	−20.03	−7.86	−3.98	−1.90
0.0628	−20.00	−7.91	−3.98	−1.96
0.0670	−20.03	−7.89	−3.87	−1.91
0.0711	−19.50	−7.89	−4.16	−1.96
0.0752	−19.73	−7.94	−4.13	−1.92
0.0793	−20.93	−7.91	−4.15	−1.95
0.0833	−20.21	−7.83	−4.06	−1.90
0.0873	−20.03	−7.94	−4.10	−1.89

heat sink is proportional to the time interval of the voltage signal, the calorimeter system was calibrated by Tris titration with HCl and electrical calibration. For the ΔH^σ measurements, the following experiment was carried out: After the ATPS systems had attained equilibrium, the top and bottom phases were separated and 1.82 mL of the bottom phase (or top phase) was placed in the calorimeter stirring at 300 rpm. When thermal equilibrium between the vessel and the heat sink was reached, 10.00 μL of the top phase (or bottom phase) was titrated into the bottom phase with a Hamilton microliter syringe at 40 min intervals. All calorimetric measurements were performed in triplicate, and the calculated relative standard deviation in the surface excess enthalpy was of the order of ± 0.5 %.

Results and Discussion

Figure 1 shows a typical microcalorimetric thermogram, expressed as heat flow P vs time, of the top phase titration into bottom phase, in which 10 μL aliquots were injected successively into the vessel 20 times. It is seen that both height and area of a peak are almost constant at low and also at high volume fractions, $\Phi = V_{\text{top}}/V_{\text{bottom}}$. The area under each peak was used to calculate the ΔH^σ value.

The surface excess enthalpies associated with the interface formation process, for the PEO1500 + citrate + H_2O ATPS, are shown in Figure 2 and Table 1. The enthalpies measured are related with two distinct processes: (i) 10 μL of the bottom phase was added to 1.82 mL of the top phase (full symbols) or (ii) 10 μL of the top phase was added to 1.82 mL of the bottom phase (open symbols).

The ΔH^σ is almost independent of which phase was added to the other, and its values are constant for the volume fraction range investigated showing that each addition of the bottom phase into the top phase (or vice versa) generated the same interface area and the same interface composition. These energies are not the surface excess enthalpy per unit area, $\Delta H^\sigma_{\text{A}}$, because in the experiment the formed area of interface was different from unit. As is well-known, the relationship between ΔH^σ and $\Delta \text{H}^\sigma_{\text{A}}$ is expressed by eq 2

$$\Delta H^\sigma_{\text{A}} = \frac{\Delta H^\sigma}{A} \qquad (2)$$

where A is the area of interface formed in each injection of 10 μL.

For the PEO1500 + citrate + H_2O ATPS system, all ΔH^σ values were negative and become more exothermic with an increase in the tie line length (TLL). In thermodynamic studies using ATPS, it is conventional to express the difference in the intensive properties of the two phases by the tie line length (TLL) parameter, which is determined by the difference in concentration of the systems forming components. TLL, expressed in weight percentage of polymers and salts, was calculated according to

$$\text{TLL} = [(C^{\text{T}}_{\text{P}} - C^{\text{B}}_{\text{P}})^2 + (C^{\text{T}}_{\text{S}} - C^{\text{B}}_{\text{S}})^2]^{1/2} \qquad (3)$$

where C_{P} and C_{S} are the polymer and salt concentrations in % (w/w), and T and B are the top and bottom phases, respectively.

The energy released from the interface formation can be considered to arise from two sources. One of them is due to the transference of the ion and macromolecule from the bulk solution to the newly formed region (interface) followed by the occurrence of polymer−ion interaction.[20] At interface, the number of contacts between PEO segments and ions is higher than in the bulk phases because the ATPS formation is a segregative process between electrolyte and macromolecules.[21] Another energy source is the conformation change that occurs when a macromolecule interacting with ions is confined at the interface. To compensate the increase in energy caused by electrostatic repulsion between ions of the same charges present around the polymer segments, the macromolecule trend is to have a less energetic conformation (more linear).[22] The polymer conformation change caused by polymer−ion interaction is a well-recognized phenomenon for which enthalpy energy change is very dependent on the salt and polymer nature. da Silva and Loh[23] have demonstrated, by calorimetric measurements, that the interaction of the Na_2SO_4 or Li_2SO_4 salts with PEO, in bulk solutions, is an endothermic process with energy in the range of (2.0 to 4.0) $\text{kJ} \cdot \text{mol}^{-1}$. However, as shown in Figure 3 and Tables 2 and 3, the interface formation process for the PEO + Na_2SO_4 + H_2O and PEO + Li_2SO_4 + H_2O ATPS systems is ever exothermic and independent of the Φ values. The electrolyte nature has a great effect on the ΔH^σ values, in which $\Delta H^\sigma_{\text{Li}_2\text{SO}_4}$ is more negative. This behavior could be explained considering that the energy released from the macromolecular conformation change is higher than the energy absorbed from the ion−polymer interaction. As expected from the polymer−ion positive enthalpy of interaction, the formation of the ion−polymer pair is entropically driven, and as a consequence, this process is affected by the polymer size and its hydrophobic nature.[3] Figures 4 and 5 show the effect of the polymer molar mass and the macromolecule hydrophobicity on the surface excess enthalpy, respectively. The numeric results are in Tables 2 and 4.

Increasing the polymer size increases the surface excess enthalpy (Figure 4), with ΔH^σ becoming more positive with an increase in TLL values. This behavior suggests that large polymer molecules, at the interface, can interact with ions, changing its conformation less. The interface formation of hydrophobic ATPS (Figure 5) releases more energy than hydrophilic ATPS, pointing out that hydrophobic macromolecules adsorb more at the interface forming a higher number of polymer−ion pairs.

Conclusion

It was possible to measure directly the surface excess enthalpy, ΔH^σ, associated with emulsion formation in ATPS systems. This energy change is very small, but the application of microcalorimetric technique makes it possible to obtain this interfacial property with great accuracy. ΔH^{σ} values are very dependent on the molar mass and hydrophobic/hydrophilic balance of the macromolecule as well as of the salt nature. The energy change due to the interface formation process was attributed to new polymer−ion interactions arisen from the ion and polymer concentrations at interface.

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