Adsorption of triblock copolymers and their homopolymers at laponite clay/solution interface. Role played by the copolymer nature†

R. De Lisi, G. Lazzara, R. Lombardo, S. Milioto,* N. Muratore and M. L. Turco Liveri

Dipartimento di Chimica Fisica "F. Accascina", Università degli Studi di Palermo, Viale delle Scienze, Parco D'Orleans II, 90128 Palermo, Italy. E-mail: milioto@unipa.it

The adsorption thermodynamics of copolymers, based on ethylene oxide (EO) and propylene oxide (PO) units, at the laponite (RD) clay/liquid interface was determined at 298 K. The copolymer nature was tuned at molecular level by changing the hydrophilicity, the architecture and the molecular weight (Mw) keeping constant the EO/PO ratio. Polyethylene (PEGs) and polypropylene (PPGs) glycols with varying Mw and their mixture were also investigated to discriminate the role of the EO and the PO segments in the adsorption process. Enthalpies of transfer of RD, at fixed concentration, from water to the aqueous macromolecule solutions as functions of the macromolecule molality were determined. They were treated quantitatively by means of a model based on two equilibria: (1) *one-to-one binding* between the macromolecule and the site on the solid and (2) *two-to-one binding* following which one macromolecule interacts with another one adsorbed onto the solid. The good agreement between the equilibrium constants obtained from calorimetry and those determined from kinetic experiments confirmed the reliability of the experimental and theoretical approaches. Almost all of the systems investigated are highlighted by the *one-to-one binding*; the L35 and 10R5 systems present both equilibria. The insights provided by the thermodynamics of adsorption of their homopolymers onto RD were fruitful in obtaining detailed information on the nature of the forces involved between RD and the copolymers. The data obtained in the present work clearly evidenced that for comparable polymer Mw, PPG is more suitable in building up a steric barrier around the RD particles and, indeed, exhibits several advantages and no drawbacks. Moreover, the parent copolymers may properly functionalize the RD surface by exploiting both their high affinity to the solid surface and the ability to self-assemble onto it as L35 and 10R5 clearly showed.

Introduction

Synthetic clays containing monodisperse disks such as fluoro-hectorites or laponite are minerals based on silicates or alumino-silicates. They not only have a well-defined structure but also possess a controlled chemical composition and low impurities and, indeed, have a large surface area. They are considered soil model in the topic of the remediation of sub-surface and aquifers contaminated by non-aqueous phase liquids.[1,2] Studies of clay aggregation were carried out to establish the fate of pollutants discharged into natural aquatic systems.[3] Laponite (RD) is also employed in various applications (for oil drilling fluids, thickness in cosmetics and pharmaceutics, building materials, paper coatings, paints, and so on) due also to the easy accessibility and low cost. The polymer adsorption onto RD clay is an issue of great relevance because polymers[4–6] are employed to inhibit the aggregation and gelation of suspensions due to the formation of steric barriers the efficiency of which depends both on the concentration and the molecular weight (Mw) of the macromolecule. Furthermore, the coated particles may assume peculiar characteristics generating novel materials like nanocomposites[7–9] of clay and polymers. Structural (small angle neutron scattering,[10] dynamic[11] and static[12] light scattering) and rheological[12] investigations evidenced that the adsorption of polyethylene glycols of different Mw onto RD inhibit the gelation process. Studies of adsorption of amphiphilic copolymers such as poly(ethylene oxides)-poly(propylene oxides)-poly(ethylene oxides) (PEO–PPO–PEO) onto RD are nearly absent. To the best of our knowledge, only the interactions between Laponites and a hexagonal mesophase of the copolymer were studied.[13] This topic is important from a scientific viewpoint because a competition between the hydrophilic PEO blocks and the less hydrophilic PPO blocks towards the solid surface is expected. Clearly, in the presence of a hydrophobic surface, the adsorption of amphiphilic molecules is controlled by hydrophobic forces[14–16] whereas it is less evident when the solid surface is hydrophilic (like RD clay) because of the eventual competition between solid and water in interacting with the macromolecule. Copolymers conveniently adjusted by changing the architecture, Mw and the hydrophilic/hydrophobic balance may functionalize the particles surface and, consequently, materials with new properties may be synthesized. Within this issue, the acquaintance of the thermodynamics of the copolymer at the RD/solution interface is relevant because it provides information at a molecular level on the nature of the interactions involved in the adsorption process. On this basis, we thought it would be interesting to perform a systematic calorimetric study of aqueous systems formed by PEO–PPO–PEO and RD clay where the copolymer hydrophilicity, the architecture and the molecular weight, keeping constant the PEO/PPO ratio, were changed. Experiments to aqueous solutions of polyethylene

and polypropylene glycols (homopolymers) at some Mw were extended to evidence the role of the PEO and the PPO blocks on the RD adsorption. To interpret quantitatively the experimental enthalpy a theoretical approach is proposed. Kinetic measurements provided information, which corroborated the reliability of the thermodynamic insights.

Experimental

Materials

Laponite RD grade was a gift from Rockwood Additives Ltd. Polyethylene glycols (400, 900 and 20 000 g mol^{-1}) and polypropylene glycols (425, 725 and 1200 g mol^{-1}) are Fluka products. The copolymers studied are poly(ethylene oxides)–poly(propylene oxides)–poly(ethylene oxides) denoted as EO_a-PO_bEO_a where a and b are the number of the repetitive units of the ethylene oxide (EO) and propylene oxide (PO), respectively. They were obtained as gifts from BASF AG (Ludwigshafen) and are listed in Table 1. The copolymers and polymers were not purified because their standard partial molar volumes (V_P^o), determined by density, are reliable. As concerns the copolymers, they are in a good agreement with those reported elsewhere.[17,18] Whenever it is possible to make comparison, the V_P^o values of homopolymers agree with the literature data;[19] moreover, their values are consistent with those calculated by the additivity using the EO and PO contributions.[20]

The mixtures were prepared by using water from reverse osmosis (Elga model Option 3) having resistivity higher than 1 MΩ cm^{-1}.

The RD clay has the molecular formula[21] $Si_8(Mg_{5.45}Li_{0.4})O_{20}(OH)_4Na_{0.7}$ which is the unitary cell of the disk-like shape clay platelet having a diameter of about 25 nm and a thickness of 1 nm.[22]

Each RD dispersion was prepared by gradually adding the necessary amount of powder to a known mass of water under continuous and vigorous stirring. Once that resulted clear, it was left for $ca.$ 1 h under stirring before use. The dispersions were used within 6 h from their preparation. The RD–water mixtures at pHs < 8 are not stable because of the release of Mg^{2+} ions which occurs on a time-scale of several weeks[21] or even months.[23] The pH of our dispersions (1% w/w) is 10.05 (it slightly depends on the RD concentration) and after 24 h it is nearly unchanged (pH = 9.98). Tawari et $al.$[3] ascribed this high value to the dissociation of the hydroxylic groups from the edge of the disk-platelet. Moreover, the pH of the water + copolymer + RD ternary systems maintained nearly the same value.

Kinetic measurements

The experiments of the adsorption process of block copolymers onto RD were carried out by means of a HI-TECH SF-61 stopped-flow CAK-501 with an electrical conductivity detection unit. The apparatus was equipped with thermostated compartments at 298.0 ± 0.1 K and interfaced to a computer for both data collection and analysis.

The rates of the adsorption process were followed by monitoring the change of the electrical conductivity of the

Table 1 Copolymer samples used in the experiments

Sample	Structure	Mw/g mol^{-1}
L35	$EO_{11}PO_{16}EO_{11}$	1900
10R5	$PO_8EO_{23}PO_8$	1950
L64	$EO_{13}PO_{30}EO_{13}$	2900
F68	$EO_{76}PO_{29}EO_{76}$	8350
F88	$EO_{103}PO_{39}EO_{103}$	11 400
F108	$EO_{132}PO_{50}EO_{132}$	14 600

aqueous systems obtained by mixing the copolymer solution and the RD dispersion. In all of the cases studied, the electrical conductivity monotonically increases reaching a plateau value. This result indicates that the copolymer adsorption onto RD leads to sodium ions release and that the desorption process is not favoured.

All of the experiments were carried out at fixed copolymer concentration and varying RD composition, and $vice$ $versa$. The composition ranges were chosen to better monitor the electrical conductivity variations.

The concentrations were expressed on a molarity scale.

Calorimetry

The enthalpy measurements were carried out by using a flow LKB 2107 microcalorimeter at 298.15 ± 0.01 K. The mixtures were pushed into the instrument through a Gilson peristaltic pump (Minipuls 2). Flow instruments[24–26] may be used to study the adsorption process of solutes onto the solid phase by determining the properties of transfer of either the solute or the solid.

The experimental enthalpy (ΔH^{exp}) was evaluated as the difference between the thermal effect produced by the mixing process of the macromolecule solution and the RD dispersion and that due to the dilution process of the same macromolecule solution with water. To evidence the RD–macromolecule interactions, the enthalpy of transfer (ΔH_t) of the RD from water to the aqueous macromolecule solution was calculated; it corresponds to the difference between ΔH^{exp} and the enthalpy of dilution of RD with water ($\Delta H_{d,L}$). In calculating the enthalpy per mole of RD, the mass of $Si_8(Mg_{5.45}Li_{0.4})O_{20}(OH)_4Na_{0.7}$ (764.55 g mol^{-1}) was used. The concentrations were expressed as molalities.

The concentration of the RD (m_L) and the macromolecule (m_P) mixtures after the mixing process were calculated as

$$m_L = \frac{m_{L,i}\Phi_L}{(\Phi_L + \Phi_P)} \quad m_P = \frac{m_{P,i}\Phi_P}{(\Phi_L + \Phi_P)} \quad (1)$$

where $m_{L,i}$ and $m_{P,i}$ stand for the initial concentrations of the RD and the macromolecule, respectively; Φ_P and Φ_L are the flows of water in the polymer and the RD mixtures, respectively, determined by weight. The mixing ratio is $ca.$ 0.5.

To calculate m_L for the dilution of RD dispersion with water, in eqn (1) the flow of water replaces Φ_P.

The $\Delta H_{d,L}$ values were determined as functions of the RD composition. However, since RD is not a well-defined electrolyte, it was not possible to calculate the apparent molar relative enthalpy of RD in water ($L_{\Phi,L}$). Therefore, we computed the $L_{\Phi,L}$ of the final mixture relative to that of the most concentrated one ($\Delta L_{\Phi,L}$) and plotted against m_L (Fig. 1). As it can be seen, $\Delta L_{\Phi,L}$ slightly changes with m_L in the concentrated region whereas it becomes more and more endothermic upon diluting the dispersion; this is consistent with the dissociation of RD.

On the basis of these results, for the adsorption studies we decided to analyze the $m_{L,i}$ value of $ca.$ 13 mmol kg^{-1} (1% w/w) for two reasons: (1) its dilution does not involve a relevant dissociation effect and (2) the uncertainty on the enthalpy due to the m_L value is negligible.

The experiments were carried out at fixed RD composition as functions of either the copolymer or the polymer concentration over a dilute domain. Experiments dealing with micellar solutions were prevented by their high viscosity.

Results

The effect of the copolymer nature on its thermodynamics of adsorption at the RD clay/liquid interface was studied in detail. F68, F88 and F108 were chosen since they exhibit the same EO/PO ratio ($ca.$ 5) and different Mw. The L64 and F68 copolymers have comparable size of the polypropylene oxide
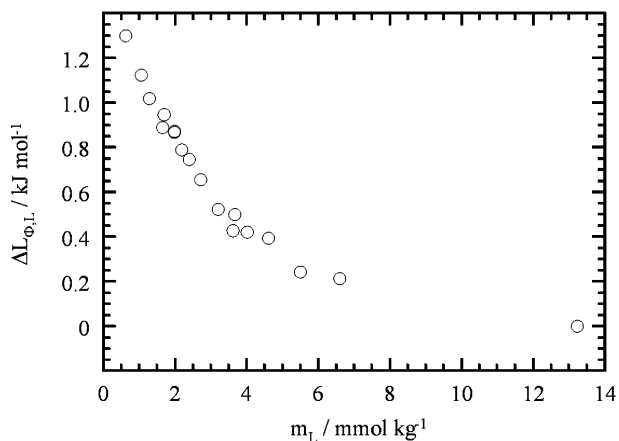
Fig. 1 Excess apparent molar relative enthalpy for RD in water as a function of concentration.

block and different number of EO units (larger for F68). The architecture of the copolymer was studied through L35 and 10R5, which differ only in the geometry, as they possess the same hydrophilic/hydrophobic balance and Mw. To highlight the role of the EO and the PO segments, calorimetric experiments were extended also to polyethylene (PEGs) and polypropylene (PPGs) glycols with varying Mw and their mixture. This information is useful to interpret the calorimetric data.

The enthalpies of transfer (ΔH_t) of RD from water to the aqueous macromolecule solutions as functions of the stoichiometric macromolecule molality (m_P) for all of the systems investigated are represented in Figs. 2–6. As a general result, the ΔH_t values are negative and the ΔH_t vs. m_P profiles are independent of the macromolecule nature with the exception of 10R5 and L35.

The profile of ΔH_t vs. m_P trend for PPGs is monotonic and independent of the molecular mass (Fig. 2). By increasing the polymer size, i.e. 425 and 725 g mol^{-1}, ΔH_t achieves a constant value at lower m_P. The low solubility of PPG 1200 in water (solutions at composition higher than 2×10^{-3} mol kg^{-1} were opalescent) allowed to register only the enthalpy decreasing curve. As for PEGs, the enthalpy profiles are the same as those obtained for PPGs (Fig. 3). In addition, an increase of Mw generates a peculiar effect on the enthalpy magnitude that is more exothermic for PEG 900.

The copolymer size, at a fixed EO/PO ratio, does not affect the dependence of ΔH_t on m_P, whereas it slightly does so at the enthalpy magnitude (Fig. 4). The hydrophobicity of the copolymer generates more exothermic enthalpies while it does not influence the profile of the ΔH_t vs. m_P curve (Figs. 4 and 5). As concerns the copolymer architecture (Fig. 6), ΔH_t in L35 decreases sharply with m_P reaching a minimum at ca. 5 mmol kg^{-1} and, then, increases with further addition of copolymer. The curve in 10R5 exhibits a less pronounced minimum. The experimental points of both copolymers are very close indicating that the geometry is not a relevant factor in governing the interactions between copolymer and RD. The location of the minimum is far below the critical micellar concentration of both copolymers (ca. 0.15 mol kg^{-1}).[27] Almost all of the enthalpy curves seem of Langmuir type whereas those for L35 and 10R5 appear to deviate from the Langmuir behaviour at larger m_P. One possibility is that such a peculiarity is explained by the Frumkin equation where the enthalpy of adsorption[21] is a function of the surface area covered. Alternatively, one may suppose that the enthalpy increase reflects an additional adsorption process correlated to the self-assembling of the copolymer. To verify which one of the two explanations matches the experimental data, ΔH_t in PEG 900 + PPG 725 equimolar solutions were determined. This mixture reasonably mimes L35 and 10R5 because both its Mw (1625 g mol^{-1}) and the EO/PO ratio (1.6) are close to those of the two copolymers. The concentration domain investigated was dictated by the
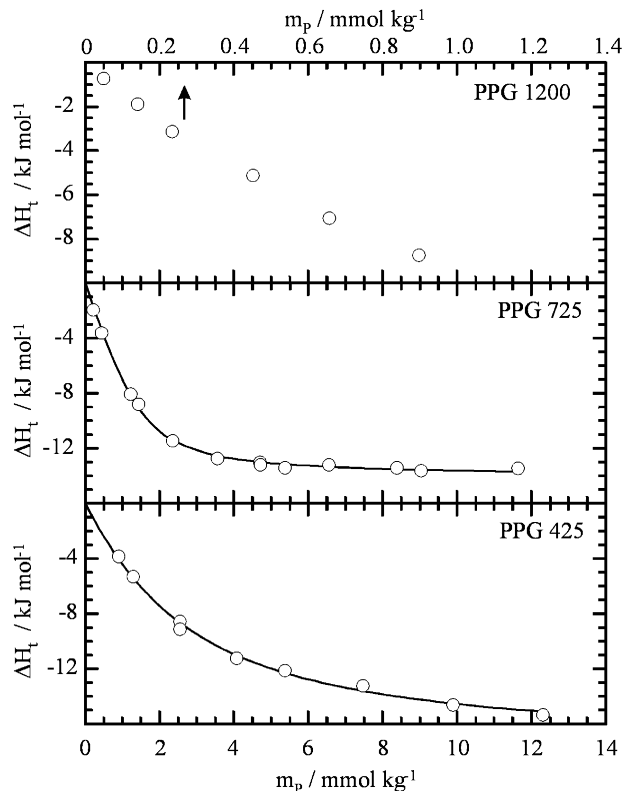

Fig. 2 Enthalpy of transfer of RD from water to aqueous PPG solutions as a function of the polymer concentration. Lines are best fits according to eqn (12) where the $x_2 \Delta H_2$ term was neglected.

solubility limit of PPG 725 in water. As Fig. 6 illustrates, ΔH_t is a monotonic decreasing curve with m_P. On this basis, one may deduce that the anomaly in the ΔH_t vs. m_P curve for both L35 and 10R5 is due to the self-assembled structures onto the solid rather than to the polymer–polymer interactions according to the Frumkin approach. A detailed discussion on this aspect will be presented in the next paragraph.

The quantitative analysis of the calorimetric data

Microcalorimetry is one of the most used thermodynamic methods to evidence surfactant–substrate interactions. The
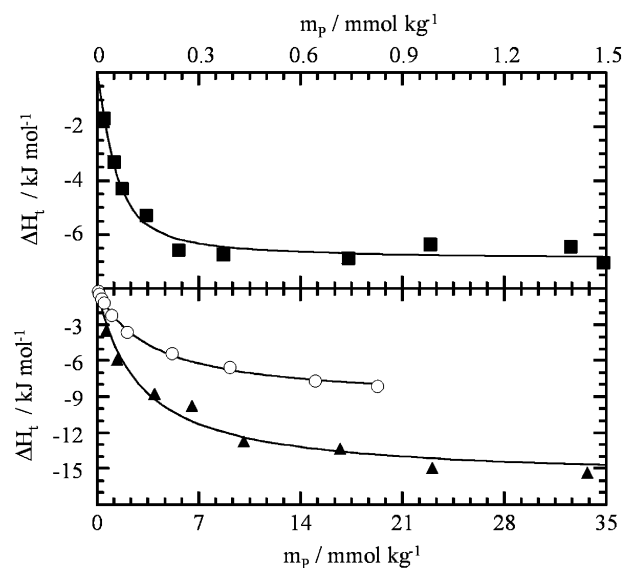

Fig. 3 Dependence on the polymer concentration of the enthalpy of transfer of RD from water to aqueous solutions of PEG 20000 (■), PEG 900 (▲) and PEG 400 (○). Lines are best fits according to eqn (12) where the $x_2 \Delta H_2$ term was neglected.
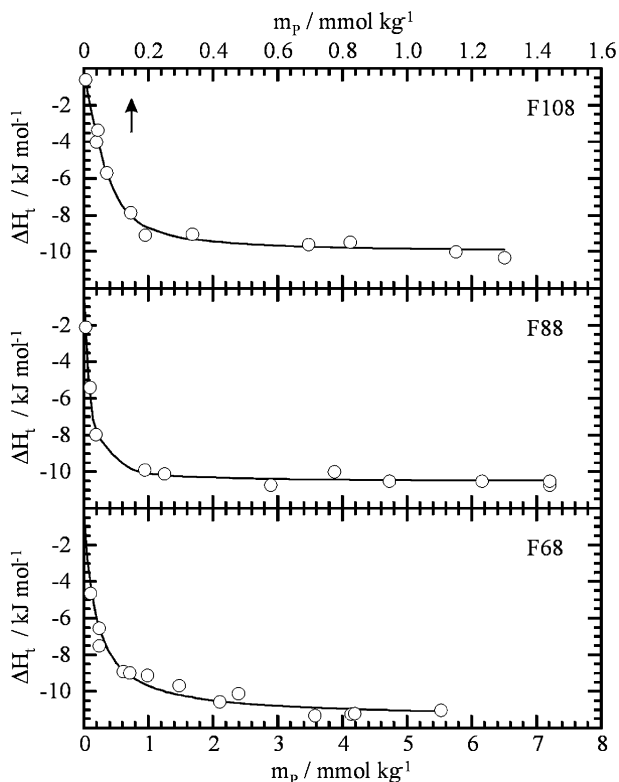
Fig. 4 Enthalpy of transfer of RD from water to aqueous copolymer solutions as a function of the copolymer concentration. Lines are best fits according to eqn (12) where the $x_2\Delta H_2$ term was neglected.

Fig. 6 Enthalpy of transfer of RD from water to aqueous macromolecule solutions as a function of the macromolecule concentration. Lines are best fit according to eqn (12).

bulk experimental property is determined as a function of internal parameters and treated by means of proper theoretical approaches to obtain information at molecular level. Such a technique was successful in describing, from a quantitative viewpoint, cyclodextrin + surfactant,[28,29] homopolymer + surfactant[30,31] and copolymer + surfactant[32–35] aqueous systems. The adsorption of conventional surfactants onto a solid substrate is generally studied through the ITC method.[36–38] However, the titration curves are combined with the isotherms of adsorption, determined from independent experiments, to obtain the enthalpy for the adsorption process.[36–38] To our knowledge, only Blandamer *et al.*[31] used the Frumkin adsorption isotherm for analyzing titration microcalorimetry data of aqueous surfactant–polymer systems.

From the qualitative analysis of the curves in Figs. 2–6, we may identify a single adsorption process which likely occurs for
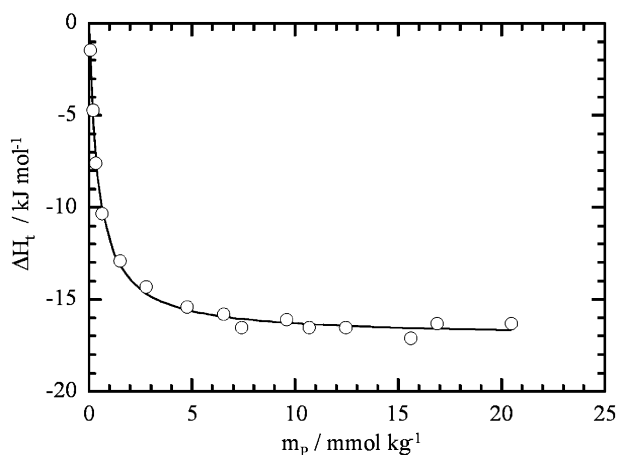

Fig. 5 Enthalpy of transfer of RD from water to aqueous L64 solutions as a function of the copolymer concentration. Line is the best fit according to eqn (12) where the $x_2\Delta H_2$ term was neglected.
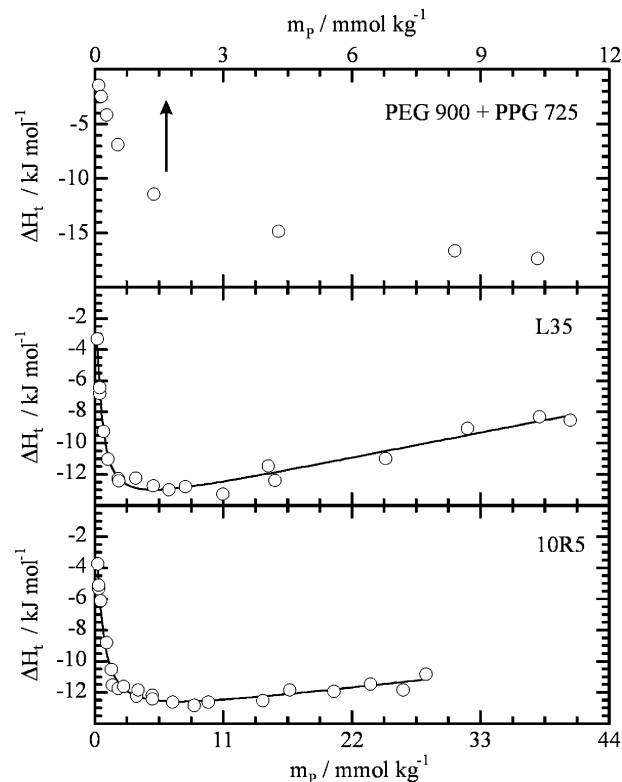
almost all of the systems investigated and, thereby, one may assume a *one-to-one binding* between the copolymer (or polymer) and the site on the solid. Moreover, to take into account the data in 10R5 and L35, an additional equilibrium *two-to-one binding* type, where one copolymer molecule interacts with another one adsorbed onto the solid, is considered. In other words, one assumes the formation of a mono-layer in the first process and of a double-layer in the second one.

The model states that RD exhibits total moles of sites per kg of water (S_t) given by

$$S_t = zm_L \tag{2}$$

where z are the moles of sites contained in 1 mole of RD.

The equilibrium constants for the two afore-mentioned bindings are

$$K_1 = \frac{S_1}{m_{P,w}S_f} \qquad K_2 = \frac{S_2}{m_{P,w}S_1} \tag{3}$$

where S_1 and S_2 represent the moles of sites per kg of water involved in the mono- and the double-layer, respectively, whereas S_f are the free sites; $m_{P,w}$ stands for the copolymer molality in the aqueous phase.

The enthalpy of transfer of RD from water to the aqueous copolymer solution may be written as

$$\Delta H_t = H_{\Phi,L}^{w+P} - H_{\Phi,L}^{w} \tag{4}$$

where $H_{\Phi,L}^{w+P}$ and $H_{\Phi,L}^{w}$ are the apparent molar enthalpies of RD in the aqueous copolymer solution and in water, respectively. $H_{\Phi,L}^{w+P}$ is given by

$$H_{\Phi,L}^{w+P} = \frac{H_T - H_B}{m_L} \tag{5}$$

where H_B and H_T are the enthalpies of the water–copolymer and water–copolymer–RD mixtures, respectively. According to the above equilibria one may write

$$H_B = 55.5H_w + m_P H_{P,w} \tag{6}$$

$$H_T = 55.5H_w + m_{P,w}H_{P,w} + m_{P,2}H_{P,2} + m_{P,1}H_{P,1} + S_f H_{L,w} \quad (7)$$

where H_w is the molar enthalpy of water whereas $H_{P,w}$, $H_{P,1}$ and $H_{P,2}$ are the partial molar enthalpies of the copolymer in the free state, mono- and double-layer, respectively. $H_{L,w}$ is the molar enthalpy of free sites.

Since the total sites may be expressed as

$$S_t = S_f + S_1 + S_2 \quad (8)$$

and the stoichiometric molality as

$$m_P = m_{P,w} + m_{P,1} + m_{P,2} \quad (9)$$

then, $m_{P,1}$ and $m_{P,2}$ correspond to S_1 and $2S_2$, respectively. By combining eqns (5)–(9) one obtains

$$H_{\Phi,L}^{w+P} = (S_1/m_L)\Delta H_1^* + (S_2/m_L)\Delta H_2^* + (S_t/m_L)H_{L,w} \quad (10)$$

here $\Delta H_1^*(H_{P,1} - H_{P,w} - H_{L,w})$ is the enthalpy change for the formation of the copolymer mono-layer and $\Delta H_2^*(2H_{P,2} - 2H_{P,w} - H_{L,w})$ is the enthalpy associated to the formation of the double-layer.

As concerns the water + RD system, one obtains

$$H_{\Phi,L}^w = (S_t/m_L)H_{L,w} \quad (11)$$

By combining eqns (2), (4), (10) and (11), the following is obtained

$$\Delta H_t = x_1 \Delta H_1 + x_2 \Delta H_2 \quad (12)$$

where x_1 and x_2 are the fractions of the sites involved in the mono- and double-layer, respectively, whereas ΔH_1 and ΔH_2 are the corresponding enthalpy changes per mole of RD.

Modelling experimental enthalpies

As a general result, the fits of the enthalpy of transfer according to eqn (12) were successful for all the systems investigated with the exception of RD + PPG 1200 system. The failure of the analysis of the latter is due to the restricted range of m_P studied. In fact, to provide accurate parameters,[28] a fitting process must be applied over a wide domain where the dependence of the property on concentration well defines the curvature related to the equilibrium constant.

The minimizing procedure was carried out by means of a non-linear least-squares fitting method. For all the systems represented in Figs. 2–5, the $x_2\Delta H_2$ term was neglected. The best fits were good (Figs. 2–5) and provided K_1, z and ΔH_1 whose values are collected in Table 2. It has to be noted that the z values depend on the nature of the system. A very low z

indicates that the amount of the adsorbed macromolecule is negligible with respect to the stoichiometric composition.

Eqn (12) in the complete form was employed to fit the 10R5 and L35 data. The K_2 and the ΔH_2 values were quite uncertain due to the smooth x_2 variation in the interval of m_P investigated as a consequence of the low K_2 (it is 1 ± 2 and 0.1 ± 1.4 kg mol^{-1} for 10R5 and L35, respectively). Comparable values were also determined for the equilibrium constant of micellization[27] of both L35 and 10R5; such similarity is consistent with the formation of a double-layer on RD. On this basis, new fits of ΔH_t were performed by fixing K_2 calculated as $-RT \ln K_2 = \Delta G_m^o$, where ΔG_m^o is the standard free energy of micellization (1.2 ± 0.1 and 1.1 ± 0.1 for L35 and 10R5, respectively). The obtained ΔH_2 values are 118 ± 4 and 72 ± 7 kJ mol^{-1} for L35 and 10R5, respectively. These endothermic enthalpies reveal the hydrophobic copolymer desolvation according to the positive enthalpy of micellization (ΔH_m) reported[39,40] for the PEO–PPO–PEO copolymers. For L35, ΔH_m is 165 kJ mol^{-1} (calculated from eqn (5) in ref. 40) whereas no ΔH_m is available for 10R5.

The standard free energy (ΔG_1^o) and entropy ($T\Delta S_1^o$) were evaluated as

$$\Delta G_1^o = -RT \ln K_1 \quad T\Delta S_1^o = \Delta H_1 - \Delta G_1^o \quad (13)$$

Modelling kinetic data

For all the systems under investigation, the data of the electrical conductivity as a function of time follow a first-order kinetic law. For L35 and 10R5, the second adsorption process was not detected. For a given copolymer, the first-order rate constant (k_{obs}) significantly varies with both the concentrations of macromolecule (M_P) and RD (M_L). An enhancement of the first-order rate constant for the more hydrophilic copolymer was observed. Interestingly, within the experimental error, the k_{obs} values are almost equal for L35 and 10R5. This indicates that the copolymer architecture plays an irrelevant role and is in agreement with the calorimetric results. At fixed M_P, the rate constant increases with M_L and, in all the cases examined, the plots of k_{obs} vs. M_L were good straight lines (Fig. 7 shows some examples). Such plots exhibit similarity with those observed for the complexes formation reaction.[41] The latter were quantitatively interpreted by assuming that in the reaction process one water molecule is replaced by the ligand. This model is formally identical to that proposed above for the formation of the copolymer mono-layer. On this basis, k_{obs} may be

Table 2 Thermodynamic properties for the adsorption of triblock copolymers and their homopolymers onto laponite at 298 K[a]

	z	$K_1 \times 10^{-3}$	ΔG_1^o	ΔH_1	$T\Delta S_1^o$
PPG 425	0.22 ± 0.04	0.52 ± 0.06	-15.5 ± 0.3	-17.7 ± 0.3	-2.2 ± 0.6
PPG 725	0.223 ± 0.008	3.7 ± 0.3	-20.4 ± 0.2	-14.03 ± 0.07	6.3 ± 0.3
PEG 400	$(1 \pm 6) \times 10^{-8}$	0.280 ± 0.007	-13.96 ± 0.02	-9.41 ± 0.09	4.55 ± 0.11
PEG 900	$(2 \pm 5) \times 10^{-5}$	0.35 ± 0.02	-14.51 ± 0.14	-15.9 ± 0.2	-1.4 ± 0.3
PEG 20000	$(87 \pm 9) \times 10^{-4}$	44 ± 6	-26.5 ± 0.3	-6.91 ± 0.06	19.6 ± 0.4
L64	$(2 \pm 8) \times 10^{-9}$	2.26 ± 0.05	-19.14 ± 0.06	-17.03 ± 0.07	2.11 ± 0.13
		2.0 ± 0.3^b	-18.8 ± 0.4^b		
F68	$(2 \pm 2) \times 10^{-9}$	5.5 ± 0.2	-21.34 ± 0.09	-11.44 ± 0.09	9.9 ± 0.2
		6 ± 1^b	-21.5 ± 0.4^b		
F88	$(14 \pm 1) \times 10^{-3}$	25 ± 2	-25.1 ± 0.2	-10.53 ± 0.04	14.6 ± 0.2
F108	$(10.4 \pm 0.8) \times 10^{-3}$	48 ± 7	-26.7 ± 0.4	-10.05 ± 0.09	16.7 ± 0.5
10R5	$(50 \pm 8) \times 10^{-3}$	2.8 ± 0.3	-19.7 ± 0.3	-13.9 ± 0.2	5.8 ± 0.5
		3.7 ± 0.2^b	-20.36 ± 0.13^b		
L35	$(63 \pm 8) \times 10^{-3}$	3.9 ± 0.4	-20.5 ± 0.3	-14.4 ± 0.1	6.1 ± 0.4
		3.6 ± 0.3^b	-20.3 ± 0.2^b		

[a] Units are: K_1, kg mol^{-1}; ΔG_1^o, ΔH_1 and $T\Delta S_1^o$, kJ mol^{-1}. [b] From the kinetic data (K_1, dm^3 mol^{-1}).
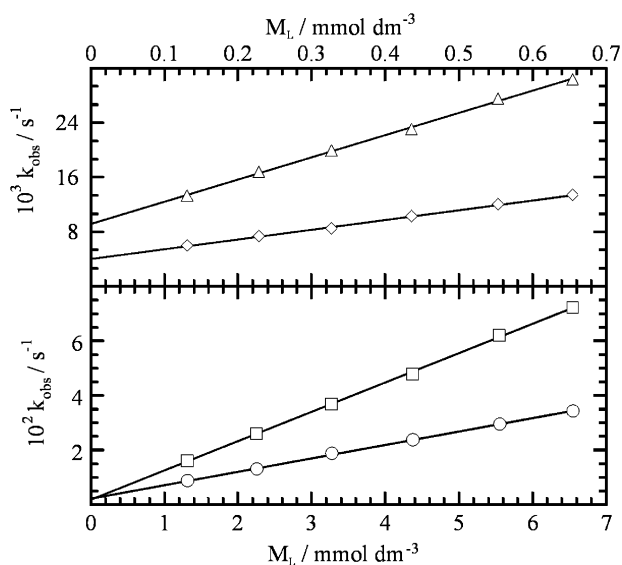
Fig. 7 Observed first-order rate constants as a function of RD concentration for L64 at 25 mmol dm^{-3} (○), F68 at 0.725 mmol dm^{-3} (□), 10R5 at 1 mmol dm^{-3} (◊) and L35 at 25 mmol dm^{-3} (△). The lines are best fits according to eqn (14).

related to the formation (k_f) and dissociation (k_d) rate constants as

$$k_{obs} = k_d + k_f M_L \qquad (14)$$

Eqn (14) enables to obtain k_d and k_f and, hence, the equilibrium constant (K_1) is obtained from the k_f/k_d ratio. For all the systems analyzed, the formation rate constant value is considerable higher than the dissociation one revealing the strong affinity of the copolymer to RD. Both k_f and k_d values increase with M_L. In addition, they depend on the copolymers nature; the increase of the hydrophilicity leads to higher kinetic constants values whereas no significant influence plays the architecture as demonstrated by the values obtained for L35 and 10R5. As for the K_1 values, for each system, it was found that they were almost independent of the copolymer concentration. Table 2 collects the mean average values. It is noteworthy that the K_1 values agree with those obtained from calorimetry (Table 2). The agreement persists if K_1 is compared on the same concentration scale. Finally, the impossibility to detect the second adsorption process evidenced by calorimetry for L35 and 10R5 can be due most likely to the low K_2 value with respect to K_1 and to the experimental technique used. Since the second adsorption process does not imply the release of sodium ions, a complicated rate law which has to underlie the electrical conductivity as a function of time, cannot be expected. This result corroborates the findings obtained by modeling calorimetric data.

Discussion

For the sake of clarity, the thermodynamics of adsorption will be divided into two parts: (i) adsorption of homopolymers and (ii) adsorption of triblock copolymers.

(i) Adsorption of homopolymers

The comprehension of the adsorbing behavior of PEGs and PPGs onto RD is preliminary to the understanding of the adsorption properties of the triblock copolymers.

For both PEGs and PPGs, ΔG_1^o decreases with Mw with a slope more negative for PPGs and, for a given Mw, ΔG_1^o(PPG) < ΔG_1^o(PEG). These results certify that the Mw raise produces the growth in the adsorbed layer that, in turns, exhibits a stronger affinity to the clay mineral surface when it is composed by PPG. Our data are consistent with literature findings.

From SANS[10] and size-excluded chromatography[12] techniques, the amount of PEGs adsorbed onto RD in water[10] and in the aqueous NaCl solution[12] was determined; this quantity increases with the polymer size.

The mechanism of polymer–RD interaction is quite complex. The RD disk particles in water presents[3] negatively charged faces and positive sites on the edge. The possible points of interaction of the polymer molecules are the –OH groups and the ether oxygens. Consequently, it may occur that the adsorption takes place *via* the attractive forces between the hydroxyl groups and the negatively charged surface, and between the ether oxygen and the positive edge. Their contributions to ΔG_1^o can be discriminated by plotting ΔG_1^o as a function of the number of monomers (*i.e.*, EO or PO units); accordingly, the intercept and the slope provide the terms for the interactions between RD and the –OH groups and between RD and a single monomer, respectively. Although our points are few, we may state that the hydroxylic groups of PEGs are more strongly bounded than those of PPGs; the opposite occurs for the ether oxygen the affinity of which is enhanced by the inductive effect of the methyl group. These results agree with recent structural[10] information following which the face thickness is constant upon changing PEGs molecular weights whereas the edge layer width changed with a power law dependence on Mw. In interpreting these results,[10] the polymer chains wrapping from one face to the other was considered a possible situation.

Peculiar are ΔH_1 and $T\Delta S_1^o$. For PPGs, both properties increase with the polymer size and for PEGs they decrease exhibiting a minimum. The evolution of such functions with Mw reflects the varying behaviour between the polymer in the adsorbed and the free states. Well known is the behaviour of aqueous solutions of PEGs and PPGs. When PEG is dissolved in water,[42] a hydrogen bond between the ether oxygen and water is formed to some extent and the water structure around the chain is enhanced. Consequently, the enthalpy of mixing between PEG and water is negative and the entropy decreases because of the reduced conformational freedom of the polymer chain. The latter, especially if long, maintains in part the conformation of its crystalline state and forms helical structures, which fit into the water lattice. The low molecular weight polymers exhibit a less ordered structure.[42,43] Spectroscopic studies showed that the polymer chain conformation in the aqueous solution is more ordered than that in organic solvent[44] or in the melt.[45] Analogously, the thermodynamic behaviour of PPGs[42] is similar to that of PEGs. However, the methyl group of the PO unit creates a sterical hindrance and generates the strain of the water structure leading to smaller hydrogen-bond energy than in the case of the EO unit. According to these reports, in the adsorption process the first step involves the partial disruption of the polymer–water interactions generating positive enthalpy and entropy. The second step deals with the polymer attachment to the RD particles and the consequent rearrangement of the chain allowing for exothermic enthalpy and entropy loss.[46] Finally, the release of the sodium ions upon the polymer adsorption takes place, evidenced by the kinetic experiments. In this case, according to data in Fig. 1, the enthalpy is expected to be positive and small.

In conclusion, as a general result, the second step controls the ΔH_1 values whereas the importance of one-step over another is system specific for $T\Delta S_1^o$.

(ii) Adsorption of triblock copolymers

Whatever is the copolymer nature, ΔG_1^o indicates a large affinity of the macromolecule to the RD surface, ΔH_1 is exothermic and $T\Delta S_1^o$ is positive. Therefore, the process is enthalpy–entropy controlled. A careful inspection of all the thermodynamic properties of adsorption may reveal the role played by the copolymer features. ΔG_1^o decreases with the

molecular weight, when keeping constant the EO/PO ratio, as ΔG_1° does for the homopolymers. To exploit whether the linking of the PEO and the PPO blocks in the copolymer assumes relevance in the driving forces of the adsorption, ΔG_1° was calculated by additivity as sum of ΔG_1° of PEG and PPG having the same molecular weights of the blocks constituting the copolymer. The calculated values (-54, -65 and -77 kJ mol^{-1} for F68, F88 and F108, respectively) are largely negative compared to the experimental ones. Therefore, one may infer that the constraints which the PEO and the PPO blocks in the macromolecular structure undergo make the adsorption process less favoured. ΔH_1 values slightly decrease with Mw whereas $T\Delta S_1^{\circ}$ ones increase. These findings likely reflect the conformational states of the macromolecule, which once removed from the water cages, assume a higher degree of flexibility with Mw.

The comparison between ΔG_1° in L64 and F68 evidences that the more hydrophilic the copolymer, the larger the affinity to the solid substrate. From the analysis of the homopolymers, we can draw the conclusions that both the EO and PO units exhibit affinity to RD that is larger for PO. Since F68 and L64 are featured by the same PPO size block, the interactions involving a larger number of EO units make ΔG_1° for F68 more negative than that for L64. The adsorption process is mainly controlled by the enthalpy for L64 whereas comparable are the enthalpy and the entropy for F68. The sequence $T\Delta S_1^{\circ}$(F68) > $T\Delta S_1^{\circ}$(L64) may be explained by invoking the more ordered state of F68 in water. The ΔH_1(L64) value is largely negative with respect to ΔH_1(F68). Such a difference is ascribable to the variation of the L64 hydration state generated by the adsorption; for instance, copolymer and water can interact in agreement with the small $T\Delta S_1^{\circ}$. These explanations also hold for the obtained kinetic trends. From the k_{obs} values the process is not diffusion controlled (k_{obs} is *ca.* 10^6–10^8 s^{-1}). However, one has to reasonably expect that F68, having higher Mw with respect to L64, adsorbs more slowly. Since the findings are opposite, one can assess that larger k_{obs} values are not the only consequence of the EO units increase but also the result of the state of F68 in water that makes the EO units more available for the interactions with RD. In turn, the higher k_{obs} reflects into larger K_1 values.

As concerns L35 and 10R5, ΔG_1°, ΔH_1 and $T\Delta S_1^{\circ}$, within the errors, are nearly independent of the copolymer architecture. The evidence that RD does not distinguish the two copolymers may provide indications on the way the copolymer is anchored to the RD particles. The macromolecule chains may wrap[10] from one face to the other of the RD particle or simply adsorb onto the edges and on the faces. The wrapping mechanism is possible from a geometrical point of view because the length of

the fully extended macromolecules (calculated by using the PO and the EO unit values[47]) is larger (12 nm) than the edge thickness of the RD particle. However, one expects that such a mechanism allows to comparable ΔG_1° and different $T\Delta S_1^{\circ}$ values for both 10R5 and L35; that is not the case here. The wrapping anchoring creates different constraints of 10R5 and L35 due to their geometry, which allows conformational states of the macromolecule to generate dissimilar $T\Delta S_1^{\circ}$. The thermodynamics near-independence of adsorption on the copolymer architecture is supported by the simultaneous independence of k_{obs}.

As Fig. 8 illustrates, the RD particle does not also discriminate the 10R5 and L35 from the PEG 900 + PPG 725 mixture in the dilute domain as a single curve is drawn through all the experimental points. This indicates that the homopolymer mixture very well mimes the amphiphilic macromolecules. Furthermore, the thermodynamics of adsorption of both PEG 900 and PPG 725 being available, ΔH_t for the mixture was calculated by assuming the formation of a polymer mixed mono-layer

$$\Delta H_t = x_{PEG}\,\Delta H_{PEG} + x_{PPG}\Delta H_{PPG} \quad (15)$$

$$K_{PEG} = \frac{x_{PEG}}{m_{PEG,w}(1 - x_{PEG} - x_{PPG})}$$

$$K_{PPG} = \frac{x_{PPG}}{m_{PPG,w}(1 - x_{PEG} - x_{PPG})} \quad (16)$$

Here ΔH_{PEG} and ΔH_{PPG} correspond to ΔH_1 in Table 2 for the polymers whereas K_{PEG} and K_{PPG} correspond to K_1.

The mass balance is

$$m_{PEG} = m_{PEG,w} \quad m_{PPG} = m_{PPG,w} + zm_L x_{PPG} \quad (17)$$

where $m_{PEG,w}$ and $m_{PPG,w}$ are the concentrations of PEG and PPG in the free state. Note that the concentration of adsorbed PEG was neglected due to its very low value.

The computed ΔH_t according to eqns (15)–(17) are represented in Fig. 8. It is interesting to observe that the experimental points of the different systems are well matched by the computed values in the dilute domain. This proves that both the PEO and the PPO blocks interact with the RD particles according to the ideal behaviour. Upon increasing m_P, the deviation of the experimental points from the calculated values takes place being positive for the copolymers, due to the formation of a double-layer, and negative for the mixture, most likely due to the polymer–polymer interactions.

Concluding remarks

The thermodynamics of both PEO–PPO–PEO and their homopolymers at the RD/solution interface was determined through a calorimetric route. A model based on two equilibria was proposed: (1) *one-to-one binding* between the macromolecule and the site on the solid and (2) *two-to-one binding* following which 1 macromolecule interacts with another one already adsorbed onto the solid. The good agreement between the equilibrium constants obtained from calorimetry and those determined from kinetic experiments confirms the reliability of the experimental and theoretical approaches. Almost all of the systems investigated are highlighted by the *one-to-one binding*. For such a process, the thermodynamic properties indicate that the copolymer, whatever its nature is, exhibits a large affinity to the RD surface and both enthalpy and entropy control the binding. The insights on the adsorbing behaviour of their homopolymers onto RD were fruitful to obtain detailed information on the nature of the forces involved between RD and the copolymers. In particular, the copolymer nature plays a role: (1) the molecular weight, when keeping constant the EO/PO ratio, increases the affinity to the solid surface and allows to slightly bigger exothermic enthalpies; (2) the more hydrophilic the copolymer is the larger is the affinity to the solid
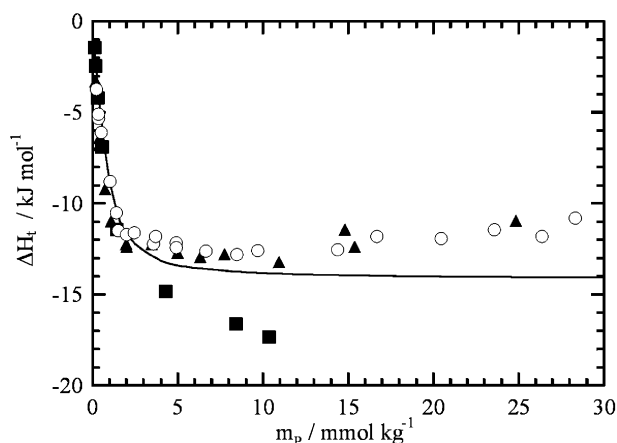

Fig. 8 Enthalpy of transfer of RD from water to aqueous solutions of 10R5 (○), L35 (▲) and PEG 900 + PPG 725 (■) as a function of the macromolecule concentration. The line is calculated according to eqns (15)–(17).

substrate but the enthalpy becomes less exothermic; and (3) RD does not discriminate between two copolymers which have the same Mw and EO/PO ratio but different geometry. Finally, the *two-to-one binding* was evidenced only for L35 and 10R5 systems; the derived thermodynamic properties are consistent with the formation of a double-layer onto the RD surface.

In the light of the thermodynamics of adsorption, we can draw the conclusion that, for comparable polymer Mw, PPG is more suitable in building up a steric barrier around the RD particles and, indeed, exhibits several advantages and no drawbacks. On the other hand, parent copolymers may be used to properly functionalize the RD surface for specific purposes by exploiting both their high affinity to the solid surface and their ability to self-assemble onto it as clearly evidenced by L35 and 10R5.

Note added in proof

During the process of publishing this paper, Nelson and Cosgrove reported SANS data on some aqueous triblock copolymer + laponite systems.[48] Their results on the adsorption process are consistent with those presented in our paper.

Acknowledgements

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