SHORT COMMUNICATION

Interactions of bentonite clay in composite gels of non-ionic polymers with cationic surfactants and heavy metal ions

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Abstract Chemically cross-linked composite gels based on bentonite clay from Manyrak deposit (Kazakhstan Republic) and nonionic polymers, i.e., poly(hydroxyethylacrylate) and poly(acrylamide), were polymerized in situ after preliminary intercalation of monomers in an aqueous suspension of bentonite clay. By means of cryo-scanning electron microscopy, it was shown that bentonite clay is well incorporated into the gel network structure with pore sizes up to 1.5 μm. The intercalated bentonite clay can adsorb cationic surfactants as well as heavy metal ions due to electrostatic interactions. Conductometric and surface tension measurements indicate not only the adsorption of surfactants and heavy metals inside the hydrogel, but also the displacement of the critical micellization concentration (CMC) of the surfactants.

Introduction

Functionalization of various adsorbents for the removal of heavy metal ions and ionic surfactants from water or wastewater has attracted great research interest in the recent years due to the advantages of achieving high efficiency and good selectivity. Rapid industrialization has led to an increased discharged wastewater containing heavy metals, which have detrimental effects on the environmental and human health. Environmental pollution caused by toxic heavy metals is one of the most hazardous problems in many densely populated cities worldwide [1].

A number of technologies to remove heavy metals from water have been developed, including electrochemical precipitation [2], reverse osmosis [3], ion exchange [4], and adsorption [5, 6]. Most of these methods are effective but also complex, and their high costs restrict their use. The reverse osmosis applications are limited by a number of disadvantages such as high operational cost (high pressure techniques) and limited pH range. Ion exchange method uses synthetic resins in a suitable process. But the disadvantages are the lack of mechanical strength and the low selectivity of the resins. Among these procedures, adsorption is one of the most economically favorable and technically easy method [7].

A number of functional groups, including carboxylate, hydroxyl, sulfate, phosphate, amide, and amino groups, have been found to be effective in metal sorption [8, 9]. Among these, the amine group is very effective for removing heavy metals. It not only chelates cationic metal ions, but also adsorbs anionic metal species through electrostatic interactions or hydrogen bonding. Polyethyleneimine (PEI), which is composed of a large number of primary and secondary amine groups in a molecule, exhibits good sorption ability for heavy metals [10, 11]. The combination of polymers containing these functional groups and an inorganic matter like porous silica and zeolites affords to obtain a highly efficient material.

Montmorillonite (MMT), among the layered silicates, is a dioctahedral smectite type (2:1) clay, meaning that it has two tetrahedral sheets sandwiching a central octahedral sheet. MMT clays are conventionally utilized as catalysts, adsorbents, metal chelating agents, and fillers for polymer composites [12–14]. It is abundant in nature and well known for its lamellar structure, high surface area, and anionic and cationic

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charges [15, 16]. These layered silicates are hydrophilic and able to swell in water, present in nature as aggregates in stacks of about micrometer sizes consisting of multilayer platelets of aluminum and silicon oxides. Metal cations originated from the isomorphic substitution of aluminosilicates by metal ions, such as Na^+, K^+, Mg^+, or Ca^+, are present between the layers. These metallic cations can be exchanged for other cationic species. The potential for replacing priority is $Ca^{2+}>Mg^{2+}>K^+=NH_4^+>Na^+$ [17].

Another very important worldwide pollution problem in our days is related to the increasing amounts of surfactants in waste water. It is already well known that especially cationic surfactants can be separated from water in a similar way like heavy metal ions due to the adsorption on MMT clays.

Due to its excellent surface properties, MMT has been used as support for hybrid nanomaterials [18]. These hybrid materials are synthesized by combining the properties of different precursors to obtain new materials with improved properties. Urbano and Rivas [19] studied the sorption performance of a polymer-clay composite based on the iminodiacetic acid group and use montmorillonite as fillers. The resin consisted of a polymer matrix of N-(4-vinylbenzyl)-iminodiacetic acid that was cross-linked with *N,N*-methylene-*bis*-acrylamide, with montmorillonite clay dispersed throughout the resin. Selectivity experiments reveal that composites present a certain selectivity towards Cu^{2+} and that montmorillonite content does not provide selectivity to the composite. Kinetic and diffusion models show that the metal ion retention occurs mainly at the surface of resin particles, suggesting a film diffusion process.

In order to improve the properties of the polymeric material, the uniform distribution of the clay nanoparticles in the polymer matrix is of high relevance. Therefore, the radical intercalation polymerization in situ of monomers on the surface of clay platelets is of special interest, resulting in a homogeneous material with uniform distribution of the mineral throughout the volume of the polymer matrix [20]. It is already well established that bentonite clay (BC) can be embedded into a hydrogel by in situ radical polymerization of nonionic monomers [21–23].

Based on this knowledge, the aim of this study was to incorporate a natural bentonite clay material with high content of MMT into a nonionic hydrogel to form a new hybrid material for the adsorption of heavy metal ions and cationic surfactants. It should be noted that Kazakhstan has large deposits of bentonites, as Manyrak (East Kazakhstan), Kyzyl-Jar (West Kazakhstan), and Kyngrak (South Kazakhstan). However, bentonite clay from Manyrak fulfills the requirements as sorbent material in hydrogels very well due to the high content of MMT. Therefore, bentonite clay from Manyrak was used in this study.

The resins consisted of a polymer matrix of 2-hydroxyethylacrylate (HEA) and acrylamide (AAm) that was cross-linked with *N,N*′-methylene-*bis*-acrylamide, while montmorillonite clay was dispersed throughout the polymer. For hydrophilic cross-linked materials such as hydrogels, the dispersed montmorillonite platelets provide improvements to the material as sorbents for ionic surfactants and metal ions, as already outlined before. The characterization of the resulting hybrid materials was performed through X-ray diffraction and cryo-high-resolution scanning electron microscopy. The ability of these hybrid materials to adsorb Cu^{2+} and Zn^{2+} as well as cationic surfactants was studied by means of conductometric titrations, zeta potential, and surface tension measurements. The adsorption experiments were carried out at different concentrations of the aqueous salt solutions. All experiments were conducted using compositions of varying clay content to investigate the influence of the MMT content on the efficiency of the material.

Experimental

Materials

2-Hydroxyethylacrylate (HEA) (purity >98 %) obtained from Aldrich (USA) and acrylamide (AAM) ($M=152.2$, $T_m=357.5$ K) from Reanal (Hungary) were used without further purification, as a cross-linking agent N,N′-methylene-*bis*-acrylamide (MBAA) from Reanal (Hungary) and as an initiator potassium persulfate (PPS) were employed. Cetylpyridinium bromide (CPB) $C_{16}H_{33}NC_5H_5Br$ and cetyltrimethylammonium bromide (CTAB) $C_{19}H_{42}BrN$ were purchased from Aldrich (USA) and used as given. Heavy metal salts, i.e., $CuSO_4 \cdot 5H_2O$ and $ZnSO_4 \cdot 7H_2O$ were obtained from JHD (China).

Bentonite clay from Manyrak deposit (East Kazakhstan Region) was purified according to the method described by Salo [24] by repeating elutriation in distilled water. The chemical composition of the purified bentonite clay was determined by means of diffraction spectral analysis (spectrograph DPhS-13, Russia):

SiO_2 : 60 %; Al_2O_3 : 9 %; Fe_2O_3 : 0.5 %; CaO
: 0.5 %; MgO : 1 %; Na_2O : 0.8 %; K_2O
: 0.5 %; H_2O : 7 %.

According to the results of X-ray diffraction (diffractometer DRON-4-07, Russia), three different phases were identified in Manyrak bentonite clay:

– α-Quartz SiO_2;
– Montmorillonite $Al_2[OH]_2\{Si_4O_{10}\}*mH_2O$;
– Amorphous phase.

Synthesis of composite gels

Composite gels of polyacrylamide (PAAm)-BC and poly(2-hydroxyethylacrylate) (PHEA)-BC were synthesized by in situ intercalation radical polymerization of an aqueous monomer solution with incorporated purified bentonite clay particles. The composition of the mixtures is given in Table 1. 100 ml of a bentonite clay suspension was mixed for 2 h by using a magnetic stirrer. After adding the monomer to the premixed bentonite suspension, the resulting system was furthermore mixed for 6 h. The mixture was tightly closed in a beaker and left overnight. The next day, the system was mixed again for 2 h. Therefore, the total time of intercalation of monomer into the clay particles was 24 h. In a next step, the cross-linking agent was added to the suspension. After heating the mixture to 60 °C, the initiator was incorporated. The suspension was put into 20-mm-sized ampoules, which were isolated from the air and placed in a thermostat. The polymerization was carried out for 2 h at 60 °C. The ampoules turned into an air thermostat for 20 h at 25 °C in order to complete the polymerization process and to link the polymer matrix [25]. The cross-linking agent concentration was between 0.05 and 1 mol%, whereas the initiator concentration was fixed at 1 mol% in relation to the monomer content. The bentonite clay concentration varied between 0.5 and 3 wt%.

The finally obtained gels were taken from ampoules and washed out from unreacted monomers with distilled water. The washing out process was controlled by detecting the amide groups and double bonds (with bromine water) in the wash water. The purified gels were dried under vacuum at 40 °C up to a constant weight and ground in porcelain mortars. In the following tests, fractions with particle size <0.1 mm were used.

Methods

Conductometric titrations were carried out with the conductometer LF-2000 (WTW, Germany) at room temperature.

Table 1 Composition of bentonite clay-polymer (BC-Pl) composites

Gel samples	[Pl] in mass%	[BC] in mass%	[MBAA] in mol.%	[PPS] in mol.%
Reference gel Pl	3	0	0.05–1	1
Composite gel BC-Pl[a]	3	0.5		
		1		
		2		
		3		

[a] Percentage calculation in relation to the monomer weight

Zeta potential measurements were performed by using a Nano Zetasizer 3600 (Malvern, UK) injecting a small portion of the pure dispersion of clay and dispersion of clay with detergent or heavy metal ions at room temperature.

Surface tension measurements were carried by using the digital tensiometer K10ST (KRÜSS, Germany) at room temperature. Starting from pure water, measurements were carried out after adding different amounts of surfactant in the absence and presence of the composite species on the bottom of the glass at room temperature. The platinum ring was cleaned after each measurement in butane/propane flame.

The morphology of bentonite clay, reference, and composite gel samples were examined by high-resolution scanning and cryo-scanning electron microscopy (SEM, cryo-SEM) by using the scanning electron microscope S-4800 from Hitachi (Japan). The respective samples were rapidly frozen in melting nitrogen and fractured in a cryo-chamber at −145 °C. After etching for 45 s at −98 °C, the samples were sputtered with a thin platinum layer. Cryo-SEM is a powerful method to visualize the network structure of different types of gels, composite gels, and hydrogels very well [26–28].

Results and discussion

Figure 1 shows different SEM and cryo-SEM micrographs of bentonite clay, homopolymer, and composite gels. In snapshots 1a and 1b, the more open layered structure of the bentonite clay in scanning (Fig. 1a) and cryo-scanning mode (Fig. 1b) can be visualized. One can see swollen clay particles due to the penetration of water molecules into the interlayer space between the clay platelets. Homopolymer gels of PAAm and PHEA (Fig. 1c, d) show a network structure with a pore size between 0.1 and 0.3 μm for PAAm and 0.6 and 1.5 μm for PHEA gels. Perhaps, this explains the more amorphous structure and elasticity of PHEA gels. Turning to cryo-SEM snapshots of composites PAAm-BC and PHEA-BC (Fig. 1e, f), one can see that the pore size of the network is not changed significantly. This means the network structure is not influenced drastically after incorporating the bentonite particles. Noteworthy, that in homopolymer gels, pores represent voids, whereas in composite gels, pores are partly filled or tightened by composite material. However, this seems to be a consequence of the aforementioned penetration of monomer molecules into the interlayer space of the clay particles during the process of intercalation, dispersion, and exfoliation of clay particles in the subsequent polymerization. This is already well known for the dispersion and delamination of filler particles with a monolayer thickness of about 1 nm [23]. Nevertheless, it should be noted here that our bentonite clay particles are still present in a layered structure, which can be concluded from the snapshot in Fig. 1e, f.
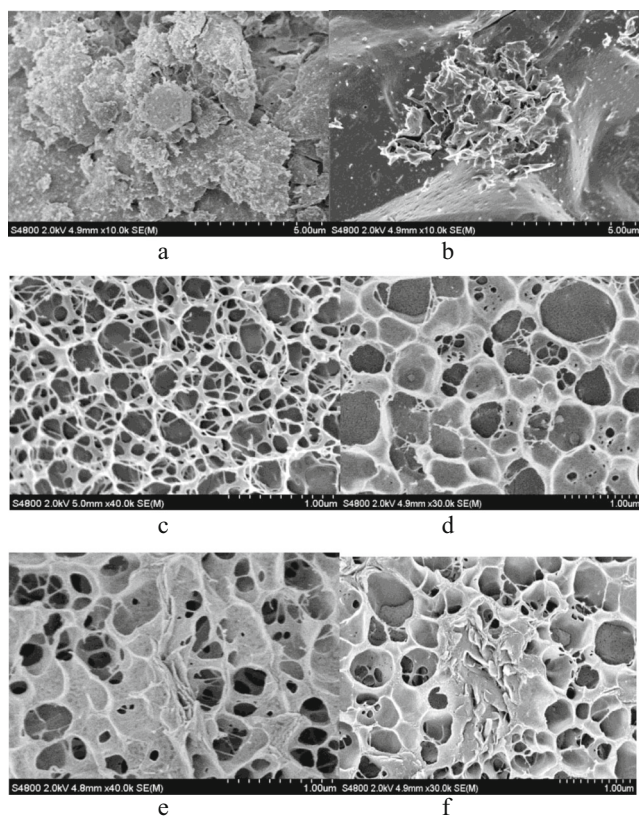
Fig. 1 SEM (**a**) and cryo-SEM (**b**) snapshots of BC, cryo-SEM snapshots of PAAm (**c**) and PHEA (**d**) homogels, and composite gels of PAAm-BC (**e**) and PHEA-BC (**f**)

Specific information about the nature of interaction between negatively charged kaolinite platelets and oppositely charged components can be obtained by means of zeta potential measurements. Already some years ago, we have shown that the adsorption of polyelectrolytes or low molecular counterions can be well detected by using zeta potential measurements based on electrophoretical light scattering [29]. However, the adsorption of oppositely charged surfactants can be detected in a similar way.

Taking this knowledge into account, the aim of our first experiments was to show that cationic surfactants, i.e., CTAB or CTB, as well as Cu2+ ions can be adsorbed and reload the bentonite platelets. Therefore, zeta potential measurements of BC suspensions were performed by injecting solutions of CTAB and CuSO₄. Results are presented in Figs. 2 and 3. One can see that the zeta potential of the clay suspension is -30 ± 3 mV for suspensions with concentration of clay in the range between 0.025 and 0.05 %, respectively.

By adding a CTAB solution (Fig. 2, curve 1), a gradual decrease of the negative zeta potential with complete neutralization at a CTAB concentration of 5.96×10^{-5} M is observed. Furthermore, a reloading with a final positive zeta potential can be registered. Decrease of the negative zeta potential can be explained by the neutralization of the negatively charged

BC platelets due to electrostatic interactions with CTAB cations and the formation BC-CTAB complexes. Because of the terminating non-polar hydrocarbon surfactant chain, the complex becomes more hydrophobic during this process up to the complete charge neutralization of BC. The following portions of surfactants will be adsorbed by means of hydrophob-hydrophob interactions, leading to the reloading and finally positive zeta potential. It has to be noted that the bentonite suspension remains stable during the whole process of adsorption. This can be explained by predominant steric (nearby zero zeta potential) and respectively electrostatic stabilizing effects (at higher zeta potential values) in dependence on the CTAB concentration.

By using a higher concentrated clay suspension (0.05 %, Fig. 2, curve 2), another picture is observed. For full neutralization of BC, more surfactants (9.40×10^{-5} M) are needed. This is plausible, since the number of particles is doubled. Nevertheless, nearby the neutralization range, coagulation phenomena can be observed. One can conclude that due to the higher particle concentration, the number of particle collisions is increased leading to larger particle aggregates which tend to coagulate. Similar effects were observed by using the other cationic surfactant, i.e., CPB.

Similar zeta potential measurements of bentonite clay suspensions were carried out with heavy metal salts, i.e., by adding CuSO₄ and ZnSO₄. After adding the first part of the CuSO₄ solution (Fig. 3), one can observe a small increase of the negative zeta potential. One can conclude that adding the first portion of salt solution to the clay particles, sulfate anions will adsorb on the positive edges of the aluminosilicate platelets. Further amounts of added salt lead to a gradual decrease of the zeta potential via electrostatic interactions between metal cations and aluminum and silica parts of clay. Nearby the full neutralization of the negative excess charge, a coagulation of the BC suspension can be observed. Similar results were obtained after adding ZnSO₄, not shown here.

According to the results of zeta potential measurements, one can say that cationic surfactants as well as divalent metal salts adsorbed at the BC platelets lead to a neutralization of the surface charge of the BC platelets.

Conductometry is a well known method to detect the critical micellization concentration by using ionic surfactants [30]. Titration curves for water and homopolymer gels (Figs. 4 and 5, curves 3, 4) are virtually identical and demonstrate that the CMC of CTAB is not influenced in the presence of the homopolymer hydrogel. This is convenient, because of homopolymer gels are nonionic, slightly swollen in water ($\alpha \sim 30$), i.e., with an electrical conductivity close to the water. The electrical conductivity is enhanced by adding CTAB molecules and undergoes a break at the CMC in full agreement with relevant literature data [30]. When the same experiments were performed in the presence of BC (Figs. 4 and 5, curves 1), the conductivity sloop is significant higher

Fig. 2 Change of zeta potential of BC after injecting a CTAB solution. [CTAB]=10^{-2} M. [BC] =0.025 % (1) and 0.05 % (2)
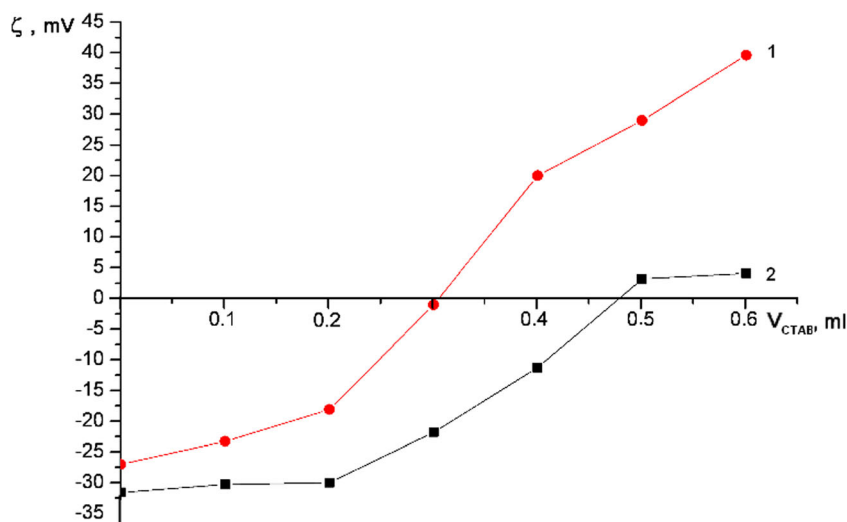
indicating the cleavage of counterions due to the adsorption of surfactants on the surface of the clay platelets. As a result of the electrostatic interaction between BC and CTAB, exchangeable cations of BC (Na$^+$, K$^+$, etc.) and Br$^-$ ions of CTAB contribute to the increased conductivity. This is in full agreement with our zeta potential measurements, already discussed before. Furthermore, the CMC is shifted to higher amounts of surfactant, which can be also related by sorption of CTAB onto bentonite clay. For systems in the presence of composites (Figs. 4 and 5, curves 2), an intermediate place between those for BC and homopolymer gels can be concluded. That means for composite gels after the first break, a second breakpoint is observed. These results can be explained as follows: In the first part, the electrical conductivity increases as usual. After reaching the first breakpoint, with further titration, the sloop becomes steeper and a second break becomes detectable. In this interval (between the two breakpoints), it becomes reasonable that CTAB molecules are adsorbed inside the composition gels. Therefore, the CMC is shifted to higher values. Taking into account the nature of interaction between composite and CTAB, one can say that electrostatic interaction between the clay component of composite and CTAB takes place after reaching the first breakpoint due to the diffusion-controlled penetration of CTAB molecules into the gel matrix.

Similar results were observed for composite for PHEA-BC. In that case, the slope becomes steeper, indicating a better diffusion and availability of the BC inside of the gel matrix. This is in full agreement with our cryo-SEM micrographs showing a more open structure with larger pores for the PHEA-BC composites (compare Fig. 1).

Similar effects can be detected by using another cationic surfactant, i.e., CPB.

Additional conductometric titrations were made with solutions of CuSO$_4$ and ZnSO$_4$. In that case, a steeper slope of the titration curve can be observed already at the beginning. One can see that the curve for the composite-BC system is located in between the curves of BC and the water reference system. This means that already at the beginning of the titration curve, the metal ions can diffuse into the gel matrix and adsorb on the

Fig. 3 Change of zeta potential of BC after injecting a CuSO$_4$ solution. [CuSO$_4$]=10^{-3} M. [BC] =0.1 % (1), 0.05 % (2), and 0.025 % (3)
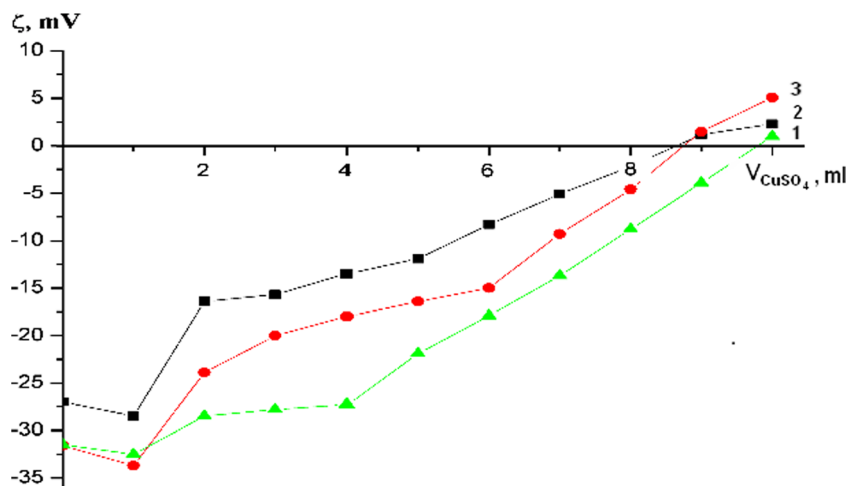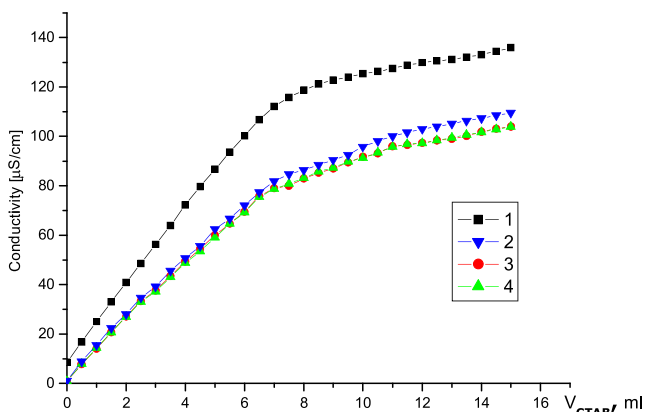
Fig. 4 Conductometric titration by adding a CTAB solution. BC (*1*). PAAm-BC (*2*). PAAm (*3*). Water (*4*). [CTAB]=10^{-2} M

clay platelets. One can explain this faster diffusion behavior due to the significant smaller dimensions of the Cu^{2+} ions in comparison to the larger more hydrophobic surfactant molecules, which are able to form micelles in solution.

Due to the fact that there is no difference in the conductivity at the starting point as well as in the very beginning of the titration curves in the presence or absence of the bentonite clay in the hydrogel as to be seen in Figs. 4, 5, and 6, one can conclude that the water penetrated into the bentonite platelets is of minor importance for the conductivity measurements.

One of the most important properties of surfactants is their ability to accumulate on the interface and decrease surface tension. Therefore, surface tension measurements are very helpful to detect the CMC of aqueous surfactant solutions. The aim of our investigations was to check if sorption phenomena inside the composite will affect the surface tension, too.

The results in Fig. 7 show that in the presence of the composite gel PAAm-BC, more significant amount of CTAB is needed to decrease the surface tension down to the
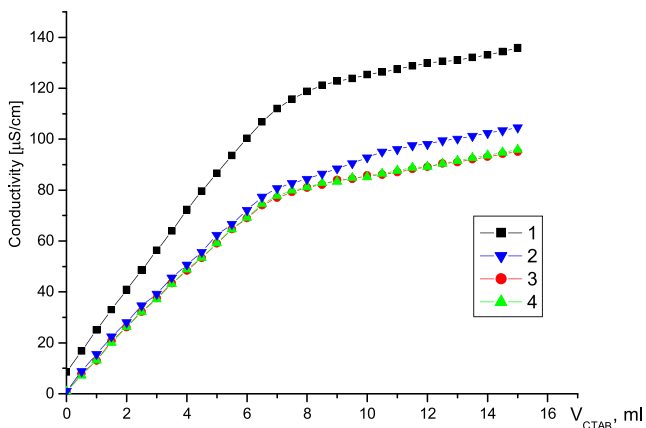

Fig. 6 Conductometric titration by solutions $CuSO_4$ (**a**) and $ZnSO_4$ (**b**). BC (*1*). PAAm-BC (*2*). PAAm (*3*). Water (*4*). [$CuSO_4$]=[$ZnSO_4$]= 10^{-3} M

ground level, this means to reach the CMC. The CMC of CTAB in water achieves at 500 μl, and in the presence of the composite gel at 720 μl, this means at 1.5×10^{-8} mol in water and 2.16×10^{-8} mol in the presence of the composite, respectively. These experiments indicate a shift of the CMC in the presence of the composite due to the surfactant adsorption

Fig. 5 Conductometric titration by solution CTAB. BC (*1*). PHEA-BC (*2*). PHEA (*3*). Water (*4*). [CTAB]=10^{-2} M
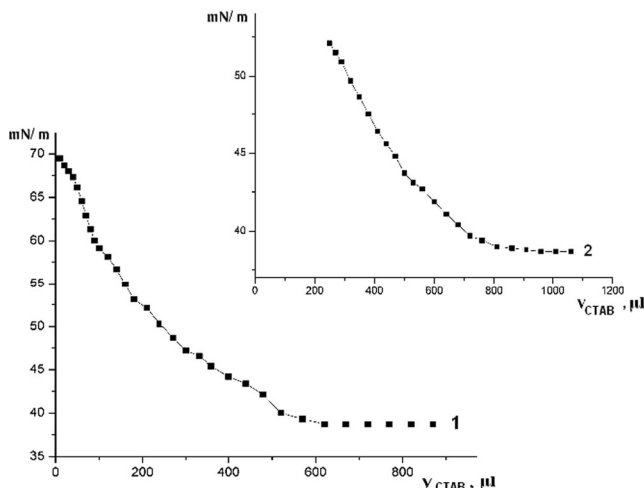

Fig. 7 Dependence of surface tension of water (*1*) and composite PAAm-BC (*2*) from quantity-injected solution of CTAB. [CTAB]=3×10^{-2} M

inside the PAAm-BC composite in agreement with our conductometric measurements, discussed before.

Conclusions

The results first of all show that cationic surfactants, like CTAB and CPB, as well as divalent metal salts, i.e., $CuSO_4$ and $ZnSO_4$, can well adsorb on bentonite clay from Manyrak deposit (Republic Kazakhstan). When the BC platelets are incorporated into a hydrogel matrix, they do not lose their properties to adsorb cationic surfactants and divalent metal ions. Especially, the more open PHEA gel matrix with larger pores, demonstrated by SEM measurements, shows good adsorption properties for both types of adsorbents. Hereby, the adsorption process is diffusion controlled. Conductivity and surface tension measurements coincide that due to the adsorption inside the hydrogel, the CMC is shifted to higher values. However, it seems to be obvious that due to a control of the pore size of the gel matrix, a furthermore improvement of the adsorption properties of the composite material should be possible. Therefore, further experiments are focused on the control of the pore size of the hydrogel matrix to make the hybrid material more effective for the adsorption of cationic surfactants and heavy metal ions.

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