Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.883191

54 (2015) 405–411
April

New hydrophobic hybrid inorganic and organic particles based on poly (n-hexadecyl-4-vinylpyridinium bromide) adsorption on micron-sized bentonite

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Received 30 March 2013; Accepted 30 December 2013

ABSTRACT

A set of copolymers poly(N-hexadecyl-4-vinylpyridinium bromide) [4VP-C_{16}Br-X] ($X = 22$, 50 and 78%) obtained by quaternization of poly(4-vinylpyridine) (P4VP) with 1-bromohexadecane ($C_{16}H_{33}Br$) at various modification percentages was perfectly characterized by conductivity, ^{1}H NMR, and by thermogravimetric analysis (TGA). New organophilic hybrid materials [BC-4VP-C_{16}Br-X] were obtained from bleaching clay (BC) and [4VP-C_{16}Br-X] copolymers. Indeed, the intercalation of these copolymers in interlayer spaces of the clay introduces new properties such as hydrophobic balance. The interlayer structure of the bentonite receives more or less easily, the polycations [4VP-C_{16}Br-X] in order to increase the interlayer volume in the mineral bentonite, then to give it an organophobic character. The characterization of the new composite materials [BC-4VP-C_{16}Br-X] by TGA shows a good stability at high temperature. In order to quantify the hydrophobic nature of the prepared organoclay, these composites were dispersed in aqueous solution in the presence of paranitrophenol (PNP) as indicating agent for the water diffusion into the material. Kinetic measurements of the retained PNP percentages show clearly that water diffusion is directly proportional to the hydrophobic nature of the material. Consequently, more the hydrophobic balance of the composite, less the water diffusion speed.

Keywords: Organoclays; Bentonite; Poly(N-hexadecyl-4-vinylpyridinium bromide); Adsorption; Paranitrophenol (PNP); Kinetics

1. Introduction

Surface modifications of clay minerals have received attention because it allows the creation of new materials and new applications [1,2]. Bentonite, which is predominantly montmorillonite clay, is characterized by an octahedral layer and a net negative surface charge. This charge imbalance is offset by exchangeable cations (Na^+ and Ca^{2+}) at the bentonite surface. The layered structure of the clay expands after wetting. Na^+ and Ca^{2+} are strongly hydrated in the presence of water, resulting in a hydrophilic environment at the bentonite surface [3].

Organoclays are clay minerals in which the inorganic exchangeable cations have been replaced by organic cations. Thus, the clay surface becomes more

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hydrophobic as a function of the organic matter amount [4]. Intercalation of cationic surfactant not only changes the surface properties from hydrophilic to hydrophobic, but also greatly increases the basal spacing of the layers. Such surface property changes affect the applications of the organoclay [5].

These hydrophobic materials have attracted much interest because they have found wide applications as adsorbents of organic pollutants, as components in the synthesis of clay-based polymer nanocomposites and as precursors in the preparation of mesoporous material [6].

Various organoclays have been synthesized using a range of surfactants, including single and dual cationic surfactants [7], anionic–cationic surfactants [8,9], and nonionic surfactants [10]. Modifications of clay minerals with organic cations also have been performed with quaternary alkylammonium salts associated with other organic compound or alkylpyridinium salts due to their high sorption efficacy and it may be useful in different applications. Polycation as hexadecyltrimethylammonium bromide [11] and dodecylpyridinium [12], for example, have been used to prepare organoclays but there is no work concerning the preparation of a new hybrid material organophiles using poly(4-vinylpyridine) (P4VP) quaternized with 1-bromohexadecane.

Side-chain polysalts having a P4VP backbone belong to a new class of comb-like polyelectrolytes, in which the solution and solid properties can be easily controlled by choosing the nature of the quaternizing agent.

The main objective of this study is to obtain well characterized new modified materials from bentonite (BC) of Maghnia modified with P4VP quaternized by 1-bromohexadecane ($C_{16}H_{33}Br$) at different percentage of quaternization. The hydrophobic property of these organomineral composites was established using paranitrophenol (PNP) as an indicating agent for water diffusion into the organoclay composites.

2. Experimental

2.1. Materials

The sample of the bleaching clay (BC) was supplied by a local company (ENOF). It was obtained by the industrial treatment of the drilling bentonite by concentrated sulfuric acid solution.

P4VP was supplied by Aldrich Company. Its average molecular weight, close to 160,000 g/mol, was determined by capillary viscosity using the empirical Mark-Houwink power law [13]. All the solvents (analytical grade) were supplied by Aldrich and used without further purification.

2.1.1. Thermogravimetric analysis (TGA)

Thermogravimetry experiments were carried out on a 2950 TGA V5.4A instrument. Measurements were performed under air atmosphere. The same conditions were used for all tests, with a heating rate of 10°C/min in the temperature range between 30 and 800°C.

2.1.2. Conductivity measurements

A standard conductivimeter CD75 Taccussel was used. The rate of quaternization of the copolymers [4VP-C_{16}Br-X] was estimated by the conductivity measurements of anions Br^- using a silver nitrate solution. Thus, the concentration of the bromide anions is calculated using the equivalent volume of this solution.

2.1.3. ^{1}H NMR analysis

Proton nuclear magnetic resonance ^{1}H NMR spectra of [4VP-C_{16}Br-X] (see Fig. 1) were recorded with a Brucker 300 MHz, at room temperature.

2.1.4. UV–visible spectrophotometry

Jenway 6405 UV–vis. spectrophotometer was used to monitor the kinetics of PNP adsorption on the organoclays [BC-4VP-C_{16}Br-X]. The absorbance was measured at 317 nm. All the measurements were carried out in a 1 cm quartz cell.

2.1.5. Preparation of poly(N-hexadecyl-4-vinylpyridinium bromide)

0.05 mol of P4VP were dissolved in 50 ml of absolute ethanol, and then introduced in 100 ml flask. A known amount of $C_{16}H_{33}Br$ was added. The mixture was stirred for 25 d at 70°C. After evaporation of excess solvent, the resulting product was dissolved in chloroform and precipitated in a large amount of hexane.

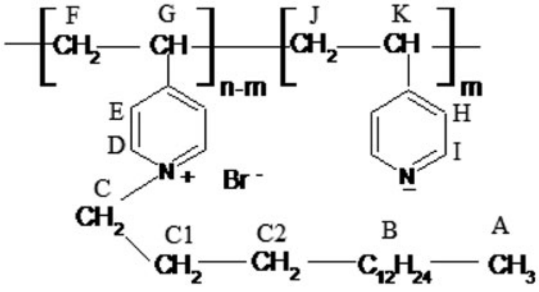

Fig. 1. Structure of poly(N-hexadecyl-4-vinylpyridinium bromide).

The product was dried at 70˚C for 24 h. Three copolymers were synthesized and named [4VP-C_{16}Br-X], where *X* corresponds to the quaternization percentage of the pyridinic moieties (*X* = 22, 50, and 78%). These samples were characterized by conductivity, ^{1}H NMR, and TGA analysis, as described below.

2.1.6. Preparation of organoclays

Two grams of bentonite (BC) was dispersed in 20 ml of absolute ethanol, and then introduced in a 50 ml flask under nitrogen. A known amount of [4VP-C_{16}Br-X] copolymers dissolved in 7 ml of ethanol previously degassed with nitrogen was added dropwise. The mixture was stirred during 24 h, centrifuged at 20 min with 4,500 rpm and dried at 75˚C during 24 h. The same procedure is used for the three copolymers. The organoclay composites are named [BC-4VP-C_{16}Br-X] and characterized by TGA, as described below.

2.2. Adsorption of PNP on organoclay composites

The hydrophobic property of these organoclay composites was established using the (PNP) as the indicating agent for the water diffusion into these composites. Fifteen parts per million of PNP solution was initially prepared. The pH of these solutions was carefully adjusted at pH = 5, by addition of 0.1 M solutions of hydrochloric acid (HCl) or sodium hydroxide (NaOH). Then, 20 mg of organoclay composites [BC-4VP-C_{16}Br-X] was introduced in these PNP solutions. The mixtures were equilibrated by stirring in a water bath for 6 h at 25 ˚C. The mixtures were then centrifuged at 4,500 rpm for 15 min. The amount of PNP present in the supernatant was analyzed using UV–visible spectroscopy at the wavelength of 317 nm. The amount of adsorbed PNP at various equilibrium times q_e (mg/g) was calculated using the following relationship:

$$q_e = \frac{(C_0 - C_r) \cdot V}{m}$$

where C_0 and C_r (mg/L) are the initial and *t* time PNP concentrations, respectively. *V* and *m* are the liquid volume (L) and the weight of dried used adsorbent (g).

3. Results and discussion

3.1. Characterization of poly(N-hexadecyl-4-vinylpyridinium bromide)

The rate of the quaternization of various copolymers was estimated by conductivity technique. The results of the analyses are represented in Table 1.

^{1}H NMR spectra confirm the presence of the various protons of the structure [4VP-C_{16}Br-X] and permit to determine the quaternization percentages of the copolymers by integrating the peak areas. Fig. 2(a)–(c) gives, respectively, the ^{1}H NMR spectra of the copolymers [4VP-C_{16}Br-X] (*X* = 22, 50, and 78%).

The chemical shifts of the signals from the three copolymers are similar. The proton integration is related to the alkyle chains $C_{16}H_{33}$ amount in each sample.

^{1}H NMR spectra of [4VP-C_{16}Br-X] are as follows:

0.92 ppm (H_A, 3H), 1.32 ppm ($H_{B+J+K+F+G}$, 30H), 1.7–2 ppm (H_{C1} 2H), 2–2.72 ppm (H_{C2} 2H), 4.5–4.6 ppm (H_C, 2H), 6.8 ppm (H_H atom at the meta position of N, 2H), 7.5–8.2 ppm (H_E atom at the ortho position of N^+, 2H), 8.24 ppm (H_I atom at the meta position of N, 2H), 8.6–8.8 ppm (H_D atom at the ortho position of N^+, 2H) [14,15].

TGA permits the quantification of the amount of the quaternized $C_{16}H_{33}Br$ onto P4VP copolymer. Fig. 3(a) shows that pure P4VP decomposes in a narrow range of temperature beyond 300˚C and up to 400˚C [2].

The first loss of weight of 3–7% was observed between 30 and 200 ˚C. This represents the removal of residual water molecules and traces of solvent from the copolymers. At 230˚C, a sudden and rapid weight loss appeared independently of the percentage of quaternization of each copolymer. This behavior is similar to that of the quaternized P4VP [16,17] and corresponds to the rapid dequaternization by breaking of C–N^+ bond. This first step was followed at about 360˚C by a second decomposition step corresponding to the slower degradation of the backbone.

The dequaternization mechanism proposed by Claret and Williams [16–18] assumes the cleavage of C–N^+ bonds with the simultaneous formation of a pyridinium ion radical associated with the counter ion and the transfer of one electron from the counter ion to a π^* orbital of the pyridinium ring.

Table 1
Estimation of the quaternization percentages in the copolymers [4VP-C_{16}Br-X]

Quaterisant (I)	Molar rate : I/P4VP	Time reaction	Quaternization % (mole/mole)
$C_{16}H_{33}Br$	1	2 d	22%
	1	7 d	50%
	1	25 d	78%

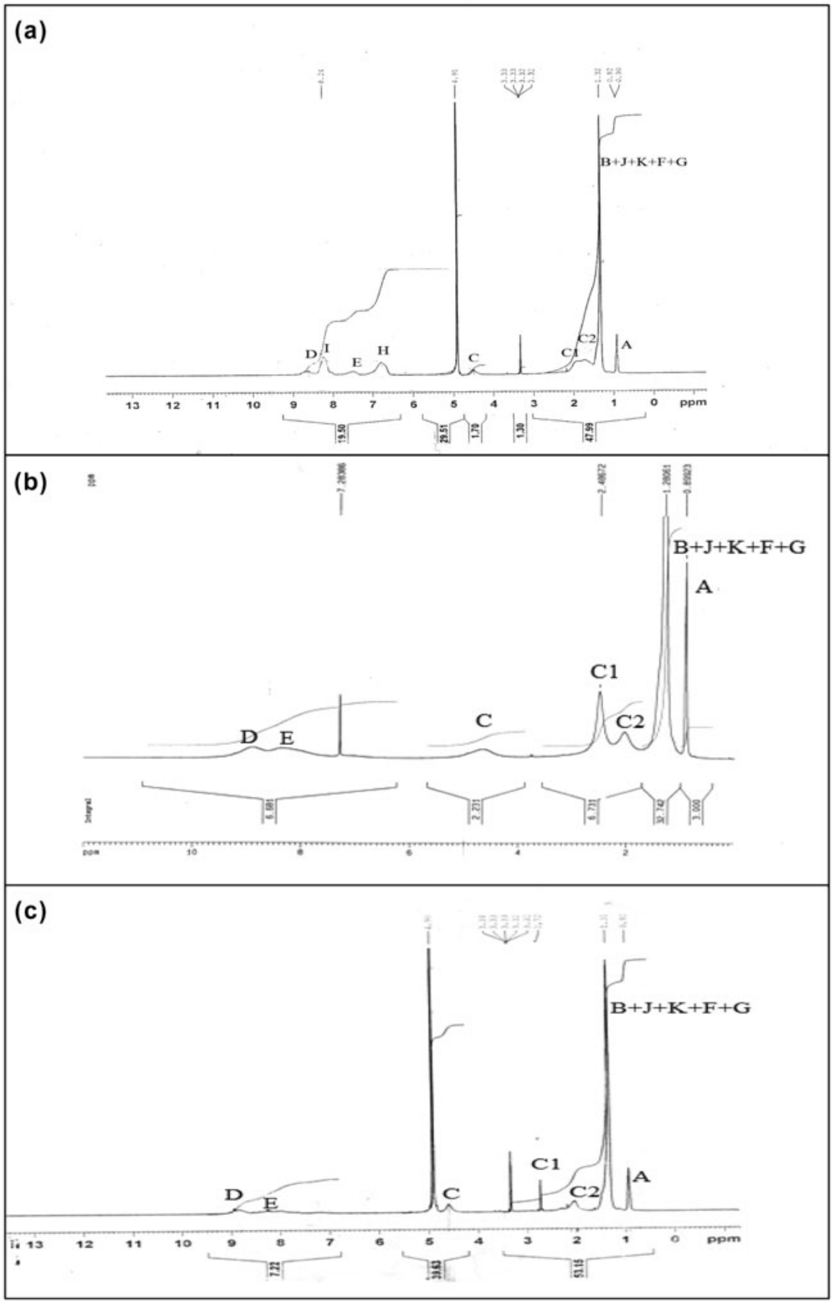

Fig. 2. ^{1}H NMR spectra of (a) [4VP-C_{16}Br-22%] (MeOD), (b) [4VP-C_{16}Br-50%] ($CDCl_3$), and (c) [4VP-C_{16}Br-78%] (MeOD).

According to this mechanism, the first decomposition step observed with our samples must correspond to the simultaneous loss of both the $C_{16}H_{33}$ and the anion. We have assumed that the percentage of quaternized P4VP could be simply estimated as the difference between the weight loss of copolymer [4VP-C_{16}Br-X] between 230 and 360˚C. An example of thermogram is given in Fig. 3(b) for [4VP-C_{16}Br-78%].

3.2. Adsorption of [4VP-C_{16}Br-X] on bentonite (BC)

The TGA thermograms allow the quantification of the amount of [4VP-C_{16}Br-X] coated onto bentonite.

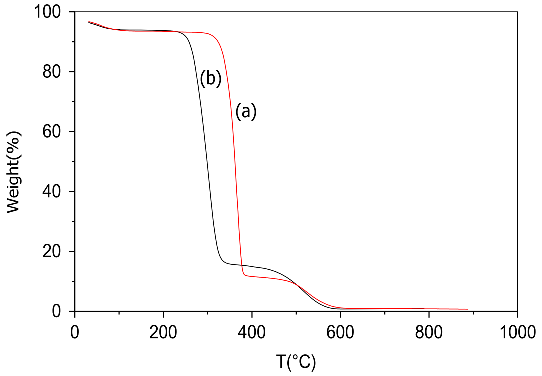

Fig. 3. TGA thermograms of (a) [P4VP] and (b) [4VP-C_{16}Br-78%].

Thermograms of natural and modified bentonites are depicted in Fig. 4. For the unmodified clay (BC), an initial weight loss between 30 and 200˚C is observed due to the residual water. There is also decomposition between 380 and 650˚C associated with dehydroxylation of the aluminosilicate [19]. We have assumed that the percentage (*w*/*w*) of coated [4VP-C_{16}Br-X] could be simply estimated as the difference between the weight loss of modified bentonite between 200 and 800˚C and that obtained for pure bentonite. 15.67% represents a maximum amount of adsorbed [4VP-C_{16}Br- 50%] which was studied here. (Table 2).

Granulometry of the treated clay was performed locally in the Civil Engineering Department (Tlemcen University) using a sedimentation technique with a 0.1% sodium hexametaphosphate solution; 95% of treated clay grains have diameter less than 100 μm. The cation exchange capacity was 48.2 mEq/100 g of treated clay and the surface area was 185 m^2/g with an average pore size of 7 nm [20]. The XRD patterns of the new hybrids show that interlayer space increases at about 22.06 Å (Figs. 5 and 6).

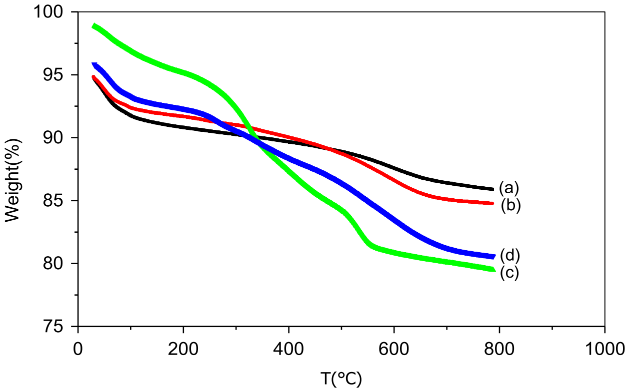

Fig. 4. TGA thermograms of: (a) BC, (b) [BC-4VP-C_{16}Br 22%], (c) [BC-4VP-C_{16}Br 50%], and (d) [BC-4VP-C_{16}Br 78%].

Table 2
Weight percentage of coated [4VP-C_{16}Br-X] on BC bentonite (2 g) in relation with initial [4VP-C16Br-X] (initial P4VP in 20 ml of ethanol, contact time = 24 h)

Sample	Initial amount of P4VP (g)	Weight loss % from 30 to 200˚C (Water)	Weight loss % from 200 to 800˚C (P4VP)
[4VP-C_{16}Br-22%]	0.2	3	6.77
[4VP-C_{16}Br-50%]	0.2	3	15.67
[4VP-C_{16}Br-78%]	0.2	3	11.72

3.3. *Hydrophobicity of material composites.*

Adsorption experiments were carried out for 6 h to find the optimal contact time. Adsorption kinetics of PNP at pH = 5 and 25˚C (Fig. 7) show that equilibrium

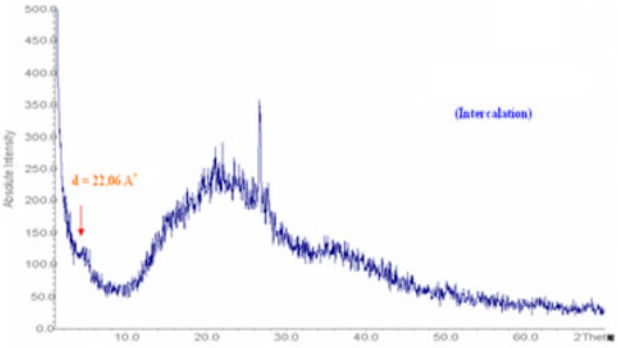

Fig. 5. XRD pattern of [BC-4VP-C_{16}Br 50%].

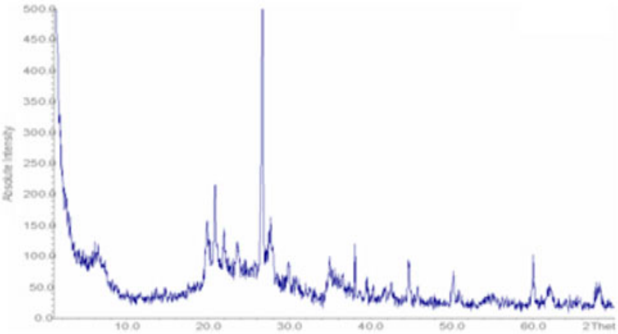

Fig. 6. XRD pattern of BC.

was attained at 90 min. for two organoclay composites [BC-4VP-C$_{16}$Br-22%] and 78% and 45 min. for [BC-4VP-C$_{16}$Br-50%].

Such plots may indicate that three adsorption steps occur. The first portion is characterized by time of damping of bentonite. The delay in the retention of PNP by the support is due to the increased hydrophobicity caused by alkyles. The second portion is fast characterized by rapid attachment of *p*-nitrophenol to the surface or the interlayer of organoclays materials with quantities of 1.31 mg/g for [BC-4VP-C$_{16}$Br-22%], 4.69 mg/g for [BC-4VP-C$_{16}$Br-50%], and 3.32 mg/g for the support [BC-4VP-C$_{16}$Br-78%]. The variation of the concentration of PNP indicates the diffusion of the aqueous solution in composite material. The third portion is slower due to the repulsive force and at this level, there is a pseudo-equilibrum between the rates of adsorption and desorption.

The results of kinetic adsorption of PNP on bentonite show that the modification of the bentonite by polycations [4VP-C$_{16}$Br-X], or *X* = 22, 50, and 78% introduced in the materials hydrophobic properties. These results become interesting in the case of the composite material prepared starting from the copolymer [4VP-C16Br-50%] or the diffusion of the PNP of the aqueous phase to interlamellaire volume of bentonite reaches its maximum values.

The observation of these results suggests that the copolymer was adsorbed on the surface of bentonite. It is associated with the negative charge of the surface to compensate the positive charges of N$^+$. Indeed, the rate of charges of the quaternized polymer changes the electrostatic balance of the interlamellar space, rather than the retention of PNP. The screen of the bentonite charges by the polyelectrolyte [4VP-C$_{16}$Br-X] makes the interlayer space less polar. Therefore, the diffusion of water molecules that carry with them the PNP molecules becomes difficult.

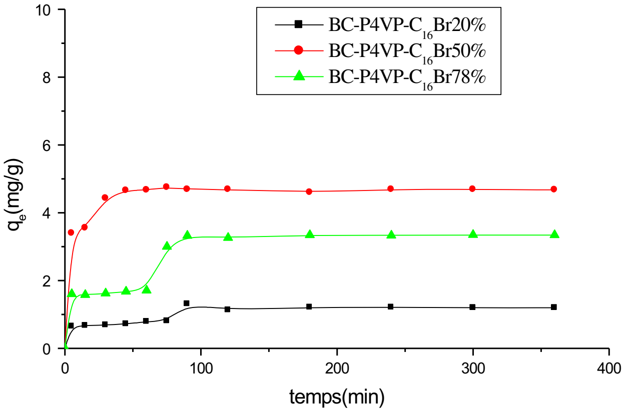

Fig. 7. Kinetics of PNP adsorption on [BC-4VPC$_{16}$Br-X] at pH = 5 of the PNP solution (*V* solution, *m* adsorbent) (10 ml, 20 mg), initial concentration of PNP 15 ppm, *T* = 298 °K.

In fact, the rate of charges increases the concentration of PNP removal by facilitating the water and the PNP molecules diffusion onto the bentonite interlayer. On the other hand, the quaternized agent C$_{16}$Br increases first the PNP retention capacity. When, the concentration of the quaternized agent C$_{16}$Br increases, the PNP removal will be lower, because the increasing of the sterical effect decreases the diffusion of the PNP molecules onto the bentonite interlayer. The hydrophobicity of the composite material is managed by the equilibrium of the balance between the rate of charges in the interlayer space and the rate of quaternized alkyls immobilized on the P4VP.

4. Conclusion

Bentonite has been successfully modified using novel cationic copolymers with three percentages of quaternization. The TGA results show intercalation of organic cations [4VP-C$_{16}$Br-X], where *X* = 22, 50, and 78% between the clay mineral layers. The ATG curves for these organoclays show four-step degradation which corresponds to degradation due to residual water desorption, dehydration, followed by decomposition of the organic modifier and the dehydroxylation of the organoclays. The hydrophobic property of these organoclays composites was established using the paranitrophenol (PNP) as indicating agent for the water diffusion into these composite. The results of kinetic adsorption of PNP on bentonite show that the modification of the bentonite by polycations [4VP-C$_{16}$Br-X], or *X* = 22, 50, and 78%, introduced in the materials hydrophobic properties. These results become interesting in the case of the composite material prepared starting from the copolymer [4VP-C16Br-50%] or the diffusion of the PNP of the aqueous phase to the interlamellar volume of bentonite reaches its maximum values.

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