Sorption Properties of Polymers Based on *N*-Substituted Maleimides

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ABSTRACT: Physicochemical and functional properties of 2,2-diallyl-1,1,3,3-tetraethylguanidinium chloride copolymers with *N*-(*n*-carboxyphenyl)maleimide, of *N*-vinylpyrrolidone with *N*-(*n*-carboxyphenyl)maleimide, and of *N*-vinylpyrrolidone with *N*-phenylmaleimide have been investigated. Specific surface area and porosity of the copolymers under investigation have been determined by using the low-temperature adsorption method. Electron microscope investigations in surfaces of the polymers have evinced that all of them have a spongy microstructure, the *N*-vinylpyrrolidone copolymer with *N*-(*n*-carboxyphenyl)maleimide being the most homogeneous of these. Sorption capacity of the copolymers toward Re(VII) ions has been investigated. The process is described by the Langmuir isotherm. The pH is the most important parameter for sorption process of Re(VII). In the conjoint presence of Re(VII) and Mo(VI) in a solution of acid and ammoniac mediums, rhenium can be separated from molybdenum by using the sorbents under investigation at pH > 4.5 or at hydrochloric acid concentrations 0.1 mol L^{-1} and more. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1978–1983, 2013

INTRODUCTION

Maleimides (MI), due to their availability, have found a number of applications as thermoreactive binders in construction materials. Materials based on maleimide binders are stable, have high fire resistance and good dielectric properties. Maleimides are stable up to 200–250°C.[1,2]
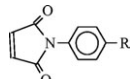
Copolymers of *N*-vinylpyrrolidone are also of a great interest. They are used in machinery, medicine, cosmetics, pharmaceuticals, and agriculture. This can be explained by the fact that polyvinylpyrrolidone has good solubility in water and in many organic solvents capable to complex with numerous inorganic, organic, and biological objects and has biocompatible and immune inertness properties.[3,4]

It is known that compounds containing guanidine group have a wide spectrum of bactericide action and are used as medications and fungicides; therefore, the presence of guanidine group in an elemental unit of a polymer has to impart high biocide action to the polymer.[5,6] Over the last years, such alkylguanidines as extraction agents and sorbents of dicyanoaurate ions from aqueous and alkaline solutions attract the attention of researchers.[7,8] From this point of view, investigation of sorption properties of copolymers based on *N*-substituted maleimides is of interest.

The aim of this work was to investigate physicochemical properties of 2,2-diallyl-1,1,3,3-tetraethylguanidinium chloride copolymers with *N*-(*n*-carboxyphenyl)maleimide, of *N*-vinyl-pyrrolidone with *N*-(*n*-carboxyphenyl)maleimide, and of *N*-vinyl-pyrrolidone with *N*-phenylmaleimide. Furthermore, sorption processes of the given copolymers with Re(VII) and Mo(VI) were investigated with the aim to see whether is it possible and under what conditions Re(VII) and Mo(VI) ions can be extracted.

EXPERIMENTAL

N-substituted maleimides (MI) were synthesized according to the method described in our previous work[9] in which ether was replaced by acetone as a solvent. The following compounds were used in this work: phenylmaleimide (PMI) (R=H, mp 89°C), carboxyphenylmaleimide (CPMI) (R=COOH, mp 240°C). 2.2-Diallyl-1.1.3.3-tetraethylguanidinium was prepared as per the method described in Ref. 10. *N*-vinylpyrrolidone (VP, fraction with bp 65°/1.5 torr, n_D^{20} = 1.5117, product of Lancaster Co.) was dried over KOH and distilled under vacuum. Initiator azobisisobutyronitrile (AIBN) and solvents used in the work were purified by means of standard methods and have characteristics in accordance to literature data.[11]

Copolymerization of PMI and CPMI was performed in ampoules, under vacuum, as per the methods described in Refs. 12 and 13. The monomers were mixed in suitable molar proportions and

copolymerization was conducted in bulk and in dimethylacetamide in the presence of initiator AIBN (3×10^{-2} mol L^{-1}).

Polymerization was finished by precipitation of the polymer. Purification of the copolymers was performed by triple precipitation from the solvent into precipitator specially selected for each "solvent/precipitator" system: dimethyl sulfoxide/water for copolymers of 2.2-diallyl-1.1.3.3-tetraethylguanidinium chloride with CPMI; chloroform/ethanol for vinylpyrrolidone with PMI; dimethyl acetamide/methanol for vinylpyrrolidone with CPMI. Copolymers were dried under vacuum at 40–50°C until a constant mass. Composition of copolymers was determined from results of elemental analysis.

The reduced h_{red} and intrinsic $[h]$ viscosity measurements were performed in an Ubbelohde capillary viscometer at 25 ± 0.1°C in dimethylacetamide.

To prepare a standard solution of rhenium(VII), NaReO$_4$ (the analytical grade) was dissolved in distilled water, whereupon the total volume in a volumetric flask was increased up to 100 mL (1 mL solution contained 0.1 mg rhenium). Solutions with lower contents of rhenium(VII) were prepared by subsequent dissolution of the standard solution. The Re(VII) contents in saturated solutions were determined using titrimetric analysis with SnCl$_2$.[14] Concentration of SnCl$_2\cdot$2H$_2$O solution was determined as per the known method.[15] The Re(VII) contents in diluted solutions (up to 20 mg L^{-1}) was determined using photometrical method, while determining residual rhenium contents in the rhodanide complex.[16] Initial solutions of Na$_2$MoO$_4$ were prepared from preparations of the analytical grade. Concentrations of molybdenum(VI) ions were determined on the KFK-3-01 conductometer while using photometrical method.[17]

To sorb, the solutions containing either only Re(VII) or Re(VII) and Mo(VI) conjointly, and hydrogen chloride acid or ammonia in respective concentration were mixed with 5.8 mg of copolymers. In 20 min, residual content of either Re(VII) ions or Re(VII) and Mo(VI) ion conjointly was determined in aqueous phase by using the KFK-3-01 conductometer.[16,17]

The static sorption capacity value in respect of metal (E^M) was determined judging from the difference in metal concentrations in the solution before and after sorption (error not over 5%).

Textural characteristics of the copolymers—specific surface area (S_{Bet}, m^2 g^{-1}), total pore volume (V_{tot}, cm^3 g^{-1}), and average pore diameter (D_{av}, Å)—were determined by using the ASAP 2020 analyzer (Micrometrics Instrument Co., USA). A weighted portion of a sample (≈ 0.3 g) taken to fifth digit was preliminary degassed at 413 K for 3 h, whereupon the sample was weighted anew. Analysis was conducted in a low-temperature regime supported by liquid nitrogen. Gaseous nitrogen was used as an adsorbate. Specific surface area values were determined by using the BET method, total pore volume and average pore diameter values were determined by using desorption isotherm and the BJH model.

Thermodynamic characteristics of sorption equilibriums—limiting adsorption value (Γ_∞, mg L^{-1}) and adsorption equilibrium constant (K)—were calculated by means of linearization of the Langmuir adsorption isotherm[18]:

$$\Gamma = \Gamma_\infty \frac{K \cdot C}{1 + K \cdot C}, \qquad (1)$$

while representing it as:

$$\frac{C}{\Gamma} = \frac{1}{K \cdot \Gamma_\infty} + \frac{C}{\Gamma_\infty}, \qquad (2)$$

where Γ is the adsorption value, mol g^{-1} and C is the equilibrium concentration of the substance in the solution, mol L^{-1}.

RESULTS AND DISCUSSION

The copolymers: 2.2-diallyl-1.1.3.3-tetraethylguanidinium chloride with CPMI (I), N-vinylpyrrolidone with CPMI (II) and N-vinylpyrrolidone with PMI (III) were obtained by radical copolymerization in the presence of the radical AIBN initiator.
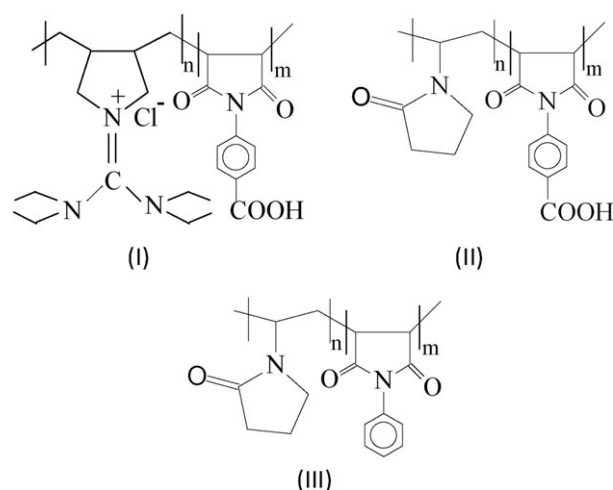

Copolymers are soluble in DMSO, DMFA and are insoluble in other common solvents. Copolymers (I) and (II) are soluble also in aqueous solution of NaOH and copolymer (III) is soluble in chloroform.

Copolymers (I) and (II) possess polyelectrolyte properties—the intrinsic viscosity of copolymer solution increases with dilution. The adding of low-molecular polyelectrolyte (1 N NaCl, 4 N LiCl) does not allow to suppress the polyelectrolyte effect due to their bad solubility in dimethylacetamide.

The intrinsic viscosity of copolymer (III) depends on the copolymer synthesis conditions. The viscosity $[h]$ of copolymer synthesized in organic solvents (dimethylacetamide) is somewhat higher than the corresponding values for the copolymer obtained in bulk. The values of intrinsic viscosity copolymer solution (dimethylacetamide, 25°C) are 0.58 dL g^{-1} in the case of copolymer synthesized in dimethylacetamide and 0.30 dL g^{-1}—obtained in bulk.

Characterizations of the (I), (II), and (III) copolymers' texture were determined using low temperature nitrogen sorption at 77
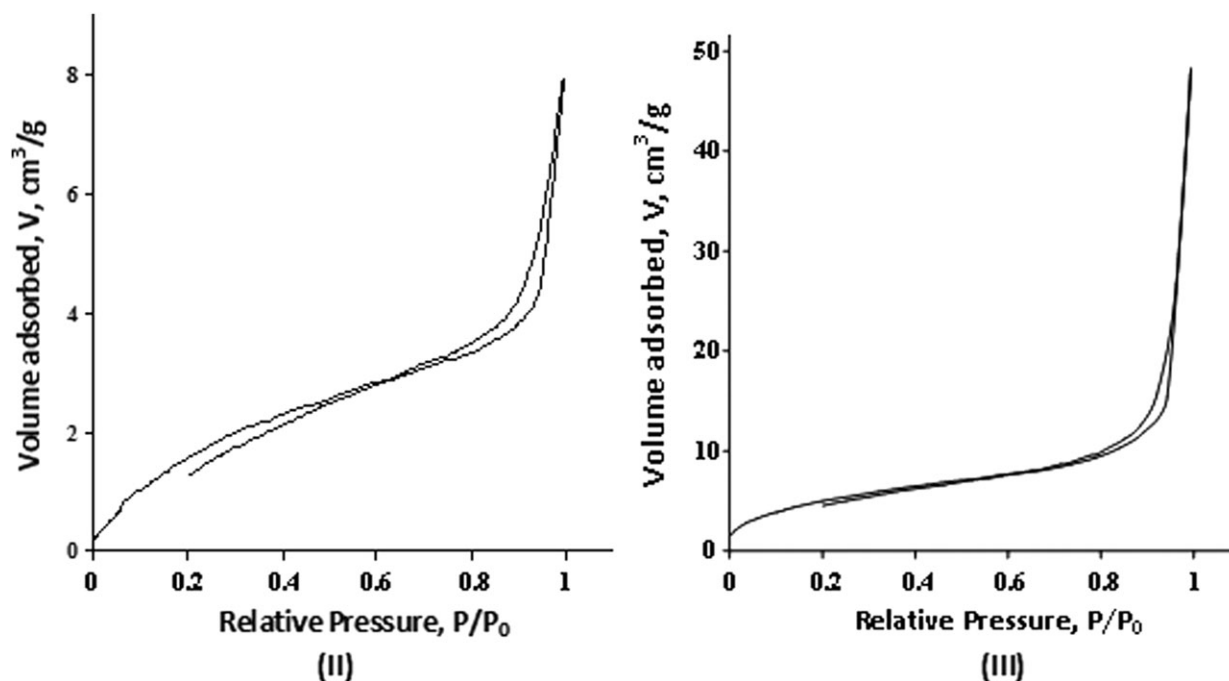
Figure 1. Adsorption/desorption isotherms of nitrogen for the copolymer (II) and the copolymer (III).

K after degassing the material under vacuum at 413 K for 3 h. Adsorption/desorption isotherms are represented in Figure 1.

There are available six basic types of isotherm.[19,20] Nitrogen adsorption isotherm plotted for the copolymer (I) is equal to the adsorption isotherm plotted for the copolymer (III). Mentioned isotherms are isotherms of third type, which describe processes on the surface with relatively weak adsorption capacity.

The isotherm plotted for the copolymer (II) pertains to the second type of adsorption isotherm describing adsorption processes followed by formation of polymolecular layers.[21]

Standard calculation models were used for processing the data, and results are represented in Table I.

Thus, the copolymers (I) and (III) are macro-porous (the generalized Langmuir theory is fair for such sorbents, pores playing

Table I. Structural Characteristics of the Samples as per the Low-Temperature (77 K) Adsorption/Desorption of Nitrogen

| Structural characteristics of the samples as per the low-temperature (77 K) adsorption/desorption of nitrogen		(I)	(II)	(III)
Specific surface area, S (m^2 g^{-1})	• As per the Langmuir method	33.5	6.1	17.5
	• As per the BET method	36	7.0	18.1
	• As per the Halsey method	51.6	11.5	23.2
	Total adsorption surface area of pores as per the BJH method in the 1.7–300 nm interval	35	3.9	14.1
	Total desorption surface area of pores as per the BJH method in the 1.7–300 nm interval	40.8	7.1	17.4
Specific pore volume, V (cm^3 g^{-1})	• Adsorption (total) volume	0.198	0.012	0.074
	• Micropore volume	0.0083	0.003	0.0026
	Total adsorption pore volume as per the BJH method in the 1.7–300 nm interval	0.192	0.01	0.07
	Total desorption pore volume as per the BJH method in the 1.7–300 nm interval	0.199	0.01	0.075
Pore size (Å)	• Average adsorption width (the BET method)	220	70	165
	• Average adsorption width (the BJH method)	219	103	200
	• Average desorption width (the BJH method)	195	70	173
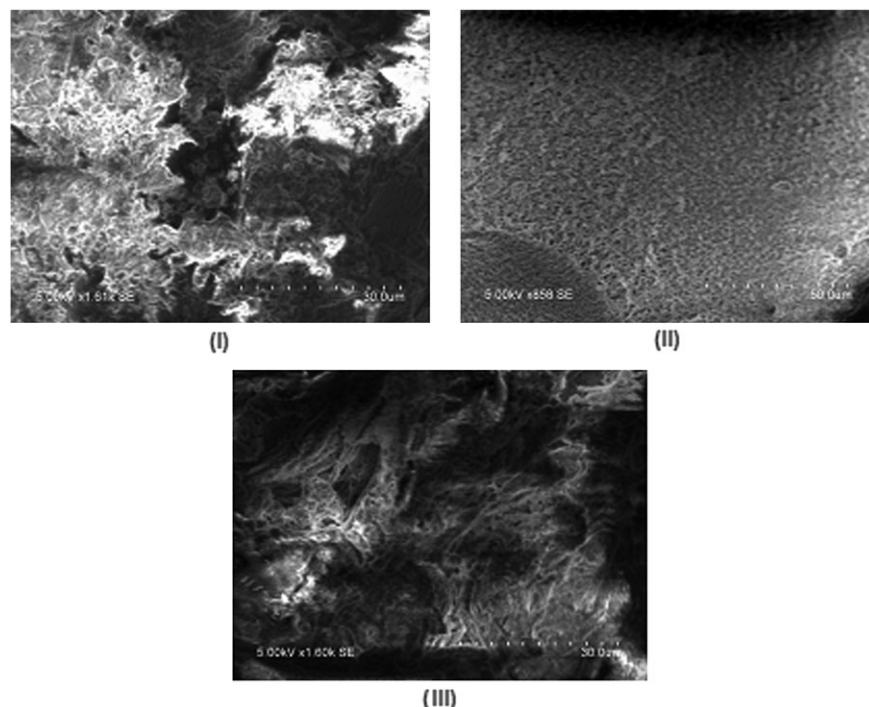
Figure 2. Microstructures of the copolymers (I), (II), and (III).

the role of transportation channels), whereas the copolymer (II) can be regarded as a transitional pore body. On pore walls of such bodies, polymolecular adsorption takes place under moderate relative pressures while resulting in capillary condensation on the increase in relative pressure values.

Electron microscopy investigations in copolymers' surfaces have shown that all three copolymers have a spongy microstructure and that copolymer (II) is the most homogenous (Figure 2).

Further on, sorption capacity of all three synthesized copolymers as adsorbents for Rhenium(VII) was investigated.

The porous structure can appreciably influence the adsorption kinetics. On the porous materials adsorption, the substance transfer stage inside the pores starts, this stage being featured

mainly by the diffusion mechanism. Frequently, this stage determines adsorption equilibrium period.

The study of the rhenium sorption kinetics process has shown that the maximal fill-up degree of the sorbents' surface (I–III) is achieved within 20 min (Figure 3). After that, desorption process starts, the E^M value decreases, rhenium ions are returning back to the solution. In Figure 3, sorption capacity versus time for the sorbent (II) has been plotted. This dependence is similar for sorbents (I) and (III). Furthermore, temperature dependence of Re(VII) adsorption was investigated in neutral media. Higher temperatures increase rhenium desorption process (Table II).

It is visible from the result shown in Table II that efficiency is appreciably dependent on the pH value of solutions
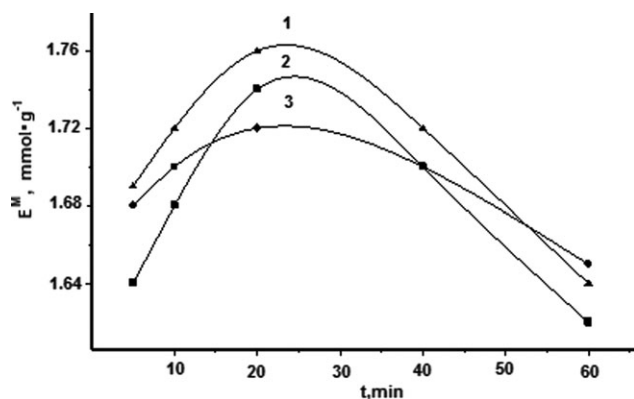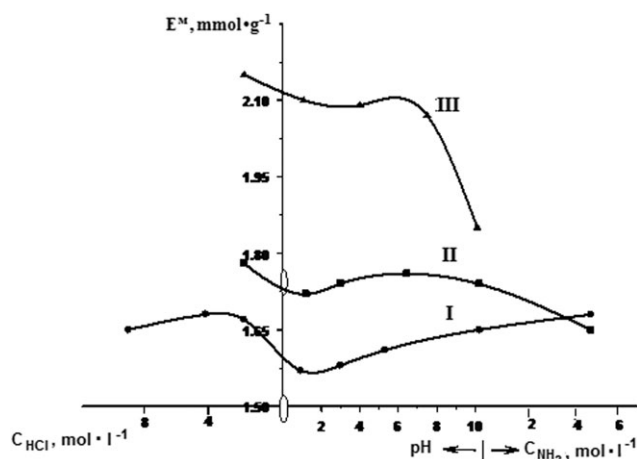

Figure 3. Sorption capacity versus time for the sorbent (II). 1—pH 6.5; 2—pH 10; 3—pH 1.2.

Table II. Re(VII) Sorption by Sorbents (I), (II), and (III) versus Temperature

Sorbent	pH	E^M (mmol g^{-1})		
		22°C	50°C	80°C
Copolymer (I)	1.2	1.56	–	–
	7.1	1.60	1.48	1.10
	10.1	1.65	–	–
Copolymer (II)	1.2	1.72	–	–
	6.5	1.76	1.50	1.20
	10.2	1.75	–	–
Copolymer (III)	1.1	2.05	–	–
	7.5	2.10	1.10	1.00
	10.1	1.85	–	–

Figure 4. Sorption capacity of the copolymers (I), (II), and (III) at different pH values for Re(VII) ions. $C_{Re(VII)} = 297.92$ mg L^{-1}, $m_{(I), (II), and (III)} = 5.8$ mg, $V_{aqueous\ phase} = 25$ mL, $\tau = 20$ min.

(hydrochloric acid and ammonia concentrations). The acidity of reaction medium has an effect on both a chemical form of a metal in solution and sorption capacity of the sorbent. In diluted solutions of acids and alkalis, the Re(VII) is present as a weakly hydrated perrhenate of the ReO$_4^-$ ion.[14] The profile of the pH value's influence on the sorption degree of rhenium is represented in Figure 4.

The statistical Re(VII) sorption capacity value (E^M) from HCl and NH$_3$ solutions equals approximately 1.65 for (I), 1.8 for (II), and 2.1 for (III) which is, apparently, attributed to the steric factor. Further increase in the hydrogen chloride acid concentration leads to the decrease in Re(VII) extraction.

The obtained data indicate a possibility to effectively extract rhenium(VII) by means of the sorbents (I–III) from solutions at hydrochloric acid's concentration over 0.1 mol L^{-1} and at that of ammonia—over 5 mol L^{-1}.

A weakly acid medium is most applicable in the rhenium extraction industry, therefore dependency of rhenium ions' adsorption of the copolymer (I) versus Re concentrations was investigated at pH 5.3. The rhenium(VII) adsorption process was described by the Langmuir isotherm linearized in the $C_{Re(VII)}/E^M - C_{Re(VII)}$ coordinates [Figure 5(a,b)].

Limiting adsorption, equilibrium constant in the Langmuir equation, and the Gibbs energy characterize a sorbent and evince its expediency. Especially important is the limiting adsorption value indicating an adsorbate's maximal quantity which can be extracted by one mass unit of an adsorbent.

Calculated were: values of limiting sorption capacity (E_∞) for the copolymer (I) equaling 0.71 mol Re(VII)·g^{-1} of the sorbent and K (adsorption equilibrium constant) value equaling 7.8 L mol^{-1}. Variation of the standard Gibbs energy in the adsorption process calculated as per the equation:

$$\Delta G^0 = -RT \ln K \tag{3}$$

was equal to -22.3 kJ mol^{-1}.
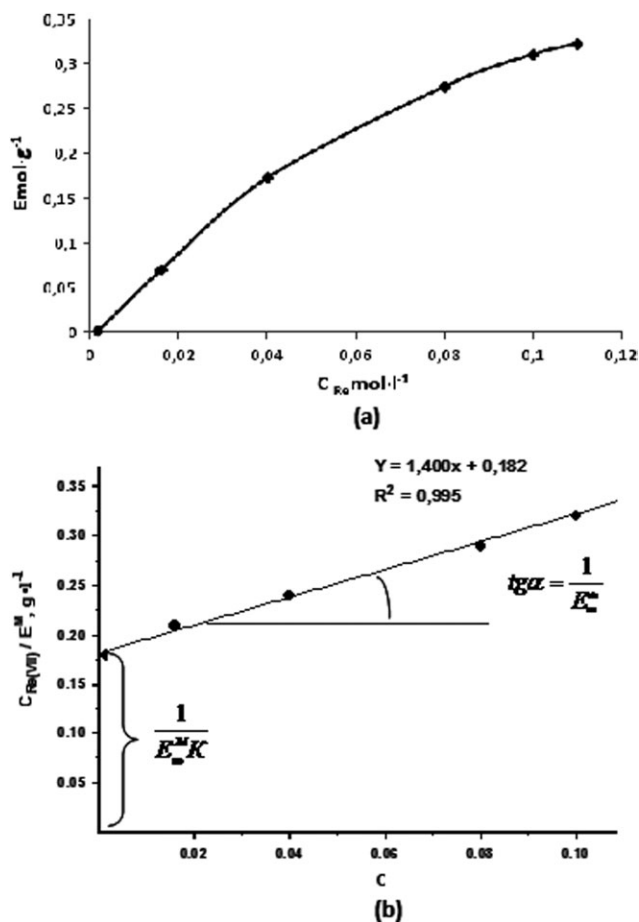
Figure 5. Rhenium(VII) adsorption isotherm by the sorbent (I) (a) and its linearization (b): $m_{(I)} = 5.8$ mg, pH 5.3, $V_{aqueous\ phase} = 25$ mL, $\tau = 20$ min.

Due to the fact that molybdenite concentrates are basic source of Re(VII), and its extraction proceeds concurrently with the ores processing,[14] efficiency of the Re(VII) in the presence of molybdenum in aqueous mediums was evaluated.
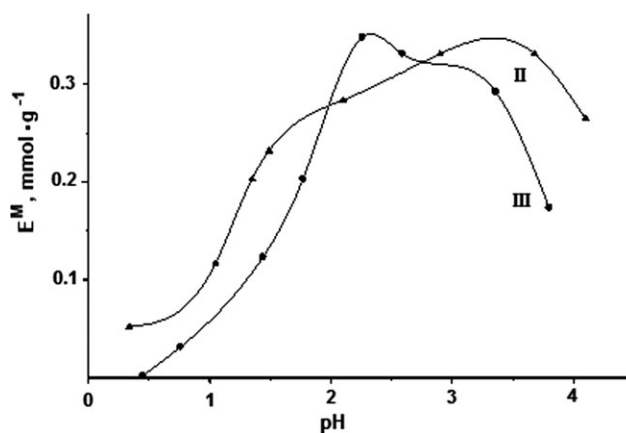
Figure 6. Sorption capacity of the copolymers (II) and (III) at different pH values for Mo(VI) ions. $C_{MIII\ (VI)} = 18.2$ mg L^{-1}, $m_{(I), (II), and (III)} = 5.8$ mg, $V_{aqueous\ phase} = 25$ mL, $\tau = 20$ min.

Table III. Extraction Degree and Sorption Capacity of Copolymers (II) and (III) for Mo(VI) Ions

Sorbent	pH	R (%)	E^M (mmol g^{-1})
Copolymer (II)	2.51	12.7	0.9611
	3.75	5.5	0.4136
	6.77	–	–
	9.97	–	–
	C_{HCl} = 2.4 M	–	–
Copolymer (III)	2.86	11.2	0.9078
	3.65	16.0	1.2610
	6.83	–	–
	10.07	–	–
	C_{HCl} = 2.4 M	–	–

$m_{copolymer}$ = 6 mg, $C_{Mo(initial)}$ = 182 mg L^{-1}, V = 25 mL, τ = 30 min.

Sorption capacity of the copolymers (II) and (III) with respect to molybdenum(VI) ions was investigated (Figure 6).

From Figure 6, it is visible that maximum sorption of the copolymer (III) toward Mo(VI) is achieved in pH range 2–2.2, where E^M is at value 0.35–0.4 mmol g^{-1}. When copolymer (II) is used as sorbent, E^M is 0.33 mmol g^{-1} in pH range 2.75–3.65. At pH less than 0.5 and over 4.5, extraction of molybdenum(VI) does not take place. On the 10-fold increase of the concentration, sorption capacity of the copolymers (II) and (III) with respect to molybdenum(VI) ions increases (Table III). At that, sorption profile does not vary.

From the given results (Figures 3 and 5), it is seen that sorption capacity of copolymers (I), (II) and (III) is higher for Re(VII) than that for Mo(VI). Thus, rhenium can be separated from molybdenum by our new sorbents at HCl concentrations over 0.1 mol L^{-1} in the conjoint presence of Re(VII) and Mo(VI) in acid and ammoniac solutions.

CONCLUSIONS

Thus, physicochemical and functional properties of the new maleimide-based copolymers have been investigated. All the copolymers have spony structure, whereas the N-vinylpyrrolidone copolymer with N-(n-carboxyphenyl)maleimide is the most homogeneous. Sorption capacity of the copolymers towards Re(VII) and Mo(VI) ions has been investigated. From the obtained results which showed that sorption capacity of Re(VII) on the copolymers I–III is higher than that for Mo(VI) in a solution of acid and ammoniac mediums, rhenium can be separated from molybdenum by using the sorbents under investigation at pH < 0.1 and pH > 4.5.

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