

The Peculiarities of Interactions in the System Containing Polyethyleneimine and Unithiol

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Abstract

Interaction processes of polyethyleneimine (PEI) with unithiol were investigated by potentiometric, conductometric and viscosimetric methods. It was stated that in the PEI-unithiol system a complex acid-basic interaction resulted in the formation of salt complex of 2:1 composition. On the basis of experimental data it was stated that complex PEI-unithiol is perspective as a polyadsorbent for many metal ions.

Introduction

Nowadays the creation of highly effective adsorbents on the basis of polymer and low molecular substances with the aim to purify industrial sewage water concentrating and removing carcinogenic and toxic metal ions is an actual problem. In connection with this investigations of interaction processes of polymers with low molecular ligands possessing a great ability to form complexes with transition metal ions are of great scientific and practical interest. One of these promising compounds is universal thiol, bidentate ligand – unithiol (sodium 2,3-dimercaptopropanesulphonate) [1].

This paper presents the results of investigation of PEI (polyethyleneimine) – unithiol (Un) system with the help of potentiometric, conductometric and viscosimetric methods.

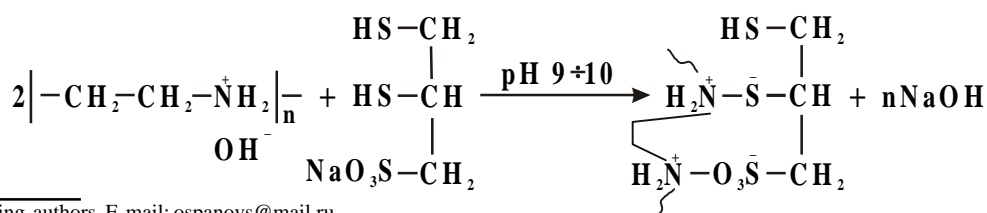
Experimental

Potentiometric investigations were carried out on the ionometer E-130 using silver chloride and glass electrodes with in 0.02 pH units. Conductometric investigations were carried out in electrolytical cells

with the help of alternating current bridge P 5010 using platinum electrodes. Viscosity was determined by using Ubbelohde viscosimeter with the hanging level, distilled water being used as a solvent. All investigations were carried out under thermostated conditions at $(25.0 \pm 0.1)^\circ\text{C}$.

Results and discussion

In aqueous solution unithiol is completely dissociated on the sulfogroup and slightly dissociated on sulfhydryl ones. A water soluble polymer, polyethyleneimine (PEI) was used as a polymer matrix. Its aqueous solution has an alkaline reaction, however, the main properties of PEI are marked weaker than those of low molecular analogs. Mixing of polyethyleneimine aqueous solutions with unithiol solution is accompanied at the initial step by the decrease of the solution pH due to the removal of sodium hydroxide from compounds involved (Fig.1), the mole ratio PEI:Un ($n=0.5$, $n=C_{\text{Un}}/C_{\text{PEI}}$) corresponding to the formation of a salt complex of 2:1 composition. Schematically this reaction taking into account the dominating presence of unithiol in the solution at pH 9-10 (2) can be presented as follows:



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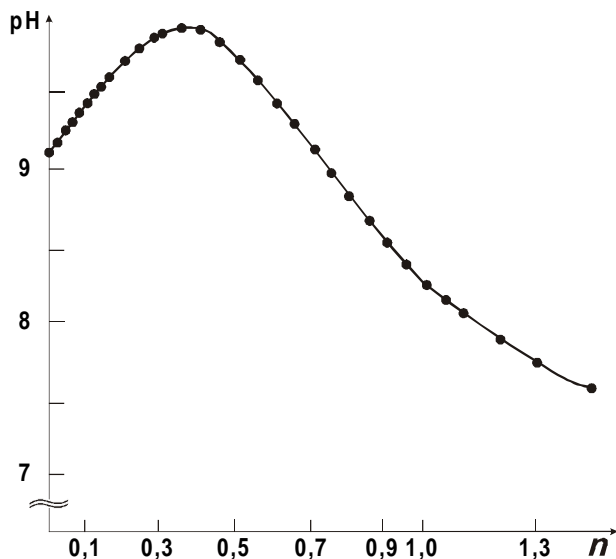


Fig. 1. The curve of potentiometric titration of PEI with unithiol: $C_{PEI} = 3.33 \cdot 10^{-3}$ base-mole/l, $C_{Un} = 1 \cdot 10^{-2}$ mole/l, $n = C_{Un}/C_{PEI}$.

The observed displacement of a stronger mineral base by a weak one takes place in cases of displacement of low molecular bases by high molecular ones, the latter due to their polymer nature being able to bind organic ions not only electrostatically but also hydrophobically providing cooperativeness of their interactions.

Interaction of organic ions with polyethyleneimine is influenced by pH as the depth of the reaction proceeding (1) is regulated by the hydroxyl-ions formed. Binding the formed OH-ions with an acid one can increase the degree of electrostatic filling of PEI macromolecules with unithiol. The degree electrostatic binding (θ) of reagents was calculated using the curves of potentiometric titration of PEI with hydrochloric acid in the absence and presence of different amounts of unithiol. The calculation of θ was done with the help of the well-known equation [2]:

$$\theta C_0 = g_{HCl}/V + [OH^-] - \sqrt{K/K_w C_0}$$

where θ - the degree of electrostatic binding; g_{HCl} - the amount of HCl added when titrating PEI, g-equiv.; $[OH^-]$ - concentration of OH⁻ ions in the mixture; K - polyelectrolyte dissociation constant; K_w - ionic product of water; C_0 - total concentration of functional groups of polyelectrolyte, base-mole/l.

Maximum degree of electrostatic binding of PEI with unithiol is 20-25%. The degree of electrostatic interaction of unithiol with PEI is less than that of for PEI-anionic SAS systems with long hydrocarbon

radicals [2,3]. This can be accounted for a greater hydrophilicity of unithiol in comparison with SAS, e.g. with sodium dodecylsulphate. Besides, the bounds being formed are stabilized by hydrophobic interaction of the hydrocarbon radical of the second component.

Dependence of the degree of electrostatic binding on pH of the solution (Fig.2) shows that decrease of pH results in sharp increase of θ , thus indicating reversibility and cooperativeness of the reaction of PEI with unithiol, and the product of the reaction is a salt complex with composition 2:1.

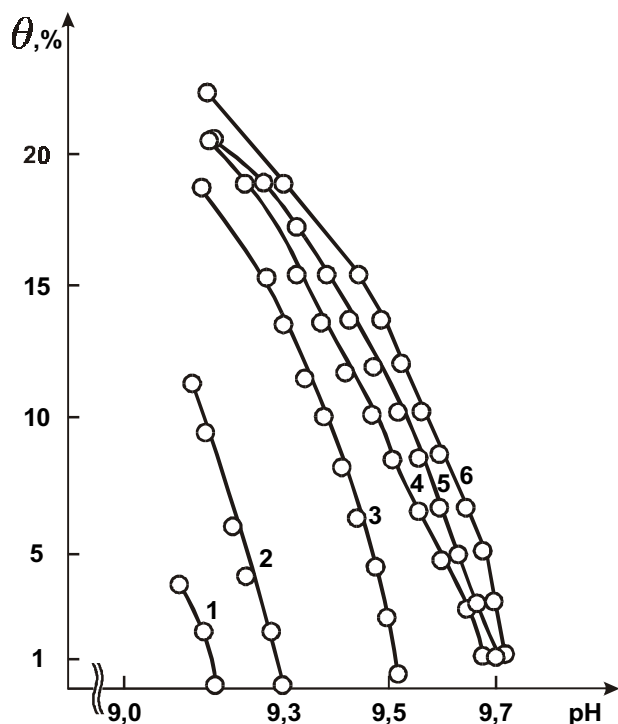


Fig. 2. Dependence of the degree of electrostatic interaction (θ , %) of unithiol with PEI on pH of the solution: $n = C_{Un}/C_{PEI}$. 1. $n=0,05$; 2. $n=0,1$; 3. $n=0,3$; 4. $n=0,5$; 5. $n=0,6$; 6. $n=0,7$.

The results of conductometric investigation of PEI - unithiol system confirm these data. Fig.3 shows the curve of conductometric titration of PEI with unithiol. As it is seen in the figure, the optimum mole ratio for this system is 0.5 : 0.6, i.e. one molecule of unithiol for two monomer chains of PEI which is in good agreement with the data of potentiometric investigations.

The results of conductometric titration of PEI-Un mixtures of different composition with hydrochloric acid (Fig.4) showed that increase of unithiol concentration in the mixtures result in increase of the solution electroconductivity which is connected with

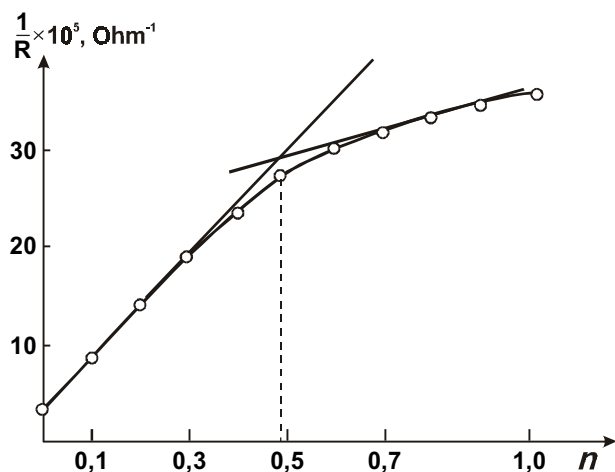
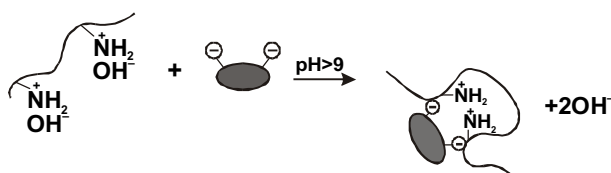



Fig. 3. The curve of conductometric titration of PEI with unithiol: R – resistance, Ohm

the formation of sodium hydroxide in the course of the reaction. Identity of the curves of conductometric titration indicates the fact that a compound of one composition is being formed in the system.

Thus, the formation of a salt complex PEI-unithiol results in increase of electroconductivity, pH of the solution and, as it is seen from equation 1, probably, in the change of conformation of PEI macromolecules.

Experimental data of viscosimetric investigation of PEI-unithiol system (Fig.5) showed that addition of PEI results in decrease of the system viscosity, i.e. as a results of electrostatic interaction of the reacting components neutralization of the charge on the polymer takes place and the macromolecule change its form to a more compact one according to the following scheme:



where  - unithiol - ion of (HUn²⁻).

Conclusions

Thus, on the basis of experimental data formation of a salt complex of 2:1 composition was stated to take place in PEI-Un system where binding occurs on account of SO₃ – group of unithiol while SH – group remains unchanged. This fact allows to make a conclusion about the prospects of the given complex to be used as an adsorbent for many transition metals.

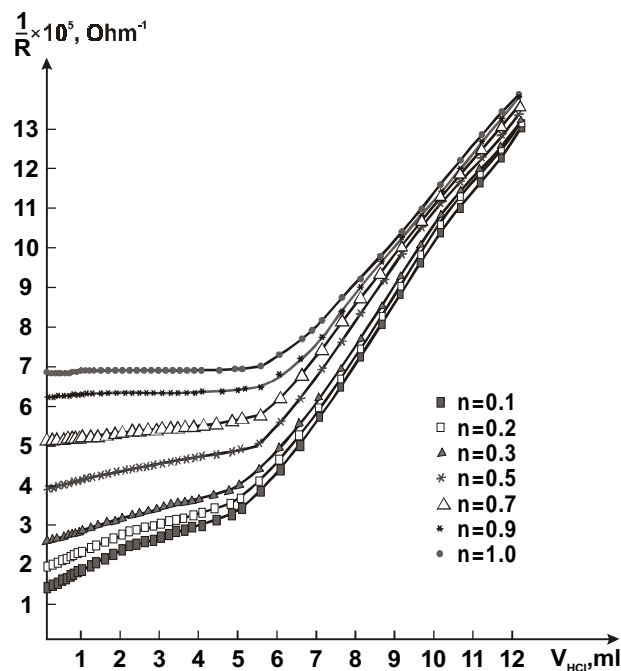


Fig. 4. The curve of conductometric titration of PEI-unithiol mixtures with hydrochloric acid: $n = C_{Un} / C_{PEI}$, R – resistance, Ohm

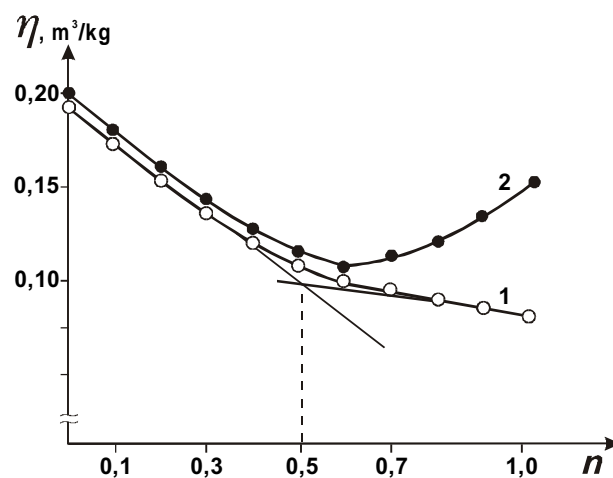


Fig. 5. Viscosity dependence of PEI-unithiol mixtures on the relative concentration of unithiol: η - viscosity, m³/kg, $n = C_{Un} / C_{PEI}$.

Besides, high local concentration of active centers (SH – group of unithiol) due to the aimed “planting” of unithiol into a polymer matrix provides an effective binding degree of metal ions. Preliminary data on precipitation of some non-ferrous and rare metals showed high sorption ability of this complex. In particular, we have suggested a method of purification of sewage from mercury, copper, cobalt, nickel, iron ions on the basis of the polymer composition developed by us. Its composition and method of preparation is not

to be reported here for we have applied for a patent of the Republic of Kazakhstan on it. The results of quantitative determination of these ions in the solutions of

industrial wastes and sewage waters are treated by the method of mathematical statistics and given in Table 1.

Table 1

The results of quantitative determination of metal ions in different sewage waters on the basis of PEI-Un-Mⁿ⁺ composition

№ sewage	The degree of Purification					
	Hg ²⁺	Cu ²⁺	Co ²⁺	Ni ²⁺	Fe ³⁺	Fe ²⁺
1	91,8±1,7	91,5±1,7	88,8±0,9	86,9±0,8	79,0±0,7	71,6±1,7
2	96,4±1,3	93,3±0,8	90,7±1,9	89,1±0,9	82,8±2,4	74,6±0,9
3	97,7±1,5	93,3±1,4	90,6±1,2	89,6±0,9	82,4±0,9	74,2±0,9

The results of these investigations confirmed the perspectiveness of a polymer composition on the basis of polyethyleneimine and unithiol for the deposition of many metal ions.

References

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