Chemistry of Natural Compounds, Vol. 40, No. 4, 2004

PREPARATION AND ION-EXCHANGE PROPERTIES OF P-CONTAINING CELLULOSE DERIVATIVES FROM CERTAIN PLANT SPECIES

B. Kh. Ubaidullaev, A. M. Kudratov, and Z. S. Salimov UDC 661.183.543.123

Phosphoric-acid esters (PAE) of cellulose are biologically active substances that are especially suitable for use in medicine, for example, to stabilize blood and prepare de-ionized milk [1-4]. However, the exchange capacity, which determines the biological activity of the products obtained by phosphorylation of cotton cellulose, is insufficient (less than 5-6.3 mg-eq/g). Considering that the chemical structure of cellulose as an anhydro-β-D-glucose has three hydroxyls, the reactivity of which depends on both their position in the molecule and on the structural morphology of the polymeric substrate, it is interesting to study the possibility of preparing biologically active PAE with a high exchange capacity by using wastes of ground *Armeniaca vulgaris* Lam., *Amygdalus* L., *Populus* L., *Oryza* L., and *Gossypium* L. [5] and expanding their applications. This was the goal of our research.

The chemical transformations occurring in the cellulose macromolecule upon phosphorylation in the presence of carbamide [6] determine its ion-exchange properties and biological activity [2, 3, 7]. These are represented as follows:

$$[C_6H_7O_2(OH)_3]_x + mxH_3PO_4 \leftrightarrow [C_6H_7O_2(OH)_{3-m}OPO(OH)_2]_x + mxH_2O.$$

Table 1 lists the elemental analyses (P, C, H) of the ground samples (less than 1 mm) of plant material and PAE prepared from them for identical treatment conditions (esterification temperature 80°C, 30 min, C_{H_2O} 36.6 g, $C_{carbamide}$ 42.5 g, $C_{H_3PO_4}$ 19.1 g, bath module 2.8). The PAE of *Armeniaca vulgaris* Lam. and Oryza L. (8.0 and 12.0 mg-eq/g) had the highest increase of P (11.5-15.4%) and, therefore, the highest exchange capacity, after esterification of various (by nature) cellulose samples.

Table 2 gives various calculated kinetic reaction orders for phosphorylation and changes of P-content of *Armeniaca vulgaris* Lam., *Amygdalus* L., *Populus* L., and *Oryza* L. samples. The reaction order (greater than 2) for all samples and the rate constants increase in the order: *Oryza* L. > *Armeniaca vulgaris* L. > *Amygdalus* L. > *Gossypium* L. > *Populus* L.

The ion-exchange properties of the plant materials depends substantially on the density and swelling [1]. Table 3 gives the swelling of the ion-exchange materials prepared from *Armeniaca vulgaris* L. as a function of density. The swelling of samples from particulate wastes of *Armeniaca vulgaris* Lam. decreases as the exchange capacity and density characteristics increase. This indicates that the structural elements become more dense after chemical transformations in macromolecular cellulose. Evidently, this is explained by the various rates and reaction orders for phosphorylation of various types of cellulose. Thus, the maximal densities and swellings for PAE from *Amygdalus* L., *Populus* L., and *Oryza* L. are 1.285 g/cm^3 and 144%, 1.330 g/cm^3 and 386%, and 0.950 g/cm^3 and 330%, respectively.

The ion-exchange materials from particulate wastes of *Armeniaca vulgaris* Lam. showed selectivity for Zn, Ca, and Co ions in purifying wastewater from the Mardzhanbulak gold-extraction plant. The activity was Zn > Ca > Co. For wastewater from the Shorbulak poultry farm, for U and Mg, U > Mg. The dymanic exchange capacity for Ca ions was >260 g-eq/m^3.

Institute of General and Inorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (99871) 162 79 90, e-mail: igic@uzsci.net. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 335-336, July-August, 2004. Original article submitted April 7, 2004.

 0009-3130/04/4004-0410

TABLE 1. Elemental Composition of Ion Exchangers Based on Various Plant Species

Sample	P	C	H	Exchange capacity, mg-eq/g
	%			
Armeniaca vurgaris Lam. (init.)	0.02	49.0	7.86	-
Armeniaca vurgaris Lam. (PAE)	11.5	46.1	7.34	8.0
Amygdalus L. (init.)	0.01	49.8	7.22	-
Amygdalus L. (PAE)	9.6	46.5	7.37	7.5
Oryza L. (init.)	0.06	46.3	8.39	-
Oryza L. (PAE)	15.4	30.1	7.42	12.0
Populus L. (init.)	0.01	45.7	8.51	-
Populus L. (PAE)	5.1	43.4	8.18	4.0

TABLE 2. Calculated Reaction Orders (n) and Rate Constants (K) for Phosphorylation of Various Samples

Sample	n	K, min^{-1}
Oryza L.	5.705	0.4939
Armeniaca vurgaris Lam.	6.145	0.8545
Amygdalus L.	9.144	2.9048
Gossypium L.	12.43	13.3174
Populus L.	15.30	70.00

TABLE 3. Swelling and Density of PAE from Ground (1.0 mm Size) *Armeniaca vulgaris* Lam. as Functions of Exchange Capacity

Exchange capacity, mg-eq/g	Swelling, %	Density, g/cm^3
6.8	275	1.360
7.2	262	1.365
7.7	250	1.370
8.0	247	1.373
8.2	239	1.377

REFERENCES

1. I. S. Skorynina, S. S. Gusev, I. K. Vorobaeva, and I. N. Ermolenko, *Vysokomol. Soedin., Ser. A*, **12**, No. 11, 2542 (1970).
2. E. D. Buglov, I. I. Ermolenko, S. I. Dovgalev, I. I. Danilov, I. P. Lyubliner, and K. I. Gorel′nik, *Preparation of Citrate-free Blood Using Cellulose Phosphate* [in Russian], Nauka i Tekhnika, Minsk (1971).
3. E. D. Buglov, I. N. Ermolenko, S. I. Dovgalev, I. P. Lyubliner, and M. L. Longin, Pat No. 191,062 (1967); *Byull. Isobret.*, No. 3 (1967).
4. M. L. Longin and I. N. Ermolenko, Pat. No. 195,308 (1966); *Byull. Izobret.*, No. 9, 1967).
5. *Flora of Uzbekistan* [in Russian], Izd. Akad. Nauk UzSSR, Tashkent (1962).
6. I. Kh. Khakimov and B. E. Geller, *Chemical Transformations of Cellulose* [in Russian], Fan, Tashkent (1976).
7. A. M. Kudratov and B. Kh. Ubaidullaev, *Uzb. Khim. Zh.*, No. 6, 56 (2002).