

WATER VAPORS ADSORPTION BY POLY(DIALLYLAMMONIUM) POLYMERS

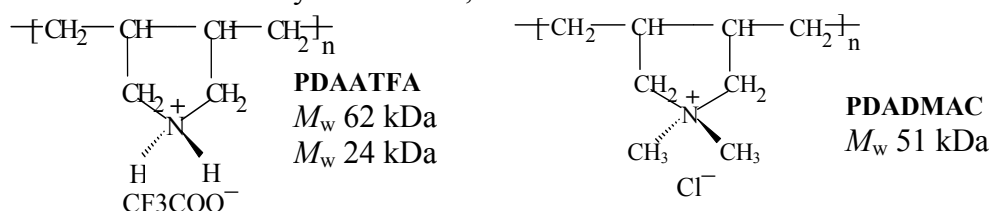
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The interrelation between the structure and adsorption properties of swelling polymers with respect to water vapor has been investigated. The studies of porous structure of hydrophilic-hydrophobic swelling polymers based on cationic polyelectrolytes using the data of physical adsorption of non-polar molecules, such as nitrogen or argon, give minor values of specific surface and negligible porosity. Adsorption properties of such polymers as well as their free volume can be determined from the water adsorption data unlike the nitrogen vapors adsorption isotherms.

Secondary and tertiary poly(diallylammonium) salts (PDAAS) with trifluoroacetate anion as counterion are novel water-soluble polymers (cationic polyelectrolytes), which have been synthesized recently [1,2]. Pyrrolidinium links of these polymers combine high hydrophobicity with the high hydrophilicity of secondary/tertiary ammonium groups, which are able to form hydrogen bonds therewith. One may expect that owing to these factors, the non-quaternary PDAAS will acquire properties other than those of quaternary poly(diallylammonium) salts, in particular known common polymer poly(diallyldimethylammonium) chloride (PDADMAC). This is proved by the high antimicrobial activity of PDAAS aqueous solutions, unlike the quaternary polymers of this series [2, 3]. Presence of $>NH_2/>NH^+$ groups in the structure of links of secondary/tertiary PDAAS as well as another counterion could provide supramolecular structure and swelling properties of PDAAS, in particular studied secondary PDAATFA, other than those of PDADMAC.



Here, we have studied the water vapors adsorption isotherms, which were measured using vacuum adsorption equipment with McBain microbalance. The water vapors isotherms have the sigmoid shape and can be attributed to the Type II according to the Brunauer classification. This form of isotherm of adsorption indicates that the energy of interactions between water molecules are higher than the energy of polymer-water interactions. The model of two stage localized adsorption (equation Dubinin-Serpinsky-2) pretends the best approximation of experimental data of water adsorption on polymers. It should be taken into consideration the changes in adsorption properties with increasing relative pressure, the rate of adsorption and amount of primary adsorption centers (PAC). Using the comparative plots it was showed that the value of PAC for PDAMAC are larger than that for PDAATFA. This fact as well as the higher values of adsorption at the small and medium relative pressures indicates the more porous structure of PDADMAC. However at the high P/P_s adsorption by PDAATFA sharply increases that obviously relates to swelling of hydrophilic macrochains. This results in close maximum adsorption values (a_m) of 35 mmol/g for PDADMAC and PDAATFA for the samples with close polymerization degree ($P_w \cong 300$). It was demonstrated that a_m for PDAATFA depends on the polymer length, increases with the substantial decreasing of P_w (up to 114) that is probably relates to a less hydrophobic interactions and selfassociations of a shorter macrochains.

1. Timofeeva, L. M.; Kleshcheva, N. A.; Vasilieva, Y. A.; Gromova, G. L.; Timofeeva, G. I.; Filatova, M. P. *Polym. Sci., Ser. A* **2005**, *47*, 273-282.
2. Timofeeva, L. M.; Kleshcheva, N. A. RU Patent 2272045, 2006 (priority September 28, 2004).
3. L. M. Timofeeva, N. A. Kleshcheva, A. F. Moroz, L. V. Didenko. *Biomacromol.* **2009**, *10*, 2976-2986.