

Thermodynamics of swelling of polymeric sorbents in aqueous solutions

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It is known that for real systems, the Gibbs free energy of swelling of polymeric sorbents [1] in water or in aqueous solutions changes according to the following formula:

$$\Delta G_{\bar{n}} = RT \ln \bar{a}_w \quad (1)$$

where: $\Delta G_{\bar{n}}$ - change in Gibbs free energy of swelling, R-gas universal constant, T-temperature, \bar{a}_w - activity of sorbed water in the polymer sorbent phase.

If the standard state of water in polymer sorbents and solutions are the same, then the activity of water in both phases will be the same $\bar{a}_w = a_w$, and the change in the Gibbs free energy of swelling in this case is described by the following formula [2]:

$$\Delta G_{\bar{n}} = RT \ln a_w = RT \varphi \ln N_w = RT \varphi \ln(1 - N_{AX}) = RT \varphi \ln \left(1 - \frac{vm}{\left(\frac{1000}{M_w}\right) + vm} \right) \approx$$
$$RT \varphi \ln \left(1 - \frac{vmM_w}{1000} \right) \quad (2)$$

where: m is the molal concentration of the solution, φ is the molal osmotic coefficient of the solute, M_w is the molecular weight of the solvent, v is the number of ions in the molecule of the solute.

In this paper, experimental results show the dependence of the change in the Gibbs differential free energy of swelling of polymeric sorbents in water or in aqueous solutions on the amount of water sorbed by the polymer, on the nature of the functional groups of polymers, on the ionic form, on the amount of divinylbenzene, and on the activity of water in the external solution.

The dependences of the change in the Gibbs differential free energy of swelling on the counterions of polymer sorbents, on the concentration of the equilibrium solution, and on the coions of the solution were studied using the KB-4 cation exchanger from different solutions of sodium, potassium, ammonium and calcium salts, as well as hydrochloric acid with different concentrations.

Experiments to study the dependence of the change in the Gibbs differential free energy of swelling on the number of cross-links of polymeric sorbents and on the activity of water in an equilibrium solution were carried out on the nitrate form of the APA anion exchange resin containing 4, 12 and 20% cross-links from NH_4NO_3 solutions of various concentrations.

From the experimental data, it was revealed that the change in the Gibbs differential free energy of swelling is directly proportional to the counterions of polymeric sorbents and to the concentration of the equilibrium solution and does not depend on the coions of the equilibrium solution. In addition, it was shown that the amount of water sorbed by the ARA anion exchanger and the change in the Gibbs free energy of swelling are directly proportional to the amount of cross-links of the polymer sorbent.

References:

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2. Иванов В. А., Карпюк Е. А. //Термодинамика ионного обмена. Москва 2016. 134 с