ISSN 0036-0244, Russian Journal of Physical Chemistry, 2006, Vol. 80, No. 8, pp. 1300–1304. © Pleiades Publishing, Inc., 2006.
Original Russian Text © E.M. Tazhbaev, E.S. Mustafin, M.Zh. Burkeev, B.K. Kasenov, 2006, published in Zhurnal Fizicheskoi Khimii, 2006, Vol. 80, No. 8, pp. 1477–1481.

Enthalpy of Swelling of Crosslinked Copolymers of Acrylic Acid β-Vinyloxyethylamide in Water and Ethanol

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Received June 28, 2005

Abstract—The thermodynamics of swelling of copolymers of acrylic acid β-vinyloxyethylamide with acrylamide and N-vinylpyrrolidone of various compositions in water and ethanol is investigated. It is established that the swelling of the copolymers in water is characterized by high negative enthalpy values and that the swelling in ethanol is an endothermic process. It is found experimentally that the hydrogels obtained experience contraction at elevated temperatures.

DOI: 10.1134/S0036024406080231

In recent years, polymer gels, which represent crosslinked polymers swollen in a solvent, have come to the attention of researchers. The interest is due to their unique properties, the most important of which is the sorption of large volumes of solvents, which can be tens and even hundreds of times larger than the volume of the polymer. Moreover, gel samples exhibit reversible jump-type changes in dimensions in response to small changes in the surrounding medium (pH, temperature, presence of low-molecular compounds, etc.). These properties of gels offer great promise for their use in medicine, industry, plant growing, the home, and in other fields. Their use can be substantially extended after the development of a general theory of swelling, which is necessary to control micro- and macroscopic properties of gels [1–3].

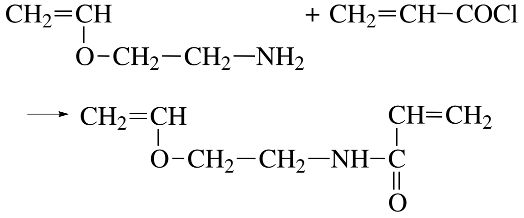
We investigated gels based on copolymers of a new divinyl monomer, acrylic acid β-vinyloxyethylamide (AAVOEA) [4, 5]. Previously [6, 7], it was established that the swelling ratio of copolymers of AAVOEA with acrylamide (AA) and N-vinylpyrrolidone (VP) essentially depends on external factors: pH of the medium, the presence of an organic solvent or an electrolyte, etc. The investigation of the thermodynamics of collapse and swelling of polymers [8] provides data on the thermodynamic affinity of solvents to polymers and insight into the energy nature of polymer–solvent interactions. Such investigations also provide a means of estimating the thermodynamic stability of polymer–solvent binary systems and its temperature dependence, predicting their collapse on cooling or heating, and, finally, relating thermodynamic parameters of swelling to the structure of base units of polymers.

In this connection, we studied the swelling of copolymers of AAVOEA with AA and VP in water and ethanol at 278 K by thermochemical methods.

EXPERIMENTAL

The enthalpy of swelling or the integral heat of swelling was measured on a DAK I-IA differential automatic calorimeter. Experimental error and the homogeneity of set of variances in the determination of heat effects were calculated using the Student criterion and the Bartlett test [9].

AAVOEA was synthesized by condensation of monoethanolamine monovinyl ether and acryloyl chloride [5] by the reaction



$$CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}NH_2 + CH_2{=}CH{-}COCl \longrightarrow CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}NH{-}C({=}O){-}CH{=}CH_2$$

in a yield of 82% ($T_b = 363$ K at $p = 2$ mm Hg, $d_4^{20} = 1.0824$, and $n_D^{20} = 1.4786$). The product was identified using IR spectroscopy and chemical analysis.

Copolymers of AAVOEA with AA and VP were synthesized by copolymerization of the monomers in the presence of a radical initiator, azobis(isobutyronitrile). The comonomers were mixed in the molar ratios 10 : 90, 15 : 85, and 25 : 75 (mol %). The conversion of comonomers varied over the range 67.3–86.9 wt % according to their nature and proportion in the initial mixture. Volumes of gel samples were measured after their synthesis (V_0) and after the attainment of the equilibrium swelling value (V) using a KI-8 cathetometer. Initial samples had the shape of a sphere with an average diameter of 0.2 cm.

Table 1. Enthalpies of swelling of copolymers in water at polymer weight fractions of (I) 0.0018, (II) 0.0014, and (III) 0.0010

m, g	$-\Delta H_{swell}$, J/g	m, g	$-\Delta H_{swell}$, J/g	m, g	$-\Delta H_{swell}$, J/g
AAVOEA–AA copolymer of composition 28 : 72 (mol %)					
I		II		III	
0.0090	32.44	0.0068	28.23	0.0048	26.66
0.0090	32.44	0.0068	28.08	0.0048	26.66
0.0091	32.42	0.0069	28.26	0.0047	27.23
0.0090	33.00	0.0066	28.33	0.0046	26.30
0.0091	33.41	0.0068	28.23	0.0048	26.45
	(32.74 ± 0.5)		(28.22 ± 0.1)		(26.66 ± 0.4)
AAVOEA–VP copolymer of composition 6 : 94 (mol %)					
I		II		III	
0.0091	79.78	0.0069	75.22	0.0046	73.91
0.0090	79.78	0.0068	76.03	0.0046	74.56
0.0091	79.36	0.0068	76.03	0.0047	74.04
0.0092	79.33	0.0067	76.86	0.0045	72.00
0.0090	78.88	0.0070	75.29	0.0045	74.66
	(79.43 ± 0.4)		(75.88 ± 0.8)		(73.83 ± 1.3)
AAVOEA–VP copolymer of composition 53 : 47 (mol %)					
I		II		III	
0.0094	100.85	0.0069	88.26	0.0045	82.87
0.0092	101.08	0.0068	89.00	0.0046	84.13
0.0092	101.08	0.0067	88.66	0.0047	84.04
0.0093	100.64	0.0068	88.38	0.0045	81.55
0.0091	101.00	0.0069	88.26	0.0047	83.19
	(100.93 ± 0.2)		(88.51 ± 0.4)		(83.16 ± 1.3)

Note: Average values are parenthesized.

Calorimetric experiments consisted in the measurement of the heat evolved upon crushing ampoules with polymer samples in excess of the solvent. Enthalpies of swelling of copolymers AAVOEA with AA and VP in water and ethanol were measured in the regime of automatic compensation of heat at polymer weight fractions from 0.00028 to 0.002. With greater weight fractions, the time of thermal response increases, which decreases the reliability of results. Registration was performed by a KSP-4 recording potentiometer and, in parallel, by an IP-4 precision integrator. Prior to testing, samples were allowed to stand in a thermostat for 2 h. Before proceeding to experimentation, the instrument was calibrated against the power evolved by the built-in heater at a calibration voltage. Performance of the calorimeter was checked by measuring the heat of dissolution of triply recrystallized KCl at the dilutions (salt-to-water molar ratios) 1 : 1600, 1 : 2400, and 1 : 3200. The obtained average value of the heat of dissolution of KCl in water (17860 ± 283 J/mol) agrees satisfactorily with the value recommended in [10] (17577 ± 34 J/mol).

RESULTS AND DISCUSSION

From the experimental data listed in Table 1, it is seen that the swelling of the copolymers in water is characterized by great negative enthalpies of swelling. The exothermic effect of swelling of the copolymers in water is due probably to the formation of polymer–water solvation complexes. The enthalpy of swelling of AAVOEA–AA copolymer varies with the polymer concentration in the system (Fig. 1): the specific enthalpy of the process increases with the polymer concentration. In the swelling of copolymers of AAVOEA with N-vinylpyrrolidone, the heat evolution is higher than that for its copolymers with acrylamide, which correlates with the data [6, 7] on swelling values of these copolymers in water.

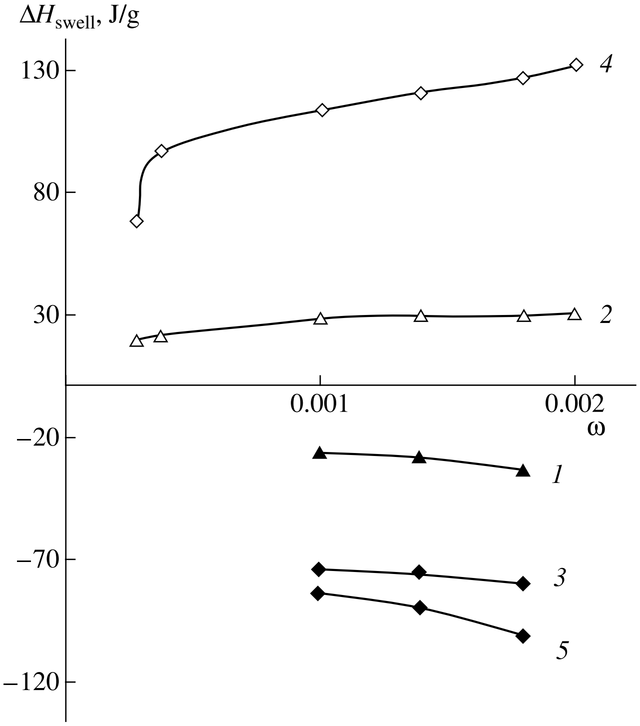


Fig. 1. Dependences of the enthalpy of swelling ($\Delta H_{\mathrm{swell}}$) of copolymers in (*1*, *3*, *5*) water and (*2*, *4*) ethanol on the polymer weight fraction in the system (ω): (*1*, *2*) AAVOEA–AA copolymer of composition 28 : 72 mol %; AAVOEA–VP copolymers of compositions (*3*, *4*) 6 : 94 and (*5*) 53 : 47 mol %.

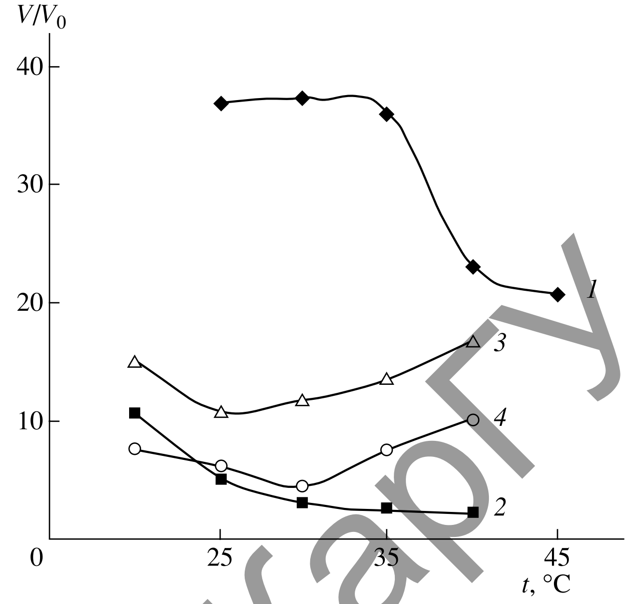


Fig. 2. Effect of the temperature on the swelling of hydrogels of AAVOEA–VP copolymers of compositions (*1*) 6 : 94 and (*2*) 23 : 77 mol % and AAVOEA–AA copolymers of compositions (*3*) 12 : 88 and (*4*) 17 : 83 mol %.

It is remarkable that the exothermic effect of swelling of AAVOEA–VP copolymers increase with the number of AAVOEA links responsible for the crosslinking of the copolymer. As the extent of crosslinking of the polymer is increased, the access of solvating molecules to links of polymer chains must seemingly become more and more limited, and, consequently, the enthalpy of swelling must decrease. However, the experimentally observed dependence of the heat evolved in swelling on the extent of crosslinking is quite the reverse. This suggests that the solvation of AAVOEA links with water molecules provides a greater gain in energy as compared to the solvation of VP links: AAVOEA links containing more functional groups must sorb more water molecules.

For the investigated polymers, the enthalpies of swelling are several times higher than those for the majority of known polymers [8], even though the measurements of heats of swelling were carried out in highly dilute systems. High enthalpies of swelling are indicative of high affinity of water to the investigated polymers.

High exothermic effects of swelling of copolymers of AAVOEA in water suggest that, owing to the enthalpy component of the total Gibbs energy, an increase of the temperature will favor the displacement of equilibrium in the direction reverse to the process of swelling of hydrogels. Temperature dependences of the volume of hydrogels experimentally determined for copolymers of AAVOEA with VP and AA are presented in Fig. 2. It is seen that, as the temperature is increased from 20 to 45°C, gels of AAVOEA–VP copolymers exhibit contraction. In this case, the character of variation of the volume is indicative of an abrupt phase transition: swelling values of the copolymers remain virtually constant to some critical temperature, and, in a certain temperature range, the sorption capacity of the hydrogels changes by jump. The magnitude of the jump occurring in this temperature range depends on the composition of the polymer. An increase of the proportion of VP links in the copolymer (or a decrease of the number of AAVOEA links) is accompanied by the displacement of the transition toward the region of higher temperatures. In this case, the hydrogels show changes in volume more than 40%.

The significant decrease in volume of hydrogels observed at elevated temperatures can be due not only to the exothermic effect of swelling of the copolymers but also to an enhancement of the hydrophobic attraction. According to present views [11], the basic reason for hydrophobic interactions is the gain in entropy due to the disruption of the water structure in the vicinity of hydrophobic groups. As the temperature is increased, the entropy component of the total free energy increases, and, consequently, the role of hydrophobic interactions increases too. Thus, the abrupt transition of hydrogels of copolymers of AAVOEA with VP from the swollen to collapsed state at elevated temperatures

Table 2. Enthalpies of swelling of copolymers in ethanol at polymer weight fractions of (I) 0.00028, (II) 0.00037, and (III) 0.0017

m, g	ΔH_{swell}, J/g	m, g	ΔH_{swell}, J/g	m, g	ΔH_{swell}, J/g
AAVOEA–AA copolymer of composition 28 : 72 mol %					
I		II		III	
0.0029	30.00	0.0019	21.05	0.0014	19.29
0.0030	30.00	0.0019	21.58	0.0015	18.66
0.0029	30.34	0.0017	21.18	0.0014	18.57
0.0029	30.69	0.0018	21.11	0.0014	18.57
0.0029	30.34	0.0019	22.10	0.0014	19.28
	(30.28 ± 0.3)		(21.40 ± 0.5)		(18.88 ± 0.4)
AAVOEA–VP copolymer of composition 6 : 94 mol %					
I		II		III	
0.0030	130.66	0.0019	95.79	0.0013	66.15
0.0029	133.10	0.0019	96.31	0.0013	68.46
0.0029	131.38	0.0019	95.79	0.0014	68.57
0.0028	131.43	0.0018	97.78	0.0014	68.57
0.0028	132.14	0.0018	97.22	0.0014	68.57
	(131.74 ± 1.1)		(96.58 ± 1.2)		(68.06 ± 0.9)

Note: Average values are parenthesized.

is caused by the enthalpy and entropy components of the total free energy of the process.

In analogous conditions, hydrogels of copolymers of AAVOEA with AA behave somewhat differently. From the experimental data (Fig. 2), it is seen that temperature dependences of the swelling value of the hydrogels behave in an extreme fashion. As the temperature is increased, the hydrogels exhibit contraction and then, at a certain temperature, continue to swell. It may be suggested that, above some critical temperature, hydrolysis of acrylamide links becomes the determining factor in swelling of these hydrogels. The presence of charged groups of like sign formed by hydrolysis leads to mutual repulsion of macromolecules and the transition of subchains from the compact globular conformation to the looser coil conformation.

Swelling of copolymers essentially depends on the nature of the solvent [1–3]. To gain a better insight into thermodynamic affinity of ethanol to polymers, we determined enthalpies of swelling of copolymers of AAVOEA with AA (28 : 72 mol %) and VP (6 : 94 mol %) in ethanol.

Previously [4, 5, 12], it was shown that hydrogels of copolymers of AAVOEA with AA and VP substantially decrease in size on the addition of an organic solvent to the polymer–water system. A probable reason for this behavior is the deterioration of the thermodynamic solvent quality. Indeed, the swelling of the copolymers in ethanol is attended by significant endothermic effects (Table 2). Consequently, the formation of polymer–ethanol solvation complexes is energetically unfavorable. Moreover, ethanol is less polar than water and, as the solvent, less favorable to the dissociation and the formation of charged fragments in macromolecular chains. Both the factors adversely affect the swelling of the investigated hydrogels. For the AAVOEA–AA system, the endothermic effect of swelling is less than that for the AAVOEA–VP system. In the swelling the copolymers in ethanol, ΔH_{swell} also depends on the ratio between components in the polymer–solvent system (Fig. 1).

Thus, the obtained thermodynamic characteristics of swelling show that the thermodynamic affinity of water to copolymers of AAVOEA with AA and VP is higher than that for ethanol. The enthalpies of swelling of the copolymers correlate with the published values and provide better insights into how the temperature and the nature of the solvent influence the stability of polymer–solvent binary systems.

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