

Study of the velocity of swelling of the sodium salt of carboxymethylcellulose in aqueous solutions of electrolytes

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The influence of aqueous solutions of electrolytes on the velocity of swelling of the sodium salt of carboxymethylcellulose (NaCMC) was studied. Carboxymethylcellulose was partially plastified by 13 % addition of glycerol (referred to the mass of NaCMC). It has been found that the transport process of diffusion of the solution of electrolyte into the solid sample obeys the Fick's law. The measured apparent mean diffusion coefficients D of the investigated systems are in the interval $\langle 1.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}; 9.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \rangle$. Their values decrease with increasing concentration of the solution of electrolyte. Similarly, they also decrease with the magnitude of charge and radius of the solvated ions. An analogous trend was also exhibited by the measured values of molar conductivities. The values of activation energy of swelling E_s and isothermal activation volume work $RA_{s,s}$, are in the intervals $\langle 15 \times 10^3 \text{ J mol}^{-1}; 25 \times 10^3 \text{ J mol}^{-1} \rangle$ and $\langle 8 \times 10^3 \text{ J mol}^{-1}; 12 \times 10^3 \text{ J mol}^{-1} \rangle$.

Изучено влияние водных растворов электролитов на скорость набухания натриевой соли карбоксиметилцеллюлозы (NaCMC), частично пластифицированной 13%-ной добавкой глицерина (относительно массы NaCMC). Обнаружено, что транспортный процесс диффузии раствора электролита в твердом образце подчиняется закону Фика. Измеренные средние кажущиеся коэффициенты диффузии D изучаемых систем лежат в интервале $\langle 1,5 \cdot 10^{-10} \text{ м}^2 \text{ с}^{-1}; 9,5 \cdot 10^{-10} \text{ м}^2 \text{ с}^{-1} \rangle$, причем их величины уменьшаются при увеличении концентрации раствора электролита, как и при возрастании заряда и радиуса сольватируемых ионов. Аналогичную зависимость имели и измеренные величины молярных проводимостей. Величины активационной энергии набухания E_D или изотермической активационной объемной работы $RA_{s,s}$, лежат в интервалах $\langle 15 \cdot 10^3 \text{ Дж моль}^{-1}; 25 \cdot 10^3 \text{ Дж моль}^{-1} \rangle$ и $\langle 8 \cdot 10^3 \text{ Дж моль}^{-1}; 12 \cdot 10^3 \text{ Дж моль}^{-1} \rangle$ соответственно.

The properties of aqueous solutions of electrolytes are, to a great extent, affected by the interactions between ions and water (electrostatic and van der Waals interactions) while the existing quasi-crystalline structure of water is disturbed by the present ions [1]. The order in the liquid changes by the effect of ions and a new quasi-crystalline lattice is formed. According to *Frank and Evans* [2], an aqueous solution of electrolyte consists of three-layer clusters (aggregates) (Fig 1). The first layer (A) contains water molecules firmly bound by the ion—dipole forces eliminating the possibility of their rotation (primary hydration sphere), the structure in the second layer is less compact (B) (nonorganized water) while the third layer (C) consists of normal water with no structural changes.

This phenomenon of quasi-crystalline structural transformations is connected with the so-called structure breaking [3]. According to *Ruckov* [4], we may, in the main, regard the Li^+ cation as the important disturber of the quasi-crystalline tetrahedral structure of water while the Na^+ and K^+ cations contribute to structure breaking in much lesser degree owing to a smaller polarization effect resulting from substantially smaller surface charge density.

According to present opinions, there are two points of view for elucidating the mutual influencing of the particles of dissolved electrolyte and the molecules of water. The first view is based on the idea of an existing “bond” between an ion and certain number of water molecules, i.e. the formation of a thermodynamically stable aggregate ion—water molecule (thermodynamic hydration) [5]. According

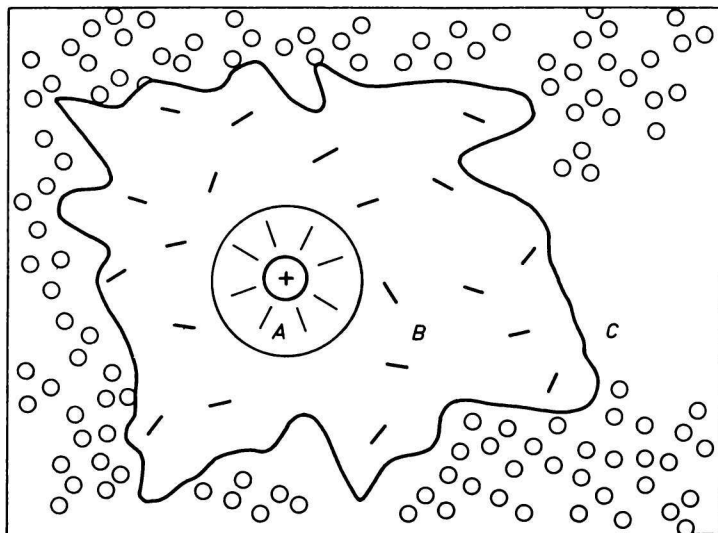
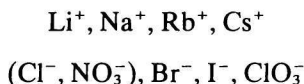


Fig. 1. Schematic representation of the hydration of ion.
A. Primary hydration; B. nonorganized water; C. normal water.

to the second point of view, we may conceive the hydration on the basis of a change in intermolecular interactions, *i.e.* the hydration results from the effect of ions on the translational motion of water molecules which surround these ions. The stability of the nearer ion's envelope is appreciated according to the rate of the exchange of these ions for water molecules from the second more distant layer which, in contrast to the bond strength resulting from thermodynamic hydration, is not dependent on the total energy of interactions but depends on its change in small dimensions in the proximity of ion. This so-called critical solvation is connected with the kinetic properties of solutions (viscosity, conductivity, diffusion coefficient [6]). In principle, both theories are in conformity with the idea of the structure of electrolyte solutions.

Valuable information about the bonds (or energetic characteristics of bonds) in aqueous solutions of electrolytes is given by infrared spectra. On this basis, *Bakeev* [7] divides cations and anions into two groups. The first group comprises the cations which have positive effect on the bond strength between water molecules in the order Li^+ , Na^+ , and K^+ while the second group contains the anions which reduce the bond strength between water molecules in the order Cl^- , I^- . The *Bakeev* views are in good agreement with general conception that the disturbing effect (structure breaking) increases with ionic radius [1] in the order



All these effects influence the effective value of the volume of solvated cation and significantly determine the ability of motion of the aqueous penetrant entering the solid polymer membrane. As the problem of interfacial diffusion in the system carboxymethylcellulose (s)—aqueous solutions of electrolytes (l) was not paid sufficient attention in literature, we investigated in this study the diffusion process of swelling of NaCMC in aqueous solutions of LiCl , NaCl , KBr , KI , CaCl_2 , and FeCl_3 . The determined values of kinetic parameters give reliable information about internal order of a solid sample of polymer.

Experimental

The experimental measurements were carried out with the sodium salt of CMC (Tylose, product of GFR). On the basis of viscosimetric measurements, it was characterized, by these parameters: $[\eta] = 9.6 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$, $M_r = 7.6 \times 10^5$ (0.2 M-NaCl, $\Theta = 25^\circ \text{C}$, $K = 4.3 \times 10^{-4}$, $a = 0.74$ [8]).

The salts LiCl , NaCl , KCl , KBr , KI , CaCl_2 , and FeCl_3 were anal. grade chemicals (Lachema, Brno).

The CMC films were prepared by fast plaster casting on Petri dishes from 2 % solution of CMC heated to 80 °C which was filtered through a fritted disk S-3. A 13 % addition of glycerol (referred to the mass of CMC) was used as softener. The films thus prepared were of 0.11–0.14 mm width. They were dried for 24 h at 65 °C.

The thickness of the surface swollen layer (SSL) δ was measured in a simple experimental optical device which was described [9] earlier. The kinetic measurements in the system NaCMC—electrolyte were performed at temperatures $\theta/^\circ\text{C}=20, 25, 30, 35, 40,$ and 45 ± 0.1 .

The values of apparent mean diffusion coefficients D were obtained from the following formula [9]

$$\delta^2 = 2Dt \quad (1)$$

the relative error being $\pm (3\text{--}5)\%$. The values of the activation parameters were determined with relative error $\pm (5\text{--}10)\%$.

The conductivity of the solutions of electrolytes was measured at 25 °C by a conductometer OK 102 (Hungary). The resistivity of the conductivity vessel was found by the use of 0.1 M-KCl. The mean quadratic deviation of these measurements was $\pm 3\%$.

Results and discussion

The course $\delta = f(t)$ for 1.0 M aqueous solutions of the investigated electrolytes as well as for distilled water at 25 °C (Fig. 2) shows clearly that the diffusion follows the Fick's law. This character is also documented by linear relationship in Figs. 3 and 4.

The graphical course of the equation $\delta^2 = f'(t)$ (Fig. 3) suggests that eqn (1) describes well the temporal dependence of the total thickness of SSL δ in a relatively wide time and concentration interval, while the sample surface is saturated immediately after the both phases came into contact. The observed dissipation of experimental points is evidently due to several factors, especially fluctuation of the thickness of film, uneven distribution of aggregate structures in the volume of sample and unevenness of section. A great influence on the value of apparent mean diffusion coefficient is exhibited by the thermal history of the sample [10].

Starting from the time—concentration relationships of the squared thickness δ^2 of SSL of the investigated systems (an example for the system NaCMC—CaCl₂ is in Fig. 4), we obtain that the values of diffusion coefficients are in the interval $(1.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}; 9.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1})$, the relative error being $\pm (3\text{--}5)\%$. The progress of the functional relationship between the apparent mean diffusion coefficient D and the concentration of the investigated electrolytes (Fig. 5) indicates a decrease in the value of D with increasing concentration of electrolyte. The observed trend of the concentration dependence D is in good agreement with the concentration dependence of the molar conductivity Λ_i of the i -th ion of the

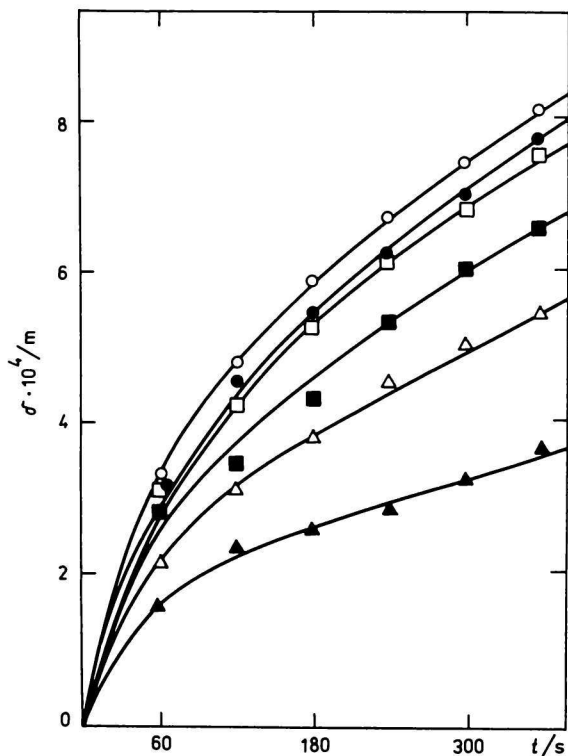


Fig. 2. The thickness of SSL δ as a function of time t at 25 °C for the system NaCMC—electrolyte. \circ distilled water; \bullet KI; \square KCl; \blacksquare LiCl; \triangle CaCl₂; \blacktriangle FeCl₃ ($c = 1.0 \text{ mol dm}^{-3}$).

investigated electrolyte (Figs. 5 and 6). This fact reveals a very close relation of these two fundamental kinetic properties, *i.e.* diffusion coefficient and conductivity, for the solutions of electrolytes. It is obvious that the relationship between diffusion coefficient D and molar conductivity Λ is quite intricate. Evidently, an important factor is the change in mobility of segments hardened by the organized solvation sphere which reduces the intensity of the process giving rise to free volume. It results from the investigated concentration dependences that the influence of cation on swelling (*i.e.* on the basis of decreasing mobility of cations) increases with the magnitude of charge in the order Na^+ , Ca^{2+} , Fe^{3+} and simultaneously in the order K^+ , Na^+ , Li^+ , which is surely connected with numerous physicochemical quantities such as thermodynamic factor, mobility [10], relative permittivity, geometrical shape of diffusing penetrants as well as the radius of the solvated particle which is the greater for a certain ion, the stronger is the electrostatic field on its "surface". In this way, we may explain the apparent

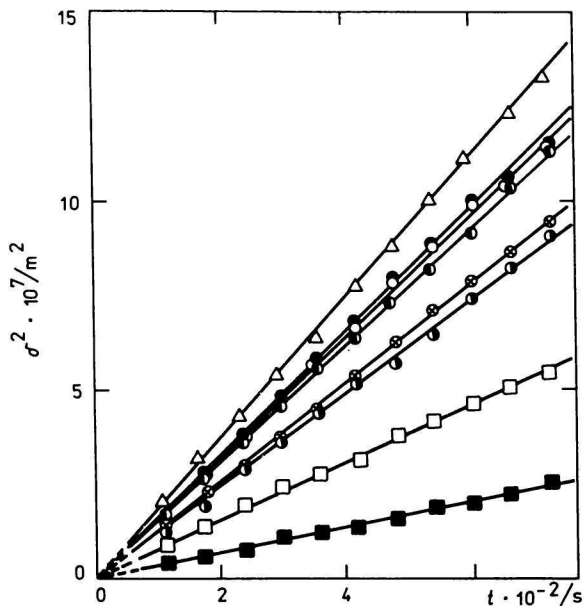


Fig. 3. Squared thickness of SSL δ^2 as a function of time t at 25 °C for the system NaCMC⁻—electrolyte. Δ distilled water; \bullet KI; \circ KBr; \bullet KCl; \otimes NaCl; \bullet LiCl; \square CaCl₂; \blacksquare FeCl₃ ($c = 1.0 \text{ mol dm}^{-3}$).

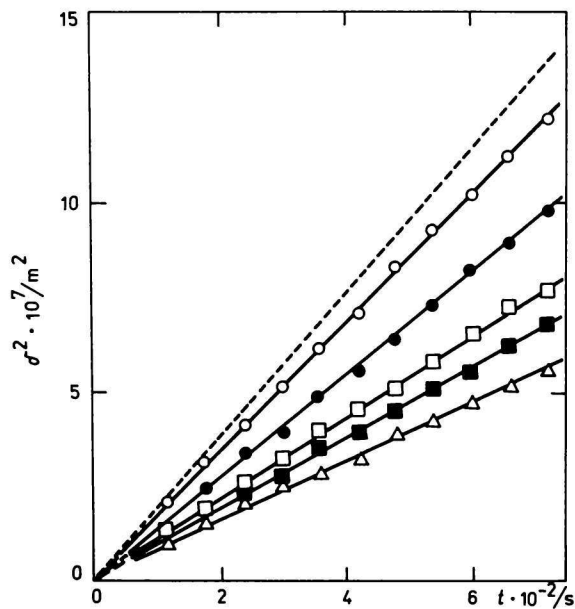


Fig. 4. Squared thickness of SSL δ^2 as a function of time t at 25 °C for the system NaCMC—CaCl₂ ($c / (\text{mol dm}^{-3})$). \circ 0.1; \bullet 0.3; \square 0.5; \blacksquare 0.7; \triangle 1.0.

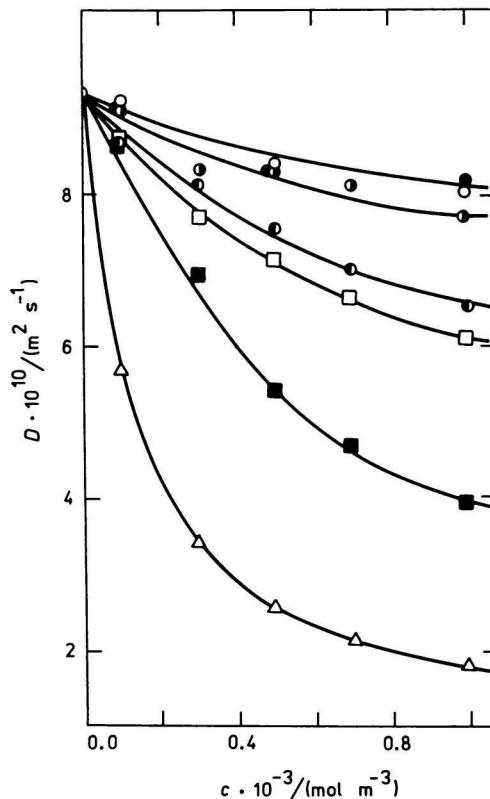


Fig. 5. Variation of the apparent mean diffusion coefficient D with concentration c at 25 °C for the system NaCMC—electrolyte.
 ● KI; ○ KBr; ● KCl; ○ NaCl; □ LiCl;
 ■ CaCl₂; △ FeCl₃.

inconsistency with crystallographic data that the smallest Li⁺ ion should be the most mobile [1].

Anions have substantially smaller influence on swelling, which may be explained by their low ability to solvate in solution. That is caused by their smaller surface density of charge and their hydration radius increases (*i.e.* the value of diffusion coefficient D decreases) in the order Cl⁻, Br⁻, I⁻

The influence of cations and anions on the strength of the bond due to solvation was documented by *Bakeev* [7] on the basis of infrared spectra. His conclusions are in agreement with our opinion as well as with the general views concerning the influence of ions on structure breaking [1].

On the basis of temperature—time relationships (Fig. 7) we may unambiguously state that the value of diffusion coefficient D increases with temperature, which is in accordance with the general theory of diffusion processes in polymers. The values of diffusion coefficient D in the investigated temperature interval (20 °C; 45 °C) varied in the region ($1.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$; $15 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).

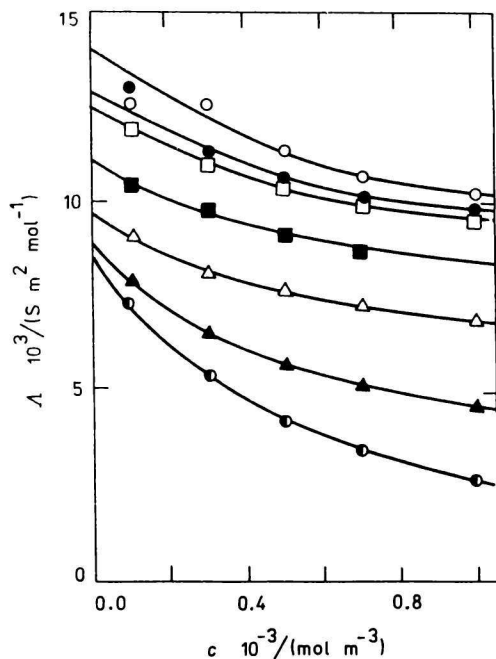


Fig. 6. Variation of molar conductivity Λ with concentration c at 25 °C.

○ KCl; ● KBr; □ KI; ■ NaCl; △ LiCl;
▲ CaCl₂; ● FeCl₃.

It results from Fig. 8 that the temperature dependence of diffusion coefficient D may be described by the common equation of the Arrhenius type [10]

$$D = D^0 \exp(-E_s/RT) \quad (2)$$

The values of preexponential factors D^0 and activation energies E_s calculated from eqn (2) are listed in Table 1. In this table, there are also values $RA_{\delta,s}$ (600 s) and

Table 1

Values of activation parameters D^0 , E_s , δ^0 (600 s), and $RA_{\delta,s}$ (600 s) of the investigated systems

Electrolytes	$\frac{D^0 \cdot 10^6}{\text{m}^2 \text{s}^{-1}}$	$\frac{E_s \cdot 10^{-3}}{\text{J mol}^{-1}}$	$\frac{\delta^0 (600 \text{ s})}{\text{m}}$	$\frac{RA_{\delta,s} (600 \text{ s}) \cdot 10^{-3}}{\text{J mol}^{-1}}$
Distilled water	0.8	16.7	0.032	8.5
1.0 M-LiCl	13.1	24.6	0.10	11.9
1.0 M-NaCl	4.0	21.6	0.052	10.1
1.0 M-KCl	1.1	18.1	0.23	7.9
1.0 M-KBr	3.0	20.2	0.068	10.5
1.0 M-KI	0.9	17.2	0.037	8.9
1.0 M-CaCl ₂	2.4	21.4	0.061	11.0
1.0 M-FeCl ₃	1.6	17.8	0.047	9.3

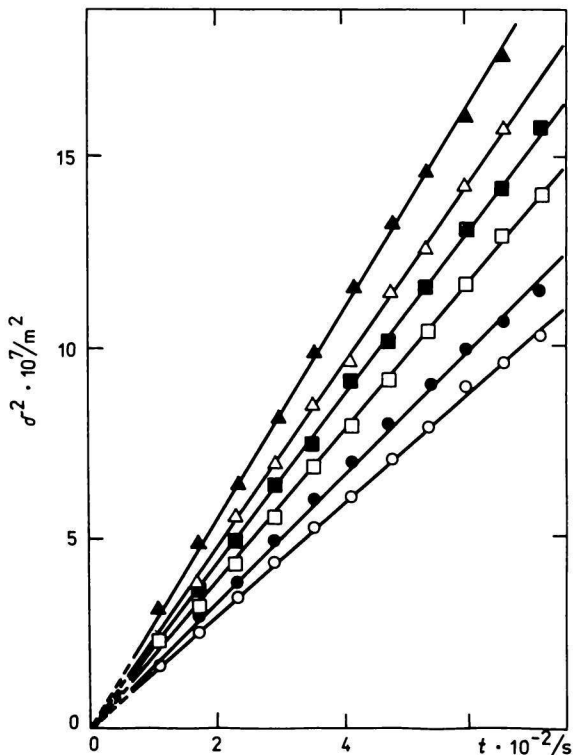


Fig. 7. Squared thickness of SSL δ^2 as a function of time t for the system NaCMC—1.0 M-KI at different temperatures.

○ 20 °C; ● 25 °C; □ 30 °C; ■ 35 °C; △ 40 °C; ▲ 45 °C.

δ^0 (600 s) which result from the equation put forward by *Ueberreiter* and *Asmussen* [11]

$$\delta = \delta^0 \exp(-A_\delta/T) \quad (3)$$

The analysis of eqn (3) has shown [12, 13] that the expression $RA_{\delta,i}$ ($i = s$ or d) stands for the isothermal activation volume work done under the internal pressure when the macromolecular coils pass from the solid polymer phase into the phase of swollen gel SSL — $RA_{\delta,s}$ (swelling) or from SSL into solution — $RA_{\delta,d}$ (dissolution). The value of this work depends on the character of solvent and structure of polymer. For the investigated system NaCMC—electrolyte, it reaches the value 8×10^3 — 12×10^3 J mol⁻¹, the relative error being 5—11 %. We may assume that the value of this work must be significantly affected by the value of equilibrium constant of the process of polymer solvation and this work increases

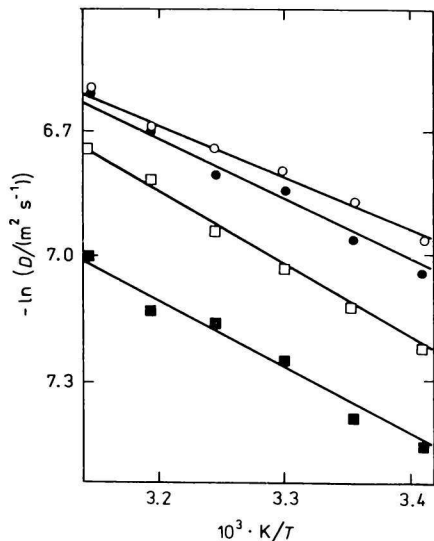


Fig. 8. Variation of the apparent mean diffusion coefficient D with temperature for the system NaCMC—electrolyte ($c = 1.0 \text{ mol dm}^{-3}$).
 ○ Distilled water; ● KBr; □ LiCl; ■ CaCl₂.

with decreasing solvation ability of the solvent. In this way, we may explain the lower values of $RA_{\delta,s}$ and E_s found in this study when compared with the data found for other systems [10, 14].

References

1. Dvořák, J., Koryta, J., and Boháčová, V., *Elektrochemie*. (Electrochemistry.) Academia, Prague, 1978.
2. Frank, H. S. and Evans, M. W., *J. Chem. Phys.* 13, 507 (1965).
3. Erdey-Grúz, T., *Transport Phenomena in Aqueous Solutions*. Akadémiai Kiadó, Budapest, 1974.
4. Ruckov, A. P., *Kolloid. Zh.* 15, 284 (1953).
5. Krestov, G. A., *Termodinamika ionnykh protsessov v rastvorakh*. Khimiya, Leningrad, 1968.
6. Samoylov, O. Y., *Struktura vodnykh rastvorov elektrolitov i gidratsiya ionov*. Izd. Akad. Nauk SSSR, Moscow, 1957.
7. Bakeev, M. I., *Gidratsiya i fiziko-khimicheskie svoystva rastvorov elektrolitov*. Nauka, Alma-Ata, 1978.
8. Brandrup, J. and Immergut, E., *Polymer Handbook*. 2nd Editon. J. Wiley, New York, 1975.
9. Kellö, V., Lapčík, L., Hrivnák, S., Polavka, J., Panák, J., Repka, J., Očadlík, J., and Kalíšek, V., *Chem. Zvesti* 32, 175 (1978).
10. Polavka J., CSc. Thesis. Slovak Technical University, Bratislava, 1976.
11. Ueberreiter, K. and Asmussen, F., *J. Polym. Sci.* 57, 187 (1962).
12. Lapčík, L. and Kellö, V., *IUPAC Preprints*, Vol. 2, p. 645. Madrid, 1974.
13. Valko, L. and Lapčík, L., *Zborník prác Chemickotechnologickej fakulty SVŠT*. Bratislava, 1967.
14. Polavka, J., Lapčík, L., and Valášek, J., *Chem. Zvesti* 34, 63 (1980).

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