ELSEVIER

Polymer 43 (2002) 743–748

polymer

www.elsevier.com/locate/polymer

Flory–Huggins parameter of interaction in polyelectrolyle solutions of chitosan and its alkylated derivative

A.P. Safronov[a,*], A.Yu. Zubarev[b]

[a]Department of Chemistry, Urals State University, 51 Lenin St., 620083 Yekaterinburg, Russia
[b]Department of Mathematics, Urals State University, 51 Lenin St., 620083 Yekaterinburg, Russia

Received 20 February 2001; received in revised form 16 May 2001; accepted 11 July 2001

Abstract

The enthalpy of dilution of chitosan and alkylchitosan solutions in aqueous 0.3 M acetic acid was experimentally studied over the entire concentration range at 298 K, and the values of Flory–Huggins interaction parameter were determined with the help of a new scaling approach which took into account the electrostatic contribution to the enthalpy of dilution of polyelectrolyte solutions. That made it possible to estimate separately the excluded volume contribution to the enthalpy of dilution and, thus, to calculate the values of χ which appeared to be -0.01 for chitosan and -0.21 for alkylchitosan. It was found out that χ did not depend on the presence of salt in the solution. The hydrophobic modification of chitosan enhanced interaction with water due to the hydrophobic hydration in the aqueous solution. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Enthalpy of dilution; Calorimetry; Polyelectrolytes

1. Introduction

Without doubt, Flory–Huggins parameter of interaction — χ, is of the very special importance in polymer solutions. Originally, it was taken from Hildebrand theory of regular solutions to characterize the energy of interaction of polymer segments with solvent molecules within the framework of Flory lattice model [1]. It was included in the well known expression for the chemical potential ($\Delta\mu_1$) of a solvent

$$\Delta\mu_1 = RT\left\{\ln(1-\varphi_2) + \left(1-\frac{1}{p}\right)\varphi_2 + \chi\varphi_2^2\right\} \qquad (1)$$

where p is the degree of polymerization and φ_2 is the volume fraction of polymer in solution.

Although, since then, many other theoretical approaches were introduced to describe solute–solvent interactions in liquid solutions [2], none of them managed to replace Flory–Huggins parameter χ, while considering polymer solutions.

The entropy term in the expression (1) was reconsidered several times, the last one according to De Gennes scaling concept [3]. But, no matter how sophisticated a theory might be, it reserved a place for Flory–Huggins parameter of interaction. On one hand, the importance of χ parameter for theory, stems from being the only way to take into account the specific chemical nature of polymer and solvent. On the other hand, parameter χ cannot be calculated and is either taken from experiment or (more often) referred to as adjustable. Thus, it appears to be a sort of a junction between theory and experiment in polymer solutions.

Experimental determination of χ in non-electrolyte solutions is described elsewhere [4]. Basically, one can (i) use expression (1) to fit experimental data on the chemical potential of the solvent measured by means of osmotic pressure, vapor sorption, light scattering, etc.; (ii) calculate χ from the position of binodal on the phase diagram of polymer solution if there is a liquid–liquid phase separation; (iii) analyze the enthalpy of dilution (ΔH_{dil}) of polymer solution.

However, none of these approaches can be used when the dissolved polymer is a polyelectrolyte. In this case, (i) the chemical potential of the solvent depends rather on the presence of counter-ions than on χ; (ii) usually there is no liquid–liquid phase separation in the solution; (iii) the enthalpy of dilution depends not only on χ (excluded volume interactions) but on electrostatics, as well.

Nevertheless, we believe that the enthalpy of dilution might provide the reliable information on χ, if we manage to estimate the electrostatic contribution to the experimental

---

* Corresponding author. Tel.: +7-3432-616-049; fax: +7-3432-557-401.
E-mail addresses: alexander.safronov@nsu.ru (A.P. Safronov), andrey.zubarev@usu.ru (A.Yu. Zubarev).

PII: S0032-3861(01)00513-4

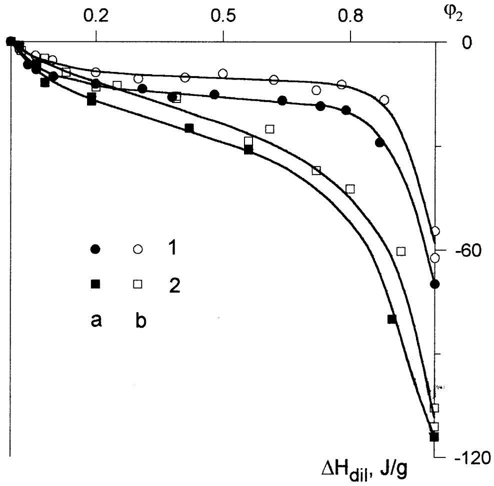

Fig. 1. The enthalpy of dilution of chitosan (1) and alkylchitosan (2) solutions in aqueous 0.3 M acetic acid over the entire concentration range, at 298 K. (a — salt-free solution; b — 0.2 M CH_3COONa present).

values of ΔH_{dil}. The objective of the present study was to find a way to do this and thus to determine Flory–Huggins interaction parameter χ for the solutions of the natural polysaccharides of practical importance: chitosan and its hydrophobically modified derivative — alkylchitosan.

2. Experimental

Chitosan is the derivative of the natural polysaccharide — chitin, obtained by the deacetilation of acetamide groups. The samples of chitosan and its alkylated derivative were kindly supplied by Prof. M. Rinaudo (CERMAV/CNRS, France) and contained monomer units: (I) — with amino groups Chit-NH_2, (II) — with acetamide groups Chit-$NHCOCH_3$ and (III) with dodecylamino groups Chit-$NHC_{12}H_{25}$. The content of different units was determined by ^{1}H-NMR which gave for chitosan sample 88% of units (I), 12% of units (II) and for alkylchitosan sample — 84% of units (I), 12% of units (II), 4% of units (III). The mean-weight molmass of the polymers, determined by static light scattering, was 2×10^5.

Chitosan becomes water soluble only after neutralization by an acid. In order to do this, both chitosan and alkylchitosan were dissolved in 1 M acetic acid. Thus, each unit of the types (I) and (III) was converted into the salty form

$$\text{Chit-NH}_2 + H^+A^- \rightarrow \text{Chit-NH}_3^+A^-$$

Thin films were cast from these solutions and vacuum dried.

All calorimetric measurements were carried out using commercial isothermal Calvet microcalorimeters: DAK-1-1 (Chernogolovka) with 10 ml cells and sensitivity 10^{-6} J/s and MID-200 (Ethalon, Almaty) with 100 ml cells and sensitivity 5×10^{-6} J/s. The values of heat effects from 0.05 to 1 J were measured with ca. 5% accuracy, the values of heat effects 0.005–0.05 J with ca. 10%. All calorimetric measurements were made at 298 K.

We experimentally measured the heat effects of the dilution of chitosan and alkylchitosan acetates over the entire concentration range, by mixing certain amounts of the solution and the solvent. The solutions were prepared in the glass vessels ca. 0.3 ml in volume. In each case, the vessel contained 4 mg of the dissolved polymer. The solutions of low and moderate concentration up to 50% of polymer were prepared directly by pouring the necessary amount of solvent into a vessel; the solutions of higher concentration were prepared by the sorption of solvent vapor on the polymers. Then, the vessels were sealed and stored for several weeks in order to reach equilibrium. The heat of dilution (ΔH_{dil}) was measured when the sealed vessel was broken in the calorimetric cell containing 4 ml of the solvent. The final concentration of the solution was ca. 1 g/l.

3. Results and discussion

The enthalpy of dilution is defined as the heat evolved (or absorbed) while the solution of the given initial concentration φ_i is diluted by the solvent to the final concentration φ_f. As the initial and the final solutions contain the same amount of polymer, the value of ΔH_{dil} is usually referred to 1 g of polymer, or 1 mol of repeating units. Thereafter, the values of ΔH_{dil} are plotted against the initial concentration of the solution.

Fig. 1 represents the values of ΔH_{dil} in the solutions of chitosan and alkylchitosan acetates in 0.3 M aqueous acetic acid at 298 K, over the entire concentration range. The dilute acetic acid was preferred instead of pure water, to prevent hydrolysis. As it was shown in Ref. [5], the dissociation of the acetic acid itself is low, it does not provide considerable amount of acetate ions in the solution and does not affect the properties of the polyelectrolyte. We studied both salt-free solutions and the solutions with added salt: 0.2 M CH_3COONa.

The enthalpy of dilution is negative for all cases which means that, the dilution of any solution to the final concentration 1 g/l is energetically favorable. The values of ΔH_{dil} for alkylchitosan are more negative than for chitosan, and for both polymers, they are more negative in the salt-free solutions ,than in the presence of salt. Despite this, the curves are rather similar in shape. One can distinguish three parts on each — the first one in less concentrated solutions has positive curvature, the second part at medium concentrations is almost linear and the third part at high concentrations has negative curvature.

We believe that the complicated character of the concentration dependence of ΔH_{dil} reflects the superposition of several contributions to the energy of the solution. First, it is the excluded volume interaction. Its contribution to the value of ΔH_{dil} can be obtained from Eq. (1). The last term in Eq. (1) is the partial enthalpy of the solvent Δh_1 which is the heat evolved (or absorbed) while the infinitesimal amount of solvent is added to the solution of definite concentration. Using the general thermodynamic formula [6] and assuming that φ_f is close to zero, one can easily derive from Δh_1, the expression for the enthalpy of dilution

$$\Delta H_{dil} = \chi RT \varphi_2 \tag{2}$$

Thus, the excluded volume interaction should provide the linear dependence of ΔH_{dil} on the initial concentration of the solution. One may observe this linearity at the central part of the curves, presented in Fig. 1.

Second, at higher concentrations the values of ΔH_{dil} become more negative than extrapolated linear dependence. This deviation is provided by the glassy nature of chitosan and alkylchitosan. Long ago, it was shown [7,8] that the dissolution of glassy polymers is accompanied by a large exothermic effect due to the metastable structure of the glass. Theoretical consideration of this contribution to the energy of solution can be found in Ref. [9]. For the enthalpy of dilution, it yields the following:

$$\Delta H_{dil,gl} = \epsilon_{22} \varphi_v^0 \varphi_2^{(1/\varphi_v^0 - 2)} \tag{3}$$

where ϵ_{22} is the energy of cohesion of polymer and φ_v^0 is the concentration of voids in the loose glassy structure of polymer.

However, the influence of the glassy nature of the polymers is essential only in highly concentrated solutions, and rapidly tends to zero with the increase of the solvent content. Basically, this is the energy aspect of the process of plasticization of a glassy polymer by a solvent.

At low concentrations of the solution, the dependence of ΔH_{dil} is not linear either. Hence, in addition to Eqs. (2) and (3), we should take into account the third contribution to the values of ΔH_{dil} provided by the electrostatic energy of polyelectrolyte. Electrostatic interactions are the only long-range forces in the solution and this makes them dominant at low content of the polymer.

The conventional theoretical approach [10], based on Lifson–Katchalsky consideration of the charged elongated macromolecule [11], is restricted to the dilute solutions of polyelectrolytes where macromolecules are far apart from each other and do not overlap. As it was shown in Ref. [12], for chitosan solutions in 0.3 M acetic acid, this condition is fulfilled only at concentrations below $c^* = 0.3$ g/l.

Hence, all the solutions under consideration in the present study (including that at φ_f) contain overlapping charged macromolecules of chitosan or alkylchitosan, and we should admit that, there is no adequate theoretical consideration of such systems. We have tried to develop the one based on the scaling concept.

4. Theoretical model

Let us consider a system of strongly charged polyelectrolyte chains with counter-ions in a salt-free solution. The average distance between chains (ξ) is much less than their contour length (L). The total electrostatic energy of the solution may be separated into the following parts:

E_a — the energy of the counter-ions adsorbed on the charged chains;
E_D — Debye electrostatic energy of the ionic system;
E_{el} — the elastic energy of the stretched charged chains.

The estimation of these terms is given below.

4.1. The energy of adsorbed counter-ions

Let us consider a straight charged segment of a macromolecule. We denote the linear charge density of the segment itself by ρ_0 and the charge density of the segment with adsorbed counter-ions by ρ. Let r_1 be the characteristic radius of the region, where the adsorbed counter-ions are located. It is equal to the diameter of the chain by an order of magnitude. The electrostatic potential ψ at a distance r from the quasi-cylindrical segment is given by a standard equation of electrostatics

$$\psi = -2\rho \ln r + C \tag{4}$$

if r is less then Debye radius r_D. Estimations [13] show that $r_D \approx \xi$. If $r > r_D$, the potential ψ rapidly decreases and tends to the value of the mean electrostatic potential of the solution ψ_D. We can therefore use the following boundary condition: $\psi \to \psi_D$, when $r \to \xi$. It effectively takes into account the presence of other chains in the system. The similar boundary conditions are often used in cell models for composites [14]. We have to use this approximation because the detailed analysis of the many-chain system, is hopeless. It should be noted that this boundary condition is different from that used by Lifson and Katchalsky [11]: ($\partial\psi/\partial r \to 0$, when $r \to \xi$).

Returning to Eq. (4), we find that $C = \psi_D$. It is convenient to introduce the value ψ_1 — the excess electrostatic potential over the mean potential of the solution

$$\psi_1 = -2\rho \ln \frac{r_1}{\xi} \tag{5}$$

Below, for the sake of simplicity, we use the two-region model for polyelectrolyte solution [13]. For example, we suppose that, in the region 1, which is close to the segment ($r < r_1$) the electrostatic potential is constant and equal to $\psi_1 + \psi_D$, the counter-ions are effectively 'condensed' in this region, and their concentration is c_1. In the region 2 ($r_1 < r < \xi$), the potential equals to ψ_D, the counter-ions are effectively 'free', and their concentration is c_2. The concentrations c_1 and c_2 are connected by Boltsman relation

$$c_1 = c_2 \exp\left(\frac{q\psi_1}{kT}\right),$$

q being the charge of the counter-ion.

The further treatment, similar to that described in Ref. [13], leads to the known equation for the fraction of free counter-ions β

$$\ln\frac{1-\beta}{\beta} = \ln\frac{\varphi^{1-u\beta}}{1-\varphi} \tag{6}$$

where φ — is the volume fraction of charged chains in the solution and u — is the charge density parameter defined by:

$$u = \frac{e^2}{DkTb} \tag{7}$$

where e is the elementary charge, b the monomer length; D is the dielectric constant.

Let us now estimate the excess energy of the counter-ions adsorbed on the chain in the region 1, as compared to the mean electrostatic energy of the solution. The electrostatic energy of a unit length of a segment with the charge density ρ in the potential ψ_1 is:

$$E = \frac{\rho\psi_1}{2D} = -\frac{\rho_0^2\beta^2}{D}\ln\varphi \tag{8}$$

We took into account Eq. (5) and estimation $r_1/\xi \approx \varphi$. In order to get E_a, we should subtract from Eq. (8), the energy of the charged chain itself in its own potential: $-2\rho_0 \ln\varphi$. As a result, we obtain the energy of adsorbed counter-ions per 1 mol of charged units ($q = e$, uni/uni valent polyelectrolyte)

$$E = -\frac{\rho_0^2\beta^2}{D}\ln\varphi - \left(-\frac{\rho_0^2}{D}\ln\varphi\right) = \frac{e^2 N_a}{bD}(1-\beta^2)\ln\varphi \tag{9}$$

assuming $\rho_0 = e/b$.

4.2. Debye energy of the solution

In the first rough approximation, the value of E_D for the polyelectrolyte solution of concentration above c^* can be estimated by the same way as for the solution of the ordinary electrolyte [15]

$$E_D = -\frac{q^3}{D^2}\sqrt{\frac{8\pi}{kTV}}(N_a\beta)^{3/2} \tag{10}$$

where V is the volume of the solution.

However, the fact that the charged monomer units are connected with each other in a chain, lowers $|E_D|$ as compared to Eq. (10). Therefore, Eq. (10) is an upper estimation for Debye energy of the polyelectrolyte solution. Let us rewrite Eq. (10) in a form:

$$E_D = -\frac{q\rho_0}{D}N_a\epsilon_D, \qquad \epsilon_D = A\frac{q^2}{D\rho_0\sqrt{kTV}}\sqrt{\frac{N_a}{V}}\beta^{3/2},$$

$$A = \sqrt{8\pi}$$

Let N be the number of macromolecules in the solution. Taking into account the condition of the electric neutrality of the solution

$$N_a q = N\rho_0 L, \tag{11}$$

we get:

$$\sqrt{\frac{N_a}{V}} = \sqrt{\frac{N\rho_0 L r_1^2}{qVr_1^2}} = \sqrt{\frac{\rho_0}{qr_1^2}\varphi},$$

and

$$\epsilon_D = A\frac{q^2}{D\rho_0 r_1\sqrt{kT}}\sqrt{\frac{\rho_0\varphi}{q}}\beta^{3/2} = \frac{Ab}{r_1}\sqrt{\frac{u\varphi}{D}}\beta^{3/2}$$

Assuming that $r_1 \approx b$, finally we get Debye energy per 1 mol of charged units in uni/uni-valent polyelectrolyte solution of concentration above c^*

$$E_D = -\frac{e^2 N_a}{b}\left(\frac{\beta}{D}\right)^{3/2}\sqrt{Au\varphi} \tag{12}$$

.

4.3. The elastic energy of the stretched charged chain

Assuming that, due to the electrostatic repulsion of monomer units the macromolecular coil is elongated, let us suppose it to be quasi-cylindrical. We denote by h — the characteristic length of the elongated coil in the direction of its long axis, by $Q = b\rho_0 L$ the overall charge of a chain with the adsorbed counter-ions.

The electrostatic energy of charging a cylinder from the zero charge to Q according to the standard approach [15] by an order of magnitude is:

$$E \cong \frac{Q^2}{Dh} \tag{13}$$

The entropy losses of the stretched chain might be estimated using de Gennes Eq. (3):

$$S \cong -\frac{h^{5/2}}{B}, \qquad B = a_m^{5/2}p^{3/2}$$

where a_m — is the radius of a monomer unit, p — is the degree of polymerization.

Hence, the free energy of a stretched coil is:

$$F \cong \frac{Q^2}{Dh} + T\frac{h^{5/2}}{B}$$

Minimizing free energy, we find the estimation for the value of h.

$$h = \left(\frac{BQ^2}{T}\right)^{2/7} = \left(\frac{a_m}{b}\right)^{5/7}u^{2/7}\beta^{4/7}L \tag{14}$$

Substituting Eq. (14) in Eq. (13), we obtain the estimation for the elastic energy of one chain

$$E_{el,1} = \rho_0^2\left(\frac{\beta}{D}\right)^{10/7}u^{-2/7}\left(\frac{b}{a_m}\right)^{5/7}L$$

Multiplying it by the number of macromolecules in the solution and taking Eq. (11) into account, we get the elastic

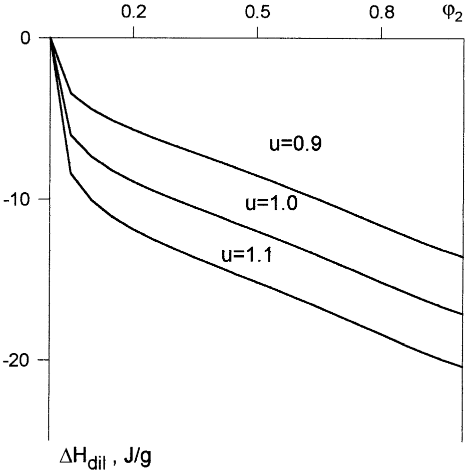

Fig. 2. Calculated concentration dependence of the enthalpy of dilution of polyelectrolyte solution over the entire concentration range including contributions from the excluded volume interactions and the electrostatic interactions.

energy per 1 mol of charged monomer units.

$$E_{\mathrm{el}} = \frac{N_{\mathrm{a}}e^2}{b}\left(\frac{b}{a_{\mathrm{m}}}\right)^{5/7} u^{-2/7}\left(\frac{\beta}{D}\right)^{10/7} \tag{15}$$

Thus, the total electrostatic energy per 1 mol of charged units of uni/uni-valent polyelectrolyte in the solution of any concentration above the c^* is the sum of Eqs. (9), (12) and (15)

$$E_{\mathrm{tot}} = \frac{e^2N_{\mathrm{a}}}{b}\left[\frac{1-\beta^2}{D}\ln\varphi - A\left(\frac{\beta}{D}\right)^{3/2}\sqrt{u\varphi} + \left(\frac{b}{a_{\mathrm{m}}}\right)^{5/7}\left(\frac{\beta}{D}\right)^{10/7}u^{-2/7}\right] \tag{16}$$

Taking into account that in the condensed phases volume changes are small, we may calculate the concentration dependence of the enthalpy of dilution directly from the values of the energy of polyelectrolyte solution at the initial and the final concentration

$$\Delta\mathrm{H}_{\mathrm{dil,el}}(\varphi_{\mathrm{i}} \rightarrow \varphi_{\mathrm{f}}) = E_{\mathrm{tot}}(\varphi_{\mathrm{f}}) - E_{\mathrm{tot}}(\varphi_{\mathrm{i}}) \tag{17}$$

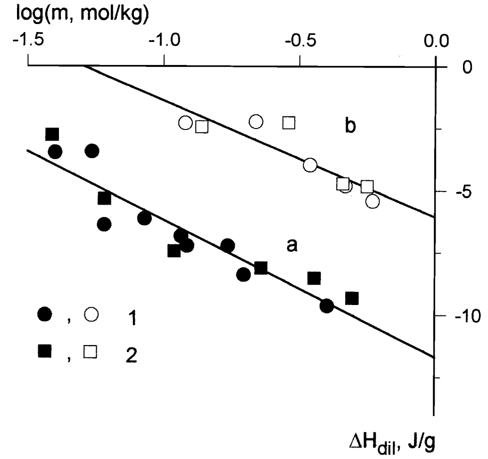

Fig. 3. The enthalpy of dilution of chitosan (1) and alkylchitosan (2) semi-dilute solutions in aqueous 0.3 M acetic acid at 298 K. (a — salt-free solution; b — 0.2 M CH_3COONa present). Symbols — experimental values, solid lines — interpolation according to Eq. (17).

Fig. 2 represents the calculated concentration dependence of $\Delta H_{\mathrm{dil,el}}$ over the entire concentration range, at 298 K for the different values of the charge density parameter u (Eq. (7)). The curves are qualitatively similar to that presented at Fig. 1 except for the region of highly concentrated solutions where the experimental values are strongly influenced by the glassy nature of chitosan and alkylchitosan. Let us, for the sake of simplicity, restrict further consideration to low and moderately concentrated solutions where we can neglect this influence and, hence, not take into account contribution (3) to the enthalpy of dilution. In this case:

$$\Delta\mathrm{H}_{\mathrm{dil}} = \chi RT\varphi_2 + \Delta H_{\mathrm{dil,el}}, \tag{18}$$

where $\Delta H_{\mathrm{dil,el}}$ is determined according to Eq. (17).

The proposed theory contains only one parameter in $\Delta H_{\mathrm{dil,el}}$ — the charge density parameter u. (Note that β depends on u according to Eq. (6)). It can be determined using the values of the enthalpy of dilution at low concentrations where the contribution of the excluded volume interactions is negligible and long-range electrostatic interactions are dominant.

Fig. 3 represents the values of $\Delta H_{\mathrm{dil,el}}$ for semi-dilute solutions ($1 < c < 10$ g/l) of chitosan and alkylchitosan versus the logarithm of the molality of the solution, at 298 K. The plots for the salt-free solution and the solution with 0.2 M CH_3COONa are almost linear in accordance with such data for other polyelectrolytes [16,17]. There is no difference between chitosan and alkylchitosan, which is quite reasonable because both are totally ionized. However, in salt-free solutions, the values of $\Delta H_{\mathrm{dil,el}}$ are more exothermic than, at the presence of salt.

The experimental values were interpolated with the theoretical expression (17) using u as adjustable parameter. It gave $u = 1.05$ for the salt-free solutions of chitosan and alkylchitosan and $u = 0.95$ for the solutions with added 0.2 M CH_3COONa. Using the value of u, one can estimate the average distance between charges in the macromolecule according to Eq. (7). The value $u = 1.05$ yields $b = 7.0$ Å, which is in a good agreement with the geometrical parameters of chitosan monomer units connected by β-glucoside bond (7.3Å between adjacent nitrogen atoms). Of course, the lower value of u in the solution with 0.2 M CH_3COONa does not mean that the average distance between charges, somehow increased. In fact, the electrostatic energy of the polyelectrolyte solution, in the presence of salt is not covered by expressions (9), (12) and (15) which should be generalized for it. However, taking into account the similarity of the curves at Fig. 1, for the sake of simplicity, we used the same theoretical expressions. In this case, $u = 0.95$ is an 'apparent' value indicating that the addition of salt

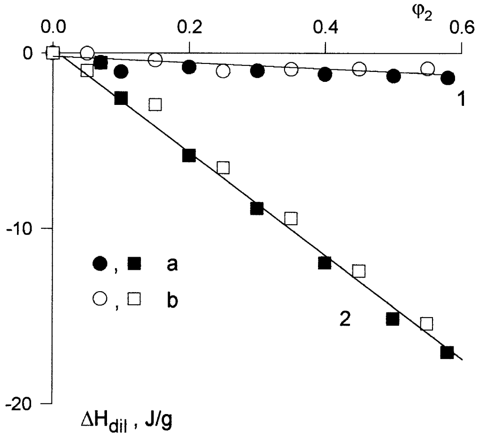

Fig. 4. The excluded volume (Flory–Huggins) contribution to the enthalpy of dilution of chitosan (1) and alkylchitosan (2) solutions in aqueous 0.3 M acetic acid at 298 K in a wide concentration range. (a — salt-free solution; b — 0.2 M CH_3COONa present). Symbols — the result of subtracting from experimental data the values of $\Delta H_{\mathrm{dil,el}}$ calculated according to Eq. (17), solid lines — interpolation by means of Eq. (2).

effectively decreases the electrostatic interactions in the solution.

Using the values of u, let us calculate $\Delta H_{\mathrm{dil,el}}$ in the low and moderately concentrated solutions of chitosan and alkylchitosan according to Eq. (17) and subtract them from the experimental values of ΔH_{dil} according to Eq. (18) in order to obtain the excluded volume contribution to the enthalpy of dilution. Fig. 4 represents the result of the subtraction. One can see that the values of the enthalpy are negative and their concentration dependence is linear in accordance with expression (2). The slope of the linear interpolation gives the value of χ. Thus, for chitosan solutions, the obtained value of χ is: -0.01 both in the absence and in the presence of salt, for alkylchitosan solutions, the value of χ is more negative: -0.21.

Concerning this values let us point out the following:

First, aqueous 0.3 M acetic acid is a good solvent both for chitosan and alkylchitosan, which is obviously, due to the hydrogen bonds formation between water molecules and polar groups of chitosan repeating units.

Second, the addition of salt does not change the value of χ and so does not affect the excluded volume interaction, which is quite reasonable because the latter is not electrostatic.

Third, hydrophobically modified chitosan interacts with aqueous 0.3 M acetic acid better than chitosan itself.

The last is rather unexpected at the first sight. However, let us take into account that water solutions provide an opportunity for hydrophobic hydration of non-polar groups. Although, the details of this process are still under discussion, and there is no adequate theory for it, it was shown for many aqueous solutions [18–20] that hydrophobic hydration provides exothermic heat effects. Probably, this is due to the extra structuring of water around hydrophobic moieties. Hence, we assume that this might be the reason for hydrophobically modified chitosan to improve the interaction with the aqueous media.

Acknowledgements

The authors are grateful to the INTAS Foundation for the financial support of the research (grant 96-1193). They also acknowledge the partial support of CRDF (grant REC. 005. 2000). APS appreciates fruitful discussions with Prof. A.R. Khokhlov and Prof. M. Rinaudo that inspired the work.

References

[1] Flory PJ. Principles of polymer chemistry. Ithaca: Cornell University Press, 1953.
[2] Walas MS. Phase equilibria in chemical engineering. Boston: Butterworths, 1985.
[3] De Gennes P-G. Scaling concepts in polymer physics. Ithaca: Cornell University Press, 1979.
[4] Kamide K, Matsuda S, Saito M. Polym J 1988;20(1):31–43.
[5] Rinaudo M, Pavlov G, Desbrieres J. Polymer 1999;40(25):7029–32.
[6] Prigogine I, Defay R. Chemical thermodynamics. London: Longmans and Green, 1954.
[7] Schulz GV, Hellfritz H. Z Elektrochem 1953;57(9):835–41.
[8] Tager AA, Kargin VA. Colloidny Z 1952;14(5):367–71.
[9] Safronov AP, Tager AA. Vysokomol Soedin Ser A 1991;33(10):2198–205.
[10] Manning G. J Chem Phys 1969;51:924–33.
[11] Lifson S, Katchalsky A. J Polym Sci 1954;13(1):43–45.
[12] Buhler E, Rinaudo M. Macromolecules 2000;33(6):2098–106.
[13] Grosberg AYu, Khokhlov AR. Statistical physics of macromolecules. New York: AIP Press, 1994.
[14] Christensen RM. Mechanics of composite materials. New York: Wiley, 1979.
[15] Landau LD, Lifshiz YeM. Statistical physics 1964.
[16] Scerjanc J, Dolar D, Leskovsek D. Z Phys Chem Neue Folge 1967;56:207–17.
[17] Mita K, Okubo T. J Chem Soc Faraday Trans I 1974;70:1546–50.
[18] Nemethy G, Sheraga HA. J Chem Phys 1962;36(12):2401–17.
[19] Tager AA, Safronov AP, Sharina SV, Galaev IYu. Colloid Polym Sci 1993;271(9):868–72.
[20] Tager AA, Safronov AP, Sharina SV, Galaev IYu. Colloid Polym Sci 1994;272(10):1234–9.