Behavior of Linear and Cross-Linked Polyelectrolytes in Metal Salt Solutions

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Summary: Comparison of swelling properties of linear and cross-linked polyelectrolytes on the basis of diffusion theory is carried out. It is shown that viscosity of both positively and negatively charged macromolecules in solutions containing low-molecualr ions may be predicted with the help of generalized Fuoss's law.

Keywords: gel; polyelectrolytes; swelling ratio; viscosity

Introduction

Polyelectrolyte macromolecules[1–3] and related cross-linked networks[4–6] were intensively studied in the last few decades. New trends in this branch of polymer science and technology are mostly connected with nanotechnology, molecular biology and some other disciplines devoted to understanding connection between living and non-living nature[5,6]. A "molecular assembler" proposed by K. Drecksler[7], and aimed to the creation of structures to molecular or supramolecular level of organization is the most noticeable example. Furthermore, information carriers both in biological organisms and in artificial electronics are charged particles (monomer units of DNA and electrons, respectively) easily managed by external electromagnetic fields. It is than of developing of a general theoretical description of fundamental properties of polyelectrolytes applicable to different lyte systems. The most part of such properties are closely connected with the extremely high swelling of linear and cross-linked charged macromolecules. Indeed, polyelectrolyte hydrogels[5,6], which can sorb extremely large amounts of water, are often classified as "intelligent materials" due to their high sensitivity to external stimuli (changing of temperature, ionic strength and chemical composition of surrounding medium as well as electric current and magnetic field).

Some theories, which are able to give interpretation of swelling of polyelectrolyte coils and networks separately, were already[4,8] developed. Nevertheless some restrictions of applicability of thermodynamics itself became significant for further understanding of the processes in polyelectrolyte systems important for biophysical and nanotechnological purposes. For example, some metastable states may be formed in polyelectrolytes systems during chemical reactions[6,9]. Consequently, an alternative non-thermodynamic description of polyelectrolyte swelling and related phenomena appeared useful.

Experimental

The dependence of viscosity of aqueous solutions of polydiallyldimethylammoniumchloride and polyacrylic acid (Mw = 250 000) on concentration of polymer c at different concentrations of low-molecular salts are investigated by standard methods at room temperature.

The experiments were carried out in accordance with the method already described[10,11]. The fixed amount of salt solution (or their mixture) was added to the polymer solution of given concentration.

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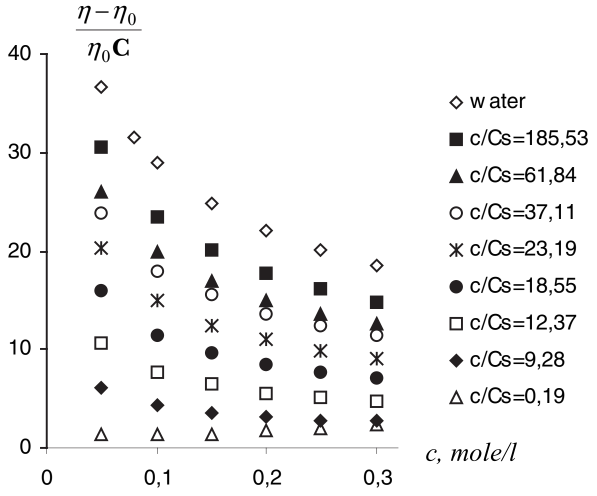

Figure 1.
Dependence of reduced viscosity of polydiallyldimethylammoniumchloride containing $K_3[Fe(CN)_6]$ aqueous solutions on polymer segment concentration.

Then this mixture was diluted by distilled water in order to keep the ratio c/C_s (polymer segmental concentration to salt concentration) fixed.

Results

An example of experimentally obtained dependence of reduced viscosity $(\eta-\eta_0)/c\eta_0$ of solutions of polydiallyldimethylammoniumchloride containing $K_3[Fe(CN)_6]$ polymer segment concentration are presented at the Figure 1 as obtained at different ratios of **polymer segment concentration c to salt concentrationC_S**. Similar types of dependence of reduced viscosity are well known in the literature.

We have to underline that namely such way of dilution of investigated polymeric system gives a set of straight lines in double

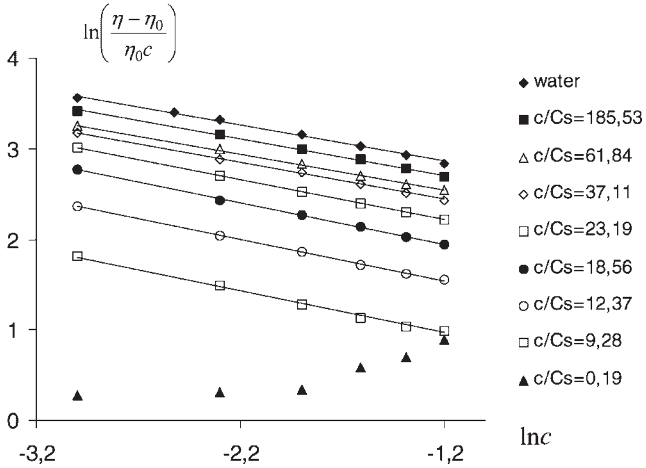

Figure 2.
The dependence of reduced viscosity of polydiallyldimethylammoniumchloride containing $K_3[Fe(CN)_6]$ aqueous solutions on polymer segment concentration in double logarithmic scale.

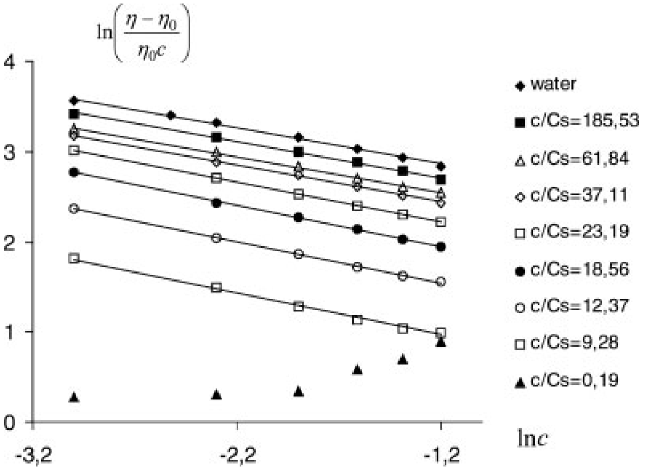

Figure 3.
The dependence of reduced viscosity of polyacrylic acid containing Na_2SO_4 aqueous solutions on polymer segment concentration in double logarithmic scale.

logarithmic scale (the same dependencies as at Figure 1 are presented at Figure 2 in double logarithmic scale). Similar set of dependencies was obtained in solution of polyacrilic acid in NaCl (Figure 3), $K_3[Fe(CN)_6]$, $CuSO_4$, poly(0.75 sodium acrylate – 0.25 acrylic acid) and of carboxymethyl cellulose in mentioned salts[10,11], etc.

Generalized Diffusion Theory of Polyelectrolyte Hydrogels Swelling

In accordance with the theory[12] of swelling pressure is determined by the double electric layer that is formed at hydrogel surface due to thermal motion of low-molecular ions. Similar double layers are formed in different physical and physico-chemical conditions and quantitatively interpreted as follows. As a result of Brownian motion, counterions partly leave the surface layer of the hydrogel. In stationary case this thermal flow of free counterions is compensated by electrostatic attraction of these particles to the charged frame of the network. As a result, an electric double layer is formed near the surface of the specimen, while charged particle partly is penetrating into the solution. It is supposed that the concentration of functional groups inside the gel in constant.

On the one hand, the field of the double layer acts on the mobile ions, preventing them to leave the volume of the specimen, but this field acts on non-compensated charge of the network in the surface layer. The last force F contributes to the swelling pressure of the hydrogel.

$$F = \int_V \rho(x)E(x)dV \qquad (1)$$

where $\rho(x)$ is density of uncompensated charge (both volume V inside and outside hydrogel may be used due to third Newton's law). Supposing that the surface of the specimen is plane (i.e. that double layer is thin in comparison with the dimension of the specimen), one can rewrite (1) as:

$$\pm P = \int_{0(l)}^{l(\infty)} \rho(x)E(x)dx \qquad (2)$$

Limits $(0,l)$ in (2) correspond to calculation of the pressure (force) acting on uncompensated charge inside the gel, and (l,∞) – outside it. Using the Boltzmann's distribution in (2), one can obtain the next expression for uncompensated charge[1]:

$$\rho(x) = q_0 \sum_i z_i \exp\left(-\frac{z_i q_0 \phi(x)}{kT}\right) - N(x) \tag{3}$$

where Z_i – charge number of ion i, k – Boltzmann's constant, T – absolute temperature, q_0 – elementary charge. Integral (2) may be calculated analytically in the most general case, while

$$\frac{dE}{dx} = 4\pi\rho(x) \tag{4}$$

Substituting (3) and (4) in (2), we get:

$$\pm P = \frac{1}{8\pi} \int_{0(l)}^{l(\infty)} \frac{d}{dx}(E^2) = q_0 \int_{0(l)}^{l(\infty)} \left[\sum_i z_i n_{i0} \exp\left(-\frac{z_i q_0 \phi(x)}{kT}\right) - N(x)\right] E(x)dx$$

Taking into account (4), the latter integral may be rewritten as:

$$P(x)|_0^x = E^2(x) = \left\{kT \sum_i n_i \exp\left(-\tfrac{z_i q_0 \phi(x)}{kT}\right) - N(x)\phi(x)\right\}\Bigg|_0^x \tag{5}$$

the pressure acting on all the layers varying between 0 and x. The expression (5) may be considered as the first integral of Poisson-Boltzmann equation too. The function $N(x)$ formally may be presented as:

$$N(x) = N_0 = \begin{cases} N_0, & 0 < x \le l \\ 0, & l < x \end{cases}. \tag{6}$$

(6), in particular, gives the possibility to calculate the integral (2) analytically, i.e. this result is obtained for homogeneous gel. Substituting real limits if integrating in (5), one can get expression for pressure acting on the surface layers of the gel

$$P_s = P(l)|_l^\infty = -E^2(l) = kT\left(\sum_i n_i(\infty) - \sum_i n_i(l)\right) \tag{7}$$

and the surface layers of the solution:

$$P_g = P(x)|_0^l = E^2(l) = kT\left(\sum_i n_i(l) - \sum_i n_i(0)\right) - N_0 q_0(\phi(l) - \phi(0)) \tag{8}$$

By summing right and left parts of Equations (7) and (8) we obtain an expression for the potential different between gel interior media and its surface:

$$\Delta\phi_g = \phi(l) - \phi(0) = \frac{kT}{q_0 N_0}\left(\sum_i n_i(\infty) - \sum_i n_i(0)\right) \tag{9}$$

In other words, the ionic component of swelling pressure of a polyelectrolyte gel immersed in the solution containing arbitrary mixture of low molecular ions is given by expression:

$$P = kT\left(\sum_i n_i(l) - \sum_i n_i(0)\right) \tag{10}$$

where concentration of each sort of ions may be calculated with the help of Boltzmann's distribution by taking into account real expression for surface potential difference.

Thus, in accordance with diffusion theory, swelling pressure is determined by the difference between total ionic concentrations at the surface and in gel bulk and can be written as:

$$P = kT\left(\sum_i n_i(\infty) - \sum_i n_i(0)\right) \tag{11}$$

Nevertheless, one should note, that interactions between different types of ions and charged network leads to decreasing of theoretical value of osmotic pressure also[13].

One of the most important (for further consideration) result of diffusion theory

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[1] In order to simplify expressions the case $\varepsilon = 1$ is under consideration.

may be obtained from expression (9) directly. Namely, the difference

$$\Delta N = \sum_i n_i(\infty) - \sum_i n_i(0) \tag{12}$$

determines the contribution of electrostatic interactions in common behavior of the system under consideration ΔN is called "parameter of similarity". The theory proposed in[10,11] is briefly considered in next section in order to show that some similarity can be obtained for linear polymers in complicated salt solutions too. This fact gives possibility to modification of the Fuoss's regularity[14] and its generalization to solutions containing arbitrary mixture of high- and low-molecular weight electrolytes.

Generalization of Fuoss's Regularity: Polyelectrolyte Effect in Complex Solutions

The majority of articles in the field are devoted to the investigation of polyelectrolyte behaviour in pure solvents or solutions containing one low-molecular component only. Indeed, the main purpose of modern theoretical investigations of polyelectrolyte macromolecules is mainly to obtain a complete theory based on calculations *ab initio*, when macroscopic parameters of the systems may be calculated through the microscopic ones. The problem, unfortunately, is too complicated to be solved in a general case in an analytical way.

Quite general description of polyelectrolyte macromolecules in complex solutions may be based on comparison of the properties of a polyelectrolyte molecule in a complex solution with the properties of this molecule some in simple case. Obviously, such comparison allows predicting polyelectrolyte solutions behaviour in large number of practical applications on the basis of restrictive experimental data. It was shown[10,11] that such approach gives possibility to develop a theory, which is applicable to any polyelectrolyte solution.

Nowadays two different theoretical approaches for the description of polyelectrolytes are well known. The former is based on the Debye-Hückel model currently used in thermodynamics calculations[17] both for linear and cross-linked charged polymer systems. The latter is usually connected with the Donnan model which considers the potential difference between interior of macromolecular coil and the surrounding solution[18].

The most known tool allows analysing the potential spatial distribution is the Poisson – Boltzmann equation. (The first integral of this equation gives possibility to describe swelling properties of polyelectrolyte gel completely, as it was shown in previous section). It is necessary to underlain, that Poisson – Boltzmann equation use the *averaged* spatial potential and *averaged* electric field magnitude. Consequently symmetrization of a problem is quite natural in any model based on using of this equation. In particular, separate polymer coil may be considered as a system having spherical symmetry.

In particular, this is a base for describing the swelling of macromolecular coils in the same way, as description of polyelectrolyte hydrogels. Namely, such swelling is considered as a result of balance between elastic pressure and ionic pressure, which, taking into account analogies with formula (2) may be given as:

$$P = \frac{q_0}{r_0^2} \int_0^{r_0} \left(\sum_{i=1}^{\alpha} N_i(r) - N_0(r) \right) \frac{d\varphi}{dr} r^2 dr \tag{13}$$

Moreover, the well-known anomalous behaviour of polyelectrolytes in semi-diluted solutions (increasing of reduced viscosity with decreasing of segmental concentration) firstly reported by Fuoss and Strauss, in the Donnan model may be interpreted as the *influence* of a charged macromolecular coil on the neighbouring ones. If the potential having the spherical symmetry is used for the description of isolated coil, then one have to describe any deformations of this potential using the model, which have the same type of symmetry. Consequently, random coil-coil

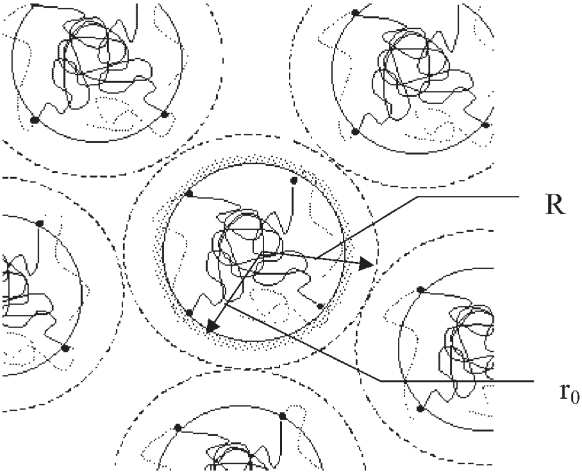

Figure 4.
Spherical symmetry in coil-coil interactions.

interactions are taken into account by the scheme given in Figure 4.

Random influence of neighbouring coils on each other in model of averaged electric field may be taken into account through a boundary condition, which supposes that magnitude of electric field is equal to zero at the surface of a sphere (R), (Figure 5).

Obviously, all theoretical models based on Poisson-Boltzmann equation may differ from each other by boundary conditions and their interpretation only. Thus, the proposed model is quite close to the one employed in[15]. In this work an isolated polyelectrolyte system was considered; this supposition corresponds to zero boundary conditions for potential and its derivative at $x \to \infty$:

The proposed model allows description of examined coil and coil-coil interactions by the following boundary conditions:

$$\varphi_1(\rho) \to 0, \frac{d\varphi_1}{d\rho} \to 0, \quad \rho \to 0, \tag{14}$$

(centre of the coil)

$$\varphi_1(\rho)|_r = \varphi_2(\rho)|_r, \left.\frac{d\varphi_1}{d\rho}\right|_r = \left.\frac{d\varphi_2}{d\rho}\right|_r \tag{15}$$

(surface of the coil)

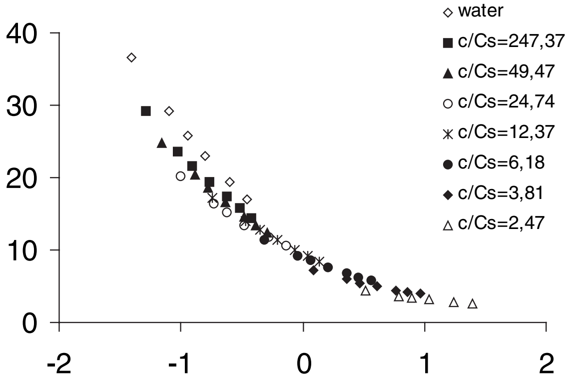

Figure 5.
Master curve of reduced viscosity of polydiallyldimethylammoniumchloride in solution containing Na_2SO_4.

$$\left.\frac{d\varphi_2}{d\rho}\right|_R = 0 \text{ (description of coil} \\ \text{– coil interactions)} \qquad (16)$$

Potentials $\varphi_1(\rho)$ and $\varphi_2(\rho)$ satisfy to two different forms of Poisson-Boltzmann equation[15]. In the first case the charge of polyelectrolyte ion $N(\rho)$ should be taken into account. In the second case spatial charge is formed by low-molecular weight ions only.

Mentioned equations may be written as:

$$(\nabla_\perp)^2\varphi_1(r) = \frac{4\pi q_0}{\varepsilon}\left[\sum_{i=1}^{\alpha} z_i N_{i0}\exp\left(-\frac{z_i q_0 \varphi_1}{kT}\right) - N_0(r)\right] \qquad (17)$$

$$(\nabla_\perp)^2\varphi_2(r) = \frac{4\pi q_0}{\varepsilon}\sum_{i=1}^{\alpha} z_i N_{i0}\exp\left(-\frac{z_i q_0 \varphi_2}{kT}\right) \qquad (18)$$

where $(\nabla_\perp)^2 = \frac{1}{\rho^2}\frac{\partial}{\partial\rho}\rho^2\frac{\partial}{\partial\rho}$ is a spherical part of laplasian, q_0- elementary charge, ε is the relative permittivity.

Equations (17) and (18) are similar to the ones used in a previous paper[15]. The main difference is connected with constant N_{0i}. One can not use neutrality condition solving Equations (17) and (18), valid for macroscopic gels, whereas the dimension of the coil is comparable with the Debye's length. Consequently, the concentrations of mobile ions at the centre of the coil are not equal to each other, and constants N_{0i} themselves ought to be found from boundary conditions.

Indeed, one can select zero point for electrostatic potential arbitrary; consequently the system (14)–(16) contains 5 conditions instead of 4. The additional condition, which allows obtaining N_{0i}, is the neutrality of the system as a whole.

It was shown[10,11] that Poisson – Boltzmann equations may be linearized (such procedure is not correct in the case of macroscopic gel specimen).

$$(\nabla_\perp)^2\varphi_1(r) = \frac{4\pi q_0}{\varepsilon}\left[\sum_{i=1}^{\alpha} z_i N_{i0} - N_0(r)\right] - \frac{4\pi}{\varepsilon}\left[\sum_{i=1}^{\alpha}\frac{z_i^2 q_0^2}{kT}N_{i0}\right]\varphi_1 \qquad (19)$$

$$(\nabla_\perp)^2\varphi_2(r) = \frac{4\pi q_0}{\varepsilon}\sum_{i=1}^{\alpha} z_i N_{i0} - \frac{4\pi}{\varepsilon}\left[\sum_{i=1}^{\alpha}\frac{z_i^2 q_0^2}{kT}N_{i0}\right]\varphi_2 \qquad (20)$$

One can see (22), (23), that the influence of low-molecular components on behaviour of the system may be completely described by two parameters only. One of them is the well-known Debye's length λ, which is given by relation:

$$\frac{1}{\lambda^2} = \frac{4\pi}{\varepsilon}\sum_{i=1}^{\alpha}\frac{z_i^2 q_0^2}{kT}N_{i0} \qquad (21)$$

And the second determines the deviation of ions density from neutrality in the middle of coil:

$$Q = \sum_{i=1}^{\alpha} z_i N_{i0} - N_0(0) \qquad (22)$$

As it was mentioned before, in addition to 2 the differential Equations (19), (20) the system should satisfy 5 boundary conditions (14)–(15). Taking into account, that the solutions of differential equations contain $2 \times 2 = 4$ arbitrary constants, one can conclude, that either (21), of (22) should be determined from boundary conditions too.

Equations (19) and (20) may be rewritten in dimensionless variables $\xi = \rho/R$, and it is easy to see that electrostatic behaviour of the system is managed by the only one dimensionless parameter (R/λ). It is convenient to consider a parameter:

$$(\lambda/R)^3 = \left(\frac{4\pi M_0}{3M_f}\right)\lambda^3 N_A \qquad (23)$$

as a *parameter of similarity* for polyelectrolyte solutions containing arbitrary mixtures of low molecular weight ions (M_0– polymer chain mass, M_f – polymer segment mass, c – segmental concentration of polymer, N_A Avogadro's number). In (23) it is taken into account that radius R may be expressed through the segmental concentration of the polymer:

$$R = 3\sqrt{\frac{3M_f}{4\pi N_A M_0 c}} \tag{24}$$

The analogy with the description of polyelectrolyte hydrogels in diffusion theory[12] is clear. Namely, the force resulting in coil swelling is determined by the action of the averaged electrostatic field on non-compensated charges inside the coil. Equations (19)–(20) show that the profile of electrostatic potential for the same geometry of the coil and the same ratio (R/λ) will be the same. In other words, averaged radius of the coil r for a given polymer and temperature is the function of the obtained parameter of similarity (R/λ).

Comparison with Experimental Data

Expression (28) means that the product $c\lambda^3$ may be used for comparison of theoretical and experimental results instead of ratio R/λ. In other words we can propose the next experimentally proven generalisation of Fuoss's regularity[10,11]:

$$\frac{\eta - \eta_0}{\eta_0 C_n} = M(\lambda^3 C_n N_A)^m + L \tag{25}$$

where M and L are constants for a given type of polymer. Constant L is practically equal to zero when the chain is flexible, for example in the case of polyacrilic acid.

For the given ratio of **polymer segment concentration *c* to salt concentration$\mathbf{C_S}$** the parameter of similarity is numerically equal to:

$$\lambda^3 c N_A \approx \frac{1}{\sqrt{c}} 4,82 \cdot 10^{-2}\left(1 + \sum p_i z_i^2\right)^{-\frac{3}{2}} \tag{26}$$

where ρ_i is the ration of concentration of ions of each type i to polymer segment concentration. It is easy to see, that in logarithmic scale curves, which correspond to different values of ρ_i should be shifted in respect to each other in accordance with the relation:

$$\ln(\lambda^3 c N_A) = -\frac{1}{2}\ln c - \frac{3}{2}\ln\left[4,82 \cdot 10^{-2}\left(1 + \sum p_i z_i^2\right)\right] \tag{27}$$

Consequently, the master curves of reduced viscosity may be obtained by shifting initial the dependence (Figures 2 and 3) in logarithmic scale. An example of master curve is presented at Figure 5. One can see that all experimentally obtained results actually may be described by the corresponding master curves with a satisfactory accuracy. The same results were obtained for the other investigated systems[7].

Thus, using of parameter of similarity gives possibility to obtain modified form of Fuoss's law, which allows prediction of the viscosity of complex polyelectrolyte solutions, containing both several low-molecular weight compounds and macromolecules.

We should underline, that the theoretical interpretation of obtained result is given on the base of Poisson-Boltzman equation and diffusion theory of polyelectrolytes swelling in low-molecular salt solutions. Direct comparison of swelling curve of polyelectrolyte network and master curve of reduced viscosity shows that these curves differs from each other by a multiplication constant multiplier only.

Conclusion

It has been shown that swelling of both linear and cross-linked polyelectrolytes may be theoretically described from a common point of view based on diffusion theory of surface double electric layers. Besides, behavior of macromolecule chains and networks in solutions containing arbitrary mixture of low-molecular weight ions may be reduced to calculation of parameters of similarity.

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