Scattering from Multicomponent Polymer Mixtures: Weakly Charged Polymers

M. Benmouna[†] **and T. A. Vilgis**[*]

Max-Planck-Institut für Polymerforschung, Ackermannweg 10,
Postfach 31 48, D-6500 Mainz, FRG

Received October 25, 1990; Revised Manuscript Received February 8, 1991

ABSTRACT: The static scattering properties of weakly charged homopolymers and copolymers in solution are investigated by using the generalization of Zimm's equation to multicomponent polymer systems. The interaction matrix is modeled as a sum of the short-range excluded-volume matrix and the long-range Debye–Hückel matrix. Several cases are considered, depending on the charge distribution among species. If the species are charged equally, the scattering behavior is essentially controlled by the thermodynamic parameter χ. If the species have opposite charges, the electrostatic attraction enhances significantly their compatibility. The case of a mixture of weakly charged and neutral polymers is also investigated, and the results are consistent with those reported by Joanny and Leibler. The description of counterions and salt ions is also discussed. It is argued that when these ions are considered as point particles, their role should be limited to the screening of electrostatic interactions and the electroneutrality condition.

1. Introduction

In a preceding paper[1] we have discussed theoretical models to derive the general result for the static structure matrix **S** of a multicomponent system

$$\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}_0^{-1}(\mathbf{q}) + \mathbf{V} \qquad (1)$$

where $\mathbf{S}_0(\mathbf{q})$ is the bare (or single-chain) structure matrix and **V** the interaction matrix; $q = (4\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength of the incident radiation and θ the scattering angle. The purpose of the present paper is to show how this result can be generalized to mixtures of weakly charged polymers. Polyelectrolyte solutions have frequently been described as multicomponent mixtures, and the strong coupling between polyions and counterions in the salt-free solutions and between polyion–counterions–co-ions in solutions with added salt play an essential role in determining the static scattering properties of these mixtures. Therefore, the use of matrix formulation to describe these properties in polyelectrolyte solutions is fully justified. However, here, this justification is not essentially due to the fact that counterions and co-ions are considered as components in the mixture. In fact, we shall argue that when counterions and co-ions are treated as point particles, their contribution is limited to the screening of Coulomb potential and to the realization of the global electroneutrality condition. It is only in the situation where these relatively small ions have finite sizes, nonzero contrast factors with respect to the solvent, and can be characterized by thermodynamic interactions (excluded-volume parameters) in addition to their electrostatic interactions that their "status" as full components in the mixture is justified. The matrix formulation is used here mostly because we consider mixtures of selectively charged homopolymers and copolymers in solution. This is implemented here as a direct generalization of eq 1 by redefining the excluded-volume parameters to account for the long-range Coulomb interaction. We consider specifically ternary mixtures of two charged homopolymers A and B in a solvent and a charged block copolymer AB in a solvent. Needless to say, eq 1 has already been applied to various mixtures of neutral polymers and copolymers and in particular the case of ternary mixtures has been examined in detail from both the theoretical[2,3] and the experimental[4] sides. Because the expressions of the elements of **S** are particularly useful in this work, we briefly recall the result in the next section.

2. Ternary Mixtures of Two Polymers A and B and a Solvent

For charged polymers, the equation remains valid with an appropriate modification of the interaction matrix, which we denote as **U**. Therefore, eq 1 becomes

$$\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}_0^{-1}(\mathbf{q}) + \mathbf{U} \qquad (2)$$

where the matrices are square and 2 by 2. We recall that $\mathbf{S}_0$ has zero off-diagonal elements for homopolymers and contains nonzero off-diagonal elements if AB is a copolymer. For simplicity, we shall consider these two cases separately.

2.1. Homopolymers AB and a Solvent.

The matrix $\mathbf{S}_0$ is

$$\mathbf{S}_0 = \begin{bmatrix} S_\mathrm{a}^0 & 0 \\ 0 & S_\mathrm{b}^0 \end{bmatrix} \qquad (3)$$

where $S_\alpha^0 = \phi_\alpha N_\alpha P_\alpha(q)$ (α = a, b) with $\phi_\alpha \equiv n_\alpha N_\alpha$, n_α being the number of chains of type α per unit volume, N_α their degree of polymerization, and $P_\alpha(q)$ their form factor. Substituting eq 3 into eq 2 gives

$$\mathbf{S}^{-1} = \begin{bmatrix} \dfrac{1}{S_\mathrm{a}^0} + U_\mathrm{aa} & U_\mathrm{ab} \\ U_\mathrm{ab} & \dfrac{1}{S_\mathrm{b}^0} + U_\mathrm{bb} \end{bmatrix} \qquad (4)$$

It is a straightforward matter to invert this matrix and find

$$S_\mathrm{aa}(q) = S_\mathrm{a}^0(1 + U_\mathrm{bb}S_\mathrm{b}^0)/\mathcal{D} \qquad (5a)$$

$$S_\mathrm{ab}(q) = S_\mathrm{ba}(q) = -U_\mathrm{ab}S_\mathrm{a}^0S_\mathrm{b}^0/\mathcal{D} \qquad (5b)$$

---

[*] To whom correspondence should be addressed.

[†] Permanent address: Physics Department, University of Tlemcen, Tlemcen, BP 119 Algeria.

0024-9297/91/2224-3866$02.50/0

and

$$\mathcal{D} = 1 + U_{aa}S_a^{\ 0} + U_{bb}S_b^{\ 0} + (U_{aa}U_{bb} - U_{ab}^{\ 2})S_a^{\ 0}S_b^{\ 0} \qquad (5c)$$

In the reciprocal form we have

$$1/S_{aa} = 1/S_a^{\ 0} + U_{aa} - U_{ab}^{\ 2}S_b^{\ 0}/(1 + U_{bb}S_b^{\ 0}) \qquad (6a)$$

$$1/S_{ab} = U_{ab} - (1 + U_{aa}S_a^{\ 0} + U_{bb}S_b^{\ 0} + U_{aa}U_{bb}S_a^{\ 0}S_b^{\ 0})/U_{ab}S_a^{\ 0}S_b^{\ 0} \qquad (6b)$$

$S_{bb}(\mathbf{q})$ can be deduced from $S_{aa}(\mathbf{q})$ by exchanging the indices a and b. It is also useful to recall the expression of the measured intensity including the scattering lengths *a* and *b* of monomers A and B, respectively:

$$I(\mathbf{q}) = \frac{a^2S_a^{\ 0} + b^2S_b^{\ 0} + (a^2U_{bb} + b^2U_{aa} - 2abU_{ab})S_a^{\ 0}S_b^{\ 0}}{1 + U_{aa}S_a^{\ 0} + U_{bb}S_b^{\ 0} + (U_{aa}U_{bb} - U_{ab}^{\ 2})S_a^{\ 0}S_b^{\ 0}} \qquad (7)$$

2.2. Block Copolymer AB and a Solvent. The essential modification with respect to the former case is the introduction of off-diagonal elements $S_{ab}^{\ 0}$. Equation 2 becomes

$$\mathbf{S}^{-1}(q) = \begin{bmatrix} S_b^{\ 0}/\delta + U_{aa} & -S_{ab}^{\ 0}/\delta + U_{ab} \\ -S_{ab}/\delta + U_{ab} & S_a^{\ 0}/\delta + U_{bb} \end{bmatrix} \qquad (8)$$

where $\delta = S_a^{\ 0}S_b^{\ 0} - S_{ab}^{\ 0\,2}$, $S_a^{\ 0} = U^2\phi NP_a(q)$, $S_b^{\ 0} = (1 - U)^2\phi NP_b(q)$, and $S_{ab}^{\ 0} = S_{ba}^{\ 0} = U(1 - U)\phi NP_{ab}(q)$, U being the fraction of A monomers within a chain, ϕ the total number density, and N the total degree of polymerization. P_{ab} is the intramolecular interspecies form factor. It is easy to calculate the inverse of $\mathbf{S}^{-1}$ and to obtain

$$S_{aa}(\mathbf{q}) = (S_a^{\ 0} + U_{bb}\delta)/\Delta \qquad (9a)$$

$$S_{ab}(\mathbf{q}) = S_{ba}(\mathbf{q}) = (S_{ab}^{\ 0} - U_{ab}\delta)/\Delta \qquad (9b)$$

where

$$\Delta = 1 + U_{aa}S_a^{\ 0} + U_{bb}S_b^{\ 0} + 2U_{ab}S_{ab}^{\ 0} + (U_{aa}U_{bb} - U_{ab}^{\ 2})\delta \qquad (9c)$$

The reciprocal expressions of $S_{ij}(q)$ are not simple and will not be needed here. $S_{bb}(q)$ can be deduced from eq 9a, and the total scattering intensity becomes

$$I(\mathbf{q}) = \{a^2S_a^{\ 0} + b^2S_b^{\ 0} + 2abS_{ab}^{\ 0} + (a^2U_b + b^2U_a - 2abU_{ab})\delta\}/\Delta \qquad (10)$$

where *a* and *b* are the scattering lengths of species a and b. In the next sections, we define explicitly the interaction matrix **U** for weakly charged polymers and use the results presented in this section to calculate $S_{ij}(q)$ and see how they are modified by the electrostatic potentials.

2.3. Generalized Interaction Parameters. We assume that, for weakly charged polymers, the total interaction matrix **U** can be written as a sum of the bare excluded-volume matrix **V** and a long-range electrostatic matrix $\mathbf{U}_e$; i.e.

$$\mathbf{U} = \mathbf{V} + \mathbf{U}_e \qquad (11a)$$

where

$$\mathbf{V} = \begin{bmatrix} v_{aa} & v_{ab} \\ v_{ab} & v_{bb} \end{bmatrix}; \quad \mathbf{U}_e = \alpha(\mathbf{q})\begin{bmatrix} f_a^{\ 2} & \epsilon_{ab}f_af_b \\ \epsilon_{ab}f_af_b & f_b^{\ 2} \end{bmatrix} \qquad (11b)$$

$$\alpha(\mathbf{q}) \equiv 4\pi l/(q^2 + \kappa^2) \qquad (11c)$$

$l \equiv e^2/\epsilon kT$ is the Bjerrum length equal to about 7 Å for water at 25 °C. $\epsilon_{ab} = +1$ if monomers A and B have charges of the same sign, and $\epsilon_{ab} = -1$ otherwise; f_ae and f_be are the charges carried by A and B monomers, respectively. The Debye–Hückel screening length is given by

$$\kappa^2 \equiv 4\pi l\phi_{ci} \qquad (11d)$$

where ϕ_{ci} is the number density of counterions, and the overall electroneutrality requires that

$$f_a\phi_a + \epsilon_{ab}f_b\phi_b = \phi_{ci} \qquad (11e)$$

In the case of added salt, the additional counterions and the co-ions both contribute to the screening and eq 11d becomes

$$\kappa^2 = 4\pi l\sum_i \phi_{ci} \qquad (11f)$$

The sum in this equation runs over all free-point ions in the system. We assume that the charge fractions f_{ci} of these ions are equal to 1 for simplicity. As pointed out earlier, if these ions have finite size, they must be treated as full components and not as fictitious particles that contribute to the screening only. This point will be discussed in more detail later. Note that we have introduced eq 11 as an assumption. This is in fact not necessary, as was shown independently in ref 5 and refs 6 and 7. In the paper by the Russian group the free energy has been written as a function of all components. Minimization of this free energy with respect to the counterion concentration gives immediately the screened form of the interaction potential. Alternatively in ref 5 and refs 6 and 7 the free energy functional at all concentrations has been formulated. Integrating out the counterions and writing the effective Edwards Hamiltonian for the "dressed" polyion leads similarly to eq 11 (compare also section 5 and see ref 7 for details).

Recalling the expressions of v_{ij} in terms of the Flory interaction parameters χ_{ij} and the solvent fraction φ_s, one has[2]

$$U_a = 1/\varphi_s - (2\chi_{as} - \alpha f_a^{\ 2}) \qquad (12a)$$

$$U_{ab} = 1/\varphi_s - (\chi_{as} + \chi_{bs} - \chi_{ab} - \epsilon_{ab}\alpha f_af_b) \qquad (12b)$$

Equation 12a shows that the repulsion electrostatic AA interaction has a net effect of reducing the apparent χ_{as} and therefore increasing the quality of the solvent. Equation 12b shows that if $\epsilon_{ab} = 1$, the net effect of electrostatic repulsion is to increase the incompatibility of the two polymers, and if $\epsilon_{ab} = -1$, the attractive long-range electrostatic forces tend to compensate for the effect of thermodynamic repulsion due to χ_{ab}; this can be seen as a net "compatibilizing effect". These observations are general and apply to homopolyelectrolytes and copolyelectrolytes as well. We shall now calculate $S_{ij}(\mathbf{q})$ for these two systems separately.

3. Mixtures of Two Selectively Charged Polyions and a Solvent

In this section, we consider a ternary mixture of two polyions A and B with different charge distributions and a solvent. The latter includes counterions and eventually salt ions to ensure the screening of electrostatic interactions and the electroneutrality condition, in addition to the real solvent. Of course, polyions A and B may have different sizes (masses, form factors, etc.), different thermodynamic properties (excluded volumes), and different scattering lengths (or $\partial n/\partial c$). The matrix $\mathbf{S}^{-1}$ remains relatively simple in this case:

$$\mathbf{S}^{-1}(\mathbf{q}) = \begin{bmatrix} \dfrac{1}{S_a{}^0} + v_{aa} + \alpha(\mathbf{q})f_a{}^2 & v_{ab} + \epsilon_{ab}\alpha(\mathbf{q})f_af_b \\ v_{ab} + \epsilon_{ab}\alpha(\mathbf{q})f_af_b & \dfrac{1}{S_b{}^0} + v_{bb} + \alpha(\mathbf{q})f_bf_b{}^2 \end{bmatrix} \tag{13}$$

The partial structure factors and the total intensity can be readily obtained from eqs 5 and 7. We only note that, unlike the case of neutral homopolymers, the cross term $S_{ab} \neq 0$ when $v_{ab} = 0$ since the AB correlations are maintained through electrostatic potential in the absence of thermodynamic correlations. Let us examine closely the denominator $\mathcal{D}$, which is common to all scattering quantities. $\mathcal{D}$ has been written before, but we could obtain it directly from the determinant of $\mathbf{S}^{-1}$ in eq 13. It can be put in the form

$$\mathcal{D} = \mathcal{D}_{\text{neutral}} + \alpha(\mathbf{q})\,\{f_a{}^2S_a{}^0 + f_b{}^2S_b{}^0 + v_eS_a{}^0S_b{}^0\} \tag{14a}$$

where $\mathcal{D}_{\text{neutral}}$ is the denominator in the absence of charges

$$\mathcal{D}_{\text{neutral}} = 1 + v_aS_a{}^0 + v_bS_b{}^0 + (v_av_b - v_{ab}{}^2)S_a{}^0S_b{}^0 \tag{14b}$$

and v_e is given by

$$v_e = v_af_b{}^2 + v_b{}^2f_a{}^2 - 2\epsilon_{ab}v_{ab}f_af_b \tag{14c}$$

Assuming that the solvent has the same quality for A and B polymers

$$v_a = v_b = v_{ab} - \chi = v \tag{15}$$

where χ is proportional to the Flory–Huggins interaction parameter, we obtain

$$\mathcal{D} = 1 + v(S_a{}^0 + S_b{}^0) - \chi(\chi + 2v)S_a{}^0S_b{}^0 + \alpha(\mathbf{q})\,\{f_a{}^2S_a{}^0 + f_b{}^2S_b{}^0 + [v(f_a - \epsilon_{ab}f_b)^2 - 2\epsilon_{ab}\chi f_af_b]S_a{}^0S_b{}^0\} \tag{16}$$

Let us consider the $q = 0$, which is related to the thermodynamic limit, put $x = \phi_a/\phi$, the fraction of polymer A in the mixture, and assume for simplicity that the degrees of polymerization are equal $N_a = N_b = N$; we have

$$\mathcal{D}(0) = 1 + v\phi N - \chi(\chi + 2v)\phi^2N^2x(1-x) + \alpha(0)\,\{[f_a{}^2x + f_b{}^2(1-x)]\phi N + [v(f_a - \epsilon_{ab}f_b)^2 - 2\epsilon_{ab}\chi f_af_b]\phi^2N^2x(1-x)\} \tag{17a}$$

Several limits can be discussed.

(i) $f_a = f_b = f$ ($\epsilon_{ab} = 1$). This means that the two polymers have the same charges. In this case $\mathcal{D}$ becomes simple

$$\mathcal{D}(0) = \mathcal{D}(0)_{\text{neutral}} + \alpha f^2\phi N(1 - \chi/\chi_c) \tag{17b}$$

with

$$\mathcal{D}(0)_{\text{neutral}} \approx v\phi N(1 - \chi/\chi_c) \tag{17c}$$

$$\chi_c{}^{-1} = 2x(1-x)\phi N \tag{17d}$$

where we have neglected in eq 17c one and the term in $\chi^2(\chi/v \ll 1)$. This gives

$$\mathcal{D}(0) \approx (v + \alpha f^2)\phi N(1 - \chi/\chi_c) \tag{17e}$$

This clearly shows that when the two polymers are charged the same way, the phase separation is completely governed by the thermodynamic parameter χ. Equation 17e shows that the excluded-volume parameter v is enhanced by the quantity αf^2 reflecting electrostatic repulsion. These remarks will be made later in different conditions, and this behavior is, of course, expected.

(ii) $f_a = f_b = f$ ($\epsilon_{ab} = -1$). This means that polymers A and B carry opposite charges and therefore they have an attractive electrostatic potential. Let us see how $\mathcal{D}(0)$ is modified in conditions similar to those in eq 17e. It is an easy matter to find in this case that

$$\mathcal{D}(0) \approx v\phi N\{1 - \chi/\chi_c\} + \alpha f^2\phi N\{1 + 4v\phi Nx(1-x)\} \tag{17f}$$

This shows clearly an effect of compatibilization due to the electrostatic term. If $\chi \approx \chi_c$, the denominator has an additional large positive term, which prevents phase separation. We note that this term goes like $(2f\phi N)^2$. This behavior is expected for oppositely charged polymers.

(iii) $f_a = f$; $f_b = 0$. This corresponds to the mixture of charged and neutral polymers in solution. In this limit, we find

$$\mathcal{D}(0) \approx v\phi N(1 - \chi/\chi_c) + \alpha f^2x\phi N\{1 + v\phi N(1-x)\} \tag{17g}$$

One can make the same observation as in the case where $f_b = f$ but $\epsilon_{ab} = -1$ with an attractive potential 4 times larger because of $(2f)^2$. This is consistent with the observations of Joanny and Leibler,[6] who considered poor solvent conditions and observed that the peak in $S_{aa}(q)$ disappears by adding a small amount of neutral polymers. They interpreted this observation as a destruction of the mesophase structure and collapse of the charged polymer. Vilgis and Borsali[7] have also considered this system within the Edwards Hamiltonian method and derived the corresponding structure factors $S_{ij}(q)$. Here, we only reproduce $S_{aa}(q)$, which is identical with the result reported in the above references:

$$S_{aa}(q) = (q^2 + \kappa^2)\left(\frac{1}{S_b{}^0} + v\right)/(q^2 + \kappa^2) \times \left\{\frac{1}{S_a{}^0S_b{}^0} + v\left(\frac{1}{S_a{}^0} + \frac{1}{S_b{}^0}\right) + 4\pi lf_a{}^2\left(\frac{1}{S_b{}^0} + v\right)\right\} \tag{18a}$$

In the reciprocal form, this equation can be written simply as

$$S_{aa}{}^{-1}(\mathbf{q}) = S_{aa}{}^{-1}(\mathbf{q})_{\text{neutral}} + \alpha(\mathbf{q})\,f_a{}^2 \tag{18b}$$

with

$$S_{aa}{}^{-1}(\mathbf{q})_{\text{neutral}} = S_a{}^0(\mathbf{q})^{-1} + v(1 + vS_b{}^0)^{-1} \tag{18c}$$

Intermediate Solvent Conditions. This is perhaps an extreme case, but it is quite interesting and possible to realize experimentally. An example[8] is given by the 50/50 mixture of sulfonated PSH and PSD in a mixture of undeuterated and deuterated benzene to be studied by neutron scattering. The scattering intensity is obtained from eq 7 by letting $a = -b$, the composition $x = {}^1/_2$ and hence

$$S_a{}^0 = S_b{}^0 = \frac{\phi N}{2}P \tag{19a}$$

If we consider the neutral polymers case with

$$v_a = v_b = v_{ab} - \chi = v \tag{19b}$$

and substitute eq 19a,b into eq 7, we obtain the known bulk result with the reduced interaction parameter $\phi\chi$, namely

$$\frac{I(\mathbf{q})}{a^2} = \frac{\phi NP(\mathbf{q})}{1 - \frac{\chi}{2}\phi NP(\mathbf{q})} \tag{19c}$$

or in the reciprocal form

$$\frac{a^2}{I(\mathbf{q})} = \frac{1}{\phi NP(\mathbf{q})} - \frac{\chi}{2} \tag{19d}$$

where we recall that $P_a = P_b = P(\mathbf{q})$, $\phi = \phi_a + \phi_b$, and $N = N_a = N_b$. Therefore, it would be interesting to check if this simplification is maintained for charged polymers. Substituting eq 19a–d and $a = -b$ in eq 7 after a straightforward manipulation gives

$$\frac{I(\mathbf{q})}{a^2\phi N} = \frac{P\left[1 + \left(\upsilon + \frac{\chi}{2}\right)\phi NP\right] + \alpha(\mathbf{q})\,\phi NP^2 A}{\left[1 - \frac{\chi}{2}\phi NP\right]\left[1 + \left(\upsilon + \frac{\chi}{2}\right)\phi NP\right] + \alpha(\mathbf{q})\,\phi NPB} \tag{20a}$$

where

$$A \equiv \left(\frac{f_a + \epsilon_{ab} f_b}{2}\right)^2 \tag{20b}$$

and

$$B \equiv \frac{f_a^{\,2} + f_b^{\,2}}{2} + \upsilon\left(\frac{f_a - \epsilon_{ab} f_b}{2}\right)^2 \phi NP - \frac{1}{2}\epsilon_{ab}\chi f_a f_b \phi NP \tag{20c}$$

We see that in the neutral limit $\alpha = 0$ and we recover the previous result. Several cases can be considered.

(i) $f_a = f_b = f$ ($\epsilon_{ab} = +1$). This means that both polymers have the same charges. A and B become

$$A = f^2;\quad B = f^2\left[1 - \frac{\chi}{2}\phi NP\right] \tag{21a}$$

Substituting eq 21a into eq 20a yields

$$\frac{I(\mathbf{q})}{a^2\phi N} = \frac{P(\mathbf{q})}{1 - \frac{\chi}{2}\phi NP(\mathbf{q})} \tag{21b}$$

which is exactly the result in the neutral limit. It is surprising to find that the peak is completely controlled by the thermodynamic χ parameter independently of the charge carried by the polymer, if there is no polydispersity in the charge distribution.

(ii) $f_a = f_b = f$ ($\epsilon_{ab} = -1$). This means that charges carried by polymers A and B are of opposite signs but have the same strength f. In this case

$$A = 0;\quad B = f^2\left[1 + \left(\upsilon + \frac{\chi}{2}\right)\phi NP\right] \tag{22a}$$

Substituting eq 22a into eq 20a yields

$$\frac{I(\mathbf{q})}{a^2\phi N} = \frac{P(\mathbf{q})}{1 - \frac{\chi - \chi_e}{2}\phi NP(\mathbf{q})} \tag{22b}$$

with

$$\chi_e = 2\alpha(\mathbf{q})\, f^2 \tag{22c}$$

This means that the electrostatic attraction between A and B polymers (χ_e parameter is attractive) reduces the thermodynamic repulsive χ parameter. This compatibilization is, of course, expected. Similar compatibilization effects have been first observed theoretically and experimentally in ref 9. It has been discussed previously also by one of us.[10]

(iii) $f_a = f$; $f_b = 0$. This corresponds to a mixture of charged and neutral polymers. We have

$$A = (f^2/4);\quad B = (f^2/2)\left(1 + \frac{1}{2}\upsilon\phi NP\right) \tag{23a}$$

Substituting eq 23a into eq 20a gives $I(q)$, which is not as simple as for $S_{aa}(q)$. It is perhaps more appealing to write $I(q)$ in the reciprocal form

$$\frac{a^2\phi N}{I(\mathbf{q})} = \frac{1 - \chi\phi NP/2}{P} + \beta\frac{1 + \left(\upsilon + \frac{\chi}{2}\right)\phi NP}{1 + \left(\upsilon + \frac{\chi}{2}\right)\phi NP + \beta P} \tag{23b}$$

with

$$\beta \equiv \chi f^2 \phi N/4 \tag{23c}$$

The first term in the right-hand side is the result for the neutral polymer. The second term contains the effect of changes but depends on all other properties such as υ, χ, and ϕNP. This was not the case for $S_{aa}(\mathbf{q})$ where the second term was equal to β (within a constant factor) (cf. eq 18b).

4. A Charged Copolymer AB and a Solvent

The extension of our discussions above to copolyelectrolytes is straightforward. For simplicity, we shall consider a diblock AB copolymer and try to identify the effect of a selective charge distribution along the chains in addition to other possible differences of geometrical, optical, or thermodynamical natures. The general expressions of $S_{ij}(\mathbf{q})$ (i, j = a, b) were already given in section 2 with the appropriate interaction parameters including the long-range Coulomb potentials (see eqs 8–11). We shall first discuss the case of a dissymmetric copolymer before turning to the special but more interesting case of a symmetric diblock copolymer.

4.1. Dissymmetric Charged Copolymers. We limit our discussions to $S_{aa}(q)$, but the other structure factors can be dealt with in the same way. We have in general

$$S_{aa}(q) = (S_a^{\,0} + U_b\delta)/\Delta \tag{24a}$$

with

$$U_b = \upsilon_b + \alpha(q)\, f_b^{\,2};\quad \delta \equiv S_a^{\,0} S_b^{\,0} - S_{ab}^{\,0\,2} \tag{24b}$$

$$\Delta = \Delta_{\text{neutral}} + \alpha(q)\,\{f_a^{\,2} S_a^{\,0} + f_b^{\,2} S_b^{\,0} + 2\epsilon_{ab} f_a f_b S_{ab}^{\,0} + (f_a^{\,2}\upsilon_b + f_b^{\,2}\upsilon_a - 2\epsilon_{ab}\upsilon_{ab} f_a f_b)\delta\} \tag{24c}$$

A particularly simple result is obtained when block B is not charged ($f_b = 0$). Therefore, letting $f_b = 0$ in eq 24, we obtain

$$\frac{1}{S_{aa}(\mathbf{q})} = \frac{1}{S_{aa}(\mathbf{q})_{\text{neutral}}} + \alpha(\mathbf{q})\, f_a^{\,2} \tag{25a}$$

where $S_{aa}(q)_{\text{neutral}}$ is given by

$$S_{aa}(\mathbf{q})_{\text{neutral}} = \frac{S_a^{\,0} + \upsilon_b\delta}{\Delta_{\text{neutral}}} \tag{25b}$$

This result is consistent with the result obtained for homopolymers in similar conditions ($f_b = 0$); see eq 18. One notes that the electrostatic term does not depend on the copolymer nature of the chain. It depends on the strength of the charge only. One can consider other cases depending on thermodynamic properties and charge distribution. If the two blocks are identical except for their scattering length, Δ becomes very simple but the copolymer nature is, of course, still reflected in $S_{aa}(\mathbf{q})$ since it has the form

$$S_{aa}(\mathbf{q}) = \frac{S_a^{\,0} + (\upsilon + \alpha f^2)\delta}{1 + (\upsilon + 4\alpha f^2)S_t^{\,0}} \tag{26a}$$

where

$$S_t^{\,0} = S_a^{\,0} + S_b^{\,0} + 2S_{ab}^{\,0} \tag{26b}$$

Another case would be $\epsilon_{ab} = -1$, which means that the two blocks have opposite charges. $S_{aa}(q)$ becomes

$$S_{aa}(\mathbf{q}) = \frac{S_a^{\ 0} + (v + \alpha f^2)\delta}{1 + vS_t^{\ 0} + \alpha f^2\{S_a^{\ 0} + S_b^{\ 0} - 2S_{ab}^{\ 0} + 4v\delta\}} \tag{27a}$$

it is interesting to note that for $q = 0$

$$S_{aa}(q) = \frac{S_a^{\ 0}(q)}{1 + vS_t^{\ 0}(q{=}0)} \tag{27b}$$

which means that $S_{aa}(q{=}0)$ is not modified by the charge distribution. The total intensity $I(\mathbf{q})$ has the same property since the numerator of $I(q)$ at $q = 0$ is always $a^2S_a(0) + b^2S_b(0) + 2abS_{ab}(0)$.

4.2. Symmetric Diblock Copolymers (50/50). An important simplification is obtained when the two blocks A and B are geometrically identical; i.e.

$$S_a^{\ 0} = S_b^{\ 0} = \frac{\phi N}{4}P_{1/2};\quad S_{ab}^{\ 0} = \frac{\phi N}{4}(2P_T - P_{1/2}) \tag{28}$$

where $P_{1/2}$ and P_T are the form factors or one block and the total chain, respectively; ϕ and N are the total fraction of the polymer and the degree of polymerization, respectively. Substituting eqs 28 and 11 into eq 10 yields

$$\Delta\frac{I(\mathbf{q})}{\phi N/4} = (a - b)^2P_{1/2} + 4abP_T + (a^2U_b + b^2U_a - 2abU_{ab})\phi NP_T(P_{1/2} - P_T) \tag{29a}$$

and

$$\Delta = 1 + (U_a + U_b + 2U_{ab})\frac{\phi N}{4}P_T + (U_a + U_b - 2U_{ab}) \times \frac{\phi N}{4}(P_{1/2} - P_T) + (U_aU_b - U_{ab}^{\ 2})\frac{\phi^2N^2}{4}P_T(P_{1/2} - P_T) \tag{29b}$$

This expression is still quite complicated. It simplifies somewhat if one considers that B is isorefractive with solvent (or $S_{aa}(q)$); i.e.

$$\Delta\frac{S_{aa}(\mathbf{q})}{a^2\phi N/4} = P_{1/2} + U_b\phi NP_T(P_{1/2} - P_T) \tag{30}$$

The major simplifications are achieved in the intermediate solvent conditions, which are discussed below.

Intermediate Solvent Conditions ($a = -b$). Letting $a = -b$ in eq 29a, one can put the result into the form

$$\frac{I(\mathbf{q})}{a^2\phi N} = \frac{P_{1/2} - P_T}{1 + (U_a + U_b - 2U_{ab})\frac{\phi N}{4}(P_{1/2} - P_T)\frac{1 + U_1\phi NP_T}{1 + U_2\phi NP_T}} \tag{31a}$$

where

$$U_1 = \frac{U_aU_b - U_{ab}^{\ 2}}{U_a + U_b - 2U_{ab}};\quad U_2 = (U_a + U_b + 2U_{ab})/4 \tag{31b}$$

For neutral polymers with $v_a = v_b = v_{ab} - \chi = v$, we have $U_1 = U_2 = v + \chi/2$ and eq 31 gives the known result

$$\frac{I(q)}{a^2\phi N} = \frac{P_{1/2} - P_T}{1 - \frac{\chi}{2}\phi N(P_{1/2} - P_T)}\ \text{(neutral)} \tag{32a}$$

This is consistent with the result obtained for homopolymers in similar conditions. Indeed, as we have pointed out earlier, this is just the result one obtains for bulk copolymers with a reduced interaction $\chi\phi$ instead of χ in the bulk where $\phi = 1$. Letting $v_a = v_b = v_{ab} - \chi = v$ in eq 31a yields

$$\frac{I(\mathbf{q})}{a^2\phi N} = \frac{P_{1/2} - P_T}{1 - \left(\frac{\chi}{2} - \frac{\chi_e}{2}\right)\phi N(P_{1/2} - P_T)\frac{1 + U_1\phi NP_T}{1 + U_2\phi NP_T}} \tag{32b}$$

where

$$\chi_e = \frac{\alpha(\mathbf{q})}{2}(f_a - \epsilon_{ab}f_b)^2 \tag{32c}$$

$$U_1 = -\frac{v\alpha(f_a - \epsilon_{ab}f_b)^2 - \chi(\chi + 2v + 2\epsilon_{ab}\alpha f_af_e)}{2\chi - \alpha(f_a - \epsilon_{ab}f_b)^2} \tag{32d}$$

$$U_2 = v + \frac{\chi}{2} + \frac{\alpha}{4}(f_a + \epsilon_{ab}f_b)^2 \tag{32e}$$

Here also, we can consider similar limits as in the case of homopolyelectrolytes.

(i) $f_a = f_b = f$ ($\epsilon_{ab} = 1$). Blocks A and B are similarly charged:

$$\chi_e = 0 \tag{33a}$$

and

$$U_1 = U_2 = v + \chi/2 + \alpha f^2 \tag{33b}$$

Hence eq 32b becomes

$$\frac{I(q)}{a^2\phi N} = \frac{P_{1/2} - P_T}{1 - \frac{\chi}{2}\phi N(P_{1/2} - P_T)} \tag{33c}$$

which means that the fact that the copolymer is charged does not change the scattered intensity $I(q)$ and the shape of the peak, which is completely governed by the parameter χ. The same conclusion was reached for homopolyelectrolytes.

(ii) $f_a = f_b = f$ ($\epsilon_{ab} = -1$). Blocks A and B have charges of opposite signs. Equation 32 gives

$$\chi_e = 2\alpha(\mathbf{q})\,f^2 \tag{34a}$$

and

$$U_1 = U_2 = v + \chi/2 \tag{34b}$$

We reach again the same conclusion as for homopolymers; namely, since

$$\frac{I(\mathbf{q})}{a^2\phi N} = \frac{P_{1/2} - P_T}{1 - \left(\frac{\chi}{2} - \frac{\chi_e}{2}\right)\phi N(P_{1/2} - P_T)} \tag{34c}$$

with

$$\chi_e/2 = \alpha f^2$$

the attractive electrostatic potential αf^2 between A and B blocks tends to compensate for the repulsive thermodynamic interaction due to χ.

(iii) $f_a = f$; $f_b = 0$. This is the case where half of the chain is charged and the other half is neutral. We have from eq 32a–e

$$\chi_e = \alpha f^2/2 \tag{35a}$$

$$U_1 = v + \frac{\chi^2}{2(\chi - \alpha f^2/2)} \tag{35b}$$

$$U_2 = v + (1/2)(\chi + \alpha f^2/2) \tag{35c}$$

and $I(q)$ is obtained by substituting eq 35a–c into eq 32b. The maximum of $I(q)$ should still be observed, but it is influenced by both thermodynamic and electrostatic properties as well as chain dimensions and concentrations.

In all our descriptions so far we have considered that counterions and salt ions (if salt is added) contribute to the screening of electrostatic interactions and to the overall electroneutrality condition. They are point particles having no thermodynamic interactions with their surroundings and having no contribution to the scattered intensity. What happens if these ions have finite sizes and should contribute to the scattering profile! This is the question we address in the next section.

5. Counterions and Salt Ions with Finite Sizes

Before proposing ways to extend the present formalism to counterions and salt ions with finite sizes, we want to first treat explicitly the case where these ions are point-like and argue from the results that their effective contribution is limited to the screening.

5.1. Point Particle Counterion Limit. The above formalism can be immediately extended by letting $v_b = v_{ab} = 0$ if B is the counterion species and A the polyion. Therefore

$$U_a = v + (4\pi l/q^2)f^2 \tag{36a}$$

$$U_b = 4\pi l/q^2 \tag{36b}$$

$$U_{ab} = -4\pi l f/q^2 \tag{36c}$$

Note that Coulomb interactions are, of course, not screened in the absence of salt. In the case of added salt, one can add a third component made of co-ions. The conclusion for co-ions is the same as for counterions, which we shall illustrate in this subsection. Namely, they all contribute to the screening of electrostatic potential. Inserting eq 36a–c into eq 4 gives

$$\mathbf{S}^{-1} = \begin{bmatrix} \dfrac{1}{S_a^{\,0}} + v + \dfrac{4\pi l f^2}{q^2} & -\dfrac{4\pi l f}{q^2} \\ -\dfrac{4\pi l f}{q^2} & \dfrac{1}{\phi_b} + \dfrac{4\pi l}{q^2} \end{bmatrix} \tag{37a}$$

where we have let $S_b^{\,0} = \phi_b$ as it should. The results from the calculation of the inverse of $\mathbf{S}^{-1}$ can be easily verified

$$S_{aa}^{\;-1}(q) = S_a^{\,0\;-1}(q) + v + \frac{4\pi l f^2}{q^2 + \kappa^2} \tag{37b}$$

$$S_{bb}^{\;-1}(q) = \left\{(q^2 + k^2)\left(\frac{1}{S_a^{\,0}} + v\right) + lf^2\right\} \times \left\{\frac{q^2k^2}{l}\left(\frac{1}{S_a^{\,0}} + v\right) + k^2f^2\right\}^{-1} \tag{37c}$$

$$S_{ab}^{\;-1}(q) = \left\{(q^2 + k^2)\left(\frac{1}{S_a^{\,0}} + v\right) + lf^2\right\}(k^2f)^{-1} \tag{37d}$$

where the screening length is defined by

$$\kappa^2 = 4\pi l \phi_b \tag{37e}$$

These results are identical with those obtained by Joanny and Leibler[6] and by Vilgis and Borsali.[7] The polyion–polyion structure factor is

$$S_{aa}^{\;-1}(\mathbf{q}) = S_a^{\,0\;-1}(\mathbf{q}) + v^{\mathrm{scr}} \tag{38a}$$

with

$$v^{\mathrm{scr}} = v + \frac{4\pi l f^2}{q^2 + \kappa^2} \tag{38b}$$

This shows that the effect of counterions is to screen the polyion–polyion electrostatic repulsion. The meaning of S_{ab} and S_{bb} is somewhat ambiguous especially in the high q region and in the limit of screened electrostatic potentials (or neutral polymers). Indeed in the last limit $S_{ab}(q) \to 0$ and $S_{bb}(q) \to \phi_b$, which means that counterions become part of the solvent with no specific interactions.

5.2. Counterions with Finite Size. If counterions, or eventually salt ions, cannot be considered as point particles, the treatment in section 5.1 is not valid anymore, and one should include counterions and co-ions as a second and third component if there is only one polyion species. Such a situation arises when counterions have a size in the range of q^{-1}, which means that their form factor $P(q)$ is less than 1. This generalization should be adopted when these "small ions" have specific thermodynamic properties such as excluded-volume parameters and also when they have finite contrast with respect to the solvent so that they contribute to the scattering intensity. The formalism in sections 3 and 4 can be immediately generalized to these situations.

We present two ways of implementing this generalization, the first is a straightforward application of the model above and the second uses the mean spherical approximation (MSA), which is a classical approximation in simple liquid theories.[11-13]

(a) Counterions with Excluded Volume. Here we assume that counterions have the same excluded volume as monomers, namely, $v_a = v_b = v_{ab} = v$. Therefore, if we consider that A is the polyion and B the counterions, we write

$$U_a = v + (4\pi l/q^2)f^2 \tag{39a}$$

$$U_b = v + 4\pi l/q^2 \tag{39b}$$

$$U_{ab} = v - (4\pi l/q^2)f \tag{39c}$$

where we have let f be the fraction of charge of the monomer and l that of the counterion. One may also assume that P_b is less than unity and can be, for example, represented by a small sphere of diameter d such that

$$S_b^{\,0} = \phi_b P_b;\quad N_b = 1 \tag{40a}$$

with

$$P_b = \left(\frac{3\sin x - x\cos x}{x^3}\right)^2;\quad x \equiv qd/2 \tag{40b}$$

The model developed in section 3 can be applied to this case. One needs only to substitute eqs 39 and 40 into eqs 4–7 to obtain all the results.

(b) Mean Spherical Approximation. In this approximation counterions are considered as small spheres of diameter d and they are characterized by a long-range electrostatic interaction and a short-range excluded-volume interaction. Monomers are also spheres of the same size (but this condition is not necessary). The potential between spheres of species α and β is

$$\phi_{\alpha\beta}(r) = \infty,\quad \text{for } r < d \tag{41a}$$

and

$$\phi_{\alpha\beta}(r) = l f_\alpha f_\beta / r,\quad \text{for } r > d \tag{41b}$$

This problem has been solved by Genz et al.[13] and Grimson et al.,[14] who adopted the Waisman and Lebowitz[15] solution of the MSA for a mixture of charged hard spheres of the same diameter. The solution for $U_{\alpha\beta}$ is found to be a superposition of a short-range and a long-range interaction parameter, which are both functions of q. The details are given in ref 13 and 14 where the partial structure factors are discussed as functions of the monomer concentration and other relevant properties of the system.

Finally we have to mention at the end of this section that similar observations concerning the screening behavior of counterions of finite size have been made by Khokhlov and Khatchaturian.[16] Moreover, these authors suggest that the screening of the polyions among themselves gives an additional contribution to the screening.

6. Conclusions

This paper deals with the application to charged polymer mixtures of Benoit's equation,[2] giving the generalization of the classical Zimm equation in matrix form. This application is simply made by writing the interaction matrix **U** as a sum of the ordinary excluded-volume matrix **v**, which contains the short-range thermodynamic interactions, and an interaction matrix, which describes the long-range Coulomb potential between various species of the mixture. We have discussed specifically the cases of ternary mixtures of two homopolymers A and B in a solvent and a block copolymer AB in a solvent. We have given the expressions of partial structure factors $S_{ij}(q)$ $(i, j = \text{a,b})$ and the total intensity $I(q) = \sum_{ij}a_ia_jS_{ij}(q)$ in various cases. We have discussed in particular the limit of intermediate solvent conditions where one observes interesting features that are very similar to the bulk limit. We have shown that if the two polymers A and B (either homopolymers or copolymers) have the same charge, the scattering intensity $I(q)$ is not significantly affected by the electrostatic interaction and depends essentially on the thermodynamic parameter χ. If A and B have opposite charges, their electrostatic attraction tends to reduce the thermodynamic repulsion. This means that $I(q)$ has the same form with a reduced effective parameter $\chi_{\text{eff}}(q) = \chi - \chi^{\text{e}}(q)$. We have also discussed the case where polymer A is charged and B is neutral, and we have obtained results consistent with those reported earlier by Joanny and Leibler and Vilgis and Borsali.

The Coulomb interaction matrix is modeled by a simple Debye–Hückel screened potential where the screening is entirely due to counterions and eventually salt ions if salt is added. These ions are assumed to be pointlike. We argue that this description is more adequate than the one consisting of treating them as full components in the mixture as it was done before.[6,7] We show this by considering the case of a polyion–counterion–solvent system. This description leads to an important simplification since it reduces the order of matrices by 1 in salt free solutions and by 2 when salt is added. We discuss in the last part of this paper how the present formalism can be generalized to the case where counterions, and eventually co-ions, have finite sizes, interaction parameters, and contrast factors.

The present investigation is limited to weakly charged polymers because we did not include the effect of nematic interactions, which can produce ordered or mesophase structures in the solution. This requires a generalization of the interaction matrix **U** to stiff chains including the nematic angular-dependent interactions. Few attempts in this direction were made recently by Shima et al.[17] and by van der Schoot and Odijk[18] for binary mixtures polymer–solvent, but the generalization to multicomponent stiff chains is still lacking. It is, of course, a straightforward task to introduce the effect of stiffness in the intramolecular form factors or $\mathbf{S}_0$, but the nematic interaction, which depends on the relative orientation of pairs of segments belonging to different chains, is crucial for strongly charged systems.

Acknowledgment. M.B. thanks Professor E. W. Fischer for his kind invitation to the Max-Planck-Institut für Polymerforschung during 4 months in 1990 when this work was accomplished. Both authors benefitted from interesting discussions with Professor J. F. Joanny of the Institut Charles Sadron (Strasbourg, France). We thank one of the reviewers for bringing the work of the Russian group to our attention. We thank also Dr. E. B. Zhulina for her assistance with those references.

References and Notes

(1) Vilgis, T.; Benmouna, M.; Benoit, H. Scattering from Multicomponent Polymer Mixtures: Static Theoretical Models, submitted for publication in *Macromolecules*.

(2) Benoit, H.; Benmouna, M.; Wu, W. *Macromolecules* **1990**, *23*, 1511.

(3) Akcasu, Z.; Tombakuglu, M. *Macromolecules* **1990**, *23*, 67.

(4) Ould Kaddour, L.; Strazielle, C. *Polymer* **1987**, *28*, 459.

(5) Nyrkova, I. A.; Khokhlov, A. R.; Kremarenko, Yu. *Vysokomol. Soedin.* **1990**, *32A*, 918.

(6) Joanny, F.; Leibler, L. *J. Phys.* (*Fr.*) **1990**, *51*, 545.

(7) Vilgis, T.; Borsali, R. Mean Field Theory of Concentrated Polyelectrolyte Solutions: Statics and Dynamics, accepted for publication in *Phys. Rev. A*.

(8) Duval, M.; Picot, C.; Benmouna, M.; Benoit, H. *J. Phys.* (*Fr.*) **1988**, *49*, 963.

(9) Vasilevskaya, V. V.; Starodubtzev, S. G.; Khokhlov, A. R. *Vysokomol. Soedin.* **1987**, *29B*, 930.

(10) Brereton, M. B.; Vilgis, T. A. *Macromolecules* **1990**, *23*, 2044.

(11) McDonald, I.; Hansen, J. P. *Theory of Simple Liquids*; Clarendon Press: Oxford, U.K., 1976.

(12) Hayter, J.; Penfold, P. *J. Mol. Phys.* **1981**, *42*, 109.

(13) Genz, U.; Klein, R.; Benmouna, M. *J. Phys.* (*Fr.*) **1989**, *50*, 449.

(14) Grimson, M.; Benmouna, M.; Benoit, H. *J. Chem. Soc., Faraday Trans. 1* **1988**, *85*, 1563.

(15) Waisman, E.; Lebowitz, J. L. *J. Chem. Phys.* **1972**, *56*, 3086.

(16) Khokhlov, A. R.; Khatchaturian, K. A. *Polymer* **1982**, *23*, 1742.

(17) Shima, T.; Doi, M.; Okano, K. *J. Chem. Phys.* **1988**, *88*, 2815.

(18) van der Schoot, P.; Odijk, T. *J. Chem. Phys.* **1990**, *93*, 3580.