Effect of Polymer Size on the Polyelectrolyte−Surfactant Interaction

Jun Liu, Noboru Takisawa, and Keishiro Shirahama*

Department of Chemistry, Saga University, Saga 840, Japan

Hiroshi Abe and Kazutami Sakamoto

The Central Research Institute, Ajinomoto Co. Ltd., Kawasaki-Ku, Kawasaki 210, Japan

Received: April 7, 1997; In Final Form: July 10, 1997[⊗]

The interaction between alkylpyridinium (C_{12} and C_{14}) chloride and sodium poly(aspartate) with different molecular weights is investigated in the presence of 10 mM NaCl by means of a potentiometric titration method using a surfactant-selective electrode at 25 °C. The effect of polymer size on the binding process is especially focused on: the critical aggregation concentration increases and the apparent cooperativity of binding decreases with the decreasing of polyelectrolyte molecular weight. Binding isotherms are analyzed by direct calculation of a matrix expressing the partition function and compared with the behavior in other polyelectrolyte−surfactant systems. It is found that the binding constant prominently depends on the polymer chain length when the number of binding sites is less than ca. 35. Such an end effect may be associated with the less effective superimposition of electrostatic potentials around the polymer chain in small-sized polymers. Model calculation is carried out by both the matrix method and the Satake−Yang equation, while the matrix one fits the experimental data better for the short-chain polyelectrolyte.

Introduction

Polymer−surfactant interaction is conveniently divided into two classes: binding to neutral polymers and to polyelectrolytes.[1,2] In the latter case, polyelectrolytes are viewed as a one-dimensional array of binding sites that bind ionic surfactant ions with opposite electric charge. The features of interaction between surfactant and polyelectrolyte are well expressed on binding isotherms. One of the binding features is the cooperative nature of interaction. The study on this is still of recent concerns.[3,4] The majority of experimental data have been analyzed by the Satake−Yang equation,[5] where the polyelectrolytes are supposed to be "sufficiently long" so that the end effect is negligible. However, this situation changes as the number of binding sites on a polymer molecule is reduced. It would be interesting to see the effect of polymer size on the interaction, although very few works have been published. It is said that polyphosphate binds dodecylpyridinium chloride strongly when the degree of polymerization is sufficiently high, and binding affinity is quickly lost for short phosphate chains, which has not, however, been published in a full paper.[6] Shirahama et al. reported binding isotherms for sodium dextran sulfate (DxS)−dodecylpyridinium bromide systems,[7] where the total binding affinity is found to increase with increasing binding site number of DxS. Here we will describe the interaction of tetradecylpyridinium chloride (TeP) and dodecylpyridinium chloride (DoP) to sodium poly(aspartate) (poly(Asp)), with different molecular weights. The poly(Asp) samples prepared by thermal polycondensation of aspartic acid in solid state contain both α- and β- peptide bonds in the main chain.[8] These polymers resemble real proteins in certain aspects and are expected to have a wide application in various cosmetic and sanitary products. Poly(Asp) are especially suited for the present purpose, since they have a relatively narrow molecular weight distribution ($M_w/M_n = 1.1$) in addition to a low degree of polymerization (29 and 12); it is so low that it might well be called oligo(aspartate). The coexistence of α- and β-peptide may introduce more interest in characterizing binding to copolymers.[9,10] In the present study, it is considered that these peptide bonds provide roughly the same electrostatic potentials on binding with surfactant. For comparison, we also investigated poly(Asp) with a high degree of polymerization (203). Binding isotherms are obtained by a surfactant-selective electrode and analyzed by direct calculation of a matrix expressing the partition function.

Experimental Section

The *N*-alkylpyridinium chlorides were synthesized by treating 1-alkyl bromide with dried pyridine followed by ion-exchanging the corresponding bromides in concentrated sodium chloride. The products were recrystallized three times from acetone. The critical micelle concentrations (cmc) determined by the electric conductivity method in aqueous solutions at 25 °C are 3.40 and 14.7 mM for TeP and DoP, respectively, in good agreement with the literature.[11]

Poly(Asp) samples were supplied by Ajinomoto Co. Ltd. (Japan) with different molecular weight (M_w) of 27 800, 4000, and 1700, which were determined by gel permeation chromatography (GPC) based on sodium poly(acrylate) standards, with the corresponding number of binding sites of 203, 29, and 12. For abbreviation, they are referred to as Asp203, Asp29, and Asp12, respectively. Binding isotherms were obtained by potentiometric titration using a surfactant-selective electrode. The preparation of the electrode was described elsewhere;[12,13] briefly, the surfactant-sensitive membrane was composed of partly sulfonated PVC, polymerized plasticizer (Elvaloy 742, Du Pont.), and tricresyl phosphate (Wako Pure Chemical) to improve the sensitivity (3:4:2 in weight). The electromotive force (emf) was measured with a digital voltmeter (Advantest TR6845). The asymmetric potential was usually less than ±1 mV and was not corrected for. All the experiments were carried out at 25 °C in the presence of 10 mM NaCl. The pH of the solutions was neutral (6.8−7.5), which assures nearly complete dissociation of sodium poly(aspartate), and the value nearly kept constant during titration. The solutions sometimes became turbid

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

S1089-5647(97)01198-X CCC: $14.00

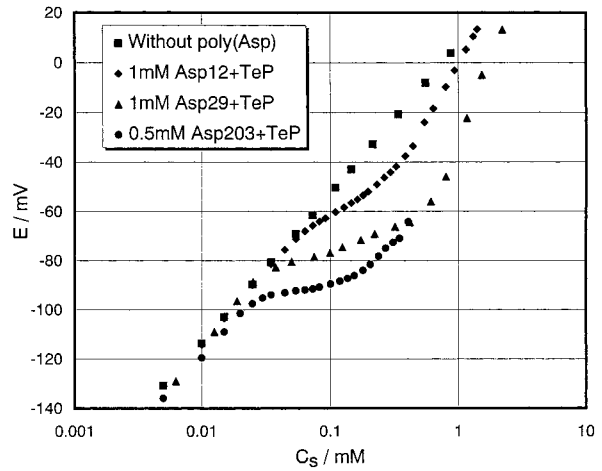

Figure 1. Plot of emf vs TeP concentration (C_s) in 10 mM NaCl with and without poly(Asp) of different molecular weights.

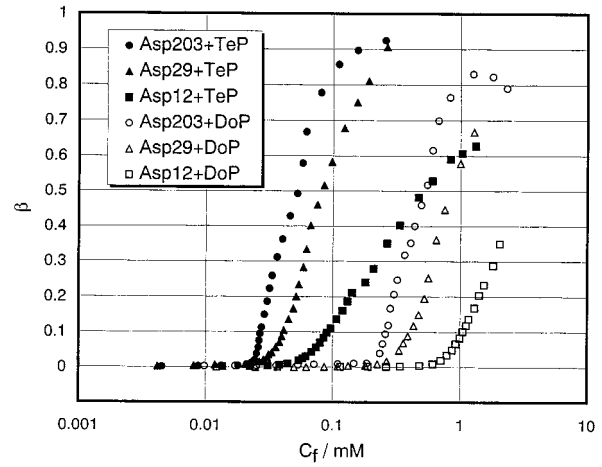

Figure 2. Binding isotherms of TeP and DoP to poly(Asp) of different molecular weights in 10 mM NaCl at 25 °C.

in the course of titration due to neutralization of charges on the polymer and subsequent aggregation. Our experiments were mostly limited before the turbid appeared, since the data thereafter are less reproducible and the precipitation is unfavorable for the PVC membrane electrode.

Results and Discussion

The typical emf responses in aqueous surfactant solutions, in the absence and presence of poly(Asp) of different molecular weights, are shown in Figure 1, where emf is plotted against the logarithm of the total TeP concentration (C_s). The electrode shows excellent performance with nearly Nernstian response from the cmc down to ca. 2×10^{-3} mM surfactant. In the presence of poly(Asp), however, a deviation from the linearity is found, suggesting that a part of surfactant is bound onto the polymer. Under the assumptions that the membrane is only sensitive to free surfactants, but not to the bound ones, and the activity coefficient of free surfactant is constant, the degree of binding (β) can be calculated by comparison the binding curves with the calibration one:

$$\beta = C_b/C_p = (C_s - C_f)/C_p \tag{1}$$

where C_b is the concentration of bound surfactant, C_f is the free surfactant concentration, and C_p is the monomer concentration of poly(Asp), as illustrated in Figure 1. Binding isotherms can be constructed by plotting the binding degree β vs free surfactant concentration (C_f) as shown in Figure 2. Two important observations are noted for both TeP and DoP cases: (1) critical aggregation concentration (cac) where binding suddenly starts increasing with decreasing number of binding sites (m); (2) slope of the cooperative binding becomes less steep with decreasing m, which implies an apparent decrease in cooperativity in the shorter-chain polymer. On the other hand, with the same Asp sample, binding of TeP is much stronger than that of DoP, with a lower cac and a little steeper slope in the former.

Binding of surfactant to polyelectrolyte can be expressed by the partition function of the one-dimensional Ising model,[14]

$$\mathbf{Z} = (1,1)\begin{pmatrix} 1 & 1 \\ s/u & s \end{pmatrix}^m \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{2}$$

with $s = KuC_f$, where m stands for the number of binding sites on a polymer, K is the intrinsic binding constant, and u a cooperativity parameter. Equation 2 generates all possible states of binding; for example, as $m = 2$, which means there are only two binding sites on the "polymer", we have

$$Z = 1 + 2s/u + s^2/u \tag{3}$$

in which the term 1 refers to the statistical weight of the situation when the sites all left unoccupied

while the second term represents the occasion with one occupied site and another unoccupied

and s^2/u is for the case where the two sites are all bound

. The binding degree of surfactant by using this partition function is given as

$$\beta = (\mathrm{d} \ln Z/\mathrm{d} \ln C_f)/m \tag{4}$$

Therefore, if the number of binding sites is available, which actually equals the degree of polymerization for poly(Asp), the binding degree can be readily obtained by the direct matrix calculation processed by Microsoft Excel.

As for an infinitely long polymer chain ($m \rightarrow \infty$), eq 4 together with eq 2 takes an explicit form, the Satake−Yang equation, which was derived from a regular solution theory[5]

$$\beta = {}^1/_2\{1 - (1 - s)/\sqrt{(1 - s)2 + 4s/u}\} \tag{5}$$

These expressions are deeply rooted in the theory originally devised for modeling the transitional conformation change of biopolymers by Zimmm and Bragg[15] and later applied to the cooperative binding of dye to poly(glutamate) by Schwarz.[14]

The Satake−Yang equation fits the experimental binding isotherms of many surfactant−polymer (with sufficiently long chains) systems quite well. Model calculations[16] by the equation have shown that, for large u values, a steep rise in binding isotherms is expected. In the present study, we supposed that the u value, which represents the hydrophobic interaction between the surfactant neighbors, remains constant even when the polymer chain becomes small, because such hydrophobic interaction is of short range and may not depend on the size of macroion. However, as shown in Figure 2, the slope of experimental binding isotherms clearly depends on the size of polymer. That indicates the polymer's end effect can also

TABLE 1: Binding Parameters

surfactant	polymer	*u*	K/mM^{-1}	*Ku*
DoP	Asp203	70	0.041	2.9
	Asp29	70	0.029	2.0
	Asp12	70	0.012	0.8
TeP	Asp203	90	0.33	30
	Asp29	90	0.23	21
	Asp12	90	0.11	9.9

reduce the apparent cooperativity on the slope, even with the same parameter *u* for a certain surfactant. Therefore, comparing with the Satake−Yang equation, the matrix method described above is more suitable to our case since the factor of polymer size has been taken into account by introducing the size parameter *m*. Thus, we carried out curve fitting by direct calculation of the matrix expression with Asp203 first. Once *u* and *K* values were determined after choosing the parameters iteratively to fit the lower half of the binding isotherm where the electrostatic potential of polyion remains nearly constant due to the ion-condensation phenomena as described by Manning,[17,18] the same *u* was employed to analyze the Asp29 and the Asp12 data using the matrix method again where only *K* is an adjustable parameter. The parameters obtained in this way are summarized in Table 1. The binding affinity *Ku* increases by about 1 order of magnitude for the addition of two CH_2 groups in each system, and the cooperativity parameter *u* also increases when the surfactant chain becomes longer. The difference per CH_2 group in ln *Ku*, the free energy of interaction, for the three poly(Asp) samples averages 1.17*kT*, very close to the value found in other polyelectrolyte−surfactant systems,[6] and once again proves that this value reflects only the difference in hydrophobic interaction between the adjacent alkyl chain of surfactants.[19] On the other hand, for the same surfactant (TeP or DoP), the *K* value, which is considered to be a function of the electrostatic potential around polyelectrolyte, decreases as the size of polyelectrolyte becomes smaller. We attribute it to a decreased superimposition of electrostatic potential on reducing the size of polyelectrolyte. At a point around a polyelectrolyte molecule, the electrostatic potential is a sort of sum over the potential exerted from the electric charges all over the polyion. This effect is valid beyond the Debye length, which is a measure of potential decay by 1/e, and so superimposed that the counterions are condensed around a polyelectrolyte molecule. Inversely speaking, this superimposition effect is getting smaller as the number of electric charges nearby or the polyion size is reduced. Such a superimposition effect makes the electrostatic potential valley on an infinite polymer chain much deeper than that of the corresponding monomer ion or short-length chain and results in a stronger intrinsic binding at lower concentration for the infinite one. As a result, the cac shifts to high concentration when the polymer size decreases. The relationship between *K* and the polymer size, *m*, can be seen more clearly in Figure 3, where ln *K* is plotted against the number of binding sites, *m*. The results measured by Miyajima and Kwak with binding of DoP to sodium polyphosphates (NaPP) of various degrees of polymerization (20) are also included in Figure 3, together with the data from Shirahama's previous work on dodecylpyridinium bromide (DoPB) and dextran sulfate (DxS) systems.[7] In all the above cases, the *K* values are nearly independent of *m* when the number of binding sites is large enough, but sharply fall at $m < 30-40$. Let us compare these three systems interacting with the same dodecylpyridinium halide; the observed order for *K* is DxS > Poly(Asp) > NaPP. The same order is also found in the overall binding constant *Ku*. It is hard to give a plausible explanation for this sequence since it may result from several factors such as the charge density of the polymers, hydrophobic character

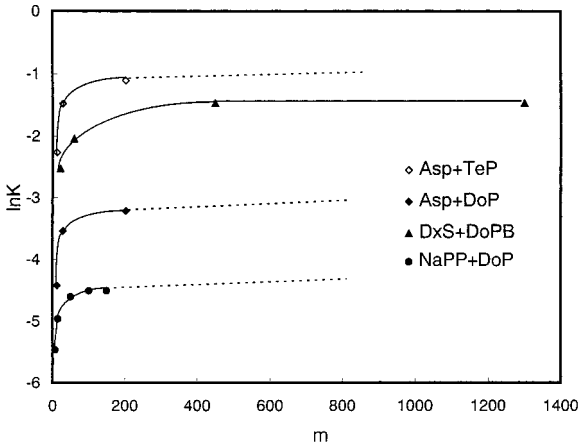

Figure 3. Relationship between binding sites number *m* and ln *K* for alkylpyridinium halide in different polyelectrolytes. Data are taken from this study (Asp + TeP, Asp + DoP), ref 19 (NaPP + DoP), and ref 7 (DxS + DoPBr).

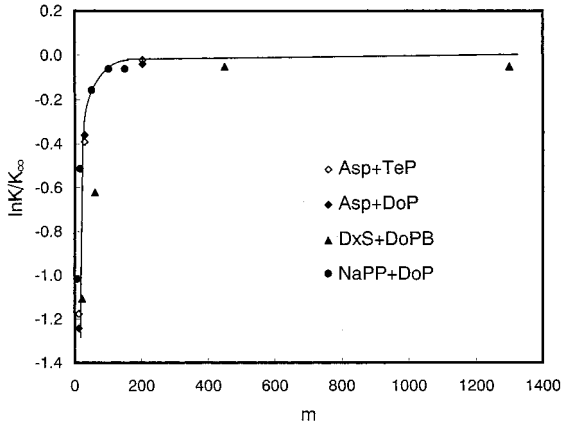

Figure 4. Effect of polymer size on ln K/K_∞ for alkylpyridinium halide in different polyelectrolytes. Data resources are the same as in Figure 3.

of the backbone, flexibility, and even detailed local structure of the polymers. Satake and Yang expressed the parameter *K* by

$$K = K_0 \exp(-Ze\psi/k_BT) \tag{6}$$

where ψ is the electrostatic potential at the polymer surface, although they did not derive any explicit expression for it.[5] In eq 6, K_0 is an intrinsic constant containing some unknown factors that represent some other contributions from the nature of the polyion-surfactant interaction besides ψ. For ease of the discussion, K_∞ is introduced as the *K* value for infinite-chain polymer, which can be derived from the intercept of a ln $K-1/m$ plot. Thus, K_0 can be eliminated in eq 7,

$$\ln K/K_\infty = (Ze/k_BT)(\psi_\infty - \psi) \tag{7}$$

We plotted ln K/K_∞, which actually represents the electrostatic potential difference between a finite-chain polymer and the infinite one, to the binding sites number *m* in Figure 4. It is found that nearly all the data points fall on the same tendency line as seen in Figure 4. Since there is uncertainty (ca. 20%) to some extent involved in the determination of *K*, it is still far-reaching to claim that such a consistency exists in all polyion−surfactant interactions. However, this asymptotic property line at least indicates that there exists a "critical binding site number" in the polyelectrolyte, below which the superimposed potential is quickly lost and the electrostatic potential is

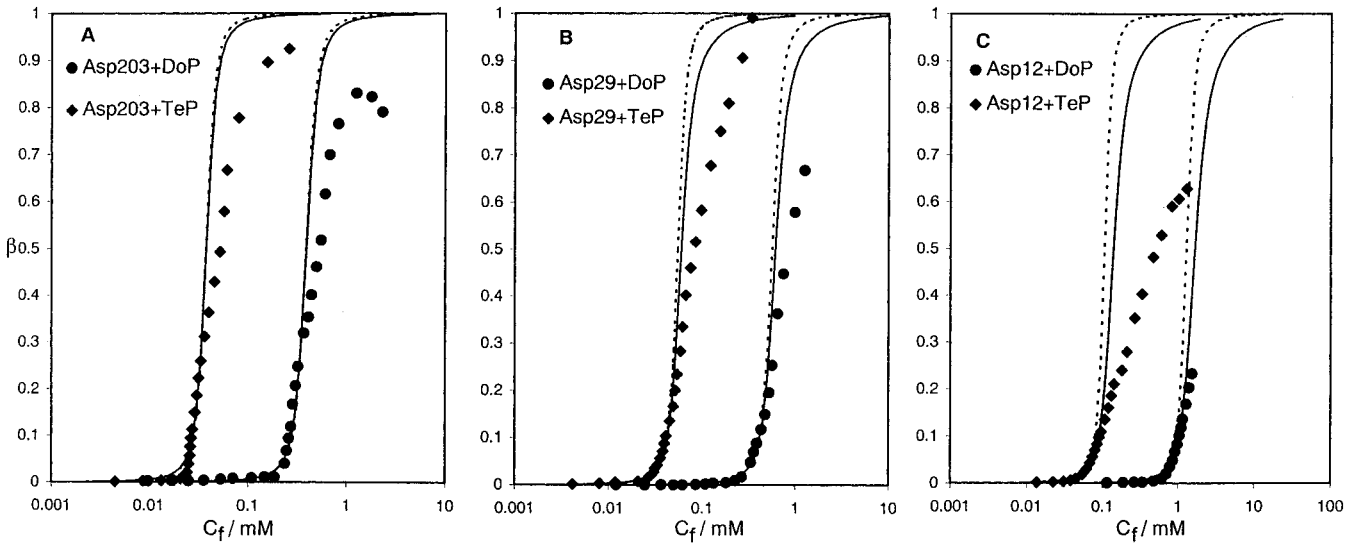

Figure 5. Calculated and experimental binding isotherms of TeP and DoP to poly(Asp) in 10 mM NaCl: solid line, fitting curve by the matrix method; dashed line, by the infinite chain model.

too weak to attract surfactant ions. Such critical binding site number is estimated as around 35 in our study. In connection with the less superimposed potential, it is interesting to note the Monte Carlo simulation by Brender and Danino[21] for short-chain (8−64 beads) polymers, where each bead is thought to carry electric charges. The effective screening effect is quickly lost when the number of beads is decreased below 32. This is closely related to a marked decrease of electrostatic potential of the short-chain polyelectrolytes, since the screening is a result of strong electrostatic attraction of counterions by the charged beads.

The fitted curves employing the parameters in Table 1 are shown in Figure 5, where the curves simulated by the Satake−Yang equation are also included for comparison. As for Asp203, there is actually no difference between the results of these two methods, while for Asp29, the curve calculated from the infinite-chain model is above the one from the matrix method at the higher β part. However, the matrix method for Asp12 provides a better fitting to the experimental data than the Stake−Yang equation (infinitely long chain) does. The calculated isotherm deviates at even lower β than the experimental binding isotherm for the short-chain poly(Asp). This could be also associated with superimposition of electrostatic potential on the polymer. The comparatively weaker electrostatic potential of short-chain polyelectrolyte, or "oligoelectrolyte", is even more easily reduced as surfactants are bound, and the breakdown of the ion condensation effect results in a sort of negative cooperativity on further binding.

Unlike the longer chain polymer, turbidity occurred even at a lower part of binding ($\beta < 0.5$) for the Asp12 sample, while in other systems a precipitate usually appears when the binding becomes saturated just below $\beta = 1$. This phenomenon may be due to the conformational change of polymer chain from the extended random coil to globules, which may happen more easily in oligoelectrolyte like Asp12, since the short chain is less stretched than the infinite one.[22] The conformational change would make the aggregates of the hydrophobic polymer−surfactant complex with more ease and subsequent precipitation in the early stage of binding. Detailed studies of the oligo-electrolyte and surfactant interactions remain a priority and are still in progress.

Acknowledgment. We thank Prof. T. Miyajima (Kyushu University, Japan) for his helpful discussion.

References and Notes

(1) Goddard, E. D. *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanbhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1992; Chapter 4.
(2) Goddard, E. D. *Colloid Surf.* **1986**, *19*, 301.
(3) Anthony, O.; Zana, R. *Langmuir* **1996**, *12*, 3590.
(4) Hansson, P.; Almgren, M. *J. Phys. Chem.* **1996**, *100*, 9038.
(5) Satake, I. ; Yang, J. T. *Biopolymers* **1976**, *15*, 2263.
(6) Hayakawa, K.; Kwak, J. C. T. *Cationic Surfactants: Physical Chemistry*; Rubingh, D., Holland, P. M., Eds.; Marcel Dekker: New York, 1991; Vol. 37, Chapter 5.
(7) Shirahama, K.; Watanebe, T.; Harada, H. *The Structure, Dynamics and Equilibrium Properties of Colloid Systems*, Bloor, D. M., Wyn-Jones, E., Eds.; Kluwer: London, 1990, p 161.
(8) Pivcová, H.; Saudek, V.; Drobník, J.; Vlasák, J. *Biopolym*ers **1981**, *20*, 1605.
(9) Shimizu, T. *Colloid Surf.* **1995**, *94*, 115.
(10) Wei, Y. C.; Hudson, S. M. *Macromolecules* **1993**, *26*, 4151.
(11) Mukerjee,P.; Myseksm, K. J. *Nature Standard Reference Data System*; U.S. National Bureau of Standards: Washington, DC, 1971; p 36.
(12) Shirahama, K.; Tashiro, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 377.
(13) Shirahama, K.; Kameyama, K.; Takagi, T. *J. Phys .Chem.* **1992**, *96*, 6817.
(14) Schwarz, G. *Eur. J. Biochem.* **1970**, *12*, 442.
(15) Zimm, B. H.; Bragg, J. K. *J. Chem. Phys.* **1959**, *31*, 526.
(16) Hayakawa, K.; Kwak, J. C. T. *Hyomen* **1985**, *23*, 169.
(17) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(18) Manning, G. S. *J. Phys. Chem.* **1981**, *85*, 870.
(19) Malovikava, A.; Hayakawa, K.; Kwak, J. C. T. *ACS Symp. Ser.* **1984**, *253*, 225.
(20) Miyajima, T.; Kwak, J. C. T.; Liu, J.; Shirahama, K. Submitted to *Colloid Polym. Sci.*
(21) Brender, C.; Danino, M. *J. Phys. Chem.* **1996**, *100*, 17563.
(22) Brender, C.; Danino, M. *J. Chem. Phys.* **1992**, *97*, 2119.