

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231699842>

Effect of Ionic Binding on the Self-Diffusion of Anionic Dendrimers and Hydrophilic Polymers in Aqueous Systems as Studied by Pulsed Gradient NMR Techniques

ARTICLE *in* MACROMOLECULES · APRIL 2007

Impact Factor: 5.8 · DOI: 10.1021/ma070372t

CITATIONS

13

READS

21

5 AUTHORS, INCLUDING:



Héloïse Thérien-Aubin

University of Toronto

39 PUBLICATIONS 427 CITATIONS

SEE PROFILE



X. X. Zhu

Université de Montréal

234 PUBLICATIONS 5,005 CITATIONS

SEE PROFILE



George Richard Newkome

University of Akron

499 PUBLICATIONS 12,952 CITATIONS

SEE PROFILE

Effect of Ionic Binding on the Self-Diffusion of Anionic Dendrimers and Hydrophilic Polymers in Aqueous Systems as Studied by Pulsed Gradient NMR Techniques

Héloïse Thérien-Aubin,[†] X. X. Zhu,^{*,†} Charles N. Moorefield,[‡] Kishore Kotta,[§] and George R. Newkome[§]

Département de Chimie, Université de Montréal, C.P. 6128, Succ. Centre-ville, Montréal, Québec, H3C 3J7, Canada, and Maurice Morton Institute for Polymer Science and Departments of Polymer Science and Chemistry, University of Akron, 170 University Cr., Akron, Ohio 44325-4717

Received February 12, 2007; Revised Manuscript Received March 17, 2007

ABSTRACT: Pulsed gradient NMR techniques including diffusion-ordered NMR spectroscopy have been used to study the self-diffusion of three carboxylated dendrimers in aqueous solutions of neutral poly(vinyl alcohol) (PVA) and of cationic poly(allyl amine) (PAAm). The ionic interaction between the cationic PAAm network and the anionic dendrimers had the most significant effect on the diffusion of the dendrimers in the system. The self-diffusion coefficients of the dendrimers in PAAm were an order of magnitude lower than in PVA and more widely distributed, and the activation energy for the displacement of the dendrimers in PAAm was higher than that in PVA. The effects of the dendrimer size, polymer concentration, and temperature on the diffusion of the dendrimers have also been studied.

Introduction

Diffusion in polymeric systems is an important issue for processes such as mass transport of plasticizers or controlled release of drugs. The diffusion of various molecules in polymeric hydrogels has been studied,^{1,2} and much has been understood on the effects of the size^{3–10} and shape^{7,8} of the diffusant, the concentration of the polymer matrix,^{3–11} and the temperature^{5–8} on the diffusion process. Physical models taking these factors into account have been established.^{3,12–14} However, various interactions between the diffusant and the matrix make the diffusion process more complex, and a better understanding of the effects of such interactions is essential in the development of more efficient polymer systems for different applications. Previously we have studied the self-diffusion of a variety of diffusants ranging from small molecules to polymers in polymer solutions.^{3–5,7,8} The study of small diffusants bearing various functional groups such as alcohol, amine, or acid in PVA⁴ showed that the self-diffusion coefficient of these molecules was mainly influenced by the size of the molecule and that the functional groups had only a small effect. The study of polymers of the same composition but with diverse molecular architectures such as linear, hyperbranched, and dendritic polymers showed that, for molecules of the same molecular weight, the energy of activation of diffusion was related to the molecular architecture of the diffusing probe⁸ and that a diffusant with a more compact molecular structure had a lower activation energy.

The presence of intramolecular interaction such as hydrogen bonding^{15,16} significantly influences the diffusion process. The nature of the polymer matrix has a large effect on the hydrogen bonding between the polymer and diffusant as observed for methyl red in poly(methyl methacrylate) and poly(vinyl acetate).¹⁷ The ionic interactions also influence the diffusion

process. The study of self-diffusion of butyrate in polyacrylamide gels showed that the self-diffusion coefficient was affected by the diffusant–diffusant interactions; the self-diffusion of the butyrate anions was strongly dependent on the butyrate concentration.¹⁸ The electrostatic interactions between a charged polymer and charged diffusing probes can be completely screened in a solution of high ionic strength.¹¹ To the best of our knowledge, the effect of ion-pairing interactions on the self-diffusion process has never been studied in detail.

The diffusion of molecules with a dendritic structure is of interest because of their potential use as carriers for various reactants and drugs. Recent studies have shown the discrepancy in the diffusion of dendrimers in comparison to that of linear polymers.⁷ Dendrimers with a more compact structure can diffuse faster than linear polymers of a similar molar mass. However, the influence of the end groups of a diffusing dendrimer and of their interactions with the surrounding environment on the self-diffusion coefficient and the activation energy of this process have not yet been addressed. We report here a study of the effect of ionic interactions as well as the temperature dependence of the self-diffusion of dendritic probes bearing carboxylic acid end groups in matrices composed of neutral and basic hydrophilic polymers.

Experimental Section

Materials. Poly(vinyl alcohol) (PVA, MW = 89–98 000, 99% hydrolyzed), poly(allyl amine) (PAAm, MW = 70 000) and deuterium oxide (D₂O) were purchased from Aldrich (Milwaukee, WI). The dendritic diffusants **1**, **2**, and **3** (Figure 1) were synthesized as described in previous reports.^{19,20}

Sample Preparation. The NMR samples were prepared by adding a D₂O solution containing 1 wt % of a diffusing probe to the polymer weighed in a 5 mm NMR tube. The final concentrations of the polymer ranged from 0 to 0.25 g·mL⁻¹. The PVA samples were sealed and heated for 24 h at 110 °C, while the PAAm samples were heated at 50 °C.

NMR Measurements of Self-Diffusion Coefficients. The stimulated echo pulse sequence developed by Tanner²¹ (STE: 90°–t₁–90°–t₂–90°–t₁–echo) was used to measure the self-diffusion

* Author to whom correspondence should be addressed. E-mail: julian.zhu@umontreal.ca.

[†] Département de Chimie, Université de Montréal.

[‡] Maurice Morton Institute for Polymer Science, University of Akron.

[§] Departments of Polymer Science and Chemistry, University of Akron.

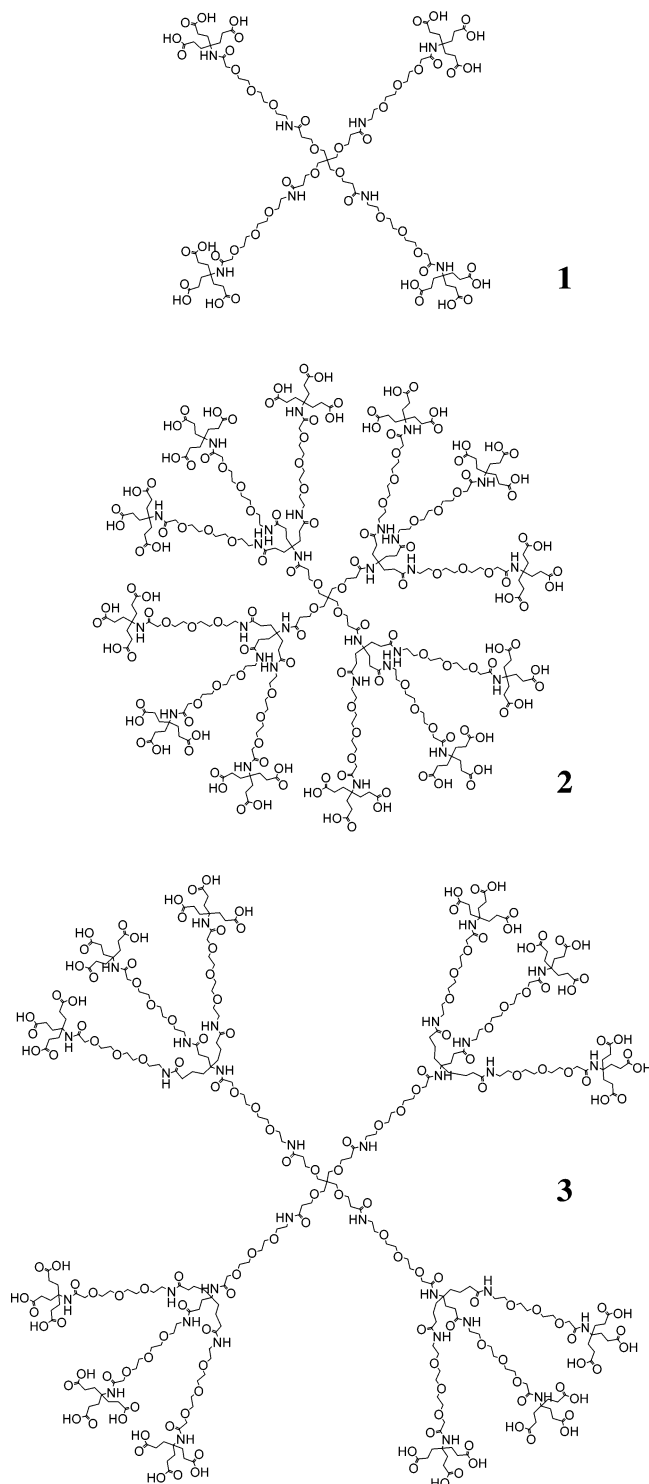


Figure 1. Chemical structures of the dendritic probes used in this study.

coefficients (D) of the diffusing probes. Measurements were performed at 25.0 °C on a wide-bore Bruker Avance-400 NMR spectrometer operating at a frequency of 400.26 MHz for protons. The interval between the gradient pulses was fixed to 100 ms, the duration of the gradient pulse was set at 1 ms for the PVA samples and the PAAm solutions and at 2 ms for the more concentrated PAAm systems. The gradient strength was varied in 32 gradient steps within a range from 0.1 to 10 T/m (the minimum and maximum varied depending on the system studied) to achieve an attenuation of at least 80% for the diffusants. Selected experiments for variable temperature studies were performed at 15.0, 25.0, 35.0, and 45.0 °C (± 0.3 °C). Temperature was calibrated with pure ethylene glycol.²²

DOSY Experiments. DOSY is a 2D NMR experiment in which the chemical shift represents one dimension and the self-diffusion coefficient the other.²³ DOSY spectra were obtained for selected STE diffusion experiments by performing inverse Laplace transform using the maximum entropy method²⁴ on each data point in the chemical shift dimension between 1.0 and 4.5 ppm.

Theoretical Background

The self-diffusion coefficients were obtained from the attenuation of the NMR signals caused by the application of gradient pulses²¹

$$A = A_0 e^{-\gamma^2 \delta^2 G^2 D (\Delta - \delta/3)} \quad (1)$$

where A_0 and A are the NMR signals in the absence and in the presence of the gradient pulses of strength G and of a duration δ , Δ is the interval between the two gradient pulses and γ the gyromagnetic ratio of the nucleus under investigation, ^1H in this case.

Equation 1 holds for a simple unhindered Brownian motion. If the system is polydisperse or inhomogeneous, a distribution of diffusion coefficients may be observed. The same effect can be observed if there is a slow exchange on the NMR time scale between different populations of the same molecules or if the movement or the Brownian motion of the molecules is hindered.^{25,26} In these cases, the attenuation of the NMR signal follows

$$A = A_0 \int f(D) e^{-\gamma^2 \delta^2 G^2 D (\Delta - \delta/3)} dD \quad (2)$$

where $f(D)$ is the distribution function of D .

To solve eq 2, an inverse Laplace transform should be performed on the system. There are different algorithms that could be used to solve this equation such as the methods based on a regularization technique^{27–30} including CONTIN^{27,28,31} or based on the maximum entropy method.^{24,32} One can also use a stretched exponential solution^{26,33} in the form of the Kohlrausch–Williams–Watts (KWW) equation^{25,26,34,35} to take into account the distribution of the diffusion coefficients

$$A = A_0 e^{-(qD)^\alpha} \quad (3)$$

where α is the stretching factor of the exponential function that represents the distribution of the self-diffusion coefficients ($0 < \alpha \leq 1$), and $q = \gamma^2 \delta^2 G^2 (\Delta - \delta/3)$. When $\alpha = 1$, eq 3 simplifies into eq 1. The smaller the α value is, the broader the distribution of D would be. A mean diffusion coefficient (\bar{D}) can be calculated from the values of D_{app} and α by

$$\bar{D} = \frac{\alpha D_{\text{app}}}{\Gamma(\alpha^{-1})} \quad (4)$$

where $\Gamma(x)$ is the gamma function. Typical fits of the attenuation of the NMR signals by the KWW equation and the inverse Laplace transform are shown in Figure 2.

Results and Discussion

Self-Diffusion of the Dendrimers in PAAm and PVA. The effects of polymer concentration and molecular size on the self-diffusion coefficients of diffusant probes in polymer systems are well-known.^{3,36} When the self-diffusion coefficient D is divided by the self-diffusion coefficient in the absence of the polymer (D_0), the D/D_0 value (also known as reduced or normalized self-diffusion coefficient) is related to the specific interactions between the polymer network and the molecular

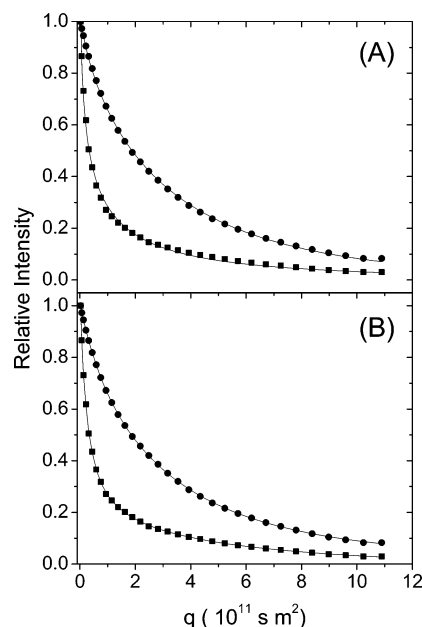


Figure 2. Attenuation of the NMR signals of dendrimer **2** (■) and PAAm (●) with the increasing pulsed gradient strength for a polymer (PAAm)–diffusant (dendrimer **2**)–water ternary system at 25 °C ([PAAm] = 0.15 g·mL⁻¹). Experimental data points (relative signal intensity) fitted by (A) the Kohlrausch–Williams–Watts equation and (B) the inverse Laplace transform.

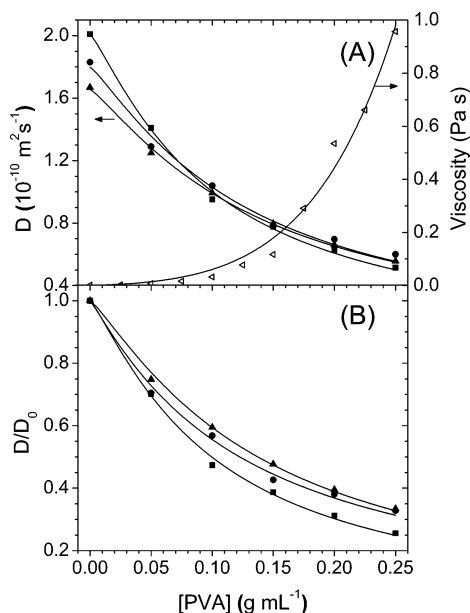


Figure 3. Variation of (A) the self-diffusion coefficient of the probe and the viscosity of the solution and (B) the reduced self-diffusion coefficient of the diffusants as a function of the PVA concentration in water at 25 °C. Dendritic diffusants: (■) **1**; (●) **2**; (▲) **3**.

probes.³⁷ In fact, Figure 3 shows that the self-diffusion coefficients of all three dendritic diffusants **1**, **2**, and **3** all exhibit similar behavior and trends as a function of polymer concentration. The most significant difference is in their D_0 values (Figure 3A). The differences between the D/D_0 values are rather small (Figure 3B), but these values for dendrimer **1** are consistently lower. This will be further discussed later. The increase in the viscosity of the polymer solutions as a function of concentration is also shown in Figure 3A.

If the self-diffusion data of the ionic dendrimers are compared in the two polymers, a significant difference is observed. Only the data for **1** are shown in Figure 4, but the self-diffusion

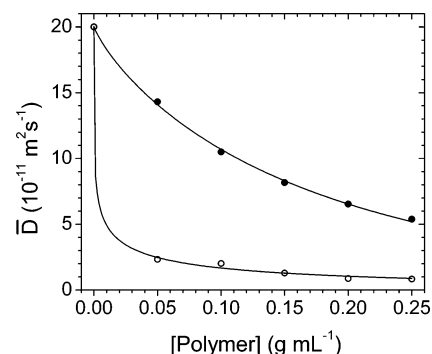


Figure 4. Self-diffusion coefficient of dendrimer **1** as a function of polymer concentration in the systems of PVA (●) and PAAm (○).

Table 1. Apparent Self-Diffusion Coefficient (D_{app}) and the Width of the Distribution (α) of the Anionic Dendritic Probes in Polymer Systems (Obtained from Eq 3)

diffusant	[polymer] (g·mL ⁻¹)	<i>T</i> (°C)	PVA		PAAm	
			D_{app} (10 ⁻¹¹ m ² s ⁻¹)	α	D_{app} (10 ⁻¹¹ m ² s ⁻¹)	α
1	0.00	25.0	20.0	0.97	20.0	0.97
	0.05	25.0	14.3	0.95	2.33	0.71
	0.10	25.0	10.5	0.90	2.02	0.33
	0.15	25.0	8.17	0.91	1.29	0.27
	0.20	25.0	6.53	0.94	0.87	0.28
	0.25	25.0	5.38	0.95	0.84	0.30
	0.15	15.0	6.00	1.00	0.89	0.28
	0.15	35.0	10.3	0.97	1.50	0.32
2	0.15	45.0	13.7	0.99	2.17	0.37
	0.15	25.0	8.01	0.92	1.96	0.38
3	0.15	25.0	7.77	0.95	1.11	0.31

coefficients for each of the dendritic probes **1**, **2**, and **3** in PAAm–water systems are about an order of magnitude lower than those of the same molecules in PVA. It is clear that the diffusion behavior of these probes in PAAm is also more complex than in PVA.

Equation 1 or even a two-component biexponential decay function cannot be used to determine the diffusion coefficient of the dendritic probes in the PAAm systems, since there is a large distribution of diffusion coefficients in the PAAm systems. Equation 3 is used to calculate the apparent diffusion coefficients (Table 1). As expected, the self-diffusion coefficient of the dendritic probes decreased with increasing PAAm concentration, but the PAAm concentration has a larger influence on the self-diffusion coefficient than that of PVA. The distribution of self-diffusion coefficients of the dendrimers also becomes wider (as indicated by a smaller α value) with increasing PAAm concentration (between 0.05 and 0.15 g·mL⁻¹), indicating an increasingly more complex system, until an entangled network is formed at a higher concentration, after which the average D and the distribution of D do not vary significantly. The critical overlap concentration (c^*)³⁸ was measured by rheology to be at ca. 0.09 g·mL⁻¹ from the concentration dependence of the zero-shear rate viscosity of the polymer solution. At polymer concentrations higher than c^* , entanglements exist between polymer chains in the solution, leading to the formation of a dynamic three-dimensional network.

DOSY Experiments. Molecular interactions between the diffusant and the polymer affect the diffusion of the different molecular species in the system. It is obvious from Figure 5 that the ionic binding has a more significant effect than hydrogen binding in the aqueous polymer systems. The distribution of the self-diffusion coefficients of the dendrimers and of the polymers can be better illustrated by the DOSY experiments, which allows the screening of a mixture on the basis of both

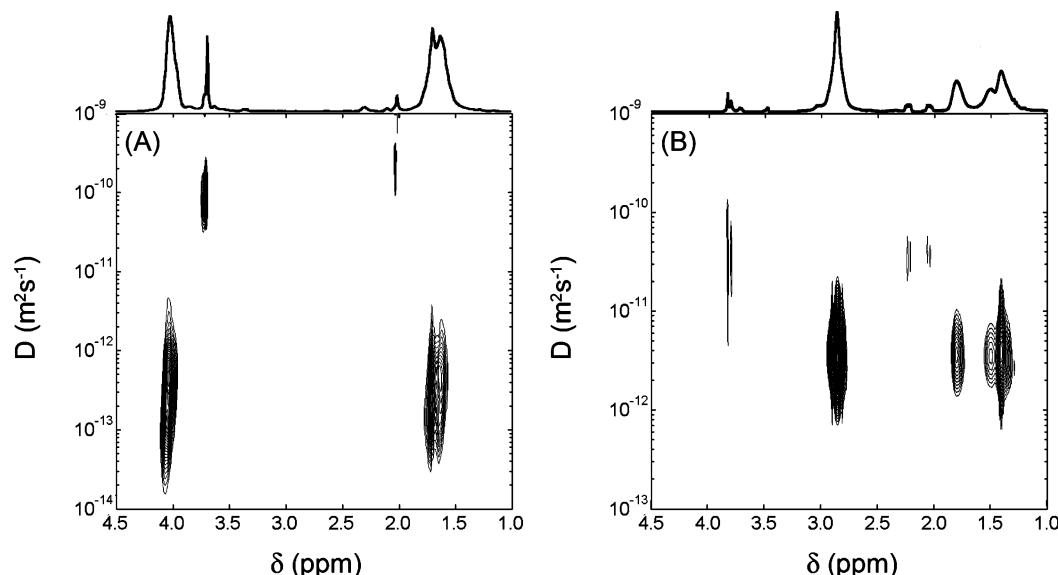


Figure 5. DOSY spectra of dendrimer **2** in two polymers ($0.15 \text{ g}\cdot\text{mL}^{-1}$) at 25°C : (A) in PVA (PVA peaks at 4.0 and 1.6 ppm and dendrimer **2** peaks at 3.7 and 2.0 ppm); (B) in PAAm (PAAm peaks at 2.9, 1.8, and 1.4 ppm and dendrimer **2** peaks at 3.8, 2.2, and 2.0 ppm).

chemical shift and self-diffusion coefficient. It is a powerful tool in the study of complex mixtures.²³ Figure 5 shows an example of the DOSY spectra of dendrimer **2** in the two polymer matrices at a polymer concentration of $0.15 \text{ g}\cdot\text{mL}^{-1}$. In the PVA system (Figure 5A), the broad peaks of PVA are observed at 4.0 (CH) and 1.6 (CH₂) ppm. The peak at 3.7 ppm is attributed to OCH₂ protons of the ethylene glycol chains of the dendrimer. A small sharp peak in the diffusion dimension is observed as expected for group undergoing unhindered Brownian motion. Figure 5A shows that the self-diffusion of the dendrimer **2** in PVA is relatively simple whereas that of the polymer is more complicated due to the extensive formation of intermolecular hydrogen bonding between PVA chains. The D values measured for the PVA provide an indication of segmental motions of the PVA chains, not necessarily the displacement of the whole polymer network. The two peaks associated with dendrimer **2** in Figure 5A do not seem to show exactly the same self-diffusion coefficient. This is mainly due to the overlapping of signals between the PVA peak at 1.6 ppm and the dendrimer peak at 2.0 ppm. In fact, weaker signals from the dendrimer (not shown because of the threshold selected in the 2D plot) show the same D value as the peak at 3.7 ppm. In the PAAm system (Figure 5B), the peaks at 1.4, 1.8, and 2.9 ppm are ascribed to the main chain methylene (CH₂) and methyne (CH) protons and the methylene protons on the side group CH₂NH₂ of PAAm. The protons of OCH₂ (3.8 ppm), CH₂CH₂COOH and CH₂CH₂COOH (2.0 and 2.2 ppm) of **2** are also observed. The DOSY spectra in Figure 5 show that dendrimer **2** has lower D values with a wider distribution of D in PAAm than in PVA, while PVA has generally lower average D values and larger distribution of D than PAAm at the same concentration.

For better comparison, the distributions of self-diffusion coefficients of the dendrimer and the polymers in the two samples corresponding to selected slices in the DOSY spectra are shown in Figure 6. The distributions of self-diffusion coefficients for the methyne (CH) peak of PVA and the OCH₂ peak of **2** are shown in Figure 6A. Figure 6B shows the distribution of the self-diffusion coefficients for the methylene protons of the side group CH₂NH₂ of PAAm and the OCH₂ protons of **2**. Comparison of the curves in Figure 6 reveals several interesting features. (1) PVA has a much lower mean D value and a much wider distribution of D than PAAm at the

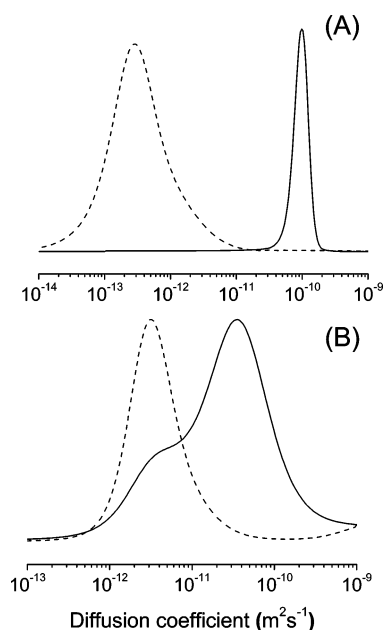


Figure 6. Distributions of self-diffusion coefficients for dendrimer **2** in aqueous polymer systems ($0.15 \text{ g}\cdot\text{mL}^{-1}$) at 25°C : (A) in PVA; (B) in PAAm. Dashed lines are for the polymer and the solid lines are for the probe.

same concentration, which could be related to the more extensive network of intermolecular hydrogen bonding in the PVA systems. (2) The average D value of the dendrimer in PAAm is lower and more widely distributed than in PVA, showing the complexity of the self-diffusion of the dendrimer in PAAm, most likely due to ionic interactions. (3) The distribution of D values for the ionic dendrimer in PAAm is even wider than that of the polymer itself. The mean self-diffusion coefficient of the polymer is still smaller than that of the dendrimer, both distributions start at a value of ca. $7 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. The distribution curve of dendrimer **2** shows a maximum at ca. $3.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ with an obvious shoulder at ca. $3.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. The shoulder correspond to the maximum of the distribution curve for the polymer PAAm, suggesting that a fraction of the dendrimer actually diffuses together with PAAm due to the strong ionic interactions between them. This observation could be related either to the exchange between the bound and the

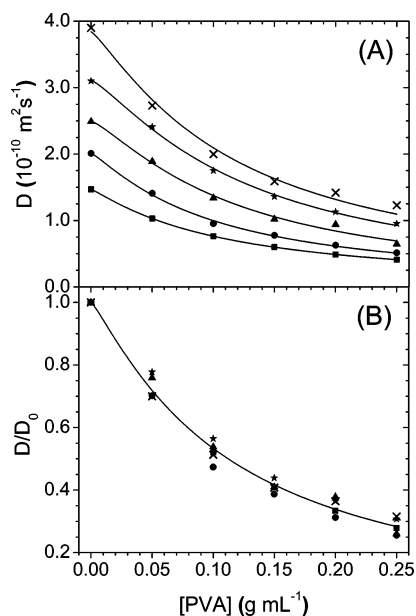


Figure 7. Temperature effect on (A) the self-diffusion coefficient and (B) reduced self-diffusion coefficient of dendrimer **1** in the PVA system: (■) 15 °C; (●) 25 °C; (▲) 35 °C; (*) 45 °C; (×) 55 °C.

Table 2. Activation Energy (in kJ mol⁻¹) of the Self-Diffusion of the Anionic Dendritic Probes in Polymer Systems

[polymer] (g·mL ⁻¹)	PVA			PAAm		
	1	2	3	1	2	3
0.00	19 ± 1	19 ± 1	18 ± 1	19 ± 1	19 ± 1	18 ± 1
0.05	20 ± 2	25 ± 2	19 ± 1	25 ± 2	29 ± 2	30 ± 6
0.10	20 ± 1	25 ± 3	21 ± 2	31 ± 9	31 ± 3	30 ± 10
0.15	20 ± 1	26 ± 3	22 ± 2	40 ± 10	51 ± 6	50 ± 10
0.20	22 ± 1	27 ± 2	21 ± 4	40 ± 10	50 ± 10	50 ± 10
0.25	24 ± 1	28 ± 2	22 ± 3	40 ± 10	53 ± 6	62 ± 9

unbound fractions of the diffusant, if the exchange is slow in comparison to the diffusion time (otherwise only a mean value would have been observed caused by time-averaging),³⁹ or to a complex transport mechanism of the diffusant, where the net displacement of the diffusant is related to the movement of PAAm.

Activation Energy of the Diffusion Process. Variable temperature experiments have been performed in an effort to better understand the diffusion processes. Figure 7A clearly shows that the self-diffusion coefficient of the dendrimer increases with temperature (Figure 7A), which is generally true for all diffusants.³ The reduced diffusion coefficients in Figure 7B show that the variation of temperature does not alter the nature of interactions between the polymer (PVA) and the diffusants under these circumstances. The temperature dependence of the \bar{D} values obtained from eq 4 can be used to determine the activation energy (E_a) associated with the diffusion of the molecular probes. The differences in E_a between the three probes are small (Table 2), even smaller than the experimental error, since the size variation of the probes is also small (Table 3).

The self-diffusion coefficients measured at various temperatures are used to estimate the diffusional activation energy. Several trends can be observed in the E_a values in Table 2. (1) The difference of E_a between the three dendrimers is small in the same polymer system, mostly within the experimental error, showing the interactions are rather similar. (2) The E_a value is dependent on the polymer concentration, since the diffusing probes require more energy to diffuse in a more hindered environment when the polymer concentration becomes higher.⁴⁰

Table 3. Comparison of the Activation Energy of Self-Diffusion between Carboxylated Dendrimer and Linear and Dendritic PEGs in Aqueous PVA Systems

diffusant	<i>M</i> (g/mol)	<i>D</i> ₀ ^a (10 ⁻¹⁰ m ² s ⁻¹)	<i>R</i> _h ^b (nm)	<i>E</i> _a (kJ/mol)
1	2111	2.01	1.22	19 ± 5
2	6358	1.83	1.34	25 ± 4
3	7227	1.67	1.47	21 ± 2
PPI(TEO) ₈	2055	1.64 ^c	1.49	28 ± 2
PPI(TEO) ₃₂	8639	0.91 ^c	2.69	36 ± 3
PEG-2000	2000	1.10 ^d	2.25	38 ± 9
PEG-8000	8000	0.64	3.77	43 ± 2

^a D_0 : D of the diffusant probe in pure D₂O measured by NMR at 25 °C.

^b R_h : Hydrodynamic radius obtained from the Stokes–Einstein equation.

^c Results from ref 7. ^d Results from ref 5.

This is especially true for the PAAm system since the polymer chains of PAAm can no longer be considered as inert obstacles for the diffusion process.⁴⁰ The net displacement of the anionic dendrimers in PAAm systems is determined by the combined movements of the dendrimer and of the polymer network. (3) The polymer has a large effect on the E_a of the dendrimers, especially at higher polymer concentrations. This provides another evidence of the strong ionic binding between the anionic dendrimers and PAAm. If the ratio of the number of acid groups to the molecular weight of the diffusant is taken as an indication of the charge density, **1** and **2** have similar density of acid groups while **3** has a lower density. The combination of the opposite effects of charge density and molecular size of the dendrimers may help explain the small difference between **2** and **3**. The increase in the density of the COOH groups should strengthen the hydrogen bonding between the diffusant and PVA.

Self-Diffusion of the Dendritic Probes. The carboxylic acid end groups of the dendritic diffusing probes seem to have an effect even on their self-diffusion coefficients in pure water in comparison to the linear,⁵ hyperbranched,⁸ and dendritic⁷ PEG polymers. They are more than 20% higher than those of the linear PEGs and of the poly(propyleneimine) dendrimers functionalized with triethyleneoxy methyl ether groups (PPI-(TEO)) of similar molecular weights. The larger D_0 values can be related to their smaller hydrated radii, which is related to the diffusion coefficient through the Stokes–Einstein equation.⁸ The hydrated structures of diffusants **1**, **2**, and **3** seem to be more collapsed than other uncharged PEGs dendrimer of comparable molecular weight (Table 3). The size of the dendrimer is known to vary with end groups and the ionic strength of the solution.¹⁹

The comparison of the self-diffusion coefficients measured for the anionic dendrimers to those of PEGs of similar molar masses measured previously⁵ reveal some interesting behaviors. The self-diffusion of **1** in the PVA–water system follows the same trend as that of linear (PEG-2000)⁵ and dendritic (PPI-(TEO)₈)⁷ PEGs (Figure 8A), while **2** has a behavior significantly different from the linear (PEG-8000) and dendritic (PPI-(TEO)₃₂)⁷ diffusants (Figure 8B). The differences among the D/D_0 values for linear,⁵ hyperbranched⁸ or dendritic⁷ PEGs are small, but the end groups of the ionic dendrimers used here have a larger effect and this effect is more pronounced for **2** or **3** than for **1**. This may be related either to the larger molecular flexibility of **1** (see Figure 1) or to the number of COOH groups on the dendrimers (12 for **1** vs 36 for **2** and **3**). The variations observed in Figure 8 are attributed to size differences among the diffusants (PEGs) chemically similar but structurally different, since size is the main factor influencing the self-diffusion of the probes⁴ in the absence of specific interactions between the diffusant and the polymer.

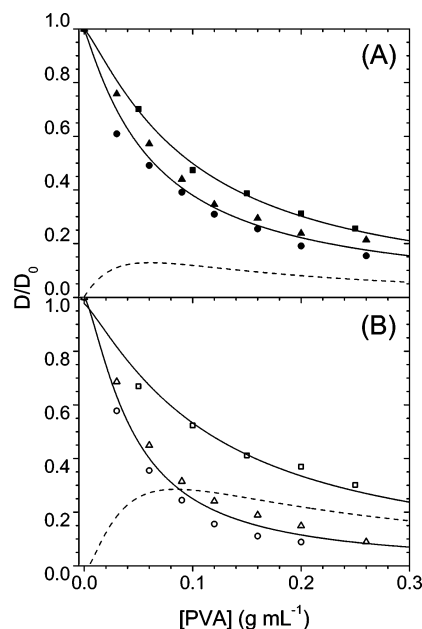


Figure 8. Reduced diffusion coefficient of selected diffusing probes as a function of PVA concentration. Diffusing probes with a molecular weight of ca. 2000 (A) and ca. 8000 (B): (■) dendrimer 1; (●) PEG-2000; (▲) PPI(TEO)₈; (□) Dendrimer 2; (○) PEG-8000; (△) PPI(TEO)₃₂. The dashed line represents the difference of the reduced self-diffusion coefficients between the two diffusants of similar molecular weights.

The activation energy of the whole diffusion process for a given polymer–diffusant–solvent ternary system can be measured from the diffusion experiments as described previously.^{5,7,8} The E_a values obtained this way do not vary with polymer concentration. E_a was shown to increase with the molecular weight of the diffusant⁵ and a more compact molecular structure (of similar molecular weight) leads to a lower E_a .⁸ The dendritic diffusants studied here are more compact and thus have lower activation energies than the linear, hyperbranched or dendritic PEGs of similar molar masses (Table 3).^{5,7}

Conclusion

The diffusion characteristics of these anionic dendritic probes differ largely from those of neutral hydrophilic probes. In a neutral polymer system such as that of PVA, where there are no specific interactions, the size of the diffusant is the main factor affecting its diffusion in a polymer. The diffusion process of the anionic dendrimers in the cationic PAAm systems is more complex than that in PVA, a result of the ionic interactions. A distribution of self-diffusion coefficients was observed, conceivably due, among other factors, to the slow exchange between the free and bound dendritic diffusants. The ionic binding of the diffusants with PAAm is stronger than their hydrogen bonding with PVA as observed by the higher activation energy.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC)

and the Canadian Research Chair program is gratefully acknowledged. G.R.N. acknowledges NSF DMR-0401780, CHE-0420987, INT-0405242, and AFSOR F49620-02-1-0428,02.

References and Notes

- (1) Peschier, L. J. C.; Bouwstra, J. A.; de Bleijser, J.; Junginger, H. E.; Leyte, J. C. *Biomaterials* **1993**, *14*, 945.
- (2) Skirda, V. D.; Aslanyan, I. Y.; Philippova, O. E.; Karybants, N. S.; Khokhlov, A. R. *Macromol. Chem. Phys.* **1999**, *200*, 2152.
- (3) Petit, J. M.; Roux, B.; Zhu, X. X.; Macdonald, P. M. *Macromolecules* **1996**, *29*, 6031.
- (4) Petit, J.-M.; Zhu, X. X.; Macdonald, P. M. *Macromolecules* **1996**, *29*, 70.
- (5) Masaro, L.; Zhu, X. X.; Macdonald, P. M. *Macromolecules* **1998**, *31*, 3880.
- (6) Kwak, S.; Lafleur, M. *Colloids Surf. A* **2003**, *221*, 231.
- (7) Baille, W. E.; Malveau, C.; Zhu, X. X.; Kim, Y. H.; Ford, W. T. *Macromolecules* **2003**, *36*, 839.
- (8) Baille, W. E.; Zhu, X. X.; Fomine, S. *Macromolecules* **2004**, *37*, 8569.
- (9) Colsenet, R.; Söderman, O.; Mariette, F. *Macromolecules* **2005**, *38*, 9171.
- (10) Colsenet, R.; Söderman, O.; Mariette, F. *Macromolecules* **2006**, *39*, 1053.
- (11) Zhang, Y.; Amsden, B. G. *Macromolecules* **2006**, *39*, 1073.
- (12) Cukier, R. I. *Macromolecules* **1984**, *17*, 252.
- (13) Amsden, B. *Macromolecules* **1998**, *31*, 8382.
- (14) Masaro, L.; Zhu, X. X. *Prog. Polym. Sci.* **1999**, *24*, 731.
- (15) Masaro, L.; Zhu, X. X. *Langmuir* **1999**, *15*, 8356.
- (16) Masaro, L.; Zhu, X. X. *Macromolecules* **1999**, *32*, 5383.
- (17) Lee, H.; Chang, T. *Macromolecules* **2001**, *34*, 937.
- (18) Darwish, M. I. M.; van der Maarel, J. R. C.; Zitha, P. L. J. *Macromolecules* **2004**, *37*, 2307.
- (19) Young, J. K.; Baker, G. R.; Newkome, G. R.; Morris, K. F.; Johnson, C. S., Jr. *Macromolecules* **1994**, *27*, 3464.
- (20) Newkome, G. R.; Kotta, K. K.; Mishra, A.; Moorefield, C. N. *Macromolecules* **2004**, *37*, 8262.
- (21) Tanner, J. E. *J. Chem. Phys.* **1970**, *52*, 2523.
- (22) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.
- (23) Johnson, C. S., Jr. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34*, 203.
- (24) Steinbach, P. J.; Ionescu, R.; Matthews, C. R. *Biophys. J.* **2002**, *82*, 2244.
- (25) Nystrom, B.; Walderhaug, H.; Hansen, F. K. *J. Phys. Chem.* **1993**, *97*, 7743.
- (26) Abrahmsen-Alami, S.; Persson, K.; Stilbs, P.; Alami, E. *J. Phys. Chem.* **1996**, *100*, 4598.
- (27) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213.
- (28) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 229.
- (29) Tikhonov, A. N. *Nonlinear ill-posed problems*. Chapman & Hall: London, 1998; p 387.
- (30) Twomey, S. *J. Franklin Inst.* **1963**, *275*, 121.
- (31) Huo, R.; Wehrens, R.; Van Duynhoven, J.; Buydens, L. M. C. *Anal. Chim. Acta* **2003**, *490*, 231.
- (32) Delsuc, M. A.; Malliavin, T. E. *Anal. Chem.* **1998**, *70*, 2146.
- (33) Abrahmsen-Alami, S.; Stilbs, P. *J. Colloid Interface Sci.* **1997**, *189*, 137.
- (34) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.
- (35) Walderhaug, H.; Hansen, F. K.; Abrahmsen, S.; Persson, K.; Stilbs, P. *J. Phys. Chem.* **1993**, *97*, 8336.
- (36) Zhu, X. X.; Macdonald, P. M. *Macromolecules* **1992**, *25*, 4345.
- (37) Zaikov, G. E.; Iordanskij, A. L.; Markin, V. S. *Diffusion of Electrolytes in Polymers*; VSP: Utrecht, The Netherlands, 1988; p 321.
- (38) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
- (39) Cohen, Y.; Avram, L.; Frish, L. *Angew. Chem.* **2005**, *44*, 520.
- (40) Pickup, S.; Blum, F. D. *Macromolecules* **1989**, *22*, 3961.

MA070372T