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- (21) It is known that some racemization is unavoidable during polypeptide synthesis by the activated ester method. No direct evaluation for the extent of racemization in the present polypeptide was made. However, poly[Lys(Z)-Lys(Z)-napAla] obtained by the activated ester method (number of repeating units > 10) showed similar but stronger CD ($\Delta\epsilon_{230} = 6 \times 10^5$ in TMP) than Boc-(Ala-napAla-Aib)₆-OBzl obtained by stepwise condensation ($\Delta\epsilon_{228} = 4.8 \times 10^5$ in TMP; Nishino, N., Private communication). Therefore, the racemization is not so serious under the condition employed in this series of study.

Iodine-127 and Potassium-39 NMR Study of the Interaction of Ions with Water-Soluble Polymers

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ABSTRACT: Thermodynamic parameters including the equilibrium constant for the binding of iodide anion with polymers in aqueous solutions have been determined from the excess line widths of the ¹²⁷I NMR. Comparison of these parameters with the NMR line widths suggests that a specific binding exists to cause severe line broadening of the ¹²⁷I NMR in solutions of poly(vinylpyrrolidone) (PVP), isotactic poly(2-hydroxyethyl methacrylate), and poly(acrylamide). Even in the absence of significant polymer-iodide binding, the asymmetric hydration of iodide anions in the solutions of poly(ethylene oxide) and poly(vinyl alcohol) seems to cause moderate line broadening. The magnitude of the binding constant of iodide anions can be related to the dipole moment of the polymer segment, which suggests that an electrostatic interaction is responsible for the specific iodide binding with PVP. The ¹²⁷I NMR line widths obtained with different alkali ions and the ³⁹K NMR data indicate no effects of counteraction on the ¹²⁷I NMR.

Introduction

The recently developed multinuclear NMR technique¹⁻³ can be expected to give detailed information on polymer salt solutions. The information obtained can be discussed at the microscopic level and should provide direct information about the behavior of ions. Furthermore, by selecting the nucleus to observe, one can obtain information about individual ions in the presence of water-soluble polymers. These characteristics give the technique a great potentiality for investigating a complex mixture of ionic species in polymer salt solutions. ¹²⁷I NMR has only rarely been utilized for studies of macromolecular systems because of its poor detection limits caused by extreme line broadening. The NMR of iodide ion has been used in some cases to study ionic interaction^{4,5} in aqueous salt solutions. But, there are only a few reports⁶⁻⁸ on studies for macromolecular systems using ¹²⁷I NMR as a chemical probe.

The purpose of this study is to examine the origin of the line broadening of ¹²⁷I NMR in a macromolecular system, the binding of iodide anions with water-soluble polymers, and the behavior of counteraction ³⁹K during the iodide binding. We have studied the polymer-iodide interactions in aqueous solution by measuring ¹²⁷I and ³⁹K NMR line widths for seven water-soluble polymers.

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Table I
Physical Properties of Water-Soluble Polymers Used in This Study

polymer	10 ⁻⁴ MW ^a	[η] ^b	M ^c	V ^d	ρ_a ^e	μ^f
PEO	1.85	0.348	44.1	39.2	1.125	0.418
PVAL	2.50	0.392	49.1	39.5	1.243	0.447
PAAM	1.00	0.036	71.1	54.6	1.302	1.051
PAAMA	20.00	3.433 ^h	73.4			
PAAMB	20.00	26.280 ^h	87.1			
iso-PHEMA	5.40 ^g	0.040	130	102.0	1.274 ⁱ	0.769
PVP	4.00	0.235	111.1	88.9	1.25	4.07 ^j

^a Nominal molecular weights stated by Polysciences Co. ^b Intrinsic viscosity measured at 298 K in water and expressed in dL/g. ^c Molar weight (g/mol). ^d Molar volume (cm³/mol). ^e Density (g/cm³). ^f Average dipole moment calculated according to the Debye equation (D). ^g Measured by using the Mark-Houwink equation reported in ref 9. ^h Reduced viscosity measured at a concentration of 0.5 g/dL. ⁱ Reference 28. ^j Reference 23.

Experimental Section

Materials. Poly(vinylpyrrolidone) (PVP), poly(ethylene oxide) (PEO), poly(vinyl alcohol-co-vinyl acetate) (PVAL) containing 12 mol % acetate, poly(acrylamide) (PAAM), poly(acrylamide-co-acrylic acid) sodium salt containing 10 mol % carboxyl (PAAMA), and poly(acrylamide-co-acrylic acid) sodium salt containing 70 mol % carboxyl (PAAMB) received from Polysciences Co. were dried under vacuum over P₂O₅. Isotactic poly(2-hydroxyethyl methacrylate) (iso-PHEMA) was prepared by the same procedure as reported earlier.⁹ In Table I the physical properties¹⁰ of the polymers such as molecular weight, intrinsic viscosity in water at 298 K, molar volume, molar weight,

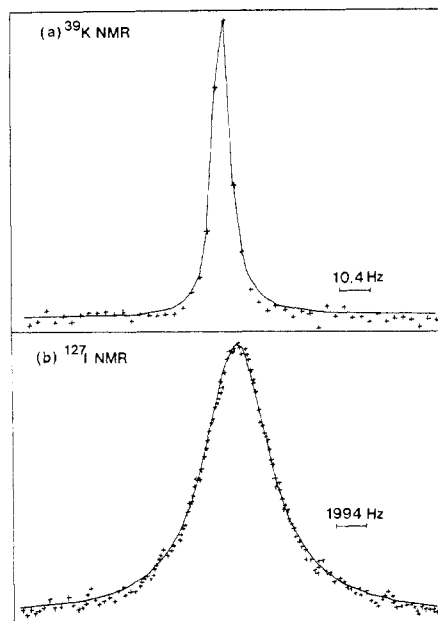


Figure 1. ^{127}I and ^{39}K NMR line shapes obtained for 0.1 M iso-PHEMA solutions containing 0.1 M KI at 298 K in the presence of 10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$.

density, and the average dipole moment calculated by the Debye equation¹⁰ are summarized. All the salts (Aldrich, $\geq 99\%$) were dried under vacuum over P_2O_5 . A small amount of $\text{Na}_2\text{S}_2\text{O}_3$ (10^{-3} M) was added to the polymer solution to prevent the oxidation of iodide anion,⁷ which caused a severe ^{127}I NMR line broadening. Water was distilled three times.

Measurements. The NMR experiments were performed on a Bruker AM 300 spectrometer operating at 60 MHz for ^{127}I and 14 MHz for ^{39}K , respectively. Samples were placed in conventional 10-mm-o.d. Pyrex NMR tubes without degassing. The ^{127}I NMR spectrum was obtained without field locking. For ^{39}K NMR, D_2O sealed in a 5-mm NMR tube was placed in the middle of the 10-mm NMR tube for field locking. The temperature was controlled by flowing heated air around the sample tube located in the NMR probe head. The line widths at half-height were obtained from the Lorentzian curve fitting. Typical line shapes for ^{127}I and ^{39}K NMR spectra are shown in Figure 1, where "+" marks are data points and the line is a calculated Lorentzian line shape best fit to the data. The measurements of the line width were repeated at least three times for the same experiment. The errors in measuring the line width were estimated to be $\pm 5\%$.

Results and Discussion

Rapid Exchange between Free and Polymer-Bound Iodide Anions. Like ^{35}Cl and ^{81}Br , ^{127}I is a nucleus having a quadrupole moment, and its quadrupole relaxation usually results in severe line broadening. Its quadrupole relaxation mechanism was recently discussed by Lindman and Forsén.¹ One of the most important characteristics of the ^{127}I NMR for aqueous iodide solutions is that the relaxation rate increases as the hydration shell surrounding the iodide ion becomes more asymmetric due to the presence of another solute in the solution. Therefore the excess line width, which is a difference between the ^{127}I NMR line width obtained from an aqueous iodide solution and that from a solution containing another solute (e.g., macromolecule) under the same iodide concentration, should generally be proportional to the concentration of the solute at low concentrations even when there is no specific binding between the iodide anion and the solute.

If the macromolecular solute dissolved in the aqueous iodide solution has a specific binding interaction with the iodide anion, the ^{127}I nuclear spin system can relax

Table II
The Line Widths at Half-Height of ^{127}I NMR and the Activation Energy^a for the Quadrupole Relaxation Obtained from an Aqueous Solution of Polymer^b Containing 0.1 M KI

polymer	$\Delta\nu_{1/2}^c$	E_a^d
none	1.75	3.56
0.1 M PEO	2.23	3.56
0.5 M PEO	4.05	4.71
1.0 M PEO	6.31	5.50
0.1 M PVAL	2.50	4.11
0.5 M PVAL	5.13	5.68
1.0 M PVAL	8.20	6.36
0.1 M iso-PHEMA	5.33	8.66
0.1 M PAAM	1.91	2.98
0.5 M PAAM	2.92	3.87
1.0 M PAAM	4.57	5.09
0.1 M PAAMA	2.18	3.68
0.5 M PAAMA	4.46	5.43
1.0 M PAAMA	7.02	6.20
0.1 M PAAMB	1.69	2.68
0.5 M PAAMB	1.83	3.00
0.1 M PVP	10.12	8.35
0.15 M PVP	18.32	10.41

^a Measured in the range 25–55 °C. ^b Contain 10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$ to avoid the oxidation of iodide anion. ^c Expressed in kHz. ^d Expressed in kcal/mol.

very fast while the two are bound together since the bound iodide can have a different quadrupole coupling constant and rotational correlation time compared with the free iodide. Usually, a binding between an ionic species and a neutral species is a weak interaction. If the polymer–iodide binding is sufficiently weak, there can be a rapid exchange between the polymer-bound and the free iodides.

As Figure 1 shows, the ^{127}I and ^{39}K NMR line shapes obtained from our aqueous polymer–iodide solutions are Lorentzian. The ^{127}I NMR line widths, as listed in Table II, for the aqueous iodide solutions of PVP and iso-PHEMA are significantly broader than that obtained for the solution without polymers. However, no separation of the two NMR lines corresponding to the polymer-bound and the free iodides was observed. The excess ^{127}I NMR line widths, as Figure 2 shows, increased proportionally to the polymer concentration. The line width was not affected by the small amount of $\text{Na}_2\text{S}_2\text{O}_3$ (10^{-3} M) added to prevent the oxidation of iodide ions, and thus the line broadening is certainly not a result of a chemical exchange^{13,14} of ^{127}I between I^- and I_3^- .

To establish that there exists a specific polymer–iodide binding and that the fast-exchange limit is applicable in treating the binding problem, we made an Arrhenius plot (shown in Figure 3) of the ^{127}I NMR line width at half-height ($\Delta\nu_{1/2}$) at aqueous polymer–iodide solution temperatures of 25–55 °C. At lower temperatures, the line broadening makes detection more difficult. Good linearity of the Arrhenius plot with a positive slope clearly demonstrates that, if the polymer–iodide binding exists, the fast exchange can be assumed for the ^{127}I NMR relaxation under our experimental conditions. From the Arrhenius plot, we also obtain the activation energy listed in Table II. The activation energy of 10.41 kcal/mol obtained for 0.15 M PVP is much larger than the corresponding values for other polymers obtained even at much higher concentration and therefore is difficult to consider for a simple reorientation but can be attributed to a specific polymer–iodide binding.

Determination of Binding Constants.¹ To determine the polymer–iodide binding constants from NMR line widths, we obtained the excess ^{127}I NMR line widths

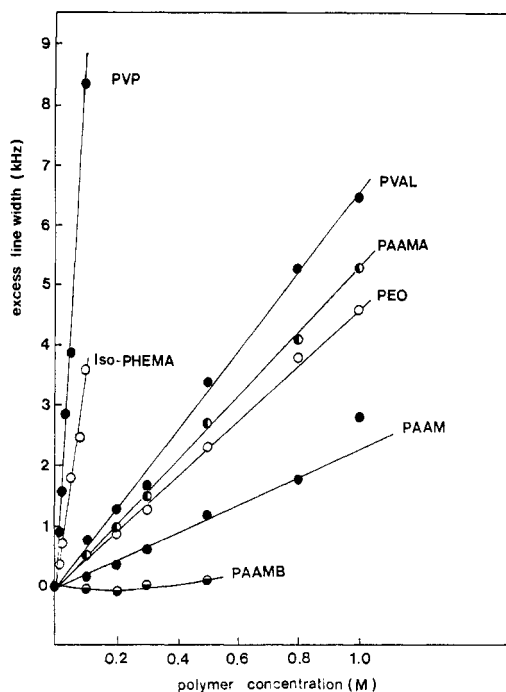


Figure 2. Excess line widths of ^{127}I NMR as a function of concentration for aqueous polymer solutions containing 0.1 M KI at 298 K in the presence of 10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$.

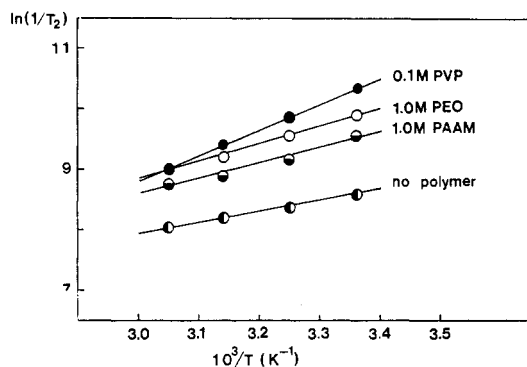


Figure 3. Temperature dependence of the ^{127}I NMR relaxation rate obtained for aqueous polymer solutions containing 0.1 M KI in the presence of 10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$.

as a function of polymer concentration under the same total iodide concentration (see Table III). We then made the assumption that there was on the macromolecule only one class of iodide binding site characterized by the binding constant $k_b(\Gamma^-)$. We also assumed that the total iodide concentration $[\Gamma^-]_{\text{tot}}$ was very much higher than the total macromolecular concentration $[\text{M}]_{\text{tot}}$ so that the fraction of free iodide ions, p_f , could always be put equal to unity. From mass law considerations the fraction of the bound iodide ions could then be written as follows:

$$p_b = \frac{n_b[\text{M}]_{\text{tot}}k_b(\Gamma^-)}{1 + k_b(\Gamma^-)[\Gamma^-]_{\text{tot}}} \quad (1)$$

where n_b is the number of binding sites. With the assumption of a rapid iodide exchange between the two states, the observed relaxation rate $1/T_2$ could be written as the following weight average:

$$\frac{1}{T_2} = \frac{1}{T_{2f}}p_f + \frac{1}{T_{2b}}p_b \quad (2)$$

where T_{2f} and T_{2b} were the relaxation times of the free and bound iodides, respectively. Substituting eq 1 into

eq 2 gave the following equation:

$$\Delta\left(\frac{1}{T_2}\right) = [\text{M}]_{\text{tot}} \left[\frac{n_b k_b(\Gamma^-)(T_{2b})^{-1}}{1 + k_b(\Gamma^-)[\Gamma^-]_{\text{tot}}} \right] \quad (3)$$

where $\Delta(1/T_2)$ was the excess relaxation rate. The reciprocal of eq 3 took on the form

$$\frac{[\text{M}]_{\text{tot}}}{\Delta(1/T_2)} = \frac{1}{n_b(T_{2b})^{-1}k_b(\Gamma^-)} + \frac{[\Gamma^-]_{\text{tot}}}{n_b(T_{2b})^{-1}} \quad (4)$$

As Figure 4 shows, a plot of $[\text{M}]_{\text{tot}}/\Delta(1/T_2)$ versus $[\Gamma^-]_{\text{tot}}$ gave a straight line with the slope T_{2b}/n_b and the intercept $T_{2b}/(n_b k_b(\Gamma^-))$, from which $k_b(\Gamma^-)$ listed in Table IV was determined. The binding constant for potassium cations in Table IV was similarly determined from the measurement of the excess ^{39}K NMR line widths.

Thermodynamic Parameters for Polymer-Iodide Binding. Comparison of the excess line widths of Figure 2 and the intrinsic binding constants in Table IV suggests that PVP and iso-PHEMA exhibit very large excess ^{127}I NMR line widths due to polymer-iodide binding. Among other polymers with marked excess line widths, PAAM has a binding constant of 1.3 M^{-1} , which is comparable to that of iso-PHEMA, where its excess line width is even smaller than that of PEO with a smaller binding constant of 0.3 M^{-1} . This finding can be explained in terms of the asymmetric hydration of iodide anions caused by a water-structure enhancement effect due to nonpolar groups of the polymers. This type of line broadening was previously pointed out in other cases.¹⁶⁻¹⁸ The concept of asymmetric hydration means that the arrangement of water molecules around an ion is distorted by the presence of other species in the solution. The more symmetric the hydration of a quadrupolar nucleus is, the lower is its relaxation rate.

To obtain thermodynamic parameters¹ on the iodide binding with PVP, we studied the ^{127}I NMR relaxation as a function of temperature with varying total iodide concentration at a fixed PVP concentration. The equilibrium constant and the free energy change for the binding process decreased with increasing temperature. The enthalpy and entropy changes were both negative at all temperatures listed in Table V, suggesting that an electrostatic interaction can be responsible for the iodide binding with PVP.

It is necessary to consider further the nature of binding forces involved in the PVP-iodide binding process. According to the principle of hard and soft acids and bases,^{21,22} iodide anion has been known as a soft base, and hence it would prefer to coordinate to a soft acid with high polarizability. It seems plausible to state that additional stability due to London forces will always exist in a complex formed between a polarizable acid and a polarizable base.²¹

The polarizability may be related to the average dipole moment. To examine the relationship between the binding constant and the dipole moment present in the polymer segment, we calculated the average dipole moment according to the Debye equation.¹⁰ For PVP, however, we chose the dipole moment reported²³ for *N*-methylpyrrolidone whose structure is a fairly close analogue of the monomer unit of PVP. PVP has the largest average dipole moment of 4.07 D^{23} as shown in Table I. Figure 5 shows a good correlation between the magnitude of the intrinsic binding constant and average dipole moment of the polymer.

The Behavior of Counterions. Interpretation of counterion NMR relaxation in polyelectrolyte solutions

Table III
The Line Widths^a at Half-Height of ¹²⁷I NMR in 0.1 M PVP as a Function of the Total Iodide Concentration in the Range 0.01–1.0 M

T, K	total iodide concentration, M									
	0.01	0.03	0.05	0.08	0.10	0.20	0.30	0.50	0.80	1.0
308		6.29	5.96	5.95	5.86	5.36	4.71	3.98	3.39	2.98
318	4.80		4.69	4.26	3.98	3.81	3.44	3.02	2.61	2.52
328	3.46		3.44	3.40	3.17	3.05	2.81	2.46	2.17	2.10

^a Expressed in kHz.

Table IV
Intrinsic Binding Constants^a for the Binding^b of Polymer with Iodide and Potassium Ions in Aqueous Solution Measured at 298 K

polymer	$k_b(\text{I}^-)^c$	$k_b(\text{K}^+)^d$
PVP	3.0	0.2
iso-PHEMA	1.4	
PAAM	1.3	
PEO	0.3	0.1

^a Expressed in M^{-1} and the errors were estimated to be $\pm 10\%$.

^b In 0.1 M water-soluble polymer as a function of total ion concentration in the range 0.01–0.1 M. ^c Denotes the intrinsic binding constant of iodide anion. ^d Denotes the intrinsic binding constant of potassium cation.

Table V
Intrinsic Binding Constant and Other Thermodynamic Parameters for PVP–Iodide Binding^a as a Function of Temperature

T, K	$k_b(\text{I}^-)^b$	ΔG^c	ΔH^c	ΔS^d
298	2.97	-645.6	-5067	-14.84
308	2.29	-507.9	-5067	-14.80
318	1.69	-328.6	-5067	-14.90
328	1.37	-202.0	-5067	-14.83

^a In 0.1 M PVP solution as a function of total iodide concentration in the range 0.01–1.0 M. ^b Intrinsic binding constant expressed in M^{-1} . ^c Expressed in cal/mol. ^d Expressed in entropy unit (eu).

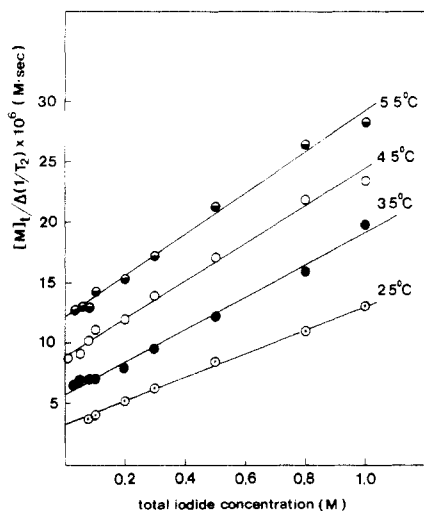


Figure 4. Plots of $[M]_{\text{tot}}/\Delta(1/T_2)$ versus $[I^-]_{\text{tot}}$ for a 0.1 M PVP solution as a function of temperature. $[M]_{\text{tot}}$ is the total concentration of PVP, $[I^-]_{\text{tot}}$ is the total concentration of iodide, and $\Delta(1/T_2)$ is the excess relaxation rate.

has recently been treated theoretically by Halle et al.²⁴ To examine the behavior of a counteranion during the binding of iodide anion with the polymer, we carried out ¹²⁷I NMR line-width measurements with various alkali iodides such as NaI, KI, RbI, and CsI. Table VI indicates no effect of counteranions on ¹²⁷I NMR line width, suggesting that the polymer–salt binding is specific to iodide, irrespective of cations. Furthermore, we mea-

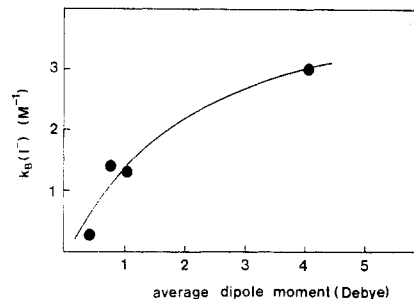


Figure 5. Correlation between the intrinsic binding constant for the polymer–iodide binding and the average dipole moment of the polymer segment.

Table VI
The Excess Line Widths of ¹²⁷I NMR Measured at 298 K as a Function of PVP Concentration in Aqueous PVP Salt Solutions^a

concn, M	$\Delta\nu_{\text{ex}}^b$			
	NaI	KI	RbI	CsI
0.01	0.84	0.88	0.92	0.82
0.02	1.52	1.54	1.62	1.59
0.03	2.34	2.68	2.52	2.55
0.05	3.85	3.82	4.21	4.09
0.1	8.16	8.37	7.89	7.85

^a Containing 0.1 M salt. ^b Expressed in kHz.

Table VII
The ³⁹K NMR Line Widths and the Activation Energy for the Quadrupole Relaxation Obtained from Aqueous Polymer Solutions^a Containing 0.1 M KI

polymer	$\Delta\nu_{1/2}^b$	E_a^c
none	6.61	1.90
0.1 M PEO	7.08	2.53
1.0 M PEO	14.23	3.92
0.1 M PVAL	6.44	2.32
1.0 M PVAL	6.87	2.84
0.1 M iso-PHEMA	6.63	3.19
0.1 M PAAM	6.37	
1.0 M PAAM	7.37	2.78
1.0 M PAAMA	9.89	2.10
0.1 M PAAMB	8.68	2.16
0.5 M PAAMB	11.55	3.29
0.1 M PVP	6.86	
1.0 M PVP	7.92	

^a Contain 10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$ to avoid the oxidation of iodide anion.

^b Measured at 298 K and expressed in Hz. ^c Measured in the range 25–55 °C and expressed in kcal/mol.

sured the ³⁹K NMR line width as a function of temperature in the same polymer solution used in the ¹²⁷I NMR experiment. The positive slope of the plot shown in Figure 6 indicates that the motion of ³⁹K is in an extremely narrowing region.²

The ³⁹K line widths and the activation energies increased by only a small amount with increasing concentration of PVP and PAAM from 0.1 to 1 M as shown in Table VI. This result provides evidence that potassium ion is not directly associated with PVP, PAAM, and iso-PHEMA. The binding constants of potassium cation listed in Table

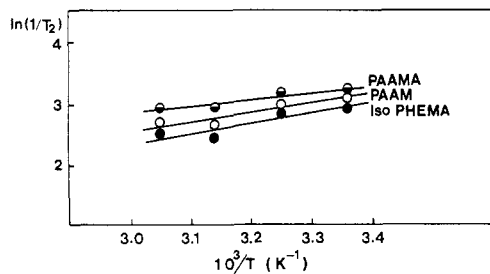


Figure 6. Temperature dependence of the ^{39}K NMR relaxation rate obtained for aqueous polymer solutions containing 0.1 M KI in the presence of 10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$.

IV also support the evidence mentioned above. Our results that the iodide anion is responsible for the complexation of the polymer with the ion irrespective of cations agree with those reported by others.²⁵⁻²⁷

It may be possible to speculate that loss of molecules of water of hydration might broaden the signal from some potassium nuclei, rendering the signal too broad for detection. However, by comparing the signal intensity obtained in the presence of the polymer with that of only potassium iodide, we established that all of the ^{39}K in the samples contributed to the observed Lorentzian lines. Therefore, we can exclude the possibility that a small fraction of the potassium signal is too broad to detect.

It should be noticed that the cation (^{23}Na and ^{85}Rb) nuclear quadrupole relaxation⁴ in aqueous solution is only slightly altered by the presence of organic anions, such as alkanoate ions and alkali-substituted BH_4^- ions. The difference between alkali cations and halogen anions in this respect may be due either to a specific anion-water interaction that is not operating in the case of cation or to the hydration of cations, which may make incorporation of these ions in the structure-modified water lattice less extensive.

Conclusions

In this work, the binding affinity of iodide anions to polymers in aqueous solution was found to follow the order $\text{PVP} > \text{iso-PHEMA} > \text{PAAM} > \text{PEO} \approx \text{PVAL} > \text{PAAMA} > \text{PAAMB}$. Severe line broadening in ^{127}I NMR observed for PVP, iso-PHEMA, and PAAM is mainly caused by the specific binding of the iodide anion on these polymers. The lesser line broadening for PEO and PVAL is rather due to the asymmetric hydration of iodide anions, which is affected by the polymer-water interaction.

The magnitude of the intrinsic binding constant of iodide anions appears to be related to the average dipole moment of the polymer segment. The thermodynamic parameters, obtained as a function of temperature, indicate that the electrostatic interaction can be responsible for the specific iodide binding with PVP. Therefore, the attrac-

tive force between the polarizable iodide anions and the electric dipoles of polymers is suggested to cause the polymer-iodide binding or the adsorption of iodide ions on the polymers.

The ^{127}I NMR line widths for the alkali PVP solutions of PVP and alkali iodides such as NaI, KI, RbI, and CsI and ^{39}K NMR data indicate that there are no significant effects of counterions on the specific iodide binding with the polymers.

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