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Proton NMR Chemical Shift Induced by Ionic Association on a Poly(ethylene oxide) Chain

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When a polymer strongly binds metal ions in solution, a substantial number of counterions can also be bound to it, if the polarity of the solvent is not too high. This is actually observed for poly(ethylene oxide) (PEO) and sodium thiocyanate in nitromethane[1] and PEO and barium salts in methanol.[2] The phenomenon may be regarded as an ionic association between the cation of the PEO–metal complex and counteranion and resembles the ion condensation of polyelectrolytes. Although our previous conductivity studies have disclosed directly the presence of ionic association, the analytical calculation is quite intricate because of the strong interactions between metal cations that were bound to the same PEO chain.[1,2] Thus the simultaneous use of a more straightforward analytical method may be desirable.

^{1}H and ^{13}C NMR spectroscopy have frequently been applied to the investigation of ionic association, especially ion pair formation between alkali metal ions and carbanions.[3,4] Downfield shifts of ^{1}H and ^{13}C signals were induced by the shift of the ion pair equilibrium toward tight ion pairs from free ions or solvent separated ion pairs. Here we wish to report the possibility of estimating by ^{1}H NMR the ionic association between alkaline earth metal cations and counteranions on the PEO chain.

It has been well established that PEO forms complexes with alkali and alkaline-earth metals in several organic solvents.[5] A ^{1}H NMR study of PEO oligomers in methanol showed that a downfield shift of the methylene protons was induced by the complexation with potassium ion, although the absolute values of the chemical shift differences were small.[6] On the other hand, a relatively large chemical shift was observed in the case of the complexation with alkaline-earth metal ions in the same solvent.[7] This was also considered to be induced by metal complexation, although the absolute chemical shift values were much different from those observed for alkali metal cations.

Commercial PEO samples with an average molecular weight of 2 × 10^4 were used. ^{1}H NMR spectra were measured on a JEOL JNM-PMX60SI spectrometer in deuterated methanol. The methylene protons of dioxane in benzene solution, which was added as an external standard, were taken as a reference. Chemical shift values were measured downfield with respect to the methylene signal of PEO in the absence of salt.

Figure 1 shows a plot of the ^{1}H NMR chemical shift as a function of the $[\mathrm{Ba}^{2+}]/[\mathrm{PEO}]$ ratio for barium thiocyanate and barium chloride in deuterated methanol. As shown in the figure, the addition of barium salts causes a downfield shift of the methylene protons of PEO. Both curves seem to saturate at a certain value of the ratio $[\mathrm{Ba}^{2+}]/[\mathrm{PEO}]$. These curves correspond well to the conductivity curves of our previous study,[2] since the ratio $[\mathrm{Ba}^{2+}]/[\mathrm{PEO}]$ at which the chemical shift or conductivity approaches an asymptotic value is very similar. Thus it is natural to consider that the chemical shift is induced by the complexation of PEO with Ba^{2+} ion. However, it should be noted that the asymptotic values of the chemical shift are very much different for these two barium salts.

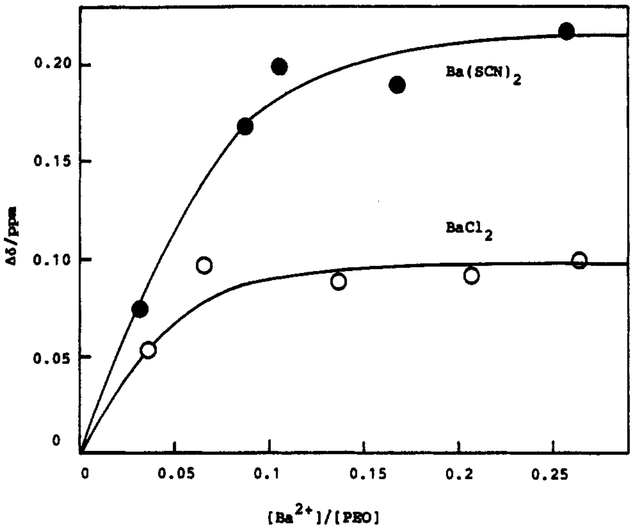

Figure 1. ^{1}H NMR chemical shifts $\Delta\delta$ in the presence of Ba(SCN)$_2$ and BaCl$_2$ plotted against $[\mathrm{Ba}^{2+}]/[\mathrm{PEO}]$ in deuterated methanol. $\Delta\delta$ is defined as the chemical shift of methylene protons as measured from the signal of dioxane added as a external standard. $[\mathrm{Ba}^{2+}] = 0.05$–$0.20$ M.

For simplicity, if the electrostatic interactions along the polymer chain are neglected, the barium ion binding is simply represented by the following equilibria

$$\mathrm{PEO} + \mathrm{Ba}^{2+} \overset{K_c}{\rightleftharpoons} [\mathrm{PEO{\cdot}Ba}^{2+}]$$

$$[\mathrm{PEO{\cdot}Ba}^{2+}] + \mathrm{X}^- \overset{K_a}{\rightleftharpoons} [\mathrm{PEO{\cdot}BaX}^{+}] \qquad (1)$$

where X$^-$ is the counteranion and K_c and K_a are the binding constant and ionic association constant on the PEO chain, respectively. Assuming that four oxymethylene units form a binding site for the barium ion,[8] we could calculate K_c and K_a using a one-dimensional lattice model. According to our conductimetric study,[2] K_c was comparable for Ba(SCN)$_2$ and BaCl$_2$, while K_a was 10 times larger for Ba(SCN)$_2$ in methanol. This result was explained by the effect of solvation on anionic species. For the small Cl$^-$ anion, the free energy of desolvation is more positive than for the SCN$^-$ anion, which is less favorable for ionic association on the PEO chain.

Figure 2 shows plots of the fractional occupation of bound ions, θ_M, and that of bound ion pairs, θ_{MX}, against $[\mathrm{Ba}^{2+}]/[\mathrm{PEO}]$ for Ba(SCN)$_2$ and BaCl$_2$. θ_M and θ_{MX} were calculated by the one-dimensional lattice model using averaged K_c and K_a values obtained in our previous report.[2] It should be noted that θ_{MX} for Ba(SCN)$_2$ was far larger than that for BaCl$_2$, while the reverse was found for θ_M. Accordingly, the larger ^{1}H NMR chemical shift for Ba(SCN)$_2$ solutions cannot be ascribed to the bound Ba^{2+} ions but principally to the bound ion pairs BaSCN$^+$. The chemical shift $\Delta\delta$ is represented by the weighted sum of the chemical shifts due to the bound ion, $\Delta\delta_M$, and bound ion pair, $\Delta\delta_{MX}$, then

$$\Delta\delta = \theta_M \Delta\delta_M + \theta_{MX} \Delta\delta_{MX} \qquad (2)$$

Figures 1 and 2 suggest that $\Delta\delta_{MX}$ is much larger than $\Delta\delta_M$. To confirm this observation, the chemical shifts due to several alkaline-earth metal salts were measured at a fixed $[\mathrm{Ba}^{2+}]/[\mathrm{PEO}]$ ratio of ca. 0.25.

Table I shows the θ_M and θ_{MX} values together with chemical shifts for several barium and strontium salts. θ_M and θ_{MX} values were calculated by using average values of

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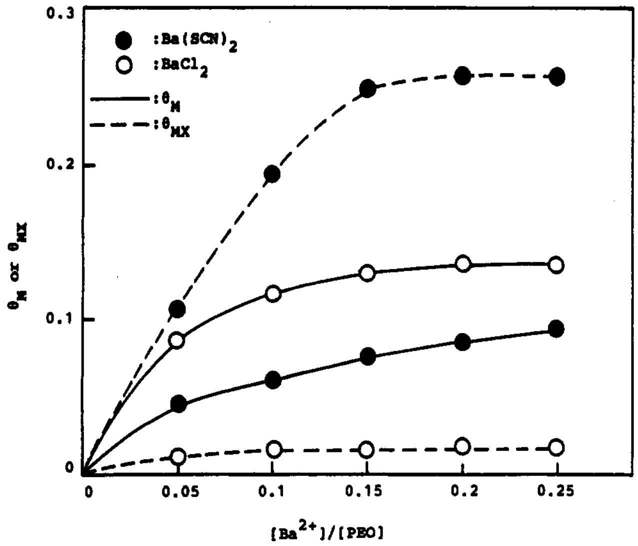

Figure 2. Fractional occupation of free ions and ion pairs, θ_M and θ_{MX}, calculated as a function of [Ba^{2+}]/[PEO], assuming that [Ba^{2+}] is 0.075 M.

binding constant obtained at various concentrations in our previous study.[2] It is clear at first glance that the chemical shift is better correlated with the θ_{MX} than the θ_M. The correlation coefficient of linear regression between the chemical shift and the θ values was 0.769 for bound ion pairs and 0.355 for bound ions. Thus a good correlation was found between the chemical shift and θ_{MX}, while no correlations were found between the chemical shift and θ_M.

In conclusion, the present study discloses a new aspect of the proton NMR chemical shift induced by ionic association on a polymer chain. A possible interpretation of this effect is the polarization due to the bound anion, which is located just outside of the helical PEO–Ba^{2+} complex.[9]

Table I
^{1}H NMR Chemical Shift and Fractional Occupation of Free Ions and Ion Pairs in the Presence of Barium or Strontium Salts

salt	$\Delta\delta$/ppm[a]	θ_M[b]	θ_{MX}[b]
Ba(SCN)$_2$	0.217	0.095	0.258
BaBr$_2$	0.213	0.109	0.094
BaCl$_2$	0.098	0.137	0.015
Sr(SCN)$_2$	0.158	0.033	0.058
SrCl$_2$	0.047	0.026	0.017

[a] [Ba^{2+}] = 0.05–0.20 M; [Ba^{2+}]/[PEO] $\simeq$ 0.25. [b] Calculated for [Ba^{2+}] = 0.075 M and [PEO] = 0.3 M.

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Registry No. PEO, 25322-68-3; Ba(SCN)$_2$, 2092-17-3; BaBr$_2$, 10553-31-8; BaCl$_2$, 10361-37-2; Sr(SCN)$_2$, 18807-10-8; SrCl$_2$, 10476-85-4.