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NMR STUDY OF ^{23}Na COMPLEXING BY POLYETHERS, SILOXANES AND POLYAMIDES

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Abstract—Complexation of Na^+-ion with polyethers and polyamides is studied by using ^{23}Na NMR spectroscopy. The variation of the linewidth and the position of the ^{23}Na NMR signal give evidence for the interaction of oxygen atoms of poly(ethylene oxide) in acetonitrile and those of siloxanes in T.H.F. with the solvated ion. In addition chemical shift data are given for perturbation of the Na^+ solvation shell by interaction of the ion with substituted amides and polyamides in T.H.F.

Biological systems [1,2] and ionic solvation [3–7] have been investigated by alkali NMR spectroscopy and it has been shown that this technique (particularly ^{23}Na NMR) is a very sensitive probe of the immediate environment of alkali metal ions. The magnitude of ^{23}Na chemical shift and line broadening give information on the ion-ion, ion-solvent or ion-dipole interactions. In this work complexation of Na^+ with various polymers (polyethers and polyamides) is studied using ^{23}Na NMR.

POLY(ETHYLENE OXIDE) AND SILOXANES

Since Pedersen's first synthesis [8] of macrocyclic compounds, crown ethers [9–11] or cryptates [12] have been the subject of extensive examination of the complexing ability of these molecules towards alkali metal ion. Few data are available on complexes of poly(ethylene oxide) with neutral salts in organic solvents [13] and we present here a study of the interaction of sodium ion with poly(ethylene oxide) in acetonitrile and with siloxanes in tetrahydrofuran. For siloxanes, we selected cyclic compounds containing as binding sites three oxygens $(Me_2SiO)_3$ or four oxygens $(Me_2SiO)_4$ and a linear compound containing six oxygens $Me_3Si(OSiMe_2)_5OSiMe_3$. In addition, data for linear high molecular weight siloxanes are reported.

EXPERIMENTAL

Poly(ethylene oxide) and siloxanes (Union Carbide) were reagent grade quality and were not further purified except for drying. The sodium salt used was ϕ_4 B Na. Acetonitrile was dried over activated molecular sieves. T.H.F. was fractionally distilled over Na. Sodium 23 nuclear magnetic measurements were made at ambient or low temperature on a modified Varian DA 60 spectrometer by using the side band technique with a V 4333 probe at 23.3 MHz and 1.4092 T in the internal lock mode. Cylindrical non-spinning sample tubes of about 10 mm diameter were used.

Chemical shifts of ^{23}Na resonance are expressed in ppm with shifts downfield from the reference (a saturated sodium chloride solution) being positive.

Results

The ^{23}Na nucleus has a quadruple moment and its magnetic resonance absorptions will be characterized by two parameters: Chemical shift and linewidth, depending on the coupling of the nuclear quadruple with electric field gradients at the nucleus and on the correlation time for reorientation of these field gradients.

Poly(ethylene oxide)

Popov [3] reported that ^{23}Na resonance line is not concentration dependent for $Na\ B(C_6H_5)_4$ dissolved in acetonitrile (D = 37.5) in the concentration range 0.5–0.1 M. $\delta = 7.77$ $(Na^+) = 0.125$ M.

The effect of concentration and molecular weight of polyethylene oxide on the chemical shift is shown in Fig. 1 and Table 1.

The addition of poly(ethylene oxide) to solutions of $Na\ B(C_6H_5)_4$ markedly affects the linewidth and the position of the ^{23}Na NMR signal, indicating a change in solvation shell around the Na^+-ion. The oxygen atoms of the poly(ethylene oxide) chain are separated from the solvent through Na^+-interaction.

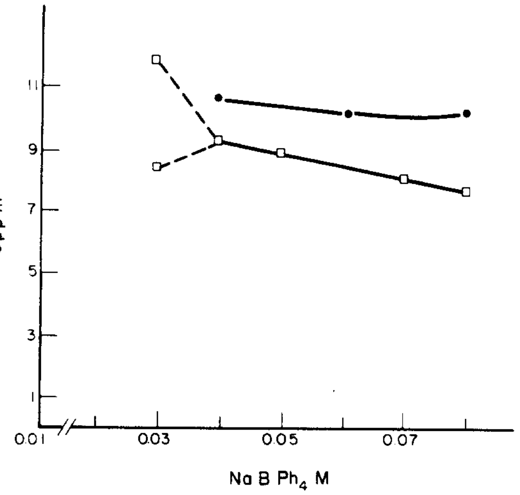


Fig. 1. Solvent acetonitrile poly(ethylene oxide) 2%. □—$\bar{M}_w$ = 30,000; ●—$\bar{M}_w$ = 10,000.

Table 1. Position and width of the Na resonance of poly(ethylene oxide) complexes

Polyethylene oxide 2%	$\overline{M}_w = 6.000$	$T = 22°$
$(Na^+) = 0.06$ M	$\delta = 10.5$	$\Delta\nu 1/2 = 240$ Hz
Polyethylene oxide 3%	$\overline{M}_w = 6.000$	$T = 22°$
$(Na^+) = 0.05$ M	$\delta = 9.70$	$\Delta\nu 1/2 = 260$ Hz

Comparison of these data shows:

(1) An increase of the chemical shift with decreasing molecular weight; (2) An increase of the chemical shift with decreasing polymer concentration; (3) The variation of chemical shift with ion concentration is more important with one polymer ($\overline{M}_w = 30{,}000$). For solutions containing this polymer and low ion concentration ($(Na^+) = 0.03$ M), 2 peaks can be observed at ambient temperature indicating that the exchange between the free and complexed sites is slow even at room temperature. Shifts for the 2 peaks are presented in Fig. 2 as a function of the temperature. At $-26°$ the band is very broad ($\Delta\nu 1/2 = 430$ Hz) but one peak corresponds probably to the free Na^+-ion ($\delta = 7.75$).

Cyclic and linear siloxanes

Sodium tetraphenylborate is a separated ion pair [14] in T.H.F. (D = 7.6) and shows no concentration dependence for the $^{23}Na^+$ resonance line ($\delta = 8.00$; $\Delta\nu 1/2 = 22$ Hz).

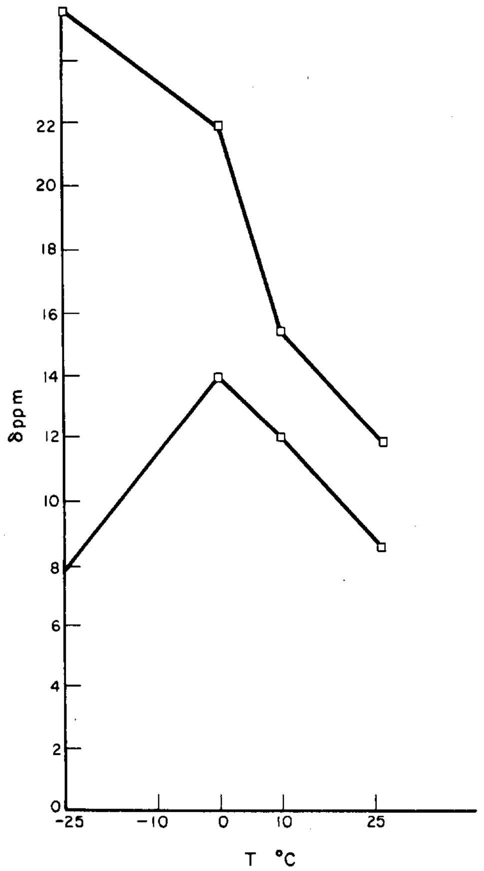


Fig. 2. Solvent acetonitrile poly(ethylene oxide) 2%. $\overline{M}_w = 30{,}000$; $(Na^+) = 0.03$ M.

Addition of siloxanes to a solution of Na B $(C_6H_5)_4$ ion pairs in T.H.F. broadens slightly the line indicating that the solvation shell is replaced by the complexing agent. Figure 3 shows that chemical shift is also affected by the complexing agent. Chelation in the solvating siloxanes causes a downfield shift on the Na resonance and this effect is more important for the $Me_3Si(OSiMe_2)_5OSiMe_3$.

Figure 3 shows the effect of complexing with the high molecular weight siloxanes on the position of the ^{23}Na resonance. The width is narrow and nearly constant with concentration and molecular weight ($\Delta\nu 1/2 = 32$ Hz). Ion pairs overlap occurs almost exclusively between the Na ion orbital and the oxygen atom orbitals of the ether molecules in its first solvation shell. A downfield shift is observed, consistent with an increase in overlap.

A temperature variation for the polymer of $\overline{M}_w = 2.48 \times 10^6$ shows that 2 peaks can be observed at low temperature (0°, $-50°$) due to the free and the complexed sodium ion, the exchange between the 2 sites being slow. But for the polymer $\overline{M}_w = 2.90 \times 10^5$ the exchange is faster and one line is observed in this temperature domain.

There is a slight broadening of the linewidth of ^{23}Na resonance with the polymer compared to the cyclic siloxanes. The linewidth suggests that the siloxanes separated ion pair is not spherically distributed around the Na^+ cation.

N,N' DISUBSTITUTED PROPIONAMIDES AND POLYACRYLAMIDES

The interactions between salts and biological polymers have been the subject of extensive work

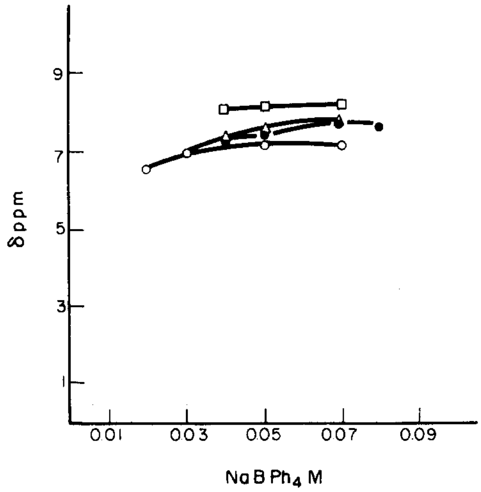
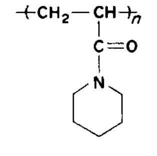
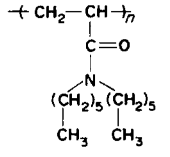


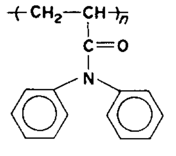
Fig. 3. Solvent T.H.F. ●—$(Me_2SiO)_3$ 0.09 M; □—$Me_3Si(OSiMe_2)_5OSiMe_3$ 0.038 M; ○—Polymer 0.1% $\overline{M}_w = 2.48\ 10^6$; △—Polymer 0.5% $\overline{M}_w = 1.17\ 10^5$.

[15–20]. Amide models have been used to determine the interaction sites of salts by i.r., ^{1}H and ^{13}C NMR spectroscopy [21,32]. The authors consider generally that the fixation of cation takes place on the carbonyl group. With the technique used in this work, we investigated the Na$^+$ solvation shell perturbation by interaction of the ion with amides and polyamides.

The choice of the substituents bound to the nitrogen atom enables modification of the steric hindrance and the inductive effect at the carbonyl site. The *N,N'*-disubstituted polyacrylamides studied are polyacrylopiperidide (**I**), poly(*N,N'* di *n*-hexyl)acrylamide (**II**) and poly(*N,N'* diphenyl)acrylamide (**III**).


(I)


(II)


(III)

In addition, two *N,N'*-disubstituted propionamides (*N,N'* di-*n*-hexyl propionamide and propionopiperidide) have been synthesized.

Experimental

Syntheses of monomers and polymerization methods have been described [33]. The polyacrylamides were prepared by radical polymerization which leads to atactic polymers. The *N,N'*-disubstituted propionamides were obtained by reaction of propionylchloride with a secondary amine.

Results and discussion

Propionamides. Addition of amide to a solution of Na B Ph$_4$ ion pair in T.H.F. [14] strongly broadens the ^{23}Na NMR signal and shifts it, indicating that the T.H.F. solvation shell is replaced by the amide group. Shifts for solutions of dihexylpropionamide and piperidine propionamide are presented Fig. 4 as a function of the concentration of sodium ion.

The di-*n*-hexylpropionamide is a stronger electron donor than propionopiperidide and this must cause a larger downfield shift, but this effect is not observed for the monomers. The bulky substituents probably do not favour the approach of sodium ion on the carbonyl site.

The linewidth is almost not concentration dependent. Examples are given below for the amides studied: di-*n*-hexyl propionamide 0.06 M, Na B Ph$_4$ 0.08 M, $\delta = 7.20$ $\Delta\nu 1/2 = 66$ Hz; Piperidine propionamide 0.1 M, Na B Ph$_4$ 0.1 M, $\delta = 7.20$, $\Delta\nu 1/2 = 55$ Hz.

Polyacrylamides. Shifts of the ^{23}Na NMR resonance signal of ternary mixtures T.H.F., polyacrylamides and Na B Ph$_4$ are presented in Fig. 5.

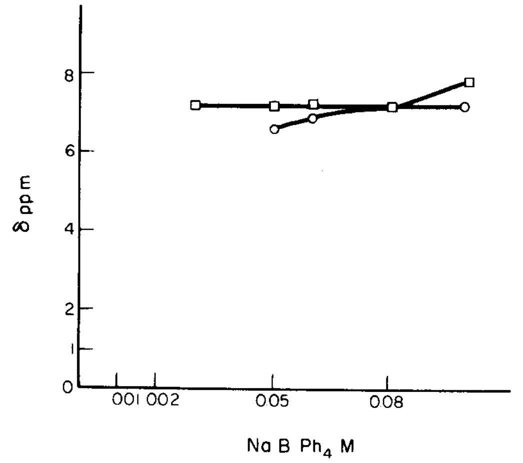


Fig. 4. Solvent T.H.F. □ *N,N* di-*n*-hexylpropionamide 0.06 M; ○ Propionopiperidide 0.1 M.

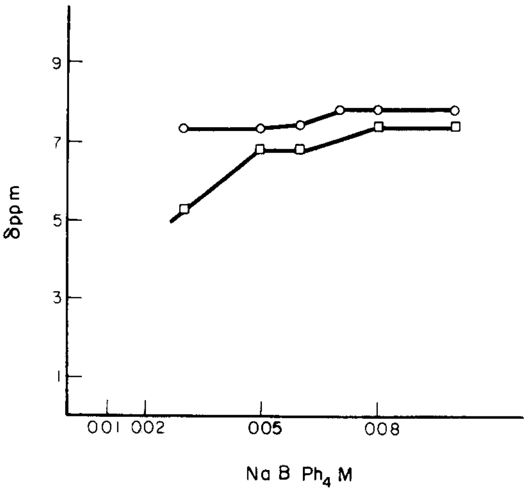


Fig. 5. Solvent T.H.F. □ Poly *N,N* di-*n*-hexylacrylamide 1.5%; ○ Poly *N,N* di-*n*-phenylacrylamide 1.5%.

Two observations can be made. (i) The NMR resonance is shifted downfield from *N,N* di-*n*-hexyl propionamide to the corresponding polymer solution. This result is consistent with a stronger interaction of Na$^+$ ion with the carbonyl site due to a cooperative effect. (ii) The NMR resonance is shifted downfield from polymer (**III**) to polymer (**II**). The aromatic ring decreases the electronic density on the nitrogen atom and the di-*n*-hexyl derivative is a stronger electron donor. Therefore the Na resonance signal appears downfield.

The influence of the substituents on the nitrogen atom is indicated by a drastic change of the linewidth

Table 2. Inherent viscosity in benzene at 25°

Polymer	Inherent viscosity [33] (ml/g)	
Polyacrylopiperidide	10.0	**(I)**
Poly-*N,N'* dihexylacrylamide	22.1	**(II)**
Poly-*N,N'* diphenylacrylamide	8.5	**(III)**

related to the correlation time τc characteristic of the solvent in the vicinity of the nucleus.

Compound (**II**)	1,5%	$Na^+ = 0.1$ M	$\delta = 7.40$	$\Delta\nu 1/2 = 150$ Hz
Compound (**III**)	1,5%	$Na^+ = 0.1$ M	$\delta = 7.85$	$\Delta\nu 1/2 = 34$ Hz

Polyacrylopiperidide (**I**) has a large downfield shift ($\Delta\delta$ 5.1) but the signal is very broad ($\Delta\nu 1/2 \sim 400$ Hz) and measurements were not accurate.

CONCLUSION

The ternary system of polymer, solvent and salt have been studied by ^{23}Na NMR spectroscopy. The technique provides information on the ion dipole interaction in solution. The oxygen atoms of the poly(ethylene oxide) chain are separated from the solvent through Na^+ interaction. Low molecular weight siloxanes show little influence on the alkali resonance signal, but for the polymers there is a clear change in the magnitude of the shift.

The sensitivity of ^{23}Na NMR in detecting steric or inductive effect has been illustrated in systems of some polyamides with Na^+.

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