Investigation of Cation−Anion Interactions in 2-Propanol Solutions of Sodium Alkoxides and Thiolates by ^{23}Na-NMR Spectroscopy

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Cation–anion interactions in 2-propanol solutions of sodium salts NaY (Y = MeS, *i*PrS, *t*BuS, *i*PrO, SCN, ClO_4, Ph_4B) have been studied by ^{23}Na-NMR spectroscopy. The analysis involved measurements of chemical shift and T_1 as a function of salt concentration in both the absence and presence of the Na^+-complexing agent 18-crown-6. The results indicate that the interactions of Na^+ with alkoxides and thiol anions are very different from those with charge-delocalized anions (SCN^-, ClO_4^-, Ph_4B^-), and that the degree of association in NaSR salts is greater for R = *t*Bu than for R = Me.

Introduction

Ion association phenomena are important in solvents of low ionizing power such as 2-propanol.[1] Thus, while MeO^-K^+ and EtO^-K^+ are largely dissociated in the parent alcohols, *i*PrO^-K^+ in 2-propanol is strongly ion-paired.[2] Ion pairing is often inferred from the results of reactivity studies. In the most common approach, the reactivity of an anionic nucleophile Y^- in the presence of an alkali metal ion M^+ is compared with that in the presence of the same metal ion as its crown ether complex, M^+−crown.[3] If MY is ion-paired, complexation of M^+ will normally lead to an enhancement of the nucleophilic reactivity of Y^-, an effect that can clearly be attributed to a diminution of the stabilizing cation−anion interaction.[3] Similar rate enhancements are often observed if the alkali metal cation is replaced by a tetraalkylammonium or -phosphonium ion,[4] species in which the charge on the heteroatom is shielded by the bulky alkyl groups.

The situation is more complex for systems involving competing reactions, which, under otherwise identical experimental conditions, can give different products depending only on the extent of cation−anion association.[5] Ion association phenomena thus need to be properly understood and considered in the context of planning new synthetic procedures.

As expected, in view of the above considerations, we found that the S_NAr reaction of *ortho*- and *para*-chloronitrobenzene with sodium thiolates (RSNa) in 2-propanol becomes faster when the sodium ion is complexed with the ether 18-crown-6 ($k^{crown} > k$).[6] Interestingly, the rate increase is greater for R = *t*Bu than for R = Me. Thus, in the reaction with *para*-chloronitrobenzene, the ratio k^{crown}/k is 15.6 for *t*BuS^- and 6.6 for MeS^-.[6] It was suggested that this difference might imply a somewhat greater degree of association in the case of the *tert*-butyl thiol anion.[6] In order to test this proposal experimentally, we have resorted to ^{23}Na-NMR analysis, which can provide information on the solvation of the ^{23}Na nucleus under investigation.

The ^{23}Na nucleus ($I = 3/2$) is 100% abundant in nature. Its high magnetogyric ratio ($\gamma = 7.0808493 \cdot 10^7\ s^{-1}\ T^{-1}$, which is larger than that of ^{13}C) and moderate nuclear quadrupole moment ($Q = 10.89\ fm^2$)[7] render its observation easy.[8,9] Its relaxation is dominated by the quadrupolar mechanism, which depends on the modulation of the electric field gradient (efg) at the nucleus (due to the surrounding electronic distribution) caused by molecular motions. Hence, the longitudinal relaxation rate $1/T_1$ in the extreme narrowing limit (generally attained for small molecules in a non-viscous solution) is given by Equation (1).

$$\frac{1}{T_1} = \frac{3\pi^2}{10}\frac{2I+3}{I^2(2I-1)}\chi\tau_c \tag{1}$$

Here, $\chi = eQq_{zz}/h$ is the nuclear quadrupolar coupling constant, q_{zz} is the largest principal component of the efg tensor $\boldsymbol{q}$, $\varepsilon = |q_{xx} - q_{yy}|/q_{zz}$ its asymmetry parameter, and τ_c is the rotational correlation time (the asymmetry parameter has been omitted since it is very small for a monoatomic ion). Since sodium chemistry consists almost entirely of compounds containing the Na^+ ion, in which the ^{23}Na nucleus is surrounded by a symmetrical charge distribution (which can, however, be perturbed by intermolecular efg's), T_1 values fall in a convenient range for signal detection, i.e. 1−10 ms, which corresponds to line widths of 10^1−10^2 Hz.[9]

From Equation (1), it is apparent that ^{23}Na relaxation is affected by two factors, namely the electric field gradient, which is directly related to the symmetry of the immediate surroundings of the ion, and the correlation time τ_c, which is a measure of the rate of tumbling of the species carrying the sodium ion in solution. It can readily be seen that both quantities are affected by solute−solvent and solute−counterion interactions. However, the correlation time is also related to the solution viscosity η through the expression $\tau_c = \eta V_m/kT$, where V_m is the hydrodynamic vol-

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ume of the tumbling species.[9] Therefore, by monitoring changes in T_1 as a response to, e.g., a change in the solvent or counterion, one can get evidence for the onset of, e.g., Na^+−counterion interactions. Moreover, if the observed relaxation rate is corrected for the solution viscosity, one can obtain the net (albeit combined) effect of efg and V_m, which are supposedly more closely related to the phenomena under investigation. However, it should be pointed out that any such influence is generally non-specific as it is due to the interaction with the electronic distribution rather than with individual spins.

The ^{23}Na nuclear shielding in Na^+ salts is only moderately affected by factors such as the nature of the solvent and counterion,[9] which is not surprising because the closed-shell Na^+ ion lacks any low-lying electronic state providing a paramagnetic contribution to its shielding. As a consequence, such shifts span a range of only ca. 20 ppm. However, owing to the normally narrow line widths, such changes are easily detectable. Several theoretical models have been proposed to account for the small solvent/counterion effect on the shielding, notably dealing with the overlap between the outer p orbitals of the ion and orbitals of other species, i.e. the counterion and solvent. In fact, infinite-dilution shifts are found to correlate with the donor number of the solvent.[8]

In the present investigation, we have analyzed specific Na^+−anion interactions in 2-propanol solution by measuring ^{23}Na-NMR chemical shifts and T_1 values as a function of salt concentration in the absence and presence of 18-crown-6 ether. Besides the thiol derivatives of immediate concern (*t*BuSNa and MeSNa), various other NaY compounds (Y = *i*PrS, *i*PrO, SCN, ClO_4, Ph_4B) have also been analyzed under the same experimental conditions.

Table 1. ^{23}Na chemical shifts and relaxation times in 2-propanol

Solute/conc.	δ[a]	T_1[b]	η/η_0[c]	$1/\eta T_1$
MeSNa				
0.1	3.6	1.4	1.107	321.2
0.05	3.5	1.5	1.062	302.0
0.01	3.5	1.8	1.013	270.6
0.005	3.2	1.7	1.006	281.9
0.001	2.0	–	1.004	–
***t*BuSNa**				
0.1	3.8	1.1	1.110	409.3
0.05	3.8	1.2	1.054	381.6
0.01	3.4	1.4	1.011	341.8
0.005	3.1	1.5	0.998	327.8
0.001	2.5	–	1.000	–
***i*PrSNa**				
0.1	3.9	1.1		
0.05	3.6	1.4		
0.01	3.5	1.5		
0.005	2.7	1.6		
0.001	2.0	–		
***i*PrONa**				
0.1	3.6	1.2	1.088	379.0
0.05	3.6	1.4	1.046	330.3
0.01	3.5	1.5	1.005	325.5
0.005	3.4	1.6	1.003	313.6
0.001	1.7	–	–	–
$NaBPh_4$				
0.1	1.4	1.5	1.208	274.4
0.05	1.5	1.6	1.102	280.0
0.01	1.8	1.7	1.024	273.8
0.005	1.8	1.8	1.010	265.5
0.001	1.9	–	–	–
$NaClO_4$				
0.1	−0.6	2.5		
0.05	−0.5	2.5		
0.01	0.2	2.4		
0.005	0.5	2.1		
0.001	1.1	–		
NaSCN				
0.1	2.27	2.4	1.086	185.9
0.05	2.34	2.2	1.048	214.8
0.01	2.16	1.9	1.013	251.0
0.005	2.20	2.0	1.012	244.9
0.001	2.18	–	–	–

[a] Chemical shifts in ppm relative to external 1 M aqueous NaCl. – [b] T_1 values in ms. – [c] Viscosities are relative to pure 2-propanol.

Results

^{23}Na-NMR Spectra of Sodium Salts in 2-Propanol

^{23}Na-NMR spectra of several sodium alkoxides and thiolates, as well as of sodium perchlorate, tetraphenylborate, and thiocyanate, were recorded at various concentrations (10^{-3}−0.1 M) in 2-propanol at 25 °C. In some cases, we also determined the viscosities of the salt solutions relative to that of the pure solvent (η/η_0), which can be converted to absolute viscosities recalling that for pure 2-propanol η_0 = 2.038 mPa s at 25 °C.[7] ^{23}Na chemical shifts, longitudinal relaxation times (T_1), and relative viscosities are collected in Table 1. Chemical shifts, relaxation rates ($1/T_1$), and corrected relaxation rates ($1/\eta T_1$) are plotted vs. the salt concentration in Figure 1, Figure 2, and Figure 3.

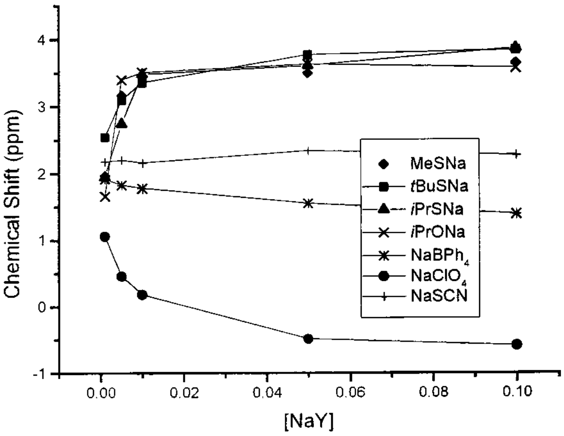

Figure 1. ^{23}Na chemical shifts of sodium salts as a function of concentration in 2-propanol

^{23}Na-NMR Spectra in the Presence of 18-Crown-6 Ether

We also recorded ^{23}Na-NMR spectra of the above sodium salts, at a constant 0.1 M concentration in 2-propanol, in the presence of increasing amounts (0.01−2.0 equivalents) of 18-crown-6 ether (18C6). As reported previously for other solvent/crown ether systems,[10] exchange of Na^+ is fast in 2-propanol at room temperature, and only one signal is observed even when 18-crown-6 is used in less than

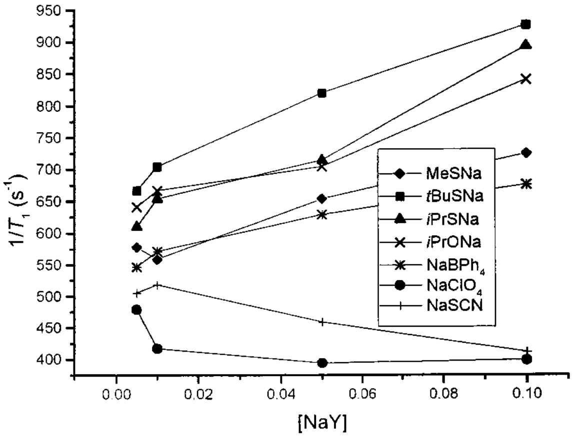

Figure 2. ^{23}Na relaxation rates ($1/T_1$) of sodium salts as a function of concentration in 2-propanol

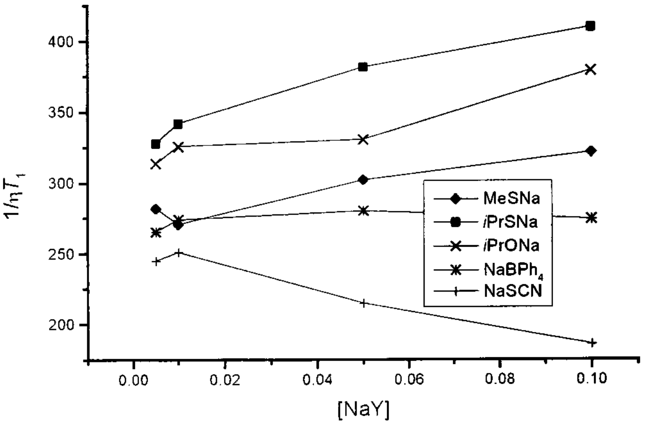

Figure 3. ^{23}Na relaxation rates, corrected for viscosity [$1/(\eta T_1)$], of sodium salts; data as in Figure 2

equimolar amounts. However, only a minimal amount of 18C6 (< 0.01 equivalents) could be added to $NaClO_4$ before precipitation occurred. Likewise, addition of even a trace amount of the crown ether to $NaBPh_4$ led to precipitation. The latter occurrence is unfortunate, since it prevents us from comparing our data in *i*PrOH with those obtained by Popov et al. for $NaBPh_4$ in THF, where slow exchange was observed.[11] For the other salts, we determined ^{23}Na chemical shifts and T_1 values as before. These data are collected in Table 2; relaxation rates are plotted vs. the [18C6]/[NaY] ratio in Figure 4. We also measured the chemical shift of a 0.1 M NaSCN solution containing one equivalent of 1,2-dimethoxyethane (δ = 1.9).

Table 2. ^{23}Na chemical shifts and relaxation times of sodium salts (0.1 M in 2-propanol) in the presence of 18-crown-6

[18C6]/[Na]	δ[a]	T_1[b]
MeSNa		
0.1	2.2	1.3
0.5	−5.8	1.1
1.0	−12.4	1.0
2.0	−12.6	1.1
***i*PrSNa**		
0.1	2.1	1.0
0.5	−5.8	0.9
1.0	−12.5	1.0
2.0	−12.6	1.0
***t*BuSNa**		
0.1	2.7	1.0
0.5	−6.1	0.8
1.0	−12.4	1.0
2.0	−12.6	1.1
***i*PrONa**		
0.1	2.1	1.0
0.5	−10.8	0.9
1.0	−12.7	1.0
2.0	−12.8	1.1
$NaClO_4$[c]		
0.1	−12.9	1.3
NaSCN		
0.1	−0.4	1.9
0.5	−4.7	1.5
1.0	−12.4	1.1
2.0	−12.4	1.1

[a] Chemical shifts in ppm relative to external 1 M aqueous NaCl. − [b] T_1 values in ms. − [c] < 0.01 equiv.

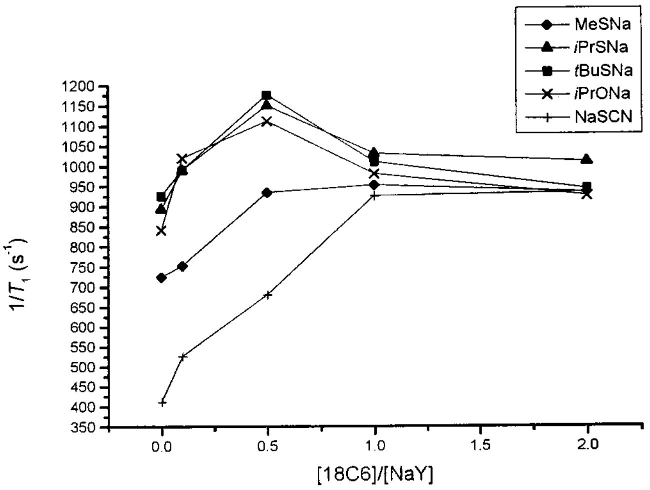

Figure 4. ^{23}Na relaxation rates ($1/T_1$) of sodium salts (0.1 M in 2-propanol) in the presence of 18-crown-6

Discussion

Chemical Shifts

The ^{23}Na chemical shift of all salts tends to a common value ($\delta \approx 2$) at infinite dilution in *i*PrOH (see Figure 1). For thiol anions and 2-propoxide salts, the ^{23}Na nucleus is deshielded with increasing concentration and the chemical shift reaches a plateau value (δ = 3.6−3.8). The gradient is steeper for *t*BuS$^-$ than for MeS$^-$, i.e. at any given concentration (within the observed range) the deviation from the infinite-dilution shift is larger with *t*BuS$^-$ than with MeS$^-$ as the counterion. The chemical shift of $NaClO_4$ shows a similar shielding, whereas those of NaSCN and $NaBPh_4$ remain constant to within 0.3 ppm throughout the accessible concentration range.

It is beyond the scope of this work to analyze the detailed effect of the counterion on the sodium shielding, specifically the reasons why it can act in both directions (cf. *i*PrONa and $NaClO_4$). However, the trend observed with ClO_4^-, SCN$^-$, and Ph_4B^- clearly indicates that the interactions of Na$^+$ with these charge-delocalized anions are very different from those with the simpler "monodentate", charge-localized thiolate and alkoxide anions.

Relaxation Rates

As with the chemical shifts, at the lowest concentration investigated all the salts exhibit a similar ^{23}Na T_1 value (1.6−2.0 ms). For all the anions except ClO_4^- and SCN^-, a decrease in T_1 is observed with increasing salt concentration. This behavior is partly due to the increase in viscosity on going from 10^{-3} to 0.1 M (generally 10%; 20% in the case of $NaBPh_4$). However, when the changes in T_1 are corrected for the effects of viscosity (Figure 3), the decrease in this parameter noted above for thiolates and *i*PrO$^-$ is still apparent (increase in $1/\eta T_1$), as could be anticipated considering the small viscosity changes in these solutions. The contrasting behavior of $NaBPh_4$ and NaSCN (for which T_1 increases with increasing salt concentration) also remains apparent. Since the effect of viscosity on the correlation time has been compensated for, any residual change should be due to a larger volume of the tumbling unit, i.e. association with the counterion. Hence, the measurement of T_1 values provides a qualitative assessment of the increasing extent of ion pairing upon increasing the salt concentration (for alkoxides and thiolates). The constant or decreasing relaxation rates for $NaBPh_4$ and NaSCN may be ascribed to different efg's at sodium induced by the solvent and counterions, the latter being very different in nature (a very bulky and a small, linear anion). Clearly, further experimental evidence is needed to test this hypothesis.

Although the extent of ion pairing is normally evaluated from the variation of chemical shift with concentration, we chose instead to employ T_1 relaxation data, which provide more information on the factors that affect ion-pair formation. The relative degrees of ion pairing for MeSNa and *t*BuSNa could be qualitatively estimated as follows. At every salt concentration studied, the values of $1/T_1$ and $1/\eta T_1$ for MeSNa were invariably lower than for *t*BuSNa, the ratio of the latter parameters being consistently ca. 0.8 (Table 1). As implied by Equation (1), an increase in $1/T_1$ may be due to an increase in efg, e.g. due to a lower symmetry about Na$^+$, or to an increased correlation time (slower motion). When comparing similar counterions such as MeS$^-$ and *t*BuS$^-$, efg changes are probably only very small, since the efg decreases as $1/r^3$ with increasing distance from the Na nucleus and only the effect of the close sulfur atom can be felt. Hence, we expect the value of $1/\eta T_1$ to be essentially due to the different hydrodynamic volumes of the species carrying the sodium ion. From this standpoint, the faster relaxation of *t*BuSNa might be considered as being simply due to the greater molecular weight (M) of the counterion, since $V_m \propto M$,[9] without necessarily implying a different degree of ion pairing. However, such a possibility is ruled out by consideration of the following simplified model. If we assume that the sodium ion is exchanging between two sites, i.e. an ion pair and a solvated Na$^+$(*i*PrOH)$_n$ ion, we may visualize the ion pair as resulting from the replacement of a solvent molecule by a counterion in the solvation shell, i.e. [Na$^+$(*i*PrOH)$_{n-1}$(RS$^-$)]. If this is the case, it can easily be seen that when R = Me, ion pairing actually causes a *decrease* in V_m, whereas with R = *t*Bu V_m is *increased*. Of course, such changes will take place, and will be reflected in the experimentally measured T_1 according to the extent to which ion pairing actually occurs.[12] Detailed consideration of individual relaxation rates based on Equation (1), assuming that nuclear quadrupolar coupling constants change to the same extent (or not at all) for the two systems (see above), leads to the expression designated as Equation (2).

$$\frac{\left(\frac{1}{\eta T_1}\right)_{\mathrm{Me}}}{\left(\frac{1}{\eta T_1}\right)_{t\mathrm{Bu}}} = \frac{V_m^0 + k(M_{\mathrm{MeS}} - M_{\mathrm{S}})x_{\mathrm{IP}}^{\mathrm{Me}}}{V_m^0 + k(M_{t\mathrm{BuS}} - M_{\mathrm{S}})x_{\mathrm{IP}}^{t-\mathrm{Bu}}} \qquad (2)$$

Here, V_{m}^0 is the hydrodynamic volume of the solvated sodium ion, M_{i} denotes molecular weights (S = solvent, *i*PrOH), x_{IP} denotes ion-pair mol fractions, and k is a proportionality constant between V_{m} and M. Since $M_{\mathrm{MeS}} - M_{\mathrm{S}} < 0$, whereas $M_{t\mathrm{BuS}} - M_{\mathrm{S}} > 0$, $x_{\mathrm{IP}}^{\mathrm{tBu}}$ must be larger than $x_{\mathrm{IP}}^{\mathrm{Me}}$ for the left-hand side of Equation (2) to be < 1 as is found experimentally.

Thus, trends in T_1 for MeSNa and *t*BuSNa again indicate a greater degree of association of the latter, in accordance with the conclusions drawn from the chemical shift data described above, and with the previous interpretation on the basis of reactivity data.[6]

Effect of Crown Ether

The change in chemical shift caused by addition of the crown ether can be used to monitor the complexation reaction. Addition of the crown ether results in a progressive shielding until a constant value of $\delta = -12.6$ is reached when one equivalent of the crown has been added,[11] irrespective of the counterion. This is consistent with the formation of a stable complex (since no constant shift would be attained otherwise[10e]) and with the large complexation constant for binding of Na$^+$ by 18-crown-6 ($K = 2\cdot10^4$ L mol^{-1} in methanol).[12] The lack of any further change when [18C6]/[NaY] > 1 also indicates that no larger complexes are formed.

Such effects are quite different from those exerted by 1,2-dimethoxyethane (DME), which is chemically similar to crown ethers but is unable to form specific complexes. In fact, the ^{23}Na chemical shift in the presence of DME is rather similar to that in pure 2-propanol, whereas the addition of just 0.1 equivalents of 18C6 brings the chemical shift to $\delta = -0.4$. Hence, the observed shielding is clearly due to a specific ion−crown interaction rather than a mere solvent effect.

The addition of the crown ether also results in a decrease in the relaxation times, which again reach an essentially constant value of 1.1 ms at [18C6]/[NaY] = 1. However, such a decrease is only apparent for NaSCN, whereas changes in T_1 are much smaller for the other salts. The decrease in T_1 stems from two main factors, i.e. the increase in the efg at sodium (due to the lower symmetry in the complex) and the increase in correlation time as Na$^+$ becomes bound to a large molecule. For some salts (*i*PrSNa, *t*BuSNa, *i*PrONa, and to a small extent for MeSNa), $1/T_1$ exhibits a shallow maximum at [18C6]/[NaY] = 0.5. Similar behavior has previously been reported for $NaBPh_4$ in nitromethane,[10e] where a minimum in the line width was detected at [15C5]/[$NaBPh_4$] = 1. This was ascribed to the formation of a 2:1 $Na(15C5)_2^+$ sandwich-type complex, in which the electric field gradient was smaller by virtue of the higher symmetry, and hence led to a slower relaxation rate (narrower line width). However, in such cases the stepwise complexation was also reflected in the chemical shifts, which also exhibited a minimum at the same crown/sodium ratio. Since no evidence was found to suggest that larger complexes are formed in our system (see above), the slight anomaly in relaxation rates may be due to an exchange process between solvent/counterion and the crown ether, or possibly due to the formation of 2:1 complexes to which ^{23}Na chemical shifts happen to be insensitive.

Conclusions

Since ^{23}Na chemical shifts and relaxation rates depend on the solvation of the ^{23}Na nucleus, both quantities are reliable probes for cation−anion interactions in solutions of NaY salts in solvents of low ionizing power such as 2-propanol. The results show that solvation of Na^+ in 2-propanol is largely dependent on the type of counterion and its concentration. Specifically, a remote substituent effect can be appreciated in the case of thiol anions RS^-, among which binding to Na^+ is greater for R = *t*Bu than for R = Me. A greater charge density on the heteroatom can reasonably be expected in the former anion, due to the inductive effect of the *tert*-butyl group, thus leading to a stronger interaction with the counterion.[6]

Experimental Section

Reagent-grade 2-propanol was fractionally distilled from Mg turnings and stored over molecular sieves under argon. Solutions of *i*PrONa were prepared by reaction of Na with 2-propanol under argon. Their concentrations were determined by titration with standardized HCl solutions. All other NaY compounds were commercial samples of reagent-grade purity and were used as received. 18-Crown-6 (Fluka) was vacuum-dried prior to use.

^{23}Na-NMR spectra were recorded unlocked at 298 K with a Bruker AM 400 instrument operating at 9.4 T (105.84 MHz for ^{23}Na) using a 5-mm broad-band probe. Typically, a 4-kHz spectral window was digitized in 256 data points and the $\pi/2$ pulse was ca. 9 μs. Chemical shifts are quoted relative to 1 M aqueous NaCl as an external reference. Relaxation times were determined using the inversion-recovery sequence, employing 12 delay values between 0.01 and 7 ms and a relaxation delay of 10 ms. Viscosities were determined with an Ubbelohde viscosimeter at 298 K.

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