Sodium-23 Nuclear Magnetic Resonance on Sodium Borate Solutions. Anion, Solvent, and Viscosity Effects[1]

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Abstract: Densities and viscosities are reported for the polyethers $CH_3\{OCH_2CH_2\}_nOCH_3$, with $n = 3$ and $n = 4$, and are compared with literature data for the lower analogs with $n = 1$ and 2. The data indicate an increase in solvent structure with increasing chain length of the ether molecules and with decreasing temperature. Shift and line widths in the ^{23}Na nmr spectra of ether solutions of $NaBH_4$ and $NaBPh_4$ are given as a function of temperature. The influence of anion, temperature, and solvent on the shift is discussed. The line width often appears to be a linear function of the viscosity of the pure solvent divided by the absolute temperature.

In the past decade the structure of ion pairs in solution has been successfully studied by conductivity experiments and electron spin resonance (esr) and ultraviolet spectroscopy to which recently have been added infrared and nuclear magnetic resonance (nmr) spectroscopy. Regarding ion pair structure the latter technique has been mainly concerned with proton nmr on solutions of diamagnetic[3,4] and paramagnetic salts,[5] while also a few alkali nmr studies of diamagnetic salts have been reported.[6,7] In recent years, however, also the alkali nmr spectra of *paramagnetic* radical ion pairs have proven to give valuable information about ion pair structure.[8-10] Since in the latter spectra shifts and line widths are not only governed by the mechanisms which are normally operative in diamagnetic compounds, but in addition by the paramagnetism of an unpaired electron, it is of interest to establish how shifts and line widths in solutions of diamagnetic salts can vary with anion, temperature, and solvent in order to obtain a clearer view of the effect of the electronic paramagnetism on the alkali nmr spectra of radical ion pairs. We therefore undertook a study of the ^{23}Na nmr spectra of solutions of sodium tetrahydroborate ($NaBH_4$) and sodium tetraphenylborate ($NaBPh_4$) in the ethers tetrahydrofuran (THF), dimethoxyethane (DME), diglyme (Dg), triglyme (Tg), and tetraglyme (Ttg). The latter four compounds have the formula $CH_3(OCH_2CH_2)_nOCH_3$ in which n ranges from 1 to 4, respectively. In addition a solution of $NaBPh_4$ in 2-methyltetrahydrofuran (MTHF) was studied. Study of a corresponding $NaBH_4$ solution was prohibited because of the limited solubility of this salt in MTHF.

The choice of salts and solvents was motivated by the fact that much is known about their properties. The solvating power of the above-mentioned ethers is known to increase in the order MTHF < THF < DME < Dg < Tg < Ttg.[11,12] Especially Tg and Ttg are known to be strongly chelating agents for Na ions.[12] Further, the behavior of $NaBPh_4$ in solution is known from conductivity experiments. For instance in ether solutions and at high concentrations (0.1–1.0 M) $NaBPH_4$ is nearly completely present in the form of ion pairs and dissociation and triple ion formation are negligible.[4] Furthermore, it is known that in the above-mentioned ethers an equilibrium between contact and solvent separated ion pairs of $NaBPh_4$ exists which shifts toward the solvent separated ion pairs as the temperature is lowered or the solvating power of the solvent is increased. For instance, the temperature at which there are equal amounts of both types of ion pair present changes from $T = -18°$ in MTHF to $T > 40°$ in THF.[13]

Apart from the variation of the shift, the variation of the line width with temperature is of interest. If the structure of the ion pair does not vary with temperature, standard theories predict the line width to be proportional to the viscosity η of the solution divided by the absolute temperature T.[14] It has been argued[9] that replacing η by the viscosity η_0 of the pure solvent would not significantly change this proportionality. This can be seen as follows. The relation between η and η_0 for a given concentration c of electrolyte is given by the Jones-Dole equation[15]

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc$$

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(1) Supported in part by a grant from the UNC Materials Research Center (Contract DAHC15 67 C 0223 with the Advanced Research Projects Agency).

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which has been applied successfully to aqueous electrolyte solutions,[15] to nonaqueous solutions of completely or partly dissociated salts,[16–22] and to nonaqueous solutions of completely associated salts.[23] The equation is usually assumed to be valid up to concentrations of 0.1 M but often appears to be applicable up to concentrations of 0.5 M and higher,[17–19,21,23] while also in some cases the same equation has been used with different values for the coefficients for different concentration regions.[20] Other equations have been proposed for the high concentration range which were obtained from the Jones–Dole equation by adding a term Dc^2 [18,21,24] or $Dc \log c$.[20,25] Still other equations are based on a power expansion in the concentration[18] or on a purely logarithmic dependence of η/η_0 on C.[15] For the Jones–Dole or extended Jones–Dole equations the deviation of η/η_0 from 1 often appears to be determined almost completely by the Bc term.[15,18,20,21,24] Thus, if B varies only slightly with temperature, as has been observed for a large number of nonaqueous electrolyte solutions,[16,17,21–23] η will be proportional to η_0 over a wide range of temperatures and so will the line width. Since the ion pair structures of $NaBH_4$ and $NaBPh_4$ in, for instance, Tg and Ttg most probably do not vary appreciably with temperature, it was of interest to check whether the Na nmr line widths of these solutions would be proportional to η_0/T indeed. To this purpose the density and viscosity of Tg and Ttg were determined.

The results of the density and viscosity measurements are compared with similar data from the literature for DME and Dg and are briefly commented on in Results and Discussion. This section also contains the results and discussion of the nmr experiments. Experimental details follow.

Experimental Section

Densities. Densities of Tg and Ttg were determined about every 10° from −35 to 90° with ordinary stem pycnometers which were calibrated with mercury. The density of mercury was taken from ref 26. The cubic expansion coefficient of the glass of the pycnometer was determined as $((2.3 \pm 0.1) \times 10^{-5})/°C$. In all weighings apparent mass was reduced to true mass.[27]

Viscosities. Viscosities of Tg and Ttg were determined every 10° from −25 to +105° with Ubbelohde viscometers.[28] The viscometers were calibrated by measuring the flow time t of a calibration liquid at a series of temperatures and fitting the data to an equation of the type[15]

$$\eta/dt = C_1 + C_2/t^2$$

in which η and d are the viscosity and density of the liquid, respectively, and C_1 and C_2 are the constants to be determined. Distilled water and 40 and 80 wt % solutions of glycerol in water were used as calibration liquids. Exact compositions of the latter two mixtures were determined from their densities at 20°. Densities and viscosities of the calibration liquids at the temperatures used for the calibration were determined by interpolation from literature tables (water, ref 15, glycerol–water, ref 29, 30). Viscometers were filled by pouring the liquids over a paper filter and a subsequent sintered glass filter. The latter proved necessary to obtain reproducible data. Tt and Ttg were dried during a few days on the vacuum line over a Na mirror and transferred to storage bulbs by distillation. Measurements of the viscosities of Tg and Ttg were performed under dry nitrogen. Measurements of the flow time, which could be read with an accuracy of ±0.1 sec, were repeated three times at each temperature.

Nmr Shifts. ^{23}Na nmr experiments were performed on a Varian DP60 spectrometer operating in the HR mode and equipped with a V4210 transmitter stabilized at 15.1 MHz with a home-built crystal stabilizer. Shifts were measured with respect to a 1 M $NaCl-H_2O$ solution of which the resonance signal was determined at room temperature several times during a run by exchanging sample and reference. The estimated accuracy of the shift measurements is ±0.5 ppm. Differences in volume susceptibilities of reference and sample were assumed to be negligibly small.

Nmr Line Widths. Values for the line width T_2^{-1} were calculated, on the assumption of a Lorentzian line shape, from the measured derivative peak–peak width ΔH by $T_2^{-1} = {}^1/_2\sqrt{3}\gamma_N\Delta H$ in which γ_N is the gyromagnetic ratio of the ^{23}Na nucleus. A computer program based on the theory of Howarth and Richards,[31] Howarth's tables,[32] and the theory of Wahlquist[33] was used to correct for finite modulation frequency and amplitude. The estimated accuracy of the line width measurements is ±10%.

Temperature. During the density and viscosity measurements the temperature was kept constant within ±0.05°. The temperature was measured to the same precision with a copper–constantan thermocouple which had been calibrated against a primary standard at the Technical University Delft and which was provided with an electronic zero point compensation. In the nmr experiments the temperature was kept constant within ±1° and measured to about the same precision with a copper–constantan thermocouple.

Samples. $NaBPh_4$ (Merck p.a.) and $NaBH_4$ (Fluka, purum) were taken from stock and used after recrystallization. Drying of the solvents and preparation of the samples on the vacuum line were performed as described elsewhere.[34] Samples were between 0.1 and 0.5 M in concentration and care was taken that no saturation occurred in the solution. As sample tubes 10-mm o.d. Wilmad tubes were used.

Calculations. All calculations were performed on the Raytheon 706 computer of the Chemistry Department of the University of North Carolina at Chapel Hill. All interpolations were performed by the Aitken-Lagrange method.[35,36] Smoothing of the viscosity data was performed by the least-squares Chebyshev polynomial method[36–38] and smoothing of the chemical shift *vs.* temperature data was performed by a three point first degree polynomial smoothing procedure.[36] Use was made of the appropriate subroutines of the IBM Scientific Subroutine Package. For least-squares linear regression analyses standard theory was employed.[39]

Results and Discussion

Densities. It appeared that over the investigated range of temperatures the densities of Tg and Ttg could be well fitted to an equation of the type

$$d(T) = a_0 + a_1(T - T_0)$$

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Table I. Values for the Constants in the Equation of the Density as a Function of Temperature for DME, Dg, Tg, and Ttg[a]

	a_0, g/ml	$a_1 \times 10^4$, g/ml, °C	T_0, °C	Density, g/ml, at 0°	Investigated range of temp, °C	Ref
DME	0.912 ± 0.001	−10.7 ± 0.3	−22.26	0.8876	−78 to +36	*b*
Dg	0.988 ± 0.001	−10.1 ± 0.3	−21.87	0.9657	−78 to +36	*b*
Tg	0.9853 ± 0.0005	−9.5 ± 0.1	20.58	1.0049	−35 to +90	*c*
Ttg	1.0114 ± 0.0004	−9.1 ± 0.1	20.58	1.0302	−35 to +90	*c*

[a] Quoted uncertainties equal to three times the statistical standard deviation. [b] Reference 40. [c] This work.

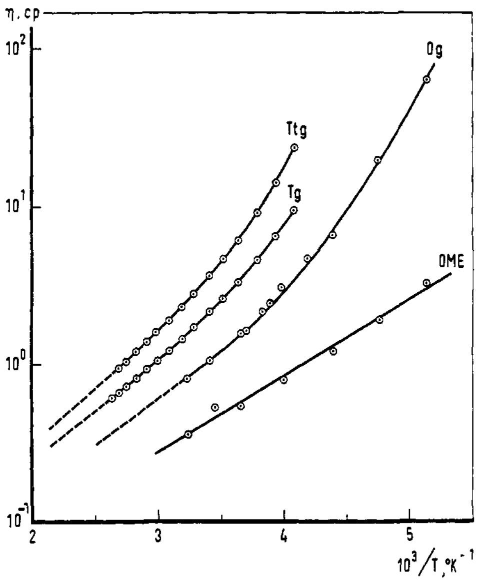

Figure 1. Semilogarithmic plot of the viscosities of DME, Dg, Tg, and Ttg as a function of the inverse absolute temperature. Solid curves represent least-squares polynomial fits of the experimental points. Data for DME and Dg were taken from ref 31 and 32.

in which T is the temperature and a_0, a_1, and T_0 are constants. For comparison a similar analysis was performed on available literature data of DME and Dg.[40] In each analysis T_0 was chosen so as to make the covariance of a_0 and a_1 zero.[39] Values for a_0, a_1, and T_0 are reported in Table I.

The data in Table I show that the density at a given temperature increases and the temperature gradient of the density decreases along the series DME, Dg, Tg, Ttg. This can be considered as evidence for an increasingly closer packing of the molecules in the liquid with increasing chain length of the ether molecules which supports a similar conclusion reached on the basis of the viscosity data (see next paragraph).

Viscosities. Experimental data on the viscosities of Tg and Ttg are presented in Figure 1. For comparison literature data for DME[40] and Dg[41] are also presented. The experimental data for the logarithm of the viscosity of Tg and Ttg were smoothed by approximating them according to a least-squares procedure with a polynomial in $1/T$. The appropriate degree of the polynomial was determined by testing for loss of significance of the coefficients in the polynomial expansion on the assumption of a Gaussian distribution of the error in the coefficients.[38] A 99.7% confidence interval was used for this analysis. A similar analysis was performed on the above-mentioned literature data for the viscosities of DME and Dg. It turned out that for DME, Dg, Tg, and Ttg ln η could very well be presented by a first, a second, a third, and a fourth degree polynomial in $1/T$, respectively. (The linear dependence of the logarithm of the viscosity of DME on $1/T$ has been noted earlier.[42]) A selection of smoothed data is given in Table II and smoothed plots have been drawn in Figure 1. The least-squares fit to the viscosity data of DME is given by $\ln \eta = (1.10 \pm 0.15)(10^3/T - 4.089)$ in which η and T are given in cP and °K, respectively.

Table II. Smoothed Values of the Viscosities of Dg, Tg, and Ttg at a Series of Temperatures

	η, cP		
T, °C	Dg[a]	Tg[b]	Ttg[b]
−80	72		
−75	47		
−70	31.4		
−65	21.9		
−60	15.8		
−55	11.7		
−50	8.9		
−45	6.9		
−40	5.5		
−35	4.47		
−30	3.69		
−25	3.09	8.18	19.12
−20	2.63	6.71	14.75
−15	2.26	5.59	11.68
−10	1.97	4.73	9.46
−5	1.74	4.05	7.81
0	1.55	3.51	6.55
10	1.39	3.07	5.57
15	1.26	2.71	4.80
20	1.14	2.41	4.18
25	1.06	2.16	3.67
30	0.978	1.953	3.25
35	0.911	1.773	2.90
40	0.853	1.618	2.60
45	0.803	1.483	2.35
50		1.365	2.14
55		1.262	1.949
60		1.171	1.787
65		1.089	1.645
70		1.017	1.521
75		0.951	1.411
80		0.893	1.313
85		0.839	1.226
90		0.790	1.148
95		0.746	1.079
100		0.705	1.016
105		0.668	0.959
		0.634	0.908

[a] Estimated accuracy ±1%. [b] Estimated accuracy ±0.5%.

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According to Eyring[43] the viscosity of a liquid obeys the equation

$$\eta = \frac{hN}{V} \exp \Delta G^{\ddagger}/RT = \frac{hN}{V} \exp (\Delta H^{\ddagger}/RT - \Delta S^{\ddagger}/R)$$

in which h is Planck's constant, N is Avogadro's number, V is the molar volume of the liquid, R is the gas constant, T is the absolute temperature, and $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are the free enthalpy, the enthalpy, and the entropy of activation for viscous flow, respectively. If $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are independent of temperature ln η becomes a linear function of $1/T$. This behavior is observed for DME. As Figure 1 shows, however, the plot of ln η *vs.* $1/T$ is nonlinear for the higher analogs of DME. Nonlinear behavior like this has been observed for other liquids composed of chainlike molecules and is usually considered as being caused by an increase in $\Delta H^{\ddagger}$ with decreasing temperature.[43,44] This in turn is caused by an increase in the structure of the liquid.[43,44] Figure 1 shows that the slope in the plots of ln η *vs.* $1/T$ increases at a given value of $1/T$ along the series DME, Dg, Tg, and Ttg, while for a given compound the slope also increases with an increase in $1/T$. We conclude, therefore, that toward lower temperatures the rotational and conformational mobility in the liquid phase of the molecules of polyethers of the formula $CH_3(OCH_2CH_2)_nOCH_3$ becomes progressively restricted due to an increase in the structure of the liquid and that this effect becomes more pronounced with increasing n.

Shifts. The shifts of the ^{23}Na nmr signals for the $NaBPh_4$ and the $NaBH_4$ solutions are presented in Figure 2 as a function of the temperature. The experimental findings can best be explained by looking at the results for the solutions in DME through Ttg first. From Figure 2(c)–(f) the following observations can be made. (i) The Na nmr signals from the $NaBPh_4$ solutions appear 6–8 ppm upfield from the signals of the corresponding $NaBPh_4$ solutions. (ii) In Tg and Ttg the Na resonance is shifted 2–4 ppm upfield for both salts compared with the corresponding solutions in DME and Dg. (iii) In a given solvent the temperature dependence of the shift is the same for both salts except for the Ttg solution where the scatter in the experimental points for the $NaBPh_4$ salt does not allow a definite conclusion.

The first observation points to the influence of the anion on the shift. The position of the Na resonance depends primarily on the structure of the first solvation shell of the cation, and since $NaBPh_4$ forms solvent separated ion pairs in DME through Ttg, the influence of the anion can be explained if we assume that $NaBH_4$ forms contact ion pairs in these solvents. This assumption is not unreasonable in view of the small radius of 1.1 Å of the BH_4^- ion[45] and the resulting large increase in the absolute value of the Coulomb energy which will occur upon formation of a contact ion pair. The second and third observations, however, demonstrate the influence of the solvent on the shift. Apparently the solvent takes part in the solvation of the cation in solutions not only of the $NaBPh_4$ salt but also of the $NaBPh_4$ salt. The following discussion of the influence of anion, temperature, and solvent on the Na nmr shift will therefore be based on the assumption that in the solvents used in this study $NaBH_4$ forms contact ion pairs in which the Na ion is peripherally solvated by solvent molecules.[48]

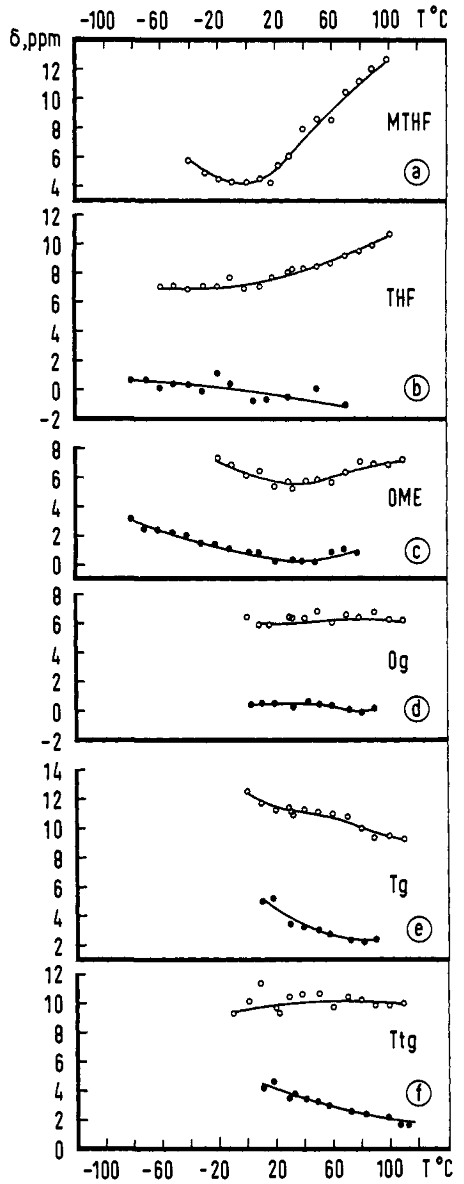

Figure 2. Shift of the ^{23}Na nmr signals from ether solutions of $NaBH_4$ (●) and $NaBPh_4$ (○) *vs.* temperature. A room temperature 1 *M* NaCl–H_2O solution was used as a reference. A positive sign indicates an upfield shift. Solutions are in (a) MTHF, (b) THF, (c) DME, (d) Dg, (e) Tg, and (f) Ttg.

a. Influence of the Anion. In our case the influence of the anion on the resonance of the cation may originate from the presence of ring currents in the anion, the electrostatic dipole polarization of the metal

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[45] This value is calculated from the covalent radii of boron (0.81 Å) and hydrogen (0.30 Å).[46] The charge on the anion may increase the bond length slightly.[47] Compare also with the B–H distance of 1.21 Å for the nonbridging H atoms in $Al(BH_4)_3$.[46]

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core electrons by the anion, and orbital overlap between the cation and atoms in its first solvation shell.

Ring currents are present in the BPh_4^- ion. To obtain an upper limit for their effect on the Na resonance position we assume that the Na ion is right above the center of one of the phenyl rings at the shortest distance possible, which in a solvent separated ion pair will be of the order of 5 Å.[49] At this distance the ring current produces a diamagnetic (upfield) shift of 0.5 ppm.[50] Even if the conformation of the phenyl rings in the anion would be such that the ring currents of three rings would cooperate, the resultant shift would be smaller than 1.5 ppm, which, although of the right sign, is too small to explain the observed difference in shift between the $NaBPh_4$ and the $NaBH_4$ solutions.

Halliday, *et al.*,[51] have shown that in solutions of the Na halides electrostatic dipole polarization effects may become important for small anions. In the $NaBPh_4$ solutions the effect can be assumed to be negligible because of the large separation between cation and anion in the ion pair. However, in the $NaBH_4$ ion pairs the BH_4^- ion presumably is in contact with the Na^+ ion. Since the radius of the BH_4^- ion is even smaller than that of the F^- ion (1.1 Å compared with 1.36 Å[46]) polarization of the Na core electrons in the $NaBH_4$ ion pairs might in part be responsible for the observed downfield shift of the Na resonance of the $NaBH_4$ solutions compared with $NaBPh_4$ solutions.

In general, however, chemical shift differences for a given cation in solution are determined by the overlap of orbitals of the cation with orbitals of atoms in its first solvation shell.[51,52] In the solvent separated $NaBPh_4$ ion pairs overlap occurs almost exclusively between the Na ion and the oxygen atoms of the ether molecules in its first solvation shell, while in the $NaBH_4$ ion pairs part of the solvent molecules has been replaced by the BH_4^- ion. Apparently, when one or more ether molecules are replaced by the BH_4^- ion the overlap of the Na orbitals with those of the solvation shell increases resulting in a paramagnetic (downfield) shift of the resonance of the $NaBH_4$ solutions. This explanation is consistent with the observation that the Na resonance of a NaI solution in THF is shifted even further downfield than the Na nmr signal of a $NaBH_4$ solution in THF.[6a] That the overlap of a Na^+ ion with a I^- ion is larger than with a BH_4^- ion is understandable in view of the smaller radius and lower symmetry of the latter anion.

We conclude that on the assumption that $NaBPh_4$ and $NaBH_4$ form solvent separated and contact ion pairs, respectively, in the ethers used in our study, the observed differences in the chemical shift of the Na nucleus can be explained by taking into account overlap effects and electrostatic dipole polarization of the core electrons of the Na ion. The relative magnitude of these two effects would have to be established by a detailed calculation.

b. Influence of the Temperature. In the solution of $NaBPh_4$ in MTHF there is a marked influence of the temperature on the Na nmr shift toward high temperatures while a similar though less pronounced effect is observed for the $NaBPh_4$–THF solution (see Figure 2(a) and (b)). In MTHF and THF ion pairs of $NaBPh_4$ change their structure toward high temperatures from solvent separated to contact ion pairs. The effect of the temperature on the shift is therefore probably caused by a change in the structure of the ion pairs. Apparently replacement of solvent molecules by BPh_4^- ions in the first solvation shell of the cation decreases the orbital overlap of the Na ion with its first solvation shell. This may have to do with the fact that the rings in the BPh_4^- ion are π-electron systems.[52] Also the ring currects may contribute to the upfield shift of the Na resonance when the distance between Na ion and BPh_4^- ion becomes small.[50]

A positive slope of the shift *vs.* temperature plots is observed also for the DME solutions toward high temperatures (see Figure 2(c)) and might point to a decrease in orbital overlap between the Na ion and the oxygen atoms of the solvent. The decrease in overlap may be caused for instance by a change in the configuration of the solvent molecules around the cation due to increased thermal movement. However, at low temperatures often a part with a negative slope is observed in the shift *vs.* temperature plots. It is possible that at low temperatures a new mechanism like ion cluster formation comes into play which counterbalances the effect of increased orbital overlap of cation and solvent. However, a detailed explanation must await further experiments.

c. Influence of the Solvent. Regarding the influence of the solvent on the position of the Na signal it is striking that there appears to be no marked difference in the shift of a given salt along the series of solvents MTHF, THF, DME, and Dg, although the increasing solvating strength of these solvents in this order is expected to cause an increasing downfield shift of the Na nmr signal.[6a,52] For both $NaBPh_4$ and $NaBH_4$, however, there is a clear change in the magnitude of the shift of about 2–4 ppm at the transition from these solvents to Tg and Ttg. Although it is known that Tg and Ttg molecules interact strongly with Na ions, as pointed out in the introduction, and a change in shift is therefore not surprising, the change is in the wrong direction since, as the experimental evidence in Figure 2 shows, chelation with the strongly solvating Tg or Ttg molecules causes an upfield shift of the Na resonance instead of a downfield one.

Line Widths. The Na line widths measured in solutions of $NaBH_4$ and $NaBPh_4$ in Tg and in Ttg are presented in the Figure 3a and b as functions of η_0/T in which η_0 is the viscosity of the pure solvent. Plots obtained for solutions in Dg and DME resembled the plots of Figure 3b. Line width measurements on solutions in THF and MTHF could not be made because of inaccuracies due to field inhomogeneity, overmodulation, and saturation broadening.

Figure 3b shows that the line width is a linear function of η_0/T which seems to justify the replacement of the viscosity of the solutions by that of the pure solvent according to the reasoning put forward in the introduction. The method should be used with care, however, since, as Figure 3a shows, in some cases a certain amount of curvature in the plot may become apparent

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(49) This value is the sum of the distance of the Na nucleus to the plane of an aromatic anion in a contact ion pair (2.0–2.5 Å)[9] and twice the van der Waals radius of oxygen (2.8 Å).[46]

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especially when the variation of the line width over a large region of temperature is considered.[53] The curvature may be caused by a negative temperature coefficient of the B coefficient in the Jones–Dole equation or cluster ion formation at low temperatures. However, at the moment a detailed explanation is lacking.

Some of the plots in Figure 3 have a nonzero intercept. This has been observed for other electrolyte solutions[54] and is probably not due to the replacement of η by η_0.

Conclusion

Numerical analysis of the viscosity data of the polyethers $CH_3(OCH_2CH_2)_nOCH_3$ with $n = 1, 2, 3$, and 4 showed that the logarithm of the viscosity can be presented to a high degree of precision by a polynomial of degree n in $1/T$. This observation can be qualitatively understood in terms of an increase in structure of the liquid as the chain length of the polyether molecules increases and the temperature decreases.

The analysis of the Na nmr shift as a function of the temperature for ether solutions of $NaBPh_4$ and $NaBH_4$ has demonstrated that the transition from solvent separated to contact ion pairs and the nature of the anion can have a pronounced effect on the position of the alkali nmr signal. It is of interest to note that the observed effects are of the correct sign and of the right order of magnitude to explain the difference between esr and nmr alkali hyperfine coupling constants, which has been observed for a number of alkali radical ion pairs.[10]

For ethers of the type used in this study the influence of the solvent on the position of the alkali resonance signal will usually be small unless there is reason to expect the presence of a specific interaction between solvent and alkali ion as in the case of Na ions and the solvents Tg and Ttg. It is worthwhile to point out that the effect observed in the latter two cases nicely accounts for the anomalies in the temperature behavior of the Na nmr hyperfine splitting constants observed for solutions of sodium biphenyl in Tg and Ttg.[9]

Finally, an analysis of the line width data has indicated that for a semiquantitative analysis the use of the viscosity of the pure solvent instead of the viscosity of the solution itself usually will be allowed.

Acknowledgment. The author thanks Professor E. de Boer for valuable discussions and advice and Professor C. S. Johnson, Jr., for permission to use the computer of the Chemistry Department of the University of North Carolina at Chapel Hill. The experimental assistance of Dr. C. Corvaja, Dr. B. M. P. Hendriks, and Dr. A. A. K. Klaassen is gratefully acknowledged. Dr. O. Howarth kindly supplied correction tables for modulation broadening. Part of this work has been carried out at the University of Nijmegen, under the auspices of the Netherlands Foundation for Chemical Research (S.O.N.), and with the aid of the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

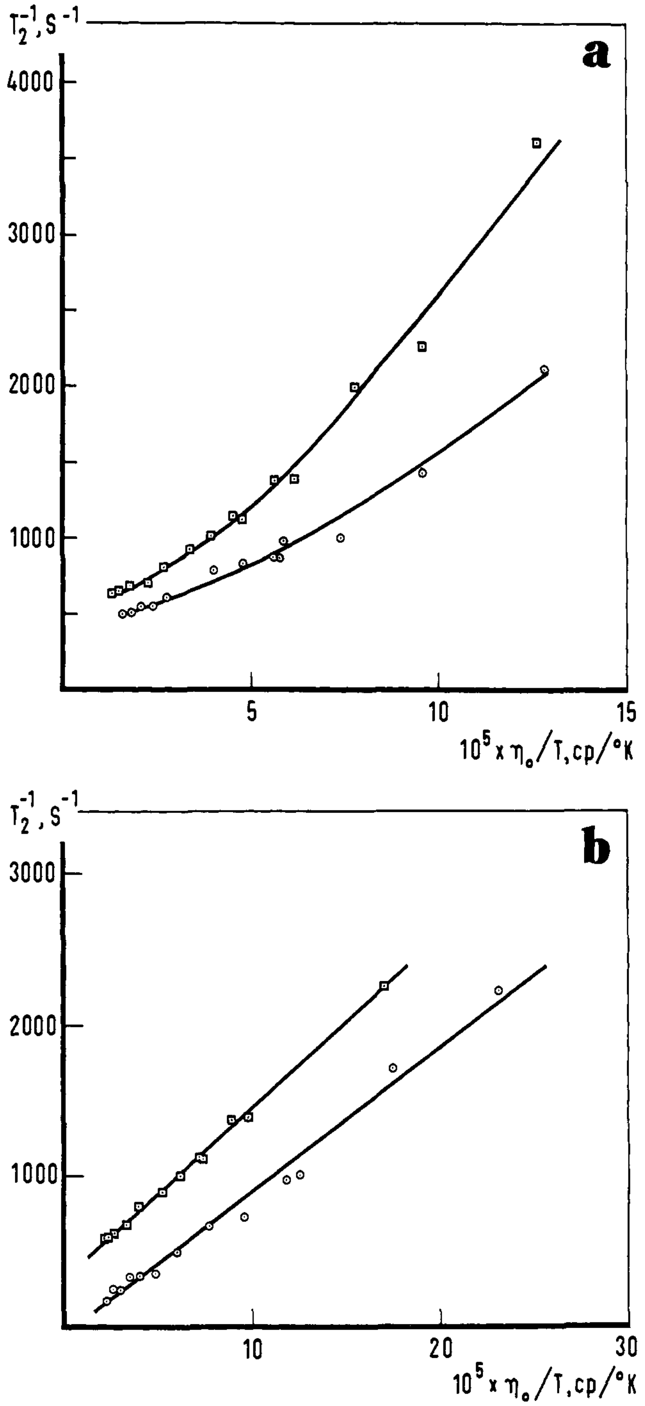

Figure 3. Widths of the ^{23}Na nmr lines from solutions of $NaBH_4$ (▣) and $NaBPh_4$ (⊙) *vs.* the viscosity of the pure solvent divided by the absolute temperature (a) in Tg, (b) in Ttg.

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