Complexation of Lithium, Sodium, and Potassium Carbanion Pairs with Polyglycol Dimethyl Ethers (Glymes). Effect of Chain Length and Temperature

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Abstract: The coordination of fluorenyllithium, -sodium, and -potassium with polyglycol dimethyl ethers (glymes) of the general formula $CH_3O(CH_2CH_2O)_xCH_3$ ($1 \leq x \leq 6$) in dioxane, tetrahydrofuran, or tetrahydropyran as solvent was investigated by means of optical and nmr spectroscopy. The complexation of glyme with the contact ion pairs leads to either glymated contact ion pairs or glyme-separated ion pairs or to a mixture of both, depending on the radius of the cation and the chain length of the glyme. With fluorenylsodium, the glyme-separated ion pairs with glyme-5 ($x = 4$), glyme-6 ($x = 5$), and glyme-7 ($x = 6$) are 1:1 coordination complexes, but with glyme-4 and probably also glyme-3 the separated ion pair contains two glyme molecules. With the potassium salt, glyme-6 and glyme-7 yield essentially glyme-separated 1:1 complexes, but glyme-4 and glyme-5 give mainly glymated contact ion pairs and a second glyme molecule is needed to convert them to the separated ion pairs. The various complexation constants rapidly increase with increasing number of oxygen atoms in the chain, but level off above a certain value of x, depending on the size of the cation. Temperature dependence studies show that the effectiveness of the glymes as coordinating agents of alkali ions is largely due to a small loss in entropy as compared to solvent-separated ion-pair formation in THF.

As reported in a previous communication, polyglycol dimethyl ethers or glymes of the general formula $CH_3O(CH_2CH_2O)_xCH_3$ form 1:1 coordination complexes with lithium and sodium salts of carbanions in low dielectric constant solvents like THF or dioxane.[1] The optical absorption spectra of the glyme complexes of fluorenyl carbanion salts were found to be identical with that of the solvent-separated fluorenyl ion pair, *e.g.*, fluorenylsodium in oxetane or fluorenyllithium in 1,2-dimethoxyethane.[2] By adding different quantities of glyme to fluorenyllithium in dioxane or fluorenylsodium in THF it was possible to measure the equilibrium constant of the reaction

$$F^-,M^+ + G \rightleftarrows F^-,G,M^+ \qquad K_i$$

The contact ion pair F^-,M^+ and the glyme-separated ion pair F^-,G,M^+ have distinctly different absorption maxima, and their fractions can therefore be easily determined. The equilibrium constant K_i represents a quantitative measure of the effectiveness of the glyme molecule to solvate alkali ions.

The present study comprises a more thorough investigation of the coordination of glyme molecules with alkali ions, particularly where it concerns the effect of chain length on the value of the constant K_i. Polyglycol dimethyl ethers with $x = 2$, 3, 4, 5, and 6 were used. We also extended our studies to include the fluorenylpotassium salt, where the coordination with glymes appears to follow a more complex pattern. The glyme may coordinate externally with the contact ion pair, which is in equilibrium with the glyme-separated ion pair. The former species can also react with a second glyme molecule to form the separated ion pair. The conclusions arrived at from measurements of optical spectra were in a number of cases confirmed from data on the nmr spectra of glyme molecules complexed to a fluorenyl carbanion pair. The temperature dependence of the above ion pair equilibrium was also measured in order to obtain the thermodynamic quantities for glyme-separated ion pair formation.

Experimental Section

Purification of the solvents used in this investigation (tetrahydrofuran, tetrahydropyran, and dioxane) has been described elsewhere.[2] The methyl tetrahydrofurfuryl ether was obtained from the Aldrich Co. and purified in the same manner as THF. Mono-, di-, tri-, and tetraglyme were acquired from Eastman Chemical Co., while the hexaglyme was kindly supplied to us by Dr. Ugelstad of the Norges Tekniske Hogskole in Trondheim. The pentaglyme (bp 153–155°, 3 mm) was prepared in 50% yield from 1,2-bis(2-chloroethoxy)ethane and the sodium derivative of ethylene glycol monomethyl ether. The respective glymes were first stirred on sodium–potassium alloy and filtered, and the clear solvent then distilled under high vacuum. In some cases the purification needed repeating until a stable deep blue color was obtained. The solvent was then filtered again under vacuum and distilled (the blue color disappears on heating). This purification removes all the residual water, alcohols, or glycols, as indicated by the fact that a 100-fold excess of the pure glyme added to a fluorenyl carbanion solution does not change the carbanion concentration.

The carbanion salts were all prepared in THF. Although the salt can be made by stirring fluorene in THF on the corresponding metal mirror, this procedure is not preferred since it introduces impurities in the solution through electron transfer reactions.[3] The lithium was obtained in THF from butyllithium and fluorene, and the THF later replaced by dioxane. The sodium and potassium salts were prepared from fluorene and the corresponding salts of the dianion of 1,1-diphenylethylene.[4] This procedure yields a stable fluorenyl salt solution with a well-characterized optical spectrum.

In the actual experiment, a mixture of glyme and a solvent in which the carbanion salt is a contact ion pair was added to the carbanion solution. For fluorenyllithium, dioxane was used as the nonsolvating medium, while THF was used for the sodium and potassium salts, both of which exist as contact ion pairs in THF at 25°. Aliquots of a fluorenyl solution with enough glyme added to form almost 100% glyme-separated ion pairs were added under vacuum through a Teflon stopcock to a solution of the same carbanion salt at about the same concentration but without glyme pres-

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(1) L. L. Chan and J. Smid, *J. Amer. Chem. Soc.*, **89**, 4547 (1967).

(2) (a) T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 308 (1966); (b) L. L. Chan and J. Smid, *ibid.*, **90**, 4654 (1968).

(3) J. J. Eisch and W. C. Kasha, *J. Org. Chem.*, **27**, 3745 (1962); E. G. Janzen and J. L. Gerlock, *J. Organometal. Chem.*, **8**, 354 (1967).

(4) T. Ellingsen and J. Smid, *J. Phys. Chem.*, **73**, 2712 (1969).

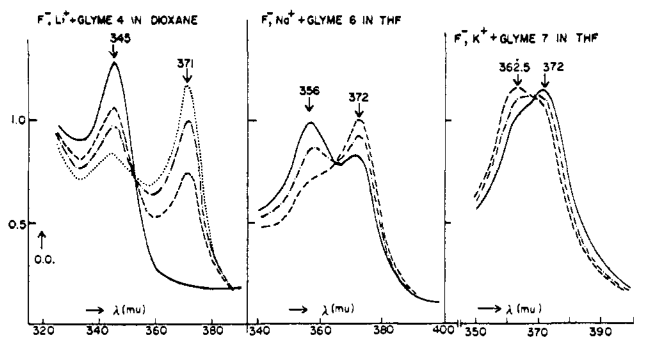

Figure 1. Spectral changes on addition of glyme-4 to F^-,Li^+ ($\approx 1.5 \times 10^{-3}$ *M* in dioxane), of glyme-6 to F^-,Na^+ ($\approx 2 \times 10^{-3}$ *M* in THF), and of glyme-7 to F^-,K^+ (5×10^{-4} *M* in THF): $[\text{glyme-4}]_0 = 0.0$ (—), 6.46×10^{-3} (- - - -), 11.3×10^{-3} (-·-·-), and 24.3×10^{-3} *M* (. . . .); $[\text{glyme-6}]_0 = 1.34 \times 10^{-3}$ (——), 2.64×10^{-3} (-·-·-), and 4.32×10^{-3} *M* (- - -); $[\text{glyme-7}]_0 = 1.02 \times 10^{-3}$ (- - -), 2.78×10^{-3} (-·-·-), and 4.8×10^{-3} *M* (——).

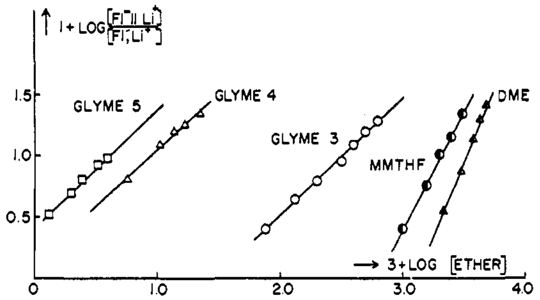

Figure 2. Coordination of 1,2 dimethoxyethane, 2-methoxymethyltetrahydrofuran, and glyme-3, -4, and -5 to fluorenyllithium in dioxane at 25°.

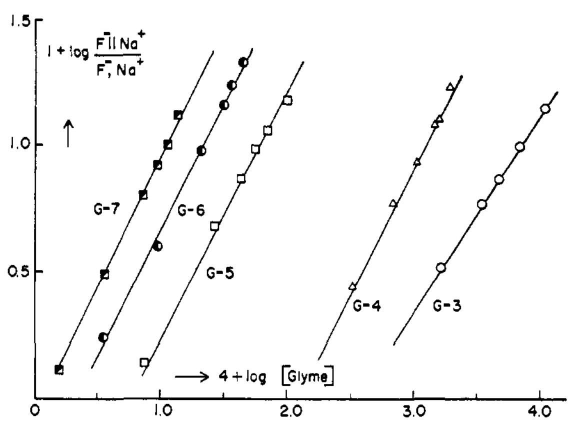

Figure 3. Glyme-separated ion pair formation of fluorenylsodium in THF at 25° with glyme-3, -4, -5, -6, and -7.

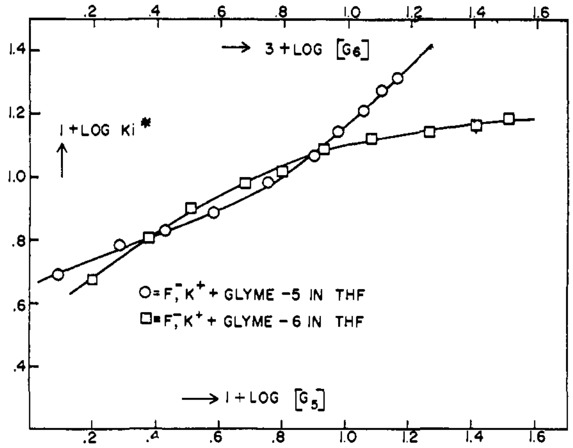

Figure 4. Plots of log K_i *vs.* log [glyme] for F^-,K^+ in THF with glyme-5 (○) and glyme-6 (□).

ent. After each addition, the optical spectrum between 340 and 400 mμ was recorded. The concentration of F^-,Li^+ in dioxane was about 1.5×10^{-3} *M* (limited because of solubility), that of F^-,Na^+ about 2×10^{-3} *M*. In the case of F^-,K^+, concentrations were between 6×10^{-4} and 6×10^{-3} *M*.

The fractions of the two ion pairs can be calculated since the spectra of the "pure" ion pairs are known. For the glyme-separated ion pairs the spectra were recorded in the presence of excess glyme, the λ_{max} in all cases being at 372 mμ. The respective maxima for the contact ion pairs are 347 mμ for F^-,Li^+ in dioxane, 355 mμ for F^-,Na^+ in THF, and 362.5 mμ for F^-,K^+, also in THF.

For enthalpy and entropy measurements, spectra were recorded for F^-,Na^+ in THF between 0 and +50°, adding enough glyme to obtain about equal fractions of the two kinds of ion pairs at 25°. The spectral changes of the pure ion pairs with temperature were also recorded, since these changes must be incorporated in the calculation of the ion pair fractions at different temperatures in the THF-glyme mixtures.[2]

Results and Discussion

Typical examples of spectra of fluorenyl salts in mixtures of glymes with either dioxane or THF are shown in Figure 1 (the number behind each glyme refers to the number of oxygen atoms in the molecule; *e.g.*, glyme-6 is pentaethylene glycol dimethyl ether or pentaglyme). The stoichiometry of the equilibrium between contact and glyme-separated ion pair is indicated by the appearance of an isosbestic point. As described in the Experimental Section, the fraction of the two kinds of ion pairs can be calculated since the pure ion pair spectra are known. It should be stressed that, unlike in the pure solvents, the glyme-separated ion pairs, at least those of F^-,Li^+ and F^-,Na^+ have extinction coefficients which are higher by a factor of 1.2 than those of the contact ion pair. This ratio should be taken into account when calculating the values for the equilibrium constant.

Assuming that the coordination by glyme can be represented by a simple equilibrium

$$F^-,M^+ + nG \rightleftharpoons F^-,G_n,M^+$$

one can find the number of glyme molecules, *n*, involved in the reaction by plotting log K_i^* *vs.* log [G], where K_i^* represents the ratio $[F^-,G_n,M^+]/[F^-,M^+]$. The concentration [G] is of course the free glyme concentration, and is equal to $[G]_0 - n[F^-,G_n,M^+]$. In a number of cases $[G]_0 \gg [F^-,G_n,M^+]$ and therefore $[G]_0 \approx [G]$. Where this is not the case, corrections must be made for the glyme bound in the glyme-separated ion pair.

Plots of log $[F^-,G_n,M^+]/[F^-,M^+]$ *vs.* log [G] are shown in Figures 2, 3, and 4 for the respective fluorenyl salts. It appears that for the lithium and sodium salt the slopes are equal or very close to $n = 1$ for glymes with $x \geqslant 2$, with the possible exception of the system F^-,Na^+-diglyme (glyme-3), where the slope is about 0.85. On the other hand, the plots for F^-,K^+ show considerable curvature. With glyme-5 the slope is less than 0.5 at low glyme concentration, but the curve eventually approaches a slope close to 1 at higher glyme concentrations. The same behavior is found for glyme-4, both in THF and tetrahydropyran (THP). With glyme-6 the initial slope is again substantially less than 1 (about 0.7), and becomes even smaller at higher glyme concentrations. In fact, the ratio of glyme-separated to contact ion pairs appears to approach a maximum value of about 2.0. A similar behavior is observed with F^-,K^+ and glyme-7 in both THF and THP. Eventually, at much higher glyme-6 and glyme-7 concentrations, the K_i^* value increases again and the fraction of contact ion pairs becomes negligibly small.

Let us first consider the results for the lithium and sodium salt. The values for the equilibrium constant K_i are listed in Table I. Unless specified, the value of n was taken to be 1. Some of the previously reported data for F^-,Na^+ differ slightly from those presented here, presumably because in our earlier work the sodium salt was prepared on a sodium mirror. These samples are less reliable because of side reactions.

Table I. Equilibrium Constants for Glyme-Separated Ion Pair Formation of Fluorenyl Alkali Salts at 25°

Glyme (x)	$K_i{}^a = [F^-,G,M^+]/[F^-,M^+][\text{glyme}]$ F^-,Li^{+b}	F^-,Na^{+b}
DME (1)	0.055 (n = 2.4)	*c*
2-(CH_3OCH_2)THF	0.25 (n = 2)	*d*
Glyme-3 (2)	3.1	1.4
Glyme-4 (3)	130	9.0
Glyme-5 (4)	240	170
Glyme-6 (5)		450
Glyme-7 (6)		800

[a] All K_i values were calculated by taking $n = 1$, except for DME ($n = 2.4$) and 2-(methoxymethyl)tetrahydrofuran ($n = 2$). [b] Dioxane was used as solvent for the lithium salt, THF for the sodium salt. [c] No titration carried out. Fraction of solvent-separated ion pairs at 25° is about 0.9 in pure DME. [d] At room temperature only solvent-separated ion pairs in the pure solvent.

The high solvating power of the glyme molecules with respect to cations is a striking example of the importance of cooperative effects in coordination phenomena. This is already apparent in such solvents as 1,2-dimethoxyethane (DME) and 2-(methoxymethyl)-THF, both of which exhibit considerably greater solvating power than THF, in which solvent F^-,Na^+ is a contact ion pair at room temperature and F^-,Li^+ solvent separated for 80%.[2] Since the THF oxygen in 2-(methoxymethyl)-THF is more basic and also more exposed than the O atoms of DME, it is understandable that the former compound is a better solvating agent for alkali ions than the latter at least as measured in terms of solvent-separated ion pair formation. Also, the number of poorly solvating conformations that these two molecules may assume is larger in DME, making it also less favorable as a coordinating agent. For both solvents the number of solvent molecules participating in the equilibrium reaction is two (or possibly somewhat higher for DME).

The observed value of $n = 1$ for glymes with $x \geqslant 2$ suggests that on formation of the glyme-separated ion pair only one glyme molecule becomes coordinated with the Li^+ or Na^+ ion. However, it should be realized that in our experiments one measures the difference in solvation state between glyme-separated and contact ion pair. It is conceivable that the contact ion pair already is coordinated on the outside by a glyme molecule, and that the glyme-separated ion pair may actually contain two glyme molecules

$$F^-,M^+,G + G \rightleftarrows F^-,G,M^+,G$$

The species F^-,M^+,G are expected to have closely similar absorption maxima as F^-,M^+ which is solvated on the outside by the solvent itself (THF or dioxane). In some cases this external solvation was detected by small bathochromic shifts, as in the case of F^-,Li^+ in mixtures of dioxane and hexamethylphosphoramide[2b] or amines.[5] We will show that nmr experiments can shed more light on the stoichiometry of the coordination complexes with glymes. But even without these data one can calculate that in most cases the glyme-separated ion pair represents a 1:1 complex. For the above equilibrium the free $[G] = [G]_0 - [F^-,M^+]_0 - [F^-,G,M^+,G]$, where $[F^-,M^+]_0$ is the total ion pair concentration. When calculating the data in this way, the plots of Figures 2 and 3 would strongly deviate from linearity and lead to inconsistent results. Only when $[G]_0 \gg [F^-,M]_0$ (as for glyme-3 with F^-,Li^+ or F^-,Na^+, or glyme-4 with F^-,Na^+) does the assumption of a glymated contact ion pair not affect the slope of the relevant plots of Figures 2 and 3. All that one can say in these cases is that the equilibrium between the two kinds of ion pairs involves only one glyme molecule. The problem of formation of glymated contact ion pairs will be dealt with in more detail when the results obtained with the potassium salt are discussed.

The values obtained for K_i (see Table I) reveal a strong increase in the complexation constant of the glymes with fluorenyllithium up to glyme-4, followed by only a small increase in the K_i for glyme-5. This probably indicates that not more than four oxygen atoms can coordinate with Li^+ all at the same time, and the fifth oxygen in glyme-5 cannot be utilized because of crowding in the solvation shell. For the sodium salt a similar trend is found, but the strongest increase in K_i is now observed when glyme-4 is replaced by glyme-5. Beyond glyme-5, the K_i value increases only moderately when glyme-6 or glyme-7 is used. The interaction of a Na^+ ion with an oxygen atom of the glyme is expected to be weaker than with the smaller Li^+ ion. In spite of the decreased coulombic interaction, one apparently needs a glyme molecule with at least five oxygen atoms to obtain a high complexation constant for formation of glyme-separated F^-,Na^+ ion pairs (*i.e.*, a value of K_i comparable to that for the system glyme-4 and F^-,Li^+). Because of the larger diameter of the Na^+ as compared to the Li^+ ion, they can apparently all be coordinated to the Na^+ ion at once. We would like to point out that the coordination of glyme or other ethers with alkali ions is not of a purely donor–acceptor type, and there are no compelling reasons to assume, as has been suggested,[6] that the oxygen atoms should be tetrahedrally arranged around the Li^+ and Na^+ ion. For example, some of the strongest coordinating agents for Na^+ ions are the cyclic polyethers which possess a nearly planar polyether ring with six-coordinating oxygen atoms.[7]

That K_i still increases beyond glyme-5 for F^-,Na^+ is to be expected for purely statistical reasons. Using a similar reasoning as given by Ugelstad, *et al.*,[8] if p is the maxium number of glyme oxygen atoms to be coor-

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[5] R. Smyk, M.S. Thesis, State University of New York College of Forestry, 1967.

[6] A. I. Shatenshtein and E. S. Petrov, *Usp. Khim.*, **36**, 269 (1967).

[7] C. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); K. H. Wong, G. Konizer, and J. Smid, *ibid.*, **92**, 666 (1970).

[8] J. Ugelstad and O. A. Rokstad, *Acta Chem. Scand.*, **18**, 474 (1964).

dinated to Na^+ ions, and q the total number of oxygen atoms available in the glyme, then the total number of possible ways, W, to coordinate the glyme with the cation is

$$W = \frac{q!}{p!(q-p)!}$$

For $p = 5$ and $q = 7$ (glyme-7), this would be 21. Of course, it is unlikely that each combination of five oxygen atoms would be equally probable. Shatenshtein[6,9] observed that the solvating power of ethers containing two oxygen atoms in the chain sharply decreases when the two atoms are more than two carbon atoms apart. Hence, it is not unrealistic to assume that only the combinations where coordination sites involve neighboring oxygen atoms are favorable for complex formation. The number of these combinations is given by $W = q - p + 1$; *i.e.*, for glyme-7 and Na^+ ($p = 5$) this will be 3. Hence, if indeed the maxium coordination number were 5 for Na^+ and if the ΔH_i of coordination remains the same, the change from glyme-5 to glyme-6 would change K_i by a factor of 2. The increase is by a factor 3 if glyme-7 is used instead of glyme-5. Experimentally the K_i values increase by factors of 2.5 and 4.5, respectively. Of course, these calculations are only approximate; nevertheless, the above consideration indicates that our K_i values appear to be reasonable.

Glyme-separated ion pair formation does not appear to depend strongly on the anion as long as the interionic distances in the respective ion pairs are comparable. Recent electron spin resonance measurements have shown that in tetrahydropyran the complexation constant for glyme-5 with sodium naphthalene is about 200–300 M^{-1} at 25°,[10] close to the value of 170 for F^-,Na^+.

Also, kinetic measurements of polymerization rates of polystyrylsodium in tetrahydropyran in the presence of glyme-5 have yielded a value of 90 M^{-1} for the equilibrium constant of the reaction $\sim S^-,Na^+ + G \leftrightarrows S^-,G,Na^+$, with $\sim S^-$ representing a benzyl-type carbanion.[11] Only when the anion is bulky, and the interionic distance in the contact ion pair is considerably increased, does one expect an increase in the complexation constant because of a decreased stability of the contact ion pair. The limiting case would be the free Na^+ ion, for which the complexation constant in tetrahydropyran was found to be 1.7×10^5 M^{-1}.[11] This value is expected to vary strongly with solvent, since the complexation of glyme with the solvated Na^+ ion requires first the desolvation of the cation. One would expect, for example, that in THF the complexation constant for the free Na^+ ion with glyme-5 is smaller than in THP.

In comparing the data for F^-,Li^+ in glyme–dioxane mixtures with those of F^-,Na^+ in glyme–THF one may argue that such a comparison would be invalid because of the pronounced difference in dielectric constant between dioxane ($D = 2.2$) and THF ($D = 7.4$). Some of the fluorenylsodium–glyme experiments were therefore repeated in dioxane. Although the results proved to be less reliable than in THF, plots of log K_i* *vs.* log [G] again show straight lines with $n = 1$. The K_i values are lower than those for THF, but only by a factor of about 4. This difference of course is very small if one realizes that the free ion dissociation constant of F^-,Na^+ in the two solvents differs by many powers of ten. Other evidence for the small change in K_i with changing dielectric constant is found in the formation of separated ion pairs of F^-,Na^+ and triisopropanolamine borate in dioxane, THP, and THF.[5] The respective K_i values were found to be 72, 104, and 102. Dielectric saturation makes the effective dielectric constant much smaller than the macroscopic dielectric constant, and while separation to a glyme-separated ion pair will be somewhat favored by the neighboring dipoles of a more polar solvent the effect is apparently small. The small change in K_i may also be due to a compensating effect. A less polar solvent is expected to yield a tighter ion pair, making separation more difficult. However, peripheral solvation of the contact ion pair is of greater importance in a more polar solvent like THF. These solvent molecules, or at least part of them, must be removed before the glyme can surround the alkali ion, and this process requires more energy for THF than for dioxane.

The strong solvating power of glymes with respect to alkali ions (comparable to that of such strongly polar solvents as dimethyl sulfoxide or hexamethylphosphoramide[2]) has been observed by other investigators. For example, Down, *et al.*,[12] studied the solubility of sodium and its alloy with potassium in different glymes, and while no quantitative data were obtained, the intensities of the blue metal solutions were shown to increase with the number of oxygen atoms in the glyme. Ugelstad and his coworkers[8,13] determined the effect of glyme structure on the rate of isomerization of 3-butenylbenzene and allylbenzene with potassium *t*-butoxide and the alkylation of alkyli phenoxides with butyl halides. The results of their experiments (carried out in the pure glymes) show a strong increase in the rate with an increase in the chain length of the glyme. For example, glyme-5 increases the rate of reaction of sodium phenoxide with butyl bromide by a factor of 180 compared to the rate of the same reaction in DME. With potassium phenoxide, the respective rates in glyme-3, -4, -5, and -7 are 8, 51, 72, and 200, all relative to DME. The rate increase in this case is largely due to an increase in the concentration of reactive free ions, due to the glyme interaction with the alkali ion. Whether glyme-separated ion pairs also play a role is not known. One must also be aware in this case of ion pair association, particularly when dealing with the planar phenoxides. This association, if present, may be strongly affected on addition of glymes because of improved ion pair solvation, and this in turn could change the reaction rate. Recent studies by Shinohara, *et al.*,[11] have also shown that addition of small quantities of glymes can dramatically increase the rate of anionic polymerization of styrene in tetrahydropyran. For example, at polystyrylsodium concentrations of 5×10^{-5} M, the polymerization rate increases by nearly a factor of 200 when glyme-5 is present at a concentration of 10^{-3} M. The formation of reactive glyme-separated ion pairs and an increase

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[9] A. I. Shatenshtein, E. S. Petrov, and M. I. Belousova, *Org. Reactiv.* (USSR), 1, 191 (1964); *Reakts. Sposobnost Org. Soedin.*, 1, 191 (1964); A. I. Shatenshtein, E. S. Petrov, and E. A. Yakovleva, *J. Polym. Sci., Part C*, 16, 729 (1967).

[10] K. Höfelmann, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 4645 (1969).

[11] M. Shinohara, J. Smid, and M. Szwarc, *ibid.*, **90**, 2175 (1968).

[12] J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959).

[13] J. Ugelstad, A. Berge, and H. Listou, *Acta Chem. Scand.*, **19**, 208 (1965).

in the fraction of reactive free ions was found to be responsible for this effect.

Temperature Dependence of K_i

The temperature dependence of glyme-separated ion pair formation of F^-,Na^+ was studied between 0 and 50°, and the respective plots of log K_i *vs.* $1/T$, shown in Figure 5, all show a reasonably linear relationship. The thermodynamic parameters ΔH_i and ΔS_i can be calculated from these plots, and their values are reported in Table II. The uncertainties in the ΔH_i values may be as much as 20%, due to the assumptions made in calculating the ion pair fractions from the temperature dependence of the absorption spectra.

Table II. Enthalpies and Entropies of Glyme-Separated Ion Pair Formation from the Fluorenylsodium Contact Ion Pair in THF

Glyme	$-\Delta H_i$, kcal/mol	$-\Delta S_i$, eu
3	2.8	9
4	5.4	14.5
5	7.1	14
6	9.2	18.5
7	9.0	17

With the exception of glyme-3, the enthalpy values do not differ greatly from the ΔH_i value of -7.6 kcal/mol found for solvent-separated ion pair formation in pure THF.[2a] The effectiveness of the glymes as coordinating agents is therefore, not unexpectedly, largely due to a smaller loss in entropy compared to solvents like THF. Actually, separation of two oppositely charged ions from a contact ion pair distance to a solvent-separated ion pair distance involves a considerable loss of entropy, probably as much as 20 to 30 eu. Hence, the observed value of approximately 14–18 eu indicates that the complexation of glyme may involve the release of one or two THF molecules, which is not unlikely since the contact ion pairs are probably solvated with two THF molecules.

In THF itself the entropy loss on solvent-separated ion pair formation is considerably larger than 30 eu, since more THF molecules become bound to the Na^+ ion. The low $-\Delta H_i$ value for glyme-3 is somewhat surprising and may indicate a more complicated solvation mechanism.

Coordination of Glymes with Fluorenylpotassium. Glymated Contact Ion Pairs

To explain the behavior of fluorenylpotassium in mixtures of glyme and THF (or THP), let us first consider the case of glyme-6 and glyme-7. It is well known that specific solvation of contact ion pairs in mixtures of solvating agents does not necessarily lead to separated ion pairs. For example, polystyryl- or polyisoprenyllithium[14] and diphenylhexyllithium[15] form complexes in hydrocarbon solvents with one or two ether molecules such as THF. Similar phenomena are observed on addition of small quantities of DMSO,[2a] hexamethylphosphoramide,[2b] or ethylenediamine[5] to fluorenyllithium in dioxane, although separated ion pair formation occurs simultaneously. One may, therefore, expect a competition between formation of glymated contact ion pairs and glyme-separated ion pairs, and the formation constants of these two kinds of glyme-coordinated ion pairs will depend on the size of the cation, the chain length of the glyme, the temperature, and the nature of the solvent in which the complex formation takes place. In fact, such a situation was recently encountered in the work of Slates and Szwarc,[16] who found that the large increase in sodium–biphenyl radical ion concentration when biphenyl and sodium are stirred in mixtures of THP and glymes (as compared to that in pure THP) could not be rationalized from the observed formation of glyme-separated B^-,G,Na^+ ion pairs (actually, no separated ion pairs could be detected in the mixtures with glyme-3). They suggested that in addition to the separated ion pairs one also forms the isomeric glymated contact ion pairs, *i.e.*, B^-,Na^+,G.

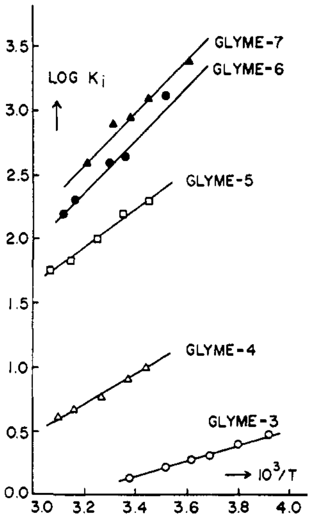

Figure 5. Temperature dependence of glyme-separated ion-pair formation of F^-,Na^+ in THF with different glymes.

The formation of two kinds of glymated ion pairs can explain our results for fluorenylpotassium with glyme-6 and -7. Let us assume that the glyme reacts with the F^-,K^+ to form a glymated contact ion pair, which is in equilibrium with a glyme-separated ion pair, *i.e.*

$$F^-,K^+ + G \rightleftarrows F^-,K^+,G \qquad K_1$$

$$F^-,K^+,G \rightleftarrows F^-,G,K^+ \qquad K_2$$

Experimentally we measure the quantity K_i^*, which is the ratio of separated to contact ion pairs. However, the contact ion pair spectrum now results from two species, *i.e.*, F^-,K^+ and F^-,K^+,G, which have identical spectra. Since

$$K_i^* = \frac{F^-,G,K^+}{F^-,K^+ + F^-,K^+,G}$$

one can easily show that the following relationship will hold.

$$\frac{1}{K_i^*} = \frac{1}{K_2} + \frac{1}{K_1K_2[G]} \tag{1}$$

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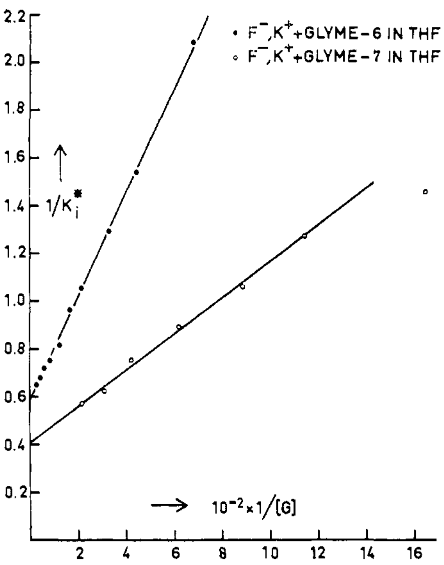

Figure 6. Plots of $1/K_i^*$ *vs.* 1/[glyme] for F^-,K^+ in THF with glyme-6 (●) and glyme 7 (○).

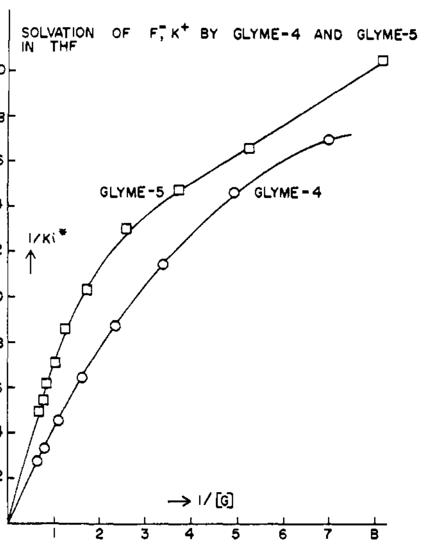

Figure 7. Plots of $1/K_i^*$ *vs.* 1/[glyme] for F^-,K^+ in THF with glyme-4 and -5, respectively.

A plot of $1/K_i^*$ *vs.* 1/[G] should yield a straight line from which the equilibrium constants K_1 and K_2 can be evaluated. The resulting plots for glyme-6 and glyme-7 in THF are shown in Figure 6, and a good linear relationship between $1/K_i^*$ and 1/[G] is indeed obtained.

The glyme concentration in eq 1 is the free glyme concentration, given by

$$[G] = [G]_0 - [F^-,G,K^+] - [F^-,G,K^+]/K_2$$

In the experiments with glyme-6 and -7, the total concentrations of F^-,K^+ and glyme are not too different, and the corrections are therefore important. Since the F^-,G,K^+ is measured spectrophotometrically, one can first plot $1/K_i^*$ *vs.* 1/[G] with $[G] = [G]_0 - [F^-,G,K^+]$. The resulting intercept can then be used to calculate the concentration of glymated contact ion pairs, which is equal to $[F^-,G,K^+]/K_2$, and [G] is then recalculated. The second correction usually does not affect K_2 but it changes the slope of the plot.

In the experiments shown in Figure 6, the total $[F^-,K^+]$ was approximately 6×10^{-4} *M*. The work was repeated at $[F^-,K^+] = 6 \times 10^{-3}$ *M*. The results are very similar to the low concentration data (see Table III), and may therefore be interpreted as an additional justification for the proposed mechanism. It also indicates that the dissociation into free ions (the free fluorenyl ion has the same absorption maximum as the separated ion pair) is negligibly small under the conditions of our experiments. However, at lower F^-,K^+ concentrations one must take the presence of free ions into account (see ref 4 for the relevant dissociation constants of fluorenylpotassium ion pairs).

The above solvation mechanism predicts that it is not possible to convert all the fluorenylpotassium ion pairs into the glyme-separated form, but that the ratio of glyme-separated to all contact ion pairs approaches the value K_2 as the glyme concentration increases. This behavior is reflected in the log K_i^* *vs.* log [G] plot for glyme-6, which levels off at higher concentration (Figure 4). However, it appears that at much higher glyme concentration all contact ion pairs are eventually converted into the separated ones. This is particularly noticeable in the results for glyme-4 and glyme-5. Plots of $1/K_i^*$ *vs.* 1/[G] for these glymes are shown in Figure 7, and the lines are obviously curved. The curve passes through the origin, indicating complete glyme-separated ion pair formation at higher glyme concentration. As expected, in pure glyme-4, -5, -6, or -7 the spectrum of F^-,K^+ only shows separated ion pairs. Only in pure glyme-3 can one still observe a considerable fraction of contact ion pairs.

The solvation mechanism for glyme-6 and glyme-7 can be extended to glyme-4 and glyme-5 if an additional solvation step is included, whereby a glymated contact ion pair is converted into a separated ion pair as more glyme is added. This means that species must be postulated which contain at least two glyme molecules, a reasonable proposition considering the results of nmr studies on the glyme complexes (see next section). The mechanism of solvation is then described by the following three steps

$$F^-,K^+ + G \rightleftarrows F^-,K^+,G \qquad K_1$$

$$F^-,K^+,G \rightleftarrows F^-,G,K^+ \qquad K_2$$

$$F^-,K^+,G + G \rightleftarrows F^-,G,K^+,G \qquad K_3$$

The experimental quantity K_i^* is now equal to

$$K_i^* = \frac{F^-,G,K^+ + F^-,G,K^+,G}{F^-,K^+ + F^-,K^+,G}$$

It is easily shown that the following relationship holds.

$$K_i^* = \frac{K_2 + K_3[G]}{1 + 1/K_1[G]} \tag{2}$$

To simplify this relationship the assumption is made that for glyme-4 and glyme-5 conditions are such that $K_1[G] \gg 1$. This is not unreasonable since the concentrations of the glymes are between 0.05 and 1.5 *M*, whereas those for glyme-6 and -7 were between 0.04 and 0.0005 *M*. For $K_1[G] \gg 1$ (which means that essentially all the F^-,K^+ contact ion pairs are externally coordinated with a glyme molecule), eq 2 reduces to the simple expression

$$K_i^* = K_2 + K_3[G] \tag{3}$$

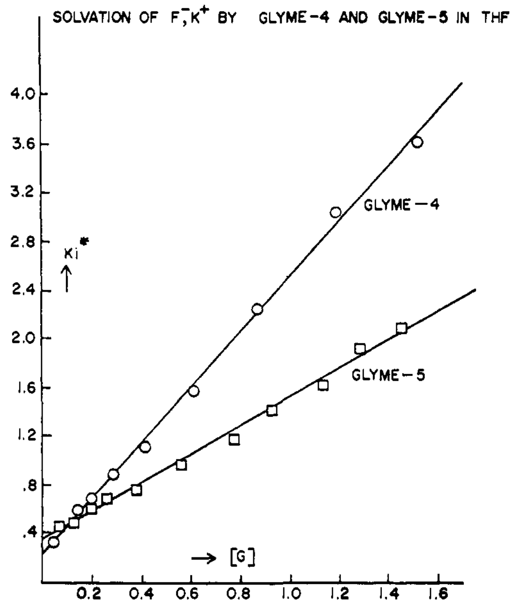

Figure 8. Plots of K_i^* *vs.* [glyme] for F^-,K^+ in THF at 25° with glyme-4 and -5, respectively.

Hence, K_i^* should change linearly with [G] (of course, K_i^* is equal to zero for $[G] = 0$; the above equation only holds for [G] sufficiently large so that $K_1[G] \gg 1$). Since for glyme-4 and -5 the $[G]_0 \gg [F^-,K^+]$ (the total $[F^-,K^+]$ is approximately 10^{-3} *M*) one may simply take $[G] = [G]_0$. Plots of K_i^* *vs.* [G] are shown in Figures 8 and 9 for both glyme-4 and -5 in THF and THP, respectively. There is indeed a good linear relationship, with the intercept yielding the value of K_2, the slope being equal to K_3. It seems therefore justified to assume that indeed all F^-,K^+ contact ion pairs are glymated with glyme-4 and -5 in the concentration range of glyme needed to form glyme-separated ion pairs.

In mixtures of THF and glyme-3, a plot of K_i^* *vs.* [G] yields a good straight line at lower [G] (*i.e.*, below 5 *M*), which passes through the origin (see Figure 10). Only at the two highest concentrations (the last point represents pure diglyme) do the points deviate, but this may be due to the fact that we have assumed the activity coefficients for the glyme to be equal to 1. It is again likely that the contact ion pairs are all glymated in glyme-3. Apparently, $K_2 = 0$; *i.e.*, no isomerization of the glymated contact ion pair to the separated one occurs. A second glyme molecule is needed to form the latter species, but the value for K_3 is much lower than that for glyme-4 or -5.

Values for the equilibrium constants K_1, K_2, and K_3 for the three solvation equilibria are collected in Table III. Values of K_1 for external coordination of glymes with the F^-,K^+ contact ion pairs could only be obtained for glyme-6 and -7. For glyme-4 and -5 the assumption $K_1[G] \geqslant 1$ led to the simplified eq 3 and the plots of Figures 8 and 9 show that linearity is maintained even down to $[G] \approx 0.05$ *M*. This means that the K_1 values for glymes-4 and -5 must be close to 50 M^{-1} or higher. Those for glyme-6 and -7 are 250 M^{-1} and 530 M^{-1}, respectively.

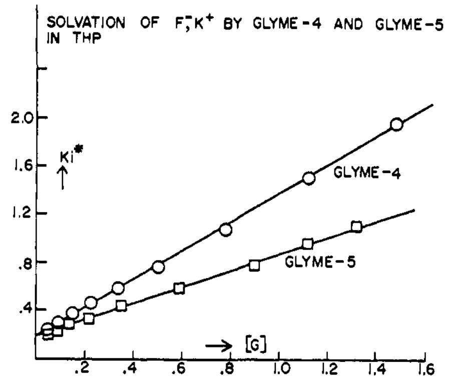

Figure 9. Plots of K_i^* *vs.* [glyme] for F^-,K^+ in THP at 25° with glyme-4 and -5, respectively.

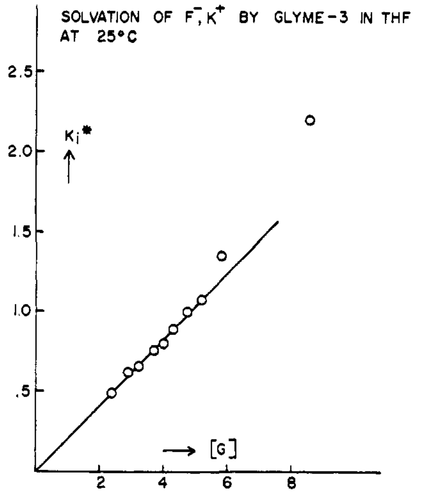

Figure 10. Plot of K_i^* *vs.* [glyme] for F^-,K^+ and glyme-3 in THF at 25°.

Table III. Equilibrium Constants for Glyme-Coordinated Ion Pair Formation of Fluorenylpotassium[a] in THF and THP at 25°

Glyme	Medium	K_1, M^{-1}	K_2	K_3, M^{-1}
Glyme-3	THF		0	0.21
Glyme-4	THF	>50	0.24	2.27
	THF[b]	>50	0.30	2.2
	THP	>50	0.18	1.2
Glyme-5	THF	>50	0.35	1.07
	THF[b]	>50	0.28	0.92
	THP	>50	0.18	0.69
Glyme-6	THF	250	1.75	
Glyme-7	THF	530	2.5	
	THP	1700	2.7	

[a] Concentration of F^-,K^+ between 1×10^{-3} and 5×10^{-4} *M*.
[b] Concentration of $F^-,K^+ \approx 6 \times 10^{-3}$ *M*.

The differences in K_1 values for the four glymes are considerably smaller than the increase in the equilibrium constant K_i for glyme-separated ion pair formation of F^-,Na^+, which increases from 9 to 170 M^{-1} when glyme-4 is replaced by glyme-5. The comparatively small increase in K_1 may indicate that on the periphery of the K^+ ion in the contact F^-,K^+ ion pair there is room for only four or at most five oxygen atoms. The larger number of available coordination sites in the higher glymes would increase K_1 only by a statistical factor. When changing from glyme-6 to -7, K_1 would then increase by a factor of 2, assuming no other factors (*e.g.*, steric hindrance) become of importance. This seems to be experimentally the case (see Table III). Calculations show that for glyme-3 K_1 may be as low as 5 M^{-1}, but no accurate value can be determined. A low K_1 value for glyme-3 is plausible if the maximum coordination number on the periphery of the K^+ ion in the contact ion pair is four.

The K_1 value in THP appears to be appreciably higher than in THF. This is to be expected, since in the process of glymation the alkali ion must be stripped of its primary solvation layer of solvent molecules, and this will cost more energy for THF than for the less basic THP.

The process of isomerization to the glyme-separated ion pair involves a loss in coulombic interaction energy, and the separation of charges must therefore be counterbalanced by additional coordination with other oxygen atoms of the glyme. For F^-,Na^+, high complexation constants for separated ion pair formation were only obtained for glyme-5 and higher glymes. Apparently, the weaker interactions with the larger K^+ ions demand that at least six oxygen atoms must be coordinated with this ion for an effective separation. The K_2 values for glyme-4 and -5 are both small, but a large increase is observed for glyme-6, and even more for glyme-7. In the case of glyme-4 and -5, the glyme-separated ion pair, *i.e.*, F^-,G,K^+, is also likely to contain an additional one or two THF molecules. This is not necessary for glyme-6 or glyme-7, which represents a substantial gain in entropy.

The K_2 values in THP appear to be slightly lower than in THF, at least for glyme-4, -5, and -6. This is consistent with the results obtained for F^-,Na^+, where the equilibrium constants for separated ion pair formation decrease in lower dielectric constant media, but, due to dielectric saturation, the effect is small.

The ion pair separation induced by a second glyme molecule as determined by the value for K_3 is small for glyme-3 ($K_3 = 0.2\ M^{-1}$), but increases by more than a factor of 10 for glyme-4, then appears to drop slightly for glyme-5. This decrease in K_3 when changing from glyme-4 to glyme-5 is also found in THP. In the latter solvent the K_3 values are again slightly smaller than in THP, consistent with the trend found for the K_2 values.

The sharp increase for glyme-4 may indicate that the K^+ ion may coordinate with a maximum of seven or possibly eight oxygen atoms which are part of one or two glyme molecules. The small decrease in K_3 for glyme-5 could be due to steric hindrance. This becomes important as the chain length increases and two glyme molecules are complexed to the K^+ ion. For glyme-6 and -7, no K_3 values could be measured, but they are not negligibly small as only glyme-separated ion pairs exist at higher glyme concentrations. Since eq 1 was shown to hold for glyme-6 up to $[G] = 4 \times 10^{-2}\ M$, the product $K_3[G]$ must be considerably smaller than K_2 (see eq 2); hence $K_3[G] \ll 1.75$, or $K_3 \ll 40\ M^{-1}$.

Nmr Spectra of Fluorenyl Salt–Glyme Complexes

Coordination of ethers with alkali cations causes a downfield shift in the nmr spectrum of the α protons, due to an increased electronegativity of the O atom.[17,18] However, when complexed to alkali fluorenyl salts, the diamagnetic anisotropy induced by the aromatic ring strongly shields the ether protons. Large upfield shifts, for example, have been reported for the ether protons (particularly the α protons) of F^-,Li^+–THF or F^-,Li^+–DME complexes in benzene[19] and for the 1:1 complexes of glymes with F^-,Li^+.[1] In the latter case, addition of an equimolar quantity of glyme-4 or glyme-5 to the solvent-separated ion pair of fluorenyllithium in pure THF causes a 30-cps upfield shift of certain glyme proton peaks, while at the same time the THF protons move back downfield close to their values observed in pure THF. This indicates that in the solvation shell of the Li^+ ion the THF is now largely replaced by the glyme molecule.

Fluorenylsodium is a contact ion pair in THF at 25°, but addition of equimolar quantities of glyme-5, -6, or -7 to a 0.1 M solution of F^-,Na^+ in THF converts it to a glyme-separated ion pair, since its optical absorption spectrum in the 430–520-mμ region (the solution is too concentrated to observe the 372-mμ peak) is identical with that of F^-,Na^+ in oxetane, in which only solvent-separated ion pairs were shown to exist.[2b] The proton peaks of the glymes are also strongly shifted upfield (see Table IV), and the peak pattern differs from that of the pure glyme, with the CH_3 protons shifting less than the CH_2 protons. In some cases the peak pattern is complex and no assignments of protons could as yet be made. The nmr spectrum of the complexed glymes is also sensitive to changes in temperature. This may indicate that in the glyme-separated ion pair the average position of the glyme with respect to the fluorenyl carbanion is temperature-dependent, and that more than one glyme-separated ion pair structure may exist. This was also suggested by Höfelmann, *et al.*,[10] in rationalizing some of their results of esr studies with glyme-separated ion pairs of radical anions.

The most interesting case in the F^-,Na^+ series is the complexation with glyme-4. For the higher glymes (-5, -6, and -7), the K_i values are all larger than 100 M^{-1} (see Table I) and at glyme concentrations of $10^{-1}M$ and $[F^-,Na^+] \approx 10^{-1}M$ more than 80% of the F^-,Na^+ is present as a glyme-separated ion pair. However, for glyme-4 the K_i is only 9 M^{-1}, and an equimolar mixture of F^-,Na^+ and glyme-4 (both 0.1 M in THF) should contain only 36% glyme-separated ion pairs. Experimentally, one can show from the optical absorption spectrum that under these conditions indeed about 40% separated ion pairs are present. However, the nmr spectrum of the glyme molecule indicates that almost all of the glyme is bound to F^-,Na^+ since the upfield shift is comparable to that of the F^-,Na^+–glyme-5 complex (see Table IV). In the latter case we know that almost all glyme is bound in the form of a glyme-separated ion pair. This strongly suggests that most of the glyme-4 is coordinated to F^-,Na^+ in the form of a glymated contact ion pair. Hence, in the optical experiments (where similar glyme-4 concentrations ($\approx 10^{-1}\ M$) were used but low F^-,Na^+ concentrations ($\approx 10^{-3}\ M$) in order to measure the equilibrium constant K_1) one actually deals with F^-,Na,G contact ion pairs and the equilibrium should be written as

$$F^-,Na^+,G + G \rightleftarrows F^-,G,Na^+,G$$

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Table IV. Nmr Chemical Shifts[a] for Complexes of Glymes with Fluorenyl$^-$,Na$^+$ and Fluorenyl$^-$,K$^+$ in THF at 40°

System	Glyme peaks[b] CH$_3$	CH$_2$ (ext)	CH$_2$ (int)
Glyme-4, -5, -6, and -7	6.73	6.51	6.47
F$^-$,Li$^+$-glyme-5 (1:1)	7.23	7.13	7.05
F$^-$,Na$^+$-glyme-7 (1:1)	6.98	6.96	6.95
F$^-$,Na$^+$-glyme-6 (1:1)	7.03	6.97	6.95
F$^-$,Na$^+$-glyme-5 (1:1)	6.98	6.97	
F$^-$,Na$^+$-glyme-4 (1:1)	7.00	6.97	
F$^-$,Na$^+$-glyme-4 (1:2)	6.94	6.90	
F$^-$,K$^+$-glyme-4 (1:1)	6.95	6.93	
F$^-$,K$^+$-glyme-7 (1:1)	7.01	6.95	

[a] In τ scale downfield from TMS. [b] Assignments of glyme proton peaks is only certain in the pure glymes, but not in the complexes. Some of the peaks also move considerably more upfield at lower temperatures.

One expects therefore two glyme-4 molecules coordinated to a glyme-4-separated F$^-$,Na$^+$ ion pair.

To check this point further, we looked at the nmr spectrum of glyme-4 in a mixture of 0.2 *M* of F$^-$,Na$^+$ and 0.44 *M* of glyme-4 in THF. The optical absorption spectrum shows approximately 75% glyme-separated ion pairs (peak overlap makes calculation of ion pair fractions from the visible region of the optical absorption spectrum less reliable). More important, the chemical shifts of the glyme protons are still very close to those of an equimolar solution of glyme-4 and F$^-$,Na$^+$ in THF.

This is an another strong indication that the glyme-4-separated F$^-$,Na$^+$ ion pairs actually contain two glyme-4 molecules (the slightly larger than 2:1 ratio of glyme-4 to F$^-$,Na$^+$ should of course bring the peaks somewhat downfield because of the free ether which is present, and even at an exact 2:1 ratio there is still some free glyme present). On the other hand, the nmr spectrum of a THF solution containing a 2:1 ratio of *glyme-5* over F$^-$,Na$^+$ was close to the weighted average of the spectra for pure glyme-5 and that of a 1:1 ratio of glyme-5 to F$^-$,Na$^+$. In this case the glyme-separated ion pair contains only one glyme-5 molecule, and the noncoordinated glyme will rapidly exchange with the coordinated glyme. No nmr measurements were done for systems containing glyme-3, but it is not unlikely that the separated ion pairs with both F$^-$,Li$^+$ and F$^-$,Na$^+$ also contain two glyme-3 molecules.

Nmr data for F$^-$,K$^+$ and glymes in THF show that a mixture of 0.25 mol of F$^-$,K$^+$ and 0.25 mol of glyme-4 yields essentially the same upfield shift for the glyme protons as a mixture of 0.3 mol of F$^-$,K$^+$ and 0.3 mol of glyme-7 (see Table IV). However, one determines from the visible region of the optical absorption spectrum that the former mixture contains only 20% glyme-separated ion pairs in THF at 25° and the latter mixture close to 80%. From a calculation of the known K_2 values (see Table III) the respective percentages are expected to be 20 and 70%, which is indeed close to the experimental values. The almost identical chemical shifts for the glymes in the two systems suggests, therefore, that practically all the glyme-4 is bound to the potassium salt, but mainly in the form of a glymated contact ion pair. This observation supports therefore the conclusions arrived at from our optical absorption data, namely that the glyme-4 coordinates first externally to F$^-$,K$^+$ and that a second glyme-4 molecule is needed to convert these ion pairs to glyme-separated ones.

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A Corrected Primary Solvation Number of Magnesium(II) in Liquid Ammonia

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Abstract: The primary solvation number of magnesium(II) in anhydrous liquid ammonia has been redetermined and been found to be six. The redetermination incorporates an improved procedure for obtaining anhydrous solutions and the use of a proton nmr complete line-shape analysis.

Magnesium(II) represents one of the few metallic cations for which solvation numbers in solution can be obtained by straightforward proton magnetic resonance signal integration.[1-4] In three of the solvents studied, methanol,[1] water,[3] and aqueous acetone,[4] the primary solvation number is six while in the third, ammonia, it was measured as five.[2] Because of the biochemical inportance of Mg(II)–nitrogen coordination such five-coordination should be investigated further to

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