# 136. Coordinating Abilities Towards Sodium of Oxygenated Solvents

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(17. II. 76)

*Summary.* Tetracoordination of the sodium cation is indicated by the $^{23}$Na-NMR. chemical shifts for $NaClO_4$ in binary mixtures of ether and alcohol solvents. Solvent exchange occurs by a sequential process, and involves one or several intermediates. In competition with tetrahydrofurfuryl alcohol, whereas glyme corresponds to monocyclic intermediates, diglyme and triglyme[1]) favor formation of bicyclic intermediates. The relevant conformational factors are analysed, and also serve to explain the better coordinating abilities of diglyme and triglyme, as compared to glyme. The mechanism for solvent exchange is discussed.

$^{23}$Na-NMR. holds great promise for studying the interactions of salts with biomolecules, or simpler organic models. Already, the $^{23}$Na chemical shifts have been related, in the pioneering studies by *Bloor & Kidd* [1] and by *Popov et al.* [2], to the *Lewis* basicity and the *Gutmann* donicity number [3] of the solvent. The $^{23}$Na shifts have served to confirm the «tight» or «loose» character of various ion pairs [4], together with their aggregation number [5]. In most solvents, sodium perchlorate exists as the loose, solvent-separated ion pair [6]. This salt will be our probe, in the present study, for establishing the composition and the geometry of the sodium solvation shell in various oxygenated donors, cyclic or acyclic. The procedure consists of relating shifts to the numbers of coordinating molecules, when the two components of a binary mixture compete for complexation of the sodium cation. It will serve to establish the stepwise equilibria and the attendant stoichiometries, in the interconversion between $Na^+$ symmetrically solvated by species A, and $Na^+$ symmetrically solvated by species B. Such an approach has been explored by *Greenberg & Popov* [7], in the formalism developed recently by *Covington* [8], for all possible binary solvent mixtures of nitromethane, acetonitrile, hexamethylphosphoramide, dimethylsulfoxide, pyridine and tetramethylurea. We shall consider ether and poly-ether solvents, with the additional incentives of acquiring insight into the dissociative or associative nature of the mechanism for solvent exchange, and into the geometry of the corresponding transition states.

## Experimental Part

The NMR. spectra are obtained with a *Bruker* HFX-90 FT spectrometer at 23.80 MHz. The chemical shifts are referred to sodium chloride at infinite dilution in water, and measured as indicated in a previous article [5]. They are accurate to ± 0.1 ppm. Whenever possible, the solvents are of analytical reagent grade: tetrahydrofuran (*Baker Analysed Reagent*), methanol (*Merck, 'Pro Analysi'*), dimethoxyethane (*Aldrich*, 99.5%), tetrahydrofurfuryl alcohol (*Aldrich*, 99%), 3-hydroxytetrahydrofuran (*Aldrich*, 99%), diglyme and triglyme (*Aldrich*, 99%) are dried

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[1]) For abbreviations see Table 1.

on grade 4 *Fischer* activated molecular sieve; 2-hydroxymethyltetrahydropyran (*Aldrich*, 98%) and ethylene glycol (*U.C.B.*, pur) are dried and redistilled over $MgSO_4$. Sodium perchlorate (*U.C.B.*, pour analyse) is dessicated under vacuum for 6 h.

We checked that the $^{23}Na$ chemical shift and linewidth in THF solvent, dried as indicated above, agree with those reported by *Van Geet* for Na $B(C_6H_5)_4$ [9], and by *Popov* for $NaClO_4$ [6]. Our measurements with Na $B(C_6H_5)_4$ in pure solvents and solvent mixtures are reported elsewhere [10].

*The sodium cation is tetra-coordinate.* The $^{23}Na$ chemical shifts in the pure solvents are listed in Table 1, together with the abbreviations that will henceforth be used.

Table 1. *$^{23}Na$ chemical shifts for $NaClO_4$ 0.1 M in the pure solvents*

| Solvent | Abbreviation | $\delta$ ($\pm$ 0.1 ppm)[a] |
|---|---|---|
| MONODENTATE | | |
| methanol | MeOH | 3.9[b] |
| tetrahydrofuran | THF | 8.2[b] |
| (*RS*)-3-hydroxytetrahydrofuran | THF-3-OH | 6.0 |
| BIDENTATE | | |
| ethyleneglycol | EG | 2.5 |
| dimethoxyethane (monoglyme) | MG | 8.6 |
| 1,5-dimethoxy-3-oxa-pentane (diglyme) | DG | 8.4 |
| 1,8-dimethoxy-3,6-dioxa-octane (triglyme) | TG | 9.4 |
| (*RS*)-tetrahydrofurfuryl alcohol | THFu | 3.4 |
| (*RS*)-2-methanol-tetrahydropyran | THPu | 3.4 |

[a] With reference to NaCl at infinite dilution in $H_2O$; shifts have been corrected for bulk susceptibility [5].

[b] See also [6].

We report results obtained with the binary mixtures in Table 2. These were selected because of a large chemical shift difference between the two pure components. Furthermore, they include cases of competition between monodentate ligands, monodentate and bidentate, bidentate and bidentate.

Table 2. *Binary mixtures studied*

| *Monodentate-monodentate* | *Monodentate-bidentate* | *Bidentate-bidentate* |
|---|---|---|
| MeOH/THF | THF/THFu | MG/THFu |
| THF-3-OH/THF | THF/THPu | DG/THFu |
| | THF/EG | TG/THFu |

THF and THFu are chosen as reference solvents, the former because it is a good donor very generally used, the latter because of its structural resemblance to a fragment from antibiotics known to strongly complex the $Na^+$ cation, such as nonactin, valinomycin, or monensin [11]. The experimental points are shown (Fig. 1 and 2). Analysis of the data is based upon the two premises, of sodium tetracoordination [12], and of stepwise replacement of coordinated solvent molecules [13] (*Scheme 1*). Other treatments fail to reproduce the observed shifts.

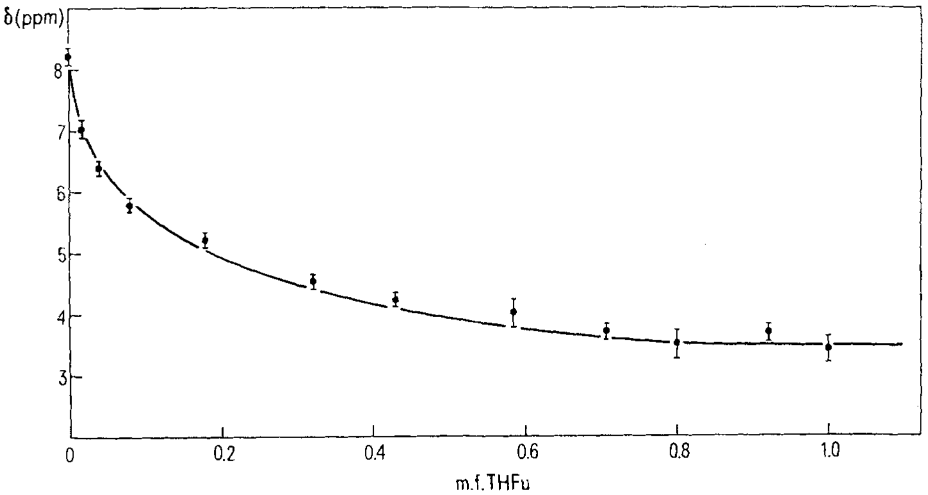


Fig. 1a. $^{23}$*Na chemical shift for* $Na^+ClO_4^-$ *in binary mixtures of tetrahydrofuran and tetrahydrofurfuryl alcohol, as a function of composition*

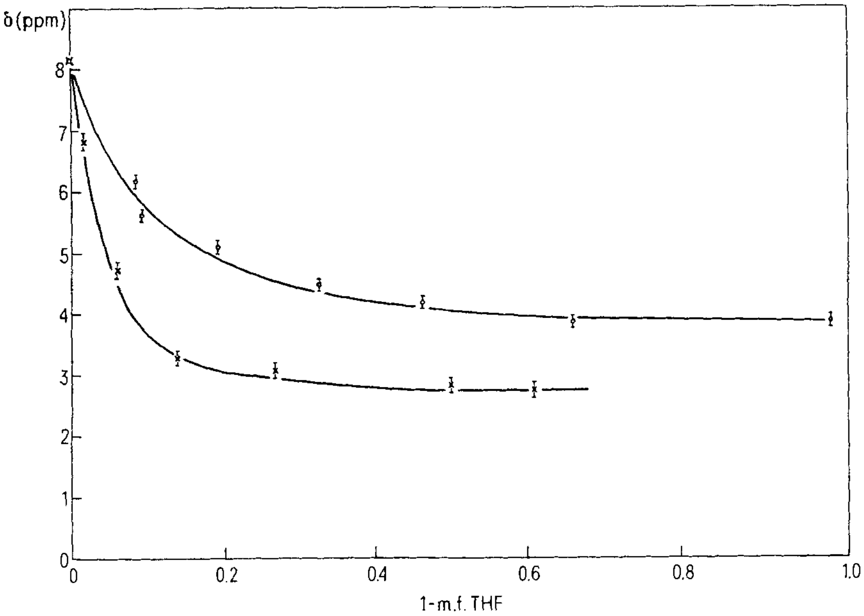


Fig. 1b. $^{23}$*Na chemical shifts for* $Na^+ClO_4^-$ *in binary mixtures of tetrahydrofuran with ethylene glycol (crosses), and tetrahydrofuran with tetrahydropyran (open circles), as a function of composition*

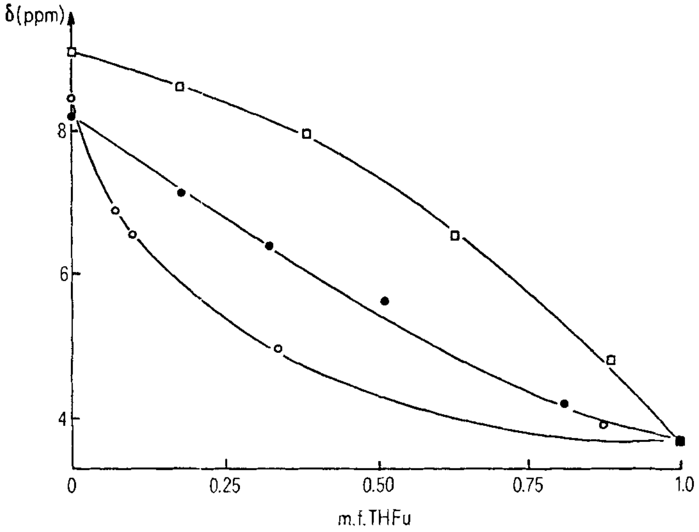
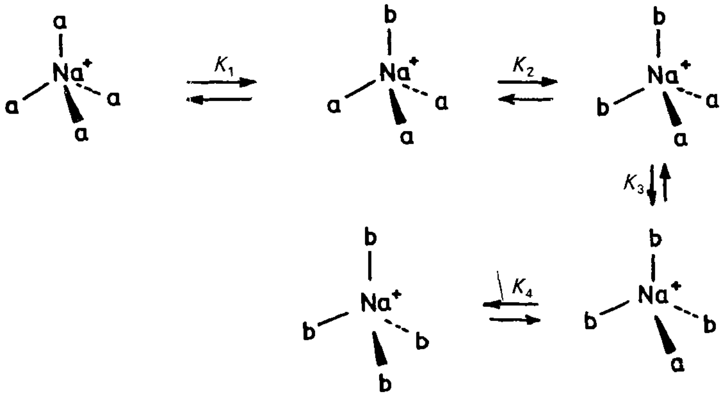


Fig. 2. *$^{23}$Na chemical shift for $Na^+ClO_4^-$ in binary mixtures of glyme (open circles), diglyme (filled circles), and triglyme (open squares), in competition with tetrahydrofurfuryl alcohol, as a function of composition*

*Scheme 1*

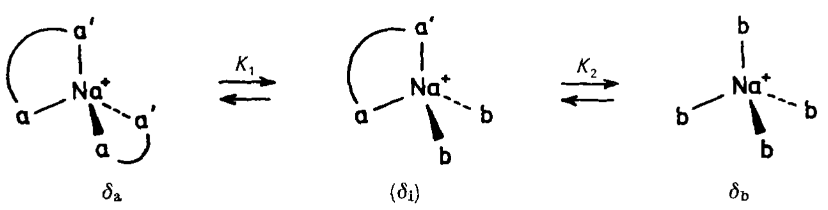


In this and the following schemes, we *represent* the sodium cation as symmetrically coordinated. The $Na^+$-O bond is characterized by $-\Delta G°$ values greater than thermal energies by at least one order of magnitude. For instance, hydration of $Na^+$ by six water molecules corresponds to $\Delta G° = -98.5$ kcal.mol$^{-1}$ [14], *i.e.* to an average bond strength $\Delta H° \simeq 16$ kcal.mol$^{-1}$ [15]. The sodium cation is expected to be at *van der Waals* contact from the oxygen donor atoms: for the $Na^+$-18-crown-6 polyether complex, *Dunitz et al.* [16] report $Na^+ \cdots O$ distances of 2.55 ± 0.10 Å, close to the sum of the ionic radius for sodium, 0.95 Å, and the *van der Waals* radius for oxygen, 1.40 Å.

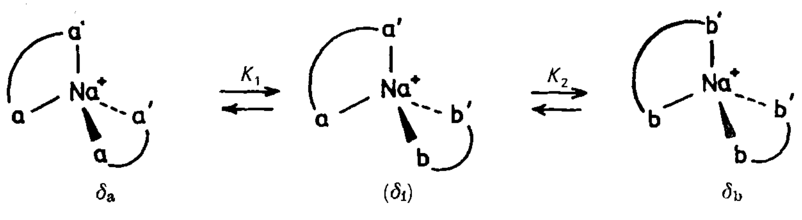
*Clementi et al.* [17] performed theoretical calculations at the *Hartree-Fock* level on the interaction between water and alkali metal cations: for small clusters such as $Na^+(H_2O)_4$ the symmetrical (tetrahedral) configuration is of lowest energy. This conclusion extends into the liquid phase: the NMR. relaxation study by *Melendres & Hertz* [18] indicates a fully oriented shell of water or methanol solvent molecules around the sodium cation, with the solvent dipoles preferentially oriented towards it. In the present study, the very simple description of coordinated sodium in the configuration of highest symmetry, *i.e.* as a tetrahedron, leads to an internally-consistent picture, accounting for all of the changes observed in the chemical shifts and in the linewidths, when the donor solvent is varied. Such an assumption amounts to the notion that the solvent molecules distribute themselves around the sodium cation so as to minimize repulsion of like charges and steric repulsions. The result is equivalent to the familiar VSEPR description of *Gillespie-Nyholm* [19]: a tetrahedral geometry corresponds to tetracoordination, while pentacoordination is represented by the trigonal bipyramid arrangement.

In most of the cases we studied, at least one of the two solvents pitted in competition against one another was bidentate. The following simplified description then applies (*Schemes 2 and 3*). Any treatment in which the number of coordinating oxygen atoms does not remain invariant in the initial ($a_4$), intermediate ($a_2b_2$), and final ($b_4$) states, fails to account quantitatively for the data. The appropriate equations are the following [8]:

*Scheme 2*



*Scheme 3*



$$\Delta = \frac{K_1Y + 2\,K_1K_2Y^2 + 3\,K_1K_2K_3Y^3 + 4\,K_1K_2K_3K_4Y^4}{4\,(1 + K_1Y + K_1K_2Y^2 + K_1K_2K_3Y^3 + K_1K_2K_3K_4Y^4)}$$

$$\text{with } Y = \frac{[\text{solvent b}]}{[\text{solvent a}]} \quad \text{in } \textit{Scheme 1},$$

and:

$$\Delta = \frac{K_1Y' + 2\,K_1K_2(Y')^2}{2\,[1 + K_1Y' + K_1K_2(Y')^2]}$$

with $Y' = \frac{[\text{solvent b}]}{[\text{solvent a}]}$ in *Scheme 2.*

The observable $\Delta$ is defined as:

$$\Delta = \frac{\delta_{obs} - \delta_a}{\delta_b - \delta_a}\,.$$

This treatment assumes that the observed $^{23}$Na chemical shift is the fast-exchange weighted average of the various species involved: an initial state characterized by a chemical shift $\delta_a$, a final state with chemical shift $\delta_b$, and an intermediate whose chemical shift $\delta_i$ is assumed to be the algebraic mean $\delta_i = 1/2\,(\delta_a + \delta_b)$ [8] [9] [20]. The curves through the experimental points in Fig. 1 and 2 result from these expressions. The quality of the fit would seem to vouch for the essential correctness of the analysis we have just outlined. The resulting parameters are gathered in Table 3.

Sodium tetracoordination by oxygen ligands, with nuclear magnetic resonance as the method of study, is not surprising and has already been reported by several authors [8] [9] [21]. As we shall see, this concept is consistent with all of our observations, and offers a rational and convenient framework for discussing the mechanism for solvent exchange. The validity of the sequential process, formally summarized above (*Schemes 1–3*), passes scrutiny: solvent exchange occurs as a succession of individual steps, in which each solvent molecule becomes coordinated in turn to the cationic center, with displacement of another solvent molecule. Deferring discussion of the values obtained for the equilibrium constants $K_1$ and $K_2$ (Table 3) to another section, we shall consider first interpretation of their $K_1/K_2$ ratios.

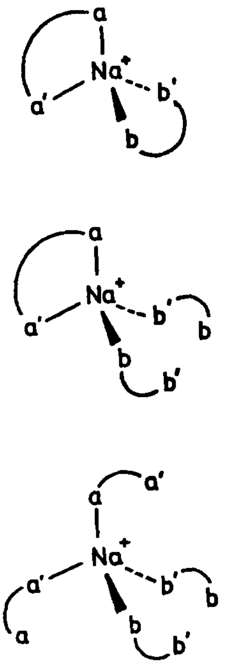
Table 3. *Solvation numbers and equilibrium constants*

| *Solvent a* ($n_a$) | *Solvent b* ($n_b$) | $K_1$ | $K_2$ |
|---|---|---|---|
| THF (4) | MeOH (4) | $K = 14.3$[a] | |
| THF (4) | THF-3-OH (4) | $K = 314$[a] | |
| THF (4) | THFu (2) | 710 ± 25 M | 20 ± 2 M |
| THF (4) | THPu (2) | 600 ± 90 M | 21 ± 2 M |
| THF (4) | EG (2) | 580 ± 70 M | 115 ± 13 M |
| MG (2) | THFu (2) | 18 ± 2 | 2 ± 0.8 |
| DG (2) | THFu (2) | 2.7 ± 0.4 | 0.7 ± 0.1 |
| TG (2) | THFu (2) | 1.2 ± 0.2 | 0.3 ± 0.07 |

[a] For the competition experiments between monodentate ligands, the data is not accurate enough for reliable determination of *four* individual equilibrium constants $K_1$—$K_4$. The overall equilibrium constant $K$ has been derived according to the treatment by *Covington et al.* [18].

*Symmetry of the intermediate and statistical numbers.* Depending upon the monodentate or bidentate character of solvents A and B, the intermediate structure ($a_2b_2$) may be acyclic, monocyclic, or bicyclic (*Scheme 4*):

*Scheme 4*



BICYCLIC notation: (aa') (bb')

MONOCYCLIC notation: (aa') (b) (b')

ACYCLIC notation: (a) (a') (b) (b')

We leave aside in this paper, for simplicity's sake, the consequences of using chiral ligands such as THFu, which increases further the number of isomeric structures to be considered. Likewise, a simplifying feature in our analysis is the assumption of a single formal intermediate characterized by a chemical shift $\delta_i = 1/2\,(\delta_a + \delta_b)$ rather than the true manifold of *all* the intermediates really involved in the interconversion. This point is further examined in the accompanying article. In such a formal classification, and because of the symmetry for the tetrahedron, the intermediate can be derived from the initial state as indicated in Table 4.

Comparison of the experimental values for $K_1$ and $K_2$ (Table 3) with the statistical ratios $K_1/K_2$ (Table 4) is performed in Table 5.

We single out for consideration ligands such as THFu, THPu, or MG: the bicyclic structure is avoided in the MG/THFu competition experiment; likewise, the monocyclic structure appears to be avoided in the THF/THFu and THF/THPu experiments.

True, the local structure (*Scheme 5*) causes unfavorable strain:

*Scheme 5*

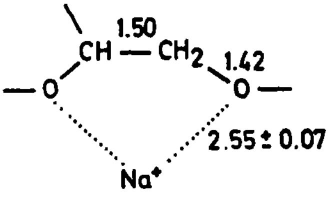


Table 4. *Symmetry numbers for the various pathways*

| Initial | | Intermediate | | Final | $K_1/K_2$ |
|---|---|---|---|---|---|
| | | monodentate-monodentate | | | |
| (a) (a) (a) (a) | $\underset{2}{\overset{12}{\rightleftarrows}}$ | (a) (a) (b) (b) | $\underset{12}{\overset{2}{\rightleftarrows}}$ | (b) (b) (b) (b) | 36 [13] |
| | | bidentate-monodentate | | | |
| (aa′) (aa′) | $\underset{12}{\overset{8}{\rightleftarrows}}$ | (a) (a′) (b) (b)<br>ACYCLIC | $\underset{12}{\overset{2}{\rightleftarrows}}$ | (b) (b) (b) (b) | 24 |
| (aa′) (aa′) | $\underset{2}{\overset{4}{\rightleftarrows}}$ | (aa′) (b) (b)<br>MONOCYCLIC | $\underset{12}{\overset{2}{\rightleftarrows}}$ | (b) (b) (b) (b) | 12 |
| | | bidentate-bidentate | | | |
| (aa′) (aa′) | $\underset{2}{\overset{8}{\rightleftarrows}}$ | (a) (a′) (b) (b′)<br>ACYCLIC | $\underset{8}{\overset{2}{\rightleftarrows}}$ | (bb′) (bb′) | 16 |
| (aa′) (aa′) | $\underset{2}{\overset{8}{\rightleftarrows}}$ | (a) (a′) (bb′)<br>MONOCYCLIC | $\underset{4}{\overset{2}{\rightleftarrows}}$ | (bb′) (bb′) | 8 |
| (aa′) (aa′) | $\underset{2}{\overset{4}{\rightleftarrows}}$ | (aa′) (b) (b′)<br>MONOCYCLIC | $\underset{8}{\overset{2}{\rightleftarrows}}$ | (bb′) (bb′) | 8 |
| (aa′) (aa′) | $\underset{2}{\overset{4}{\rightleftarrows}}$ | (aa′) (bb′)<br>BICYCLIC | $\underset{4}{\overset{2}{\rightleftarrows}}$ | (bb′) (bb′) | 4 |

Table 5. *Statistical ratios* $K_1/K_2$ *and structure of the intermediate*

| Solvent A | Intermediate | Solvent B | $K_1/K_2$ | |
|---|---|---|---|---|
| | | | Calc. | Exper. |
| DG | bicyclic | THFu | 4 | 4 ± 1 |
| TG | bicyclic | THFu | 4 | 4 ± 1 |
| MG | monocyclic | THFu | 8 | 9 ± 1 |
| THF | acyclic | THFu | 24[a] | 36 ± 4 |
| THF | acyclic | THPu | 24[a] | 29 ± 5 |
| THF | ? | EG | ? | (5 ± 1)[b] |

[a] 36 if the intermediate can be indifferently acyclic or monocyclic.

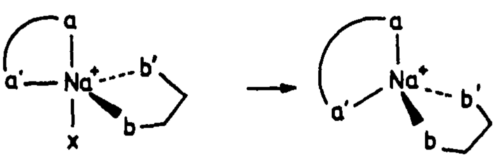
[b] With ethylene glycol ($\varepsilon = 39$), another equilibrium is superimposed, that between the solvent-separated and the dissociated ion pairs.

values for the O–C, C–C bond lengths, O–Na distances [16] and the O–C–C bond angle leads to an O–$Na^+$–O angle of *ca.* 76°, *i.e.* much smaller than the required tetrahedral angle of 109.5°. However, the initial and the final states in these experiments also suffer from the same angular strain. Hence, access to the bicyclic MG/THFu intermediate (or to the monocyclic THF/THFu intermediate) is kinetically, rather than thermodynamically, forbidden.

*A plausible geometry for the transition states.* Solvent exchange in tetracoordinate species is expected to proceed by an *associative* mechanism [22]. In the transition state for the process, the coordination number increases by one unit relative to the initial and final states for the individual step. Geometrically, one will be dealing with trigonal bipyramids in these *pseudo-$S_N2$* processes. The entering and the departing solvent molecules will occupy apical positions, 180° apart. This working hypothesis is simple, has precedence in the literature, and explains satisfactorily the observations above reported.

More specifically, a bicyclic intermediate requires as the antecedent transition state a trigonal bipyramid in which an MG (or THFu, or THPu) molecule spans equatorial position, 120° apart (*Scheme 6*). Such a transition state would suffer from considerable angular strain, as the 'normal' *ca.* 76° O–$Na^+$–O angle is forced to open to 120°: with MG (or THFu, or THPu) bidentate ligands, the two coordinating oxygen atoms occupy preferentially apical-equatorial sites. With the higher glymes, DG and TG, there is enough additional flexibility that these ligands can and do bind in the equatorial-equatorial disposition without undue strain. A similar argument explains the preference for acyclic intermediates in competition experiments such as between THF and THFu. The same geometrical factor also accounts for the relative values of the equilibrium constants for transfer of the $Na^+$ cation between the various oxygenated solvents, to be considered now.

*Scheme 6*



∈ (a, a', b, b')

*The* Gibbs *free enthalpies of solvation* $\Delta G°$. The overall process for preferential solvation of the $Na^+$ cation by solvent B relative to solvent A corresponds to the equilibrium:

$$(\mathrm{Na}^+)_{\mathrm{nA}} + \mathrm{mB} \overset{K}{\rightleftarrows} (\mathrm{Na}^+)_{\mathrm{mB}} + \mathrm{nA}$$

with $K > 1$. The corresponding values of $\Delta G° = -RT \ln K$ are listed in Table 6, together with the values of m and n, relative to THF, arbitrarily chosen as the reference solvent.

The observed $\Delta G°$ values have to be corrected for the large entropy contributions associated with loss of translational and (internal)rotational degrees of freedom. Obviously, if solvent A is THF and solvent B one of the glymes, the process $n = 4 \rightarrow m = 2$ is favored entropywise, because of the gain in translational entropy upon liberation of n-m (= 2) THF molecules. This term, related to the so-called chelate [23] or macrocyclic effect [24], is evaluated from the *Kohler* modification [25] of the *Sakur-Tetrode* relationship, incorporating the reduction in the translational free volume of the molecules between the gas and the liquid phase.

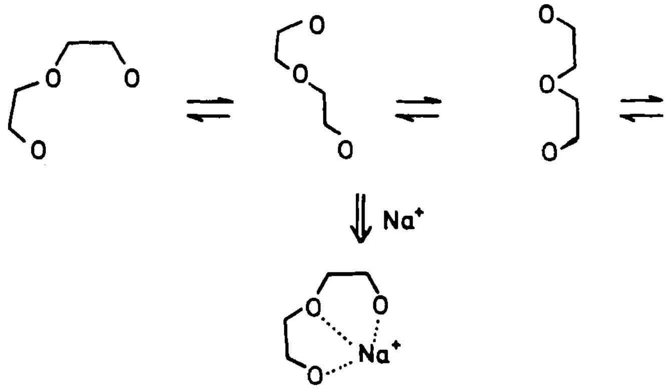
Table 6. *$\Delta G^\circ$ values for transfer of $Na^+$ between oxygenated solvents*

| Solvent (n or m) | $\Delta G^0_{tr}$: exper. | corr.[a]) (± 0.1 kcal.mol$^{-1}$) |
|---|---|---|
| THF (4) | 0.0 | 0.0 |
| MG (2) | −3.7 | 2.5 |
| DG (2) | −5.3 | −4.7 |
| TG (2) | −6.4 | −11.2 |
| EG (2) | −6.6 | 0.7 |
| THFu (2) | −5.7 | 2.0 |
| THPu (2) | −5.6 | 1.8 |
| THF-3-OH (4) | −3.4 | −5.7 |
| MeOH (4) | −1.6 | −1.0 |

[a]) See text.

For a bidentate solvent, bi-coordination of two of its oxygen heteroatoms amounts to a formal cyclization, with an entropy loss per internal rotation – *i.e.* per C–O or C–C bond frozen into one of its three rotamers – of 2.70–4.30 e.u. [26]. Since we are not dealing here with cyclization *senso strictu*, we have selected the lower limit of 2.70 e.u., which also happens to be close to the value of R ln 3 appropriate to an idealized model with three equivalent potential wells separated by infinite barriers. The loss of internal rotation is usually the largest contribution to changes in entropy upon cyclization [26], and such a correction is important in comparing, say MG with TG; whereas the former molecule must select one conformation out of a possible 81, the probability become 1:59,049 for TG.

*Scheme 7*



These are clearly the two most important corrections that have to be performed. Judging from the internal consistency of the corrected data, they appear to be appropriate. Comparing the values for the glymes (Table 6), the terminal oxygen atoms in diglyme are better than their counterparts in glyme, by approximately 1.7 kcal.mol$^{-1}$ per oxygen atom if one neglects the contribution of the central oxygen atom in diglyme. Likewise, the stabilization afforded by the four oxygen atoms in triglyme is superior by approximately 1.7 kcal.mol$^{-1}$ per oxygen, compared to glyme.

Possession of the $OCH_2CH_2O$ fragment is not restricted to glyme: a similar unit characterizes the EG, THFu, THPu molecules, and it destabilizes them indeed by the same amount, *viz.* approximately 7 $kcal.mol^{-1}$ (or 1.7 kcal per oxygen atom). We shall summarize in the next section the appropriate conformational analysis, which offers a justification for this effect.

Turning finally to the comparison between glyme and ethylene glycol, we note that an OH function is better than the $OCH_3$ group by approximately 0.5 $kcal.mol^{-1}$. A similar result, *viz.* 0.3 $kcal.mol^{-1}$, obtains from a comparison of the THF and MeOH values, which would tend to indicate similar coordinating abilities by each oxygen atom type. They do not differ very greatly indeed in their donating aptitudes, as measured by the *Gutmann* donicities [3]. This stabilization by the OH groups probably originates in the increased acidity or hydrogen bond strength of the alcohol functions coordinated to the cation as shown recently by *Symons* [27]: in solvents of high dielectric constant such as methanol or ethylene glycol, there will be increased hydrogen bonding in the solvation shell (or towards the counter-anion), with virtually no entropy loss since *Parker et al.* [28] have shown that the degree of 'tightness' of the solvation shell does not affect significantly the entropy term. As for 3-hydroxytetrahydrofuran, the large stabilization observed points to a bridged solvent-separated ion pair in which both the anion and the cation coordinated to the solvent molecule.

*Conformational analysis of the interaction with the glymes.* In the convenient notation of *Dale* [29], diglyme is represented as shown in Fig. 3a, in its stable conformation characterized by *anti*(a)O–C bonds and *gauche*(g)C–C bonds [29]. Such a conformation is nearly ideal for complexation of sodium by the terminal oxygen atoms, at a distance of about 2.5 Å [16] and with a nearly tetrahedral O(1)–$Na^+$–O(3)

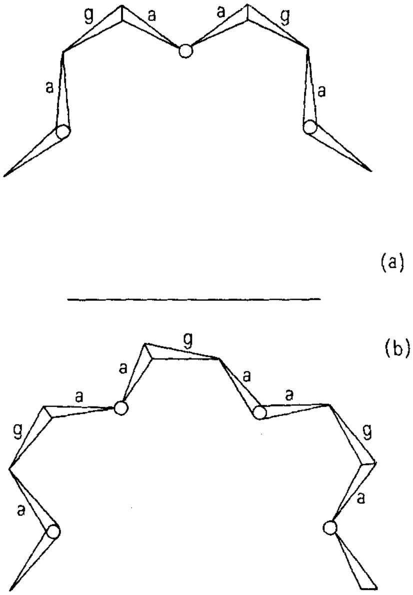
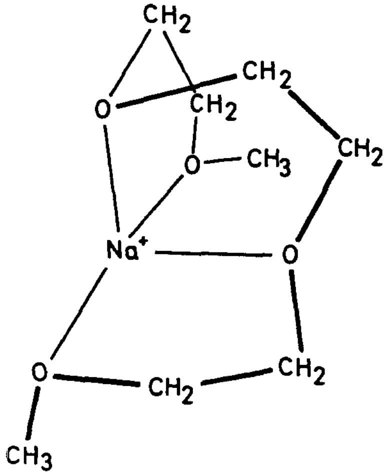


Fig. 3. *Stable conformations for diglyme (a) and triglyme (b)*

angle. Furthermore, in this conformation the central oxygen O(2) is also within bonding distance of $Na^+$, one of its electron pairs 'pointing' in that direction in a manner reminiscent of apical attack, *i.e.* along the normal to the face of the tetrahedron defined by O(1), O(3), and another oxygen atom from the second coordinating molecule.

With triglyme (Fig. 3b), the $(CH_2CH_2O)$ fragments adopt the ideal sequence $ag^+a$, $ag^-a$, $ag^+a$, and the four oxygen atoms are disposed at a bonding distance, approximately 2.5 Å [16], from the sodium cation. From the recent X-ray study of *Dunitz et al.* [16], sodium-oxygen distances of 2.452, 2.474, 2.550, 2.576, 2.624 and 2.623 Å are measured in the $NaNCS.H_2O$ complex of a cyclic hexa-ether. The conformation of Fig. 3b resembles markedly half of that established for this hexa-ether complex [16]. However, for geometrical reasons, it would be impossible conversely for a *single* triglyme molecule to complex the $Na^+$ cation while maintaining tetrahedral coordination (*Scheme 8*). It would force all four of the $Na^+$–O bonds into the same half-sphere, with considerable strain. Once the entropy price of coordinating a second triglyme molecule is paid, *viz.* a (9 $kcal.mol^{-1}$)-equivalent, then the $Na^+$ cation achieves effective octacoordination (Fig. 3b). From this argument, we can put a lower limit of 5 $kcal.mol^{-1}$ on the strength of each $Na^+$–O bond in triglyme; we know however that the true value is significantly higher, close to a $\Delta H°$ of $-16$ $kcal.mol^{-1}$ [15].

*Scheme 8*



## REFERENCES

[1] *E. G. Bloor & R. G. Kidd*, Canad. J. Chemistry *46*, 3425 (1968).

[2] *R. H. Erlich, E. Roach & A. I. Popov*, J. Amer. chem. Soc. *92*, 4989 (1970); *R. H. Erlich & A. I. Popov*, J. Amer. chem. Soc. *93*, 5640 (1971).

[3] *V. Guttmann & U. Mayer*, 'Structure and Bonding', Springer-Verlag, Berlin 1972, vol. 12, p. 113.

[4] 'Ions and Ion Pairs in Organic Reactions', M. Szwarc, ed. Wiley-Interscience, New York 1972.

[5] *C. Detellier & P. Laszlo,* Bull. Soc. chim. Belges *84,* 1081 (1975).
[6] *M. S. Greenberg, R. L. Bodner & A. I. Popov,* J. phys. Chemistry *77,* 2449 (1973).
[7] *R. H. Erlich, M. S. Greenberg & A. I. Popov,* Spectrochim. Acta *29A,* 543 (1973); *M. S. Greenberg & A. I. Popov,* Spectrochim. Acta *31A,* 697 (1975).
[8] *A. K. Covington, T. H. Lilley, K. E. Newman & G. A. Porthouse,* J. chem. Soc. Faraday I *69,* 963 (1973); *A. K. Covington, K. E. Newman & T. H. Lilley,* J. chem. Soc. Faraday I *69,* 973 (1973); *A. K. Covington, I. R. Lantzke & J. M. Thain,* J. chem. Soc. Faraday Trans. I, *1974,* 1869; *A. K. Covington & J. M. Thain,* J. chem. Soc. Faraday Trans. I, *1974,* 1879.
[9] *A. L. Van Geet,* J. Amer. chem. Soc. *94,* 5583 (1972).
[10] *C. Detellier,* Thèse de Doctorat, Université de Liège 1976.
[11] *W. Simon, W. E. Morf & P. Ch. Meier,* 'Structure and Bonding', Springer-Verlag, Berlin 1973, vol. 16, p. 113.
[12] *A. T. Tsatsas, R. W. Stearns & W. M. Risey,* J. Amer. chem. Soc. *94,* 5247 (1972).
[13] *F. A. Cotton & G. Wilkinson,* 'Advanced Inorganic Chemistry', 3rd Edition, Wiley, New York 1972 p. 646.
[14] *W. E. Morf & W. Simon,* Helv. *54,* 2683 (1971); *W. E. Morf,* Ph. D. Thesis, E.T.H. Zürich 1972, p. 48; *S. Goldman & R. G. Bates,* J. Amer. chem. Soc. *94,* 1476 (1972).
[15] *P. Laszlo,* 'Leçons de Chimie', Hermann, Paris 1974, vol. 2, p. 87.
[16] *M. Dobler, J. D. Dunitz & P. Seiler,* Acta crystallogr. *B30,* 2741 (1974).
[17] *H. Kistenmacher, H. Popkie & E. Clementi,* J. chem. Physics *61,* 799 (1974).
[18] *C. A. Melendres & H. G. Hertz,* J. chem. Physics *61,* 4156 (1974).
[19] *R. J. Gillespie,* 'Molecular Geometry', Van Nostrand-Reinhold, London 1972.
[20] *L. S. Frankle, C. H. Langford & T. R. Stengle,* J. phys. Chemistry *74,* 1376 (1970).
[21] *E. S. Amis,* 'Solutions and Solubilities', I-3, M.R.J. Dack, Ed., Techniques of Chemistry (A. Weissberger, Ed.), vol. III, Wiley, New York 1975; *J. W. Akitt,* J. chem. Soc., Dalton *1973,* 42; *A. K. Covington, K. E. Newman & M. Wood,* J. chem. Soc., Chem. Commun. *1972,* 1234; *J. F. Vogrin & E. R. Malinowski,* J. Amer. chem. Soc. *97,* 4876 (1975).
[22] *J. J. Delpuech, M. R. Khaddar, A. A. Péguy & P. R. Rubini,* J. Amer. chem. Soc. *97,* 3373 (1975).
[23] *A. E. Martell,* 'Advances in Chemistry Series no. 62', American Chemical Society, Washington D.C. 1967, p. 272.
[24] *D. K. Cabiness & D. W. Margerum,* J. Amer. chem. Soc. *91,* 6540 (1969); *D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati & N. Tokel,* 'Advances in Chemistry Series no. 100', American Chemical Society, Washington D.C. 1971, p. 44; *R. W. Izatt, D. J. Eatouch & J. J. Christensen,* 'Structure and Bonding', Springer-Verlag, Berlin, 1973 vol. 16, p. 161; *P. Paoletti, L. Fabrizzi & R. Barbucci,* Inorg. Chemistry *12,* 1961 (1973); Inorg. chim. Acta Rev. *7,* 43 (1973); *F. P. Hinz & D. W. Margerum,* J. Amer. chem. Soc. *96,* 4993 (1974); *A. Dei & R. Gori,* Inorg. chim. Acta *14,* 157 (1975); *T. E. Jones, L. L. Zimmer, L. L. Diaddario, D. B. Rorabacher & L. A. Ochrymowycz,* J. Amer. chem. Soc. *97,* 7163 (1975).
[25] *F. Kohler* 'The Liquid State', Verlag-Chemie GmbH, Weinheim/Bergstr. 1972, pp. 222–224.
[26] *M. I. Page,* Chem. Soc. Rev. *2,* 295 (1973).
[27] *M. C. R. Symons,* Spectrochim. Acta *31A,* 1105 (1975); see also *I. D. Kuntz & C. J. Cheng,* J. Amer. chem. Soc. *97,* 4852 (1975).
[28] *G. R. Hedwig, D. A. Owensby & A. J. Parker,* J. Amer. chem. Soc. *97,* 3888 (1975).
[29] *J. Dale,* Tetrahedron *30,* 1683 (1974).