Isotopic Shifts in Chemical Exchange Systems. 1. Large Isotope Effects in the Complexation of Na^+ Isotopes by Macrocyclic Polyethers

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Abstract: The complexation of $^{24}Na^+$ and $^{22}Na^+$ by 18 of the most widely used macrocyclic polyethers (crown ethers and monocyclic and bicyclic aminopolyethers) has been investigated in view of possible equilibrium isotope shifts. Solvated salts and polyether complexes were distributed differently into two phases and isotope ratios determined in both phases. Chloroform/water systems were shown to be particularly suitable to the investigations allowing favorable distribution for Na^+ and 13 of the 18 polyethers employed. With crown ethers $^{24}Na^+$ enrichment varied from nonsignificant values (for large crown ethers) up to 3.1 ± 0.4% (18-crown-6). In the case of bicyclic aminopolyethers, ligands with cages of optimum size to accommodate Na^+ showed $^{24}Na^+$ enrichment between O (nonsignificant) $(2.2._B2._B)$ and 5.2 ± 1.8% (2.2.1). In contrast, for 2.2.2. and its derivatives, being too large for Na^+, $^{22}Na^+$ enrichment varying from O (nonsignificant) $(2.2.2._D)$ up to 5.4 ± 0.5% (2.2.2.) has been observed. These values are remarkably high. They are explained by different bonding in solvate structure and polyether complex by using the theoretical approach of Bigeleisen.

Differences in the behavior of isotopic atoms and of molecules of varying isotopic composition that are caused by differences in the mass of the isotopes are generally referred to as "isotope effects". If one considers only chemical systems, then the different nuclear mass of the isotopic atoms and molecules affects the position of the thermodynamic equilibria (equilibrium isotope effects) and the rate of chemical reactions (kinetic isotope effects). It is important to bear in mind that these are nonclassical effects, i.e., they must be explained on the basis of quantum theory.[1,2]

1. Equilibrium Isotope Effects. The numerical computation of equilibrium isotope effects, like that of all thermodynamic functions and constants of matter, belongs to the realm of statistical thermodynamics.

The simplest possible starting point for statistical investigations is given by the partition function which, for the molecule, is defined by eq 1,[3] where E_l is the total energy of the molecule in a particular state, i.e., an eigenvalue of the molecular Schrödinger equation, and l is a set of quantum numbers defining the state; k is Boltzmann's constant and T the (absolute) temperature. The summation is over all quantum mechanically allowed molecular states. Equilibrium isotope effects are characterized by the equilibrium constant of isotope-exchange reactions.

$$Q = \sum_l e^{-E_l/kT} \tag{1}$$

$$n^1\mathrm{AX} + m^2\mathrm{AY} \rightleftarrows n^2\mathrm{AX} + m^1\mathrm{AY} \tag{2}$$

One has

$$K = \frac{[Q(^2\mathrm{AX})]^n[Q(^1\mathrm{AY})]^m}{[Q(^1\mathrm{AX})]^n[Q(^2\mathrm{AY})]^m} = \left[\frac{Q(^2\mathrm{AX})}{Q(^1\mathrm{AX})}\right]^n \Big/ \left[\frac{Q(^2\mathrm{AY})}{Q(^1\mathrm{AY})}\right]^m \tag{3}$$

In the case of two nonlinear molecules containing n atoms of arbitrary isotopic composition without internal rotators the partition ratio Q_2/Q_1 is given by eq 4[3] with M_1 = sum of mass of the lighter molecule, M_2 = sum of mass of the heavier molecule, I_{a1} = main moment(s) of inertia of the lighter molecule, I_{a2} = main moment(s) of inertia of the heavier molecule, S_1 = symmetry number of the lighter molecule, S_2 = symmetry number of the heavier molecule, $u_i = ((\mathrm{h\ c})/kT)\omega_i$ and ω = wavenumber. From eq 4 we can get by taking into account the product rule of Teller and Redlich, by neglecting the translational and rotational partition function, and by using the simplifications that the difference between u_{1i} and u_{2i} is small, which is justified in practice for all systems except hydrogen and u is small at room temperature and higher temperatures eq 5 according to Bigeleisen[5] with $f = Q'_2/Q'_1$,

$$\frac{Q_2}{Q_1} = \left(\frac{M_2}{M_1}\right)^{3/2}\left(\frac{I_{a2}I_{b2}I_{c2}}{I_{a1}I_{b1}I_{c1}}\right)^{1/2}\frac{S_1}{S_2}\prod_{i=1}^{3n-6}\frac{e^{-u_{2i}/2}}{e^{-u_{1i}/2}}\frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \tag{4}$$

$$\ln\left(\frac{S_2}{S_1}\right)f = \frac{1}{24}\left(\frac{h}{kT}\right)^2\sum_{i=1}^{3n-6}(1/m_{1i} - 1/m_{2i})a_{ii} \tag{5}$$

$Q' = Q/\prod_{k=1}^{n} m_k^{3/2}$, m_{1i} = mass of the lighter isotope, m_{2i} = mass of the heavier isotope, and a_{ii} = force constant for the motion of this atom (in Cartesian coordinates). From eq 7 and 10 V one deduces to a first approximation the following rules governing equilibrium isotope effects. (1) Isotope effects are only observed if there is a change in the force constants of the bonds while their character is retained between the isotope and the rest of the molecule. (2) Since by definition $m_{1i} < m_{2i}$, $(S_2/S_1)f > 1$. This means that the heavier isotope prefers that bond formation which has the larger vibrational function and consequently the lighter isotope is connected with the smaller Q_v. (3) Isotope effects of the different degrees of freedom are additive. (4) For molecules containing the same elements and similar structure a pair of larger isotopic molecules possesses a greater number of degrees of freedom of vibration and therefore a larger reduced partition ratio than an analogous pair of smaller isotopic molecules. One has, e.g., for the ions SO_3^{2-} and SO_4^{2-} at T = 273.15 K[6]

$$\frac{S_2}{S_1}f\left(\frac{^{34}SO_3^{2-}}{^{32}XO_3^{2-}}\right) = 1.096 \tag{6}$$

$$\frac{S_2}{S_1}f\left(\frac{^{34}SO_4^{2-}}{^{32}SO_4^{2-}}\right) = 1.101 \tag{7}$$

(5) From the definition of $u_1 = hC(\omega_i/k)T$ it follows for all pairs of isotopic molecules

$$\lim_{T\to\infty}\frac{S_2}{S_1}f = 1$$

(1) Waldmann, L. *Naturwissenschaften* **1943**, *31*, 205.
(2) Bigeleisen, J.; Goeppert Mayer, M. *J. Chem. Phys.* **1947**, *15*, 261.
(3) Roginski, S. S. "Theoretische Grundlagen der Isotopenchemie"; VEB Deutscher Verlag der Wissenschaftaen: Berlin, **1962**.
(4) Redlich, O. *Z. Phys. Chem., Abt. B* **1935**, *28*, 371.
(5) Bigeleisen, J. Lee, J. W.; Mandel, R. *Annu. Rev. Phys. Chem.* **1973**, *24*, 407 (1973).
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Consequently there are no isotope effects at high temperatures.

2. Determination of Equilibrium Isotope Effects in Two-Phase Mixtures. The present investigation considers equilibrium isotope effects between the solvate structure of isotopic cations and their complexes with macrocyclic polyethers.

$$^1A^+ + L \rightleftarrows {}^1AL^+ \qquad (8)$$
$$^2A^+ + L \rightleftarrows {}^2AL^+$$

In order to calculate the quotient of the equilibrium constants of the complexation reactions, one needs to know the concentrations of the individual species in solution of the various isotopes. Since this is difficult to obtain by direct measurement of the concentrations, an indirect determination is preferred in which the species are distributed between two suitable phases with different distribution coefficients. The relevant equilibrium can then be characterized by the separation factor, defined as the quotient of the isotope ratios in the two phases.[7]

Separation factor

$$SF = (^1A/^2A)_{\text{phase I}}/(^1A/^2A)_{\text{phase II}} \qquad (9)$$

The relation between isotope effects and separation factor can be derived from other measurable quantities.

One defines as the quotient of the total cation concentration in the two phases

$$K_{sum} = \frac{[A^+]_{\text{phase I}} + [AL^+]_{\text{phase I}}}{[A^+]_{\text{phase II}} + [AL^+]_{\text{phase II}}} \qquad (10)$$

Considering furthermore the complexation equilibrium constant of phase I

$$K_i = \frac{[AL^+]_i}{[A^+]_I[L]_I} \qquad (11)$$

and the equilibrium constant of the distribution of the complexes between the phases

$$K_{compl} = \frac{[AL^+]_I}{[AL^+]_{II}} \qquad (12)$$

one obtains from eq 10

$$K_{sum} = \frac{K_{compl} + K_{compl}K_I[L]_I}{K_I[L]_I} \qquad (13)$$

with the assumption that the concentration of the cation in phase II is negligible. When we solve for the stability constant

$$K_I = \frac{K_{compl}}{K_{sum}[L]_I - K_{compl}[L]_I} \qquad (14)$$

the ratio of the equilibrium constants of isotopes ^1A and ^2A becomes

$$\alpha = \frac{K_{I^1A}}{K_{I^2A}} = \frac{K_{compl\,{}^1A}}{(K_{sum\,{}^1A} - K_{compl\,{}^1A})} \frac{(K_{sum^2A} - K_{compl\,{}^1A})}{K_{compl\,{}^2A}} \qquad (15)$$

One does not expect an isotope effect of the cation complex in the distribution between the phases.

$$K_{compl\,{}^1A} = K_{compl^2A} = K_{compl} \qquad (16)$$

Equation 15 can then be simplified

$$\alpha = \frac{K_{sum\,{}^1A} - K_{compl}}{K_{sum\,{}^2A} - K_{compl}} \qquad (17)$$

In order to compute the isotope effect from the measurable quantity K_{sum}, one needs to know the distribution coefficient K_{compl} for the complexed cation. Equation 17 also shows that in the computation of the isotope effect the relative magnitude of the distribution coefficient and K_{sum} play an important role. α will be greater the more similar the two quantities become.

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3. The Properties of Macrocyclic Polyethers with regard to Isotope Effects in Complex Formation. This paper investigates possible isotopic shifts in the complexation of sodium isotopes by macrocyclic polyethers. These and similar aminopolyethers have found widespread interest since their introduction through the work of Pedersen[8] and Lehn,[9] and the results have been published in several papers.[10,11] One of their most remarkable properties is the capability to complex alkali and alkaline-earth ions. The complexation consists of two simultaneous processes:[12-14] a more or less complete removal of the solvate sphere of the cation and conformational changes in the ligand. By stepwise formation of polar–dipolar interactions the cation is pulled into the inner cavity of the ligand. In the final complexed state the macrocycle has undergone such conformational changes as to provide a circular envelope around the cation, and the dipoles of the donor atoms are directed toward the central charge.

Due to the conformational lability of the complex and the relative weakness of the individual polar–dipolar interactions, which only by multiple interactions lead to the high (thermodynamic) stability, decomplexation is easily achieved. The complexation processes take place in reverse, but more slowly, so that decomplexation of the cation becomes rate determining.[13]

In essence, complexation while the fundamental bonding scheme is retained leads to bond modifications that affect the vibrational energy levels of the cation. The coordination number is lower than in the solvate complex. The donor atoms are bridged by ethylene units that are more or less flexible and thus impose structural constraints. In the resultant cage the cation is fixed but able to vibrate. In comparison with the cation vibrations the ligand cage is flexible and under suitable conditions is able to resonate. When donors other than oxygen (e.g., nitrogen) are incorporated, a different, but related, bonding scheme is conferred to the cation.

The nature of these bonds and their combined effect in a macrocycle suggest the presence of a larger number of vibrational degrees of freedom in macrocycle complexes which should therefore be particularly suitable for the detection of isotope effects. Due to the aforementioned kinetics of exchange it is permissable to assume equilibrium to be established.

The variety of monocyclic and polycyclic polyethers and aminopolyethers leads itself to a wide range of investigations on isotope effects. A systematic study should allow general statements about the influence of various bonding situations involving isotopic ionic nuclides in hydrated and complexed forms.

Thus far only a few results in this direction have been reported. Jepson and DeWitt in their study of the calcium isotopes $^{40}Ca/^{44}Ca$ with dicyclohexano-18-crown-6 (named according to ref 10 and 11) found the effect to be 1.004.[15] Heumann and Schiefer observed a shift of 1.005 for the ratio $^{44}Ca/^{40}Ca$ on elution of matrix-bound aminopolyether 2.2.2. with $CH_3OH/CHCl_3/H_2O$.[16] Very recently they reported an effect of 1.007 in the extraction system with 2.2.2. in $CHCl_3$.[17] The present study deals with the occurrence of isotope effects in the complexes of sodium with the most common macrocyclic polyethers and aminopolyethers. The choice of sodium as cation was suggested by its ability to form well-defined complexes with practically all polyethers.

Experimental Section

The aminopolyethers were obtained from E. Merck, Darmstadt, 15-crown-5, 18-crown-6 from Fluka, Buchs, and 21-crown-7 and dicyclohexano-24-crown-8 from Parish. They were all used without further purification.

Our investigation employed the radioactive sodium isotope ^{22}Na ($t_{1/2}$ = 2.602 a; γ = 1274.5 KeV) and ^{24}Na ($t_{1/2}$ = 15.0 h; γ = 1368.6, 2754.1,

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(13) Cox, B. G.; Schneider, H.; Stroka, J. *J. Am. Chem. Soc.* **1978**, *100*, 4746.
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(15) Jepson, B. E.; DeWitt, R. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1175.
(16) Heumann, K. G.; Schiefer, H. P. *Angew. Chem.* **1980**, *92*, 406.
(17) Schiefer, H. P. Dissertation, Regensburg, **1979**.

Table I. Main Sources of Error on the Separation Factors

sources of error	tolerable error in 1:100, to hold the overall error 1:100	remarks
pipetting, weighing	30	all volumes were weighed; not decisive, because the ratio of the isotopes counts and not the specific activity
drift of the measuring system	5.3	was held by a stabilizer 1:100
time correction for the ^{24}Na determination	38	was held 2:100 by an integrated chronometer system
determination of the background	33	was held under 2:100 by long-time determination
first measuring of the activity of the starting solution (^{22}Na and ^{24}Na)	0.32	was achieved by measuring 5×10^5 counts
second measuring of the starting solution (^{22}Na	0.32	was achieved by measuring 5×10^5 counts
first measuring of the activity of the treated sample (^{22}Na and ^{24}Na)	0.084	was achieved by measuring 1.2×10^6 counts
second measuring of the activity of the treated sample (^{22}Na)	0.086	was achieved by measuring 1.2×10^6 counts

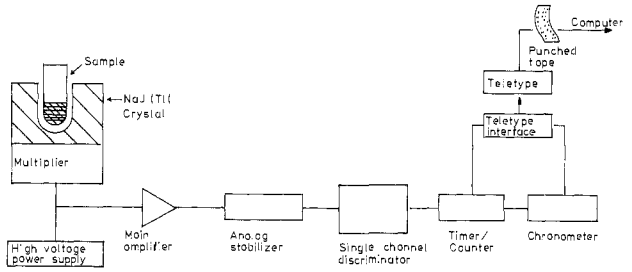

Figure 1. Measuring system.

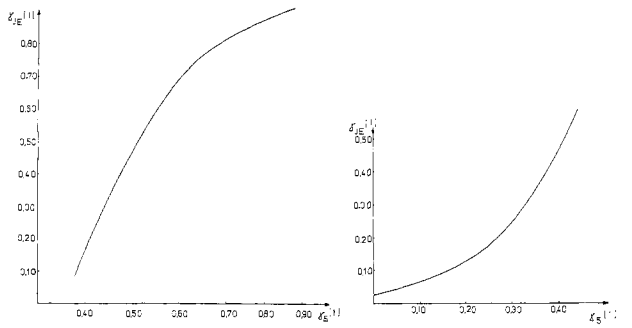

Figure 2. 2.2.1. distribution in aquesou solution (left) and Na^+ distribution in aqueous solution (right).

3850, 4230 KeV). They were measured by a high precision measuring system with a well-typed scintillation detector by the γ-rays of the nuclides by utilizing their different half-lives.

The first two-phase system investigated consisted of the cation exchanger, Dowex HCR-W, and an aqueous solution, and the sodium isotopes were allowed to equilibrate between the two phases in the presence of various polyethers.

Determination of complex formation constants according to the method of Schubert and Fronaeus[18] is possible only if the cation exchanger exclusively or at least preferentially takes up uncomplexed cations. In our case the equivalent part of the polyether 2.2.1 (^{14}C labeled) on the exchange resin ($\pm_{IE}$) is plotted (Figure 2) against the equivalent part in solution (γ_S). The equivalent part is defined as $\gamma_A = Z_A m_A/(Z_A m_A + Z_B m_B)$ with Z = electrochemical valence, m = molarity, and A and B = phase A and B, respectively. As the figure shows the above-mentioned condition is not fulfilled and the complex rather than the ^{24}Na cation binds to the exchanger. Consequently, this system is not suited for our investigations. However, the graph suggests a possible means of regenerating and purifying aminopolyethers through adsorption on cation exchangers and this is being further pursued.[19]

A suitable system has been found in the two-phase water/chloroform system. Here the conditions of only slight miscibility and preferential solubility of the complex in one of the phases are met satisfactorily. One can then determine separation factors according to eq 14.

Figure 3 shows the general work routine in these investigations. All quantities that might possibly influence the accuracy of the results have been carefully checked. The main sources of error are listed in Table I and their influence on the separation factor is also given.

As can be seen, the most serious source of error is contained in the determination of starting (standard) and sample activities where sample activities must be accurate at the 1:1000 level to allow significant conclusions at the 1:100 level. This puts high demands on measuring techniques which were achieved by a single channel measuring system with very high precision (see Figure 1) and electronic stabilizers for, in particular, spectrum amplification.

Possible long-term instability of the measuring apparatus was monitored by repeated measurement of reference samples of known activity and the results were corrected for these effects. Data evaluation was done by using a specifically designed computer program, and calculations were carried out on TR440 computer at the university computing center. Statistical tests were incorporated into the program to obtain criteria for significance [t test, Nalimov test, χ^2 test].

Experimental monitoring of measuring technique, experiment, and evaluation showed separation factor = 0.9970 ± 0.0081 in good agreement with the expected value of 1.0000.

The distribution of Na^+ between the phases is shown in Table II for various poly- and aminopolyethers. All data are for Na^+ and polyether concentrations of 0.1 mmol and 10 mmol of tetraethylammoniumchloride at pH ≥8. There are two classes of polyethers not suitable for the detection of isotope effects: Ligands with very large distribution coefficients, complexes of which are only sparingly soluble in the organic

Table II. Distribution of Na^+ between the Phases

polyether	K_{sum} [H_2O/$CHCl_3$, g/g]	polyether	K_{sum} [H_2O/$CHCl_3$, g/g]
2.2.1.	1.7	dicyclohexano-18-crown-6	100
2.2.2.	49	18-crown-6	7000
2.1.1.	230	15-crown-6	17200
$2.2.2._B$	60	dicyclohexano-24-crown-6	40000
$2.2._B2._B$	62	21-crown-7	61500
$2.2.2._D$	320		

Table III. Separation Factors (SF) of Crown Ethers [SF = ($^{24}Na/^{22}Na$) in Chloroform/($^{24}Na/^{22}Na$) in Water]

crown ether	SF	SD[a]		Na^+ complex stability constant (log K_B)
21-crown-7	1.066	0.056	(68%, 8)	unknown
18-crown-6	1.031	0.004	(68%, 7)	0.3
dicyclohexano-18-crown-6	1.007	0.011	(68%, 14)	1.6
dicyclohexano-24-crown-8	1.005	0.025	(68%, 7)	unknown
15-crown-5	0.976	0.027	(68%, 7)	0.3

[a] SD = standard deviation.

(18) Schubert, J.; Fronaeus, St. *J. Phys. Colloid. Chem.* **1948**, *52*, 340.
(19) Shih, J. S.; Lin, L.; Popov, A. I.; *J. Inorg. Nucl. Chem.* **1977**, *3*., 552.

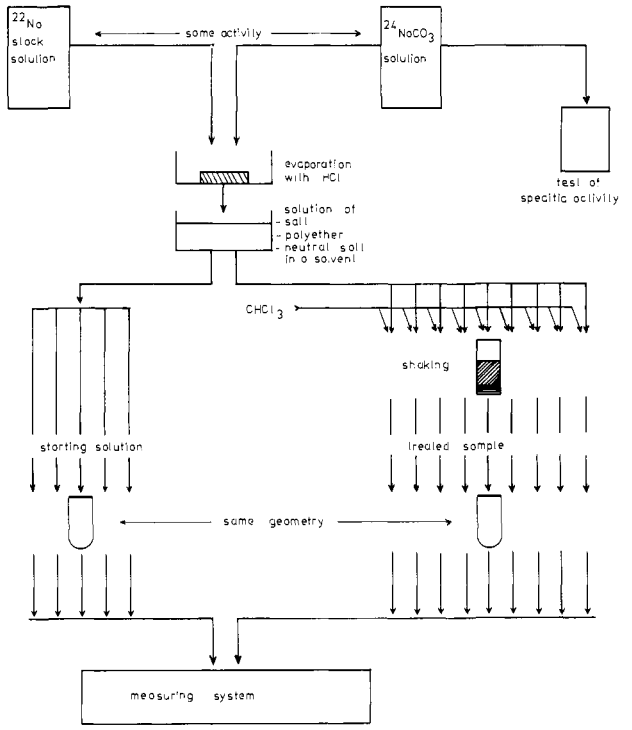

Figure 3. General work routine.

Table IV. Separation Factors (SF) of Aminopolyethers [SF = (^{24}Na/^{22}Na) in chloroform/(^{24}Na/^{22}Na) in water]

amino-polyether	SF	SD[a]	cavity size, pm	Na^+ complex stability constant ($\log K_s$)
2.2.1.	1.052	0.018 (68%, 21)	220	5.4
2.2.2.$_B$	1.030	0.004 (68%, 12)	unknown	4.0
2.2.1.	1.03	0.022 (68%, 7)	160	2.8
2.2.$_B$2.$_B$	1.0025	0.015 (68%, 5)	unknown	3.3
2.2.2.$_D$	0.989	0.021 (68%, 8)	unknown	unknown
2.2.2.	0.946	0.005 (68%, 14)	280	3.9

[a] SD = standard deviation.

phase (e.g., dicyclohexano-18-crown-6); ligands forming emulsions, these include all monocylic aminopolyethers. Attainment of equilibrium between the phases was determined by measuring the distribution of Na-activity and of ^{14}C-labeled aminopolyethers. In all cases equilibrium was established in less than 60 min.

Results and Discussion

Table III shows the separation factors in $CHCl_3/H_2O$ for various crown ethers as compared with the stability constants of the sodium complexes[10,11] in water. In most cases isotopic shifts are in the direction of the heavier isotope ^{24}Na. When standard errors are neglected, the effect decreases in the order 21-crown-7, 18-crown-6, dicyclohexano-18-crown-6, and dicyclohexano-24-crown-8. The lighter isotope $^{22}Na^+$ is, however, found to be enriched in 15-crown-5, but the significance of these data is hampered by the statistics of radiometric measurement, since accuracy decreases with decreasing concentration of Na^+ in the chloroform phase. If one takes into account the varying spreads of error, the best one can infer from the observed order is that there appears to be a correlation between the direction of the effect and decreasing ring size and number of oxygen donors in the macrocyclic system.

The results for the analogous determination of separation factors for bicyclic aminopolyethers are shown in Table IV. For comparison we also list the corresponding stability constants of their Na complexes[10,11] in water and the diameter of the ligand cage.[10,11] Remarkably high isotopic shifts are in some cases found and are in either direction. The reversal of the effect in going from 2.2.1.

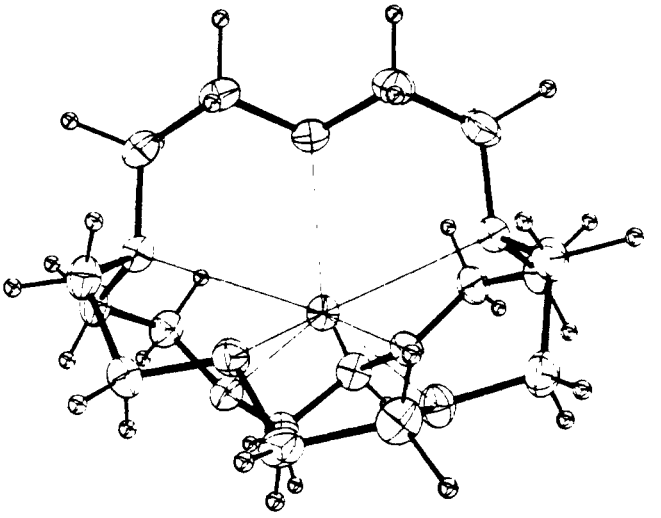

Figure 4. X-ray structure of $[Na^+\subset 2.2.1.]^+SCN^-$.

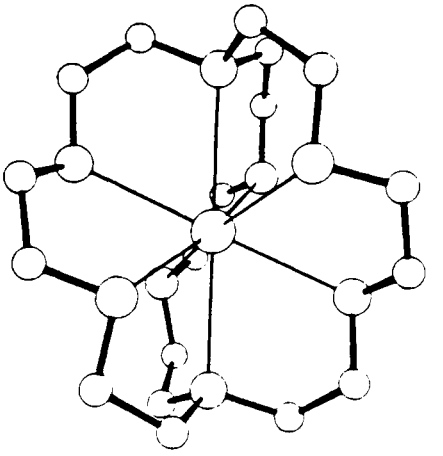

Figure 5. X-ray structure of $[Na^+\subset 2.2.2.]^+SCN^-$.

to the larger 2.2.2. appears to be particularly striking. Na^+ (d = 204 pm)[20] has optimal size for the cage of 2.2.1., consequently its complex is the most stable. On the other hand, it is too small for 2.2.2., the latter cage being optimal for K^+. Attachment of benzene rings decreases the effective volume of the cage, and the ligand structure becomes more rigid. These conditions are again more favorable for complexing of sodium as evidenced by stability constants. Even in the uncomplexed 2.2.1. the cage appears to be too small for Na^+, but changes in the ligand structure make incorporation possible and ^{24}Na is preferentially bound in 2.2.1., 2.2.2.$_B$, 2.1.1., and 2.2.$_B$2.$_B$, the effect decreasing in this order. In contrast, enrichment of the lighter isotope is observed for the ligands 2.2.2. and 2.2.2.$_D$ that are too large for Na^+.

The results thus obtained support our earlier assumption that macrocyclic polyethers and aminopolyethers are systems particularly sensitive to isotopic shifts. This had also been evident from the 1972 work of Raede and Wagener which showed an isotopic shift toward $^{24}Na^+$ in the complexation with the macrocyclic antibiotic monactin.[21]

Beyond the magnitude of the effects the most surprising result appears to lie in the reversal on going from 2.2.1. to 2.2.2.; in the meantime this has also been demonstrated by Heumann and Schiefer in the case of Ca isotopes employing mass spectrometric techniques.[17] In order to explain these effects, one has to go beyond the simple match of cation/ligand size referred to above.[22,23] From

(20) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *25*, 925.
(21) Wagener, K.; Raede, H. S. *Radiochem. Acta* **1972**, *18*, 141.
(22) Myers, Th. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 329.
(23) Lamb, J. D.; Izatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 475.

the X-ray crystal structures of the sodium complexes of 2.2.1.[24] and 2.2.2.[25] it can be seen that in the 2.2.1. complex Na^+ is unsymmetrically located in the cage with other oxygens at 249.1, 249.9, 245.1, 251.9, and 244.6 pm and in 2.2.2. on the other hand, Na^+ is symmetrically surrounded by oxygen atoms, but distances are ca. 10 pm larger than in 2.2.1.

In both complexes the sodium ion at the center of an extended system possesses a large number of vibrational degrees of freedom which is further enhanced by the flexibility of the ligand. The fundamental bonding pattern is the same as in the solvate structure. The macrocyclic effect of the ligand does, however, lead to a higher degree of order, which opens up additional vibrational modes that are variable with regard to the ligand topology. Evidently then, macrocyclic polyethers are systems which are particularly sensitive to change in mass and which may even show resonance effects with masses of certain magnitudes. More specifically (1) in the Na^+ complex of 2.2.1. the sum of the vibrational partition functions is larger than that of the solvate complex (accordingly (see Equilibrium Isotope Effects) enriched in the polyether complex), (2) the 2.2.2. complex with sodium shows longer lengths between Na^+ and ether oxygens and thereby seriously alters the vibrational system so that compared with the solvate system the vibrational partition function is smaller and the lighter isotope preferentially bound), (3) attachment of nonrigid substituents, as, e.g., dodecyl groups, enhances ligand flexibility and the number of vibrational modes are increased for the cation, leading to decreased ^{22}Na enrichment, and (4) introduction of benzene rings into one or more ethylene bridges gives increased rigidity of the ligand and decreased cage volume.

As a consequence, the complex of Na^+ with $2.2.2_B$. becomes more stable than that with 2.2.2. and bonding is more like that in the complex with 2.2.1.. On the other hand, the complex as a whole is more rigid due to incorporation of a benzene nucleus and its vibrational partition function is less than in Na^+ 2.2.1.. However, the latter is larger than in the solvate complex, as shown by the $^{24}Na^+$ enrichment of 3.0 ± 0.4%. Further incorporation of benzene rings leads to more pronounced rigidity and there is no significant separation factor observed for $2.2_B.2_B$..

It is now possible to interpret the results found by Lee and Begun[26] for lithium isotopes on cation exchangers in which isotopic shifts depended on cross-linking of the exchanger, effects becoming larger with higher cross-linking. This can be explained by the different degrees of hydration of lithium cations on the exchanger which depends on the cross-linking. In the case of the hydrated systems more ordered structures can be formed, affecting the number of vibrational modes and the resultant partition function.

While these considerations allow qualitative predictions based on the work of Bigeleisen (eq 5) necessitate the exact analysis and characterization of the individual vibrational modes of the complexes. Further experimental work needs to be done to achieve this objective.

Even though these isotope effects involving sodium are only of interest in a theroetical context, their investigation is of more fundamental importance. Present methods of isotopic enrichment allow isotopes of sufficient purity to be obtained, but costs are very often prohibitive due to the smallness of the effects and the consequent expenditure of energy.

Chemical exchange methods are more economical, as, e.g., in the systems H_2O/HDS and HD/H_2O, respectively. However, these chemical systems have shown large isotope effects only in the case of exchange equilibria involving covalently bound nuclides. This is due to ion solvation, which it has not been possible to overcome without severe changes of bonding.

Macrocyclic polyethers now seem to offer the possibility of bonding interactions similar to those in the solvate complex while possessing a larger vibrational partition function that leads to equilibrium isotope effects and sufficiently fast kinetics of exchange, allowing the effects to be attained in finite time.

The use of macrocyclic polyethers or similar substances should therefore enable isotope enrichment by chemical exchange to be extended to ionic products.

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Microwave Spectrum and Unusual Geometry of Propadienone (Methylene Ketene)

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Abstract: The microwave spectra of several isotopic species of propadienone, $CH_2{=}C{=}C{=}O$, have been analyzed to elucidate the geometry of this somewhat peculiar molecule. The heavy chain of atoms is found to be bent at the middle carbon by approximately 26° from the linear configuration. The nonlinearity is confirmed by the identification of cis and trans forms of monodeuteriopropadienone, by the lack of intensity alternation in the spectral lines, and by a substantial perpendicular component of the dipole moment [μ_b = 0.7914 (6) D; μ_a = 2.156 (3) D; μ_{total} = 2.297 (3) D]. Both the geometry and the dipole moment are at variance with recent results of elaborate molecular orbital calculations.

The microwave spectrum of propadienone (H_2C_3O) was first observed in these laboratories as a means of demonstrating unambiguously the generation of the compound by flash vacuum pyrolysis.[1] The analysis of the spectra of H_2C_3O, HDC_3O, and D_2C_3O implied that the molecule was probably planar.[2] However the moments of inertia suggested the presence of in-plane distortion or large-amplitude vibration and that the molecule is not a simple relative of formaldehyde and ketene. This structural uncertainty has been resolved from a more extensive study of the rotational spectra of some isotopic species of propadienone. We present here

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