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FAST ATOM BOMBARDMENT OF CROWN ETHER/CATION COMPLEXES IN SOLUTION

INFERENCES ON MECHANISMS OF ENERGY TRANSFER

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Abstract—Mechanisms of energy transfer leading to the mass spectrometric detection of ionized species during fast atom bombardment are discussed. These mechanisms may be of an equilibrium or non-equilibrium nature but consideration of either mechanism suggests that the observed mass spectral peak heights for desorbed ionic species should be proportional to the concentrations of these species in solution. Solutions of crown-ethers with added metallic salts provide a means for testing this deduction. Under fast atom bombardment, a wide range of metal ions has been found to desorb as crown ether/cations and the technique affords a sensitive means of detecting metal ions in solution. The variation in concentration of a crown ether/cation complex in solution at normal temperatures with different molar ratios of crown ether to added metal salt is reflected accurately by the accompanying changes in mass spectral peak heights of the crown ether/cations. From the mass spectral data, it seems possible that quantitative determination of crown ether/metal salt stability constants can be effected simply. Methods for extracting such information are discussed.

Bombardment of substances on a surface with fast atoms results in ionized species being desorbed.[1,2] This ionization method is of fast-increasing importance in mass spectrometry and has been compared to other methods (laser desorption, ^{252}Cf-recoil, secondary ion emission and "in-beam" ionization)[3] in which it is believed that the incoming particle or packet of energy loses its energy through a collisional cascade process with a substrate. Rapid deposition of this energy leads to fast, localized heating under non-equilibrium conditions so that sufficient translational energy can be taken up leading to desorption of ions before sufficient vibrational energy can be absorbed to cause thermal decomposition. The partition of this transferred energy into various states (rotational, vibrational, electronic, translational) which results in the ejection of an ionized species has not been discussed. In work designed to use crown ethers to analyse for metal ions in solution, we have used fast atom bombardment to examine solutions of metal salts containing various crown ethers such as 18-crown-6. We have found that many metal ions can be vaporized successfully as crown ether/cation complexes by fast atom bombardment. For example, chlorides, acetates, nitrates and iodides of Li, Na, K, Cs, Rb, Cu(II), Co(III), Ni(II), Ce(III), La(III), Hg(II), Tl(I) and Th(IV) (all salts of general formula, $M^{n+}X_n$) yield unipositive ions corresponding to $[C + M + X_{n-1}]^+$, where C represents the crown-ether. This analytical aspect of the work will be described elsewhere. It is noteworthy that these crown ether/cation complexes dissolved in glycerol, under fast atom bombardment conditions, gave spectra of these unipositive ions and, in contrast, no background ions from glycerol could be detected. The crown ether/salt complexes exist as ions in solution and therefore none of the translational energy of the incoming fast atom is required for ionization but is used to overcome interionic (Coulombic) forces and so separate the crown/cation complexes from their counter ions. Similar effects have been observed with laser desorption and the other methods for ionizing molecules which depend essentially on depositing sufficient energy to desorb cationized or anionized species in so short a time that there appears to be little uptake of excess of vibrational energy, as demonstrated by a general lack of fragmentation of even thermally labile molecules. Very often in these methods of "ionization" little or no direct ionization occurs and the desorbed ions are adducts[4] as, for example, in the production of protonated "quasi-molecular" ions, $[M + H]^+$. Indeed, ions may be detected mass spectrometrically simply by heating metal salts to about 700°.[5] We consider here the partition of the kinetic energy transferred from a fast atom to a solution containing a crown ether and a metal salt and then show how the conclusions arising from these considerations may be tested by a comparison of the mass spectra obtained by fast atom bombardment of these solutions with solution phenomena associated with crown ether/cation stability constants.

For a dilute solution of a crown ether/metal salt, a total energy partition function (Q) can be written as in eqn (1) where

$$Q = Q_{tr} \cdot Q_{rot} \cdot Q_{vib} \cdot Q_{el} \cdot Q_{solvent} \quad (1)$$

Q_{tr}, Q_{rot}, Q_{vib} and Q_{el} are individual partition functions for energy appearing in translational, rotational, vibrational and electronic modes of the crown ether/cation complex and $Q_{solvent}$ is a partition function for all of the energy states arising in the solvent. As only dilute solutions are considered then $Q_{solvent}$ can be regarded as constant. For any one crown ether, the partition functions, Q_{rot}, Q_{vib}, Q_{el} can be expected to remain reasonably constant with variation in the complexing metal ion because they derive mostly from rotational, vibrational and electronic modes of the crown ethers.[6] Therefore, for any particular crown ether, the energy partition functions for a series of cation complexes can be separated into two sets as in eqn (2) in which

$$Q = Q_{tr}[Q_{int} \cdot Q_{solvent}] \quad (2)$$

$Q_{int} = Q_{rot} \cdot Q_{vib} \cdot Q_{el}$ and the energy deposited (E) by a fast atom can appear in the various states of the solution according to eqn (3). The energy terms include one for translational energy

$$E = RT^2(d\ln Q/dT) = RT^2(d\ln Q_{tr}/dT) + RT^2(d\ln Q_{int} \cdot Q_{solvent}/dT) \quad (3)$$

and a compound one for the rotational, vibrational, electronic and solvent energies. The total energy available from the translation motion of the fast atom is $1/2\,mv^2$ (= E) where m and v are the mass and velocity of the atom. To a first approximation, *under equilibrium conditions*, the energy available from the translation energy of the fast atom will be shared between the translational, rotational, vibrational and electronic modes of the crown ether/cation complex and similar modes in the solvent according to the partition functions. If the imparted translational energy is sufficient to overcome the attractive electrostatic forces[7] ($z_1z_2e^2/4\pi\epsilon_0 r$) between the crown ether/cation complex and its counter ions, then crown ether/cations can appear in the vapour phase without there being any specific ionization process, i.e. the fast atom induces desorption of existing ions.

For desorption of complexed cations from solution, the expression (4) must be satisfied, i.e. the translational energy

$$RT^2(d\ln Q_{tr}/dT) > z_1z_2e^2/4\,\pi\epsilon_0 r \quad (4)$$

of the crown ether/cation complex must exceed the electrostatic energy between them and their counter ions.[7] For translational energy, $RT^2(d\ln Q_{tr}/dT) = 3/2\,kT$ so that for crown ether/cation complexes to desorb, a localized "temperature" (T) must be created in a small volume around the impacting fast atom. This energy must be sufficient to desorb ions before being dissipated into the bulk of the solution and suggests that only species near or at the solvent surface will be desorbed strongly (further into the bulk of the solvent, excess of translational energy will be dissipated by multiple collisional effects). For crown ether/cation complexes to desorb, expression (5) must hold and inserting values[8] into this

$$\frac{3}{2}kT > z_1z_2e^2/4\pi\epsilon_0 r \quad (5)$$

expression indicates that a localized "temperature" of about 860°K is needed. This estimated minimum "temperature" compares favourably with experimental temperatures needed to desorb ions from a heated filament. For example, Cotter has found[5] that temperatures in the range 973–1273°K are sufficient to desorb quaternary ammonium cations and Stoll found[5] that temperatures of 900°K were sufficient to desorb a benzo-15-crown-5/sodium ion complex. It is assumed in the following discussion that this localized high temperature desorbs the crown ether/cation complexes in so short a time that the bulk solution concentration of crown ether/cation complex is not disturbed. That this assumption is not unreasonable is supported by the results derived below and the fact that, even with complex thermally-labile molecules, fast atom bombardment does not normally give thermally degraded species, i.e. desorbing ions do not appear to be excessively ro-vibrationally excited.

From the Boltzmann distribution, $n_r = (N/Q_{tr})\exp(-E/kT)$, where n_r is the number of ions with sufficient translational energy (E) to desorb and N is the total number of such ions in solution. For two different cations (M_1^+, M_2^+) competing for the same crown ether in solution then, $n_r' = (N'/Q_{tr}')\exp(-E/kT)$ and $n_r'' = (N''/Q_{tr}'')\exp(-E/kT)$. If, for a series of crown ether/cations, $Q_{tr}' = Q_{tr}''$, then $n_R'/n_R'' = N'/N''$, i.e. under conditions of fast atom bombardment, for a series of complexes of various metal ions with any one crown ether, the number of ions desorbed should be proportional to the numbers existing in solution, at the temperature of the bulk of the solution.[9] This conclusion may be expressed mathematically by eqn (6) in which $C_{complex}$ is the concentration

$$C_{complex} = t \cdot p \quad (6)$$

of crown ether/cation complex in solution, p is the peak height observed in the mass spectrum at the m/z value for the crown ether/cation and t is a proportionality constant,[10] termed here the "transfer coefficient". The above treatment indicates that observed mass spectral peak heights are proportional to the concentration of crown ether/cation complexes in solution so that any changes induced intentionally in the solution should be reproduced by corresponding proportional changes in peak heights. This inference affords a means of testing the above treatment, as is shown later. The above treatment has shown that, by considering equilibrium conditions, it may be concluded that fast atom bombardment will desorb ionic species, in proportion to their concentrations in solution, allowing for variations in electrostatic energies between ions. However, before we show how this deduction may be tested, we suggest here that non-equilibrium conditions might also yield a similar conclusion. Ion/molecule reactions are well-known in the gas-phase.[11] Generally, the close passage of an ion to a molecule leads to their mutual attraction and, for orbiting collisions, to the ion and molecule rotating about a joint centre of gravity. In all of the work on ion/molecule collisions, the ions are usually moving with greater velocities and larger kinetic energies than the molecules they encounter. In fast atom bombardment of a solution containing ions, it is the neutral species that has the greater velocity but, apart from considerations of the changes that must be accounted for in changing state from the gas phase to the liquid phase, the encounter between the atom and ion can still be described by ion/molecule collisional phenomena. Thus, the fast atom, in passing close to an ion (at or near the surface of a solution), can set up a rotational moment about their joint centre of gravity as the ion is accelerated into the attractive potential well between them. The ion, moving at thermal energies is accelerated and given extra kinetic energy as the fast atom slows down. If the atom/ion collisional interaction allows sufficient time for only a partial rotation before the atom leaves the vicinity of the collision, the ion will have received translational energy approximately in the opposite direction to the trajectory of the incoming fast atom, i.e. the ion is accelerated (desorbed) from the surface of the solution. An orbiting collision, such as might well occur when the fast atom has slowed down in its passage into the bulk of the solution, will lead to scatter of ions in all directions, mostly into the solution. As atoms have no vibrational or rotational energy and, in FAB experiments, are not electronically excited, the only means of increasing the rovibrational energy content of the species in solution will result from some (generally inefficient) conversion of collisionally-induced rotational energy into vibrational energy or will result from direct collision between atom and ion; in this last instance, the ion suffering collision will be scattered away from direction of the incoming atom and is unlikely to be desorbed from the surface of the solution, except by back-scattered fast atoms. By multiple collisions (cascade) of this sort, the kinetic energy of the fast atom can be dissipated but the desorbed ions will not have gained a large excess of vibrational energy and should not fragment. It is noteworthy that the best responses from fast atom bombardment arise with pre-ionized species, e.g. with glycerol solutions, molecules are desorbed as $(M + H)^+$ ions or clusters; in the presence sodium salts, sugars give $[M + Na]^+$ ions, ammonium salts give good spectra. The direct ionization of a molecule to yield M^+ or M^- ion-radicals is apparently much rarer and, seemingly, a much less efficient process. Direct ionization presumably occurs by charge-exchange during very close (grazing) encounters when the electronic fields of the fast atom and bombarded molecule are mutually distorted. This non-equilibrium view of fast atom bombardment as a random process does not require there to be a localized "high temperature" at the point of impact. Ions can be desorbed from solutions at normal temperatures with kinetic energy equivalent to that attained under thermal equilibrium conditions by species at high temperature without the ions ever having been subjected to high temperature. Therefore, kinetic energy can be imparted to ions to eject them back almost along the trajectory of the incoming fast atom with little or no excess of ro-vibrational energy appearing in the desorbed ions. As this process is random then, statistically, ions will be desorbed in proportion to their concentrations in solution, again allowing for differential effects caused by electrostatic and solvent interactions between oppositely charged ions in solution. Therefore, by considering the transfer of kinetic energy of a fast atom into kinetic energy of a desorbed ion as either an equilibrium or a non-equilibrium process, one can reach the same conclusion viz the mass spectral peak heights observed for desorbed ionic species should be proportional to the concentrations of those species in solution *at the bulk temperature of the solution.* Any effects due to changes induced in those concentrations should be reflected in proportional changes in mass spectral peak heights. Such changes and the observed effects are now discussed.

For a metal ion (M_1^+) in equilibrium with a crown ether in solution (eqn 7), the corresponding stability constant (K_1) is given by eqn (8) in which r is the concentration

$$\text{Crown ether} + M_1^+ \rightleftharpoons \text{Crown ether}/M_1^+ \qquad (7)$$

$$K_1 = r/(c - r) \cdot (a - r) \qquad (8)$$

of the crown ether/cation complex and c, a are the respective initial concentrations of crown ether and metal ion. By inserting values for K_1, c and a into eqn (8), the concentration of crown ether/M_1^+ complex (r) can be calculated. With $K_1 = 20{,}000$[12] and $c = 0.008$ M, the concentrations (r) were calculated for successive additions of potassium chloride, each addition increasing the concentration of KCl by 0.001 M. Figure 1 shows the calculated variation of the concentration of crown ether/K^+ complex in aqueous glycerol solution with increasing quantities of added KCl. The initial part of the graph is linear as virtually all of the added KCl is complexed to an excess of crown ether. As the molar quantity of KCl approaches that of the crown ether, the graph curves over and, close to a molar ratio for KCl/crown ether of about one, becomes almost horizontal. Further additions of KCl produce almost no more crown ether/K^+ complex because all of the crown ether has been used up in complexation. Experimentally, seven solutions of KCl in glycerol/water containing 18-crown-6 were prepared; in each successive solution, the molar ratio of KCl to 18-crown-6 was increased over the previous one so as to cover a range of molar ratios from zero to about 1.3. Each of these solutions was examined by FAB and the mass spectral peak heights at m/z 303 (18-crown-6/K^+) and m/z 265 (18-crown-6/H^+) were measured. The percentage relative peak heights for each solution at m/z 303 and 265 were calculated and plotted against the molar ratio of KCl to 18-crown-6. Figure 2 shows the curves obtained. Two features of the curves are immediately obvious. Firstly, the variation in peak heights at m/z 303 for the 18-crown-6/K^+ complex is very similar to the calculated variation in concentration for a crown ether/K^+ complex in solution shown in Fig. 1.

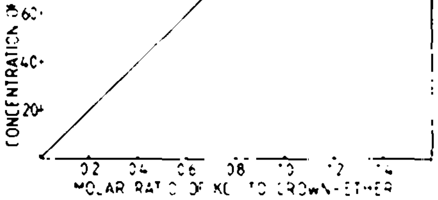

Fig. 1. The calculated variation in concentration of crown ether/K^+ complex produced by successive additions of 0.001 mole of KCl to a 0.008 molar solution of 18-crown-6 for which a stability constant of log K = 4.3 was used.

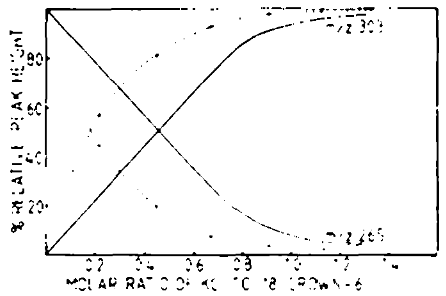

Fig. 2. The variations in observed percentage relative peak heights for 18-crown-6/H$^+$ at *m/z* 265 and for 18-crown-6/K$^+$ at *m/z* 303 produced by successive additions of KCl to an 0.008 molar solution of 18-crown-6 in glycerol/water; (a) the lines ----- represent the observed experimental data (b) the lines—— represent data corrected for differences in sensitivity response (transfer coefficients) of the FAB technique to 18-crown-6/H$^+$ and 18-crown/K$^+$.

Secondly, as the peak height for the 18-crown-6/K$^+$ complex at m/z 303 increases with increasing molar ratio of KCl to crown ether, the peak height at *m/z* 265 corresponding to 18-crown-6/H$^+$, decreases and reaches a limiting value when almost all the crown ether is complexed to K$^+$. These experimental data need to be corrected[9, 10] for the different sensitivities of the FAB/mass spectrometer system towards 18-crown-6/H$^+$ and 18-crown-6/K$^+$ by estimation of the respective transfer coefficients. These were obtained readily. Thus, for the first solution examined (containing no KCl), a peak height of 67 units at *m/z* 265 was observed for a 2.42×10^{-2} molar solution of 18-crown-6. At a mole ratio of KCl to 18-crown-6 of one, practically all of the KCl has complexed with the crown ether. Thus, a peak height of 200 units corresponds to a 1.69×10^{-2} molar solution of 18-crown-6/K$^+$ (Experimental for data). From these values, the relative sensitivities of detection of the peaks at *m/z* 303 to *m/z* 265 are in the ratio of 4.3:1. This ratio was used to correct the peak heights for *m/z* 265 and new percentage relative peak heights at *m/z* 303, 265 were calculated and are shown also on Fig. 2 as a graph. The corrected curve for the peak heights of the 18-crown-6/K$^+$ complex at *m/z* 303 is very similar to the one depicting calculated concentrations for the complex in solutions of KCl and a crown ether (in Fig. 1). Both experimental and calculated curves have an initial linear portion, curve over quite sharply near a mole ratio of KCl to crown ether of one and then become almost horizontal. These results strongly imply that the FAB technique is capable of giving quantitative information on phenomena occurring in solution. Further support for this deduction arises from the crossover point for *m/z* 303, 265. This cross-over point lies at 50% relative peak height and a molar ratio of 0.5. It can be shown[11] that, if the stability constant for a crown ether/cation complex is large (as it is here) and/or the concentration a crown ether used is large, then the two curves can be predicted to cross at a mole ratio of 0.5. The results suggest that FAB spectroscopy can be used to obtain data on stability constants of crown ether/cation complexes. The results also demonstrate that FAB appears to give information from solutions whose bulk temperatures are not seriously disturbed by the atom bombardment, even though a high localized "temperature" is required to eject ions from solutions. These data suggest that an impacting fast atom loses its kinetic energy very rapidly as it enters the solution, depositing sufficient kinetic energy in a short time into some ionic species in solution so that they can leave the surface against the attractive electrostatic forces of the counter ions aided by the ion accelerating electrode of the mass spectrometer. Presumably the remaining energy deposited by the fast atom is dissipated as vibrational and rotational energy in the solution and then lost to the surrounding system. Some indication of the importance of the electrostatic attraction between ions as a factor in the production of FAB spectra with crown ethers can be gained from the above ratio of transfer coefficients for 18-crown-6/H$^+$ and 18-crown-6/K$^+$ and by a comparison of the behaviours of $HgCl_2$ and $Hg(OAc)_2$. In glycerol/water containing 18-crown-6, $HgCl_2$ yielded no mercury-containing ions in the FAB mass spectrum of the solution but $Hg(OAc)_2$ yielded the expected ions corresponding to $[18\text{-crown-}6/HgOAc]^+$.

For two metal ions (M_1^+, M_2^+) having the same counter ion and competing for the same crown ether in solution, the stability constants (K_1, K_2) are given by eqns (9) in which s is

$$K_1 = r/(c - r - s)\cdot(a - r);\ K_2 = s/(c - r - s)\cdot(b - s) \tag{9}$$

the concentration of the crown ether/M_2^+ complex and b is the initial concentration of metal ion (M_2^+). Given suitable values for c, a, b, K_1 and K_2 the concentrations of complexes (r, s) can be calculated.[14] Similarly, these calculations can be extended to include other metal ions and Fig. 3 shows typical results obtained for the variation in concentration of crown ether/cation complexes of three different metal ions (M_1^+, M_2^+, M_3^+) competing for a limited amount of a crown ether. For these calculations, values for the stability constants were assumed ($K_1 = 20{,}000$, $K_2 = 500$, $K_3 = 2000$)[12] and c was put equal to 0.0174 mole.l^{-1}. The three metal ions were considered to be added as aliquots of a mixture containing all three ions as their salts; each aliquot contained 0.002, 0.004 and 0.002 mole.l^{-1} respectively of each metal salt. In the corresponding experimental work, a solution of a dicyclohexyl-18-crown-6 in glycerol was treated with aliquots of an aqueous glycerol solution containing KCl, NaCl and CsCl. After addition of each

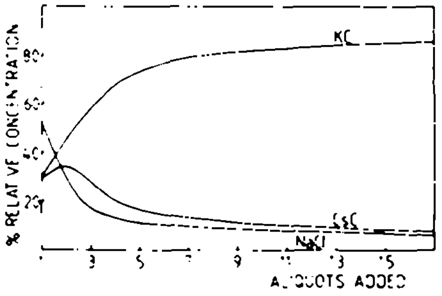

Fig. 3. Variations in calculated percentage relative concentrations of dicyclohexyl-18-crown-6 complexes of NaCl, KCl and CsCl produced by successive additions of aliquots of a solution of a mixture of the three salts. Initial concentration of crown ether was 0.0174 mole.l^{-1} and each aliquot contained 0.002, 0.004 and 0.002 mole.l^{-1} of KCl, NaCl and CsCl respectively.

aliquot, FAB mass spectral peak heights at *m/z* 395, 411 and 505 (corresponding to dicyclohexyl-18-crown-6 plus Na^+, K^+ and Cs^+ respectively) were measured. Typical results are shown in Fig. 4. A comparison of Figs. 3 and 4 shows that the (uncorrected) variations in mass spectral peak heights for the dicyclohexyl-18-crown-6 complexes of Na^+, K^+ and Cs^+ correspond very closely to the calculated changes in concentrations of these complexes in solution. This result suggests that the assumptions made in the above theoretical treatment are not unreasonable and that it is possible to extract information on solution behaviour by the use of fast atom bombardment mass spectrometry.

For internal consistency and to obviate the effects of small fluctuations in peak heights during measurements, the measured peak heights were converted to percentage relative peak heights. We are examining an alternative method for obviating fluctuations in peak heights during their measurement by incorporating into the solutions a small quantity of a standard ionic substance which does not form a complex with crown ethers. Typical curves of actual peak heights obtained for mixtures of CsCl and KCl added to a solution of 18-crown-6-in glycerol/water are shown in Fig. 5. The mole ratio of CsCl to KCl was 2:1. Initially, because of its greater concentration, CsCl forms more crown ether/cation complex than does KCl despite the latter having a greater stability constant than the CsCl. However, as the concentration of CsCl and KCl build up, the crown ether/K^+ complex is found in larger and larger amounts and, eventually, almost all the crown ether is used up in complexation with K^+. Thus, the concentration of crown ether/Cs^+ reaches a maximum and then falls away, reflecting its smaller stability constant. This behaviour can be used to extract stability constants from the mass spectral data. Unfortunately, stability constant data for crown ether/cation complexes in glycerol or glycerol/water derived from independent physical methods are not available. The common solvents for measurement of these data are water or methanol, both of which are too volatile for our apparatus in its present form. Therefore, until such time as these data become available or we can modify our apparatus to allow use of aqueous or methanolic solvents, we indicate here how the stability constants can be obtained from mass spectral data.

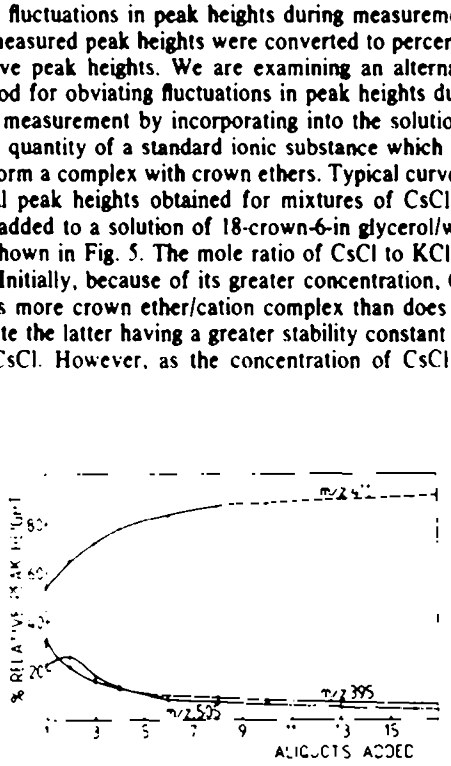

Fig. 4. Observed percentage relative mass spectral peak heights for dicylcohexyl-18-crown-6 complexes with K^+ (at *m/z* 411), Na^+(*m/z* 395) and Cs^+(*m/z* 505). The metal ions were introduced as chlorides by addition of aliquots of a solution containing a mixture of the three salts in aqueous glycerol to a solution of dicyclohexyl-18-crown-6 in the same solvent.

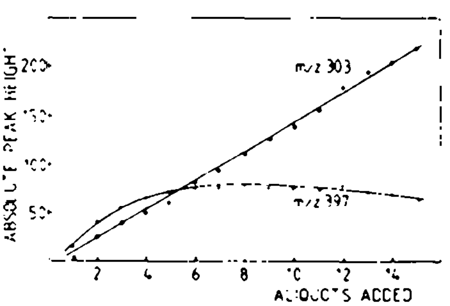

Fig. 5. The observed variation in absolute peak heights at *m/z* 303 and *m/z* 397 for 18-crown-6 complexes of K^+ and Cs^+ in aqueous glycerol. KCl and CsCl were added as aliquots of a solution containing a mixture of them to an aqueous glycerol solution of 18-crown-6.

It can be shown[15] that, where two curves cross as for the M_1^+ and M_2^+ complexes shown in Fig. 5 for which the stability constant, $K_1 \gg K_2$, then, at the cross-over point, K_2 can be calculated from eqn (10). In this expression,

$$K_2 = (n-1)(c-2a)^{-1} \qquad (10)$$

n is the (constant) ratio of M_1^+ to M_2^+ in each aliquot, a is the total amount of added ion (M_1^+) and c is the initial concentration of crown ether. From the experimental data, the mass spectral peak heights (p) must be converted into solution concentrations by derivation of the transfer coefficients (t; eqn 6). These transfer coefficients may be obtained by measurement of the peak heights for a crown ether/cation complex in the presence of a large excess of crown ether. Under these conditions, the concentration of crown ether/cation complex in solution is known to be equal to the concentration of added metal ion.[10] Thus, both c complex and p are known and t can be derived. This value of t can be used to convert any observed peak height into a solution concentration. Again, for two ions (M_1^+, M_2^+) competing for a crown ether for which $K_1 \gg K_2$, one of the curves will reach a maximum and then decrease (curve for *m/z* 395 in Fig. 5). At this maximum, it can be shown[16] that expression (11) applies. Thus, at the

$$s = (c-2a)/(1-1/n) \qquad (11)$$

maximum, independently of any peak height values, the concentration of the crown ether/M_2^+ complex (s) can be calculated and compared with the value derived from the transfer coefficient. This technique provides an independent check on the transfer coefficient (t) found by other means.[10]

Quantitative aspects of this work are being examined and the work is being extended to examine the effects of counter ions and competing crown ethers.

EXPERIMENTAL

Spectra were measured on VG Micromass ZAB-2F and 70-70F instruments using bombardment by fast xenon or argon atoms. The probe tip was coated with 2 μl of glycerol and 1 μl of each analytical soln was added. The sample was placed in the ion source and 2 min were allowed for the source pressure to settle. The atom gun was turned on and a further 1 min allowed to elapse before a spectrum was recorded (a total 3 min after insertion of sample). Further spectra were recorded at 4 and 5 min from insertion of sample and peak heights (self-consistent arbitrary units) at the required *m/z* values were averaged over the 3 runs.

Additions of KCl *to a solution of* 18-*crown*-6. A standard soln (A) was prepared by dissolving 18-crown-6 (31.9 mg) in glycerol/water (1:1; 5 ml). A second standard soln (B) was prepared by dissolving KCl (20.2 mg) in water (5 ml). For the measurements required for Fig. 2, seven solns (K1 – 7) were prepared by mixing standard (A; 100 μl) with 0, 10, 20, 30, 40, 50 and 60 μl of standard B. The following average peak heights were recorded (soln; *m/z* 265; *m/z* 303): K1, 67, 11; K2, 62, 93; K3, 25, 109; K4, 13, 185; K5, 5, 205; K6, 2, 197; K7, 2, 312. Soln K1 gave a peak height of 11 units at *m/z* 303 although no KCl had been added. This background value was subtracted from the peak heights for *m/z* 303 in solns K1-7. Percentage relative peak heights were calculated for each soln for *m/z* 265, 303 and were used as data for Fig. 2.

Additions of NaCl, KCl *and* CsCl *to a solution of dicyclohexyl*-18-*crown*-6. Dicyclohexyl-18-crown-6 (97 mg) was dissolved in a mixture of glycerol/water (1:2, 9 ml) to give a standard soln (P). A mixture of NaCl (1.4684 g), KCl (0.9226 g) and CsCl (2.1100 g) was dissolved in glycerol/water (1:2, 50 ml) to give a standard soln (Q). Each analytical soln (M1–11) was prepared by addition of x μl of soln Q to 600 μl of soln P and making this mixture up to a final volume of 1 ml. The following solns were prepared (x is given in parentheses): M1(10), M2(20), M3(30), M4(40), M5(60), M6(80), M7(100), M8(130), M9(160), M10(200), M11(300). For each soln, the following average peak heights were recorded (soln, *m/z* 395, *m/z* 411, *m/z* 505): M1(2.6, 5.6, 2.5); M2(3.2, 8.9, 4.0); M3(5.9, 23.5, 6.2); M4(4.7, 25.4, 5.1); M5(5.4, 56.9, 4.5); M6(6.7, 72.3, 4.8); M7(3.2, 39.8, 2.4); M8(4.8, 74.0, 3.3); M9(3.3, 51.6, 1.7); M10(2.2, 32.5, 0.9); M11(1.1, 17.6, 0.4). For Fig. 4, these peak heights were converted into percentage relative peak heights for each aliquot (M1–11).

Additions of KCl, CsCl *to a solution of* 18-*crown*-6. A soln (R) in water was prepared such that 1 μl delivered 2×10^{-10}M of KCl and 4×10^{-10}M CsCl. A soln (S) in MeOH was prepared such that 1 μl delivered 1×10^{-8}M of 18-crown-6. For each of the experiments (N1–15), 2 μl of soln (S) were added to 3 μl of glycerol on the probe tip and x μl of soln (R) were added. The following average peak heights were recorded (soln, x, *m/z* 303, *m/z* 397): N1, 1, 5.3, 18.2; N2, 2, 25, 41; N3, 3, 40.2, 53; N4, 4, 49.2, 61; N5, 5, 64.2, 67; N6, 6, 82.2, 74; N7, 7, 89.2, 73; N8, 8, 112.2, 78; N9, 9, 122.2, 76; N10, 10, 136.2, 74; N11, 11, 156.2, 74; N12, 12, 182.2, 80; N13, 13, 193, 72; N14, 14, 204, 68; N15, 15, 226, 65. These peak heights and aliquots (N1–15) were used in Fig. 5.

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[7] An electric field is usually applied to the sample to direct any desorbed ions into the analyser of the mass spectrometer. This applied field will tend to separate (polarize) cations and anions in soln before arrival of the fast atom. The term to the right of expression (4) should be reduced by $(z_1 + z_2)$ eV, where V is the potential of the applied electric field. Except for very large values for V, this polarization term is small compared with the total electrostatic energy between ions and has been ignored in this treatment.

In the electrostatic term on the right of expression (4), z_1 and z_2 are the electric charges on the cation and anion of the metal salt used, e is the electronic charge, ϵ_0 is the permittivity of the solution and r is the distance between charges. For closest approach (maximum electrostatic energy) and using standard atomic radii for K^+Cl^-, then $r = 3.14 \times 10^{-10}$ m and $z_1z_2e^2/4\pi\epsilon_0 r = 1.74 \times 10^{-20}$J ($\epsilon_0$ for glycerol $= 3.76 \times 10^{-10}$). This value for the electrostatic energy of KCl in dilute solution containing crown ether is a reasonable approximation because the crown ether in its complex with K^+ tends to fill its co-ordination sphere and prevent build-up of an anionic and/or solvation atmosphere. Nevertheless, variations in this electrostatic term can be expected depending on the ions, their electronic charge and solvation, and, for quantitative work, mass spectral peak heights will need correction (see, ref. 9).

[8] With $k = 2.1 \times 10^{-23}$ J K^{-1}, expression (5) becomes $2.1 \times 10^{-23} \times T > 1.74 \times 10^{-20}$ and therefore, T > 860°K.

[9] If the electrostatic energies of separation of crown ether/cation complexes from their counter ions are significantly different for M_1^+, M_2^+, then E does not cancel out (i.e. the "temperatures" of desorption calculated as in Ref. 8 will be different for the two crown ether/cation complexes). In this case, $n'_r/n''_r = (N'/N'') \exp(-[E' - E'']/kT)$ and the observed peak heights must be corrected for the differing electrostatic energies. This correction is made automatically if transfer coefficients (expression (6) and Ref. 10) are determined experimentally. Assessment of the difference, $E' - E''$, from ionic cohesion energies or similar thermodynamic data is difficult because of solvation effects and incomplete complexation of the metal ion by the crown ether. Using $r = 3.4 \times 10^{-10}$ m for CsCl, the electrostatic attraction between Cs^+ and Cl^- is 1.61×10^{-20} J, compared with 1.74×10^{-20} J for K^+Cl (Ref. 7), and yields a minimum temp. for desorption of 767°K, i.e. almost 100° less than that required for KCl. These admittedly simplistic calculations suggest that a crown ether/Cs^+ complex will be easier to desorb from soln than a crown ether/K^+ complex and that $n'_r/n''_r \neq N'/N''$. However, a suitable correction for this difference in sensitivity can be made by measurement of the transfer coefficient as discussed in Ref. 10.

[10] From Eqns (9), $r^2 - r(c + a - s + 1/K_1) + a(c - s) = 0$; for a single cation species, $s = 0$ and $1/K_1 \simeq 0$ for a reasonably stable crown ether/cation complex or c is made $\gg 1/K_1$. Solving this equation for r then gives $r = a$. Thus, for large stability constants (K_1) or for values of the crown ether concentration (c) much greater than the reciprocal of the stability constant, the concentration of a crown ether/cation complex in soln is simply equal to the amount of added metal salt. This situation can be seen in the curve for KCl in Fig. 1 where the early part of the curve is linear. In the early portions of all curves where $c \gg 1/K_1$, the concentration of crown ether/cation complex in soln is equal to the concentration of cation, i.e. $C_{complex}$ of equation (6) is known. Therefore, by measurement of the mass spectral peak height (p) for the crown ether/cation and knowing $C_{complex}$, the transfer coefficient (t) can be calculated. For example, from the experimentally observed linear portion of the curve for 18-crown-6/K^+ complex, after addition of 0.49×10^{-2} mole. l^{-1} of KCl, the peak height at *m/z* 303 is 60 units so that, $t = 0.8 \times 10^{-4}$ mole.l^{-1} per unit of peak height. The transfer coefficient also accounts for variation in response of the mass spectrometer to different masses.

[11] See, for example, T. A. Lehman and M. M. Bursey, *Ion Cyclotron Resonance Spectrometry*, pp. 132–138. Wiley, New York (1976).

[12] Values of K_1, K_2, K_3 in glycerol/water were estimated very approximately from equilibrium constants for K^+, Cs^+ and Na^+ complexed with 18-crown-6 in methanol and water at 25° or with dicyclohexyl-18-crown-6. (H. K. Frensdorff, *J. Am. Chem. Soc.* **93**, 600 (1971).

[13] From eqn (8), if the concentration of crown ether equals the concentration of crown ether/cation complex, $2r = c$ and $(a - r) = 1/K_1$. If $c = n \cdot a$, then $(c/n - c/2) = 1/K_1$ and $1/n = 1/K_1c + 1/2$. Therefore, when $K_1 \cdot c \gg 1$, $1/K_1c \to 0$ and $1/n = 1/2$. In the example discussed in the text, $K_1 = 20{,}000$ and $c = 0.008$, so that $1/K_1c = 0.006$ and $1/n \simeq 0.5$.

[14] An iterative computer programme was used to solve these interdependent equations. Initially, $s = 0$ (corresponding to the

smaller stability constant) to calculate a value for r. This value of r is used to calculate a new value for s and so on until the values for r, s do not change by more than 10^{-6} per cent at each iteration. This approach is readily extended to more than two competing ions. For Fig. 3, percentage relative concentrations were calculated, i.e. $100\, r/(r+s)$ and $100\, s/(r+s)$.

[15] Where two curves cross as in Fig. 1, $r = s$ in eqns (9). Combining these equations and eliminating s gives, $r\,(2b - 2a + 1/K_2 - 1/K_1) = c(b - a)$; as shown in Ref. 10, for $1/K_1 \gg 0$ then $r = a$ and the combined equations reduce to $K_2 = [(n-1)(c-2a)]^{-1}$.

[16] If $c \gg 1/K_1$ or K_1 is large then $r = a$ (Ref. 10) and $dr/da = 1$. For aliquots of two ions (M_1^+, M_2^+) where $n \cdot a = b$ (i.e. the concentration of ion M_2^+ is n times the concentration of ion M_1^+ in each aliquot) then $n \cdot da/db = 1$. Therefore, $dr/db = (dr/da)\cdot(da/db) = 1/n$. From the expression for K_2 in eqns (9) we have, if $1/K_1 \approx 0$, $s^2 - s(c + b - r + 1/K_2) + b(c - r) = 0$, and, from this by differentiation, $2s(ds/db) - (c + b - r + 1/K_2)(ds/db) + (s - b)(dr/db) + c - r - s = 0$. At the curve maximum, $ds/db = 0$ and, recalling that $dr/db = 1/n$, we have $s = (c - 2a)/(1 - 1/n)$.