Volume changes in complex formation between crown ethers of cryptand-222 and alkali metals in various solvents

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Abstract

The volume changes ΔV^{∞} in crown ether or cryptand-222 + metal salt reactions are large. These reactions are interesting in that the metal ion is apparently enveloped by the larger organic molecule and as a result these measurements can shed light on the processes involved. In this work, we have shown that ΔV^{∞} not only reflects the proposed simple mechanism but also is a measure of the electrostriction effect of the metal ion on the solvent.

INTRODUCTION

The reaction between some crown ethers or cryptand-222 and some metal ions are interesting in that the large host molecule appears to envelope the metal ion.[1-2] In this work, we have focussed on four crown ethers: 18-crown-6 ether (18C6E), dibenzo-18-crown-6 ether (B$_2$18C6E), dicyclohexano-18-crown-6 ether (C$_2$18C6E) and 15-crown-5 ether and cryptand-222 (C222). These compounds range in cavity size, solubility in various solvents and in rigidity. A number of laboratories have contributed to the results discussed in this paper. They include volume changes for reactions between the above host molecules and sodium, potassium and cesium chlorides and iodides. These metal ions range in ionic radii from a size which is smaller than that of the host ligand to that which is larger. Both chloride and iodides have been investigated in order to ascertain the effect of the "spectator ion". These reactions have been carried out in various solvents such as water, acetonitrile (AN), dimethylsulphoxide (DMSO) and methanol (MeOH). These ranged from being highly compressible to being weakly compressible. The reaction can be thought of

as the following:

$$M^+ X^- \quad + \quad CE \quad \rightarrow \quad M.CE^+ \quad + \quad X^- \quad (1)$$
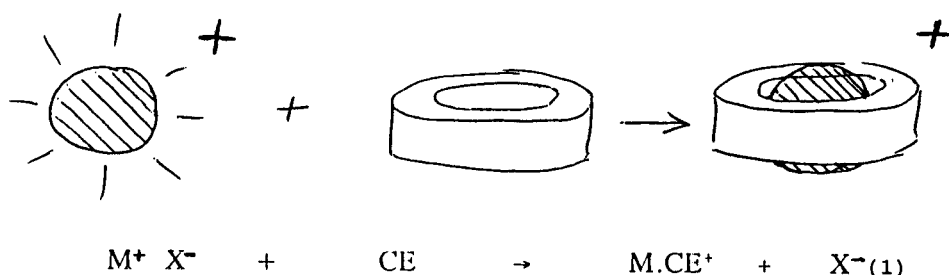
The equilibrium constant for these reacts is important as it strongly influences the way the experiment and calculations are carried out. For the reaction[2] in AN and in MeOH, log K = 4, where as for water log K = 0.3. The value of log K for the reactions in DMSO ranged from 1 to 3.

MEASUREMENTS

We have measured the volume changes at infinite dilution ΔV^∞, for the systems:

$$CE + MX \rightarrow MX.CE \tag{2}$$

where $\Delta V^\infty = V^\infty_\phi(MX.CE) - V^\infty_\phi(MX) - V^\infty_\phi(CE)$ (3)

and where V^∞_ϕ refers to the apparent molar volume V_ϕ extrapolated to infinite dilution. The quantity V^∞_ϕ is identical to the partial molar volume at infinite dilution $V_1(x_1 = 0)$ where 1 refers to the solute. Equation (3) can be expanded to

$$\Delta V^\infty = V^\infty_\phi(CE.M^+) + V^\infty_\phi(X^-) - V^\infty_\phi(M^+) - V^\infty_\phi(X^-) - V^\infty_\phi(CE) \tag{4}$$

i.e. $\Delta V^\infty = V^\infty_\phi(CE.M^+) - V^\infty_\phi(M^+) - V^\infty_\phi(CE)$ (5)

Hepler[3] has shown that

$$V^\infty_\phi(M^+) = Ar^3 - B/r \tag{6}$$

where r is the ionic radius of the ion and A and B are empirical constants. Ar^3 is the contribution of the intrinsic volume of the ion while $-B/r$ is the contribution of the electrostriction effect of the ion on the solvent. Rewriting (5) we have

$$\Delta V^\infty = \Delta V^m_\phi(CE.M^+) - V^\infty_\phi(M^+, \text{ intrinsic})$$
$$- V^\infty_\phi(M^+, \text{ electrostriction}) - V^\infty_\phi(CE) \tag{7}$$

If the crown ether does not undergo a volume change on complex formation and the intrinsic volume of M^+ is the same when bound to the CE, as it is in solution then,

$$\Delta V^\infty = V^\infty_\phi(M^+, \text{ electrostriction}) \tag{8}$$

or using the Hepler notation:

$$\Delta V^\infty = B/r. \tag{9}$$

EXPERIMENTAL (ref. 4)

The density d of each solution was obtained from the density of pure solvent d_o and the periods of vibration of the tube when it contained the solution (τ) and the pure solvent (τ_o) using the relationship

$$d = d_o + D(\tau^2 - \tau_o^2) \tag{10}$$

where D is the density meter constant.

The apparent molar volume V_ϕ is given by:

$$V_\phi = M/d_o - 1000(d - d_o)d_oC \tag{11}$$

where M is the molar mass of the solute and c the concentration.

At infinite dilution V^∞_ϕ of each non-ionic solute can be related to V_ϕ through

$$V_\phi = V^\infty_\phi + aC \tag{12}$$

where a is a constant.

For ionic species (MX) and (CE.MX) V_ϕ was related to V^∞_ϕ through

$$V_\phi - 2/3\delta_v C^{1/2} = V^\infty_\phi + bC \tag{13}$$

where δ_v is the Debye Hückel term.

In our laboratory the V_ϕ values for the complex were obtained by weighing equimolar amounts of the crown ether or cryptand and the metal salt followed by dissolving the complex in one of the chosen solvents. The V_ϕ results extrapolated to infinite dilution were then used to calculate V^∞_ϕ using equation (3). The technique did not take into account any unreacted species as it was assumed that K was large and that almost all the reactant reacted. For log K = 4 this assumption is valid within experimental error. For the water system measured by Høiland, a different technique was used

TABLE 1 : V^∞_ϕ FOR METAL SALTS IN VARIOUS SOLVENTS
The results in parenthesis have been obtained from the literature.[4]

	MeOH	AN	DMSO
NaCl	-7.9 (-5.5)	-	-
KCl	(5.7)	-	-
CsCl	(16.2)	-	-
NaI	9.2 (12.7)	4.7 (4.7)	34.1 (33.4)
KI	20.2 (22.3)	16.4 (15.6)	40.8 (41.9)
CsI	30.8 (33)	27.7 (26)	53.2 (53.5)

which took unreacted species into account. Results for V^∞_ϕ for
metal salts in solvent have been reported in the literature [4]
and have been repeated in my laboratory. A summary is given in
Table 1. Results for V^∞_ϕ for crown ether and cryptand-222 in
various solvents is given in Table 2.

TABLE 2 : V^∞_ϕ FOR CE COMPOUNDS IN VARIOUS SOLVENTS
The result given in parenthesis has been obtained from the
literature.[4]

	MeOH	AN	DMSO
18C6E	226.2	229.2	234.4
B$_2$18C6E	279	270.9 (271.7)	288.7 (288.3)
C222	322.5	329.8	340.8
15C6E	184.3	185.3	192.8
C$_2$18C6E	319.9	325.2	352.6

The results for 18C6E have been graphed in Figure 1. Results
for $V\infty_\phi$ for the crown ether metal complex are tabled in Table 3.
The data for 18C6E in MeOH has been graphed in Figure 2.
Results for ΔV^∞_ϕ are given in Table 4(a), (b), (c) and (d).
The results include ΔV^∞ for the reaction of 18C6E, B$_2$18C6E,
C222, 15C5E and C$_2$18C6E with NaCℓ, KCℓ, CsCℓ, NaI, KI and CsI
in the solvents MeOH, AN, DMSO and water. The table also
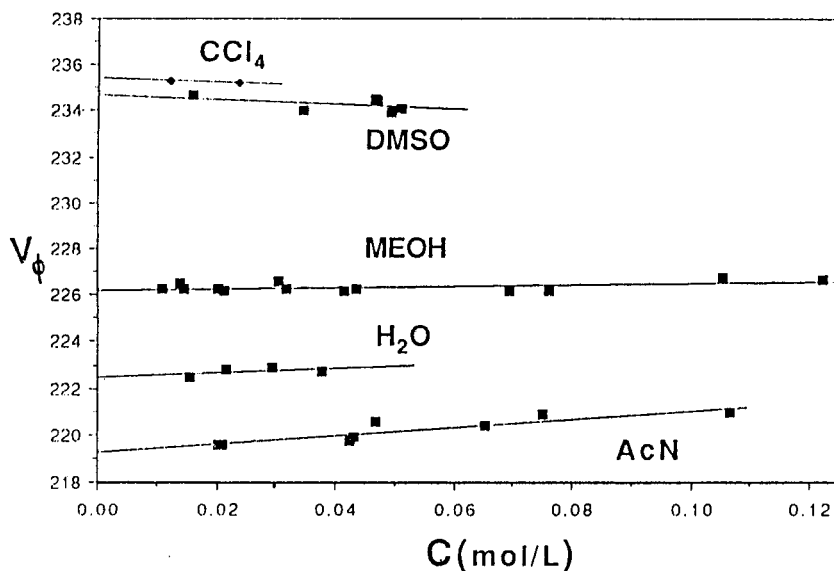includes the Hepler calculated values of B/r.[3]

FIGURE 1: V_ϕ (18-CROWN-6 ETHER) VS C

TABLE 3 : V$^\infty_\phi$ FOR METAL SALT-CROWN ETHER COMPLEX
The results in parenthesis have been obtained from the
literature.[1]

Salt	V$^\infty_\phi$(MeOH)	V$^\infty_\phi$(AN)	V$^\infty_\phi$(DMSO)	Salt	V$^\infty_\phi$(MeOH)	V$^\infty_\phi$(AN)	V$^\infty_\phi$(DMSO)
18C6E				**15C5E**			
NaCl	233.0	-	-	NaCl	190.7	-	-
KCl	245.2	-	-	KCl	-	-	-
CsCl	249.9	-	-	CsCl	-	-	-
NaI	-	251.4	271.3	NaI	208.4	211.1	-
KI	261.5	260.9	277.9	KI	215.9	214.8	-
CsI	-	262.4	283.6	CsI	220.5	224.0	-
B₁18C6E				**C₁18C6E**			
NaCl	-	-	-	NaCl	-	-	-
KCl	-	-	-	KCl	-	-	-
CsCl	-	-	-	CsCl	-	-	-
NaI	300.8	(300.4)	(326.4)	NaI	347.8	355.6	377.9
KI	312	(308.9) 307.5	(331.0) 330.3	KI	353.7	357.1	380.2
CsI	315.6	(315.6) -	(339.1) 339.9	CsI	358.4	364.2	395.5
C222							
NaCl	336.9	-	-				
KCl	329.5	-	-				
CsCl	347.7	-	-				
NaI	347.4	353.3	384.9				
KI	355.4	362.5	391.8				
CsI	363.7	369.3	402.1				
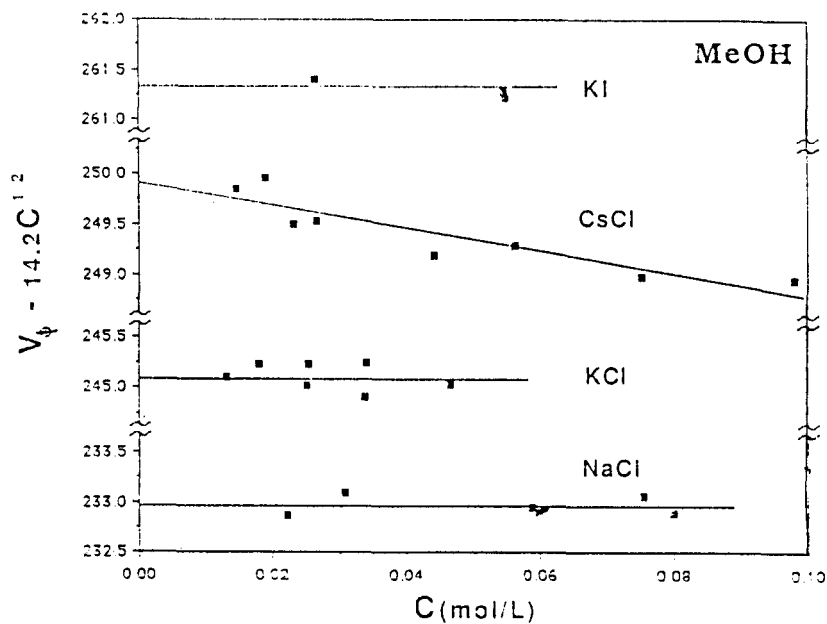
**FIGURE 2: THE LIMITING APPARENT MOLAR VOLUMES OF 18-CROWN-6
ETHER COMPLEXES IN METHANOL**

TABLE 4(a) : ΔV^∞_ϕ FOR COMPLEXATION BETWEEN ALKALI METAL IONS AND CROWN ETHERS OR CRYPTAND-222 IN METHANOL AND HEPLER'S RESULTS

The data in parenthesis refers to the literature[4-6]

	18C6E	B₂18C6E	C222	15C5E	C₂18C6E	B/r⁺
NaCl	(12)	(15)	15	14	-	18
KCl	(13)	(11)	13 (16)	-	-	13
CsCl	(6)	(4)	10 (7)	-	-	10
NaI	-	(9)	16	15	19	18
KI	(13)	(11)	13	11	14	13
CsI	-	(4)	10	1	8	10

TABLE 4(b) : ΔV^∞_ϕ FOR COMPLEXATION BETWEEN ALKALI METAL IONS AND CROWN ETHERS OR CRYPTAND-222 IN ACETONITRILE (AN) AND HEPLER'S RESULTS

	18C6E	B₂18C6E	C222	15C5E	C₂18C6E	B/r⁺
NaCl	-	-	-	-	-	25
KCl	-	-	-	-	-	18
CsCl	-	-	-	-	-	14
NaI	(28)	25	25	21	19	25
KI	(26)	(21) 22	16	13	12	18
CsI	(17)	17	11	-13	16	14

TABLE 4(c) : ΔV^∞_ϕ FOR COMPLEXATION BETWEEN ALKALI METAL IONS AND CROWN ETHERS OR CRYPTAND-222 IN DIMETHYL SULPHOXIDE (DMSO) AND HEPLER'S RESULTS

The results in parenthesis have been obtained from the literature.[4]

	18C6E	B₂18C6E	C222	15C5E	C₂18C6E	B/r⁺
NaCl	-	-	-	-	-	13
KCl	-	-	-	-	-	9
CsCl	-	-	-	-	-	7
NaI	(4)	4	2	-	-9	13
KI	(2)	(0) 2	1	-	-13	9
CsI	(-4)	(-2) -3	3	-	10	7

TABLE 4(d) : ΔV^∞_ϕ FOR COMPLEXATION BETWEEN CROWN ETHERS OR CRYPTAND-222 IN WATER AND HEPLER'S RESULTS

The results given were reported by Høiland.[7-8]

	18C6E	B₂18C6E	C222	15C5E	C₂18C6E	B/r⁺
NaCl	(12)	-	(14)	-	-	11
KCl	(13)	-	(17)	-	-	8
CsCl	(9)	-	-	-	-	6
NaI	-	-	-	-	-	11
KI	-	-	-	-	-	8
CsI	-	-	-	-	-	6

The atomic dimension of the crown ether cavity and the ionic
radii is given in Table 5.

TABLE 5 :   ATOMIC DIMENSIONS

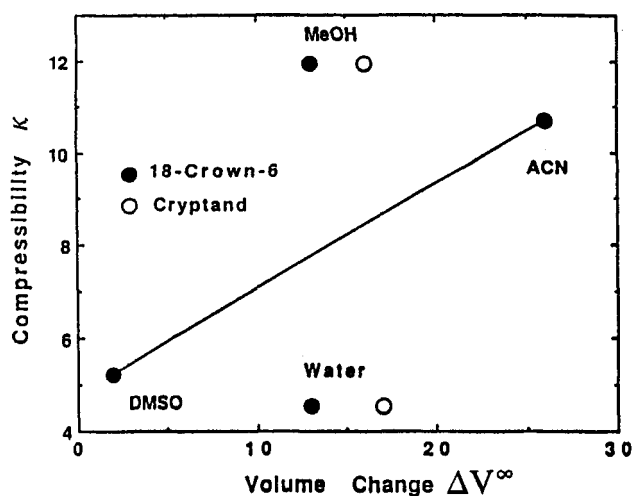| ligand	hole diameter/Å
15C5	1.7 - 2.2
18C6	2.6 - 3.2
ion	ionic diameter/Å
Na$^+$	1.9
K$^+$	2.7
Cs$^+$	3.3

FIGURE 3:   A PLOT OF SOLVENT COMPRESSIBILITY VS
VOLUME CHANGE ΔV$^\infty$ FOR 18C6E AND C222 WITH Na$^+$
IN MeOH, AN, DMSO AND H$_2$O

DISCUSSION

In most cases the reaction of 18C6E, C222, B$_2$18C6E and C$_2$18C6E
with Na$^+$ or K$^+$ and in some cases Cs$^+$ ions result in

$$\Delta V^\infty = B/r \qquad\qquad (9)$$

This gives credence to the simple concept of the host molecule
enveloping the cation and also to Hepler's theory.[3] This does
seem to be true even in the case of the reaction of Cs$^+$ with
18C6E, B$_2$18C6E, C$_2$18C6E and C222 in spite of the fact that the
diameter of the Cs$^+$ is reported to be larger than the diameter
of the cavity of the host ligand.

The ΔV$^\infty$ for the reactions of 15C4E with Cs$^+$ ions in MeOH and
AN is very much less than the calculated value of B/r and this
could be a result of the incompatability of the host cavity
and the Cs$^+$ ionic diameter.

The ΔV$^\infty_\phi$ results in DMSO do not appear to be related to B/r.
This could be a result of the low value of the equilibrium
constant for the reactions in DMSO or that a 1:2 complex takes

place between the ion and the host ligand in this solvent.
It must also be remembered that our experimental technique is
based on the fact that the equilibrium constant is large.
Attempts to relate the ΔV$^\infty_\phi$ values to the compressibility of
the solvent (after all the compressibility should be closely
related to the electrostruction effect of the ion on the
solvent) proved invane. Results for 18C6E and C222 with Na$^+$
in MeOH, AN, DMSO and H$_2$O are given in Figure 3.

Even the relationship between the partial molar compressibility
of the ion (K^+ in this case) vs ΔV^∞ for 18C6E with K^+ in MeOH,
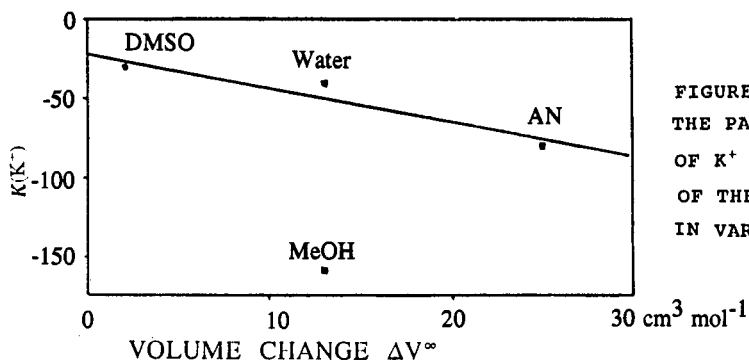AN, DMSO and H_2O proved unsatisfactory as can be seen in Figure 4.

FIGURE 4:
THE PARTIAL MOLAR COMPRESSIBILITY
OF K^+ VS ΔV^∞ OF COMPLEX FORMATION
OF THE 18-CROWN-6 ETHER, K^+ COMPLEX
IN VARIOUS SOLVENTS

It is interesting to note the volume differences between
$B_2$18C6E and 18C6E and $C_2$18C6E and 18C6E:

$$V^\infty_\phi(B_2 18C6E - 18C6E) = 52 - 54 \text{ cm}^3\text{mol}^{-1}$$
$$V^\infty_\phi(C_2 18C6E - 18C6E) = 94 - 116 \text{ cm}^3\text{mol}^{-1}$$

The two cyclohexyl rings occupied a very much larger volume at
infinite dilution than do the two benzene rings.

Before concluding this paper it is interesting to note that
the partial molar volume at infinite dilution ($V_1(x_1 = 0) = V^\infty_\phi$)
for 18C6E appear to be dependent on the molar volume of the
solvent, V^0_2. The larger the value of V^0_2 the larger is
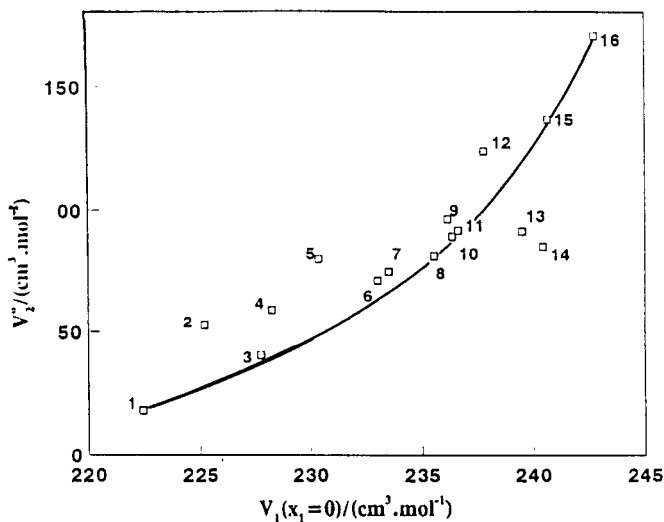($V_1(x_1 = 0)$. This result is summarised in Figure 5.

FIGURE 5:
PARTIAL MOLAR VOLUMES AT INFINITE
DILUTION $V_1(x_1 = 0)$ FOR 18C6E IN
VARIOUS SOLVENTS VS SOLVENT MOLAR
VOLUMES V^0_2[9]

A similar relationship exists for C222 in various solvents as
given in Figure 6. It almost appears as though the distortion
of the solvent by addition of 18C6E or C222 species depends
very much on the molar volume of the solvent species. The
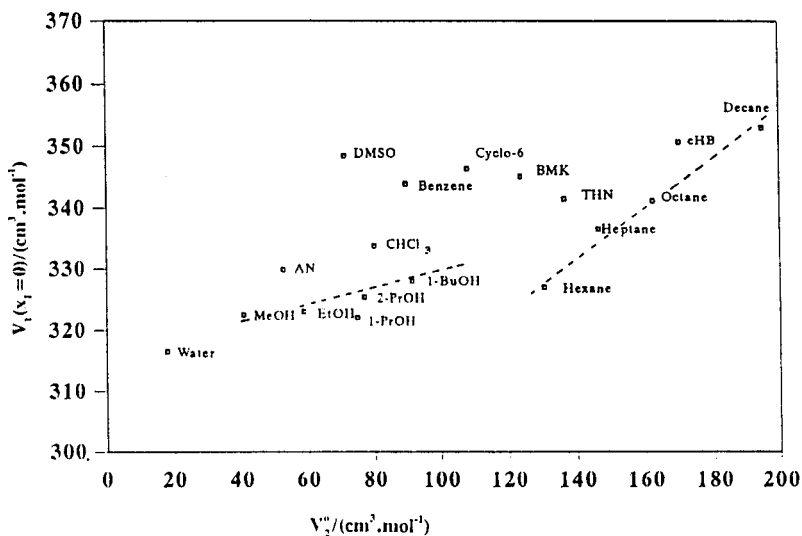larger the molar volume of the solvent species, the greater is

FIGURE 6:
PARTIAL MOLAR VOLUMES AT
INFINITE DILUTION $V_1(x_1 = 0)$
FOR C222 IN VARIOUS SOLVENTS
VS SOLVENT MOLAR VOLUME V''_2

the distortion of adding 18C6E or C222. The results are also independent of the polar nature of the solvent. The phenomena has been sketched in Figure 7.
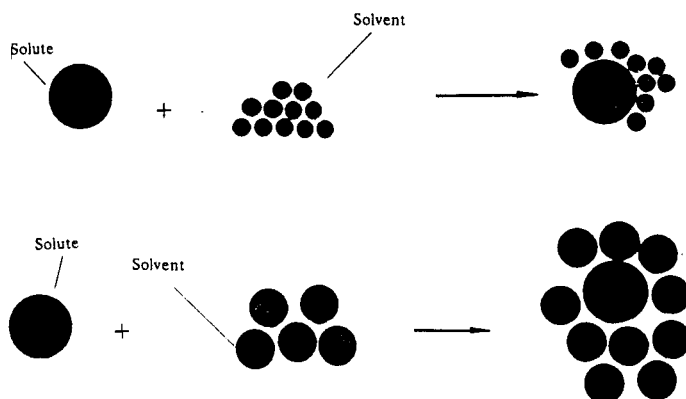

FIGURE 7: OUR PARTIAL MOLAR VOLUME AT INFINITE DILUTION
Results indicate that the addition of a solute such as 18C6E
or C222 produces a volume distortion which increases with
increasing size of the solvent molar volume.

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