

# CROWNS IN ALKALI ALKOXIDE-CONJUGATE ACID SOLUTIONS: A REMARKABLY LOW PROPENSITY TO COMPLEX FORMATION\*

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Complexing ability of the macrocyclic polyethers 18-crown-6, 15-crown-5 and 12-crown-4 has been investigated ebulliometrically in the homologous series of 0.6 molal ROM-ROH solutions ( $M = K, Na, Li$ ;  $R = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, t-C_4H_9$ ). The values of complexation constants have been estimated in all the 54 crown-ROM combinations and the effects of cation, crown-cavity size and solvent have been examined. Two intriguing facts emerged from a comparison of the new results with the pertinent literature data. Firstly, it was found that the cation-crown cavity-complex stability variation in the ROM-ROH series disagrees with the well-known principle of steric match, the propensity of crowns to complexation decreasing in most instances in the order 15-crown-5 > 12-crown-4 > 18-crown-6 for the potassium and 12-crown-4 > 15-crown-5 > 18-crown-6 for the sodium alkoxide. An energetical preference of 2:1 over 1:1 crown-ROM complexes is presumably the responsible factor. Secondly, and even more importantly, it was found that complexation constants obtained in this study are strikingly small, the values for complexation of potassium and sodium alkoxides with 18-crown-6 being smaller by 3-7 power of ten than those which were previously obtained for the alkali ions, at lower concentrations. Evidence is provided that the difference does not originate from ion-pairing but from the operation of some effect which so far escaped notice.

The effects controlling complexation of alkali ions with polydentate ligands have been subject of studies in the past decade. In spite of effort already expended<sup>1-4</sup>, some important problems still await exploration. In particular, the effects of medium and counterion — both being large and complex — present a field ripe for further investigation.

As a part of our vested interest<sup>5</sup> in alkoxide-promoted reactions, we have recently initiated<sup>6</sup> a systematic investigation of crown-complex formation in alkali alkoxide-conjugate acid solutions. In this paper we report results of a detailed ebulliometric study revealing astonishingly low propensity of three standard crowns, 18-crown-6 (18C6), 15-crown-5 (15C5) and 12-crown-4 (12C4), to complex formation in a wide scale of 0.6 molal ROM-ROH solutions ( $R = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, t-C_4H_9$ ;  $M = Li, Na, K$ ).

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## EXPERIMENTAL

**Materials:** Alkali alkoxide solutions were prepared as described previously. The macrocyclic ligands 18C6, 15C5 and 12C4 were prepared by known procedures<sup>7-9</sup> and re-crystallized from hexane under dry-ice cooling.

**Ebulliometry:** Performed in a quartz apparatus under analogous conditions as we employed previously<sup>6,10</sup>. Reliability of the procedure was tested by determining molecular weights of 18C6, 15C5, and 12C4 in all the investigated solvents. Ebulliometric constants ( $K_E$ ) for the solvent series were available from our previous work<sup>10</sup>. In most instances, a very satisfactory agreement was obtained between theory and experiment, the difference being, in 0.05–1.2 molal region, less than 5–7%. Exceedingly high molecular weights were persistently obtained for all the three crowns in water (120–140% of theory). It is suggested that hydrophobic interactions are responsible for this anomaly, inviting the ligand molecules to flock together and aggregate.

## RESULTS

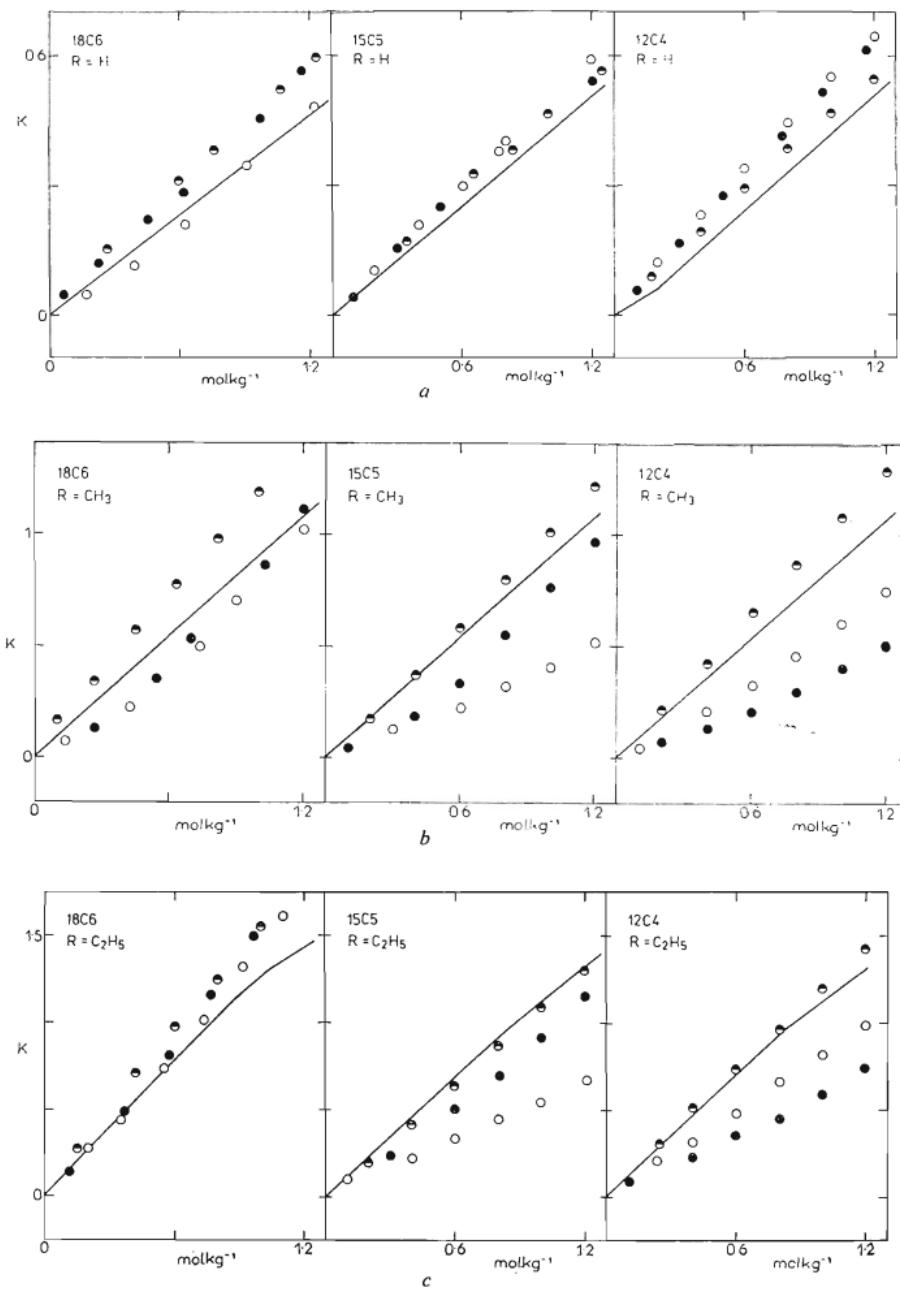
We pointed out already in our preliminary paper<sup>6</sup> that ebulliometric titration may serve as a simple tool for assessment of crown complex formation. Independence on the nature of solvent, ligand and cation, as well as operational capability at relatively high solute concentrations make the ebulliometry particularly suited for the present study which covers a wide scale of ROM–ROH solutions.

The procedure consists of measuring changes in boiling point temperature,  $\Delta T$ , induced by a gradual addition of the macrocyclic ligand to the appropriate ROM–ROH solution. Subsidiary data can be obtained from reverse ebulliometric experiments, in which alkoxide is being added to the macrocyclic ligand dissolved in the corresponding alcohol. Results of the ebulliometric measurements accomplished with three macrocyclic ligands (18C6, 15C5 and 12C4) in a homologous series of ROM–ROH solutions ( $R = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, t-C_4H_9; M = Li, Na, K$ ) are summarized in Figs 1–3. The values of  $\Delta T$  obtained upon a gradual addition of two equivalents of the crown to boiling 0.6 molal ROM–ROH solution are plotted in Figs 1 and 2. The values of  $\Delta T$  from the reverse experiments, in which 0.5 equivalent of ROK was gradually added to the 1.2 molal solution of crown in the corresponding alcohol are plotted in Fig. 3.

**Assessment of the fraction of the complexed form of crown present in ROM–ROH solution:** Since  $\Delta T$  is a colligative property, complex formation can be simply assessed from the data involved in Figs 1–3. For evaluation of the overall fraction of the complexed crown,  $\alpha$ , in 0.6 molal ROH–ROH solution we have used the equation

$$\alpha = \frac{\Delta T_{(ROH)} - \Delta T_{(ROM-ROH)}}{\Delta T_{(ROH)}}, \quad (1)$$

where  $\Delta T_{(ROM-ROH)}$  and  $\Delta T_{(ROH)}$  are boiling point elevations induced, in experiments from Figs 1 and 2, upon addition of a given amount of crown to the ROM–ROH



solution and to the corresponding pure solvent, respectively. The equation (1) rests on the tacit assumption that the state of ionic association in the alkoxide solution does not change upon addition of crown. It will be demonstrated later in this paper that this assumption approximately holds.

*Calculation of stability constants:* The concentration stability constants for 1 : 1 complex,  $\beta_1$ , is defined by

$$\beta_1 = [\text{MOR.L}] / [\text{MOR}][\text{L}], \quad (2)$$

where  $[\text{MOR.L}]$ ,  $[\text{MOR}]$ , and  $[\text{L}]$  are the molal concentrations of the 1 : 1 complex, uncomplexed alkoxide, and the uncomplexed ligand, respectively. Similarly, the concentration stability constant for 2 : 1 (sandwich) complex,  $\beta_2$ , is defined by

$$\beta_2 = [\text{MOR.L}_2] / [\text{MOR}][\text{L}]^2, \quad (3)$$

where  $[\text{MOR.L}_2]$  is the molal concentration of the 2 : 1 complex and  $[\text{MOR}]$  and  $[\text{L}]$  have the same meaning as above. If  $\alpha$  is the overall fraction of the complexed ligand from Eq. (1) and  $y$  is the fraction bound in the form of the 2 : 1 complex, the two stability constants can be expressed as

$$\beta_1 = \alpha - y / \{[\text{MOR}]_t - (\alpha - 0.5y)[\text{L}]_t\} (1 - \alpha) \quad (4)$$

and

$$\beta_2 = 0.5y / \{[\text{MOR}]_t - (\alpha - 0.5y)[\text{L}]_t\} (1 - \alpha)[\text{L}]_t, \quad (5)$$

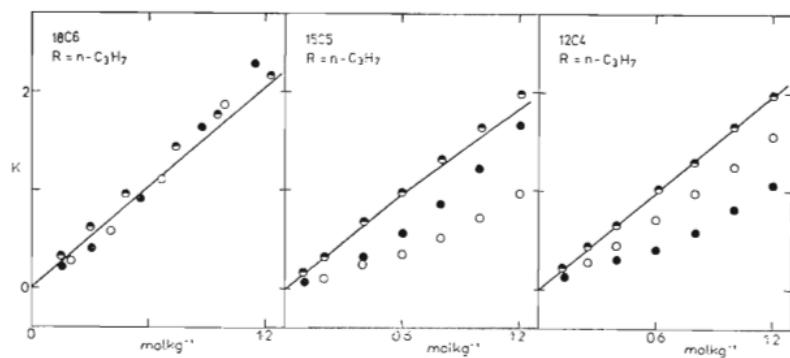
where  $[\text{MOR}]_t$  and  $[\text{L}]_t$  are the analytical concentrations of alkali alkoxide and ligand, respectively, present in the investigated solution. Simultaneous solution of Eqs (4) and (5) presents a rather tedious task<sup>11</sup> which however can be avoided in limiting situations. Thus, if 1 : 1 complex prevails over the 2 : 1 complex so that  $\alpha \gg y$ , the Eq. (4) reduces to

$$\beta_1 = \alpha / \{[\text{MOR}]_t - \alpha[\text{L}]_t\} (1 - \alpha) \quad (6)$$

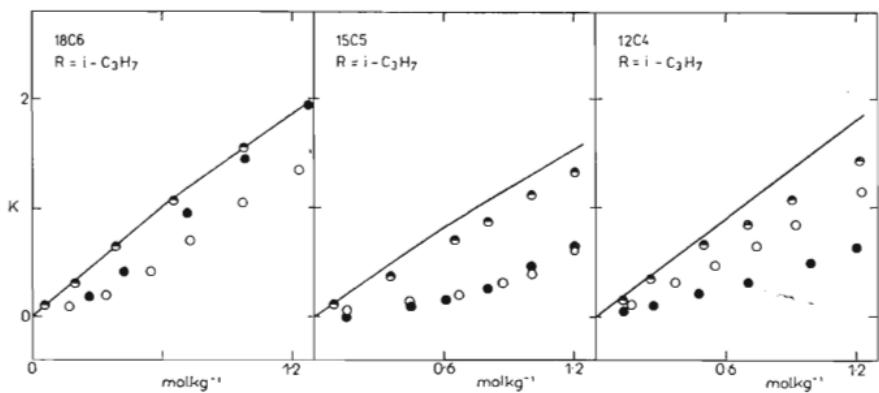
and  $\beta_2$  can be ignored. If, on the other hand, the 2 : 1 complex prevails so that

FIG. 1

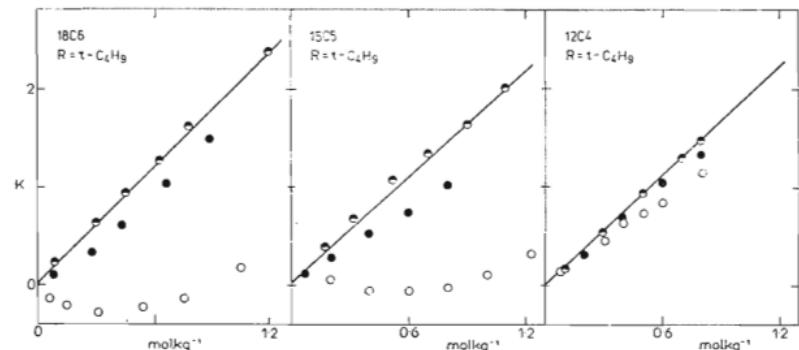
Changes in boiling point temperature,  $\Delta T$  (K), induced in 0.6 molal ROM-ROH solution [*a*: R = H; *b*: R = CH<sub>3</sub>; *c*: R = C<sub>2</sub>H<sub>5</sub>; M = K (○), Na (●), Li (◐)] and in the corresponding pure solvent (ROH; full line) upon addition of crown (18C6, 15C5, 12C4)



a



b



c

$\alpha \doteq y$ , the Eq. (5) reduces to

$$\beta_2 = 0.5\alpha / \{ [MOR]_t - 0.5\alpha [L]_t \} (1 - \alpha) [L]_t \quad (7)$$

and  $\beta_1$  can be ignored.

## DISCUSSION

The overall fractions of the complexed crown,  $\alpha$ , which were assessed ebulliometrically in the boiling 0.6 molal ROM-ROH solutions containing one equivalent of the macrocyclic ligand are summarized in Table I.

It is immediately apparent that complexation is very incomplete in majority of the examined solutions. Of the total 54 crown-ROH combinations included in Table I, only 2 give rise to a practically complete complexation ( $\alpha \sim 1$ ). An incomplete complexation ranging between 10–80% is found ( $\alpha = 0.1$ –0.8) in 25 crown-ROH combinations, whereas in the remaining 27 solutions the complexation is immeasurably small ( $\alpha < 0.1$ ).

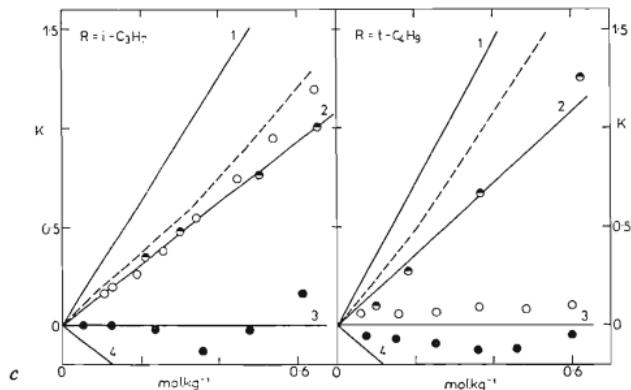
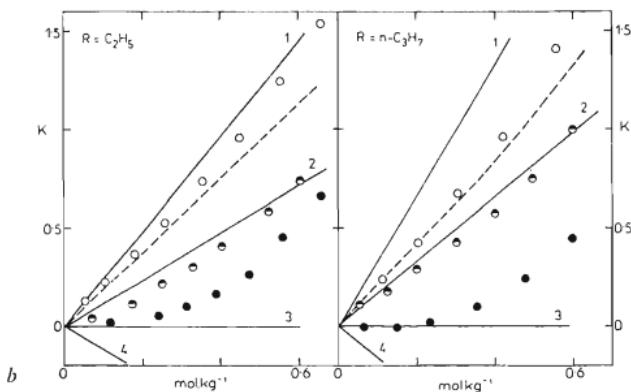
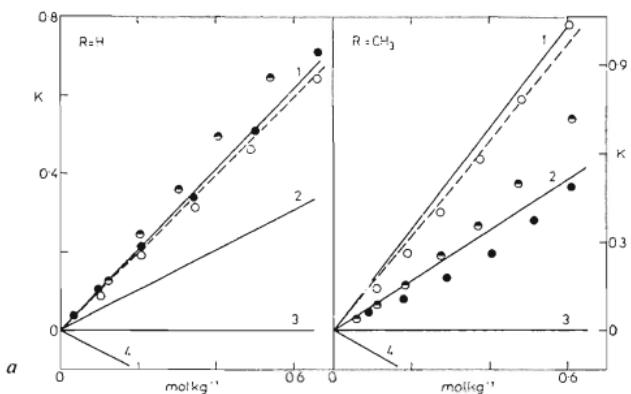
*Complex structure inferred from crown cavity-cation diameter- $\alpha$ -value correlation:* A correlation between ligand cavity and cation diameter has been frequently invoked in literature<sup>11–17</sup> in discussing stabilities of macrocyclic (crown) as well as macrobicyclic (cryptand) ligand–metal ion complexes. In most instances it has been found that the most stable complexes arise from such ligand–ion combinations which sterically match (Table II).

In a striking contrast, inspection of the present results in Table I reveals an entirely different pattern of complex stability variation, the highest proportions of the complexed crown being found in such ligand–ion combinations which apparently do not match. In all the ROM-ROH system under study (except for  $R = t\text{-C}_4\text{H}_9$ ), the  $\alpha$  values decrease in the order 15C5 < 12C4 < 18C6 for the potassium and 12C4 < < 15C5 < 18C6 for the sodium alkoxide indicating a distinct propensity of the alkali salts to coordinate preferentially with crowns which possess cavity smaller than is the cation diameter (Table II).

A simple explanation for this behaviour can be provided when a possible formation of 2:1 crown-ROH complexes is taken into account. It is generally assumed that 1:1 complexes arise preferentially or exclusively whenever the ligand cavity

Fig. 2

Changes in boiling point temperature,  $\Delta T$ (K), induced in 0.6 molal ROM-ROH solution [ $a: R = n\text{-C}_3\text{H}_7$ ;  $b: R = i\text{-C}_3\text{H}_7$ ;  $c: R = t\text{-C}_4\text{H}_9$ ;  $M = K (\circ)$ ,  $Na (\bullet)$ ,  $Li (\square)$ ]<sup>1</sup> and in the corresponding pure solvent (ROH; full line) upon addition of crown (18C6, 15C5, 12C4)



is equal to or larger than diameter of the alkali cation. However, if cation diameter exceeds that of the ligand cavity, part of the ion remains exposed to solvent and the fraction of the ion in the cavity is less bound with ether oxygen. Accordingly, formation of 2:1 crown-cation complexes becomes more competitive and may prevail eventually over the 1:1 complexed species. Such a preference has been already noted in literature in several instances. Thus, it has been reported that benzo-15C5 upon treatment with potassium salts deposits 2:1 crown-sodium salt complexes<sup>18-20</sup>, regardless of the educts ratio. Similarly, it has been found that 12C4 when treated with sodium salts yields crystalline 2:1 complexes<sup>21-22</sup>. A scattered evidence indicates that the 2:1 complexes may prevail also in solution. According to Izatt<sup>23</sup>, the 2:1 complex of benzo-15C5 with potassium chloride in 80% aqueous methanol is more stable ( $\log \beta_2 = 4.8$ ) than the corresponding 1:1 complexed species ( $\log \beta_1 = 2.2$ ). Desreaux<sup>24</sup> reports that 2:1 complex arising from 12C4

TABLE I

The fraction of the complexed crown,  $\alpha$ , resulting upon addition of 1 equivalent of macrocyclic ligand to the boiling 0.6 molal ROM-ROH solution

R	M = K			M = Na			M = Li		
	18C6	15C5	12C4	18C6	15C5	12C4	18C6	15C5	12C4
H	≤0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH <sub>3</sub>	0.2	0.6	0.3	0.2	0.4	0.6	0.0	0.0	0.0
C <sub>2</sub> H <sub>5</sub>	0.0	0.5	0.3	0.0	0.3	0.5	0.0	0.0	0.0
n-C <sub>3</sub> H <sub>7</sub>	0.0	0.6	0.3	0.0	0.4	0.6	0.0	0.0	0.0
i-C <sub>3</sub> H <sub>7</sub>	0.5	0.8	0.5	0.2	0.8	0.8	0.0	0.2	0.2
t-C <sub>4</sub> H <sub>9</sub>	1.0	1.0	0.3	0.3	0.3	0.1	0.0	0.0	0.0

←

FIG. 3

Changes in boiling point temperature,  $\Delta T$  (K), induced in 1.2 molal 18C6-ROH solution (○), 1.2 molal 15C5-ROH solution (●), 1.2 molal 12C4-ROH solution (◐), and in the pure solvent (ROH; broken line) upon addition of ROK ( $a$ : R = H, CH<sub>3</sub>;  $b$ : R = C<sub>2</sub>H<sub>5</sub>, n-C<sub>3</sub>H<sub>7</sub>;  $c$ : R = i-C<sub>3</sub>H<sub>7</sub>, t-C<sub>4</sub>H<sub>9</sub>). A comparison with the model system traces calculated for various modes of complexation: 1 formation of uncomplexed dissociated ions ( $K^+ + RO^-$ ); slope =  $2K_E$ ; 2 formation of uncomplexed ion pairs (KOR) or formation of the dissociated 1:1 complex  $[K^+(crown) + RO^-]$ ; slope =  $K_E$ ; 3 formation of the ion-paired 1:1 complex [KOR(crown)] or formation of the dissociated 2:1 complex  $[K^+(crown)_2 + RO^-]$ ; slope = 0; 4 formation of the ion-paired 2:1 complex [KOR(crown)<sub>2</sub>]; slope =  $-K_E$

and sodium perchlorate in propylene carbonate is more stable ( $\log \beta_2 = 6.3$ ) than the corresponding 1:1 species ( $\log \beta_1 = 3.5$ ).

We are therefore inclined to assume that relative stabilities of 2:1 and 1:1 complexes underlie the pattern of  $\alpha$ -value variation in Table I. In line with the above arguments we suggest that energetical preference of 2:1 over 1:1 complexes is responsible for the observed decrease of  $\alpha$ -values in the order  $15C5 > 12C4 > 18C6$  for the potassium and  $12C4 > 15C5 > 18C6$  for the sodium cation, reflecting the stability order of the complexes  $MOR(15C5)_2 > MOR(12C4)_2 > MOR(18C6)$  in the former ( $M = K$ ) and  $MOR(12C4)_2 > MOR(15C5) > MOR(18C6)$  in the latter ( $M = Na$ ) cation series.

As it concerns the different  $\alpha$ -value variation which in  $t\text{-C}_4\text{H}_9\text{OM}-t\text{-C}_4\text{H}_9\text{OH}$  solution is found to follow the order  $18C6 > 15C5 > 12C4$  for the potassium as well as for the sodium cation, we suggest that it indicates a prevalence of the 1:1 over 2:1 complexes, regardless of crown *vs* cation diameter ratio. Enhanced ligation ability of alkoxide anion in the low polar, ion-pairing solvent is probably responsible for this exception, allowing the counterion to compete efficiently with the second molecule of crown for entrance into the cation coordination sphere.

*Effect of medium on complex stability:* Solvent effects on stability of crown-alkali ion complexes have been already subject of several studies<sup>25-29</sup>. For comparison

TABLE II  
Principle of steric match in alkali ion-crown and alkali ion-cryptand complex formation: literature data

Ligand	Medium	Complex stability ( $\log \beta$ )		
		$\text{Li}^+$ (0.136) <sup>a</sup>	$\text{Na}^+$ (0.194) <sup>a</sup>	$\text{K}^+$ (0.266) <sup>a</sup>
$18C6^b$	$\text{H}_2\text{O}$	— <sup>c</sup>	0.8	2.0
(0.26—0.32) <sup>d</sup>	$\text{CH}_3\text{OH}$	— <sup>c</sup>	4.4	6.1 <sup>c</sup>
$15C5^b$	$\text{H}_2\text{O}$	— <sup>c</sup>	0.7	0.7
(0.17—0.22) <sup>d</sup>	$\text{CH}_3\text{OH}$	— <sup>c</sup>	3.5	3.8
[2.2.2] <sup>e</sup>	$\text{H}_2\text{O}$	<2.0	3.9	5.4
(0.28) <sup>d</sup>	$\text{CH}_3\text{OH}-\text{H}_2\text{O}$	1.8	7.2	9.8
[2.2.1] <sup>e</sup>	$\text{H}_2\text{O}$	2.5	5.4	3.9
(0.22) <sup>a</sup>	$\text{CH}_3\text{OH}-\text{H}_2\text{O}$	4.2	8.8	7.4
[2.1.1] <sup>e</sup>	$\text{H}_2\text{O}$	5.5	3.2	<2.0
(0.16)	$\text{CH}_3\text{OH}-\text{H}_2\text{O}$	7.6	6.1	2.3

<sup>a</sup> Ionic diameter (nm). <sup>b</sup> Crown; values from refs<sup>15,16</sup>. <sup>c</sup> Immeasurably low. <sup>d</sup> Cavity diameter (nm). <sup>e</sup> Cryptand; values from ref.<sup>14</sup>.

with these studies it appeared desirable to convert the  $\alpha$ -values from Table I into stability constants. Approximately, it has been done using the Eqs (6) and (7). The calculation is based on the simplifying assumption that the 1:1 crown-ROH complex prevails greatly over the 2:1 species (Eq. (6)) or that the reverse holds (Eq. (7)). Justifiability of the approximation rests on the arguments outlined above. The calculated values are summarized in Table III. Inspection of Table III shows that values of the complexation constants increase in the homologous series in the order  $\text{H} < \text{C}_2\text{H}_5 < \text{CH}_3 < \text{n-C}_3\text{H}_7 < \text{i-C}_3\text{H}_7$  following thus more or less regularly (with exception of  $\text{R} = \text{CH}_3$ ) the order of a decreasing solvent polarity. Such a correlation appears to be reasonable if the complexation is viewed as a competition between macrocyclic ligand and solvent for the cation coordination sites.

At variance with the simple concept are the complexation constants found in the least polar ROM-ROH combination ( $\text{R} = \text{t-C}_4\text{H}_9$ ), the values for complexation of sodium t-butoxide with 12C4 and 15C5 and of potassium t-butoxide with 12C4 being much smaller than the corresponding ones found for the more polar homologues. Ion-pairing may account well for this exceptional behaviour. We pointed out already earlier in this paper that also anion can compete, in low polar solvents, with the macrocyclic ligand for coordination with the cation and diminish thus stability of the crown complexes in tert-butanol.

*Disagreement with the data reported in literature:* Stability of complexes of alkali salts with 18C6 in some of the protic solvents employed in this study was investigated already previously by several research groups. Izatt with coworkers<sup>15,16</sup> and Frensdorff<sup>11</sup> measured the complexation constants in methanol and water,

TABLE III

Approximate stability constants of 1:1 and 2:1 crown-metal complexes ( $\beta_1$  and  $\beta_2$ , respectively) determined in boiling 0.6 molal ROM-ROH solutions

R	M = K			M = Na		
	18C6 ( $\beta_1$ ) <sup>a</sup>	15C5 ( $\beta_2$ ) <sup>b</sup>	12C4 ( $\beta_2$ ) <sup>b</sup>	18C6 ( $\beta_1$ ) <sup>a</sup>	15C5 ( $\beta_1$ ) <sup>a</sup>	12C4 ( $\beta_2$ ) <sup>b</sup>
H	≤ 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
CH <sub>3</sub>	0.7	6.0	1.1	0.5	1.7	8.0
C <sub>2</sub> H <sub>5</sub>	< 0.2	4.5	1.1	< 0.2	1.0	4.2
n-C <sub>3</sub> H <sub>7</sub>	< 0.2	8.6	1.0	< 0.2	2.0	7.4
i-C <sub>3</sub> H <sub>7</sub>	2.8	46	3.0	0.5	37	27
t-C <sub>4</sub> H <sub>9</sub>	> 600	> 600 <sup>a</sup>	0.8 <sup>a</sup>	0.7	1.1	< 0.2 <sup>a</sup>

<sup>a</sup> Calculated from data in Table I using the Eq. (6). <sup>b</sup> Calculated from data in Table I using the Eq. (7).

the former authors employing titration calorimetry, and the latter potentiometry with ion-selective electrodes. In addition, Agostiano<sup>25</sup> and his colleagues measured the complexation constants in methanol, ethanol and n-propanol by a polarographic procedure. The results of the previous measurements are compared with the present ones in Table IV.

A stunning disagreement between the previous and the present results becomes immediately apparent from the comparison, the literature values for the potassium and sodium ion complexation being larger by 3–8 logarithmic units than the present ones. The consistency of the literature values obtained by different procedures makes the disagreement even more surprising.

Seeking explanation for the disparate results, we must therefore first consider possible flaws in the ebulliometric measurement. As it was pointed out earlier in this paper, evaluation of the experimental data from Figs 1 and 2 rests on the assumption that state of ionic association in the investigated solution does not change upon addition of the macrocyclic ligand, so that dissociated ions remain dissociated and ion pairs remain ion-paired, regardless of complex formation. That this assumption is of a crucial importance is evident from a simple consideration of the traces 1 in Fig. 4a and 2 in Fig. 4b showing that erratically low values of complexation constants would be obtained using the Eq. (1), if the complexation were attended by a dissociation of ion pairs.

TABLE IV

Reported constants of complexation of alkali ions with 18C6 compared with the corresponding values from the present study (figures in parentheses)

Solvent	$\log \beta$		
	$M = K$	$M = Na$	$M = Li$
$H_2O$	2.06 <sup>a</sup> ; 2.03 <sup>b</sup> ( $\leq -0.7$ ) <sup>d</sup>	0.3 <sup>a</sup> ; 0.8 <sup>b</sup> ( $< -0.7$ ) <sup>d</sup>	— ( $< -0.7$ ) <sup>d</sup>
$CH_3OH$	5.97 <sup>c</sup> ; 6.10 <sup>a</sup> ; 6.06 <sup>b</sup> ( $-0.15$ ) <sup>d</sup>	4.21 <sup>c</sup> ; 4.32 <sup>a</sup> ; 4.36 <sup>b</sup> ( $-0.3$ ) <sup>d</sup>	< 2.0 <sup>c</sup> ( $< -0.7$ ) <sup>d</sup>
$C_2H_5OH$	6.58 <sup>c</sup> ( $< -0.7$ ) <sup>d</sup>	4.70 <sup>c</sup> ( $< -0.7$ ) <sup>d</sup>	< 2.0 <sup>c</sup> ( $< -0.7$ ) <sup>d</sup>
n-C <sub>3</sub> H <sub>7</sub> OH	7.24 <sup>c</sup> ( $< 0.7$ ) <sup>d</sup>	4.90 <sup>c</sup> ( $< -0.7$ ) <sup>d</sup>	< 2.0 <sup>c</sup> ( $< -0.7$ ) <sup>d</sup>

<sup>a</sup> Potentiometric value; ref.<sup>1</sup>. <sup>b</sup> Calorimetric value; refs<sup>15,16</sup>. <sup>c</sup> Polarographic value for dicyclohexyl 18C6; ref.<sup>25</sup>. <sup>d</sup> Logarithmed value from Table III.

Arguments are, however, available which speak against such an eventuality. First, we have shown previously<sup>10</sup> that alkali alkoxides are almost completely dissociated in the boiling 0.6 molal  $\text{MOH}-\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OM}-\text{CH}_3\text{OH}$  and  $\text{C}_2\text{H}_5\text{OM}-\text{C}_2\text{H}_5\text{OH}$  solutions ( $M = \text{K, Na, Li}$ ), the apparent degrees of their association being close to the value 0.5 which is the theoretical limit for dissociation. No substantial dissociation of ion pairs can therefore ensue on addition of crown to these solutions. Second, the results of the reverse ebulliometric titration of 18C6 with ROK in Fig. 3 shows that the experimental points for  $R = \text{H, CH}_3, \text{C}_2\text{H}_5$  are very close to the theoretical trace 1 corresponding to the absence of complexation but evidently lie astray from the traces 2-4 calculated for the formation of various crown-ROK complexes.

Since principal soundness of the basic ebulliometric assumption thus appears to be beyond reasonable doubts, at least as it concerns the three lower homologues

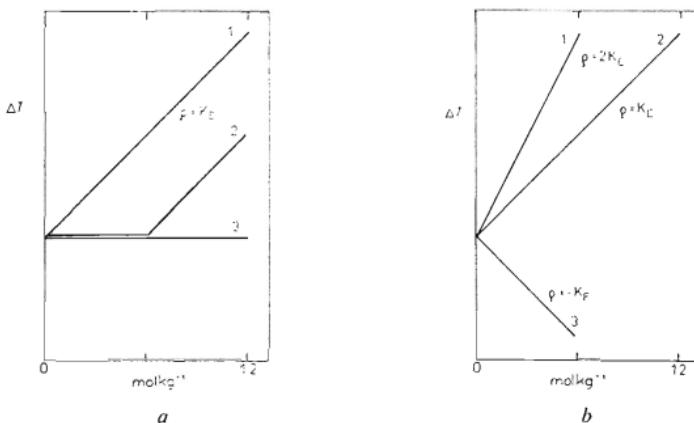


FIG. 4

Ebulliometric model system traces calculated for different modes of complexation in 0.6 molal  $\text{ROM}-\text{ROH}$  solution upon addition of crown. *a* Traces calculated under the assumption that state of ionic association in the model system does not change upon addition of crown: 1 a crown dissolution, unaccompanied by complex formation; 2 formation of the dissociated 1:1 complex  $[\text{M}^+(\text{crown}) + \text{RO}^-]$  from dissociated alkoxide ions ( $\text{M}^+ + \text{RO}^-$ ), or formation of the ion-paired 1:1 complex  $[\text{ROM}(\text{crown})]$  from ion-paired alkoxide species ( $\text{MOR}$ ); 3 formation of the dissociated 2:1 complex  $[\text{M}^+(\text{crown})_2 + \text{RO}^-]$  from the dissociated alkoxide ions ( $\text{M}^+ + \text{RO}^-$ ), or formation of the ion-paired 2:1 complex  $[\text{ROM}(\text{crown})_2]$  from the paired alkoxide ( $\text{MOR}$ ) species. *b* Traces calculated under the assumption that state of ionic association in the model system changes upon addition of crown: 1 a crown dissolution accompanied by dissociation of alkoxide ion pairs ( $\text{MOR}$ ); 2 formation of the dissociated 1:1  $[\text{M}^+(\text{crown}) + + \text{RO}^-]$  and/or 2:1  $[\text{M}^+(\text{crown})_2 + \text{RO}^-]$  complexes from ion-paired alkoxide ( $\text{MOR}$ ); 3 formation of the ion-paired 1:1  $[\text{MOR}(\text{crown})]$  and/or 2:1  $[\text{MOR}(\text{crown})_2]$  complexes from dissociated alkoxide ions ( $\text{M}^+ + \text{RO}^-$ ).

(R = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>), we must next consider the experimental differences which may also account for the conflicting results in Table IV. The most obvious difference concerns temperature, all the measurements reported in literature being conducted at 25°C. However, this factor can be safely excluded from consideration on basis of our observation<sup>30</sup> that complexation of 18C6 with 0.6 molal KOH in aqueous solution is negligible also at room temperature. Another apparent difference concerns the nature of counterion, alkali chlorides being examined in all the previous studies referred to in Table IV. There is, however, evidence in literature suggesting that change of counterion, alone, does not affect the complex formation, at least in water and methanol. Chloride was replaced by hydroxide<sup>11</sup> and perchlorate<sup>21</sup> anion, but there was no detectable effect on the stability of crown complexes with sodium cation. Lastly, difference in salt concentration has to be taken into account since all the previous measurements have been conducted in more diluted solutions. Again, however, no clear-cut indication that salt concentration affects crown complex formation is apparent from the available literature evidence. Frensdorff<sup>11</sup> admittedly reports that sodium complexing with dicyclohexyl-18C6 is weakened somewhat as the cation concentration rises in 0.001–0.01 molal region. However, no significant difference is found (Table IV) between the constants of alkali ion complexation with 18C6, obtained respectively in 0.002–0.01 molal (by potentiometry) and in 0.1 molal (by titration calorimetry) solution. Moreover, influence of ionic strength on complexation of sodium ion with 18C6 was specifically investigated<sup>31</sup> in methanol. A decrease of the complex stability was observed on increasing ionic strength from  $I_e = 0.005$  to  $I_e = 0.5$  (in mol dm<sup>-3</sup>) but the overall change in  $\log \beta$  was less than 0.3 logarithmic unit.

As a corollary, the operation of some powerful effect which so far escaped notice in literature has to be responsible for the disagreement in Table IV.

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