DEGREES OF ASSOCIATION OF ALKALI TERT-BUTOXIDES IN TERT-BUTANOL IN THE ABSENCE AND IN THE PRESENCE OF CROWNS: AN EBULLIOMETRIC STUDY*

Václav PECHANEC[a], Oldřich KOCIÁN[a], Vlastimil HALAŠKA[b], Magdalena PÁNKOVÁ[a] and **Jiří ZÁVADA[a]

[a] *Institute of Organic Chemistry and Biochemistry,*
Czechoslovak Academy of Sciences, 166 10 Prague 6 and
[b] *Institute of Macromolecular Chemistry,*
Czechoslovak Academy of Sciences, 162 06 Prague 6

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Association degrees have been determined in 0·03–0·8 molal t-C_4H_9OLi–t-C_4H_9OH, t-C_4H_9ONa–t-C_4H_9OH and t-C_4H_9OK–t-C_4H_9OH solutions in the absence and also in the presence of three different crowns (18-crown-6, 15-crown-5 and 12-crown-4). It has been found that presence of any of the three crowns does not affect association degree in the alkoxide solutions. t-C_4H_9OLi is on average dimeric in 0·03 molal and tetrameric in 0·4–0·8 molal solution, whereas t-C_4H_9ONa and t-C_4H_9OK are in the full concentration range monomeric ion pairs, in the absence as well as in the presence of the crowns. Of the nine tert-butoxide–crown combinations studied, only two, t-C_4H_9OK–18-crown-6 and t-C_4H_9OK–15-crown-5, yielded complexes quantitatively, in the form of 1 : 1 complexed ion pairs. An incomplete complex formation (10–30%) has been observed with the combinations t-C_4H_9OK–12-crown-4, t-C_4H_9ONa–18-crown-6, t-C_4H_9ONa–15-crown-5, t-C_4H_9ONa–12-crown-4. No complex formation has been detected with t-C_4H_9OLi, in combination with any of the three crowns. Complex stability decreases in the order $\overset{(+)}{K} > \overset{(+)}{Na} > \overset{(+)}{Li}$, regardless of the crown cavity size. At variance with the prevailing opinion it indicates that steric fit between cation and crown is not the main factor which controls complex stability in the solution. A cooperative influence of anion on crown complex stability is considered in terms of the theory of hard and soft acids and bases.

Crown ethers (crowns) have been used amply for diagnosis of base association effects in alkali alkoxide-promoted reactions[1–10]. Yet, very little is known[1,11,12] about the effect of crown on base association in the alkoxide solutions.

In this paper we have examined, ebulliometrically, the association equilibrium (Eq. (*1*)) in 0·03–0·8 molal solutions of lithium, sodium and potassium tert-butoxide

$$\overset{(-)}{RO} + \overset{(+)}{M} \rightleftharpoons (ROM) \rightleftharpoons (ROM)_2 \rightleftharpoons (ROM)_3 \rightleftharpoons (ROM)_4 \rightleftharpoons (ROM)_n \qquad (1)$$

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** To whom correspondence should be addressed.

in tert-butanol, in the absence and also in the presence of crowns. Three crowns differing greatly in cavity size, 18-crown-6, 15-crown-5, 12-crown-4, have been employed in this study, in combination with each of the three alkali alkoxides. Degrees of association have been determined in the alkoxide solutions in the absence as well as in the presence of crowns. Crown-complex stabilities have been assessed for all alkoxide-crown combinations studied.

Cooperative influence of cation, anion, solvent and crown upon ionic association and crown-complex formation has been examined on basis of these results and some pertinent literature data.

EXPERIMENTAL

Materials: Dry tert-butanol (less than 0·006% of water; K. Fischer) was prepared as described previously[10]. The lithium and sodium metals employed were reagent grade and potassium metal analytical grade (Erba) products. 18-Crown-6, 15-crown-5 and 12-crown-4 were prepared by described procedures[13-15] and the purity was checked gas-chromatographically (>98%). Impurities present in 12-crown-4 were removed by a repeated crystallization from hexane in a dry-ice bath.

Ebulliometric measurements: Performed in a quartz ebulliometer equipped with a Beckman thermometer. The effect of atmospheric pressure fluctuation was excluded by a simultaneous determination of boiling point of tert-butanol in another apparatus. The apparatus were protected against moisture and CO_2 by absorption tubes.

Alkoxide solutions: Prepared *in situ* in the ebulliometer by a portionswise addition of weighted pieces of the freshly cut metal to the boiling solvent. Each portion of the metal was allowed to dissolve completely prior further addition enabling thus a series of measurements for several alkoxide concentrations to be conducted within a single ebulliometric run.

Solubility of alkali tert-butoxides in boiling tert-butanol: t-C_4H_9OK: 1·9 mol/1 000 g at 88·6°C; t-C_4H_9ONa: 0·89 mol/1 000 g at 83·4°C; t-C_4H_9OLi: 1·1 mol/1 000 g at 82·4°C.

Evaluation of experimental data: The apparent molecular weights, M_{app}, were calculated from the equation

$$M_{\text{app}} = K_{\text{E}} \frac{w_1}{w_2 \, \Delta T}, \qquad (2)$$

where K_{E} is the ebullioscopic constant of tert-butanol (*vide infra*), w_1 is the weight of the metal alkoxide corresponding to the dissolved metal, w_2 is the weight of tert-butanol corrected on the amounts of the alcohol consumed in the formation of the alkoxide, and ΔT is the difference between the boiling point of the measured alkoxide solution and that of pure tert-butanol. The apparent degrees of association, n_{app}, were calculated from the equation

$$n_{\text{app}} = \frac{M_{\text{app}}}{M_{\text{theor}}}. \qquad (3)$$

Ebulliometric constant: Calculated from the heat of vaporization of tert-butanol[16]. The obtained value ($K_{\text{E}} = 1{\cdot}79$) gave in molecular weight determination of crowns the following results. 12-Crown-4: M_{app} 170 ± 3 (M_{theor} 176·2); 15-crown-5: M_{app} 223 ± 5 (M_{theor} 220·2); 18-crown-6: M_{app} 236 ± 5 (M_{theor} 264·3).

Effect of glass surface: Erratic values of M_{app} for the alkali alkoxides were obtained in the preliminary experiments using a standard soft-glass ebulliometer. Reaction of the alkoxides with the glass surface (ion exchange) was presumably the responsible factor. Washing of the glass apparatus with mineral acids markedly deteriorated reproducibility of the measurement.

Thermoelectric measurements: The apparatus and experimental procedure were described elsewhere[17].

RESULTS AND DISCUSSION

Association in the Absence of Crowns

The ebulliometrically determined association degrees n_{app} of lithium, sodium and potassium tert-butoxides in tert-butanol are plotted as a function of concentration in Fig. 1. Striking differences in association of the three alkoxides are immediately apparent. For lithium tert-butoxide, the association degree is distinctly higher than

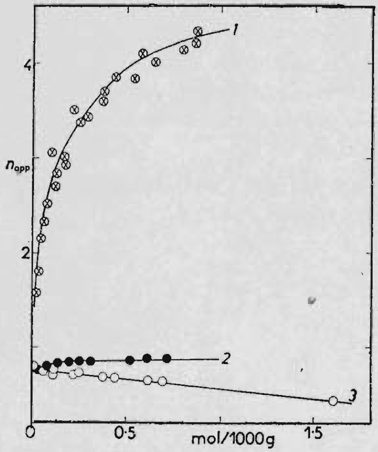


FIG. 1

Apparent degree of alkoxide association (n_{app}) as a function of molal concentration in boiling $t-C_4H_9OLi-t-C_4H_9OH$ *1*, $t-C_4H_9.ONa-t-C_4H_9OH$ *2* and $t-C_4H_9OK-t-C_4H_9.OH$ *3* solutions. Experimental points for each alkoxide are from three independent runs

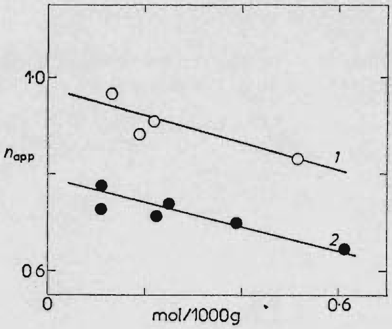


FIG. 2

Effect of temperature on the apparent degree of alkoxide association (n_{app}) in 0·1—0·5 molal $t-C_4H_9OK-t-C_4H_9OH$ solution: values determined at 25°C *1* and in the boiling solution *2* unity over the full concentration range studied and the tendency to formation of higher aggregates sharply increases with rising concentration, the value of n_{app} being approximately 2 in a 0·03 molal and about 4 in 0·8 molal solution. For sodium and potassium tert-butoxide, on the other hand, the association degrees in the same concentration range are lower than unity. A near-independence of n_{app} on concentration is observed for the sodium alkoxide. A marked decrease of n_{app} with increasing concentration is found, surprisingly, for the potassium alkoxide.

These findings disagree very considerably with the previous studies[17,18] in aprotic solvents which showed that n_{app} of alkali tert-butoxides are much higher than unity and independent on concentration (in 00·6–0·3 molal region), regardless of solvent polarity (ε) and identity of cation. On comparison with the aprotic solvents (Table I), the ability of tert-butanol to support association of the alkoxide ions thus appears to be remarkably low.

A simple explanation for this exceptional behaviour of tert-butanol can be provided when capability of protic solvents to solvate effectively cations as well as anions is taken into account. In accord with the donor–acceptor theory of outer-sphere solvation[20], coordination of molecules of tert-butanol in the inner sphere of a cation leads to an increase of acidity of the hydrogen atoms. "Free" tert-butanol molecules interact therefore preferentially with the latter providing electrons from the oxygen atoms (Scheme 1*A*). For the same reason, also tert-butoxide anions are solvated preferentially by the inner-sphere hydrogen bonds (Scheme 1*B*). Formation of solvent-separated ion pairs is thus greatly favored, particularly at low concentra-

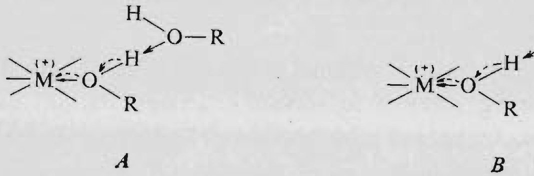
TABLE I

Association degrees, n_{app}, of alkali tert-butoxides in aprotic solvents

Solvent	ε (25°C)[a]	Degree of association		
		t-C_4H_9OLi	t-C_4H_9ONa	t-C_4H_9OK
Cyclohexane	2·0	6·1[b]	7·6[b]	—
Benzene	2·3	6·2[c]	8·3[c]	—
Toluene	2·4	5·8[c]	—	3·8[c]
Tetrachloromethane	2·2	5·9[c]	7·5[c]	—
Diethyl ether	4·2	5·9[c]	4·3[c]	—
Tetrahydrofuran	7·4	4·1[c]	3·9[c]	3·9[c]
Pyridine	12·3	4·0[c]	3·9[c]	4·0[c]
Dimethyl sulphoxide	48·9	4·0[d]	—	2–3[d]

[a] From ref.[19]. [b] Determined ebulliometrically; ref.[17]. [c] Determined by vapor-pressure osmometry; ref.[17]. [d] Determined by cryoscopy; ref.[18].

tions. On increasing the solute concentration, solvation layers are gradually reduced and a collapse of the solvent-separated species may result leading to contact ion pair monomers and/or higher aggregates. When propensity of alkali cation to association with tert-butoxide anion is very strong, as it is assumedly the case of the small lithium ion, coulombic forces squeeze out solvent molecule separating the opposite ions already at a very low alkoxide concentration and further desolvation accompanying the contact ion pair aggregation is also easy. However, when the propensity of alkali cation to association is weaker, as it is probably with the larger sodium and potassium ions, the coulombic energy gain accruing from the ion pair aggregation does not compensate the loss of solvation energy and contact or solvent-separated ion pair monomers remain prevalent even at high alkoxide concentrations.



SCHEME 1

Ideally, values of n_{app} equal or close to unity would be expected when ion pair monomers prevail in the alkoxide solutions. However, as Fig. 1 shows, the values of n_{app} obtained for sodium and potassium tert-butoxides are significantly lower than unity. Moreover, the value of n_{app} decreases steadily with rising concentration of the latter alkoxide, being approximately 0·78 in 0·05 molal, 0·64 in 0·7 molal and 0·45 in 1·6 molal solution. This might be taken to indicate increasing proportion of free ions in the alkoxide solution; n_{app} equal to 0·5 corresponds, formally, to a complete dissociation into free ions. However, a consideration of the Bjerrum's theory of ion pairs[21] in solvents with low dielectric constants ($\varepsilon_{\text{t-BuOH}} = 12{\cdot}2$)[19] and, particularly, conductivity data obtained in $\text{t-}C_4H_9ONa$–$\text{t-}C_4H_9OH$ and $\text{t-}C_4H_9OK$–$\text{t-}C_4H_9OH$ solutions[12,22] exclude any sizeable proportion of free ions in the concentration range studied. Hence, the observed negative deviation of n_{app} from unity has to be consequence of a non-ideal solution behaviour of the ion pairs.

Pronounced deviations from ideality of solution behaviour were previously noted[23] in measurements of n_{app} of some organolithium compounds in diethyl ether and tetrahydrofuran and explained plausibly in terms of strong specific solute–solvent interactions reducing solvent vapour pressure below that computed from the Raoult's law. In accordance with the concept of outer-sphere solvation we assume that such interactions operate also in the solutions of sodium and potassium tert-butoxide; boiling point elevation (ΔT) in the two solutions are therefore exaggeratedly high and the values of n_{app} are anomalously low. Equilibrium between solvent–separated and contact ion pairs[24] is probably responsible for the quantitative difference which in this respect exists between the sodium and potassium tert-butoxide (Fig. 1). Evidence will be presented in the following section suggesting that the equilibrium is cation dependent, the sodium ion preferring the contact and potassium ion the solvent-separated species in the solution. This may explain well why n_{app} declines with rising concentration only for the potassium alkoxide because solute–solvent interactions are evidently much stronger for the solvent-separated (outer-sphere solvated) than for contact ion pairs.

In order to assess possible dependence of n_{app} on temperature, we complemented the ebulliometric study by determination of n_{app} at room temperature using the thermoelectric method* (vapour phase osmometry). A comparison of the values of n_{app} determined for $t\text{-}C_4H_9OK\text{–}t\text{-}C_4H_9OH$ system by the two different procedures (Fig. 2) shows that the values determined at room temperature are distinctly higher than those in the boiling solution but still lower than unity. The changes of n_{app} with alkoxide concentration at the two different temperatures are almost parallel.

Summing up the present evidence, we see that the propensity of alkali tert-butoxides to *association* (in tert-butanol) increases in the order $\overset{(+)}{K} < \overset{(+)}{Na} < \overset{(+)}{Li}$. It contrasts remarkably with the previous reports by Smid and coworkers that propensity of fluorenyl alkali salts[25–27] and alkali tetraphenylborides[28,29] (in tetrahydrofuran) to *dissociation* follows the order $\overset{(+)}{K} < \overset{(+)}{Na} < \overset{(+)}{Li}$.

A simple explanation for this apparent divergency of cation effects can be provided when a competition between anion and solvent[30] for coordination with a cation is considered. Tert-butoxide anion possesses a localized negative charge and is a hard nucleophile. On the other hand, fluorenyl and tetraphenylboride anions with dispersed negative charges are soft nucleophiles. In accordance with the theory of hard and soft acids and bases[31,32], the hard tert-butoxide anion binds strongly lithium cation which is a hard electrophile but weakly potassium cation which is a soft electrophile. As a result, solvation of the former cation is weak and of the latter strong. For the fluorenyl and tetraphenylboride anions the situation is exactly opposite. This may explain the difference between our system and the systems investigated by the American authors[25–29] because cation coordination with anion promotes association whereas cation solvation provides driving force for ion-pair separation and dissociation.

Association in the Presence of Crowns

In order to assess the effect of crown ethers on association of alkali alkoxides, we examined changes in ebulliometric behaviour of three 0·6 molal $t\text{-}C_4H_9\overset{(-)}{O}\overset{(+)}{M}\text{–}t\text{-}C_4H_9OH$ solutions $(\overset{(+)}{M} = \overset{(+)}{Li}, \overset{(+)}{Na}, \overset{(+)}{K})$ upon addition of three different crowns. Fig. 3*a* summa-

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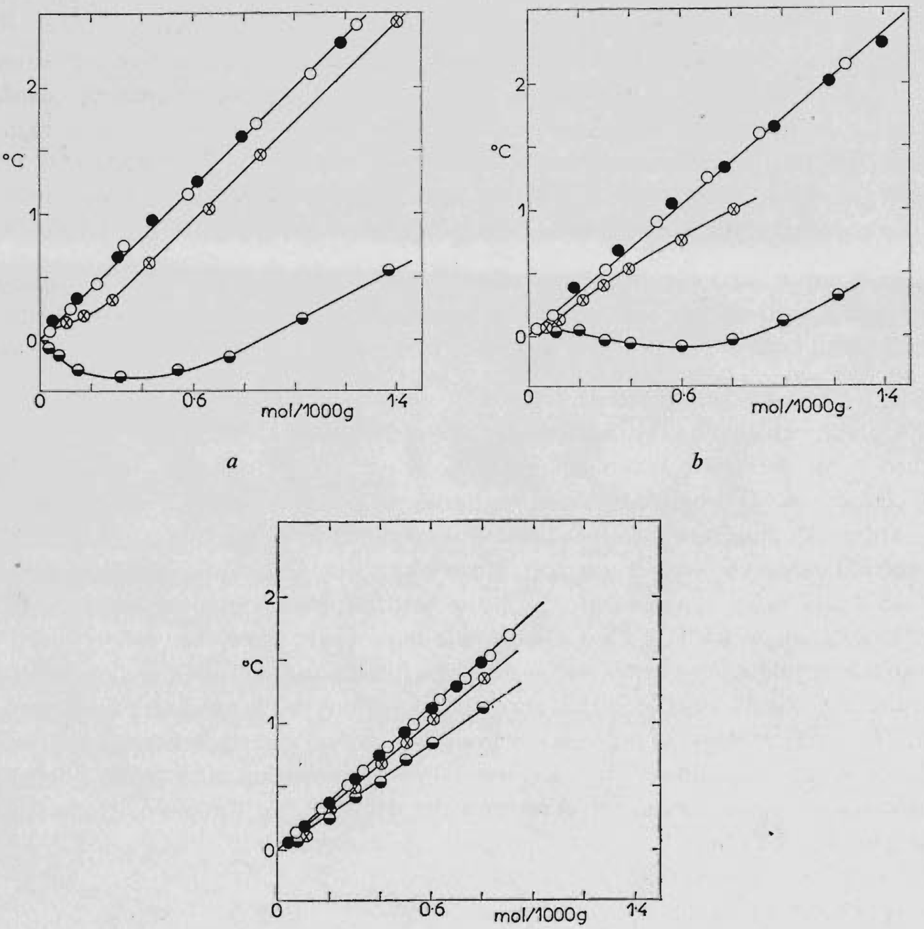
* Experiments performed by V. H. in the Institute of Macromolecular Chemistry.

rizes the changes in boiling point, ΔT, of the three tert-butoxide solutions induced by a gradual addition of 18-crown-6. Figs 3*b* and 3*c* summarize the corresponding changes induced by 15-crown-5 and 12-crown-4, respectively.

Inspection of these results reveals immediately a prominent effect of cation. In the solution of lithium tert-butoxide, each of the three crown induced boiling point elevations which within limits of experimental error are identical with those arising



a *b*

c

FIG. 3

Changes of boiling point, ΔT, of 0·6 molal t-C_4H_9OLi–t-C_4H_9OH solution (●), 0·6 molal t-C_4H_9ONa–t-C_4H_9OH solution (⊕), 0·6 molal t-C_4H_9OK–t-C_4H_9OH solution (◒) and of pure tert-butanol (○) as a function of molal concentration of added crown: *a* 18-crown-6; *b* 15-crown-5; *c* 12-crown-4 correspondingly in tert-butanol. In the solutions of sodium and potassium tert-butoxide, on the other hand, the three crowns induced boiling point elevations which are significantly smaller than those arising in tert-butanol. Regardless of crown size, the elevations are always much smaller in the potassium than in the sodium tert-butoxide solution. No boiling point elevation at all arose in the potassium alkoxide solution upon addition of one equivalent of 18-crown-6 or 15-crown-5; instead, a significant boiling point depression (Figs 3*a* and 3*b*) results.

Before attempting to interpret these findings, we have first to consider possible changes which in the alkoxide solutions may arise upon addition of crown. For lithium tert-butoxide which in the 0·6 molal solution exists largely in tetrameric form (Fig. 1) following changes may hypothetically occur: *1*) Formation of 1 : 1 crown-complexed tetramers $(\mathrm{ROM\text{-}CE})_4$; the overall number of solute molecules in the solution would not change. *2*) Formation of 1 : 1 crown-complexed trimers, dimers and monomers, or formation of sandwich complexes (ROM–CE–MOR or CE–ROM–CE); the overall number of solute molecules would increase slower than in the case of a mere crown dissolution. *3*) Formation of crown-complexed dissociated ions $(\overset{(+)}{\mathrm{M}}\text{–CE} + \overset{(-)}{\mathrm{RO}})$; the overall number of solute molecules would increase faster than in the case of a mere crown dissolution.

Since sodium and potassium tert-butoxide exist in the 0·6 molal solution in monomeric form, entirely different changes may arise upon addition of crowns: *1*) Formation of 1 : 1 crown-complexed monomers (ROM–CE), or formation of the sandwiches (CE–ROM–CE); the overall number of solute molecules would not change. *2*) Formation of crown-complexed dissociated ions $(\overset{(+)}{\mathrm{M}}\text{–CE} + \overset{(-)}{\mathrm{RO}})$; the overall number of solute molecules would increase in exactly the same manner as in the case of a mere crown dissolution. *3*) Formation of the sandwiches (ROM–CE–MOR); the overall number of solute molecules would decrease upon addition of crown.

Since ΔT is a colligative parameter depending only on quantity of molecules of solute, distinction can be made among the above alternatives by comparing the experimental points from Figs 3*a* – 3*c* with the theoretical traces calculated for the individual complexation modes.

Fig. 4*a* presents such a comparison for 0·6 molal solution of lithium tert-butoxide. It is immediately seen that no correlation exists between the experimental points and the calculated traces *1* – *4* for the alternative complexation modes. However, a very reasonable correlation exists between the experimental points and the calculated trace *5* for a mere dissolution of a crown; a perfect correlation with the experimental* traces corresponding to the dissolution of the individual crowns was already noted in Figs 3*a* – 3*c*. It indicates that no perceptible complexation took

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* Difference between the calculated and experimental traces for crown dissolution arises from the difference between M_{theor} and M_{app} in molecular weight determination of the crown.

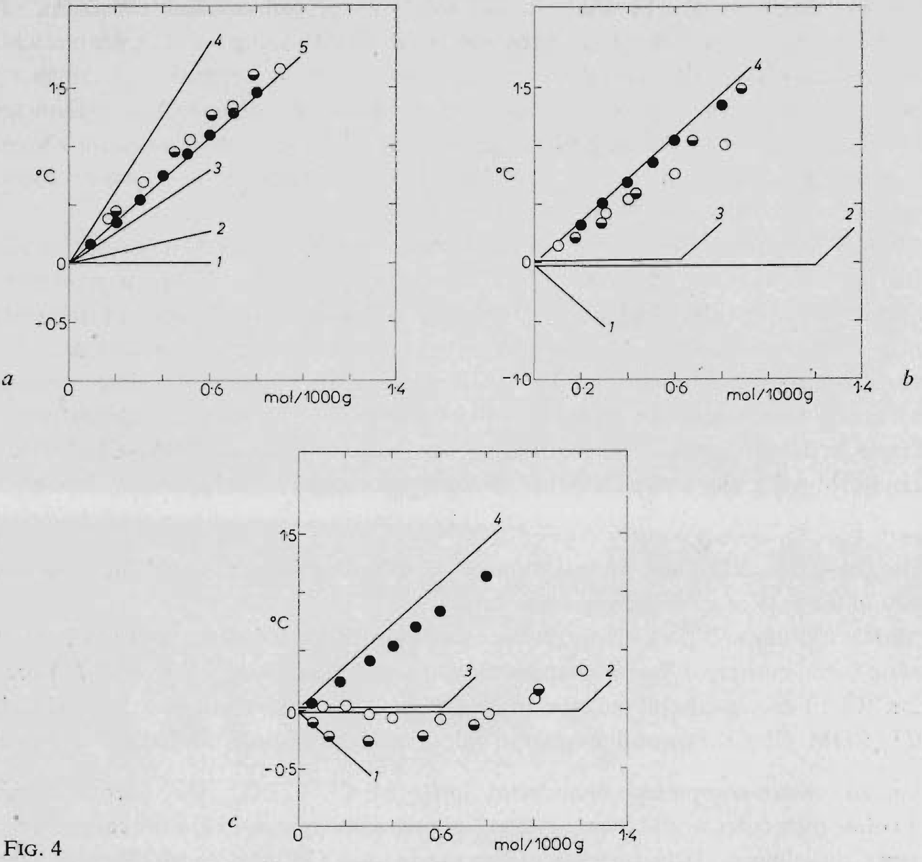

FIG. 4

A comparison between experimental values of ΔT and calculated model system traces for complex formation upon addition of 18-crown-6 (⊖), 15-crown-5 (○) and 12-crown-4 (●) to three different alkoxide solutions.

a: 0·6 molal $t\text{-}C_4H_9OLi\text{–}t\text{-}C_4H_9OH$ solution; *1* calculated trace for the formation of $(\text{ROLi-CE})_4$ from $(\text{ROLi})_4$; *2* calculated trace for the formation of $(\text{ROLi-CE})_2$ from $(\text{ROLi})_4$; *3* calculated trace for the formation of (ROLi-CE) from $(\text{ROLi})_4$; *4* calculated trace for the formation of $(\overset{+}{\text{Li}}\text{-CE})$ and $(\overset{-}{\text{RO}})$ from $(\text{ROLi})_4$; *5* calculated trace for a dissolution of crown. *b*: 0·6 molal $t\text{-}C_4H_9ONa\text{–}t\text{-}C_4H_9OH$ solution; *1* calculated trace for the formation of (RONa-CE-NaOR) from (RONa); *2* calculated trace for the formation of (CE-NaOR-CE) from (RONa) followed by crown dissolution; *3* calculated trace for the formation of (RONa-CE) from (RONa) followed by crown dissolution; *4* calculated trace for the formation of $(\overset{+}{\text{Na}}\text{-CE})$ and $(\overset{-}{\text{RO}})$ from (RONa) or, alternatively, for crown dissolution. *c*: 0·6 molal $t\text{-}C_4H_9OK\text{–}t\text{-}C_4H_9OH$ solution; *1* calculated trace for the formation of (ROK-CE-KOR) from (ROK); *2* calculated trace for the formation of (CE-KOR-CE) from (ROK) followed by crown dissolution; *3* calculated trace for the the formation of (ROK-CE) from (ROK) followed by crown dissolution; *4* calculated trace for the formation of $(\overset{+}{\text{K}}\text{-CE})$ and $(\overset{-}{\text{RO}})$, or, alternatively, for a crown dissolution place in the lithium alkoxide solution upon addition of any of the three crowns. Fig. 4*b* provides an analogous comparison for 0·6 molal solution of sodium tert-butoxide. Formally, a very incomplete complexation as well as a very complete dissociation would be compatible with the apparent correlation between the experimental points and the calculated trace *4*. However, the circumstantial evidence provided by Figs 4*c* and 6 rules out (*vide infra*) the latter alternative. Fig. 4*c* examines correspondingly 0·6 molal solution of potassium tert-butoxide. For 12-crown-4, a very incomplete complexation is again deduced from the correlation of the experimental points with the theoretical trace *4*, analogously as it was in Fig. 4*b*. For 15-crown-5 and 18-crown-6, on the other hand, a very complete complexation leading to 1 : 1 complexed ion pairs, ROK–CE, and/or to the sandwiches ROK–CE–ROK and CE–KOR–CE follows from the correlation of experimental points with the calculated traces *1*–*3*. Apparently, no dissociation leading to the crown-complexed ions (trace *4*) took place in the alkoxide solution.

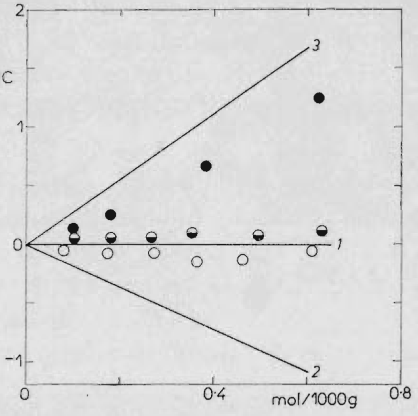

FIG. 5

Changes of boiling point, ΔT, of 1·2 molal solution of 18-crown-6 (◒), 1·2 molal solution of 15-crown-5 (○) and 1·2 molal solution of 12-crown-4 (●) in tert-butanol as a function of molal concentration of added t-C_4H_9.OK. A comparison between experimental values and calculated model traces: *1* Calculated trace for the formation of (ROK-CE); *2* calculated trace for the formation of (CE-KOR-CE); *3* experimental trace for a dissolution of t-C_4H_9OK in tert-butanol

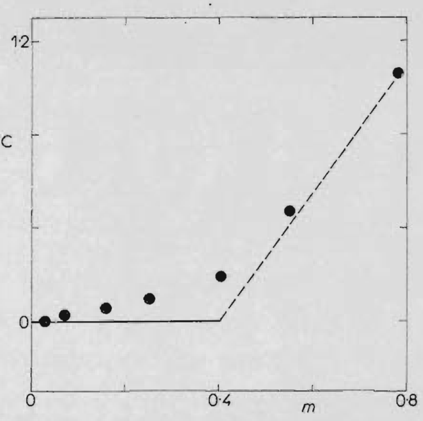

FIG. 6

Changes of boiling point temperature, ΔT, of a mixed 0·4 molal solution of 18-crown-6 and t-C_4H_9ONa (1 : 1) in tert-butanol upon addition of two equivalents of t-C_4H_9.OK. A comparison between the experimental values (●) and calculated trace for formation of (t-C_4H_9OK–CE) complex (full line) followed by t-C_4H_9OK dissolution (dotted line; from data in Fig. 1)

In order to probe feasibility of the sandwich CE–KOR–CE formation, we performed a series of "inversed" experiments in which ΔT was measured upon addition of t-C_4H_9OK to a large excess of a crown dissolved in tert-butanol. The experimental data obtained in 1·2 molal solutions of 18-crown-6, 15-crown-5 and 12-crown-4 are compared with the theoretical traces for the alternative complexation modes in Fig. 5. Significantly, no marked deviation of the experimental points from the calculated trace for 1 : 1 complex formation *1* is obtained in the 1·2 molal solutions of 18-crown-6 and 15-crown-5. At variance with the results from Fig. 4*c* it indicates that no substantial formation of the sandwiches (CE–KOR–CE) took place under conditions of the "inversed" experiment, in spite of the very favourable crown : t-C_4H_9OK ratios in the solution.

It was pointed out in the preceding section that strong specific solute–solvent interactions induce in t-C_4H_9OK–t-C_4H_9OH solution a deviation from ideality by enhancing exaggeratedly the boiling point. Upon complexation with 18-crown-6 and 15-crown-5, molecules of tert-butanol are stripped from the potassium cation and the solute–solvent interactions are thus substantially reduced. This, obviously, has to affect boiling point in an opposite direction because ideality of the solution is partly restored by the cation desolvation. We assume that the desolvation accounts for the negative deviation of experimental points from the theoretical trace for 1 : 1 complex formation in Fig. 4*c*. In the "inversed" experiment shown in Fig. 5 we examine, in actual fact, a complexation of "naked" molecules of t-C_4H_9OK and the effect of desolvation does not therefore operate.

In another „inversed" experiment, we measured ΔT upon addition of t-C_4H_9OK to a 0·4 molal solution of 18-crown-6 in tert-butanol containing equimolal amounts of t-C_4H_9ONa. Similarly as in the experiment from Fig. 5, no marked boiling point elevation arose upon addition of one equivalent of t-C_4H_9OK to this mixed solution (Fig. 6). It indicates that coordination sites of the crown had not been filled by sodium ions, in accordance with the suggestion we made earlier discussing the experiments from Fig. 4*b*.

Summing up the evidence from Figs 3–6, we see that crown-complex stability in t-C_4H_9OM–t-C_4H_9OH system varies with cation and crown size in the order (ROK–18-crown-6) $\sim$ (ROK–15-crown-5) $\gg$ (ROK–12-crown-4) $\sim$ (RONa–15-crown-5) > (RONA–18-crown-6) > (RONa–12-crown-4) > (ROLi–crowns). Thus, complex stability decreases always in the order $\overset{(+)}{K} > \overset{(+)}{Na} > \overset{(+)}{Li}$, regardless of the crown-cavity size. It indicates that steric fit between cation and crown cannot be the sole decisive factor in the formation of crown complexes, as it was previously believed; a reverse order of complex stabilities would be otherwise obtained for 12-crown-4.

At variance with the present results, Smid and coworkers[33] observed that 18-crown-6-ethers form much stronger complexes (in tetrahydrofuran) with sodium than with potassium salt of fluorene. We have pointed out earlier in this paper that tert-

-butoxide and fluorenyl anions exhibit a divergent propensity to coordination with alkali cations, the former preferring $\overset{(+)}{\mathrm{Li}} > \overset{(+)}{\mathrm{Na}} > \overset{(+)}{\mathrm{K}}$ whereas the latter $\overset{(+)}{\mathrm{K}} > \overset{(+)}{\mathrm{Na}} > \overset{(+)}{\mathrm{Li}}$. This may explain well the diverse order of crown-complex stabilities in the two compared systems because anions in low polar solvents can compete efficiently with the macrocyclic ligands for coordination with the cations.

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