EFFECTS OF STRUCTURE AND CONCENTRATION ON IONIC ASSOCIATION IN ALKALI ALKOXIDE–CONJUGATE ACID SOLUTIONS: RELUCTANCE TO FORMATION OF ION-PAIR AGGREGATES*

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Degrees of ionic association, n_{app}, were ebulliometrically determined in $0.06 - 0.6$ molal region for eighteen ROM—ROH base-conjugate acid combinations (R = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, t-C_4H_9; M = Li, Na, K) and found to range between the extremes 0.5 and 4.0. Presence of ion-pair aggregates ($n_{app} > 1$) was established only in two of the examined combinations (i-C_3H_7OLi–i-C_3H_7OH and t-C_4H_9OLi–t-C_4H_9OH).

Association of alkali alkoxide ions to form ion pairs and higher ion aggregates in solution

$$\overset{(+)}{M} + \overset{(-)}{OR} \;\rightleftharpoons\; \overset{(+)(-)}{(MOR)} \;\rightleftharpoons\; \overset{(+)(-)}{(MOR)_n} \qquad (A)$$
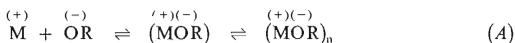
attracted much attention in the past decades in connection with solving mechanism of alkoxide-promoted reactions[1-7] and also as a problem of a considerable interest on its own right[8-13].

An important but not yet fully explored facet of this intriguing problem concerns participation of ion-pair aggregates ($n > 1$) in the equilibrium (A). In aprotic solvents, presence of these aggregates was amply investigated[8,9] by a variety of colligative property measurements (ebulliometric, cryoscopic, thermoelectric). With a single exception of our previous study[13], no such investigation has been however conducted in protic solutions.

In order to supplement the lacking information which appeared requisite also in context with our other studies[2,14], we have undertaken a systematic study of ionic association in a homologous series of alkali alkoxide–conjugate acid solutions. In this paper we report the association degrees n_{app} determined by ebulliometry for eighteen ROM–ROH combinations (R = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, t-C_4H_9; M = Li, Na, K) in $0.06 - 0.6$ molal solutions.

EXPERIMENTAL

Materials: Alcohols were kept over molecular sieves for a week and fractionated. The middle cuts were collected and stored again over molecular sieves (content of H_2O was less than 0.01%; K. Fisher). Alkali metals employed were reagent grade and alkali hydroxides analytical grade (LACHEMA).

Ebulliometry: Performed with a quartz ebulliometer, analogously as it was described in the previous paper[13]. The solutions of alkali alkoxides were prepared *in situ* in the ebulliometer by a portionwise addition of weighted pieces of freshly-cut metal to the appropriate boiling alcohol. Each portion of the metal was allowed to dissolve completely prior further addition allowing thus a series of boiling point determinations for different alkoxide concentration to be made in a single experimental run. The hydroxide solutions were prepared by a gradual addition of hydroxide pellets to boiling water in the ebulliometer.

Evaluation of experimental data: The apparent degree of association, n_{app}, was calculated from the equation

$$n_{app} = M_{app}/M_{theor}, \qquad (1)$$

where M_{theor} is the theoretical molecular weight corresponding to the monomeric alkali salt unit and M_{app} is the experimental value obtained from the equation

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

where K_E is the ebullioscopic constant, w_1 is the weight of the dissolved alkali salt, w_2 is the weight of the solvent (corrected, if necessary, on the amount of alcohol consumed in the alkoxide formation), and ΔT is the difference between the boiling point of the given solution and that of the pure solvent. The results are summarized in Table I.

Ebullioscopic constants: Calculated from the reported[15] heats of vapourisation of individual solvents. The following values of K_E have been employed in this study: 0.515 (H_2O); 0.85 (CH_3.OH); 1.20 (C_2H_5OH); 1.66 (n-C_3H_7OH); 1.57 (i-C_3H_7OH); 1.79 (t-C_4H_9OH).

RESULTS AND DISCUSSION

A cursory inspection of the experimental results summarized in Table I immediately shows that the apparent degree of association is a composite function of several variables.

The effect of solvent: Table II compares the association degrees determined in 0.3 ± 0.05 molal ROM–ROH solutions with dielectric constants of the corresponding solvents. The lowest association degrees are found in the most polar solvents H_2O and CH_3OH ($\varepsilon = 78.5$ and 32.6, respectively), with the values of n_{app} approaching the theoretical limit expected for a complete ionic dissociation (0.5). A gradual rise of n_{app} towards the value of 1 corresponding to the prevalence of monomeric ion pairs in solution is observed along the series CH_3OH, C_2H_5OH, n-C_3H_7OH

TABLE I
Apparent degrees of association in 0·06--0·6 molal ROM–ROH solutions $\overset{(-)(+)}{\text{ROM}}$

Li$^{(+)}$		Na$^{(+)}$		K$^{(+)}$	
$m^{a,b}$	$n_{app}{}^{b}$	$m^{a,b}$	$n_{app}{}^{b}$	$m^{a,b}$	$n_{app}{}^{b}$
R = H					
0·06	0·58	0·06	0·56	0·11	0·57
0·19	0·59	0·22	0·55	0·21	0·55
0·29	0·62	0·31	0·55	0·32	0·55
0·38	0·63	0·40	0·55	0·42	0·55
0·51	0·64	0·50	0·54	0·52	0·56
0·61	0·65	0·61	0·54	0·63	0·55
R = CH$_3$					
0·06	0·59	0·10	0·59	0·06	0·59
0·11	0·60	0·17	0·59	0·11	0·58
0·22	0·61	0·26	0·59	0·22	0·57
0·32	0·62	0·35	0·57	0·33	0·55
0·45	0·62	0·45	0·56	0·46	0·52
0·62	0·62	0·60	0·53	0·61	0·51
R = C$_2$H$_5$					
0·09	0·64	0·12	0·63	0·08	0·63
0·15	0·67	0·20	0·66	0·14	0·64
0·28	0·70	0·30	0·66	0·22	0·65
0·37	0·70	0·38	0·66	0·41	0·65
0·49	0·71	0·48	0·66	0·50	0·65
0·62	0·71	0·61	0·65	0·62	0·63
R = C$_3$H$_7$					
0·07	0·90	0·07	0·90	0·09	0·89
0·12	0·90	0·17	0·87	0·15	0·86
0·23	0·93	0·26	0·86	0·23	0·85
0·35	0·94	0·35	0·83	0·35	0·82
0·47	0·97	0·45	0·82	0·37	0·78
0·61	0·98	0·61	0·79	0·63	0·75
R = i-C$_3$H$_7$					
0·06	1·06	0·06	0·85	0·09	0·90
0·11	1·12	0·10	0·85	0·16	0·89
0·21	1·29	0·15	0·85	0·23	0·87
0·31	1·41	0·26	0·84	0·34	0·84
0·50	1·62	0·44	0·83	0·46	0·83
0·60	1·70	0·61	0·81	0·61	0·78

TABLE I

(Continued)

Li$^{(+)}$		Na$^{(+)}$		K$^{(+)}$	
$m^{a,b}$	$n_{app}{}^{b}$	$m^{a,b}$	$n_{app}{}^{b}$	$m^{a,b}$	$n_{app}{}^{b}$
		R = t-C$_4$H$_9$			
0·06	2·08	0·07	0·79	0·09	0·78
0·10	2·77	0·14	0·79	0·11	0·75
0·18	3·14	0·20	0·84	0·19	0·74
0·26	3·40	0·28	0·84	0·24	0·73
0·30	3·76	0·53	0·85	0·41	0·69
0·59	3·98	0·64	0·86	0·63	0·63

[a] Alkoxide molality in mol kg^{-1}. [b] Average values from three repeated experiments.

n-C$_3$H$_7$OH, i-C$_3$H$_7$OH, as the dielectric constant of solvent is being diminished. A less regular pattern evolves on going from i-C$_3$H$_7$OH to the least polar t-C$_4$H$_9$OH: n_{app} increases further only for the lithium alkoxide whereas for the potassium decreases markedly and for the sodium levels out.

According to the Bjerrum theory[15,16], ionic association depends inversely on dielectric constant. Thus, with exception of the irregularity observed in tert-butanol, the ebulliometric results are in a qualitative accord with this theory[17] as well as with the scattered conductivity experiments suggesting that ionic association is negligibly small[18,19] in MOH–H$_2$O and CH$_3$OM–CH$_3$OH, substantial[6,19] in C$_2$H$_5$OM––C$_2$H$_5$OH and greatly prevalent[20,21] in t-C$_4$H$_9$OM–t-C$_4$H$_9$OH solutions.

Apparent degrees of association have been reported previously[8,9] for alkali tert-butoxides in various aprotic solvents covering a wide range of dielectric constants. A comparison of n_{app} obtained in aprotic and protic solvents with similar ε can be accordingly made (Table III). In pyridine ($\varepsilon = 12.3$) e.g., the observed values of $n_{app} \sim 4$ for M = Li as well as Na and K indicate that all the three alkali tert-butoxides are on average tetrameric species in the aprotic solution. In contrast, in the protic solvent tert-butanol possessing almost identical dielectric constant ($\varepsilon = 12.2$), only lithium tert-butoxide is tetrameric, whereas $n_{app} < 1$ for the sodium and potassium alkoxides suggests that the latter two are monomeric species (any sizeable presence of free ions is excluded by conductometric studies[20,21]). Similarly, lithium as well as potassium ter-butoxides in dimethyl sulphoxide ($\varepsilon = 48.9$) are oligomeric ion pairs (tetramers and trimers, respectively), whereas in methanol free methoxide

ions prevail, in spite of the lower dielectric constant of the latter (protic) solvent ($\varepsilon = 32\cdot6$). The much lower propensity to ionic association observed in the protic solutions arises assumedly from $\overset{(-)}{RO}\ldots\overset{(+)}{HOR}$ hydrogen bonding which leads to dissipation of the negative charge and disfavours thus both ion pairs as well as ion aggregates in the equilibrium (A).

The effect of cation: According to the Bjerrum theory, tendency to formation of ion pairs (or aggregates) decreases with increasing radii of ions. As it concerns alkali salts, this prediction is however ambiguous, because radii of the bare (unsolvated) cations increase in the order $\overset{(+)}{Li} < \overset{(+)}{Na} < \overset{(+)}{K}$, whereas those of the solvated ones follow usually[11,19,22] (in donating solvents) the opposite order $\overset{(+)}{Li} > \overset{(+)}{Na} > \overset{(+)}{K}$.

TABLE II

Relationship between dielectric constant of pure solvent (ε) and apparent association degree (n_{app}) in $0\cdot3 \pm 0\cdot05$ molal $\overset{(-)(+)}{ROM}$–ROH solution

ROH	$\varepsilon_{(25°C)}$	n_{app}		
		$Li^{(+)}$	$Na^{(+)}$	$K^{(+)}$
H_2O	78·5	0·62	0·55	0·55
CH_3OH	32·6	0·62	0·57	0·55
C_2H_5OH	24·3	0·70	0·66	0·65
$n\text{-}C_3H_7OH$	20·1	0·94	0·83	0·82
$i\text{-}C_3H_7OH$	18·3	1·41	0·84	0·84
$t\text{-}C_4H_9OH$	12·2	3·76	0·84	0·70

TABLE III

Association degrees (n_{app}) in $0\cdot3$ molal solutions of alkali tert-butoxides in aprotic solvents: the effect of dielectric constant (ε) and cation

Solvent	$\varepsilon_{(25°C)}$	n_{app}		
		$t\text{-}C_4H_9OLi$	$t\text{-}C_4H_9ONa$	$t\text{-}C_4H_9OK$
Diethyl ether	4·2	5·9[a]	4·3[a]	—
Tetrafuran	7·4	4·1[a]	3·9[a]	3·9[a]
Pyridine	12·3	4·0[a]	3·9[a]	4·0[a]
Dimethyl sulphoxide	48·9	4·0[b]	—	3·0[b]

[a] From ref.[8]; [b] From ref.[9].

As Table II shows, the association degree n_{app} decreases, in any of the six ROM$-$
$-$ROH triads investigated, in the order $\overset{(+)}{Li} > \overset{(+)}{Na} > \overset{(+)}{K}$, expected from consideration of the bare alkali ions. Analogous pattern of results has been previously found, by conductivity measurements, only for a rather limited[16] group of alkali salts possessing very hard anions (*e.g.* fluorides, acetates, hydroxides). Majority of alkali salts which posses soft anions (iodides, bromides, chlorides[16], thiocyanates[22,23], tetraphenyl-boronates[24,25] *etc.*) follow the opposite order of n_{app}, $\overset{(+)}{Li} < \overset{(+)}{Na} < \overset{(+)}{K}$, correlating with size of the solvated ions.

A plausible explanation can be given for this dichotomy of cation effects in terms of the Eisenman theory[26] of anionic field strenght. A scale of relative interaction energies between oppositely charged ions can be set empirically for different alkali salts by comparing free energies of hydration with crystal-lattice free energies. Calculation shows that for large anions, with low anionic field strenght, the interaction energy decreases in the order $\overset{(+)}{K} > \overset{(+)}{Na} > \overset{(+)}{Li}$ whereas for small anions with very high anionic field the reverse order holds. Another explanation was invoked by Robinson and Harned[27,28] in terms of a „localized hydrolysis". A modified version of the latter concept was considered in our previous paper[13].

The effect of alkoxide concentration: Inspection of Table I shows that n_{app} varies also with alkoxide concentration and that the variation is cation-dependent. For lithium alkoxide, a gradual increase of n_{app} with concentration is found in all the six solvents examined. For potassium alkoxide, on the other hand, a gradual decrease of n_{app} with increasing concentration (in CH_3OH, n-C_3H_7OH, i-C_3H_7OH, t-C_4H_9.OH), or a near-independence on concentration (in H_2O, C_2H_5OH) is in actual fact observed. A situation which is intermediate between those for the lithium and for the potassium is found for the sodium alkoxide.

This disparate behaviour disagrees with the conductivity measurements accomplished in $0.05-1.0$M $\overset{(-)(+)}{C_2H_5OM}-C_2H_5OH$ solution showing that ion-pairing increases[6] with concentration regardless of the identity of cation. A general increase of ion-pairing with concentration is postulated also in the Bjerrum theory of ion pairs[16].

We suggested already previously[13] that strong specific solute–solvent interactions may cause anomalous ebulliometric behaviour in ROK–ROH and RONa–ROH solution, such as is now observed in Table I. Solvate formation is assumed to diminish number of free molecules of solvent in the solution reducing thus vapour pressure below that corresponding to ideality. A strong support for this assumption is provided by the concomitant observation[13] that this anomaly disappears upon cation complexation with 18-crown-6.

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Translated by the author (J. Z.).