Effect of Metal Salts on the Cloud Point of Alkyl Crown Compounds

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Summary The salt effect on the cloud point of alkyl crown compounds has been studied; alkali metal salts salt the crown compounds in or out selectively according to the cation and the ring size of the crown compound.

CROWN compounds bearing long alkyl groups and their complexes with metal salts have attracted attention as surfactants and their surface-active properties have been investigated recently.[1] We have also synthesized some of this new type of surface-active crown compounds,[2] and we now describe an unusual salt effect on the cloud point of their aqueous solutions.

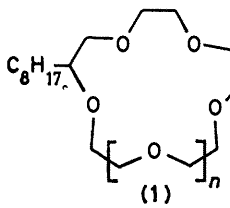
There have been many reports on the effect of inorganic electrolytes on the cloud point of aqueous solutions of polyoxyethylated non-ionic surfactants,[3,4] and it is well known that the alkali metal salts, which do not form stable complexes with ether or dioxan, do not interact with the polyoxyethylene chain in water and cause a depression of the cloud point by a salting-out effect, unless their counter-anions are polarizable and effective in destructuring water.[4]

The cloud points of aqueous solutions of the octyl crown ethers (**1a** and **b**) and the *N*-octyl monoaza-crown ethers (**2a**—**c**) were determined in the presence and absence of metal salts; it was found that some alkali metal salts, which lowered the cloud points of the corresponding noncyclic polyoxyethylene derivatives (**4**) and (**5**), selectively raised those of the alkyl crown compounds (Table).

TABLE. Cloud points of alkyl crown compounds and the corresponding open-chain derivatives in the presence or absence of metal chlorides[a]

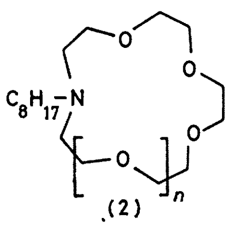
Sample	No metal salt	Cloud point and ΔCP[b] (T/°C)				
		LiCl (ΔCP)	NaCl (ΔCP)	KCl (ΔCP)	RbCl (ΔCP)	CsCl (ΔCP)
(**1a**)	13·0	12·5 (−0·5)	26·4 (+13·5)	20·0 (+ 7·0)	17·0 (+ 4·0)	13·0 (+ 0·0)
(**1b**)	28·5	26·0 (−2·5)	41·0 (+12·5)	71·5 (+43·0)	55·0 (+26·5)	40·0 (+11·5)
(**2a**)	23·0	22·5 (−0·5)	31·0 (+ 8·0)	24·0 (+ 1·0)	18·0 (− 0·5)	17·0 (− 6·0)
(**2b**)	33·5	31·5 (−2·0)	41·5 (+ 8·0)	60·5 (+27·0)	46·5 (+13·0)	36·5 (+ 3·0)
(**2c**)	45·5	42·0 (−3·5)	39·0 (− 6·5)	50·0 (+ 4·5)	52·5 (+ 7·0)	49·5 (+ 4·0)
(**4**)	69·5	63·0 (−6·5)	56·5 (−13·0)	56·5 (−13·0)	56·5 (−13·0)	57·0 (−13·5)
(**5**)	79·0	69·5 (−9·5)	61·5 (−17·5)	61·0 (−18·0)	61·0 (−18·0)	61·0 (−18·0)

[a] 1 molal salt solutions including 1 wt.% of sample. [b] Net cloud point changes with and without salts.



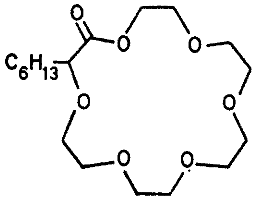
(1)

a; n = 1
b; n = 2

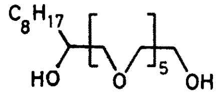


(2)

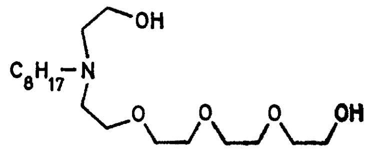
a; n = 1
b; n = 2
c; n = 3



(3)



(4)



(5)

log *K* values (K^+; H_2O; 25 °C): (**1b**), 1·7; (**2b**), 2·4.

The degree of cloud point change was found to depend strongly on the type of metal cation and the ring size of the crown compounds. Thus, potassium markedly raised the cloud point of the 18-crowns (**1b**) and (**2b**), whereas sodium and rubidium were found to be most effective for salting-in the 15-crowns (**1a**) and (**2a**) and the 21-crown (**2c**), respectively.

The cloud point of the 3-hexyl-2-oxo-18-crown-6 (**3**) (0·5%) was determined as 30 °C. It increased to 56·5 °C on the addition of potassium chloride (3 molal) and decreased to 28 °C in the presence of sodium chloride (3 molal).

The cloud point increase of nonionic surfactants on the addition of metal salts has been interpreted as arising from a complexation of the cations to the ether oxygens.[4] In view of the relatively good correlation between the stability constants of 18-crown-6 derivatives for alkali metal cations[5] and the change in cloud point of octyl18-crown-6 and octylmonoaza-18-crown-6 in the presence of these cations, the cloud point may be useful as a measure of complexing abilities of alkyl crown compounds with cations in water.

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[1] T. Kuwamura and T. Kawachi, *Yukagaku*, 1975, **28**, 195; Y. Moroi, E. Pramauro, M. Grätzel, E. Plizzeti, and P. Tundo, *J. Colloid Interface Sci.*, 1979, **69**, 341.

[2] T. Mizuno, Y. Nakatsuji, S. Yanagida, and M. Okahara, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 481; I. Ikeda and M. Okahara, Abstracts of 7th International Congress of Heterocyclic Chemistry, Aug. 12—19, 1979, T1645A, p. 97; P-L. Kuo, M. Miki, I. Ikeda, and M. Okahara, *J. Am. Oil Chem. Soc.*, in the press.

[3] M. J. Schick, 'Nonionic Surfactants,' Dekker, New York, 1967, ch. 17, and references cited therein.

[4] H. Schott, *J. Colloid Interface Sci.*, 1973, **43**, 150; H. Schott and Sue Kyu Han, *J. Pharm. Sci.*, 1975, **64**, 658; F. Tokiwa and T. Matsumoto, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 1645.

[5] H. K. Frensdorff, *J. Am. Chem. Soc.*, 1971, **83**, 600; R. M. Izatt, R. E. Terry, B. L. Haymore, H. D. Hansen, N. K. Dalley, A. G. Avondett, and J. J. Christensen, *ibid.*, 1976, **98**, 7620.