

On the Temperature Dependence of the Solubility of some Long-chain Alkali *n*-Alkanoates

G. Spinolo and M. Zangen *

Centro di studio per la termodinamica ed elettrochimica dei sistemi salini fusi e solidi del C.N.R.
c/o Istituto di Chimica-Fisica e di Elettrochimica della Università, Pavia, Italy

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Solubility measurements allowed to put into evidence a marked Krafft-effect in the ethanolic solutions of the Na and K soaps from *n*-octanoate to *n*-dodecanoate. The co-ordinates of the Krafft-points exhibited a pronounced alternating character when odd and even homologues were employed as the solutes. The behaviour of a number of alkali soaps in different solvents is also briefly discussed.

1. Introduction

It was known for a long time that salts in which either the cationic or the anionic charge is at the end of a long hydrocarbon chain may exhibit in a number of solvents a quite peculiar solubility dependence on temperature. The name "Krafft-point" was adopted to single out (in a T/K vs x plot; x = molar fraction of the solute) the characteristic temperature and composition values in the neighbourhood of which the slope of the curve markedly decreases by moderately increasing x ¹. Various theories were proposed to explain this phenomenon², often relating it to the formation of large solute aggregates (so-called micelles): none of them, however, seems to be able to account for all the experimental facts observed, e. g., in a recent study on the temperature dependence of the solubility of dodecylammonium halides³.

Concerning the latter investigation, it is here to be mentioned that some evidence was obtained about a possible parallelism between the existence in the crystalline salts of solid state transitions (sstr's) involving large ΔH values and the occurrence of Krafft-effects when the same salts were dissolved in proper solvents. It seemed therefore interesting to look for an analogous parallelism in the case of the alkali *n*-alkanoates where, unlike alkylammonium halides, the negative-instead of the positive-charge is at the end of the hydrocarbon chain: the present paper deals with the temperature-solubility depen-

dence in several solvents of the MC_8 - MC_{12} soaps **, the thermal behaviour of which was recently investigated by our group⁴.

2. Experimental

The salt preparation was described elsewhere⁴ and reagent grade solvents were employed.

In preliminary experiments the solvent was added dropwise to a known amount (50–100 mg) of salt until complete dissolution was reached on boiling: as a rule, only systems which on subsequent cooling to room temperature exhibited an extensive precipitation were further investigated.

The required solubilities were determined as follows.

For measurements above room temperature clear solutions of known composition (contained in a Pyrex tube immersed into a thermostated transparent oil bath and vigorously stirred by means of a Chemap vibromixer type E-1) were slowly cooled until the onset of precipitation. The temperature at which the latter occurred was taken (with an accuracy of ± 0.2 K) by means of a Chromel-Alumel thermocouple (checked by comparison with a certified, Pt/Pt, Rh one) in connection with a Leeds & Northrup K-3 potentiometer.

For measurements between room and ice temperature the solutions saturated at the required T -values were quickly filtered: known amounts of them were then evaporated under vacuum, and the solid residues were finally weighed.

Since Krafft-effects could arise in a more or less marked way in the different cases, Krafft-points could be singled out either as the intersections of (nearly) straight branches of the solubility curves, or by extrapolation: examples are shown in Figure 1.

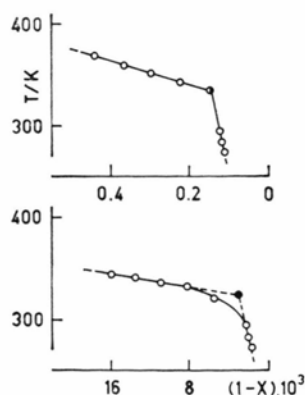


Fig. 1. Solubility curves of RbC_{10} in nitromethane (upper section) and LiC_{11} in formamide (lower section); empty circles: experimental data; filled circles: Krafft-points.

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Reprint requests to Dr. G. Spinolo, Istituto di Chimica-Fisica e di Elettrochimica della Università, Viale Taramelli 16, I-27100 Pavia (Italy).

** The *n*-alkanoate where the number of carbon atoms is $n_C = a$ is here briefly indicated as MC_a (M = alkali metal).

3. Results and Discussion

It is preliminarily to be said that: (i) in the case of dodecylammonium halides, benzene and carbon tetrachloride as well as alcohol and formamide could be suitably used³; (ii) the changed mechanism of dissolution, however, caused in our preliminary experiments only solvents like water, alcohols, formamide and nitromethane to be selected as promising for more or less large *n*-alkanoate groups; (iii) a number of practical reasons [among which, e. g., the fact that the adopted experimental technique allowed to get satisfactory results only when Krafft-points occurred at $(1-x) > 0.0001$, and the necessity to collect series of directly comparable data] finally suggested to focus attention on Na, K and Rb soaps dissolved in either methanol, or ethanol, or 2-propanol.

Remarkable temperature-solubility effects were first detected in the ethanolic solutions of the $KC_8 - KC_{12}$ salt series, for which (in the pure state) sstr's involving at least 2 kcal mole^{-1} were previously observed at $325 < T/K < 370$ ^{4b}: the pertinent Krafft-point co-ordinates are summarized in Table I.

Table I. Krafft-points in solutions of potassium soaps.

Solvent	Solute	$(1-x) \cdot 10^2$	T/K
Ethanol	KC_8	2.0 ₅	292
	KC_9	0.8	307
	KC_{10}	1.2 ₅	301
	KC_{11}	0.4	301
	KC_{12}	0.5	296
2-propanol	KC_8	0.7	301
	KC_9	0.2 ₅	311
	KC_{10}	0.3	304

An odd-even alternating character was apparent both in Krafft-point temperatures and compositions (see Fig. 2) and, as a matter of fact, the trend of the former quantities looked analogous to that already pointed out for sstr's.

In the same solvent the $NaC_8 - NaC_{12}$ soaps behave quite similarly (see Fig. 3), though Krafft-points were displaced towards higher x and T/K values. On this purpose, it is also interesting to note that in the pure salts the main sstr's too occur at higher temperatures when, the anion being the same, K^+ is replaced by Na^+ as the cation^{4c}.

In both series the influence of the hydrocarbon chain length was noticeable in the fact that the longer the chain, the more marked was the Krafft-effect.

A few more data were drawn from measurements carried out on solutions of $KC_8 - KC_{10}$ in 2-propanol and of NaC_{11} , NaC_{12} in methanol. As the solvent

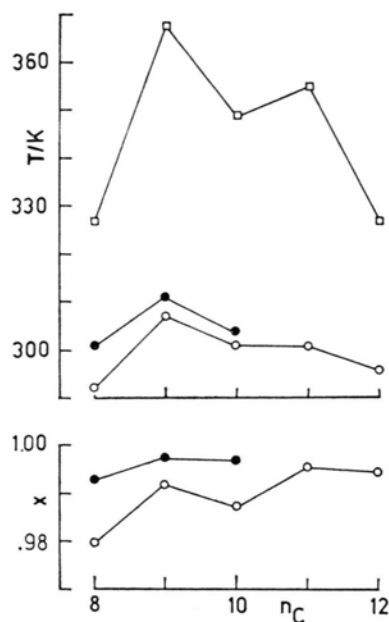


Fig. 2. Temperatures and compositions of Krafft-points taken in solutions of K *n*-alkanoates in ethanol (empty circles) and 2-propanol (filled circles); for the sake of comparison, the sstr temperatures are also given (squares).

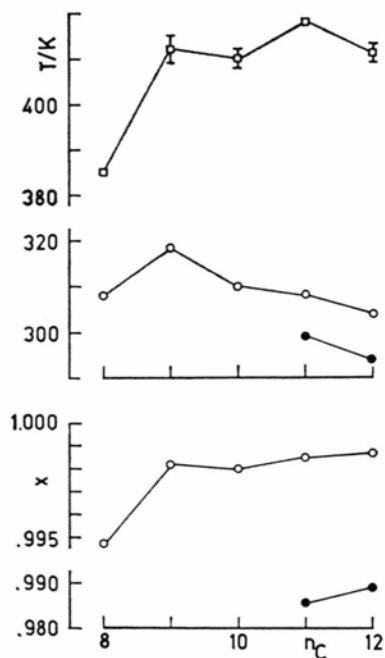


Fig. 3. Temperatures and compositions of Krafft-points taken in solutions of Na *n*-alkanoates in ethanol (empty circles) and methanol (filled circles); for the sake of comparison, the sstr temperatures of the crystalline salts are also given (squares).

effectiveness of 2-propanol and methanol on alkali soaps is respectively lower and higher than that of ethanol, Krafft-points are caused to move towards x and T/K values respectively higher and lower than those observed in ethanol, but the correlations put into evidence in the case of the latter solvent still look as valid (see Figs. 2 and 3).

Let us now consider Rb^+ as the cation and, the solubility of rubidium soaps in methanol and ethanol being too large, 2-propanol as the solvent. Should in particular the extreme representatives of the series be taken into account, it may be noted that (i) both crystalline RbC_8 and RbC_{12} were known to undergo two sstr's, respectively at 283.5 K (0.6 kcal mole⁻¹) and 303.3 K (2.0), and at 334 K (4.4) and 360 K (0.5); (ii) consequently, and owing to the well known similarity between the behaviours of K and Rb salts, Krafft-effects were reasonably to be expected for RbC_8 not far from (and likely below) the ice point and for RbC_{12} not far from (and likely above) room temperature, respectively; (iii) the expectation did agree with the experimental facts. An impressive evidence of the absence (in the case of RbC_8) or existence (in the case of RbC_{12}) of a Krafft-effect within the temperature range investigated is given by the continuity and, respectively, by the discontinuity of the $\ln(1-x)$ vs T^{-1}/K^{-1} plot (see Figure 4).

In conclusion: (i) in long chain alkali *n*-alkanoates, as well as in dodecylammonium halides³, the occurrence (in solution) of Krafft-effects appears to be correlated to the existence (in the crystalline state) of sstr's involving large ΔH values; (ii) the

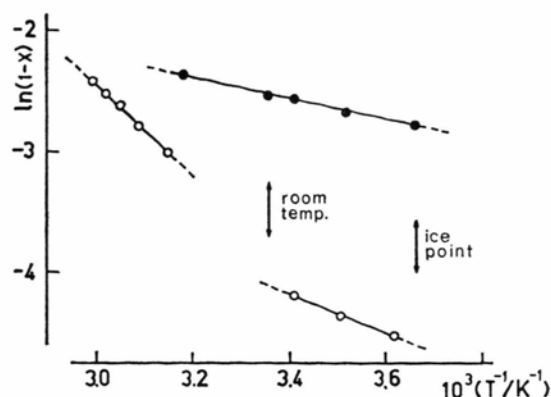


Fig. 4. Solubilities of RbC_8 (filled circles) and RbC_{12} (empty circles) in 2-propanol.

latter phenomenon, however, cannot be looked at as a cause of the sudden increase in the solubility dependence on temperature^{*}; (iii) still, it may be said that, by increasing the temperature, salts (with organic cation or anion) easily undergoing, because of their structures, high entropy sstr's look as having a definite tendency to replace, in the presence of an appropriate solvent, a given mode of dissolution with a new one involving a much larger entropy change.

* Could it be so, the solid phase stable at higher temperatures should obviously exhibit the lower entropy of solution, which is conflicting with the fact that, in a $\ln(1-x)$ vs T^{-1} plot, the slope of the liquidus is always greater above than below a Krafft-point; see, e. g., the case of RbC_{12} in 2-propanol shown in Figure 4.

¹ J. E. Ricci, *The Phase Rule and Heterogeneous Equilibrium*, Dover Pub., New York 1966, p. 83.

² see, e. g.: (a) R. C. Murray and G. S. Hartley, *Trans. Faraday Soc.* **31**, 183 [1935]; (b) K. Shinoda and E. Hutchinson, *J. Phys. Chem.* **66**, 577 [1962]; (c) R. C. Little and C. R. Singleton, *ibid.* **68**, 3453 [1964].

³ W. Tuler Magnuszewski, Thesis, Hebrew University of Jerusalem, 1975.

⁴ (a) Cs soaps: M. Sanesi, P. Ferloni, M. Zangen, and P. Franzosini, *Z. Naturforsch.* **32a**, 285 [1977]; (b) K soaps: P. Ferloni, G. Spinolo, M. Zangen, and P. Franzosini, *ibid.* **32a**, 329 [1977]; (c) Li and Na soaps: P. Ferloni, M. Zangen, and P. Franzosini, *ibid.* **32a**, 627 [1977]; (d) Rb soaps: P. Ferloni, M. Zangen, and P. Franzosini, *ibid.* **32a**, 793 [1977].