The Relative Stability of the Alkali Metal Chelates of Dibenzoylmethane

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Brändström [1] has recently discussed the evidence bearing on the relative stability of the sodium and potassium chelates of β-ketoesters. He concludes that K^+ has a stronger tendency than Na^+ to give a chelate ring with the anion of a β-ketoester. Since none of the evidence previously available involves a direct measurement of these tendencies to form chelate rings, it seems worthwhile to consider some recent measurements in our laboratory on the tendencies of the alkali metal ions to form chelate rings with dibenzoylmethane (HCh) which is very closely related to the β-keto-esters.

By making potentiometric measurements in 75 % dioxane — 25 % water instead of pure water, it becomes possible to measure differences in chelate stability which are not measurable in water [2-5]. Thus, by using tetramethylammonium hydroxide as the titrating agent (the tetramethylammonium ion is a non-chelating ion), it became possible to make measurements which permit the calculation of formation constants (as defined by Bjerrum [6]) for the alkali metal chelates of dibenzoylmethane. The results of such measurements at 30° (4×10^{-3} mole of HCh and 1×10^{-3} mole of M^+ in 100 ml solution) expressed as log K are:

Li^+ (LiNO$_3$)	5.95	K^+ (KCl)	3.67
Na^+ (NaCl)	4.18	R^+ (RbNO$_3$)	3.52
		Cs^+ (CsCl)	3.42

The order of variation with atomic number from metal to metal is the same here as for the alkali earths and other periodic groups. Thus the direct measurements obtained here show that the tendency to form the sodium chelate is definitely greater than that for the potassium chelate.

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2. Van Uitert, L. G. and Haas, C. G., Jr. *J. Am. Chem. Soc.* 75 (1953) 451.
3. Van Uitert, L. G., Haas, C. G., Jr., Fernelius, W. C. and Douglas, B. E. *J. Am. Chem. Soc.* 75 (1953) 455.
4. Van Uitert, L. G., Fernelius, W. C. and Douglas, B. E. *J. Am. Chem. Soc.* 75 (1953) 457, 2736, 2739, 3862.
5. Van Uitert, L. G. and Fernelius, W. C. *J. Am. Chem. Soc.* 76 (1954) 375, 379.
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A Remark to the Paper of W. C. Fernelius and L. G. Van Uitert on the Relative Stability of the Alkali Metal Chelates of Dibenzoylmethane

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The very interesting measurements of Fernelius and Van Uitert [1] on the relative stability of the alkali metal chelates of dibenzoylmethane which were performed in a dioxane-water mixture are in good agreement with the evidence obtained by Brändström [2-3] given in papers probably not yet accessible to Fernelius and Van Uitert. The paper of Brändström [4] cited by them deals with the behaviour in solvents of a much lower polarity (toluene and tert-butyl alcohol) where the situation may be quite different from that in a more polar medium [3] and where unfortunately no exact measurements seem possible.

The interesting high value of the formation constant obtained with Cs^+ together with the fact that the alkali chelates appear to be of a pure ionic type might give rise to the question if the tetramethylammonium ion is an absolutely non-chelating ion.

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3. Brändström, A. *Arkiv Kemi* 7 (1954) 181.
4. Brändström, A. *Acta Chem. Scand.* 7 (1953) 223.

The System CaO-CaF$_2$

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In studies on the electrical conductivity of the system CaO — CaF$_2$ it has been shown that there exists a gap of miscibility in the liquid state on the CaF$_2$-rich side of the diagram.

Previously this system had only superficially been studied by Eitel [1] as part of a greater work with the method of thermal analysis. In his work, he reported a value for the eutectic point. However, Eitel did not use the highest grade of purity of CaF$_2$ and thus found a melting point for the fluoride which was too low. The true melting point has been determined by Naylor [2] and found to coincide with the one in this work.

The experiments were carried out in a high frequency furnace and the temperature was measured with a Pt : Pt — 10 % Rh thermocouple. The resistances of the melts were measured between molybdenum electrodes, the cell constant of which was determined using 0.1 N KCl. The determinations were made in carbon crucibles with thoroughly weighed and blended mixtures of CaO and CaF$_2$, A.R. grade. All experiments were carried out in a purified nitrogen atmosphere. The carbide contamination from the carbon crucibles could be shown to be negligible with
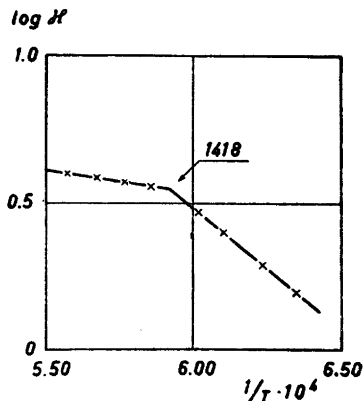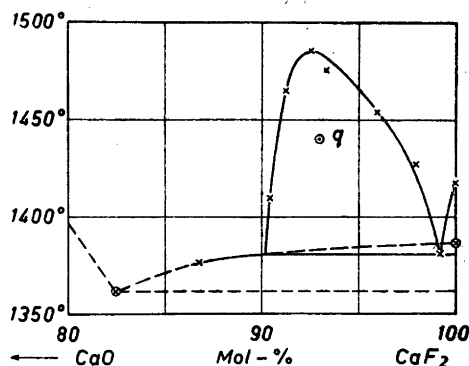
log $\varkappa$

Fig. 1.

mixtures up to about 15 mol-% CaO. From measured values of the resistances, the conductivities ($\varkappa$) were computed in the usual way. Phase transitions are found as discontinuities in the curves of log $\varkappa$ as a function of $1/T$. An example (pure CaF$_2$) of these curves is shown in Fig. 1. All results are summarised in the equilibrium diagram (Fig. 2), where crosses ($\times$) are from this investigation, while crosses with rings ($\oplus$) and the dotted lines are from Eitel. The diagram shows a gap of miscibility with a maximum at about 92.5 mol-% CaF$_2$ and 1 485° C. The gap goes from 0.8 mol-% to about 10 mol-% CaO.

The point q represents an experiment in which a mixture has first been heated to 1 510° C after which it has been cooled down to 1 440° C and kept at this temperature for two hours and then quenched. The result was two phases with a sharp boundary.

Finally, it may be remarked that the electrical conductivity of CaF$_2$ at the melting point (1 418° C), $\varkappa = 3.56$ ohm^{-1}cm^{-1}, is of the same magnitude as that of CaCl$_2$, $\varkappa = 4.17$ ohm^{-1}cm^{-1}, extrapolated to the same temperature [3].

Fig. 2.

1. Eitel, W. *Zement* 27 (1938) 469.
2. Naylor, B. F. *J. Am. Chem. Soc.* 67 (1945) 150.
3. Drossbach, P. *Elektrochemie geschmolzener Salze*, Berlin, 1938, p. 72.