

## ON THE ASSOCIATION AND PRECIPITATION OF $\text{CaCl}_2$ IN $\text{NaCl}$ CRYSTALS

ARNOŠT KESSLER, Bratislava

### INTRODUCTION

It is known (cf. [1]) that ion transport effects in the *structure sensitive region* of polar crystals are influenced by association and precipitation of the divalent admixtures. Several authors [2, 3, 4, 5] could observe an effect of precipitation on conductivity. But often one and the same effect is explained once by complex formation [6], another time by precipitation [7]. The association energy as evaluated from experimental data exhibits considerable differences. Data reported e. g. for calcium complexes are .08 eV [8], .31 eV [9], .6 eV [10]. (Compare the stray of the activation energy of migration, which is reported to be .72— .85 eV [11].) Theoretical calculations give .38 eV [12].

Kessler and Mariani [13] performed recently measurements on slowly cooled  $\text{NaCl} : \text{CaCl}_2$  crystals grown by the Kyrponoulos method in an inert atmosphere. They found the conductivity to differ considerably from that reported earlier by Bean [14]. This difference seems to be satisfactorily explained by precipitation and gives an insight into the possible reasons of the wide stray of the association energy as established from experimental data (see below).

### COMPARISON OF EXPERIMENTAL RESULTS [13], [14]

In Fig. 1a the conductivity isotherms from both measurements and in Fig. 1b the  $\text{tg } \delta_{\text{rel. max}}$  vs. impurity concentration  $c$  [13] are given. The difference in conductivity is obviously caused by precipitation, because equilibrium association is achieved quickly enough to rule out any possibility of Bean's results answering a lower degree of association than the results of Kessler and Mariani and there has hardly been known a process, which could cause an increase in the conductivity in case of the measurements performed by Bean except the freezing in of a calcium concentration exceeding the solu-

bility. Further, slightly alkaline  $\text{NaCl} : \text{CaCl}_2$  crystals (cf. Fig. 1a and [13]) exhibited at higher concentrations a higher conductivity than neutral  $\text{NaCl} : \text{CaCl}_2$  in spite of the fact, that by anion doping the conductivity in general decreases [15, 16, 17]. This might perhaps be due to an increase in solubility by the anion admixtures (cf. [18]).

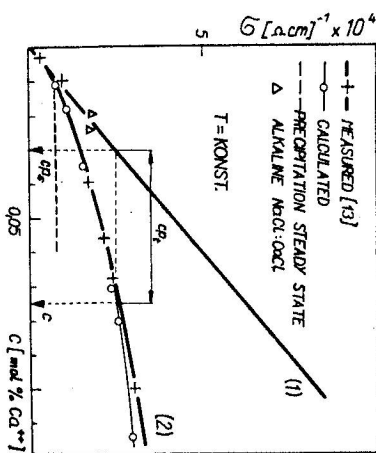


Fig. 1a. Conductivity isotherms as reported (1) by Bean, (2) by Kessler and Mariani. Isotherm calculated, basing on trimer formation,  $K_3 = 1.6 \times 10^8$ .

As known (cf. Lillard [1] § 29) the  $\text{tg } \delta_{\text{rel. max}}$  is proportional to  $pc$ , where  $p$  is the degree of association of complexes. If  $p < 1$ ,  $p$  should increase with  $c$ . The  $\text{tg } \delta_{\text{rel. max}}$  vs.  $c$  should therefore be either linear with  $c$  for  $p = 1$  as observed by Haven [19] or concave, if  $p < 1$ . Hence, the only reasonable explanation of the convex shape of the experimental curve is precipitation in accord with the findings concerning conductivity.

### DETAILED DISCUSSION OF THE INFLUENCE OF PRECIPITATION ON CONDUCTIVITY

Cook and Dryden [20, 21] and others observed a successive transformation of the calcium complexes into so called trimers at about  $100^\circ$  above room temperature, 3 complexes  $\rightleftharpoons$  1 trimer, followed eventually after a *transient equilibrium state* by a slow formation of even higher complexes. Let us denote by  $cp_3$  the fraction of associated and dissociated complexes and by  $cp_1$  the fraction of trimers,  $p_3 + p_1 = 1$ . The equilibrium between associated and dissociated complexes then should be

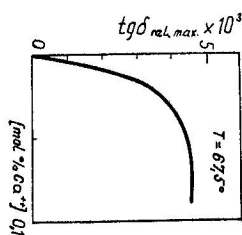


Fig. 1b. Dielectric loss maximum in dependence on the calcium content [13].

$$\frac{p}{(1-p)^2} = cp_s K_k(T) \quad (1)$$

and that between complexes and trimers at low temperature

$$\frac{p_t}{(p_s p)^3} \doteq \frac{p_t}{p_s^3} = c^2 K_t(T) \quad (2)$$

If a crystal is cooled slowly enough or stored over a sufficiently long period, an *equilibrium* should be obtained corresponding at least approximately to (2) at a certain temperature (which cannot be too high).

(1) and (2) correspond only to a transient equilibrium and slowly higher aggregates [22] are formed in due time. Suppose they are formed by association of trimers and complexes. Then as long as  $p_s + p_t \sim 1$ , the decrease of  $cp_s$  with time  $t$  is

$$\frac{dcp_s}{dt} = -K'(T) \cdot (cp_s) \cdot (cp_s) = -K' c^2 p_s (1 - p_s),$$

$$\frac{p_s}{p_t} = \frac{p_{s0}}{p_{t0}} \exp(-K'ct) \quad (3)$$

The zero index denotes the respective concentration at *transient equilibrium*,  $K'$  the respective mass action constant of the process.

The comparatively short period of heating during conductivity measurement cannot cause a change in concentration of the agglomerates. In fact, as seen from Tab. 1, the relative conductivity decrease as found by Kessler and Mariani actually depends on the calcium concentration only and not on the temperature of the measurement.

If the difference in conductivity (see Fig. 1a) is really caused by precipitation, the conductivity is, if the free energy of association  $U_A$  is not too high

$$\sigma \doteq \text{const. } cp_s(1 - p) \quad (4)$$

Relative difference in conductivity between [13] and [14] and of the  $\text{tg } \delta_{\text{rel. max.}}$  [13] as compared with the straight line increase with  $c$  in dependence on temperature and  $\text{CaCl}$  concentration.

Table 1

$\text{Ca}^{2+}$ content [mol %]	diminution [%] of conductivity at $10^3/T = 1.1, 1.2, 1.3, 1.4, 1.5, 1.8, 2.3$	diminution [%] of $\text{tg } \delta_{\text{rel. max.}}$ at $10^3/T = 2.96$
.02	25 28 20 23 26 4 15	18
.05	43 55 49 48 50 29 40	44
.10	61 63 63 58 61 61 55	77

and  $cp_t = c(1 - p_s)$  should correspond to the difference of the calcium content of both kind of crystals at the same value of conductivity (cf. Fig. 1a). Putting the respective values  $p_t$ ,  $p_s$  and  $c$  into (2), we get for  $K_t$   $1.6 \times 10^3$ . The conductivity calculated on the basis of this value from (2) and (4) is in perfect agreement — as seen in Fig. 1a — with the experimental data [13].

Suppose now that higher complexes are formed according to (3) and the *transient equilibrium* of trimer formation has passed. A regression in conductivity should then occur after some time; it should proceed more quickly at higher concentrations  $c$ , hence a *virtual maximum* in the  $\sigma$  vs.  $c$  isotherm should be observed.

In fact the occurrence of a  $\sigma$  vs.  $c$  maximum was observed in some cases in  $\text{NaCl} : \text{CaCl}_2$  by Kessler and Mariani and in  $\text{NaCl} : \text{Ni}^{2+}$  by Jain and Dahiya. In  $\text{KCl} : \text{CaCl}_2$  Fröhlich and Henzel [23] observed a  $\sigma$  vs.  $c$  maximum and further the vanishing of the  $\sigma$  vs.  $c$  maximum after some time. Obviously the formation of higher complexes continued till  $\text{CaCl}_2$  microcrystals were formed and a final state of precipitation was attained. Under these conditions the expression  $c_{\text{sol}} = \exp(-U_A/RT)$  as given by Lidard [24] for the solubility  $c_{\text{sol}}$  with  $U_A$  denoting the free energy of solution should be satisfied and the  $\sigma$ -isotherm should exhibit a sharp knee with a horizontal tail (cf. Fig. 1a). This state is approached in  $\text{NaCl} : \text{ZnCl}_2$  (cf. Rothmann et al. [25] where) the  $\log \sigma$  vs.  $1/T$  curves nearly join into one single line in the precipitation region (Fig. 2a) in contrast to the usual situation, where  $\sigma$  depends on  $c$  in this region (Fig. 2b). The conclusion of Rothmann et al., that the *precipitation line* in the  $\log \sigma$  vs.  $1/T$  curves correspond to  $c_{\text{sol}}$  is confirmed by the solubility of  $\text{ZnCl}_2$  in  $\text{NaCl}$  as established by Pauliny—Tóthová and Popeliš [26].

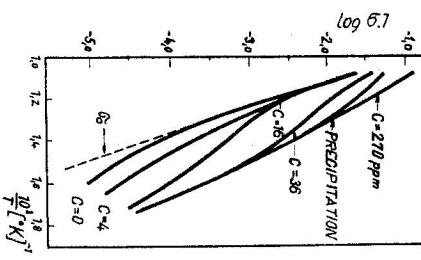


Fig. 2a. Conductivity of  $\text{NaCl} : \text{ZnCl}_2$  according to [25].

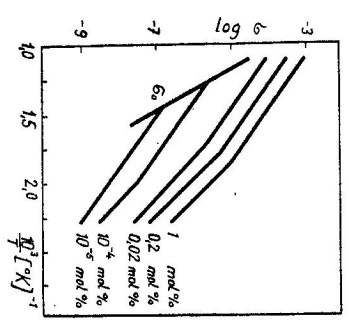


Fig. 2b. Conductivity of  $\text{NaCl} : \text{CaCl}_2$  according to [13].

It should be noted that a  $\sigma$ -isotherm as given in Fig. 1a (2) should be expected also for the simple association model in case of a high enough association energy  $U_A$ . Were it not because of the  $\sigma$ -isotherms given by Bean, one would infer perhaps something like this from curve (2), Fig. 1a. But if this were true a difference in the slope of the  $\log \sigma T$  vs.  $1/T$  should be observed between pure and highly doped crystals because (cf. [13])

$$48c \exp(U_A/kT) \ll 1; \quad \sigma T = \text{const. } c \exp(-U_p/kT),$$

$$48c \exp(U_A/kT) \gg 1; \quad \sigma T = \text{const. } |c \exp\left(-\frac{U_p + U_A/2}{kT}\right)|.$$

$U_p$  denotes the jump activation energy of the charge carriers. From the results in Fig. 2b it is apparent that this is not the case.  $U_A$  should be expected therefore  $U_A < 1 - 2 \text{ eV}$ .

It is to be noted that this low value of the association energy might be caused also by a deviation from the simple association model. It is not the purpose of this paper, however, to discuss this problem.

#### CONCLUSIONS

The discussion of the different experimental data showed that

- 1) the difference in conductivity can be satisfactorily explained by a *freezing in* and *precipitation* respectively of the calcium,
- 2) in case  $\sigma$  is in the precipitation region a function of the admixture concentration, the substitutionally built in admixtures are not in thermodynamical equilibrium with the lattice and
- 3) an uncontrolled formation of higher complexes i. e. a starting precipitation process may *simulate* eventually a high association energy, if the evaluation of the experimental data is made not carefully and complex enough. This fact is responsible perhaps for the considerable stray in association energy values as reported.

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Fyzikální ústav SAV,  
Bratislava