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DIPOLAR ATOMS IN Na-NaX SOLUTIONS? - AN OPTICAL STUDY -

Th. SCHINDELBECK, D. NATTLAND and W. FREYLAND

Institute of Physical Chemistry, University Karlsruhe, Kaiserstrasse 12, D-7500 Karlsruhe, Germany

Abstract - In a recent quantum molecular dynamics calculation of diluted Na-NaBr solutions Parrinello and coworkers found that excess electrons may localize to form dipolar Na atomic - like states. This is at variance with spectroscopic observations that F-center like states prevail in alkalimetal-alkalihalide solutions. In order to get further insight into this problem we have reinvestigated the optical absorption spectra of dilute alkalimetal-alkalihalide-NaCl solutions as a function of temperature and for various salt compositions. The main result of this study is that indeed in NaCl-rich solutions deviations from the expected F-center characteristics are visible.

1. Introduction

For years the nature of electron localization in molten alkalihalides has been controversial. Pitzer /1/ suggested, on the grounds of simple thermodynamic considerations, that F-center like states might exist. Bredig /2/ discussed in detail the phase behaviour and the electrical conductivity and concluded that at least in Na-NaX systems atomic like states should be considered. In recent years various spectroscopic studies have been performed in different fluid M-MX systems which all support the F-center model including Na-NaX solutions. These experiments comprise ESR-spectra /3/, optical absorption measurements /4/, /5/ and NMR studies /6/. The first quantum mechanical treatment of a solvated electron in molten KCl has been reported by Parrinello and Rahman /7/. Using the Feynman path integral method these authors find that the electron is highly localized thus justifying the F-center model /7/. However, at the same time these calculations demonstrate that the electron density distribution is very sensitive to the radius R_0 of the local pseudopotential, i.e. for a small $R_0 \sim 1.5 \text{ \AA}$ the electron is localized around one of the K^+ -cations. In a very recent quantum molecular dynamics (QMD) calculation on dilute Na-NaBr solutions Parrinello and coworkers emphasize this point /8/. Treating the ions classically while a quantum mechanical description is used for the electrons they find that atomic like states with some dipolar character are favoured with respect to the F-center. This depends on the strength of the alkali metal atom potential and should be most pronounced for the Li-LiX systems.

These theoretical findings have been the impetus for the present study. For experimental reasons (corrosion) we have focused on NaCl containing melts instead of LiCl. We report here optical absorption measurements on dilute M-MCl, NaCl solutions for different salt compositions. Our interest concentrates on the NaCl-rich end to see if with varying composition of the cation solvation shell and corresponding variation of the electron-cation potential, deviations from F-center characteristics occur.

2. Experimental

The experimental technique used to measure the optical absorption spectra is similar to that described in /5/. In brief, thin liquid films of the salt mixtures of the order of 20 μm have been prepared between two sapphire windows which are sealed by Ta- or Nb-wire rings. The metal concentration was determined by additive doping. The salts were cleaned by heating under vacuum up to the melting point to reduce mainly H_2O -impurities. All sample preparations and manipulations have been performed under high purity argon atmosphere. For further details reference is given to our previous paper /5/.

3. Results and discussion

In the crystalline state the optical evidence for F-centers is the validity of the Mollwo-Ivey relation, i.e. the optical excitation energy of the absorption band maximum, E , scales with the sum of the ionic radii, $R = R_+ + R_-$, $E \sim R^{-\alpha}$ (see e.g. /9/). A similar correlation is obtained in the liquid with $\alpha \sim 2$ if one plots a linear regression through all experimental data from NaX to CsX systems at a constant reduced temperature $T/T_m = 1.1$ above the melting temperature T_m using the ionic radii of the solid structures /5/. Of course, the exponent α is sensitive to changes in the interatomic potential which occurs on melting. Therefore we have replotted E vs. R using the appropriate ionic radii of the molten salts as determined by Abramo et al /10/. In this work the ionic radii have been determined from interatomic potentials fitted to experimental data of the isothermal compressibility and the structure factor. The result of this plot is shown in Fig. 1. In the presented linear regression only data of K-KX, Rb-RbX and Cs-CsX systems have been taken into account in order to see how they correlate or extrapolate to the data of the Na-NaX systems.

Within these systems a nice correlation is observed with $\alpha \sim 1.9$. However, the data points of Na-NaCl ($\ln(R/\text{\AA}) \sim 0.89$) and Na-NaBr ($\ln(R/\text{\AA}) \sim 0.93$) systematically deviate towards higher energies, outside the experimental error of E . The same trend is observed if one uses a different data set for the liquid ionic radii, like e.g. that of Senatore et al /11/. Furthermore, if one includes in this comparison the measurements of Young /12/ on Li-LiCl the deviation is even more pronounced. So we may conclude: if F-center like states occur in the heavier alkali halides and a Mollwo-Ivey type relation holds this does not apply with the same exponent α for the lighter alkali metal halides.

Fig. 1: Logarithmic plot of the absorption energy E , vs the sum of ionic radii R for different dilute M-MX melts at a constant reduced temperature $T/T_m = 1.0$ (circles from /4/, squares from /5/ and this work).

In order to follow continuously the transformation of the optical characteristics going from heavier to lighter dilute M-MX-solutions we have measured in detail the optical spectra of the following salt mixtures doped with small amounts of alkali metal below 0.5 at %: M-KCl-RbCl, M-RbCl-NaCl, M-KCl-NaCl /13/. According to the phase diagrams the salt mixtures have the following thermodynamic characteristics: the first shows ideal behaviour, the second has a deep eutectic, and the third exhibits clear signs of demixing. All observed spectra exhibit a clear asymmetry towards higher energies. The line shape of the overall absorption band can be described equally well by either two Lorentzians or two Gaussians, where the second band with small intensity takes account of the asymmetry. So the line shape is not well resolved. From this curve analysis - after background correction - the absorption maximum of the dominant band has been determined as a function of temperature and for various salt compositions - for details see /13/.

A summary of these results is presented in Fig. 2. Here the energy E of the absorption band is plotted as a function of salt composition for the three systems M-MX. M'X at two temperatures of 800 °C and 900 °C, respectively.

The main observations of this comparison of the three systems are the following:

1. In the RbCl-KCl system the energy shifts linearly with composition and the temperature dependence remains constant within experimental error. This behaviour is expected for F-centers if the cation shell - which mainly defines the changes of the potential well - varies continuously as is the case with ideal mixing.

2. In KCl-NaCl and RbCl-NaCl an incipient linear increase of E with addition of NaCl is apparent up to ~ 50 mol% NaCl. This is better demonstrated in the KCl-NaCl case where more measurements have been performed. The temperature dependence of E slightly increases with x_{NaCl} .
3. The most interesting result is the behaviour of E in the NaCl-rich solutions. The temperature coefficient $\partial E/\partial T$ is a factor of ~ 3 larger than in M-KCl, M-RbCl or M-CsCl solutions. The concentration dependence is weak. The most important observation is that down to about 60 mol% NaCl the optical energies of the two systems exhibit within experimental error the same trend. This is remarkable in view of the different thermodynamic characteristics of KCl-NaCl and RbCl-NaCl.

Fig. 2: Absorption energy E vs salt concentration x for: $M\text{-RbCl}_{1-x}\text{NaCl}_x$ (Δ) $M\text{-RbCl}_{1-x}\text{NaCl}_x$ ($\circ$), $M\text{-KCl}_{1-x}\text{NaCl}_x$ ($\square$). The full curves correspond to 800 °C, the dashed curves to 900 °C. The error bars are marked by the dashes. The amount of doped alkali metal in all cases is below 0.5 at %.

If F-centers were the only type of localized electronic states this behaviour is difficult to explain. On the other hand, one might assume that microscopic segregation of NaCl and due to this, F-center formation in these regions is energetically favoured. However, again this is difficult to reconcile with the difference in the thermodynamics of these two salt mixtures, i.e. demixing vs. compound forming tendency.

So these considerations strongly indicate that at least in NaCl melts different characters of localized electronic states must be taken into account. This is consistent with the QMD calculations mentioned in the introduction. For dipolar atomic like configurations - which contain admixing of p character into the s atomic ground state - Parrinello and coworkers predict a blue shift of the optical excitation relative to the corresponding F-center [8].

This is consistent with the data in Fig. 1. In particular, they point out that the strength of the electron-cation potential controls the relative stability of the dipolar atomic state vs. the F-center and that a gradual change from the one to the other occurs going from the Na^+ - to the K^+ -potential. This gradual transformation as probed by the optical excitation is shown in Fig. 3. It shows the optical energies of all the data of Fig. 2 at 800 °C plotted versus the sum of the ionic radii R weighted by the corresponding compositions. We are aware that these R -values do not reflect the actual nearest neighbour distances in the salt mixtures and so the slopes in this plot cannot be compared with α discussed above.

Fig. 3: Logarithmic plot of energy, E , vs average sum of ionic radii, R ; the data presented correspond to all points of Fig. 2 at 800 °C with corresponding symbols.

However, there is a clear change in slope of $\ln E$ vs $\ln R$ approaching R of NaCl-rich melts. This reflects the observations of Fig. 2 and is consistent with the above predictions of the QMD calculations.

In summary we may state that with increasing strength of the electron-cation potentials towards values like in M -NaCl solutions the optical spectra clearly deviate from the behaviour of simple F-center like states. This is in agreement with theoretical calculations according to which dipolar atomic like states should stabilize in NaX and LiX melts. A direct proof of this species should be possible via measurements of its large predicted dipole moment $/8/$, e.g. in molecular beam experiments on the corresponding M -MX clusters.

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