THERMOSONIMETRY IN FUSED SALTS

by

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ABSTRACT

Three binary systems; NaCl-CsCl, CsCl-BaCl$_2$ and LiCl-AlCl$_3$, have been chosen to test if Thermosonimetry (TS) could be used in phase-diagram studies of salt systems. In the TS technique the sample is heated at a constant rate and the sonic radiation from the sample is recorded. Whenever a change of phase takes place, an increase in the sonic activity is observed. One of the advantages of thermosonimetry is that compared to the slow diffusion of heat to the sample surface and subsequent pick-up by a thermocouple or calorimeter, the propagation of information is practically instantaneous and given by the sound velocity.

The TS results compare well with DTA measurements in the LiCl-AlCl$_3$ system and with the known phase-diagrams of the binary systems NaCl-CsCl and CsCl-BaCl$_2$. Some noise, however, is observed above and in the liquidus region in the LiCl-AlCl$_3$ system.

INTRODUCTION

The present preliminary work intends to show the potensiality of thermosonimetry in phase-diagram studies. This technique is newly developed (1), and has not previously been used to study phase-diagrams. Certain applications have already been demonstrated within the field of phase transitions, decompositions of chemical compounds and minerals and thermomechanical fracturing. In this technique one measures the sonic activity from the process in question. The technique resembles "acoustic emission spectroscopy", the main difference being that the transformations causing the sonic emission are activated thermally. The background TS-activity in the absence of a physical process involving say some change of phase, is so low that the TS signal from the physical process can be clearly identified. When liquids are present, however, reactions between the liquid and container material evaporation/condensation processes or liquid creeping on the container walls may create thermal noise which will disturb this simple picture. It is therefore of importance when investigating the usefulness of this technique in systems containing fused salts to cheque the influence of these disturbances on the TS signal.
EXPERIMENTAL

All salts were dried carefully before use. Anhydrous AlCl₃ was distilled at 200°C three to four times in a closed evacuated quartz tube to get rid of oxide impurities. The pure hygroscopic salts and their mixtures were transferred to the quartz stethoscopes in a dry-box with less than 5 ppm of water. The stethoscope-salt-container was then evacuated and sealed. Before use the salts were fused, mixed and then quenched by dipping the stethoscope in water. Fig. 1 shows the seismically mounted quartz stethoscope resting on the piezoelectric cell for conversion of the induced vibrations in the stethoscope. The electric signals from the piezoelectric cell are then processed for recording or storage. In this system the TS activity can be monitored by recording:

1. The mean signal amplitude
2. The number of sonic bursty per second (Cps)
3. The frequency of the sonic radiation.

This flexibility allows us to study different aspects of the process giving rise to sonic activity. The measurements were run with nominal heating rates of 5, 10 and 20°C per minute. The TS activity was recorded as a function of temperature over the range 25°C to 750°C. The reference temperature provided by the thermocouple (Fig. 1) was later calibrated against the alpha-beta quartz transition at 573°C.

RESULTS AND DISCUSSION

The NaCl-CsCl system

The NaCl-CsCl binary is a simple eutectic system with a β→α transition in solid CsCl at 470°C and an eutectic temperature around 500°C. Fig. 2 shows the thermosonigram obtained from the mixture 15 mol% NaCl - 85 mol% CsCl (2). The β→α transition, eutectic temperature and liquidus line can clearly be seen. When the first liquid is formed, the rearrangements of the atoms in the crystals create strong sonic emission which is picked up by the stethoscope, and when the eutectic composition is reached the TS activity decreases since one solid phase is gone. Dissolution of CsCl still takes place and creates a fairly strong sonic emission which reaches a final maximum at the liquidus temperature. An increase in the surface to volume ratio will increase the rate with which the dissolution reaction takes place, and an increase in the sonic emission might be the result when the last crystals dissolve. We are not, however, ready to give a quantitative and definite explanation of this increase in sonic activity at the liquidus temperature before more experimental information on this effect is available.
The CsCl-BaCl$_2$ system

In the CsCl-BaCl$_2$ binary, which has been studied by thermoanalysis (3), two compounds exist (see Fig. 3). One, Cs$_2$BaCl$_4$, melts congruently at 588°C and the other, CsBaCl$_3$, melts incongruently at 600°C. The system has two eutectic temperatures at 543°C and 582°C. In Fig. 3 the thermosonigram is shown. The interpretation of the experimental results is somewhat questionable. The eutectic and liquidus temperatures are clearly seen, and we think that the strong sonic activity at 622°C is due to the peritectic reaction. To correlate further the sonic data with the reported phase-diagram we have plotted the sonic transition temperatures as a function of the rate of temperature rise. On extrapolating to zero rate (isothermal heating) we find the data given in Fig. 4. The liquidus temperature coincide with the reported phase-diagram and the peritectic and eutectic temperatures are somewhat higher than those obtained by thermoanalysis.

The LiCl-AlCl$_3$ system

Five different compositions: 10, 20, 30, 40 and 46 mol% AlCl$_3$ were investigated, and since the LiCl-AlCl$_3$ phase diagram is not known, the TS data are compared with preliminary DTA curves obtained on cooling (4). The DTA cooling curves show extensive supercooling and the liquidus temperatures estimated from these data are therefore tentatively only.

In Figs. 5-8 TS results are shown for a melt containing 10 mol% AlCl$_3$. The TS curves show a strong sonic activity around 600°C which drops of abruptly just above 600°C. This reduction in activity indicates that the liquidusline is reached. Just above this temperature a final increase in the TS activity is observed. The intensity of this peak, however, is smaller than that of the main peak when the heating rate is high (5°C/min and 10°C/min), but greater when the heating rate is low (2°C/min). We tend to believe that the last peaks are representative for the melting at the liquidus temperature. In Fig. 8 the isothermal melting point for the 10/90 melt is found to be 598°C. This agrees very well with the DTA data which gives $T_f = 596°C$. At higher contents of AlCl$_3$ it was difficult to obtain reproducible thermosonigrams. The most reliable results are presented in Figs. 9-12. It is a reasonable agreement between the TS data around the liquidus-temperature and the DTA data for the 20/80 and 30/70 melts. In Fig.11, however, strong sonic activity is observed at temperatures far above the liquidus temperature. For the 46/54 melt it was not possible to obtain a DTA signal on cooling (4). The TS data shown in Fig. 12 indicate a melting temperature below 390°C. This is in agreement with a calculation of the liquidus temperature based on vapour pressure data giving 360°C (5).

On the basis of the present preliminary results it may be concluded that thermosonimetry seems to be a promising method for phase diagram studies. The very strong sonic activity which occurs at phase transi-
tions may give additional informations to data obtained through more conventional methods.

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Fig. 1. Sample mounting, stethoscope and piezoelectric converter mounted in housing.

Fig. 2. Thermosonigram of the mixture 15 mol% NaCl – 85 mol% CsCl. Heating rate: 10 °C/min.

Fig. 3. Thermosonigram of the mixture 40 mol% (CsCl)$_2$ – 60 mol% BaCl$_2$. Heating rate: 10 °C/min.

Fig. 4. Temperature of sonic transitions at the eutectic, peritectic and liquidus as function of heating rate in the CsCl-BaCl$_2$ system. Composition: 40 mol% (CsCl)$_2$ – 60 mol% BaCl$_2$. 211
Fig. 5. Sonic activity as function of temperature.
Heating rate: 2°C/min.
System: AlCl\textsubscript{3}/LiCl = 10/90.

Fig. 6. Sonic activity as function of temperature.
Heating rate: 5°C/min.
System: AlCl\textsubscript{3}/LiCl = 10/90.

Fig. 7. Sonic activity as function of temperature.
Heating rate: 10°C/min.
System: AlCl\textsubscript{3}/LiCl = 10/90.

Fig. 8. Temperature of ionic transitions as function of heating rate in the 10/90 AlCl\textsubscript{3}/LiCl mixture.
Fig. 9. Sonic activity as function of temperature. Heating rate: 20°C/min. System: AlCl₃/LiCl = 20/80.

Fig. 10. Sonic activity as function of temperature. Heating rate: 20°C/min. System: AlCl₃/LiCl = 30/70.

Fig. 11. Sonic activity as function of temperature. Heating rate: 20°C/min. System: AlCl₃/LiCl = 40/60.

Fig. 12. Sonic activity as function of temperature. Heating rate: 20°C/min. System: AlCl₃/LiCl = 46/54.