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MEASUREMENTS OF ULTRASONIC VELOCITY IN THE MOLTEN SALT MIXTURE $CdCl_2$-NaCl

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The measurement of the ultrasonic velocity was carried out for the molten salt mixture $CdCl_2$-NaCl, in mole fraction ratios, for the temperature range 580-880°C. The adiabatic compressibility was calculated for each concentration at the temperature 680°C. The isothermal velocity and excess velocity as functions of the mole fraction have been illustrated for the temperature 840°C.

1. Introduction

Measurements of ultrasonic velocity in molten salt systems carried out simultaneously with density measurements are the basic source of data necessary to calculate the adiabatic compressibility β_s of such systems. Interpretation of adiabatic compressibility in terms of its relation to ion-ion interactions leads to a direct conclusion about the microscopic structure of the molten electrolytes. Most of the ultrasonic velocity measurements have been carried out for simple molten electrolytes [1, 2]. A consequence of these investigations has been the equation of state for simple molten electrolytes established by BOCKRIS. On the basis of scaled particle theory the sum of anion-cation radia for molten alkali halides has been calculated by STILLINGER Jr.

Investigations of some binary molten electrolyte mixtures have been carried out by STERNBERG and VASILESCU [3, 4]. These authors suggest the formation of ionic complexes of the type $PbCl_3^-$, $PbCl_4^{2-}$, $PbCl_6^{4-}$, in the investigated samples. It also seems possible that similar complexes could be formed in the molten binary mixture of $CdCl_2$-NaCl.

The results of our investigations reveal some evidence for the complexing of Cd^{2+} by Cl^- ions to form $CdCl_4^{2-}$ in the molten mixture $CdCl_2$-NaCl.

2. Experimental

Apparatus. The measurements of the ultrasonic velocity were carried out using an apparatus constructed in the General Chemistry Department of the Institute of Chemistry, Jagiellonian University.

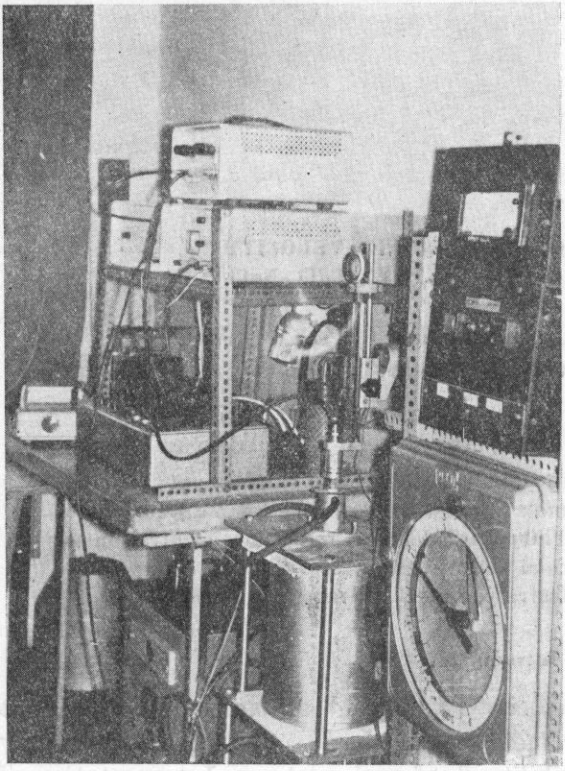

Fig. 1. General view of the apparatus for the measurement of ultrasonic velocity at high temperature

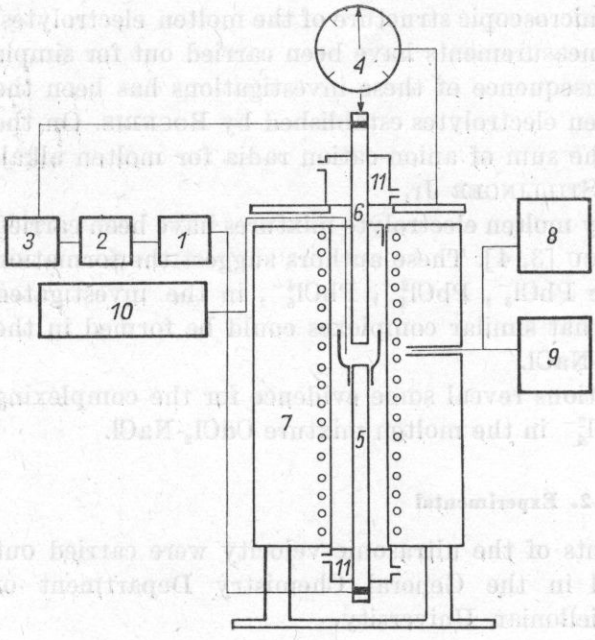

Fig. 2. Scheme of the apparatus for the measurement of ultrasonic velocity in molten salt systems

The apparatus was used to measure the velocity of ultrasound in molten salts, glass phases and alloys over the temperature range 100°-1000°C at two different ultrasonic frequencies, 5 and 10 MHz. Using a special micro-balance with a density bob, the density of a sample could be determined.

The apparatus consists of an ultrasonic generator *1*, amplifier with attenuator *3*, receiver *2*, support with a cathetometer for measuring the distance between the quartz rods with an accuracy of 10^{-5} m *4*, the vessel with the quartz delay rod and the transducer *5*, the transducing receiver with the quartz delay rod *6*, resistance oven *7*, thermal regulator *8*, temperature recorder 9, cooling coils *11* and a measurement assembly including a compensatory Wheatstone bridge *10*.

Table 1. Coefficients a and u_0 calculated from our results and compared with the results obtained by Vasilescu and Bockris

	Our results		Bockris		Vasilescu	
	a	u_0	a	u_0	a	u_0
NaCl	0.814	2402	0.915	2483	0.811	2405
$CdCl_2$	0.348	1272	0.382	1280	—	—

The electronic assembly included an ultrasonic pulse-phase UI-11 interferometer produced in Poland (IPPT PAN, Warsaw). Measurement of the ultrasonic velocity is based on the observed interference of two electrical pulses introduced simultaneously into the input of the receiver, one having passed through the ultrasonic transducers and the investigated sample, and the second

Table 2. The experimental temperature ranges for different samples

k_{mole}NaCl	Temperature range [°C]
0	580-890
0.1	580-860
0.2	600-870
0.3	610-860
0.4	500-860
0.5	600-870
0.6	580-880
0.7	640-870
0.8	630-880
0.9	755-880
1.0	above 807;

coming directly. The change of distance between the ultrasonic transducers causes a change in the resultant amplitude of the two pulses. Using the cathetometer we can measure the distance between two points having the same ampli-

tude (usually zero) for the same frequency f of the ultrasound; the velocity u can be derived from the following relationship

$$u = \Delta l f, \tag{1}$$

where Δl is the distance between the transducers.

Calibration of the apparatus. The standardizing measurements for the velocity of ultrasound were carried out in molten NaCl, temperature range 810°-920°C, and molten $CdCl_2$, temperature range 580°-880°C, at a frequency of 5 MHz. «Analar» materials were used for these measurements. The measured ultrasonic velocities in the above temperature ranges can be represented by the linear relationship

$$u = u_0 - at. \tag{2}$$

The coefficients u_0 and a, calculated from the above equation, are collected together in Table 1. Looking at this table we can compare the results for u_0 and a previously found by VASILESCU [3], BOCKRIS [1]. As can be seen from Table 1, the results are in good agreement and the error does not exceed 1.5 %.

Procedure. Measurements of the ultrasonic velocity were carried out for the mixture $NaCl/CdCl_2$ in different molar ratios. In Table 2 the temperature ranges for the different compositions are shown. The measurements were carried out three times for each sample, and the results, as a function of temperature and composition, are presented in Fig. 3.

As can be seen from Fig. 3 the relationship between the ultrasonic velocity and the temperature is linear for the whole sample range. The coefficient a changes with mixture composition from which we conclude that the investigated samples are not ideal liquids and that the observed deviations are due to the production of ionic complexes in solution.

This assumption is confirmed by the isothermal plot of ultrasonic velocity vs. mole fraction for 840°C (Fig. 4), where a negative deviation may be seen between the measured ultrasonic velocity and the additive velocities. The highest difference occurs for the mixtures 0.6 and 0.7 k_{mole} NaCl.

The excess velocity of the ultrasound u^E (Fig. 5) is calculated from the equation

$$u^E = u - u_1^0 k_1 - u_2^0 k_2 \tag{3}$$

(where u is the velocity in the mixture, and $u_1^0 k_1$ and $u_2^0 k_2$ are the velocities and molar fractions of the first and the second component of mixture, respectively) and has a minimum for the concentration 0.6-0.7, as was found above.

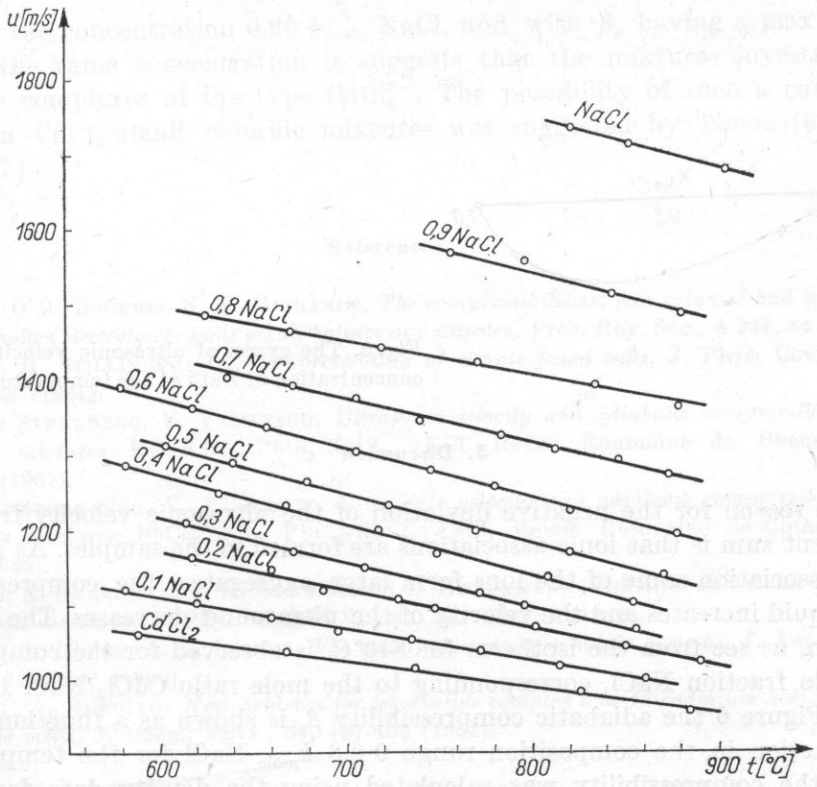

Fig. 3. Ultrasonic velocity vs. temperature in liquid mixtures of $NaCl/CdCl_2$

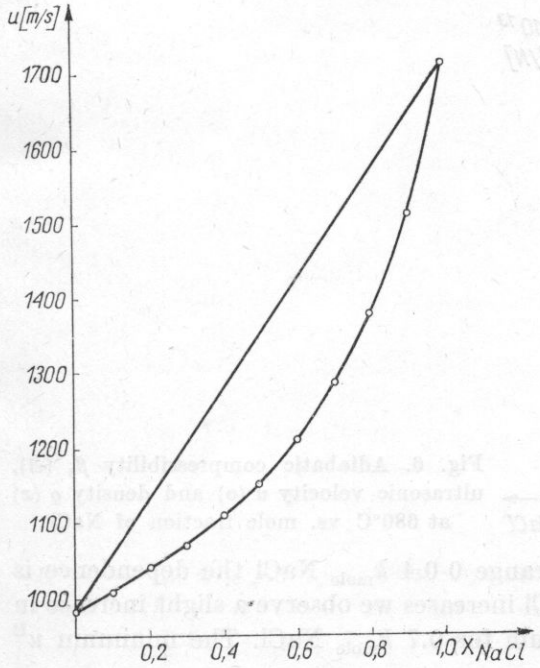

Fig. 4. Plot of ultrasonic velocity vs. mole fraction of NaCl at 840°C

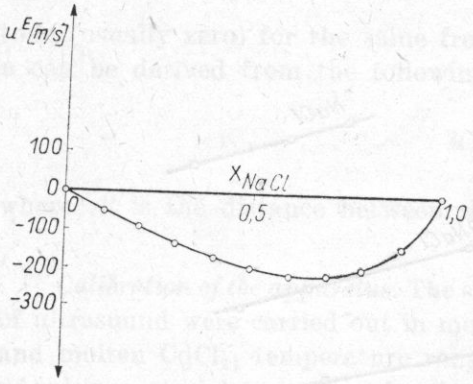

Fig. 5. The excess of ultrasonic velocity u^E vs. concentration of NaCl at the temperature 840°C

3. Discussion

The reason for the negative deviation of the ultrasonic velocity from the component sum is that ionic associations are formed in the samples. As a result of the association some of the ions form large aggregates, the compressibility of the liquid increases and the velocity of the ultrasound decreases. The highest deviation, as see from the isotherm for 840°C, is observed for the composition 0.66 mole fraction NaCl, corresponding to the mole ratio $CdCl_2$/NaCl 1:2.

In Figure 6 the adiabatic compressibility β_s is shown as a function of the mole fraction in the composition range 0-0.8 k_{mole} NaCl for the temperature 680°C; the compressibility was calculated using the density data found by

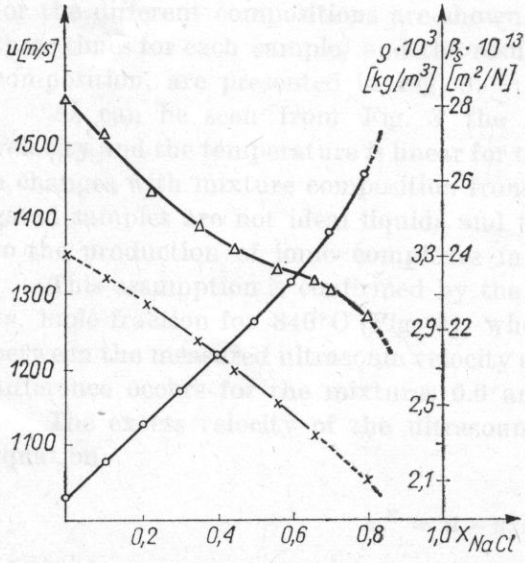

Fig. 6. Adiabatic compressibility β_s (Δ), ultrasonic velocity u (o) and density ϱ (x) at 680°C vs. mole fraction of NaCl

Heymann [5]. In the concentration range 0-0.4 k_{mole} NaCl the dependence is linear, but as the concentration of NaCl increases we observe a slight increase in compressibility up to a small maximum for 0.7 k_{mole} NaCl. The minimum u^E

occurs for the concentration 0.66 k_{mole} NaCl, and with β_s having a maximum value at the same concentration it suggests that the mixtures investigated form ionic complexes of the type $CdCl_4^{2-}$. The possibility of such a complex existing in $CdCl_2$/alkali chloride mixtures was suggested by TOPOL [6] and BREDIG [7].

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