Density and Electrical Conductivity of $NaCl-CoCl_2$ and $NaCl-NiCl_2$ Molten Mixtures

A. A. Red'kin, A. B. Salyulev, M. V. Smirnov, and V. A. Khokhlov

Institute of High Temperature Electrochemistry, 620219, GSP-146, S. Kovalevskaya 20, Ekaterinburg, Russia

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The density and electrical conductivity of cobalt and nickel dichlorides and their solutions in molten sodium chloride have been measured. The density was measured by a dilatometric method, and the electrical conductivity by an AC technique. The molar volume and equivalent conductance were calculated.

Key words: Density, Electrical Conductivity, Molten Chlorides.

Introduction

Some thermodynamic properties of chloride melts containing transitional metal chlorides have been measured, but their transport properties have not. Therefore we have measured the density and electrical conductivity of $NaCl-CoCl_2$ and $NaCl-NiCl_2$ melts.

Experimental

Chemicals. NaCl was dried under vacuum and purified by zone melting [1]. $NiCl_2$ was produced from $NiCl_2 \cdot 6H_2O$ and dried under vacuum by heating up to 200 °C. Then it was treated with chlorine at 600 °C and sublimated at 900–960 °C in a quartz tube. $CoCl_2$ was prepared from $CoCl_2 \cdot 2H_2O$ and dried under vacuum at 100 and 200 °C.

Density

The density of $CoCl_2$ and its mixtures was measured by the dilatometric method described in [2]. Tubes of transparent quartz (8 mm inner diameter) were calibrated with molten potassium chloride, using the data presented by Smirnov and Stepanov [3]. In a dry box the sample was weighted and charged into the tube. Then the tube was evacuated, filled with helium and placed into an electric furnace with holes to read the position of the meniscus with a cathetometer (Figure 1). A stainless steel bloc provided uniform temperature. The volume of the melt was 2.5–3.5 ml. In case of $NiCl_2$ and its mixtures, because of their high vapour pressure, the tube was pumped out, heated up to 150 °C and then sealed off.

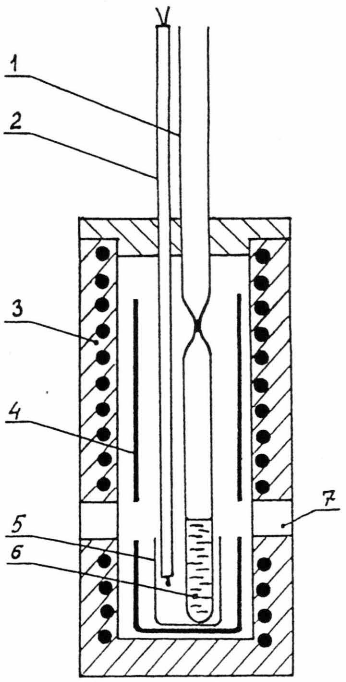

Fig. 1. The set-up for density measurements. **1** tube, **2** thermocouple, **3** furnace, **4** bloc, **5** crucible, **6** melt, **7** holes.

Reprint requests to Dr. A. A. Red'kin.

Specific Conductance

The measurements on $CoCl_2$ and its mixtures were carried out in a U-type quartz capillary cell. The constant of the cell was about 200 cm^{-1}. Platinum wire served as electrodes. The measurements were carried out at a frequency of 10 kHz. The cell was calibrated with molten sodium chloride, its conductivity being taken from [4]. The conductance of pure $NiCl_2$ and its mixtures containing more than 50 mol% $NiCl_2$ was measured in a special cell because of their high vapour pressure (Figure 2).

A graphite electrode (length 20 mm) was placed in a capillary of 2 mm inner diameter, and a second one of semi-ring form was placed close to it. The electrodes were connected with 0.5 mm tungsten wire. The lower part of the cell was soldered. In a dry box nickel dichloride was charged into the cell. Then the tube was pumped out, sealed off and placed into the electric furnace. The temperature was measured by a Pt/Pt/Rh thermocouple placed near the electrodes. The experiments were carried out with 3 cells. The first cell was calibrated with zinc dichloride, the second with lead dichloride, and the constant of the third cell was calculated using its geometric parameters. The resulting constants were 52.15, 32.25, and 40.82 cm^{-1}. Mixtures containing less than 50 mol% $NiCl_2$ were measured in the usual U-type cell.

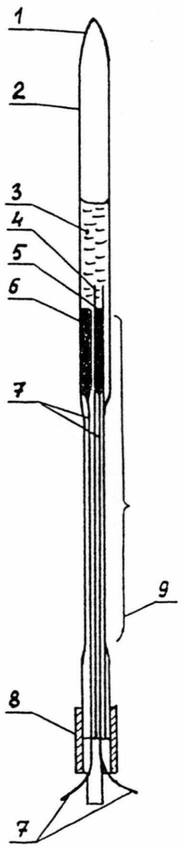

Fig. 2. The cell for specific conductivity measurements at high vapour pressure of the salt. **1** sealed off end, **2** space for melt, **3** melt, **4** quartz capillary, **5, 6** graphite electrodes, **7** tungsten wire, **8** rubber tube, **9** soldered quartz tube.

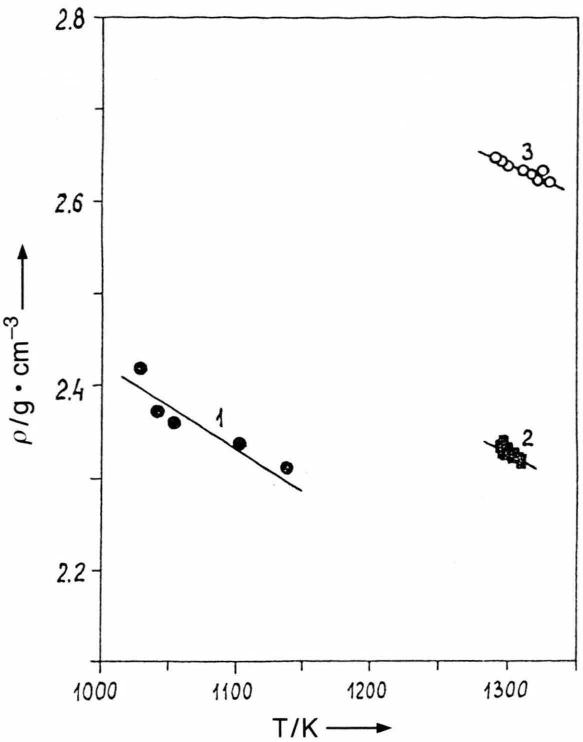

Fig. 3. The density of molten cobalt (**1**) and nickel dichlorides (**2, 3**). ■, ● our data, ○ Galka et al., – Mil'man and Burylev.

Results and Discussion

Density

The density of molten $CoCl_2$ and $NiCl_2$ is shown in Figure 3.

We suppose that the γ-ray method used by Galka for $NiCl_2$ [5] was not suitable for molten salts. The results obtained by Mil'man and Burylev on $CoCl_2$

coincide with ours. The difference amounts to less 2%. The temperature dependence of the density of the single salts and mixtures was found to be linear:

$$\varrho = a - b\,T,\ \mathrm{g/cm^3},\ T/\mathrm{K}. \qquad (1)$$

Table 1. The coefficients of the dependences of density on temperature.

Mole fraction of $Ni(Co)Cl_2$	Temperature interval T/K	$\varrho = a - b\,T$ g/cm³		
		a	$b \cdot 10^{+3}$	Δp
		$NaCl-NiCl_2$		
0.31	850–1310	2.345	0.450	0.007
0.45	1020–1310	3.055	0.922	0.007
0.73	1230–1310	3.285	0.850	0.007
1.00	1285–1310	3.776	1.110	0.005
		$NaCl-CoCl_2$		
0.25	970–1120	2.399	0.570	0.003
0.40	915–1120	2.499	0.540	0.005
0.50	780–1140	2.934	0.835	0.020
0.65	870–1120	2.783	0.620	0.008
0.78	870–1120	2.866	0.630	0.007
1.00	1020–1140	3.194	0.780	0.020

The values of the coefficients a and b are shown in Table 1. Density and molar volume isotherms are shown in Figs. 4 and 5. The densities of molten sodium chloride were taken from [3]. It turns out that these isotherms are nearly additive. The density data of molten $NaCl-CoCl_2$ mixtures by Mil'man and Burylev [6] differ from ours. For an explanation we may point out that the deviations of the molar volume from additivity for molten sodium chloride – polyvalent metal chloride mixtures were found in the review of Stepanov and Smirnov [7] to be smaller than 2%. These deviations exceed 10% in the work of Burylev and Mil'man.

Electrical Conductivity

The specific conductivity of the pure salts is shown on Figure 6. The results on the specific conductance of cobalt and nickel chloride solutions in molten sodium chloride were treated according to the polynomial

$$\varkappa = c + d\,T + e\,T^2,\ \mathrm{ohm^{-1}\,cm^{-1}},\ T/\mathrm{K}. \qquad (2)$$

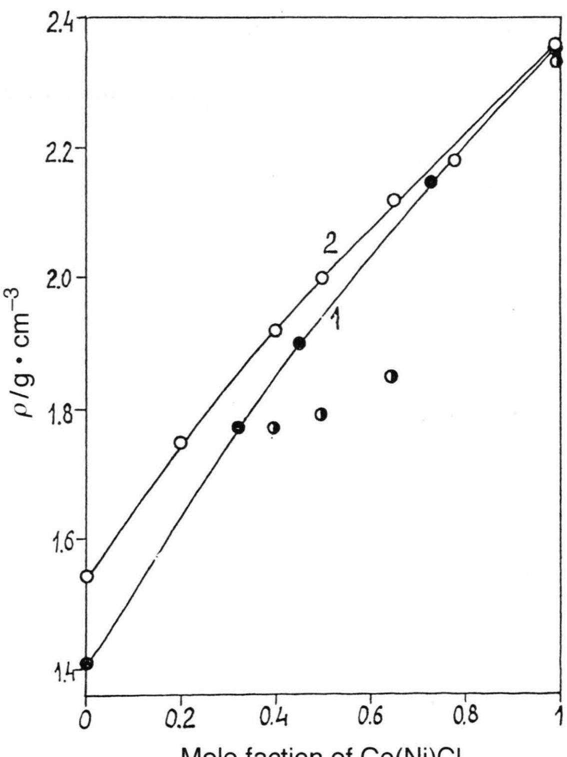

Fig. 4. Density isotherms. **1** $CoCl_2-NaCl$ (1100 K), **2** $NiCl_2-NaCl$ (1300 K), ◑ Mil'man and Burylev.

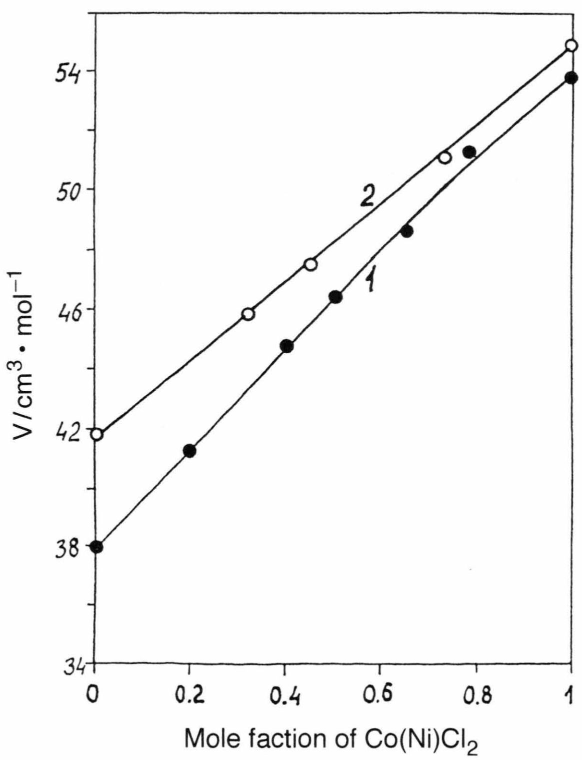

Fig. 5. Molar volume isotherms. **1** $CoCl_2-NaCl$ (1100 K), **2** $NiCl_2-NaCl$ (1300 K).

Table 2. The coefficients of the temperature dependence of the specific ($\varkappa$) and equivalent (λ) conductance.

Mole fraction of Co(Ni)Cl_2	Temperature interval T/K	$\varkappa = c + dT + eT^2$, $ohm^{-1} cm^{-1}$				$\lambda = \lambda_0 \exp(-E/RT)$	
		$-c$	$d \cdot 10^3$	$-e \cdot 10^6$	$\Delta\varkappa$	λ_0/$ohm^{-1} cm^2$	E/cal
			NaCl–$CoCl_2$				
0.20	940–1140	2.266	6.247	1.6201	0.003	390.3	3172
0.31	850–1140	1.336	4.022	0.5174	0.002	422.8	3580
0.50	870–1160	0.842	2.666	0.1418	0.006	340.4	3752
0.65	900–1200	2.378	5.258	1.5306	0.008	261.4	3732
0.78	900–1160	2.824	5.836	1.897	0.006	301.9	4546
1.00	1040–1220	1.118	1.410	−0.456	0.008	480.6	6276
			NaCl–$NiCl_2$				
0.31	890–1150	1.857	5.607	1.6134	0.006	304.0	2963
0.48	1090–1200	2.345	5.628	1.6073	0.008	299.2	3610
0.72	1223–1310	4.575	9.240	3.3073	0.006	169.9	2933
1.00	1280–1310	2.421	2.900	–	0.008	1166.8	8861

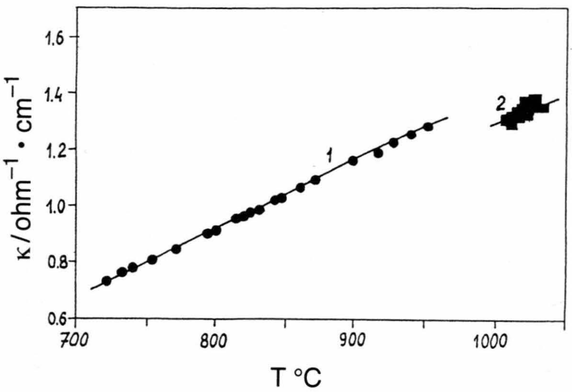

Fig. 6. The specific conductance of molten cobalt and nickel dichlorides. **1** $CoCl_2$, **2** $NiCl_2$.

The coefficients c, d, and e are shown in Table 2.

The specific conductivity of some of these mixtures below the liquidus line were also measured. The results are shown in Figure 7. The equivalent conductances were presented in exponential form

$$\Lambda = \Lambda_0 \exp(-E/RT), \ ohm^{-1} cm^2 equiv, \quad (3)$$
$$R = 1.987 \ cal \ mol^{-1} deg^{-1}.$$

The coefficients Λ_0 and E are shown in Table 2. Some isotherms of $\varkappa$ and Λ are shown in Figs. 8 and 9. The specific conductances of molten sodium chloride were

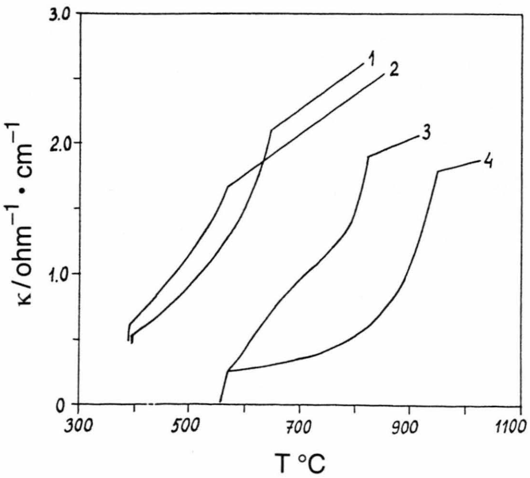

Fig. 7. The specific conductivity of some of the mixtures in the liquidus-solidus temperature range. **1** 0.20 $CoCl_2$–0.80 NaCl, **2** 0.31 $CoCl_2$–0.69 NaCl, **3** 0.48 $NiCl_2$–0.52 NaCl, **4** 0.72 $NiCl_2$–0.28 NaCl.

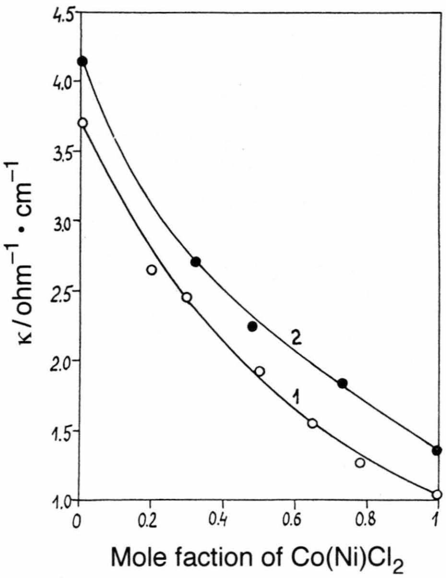

Fig. 8. Specific conductivity isotherms. **1** $CoCl_2$–NaCl (1100 K), **2** $NiCl_2$–NaCl (1300).

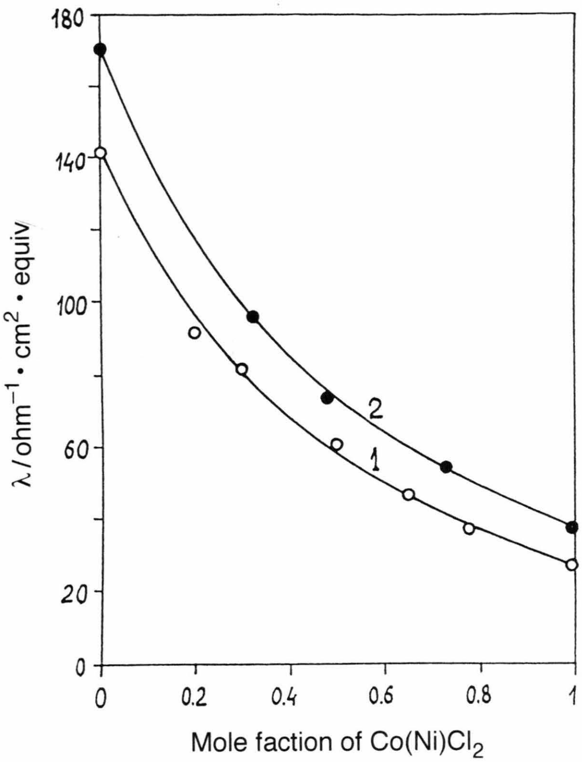

Fig. 9. Equivalent conductivity isotherms. **1** $CoCl_2$–NaCl (1100 K), **2** $NiCl_2$–NaCl (1300).

taken from [4]. An empirical equation connecting the specific conductance and the molar volume has been obtained recently. It is valid for molten salt systems where thermodynamical parameters show weak interaction between the components [8]. The specific conductance of cobalt and nickel chloride solutions in molten sodium chloride can be described in the same way that of molten rare earth metal chloride mixtures with sodium chloride, with the same correlation coefficient 0.6 for $CoCl_2$ and $NiCl_2$:

$$\varkappa = 4.9 \cdot \exp[-(2747-(33724/V))/T] \cdot \exp(53.7/V) \cdot \exp(-0.6 \cdot N), \quad (4)$$

where V = molar volume, T = temperature, N = mole fraction of dichloride.

Comparisons with experiment are given in Table 3.

Table 3. Comparison of calculated (according to (4)) and experimental specific conductivity ($ohm^{-1}\ cm^{-1}$)

N_2	$\varkappa_{exp}$	$\varkappa_{calc}$	$\lvert\Delta\varkappa\rvert$	N_2	$\varkappa_{exp}$	$\varkappa_{calc}$	$\lvert\Delta\varkappa\rvert$
NaCl–$CoCl_2$ (1100 K)				NaCl–$NiCl_2$ (1300 K)			
0.20	2.645	2.764	0.118	0.31	2.706	2.714	0.008
0.31	2.462	2.425	0.036	0.48	2.255	2.321	0.066
0.50	1.920	1.842	0.077	0.72	1.847	1.838	0.009
0.65	1.554	1.549	0.004	1.00	1.369	1.373	0.004
0.78	1.300	1.326	0.029				
1.00	0.985	1.033	0.048				

Conclusion

Now we can say that molten sodium chloride mixtures with cobalt and nickel dichlorides are close to ideal solutions. This results from thermodynamic [9], molar volume and electrical conductivity data.

Acknowledgements

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