Density and Electrical Conductivity of Molten $(2K, Fe)Cl_2$, $(2K, Co)Cl_2$, and $(2K, Ni)Cl_2$

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The density and electrical conductivity of molten $(2K, Fe)Cl_2$, $(2K, Co)Cl_2$ and $(2K, Ni)Cl_2$ have been investigated. The density was measured by the maximum bubble pressure and dylatometric methods, the electrical conductivity by an AC technique. The molar volume and equivalent conductance were calculated.

Key words: Molten chlorides, Density, Electrical conductivity.

Introduction

Chloride melts containing transition metals chlorides are in practical use. Also, molten salt mixtures containing such salts are good model liquids of ionic-covalent type interactions. Some thermodynamic properties of those mixtures were under investigation but transport ones were not. Density and electrical conductivity measurements can provide essential information about these salts.

Experimental

Preparatory

Potassium chloride was dried and purified in the usual way [1]. Ferrous chloride was prepared by the interaction of powdered iron with dried hydrogen chloride at 850 °C. At this temperature, $FeCl_2$ was vaporised and condensed in a cool zone. The salt obtained contained 99.8% pure product. $NiCl_2$ was produced from $NiCl_2 \cdot 6H_2O$. The product was dried under heating for a long time. Then it was treated by chlorine at 600 °C and sublimated at 900–960 °C in a quartz tube. $CoCl_2$ was prepared from $CoCl_2 \cdot 2H_2O$. It was dehydrated by heating up to 200 °C.

Density

The density of ferrous chloride and its mixtures was investigated by the maximum bubble pressure method [2]. The main part of the set-up is a quartz capillary with a conic end of 1 mm inner diameter, which is lowered into the melt with a micro-screw of low friction (Figure 1). Working gas was helium. The gas pressure was measured with a U-type manometer placed into a thermostat. The level difference measurements were carried out with a cathetometer with 0.005 mm precision. The sample under investigation was placed into a glasscarbon crucible, and then the sealed cell was filled with working gas and heated. This technique needed a large amount of melt (about 25 ml) but allowed the electrical conductivity to be measured in the same device using an additional capillary (Figure 1). The time of bubble creation was about 30 sec.

The density was calculated according to the formula

$$\varrho = \varrho_m \cdot (H_1 - H_2)/(h_1 - h_2),$$

where

ϱ_m = density of the manometric liquid,
$H_2 - H_1$ = difference of manometric liquid levels,
$h_2 - h_1$ = difference between final and initial depth of capillary.

The density of $NiCl_2$ and $CoCl_2$ (Figs. 2, 3) and their mixtures (Fig. 4) was measured by the dylatometric method as described in [3].

Specific Conductance

The specific conductance of ferrous chloride and its mixtures was measured in the cell for the density measurement using a quartz capillary. The constant of

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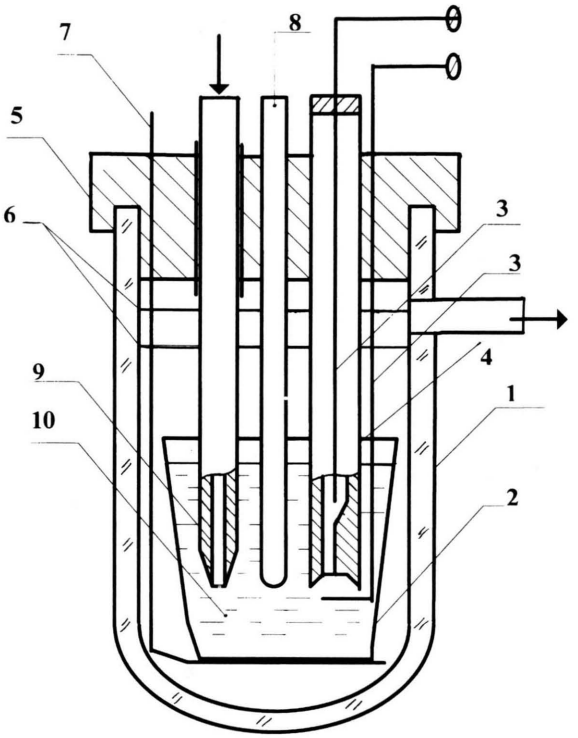

Fig. 1. Experimental cell: 1 – Quartz vessel, 2 – glasscarbon crucible, 3 – electrodes, 4 – Capillary for conductivity measurements, 5 – rubber stopper, 6 – screens, 7 – lift, 8 – thermocouple, 9 – Capillary for density measurements, 10 – melt.

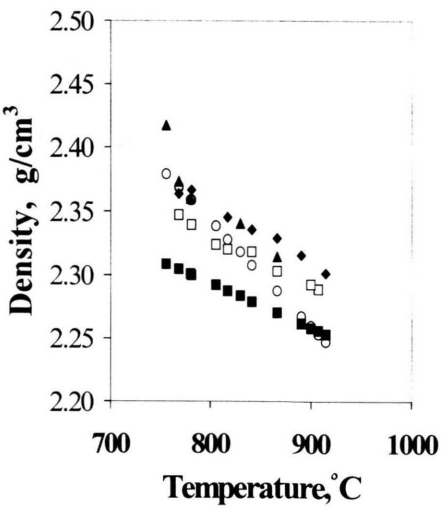

Fig. 2. The density of molten $CoCl_2$: □ – first series, ◆ – second series, ▲ – [3], ○ – [5], ■ – [6].

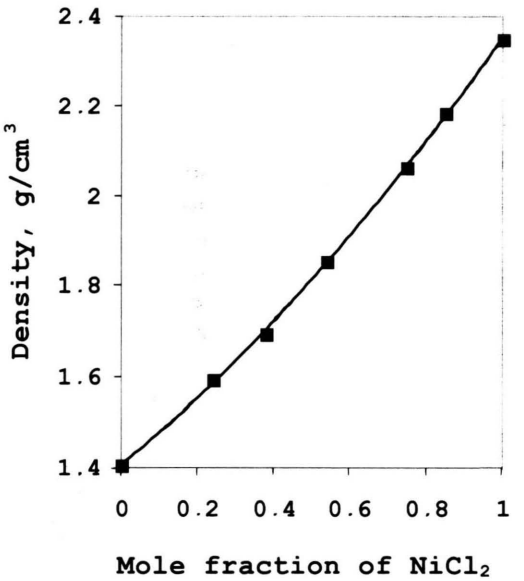

Fig. 3. The density of molten (2 K, Ni)Cl_2 (T = 1253 K).

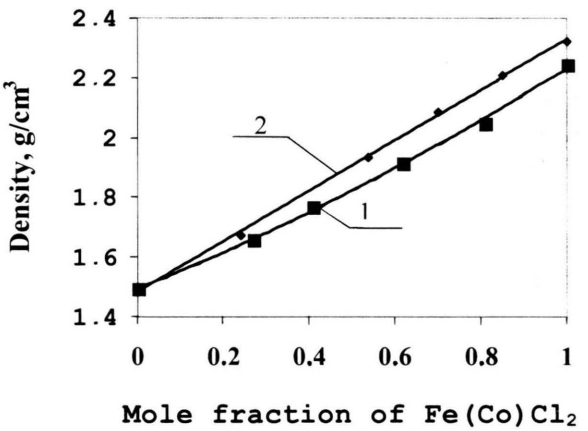

Fig. 4. The density of molten (2 K, Fe)Cl_2 and (2 K, Co)Cl_2 (T = 1100 K): 1 – (2 K, Fe)Cl_2, 2 – (2 K, Co)Cl_2.

the capillary was about 200 cm^{-1}. The electrodes were made of platinum wire. The investigation of $CoCl_2$ and its mixtures was conducted in a U-type quartz cell. All measurements were carried out at 10 kHz. The cell was calibrated using molten sodium chloride with data taken from [4]. The electrical conductance of (2 K, Ni)Cl_2 containing more than 70 mol% of $NiCl_2$ was measured in a special cell [3].

Results

Density

The measured densities as functions of temperature are well reproduced by a linear relationships, the coefficients of which are given in Table 1.

In this work we repeated our previous measurements of the density of $CoCl_2$, because there are differing results on this salt [5, 6], whereby we improved the temperature dependence. The density of molten (2 K, Fe)Cl_2 and (2 K, Co)Cl_2 mixtures has been measured before by Burylev and Mil'man [5]. The data differ considerably. Note that the temperature coefficient ($34.9 \cdot 10^{-4}$ g/cm^3/grad) obtained by these authors for $FeCl_2$ is too great for ionic salts. Data on (2 K, Co)Cl_2 have also been obtained by Takagi and Nakamura [6]. There are some differences (within 2%), but the isotherms presented in Fig. 5 show a very close trend. The molar volumes deviate positively from additivity for all three systems (Figs. 5, 6), which may result from a rearrangement of ions when mixing the pure salts. In mixtures with a common anion, divalent cations pull up more polarizable halide anions around themselves to form associates or complexes, whereby alkali cations are displaced into second coordination spheres, where they are arranged more loosely among those associates. The larger the alkali cation the freer it is and the larger the excess molar volume. The molar volume of mixtures of transition metal chlorides with NaCl is close to additive [3], while the systems measured in this work show excess molar volume because K^+ is larger than Na^+.

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

Mole fraction of $MeCl_2$	Temperature interval, T/K	$\varrho = a - b \cdot T$, g/cm^3		
		a	$b \cdot 10^4$	$\Delta\varrho$
(2 K, Fe)Cl_2				
0.27	970–1043	2.715	9.590	0.060
0.41	978–1059	2.759	9.000	0.090
0.62	835–1073	2.884	8.810	0.060
0.81	877– 966	3.153	10.00	0.070
1.00	963–1088	2.967	6.580	0.070
(2 K, Co)Cl_2				
0.24	923–1123	2.329	5.956	0.007
0.54	723–1173	2.673	6.697	0.007
0.70	1023–1173	2.942	7.779	0.007
0.85	1015–1173	2.835	5.695	0.006
1.00	1033–1200	2.756	3.939	0.007
(2 K, Ni)Cl_2				
0.24	873–1173	2.381	6.369	0.007
0.38	923–1100	2.468	6.162	0.008
0.52	950–1173	2.641	6.280	0.005
0.75	1173–1240	3.068	8.006	0.007
0.85	1233–1273	2.677	3.929	0.007

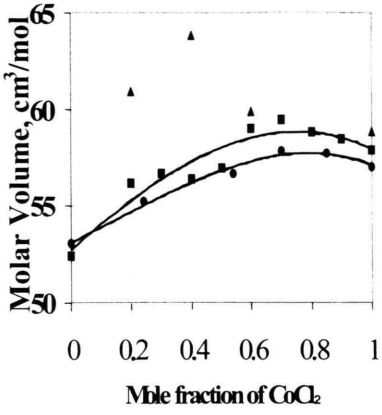

Fig. 5. Molar volume of molten (2 K, Co)Cl_2 (1253 K): ● – our data, ■ – [6], ▲ – [5].

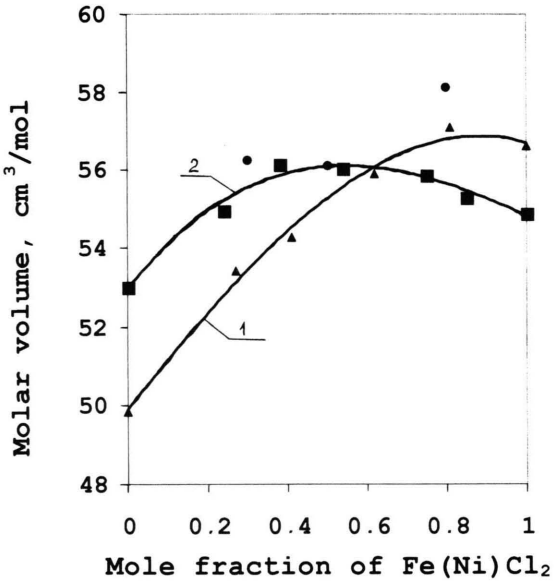

Fig. 6. Molar volume of molten (2 K, Fe)Cl_2 and (2 K, Ni)Cl_2: 1 – (2 K, Fe)Cl_2 (1100 K): ▲ – our data, ● – [5], 2 – (2 K, Ni)Cl_2 (1253 K).

Electrical Conductivity

The measured conductivities as functions of temperature were summarised by polynomials of the form

$$\chi = c + d\,T + e\,T^2,\ \text{ohm}^{-1} \cdot \text{cm}^{-1}$$

Table 2. The coefficients of the temperature dependence of the specific and equivalent conductance.

Mole fraction of $MeCl_2$	Temperature interval, T/K	$\chi = c + d \cdot T + e \cdot T^2$, $Ohm^{-1}\,cm^{-1}$				$\lambda = \lambda_0 \cdot \exp(-E/RT)$	
		$-c$	$d \cdot 10^3$	$-e \cdot 10^6$	$\Delta\chi$	λ_0/$ohm^{-1} \cdot cm^2 \cdot equiv^{-1}$	E(cal)
(2 K, Fe)Cl_2							
0.22	990–1073	−0.086	1.700	–	0.006	347.5	3092
0.33	970–1079	−0.411	1.238	–	0.015	184.2	2082
0.56	895–1071	5.650	12.60	5.340	0.003	401.2	4006
0.67	865–1063	1.496	4.419	1.300	0.008	226.5	2881
1.00	988–1072	0.410	2.000	–	0.006	301.9	3855
(2 K, Co)Cl_2							
0.24	873–1113	2.524	5.640	1.701	0.003	387.6	3773.3
0.38	673–1123	1.833	4.108	1.053	0.003	387.2	4243.4
0.54	713–1153	1.697	3.765	0.980	0.005	327.0	4328.7
0.63	973–1173	1.556	3.262	0.693	0.003	–	–
0.74	893–1173	1.341	2.965	0.616	0.008	242.0	4136.9
1.00	–	–	–	–	–	606.0	6980.3
(2 K, Ni)Cl_2							
0.10	1073–1223	0.434	2.074	–	0.003	–	–
0.22	953–1100	6.973	12.460	4.301	0.006	688.1	4941.7
0.39	873–1173	0.500	1.952	0.185	0.003	234.7	3165.3
0.50	993–1200	1.708	3.910	1.080	0.003	240.3	3656.1
0.63	1073–1223	5.600	10.39	3.792	0.005	–	–
0.72	1123–1223	2.838	5.801	1.885	0.003	214.2	3596.5
0.85	1253	1.38	–	–	0.010	–	–

The coefficients c, d, e are listed in Table 2. Representative conductivity isotherms are shown in Figure 7. The equivalent conductances were calculated using our density data. Their temperature dependences were presented in exponential form

$$\lambda = \lambda_0 \cdot \exp(-E/RT),\ ohm^{-1} \cdot cm^2 .$$

The coefficients λ_0 and E are listed in the Table 2, and typical isotherms are shown in Figure 8. The validity of an empirical equation for non-ideal mixtures [8] describing the temperature and volume dependence of the specific conductance was tested.

For molten chlorides it is:

$$\chi = 4.9 \exp[-(2\,747 - (33\,724/V))/T] \cdot \exp(53.7/V) \cdot \exp(-L \cdot N_2) + \Delta\chi ,$$

$$\Delta\chi = \Delta H(E - F \cdot N_2) ,$$

where V = molar volume, cm^3/mole, T = temperature, K, N_2 = mole fraction of the heavy component, ΔH = enthalpy of mixing, J/mol, L, E, F = empirical dimensionless coefficients.

For $FeCl_2$, $CoCl_2$ and $NiCl_2$, L=1, 0.60, 0.60, respectively. There are no full thermodynamic data for (2 K, Ni)Cl_2.

For (2 K, Fe)Cl_2 and (2 K, Co)Cl_2, $\Delta\chi$ is

$$\Delta\chi = \Delta H \cdot (1.1 - 1.1 \cdot N_2) \cdot 10^{-5},\ ohm^{-1} \cdot cm^{-1},$$

where N_2 = mole fraction of dichloride, ΔH = enthalpy of mixing, J/mol.

A comparison of the experimental and calculated data is presented in Table 3. The thermodynamic data were taken from [9]. The difference is compatible with

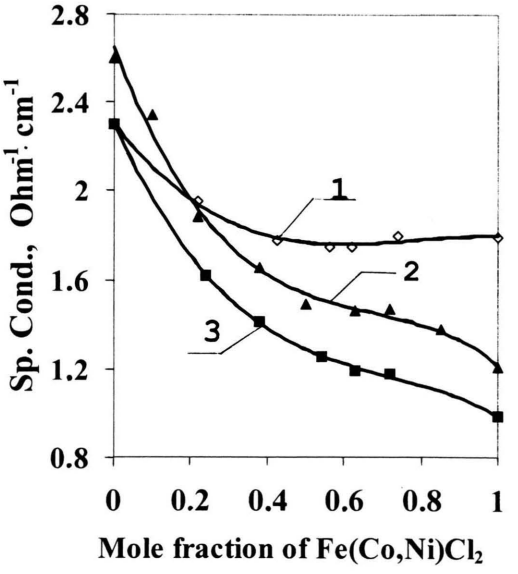

Fig. 7. Specific conductivity isotherms: 1 – (2 K, Fe)Cl_2 (1100 K), 2 – (2 K, Ni)Cl_2 (1253 K), 3 – (2 K, Co)Cl_2 (1100 K).

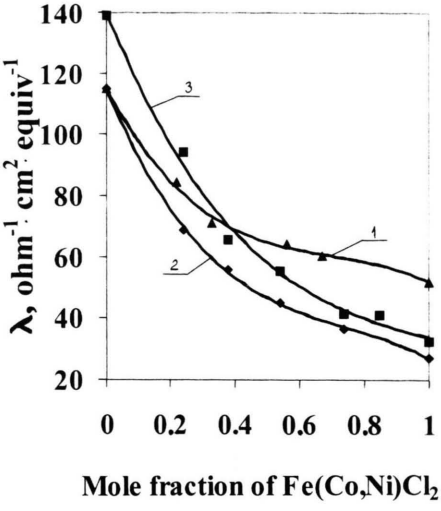

Fig. 8. Equivalent conductivity isotherms: 1 – (2 K, Fe)Cl_2 (1100 K), 2 – (2 K, Co)Cl_2 (1100 K) 3 – (2 K, Ni)Cl_2 (1253 K).

Table 3. Comparison of calculated and experimental data (T = 1100 K).

(2 K, Fe)Cl_2				(2 K, Co)Cl_2			
N_2	χ_{exp}	χ_{calc}	$\Delta\chi$	N_2	χ_{calc}	χ_{exp}	$\Delta\chi$
0.22	1.956	1.917	0.039	0.24	1.594	1.635	0.041
0.33	1.775	1.827	0.052	0.38	1.441	1.411	0.030
0.54	1.787	1.795	0.008	0.54	1.319	1.395	0.076
0.67	1.793	1.761	0.032	0.62	1.257	1.247	0.010
1.00	1.789	1.790	0.001	0.74	1.144	1.181	0.037
–	–	–	–	1.00	1.010	0.984	0.026

the summary error of the experimental determination of density, electrical conductivity and enthalpy of mixing.

Conclusion

Our results show that the mixtures studied are non-ideal.

[1] V. Yu. Shishkin and V. Mityaev, Izv. AN SSSR. Inorganic materials **18,** 1917 (1982).
[2] Physicochemical measurements at high temperature. Edited by J. O. M. Bockris et al., Butterworth publications, London 1959.
[3] A. A. Red'kin, A. B. Salyulev, M. V. Smirnov, and V. A. Khokhlov, Z. Naturforsch. **50a,** 998 (1995).
[4] G. Janz et al., J. Phys. Chem. Ref. Data, Molten salts 4, Part 2 (1975).
[5] B. P. Burylev and V. M. Mil'man, Zh. Fiz. Khim. **60,** 2217 (1986).
[6] Y. Takagi and T. Nakamura, J. Chem. Eng. Data **30,** 438 (1985).
[7] M. V. Smirnov and V. P. Stepanov, Electrochim Acta **27,** 1551 (1982).
[8] A. A. Red'kin, Extended abstracts of the 185th Electrochem. Soc. Meeting, San-Francisco 1994.
[9] G. N. Papatheodorou and O. J. Kleppa, J. Inorg. Nucl. Chem. **33,** 1249 (1971).