Chlorine Solutions in Molten Alkali Chlorides

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Electronic absorption spectra of gaseous chlorine and their saturated solutions in molten alkali chlorides were studied in wide ranges of temperature and wavelength. It was found that gaseous chlorine has a wide absorption band between 20 000 and 43 500 cm^{-1}. There is a tendency to both widening of the band and shifting of the absorption maximum to the short-waves region with rising temperature.

The absorption bands of saturated solutions of chlorine in all molten alkali chlorides show a maximum in the neighborhood of 30 000 cm^{-1}. A good correlation was found between the optical density of molten salt-Cl_2 systems and the solubility of chlorine.

Key words: Chlorine; Molten Alkali Chlorides; EAS; Solutions.

1. Introduction

Molten salts are widely used in many technological processes [1]. In the majority of processes reactive gases, such as chlorine, play an important role. It can be used for chlorination of oxides, sulfides etc. in molten salts. The chemical reaction can be reversed by varying the pressure of gaseous chlorine over the melt. Systematic research on chlorine solutions in molten chlorides is required for further technological advances.

Literature data on the electronic absorption spectra (EAS) of chlorine solutions in molten chlorides are limited and discrepant [2 – 6]. Information on the effect of temperature on the EAS of chlorine dissolved in salt melts is lacking. The spectra of gaseous chlorine and its solutions in molten salts have up to date not been correlated quantitatively, though considerations of this kind can refine our view about the nature of chlorine-molten salt systems.

In this work EAS of gaseous chlorine and its saturated solutions in molten alkali chlorides were studied in a wide range of temperature and wavelength. An attempt is made to connect quantitatively refined data on the EAS with the chlorine solubility in molten alkali chlorides.

2. Experimental

2.1. Chemicals

High-purity anhydrous gaseous chlorine was produced by electrolysis of molten $PbCl_2$ (99.5) placed in a quartz tube. A carbon rod and a molybdenum wire shielded by a quartz tube were used as anode and cathode, respectively. Gaseous chlorine was passed through mineral wool and bubbled through concentrated sulfuric acid.

The alkali chlorides were slowly heated and then melted under air to remove possible organic impurities. After melting, they were treated by dry Cl_2. The dissolved chlorine was removed using argon purge.

2.2. Procedure

The spectra were recorded with a spectrophotometer adapted to high temperature measurements. Light sources were located at a distance of about 30 cm away from the monochromator. A special moveable furnace assembly was placed between sources of light and monochromator. After the furnace an additional lens was positioned to focus the light on the input slit of the monochromator. The furnace temperature was held within ± 2 K.

Table 1. Basic parameters of gaseous chlorine electronic absorption spectra (EAS).

Optical path length l (mm)	Temperature T (K)	Pressure P (atm)	Chlorine concentration c (mol/dm^3)	Optical density D	Absorption maximum $\nu_{max} \cdot 10^{-3}$ (cm^{-1})	Maximum molar extinction coefficient ε_{max} (dm^2/mol)	Band half width $\Delta\nu_{1/2} \cdot 10^{-3}$ (cm^{-1})	Oscillator strength $f \cdot 10^2$
2.00	472	0.972	2.5101	0.2932	30.48	603.4	5.50	1.53
	717	0.972	1.6524	0.1497	30.69	529.6	6.26	1.53
3.50	275	0.980	4.3432	1.0378	30.31	682.1	4.87	1.53
	279	0.980	4.2249	1.0067	30.31	680.9	4.91	1.54
	293	0.982	4.0846	0.9696	30.33	674.1	5.00	1.58
	382	0.982	3.1330	0.6789	30.40	631.5	5.20	1.51
	486	0.982	2.4625	0.4982	30.49	607.1	5.60	1.52
	591	0.982	2.0250	0.3774	30.58	570.0	5.90	1.53
9.36	293	0.978	4.0681	2.5865	30.32	679.0	5.08	1.59
	379	0.978	3.1450	1.8572	30.40	643.8	5.33	1.58
	480	0.978	2.4833	1.3474	30.49	609.2	5.58	1.56
	581	0.978	2.0516	0.9769	30.57	574.7	5.86	1.57
	680	0.978	1.7529	0.7820	30.66	539.5	6.11	1.52
	883	0.978	1.3499	0.5176	30.84	493.2	6.71	1.52
	982	0.978	1.2138	0.4245	30.92	470.4	7.07	1.53
	1078	0.978	1.1057	0.3786	31.01	459.3	7.39	1.56
	1189	0.978	1.0025	0.3283	31.11	445.7	7.81	1.60
	1285	0.978	0.9276	0.3070	31.20	437.4	8.11	1.67
11.32	704	0.967	1.6743	0.8796	30.68	532.1	6.24	1.53
	810	0.967	1.4552	0.6953	30.78	504.3	6.70	1.55
	918	0.967	1.2840	0.5677	30.87	482.1	6.94	1.54
	1021	0.967	1.1545	0.4941	30.96	466.3	7.13	1.53
	1124	0.967	1.0487	0.4405	31.05	454.7	7.46	1.56
	1227	0.967	0.9607	0.3770	31.14	441.6	7.82	1.59
	1340	0.967	0.8797	0.3499	31.25	431.7	8.14	1.60

A two-cuvette optical scheme was applied for recording spectra of gaseous chlorine or its solutions in molten alkali chlorides. Quartz cuvettes with optical path length of about 0.8, 1, 2, 3 and 10 mm were used as the working and reference cells. Exact values of path length were determined by calibration with standard $KCrO_4$ and K_2CrO_4 solutions relative to standard cells. The working cuvette was filled with gaseous chlorine or the molten salt under study saturated with chlorine. The measurements were always carried out under a continuous atmospheric pressure of chlorine flow through the working cell. The reference cell was filled with pure dry argon for the gaseous chlorine experiment or the test molten alkali chloride, free of dissolved chlorine in the case of the molten salt experiment. In the latter case both working and reference cuvettes were charged with salt in dry box under an inert gas atmosphere.

The spectra were studied in the wavelength range from 200 to 1200 nm.

The gaseous chlorine spectra were recorded at temperatures from 273 to 1470 K. The chlorine solutions in molten alkali chlorides were studied in the temperature range starting from the melting point of the salt up to 1280 K.

In the case of gaseous chlorine the measuring errors are 0.3% for position of absorption band maximum and 1.4% for optical density (absorbance). For Cl_2 solutions in molten salts the errors rise to 2.5 and 2.0% correspondingly.

3. Results and Discussion

3.1. Gaseous Chlorine

The EAS of gaseous chlorine are recorded in the range of wave numbers (ν) from 8333 to 50 000 cm^{-1} (or wavelength from 200 to 1200 nm). In specific experiments the EAS of Ar + Cl_2 gaseous mixtures with chlorine concentrations [Cl_2] equal to 17, 33, 50, 66 and 83 vol.% have been produced. The dependence of optical density D vs. chlorine concentration [Cl_2] is a straight line, suggesting that Beer's law is valid.

There is only a wide absorption band observed between 20 000 and 43 500 cm^{-1}. The absorption band contour does not change substantially as the temper-

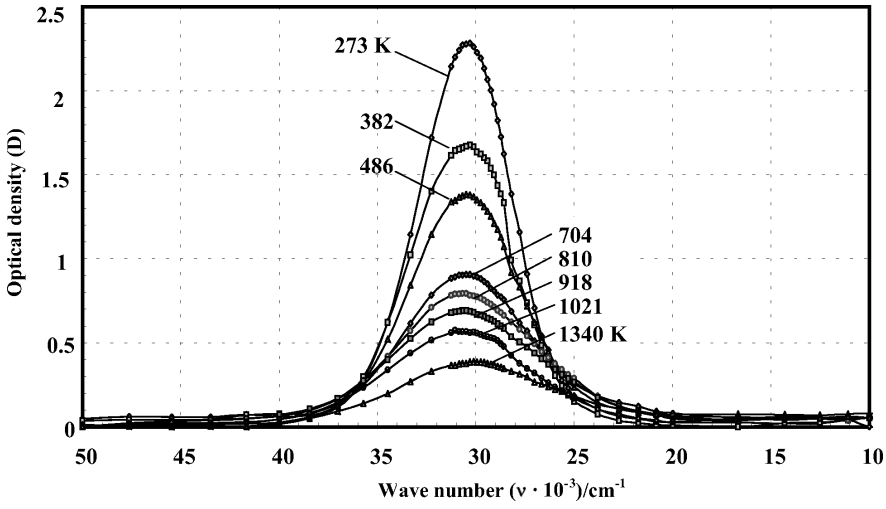

Fig. 1. The ν-dependence of $Cl_{2(gas)}$ optical density (D).

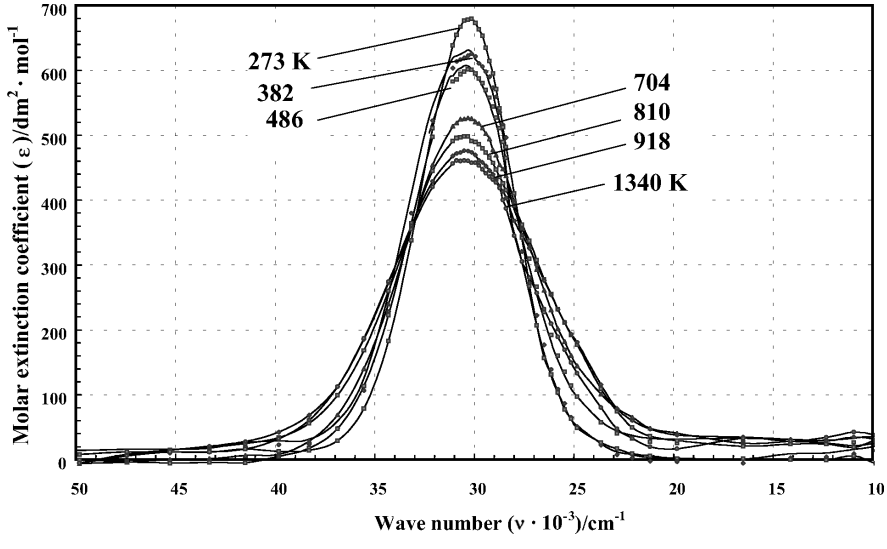

Fig. 2. The ν-dependence of $Cl_{2(gas)}$ molar extinction coefficient (ε).

ature rises from 273 to 1470 K excluding a slight tendency to band widening. The basic optic parameters of the absorption band such as optical density (absorbance) D, absorption maximum ν_{max}, maximum molar extinction coefficient ε_{max}, band half width $\Delta\nu_{1/2}$, and oscillator strength f measured under different experimental conditions are indicated in Table 1. The dependencies of optical density D as a function of wave number ν at different temperatures are shown in Figure 1.

With rising temperature the optical density at the maximum of absorption band (D_{max}) decreases, while the absorption maximum (ν_{max}) shifts slightly to the short-wave region. These changes can be closely approximated by the following equations:

$$D_{max} = 4.397 \cdot 10^{-12} T^4 - 1.914 \cdot 10^{-8} T^3 + 3.138 \cdot 10^{-5} T^2 - 2.359 \cdot 10^{-2} T + 7.413, \quad (1)$$

$$\nu_{max} = (30.063 + 8.806 \cdot 10^{-4} T) \cdot 10^3. \quad (2)$$

The lowering D_{max} is partially connected with decreasing chlorine concentration. Therefore all data on optical density were converted to molar extinction ε (dm^2/mol) by $\varepsilon = D/(c \cdot l)$ where c is the concentration expressed in Cl_2 moles per dm^3 of gas and l is the optical path length in dm. The experimental values of gaseous chlorine density ρ measured in the tempera-

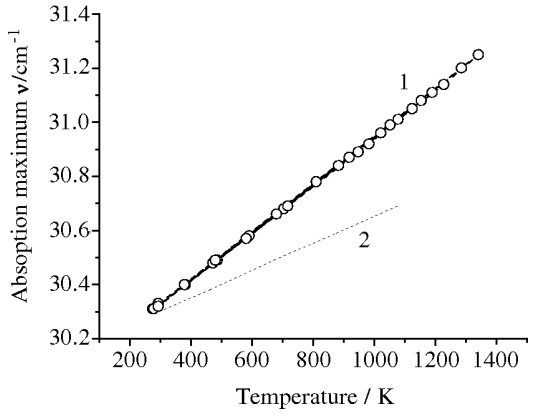

Fig. 3. The temperature dependence of $Cl_{2(gas)}$ absorption maximum ν_{max}. 1, Our data; 2, [4].

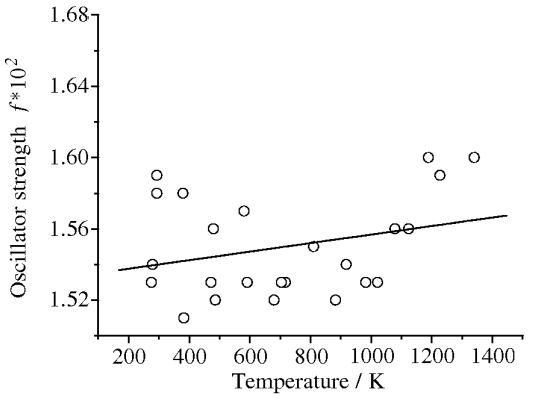

Fig. 4. The temperature dependence of $Cl_{2(gas)}$ oscillator strength f.

ture range 273 to 413 K [7] – whereas at higher temperatures up to 1470 K those were evaluated by the van der Waals equation – are used for the calculation of the molar concentration: $c = \rho/M$, where M is the molecular weight. The root-mean-square error of the extinction coefficient does not exceed 2.4%.

Similar to the optical density, the molar extinction coefficient reduces gradually with rising temperature as shown in Figure 2. The temperature dependence of ε_{max} can be described by

$$\varepsilon_{max} = -1.347 \cdot 10^{-4} T^4 + 4.414 \cdot 10^{-7} T^3 - 3.264 \cdot 10^{-4} T^2 - 0.287 T + 777.556. \quad (3)$$

The oscillator strength f related to the maximum molar extinction coefficient ε_{max} and absorption band half width $\Delta\nu_{1/2}$ by $f = 4.6 \cdot 10^{-9} \cdot \varepsilon_{max} \cdot \Delta\nu_{1/2}$ [8], is a measure of single band integral absorption. Its value grows from $1.53 \cdot 10^{-2}$ to $1.68 \cdot 10^{-2}$ with increasing temperature from 273 to 1470 K.

It is interesting that both the absorption maximum ν_{max} and oscillator strength f vary in their magnitudes approximately by 4% in the temperature range covered as shown in Figs. 3 and 4.

Andresen et al. [4] also called attention to the absorption maximum shift. For comparison the results of their estimation are shown in Fig. 3 by a dashed line. Taking into consideration that, in the temperature range under study, thermal Cl_2 dissociation to atomic state is negligible, the shift of ν_{max} to the short-wave region and expanding of the absorption band with rising temperature can not be related to new type of optical active particles (atoms). Judging by the absorption spectra found, these latter are only in an excited short-lived state as a consequence going Cl_2 molecule from basic $^1\Sigma_g{}^+$ state to high-energy repulsive $^1\Pi_u$ state [9].

The contour of absorption band observed can be closely described (Fig. 5) using the equation suggested by Sulzer and Wieland [9] for the temperature dependence of the halogen extinction coefficient if change of ν_{max} with temperature found by us experimentally (see Table 1) will be taken into consideration as well as refined values of ν at 0 K. Then this expression for gaseous chlorine at atmosphere pressure assumes the form

$$\varepsilon_T(\nu) = 750 \left(\mathrm{th} \left[\frac{403.65}{T} \right] \right)^{1/2} \cdot \exp \left(-\mathrm{th} \left[\frac{403.65}{T} \right] \left[\frac{\nu - \nu_{max}}{3085} \right]^2 \right). \quad (4)$$

3.2. Saturated Solutions of Chlorine in Molten Alkali Chlorides

EAS of saturated chlorine solutions in molten salts are studied in NaCl, NaCl-KCl (1 : 1), KCl and CsCl as a function of temperature. The absorption bands recorded are shown in Fig. 6 as dependencies of reduced optical density D_{red} ($D_{red} = \lg(I_0/I)/l$, where I_0 and I are intensities of the falling and transmitted luminous flux while l is the optical path length) vs. wave number ν.

The absorption bands are adequately represented by Gaussian curves. Analysis of (D_{red}/ν)-dependencies observed has revealed some peculiarities which escaped the attention of researchers [2, 4, 6] as a result

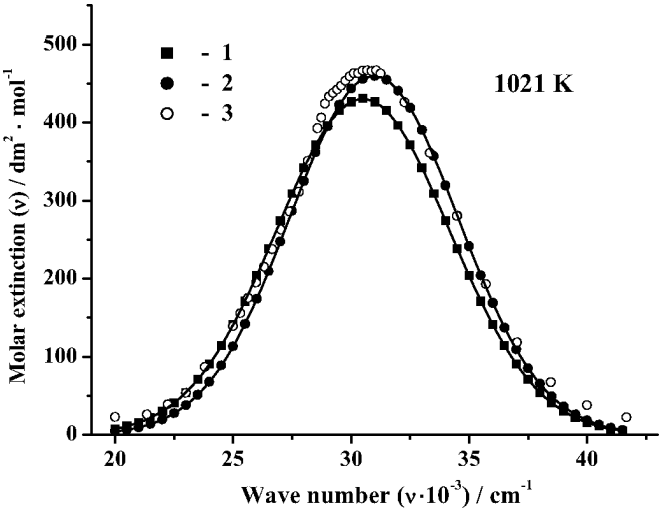

Fig. 5. Correlation between experimental and calculated values of the $Cl_{2(gas)}$ extinction coefficient at 1021 K. 1, Computed data presented in [9]; 2, values calculated with (4); 3, our experimental data.

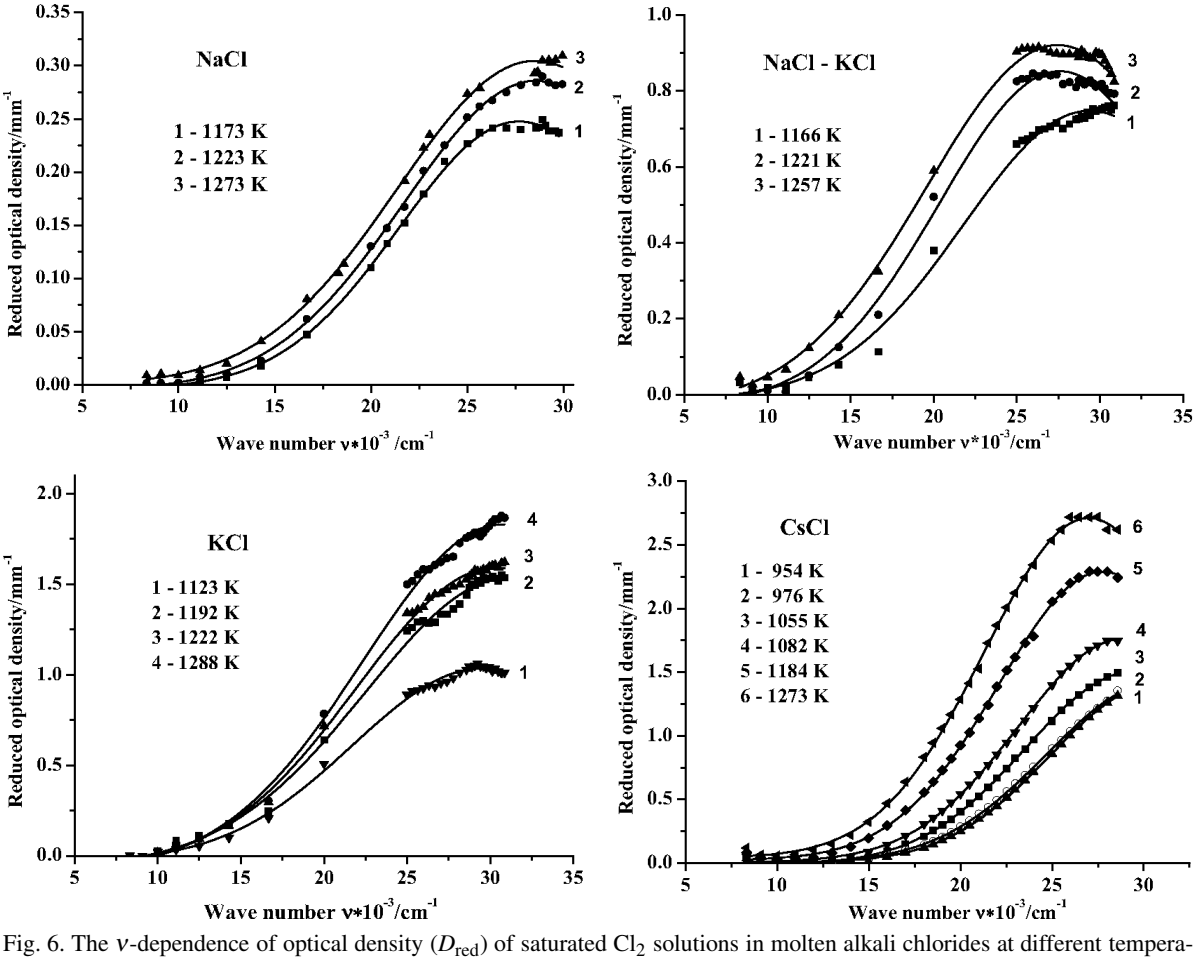

Fig. 6. The ν-dependence of optical density (D_{red}) of saturated Cl_2 solutions in molten alkali chlorides at different temperatures.

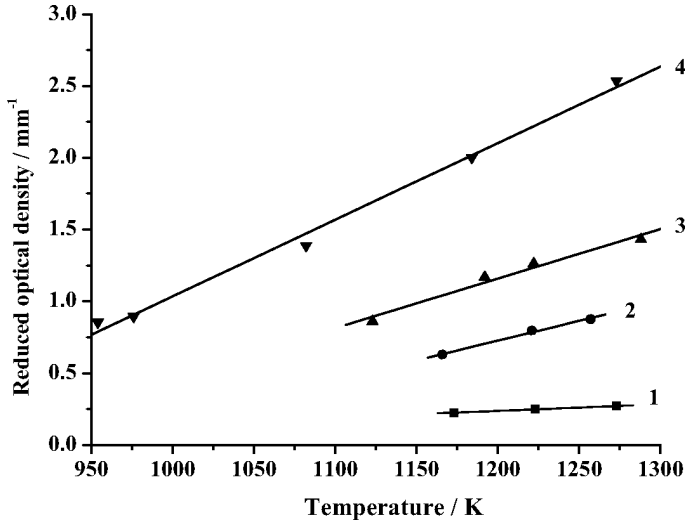

Fig. 7. Temperature dependence of optical density D_{red} ($\nu = 25000$ cm^{-1}) of saturated Cl_2 solutions in molten alkali chlorides. 1, NaCl; 2, $(NaCl\text{-}KCl)_{equimol}$; 3, KCl; 4, CsCl.

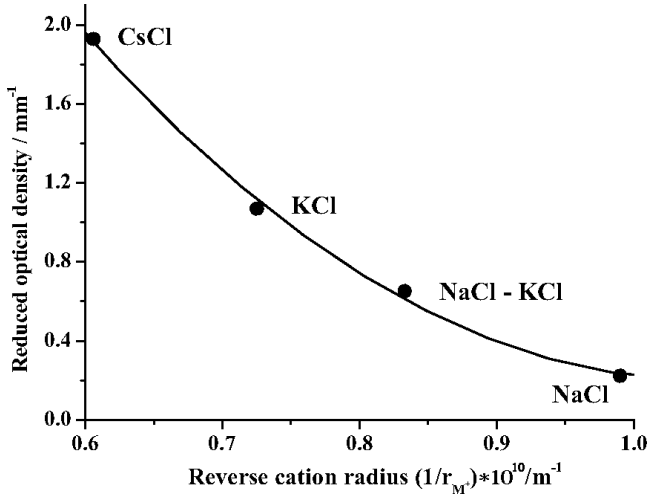

Fig. 8. Influence of ionic composition of molten salt solvent on optical density of chlorine solutions; $\nu = 25000$ cm^{-1}; $T = 1173$ K.

of scanty data on EAS of chlorine solutions in molten salts.

Firstly, it was found that the optical densities of all Cl_2 solutions are linear with temperature as illustrated in Fig. 7 where, as an example, D_{red} at the wave number 25000 cm^{-1} is plotted vs. T. It can be noted that the optical density as well as the slope of its temperature dependence change is similar to the chlorine solubility c_{Cl_2} in molten alkali chlorides [4, 10, 11].

Secondly, the measured optical densities depend on cation composition of salt solvent in much the same manner as the Cl_2 solubility in these salts. This is apparent from Figs. 8 and 9. The well-according solubility values measured by Ryabukhin [10, 11] and Andresen et al. [4] are used for correlation with our EAS data. Shannon's cation radii [12] are taken as characteristics of the salt composition.

Moreover, we have found that the curves from Figs. 8 and 9 when presented on a logarithmic scale are parallel, as can be seen graphically in Figure 10. The correlations of this sort are valid for all studied wave numbers and temperatures giving the excellent chance to calculate the chlorine solubility in unexplored molten alkali chloride mixtures by the EAS data to a good approximation.

According to computations carried out the equations for salt solvents considered are

$$\log c_{Cl_2} = 2.990 \pm 0.088 - (2.322 \pm 0.118)/r_i \quad (5)$$

and

$$\log D_{red} = 1.708 \pm 0.144 - (2.335 \pm 0.189)/r_i, \quad (6)$$

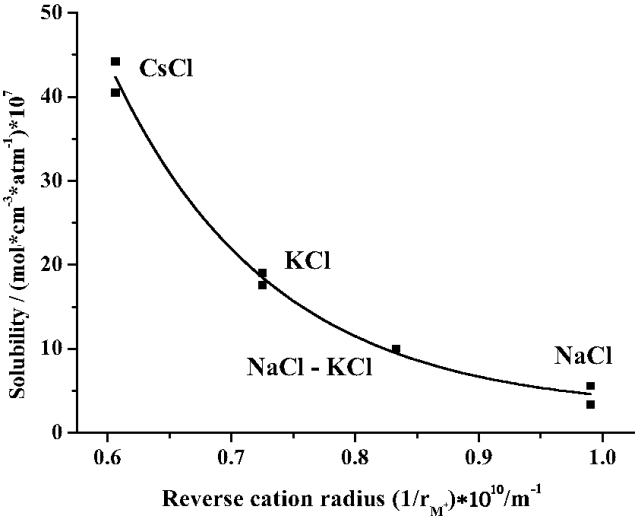

Fig. 9. Influence of ionic composition of molten salt solvent on chlorine solubility [4, 10, 11] at 1173 K.

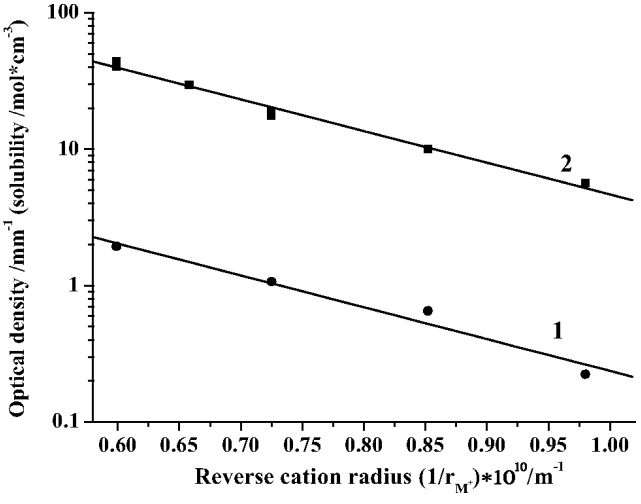

Fig. 10. Relation between reduced optical density ($\nu = 25\,000$ cm^{-1}) and chlorine solubility in molten alkali chlorides at 1173 K.

where c_{Cl_2} has the dimensionality $(\mathrm{mol}\cdot\mathrm{cm}^{-3}\cdot\mathrm{atm}^{-1})\cdot 10^7$, $D_{\mathrm{red}} - \mathrm{mm}^{-1}$ and $r_{\mathrm{i}} - \mathrm{m}\cdot 10^{10}$.

From the above equations it appears that $c_{Cl_2} = 19.14 D_{\mathrm{red}}$ at 1173 K.

In the context of the subject being discussed, it should be also noted that the EAS experiment is simpler and more correct than measuring the solubility in the presently accepted ways.

Thirdly, maybe one of the most important results of this study is solid experimental verification of the occurrence of absorption band maxima ($\nu_{\max}$) in saturated chlorine solutions in molten alkali chlorides close to 30 000 cm^{-1}. The value of $\nu_{\max}$ at the same temperature decreases approximately from 29 200 to 27 800 cm^{-1} at 1173 K on going from NaCl to CsCl. Our results correlate to some extent with data of Norwegian researchers [4]. As distinct from gaseous chlorine $\nu_{\max}$ in Cl_2 molten salt systems is shifted to the long-wave region with rising temperature.

The observed changes in the position of absorption band maxima and optical density with changing temperature and cationic composition of salt solvent allows us to coordinate them with known data on chlorine solubility in molten alkali chlorides. Indeed, the enhancement of optical density with rising temperature conforms to the growing chlorine solubility in all salts and elevating temperature coefficient of solubility on going from sodium chloride to cesium chloride. The shift of maxima of chlorine absorption bands in molten salt solutions to the long-wave region, which increases in the same direction, is additional evidence of the appearance of new low-energetic levels of elec-

tron transition in Cl_2 molecule associated most probably with ion-molecular Cl_2–Cl^- bonds produced in Cl_2-MCl systems. It is especially of interest that the degree of displacement of ν_{max} rises as the interionic energy in salt solvent decreases in direction from the Cl_2-NaCl system to the Cl_2-CsCl one.

Acknowledgement

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