

Integral cation mobility in molten $KCl - LaCl_3$

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1. INTRODUCTION

Cation mobility in molten salts has been determined with different techniques and published in many papers. They usually deal with binary (M_1, M_2)X systems, where M_1 and M_2 are monovalent cations and X is a univalent anion. The data on binary multivalent systems have been reviewed and summarized by Chandra and Chandra [1]. There are also some papers on binary (M_1, M_2, M_3)X systems, where M_1 is a monovalent, M_2 a divalent cation and X a univalent anion. Investigations performed on these systems have been reviewed by Klauer [2]. Recently, investigations of cationic mobility in systems with complex cations have been performed. With nondestructive electrochromatic method (Kramer's method) [3,4] mobilities of cations species with La^{3+} [5], Ca^{2+} [6], U^{4+} and Nd^{3+} [7] have been determined. Interference was observed during electrolysis of fused chloride salts of these cations. Relative diffusivities of cations based on mobility (D_{rel}) was also determined in these salts. Investigations were restricted by the escape of gases during and resulting by electrolysis of molten salts [8]. Only few binary systems with trivalent cations have been investigated in the whole range of compositions. These are $YCl_3 - LaCl_3$, $YCl_3 - DyCl_3$ [9] and $KCl - DyCl_3$ [10]. Integral cation mobilities were determined for these systems with nondestructive electrochromatic method. © 1995 Elsevier Science B.V. All rights reserved.

2. EXPERIMENTAL**2.1. Synthesis of $LaCl_3$ and preparation of KCl [11]**

Lanthanum (III) chloride was prepared by dehydratation of $LaCl_3 \cdot 6H_2O$ from with methanolic chloride under vacuum. Commercial $LaCl_3 \cdot 6H_2O$ (REACHEM, Soviet) or laboratory methanolic hydrate was dissolved in fused KCl then methanolic chloride (PPOCH Gdansk, Poland) in molar ratio of 1:4 with respect to lanthanum was added to the solution. Solution was filtered and slowly evaporated. Solid-dry product was placed in a quartz ampoule and gradually heated under vacuum. Sublimation of $NELaCl_3$ produced and remaining chloride contained in the solid part of the ampoule. Anhydrous $LaCl_3$ was washed in the same ampoule in order to remove traces of $NELaCl_3$. Ampoules with compound were opened in a dry-box under argon; methanolic chloride was gassed and sealed in cooled glass ampoules.

Yttrium chloride (PPOCH Gdansk, Poland) was prepared by reacting the salt under gaseous HCl . Traces of the gas were removed into the seal with argon. Molten KCl was also gassed in a dry-box under argon and sealed in cooled glass ampoules.

2.1. Migration cell.

Design of the migration cell was similar to that described in literature [2, 7, 12, 13]. It consisted of two parts - anode and cathode - connected with wet apparatus. Lower one, filled with quartz wool, enabled electric contact and ionic flow between the two parts of the cell. Upper part was designed for connection of gas spaces of the cell, equilibration of gas pressure, chloride and vapor flow. In anodic part, a typical arrangement consisting of two $PbCl_2$ and solid graphite cathode was replaced with wetted cathode of KCl and 22 vol. % of $LaCl_3$. Cathode - a graphite rod (rod diameter of 10 mm) had a channel inside the channel gas. Composition of the salt was chosen to minimize diffusion flow between cell compartments due to concentration gradients of anions. Anodic part of the cell was filled with investigated KCl - $LaCl_3$ melt. A typical migration tube immersed in the melt was slightly modified - a small, perforated quartz chip was placed on quartz wool at the top of the tube. Graphite rods were used on the chip that enabled that evolution of chlorine without frequent breaking of contact between anode and the melt (bubbles of the gas at the anode point in the quartz wool). The cell was the whole part of measuring compartment, which has been constructed in a similar way as it was described in [7].

2.2. Experimental procedure

Before the beginning of the first experiment the cell temperature was stabilized at 1023 K and the cell was flushed with argon. Then weighed amount of KCl was added in both parts of the cell and appropriate amount of $LaCl_3$ was introduced. Melts were homogenized by bubbling with purified argon for 10 minutes. A special care was taken to trap water in both parts of the cell at the same level. Then a chlorine electrode (cathode) and migration tube (previously heated to the same temperature as the melt) were introduced to the cell. The cell was equilibrated for the time 12 hours under flow of argon. During that time the cell potential migration tube and electric circuit was established. Then chlorine flow was opened and electrolysis was started. At the end of experiment migration tube was taken out of the melt and the salt in the tube solidified in several minutes. Then the tube was cut into 12 pieces of a similar length. The salt from each piece was dissolved in water, slightly acidified with HCl. Concentration of potassium was determined with AEA and lanthanum with ICP methods. Finally, relation between the concentration of each metal and the piece number was determined which, after multiplication in distance from anode, was defined as "concentration profile".

2.4. Composition of KCl - $LaCl_3$ melt

Composition of investigated KCl - $LaCl_3$ melt was changed from 1:1 to 1:6 mol. % of $LaCl_3$ in five steps (Table 1). Appropriate amount of the melt was removed from the cell after measurements in a given composition and necessary amount of $LaCl_3$ was introduced to the cell. The melt was homogenized and the salt level was controlled by immersion of graphite and an electrolytic electric contact. Proximate composition of the melt was determined by its electrical analysis before the next change.

3. RESULTS AND DISCUSSION

Electroviscosity measurements have been performed for five compositions of KCl - LaCl₃ melt in the molar ratio 8,346 to 8,792 equivalent fractions of LaCl₃ (Table 1). Measurements were carried out at 1023, 1073 and 1123 K. Characteristic parameters of measurements, values of α and the internal mobility of cations (b_{10} and b_{20}) are presented in Table 1. The temperature range of measurements and the composition of salt melts were correlated with phase diagrams of the KCl - LaCl₃ system given by H. J. Seifert et al. [14]. Details of migration model and origin of basic migration equations are briefly summarized in paper [15]. Parameter α is defined as:

$$\alpha = \frac{(b_1 - b_2)}{(y_1 b_1 + y_2 b_2)} = \left(\frac{1}{Z} \right) \left[\left(\frac{Z_2}{y_2} \right) - \left(\frac{Z_1}{y_1} \right) \right] \quad (1)$$

where:

- b_1 and b_2 - internal mobility of cations 1 and 2 (K and La, respectively),
- y_1 and y_2 - equivalent fractions of cations 1 and 2 (K and La) under migration process,
- $Z = Q/F$ - Q - electric charge, F - Faraday's constant,
- Z_1 and Z_2 - number of equivalent of cations 1 and 2 in the melt after migration process between walls and the cross-section of migration tube where original equivalent fractions y_1 and y_2 were unchanged.

Values of b_1 and b_2 have been calculated from measured conductivity σ [13], equivalent volume V_e [13] of the salt mixture and α :

$$b_1 = \left(\frac{\sigma V_e}{F} \right) (1 + \alpha y_2) \quad (2)$$

$$b_2 = \left(\frac{\sigma V_e}{F} \right) (1 - \alpha y_1) \quad (3)$$

General tendency is that values of α parameter decrease with the increase of lanthanum chloride equivalent fraction. Dependence of internal mobility of K and La cations (b_{10} and b_{20}) have been calculated with equations (2) and (3). Values of specific electrical conductivity and equivalent molar volumes are values from literature [13]. It has been found that calculated values of mobility of K⁺ and La³⁺ ions at 1023 K differ from the ones at 1073 K and 1123 K and even not so depend on equivalent molar fraction of lanthanum chloride - Figure 1. Mobility of La³⁺ is constant in investigated composition range and mobility of K⁺ only slightly increases with increase of LaCl₃ equivalent molar fraction. At 1073 K (Figure 2) as well as at 1123 K (Figure 3) mobility of La³⁺ and K⁺ depends on equivalent molar fraction of lanthanum chloride.

Table I.

Characteristic parameters of experiments, ν and internal stability of columns in various binary systems $KCl - LaCl_3$.

T	$\alpha_{12}(\%)$	Q	ν	\bar{z}	$V_m(V_m)^{1/2}$	b_{12}	b_{13}
[K]		[C]		[mol ³]	[10 ³ m ³ mol ⁻¹]	[10 ³ m ³ V ⁻¹ s ⁻¹]	
1023	0	-		791,800	41,340		8,99
	0,15 (0,346)	340	0,664	93,161	53,163 (49,895)	2,21	4,85
	0,19 (0,413)	182	0,302	97,729	55,829 (50,885)	1,41	3,77
	0,29 (0,531)	764	0,424	89,428	54,822 (51,217)	1,79	4,25
	0,43 (0,685)	756	1,314	87,868	55,790 (54,090)	2,89	4,57
	0,38 (0,792)	482	0,794	98,861	63,796 (61,261)	2,98	3,70
				58,802	69,327 (63,875)	2,12	
1073	0			202,300	49,329		9,49
	0,11 (0,346)	347	1,267	103,304	53,788 (49,892)	0,80	4,77
	0,19 (0,413)	368	0,682	97,433	55,972 (50,886)	1,48	4,13
	0,29 (0,531)	508	1,298	100,033	58,988 (57,333)	1,78	6,43
	0,43 (0,685)	756	1,192	109,578	68,943 (65,206)	2,30	7,33
	0,38 (0,792)	130	0,477	108,972	66,023 (61,245)	3,17	4,85
				181,168	69,340 (63,193)	2,43	
1123	0			212,000	47,062		10,30
	0,15 (0,346)	340	1,320	113,143	55,188 (49,452)	0,57	2,19
	0,19 (0,413)	681	1,673	109,463	58,989 (61,297)	1,87	6,11
	0,29 (0,531)	695	1,090	111,186	58,988 (58,543)	2,21	7,08
	0,43 (0,685)	467	0,888	121,868	64,805 (63,206)	3,11	7,38
	0,38 (0,792)	343	0,396	121,776	67,823 (61,892)	3,71	9,38
				113,800	70,343 (63,615)	2,77	

^a Values in parentheses are equivalent values in 10³ m³ eq⁻¹.

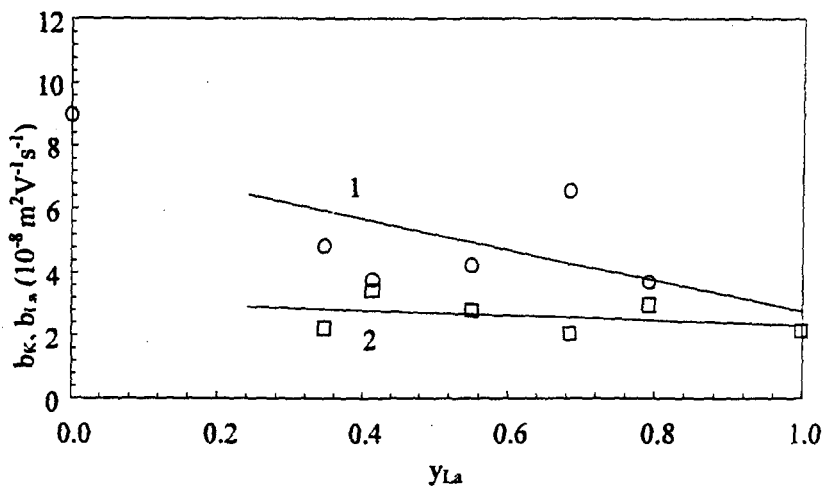


Figure 1. Isotherms of K^+ and La^{3+} mobilities at 1023 K. o - K^+ (line 1), \square - La^{3+} (line 2).

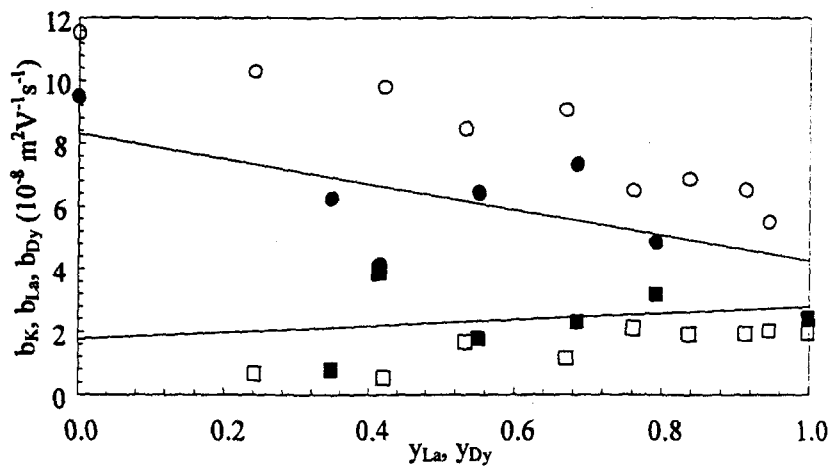


Figure 2. Isotherms of K^+ , La^{3+} and Dy^{3+} [10] mobilities at 1073 K (1093 K for Dy^{3+}). o - K^+ [10], \bullet - K^+ (this work), \square - Dy^{3+} [10], \blacksquare - La^{3+} (this work).

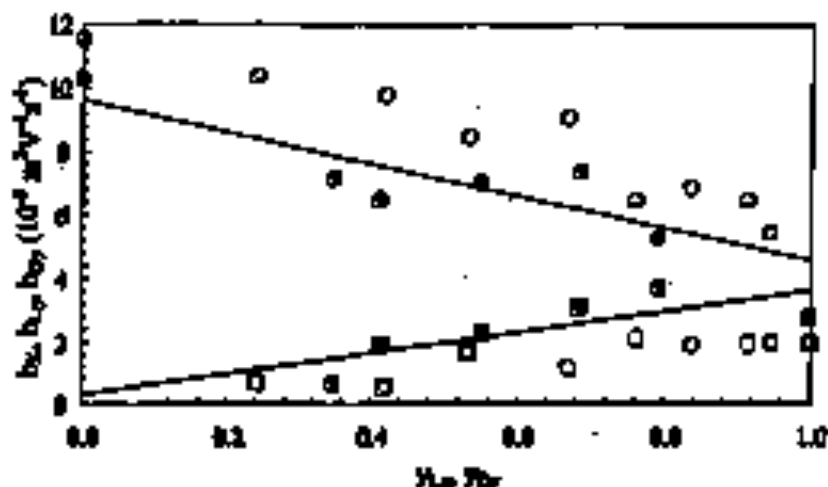


Figure 3. Isotherms of K^+ , La^{3+} and Dy^{3+} [10] mobilities at 1173 K (1073 K for Dy^{3+}), $\circ - K^+$ [10], $\square - K^+$ (this work), $\triangle - Dy^{3+}$ [10], $\square - La^{3+}$ (this work).

Binary system $KCl - DyCl_3$ was the first one of the $(M_1, M_2)X$ type [where $M_1 -$ monovalent cation, $M_2 -$ trivalent cation, $X -$ common anion] for which cation mobility was investigated at higher contents of trivalent cation [10]. These investigations were carried out only at the temperature of 1073 K. Their results have been shown in Figure 2 and Figure 3 together with results of present investigations (please note that they were carried out at different temperatures). As it was expected, there is strong similarity between both systems. Differences seem to be in the first place the source of different literature sources which was chosen for absolute conductivity and density data (please note the references and values of b_0 at $y_{A_2} = 0$). Therefore, it seems that the difference of mobility values in $KCl - LaCl_3$ and $KCl - DyCl_3$ systems due to different ionic radii of La^{3+} (0,106 nm) and Dy^{3+} (0,091 nm) is negligible in comparison to experimental errors and differences between reference values of absolute conductivity and density.

4. CONCLUSIONS

Concurrent migration experiments have been carried out for $KCl - LaCl_3$ system at 1023, 1073 and 1173 K. Detached values of stability of K^+ and La^{3+} cations at 1073 and 1173 K are very similar to those reported in literature for $KCl - DyCl_3$ system at 1073 K [10]. Mobility of K^+ and La^{3+} at 1023 K is almost independent from temperature in investigated range of composition. At 1073 and 1173 K mobility of K^+ is slightly higher and decreases whereas La^{3+} mobility increases with increase of $LaCl_3$ equivalent fraction.

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