

Transport properties in molten systems $MCl-UCl_4$ ($M = Li, Na, K, Rb, Cs$)*

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Diffusion coefficients were determined for $^{22}Na^+$, $^{86}Rb^+$, $^{137}Cs^+$, and $^{36}Cl^-$ ions in molten UCl_4 as well as in the binary $NaCl-UCl_4$, $RbCl-UCl_4$, and $CsCl-UCl_4$ mixtures containing 50 and 75 mole % UCl_4 . Values of diffusion coefficients were measured by the capillary method with application of radioactive tracers. Values of diffusion activation energy were determined and compared with values of activation energy of molar conductance. The Nernst—Einstein equation was applied to calculation of the theoretical values of cationic conductance in the investigated melts. Values of obtained conductance are compared with those determined experimentally. Concentration dependence of electric conductance is presented for $MCl-UCl_4$ systems at comparative temperatures. Besides, mechanism of charge transfer in the examined molten solutions is discussed.

Проведены измерения коэффициентов диффузии ионов $^{22}Na^+$, $^{86}Rb^+$, $^{137}Cs^+$ и $^{36}Cl^-$ так в расплавленном UCl_4 как и в двойных расплавленных системах $NaCl-UCl_4$, $RbCl-UCl_4$ и $CsCl-UCl_4$ состоящих очередно из 50 и 75 мол. % UCl_4 . Измерения сделаны методом капиллярной диффузии с применением «меченых атомов». Сравнены величины энергии активации диффузии (E_D) и молярной электропроводимости (E_λ). Вычислены теоретические величины электропроводимости катионов с помощью уравнения Нернста—Эйнштейна. Проведено сравнение вычисленной электропроводимости с экспериментальной. Указаны концентрационные зависимости удельной и молярной проводимостей при сопоставимых температурах. Обсуждается механизм переноса заряда в исследуемых расплавах.

Molten binary systems consisting of uranium(IV) chloride and alkali chlorides have been the subject of thermodynamic [1—3] as well as spectroscopic [4] and magnetochemical [5] investigations. It was found that in all $MCl-UCl_4$ systems a congruently melting compound of the M_2UCl_6 type is formed. In all cases

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considerable negative deviations of properties of uranium(IV) chloride—alkali chlorides molten mixtures from ideal solution properties have been observed [1]. These deviations increase systematically with increasing radius of alkali cation from LiCl—UCl_4 to CsCl—UCl_4 . Examination of absorption spectra of chloride melts containing UCl_4 proved the presence of UCl_6^{2-} ions in these solutions. Isotherms of molar volume of molten solutions MCl—UCl_4 satisfy the rule of additivity in temperature range 800—980 K with the exception of the CsCl—UCl_4 system [6, 7]. However, the course of concentration dependence of electric conductance, both specific and equivalent, shows negative deviations from additive values, as well as from theoretical isotherms as proposed by Markov [6—8].

Experimental

Characteristics of the reagents applied as well as the method of synthesis of uranium tetrachloride were presented in [6, 7]. Diffusion coefficients of $^{22}\text{Na}^+$, $^{86}\text{Rb}^+$, $^{137}\text{Cs}^+$ and $^{36}\text{Cl}^-$ ions were determined by the capillary method according to [9]. Quartz vessel, presented in Fig. 1 has been used. The main part of the vessel consisted of the quartz test tube (1), closed in the upper part with a special head (13). Test tube (1) contained the examined molten mixture (8). A small quartz test tube (4) was filled with a melt of the same composition with an admixture of radioactive isotope along with carrier. Test tube (4) was fixed to the rod (11) passing through the channel (10) (standard seal, Sovirel Co.). Mole fraction of active salt in this melt never exceeded the value of 10^{-5} . Temperature of the melt was measured by thermobattery (2) consisting of two thermocouples Pt/Pt,Rh. Temperature was determined

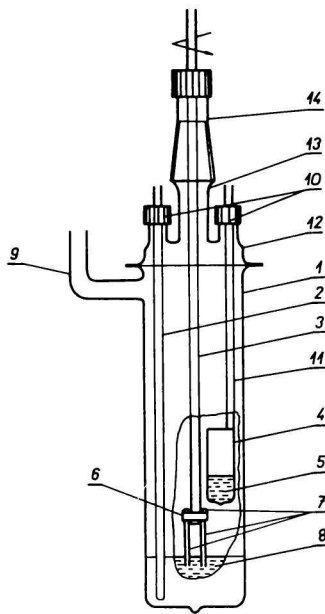


Fig. 1. Scheme of the vessel for determination of diffusion coefficients by capillary method.

1. Quartz test tube; 2. quartz protection of thermocouple; 3. quartz rod; 4. quartz vessel (active melt container); 5. active melt; 6. graphite holder; 7. quartz capillaries; 8. nonactive melt; 9. tube joining container with vacuum pump or bottle filled with argon; 10. glass channel (Sovirel type); 11. quartz rod; 12. head of the container (Pyrex glass); 13. tube with microsection; 14. rotary head with channel of Sovirel type.

with an accuracy of ± 0.3 K. To the quartz rod (3) the graphite holder (6) with six quartz capillaries (7) was fixed. In the experiments, capillaries with an internal diameter within the range 0.5—1.0 mm were used. The construction of the measuring vessel guaranteed the air-tightness and allowed to work in vacuum or in an atmosphere of hydrogen chloride or argon over the salt melt.

In order to fill the capillaries with the melt, the vessel (1) was evacuated, lower ends of capillaries (7) were immersed into the active melt (5) and then the vessel (1) was filled with argon. As a consequence, the capillaries were filled by the active melt. Consequently, the bottoms of capillaries were dipped into the nonactive melt (8) for 72 h. During the diffusion experiment, the quartz rod (3) with the set of capillaries rotated with a velocity of 2 rev./min and the temperature of melt was kept constant within ± 0.3 K. Subsequently, the capillaries were removed from the melt, weighed, and then the radioactivity of melt enclosed in capillaries was measured by means of multichannel spectrometer, type ND 1200 with Ge(Li) detector (Canberra Co.). Moreover, activities of capillaries filled with active melt (5) taken directly from test tube (4) as well as of capillaries filled with nonactive melt (8) were measured.

The values of diffusion coefficients were calculated according to eqn (6) on the basis of the determined values of specific activities of melts in capillaries applied to the diffusion experiments (A_D), those in capillaries filled with active melt (5) (A_A), and those in capillaries filled with nonactive melt (8) (A_N). Each value of diffusion coefficient represents an arithmetical mean of six values corresponding to the individual capillaries. As estimated by combination of errors, the diffusion coefficients were determined with an accuracy of $\pm 1.2\%$.

Results

Diffusion coefficients were calculated according to eqn (6) which results from the solution of the second Fick equation [10]

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

under the initial conditions

$$t = 0 \quad \begin{cases} A(x) = A_0 & \text{for } x < l \\ A(x) = 0 & \text{for } x > l \end{cases} \quad (2a)$$

$$(2b)$$

and boundary conditions

$$t > t_1 > 0 \quad \begin{cases} A(x) = f(x) & \text{for } x < l, A(0) < A_0 \\ A(x) = 0 & \text{for } x > l \end{cases} \quad (3a)$$

$$(3b)$$

where $A(0)$ is specific activity of salt in the closed end of capillary at $x = 0$, $A(x)$ specific activity of the salt column in capillary at a distance of x from the end of capillary, A_0 initial specific activity of active melt, l length of capillary, t time of diffusion, D diffusion coefficient.

In estimation of the initial and boundary conditions the concentrations of diffusing ion have been expressed by specific activities.

The average specific activity A_a of the salt column in capillary at a moment t is equal to

$$A_a = \frac{1}{l} \int_0^l A(x) dx \quad (4)$$

After a period of time t the average specific activity A_a is determined by solution of the Fick equation under the above conditions [10]

$$\frac{A_a}{A_0} = \gamma = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[\frac{-(2n+1)^2 \pi^2 D t}{4l^2} \right] \quad (5)$$

In the case when $A_a/A_0 = \gamma < 0.4$ the limitation of the sequence (5) to the first term for $n = 0$ made it possible to calculate the diffusion coefficient D with an accuracy of 0.2% [11].

Thus, the diffusion coefficient of a given ion is determined by the equation

$$D = \frac{4l^2}{\pi^2 t} \ln \frac{8}{\pi^2 \gamma} \quad (6)$$

in which

$$\gamma = \frac{A_D - A_N}{A_A - T} \quad (7)$$

where

A_A is specific activity of a capillary filled with active melt, A_D specific activity of a capillary filled with active melt after diffusion experiment, A_N specific activity of a capillary filled with nonactive melt after diffusion measurement, and T background of counter.

Table 1
Diffusion coefficients of ions in molten
50% UCl_4 + 50% NaCl mixture
 $D_i/\text{cm}^2 \text{ s}^{-1} \cdot 10^5$

Temperature K	726	753	768	775	780	788
Diffusion coefficient of $^{22}\text{Na}^+$ ion	3.39 ± 0.03	4.21 ± 0.04	4.60 ± 0.05	4.97 ± 0.05	4.86 ± 0.05	5.05 ± 0.05
Diffusion coefficient of $^{137}\text{Cs}^+$ ion	1.89 ± 0.02	2.11 ± 0.02	2.53 ± 0.03	2.60 ± 0.03	2.60 ± 0.03	2.71 ± 0.03
Diffusion coefficient of $^{86}\text{Rb}^+$ ion	—	—	3.27 ± 0.04	3.63 ± 0.05	—	4.09 ± 0.05

The values of the diffusion coefficients determined in molten $\text{MCl}-\text{UCl}_4$ mixtures are given in Tables 1—8.

Table 2

Diffusion coefficients of ions in molten
75% UCl_4 + 25% NaCl mixture
 $D_i/\text{cm}^2 \text{s}^{-1} \cdot 10^5$

Temperature K	816	844	864
Diffusion coefficient of $^{22}\text{Na}^+$ ions	1.88 ± 0.02	3.53 ± 0.04	4.32 ± 0.05
Diffusion coefficient of $^{86}\text{Rb}^+$ ion	1.58 ± 0.02	2.68 ± 0.03	3.13 ± 0.04
Diffusion coefficient of $^{137}\text{Cs}^+$ ion	1.13 ± 0.01	2.13 ± 0.03	2.54 ± 0.03

Table 3

Diffusion coefficients of ions in molten
50% UCl_4 + 50% RbCl mixture
 $D_i/\text{cm}^2 \text{s}^{-1} \cdot 10^5$

Temperature K	678	700	726	748
Diffusion coefficient of $^{22}\text{Na}^+$ ion	1.61 ± 0.01	2.01 ± 0.02	2.34 ± 0.02	2.58 ± 0.02
Diffusion coefficient of $^{137}\text{Cs}^+$ ion	0.84 ± 0.01	1.21 ± 0.01	1.61 ± 0.01	1.82 ± 0.02
Diffusion coefficient of $^{36}\text{Cl}^-$ ion	0.90 ± 0.02	1.25 ± 0.03	1.64 ± 0.04	—

Table 4

Diffusion coefficients of $^{86}\text{Rb}^+$ ion in molten
50% UCl_4 + 50% RbCl mixture
 $D_i/\text{cm}^2 \text{s}^{-1} \cdot 10^5$

Temperature K	673	674	703	730	776	974	980
Diffusion coefficient of $^{86}\text{Rb}^+$ ion	1.19 ± 0.02	1.29 ± 0.02	1.76 ± 0.03	2.05 ± 0.04	2.29 ± 0.04	2.67 ± 0.05	2.73 ± 0.05

Table 5

Diffusion coefficients of ions in molten
75% UCl₄ + 25% RbCl mixture
 $D_i/\text{cm}^2 \text{ s}^{-1} \cdot 10^5$

Temperature K	795	803	811	829	842
Diffusion coefficient of ²² Na ⁺ ion	—	—	5.64 ±0.06	7.42 ±0.07	8.44 ±0.08
Diffusion coefficient of ⁸⁶ Rb ⁺ ion	2.07 ±0.02	3.24 ±0.03	4.03 ±0.04	5.49 ±0.05	6.13 ±0.06
Diffusion coefficient of ¹³⁷ Cs ⁺ ion	—	—	2.86 ±0.03	4.03 ±0.04	4.50 ±0.05

Table 6

Diffusion coefficient of ions in molten
50% UCl₄ + 50% CsCl mixture
 $D_i/\text{cm}^2 \text{ s}^{-1} \cdot 10^5$

Temperature K	788	803	827	854
Diffusion coefficient of ²² Na ⁺ ion	3.15 ±0.03	3.55 ±0.04	4.00 ±0.04	4.35 ±0.05
Diffusion coefficient of ¹³⁷ Cs ⁺ ion	1.64 ±0.02	1.93 ±0.02	2.32 ±0.03	2.65 ±0.03

Table 7

Diffusion coefficients of ions in molten
75% UCl₄ + 25% CsCl mixture
 $D_i/\text{cm}^2 \text{ s}^{-1} \cdot 10^5$

Temperature K	815	825	838
Diffusion coefficient of ²² Na ⁺ ion	2.31 ±0.13	2.64 ±0.07	3.05 ±0.08
Diffusion coefficient of ⁸⁶ Rb ⁺ ion	1.80 ±0.11	2.18 ±0.05	2.65 ±0.07
Diffusion coefficient of ¹³⁷ Cs ⁺ ion	1.40 ±0.08	1.72 ±0.04	2.24 ±0.06

Table 8

Diffusion coefficients of ions in molten UCl_4 at 873 K
 $D_i/\text{cm}^2 \text{ s}^{-1} \cdot 10^5$

Investigated ion	$^{22}\text{Na}^+$	$^{36}\text{Cl}^-$	$^{137}\text{Cs}^+$
Diffusion coefficient	3.01 ± 0.20	2.70 ± 0.40	2.86 ± 0.20

Table 9

Values of the activation energy of cations in the systems
 $\text{MCl}-\text{UCl}_4$ ($\text{M} = \text{Na}, \text{Rb}, \text{Cs}$)
 $E_D/\text{kJ mol}^{-1}$

Molar composition of melt	Temperature K	$E_{D_{\text{Na}}}$	$E_{D_{\text{Rb}}}$	$E_{D_{\text{Cs}}}$	$E_{D_{\text{Cl}}}$
50% UCl_4 — NaCl	733	39	—	57	—
50% UCl_4 — RbCl	714	32	31	49	43
50% UCl_4 — CsCl	820	42	—	35	—
75% UCl_4 — RbCl	835	53	43	43	—
75% UCl_4 — CsCl	828	90	106	144	—

On the basis of the temperature dependences of diffusion coefficients, the activation energies of diffusion of Na^+ , Rb^+ , Cs^+ , and Cl^- ions were determined. Values of activation energy obtained for melts containing 50 mole % UCl_4 at temperature $1.10 T_1$ (T_1 is temperature of the primary crystallization of the melt of a given composition), and for melts containing 75 mole % UCl_4 at temperature $1.06 T_1$ are presented in Table 9.

Discussion

Activation energies of diffusion of alkali cations E_D as well as molar conductances E_Λ decrease with increasing temperature, however, the temperature dependence of E_D is more expressed than that of E_Λ (Fig. 2), this difference being due to the different mechanisms of both processes.

Beside ions which determine the conductance of a molten salt, uncharged particles and agglomerates of particles of various sizes also take part in the diffusion process [12]. An increase of temperature is accompanied by structural changes resulting from an increased ionization of the melt. Thus, the number of charge carriers increases and at the same time the average size of particles participating in diffusion process decreases. Consequently, the values of activation energy of both processes also decrease, though in a different way. To determine

qualitatively the way of charge transfer, the values of electric conductance of cations, Λ_i were calculated according to the Nernst—Einstein equation

$$\Lambda_i = \frac{z_i F^2 D_i}{RT} \quad (8)$$

where D_i is diffusion coefficient of the cation i , z_i charge of the cation i , and F Faraday constant.

Then, the values of Λ_i were compared (in accordance with suggestion of *Chemla* and *Lantelme* [13]) with the experimentally determined values of the electric conductance (Table 10).

Table 10

Comparison of the values of cationic conductance calculated according to the Nernst—Einstein equation, Λ_{calc} , and determined experimentally, Λ_{exp} , in the system RbCl—UCl₄

Concentration of UCl ₄ in the melts, mole %	Temperature K	Diffusion coefficient, D_{Rb} $\text{cm}^2 \text{s}^{-1} \cdot 10^5$	Λ_{exp}		Λ_{calc}		$\Lambda_{\text{calc}}/\Lambda_{\text{exp}}$
			$\Omega^{-1} \text{m}^2 \text{mol}^{-1} \cdot 10^4$	$\Omega^{-1} \text{m}^2 \text{mol}^{-1} \cdot 10^4$	$\Omega^{-1} \text{m}^2 \text{mol}^{-1} \cdot 10^4$	$\Omega^{-1} \text{m}^2 \text{mol}^{-1} \cdot 10^4$	
50	678	1.40	20.25		23.96		1.17
	700	1.70	27.65		27.20		0.98
	730	2.05	37.25		31.50		0.85
	748	2.15	42.40		32.20		0.76
75	803	3.24	125.1		45.2		0.36
	811	4.03	130.5		55.7		0.43
	842	6.15	148.9		81.5		0.55

In the investigated melts a cationic character of electric conductance was assumed and therefore the experimental values of equivalent conductance for a given composition were multiplied by the reciprocal values of equivalent fraction of alkali chlorides.

The ratio between the calculated and the experimental conductance values, Λ_{calc} , and Λ_{exp} , respectively, is higher than 0.5 for melts containing 50 mole % UCl₄, except for the system RbCl—UCl₄ where it is close to 1. In melts containing 75 mole % UCl₄ the agreement between the experimental conductance values and those calculated from the Nernst—Einstein equation is rather poor. However, it should be pointed out that the validity of the Nernst—Einstein equation is somewhat limited in molten salts. The values of the ratio $\Lambda_{\text{calc}}/\Lambda_{\text{exp}}$ may indicate the type of charge transfer in investigated systems. It may be assumed that in melts with a high content of alkali chloride, the cationic conductance is predominant. At higher concentrations of UCl₄ in the melt both uranium(IV) and chloride ions take part in the charge transfer and in molten UCl₄ a mixed anionic-cationic conduc-

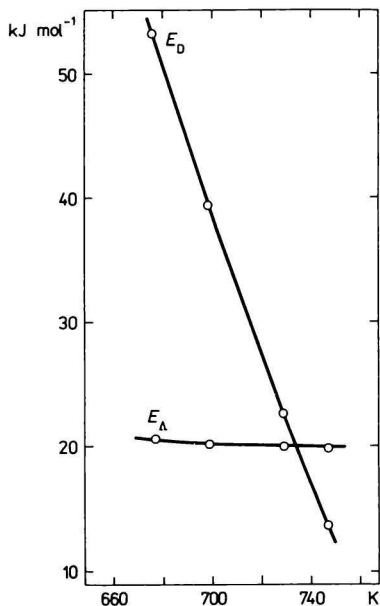


Fig. 2. Activation energy of diffusion, E_D , of Rb^+ ions and activation energy of electric conductance, E_A , as a function of temperature in the melt, containing 50 mole % UCl_4 + 50 mole % RbCl .

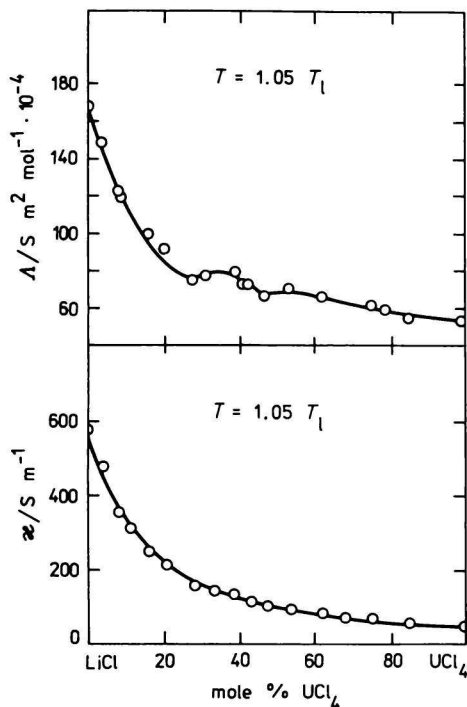


Fig. 3. Dependence of the specific electric conductance, κ , and molar conductance, Λ , on the concentration at comparative temperatures $T = 1.05 T_l$ in the $\text{LiCl}-\text{UCl}_4$ system.

tance is assumed. This assumption is confirmed by a comparison of values of relative mobilities, u_{+-} , and of the friction coefficients, r_{+-} , for molten alkali chlorides with the corresponding values for molten uranium(IV) chloride (Table 11).

Values of relative mobility, u_{+-} , were calculated from the relation

$$\Lambda_{\text{exp}} = F u_{+-} \quad (9)$$

For UCl_4 it has been assumed that $\Lambda_{\text{exp}} = \Lambda(1/4 \text{UCl}_4)$, according to IUPAC recommendation [14]. The cation-anion friction coefficients, r_{+-} , of the pure molten salts were calculated using the *Laity* equation [15]

$$r_{+-} = \frac{(z_+ + z_-) F^2}{\Lambda_{\text{exp}}} \quad (10)$$

assuming that the investigated salts are electrolytes of type I according to *Laity's* classification (they consist of only two ionic species).

Table 11

Values of relative mobilities, u_{+-} , friction coefficients, r_{+-} , and activation energy of molar conductance, E_{Λ} , in molten LiCl, NaCl, CsCl, and UCl₄

Compound	Temperature K	$u_{+-} \cdot 10^4$ cm ² s ⁻¹ V ⁻¹	$r_{+-} \cdot 10^9$ J s mol ⁻¹ cm ²	E_{Λ} kJ mol ⁻¹
LiCl	893	16.75	0.115	7.76
	923	17.35	0.111	8.32
NaCl	1083	14.13	0.137	11.92
	1123	14.81	0.130	12.04
CsCl	933	7.10	0.272	17.7
	983	8.06	0.239	20.9
UCl ₄	873	1.18	4.09	25.8
	923	1.41	3.41	22.8

The values of relative mobilities, u_{+-} , in molten UCl₄ are 10 times lower than those in molten LiCl or NaCl and 5 times lower than those in molten CsCl. Values of friction coefficients in molten UCl₄ are more than 30 times higher as compared to those in molten LiCl and 15 times higher than those in molten CsCl. These facts and the relatively high value of activation energy of electric conductance in molten UCl₄ suggest a considerable contribution of anionic conductance, in contrast with molten alkali chlorides, particularly LiCl and NaCl, with predominant cationic conductance [16].

The dependences of the specific and molar conductances on concentration at comparative temperatures $T = 1.05 T_1$ show more similarities to the liquidus curves of the investigated systems than the corresponding isotherms of these properties. The dependence of the molar conductance Λ on concentration for the system LiCl—UCl₄ shows a local maximum at the composition of Li₂UCl₆ (Fig. 3). In the systems RbCl—UCl₄ and CsCl—UCl₄ the curves of the specific and molar conductance vs. concentration at comparative temperatures show a course similar to liquidus curves on the phase diagrams of these systems [1] (Figs. 4 and 5).

The same resemblance between curves of specific (κ) and molar (Λ) conductances vs. concentration at comparative temperatures and the liquidus curves on the phase diagrams of the systems NaCl—RbCl, PbO—Bi₂O₃, and PbO—PbMoO₄ was observed by Morris and Mazumder [17]. The occurrence of maxima on the dependences of κ and Λ vs. concentration at composition corresponding to the compound M₂UCl₆ which are related with minima observed on the isotherms of activation energy of molar conductance in the same range of concentration, may be the evidence of a quasi-lattice retention of this compound in molten state. From the studies of relative mobilities of cations in binary nitrate and chloride systems it follows that relative mobility of cation is, as a rule, the highest in its mother quasi-lattice [18, 19].

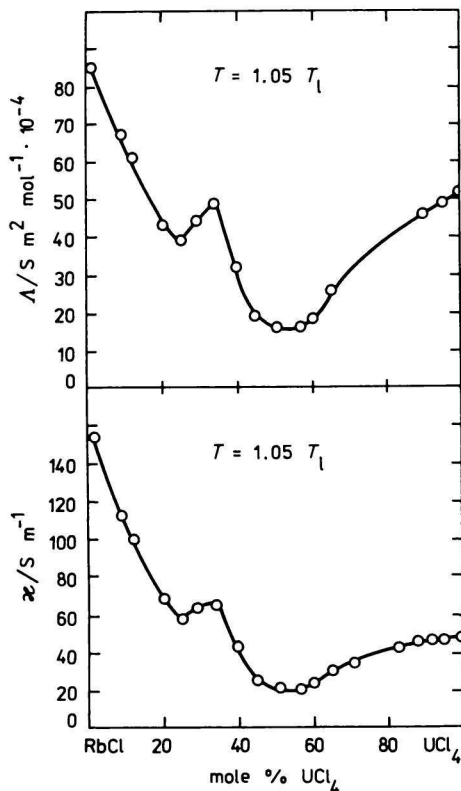


Fig. 4. Dependence of the specific electric conductance, κ , and molar conductance, Λ , on the concentration at comparative temperatures $T = 1.05 T_1$ in the RbCl— UCl_4 system.

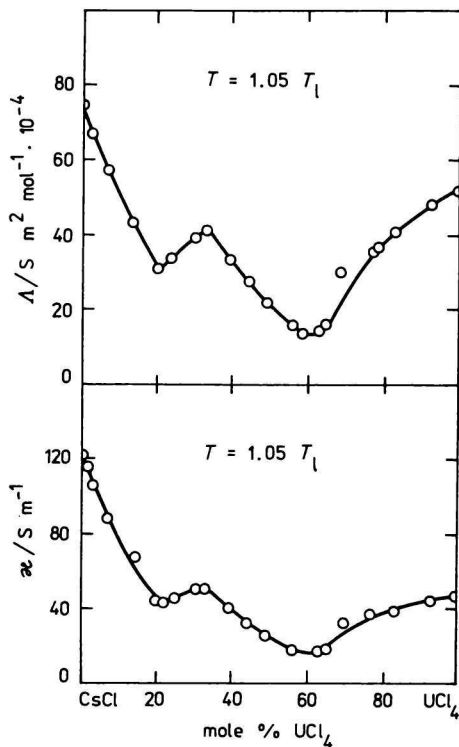


Fig. 5. Dependence of the specific electric conductance, κ , and molar conductance, Λ , on the concentration at comparative temperatures $T = 1.05 T_1$ in the CsCl— UCl_4 system.

It can be assumed that the structure of molten M_2UCl_6 compounds is similar to that in the solid state and the M^+ cations have a high migration ability. The theoretical values of cationic conductance calculated by means of the Nernst—Einstein equation support the above hypothesis. The cationic character of the electric conductance of molten compounds of the type M_2UX_6 ($\text{X} = \text{Cl}, \text{Br}$) can also be proved by comparison of electric conductance values of molten chlorides and bromides containing 33 mole % of uranium(IV) halide. The values of electric conductance of bromides are insignificantly lower (by ca. 5%) than the conductance values of corresponding chlorides [20]. Thus it is evident that in the range of high concentrations of alkali chlorides the electric conductance of molten MCl—UCl_4 mixtures exhibits a distinct cationic character.

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