Viscosity of Molten Rare Earth Metal Trichlorides
I. $CeCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$ and $ErCl_3$

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The kinematic viscosity of molten $CeCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$ and $ErCl_3$ has been measured by using a capillary viscometer. The dynamic viscosity was computed by using density data taken from the literature. The viscosity increases with going from $CeCl_3$ to $ErCl_3$. The activation energy of the viscous flow, calculated by the Arrhenius equation, rises in the same order.

Key words: Viscosity; Molten Salts; Rare Earth Metal Chlorides.

1. Introduction

Knowledge of the viscosity of rare earth halides is important for the electrolytic production and separation of the rare earth elements [1 – 3]. However, essential difference is observed between the viscosity values of the same molten rare earth salts obtained experimentally by various researchers. As a rule, the viscosity of their halides was measured with reliable experimental methods checked repeatedly on studying other molten salts. In our opinion, there are two main reasons for the discrepancies in the results of the viscosity measurements. The first is inadequate dehydration of the salts, resulting in the formation of oxyhalide impurities. The second is a not sufficiently inert gas atmosphere over the salts during handling or measurements, leading to the same effects, especially at higher temperatures.

In this study, the kinematic viscosity of molten $CeCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$ and $ErCl_3$ was measured, using a capillary viscometer made of quartz and a transparent electric furnace. The dynamic viscosity (η) has been calculated from the measured kinematic viscosity (ν) and density data taken from the literature.

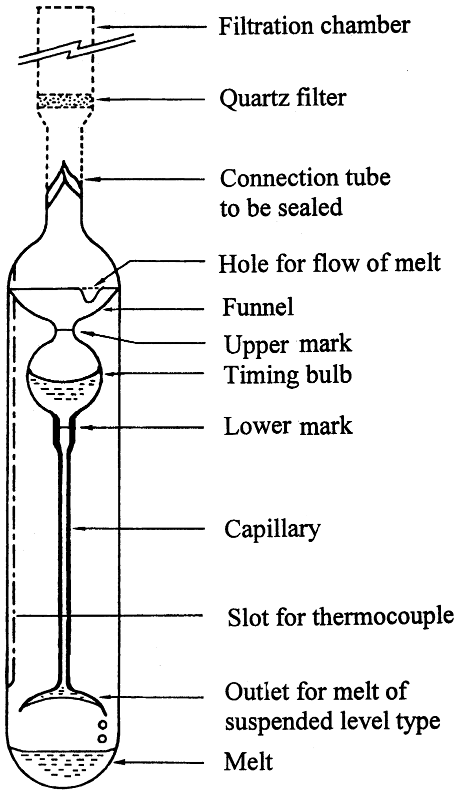

Fig. 1. The capillary viscometer made of quartz.

2. Experimental

2.1. Apparatus

The used capillary viscometer, entirely made of quartz, is shown in Figure 1. The capillary of 0.4 mm inner diameter was about 6 cm long. The capacity of the timing bulb was about 3 to 4 ml. The efflux time ranged from 100 to 600 s. The temperature was uniform within 0.5 K around the viscometer, sitting in a transparent Gold Furnace. The steel frame with the furnace could be rotated by 180° in order to enable for repeated measurements with the same melt. For more details see [4].

2.2. Chemicals

Anhydrous lanthanide chlorides were synthesized from corresponding oxides (99.9%) supplied by Soekawa Chemicals (Japan). The oxides were dissolved in concentrated HCl with subsequent crystallization of the hydrates $LnCl_3 \cdot 6H_2O$ (Ln = Ce, Nd, Sm, Dy, Er). Subsequent dehydration was carried out in an apparatus depicted in Figure 2. Most of the water was removed by heating for 40 hrs in a flow of dry N_2 up to 450 K. The resulting product is $LnCl_3 \cdot (1\text{-}2)H_2O$. Then the N_2 flow was replaced by a flow of dry HCl, and

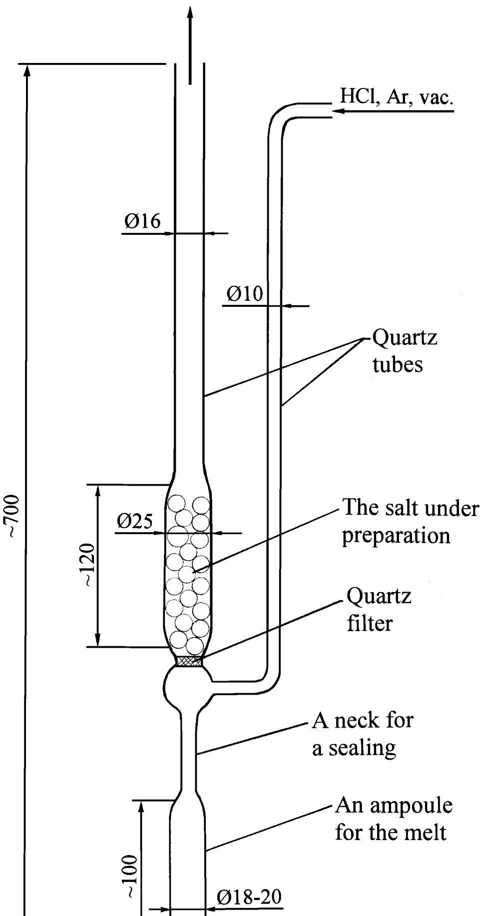

Fig. 2. Apparatus for dehydration of rare earth chlorides.

the salt was further heated up to melting. It is very important to perform the dehydration slowly to prevent the formation of oxichlorides. Gaseous HCl has low chlorinating activity and do not convert oxichlorides to pure chloride. So it is necessary to avoid oxichlorides formation from the outset. Typically the salt was melted after 3 – 10 days. After melting, HCl was further passed through the melt for ∼ 1 hr, and then it was replaced by argon for another hr. Then the melt was filtrated through the quartz filter shown in Figure 2 and the ampoule containing the salt was sealed off under vacuum. Finally, the anhydrous salt was distilled under vacuum to separate it from possible oxichlorides.

Solubility tests [5] were made in every stage. About 0.5 g of the salt were dissolved in 3 – 4 cm^3 distilled water. The solution is absolutely transparent or has a weak opalescence when oxichlorides are absent. In several cases, especially for the heavy lanthanides, hydrolysis occurs during the dissolution with hydroxide formation. In this case, 1 – 2 drops of concentrated HNO_3 were enough to suppress hydrolysis. If the solution still remained opaque after 2 drops of HNO_3, the content of oxichlorides was considered to be too high.

2.3. Procedure

In the vertical type of capillary viscometer the viscosity, η, is expressed by the well-known Hagen-Poiseuille's equation

$$\eta = \frac{\pi r^4 \rho g h}{8(L+nr)V} t - \frac{m\rho V}{8\pi(L+nr)} \frac{1}{t}, \tag{1}$$

where ρ is the density of the liquid, r and L are the radius and length of the capillary, h is the effective height of the liquid column, V the volume of the timing bulb, g the gravitational acceleration, t the time interval of the flow of liquid, and m and n are constants. For a given viscometer, the quantities in the right-hand term of (1), except t and ρ, are constant. Therefore, by introducing the kinematic viscosity ν, one can write

$$\nu = \eta/\rho = C_1 \cdot t - C_2/t, \tag{2}$$

The constants C_1 and C_2 may be determined by calibration with standard liquids. We used distillated water as a liquid of well-known viscosity. The efflux time was measured by visual observation with a digital stopwatch having 0.01 s accuracy. Temperature ranged between 2 and 65 °C.

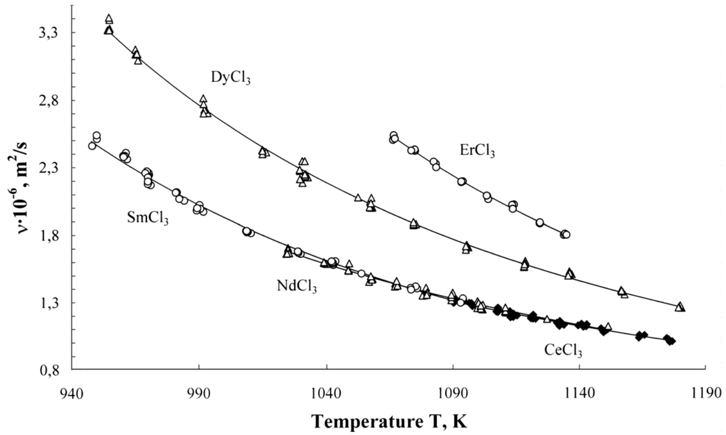

Fig. 3. Kinematic viscosity of molten $CeCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$ and $ErCl_3$.

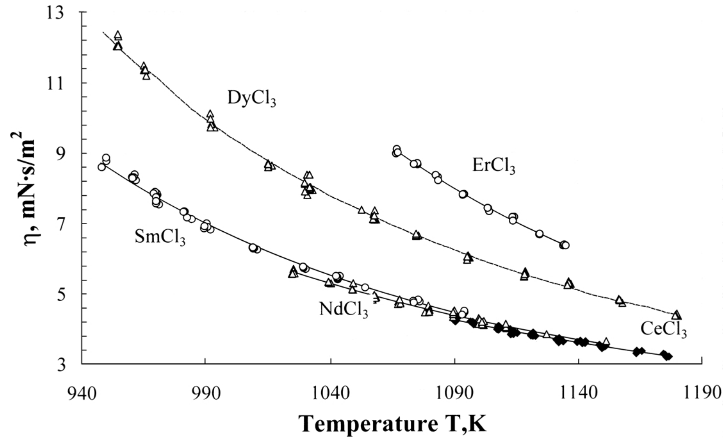

Fig. 4. Dynamic viscosity of molten $CeCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$ and $ErCl_3$.

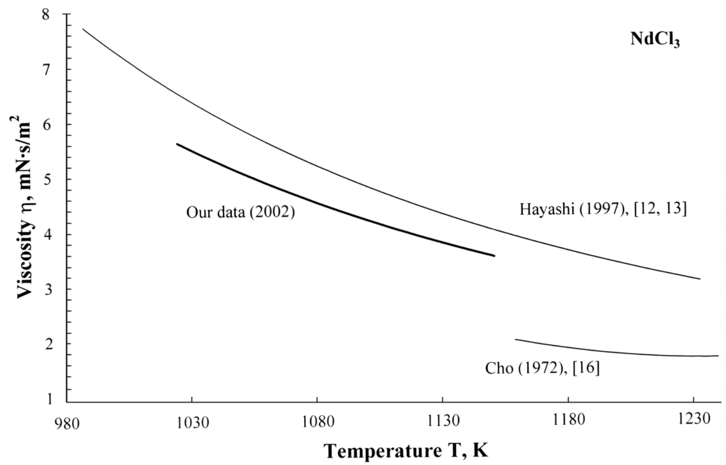

Fig. 5. Published viscosity data on molten $NdCl_3$.

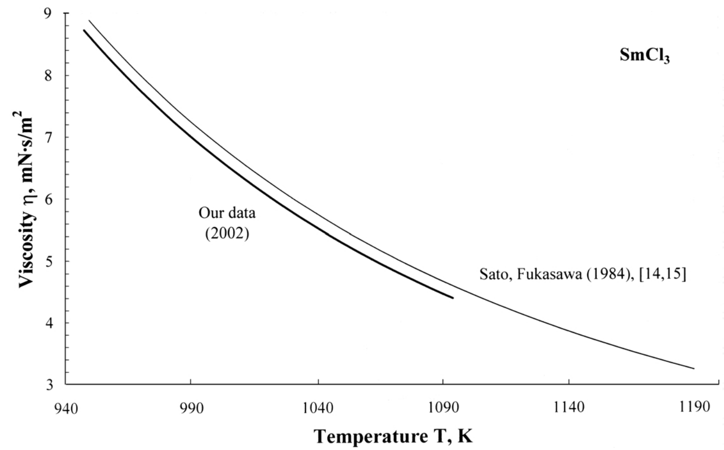

Fig. 6. Published viscosity data on molten $SmCl_3$.

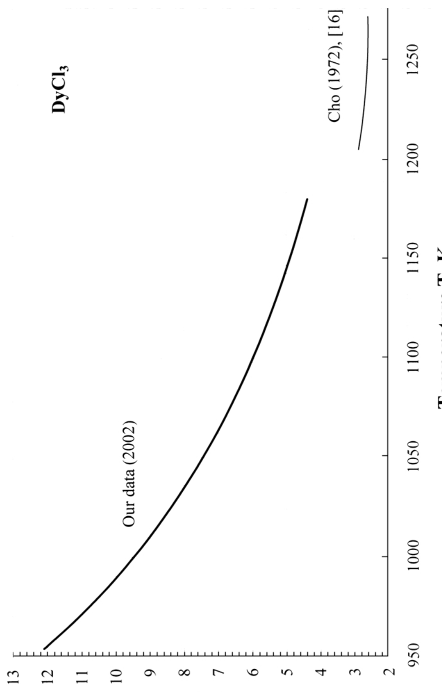

Fig. 7. Published viscosity data on molten $DyCl_3$.

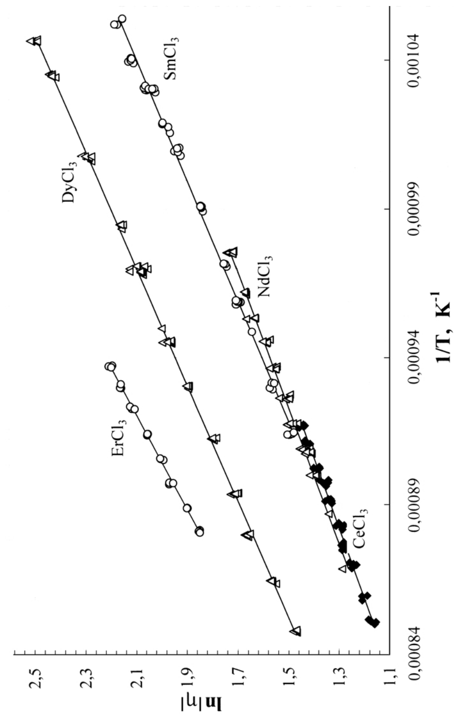

Fig. 8. Plot of ln $|\eta|$ *vs* 1/T for molten rare earth chlorides.

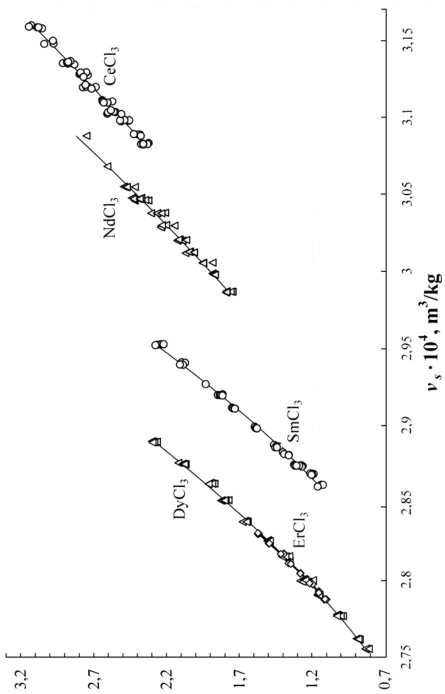

Fig. 9. Correlation between fluidity, $1/\eta$ and specific volume v_s for molten rare earth chlorides.

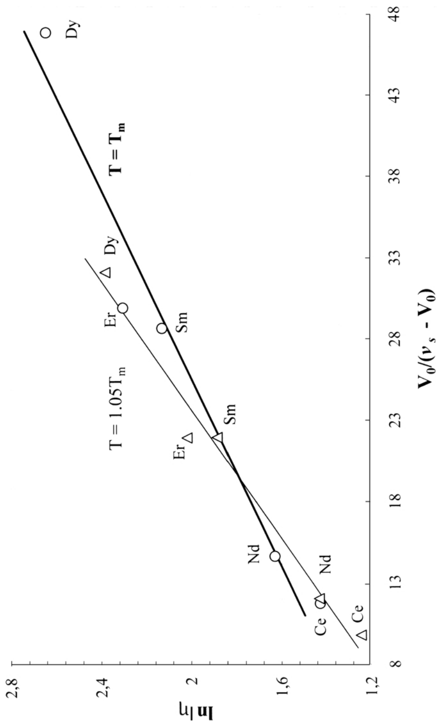

Fig. 10. Dependence of ln $|\eta|$ on the ratio of hard sphere volume, V_0 to hole volume $(v_s - V_0)$ for five molten rare earth chlorides.

Table 1. Kinematic viscosities $\nu = A \cdot \exp(E_{A/RT})$ of molten rare earth chlorides. R = 8.31441 J/(K· mol).

Salt	$A \cdot 10^{-6}$, m^2/s	E_A J/mol	Temperature range, K
$CeCl_3$	0.039180	31787.5	1090 – 1177
$NdCl_3$	0.032544	33604.7	1025 – 1151
$SmCl_3$	0.018101	38823.3	948 – 1094
$DyCl_3$	0.021089	40140.8	954 – 1180
$ErCl_3$	0.0090129	49976.1	1067 – 1135

Table 2. Densities (ρ) of molten rare earth chlorides used for the calculation of dynamic viscosities. $\rho = \rho_0 - \rho_1 \cdot 10^{-4} \cdot T$ g/cm^3 (T/K).

Salt	ρ_0	ρ_1	Ref.
$CeCl_3$	4.248	9.20	[6]
$NdCl_3$	4.2379	8.6745	Mean value of [7] and [8]
$SmCl_3$	4.2048	7.472	[9]
$DyCl_3$	4.34418	7.4828	Mean value of [7] and [10]
$ErCl_3$	4.4406	7.991143	[11]

Prior to the measurement, the sample salt was fed into a filtration chamber under vacuum. Then it was heated and filtrated. The filtration chamber was sealed off from the viscometer. Thus any contact of the sample with the atmosphere was excluded during all handling and the measurements. For more details see [4].

3. Results and Discussion

The experimental kinematic viscosity values are listed in the Supplementary Table. They are well approximated by the Arrhenius equation, the coefficients of which are shown in Table 1.

The kinematic viscosities, ν, of $CeCl_3$, $NdCl_3$ and $SmCl_3$ differ little, while for $DyCl_3$ and $ErCl_3$ ν is higher, see Figure 3.

The dynamic viscosity, η is

$$\eta = \nu \cdot \rho, \qquad (3)$$

were ρ is the density.

The densities used are shown in Table 2, [6 – 11].

The obtained dynamic viscosities are shown in Figure 4. The same tendency as in case of the kinematic viscosity is observed. For example, dynamic viscosities of $CeCl_3$, $NdCl_3$ and $SmCl_3$ coincide within 1.6% at 1100 K. Dynamic viscosities of $DyCl_3$ and $ErCl_3$ are essentially higher than others.

For the viscosities of molten $CeCl_3$ and $ErCl_3$ no literature data were found. Our data on the viscosity $NdCl_3$, $SmCl_3$ and $DyCl_3$ are compared with earlier ones in Figures 5 – 7. The viscosity of $NdCl_3$ measured in [12, 13] is 13.5 – 16.3% higher than our one.

Table 3. Dynamic viscosity of molten rare earth chlorides, $\eta = A \cdot \exp(E_{A/RT})$. R = 8.31441 J/(K · mol).

Salt	A, mN · s/m^2	E_A J/mol	Temperature range, K
$CeCl_3$	0.090841	34837.4	1090 – 1177
$NdCl_3$	0.081140	36123.0	1025 – 1151
$SmCl_3$	0.049990	40688.2	948 – 1094
$DyCl_3$	0.059842	42108.8	954 – 1180
$ErCl_3$	0.025026	52251.7	1067 – 1135

Table 4. Correlation between viscosity and specific volume (v_s of molten rare earth chlorides. Parameters of the Batschinsky's equation.

Salt	$\eta = C/(v_s - \omega)$		$v_s \cdot 10^4$, m^3/kg,
	C·10^7, m^2/s	$\omega \cdot 10^4$, m^3/kg	at $T = T_m$
$CeCl_3$	1.0101	2.8438	3.086
$NdCl_3$	0.97852	2.8130	3.005
$SmCl_3$	0.82061	2.7679	2.864
$DyCl_3$	0.92845	2.6827	2.740
$ErCl_3$	0.91676	2.6863	2.7760

Hayashi (see Fig. 5) used almost the same method as we did. However, if oxichlorides remained in the melt, they could be passed through the quartz filter and increased the apparent viscosity. The difference between viscosities of $SmCl_3$ measured now and earlier [14, 15] amounts to about 3.5%, that is close to the experimental error. It is difficult comment on the too low viscosities of $NdCl_3$ and $DyCl_3$ published in [16] because of the poor description of the sample preparation.

Plots ln $|\eta|$ *vs.* $1/T$ are shown in Figure 8. Straight lines are obtained for all melts in spite of the wide temperature range (226 K for $DyCl_3$).

As was shown by Batschinsky [17], the dynamic viscosity η of molten salts is connected with their specific volume v_s by the equation

$$\eta = C/(v_s - w), \qquad (4)$$

where C and w are constants.

The relation between the fluidity $1/\eta$ and v_s of our melts is shown in Figure 9. The difference ($v_s - \omega$) is kind of a "free" volume. The parameters of Batschinsky's equation are given in Table 4.

It is a well-known opinion that the fluidity is proportional to the "free" volume of the liquid. Higher "free" volume indicates looser structure of liquid. The hard sphere volume V_0 is independent of the temperature, whereas the specific (v_s) or molar (V_m) volume depends on temperature. Thus the difference ($v_s - V_0$) or ($V_m - V_0$) directly characterizes fluidity. Based on such ideas, it can be expected that the viscosity of molten

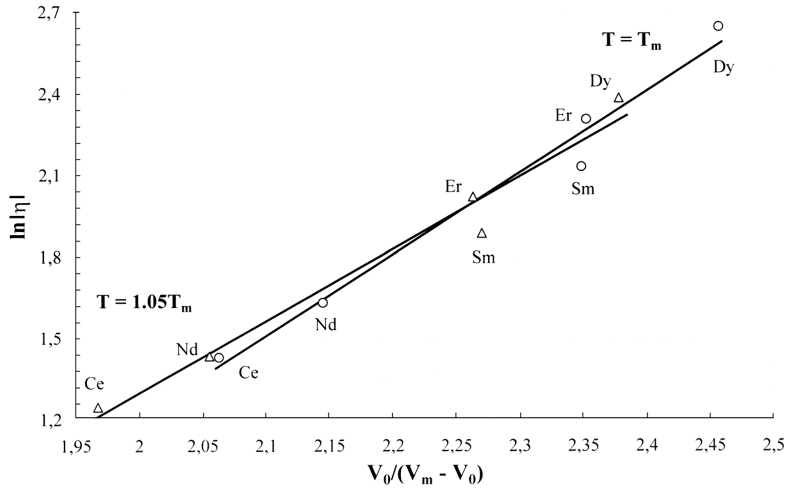

Fig. 11. Plot of $\ln|\eta|$ *vs.* $V_0/(V_m - V_0)$ for molten rare earth chlorides.

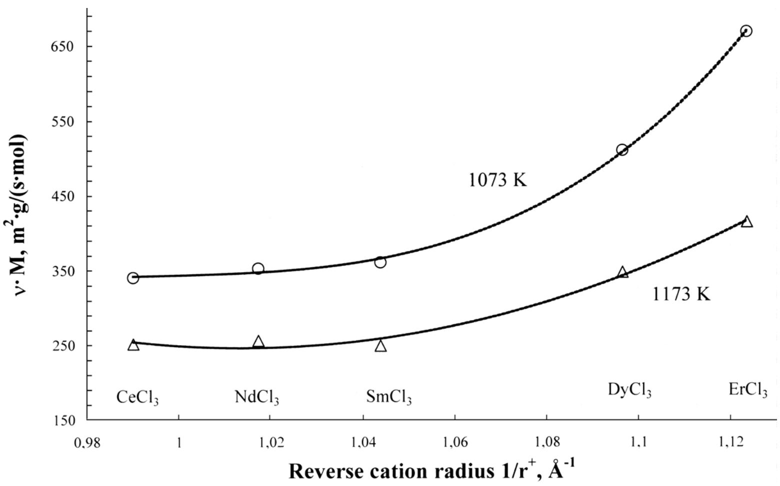

Fig. 12. Molar viscosity ($\eta \cdot V_m$) of molten rare earth chlorides *vs* $1/r^+$ of the cations.

salts is proportional to the ratio of V_0 to the "free" volume. Indeed, linear dependencies were derived in the $\ln|\eta|$ *vs.* $V_0/(v_s - V_0)$ and $\ln|\eta|$ *vs.* $V_0/(V_m - V_0)$ plots, as shown in Figs. 10 and 11.

A further essential step forward could be made to the understanding of the results obtained. It is associated with going from the dynamic viscosity to the molar one which refers to a mole of matter. The molar viscosity allows to compare different salts by the energy of interaction between particles involving complex ions. This parameter (η_M is the product of the dynamic viscosity and the molar volume V_m or, what is the same, the product of the kinematic viscosity and the molar mass M: $\eta_M = \eta \cdot V_m = \nu \cdot M$. As illustrated in Fig. 12, there is a correlation between the molar viscosity and the reverse radius of rare earth cation that may be used for estimating the viscosity of unstudied rare earth chlorides lying between cerium trichloride and erbium trichloride.

4. Conclusion

Viscosity of five molten rare earth chlorides has been measured. In all cases, the viscosity decreases with increasing temperature in the manner of the Arrhenius relationship. A straight correlation between the fluidity and the "free" volume was observed. This means validity of Batschinsky equation. Viscosity gradually increases in a row of lanthanides from $CeCl_3$ to $ErCl_3$ due to the decreasing cation size and increasing Coulomb interaction between the rare earth cation and the chloride anion.

Sublementary Table. Kinematic viscosities (ν, m^2/s) of molten rare earth chlorides. Initial data.

$CeCl_3$		$NdCl_3$		$SmCl_3$		$DyCl_3$		$ErCl_3$	
t, ^0C	$\nu \cdot 10^{-6}$	t, ^0C	$\nu \cdot 10^{-6}$	t, ^0C	$\nu \cdot 10^{-6}$	t, ^0C	$\nu \cdot 10^{-6}$	t, ^0C	$\nu \cdot 10^{-6}$
867.7	1.136	878.2	1.119	821	1.327	757.8	2.344	793.6	2.500
834.6	1.255	854.1	1.173	820.1	1.294	757.9	2.182	793.9	2.535
834.2	1.228	826.8	1.306	708.5	2.114	756.9	2.271	794.3	2.509
834.9	1.256	826.7	1.255	708.3	2.115	756.9	2.210	802.3	2.418
835.1	1.240	827.2	1.294	708	2.112	756.8	2.280	802.2	2.429
834.8	1.225	828.1	1.270	697.6	2.245	779.7	2.074	800.8	2.420
824.4	1.291	816.5	1.313	697.4	2.258	681.5	3.315	810.5	2.322
824.5	1.286	816.7	1.338	696.9	2.248	682.2	3.392	809.6	2.338
823.5	1.294	816.5	1.336	696.7	2.270	682.3	3.327	810.6	2.296
824.8	1.269	817	1.370	696.1	2.257	682.1	3.315	820.5	2.185
817	1.300	816.5	1.354	689	2.361	682	3.409	821.1	2.191
817.4	1.293	806	1.350	688.5	2.408	693.4	3.092	820.5	2.190
818.2	1.322	805.1	1.348	688.1	2.385	693.2	3.136	830.7	2.083
817.7	1.301	806.5	1.408	687.4	2.384	692.4	3.173	831.1	2.059
817.4	1.318	807	1.371	687.6	2.377	692.4	3.135	830.5	2.085
817.5	1.302	806.8	1.353	677.1	2.511	693	3.141	841.2	2.019
840.9	1.212	795.2	1.428	677	2.539	720.6	2.702	840.5	2.017
839.5	1.231	794.3	1.440	675.3	2.460	719.7	2.732	840.7	1.987
839.7	1.185	794.2	1.416	675.2	2.460	719.3	2.727	851.4	1.882
841.2	1.207	795.2	1.422	698.2	2.167	718.9	2.812	851.2	1.884
840.8	1.188	794.9	1.458	697.3	2.189	719	2.770	851.4	1.887
842.3	1.198	784	1.451	697.3	2.226	719	2.700	860.8	1.797
849.6	1.173	785.1	1.473	697.1	2.176	743.7	2.410	861.3	1.805
848.6	1.174	785.4	1.473	697.1	2.195	742.1	2.426	861.9	1.797
848.7	1.204	785.1	1.467	718.8	1.971	742.2	2.397		
847.8	1.189	784.7	1.493	717.3	2.020	742.2	2.429		
847.8	1.177	776	1.534	717.6	1.993	742.2	2.420		
859.3	1.135	776	1.538	716.2	1.980	760	2.223		
859	1.120	776.2	1.590	716.4	1.997	759.2	2.246		
859.2	1.157	775.8	1.538	737.6	1.814	759	2.233		
859.3	1.131	775.8	1.537	736.4	1.824	758.8	2.245		
858	1.144	767.3	1.586	736	1.821	758.8	2.344		
860.8	1.128	766.5	1.590	735.7	1.829	785.4	1.998		
868.5	1.114	766.2	1.596	735.9	1.831	784.9	1.997		
868.3	1.118	766.3	1.599	757.1	1.660	784.4	2.000		
869.8	1.133	766.3	1.598	756.2	1.668	784.3	2.002		

$CeCl_3$		$NdCl_3$		$SmCl_3$		$DyCl_3$		$ErCl_3$	
t, ^0C	$\nu \cdot 10^{-6}$	t, ^0C	$\nu \cdot 10^{-6}$	t, ^0C	$\nu \cdot 10^{-6}$	t, ^0C	$\nu \cdot 10^{-6}$	t, ^0C	$\nu \cdot 10^{-6}$
869.6	1.117	752.2	1.704	756.1	1.679	784.5	2.042		
866.4	1.124	752.2	1.692	756	1.678	785	2.071		
876	1.086	751.5	1.660	781	1.513	784.8	2.031		
876.4	1.073	752.6	1.665	770.8	1.605	802.6	1.877		
877	1.084	751.8	1.663	770	1.577	801.9	1.874		
875.4	1.102	828.9	1.280	769.9	1.578	801.6	1.871		
877.9	1.093	828.8	1.245	769.8	1.595	801.6	1.878		
877.3	1.087	828.1	1.251	769.8	1.589	801.6	1.878		
890.3	1.032	828.1	1.273	769.7	1.595	801.6	1.892		
890.5	1.054	838	1.220	769.3	1.605	823.2	1.706		
892.5	1.053	837.5	1.227	803	1.401	822.6	1.724		
903.5	1.007	837.7	1.231	802.4	1.417	822.6	1.717		
902.1	1.020	837.7	1.259	800.4	1.406	822.2	1.689		
901.3	1.030			800.6	1.392	822.3	1.718		
902	1.022			821.1	1.316	822.3	1.715		
902.5	1.001			820.6	1.301	845.1	1.559		
				821	1.327	845	1.559		
				820.1	1.294	845.1	1.564		
						845.6	1.604		
						845.5	1.586		
						845.3	1.579		
						863.9	1.506		
						862.9	1.515		
						863	1.527		
						863.1	1.515		
						862.5	1.495		
						884.7	1.355		
						883.9	1.375		
						883.3	1.388		
						883.5	1.377		
						883.5	1.383		
						907.2	1.254		
						906.6	1.261		
						906.7	1.273		
						906.2	1.263		
						906	1.256		

[1] Y. Yamamura, I. Wu, H. Zhu, M. Endo, N. Akao, M. Mohamedi, and Y. Sato, Molten Salt Forum **5 – 6**, 355 (1998).

[2] T. Ogawa, S. Yamagishi, F. Kobayashi, A. Itoth, T. Mikaiyama, and M. Handa, Proceeding of International Conference on Evaluation of Emerging Nuclear Fuel Cycle System, Versailles, France, 11 – 14 September 1995.

[3] J. Millat, J. H. Dymond, and C. A. Nieto de Castro, Transport Properties of Fluids. Their correlations, prediction and estimation. IUPAC, Cambridge University Press, 1996.

[4] Y. Sato, M. Fukasawa, and T. Yamamura, Int. J. Thermophys. **18**, 1123 (1997).

[5] N. M. Kulagin, D. M. Laptev, and I. S. Astakhova, Russian J. Inorg. Chem. **21**, 1401 (1976).

[6] G. W. Mellors and S. Senderoff, J. Phys. Chem. **64**, 294 (1960).

[7] K. Cho, K. Irisawa, J. Mochinaga, and T. Kuroda, Electrochim. Acta **17**, 1821 (1972).

[8] J. Mochinaga and K. Irisawa, Bull. Chem. Soc. Japan **48**, 713 (1975).

[9] Y. Sato and T. Yamamura, Met. Rev. MMIJ. **9**, 100 (1992).

[10] J. Mochinaga and Y. Shimada, J. Fac. Eng. Chiba Univ. **25**, 123 (1973).

[11] K. Fukushima, T. Ikumi, J. Mochinaga, R. Takagi, M. Gaune-Escard, and Y. Iwadate, J. Alloys Comp. **229**, 274 (1995).

[12] H. Hayashi, Y. Okamoto, T. Ogawa, Y. Sato, and T. Yamamura, Molten Salt Forum **5 – 6**, 257 (1998).

[13] H. Hayashi, Y. Kato, T. Ogawa, and Y. Sato, Development of Viscometers for Molten Salts. JAERI-Tech 97-024, **6**, 40 (1997).

[14] Y. Sato, Unpublished data.

[15] M. Fukasawa, Bachelor thesis, Tohoku University, (1984).

[16] K. Cho and T. Kuroda, Denki Kagaku, **40**, 878 (1972).

[17] A. J. Batschinski, Z. Phys. Chem. **84**, 643 (1913).