Universal features in the viscosity behaviour of salt melts and their mixtures

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Abstract. Precision viscosity measurements of the salts RbCl, RbI, KI, NaI and their binary mixtures RbCl–RbI and KI–NaI were performed. Universal features of the viscosity behaviour of these melts are discussed together with the mixed nitrate $NaNO_3$ KNO_3 and $NaNO_3$–$RbNO_3$ melts in comparison with glass forming liquids.

1. Introduction

The viscosity of salt melts has been carefully measured before [1]. However many interesting melts and especially mixtures still remain not investigated. We have performed precise viscosity measurements of a family of alkali halides and their mixtures to be able to trace the universal features of salt melt viscosity behaviour in a broader context comparing them with other liquids. One of our aims was to bridge the gap between those melts and well known glass forming liquids.

2. Experimental section

The work has been performed with the oscillational viscometer developed by Tørklep and Øye [2]. In the experiment viscosity of molten RbI, RbCl, KI, NaI and their binary mixtures RbCl–RbI (0.58 mol% of RbI) and KI–NaI (0.58 mol% of NaI) have been determined within the temperature range from the melting point up to 900–1000 °C. Viscosity is calculated from the damping constant of an oscillating cylinder immersed into the melt. The automated viscometer assembly, check-ups, experimental procedure, working equations and the detailed error analysis have been described earlier [2, 3]. The total accuracy of the vicosity measurement is estimated to be about 0.3%. The samples of RbI, RbCl, KI, NaI were p.a.-grade chemicals from Merck (RbI, RbCl, NaI) and KEBO (KI). The salts were additionally dried under vacuum at 400 °C, melted in a nitrogen atmosphere and then allowed to crystallize at a slowly decreasing temperature (3 K h^{-1}). After that procedure the clear crystals were selected and used for the sample preparation. The purified salts were weighed out within a dry box into the platinum crucible to be used in the viscometer. The operating temperature of the viscometer was reached under a stream of highly purified nitrogen. After thermal stabilization, the damping and the period of oscillations in nitrogen were measured and compared with the results obtained in the separate experiments with an

empty furnace. Five measurements have been carried out at each temperature. At least 2.5 h were allowed for the temperature to stabilize after any temperature change.

The following density equations recommended by Janz [4] were used for the viscosity computation:

$$
\begin{array}{ll}
\text{RbCl} & \rho \ (\text{g cm}^{-3}) = 3.1210 - (0.8832 \times 10^{-3})T \ (\text{K}) \\
\text{RbI} & \rho \ (\text{g cm}^{-3}) = 3.9449 - (1.1435 \times 10^{-3})T \ (\text{K}) \\
\text{KI} & \rho \ (\text{g cm}^{-3}) = 3.3594 - (0.9557 \times 10^{-3})T \ (\text{K}) \\
\text{NaI} & \rho \ (\text{g cm}^{-3}) = 3.6274 - (0.9491 \times 10^{-3})T \ (\text{K}).
\end{array}
\tag{1}
$$

The density data of the binary salt mixtures not available in the literature were obtained experimentally by Archimedian weighing. The results of the measurement fit (with an accuracy not less than in [4]) led to the following linear expressions:

$$
\begin{array}{ll}
\text{RbCl–RbI (0.58 mol\% of RbI)} & \rho \ (\text{g cm}^{-3}) = 3.6792 - (1.0811 \times 10^{-3})T \ (\text{K}) \\
\text{KI–NaI (0.58 mol\% of NaI)} & \rho \ (\text{g cm}^{-3}) = 3.534 - (0.990\,18 \times 10^{-3})T \ (\text{K}).
\end{array}
\tag{2}
$$

3. Results and discussion

The resulting experimental viscosity data are presented in table 1. Every point here is the average of five or six independent measurements.

The results within the error bars may be also presented by the exponential equations (figure 1):

$$
\begin{array}{ll}
\text{RbCl} & \eta/T \ [\text{cP K}^{-1}] = 2.3031 \times 10^{-5} \exp(4065.92/T) \\
\text{RbCl–RbI} & \eta/T \ [\text{cP K}^{-1}] = 2.341\,43 \times 10^{-5} \exp(3928.23/T) \\
\text{RbI} & \eta/T \ [\text{cP K}^{-1}] = 2.380\,94 \times 10^{-5} \exp(3890.6/T) \\
\text{KI} & \eta/T \ [\text{cP K}^{-1}] = 2.3513 \times 10^{-5} \exp(3789.4/T) \\
\text{KI–NaI} & \eta/T \ [\text{cP K}^{-1}] = 3.163\,07 \times 10^{-5} \exp(3419.95/T) \\
\text{NaI} & \eta/T \ [\text{cP K}^{-1}] = 3.3256 \times 10^{-5} \exp(3367.79/T).
\end{array}
\tag{3}
$$

We prefer these, more correct, expressions for viscosity, in accordance with [5], rather than the usually applied simplified Arrhenius formula which omits T from the denominator. Figure 1 illustrates the validity of the expressions (3). The average deviations from the lines do not exceed the experimental error of the measurement.

Another convenient (but rarely used) way to present the viscosity data is to plot the fluidity (η^{-1}) against the temperature. In accordance with a well known Hildebrand–Batchinsky argument [6] for the high-temperature region a linear dependence of fluidity on temperature is expected for usual (nonglassifying) fluids. Figure 2 presents the fluidity of one of our mixtures as a function of temperature demonstrating the linearity of the asymptotic behaviour for the high-temperature region. This linearity (originating from the roughly linear dependence of fluidity on volume [6, 7, 8] and equations (1), (2) for volume
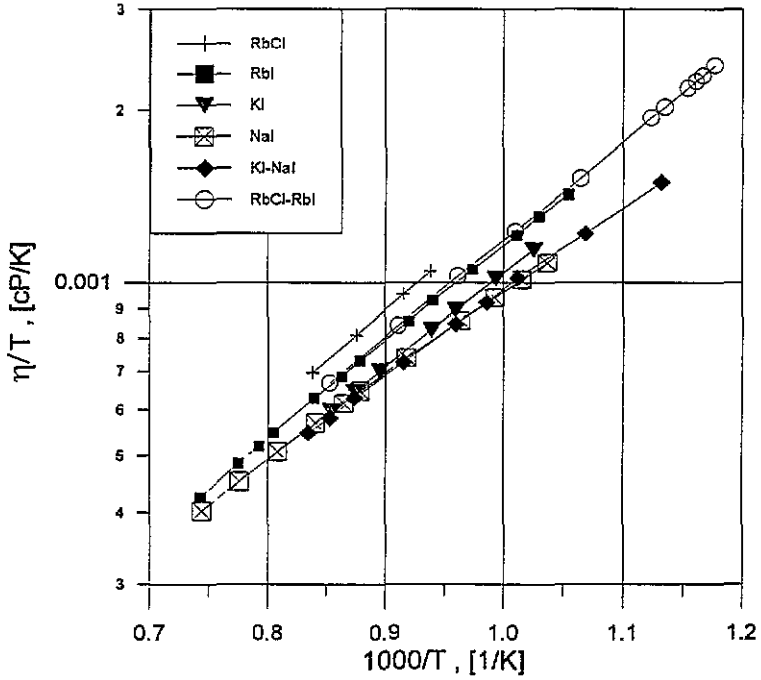
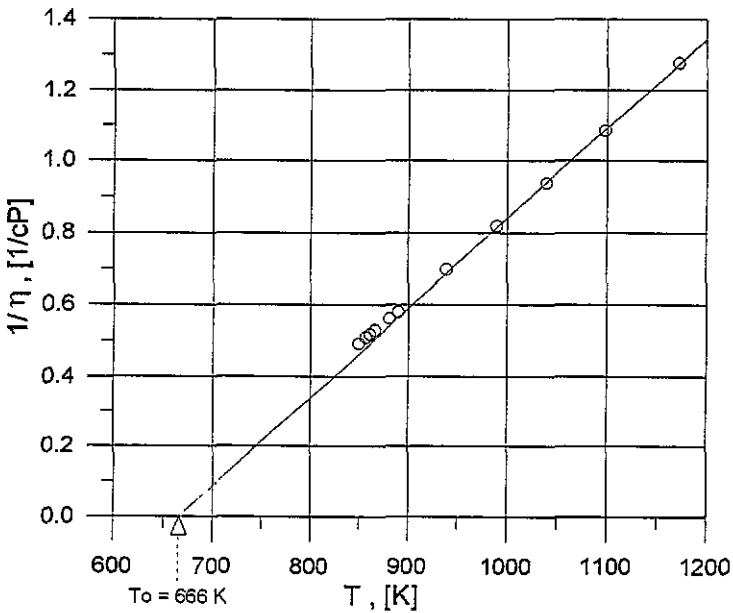**Figure 1.** Logarithmic plot of the viscosity for our experimental data.

Figure 2. Fluidity of RbCl–RbI against temperature. T_0 is the temperature where the asymptotic temperature dependence of fluidity predicts zero value.

dependence) is not in contradiction with the exponential formula (3) for viscosity of the liquids since the interval of our measurements is still rather narrow in comparison with the whole liquid state region.

Figure 2 demonstrates the way to estimate empirically a characteristic temperature T_0 where the extrapolated fluidity reaches its zero value. In fact the high-temperature mechanism of fluidity for a liquid [9] stops being valid at temperature higher than T_0 and one observes deviation from linearity as is obvious from figure 2 below 900 K. This happens when the packing of fluid is going to approach a value that interferes in some way with the diffusion motion. For salt melts such a temperature is situated usually well below the melting point. But this is different for glass forming liquids.

It has been shown by Taborek *et al* [9] in experiments with some glass formers that *the temperature T_0 derived in a similar way appears to be a significant point where the* temperature dependence of viscosity crucially changes its character. One will be able to see below that it can happen for some mixed salt melts as well.

Table 1. Experimental viscosity data.

Salt	T (K)	η (cP)	Salt	T (K)	η (cP)
KI	975.2	1.1153	RbCl	1065.4	1.1141
	1006.0	1.0227		1092.3	1.0412
	1041.4	0.9326		1142.6	0.9244
	1065.0	0.8800		1192.9	0.8297
	1117.0	0.7817			
	1144.3	0.7378	RbI	948.2	1.3560
	1171.0	0.6993		970.9	1.2710
				988.7	1.1999
NaI	964.1	1.0446		1026.4	1.0813
	984.3	0.9964		1063.2	0.9895
	1007.0	0.9472		1087.7	0.9281
	1037.5	0.8897		1138.7	0.8321
	1089.5	0.8042		1159.1	0.7944
	1138.4	0.7360		1191.2	0.7479
	1156.8	0.7110		1242.3	0.6793
	1189.7	0.6761		1261.7	0.6542
	1237.0	0.6272		1290.3	0.6246
	1288.5	0.5819		1345.6	0.5716
	1343.7	0.5403			
RbCl–RbI	849.6	2.0304	KI–NaI	869.8	1.3589
	856.9	1.9658		883.8	1.3286
	861.0	1.9319		935.8	1.1441
	866.3	1.8914		987.7	1.0064
	880.8	1.7813		1014.0	0.9363
	889.8	1.7264		1042.0	0.8809
	939.4	1.4324		1092.5	0.7913
	989.8	1.2214		1145.0	0.7210
	1039.6	1.0674		1172.6	0.6801
	1097.9	0.9223		1198.8	0.6552
	1172.6	0.7829			

The values of melting temperature T_m, extrapolated temperatures T_0 and their ratio for our salts are tabulated in table 2 (some other salt melts from the literature [1, 8] are given there for comparison).

One has to stress that T_0, generally speaking, does not coincide with the glassification point T_g. The temperature T_0 corresponds to the point of a crossover from an asymptotic diffusive (high-temperature) mechanism of viscous flow to a percolative one in accordance with other invesigators [10–13].
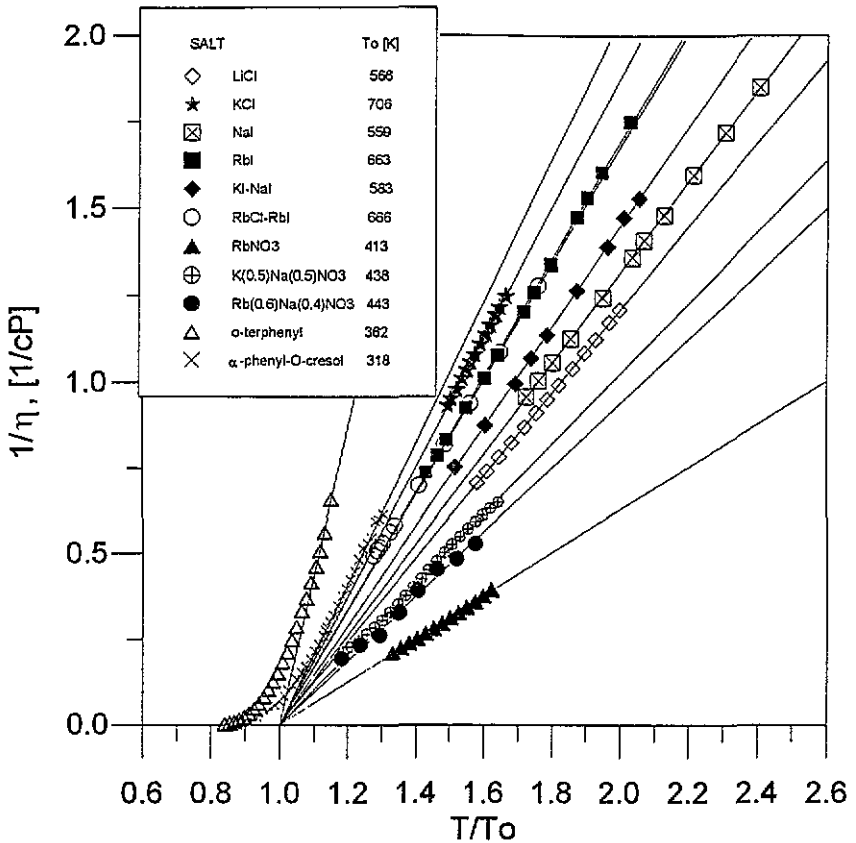

Figure 3. Fluidities of salt melts against reduced temperature.

Figure 3 presents the fluidity of a family of salt melts together with a few well known glassformers [14] to demonstrate the universal character of the asymptotic behaviour of different liquids at high temperature where the diffusion mechanism of fluidity prevails. One can also see the low-temperature deviations from this asymptotic behaviour for mixed salts with lower solidification temperatures. Thus the mixing of ions allows us to approach the range of glassification.

For the molten alkali halides the hard-sphere liquid model which has been successfully applied to liquid metals [15] and metal–metalloid glasses [16] can be used. For a hard-sphere liquid a convenient measure of density is the packing fraction ϕ—the part of the total volume of the system occupied by the spheres. If n is the total number density, x_i and r_i are mole fraction and radius of the i species, then

$$\phi = \frac{4\pi}{3} n \sum x_i r_i^3.$$

The melting point (as well as T_0) of a mixture depends on the packing fraction which can be efficiently varied by mixing ions of different sizes [17, 18]. A solidification temperature of a mixture is quite a complicated function of both the packing fraction of the liquid and a built-in disorder of the crystalline phase [17, 19]. This makes the ratio T_0/T_m not a universal figure (see table 2). This is also one of the possible reasons for the appearance of an anomalous T_0/T_m value exceeding unity for the $Rb_{0.6}Na_{0.4}NO_3$ mixture. This value suggests for $RbNO_3$–$NaNO_3$ and other mixtures that T_0 shifted considerably higher than the melting point as it is the case for the glass forming liquids. Indeed, the viscosities of $RbNO_3$–$NaNO_3$ mixtures reach unusually high values for salt melts [8]. Our resistivity measurements confirm the abnormal behaviour of $Rb_{0.6}Na_{0.4}NO_3$ [20]. We are preparing now precise viscosity measurements of this peculiar species.

In figure 4 the viscosity data of alkali halides together with some nitrates are plotted versus reduced temperature units i.e. η/T versus T_0/T. It turns out that all the graphs are straight lines with approximately the same slope. In our reduced scale this corresponds to the dimensionless relation

$$E_\eta/RT_0 = 5.9 \pm 0.1. \qquad (4)$$

Here E_η is the activation energy of viscous flow, R is the gas constant and T_0 is the extrapolated temperature from table 2.

Table 2. Melting and characteristic temperatures.

Salt	T_m (K)	T_0 (K)	T_0/T_m
LiCl[a]	883	566	0.64
NaCl[a]	1078	648	0.60
KCl[a]	1047	706	0.67
RbCl	993	694	0.70
CsCl[a]	917	655	0.71
NaI	934	559	0.60
KI	954	648	0.68
RbI	920	663	0.72
KI–NaI	853	583	0.68
RbCl–RbI	833	666	0.80
$NaNO_3$[b]	582	440	0.76
$RbNO_3$[b]	585	413	0.71
$K_{0.5}Na_{0.5}NO_3$[b]	495	438	0.89
$Rb_{0.6}Na_{0.4}NO_3$[b]	433	443	1.02

[a] Viscosity data from [1].
[b] Viscosity data from [8].

The equation (4) corresponds to the system of equations (3) where numerical values of E_η/R are written. As expected these values are roughly equal (with a coefficient from 1.1 to 1.3) to the estimated values of liquid–gas critical temperature T_c [4]. Thus (4) shows that in spite of the fact that the temperature T_0 is obtained in a quite formal way, it appears really to control the temperature dependence of viscosity at high temperature. It defines the low- and high-temperature intervals for the salt melts in their liquid state. The deviations of the data of different authors from each other exceed the differences between the substances in equation (4). Thus the found universal value of the slope (4) is really highly reliable.
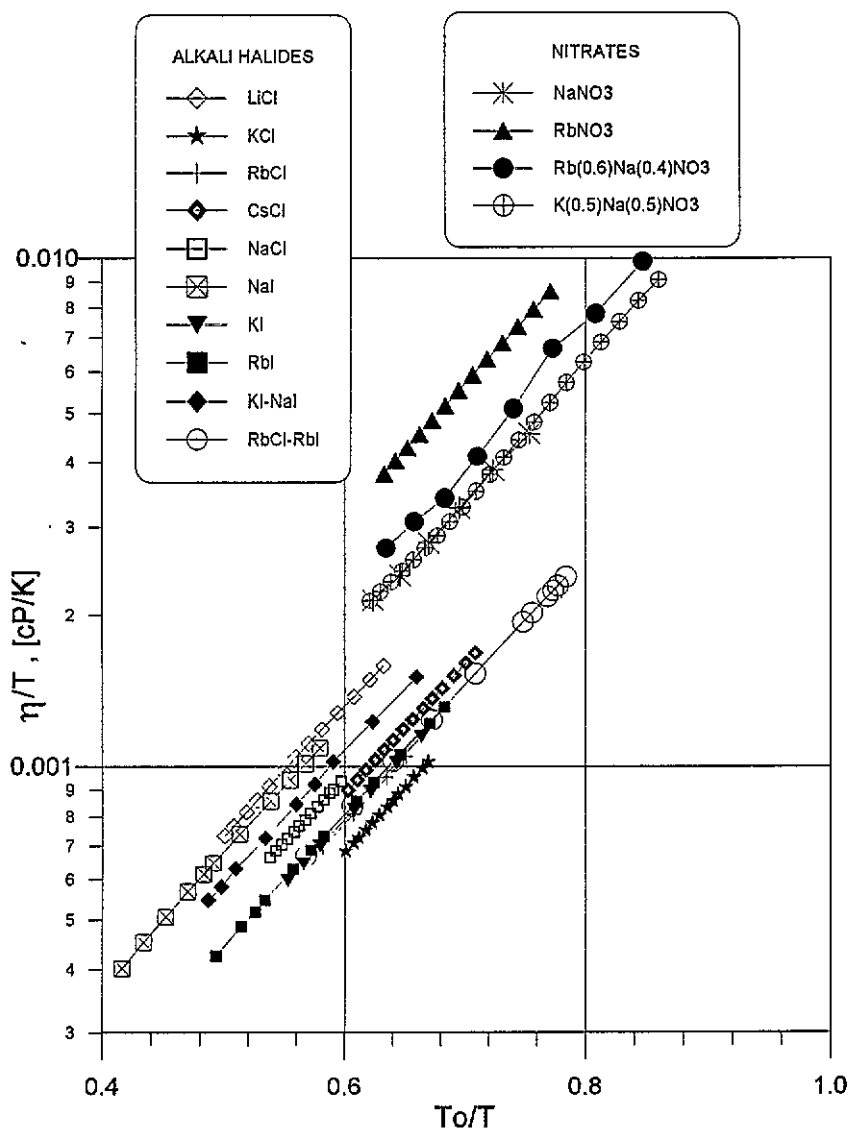
Figure 4. Viscosities of some alkali halides and nitrates as functions of the reduced temperature T_0/T.

4. Conclusions

1. Viscosity of the molten RbCl, RbI, KI, NaI and their mixtures RbCl(0.42)–RbI(0.58) and KI(0.42)–NaI(0.58) have been measured with high accuracy (0.3%).

2. The universal behaviour of the temperature dependence of viscosity in the high-temperature region has been found in scaled temperature units for all the salt melts. The activation energies of liquid flows happen to be roughly proportional to the liquid–gas critical temperatures.

3. Mixing of melts allows us to reduce the melting points and approach the crossover

regime where the diffusive mechanism of viscosity is about to change.

Acknowledgments

References

[1]   Brockner W, Tørklep K and Øye H A 1981 *J. Chem. Eng. Data* **26** 250
[2]   Tørklep K and Øye H A 1979 *J. Phys. E: Sci. Instrum.* **12** 875
[3]   Berstad D A, Knapstad B, Lamvik M, Skjølsvik P A, Tørklep K and Øye H A 1988 *Physica* A **151** 246
[4]   Janz G J 1967 *Molten Salt Handbook* (New York: Academic)
[5]   Frenkel Y I 1955 *Kinetic Theory of Liquids* (New York: Dover)
[6]   Hildebrand J H 1977 *Viscosity and Diffusion: A Predictive Treatment* (New York: Wiley)
[7]   Berg R F, Moldover M R, Rabinovich S and Voronel A 1987 *J. Phys. F: Met. Phys.* **17** 1861–6
[8]   Janz G J *et al* 1972 *J. Phys. Chem. Ref. Data* **1** No 3
[9]   Taborek P, Kleiman R N and Bishop D J 1986 *Phys. Rev* B **34** 1835
[10] Hunt A *Preprint*
[11] Sridhar S and Taborek P 1988 *J. Chem. Phys.* **88** 1170
[12] Hunt A 1992 *Solid State Commun.* **84** 701
[13] Quitmann D, Sokolov A P, Sokolov AA, Kisliuk A and Rössler E 1994 *Proc. 9th Int. Symp. on Molten Salts*
         (Pennington: Electrochem. Soc. USA)
[14] Cukiermann M, Lane J W and Uhlmann D R 1973 *J. Chem. Phys.* **59** 3639
[15] Protopapas P, Andersen H C and Parlee N A D 1973 *Chem. Phys.* **59** 15
[16] Hudson S and Andersen H C 1978 *J. Chem. Phys.* **69** 2323
[17] Voronel A, Rabinovich S, Kisliuk A, Steinberg V and Sverbilova T 1988 *Phys. Rev. Lett.* **60** 2402
[18] Berrebi D, Grigoryan L, Rabinovich S, Shasha E and Voronel A 1992 *J. Phys.: Condens. Matter* **4** 10 139
[19] Voronel A and Rabinovich S 1987 *J. Phys. F: Met. Phys.* **17** L193–6
[20] Shasha E and Voronel A 1995 in preparation