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LETTER TO THE EDITOR

Universal viscosity behaviour of regular and glassforming ionic meltsA Voronel[†], E Veliyulin[†], T Grande[‡] and H A Øye[‡][†] R and B Sackler School of Physics and Astronomy, Tel-Aviv University, 69978 Tel-Aviv, Israel[‡] Institutt for Uorganisk Kjemi, Norges Tekniske Høgskole, Universitetet i Trondheim, N-7034 Trondheim-NTH, Norway

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Abstract. Precise viscosity measurements of pure and mixed ionic melts (alkali halides and nitrates) have revealed their universal viscous behaviour. All the data are well presented by one curve which is compatible with an exponential formula at high temperatures but deviates from it in the low-temperature region. This deviation is still universal and agrees with the behaviour of glassforming liquids. The mixture $\text{Rb}_x\text{Na}_{1-x}(\text{NO}_3)$ bridges the gap between the regular and glassforming ionic melts.

Precise viscosity measurements were performed for 15 alkali halide and nitrate melts to find common trends and to compare their viscous properties with those of the known glassformer CKN ($[\text{Ca}(\text{NO}_3)_2]_{0.4}[\text{KNO}_3]_{0.6}$). The mixtures with depressed melting points seemed to be promising to cover the gap between the regular melts and glassformers. Thus the series of mixtures $\text{Rb}_x\text{Na}_{1-x}(\text{NO}_3)$ was prepared and studied in detail. The measurements were performed with the oscillational viscometer developed by Tørklep and Øye [1, 2]. The total accuracy in the obtained viscosity values was about 0.3%. Experimental details have been given elsewhere [3].

Our earlier investigation [3] showed that the viscosity of all the salts at high temperature may be well presented by the modified Arrhenius law:

$$\frac{\eta}{T} = \frac{B}{T_0} \exp\left(\frac{qT_0}{T}\right). \quad (1)$$

It was found [3] that on a semilogarithmic scale the slope $q = E_\eta/RT_0$ is a universal number for all the studied melts ($q = 5.9 \pm 0.1$) if the correct characteristic temperature T_0 for each of them has been chosen.

Figure 1 illustrates the easy way to find this parameter for a few melts. Indeed, the function (1) can be expanded into Taylor's series within the range of the liquid state. The first term of this expansion for the fluidity (η^{-1}) at medium temperatures above T_0 ($T_0 < T < 3T_0$, but not too close to T_0) is a linear function of temperature. Then the characteristic temperature T_0 may be rather accurately determined as a point where the extrapolation of this straight line from the higher temperature hits the zero fluidity value. This actually happens in the low-temperature region where the packing fraction of the liquid approaches a value that interferes with the diffusion motion. Thus the usual diffusive mechanism of viscous flow is gradually replaced by a percolative one [4]. While T_0 does not coincide with the critical temperature of the mode-coupling theory [5, 6], it is definitely

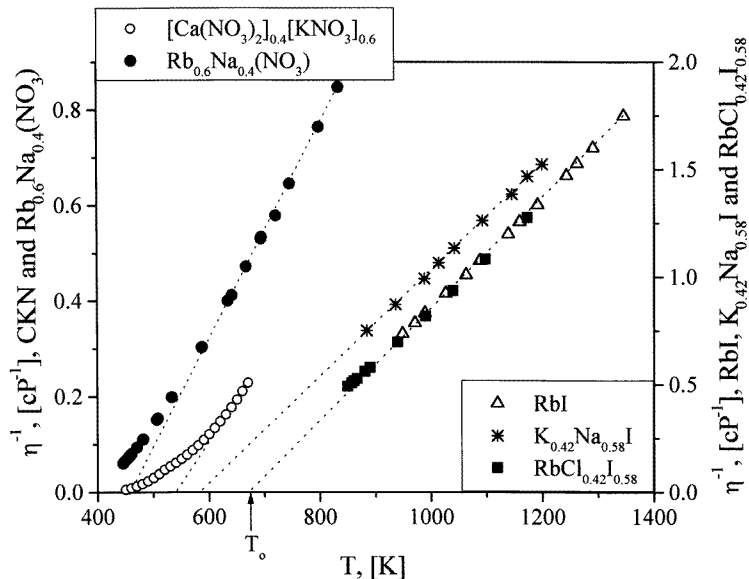


Figure 1. Fluidity as a function of temperature for some ionic melts. T_0 is the temperature where the extrapolated high-temperature linear dependence predicts a zero fluidity value.

closely related to it. For usual liquids the T_0 is situated well below the melting point, but this appears to be not the case for some of the $\text{Rb}_x\text{Na}_{1-x}(\text{NO}_3)$ mixtures. Their melting points have been found to be well below the corresponding characteristic temperatures T_0 . Only for these melts one can observe a significant deviation from (1), which is typical for glassforming liquids (see figure 1).

Table 1 presents the values of T_0 and other parameters of the equation (1) for all the

Table 1. Characteristic parameters for pure and mixed ionic melts.

Salt	T_m (K)	B (cP)	T_0 (K)	T_m/T_0	$q = E_\eta/RT_0$
NaI	934	0.0186	559	1.67	6.02
KI	954	0.0152	648	1.47	5.85
$\text{K}_{0.42}\text{Na}_{0.58}\text{I}$	853	0.0184	583	1.46	5.87
RbCl	993	0.0160	694	1.43	5.86
RbI	920	0.0158	663	1.39	5.87
NaNO_3	575	0.0264	432	1.33	5.95
$\text{RbCl}_{0.42}\text{I}_{0.58}$	833	0.0156	666	1.25	5.90
RbNO_3	583	0.0266	479	1.22	5.84
$\text{K}_{0.5}\text{Na}_{0.5}\text{NO}_3^{\text{a}}$	495	0.026 ^b	438	1.13	5.9 ^b
$\text{Rb}_{0.8}\text{Na}_{0.2}\text{NO}_3$	484	0.0245	465	1.04	5.97
$\text{Rb}_{0.7}\text{Na}_{0.3}\text{NO}_3$	449	0.0258	455	0.99	5.93
$\text{Rb}_{0.67}\text{Na}_{0.33}\text{NO}_3$	445	0.0248	459	0.97	5.95
$\text{Rb}_{0.63}\text{Na}_{0.37}\text{NO}_3$	447	0.0242	460	0.97	5.97
$\text{Rb}_{0.6}\text{Na}_{0.4}\text{NO}_3$	444	0.0245	457	0.97	5.97
$[\text{Ca}(\text{NO}_3)_2]_{0.4}[\text{KNO}_3]_{0.6}^{\text{a}}$	498	0.032 ^b	530	0.94	5.9 ^b

^a Viscosity data are from [7].

^b Estimated values.

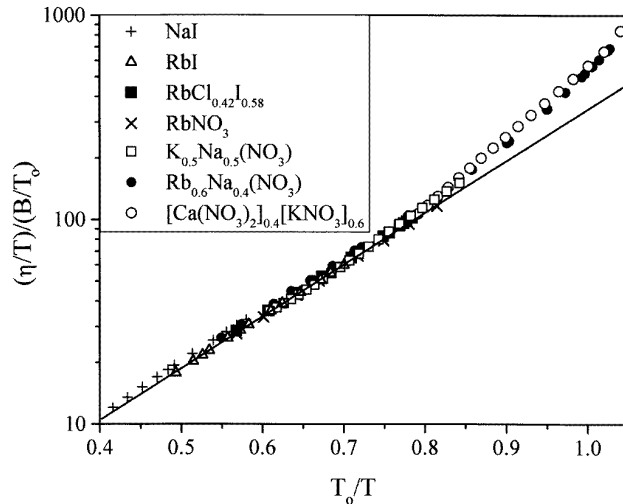


Figure 2. Viscosities of some alkali halides and nitrates against reduced temperature.

investigated melts found from the fit of our measurements. The table includes also a couple of melts from literature: in particular, the glassformer CKN. One can see that there is no noticeable gap in viscous properties between the other melts and the glassformer.

Figure 2 shows the universal graph for all the investigated melts. Some of them are not included for the sake of clearer presentation. The interesting feature of this graph is its universality even far beyond the domain of validity of the formula (1). Our mixtures $\text{Rb}_x\text{Na}_{1-x}(\text{NO}_3)$, being properly scaled, behave similarly to CKN in spite of the fact that both deviate considerably from (1). Usually CKN is presented by the Vogel–Fulcher equation [8], although this can hardly be applied to $\text{Rb}_x\text{Na}_{1-x}(\text{NO}_3)$. Actually, there is no straightforward way from (1) to the Vogel–Fulcher expression.

Our extended investigation has demonstrated the universal character of the temperature dependence of viscosity of all (pure and mixed) ionic melts including the glassformer CKN. It gives grounds to assume the basic similarity of the viscous flow mechanism in all of these melts. The mixture $\text{Rb}_x\text{Na}_{1-x}(\text{NO}_3)$ bridges the gap between the nonglassifying melts and CKN. It is interesting to note that the behaviour of $\text{Rb}_x\text{Na}_{1-x}(\text{NO}_3)$ does not differ (qualitatively or quantitatively) from that of CKN in spite of the obvious difference in the cation valency.

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