SHORT COMMUNICATIONS

VISCOSITY OF MOLTEN SILVER NITRATE*

By V. C. Reinsborough†

Viscosity measurements in molten silver nitrate were made to gain information on the structure of the melt, which e.m.f.,[1] specific heat,[2] electrical conductivity,[3] infrared,[4,5] and Raman spectrum[6,7] studies indicate is more complicated than molten salts ordinarily are. Viscosity data for silver nitrate reported in the literature do not cover the entire temperature range of interest or are not sufficiently refined.[8–11]

Experimental

A conventional, two-bulb Ubbelohde viscometer was employed following the principles and method of operation outlined by Bloom, Harrap, and Heymann.[12] Refinements and modifications will be discussed in a later paper. A molten-salt bath of approximately 100 lb of well-stirred HTS eutectic[13] served as the constant temperature medium. Temperature control could be maintained to $\pm 0{\cdot}02°$ at 250°. Calibration of the viscometer was carried out with 0·5M KCl solution using the data of Kaminsky.[14] No kinetic energy correction was found necessary. Individual runs showed a mean scatter of $\pm 0{\cdot}2\%$ in the melt.

The three samples of reagent grade silver nitrate used were recrystallized once from water shortly before use, filtered, and dried under partial vacuum while molten. Melts left for 24 hr showed no detectable changes in viscosity.

Results

The experimental results are presented as a graph of log viscosity (η in centipoise) against the reciprocal of the absolute temperature to test the system for Arrhenius viscosity behaviour, i.e. whether the equation $\eta = A\exp(E\eta/\mathbf{R}T)$ is obeyed. (T represents degrees absolute while temperatures in text are in degrees Centigrade.)

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The plot (Fig. 1) is seen to consist of two straight lines which intersect at $260 \pm 5°$. No abnormal increase of the viscosity was noted on approaching and passing through the melting point. The data can be represented by the equations:

$$\eta = 11 \cdot 37 \times 10^{-2} \exp(3 \cdot 62/\mathbf{R}T) \qquad (210\text{–}260°)$$

and

$$\eta = 21 \cdot 04 \times 10^{-2} \exp(2 \cdot 97/\mathbf{R}T) \qquad (260\text{–}310°)$$

(with activation energies of $3 \cdot 62 \pm 0 \cdot 08$ and $2 \cdot 97 \pm 0 \cdot 10$ kcal mole^{-1} respectively).

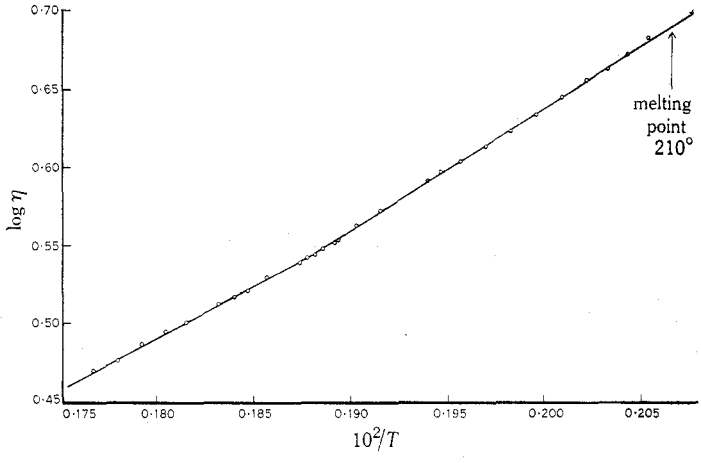

Fig. 1.—Temperature dependence of viscosity of molten silver nitrate.

These numbers are consistently 2–3% lower than those reported by Sundheim and Berlin,[8] but are in reasonable agreement with Pugsley and Wetmore[9] and the older work of Goodwin and Mailey[10] over the temperature ranges investigated by these authors (roughly 250–300°). Davis, Rogers, and Ubbelohde[11] claim continuity with Goodwin and Mailey,[10] although the Arrhenius equation in which their data are presented for the 210–250° range gives very low results.

Discussion

The point of intersection at $260 \pm 5°$ is to be compared with the transformation point of $270 \pm 5°$ noted by Bakes *et al.*[1] from e.m.f. measurements, although a further transition at 230° of opposite entropy sign reported by these authors was not detected in this investigation.

It is possible that the latter transition was associated with the solid silver halide/silver half-cell used in the e.m.f. investigation as the viscosity measurements should have been sensitive to an entropy change three times greater than that involved in the transition at 260°.

Other molten nitrate systems except lithium nitrate[11] give a straight-line Arrhenius viscosity plot (see, e.g., the recent careful work by Wellman, DeWitt,

and Ellis[15] with potassium nitrate). With silver nitrate, the two straight-line plots can be interpreted as indicating Arrhenius flow at all temperatures, but that at 260° the structural unit governing viscous flow increases in size on cooling through this temperature. Spooner and Wetmore[3] found that at 220° the Arrhenius activation for electrical migration was 3·3 kcal mole^{-1} while at 320° it had decreased to 2·7 kcal mole^{-1}. This was attributed to a diminution in structural forces in molten silver nitrate with increasing temperature. The E_η/E_Λ ratio for each temperature region is 1·10, which indicates that the species controlling viscous flow is affected in the same direction as the species controlling electrical flow on passing through the transition point.

It may be significant that lithium nitrate and silver nitrate, the two nitrates that do not show the one straight-line Arrhenius plot, are the only monovalent nitrates to show splitting of the ν_3 band in Raman[6,7] and infrared spectra.[4,5] Wilmshurst and Senderoff[4] attributed this to a loss of the threefold symmetry of the nitrate ion arising from the effect of the cation field, while Janz and James[6] further suggested that the interaction of Li^+ and Ag^+ ions leads to cubic close packing in the melt. Ion-pairing[16] and $Ag(NO_3)_2^-$ complexes[5] have also been proposed. In this regard, further temperature dependence studies of physicochemical properties of the silver nitrate melt should prove quite informative.

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