

tron transfer from the peroxo species to be oxidized occurs *through* the orbitals of the metal ion to the peroxo species to be reduced.<sup>41</sup> This mechanism is similar to the one proposed recently for systems with  $\text{Cu}(2,2'\text{-bipy})^{2+}$  as catalyst,<sup>7,42</sup> though in this system a

(41) In this connection it may be of interest to note that a cobalt(II) porphyrin is known to form a reversible  $\text{O}_2$  adduct: F. A. Walker, *J. Amer. Chem. Soc.*, **92**, 4235 (1970).

(42) H. Erlenmeyer, C. Flierl, and H. Sigel, *ibid.*, **91**, 1065 (1969).

cis arrangement of  $\text{H}_2\text{O}_2$  and  $\text{OOH}^-$  is possible, while in the present case with  $\text{Co}^{\text{II}}\text{HP}$  only a trans arrangement can occur.

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CONTRIBUTION FROM THE PHILIPS RESEARCH LABORATORIES,  
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## Viscosity of Molten Alkali Molybdates, Tungstates, and Sulfates<sup>1</sup>

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The viscosities of molten  $\text{M}_2\text{MoO}_4$  and  $\text{M}_2\text{WO}_4$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) have been determined as a function of temperature up to  $1000^\circ$  by the method of the oscillating hollow cylinder. Viscosity values, ranging from 2 to 10 cP, are higher for the tungstates than for the corresponding molybdates and decrease in the order  $\text{Li} \rightarrow \text{Na} \rightarrow \text{K}$ . In addition, viscosity values of  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  are reported, in order to allow a comparison with the behavior of other high-melting salts with complex anions. The relationships between viscosity and temperature can be represented satisfactorily by an Arrhenius equation. Values of the activation energy for viscous flow  $E_\eta$  are as follows (in kcal mol<sup>-1</sup>):  $\text{Li}_2\text{MoO}_4$ , 7.0;  $\text{Na}_2\text{MoO}_4$ , 6.8;  $\text{K}_2\text{MoO}_4$ , 5.1;  $\text{Li}_2\text{WO}_4$ , 12.0;  $\text{Na}_2\text{WO}_4$ , 9.2;  $\text{K}_2\text{WO}_4$ , 8.6;  $\text{Li}_2\text{SO}_4$ , 12.8;  $\text{Na}_2\text{SO}_4$ , 10.0. The  $E_\eta$  values found are predicted reasonably well by the semiempirical relation  $E_\eta = 3.7RT_m$ . The relatively low values of the ratio  $E_\eta/E_A$ , *i.e.*, activation energy of viscosity *vs.* activation energy of equivalent conductivity, in the case of molten alkali molybdates, tungstates, and sulfates would suggest that the melts have a more or less associated character.

### 1. Introduction

Although several physical properties of molten alkali molybdates and tungstates have been determined (density,<sup>2-8</sup> surface tension,<sup>2,8</sup> electrical conductivity,<sup>3-6,9-12</sup> thermal stability,<sup>13</sup> and volatility<sup>13</sup>), viscosity values have not yet been reported in the literature. The only indication has been given by van der Wielen, *et al.*,<sup>7</sup> who stated that alkali molybdate melts have viscosities of the order of  $10^{-2}$  P.

The viscosity values of molten molybdates and tungstates are interesting in view of the glass formation observed in the systems  $\text{M}_2\text{MoO}_4\text{-MoO}_3$ <sup>7</sup> and  $\text{M}_2\text{WO}_4\text{-WO}_3$ <sup>14</sup> ( $\text{M} = \text{alkali ion}$ ). Furthermore, they allow a comparison with other physical properties of the same molten salts, especially electrical conductivity, and with the properties of related salts with complex anions. Therefore, they may contribute to our knowledge of the transport properties of ionic liquids.

The present paper describes the determination of the

viscosities of  $\text{Li}_2\text{MoO}_4$ ,  $\text{Na}_2\text{MoO}_4$ , and  $\text{K}_2\text{MoO}_4$ , and also of  $\text{Li}_2\text{WO}_4$ ,  $\text{Na}_2\text{WO}_4$ , and  $\text{K}_2\text{WO}_4$  as a function of temperature up to  $1000^\circ$ .

Owing to the scarcity of viscosity data on high-melting salts with complex anions, viscosity values for  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  were also determined and are reported in this paper. The viscosity of molten  $\text{K}_2\text{SO}_4$  could not be measured with the described apparatus, because of the relatively high melting point of this salt.

### 2. Experimental Section

**Materials.**—As described earlier,<sup>8</sup> molybdate and tungstate samples were made from alkali carbonates (Merck p.a.),  $\text{MoO}_3$  (Merck p.a.), and  $\text{WO}_3$  (Merck). The carbonates were dried by heating at  $300^\circ$  for several hours. Weighed quantities of carbonate and trioxide were mixed thoroughly and melted together in a platinum dish at  $950\text{--}1000^\circ$  for 2 hr. The  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  used were reagent grade chemicals (Merck).

**Method.**—The method used for the determination of viscosities was that of the oscillating hollow cylinder. The melt is contained in a cylindrical crucible, which is suspended by a torsion wire. When the crucible is oscillating, the logarithmic decrement of the oscillation forms a measure of the viscosity of the melt.

The apparatus used was almost identical with that of Janz and Saegusa,<sup>15</sup> the most important difference being that the adjustable inertia pieces were omitted.

The torsion wire was a tungsten wire having a diameter of 0.4 mm. The crucible containing the melt consisted of an 80% Au-20% Pd alloy, its height was 6.0 cm, and its diameter was 2.5 cm. It was inserted in a closely fitting Inconel cradle which was suspended in a long electric furnace. The oscillating part of the apparatus was protected against air currents by Plexiglas draught shields.

Amplitudes of oscillation were determined visually with the aid of a system consisting of a lamp, a mirror, and a scale on which the maximum torsion angles  $\alpha$  could be read.

The logarithmic decrement  $\delta$  was calculated by

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$$\delta = \frac{1}{n} \ln (\alpha_0/\alpha_n)$$

where  $n$  is the number of oscillations measured and  $\alpha_0$  the initial torsion angle.

The decrement of the system only increases with viscosity up to a certain value. When the viscosity is still further increased, the decrement drops and the liquid behaves more and more as a rigid body.<sup>16</sup> In order to get an impression of the position of the viscosity of maximum decrement, the relation between viscosity and logarithmic decrement was determined for a number of water-glycerol mixtures at 22.5° (see Figure 1). Viscosity values were

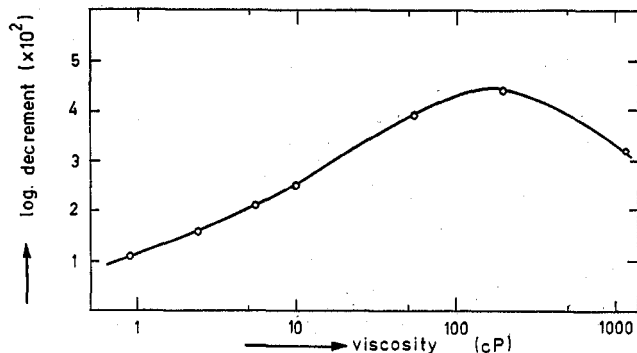


Figure 1.—Relation between viscosity and logarithmic decrement for water-glycerol mixtures.

derived from the Landolt-Börnstein tables.<sup>17</sup> For water-glycerol mixtures the maximum decrement is found at a viscosity of about 150 cP. From the work of Reeves and Janz<sup>18</sup> it is seen that the viscosity of maximum decrement is directly proportional to the density of the liquid, provided that the oscillation time, diameter of the cylinder, and height of the liquid remain constant. Therefore, for densities of the order of magnitude of those of the molten molybdates,<sup>8</sup> tungstates,<sup>9</sup> and sulfates,<sup>2</sup> the maximum decrement is attained at even higher viscosities than 150 cP. This means that no ambiguity arises in the measurements of the viscosities of these molten salts.

Equations for calculating viscosity values from logarithmic decrements have been proposed by several authors.<sup>18</sup> We have used Reeves and Janz' equation

$$I(\delta - \delta_0) \left( \frac{\tau^2}{\tau_0^2} + 1 \right) = 2\pi^2 a^3 (c + 0.2246a)(\eta\rho\tau)^{1/2} - \pi a^2 (3c + 1.844a)\eta\tau + \frac{3\pi^{1/2}}{8} ac \frac{(\eta\tau)^{3/2}}{\rho^{1/2}}$$

where  $I$  = moment of inertia of the oscillating part ( $\text{g cm}^2$ ),  $\delta$  = logarithmic decrement,  $\delta_0$  = logarithmic decrement of the empty system,  $\tau$  = oscillation time (sec),  $\tau_0$  = oscillation time of the empty system (sec),  $a$  = radius of the cylinder (cm),  $c$  = height of the liquid (cm),  $\eta$  = viscosity of the liquid ( $P$ ), and  $\rho$  = density of the liquid ( $\text{g cm}^{-3}$ ).

The logarithmic decrement and oscillation time of the empty system were  $0.63 \times 10^{-2}$  and 2.504 sec, respectively; both values remained unchanged when the temperature in the furnace was raised to 900°.

Application of the above equation to the apparatus and samples used demonstrated that the third term on the right-hand side of the equation was less than 0.1% of the second term, which again was 10% of the first. Therefore, the third term could be neglected. The resulting equation is a quadratic expression in  $\eta^{1/2}$ .

The value of the moment of inertia  $I$  was evaluated from measurements of the logarithmic decrement of liquids of known viscosity. The liquids used were water (distilled twice), toluene (Merck p.a.), and chloroform (Merck p.a.) at ambient temperatures and potassium nitrate (Merck p.a.) and lithium nitrate at elevated temperatures (the latter compound was obtained by adding lithium carbonate to nitric acid (1:1); after which the

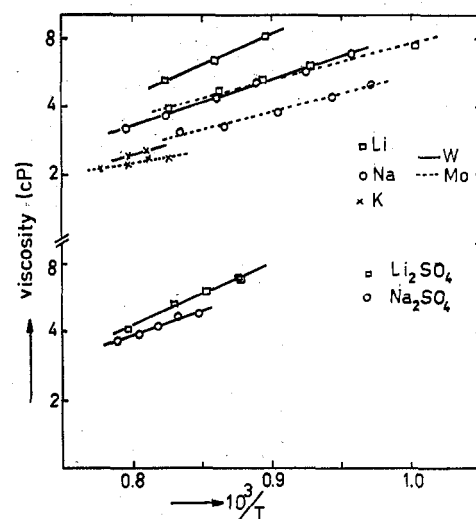


Figure 2.—Relation between viscosity and temperature for alkali molybdates, tungstates, and sulfates.

water and excess of nitric acid were evaporated; mp 255°). Viscosity and density values were derived from the "International Critical Tables," Janz and Saegusa,<sup>15</sup> and Murgulescu and Zuca.<sup>19</sup> The resulting average value of the moment of inertia  $I$  was 547  $\text{g cm}^2$ .

Temperatures were measured with a calibrated (Pt-5% Rh-Pt-20% Rh) thermocouple placed directly above the crucible.

## Results

The results of the viscosity determinations are shown in Table I and in Figure 2, in which the viscosity axis

TABLE I  
VISCOSITY VALUES,  $\eta$  (cP), AND ACTIVATION ENERGIES FOR VISCOUS FLOW,  $E_\eta$  (KCAL MOL<sup>-1</sup>), OF ALKALI MOLYBDATES, TUNGSTATES, AND SULFATES

Li <sub>2</sub> MoO <sub>4</sub>			Li <sub>2</sub> WO <sub>4</sub>			Li <sub>2</sub> SO <sub>4</sub>		
$E_\eta$	Temp, °C	$\eta$	$E_\eta$	Temp, °C	$\eta$	$E_\eta$	Temp, °C	$\eta$
7.0	723	7.48	12.0	843	8.13	12.8	866	6.92
	804	6.01		891	6.42		868	6.98
	846	5.23		942	5.27		899	6.03
	886	4.70					931	5.39
	936	3.98					981	4.09
Na <sub>2</sub> MoO <sub>4</sub>			Na <sub>2</sub> WO <sub>4</sub>			Na <sub>2</sub> SO <sub>4</sub>		
$E_\eta$	Temp, °C	$\eta$	$E_\eta$	Temp, °C	$\eta$	$E_\eta$	Temp, °C	$\eta$
6.8	756	4.95	9.2	772	6.80	10.0	907	4.89
	786	4.40		808	5.71		929	4.71
	832	3.76		850	5.13		949	4.26
	882	3.29		890	4.44		971	3.97
	926	3.13		940	3.64		994	3.70
				985	3.20			
K <sub>2</sub> MoO <sub>4</sub>			K <sub>2</sub> WO <sub>4</sub>					
$E_\eta$	Temp, °C	$\eta$	$E_\eta$	Temp, °C	$\eta$			
5.1	938	2.36	8.6	962	2.57			
	958	2.38		982	2.43			
	983	2.25						
	1014	2.10						

is logarithmic. The viscosities of alkali molybdates, tungstates, and sulfates are dependent on the nature of the alkali ion, on the understanding that the viscosity decreases in the order  $\text{Li} \rightarrow \text{Na} \rightarrow \text{K}$ . Further, the viscosities of the molybdates are lower than those of the analogous tungstates.

Although the number of measurements is limited, the conclusion is justified that the relationship between

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TABLE II  
ACTIVATION ENERGIES OF VISCOSITY AND EQUIVALENT  
CONDUCTIVITY (KCAL MOL<sup>-1</sup>) FOR MOLTEN ALKALI SALTS

Salt	Mp, °C	3.7RT <sub>m</sub>	E <sub>η</sub>	Ref	E <sub>A</sub>	Ref	E <sub>η</sub> /E <sub>A</sub>
Li <sub>2</sub> MoO <sub>4</sub>	705	7.2	7.0	<i>a</i>	(9.4)	5	(0.7)
					5.2	11	1.3
Na <sub>2</sub> MoO <sub>4</sub>	687	7.1	6.8	<i>a</i>	4.5	3	1.5
					5.7	4	1.2
K <sub>2</sub> MoO <sub>4</sub>	926	8.8	5.1	<i>a</i>	3.7	5	1.4
Li <sub>2</sub> WO <sub>4</sub>	742	7.5	12.0	<i>a</i>	5.8	6	2.1
					6.3	12	1.9
Na <sub>2</sub> WO <sub>4</sub>	700	7.2	9.2	<i>a</i>	4.5	3	2.0
					(6.4)	6	(1.4)
					4.6	10	2.0
K <sub>2</sub> WO <sub>4</sub>	921	8.8	8.6	<i>a</i>	4.8	6	1.8
Li <sub>2</sub> SO <sub>4</sub>	859	8.3	12.8	<i>a</i>	2.93	<i>b</i>	4.4
					3.93	<i>c</i>	3.3
Na <sub>2</sub> SO <sub>4</sub>	889	8.5	10.0	<i>a</i>	4.51	<i>d</i>	2.2
					4.44	<i>c</i>	2.3
Li <sub>2</sub> CO <sub>3</sub>	726	7.3	16.9	22	4.44	22	3.8
Na <sub>2</sub> CO <sub>3</sub>	858	8.3	26.3	22	4.20	22	6.3
K <sub>2</sub> CO <sub>3</sub>	899	8.6	29.5	22	4.65	22	6.3
LiCl	613	6.5	7.01	22	2.02	22	3.5
NaCl	801	7.9	9.31	22	2.99	22	3.1
KCl	776	7.7	6.59	22	3.42	22	1.9
LiNO <sub>3</sub>	255	3.9	5.10	22	3.59	22	1.4
NaNO <sub>3</sub>	307	4.3	3.89	22	3.22	22	1.2
KNO <sub>3</sub>	333	4.4	4.30	22	3.58	22	1.2
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	398	4.9	6.88	22	8.14	22	0.8

<sup>a</sup> Present results. <sup>b</sup> A. Kivist and A. Lundén, *Z. Naturforsch.* A, 20, 223 (1965). <sup>c</sup> A. M. Josefson and A. Kivist, *ibid.*, 24, 466 (1969). <sup>d</sup> A. Kivist, *ibid.*, 22, 208, 467 (1967).

viscosity  $\eta$  and absolute temperature  $T$  can be represented satisfactorily in the temperature region investigated by an equation of the Arrhenius type

$$\eta = A \exp(E_{\eta}/RT)$$

where  $A$  = preexponential factor (cP),  $E_{\eta}$  = activation energy for viscous flow (kcal mol<sup>-1</sup>), and  $R$  = gas constant (kcal mol<sup>-1</sup> deg<sup>-1</sup>). Values for  $E_{\eta}$ , calculated by the method of least squares, are also included in Table I.

To compare the results obtained with those of electrical conductivity measurements, values for the activation energy of equivalent conductivity  $E_{\Lambda}$  were evaluated from literature data.<sup>3-6,9-13</sup> In Table II it is observed that  $E_{\Lambda}$  values calculated from different literature sources show considerable mutual deviations in some cases. Nevertheless, it can be concluded that, leaving the exceptionally high  $E_{\Lambda}$  values for Li<sub>2</sub>MoO<sub>4</sub> and Na<sub>2</sub>WO<sub>4</sub> measured by Morris and Robinson<sup>5,6</sup> out of consideration, the ratio  $E_{\eta}/E_{\Lambda}$  for alkali molybdates is approximately 1.3, while that for the corresponding tungstates is approximately 2.0. Li<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> have somewhat higher  $E_{\eta}/E_{\Lambda}$  values.

Various melting point determinations of molybdates and tungstates have been reported, the results of which show only small mutual deviations. For Table II we used Hoermann's data.<sup>20</sup>

Finally, to permit further comparisons with the present results, Table II gives the melting points and values of  $E_{\eta}$ ,  $E_{\Lambda}$ , and  $E_{\eta}/E_{\Lambda}$  for a number of suitably chosen alkali salts. The  $E_{\eta}$  and  $E_{\Lambda}$  values used for these salts are those which are considered by Janz and coworkers<sup>21,22</sup> to be the most reliable values available.

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## Discussion

From the point of view of glass formation in the systems M<sub>2</sub>MoO<sub>4</sub>-MoO<sub>3</sub> and M<sub>2</sub>WO<sub>4</sub>-WO<sub>3</sub> (M = alkali metal) it is of interest that the viscosities of the molten salts M<sub>2</sub>MoO<sub>4</sub> and M<sub>2</sub>WO<sub>4</sub> are of the order of a few centipoise. Even when up to 50 mol % MoO<sub>3</sub> or WO<sub>3</sub> is added, the viscosity is not considerably raised,<sup>23</sup> which indicates that in the composition regions of relatively easy glass formation only small groups take part in viscous flow.

Present-day understanding of mass transport processes in molten salts is far from complete. A brief discussion of two simple methods of approach may illustrate the need for further clarification of the mechanisms involved.

In the first place there is the empirical relation between the melting point and the activation energy for viscous flow:  $E_{\eta} = 3.7RT_m$ . Bockris and co-workers<sup>24,25</sup> have attempted to rationalize this relation on the basis of the hole theory for ionic liquids, their approach being criticized by Angell.<sup>26</sup> It can be seen from Table II that the value of  $3.7RT_m$  provides a reasonably accurate prediction of the activation energies for most of the salts included. The alkali carbonates are an exception.

A second method of approach is to consider the value of the ratio  $E_{\eta}/E_{\Lambda}$ . Low values of  $E_{\eta}/E_{\Lambda}$  ( $\sim 1-2$ ) have been related by several authors<sup>21,27,28</sup> to the occurrence of association in the melt. Generally,  $E_{\eta}$  values are considerably higher than the corresponding  $E_{\Lambda}$  values. However, when a melt is of a somewhat associated character, both viscous flow and electrical conductance involve a cooperative motion of anions and cations, as a consequence of which  $E_{\eta}$  and  $E_{\Lambda}$  are of the same order.

From Table II it can be seen that alkali molybdates and tungstates, as also alkali nitrates and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, have low values of  $E_{\eta}/E_{\Lambda}$ . On the other hand, the  $E_{\eta}/E_{\Lambda}$  values of alkali halides and carbonates are relatively high. The sulfates seem to occupy an intermediate position. These differences in value, though admittedly small, would suggest that alkali molybdates, tungstates, and sulfates are of a more associated character than alkali halides and carbonates, which is in accordance with the classification made by Janz and Reeves<sup>21</sup> with electrical conductance as the only criterion.

The theoretical significance of the ratio  $E_{\eta}/E_{\Lambda}$  has been questioned by Angell and Moynihan.<sup>29</sup> These authors point out that the activation energies for self-diffusion of cations and anions are nearly equal in some molten salts for which association is not indicated by the value of  $E_{\eta}/E_{\Lambda}$ . Angell and Moynihan's own approach, however, does not seem to provide a satisfactory explanation for the fact that the activation energies for electrical conductance generally are lower than those for self-diffusion and viscous flow

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