Table II. pK Values of the Formed Complexes

Complexes	pK	ϵ_0
(1:1) iron	5.15 ± 0.21	12924
(1:2) iron	4.79 ± 0.05	8102
(1:3) iron	4.23 ± 0.31	3224
(1:1) copper	5.63 + 0.34	5026
(1:2) copper	11.34 ± 0.03	13012

moved by the aluminum. Citrate and nitrite ions caused high negative deviations.

Nature of the Complexes. pH and the conductometric titration of Cu^{2+} against DNRS resulted in a decrease in the pH with an increase in conductance due to hydrogen liberation with the formation of 1:1 and 1:2 complexes. These two tools permit the tracing of 1:1, 1:2, and 1:3 iron complexes. In the molar ratio method, Figure 6, in which the metal ion concentration was kept constant while that of the ligand was varied, bis copper and tris iron complexes were shown to exist. The straight line method (*3*), Figure 7, by plotting log A_s vs. log V (V was the volume of the ligand added per constant volume of the metal ion) proved the existence of a mono complex in both systems. However, the continuous variation method (*16*) for the iron system did not give reliable results due to the formation of colloidal particles at different pHs even in dilute solutions at 4×10^{-5} M. By plotting the A_s vs. the mole fraction of Cu^{2+}, Figure 8, different complexes were traced depending on the total molar concentrations of Cu^{2+} and the wavelength of the measurements. Solutions with a total molar concentration of 4×10^{-4} M in aqueous media at wavelength 355 nm, gave a sharp maximum at 0.5 mole fraction of Cu(II) indicating the formation of a complex of copper in which the metal:ligand ratio is 1:1. When this experiment was performed at pH 4 with a total molar concentration of 2×10^{-4} M and a wavelength 385 nm, another complex with the mole fraction of 0.33 was traced, indicating the formation of a 1:2 complex.

Determination of the Dissociation Constant of the Complexes. The molar ratio (*17*), the straight line (*3*), and the continuous variation methods (*16*) were used to evaluate the pK values of the complexes, based on assuming the reaction to take place as follows (*6–8*).

$$M + L \rightleftharpoons ML$$

$$K = [ML]/((M^0 - [ML])(L^0 - [ML]))$$

and

$$A_s = (M^0 - [ML])\epsilon_M + (L^0 - [ML])\epsilon_L + [ML]\epsilon_C$$

M, L, and C denotes metal, ligand, and complex, respectively. Hence

$$\frac{M^0L^0}{A_s - \epsilon} + \frac{A_s - \epsilon}{{\epsilon_0}^2} = \frac{M^0 + L^0}{\epsilon_0} + \frac{1}{K\epsilon_0}$$

Where $\epsilon = M^0\epsilon_M + L^0\epsilon_L$ and $\epsilon_0 = \epsilon_C - [\epsilon_M + \epsilon_L]$. On plotting $M^0L^0/(A_s - \epsilon_0)$ against $M^0 + L^0$ a straight line is obtained with a slope $= 1/\epsilon_0$ and an intercept equals $1/K\epsilon_0$. So, the K and ϵ_0 of the reaction can be evaluated. The results are collected in Table II.

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Viscosity of Molten $LiNO_3$

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A precise and accurate reinvestigation of the viscosity of molten $LiNO_3$ is reported, together with additional results for molten KNO_3, using an Ostwald capillary viscometer modified for molten salts studies. The temperature dependence of the results for $LiNO_3$ may be expressed by the equation $\eta = (7.283 \times 10^{-2}) \exp(4578/RT)$, and the accuracy is better than ±1.5%. The previously reported Dantuma (1928) results are found to be seriously in error, and the NSRDS recommendation based on the Dantuma data should be revised.

Viscosity techniques are generally classified into four main groups: capillary flow, oscillational, falling body, and rotational methods. The former two methods have found extensive application to ionic melts where the viscosities fall in the range 0.5–10 cP. The falling body methods are suited for liquids of higher viscosities (>40 cP) and the rotational technique, although having been used for melts with viscosities as low as 5 cP, is in general only feasible for systems of high viscosities. Capillary techniques, using both the Ostwald and Ubbelohde design, have had rather limited application at moderately high temperatures (400–900 K), the primary difficulties being the need for capillaries of known and stable dimensions and inertness to attack by molten ionic compounds.

In principle the viscosity data from these four methods should be in exact agreement, and indeed this has been shown to be possible for selected molten salts. Thus for molten KNO_3 for which some 13 independent investigations are known, an intercomparison of the capillary and oscillational techniques shows the results generally in good agreement (±1.5% agreement). With reference to $LiNO_3$, value judgments were advanced (*7*)

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Table I. Viscosity of Potassium Nitrate and Lithium Nitrate (cP)

(a) Viscosity of Potassium Nitrate

T, K	613	618	623	628	643	648	653	658	663	673	683	693	703	743
This work	2.893	2.800	2.711	2.655	2.446	2.383	2.341	2.260	2.186	2.083	1.995	1.884	1.813	1.530
Lit.[a]	2.872	2.794	2.718	2.645	2.437	2.372	2.309	2.248	2.189	2.078	1.975	1.881	1.795	1.536

(b) Viscosity of Lithium Nitrate

T, K	This work[b]	Goodwin (*5*)[b]	Protsenko (*10*)[b]	Dantuma (*3*)[c]	Murgulescu and Zuca (*9*)[c]	Zuca (*12*)[c]
540	5.240	5.159		6.237		5.330
543	5.119	5.037		6.125		5.226
555	4.635	4.579	4.604	5.689	4.783	4.827
563	4.311	4.299	4.348	5.410	4.538	4.576
570	4.167	4.071	4.134	5.172	4.333	4.367
578	3.936	3.830	3.903	4.910	4.110	4.139
583	3.733	3.689	3.765	4.750	3.976	4.002
583	3.739	3.635	3.711	4.687	3.924	3.948
592	3.585	3.457	3.530	4.470	3.747	3.768
600	3.290		3.335	4.232	3.556	3.572
607	3.260		3.176	4.030	3.398	3.411
615	3.260		3.006	3.807	3.229	3.237
622	2.992		2.869	3.620	3.090	3.095
630	2.792		2.725	3.414	2.941	2.944
637	2.748		2.610	3.241	2.822	2.822
645	2.639		2.490	3.051	2.696	2.694

[a] 110 data points, 13 investigations; least-squares analysis. [b] Capillary method. [c] Oscillational method.

in 1968 from an evaluation of the four existing studies, two capillary (*5*, *10*) and two oscillational (*3*, *9*), and with the unsatisfactory situation where the results from oscillational and capillary techniques differed significantly (from −4 to +22%), as well as poor agreement from intercomparisons of the capillary studies (0–8% divergence) and oscillational studies (4–16% divergence). Two recent publications from the Bucharest school (*2*, *12*) both include new results for $LiNO_3$ viscosities (oscillational) which differ significantly from the best value judgments advanced in the NSRDS series (*7*). The present communication reports the results of a reinvestigation of the viscosity of molten $LiNO_3$ by the capillary method, undertaken to see if divergence between the results from these two techniques could be resolved and to provide the additional input for an update of the NSRDS quality recommendations.

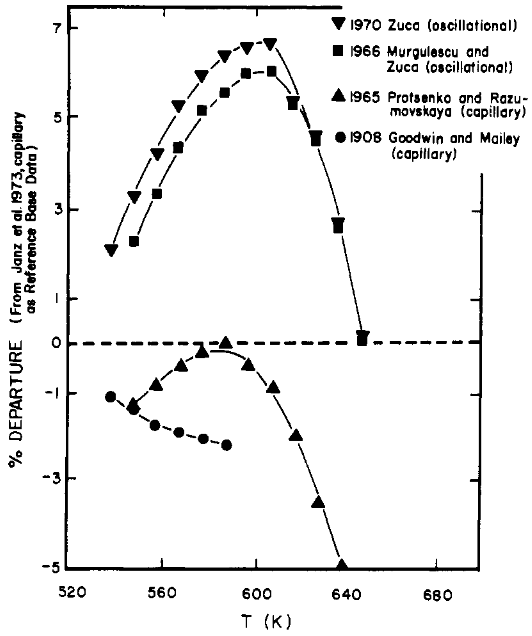

Figure 1. Percent departure analysis of the viscosity data for molten $LiNO_3$.

Experimental Section and Results

Lithium nitrate, reagent grade (Fisher Scientific Co.) and prepared from lithium carbonate and nitric acid, was used. The $LiNO_3$ was recrystallized twice from doubly distilled water and dried for 24 h at 150 °C under a vacuum of 10^{-4} mmHg. While the careful determination of the viscosity of $LiNO_3$ was the primary interest of this study, some measurements with molten KNO_3 were undertaken (as a secondary calibrant) and the results of these are also reported. KNO_3 (Fisher certified reagent grade) was recrystallized from doubly distilled water and dried using a similar procedure as given above for $LiNO_3$. Viscometers of the type described previously (*11*) were calibrated at 25 °C with two standards, *n*-hexane (Cannon Viscosity Standard No. N.4-68-1, $\eta = 0.4496$ cs/25 °C) and *n*-decane (Cannon Viscosity Standard No. N1.0-66-1, $\eta = 1.175$ cs/25 °C). Viscometers were loaded in a dry nitrogen glovebox, equilibrated for 2–6 h in a thermostated water bath at 25 °C (±0.005 °C) and measurements were made until agreement between flow times (seconds) was 0.1–0.3%. The values for the constants *C* and *E* in the Poiseuille equation (eq 1) were $C = 3.486 \times 10^{-3}$ (cs s^{-1}) and $E = 1.546 \times 10^2$ (cP s^2). Possible errors due to the vertical alignment of the capillary have been described previously (*11*), and due cognizance was taken to minimize these error sources.

$$\nu = \eta/\rho = Ct + E/t^2 \qquad (1)$$

The following procedure was used in all measurements. The dried salt samples were transferred into (filtered through a glass frit directly into) the Pyrex viscometer (using 0.33 atm of dry argon). The salt was next cooled to room temperature, over a 24-h period, for degassing (at 10^{-5} mmHg for at least 36 h) and the loaded viscometer was then vacuum sealed. The viscosities of potassium and lithium nitrate were investigated over 613–743 and 540–645 K, respectively. Measurements were carried out at increasing and decreasing temperatures with reproducibility of the experimental viscosities in the above temperature ranges being about 0.5%. Temperatures were measured with a chromel–alumel thermocouple, calibrated against a NBS Certified Pt/Pt–10% Rh thermocouple. The molten salt thermostated bath was controlled to ±0.2 °C. Absolute viscosities (η) were calculated from the measured kinematic viscosities using the

Table II. Derived Values for E_η

$LiNO_3$ investigation	Technique	E_η
This work	Capillary	4.58
Protsenko and Razumovskaya (*10*)	Capillary	4.77
Goodwin and Mailey (*5*)	Capillary	4.85
Dantuma (*3*)	Oscillational	4.34
Murgulescu and Zuca (*9*)	Oscillational	4.59
Zuca (*12*)	Oscillational	4.51

density values of Bloom et al. (*1*) for KNO_3 and those of Jaeger and Kapma (*6*) for $LiNO_3$.

The results are in Tables Ia and Ib, respectively, together with calculated values from previous measurements for $LiNO_3$. Calculated literature values at the experimental temperatures of the present investigation were generated from polynomial least-squares equations obtained using the P.D.P. Model 15 computer facility of this Laboratory. In Figure 1, the results of the various investigations (and techniques) are compared as the percent departure. This is defined as [(experimental value − recommended values)/recommended values × 100]. The results of Dantuma (*3*) 1928, oscillational) are off-scale (26% (540 K), increasing to 37.3% (610 K), decreasing to 26% (650 K)).

Discussion

The results for KNO_3 in this investigation cross-check the literature values well within the limits of experimental accuracy ($\pm 1.5\%$); indeed with the exception of one value (at 653 K), the agreement is within $\pm 1\%$ and better. One may confidently place the same reliance factor to the results for molten $LiNO_3$ since the measurements were in overlapping temperature ranges.

Examination of the temperature dependence of the viscosity data from these various studies of $LiNO_3$ shows an interesting result. A least-squares analysis was used to fit the data to an "Arrhenius" type exponential equation

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

The derived values for E_η (kcal/mol) are given in Table II. Inspection shows that the results, collectively, are more or less in accord with the temperature variance of the viscosity of molten $LiNO_3$. The sample "quality" (i.e., chemical purity) thus seems uniformly satisfactory, and the suggestion that the variance in the actual viscosity values is probably due to technique thus receives additional support from this viewpoint.

From the results of our present study (Table I, column 2) the temperature dependence of the viscosity of $LiNO_3$ may be expressed by the following equations: (a) exponential equation, $\eta = (7.283 \times 10^{-2}) \exp(4578/RT)$ cP (% standard error of estimate, 1.31); (b) power series equation, $\eta = 70.567 - 0.20188T + (0.14976 \times 10^{-3})T^2$ (% standard error of estimate, 1.12); and from the latter, the values calculated at rounded temperatures are the following [η, cP (T, K)]: 5.222 (540), 4.835 (550), 4.479 (560), 4.152 (570), 3.856 (580), 3.589 (590), 3.352 (600), 3.146 (610), 2.969 (620), 2.822 (630), 2.705 (640), 2.619 (650). The NSRDS values which we advanced earlier were based on the results of Dantuma. The present reinvestigation shows that the NSRDS recommendation for $LiNO_3$ should be revised, using the data base of Goodwin and Mailey (*5*), Protsenko and Razumovskaya (*10*), and Murgulescu and Zuca (*9, 12*) together with the results of this study to develop the "best-value" recommendation.

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Viscosity of Heavy Water at High Pressures

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The viscosity of heavy water (D_2O) was measured in the liquid and dense-gas region of up to 500 °C (773.15 K) and 800 bar (80 MPa). A capillary-type viscometer was newly constructed and used. The experimental error is estimated to be 0.5% exclusive of uncertainty in density data. Experimental results quantitatively show pressure dependence of the viscosity of heavy water in a wide range of temperatures and pressures.

Although heavy water (D_2O) is one of the important substances especially in nuclear power engineering, its properties are not satisfactorily studied. Properties of heavy water under high pressure are often calculated from those of ordinary water with simple assumptions. Available knowledge, especially of transport properties, to approve this procedure is quite limited. At atmospheric pressure, several reports on the viscosity of heavy water are available, including one by Hardy and Cottington (*4*). Principal interest in these studies is in the ratio of viscosities of H_2O to D_2O. At high pressures, three investigations are available, all of them carried out in USSR. Their experimental ranges of temperature and pressure are shown in Figure 1. Timrot and Shuiskaya (*11*) used a capillary viscometer for the temperature range 15–288 °C and for the pressure range 44–319 bar in 1959, the quoted accuracy being 2%. In 1968 and 1971, Agayev and co-workers (*1, 2*) measured in the liquid region up to 275 °C and 1200 bar. The liquid and vapor region up to 500 °C and 500 bar was measured by Rivkin and co-workers (*6, 7*)

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