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Measurement of the Electrical Conductivites of Molten $NaNO_3$–KNO_3–$NaNO_2$ and Molten LiF–NaF–KF by Displacing the Positions of Electrodes

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In order to obtain the true electrical conductance of solution in the ac bridge method, it is necessary to eliminate both the frequency effect resulting from circuitry and that of the metal/salt interfacial impedance. In this study we devised the apparatus of electrical conductances so that the interfacial impedance could be neglected by subtracting the measured resistances between two positions of electrodes which were moved through a capillary cell by using a micrometer. With this method it has been found that the same solution resistance could be obtained at any frequency without extrapolating infinitely the measured resistance against the reciprocal of frequency. The experiments were carried out for molten $NaNO_3$, KNO_3, heat transfer salt (HTS) (a mixture of molten $NaNO_3$–KNO_3–$NaNO_2$, 7:44:49 mol %), and FLINAK (a mixture of molten LiF–NaF–KF ternary eutectic, 46.5:11.5:42.0 mol %).

Introduction

For the measurement of electrical conductivity of molten salts, two different types of conductance cells have been used: the capillary cell and the immersion cell. In general, molten salts except covalent compound like the mercuric halides have higher specific conductivities than those of aqueous electrolytes. When one takes into account that the resistance value of the immersion cell (1 ~ 10 Ω) is low as compared with that of the capillary cell (500 ~ 1500 Ω), polarization effects at the surface of the electrodes of the immersion cell will make accurate measurement of resistance values practically impossible. For accurate measurement of resistance, the ac conductance bridge techniques with high cell constants are readily applicable as compared with the immersion cell.

The measured resistance in the ac bridge technique also contains the frequency effects resulting from circuitry and the electrode impedance resulting from polarization effects at the electrodes, which depend on the frequency of the applied alternating voltage. If the former effects are neglected, one can consider that the measured resistance, R_m, and the resistance associated with the electrode/solution interface, R_z, depend on the frequency of the applied current.

$$R_m = R_s + R_z \tag{1}$$

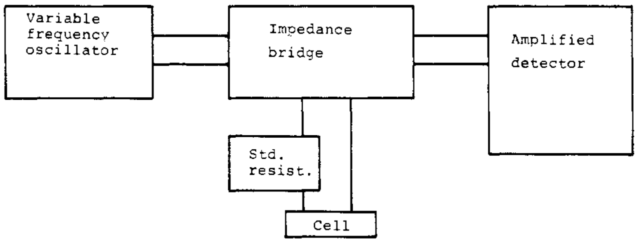

Figure 1. Experimental assembly for electrical conductivity.

R_z must be either corrected or eliminated experimentally so that R_m represents the true resistance of the solution.

In the measurements of molten salts, a value of R_m is generally extrapolated to infinite frequency with $f^{-1/2}$ or f^{-1}, where R_z is assumed to be zero. However, it has been reported that, in molten nitrates (*1*) and chlorides and fluorides (*2*), R_m is nonlinear in $f^{-1/2}$ or f^{-1}, with resistance approaching a nearly constant value at high frequencies. Although the effects of the metal/salt interfacial impedance have been studied by some investigators (*3*, *4*), the phenomena at the interface are too complicated to clarify. This polarization effect appears to lead to the error of specific conductivity of molten salts, especially fluoride melts which exhibit high ionic conductivity. The purpose of the present work is to eliminate the polarization impedance.

We devised an apparatus of electrical conductivities so that two electrodes could be moved through a capillary cell by using a micrometer. The difference of measured resistances between two arbitrarily chose electrode positions shows the true solution resistance of a melt, R_s, since the polarization impedance could be considered to have the same value at any position and be neglected by subtracting.

In order to check this method, the specific conductivities of a 1.0 demal KCl solution and of molten $NaNO_3$ and KNO_3 were measured. Then, those of heat transfer salt and FLINAK were measured since they are stable over a relatively wide range of temperatures and, to our knowledge, there are no available data for FLINAK. With this method we found that the same solution resistance, R_s, could be obtained at any frequency and that it was not necessary to extrapolate the measured resistance with respect to frequency.

Experimental Section

Figure 1 shows a schematic outline of the bridge circuit ap-

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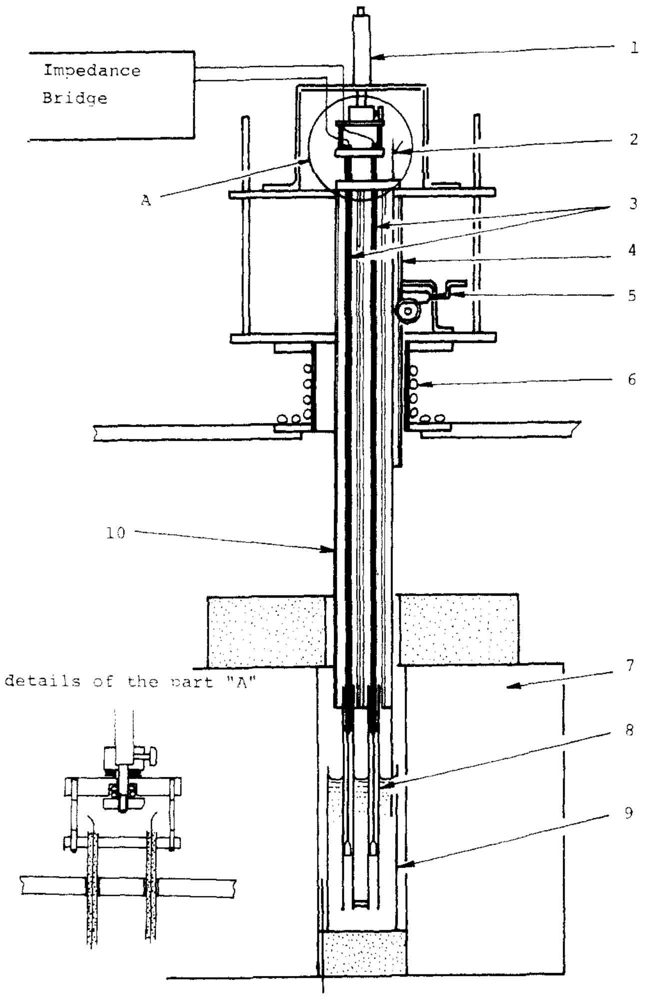

Figure 2. Apparatus for the determination of electrical conductivity: (1) micrometer; (2) Ch-Al thermocouple; (3) electrodes; (4) rack; (5) winch; (6) water cooling; (7) furnace; (8) quartz cell; (9) platinum crucible; (10) stainless pipe.

plied to these investigations. Resistance measurements were carried out with an impedance bridge (Double Wien type). The accuracy of the bridge was better than ±0.2 Ω for resistance on the order of 100 Ω in the frequency range 3~150 kHz. An amplified detector (Ando Inc. Model ED-7) was used to detect impedance and phase balance. For the generation of the alternating current feeding the bridge circuit, a generator (NF Circuit Inc. Model SY-107A) allowing a frequency range running from 10 Hz to 2 MHz has been applied.

The experimental apparatus was devised as shown in Figure 2. The assembly mainly consists of two parts: one part to make the cell assembly immerse into the proper position of the melt by using a worm gear and a rack, and the other to make only the electrodes move by means of a micrometer.

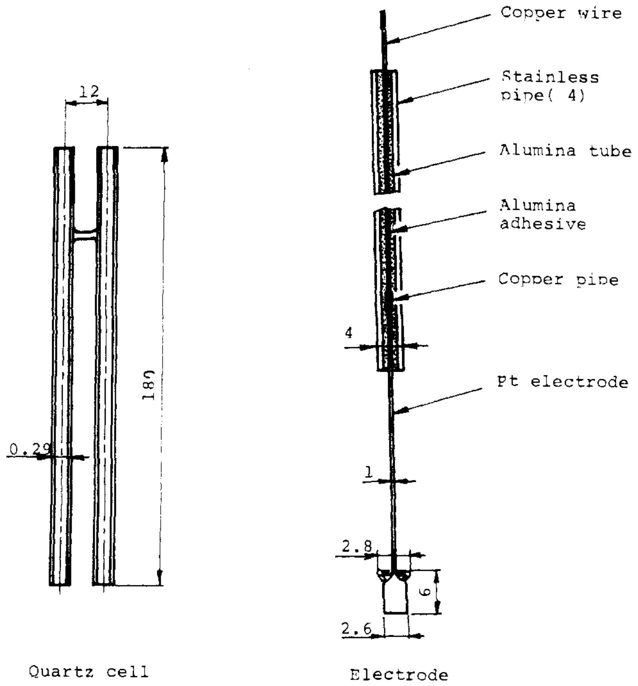

Figure 3. Scheme of a quartz cell and an electrode. Measurements are in millimeters.

Figure 3 represents conductance cells of fused quartz and platinum electrodes used in the measurements. Both of the electrodes can be moved within 5 cm in the cell at the same time by means of a micrometer; that is, the distance moved by the electrodes in the cell is at most 10 cm. In the case of the cell of 0.29-cm inside diameter, a calculated cell constant is 151.4 cm^{-1}. During the measurement, the formation of air bubbles in the cell made it difficult to get a correct value of the resistance. In order to remove air bubbles from the inside of the cell, we used a cylindrically shaped electrode. As this shape also provides large surface area for the electrode, the current might flow between the tips of the electrodes; that is, measured resistance is independent of depth of immersion.

The resistance of the KCl solution has been measured as follows. Setting the electrodes to the upper level in the cell by means of a micrometer, we slowly immersed the cell assembly into the solution by turning the worm wheel. We could observe that the electrodes touched the surface of the solution from the meter deflection of the detector. Then the cell assembly was lowered further until the level of the solution reached more than 2 cm above the lowest point of the electrodes. Test measurements proved the cell resistance to be independent of the height of this level at this value of 2 cm and above. After the cell was set at a suitable position in the solution, the electrodes were lowered in the cell by means of a micrometer. The re-

Table I. Measured Resistance for a 1 demal KCl Solution at 285 K

position of electrodes, mm	measured resistance, Ω						av resistance, Ω
	frequency, kHz	5	10	20	30	50	
0	R_0	284.55	276.05	270.4	267.9	265.45	
10	R	645.4	636.7	631.2	628.6	626.15	
	$R - R_0$	360.85	360.65	360.8	360.7	360.7	360.74
20	R	1007.65	999.15	993.65	991.3	988.45	
	$R - R_0$	723.1	723.1	723.25	723.4	723.0	723.17
30	R	1372.9	1364.3	1358.65	1356.1	1353.45	
	$R - R_0$	1088.35	1088.25	1088.25	1088.2	1088.0	1088.2
40	R	1733.4	1724.95	1719.25	1716.35	1713.9	
	$R - R_0$	1448.85	1448.9	1448.85	1448.95	1448.45	1448.8
50	R	2095.35	2086.55	2081.6	2079.3	2076.45	
	$R - R_0$	1810.8	1810.5	1811.2	1811.4	1811.0	1810.98

Table II. Measured Resistance for Molten Nitrates

temp, K	position, mm	frequency, kHz	measured resistance, Ω: 5	10	20	30	50	av resistance, Ω
			Molten KNO_3					
	0	R_0	9.0	7.85	7.0	6.7	6.25	
673	50	R	127.5	126.2	125.25	124.75	124.3	
		$R - R_0$	118.5	118.35	118.25	118.05	118.05	118.24
	0	R_0	6.7	5.9	5.35	5.1	4.85	
756	50	R	98.55	97.6	96.85	96.5	96.15	
		$R - R_0$	91.85	91.7	91.5	91.4	91.3	91.56
			Molten $NaNO_3$					
	0	R_0	6.6	5.8	5.35	5.1	4.8	
615	50	R	92.6	91.75	91.2	90.9	90.65	
		$R - R_0$	86.0	85.95	85.85	85.8	85.85	85.89
	0	R_0	5.5	4.85	4.4	4.15	3.95	
710	50	R	69.4	68.7	68.1	67.55	67.2	
		$R - R_0$	63.9	63.85	63.7	63.4	63.25	63.59

Table III. Experimental Results of Specific Electrical Conductivities for HTS and FLINAK

temp, K	electrical conductivity, Ω^{-1} m^{-1}	temp, K	electrical conductivity, Ω^{-1} m^{-1}
	HTS		
465	34.50	603	98.19
477	40.76	606	99.59
498	48.46	639	114.59
506	52.72	657	122.24
517	57.95	681	129.76
527	61.92	693	135.39
540	69.21	704	140.77
551	73.88	720	147.66
572	84.06	732	153.02
585	90.07		
	FLINAK		
767	122.29	864	195.39
784	133.22	880	207.41
802	147.23	905	223.58
821	161.19	922	235.16
840	176.56		

Table IV. Equations of Specific Electrical Conductivity

$k/(\Omega^{-1}\ m^{-1}) = A + BT$

sample	A	B	temp range, K
$NaNO_3$	−147.6 ± 1.1	0.4242 ± 0.00029	590–710
KNO_3	−116.16 ± 0.44	0.2942 ± 0.0001	634–767
HTS	−170.71 ± 0.81	0.4433 ± 0.0024	465–732
FLINAK	−447.4 ± 3.2	0.742 ± 0.006	767–922

sistance of the cell was measured at least at two positions: 2.5 and 5 cm from the upper level. The same procedure was carried out to measure the resistance of molten salts.

According to this method the specific conductivity of the melt, K, is calculated by the following equation:

$$K = K'(R_u' - R_l')/(R_u - R_l) \quad (2)$$

where K' is the specific conductivity of a 1 demal KCl solution. R and R' are measured resistances of the melt and the solution, respectively; the suffixes u and l refer to the upper and lower levels of the electrodes, respectively. The experimental error in K is determined from the measured resistance both in the KCl solution and in the investigated melt. The indeterminate error in the measured resistances is determined by the accuracy of the impedance bridge, ±0.2 Ω. This bridge accuracy is considered to affect most significantly the total experimental error for the conductivities of molten salts. Other systematic errors are estimated within ±0.4%. The expansion of the quartz cell at 673 K causes an error of ~0.04% in the value.

Temperature, measured with a calibrated Pt—Pt-Rh thermocouple, is supposed to be accurate to ±1 °C. The vertical temperature gradient along the sample was less than 4 °C for the high-temperature measurement of fluoride melts. Starting from a temperature of 5~10 °C above the melting point, the resistance of the melt is measured at intervals of 15~20 °C. Care is taken that the temperature has been constant for at least 20 min before the actual measurement is carried out.

Results and Discussion

The measured resistances R for a 1 demal KCl solution at 285 K were examined in the frequency range 5~50 kHz at different electrode positions in order to determine whether the assumption used in the experiment is appropriate. The values of R and $\Delta R = R - R_0$, which gives the real solution resistance, are represented in Table I. It can be seen that a comparison of ΔR for every frequency at each electrode position gives excellent agreement within ±0.2 Ω of the bridge accuracy.

As a preliminary experiment to examine this method for use with molten salts, we have measured the electrical conductivity of molten $NaNO_3$ and KNO_3. Table II shows the measured resistances of these nitrates at different temperatures, which represent constant values at any frequency at each temperature. This indicates that by using this method one can obtain the same solution resistance at any frequency not only for an aqueous solution but also for a molten salt without extrapolating the measured resistance against frequency.

Table V. Deviations from Additivity Rule for the Properties of HTS

temp, K		10^6(molar vol), m^3 mol^{-1}	10^3(surface tension), N m^{-1}	sound velocity, m s^{-1}	specif elec conduct, Ω^{-1} m^{-1}	10^4(equiv elec conduct), Ω^{-1} m^2	viscosity, cP
623	calcd	45.14	114.11	1765.9	116.95	49.40	2.50
	exptl	45.03	113.68	1765.1	106.0	47.73	2.35
	Δ	−0.11	−0.43	−0.8	−10.95	−1.67	−0.15
	Δ%	−0.24	−0.38	−0.05	−10	−3.5	−6.4
673	calcd	46.04	113.31	1700.4	131.3	59.68	1.95
	exptl	45.95	110.3	1698.9	127.4	58.54	1.90
	Δ	−0.09	−1.01	−1.49	−3.9	−1.14	−0.05
	Δ%	−0.20	−0.91	−0.09	−3.1	−1.9	−2.6

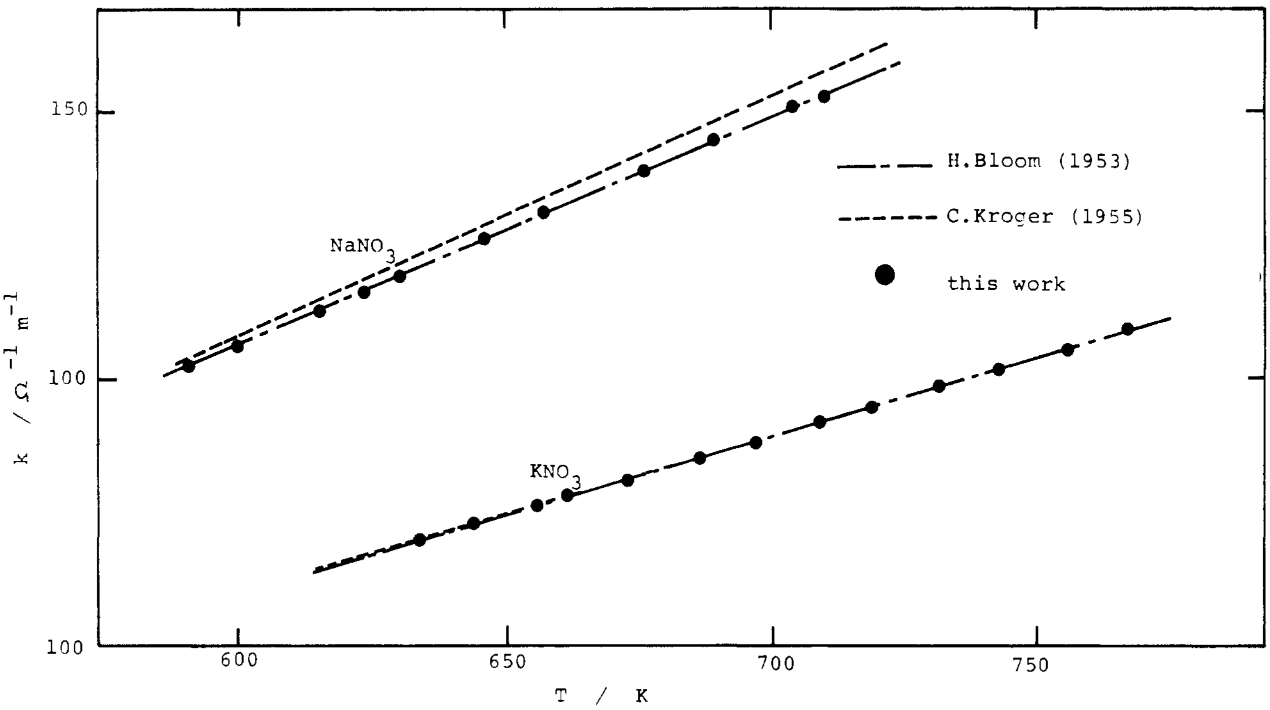

Figure 4. Specific electrical conductivities of KNO_3 and $NaNO_3$.

The specific conductivity can be calculated from eq 2. Figure 4 shows the experimental data of specific conductivity for pure $NaNO_3$ and KNO_3, which agree well, within ±0.2%, with published data. For molten $NaNO_3$, our obtained values are closer to those of Bloom et al. (*2*) than to those of Kroger (*3*). Considering the values of measured resistance and the accuracy of the impedance bridge, ±0.2 Ω, the experimental accuracy of the specific conductivities is estimated to be less than ±0.3%.

The specific conductivities were measured for molten HTS, the $NaNO_3$–KNO_3–$NaNO_2$ ternary eutectic, and for FLINAK, the LiF–NaF–KF ternary eutectic. These systems not only are utilized as heat transfer materials but also form low melting liquids with good thermal stabilities. The results of specific conductivity for HTS and FLINAK are listed in Table III and plotted against temperature in Table IV.

In Table V the deviations from the additivity rule in isotherms of electrical conductivity for HTS are compared with that of surface tension. A calculated value for each property was obtained from the following equation:

$$X_{calcd} = 0.07X_{NaNO3} + 0.44X_{KNO_3} + 0.49X_{NaNO_2}$$

The data for the surface tension of HTS were taken from ref *7*, the density of HTS from ref *8*, and other from ref *9*. As shown in the table, the percentage deviation for electrical conductivities is larger than that for surface tension; that is, transport phenomena of mixing might be affected more significantly than static ones.

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