

Figure 4. Contour diagram of differences in compressibilities of D_2O obtained from our results and work of Fine and Millero from 5° to $40^\circ C$ and 0 to 1000 bars (unit of contour is $1 \times 10^{-6} \text{ bar}^{-1}$)

secant bulk modulus equation does not have large "end effects." Since our measurements on D_2O were made relative to the equation of state for H_2O of Fine and Millero, the high-pressure specific heats of D_2O determined from our equation of state are probably of reasonable validity. High-pressure specific heat measurements on D_2O similar to those of Sirota et al. (19) would prove or disprove these speculations.

Since the specific heats of liquids are directly related to the molecular structure of a liquid, the high-pressure values of C_p and C_v for D_2O calculated from our equation of state may be useful in elucidating the structure of water.

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Received for review October 10, 1974. Accepted May 27, 1975. Research supported by the Office of Naval Research (N00014-67-A-0201-0013) and the Oceanographic Branch of the National Science Foundation (GA-17386 and GA-40532). R.T.E. supported by Navships Ocean Science Program during analysis and write-up of results. Paper taken in part from dissertation submitted by R.T.E. in partial fulfillment of the requirements for the PhD, University of Miami.

Effects of Temperature and Pressure on Conductance of Solid Electrolyte, $RbAg_4I_5$

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The effects of temperature and pressure on ionic conductance of the solid electrolyte, $RbAg_4I_5$, were investigated. The potential probe method was used in measuring the conductance with ac current imposed on the specimen to avoid contact resistance and polarization effects between the sample and the current supplying electrodes. The specific conductance, σ , was $0.288 \text{ ohm}^{-1} \text{ cm}^{-1}$ at $25^\circ C$, and the activation energy was calculated to be 1.59 kcal/mol of Ag^+ . The specific conductance increased as the pressure increased up to 8000 kg cm^{-2} . From the increase of σ with pressure and the compressibility data, an activation volume of $-0.32 \text{ cm}^3/\text{mol}$ of Ag^+ was obtained by the absolute reaction rate theory applied to the electrochemical process.

There has been considerable interest in solid electrolytes owing to recent discoveries of their highly conducting nature and of their wide range of applications (8, 10, 11, 20, 21). Compounds of the type MAg_4I_5 in which M is K^+ , Rb^+ , or NH_4^+ have high ionic conductance in the solid state owing to the exceptionally mobile Ag^+ ions (2). Rubidium silver iodide, $RbAg_4I_5$, is the most stable among these. Consequently, much attention has been focused on this electrolyte. In $RbAg_4I_5$, 16 Ag^+ ions which have high mobility are statistically distributed over 56 available tetrahedral sites per unit cell (5). Each of these tetrahedral sites has four I^- ions at its apexes.

Although the conductance of $RbAg_4I_5$ has been reported by several authors (2, 4, 12, 16, 17), the data are scattered, ranging from 0.124 to $0.279 \text{ ohm}^{-1} \text{ cm}^{-1}$, depending upon the experimental methods used (17). This scatter of data indicates that measuring techniques did not completely exclude contact resistance and polarization effects between samples and current-supplying electrodes, in spite of many efforts to avoid this problem (12, 16, 17). With aqueous solutions the

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polarization resistance problems can be avoided by the use of high-frequency ac currents (because of the high capacitance existing across the metal solution interface) and by the use of the platinized electrodes to reduce the polarization (7). With solid electrolytes, however, the two-electrode system cannot exclude resistance because the capacitance between the electrodes and the solid sample is not large enough. In the present work to study dependence of conductance upon temperature and pressure, the conducting properties of RbAg_4I_5 were investigated by a measurement technique designed to avoid the above complications.

In addition to the possibility of phase changes under high pressures reported in the literature (11, 17), high pressures applied to solid electrolytes result in changes of conductance (9, 15), the direction and magnitude of which are determined by the structure of the solid and by the conducting mechanism. Activation volume for ionic movement was obtained in this study by studying the effect of high pressures on conductance and compressibility of the electrolyte.

Experimental

The compound RbAg_4I_5 was prepared from reagent grade AgI and RbI in the manner reported by Owens and Argue (12). Particular care was taken in weighing the ingredients accurately, to 10^{-4} gram out of several grams of the total weight to obtain the stoichiometric ratio as closely as possible, because conductance of the salt is known to decrease sharply when one of the components is present even in a slight excess over the stoichiometric quantity (12). This polycrystalline mass was ground, pressed under pressure of 3000 kg cm^{-2} into a cylindrical form, and used after annealing at 150°C for about 24 hr. The polycrystalline salt obtained in this manner has a conductance similar to that of a single crystal (16).

The potential probe method used in measurement of contact resistance-free and polarization-free conductance of the solid electrolyte in this experiment is illustrated in Figure 1. There are four electrodes in contact with the solid sample. The two current-supplying electrodes, A and B, are circular silver disks attached to both ends of the cylinder of the electrolyte with the support of springs. No particular care was necessary as to the contact area between sample and electrodes since polarization and contact resistances do not affect this measurement. Two other electrodes, E and F, each in pin-point contact with the electrolyte in a line parallel to the cylinder axis, are used as potential probes. These two probes made of platinum wire are analogous to the Luggin capillary used in measurement of local potentials in liquid electrolytes. Low-frequency (300 Hz) ac current was applied to the sample through a standard precision resistor, R_p , from a low-voltage power source. The voltage amplitudes across the standard resistor and across the two probes are measured with an oscilloscope.

Since the probes should draw practically no current from the electrolyte, the potential across the probes is first amplified through a high input impedance (10^{14} ohms) differential amplifier circuit. This differential amplifier was built with two FET input stage IC operational amplifiers (Signetics 536) and a monolithic operational amplifier (Motorola 1709) in a circuit configuration described in the literature (13). The resistance of the cylindrical portion of the sample between the two probe electrodes is then obtained as the resistance of the standard precision resistor multiplied by the ratio of the voltage amplitudes across the two probes and across the standard resistor. Steady contacts at the electrode sample interface were confirmed by a distortion-free sine wave displayed on the oscilloscope.

To study the effect of temperature, the sample holder containing the cylindrical RbAg_4I_5 solid was placed inside a drying oven converted into an air thermostat with convection fans

for the time required to attain a steady temperature before making each measurement. To the sample, a 300-Hz ac current of about 1/20 A was applied from the power source. Conductance measurements were carried out at temperatures from 20° to 150°C by use of the equipment shown in Figure 1.

To study the effect of pressure, conductance measurements were carried out under pressures of up to 8000 kg cm^{-2} at 18°C with the equipment shown in Figure 2. The pressure was changed in 1000 kg cm^{-2} intervals, and enough time was given at each change of pressure before making the measurements of conductance for pressure in all directions in the specimen to reach a steady value. The measurement was repeated with reversed pressure changes. Although the force was applied uniaxially with a hand-operated hydraulic press, the pressure inside the electrolyte was considered to be closely hydrostatic (isotropic), owing to the high deformability of the electrolyte. No pressure transmitting medium was used since the solid sample itself had the flow property comparable to that of talc or pyrophyllite commonly used in high-pressure works. Although there can be a possibility of pressure gradient in the solid owing to the shear stress along the inside wall of the cylinder, the magnitude of this effect did not seem to be large enough to affect the results from the

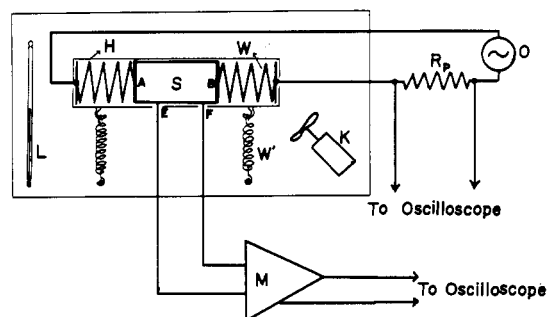


Figure 1. Assembly for measuring conductance of RbAg_4I_5 under controlled temperatures

S, sample; A, B, current-carrying silver disk electrodes; R_p , standard precision resistor (10.00 ohms); H, sample holder (Pyrex glass); K, ventilation fan; L, thermometer; M, differential amplifier; O, ac power source; W, W', springs

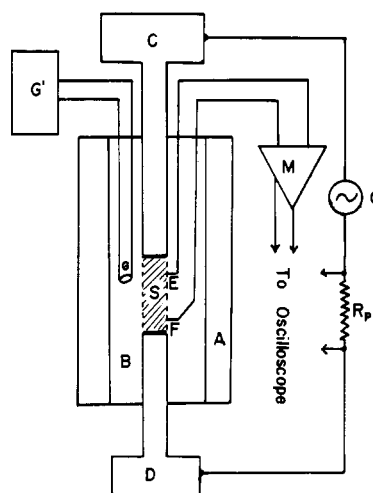


Figure 2. Assembly for measuring conductance of RbAg_4I_5 under controlled pressure

A, SKD-11 steel cylinder; B, Bakelite sleeve, thickness is exaggerated; C, D, pressure-conveying pistons, also act as current-supplying electrodes; G, G', thermistor and bridge circuit to read temperature; S, sample; R_p , standard precision resistor (10.00 ohms); E, F, Pt probe electrodes; M, differential amplifier; O, ac power source

close agreement between the measured values with increasing and decreasing pressures (see Results section).

A thermistor probe was placed in the Bakelite sleeve near the sample to confirm temperature control. Contraction of combined lengths of the sample and piston with increasing pressure up to 5000 kg cm⁻² at 18°C was measured in the experimental setup shown in Figure 2, using a traveling microscope. Because with each advance of the piston, pressures usually decreased for several minutes because of slow decrease of volumes, sufficient time had to be allowed before taking the pressure-volume readings. Contraction of the piston alone was measured separately, and this value was subtracted from the above measured value to give the compressibility of the electrolyte.

Results and Discussion

Dependence of conductance upon temperature is presented in Table I and Figure 3. The specific conductance, σ , of RbAg₄I₅ at 25°C was 0.288 ± 0.003 ohm⁻¹ cm⁻¹. This value is slightly larger than the highest value, 0.279, reported up to now (16). This suggests that some of the reported values might be lower than the true conductance, owing to improper contacts and polarization effects between the electrodes and the electrolyte, whereas the present method of measurement is completely free of such complications. The Arrhenius activation energy was calculated to be 1.59 ± 0.03 kcal/mol of Ag⁺ ions, somewhat lower than the reported value, 1.7 kcal (12).

Up to 8000 kg cm⁻², conductance increased with pressure increase (Table II and Figure 4.). On reversing the pressure change, a small degree of hysteresis was observed. The difference between the conductance values obtained with increasing and decreasing pressures was large at the instant of pressure change and then gradually decreased when allowed enough time (usually less than 1/2 hr) to about 0.004 ohm⁻¹ cm⁻¹. The "upcurve" values are listed in the table. Since the magnitude of this hysteresis effect was comparable to the scatter of the measured values in this work, its significance was considered marginal. No abrupt change in the conductance indicating a phase transition was observed in this pressure range. The average value of compressibility, β , of the electrolyte was 1.40 × 10⁻⁵ atm⁻¹ at 18°C (Table III). The activation volume was calculated by applying the absolute reaction rate theory to the electrochemical process, under the following two assumptions (3, 6, 18). Firstly, Ag⁺ ion migrates in a succession of jumps between neighboring equilibrium positions. Secondly, Ag⁺ ion has equal probability of jumping in all directions in the absence of an external field. Then the number of ions, $n(\theta)$, which jump in unit time in a direction with angle θ to the direction of the applied electric field per 1 mole of Ag⁺ ions, can be expressed as

$$n(\theta) = N \left(\frac{kT}{h} \right) e^{-\Delta G^\ddagger / RT} e^{\phi \epsilon L \cos \theta / 2 kT} \quad (1)$$

where N , ϕ , and L are Avogadro's number, electric field strength, and the distance between the neighboring equilibri-

um positions, respectively. ΔG^\ddagger and ϵ are the activation free energy and the electronic charge, respectively. Thus, the contribution of jumping ions to conductance in the field direction will be proportional to $n(\theta)L \cos \theta$. Since the ions can jump in all directions as previously assumed, the average value of $n(\theta) \cdot \cos \theta$ will be

$$\begin{aligned} \langle n(\theta) \cdot \cos \theta \rangle &= \frac{\int_0^\pi \cos \theta \exp(\phi \epsilon L \cos \theta / 2 kT) \cdot 2\pi \sin \theta d\theta}{\int_0^\pi 2\pi \sin \theta d\theta} \\ &= N \left(\frac{kT}{h} \right) e^{-\Delta G^\ddagger / RT} \frac{\int_0^\pi \cos \theta \sin \theta (1 + \phi \epsilon L \cos \theta / 2 kT) d\theta}{\int_0^\pi \sin \theta d\theta} \\ &= \frac{1}{6} N \phi \epsilon L e^{-\Delta G^\ddagger / RT} \quad (2) \end{aligned}$$

where the approximation $\exp(\phi \epsilon L \cos \theta / 2 kT) \approx 1 + \phi \epsilon L \cos \theta / 2 kT$ is used since $\phi \epsilon L \cos \theta \ll 2 kT$. Thus, the equivalent conductance, Λ , is given by

$$\Lambda = L \epsilon \langle n(\theta) \cos \theta \rangle / \phi = \frac{F}{6h} \epsilon L^2 e^{-\Delta G^\ddagger / RT} \quad (3)$$

where F is the Faraday constant. This equation is formally equivalent to similar expressions for liquid solutions by Brummer and Hills (3), Stearn and Eyring (19), Bockris et al. (1), and by Polissar (14). The specific conductance, σ , becomes, on dividing by the molar volume, V ,

$$\sigma = \frac{1}{V} \frac{FL^2 \epsilon}{6h} e^{-\Delta G^\ddagger / RT} = AV^{-1/3} \frac{F \epsilon}{6h} e^{-\Delta G^\ddagger / RT} \quad (4)$$

where A is the proportionality constant determined by the lattice dimension, $AV^{2/3} = L^2$. Hence, the effect of pressure on conductance is

$$\left(\frac{\partial \ln \sigma}{\partial P} \right)_T = \frac{1}{3} \beta - \frac{\Delta V^\ddagger}{RT} \quad (5)$$

where β and ΔV^\ddagger are compressibility and activation volume, respectively. The activation volume, ΔV^\ddagger , was calculated

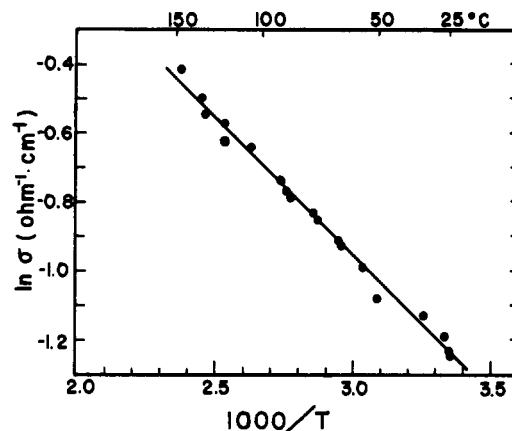


Figure 3. Effect of temperature on specific conductance of Rb₄AgI₅

Table I. Specific Conductance of RbAg₄I₅ at Various Temperatures^a

$t, ^\circ\text{C}$	25	25.3	27	34	51	56	65	66	75
$\sigma, \text{ohm}^{-1} \text{cm}^{-1}$	0.288 ±0.003	0.291	0.304	0.322	0.339	0.371	0.395	0.402	0.427
$t, ^\circ\text{C}$	77	87	89	92	107	121	132	134	147
$\sigma, \text{ohm}^{-1} \text{cm}^{-1}$	0.434	0.455	0.465	0.477	0.527	0.550	0.581	0.608	0.659

^a Standard deviation of measured values at each temperature was about 2% of the listed average, except at 25°C where a smaller deviation was obtained by finer adjustment of the temperature as presented in the table.

Table II. Specific Conductance of RbAg_4I_5 Under Applied Pressures at 18°C

P , atm	970	1940	2900	3870	4840	5810	6780	7740
σ , $\text{ohm}^{-1} \text{cm}^{-1}$	0.265	0.270	0.274	0.279	0.284	0.289	0.295	0.300
	± 0.003	± 0.003	± 0.003	± 0.003	± 0.004	± 0.004	± 0.004	± 0.004

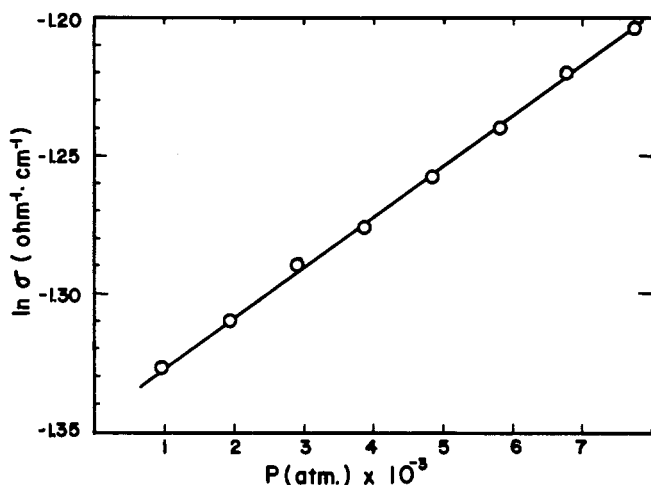


Figure 4. Effect of pressure on specific conductance of RbAg_4I_5

Table III. Measured Volume Change Of RbAg_4I_5 at 18°C Under Pressure

Press range, atm	$-\frac{1}{V} \frac{\partial V}{\partial P}$, atm^{-1}	$\bar{\beta}$, atm^{-1}
0-617	1.41×10^{-5}	1.40×10^{-5}
617-1234	1.40×10^{-5}	
1234-1851	1.38×10^{-5}	
1851-2468	1.40×10^{-5}	
2468-3085	1.39×10^{-5}	
3085-3702	1.41×10^{-5}	
3702-4319	1.41×10^{-5}	
4319-4936	1.40×10^{-5}	

from the experimental $(\partial \ln \sigma / \partial P)_T$ and β values to be $-0.32 \text{ cm}^3/\text{mol}$ of Ag^+ ion at 18°C . This result of negative activation volume is interesting in view of the fact that Radzilowski and Kummer (15) obtained a negative activation volume with Li-substituted β -alumina, whereas they obtained zero activation volume with sodium β -alumina, and positive activation volume with the β -alumina in which Na^+ is substituted by larger K^+ ions. One can expect that the large K^+ ions would experience a steric hindrance in passing through the lattice, whereas a small cation such as Li^+ would experience little steric hindrance. Hoshino et al. (9) also obtained negative activation volumes for Ag_3SBr and $\beta\text{-Ag}_3\text{SI}$.

In the process of conduction in RbAg_4I_5 in which the Ag^+ ions migrate by jumping from one tetrahedral site to the next

vacant tetrahedral site through the center of the triangular plane shared by two tetrahedra, two extreme cases can be assumed. In one case, the Ag^+ ion moves, leaving the I^- ion at the corner of the tetrahedron opposite to the shared plane unchanged in its position so that the Ag-I bond length is stretched in the transition state, but maintaining the remaining three Ag-I bond lengths unchanged. In this case, the tetrahedra in the transition state will have larger volumes than in the normal state. The other extreme case is when the Ag^+ ion migrates keeping the lengths of all four Ag-I bonds unchanged, so that the tetrahedra in the transition state have smaller volumes than in the normal state. For the above two extreme hypothetical cases, the activation volumes were calculated to be 1.8 cm^3 and $-2.2 \text{ cm}^3/\text{mol}$ of Ag^+ , respectively, using the interatomic distance data reported by Geller (5). The present result of -0.32 cm^3 falls between these two values, as expected.

Raleigh (16) reported that polycrystalline RbAg_4I_5 had 3.3% higher conductivity than a single crystal, attributing the increase of conductivity to grain boundary conduction. If such is the case with the present measurements, the absolute values of the present data may be slightly higher than the bulk conductivity which should be confirmed by measurements on a single crystal, although such measurements on a single crystal will be extremely difficult under applied pressures.

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Received for review December 2, 1974. Accepted May 28, 1975. Work supported by a research grant from the Ministry of Science and Technology.