Thermoelectric Power of the Systems $AgI\text{-}Ag_2XO_4$ (X=Mo, W)

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Determinations of the initial thermoelectric power were carried out at 1000 K in the whole composition range of the molten systems $AgI-Ag_2XO_4$ (X=Mo, W). For the composition $X_{AgI}=0.8$ the investigation was extended to the variation of the thermal emf at the "melting point" of the electrochemically noteworthy glass-like phases, obtained through rapid quenching of the melt. The hypothesis that these glass-like materials could keep the melt configuration at room temperature is contradicted by the results on the molten systems; more complex interpretations, based on the behaviour of the thermal emf at the "m.p." are proposed.

Introduction

Noteworthy ionic conductivity and electrochemical properties were recently observed in some electrolytes obtained from AgI and Ag oxysalts [1–3]. From X ray diffraction patterns and the softening phenomena much below the transition to the liquid state it was concluded that such materials have a glass-like nature [4]. This, however, cannot explain the fact that these peculiar properties are observed just in a very narrow composition range (75 ÷ 80 mole% AgI, depending on the particular system) [5]. Also, the glass-like nature itself can't be the main reason of the peculiar electrochemical properties since other glass-like materials containing mobile silver ions show a "normal" behaviour [6].

The present work is an attempt to attain some information about the thermodynamical and transport properties of the silver ions (the only carriers in these electrolytes) on the basis of determinations of the initial thermoelectric power.

The preparation of these materials requires a rapid quenching of the melt. Therefore it was tentatively supposed that the obtained glass-like phases keep the configuration of the corresponding melt. More complex interpretations are suggested, however, by the thermoelectric power variation at the "melting point" of these materials.

Experimental

AgI (Merck LAB) was directly employed after drying. Ag_2MoO_4 and Ag_2WO_4 were prepared by precipitation from aqueous $AgNO_3$ (Merck p. a.) with Na_2MoO_4 and Na_2WO_4 (Merck p. a.), respectively.

The quenching procedure for the preparation of the electrolytes and the apparatus for thermoelectric power determinations were reported elsewhere [3, 4, 7, 8].

The heat of fusion of the glass-like electrolyte $Ag_6I_4WO_4$ was estimated through DTA by comparison with the heat of fusion of $NaNO_3$ [9], the melting point of which is $T_m = 306$ °C, i. e. close to that of $Ag_6I_4WO_4$, 293 + 298 °C [4].

Results and Discussion

a) Molten Systems

Initial thermoelectric power data obtained for molten salt binaries were worked out in previous papers [7] on the basis of Temkin's model for ionic melts; however, as in the present case the components of the binaries have differently charged anions, the following statements are more adequate:

1) true molar fraction of Ag^+

$$X_{\mathrm{Ag}^+} = \frac{n_{\mathrm{Ag}^+}}{n_{\mathrm{Ag}^+} + n_{\mathrm{I}^-} + n_{\mathrm{XO}_4^=}} = \frac{2 - X_{\mathrm{AgI}}}{3 - X_{\mathrm{AgI}}}$$

2) molar entropy of the components

$$S_{\mathrm{AgI}} = (S_{\mathrm{Ag}^+})_{\mathrm{AgI}} + (S_{\mathrm{I}^-})_{\mathrm{AgI}} = [({}^0S_{\mathrm{Ag}^+})_{\mathrm{AgI}} - R \ln 1/2] + [({}^0S_{\mathrm{I}^-})_{\mathrm{AgI}} - R \ln 1/2]$$

$$\begin{aligned} S_{\mathrm{Ag_2XO_4}} &= 2\,(S_{\mathrm{Ag}^+})_{\mathrm{Ag_2XO_4}} + (S_{\mathrm{XO}_4^=})_{\mathrm{Ag_2XO_4}} \\ &= 2\,[({}^0S_{\mathrm{Ag}^+})_{\mathrm{Ag_2XO_4}} - R \ln 2/3] \\ &\quad + [({}^0S_{\mathrm{XO}_4^=})_{\mathrm{Ag_2XO_4}} - R \ln 1/3] \end{aligned}$$

where the quantities $-\nu_i R \ln X_i$ (ν_i and X_i are the number per molecule and the molar fraction, respectively, of the i-ion) are the ideal configurational

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Reprint requests to Alberto Schiraldi, Istituto di Chimica Fisica e di Elettrochimica dell'Università di Pavia, Viale Taramelli, *I-27100 Pavia* (Italien) entropy terms, whereas the $({}^0S_i)$'s contain the other entropic contributions.

3) partial molar entropy of Ag^+ in a mixture

$$(S_{Ag^+})_{X_{AgI}} = ({}^0S_{Ag^+})_{X_{AgI}} - R \ln X_{Ag^+}$$
$$= ({}^0S_{Ag^+})_{X_{AgI}} - R \ln \frac{2 - X_{AgI}}{3 - X_{AgI}},$$

4) transport quantities, referred to the common ionic species Ag^+,

$$t_I + t_{XO_4} = 1$$

where the t_i's represent the ionic Hittorf transport numbers. Accordingly, the expression for the initial thermoelectric power will contain only the heats of transport, Q_I^* and $Q^*_{XO_4}$.

With these four conditions the expression of the initial thermoelectric power, $F\varepsilon$ (F is the Faraday's constant), for a silver electrodes thermocell as established by thermodynamics of irreversible processes, i. e.

$$F\varepsilon = S_{Ag} - S_{Ag^+} - \sum_i (t_i/z_i)\, Q_i^*/T \quad (z_i = \text{ionic valence})$$

becomes in the present case

$$F\varepsilon = S_{Ag} - ({}^0S_{Ag^+})_j + R \ln X_{Ag^+} - \sum_i [(t_i/z_i)(Q_i^*/T)]_j$$
$$(j = 1, 2, 3\,^*)\,.$$

In the discussion $P_j \equiv F\varepsilon_j - R \ln X_{Ag^+}$, which contains only directly detectable parameters, will be more suitably employed. Such a function is assumed to behave ideally when:

a) $({}^0S_{Ag^+})_3 = X_1({}^0S_{Ag^+})_1 + X_2({}^0S_{Ag^+})_2$,
b) $(Q_I^*)_3 = (Q_I^*)_1$ and $(Q^*_{XO_4})_3 = (Q^*_{XO_4})_2$,
c) $t_I = X_1$ and $t_{XO_4} = X_2$,

so that

$$(P_3)_{id} = S_{Ag} - [X_1({}^0S_{Ag^+})_1 + X_2({}^0S_{Ag^+})_2]$$
$$+ X_1(Q_I^*)_1/T + X_2(Q^*_{XO_4}/2)_2/T = X_1 P_1 + X_2 P_2$$

is linear between the limits P_1 and P_2.

Deviations from this behaviour may therefore be due either to an excess entropy term defined as

$$(S^E_{Ag^+})_3 = ({}^0S_{Ag^+})_3 - [X_1({}^0S_{Ag^+})_1 + X_2({}^0S_{Ag^+})_2]$$

or to formally analogous excess transport quantities.

Table 1 reports the experimental $F\varepsilon$'s and the calculated P's for both systems at 1000 K. Deviations from the ideal behaviour are shown in Figure 1. Such deviations are the largest at $X_{AgI} \approx 0.5$ for the systems containing Ag_2MoO_4 and at $X_{AgI} \approx 0.33$ for the system containing Ag_2WO_4; at these compositions the corresponding phase diagrams report intermediate compounds incongruently melting at 523 K and 613 K respectively. Conversely in both systems no particular observation can be made about the P behaviour for the composition $X_{AgI} = 0.8$ at 1000 K and lower T's.

Tab. 1. Thermoelectric power and P values for the molten systems AgI—Ag_2MoO_4 and AgI—Ag_2WO_4 at 1000 K.

	AgI—Ag_2MoO_4		AgI—Ag_2WO_4	
X_{AgI}	$-F\varepsilon$ (e.u.)	$-P$ (e. u.)	$-F\varepsilon$ (e.u.)	$-P$ (e. u.)
1.00	11.1	9.7	11.1	9.7
0.95	11.0	9.7	10.8	9.5
0.90	10.8	9.5	10.6	9.3
0.80	10.4	9.2	10.4	9.2
0.70	—	—	9.9	8.8
0.60	9.3	8.2	—	—
0.50	8.1	7.1	8.4	7.4
0.40	8.0	7.0	—	—
0.33	8.1	7.2	7.5	6.6
0.20	8.2	7.3	7.6	6.7
0.10	8.3	7.5	8.1	7.3
0.00	8.3	7.5	8.6	7.8

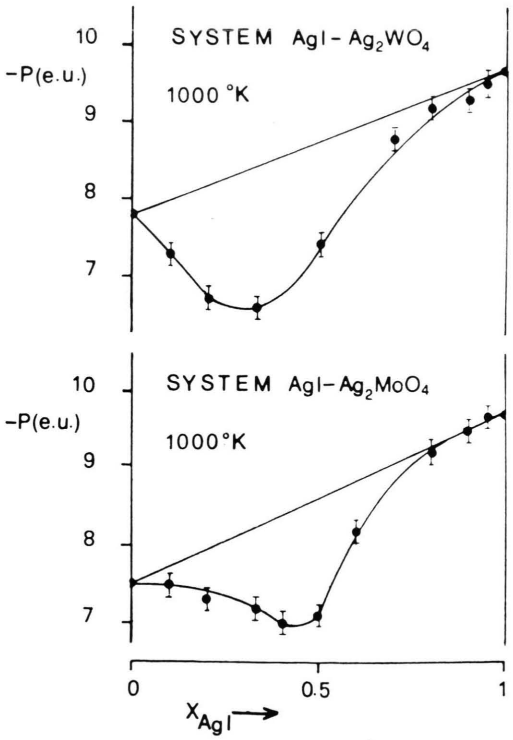

Fig. 1. P *vs* composition for the molten systems AgI—Ag_2MoO_4 and AgI—Ag_2WO_4 at 1000 K.

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* In the following 1=AgI; 2=Ag_2XO_4; 3=molten mixture.

Therefore this composition range is not as important in the molten systems as in the glass-like phases; this observation seriously contradicts the simple hypothesis of a quenched liquid state.

b) Investigation at the "Melting Point"

The initial thermoelectric power of the glass-like electrolytes of composition $X_{AgI} = 0.8$ was determined from room temperature to the point where a softening or decomposition process occurred.

The former is the case with the system containing Ag_2MoO_4, which becomes very soft and cannot be longer held between the electrodes at about 70 °C; therefore it is difficult to attain any reliable conclusion about the $F\varepsilon$ behaviour at the "melting point".

As for the system containing Ag_2WO_4 a decomposition process occurs at 298 °C, very close indeed to the definite passage to the liquid state (300 °C). In this case a comparison is possible between glass-like and molten material. Figure 2 reports the dependence of $F\varepsilon$ on T for both systems.

It is noteworthy that at the "melting point" of $Ag_6I_4WO_4$ the observed $F\varepsilon$ discontinuity is quite small, i. e. less than 10%. An analogous dependence has been observed for AgI, $RbAg_4I_5$ and other high conducting ionic solids containing AgI. Therefore a comparison with such products seems to be reliable.

In Table 2 values for the molten and solid phases at the m.p. are reported for some ionic conductors together with the entropy of fusion per silver ion contained in the molecule, $\Delta\bar{S}_m = \Delta S_m/\nu_{Ag^+}$.

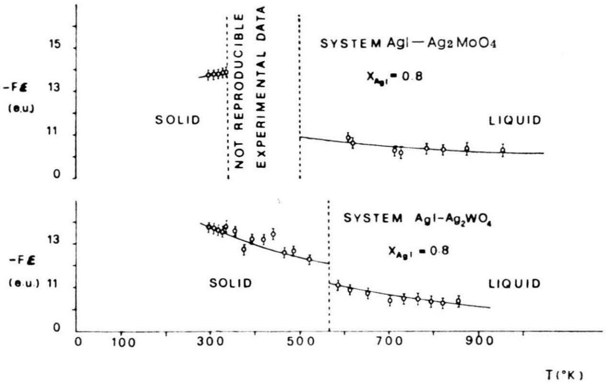

Fig. 2. Thermoelectric power *vs* T for solid and liquid $4\ AgI : Ag_2XO_4$ (X=Mo, W).

The last column reports the data of AgCl, a salt showing ordinary structural disorder and low electric conductivity.

The comparison between the quantities $\Delta F\varepsilon$ and $\Delta\bar{S}_m$ may have a particular meaning in the case of high conducting electrolytes since transport contributions to the thermoelectric power are small and close to each other in the solid and liquid phases; so that $\Delta F\varepsilon$ is a reasonable estimate of the partial

Tab. 2. Thermoelectric power of solid ($F\varepsilon_s$) and liquid ($F\varepsilon_l$) electrolytes at the respective melting points; entropies of fusion per equivalent of Ag, $\Delta S_m = \Delta S_m/\nu_{Ag^+}$; heats of transport in solid $(Q^*_{Ag^+})_s$, and liquid, $(\Sigma(t_i/z_i)Q_i^*/T)_l$, phases. (a) value extrapolated at 505 K; (b) value obtained as $1/4\,(4/5\ \Delta S_m)$ according to a procedure proposed in reference (10); (c) value obtained from the slope of $F\varepsilon_s$ *vs* $1/T$: discrepancies with respect to reference (18) may depend on the wider range of T's here investigated and on the different preparation procedure of the samples; (d) $-F\varepsilon_s$ at 343 K and $-F\varepsilon_l$ at 500 K.

	AgI $T_m = 829$ K		$RbAg_4I_5$ "T_m" = 505 K		$Ag_6I_4WO_4$ "T_m" = 566 K	$4\ AgI:Ag_2MoO_4$	AgCl $T_m = 728$ K	
$-F\varepsilon_s$ (e.u.)	12±0.7	(10)	10.5	(10)	12	14 ^{d}	12.5	(14)
$-F\varepsilon_l$ (e.u.)	11.1	(7)	9.9 ^{a}	(7)	11.2	11 ^{d}	9.3	(15)
$\Delta(F\varepsilon)$ (e.u.)	0.9		0.6		0.8	—	3.2	
$\Delta\bar{S}_m$ (e.u.)	2.7	(11)	2.96 ^{b}	(12)	2.5	—	4.0	(16)
$(Q^*_{Ag^+})_s$ (kcal mole^{-1})	2.9	(10)	2.1	(10)	0.7 ^{c}	—	6.6	(14)
$\left(\sum_i \frac{t_i}{z_i}\frac{Q_i^*}{T}\right)_l$ (kcal mole^{-1})	3.4	(7)	3.2	(13)	—	—	2.3	(15)

molar entropy variation of the silver ions through the melting point, i. e. the Ag^+ contribution to ΔS_m.

The entropy of fusion of $Ag_6I_4WO_4$ has been here evaluated from a DTA determination of the heat of fusion (about 8.3 kcal $mole^{-1}$, see Figure 3).

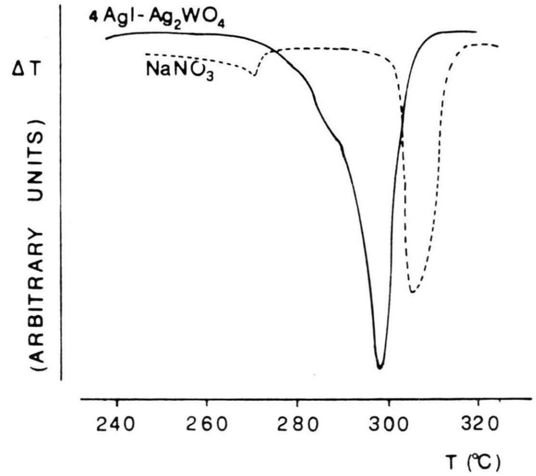

Fig. 3. DTA trace of solid 4 AgI : Ag_2WO_4 compared with that of $NaNO_3$ [9] for the quantitative determination of the heat of fusion.

The data in Table 2 concerning AgI, $RbAg_4I_5$ and $Ag_6I_4WO_4$ are close to each other and therefore it seems reasonable to suggest that $Ag_6I_4WO_4$, as well as $RbAg_4I_5$, may be compared to the α-phase of AgI both regarding electrochemical properties and the state of the silver ions.

However another interpretation is still possible. It was recently shown that the thermoelectric power of the metastable γ-phase of AgI assumes values quite close to those of the α-phase [8] and it is well known that rapid quenching of the melt and presence of other silver salts lead to a stabilization of γ-AgI [17].

Thus the constitution of the glass-like $Ag_6I_4WO_4$ might be thought as originated by a very fine dispersion of γ-AgI grains in a silver tungstate glass matrice: this interpretation might be supported by the fact that the critical composition of these compounds occurs as a rule near the eutectic in the phase diagram. Such a picture of the glass-like electrolyte structure may account both for the $F\varepsilon$ values and for the high electric a. c. conductivity which would be due to the ionic migration on the surface of the dispersed AgI particles **.

** The latter suggestion might be supported by the knowledge of the dielectric properties of the materials. In preliminary determinations of this kind it was observed that also the dielectric constant of these substances shows a sharp maximum in the same critical composition range: e. g. at 1592 Hz the capacity of pellet shaped cells (2 mm thickness, 8 mm diameter) rises from 0.8 μF at $X_{AgI}>0.8$ to 4.0 μF at $0.8 \geqq X_{AgI} \geqq 0.75$ and finally sharply decreases to 0.5 μF for $X_{AgI}<0.75$.

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