Short communication

Vapour pressure of the binary system I_2–$Ag_7I_4PO_4$

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Abstract

Previous solubility studies of absorbed gaseous iodine by $Ag_7PO_4I_4$ (API) in a wet atmosphere showed that API absorbs a great quantity of iodine (up to 1.8 mol of iodine per mol of API). The absorption rate law depends on the square root of iodine fugacity plus a constant term that represents a threshold fugacity ($f_{I_2}^0 = 0.4 \pm 0.5$ Pa) for the iodine absorption process. In this work, thermodynamic measurements carried out on the system $\{API + I_2\}$, by using solid-state galvanic cells, gives a value ($p_{I_2} = (1.2 \pm 0.7) \times 10^{-2}$ Pa at 298 K) consistent with the one previously obtained with kinetic measurements. The API compound is stable for activity values lower than the mentioned fugacity.
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1. Introduction

β-AgI, which is stable at room temperature, presents a phase transition (β → α) at 420.15 K, which improves its conductivity 10^6 times. Many attempts have been made to obtain a crystalline salt with comparable conductivity to α-AgI at room temperature by generating a crystalline structure with a rigid anionic sub-lattice. This structural arrangement contains numerous interstitial positions with equivalent or quasi-equivalent energies in which to place the Ag^+ cation [1].

A large number of electrolytes has been obtained that form double salts with AgI and have ionic conduction at room temperature. This kind of double salt can be classified into two large groups, namely:

(a) Salts obtained by cationic substitution, in which one Ag^+ ion from AgI has been partially substituted by another cation M^+ with ionic radii greater than the silver radii (for example: K^+ in KAg_4I_5, NH_4^+ in $NH_4Ag_4I_5$, Rb^+ in $RbAg_4I_5$, etc.).
(b) Salts obtained by anionic substitution, in which one I^- ion from AgI has been partially substituted by another

anion X^{y-} (for example S^{2-} in Ag_3SI, $PO_4{}^{3-}$ in $Ag_7I_4PO_4$, $AsO_4{}^{3-}$ in $Ag_7I_4AsO_4$, etc.).

For these electrolytes, the galvanic pair formed by I_2(s) as cathode and Ag(s) as anode, gives rise to the highest emf compatible with the species that make up the galvanic system. It must be pointed out, however, that many of these electrolytes are unstable in the presence of high iodine activity [2].

The compound $RbAg_4I_5$ decomposes in the presence of iodine sources if I_2 activity (in relation to solid iodine) is greater than 0.113, breaking up into RbI_3 and AgI [2,3]. On the other hand, the $(NH_4)_2Ag_4I_5$ salt turns out to be stable at $a_{I_2} \leq 0.050$, which is the activity compatible with the $(NH_4)I_3$. In the case of the salt KAg_4I_5, the absence of non-hydrated potassium polyiodides allowed the formation of a galvanic pair with $a_{I_2} = 1$ but the compound is very hygroscopic and not too stable at room temperature [4].

Ag_3SI is the most well known solid electrolyte obtained by anionic substitution. This electrolyte is not stable at $a_{I_2} > 0.030$ at temperatures higher than 338 K and decomposes according to the expression: $Ag_3SI(s) + I_2(g) \rightarrow 3AgI(s) + S(s)$ [5]. There is no thermodynamic data at room temperature although Takahashi and Yamamoto [6] have reported a stable galvanic cell having $a_{I_2} = 0.39$.

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Nomenclature

a_{I_2}	iodine activity
$\{API + yI_2\}$, $\{API + (y-1)I_2\}$	solids system formed by iodine and the elements that compose the API in their stoichiometric proportion
E	electromotive force (emf)
E^0	emf thermodynamic values of the cell using $I_2(s)/I_2(g)$ as cathode
$f_{I_2}^0$	threshold fugacity of gaseous iodine
F	Faraday constant
p_{I_2}	iodine vapour pressure
$p_{I_2}^e$	iodine vapour pressure in equilibrium with API
$p_{I_2}^0$	iodine vapour pressure of the $I_2(s)/I_2(g)$ system in equilibrium
P_+	iodine vapour pressure for $t_{e1} = 0.5$ (being t_{e1} the transport electronic number of β-AgI)
R	universal gas constant
T	absolute temperature (K)
v	rate of iodine absorption
v_c	condensation rate
v_e	evaporation rate
z	number of electrons transferred

The salt $Ag_7PO_4I_4$ (hence API), that was firstly reported by Takahashi et al. [7], is another electrolyte obtained by anionic substitution. It has also been studied by Casanova et al. [8–11], who have observed that I_2 absorption by API in a humid and dry atmosphere is followed by decomposition of the electrolyte, AgI being the only detectable product by X-ray. For a humid atmosphere, at 298.15 K, the rate of iodine absorption is

$$v = a + b p_{I_2}^{1/2} \tag{1}$$

where p_{I_2} is the vapour pressure of the iodine source.

According to observations of other electrolytes of the same family, the possibility exists that the electrolyte is stable below a determined iodine activity. In this paper the iodine activity in the system resulting from the saturation of API with I_2 vapour will be determined and it is identified as the stability threshold for iodine absorption by API.

2. Experimental

2.1. Preparation of the cells

To determine the iodine vapour pressure in some iodine compounds, the open circuit voltage in cells of the following types was measured:

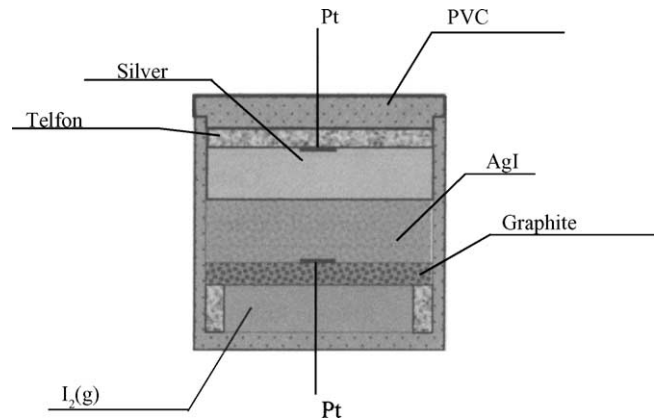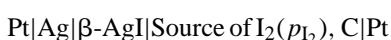$$Pt|Ag|\beta\text{-AgI}|\text{Source of } I_2(p_{I_2}), C|Pt$$

Fig. 1. Solid-state cell scheme used to measure iodine vapour pressure.

Schematic representation of the solid-state cell is shown in Fig. 1. The iodine sources used as cathodes were $2I_2$.Pi(s)/Pi(s), $RbI_3(s)/RbI(s)$ and $\{API + I_2\}(s)$ systems, where Pi represents pyrene ($C_{16}H_{10}$). The characteristics of the cell cathodes are shown in Table 1.

In cells of types I and II, all the cathodes were built by pressing a mixture of $2I_2$.Pi(s) (or $RbI_3(s)/RbI(s)$) and graphite together at 80 MPa with a platinum contact. In the same way, the anodes were built by pressing the electrolyte together with powdered silver and the corresponding platinum contact. The two sets were firmly assembled within an acrylic container by means of a threaded lid and sealed with a low vapour pressure commercial epoxy.

In type III cells, the cathode was not compacted because $\{API + I_2\}$ samples turn black under mechanical pressure. This shows that the mechanical work forces part of the absorbed iodine to the sample surface.

2.2. Materials

$2I_2$.Pi(s) was obtained following Baranek et al. [12].

$RbI_3(s)/RbI(s)$ was prepared by adding solid RbI (Aldrich 99.9% Gold Label), in stoichiometric excess, to a solution of $I_2(s)$ (Mallinckrodt A.R, bisublimated) in acetone (Merck A.R.). The solvent was later evaporated.

API was synthesised by heating a stoichiometric mixture of AgI (Aldrich 99.999%) and Ag_3PO_4 (Fluka Chem. Puriss.) up to 673 K and by immersing the melt into liquid air. It was characterised by energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), conductivity measurements and by measuring the melting point. The experimental procedures

Table 1
Characteristics of the experimental cell cathodes

Cell type	Cathode source of iodine	Geometry
I	$2I_2$.Pi(s)	Tablet
II	$RbI_3(s)/RbI(s)$	Tablet
III	$\{API + I_2\}$	Powder

and equipment used for the characterization are reported elsewhere [8,9].

Samples of $\{API + I_2\}$ were obtained by exposing API to $I_2(g)$ coming from solid iodine (Mallinckrodt A.R., bisublimated) at 298.15 ± 0.5 K, in a dry atmosphere provided by a layer of $(ClO_4)_2Mg$. The exposure time to gaseous iodine was in the range of 48–192 h.

Silver powder was obtained from an ammoniacal silver nitrate solution that was reduced by a 20% dextrose solution. The metallic powder was then calcined, ground and sifted (300 mesh).

The ground and sifted AgI was submitted to several heating cycles [13] to improve its β-AgI content. The final product was almost entirely β-AgI as found by XRD analysis.

2.3. Emf measurement

Emf measurement was carried out with a model 617 Keithley with an input impedance of 2×10^{14} Ω.

The cells were placed within a closed glass container, together with a thermistor to obtain the experimental temperature. The external electrical connections were made through leak proof electrodes sealed with low vapour pressure epoxy resin. Inside the cell, a dry atmosphere was achieved by means of a layer of $Mg(ClO_4)_2$. The container was in turn placed inside a thermostatic bath with a temperature control of ± 0.5 K.

3. Results and discussion

3.1. emf Measurements

In type I cells, temperature measurements were made close to room temperature (between 296 and 304 K).

The emf experimental data were corrected by the electronic conductivity of β-AgI according to Franco et al. [14] who used for P_+ the value of:

$$P_+ \text{(Pa)} = 4.2 \times 10^{21} \exp(104\,690\,\text{K}/T) \qquad (2)$$

P_+ being the iodine vapour pressure for transport electronic number of β-AgI $t_{e1} = 0.5$.

The values of corrected emf versus absolute temperature (T) are shown in Fig. 2, where they are compared to the values obtained by other authors [12,15]. There is good agreement within the experimental errors. The linear regression of the corrected experimental points can be expressed as:

$$E \text{(V)} = (0.6764 \pm 0.0001) + (8.1 \pm 1.4)(T \text{(K)} - 273.15) \qquad (3)$$

In type II cells the accomplished emf measurement showed linear behaviour with temperature along the whole measurement range (between 278 and 333 K). The values corrected by β-AgI electronic conductivity are shown in Fig. 3.
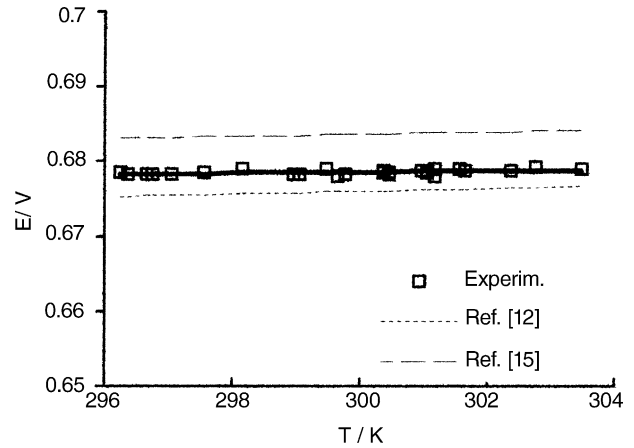

Fig. 2. Emf vs. temperature for type I cells (cathode made of $2I_2Pi/Pi$). Comparison with the values obtained by other authors.

The results of the linear regression of the experimental values are:

$$E \text{(V)} = (0.6266 \pm 0.0006)$$
$$+ (2.12 \pm 0.07)(T \text{(K)} - 273.15) \qquad (4)$$

The values reported by L.E. Topol [3] were:

$$E \text{(V)} = (0.629 \pm 0.002) + (2.00 \pm 0.16)(T \text{(K)} - 273.15) \qquad (5)$$

As it can be seen, both equations have good agreement (between 278 and 333 K). Type III cells were built with $\{API + I_2\}$ cathodes, obtained from different exposure times of powdered API to iodine vapour coming from $I_2(s)$ at 298.15 ± 0.5 K. API exposure time to iodine was varied between 48 and 192 h.

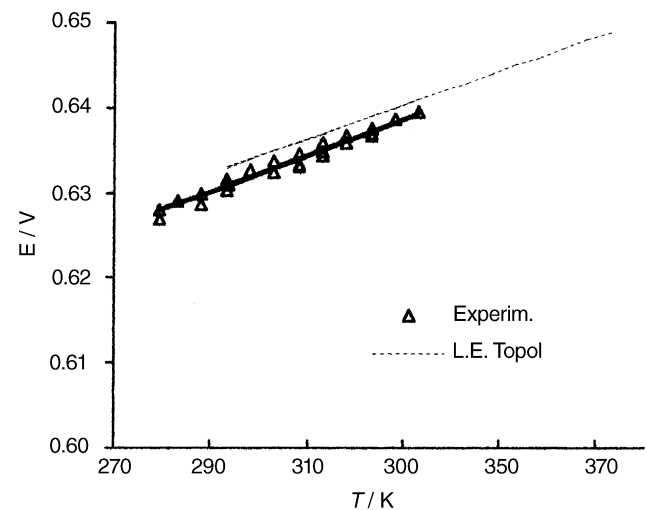As the measured emf did not depend on the exposure time to iodine, this was fixed at 48 h. After correction by β-AgI

Fig. 3. Emf vs. temperature for type II cells (cathode made of RbI_3/RbI). Comparison with the values obtained by L.E. Topol [3].
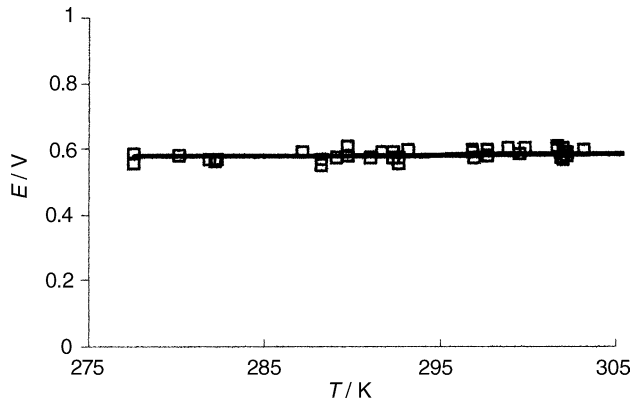
Fig. 4. Emf vs. temperature for type III cells (cathode made of $\{API + I_2\}$).

Fig. 5. Equilibrium vapour pressure of iodine vs. temperature for different iodine sources: (1) $2I_2Pi(s)/Pi(s)$; (2) $RbI_3(s)/RbI(s)$, (3) $\{API + I_2\}$.

electronic conductivity, the E versus t graph was obtained (Fig. 4).

The emf data for $\{API + I_2\}$ cathodes can be interpreted by a linear regression through the expression:

$$E\,(V) = (0.573 \pm 0.012) + (3.5 \pm 1.4)$$
$$\times 10^{-4}(T\,(K) - 273.15) \qquad (6)$$

3.2. Calculation of equilibrium pressure for the iodine sources

The equilibrium pressures for the iodine sources were obtained by:

$$p_{I_2} = p_{I_2}^0 \exp\left[(-zF/RT)(E - E^0)\right] \qquad (7)$$

where $p_{I_2}^0$ is the iodine vapour pressure of the $I_2(s)/I_2(g)$ system in the equilibrium, obtained through the expression [16,17]:

$$\log(p_{I_2}^0/p^*) = -(3512.8\,K/T) - 2.013\log(T\,(K))$$
$$+13.3740 \qquad (8)$$

Being $p^* = 1\,atm = 101\,308\,Pa$.

The emf thermodynamic values of the cell using $I_2(s)/I_2(g)$ as cathode were taken from [18] and are given by:

$$E^0(T)\,(mV) = 624.43 + \left[1.015 + 2.73 \times 10^{-4}(T\,(K))\right.$$
$$\left. -0.3586\log(T\,(K))\right] T\,(K) \qquad (9)$$

Fig. 5 shows the curves of equilibrium pressures versus temperature for the different iodine sources used as cell cathodes. The curves have been obtained by applying the formulas (7)–(9) to the emf values represented in Figs. 2–4.

The equilibrium vapour pressure of iodine for $\{API + I_2\}$ at 298.15 K is $p_{I_2}^e = (1.2 \pm 0.7) \times 10^{-2}$ Pa. This value corresponds to iodine activity that is given by the following equi-
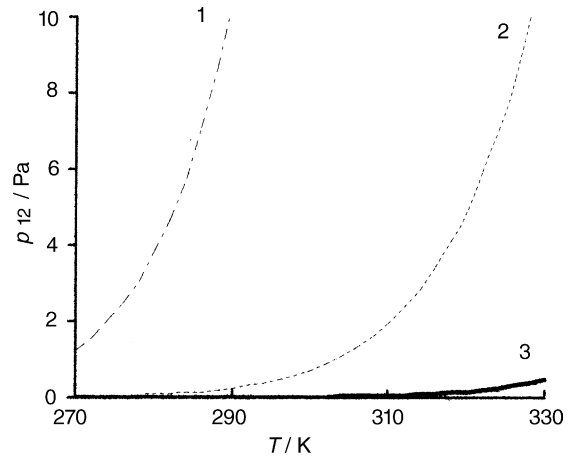
librium equation:

$$\{API + yI_2\}(s) \underset{v_e}{\overset{v_c}{\rightleftharpoons}} I_2(g) + \{API + (y-1)I_2\}(s) \qquad (10)$$

where $\{API + yI_2\}$ and $\{API + (y-1)I_2\}$ represent solids system formed by iodine and the elements that compose the API in their stoichiometric proportion. Furthermore, v_e and v_c represents the evaporation and condensation rate respectively and $v = v_c - v_e$ being the rate of iodine absorption. Equilibrium corresponds to $v = 0$.

If the activity of the iodine source is greater (lower) than the equilibrium value, the predominant observed process is evaporation (condensation). Thus, the equilibrium activity should be the same as that obtained from the expression (1): $v = a + bp_{I_2}^{1/2}$ for iodine pressure that nullifies v. This value is $(4 \pm 5) \times 10^{-1}$ Pa, which is consistent with the obtained equilibrium value. Therefore, it can be concluded that for iodine activity lower than 3×10^{-4} the $Ag_7PO_4I_4$ (API) is stable.

Acknowledgements

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