JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2003; **16:** 661–668

Electrochemical behaviour of mixtures of phenazine with iodine in the solid state[†]

Agnieszka Szadkowska, Piotr K. Wrona and Zbigniew Galus*

Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

Received 19 February 2003; revised 27 March 2003; accepted 3 April 2003

ABSTRACT: The electrochemical behaviour of mixtures of phenazine (P) with iodine (I_2) in the solid state was investigated. Three types of electrochemical experiments were conducted: (i) EMF measurements of the Ag/AgI/I_2:P system for various $I_2:P$ ratios, (ii) cyclic voltammetric (CV) experiments and (iii) potentiometric measurements of the open cell potentials after different cathodic charges were injected into the $I_2:P$ pellets. In the first case, a detailed analysis of the observed electromotive force was presented. The Gibbs free energy of the $I_2:P$ complex determined was in good agreement with earlier results. In the second case, the CV curves corresponding to the electrode processes of phenazine mixed with graphite in the solid state indicate that the mass and charge transfer, which occur in the pellets, are faster than expected. The potentiometric experiments confirm this conclusion. Additional experiments, conducted with pellets of different thickness, indicate that although, in comparison with an equilibrated pellet, the concentration profiles are modified in small layers (diffusion layers) neighbouring the electrodes, the electrode reaction probably occurs in the whole pellet. A tentative mechanism of these processes is discussed. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: phenazine; iodine; solid-state mixtures; electrochemical behaviour

INTRODUCTION

Solid-state electrochemistry has developed intensely in recent years. It is an interesting field of research with potential applications in charge storage in batteries and supercapacitors, molecular electronic sensors, displays and others.[1]

The voltammetric behaviour of various reactants in the solid state is often strongly dependent on the presence of traces of water in an investigated sample.[2–5] In the presence of water in solid hexacyanoferrates, the movement of counter-ions is faster and under cyclic voltammetric (CV) conditions one may observe the formation of current peaks, which proves that in the vicinity of the working electrode a diffusion layer develops. Similar behaviour is also observed in the case of frozen[6–13] and polymer electrolytes.[14,15] If, however, water molecules are removed from the sample by evacuation or heating, the electrochemical system often responds as a resistor and practically no current peaks are observed. The resistivity of the sample may then rise by several orders of magnitude depending of the amount of water.[3,14]

It is not easy to obtain a system with a very low water content which would exhibit non-ohmic behaviour. From the analysis of available literature data, we selected one system from which removal of water is very easy and preliminary experiments conducted proved that under CV conditions one may observe peaks of current. This system, based on a phenazine (P)–I_2 charge-transfer complex, has previously been analysed potentiometrically by Franco *et al.*[16] They carried out EMF measurements of the following electrochemical cells in the solid state:

$$\mathrm{Pt}'|\mathrm{Ag}|\mathrm{AgI}|\mathrm{P}, \mathrm{I_2} : \mathrm{P}; \mathrm{C}|\mathrm{Pt} \tag{1}$$

and

$$\mathrm{Pt}'|\mathrm{Ag}|\mathrm{AgI}|\mathrm{I_2} : \mathrm{P}, \mathrm{I_2}; \mathrm{C}|\mathrm{Pt} \tag{2}$$

for various compositions of phenazine and iodine. In these schemes $I_2:P$ denotes a complex of phenazine (P) with iodine with an excess of phenazine [Eqn (1)] or with an excess of iodine [Eqn (2)]. In both cells, the vertical bars represent the phase boundary and C stands for graphite.

From the results obtained, Franco *et al.* determined the Gibbs energy of formation of the $P:I_2$ complex. One may add that the charge-transfer complexes of iodine in solution are known and are well characterized.[17]

The aim of the present work was a further study of the thermodynamics of the EMF of cells (1) and (2) and analysis of the electrochemical processes corresponding

---

**Correspondence to:* Z. Galus, Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland.
E-mail: zbgalus@chem.uw.edu.pl

[†] Dedicated to Professor Marek T. Krygowski for his contribution to physical organic chemistry.

Contract/grant sponsor: Polish Committee for Scientific Research; *Contract/grant number:* 3 T09A 046 18.

to reduction and oxidation phenomena in the solid state observed in the absence of water under CV conditions.

EXPERIMENTAL

Materials

Phenazine (P) ($C_{12}H_8N_2$) (p.a., Aldrich) and iodine (p.a.), AgI (p.a.) and AgCl (p.a.) (POCh, Gliwice, Poland) were used without further purification. Silver powder was prepared by reduction of AgCl with formaldehyde (p.a., POCh) in NaOH solution (300 g in 750 ml of H_2O) at 70 °C. The silver deposit was carefully washed first with sulfuric acid (2%), then with ammonia (2%) and finally with water and dried at 40–50 °C.[18] Graphite (Bay Carbon), added to the Ph : I_2 complex in order to increase the conductivity, was very pure and contained traces (1 ppm) of Si.

Preparation of complexes and pellets

Mixtures of P and I_2 with the desired molar proportions were homogenized in an orbital shaker and transferred to test-tubes. After sealing, the test-tubes were heated at 80 °C for 2 days.[19] The complex was mixed with 20 wt% graphite, homogenized and ground with a mortar and pestle. From the resulting mixture, the pellets were prepared in a laboratory press used to prepare KBr IR pellets. Pellets were prepared under a pressure of 3000 kg cm^{-2}. The thickness of the pellets, in typical experiments, was 6 mm and their diameter 12 mm. The final arrangement was prepared by placing in the cell three pellets in the order Ag, AgI and P : I_2. The three pellets were then pressed together under a pressure of 3000 kg cm^{-2}.

Electrochemical cell

The system of pellets located between platinum disk contacts was placed in a Teflon tube. The working surface area of electrodes was 1.13 cm^2. The system was compressed together with a polyethylene screw. The cell was placed in a laboratory oven of capacity ~50 dm^3. During experiments the oven was preheated to a suitable value and experiments were started after 30 min from the moment when the interior of the oven reached the selected temperature.

Apparatus

EMF was measured with a V-543 voltmeter (Poland). Electrochemical experiments (CV, impedance measurements and open-circuit versus time measurements) were conducted with a CHI660 Electrochemical Workstation (USA) controlled by a Pentium computer.

RESULTS AND DISCUSSION

Three types of electrochemical experiments were carried out: (i) EMF measurements of the Ag/AgI/I_2 : P system for various I_2 to P ratios; (ii) CV experiments, carried out under different experimental conditions (sweep rates, temperatures and various I_2 : P ratios); and (iii) potentiometric measurements of the open cell potentials, after different cathodic charges were injected into the I_2 : P pellets.

EMF measurements

The EMF data obtained for samples with different phenazine–iodine (I_2 : P) compositions are presented in Fig. 1(a). These EMF values recorded after 24 h from the beginning of the experiment were stable during the next 2 days. The EMF values measured just after the preparation of the pellets were about 40 mV more positive.

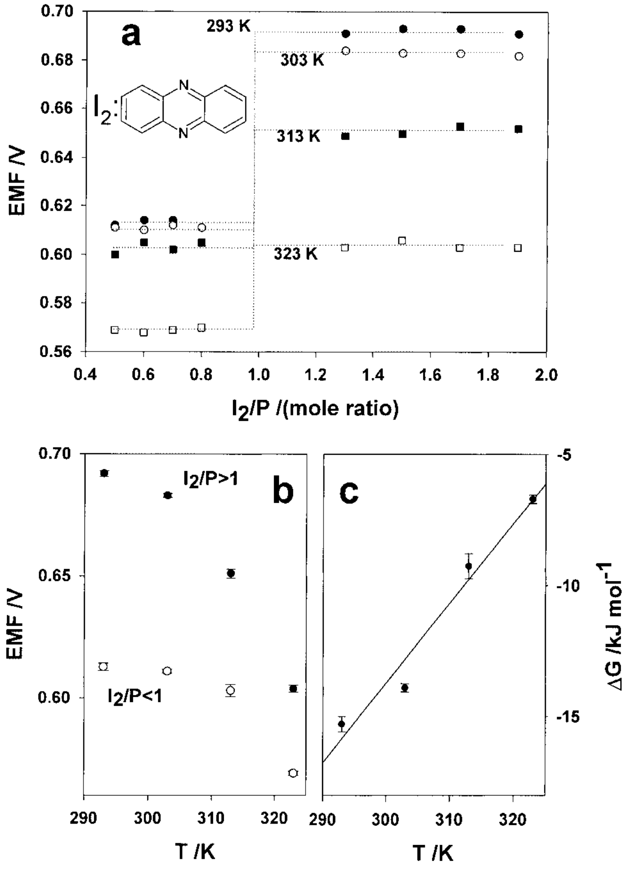

Figure 1. (a) Dependence of the EMF values on the I_2 : P ratios at various temperatures: ●, 293 K; ○, 303 K; ■, 313 K; □, 323 K. (b) Temperature dependence of the stable EMF values. (c) Dependence of the Gibbs free energy values on temperature

As follows from the results presented in Fig. 1(a), we have two regions where the EMF values do not depend on the $I_2:P$ composition; however, with rise in temperature a slight decrease was observed, as shown in Fig. 1(b).

The iodine to phenazine molar ratio in the first cell was <1, and over a wide range of compositions its EMF did not depend on the $I_2:P$ ratio. In the second cell, the $I_2:P$ ratio was >1, but its EMF did not depend of this ratio either. These two important findings should be taken into account in the analysis of the EMF of both cells.

We start our analysis with cell (2). In the left-hand electrode we have the Ag/AgI redox system. The activity of Ag^+ in the solid phase follows from the equilibrium constant, which could be interpreted as the solubility product of AgI in the solid phase:

$$K(\mathrm{AgI}) = [\mathrm{Ag}^+][\mathrm{I}^-] \;\rightarrow\; [\mathrm{Ag}^+] = K(\mathrm{AgI})/[\mathrm{I}^-] \quad (3)$$

Thus, the equilibrium potential of silver electrode could be written as

$$E = E^\circ_{\mathrm{Ag}^+/\mathrm{Ag}} + RT/F\ln\{K(\mathrm{AgI})/[\mathrm{I}^-]\} \quad (4)$$

where $E^\circ_{\mathrm{Ag}^+/\mathrm{Ag}}$ is the standard potential of the Ag^+/Ag electrode in the solid phase and $[Ag^+]$ is the activity of silver ion. The final result has a rather conventional form.

The equilibrium potential of the right-hand side electrode should be determined by the I_2/I^- system, with the equilibrium potential described as

$$E = E^\circ_{\mathrm{I}_2/\mathrm{I}^-} + RT/F\ln(p[\mathrm{I}_2])^{1/2}/[\mathrm{I}^-] \quad (5)$$

where $p[I_2]$ is the vapour pressure of iodine at a given temperature. On the other hand, the activity of iodide ions in the solid phase is determined by the equilibrium constant of AgI [Eqn (3)]:

$$[\mathrm{I}^-] = K(\mathrm{AgI})/[\mathrm{Ag}^+] \quad (6)$$

Thus

$$E = E^\circ_{\mathrm{I}_2/\mathrm{I}^-} + RT/F\ln\{[\mathrm{Ag}^+](p[\mathrm{I}_2])^{1/2}/K(\mathrm{AgI})\} \quad (7)$$

and the EMF of cell (2) is given by the difference of Eqns (4) and (7):

$$\mathrm{EMF}(2) = E^\circ_{\mathrm{Ag}^+/\mathrm{Ag}} - E^\circ_{\mathrm{I}_2/\mathrm{I}^-} + RT/F\ln\{K(\mathrm{AgI})/p[\mathrm{I}_2]^{1/2}\} \quad (8)$$

This equation is not easily interpreted as it contains the term $(p[I_2])^{1/2}$, which is a function of temperature and the properties of the solid phase. Specifically, in our case one could expect that the vapour pressure of iodine will be modified by the presence of graphite.

In the case of cell (1), the left-hand electrode remains the same, but the equilibrium potential of the right-hand electrode should be discussed. We expect that this electrode should be reversible with respect to the I_2/I^- redox couple, and the interaction of iodine with phenazine changes the vapour pressure of iodine. The equilibrium constant describing this interaction could be written as

$$\mathrm{P} + \mathrm{I}_2 = \mathrm{PI}_2 \quad (9)$$

$$K(\mathrm{PI}_2) = [\mathrm{PI}_2]/\{[\mathrm{P}][\mathrm{I}_2]\} \quad (10)$$

Assuming strong interaction of phenazine with iodine [i.e. a high equilibrium constant, Eqn (10)], one should expect that the vapour pressure of iodine, in the presence of phenazine, would be lower than in its absence.

On the other hand, analysis of the EMF values obtained for I_2 to phenazine ratios from 0.5 to 0.8 (which corresponds to $[PI_2]/[P]$ ratios from 1 to 4) reveals that the EMF values in this range of the I_2/phenazine molar ratio are not sensitive to changes in composition. Hence one should expect that when the phenazine to iodine ratio is <1, the right-hand electrode potential is sensitive to the vapour pressure of iodine, which increases with temperature.

On the other hand, when the phenazine to iodine ratio is >1, the vapour pressure of iodine results from equilibrium (9), but the activities of both phenazine and the phenazine–iodine complex do not influence the equilibrium potential. They behave, at this temperature, as if their activities were equal to one. Hence the ratio of the vapour pressure of iodine in the absence (a) and in the presence (p) of phenazine is described by an equilibrium constant, and its magnitude describes the interaction of iodine and phenazine:

$$K(\mathrm{I}_2\mathrm{P}) = p([\mathrm{I}_2])_\mathrm{a}/p([\mathrm{I}_2])_\mathrm{p} \;\rightarrow\; p([\mathrm{I}_2])_\mathrm{p} = p([\mathrm{I}_2])_\mathrm{a}/K(\mathrm{I}_2\mathrm{P}) \quad (11)$$

The vapour pressure of iodine described by Eqn (11) could be now introduced into Eqn (8), and the equation describing the EMF of cell (1) is finally obtained:

$$\mathrm{EMF}(1) = E^\circ_{\mathrm{Ag}^+/\mathrm{Ag}} - E^\circ_{\mathrm{I}_2/\mathrm{I}^-} + RT/F\ln\{(K(\mathrm{AgI})K(\mathrm{I}_2\mathrm{P})^{1/2})/p[\mathrm{I}_2]^{1/2}\} \quad (12)$$

The difference between Eqns (8) and (12):

$$\Delta\mathrm{EMF} = -RT/2F\ln K(\mathrm{I}_2\mathrm{P}) \quad (13)$$

describes equilibrium constant (11) and is not a function of the vapour pressure of iodine, and no correction for the temperature dependence of the iodine vapour pressure is necessary.

The dependence of the Gibbs free energy on temperature is shown in Fig. 1(c). The formation of the phenazine–iodine complex is exothermic [ΔG (293 K) = $-15.3 \pm 0.3\,\mathrm{kJ\,mol^{-1}}$ and $\Delta H = -104 \pm 13\,\mathrm{kJ\,mol^{-1}}$] and associated with large entropy changes ($S = -304 \pm 42\,\mathrm{J\,K^{-1}\,mol^{-1}}$). Our ΔG value is in a good agreement with earlier data reported by Aronson *et al.* ($-15.6\,\mathrm{kJ\,mol^{-1}}$)[19] and Franco *et al.* ($-14.96\,\mathrm{kJ\,mol^{-1}}$).[16] However, the latter authors reported different ΔH and S values: $-20.83 \pm 0.76\,\mathrm{kJ\,mol^{-1}}$ and $-19.7 \pm 2.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. The reasons for these differences are not known.

Electrochemical experiments

Electrochemistry of the phenazine–iodine complex at I_2 : P ratios <1. In Figs 2(a)–(e) are shown the CV curves recorded for the pellets with a molar composition $I_2 : P = 0.7$, in the temperature range 293–323 K. At each temperature, several curves were recorded. Always only the first curve was slightly different to the others.

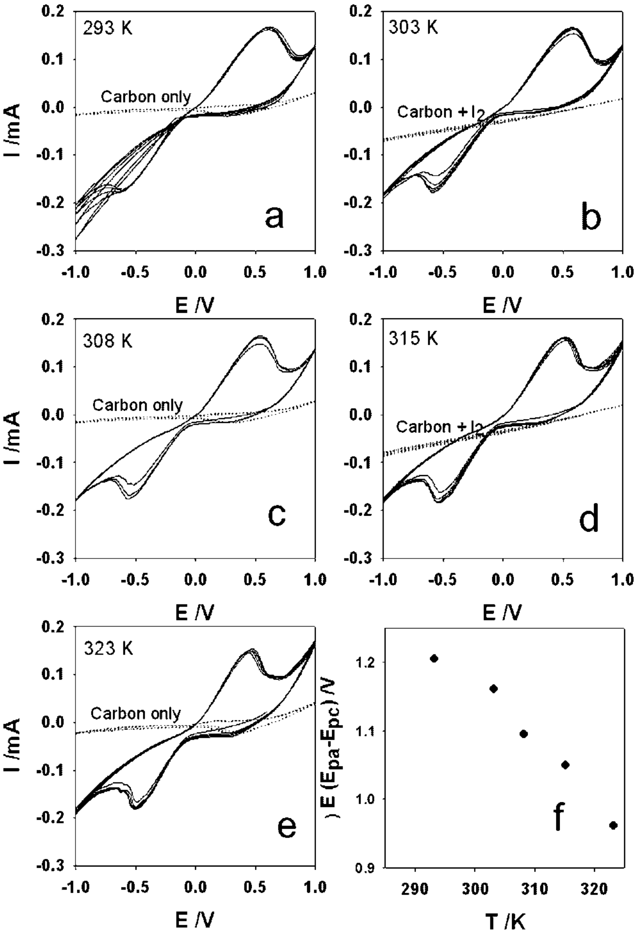

Figure 2. CV curves recorded for pellets with a molar composition $I_2 : P = 0.7$ in a range of temperatures from 293 to 323 K. In (a), (c) and (e), the CV curves of pure graphite at the same temperature are also shown. In (b) and (d), the CV curves for graphite and iodine pellets are presented. (f) Dependence of the difference of the anodic and cathodic peak potentials on temperature. Scan rate $0.05\,\mathrm{V\,s^{-1}}$

In all cases we observed the formation of anodic and cathodic peaks, which indicates that during the development of the electrochemical processes a diffusion layer is formed. One could expect that at potentials exceeding the peaks, the concentration of the electroactive species will drop to zero at the electrode surface.

Figure 2(f) shows the dependence of the difference of the anodic and cathodic peak potentials (ΔE_p) on temperature. It follows from these results that ΔE_p depends strongly on temperature since it drops by 0.3 V when temperature increases by 30 K.

For other I_2 : P compositions, but <1, the CV curves were very similar to those shown in Fig. 2.

One should say, however, that the current and peak potential values were only moderately reproducible. This resulted from the fact that, owing to not precisely controlled pressures applied to both sides of the pellets, the resistivity of the system measured by the impedance method changed in a range 1000–3000 Ω, indicating that the electrical contacts between platinum disks and I_2 : P pellets differed, to some extent, from experiment to experiment. That is why we did not determine the scan rate (v) dependence of the peak potentials, since their values are influenced by the *IR* drop, which, in this case was not precisely and adequately compensated.

In Figs 2(a), (c) and (e) are additionally shown the CV curves recorded for pellets prepared from pure graphite. In Fig. 2(b) and (d), the CV curves recorded for the graphite and iodine mixtures are also shown. All these curves were recorded at the same temperature as the curves for the $I_2 : P = 0.7$ pellets. No voltammetric peaks in the potential range $+1.0 > E > -1.0$ V were observed.

Additional analyses of the CV curves shown in Fig. 2 and those obtained for other iodine to phenazine compositions are presented in Fig. 3. In all cases an increase in current with temperature was observed (Fig. 3, top) and the dependences between current and the reciprocal of temperature were linear for all I_2 : P compositions.

In Fig. 3 (bottom) there are also shown the dependences of peak currents on scan rate and square root of the scan rate. Non-linear dependences of I_p on $v^{1/2}$ and v indicate that neither the cathodic nor anodic peak currents have a diffusional character, and that they should have in fact also migrational and capacitive components.

In Fig. 4 we present typical impedance spectra obtained at the open-circuit potentials for the pellets with a composition $I_2 : P = 0.5$ for the temperature range 293–323 K. Although we did not analyse these spectra in detail, they indicate that at least two semi-circles corresponding to two time constants should be taken into account. The semi-circles are, however, rather unsymmetrical. The real part for the first semi-circle is of the order of 4 kΩ, whereas the imaginary part is much lower, and close to 1 kΩ. Hence these semi-circles are fairly flat.

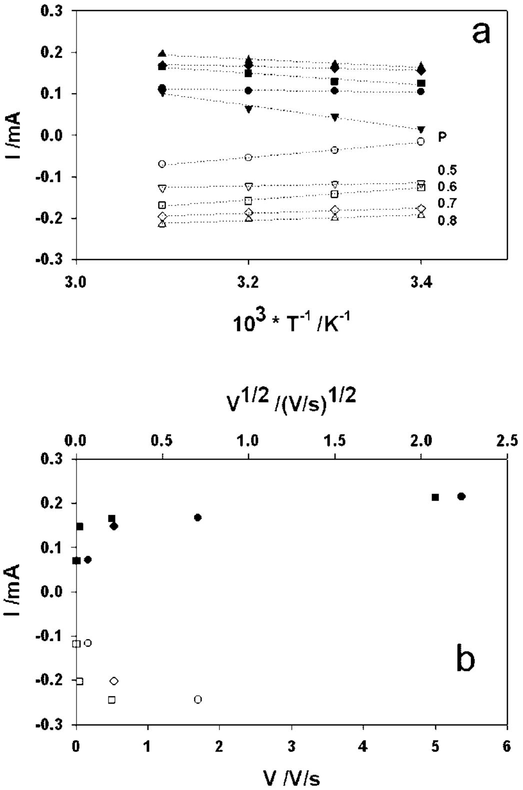

Figure 3. (a) Dependence of the anodic (filled symbols) and cathodic (open symbols) peak currents on the reciprocal of temperature for phenazine (P) and different I_2 : P ratios. Scan rate, $0.05\,V\,s^{-1}$. (b) Dependence of the anodic (filled symbols) and cathodic (open symbols) peak currents on the scan rate ($V\,s^{-1}s$) (squares) and the square root of the scan rate $(V\,s^{-1})^{1/2}$ (circles)

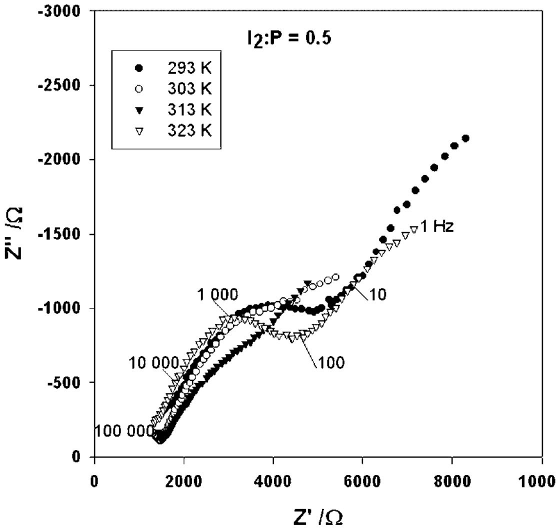

Figure 4. Impedance spectra (Nyquist plots) for a pellet with composition $I_2 : P = 0.5$, measured at the open circuit potentials at different temperatures. The frequencies of the a.c. currents (in Hz) are shown on the curve obtained at 323 K

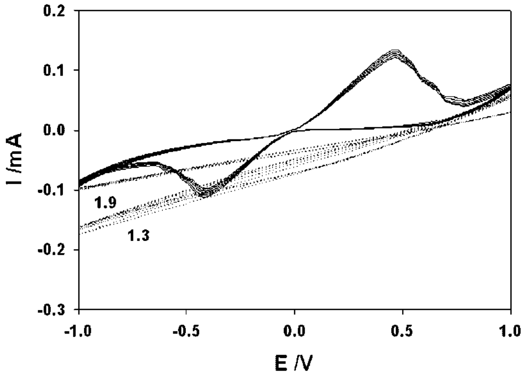

Figure 5. CV curves obtained for phenazine (solid lines) and two pellets with $I_2 : P$ ratios >1. Scan rate, $0.05\,V\,s^{-1}$

By extrapolation of the spectra to infinite frequency, we determined the resistivity of the pellets. However, the reproducibility of these data was lower than that usually observed in aqueous solutions.

Electrochemistry of solid phenazine. CV curves obtained for phenazine mixed with graphite are shown in Fig. 5. We observe the formation of cathodic and anodic peaks separated by ~0.8 V at a scan rate of $0.05\,V\,s^{-1}$. Since in this case the resistivity of the cell is of the order of 3500 Ω, after correction for *IR* the peak separation drops to about 0.4 V. However, we finally concluded that the electrode process occurring in this region of potentials is fairly fast, and the *IR* compensation was not precise and adequate enough to decrease the peak separation to values which are characteristic in aqueous solutions for the reversible redox processes ($0.059/n$ V).

Figure 5 also presents CV curves recorded for two $I_2 : P$ compositions: 1.3 and 1.9. In both cases only ohmic behaviour was observed.

Relaxation experiments. At the end of the CV experiments, when successive CV curves did not change with time, we carried out relaxation experiments. First, during 600 s, the $I_2 : P$ pellet was polarized cathodically using different initial potentials, and next the open-circuit potential was measured with time. Typical potential–time curves recorded at 323 K for pellets with the composition $I_2 : P = 0.6$ are shown in Fig. 6. Results obtained for other pellets with $I_2 : P < 1$ were similar.

The potential–time curves shown in Fig. 6 (top) were obtained after the pellets had been polarized to various negative potentials, ranging from −0.2 to −1.3 V. The initial potential observed for all curves was close to 0 V, and with time it changed to a value that was almost identical with that measured during the EMF experiments. In the bottom part of Fig. 6, the dependence of time which passed to reach a potential of 0.3 V, measured in the middle between the initial and final potential values (around 0.3 V), denoted $t_{1/2}$, on the polarization potential is shown.

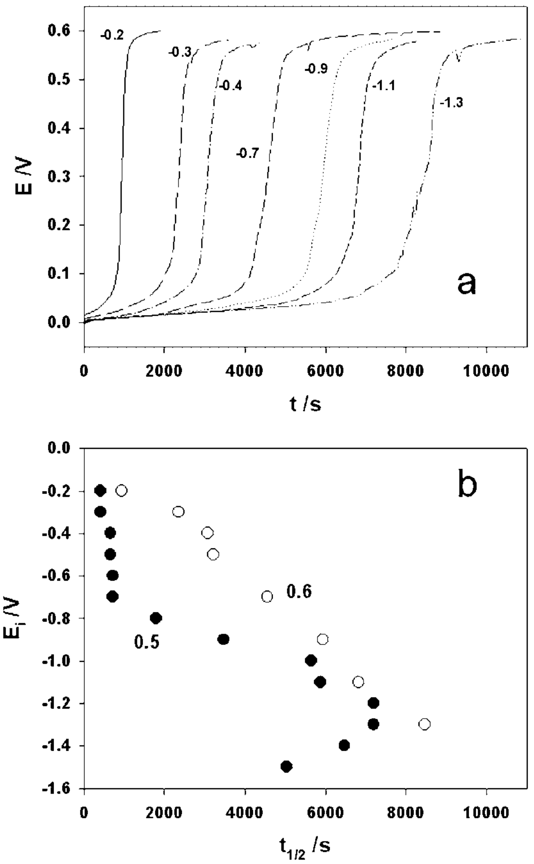

Figure 6. (a) Time dependence of the open circuit potentials measured for pellets with composition $I_2 : P = 0.6$, recorded after polarization by the potential indicated on each curve for 600 s. (b) Dependence of the half-time of the relaxation curves on the polarizing potentials for two pellets with composition $I_2 : P = 0.5$ and 0.6

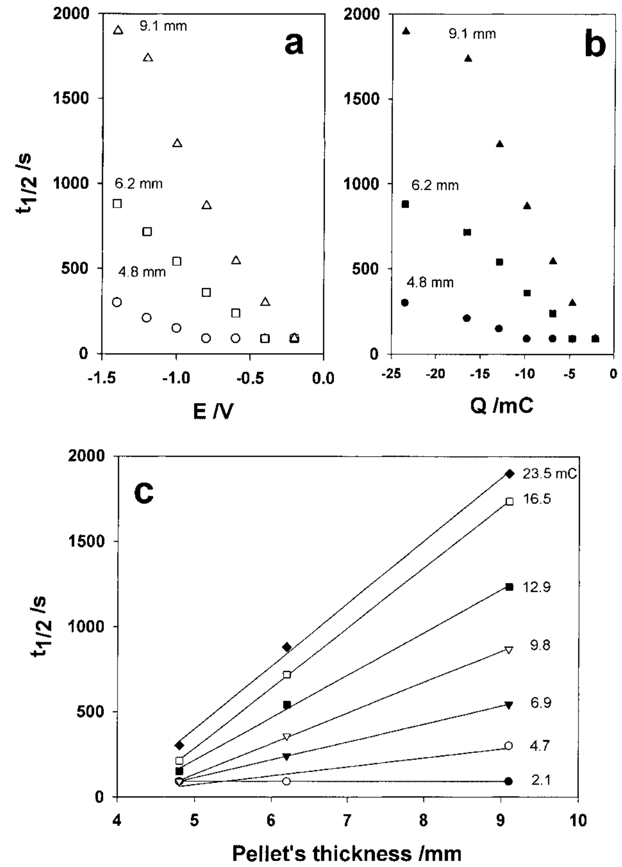

Figure 7. Dependences of the half-time on polarizing potential (a) and on polarizing charge (b) obtained for pellets with composition $I_2 : P = 0.6$ and different thicknesses (4.8, 6.2 and 9.1 mm). (c) Half-time versus pellet thickness dependence obtained for different polarizing charges

The main reason why the potential–time curves (Fig. 6, top) exhibited the shape of polarographic waves was probably the diffusion of species within the $I_2 : P$ pellets, because in the AgI pellet, the charge transport should be fast, since AgI is a relatively good electronic conductor. Therefore, we prepared three I_2–P pellets with the same composition ($I_2 : P = 0.6$) but with different thicknesses: 4.8, 6.2 and 9.1 mm. These pellets were next used in the relaxation experiments. The results obtained are shown in Fig. 7 as the dependences of $t_{1/2}$ on potential (a) and of $t_{1/2}$ on the cathodic polarization charge (b). These charges changed in a range from 2.1 to 23.5 mC. The dependence of $t_{1/2}$ on the pellet's thickness is shown in Fig. 7(c) for various cathodic charges. In all cases a linear behavior was observed.

Analysis of the cyclic voltammetric curves and the relaxation experiments. From the results presented in Fig. 1, it follows that for $I_2 : P$ ratios <1, the EMF values are of the order of 0.57 V (323 K). However, the mean value from the cathodic and anodic peak potentials of the CV curves (shown in Fig. 2) is shifted towards more negative values, and is close to 0 V. The open-circuit potential of the system, measured immediately after chronoamperometric experiments, was also close to 0 V, but it was not stable. This potential changes with time towards the initial EMF value. Probably, the products formed during the amperometric experiments react in such a fashion that the initial equilibrium is restored.

One should also note that during cathodic polarization of the working electrode being in contact with graphite or with the mixture of graphite and iodine, no voltammetric peaks are observed in the polarization range used. These observations confirm the electroactivity of phenazine. Judging from the rather large current, the electrode process of phenazine occurs with relatively high intensity. The current density estimated for voltammetric peaks is of the order of 0.1–0.2 mA cm^{-2} ($v = 0.05\ \mathrm{V\,s^{-1}}$).

During the cathodic process, phenazine is probably reduced to an anion radical:

$$P + e(Pt) = P^- \qquad (14)$$

whereas on the opposite electrode the silver cation is formed:

$$\mathrm{Ag} = \mathrm{Ag}^+ + \mathrm{e(Ag)} \tag{15}$$

Reaction (15) seems to be more probable than the oxidation reaction:

$$\mathrm{AgI} = \mathrm{Ag}^+ + \tfrac{1}{2}\mathrm{I}_2 + \mathrm{e(Ag)} \tag{16}$$

since reaction (16) should occur at significantly more positive potentials than reaction (15).

Formation of the phenazine anion radical in non-aqueous solvents has been well documented.[20–22]

Since the conductivity of β-AgI in this temperature range is relatively high, we expect that the main hindrance in the studied electrode reactions comes from the transport in the $I_2:P$ pellet. However, the mechanism of the transport in all these processes is not well understood. First in the case of a simple diffusion process, we would expect that between the pellet's thickness (x) and time needed to reach the equilibrium conditions ($t_{1/2}$), the following relation should be obeyed:

$$x = (2Dt_{1/2})^{1/2} \tag{17}$$

Thus, the relaxation time ($t_{1/2}$) should be proportional to the distance to power 2, whereas a linear relation between $t_{1/2}$ and x is observed [Fig. 7 (c)].

Assuming, however, that Eqn (17) holds, approximate calculations, with the pellet's thickness equal to 1 cm and time needed to reach the equilibrium conditions of the order of 10^3 s, gives a diffusion coefficient equal to $5 \times 10^{-4}\,\mathrm{cm^2\,s^{-1}}$. This value is orders of magnitude higher than expected. Probably, in addition to the diffusion process, some other process leading to the decomposition of the phenazine radical takes place. Although the nature of this process is not known, it is possible that adsorbed oxygen may play some role here.

The dependence of $t_{1/2}$ on the thickness of the pellets [Fig. 7 (c)] may indicate also that the relaxation occurs in the whole pellets and not in small layers (diffusion layers) neighbouring the electrodes. One should add, however, that during the chronoamperometric experiments, only a very small fraction of phenazine (around 1.5×10^{-3}% for $Q = 23.5$ mC) in the pellets was reduced.

The tentative explanation of these phenomena should be based on the following observations:

(i) The voltammetric behaviour is due to phenazine. Similar experiments carried out with the cell where instead of phenazine with graphite either graphite alone or its mixture with iodine were used did not exhibit voltammetric peaks.

(ii) To observe the voltammetric behaviour, graphite powder precisely mixed with phenazine has to be used. Without the addition of a significant amount of graphite (20 wt%), the resistance of the system is very high and only ohmic behaviour is observed.

(iii) Since the shape and position, on the potential axis, of the curves for the $I_2:P$ system are very similar to those observed for phenazine, we assumed that the CV curves for mixtures with the $I_2:P$ ratios <1 correspond to the electrode processes of free phenazine, and are not influenced significantly by the presence of the $I_2:P$ complex.

In conclusion, only a mixture of graphite with free phenazine or pellets containing $I_2:P<1$, where free phenazine exists, exhibit voltammetric behaviour.

The observed facts may lead to a tentative explanation based on the double role of graphite. The first role consists in the fast transfer of electrons from Pt electrodes to the bulk of the pellet. This transfer causes the electroreduction of phenazine. However, the occurrence of such electroreduction should be accompanied by the movement of counter-ions, in order to maintain the electroneutrality of the medium. This may be fulfilled by diffusion away of some anionic (e.g. OH^-) groups (or diffusion towards the reacting layer of some cationic groups) which may be present on the surface of the graphite.

Also, since the structure of graphite is slightly similar to that of *trans*-polyacetylene,[23] we cannot exclude, for example, the formation of holes or vacancies during the electrode process, which diffuse faster that one could expect. How these defects are formed, however, is not clear. This would be the second role of the graphite played in the charge propagation in the studied system.

Hence we do not know the detailed mechanism of transport under these conditions, but in our opinion this relatively fast transport should be related to graphite, used for the fabrication of all pellets.

CONCLUSIONS

Analysis of the EMF data of the all solid system $\mathrm{Ag|AgI|I_2:P}$, carried out for different $I_2:P$ ratios, gave the Gibbs free energy of the $I_2:P$ complex, which was in good agreement with earlier literature data. However, our enthalpy (ΔH) and entropy (S) values differ from those given by Franco *et al.*[16]

From the CV experiments it follows that phenazine in mixtures with iodine and graphite, in the solid state, is electroactive, but for $I_2:P$ ratios <1. In this case we observed the formation of anodic and cathodic peaks, which indicates that during the development of the electrochemical processes, a diffusion layer is formed. Formal analysis of the CV experiments indicates that the transport within the $I_2:P$ pellets is much faster than expected. If $I_2:P$ ratio exceeds one the $I_2:P$ complex is not electroactive in the considered range of potentials.

The latter conclusion follows also from the relaxation studies carried out just after the chronoamperometric and coulometric experiments. In this case the equilibrium state is restored orders of magnitude faster than expected.

In order to explain these phenomena, we assumed that graphite, always present in the samples studied, plays a double role in these experiments: (i) as an electron conductor and (ii) as a source of anionic (or cationic) groups, present on the surface of graphite, which diffuse into the pellet in order to fulfill the neutrality condition.

Acknowledgement

The support of the Polish Committee for Scientific Research through grant 3 T09A 046 18 is acknowledged.

REFERENCES

1. Kulesza PJ, Malik MA. In *Interfacial Electrochemistry*, Wieckowski A (ed). Marcel Dekker: New York, 1999; 673–688.
2. Rosseinsky DR, Tonge JS, Berthelot J, Cassidy JF. *J. Chem. Soc., Faraday Trans.* 1987; **83**: 231–243.
3. Wrona PK, Piela P. *Pol. J. Chem.* 1994; **68**: 1353–1367.
4. Piela P, Wrona PK, Galus Z. *J. Electroanal. Chem.* 1994; **378**: 159–164.
5. Kulesza PJ, Galus Z. *J. Electroanal. Chem.* 1992; **323**: 261–274.
6. Frese U, Iwasita T, Stimming U. *J. Phys. Chem.* 1985; **89** 1059.
7. Stimming U. In *Electrochemical Surface Science*, Soriaga MP (ed). ACS Symposium Series. American Chemical Society: Washington, DC, 1988; 275.
8. Borgeding A, Brost E, Schmickler W, Dinan T, Stimming U. *Ber. Bunsenges. Phys. Chem.* 1990; **94**: 607–612.
9. Opallo M. *J. Electroanal. Chem.* 1998; **444**: 187–194.
10. Opallo M. *J. Electroanal. Chem.* 1995; **399**: 169–178.
11. Opallo M. *J. Electroanal. Chem.* 1996; **411**: 145–152.
12. Opallo M, Tymosiak A, Borkowska Z. *J. Electroanal. Chem.* 1995; **387**: 47–52.
13. Opallo M. *J. Electroanal. Chem.* 1996; **418**: 91–97.
14. Masui H, Murray RW. *J. Electrochem. Soc.* 1998; **145**: 3788–3793.
15. Kulesza PJ, Galus Z. *Electrochim. Acta* 1997; **42**: 867–872.
16. Franco JI, Perissinotti L, Walsoe De Reca NE. *Solid State Ionics* 1985; **15**: 95–99.
17. Greenwood NN, Earnshaw A. *Chemistry of the Elements*. Pergamon Press: Oxford, 1984; 943.
18. Galecki J. *Inorganic Laboratory*. WNT: Warsaw, 1964 (in Polish).
19. Aronson S, Ri Y, Gerber AJ, Zhang YR. *J. Chem. Educ.* 1990; **67**: 432–433.
20. Pedersen SU, Christensen TB, Thomasen T, Daasbjerg K. *J. Electroanal. Chem.* 1998; **454**: 123–143.
21. Carre C, Courtieu J, Jullien J, Stahl-Lariviere H. *Spectrochim. Acta, Part A* 1986; **42**: 1201–1208.
22. Fernando KR, McQuillan AJ, Peake BM, Wells J. *J. Magn. Reson.* 1986; **68**: 551–555.
23. Smart L, Moore E. *Solid State Chemistry*. Chapman and Hall: London, 1992.