Potential Response of Solid State Potentiometric Chemical Sensors, Theoretical Approach and Teaching Experiment

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Abstract

Analytical procedures used for qualitative identification or/and quantitative determination of chemical species are based on reaction that takes place in homogeneous or heterogeneous systems. When a solid state potentiometric chemical sensor (PCS) is placed in a solution containing species which can exchange (or reversibly react) with the sensing surface an electrical potential at the surface of a solid material is formed. The species recognition process is achieved with PCS through a heterogeneous chemical reaction at the sensor surface. Reactions that take place in homogeneous solution are also important for the response of a solid state PCS to sensed species in solution. Potentiometric measurements with PCS containing membrane prepared by pressing sparingly soluble inorganic salts can be used for teaching homogeneous and heterogeneous equilibrium. Learning objective is to distinguish between homogeneous and heterogeneous equilibrium, and between single-component and multi-component systems. Homogeneous and heterogeneous systems may be a single chemical or may consist of several components.

Key words: analytical chemistry, potentiometrc sensors, teaching learning theory

Introduction

Design and use electrodes which can selectively measure the activities of ions in solution are important to both theoretical and experimental branches of chemistry. Recently several procedures, which can be adopted for student use and teaching in analytical chemistry, have been published describing the construction of ion selective electrodes.[1–6] Construction and evaluation of an iodide selective electrode employing an AgI + Ag$_2$S coprecipitate pellet-sensing membrane and internal liquid contact has been described.[7] Laboratory experiment based on the construction of a selective electrode utilizing an inexpensive and easy to construct "all-solid-state" electrode body and a polycrystalline homogeneous or heterogeneous AgI + Ag$_2$S membrane also has been described.[8]

Generally, potentiometric chemical sensors (PCS's) make use of the development of an electrical potential at the surface of a solid material when it is placed in a solution containing ions which can exchange (or reversible react) with the surface. Chemical sensor potential data are used to determine the concentration of analyte in solution. Since only cell potentials can be obtained experimentally the potential of the sensor (half-cell potential) can be calculated by the equation

$$E_{\text{cell}} = E_{\text{sensor}} - E_{\text{ref}} + E_{\text{j}} \qquad (1)$$

The first term in Equation (1), E_{sensor}, contains the information about concentration of the analyte. Two other terms: reference electrode potential, E_{ref}, and junction potential, E_{j}, are kept constants during potentiometric measurements.

There are more kinds of membranes which can be used in preparation of PCS's. One of them is sparingly soluble inorganic salt membrane. Also, there are a number of pressed powder type membranes, which are mixtures of silver sulfide and other sparingly soluble inorganic salts. Silver sulfide provides conduction properties of the membrane. The other salt in the membrane is added to obtain selectivity for an ion other than silver or sulfide. The solubility product of the other salt must be higher than that for silver sulfide. In these cases, the primary response of the sensor's membrane is to the silver ion, according to the equation at 298.15 K

$$E = \text{const} + 59.2 \text{ mV} \log a_{\text{Ag}^+} \qquad (2)$$

where a_{Ag^+} is the activity of the silver ion.

The response of Ag$_2$S + AgI membrane to the iodide ion can be understood by writing the expression for the solubility product for AgI, $K_{\text{sp}}^{\text{AgI}}$, and including this term in Equation (2).

Solubility product $\quad K_{\text{sp}}^{\text{AgI}} = a_{\text{Ag}^+} \cdot a_{\text{I}^-} \; ; \quad a_{\text{Ag}^+} = K_{\text{sp}}^{\text{AgI}} \big/ a_{\text{I}^-}$

Inclusion in Equation (2) and simplifying gives

$$E = \text{const}' - 59.2 \, \text{mV} \log a_{I^-} \qquad (3)$$

The response to other ions is again achieved via the solubility product of the respective sparingly soluble salt. It is important to note that the salt more soluble than silver sulfide is either a part of the membrane material in the bulk, or a thin layer on the surface of the membrane formed in contact with an analyte solution.

Chemical analysis

Chemical analysis is that part of analytical chemistry where the reagent, which reacts with the sample under investigation, is a chemical.[9] The fundamentals of chemical analysis deal with the chemical reactions used in analytical investigations. The most important principles for understanding of chemical analysis are equilibria in homogeneous and heterogeneous systems. The stable potential of PCS is formed due to heterogeneous equilibrium at the surface of membrane and homogeneous equilibrium in contacting solution.

The potential response of solid state PCS with $Ag_2S + AgI$ membrane has been extensively investigated in previous papers.[10–15] In this work, for this membrane, the following questions are discussed.

a) Which chemical compound on the surface of the membrane is important for the response of the sensor?

b) Which heterogeneous chemical reaction (or reactions), occurring between the electrode membrane and the sensed ions in solution, forms the interfacial potential?

c) Which homogeneous chemical reaction (reactions) in solution is (are) important for the potential response of the sensor?

Results and Discussion

Heterogeneous and homogeneous equilibrium

Potentiometric determination of penicillamine is described based on a batch experiment and flow-injection analysis (FIA) using a chemical sensor with AgI-based membrane.[16] The membrane was prepared by pressing silver salts (AgI, Ag_2S) and powdered Teflon. This AgI-based membrane detector, sensitive to the sulfhydryl group, was applied to flow-injection determination of different compounds containing sulfur.[17]

In order to understand the effect of stirring to potential response of sensor, for both kind of experiments (batch and FIA), it is necessary to develop a picture of liquid flow patterns near the surface of sensor in a stirred solution.

According to Skoog[18] three types of flow can be identified. *Turbulent flow* occurs in the bulk of the solution away from the electrode. Near the surface of electrode *laminar flow* take place. At 0.01–0.50 mm from the surface of electrode, the rate of laminar flow approaches zero and gives a very thin layer of stagnant solution, which is called the *Nernst diffusion layer* (Ndl). According Equation (2), the potential of sensor is determined by activity of Ag^+ ion in Ndl.
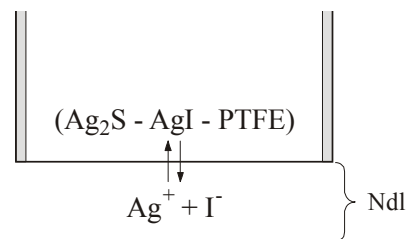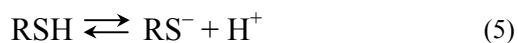

Figure 1. Heterogeneous equilibrium at the phase boundary between AgI-based membrane and solution. Ndl - Nernst diffusion layer.

When the membrane of the sensor, containing both Ag_2S and AgI, is immersed in a solution with Ag^+ or I^- ions heterogeneous equilibrium at the phase boundary is established. The potential difference between the solution phase and the solid phase of the sensor is built up by a charge separation mechanism in which silver ions distribute across the membrane/solution interface as shown in Figure 1. Each silver ion leaving the membrane phase leaves behind a negatively charge vacancy in the crystal lattice.

When the same sensor is immersed in a solution with ions, which form a less soluble salt than AgI or stable metal complexes, a new compound is formed on the membrane surface and/or in Ndl. In contact with a solution containing compounds with the -SH group, at a concentration sufficiently high to cause precipitation of RSAg, the following important equilibrium in Ndl are

$$AgI(s) \rightleftharpoons Ag^+ + I^- \qquad (4)$$

$$\left[Ag^+\right]\left[I^-\right] = K_{sp}^{AgI} = 8.3 \times 10^{-17}$$

$$RSH \rightleftharpoons RS^- + H^+ \qquad (5)$$

$$\frac{\left[RS^-\right]\left[H^+\right]}{\left[RSH\right]} = K_a$$

$$RS^- + Ag^+ \rightleftharpoons RSAg(s) \qquad (6)$$

$$\left[RS^-\right]\left[Ag^+\right] = K_{sp}^{RSAg}$$

For simplicity the equilibrium constants are expressed with concentrations instead activities of

species. Also, the sign for aqueous state (aq) of the species in solution are omitted.

If we summarize Equations (4, 5) and (6) we obtain equilibrium which illustrates new phase formation on the AgI-part of membrane in acid solution (Figure 2b).
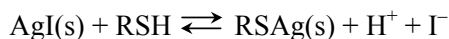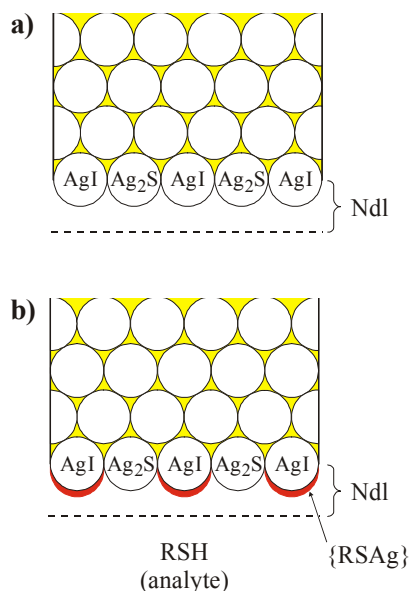
$$AgI(s) + RSH \rightleftarrows RSAg(s) + H^+ + I^- \qquad (7)$$

Figure 2. New phase formation on the more soluble AgI-part of (Ag$_2$S + AgI + Teflon)-membrane.

The equilibrium constant for the total reaction at the phase boundary may be written as

$$K_{eq} = \frac{[RSAg(s)][H^+][I^-]}{[AgI(s)][RSH]} \qquad (8)$$

If we multiply numerator and denominator in Equation 8 by [Ag$^+$] [RS$^-$] we obtain

$$K_{eq} = K_{sp}^{AgI} \frac{K_a}{K_{sp}^{RSAg}} \qquad (9)$$

The solubility product of the new phase, RSAg, formed on the Ag-part of membrane must be higher than that for silver sulphide. In the case of the RSH sensor, the solubility product term for RSAg is incorporated into the Nernst equation as follows

$$K_{sp}^{RSAg} = a_{Ag^+} \cdot a_{RS^-}$$

$$E = const + 59.2 \text{ mV} \log \left(\frac{K_{sp}^{RSAg}}{a_{RS^-}} \right) \qquad (10)$$

$$E = const' - 59.2 \text{ mV} \log a_{RS^-} \qquad (11)$$

If equilibrium constant for RSH, Equation (5), is expressed with activities of species, we can write

$$E = const' - 59.2 \text{ mV} \log \left(K_a \frac{a_{RSH}}{a_{H^+}} \right) \qquad (12)$$

or, at constant pH

$$E = const'' - 59.2 \text{ mV} \log a_{RSH} \qquad (13)$$

The above equation shows that the RSH activity controls the activity of the silver ion at the membrane surface and so controls the membrane potential. Although the silver ion distributes across the interface and is the mobile ion in the membrane the RSH is sensed indirectly.

For any experiment when solution contains small concentration of silver ion and RSH in excess {c(RSH) $>> c$(Ag$^+$)} the two equilibrium, Equations (5) and (6), exist in solution, and the solubility product of RSAg, when pH is fixed and known, can be calculated by the next equation

$$\log K_{sp}^{RSAg} = \{(E - const) / S\} + \log c(RSH) - \log \frac{K_a + [H^+]}{K_a} \qquad (14)$$

where E, S, c(RSH) and K_a denote the measured potential of the sensor, experimental slope, total or analytical concentration of RSH in solution and the dissociation constant of RSH, respectively.

The response of the electrochemical cell, with PCS containing AgI-based membrane, to Ag$^+$ ions was tested by the method of continuous decrease in the concentration of silver ions in the reaction vessel. Serial dilution of the 0,100 M standard silver nitrate solution was performed using 0.100 M perchloric acid. After decreasing the Ag$^+$ ions concentration up to the concentration 6.3×10^{-6} M different volumes of standard penicillamine (designated also as RSH) solution were added into the same perchloric acid solution of silver ions. This procedure was used in testing the response of the electrochemical cell to the increase of penicillamine concentration. Linear response was obtained in the concentration range from 2.0×10^{-5} to 1.8×10^{-2} M. The experimental slope was in good agreement with the theoretical (59 mV {p(RSH)}$^{-1}$) value postulated on an precipitation process and formation of RSAg in Ndl or on the sensing part of the detector. Similar slopes were obtained when other RSH compounds were tested (cysteine, *N*-acetil-L-cysteine, glutathione, thiopronine).

In the experiment with penicillamine[16] the solubility product, K_{sp}^{RSAg}, was determined using experimental values recorded both by batch measurements and by continuous-flow experiment. The calculated mean value, $K_{sp}^{RSAg} = 1.40 \times 10^{-20}$, obtained by batch measurements is in good agreement with the value obtained by

continuous-flow experiment. For both experiments PCS with AgI + Ag$_2$S membrane was used.

By using the experimentally established constant of solubility product, K_{sp}^{RSAg}, the dissociation constant of penicillamine,[19] K_a, and Equation (9) the equilibrium constant can be calculated.

$$K_{eq} = 8.3 \times 10^{-17} \frac{3.16 \times 10^{-11}}{1.40 \times 10^{-20}} = 1.87 \times 10^{-7}$$

The calculated value of equilibrium constant indicates that the postulated reaction 7 at the phase boundary has not gone to completion.

If we suppose that Ag$_2$S part of membrane, instead AgI part, reacts with RSH the process at the phase boundary may be expressed by the total reaction

$$Ag_2S(s) + 2\ RSH \rightleftharpoons 2\ RSAg(s) + 2\ H^+ + S^{2-} \qquad (15)$$
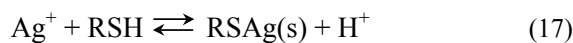
with appropriate equilibrium constant

$$K_{eq} = K_{sp}^{Ag_2S} \frac{(K_a)^2}{(K_{sp}^{RSAg})^2} \qquad (16)$$

$$K_{eq} = 6.3 \times 10^{-50} \frac{(3.16 \times 10^{-11})^2}{(1.40 \times 10^{-20})^2} = 3.21 \times 10^{-31}$$

Evidently the stable potential of the PCS with (AgI + Ag$_2$S) membrane in penicillamine solution is governed neither by the reaction (7) nor (15).

As mentioned, PCS with AgI + Ag$_2$S membrane (before the experiment with penicillamine) was immersed in a solution of Ag$^+$ ions, and the residual concentration of Ag$^+$ ions in solution including Ndl was 6.30×10^{-6} M. The formation a new solid state phase in Ndl or/and at the surface of membrane may be expressed by the next reaction:

$$Ag^+ + RSH \rightleftharpoons RSAg(s) + H^+ \qquad (17)$$

with appropriate equilibrium constant.

$$K_{eq} = \frac{[H^+]}{[Ag^+][RSH]} \qquad (18)$$

$$K_{eq} = \frac{K_a}{K_{sp}^{RSAg}} \qquad (19)$$

$$K_{eq} = \frac{3.16 \times 10^{-11}}{1.40 \times 10^{-20}} = 2.26 \times 10^9$$

The calculated value of equilibrium constant suggests completeness of the new phase formation reaction at the surface of membrane. In addition, it can be supposed that, by adsorption process, both parts of membrane, AgI and Ag$_2$S, are covered with thin layer of RSAg precipitate (Figure 3). Under these conditions, the equilibrium activity of Ag$^+$ ions and the corresponding response of PCS are governed by new heterogeneous equilibrium.

Now we can calculate the minimal concentration of penicillamine, or any other RSH compound, which cause precipitation of RSAg in acidic media.

$$K_{eq} = \frac{[H^+]}{[Ag^+] \cdot c(RSH) \cdot \alpha(RSH)} = 2.26 \times 10^9 \qquad (20)$$

$$c(RSH) \geq \frac{[H^+]}{[Ag^+] \cdot K_{eq} \cdot \alpha(RSH)} \qquad (21)$$

$$\alpha(RSH) = \frac{[RSH]}{c(RSH)} = \frac{[RSH]}{[RS^-] + [RSH]} \qquad (22)$$

If we express [RS$^-$] with dissociation constant of RSH, Equation (5), we obtain

$$\alpha(RSH) = \frac{[H^+]}{K_a + [H^+]} \qquad (23)$$

In 0.100 M perchloric acid $\alpha(RSH) \approx 1$.

$$c(RSH) \geq \frac{0.100}{6.3 \times 10^{-6} \cdot 2.29 \times 10^9 \cdot 1}$$

$$c(RSH) \geq 7.0 \times 10^{-6}\ M$$

This concentration of penicillamine may be estimated as the detection limit for describing experimental conditions.

When a sample solution containing RSH forms $Ag(SR)_n^{(1-n)+}$ complexes instead of precipitates, the equilibrium in solution may be expressed as:

$$RSH \rightleftharpoons RS^- + H^+$$
$$Ag^+ + n\ RS^- \rightleftharpoons Ag(RS)_n^{(1-n)+} \qquad (24)$$
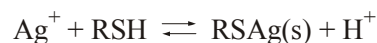

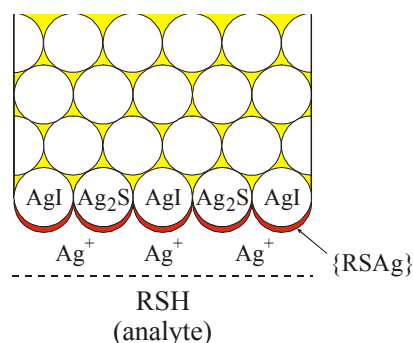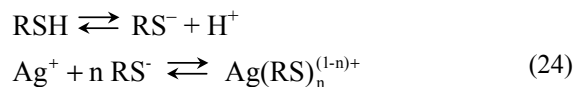$$Ag^+ + RSH \rightleftharpoons RSAg(s) + H^+$$

Figure 3. New phase formation in Ndl and its adsorption on the surface of membrane.

The equilibrium activity of Ag^+ ions and the corresponding response of PCS are now governed with these homogeneous reactions.

If the sample solution contains M^{m+} ions, which form stable complexes with iodide, the process at the phase boundary may be expressed by the total reaction

$$AgI(s) + M^{m+} \rightleftarrows MI_x^{(m-x)+} + \times Ag^+ \qquad (25)$$
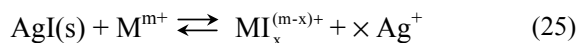
If the formation constants of $MI_x^{(m-x)+}$ species are very large a vanishing small M^{m+} ions concentration remains near the electrode surface. The electrode phase has started to dissolve and form the $MI_x^{(m-x)+}$ compounds. Consequently, if the concentration of the M^{m+} ions in solution and the solubility (stability) constant are sufficient for reaction (25) to proceed to the right, the activity of the silver ions at the phase boundary and potential of PCS are determine by the concentration of the M^{m+} ions in solution.

Application and Conclusion

The present article can be used as a laboratory experiment in teaching of analytical chemistry. The used PCS is based on a polycrystalline homogeneous or heterogeneous $AgI + Ag_2S$ membrane. An inexpensive and easy to construct "all-solid-state" electrode body[8] can be used for assembling PCS. The potential response of the PCS with membrane prepared by pressing of the sensing material is based on the reversible heterogeneous and homogeneous chemical reactions at (or near) the exposed surface of the sensor.

For compounds with -SH group, a rectilinear calibration graphs were obtained by plotting the experimental potential versus concentration of RSH. The experimental slopes were in good agreement with the theoretical $(59\,mV\{p(RSH)\}^{-1})$ value postulated on an heterogeneous reaction and formation of RSAg at the membrane of the sensor or/and into Ndl.

The utilized PCS with $AgI + Ag_2S$ membrane can be applied for calculation of the solubility product of RSAg or stability constant of $Ag(SR)_n^{(1-n)+}$ complex.

These experiments have been designed to illustrate the theoretical and the practical aspects involved in the use of PCS with $AgI + Ag_2S$ membrane. Many thiols (cysteine, *N*-acetyl-L-cysteine, penicillamine, glutathione, thiopronine) have been tested in proposed teaching experiment.

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Povzetek

Analizni posopek za kvalitativno in/ali kvantitativno določitev kemijske zvrsti temelji na reakciji v homogenem ali heterogenem sistemu. Če trden potenciometrični senzor vstavimo v raztopino zvrsti, ki lahko reverzibilno reagira s senzorsko površino, se na njej vzpostavi električni potencial. Proces razpoznavanja zvrsti se vrši prek heterogene kemijske reakcije. Potenciometrične meritve s senzorji z membranami, ki jih pripravimo s stiskanjem slabo topnih anorganskih soli, lahko uporabimo za učenje vsebin, kot sta homogeno in heterogeno ravnotežje. Pedagoški namen je, da med njima razlikujemo, kot tudi, da razlikujemo med enokomponentnimi in večkomponentnimi sistemi.