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SHORT COMMUNICATION

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Determination of the complex formation constants for some water-soluble polymers with trivalent metal ions by differential pulse polarography

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Abstract The formation of metal complexes between water-soluble polymers, poly(vinyl alcohol) [PVA], poly(*N*-vinylpyrrolidone) [PVP], poly(acrylamide) [PAAm] and poly(ethylene oxide) [PEO] with trivalent metal ions, Fe^{3+}, Cr^{3+}, and V^{3+} were studied by using differential pulse polarography (DPP). The general experimental observation is the shift of totally reversible reduction peaks ($M^{3+} + Hg + e^- \rightleftharpoons M^{2+} + Hg$) towards more negative potentials when the complexing water-soluble polymers are added to the solution of trivalent metal ions. The negative shift in potential permitted the determination of complex formation constants (K_f) between trivalent metal ions and water soluble polymers. The complex formation constants for Fe^{3+}, Cr^{3+}, and V^{3+} ions with these polymers increased in the order of $V^{3+} > Cr^{3+} > Fe^{3+}$.

Keywords Trivalent metal ions · Water-soluble polymers · Complex formation constant · Differential pulse polarography

Introduction

The removal and recovery of heavy metal ions from industrial wastewater have been taking on an increasing importance because of a combination of economic and environmental factors. As an effective settlement, chelating groups are used for enriching and separating heavy metal ions from aqueous solutions [1]. Water-soluble polymers are insoluble when they are in the form of crosslinked structure and provide an efficient way for removal of the heavy metal ions selectively from dilute solutions by complexing with their electron donor sites.

Interaction between polymer and metal ions generally consist of various weak binding forces such as coordination bonds, hydrogen bonds, charge-transfer interaction, hydrophobic interaction, etc. Although these interactions are weak, they are significant and act multiply and dynamically. Because they are plural, these binding forces cooperatively play an important role in polymer-metal complexes. The electron-transfer processes of the complex moieties of polymer-metal complexes are often affected by the dynamic conformational change of the molecular environment around the complexes [2, 3].

The potential for the reduction of metallic ions are greatly affected by the presence of species that form complexes with those ions. The half-wave potential ($E_{1/2}$) or peak potential (E_p) for the reduction of a metal complex is generally more negative than that for the corresponding simple metal ion. For small pulses amplitudes, the potential at maximum current (peak potential, E_p) is close to the $E_{1/2}$ polarographic potential, such that E_p was measured in this study. In fact, the negative shift in potential permits elucidation of the composition of the complexed ion and the determination of its complex formation constant provided that the electrode reaction is reversible. Thus for the reactions

$$M^{n+} + Hg + ne^- \rightleftharpoons M(Hg)$$

and

$$M + pL \rightleftharpoons ML_p$$

Lingane [4] derived the following relationship between concentrations of ligand (L) and shift in half-wave potential:

$$\left(E_{1/2}\right)_c - E_{1/2} = -\frac{0.0591}{n}\log K_f - \frac{0.0591p}{n}\log L \qquad (1)$$

where $(E_{1/2})_c$ and $E_{1/2}$ are the half-wave potentials for the complexed and uncomplexed cations, respectively, K_f is the complex formation constant, *p* is the molar ratio of complexing agent to cation, and *n* is the number of electrons transferred for reduction. Different experimental techniques such as potentiometric [5], voltammetric [6, 7], or spectrophotometric [2] techniques are reported in the scientific literature for the measurements of K_f. In this study, the shift of the half-wave potential is measured as mentioned in electrochemistry textbooks [8]. Effect of complexing agent on polarographic half-wave potentials at the dropping mercury electrode is applicable whenever the electron transfer is reversible, as in the case for the $M^{3+} + e^- \rightleftharpoons M^{2+}$ where M is Fe, Cr, or V.

Experimental

Apparatus A polarographic analyzer system (PAR 174 A), equipped with a mercury drop-timer, was used. The drop time of mercury electrode was approximately 2–3 s (2.75 mg/s). A Kalusek electrolytic cell with reference-saturated electrode (SCE), separated by liquid junction was used in three electrode configuration. Counter electrode was platinum wire. The polarograms were recorded with a Linseis LY 1600 X-Y recorder. Pulse polarograms were recorded under the conditions of a drop life of 1 s, a scan rate of 5 mV/s, pulse duration of 50 ms, and pulse amplitude of 50 mV.

Chemicals Poly(*N*-vinyl 2-pyrrolidone) (PVP) ($M_w = 120{,}000$ g/mol), poly(ethylene oxide) (PEO) ($M_w = 10{,}000$ g/mol) poly(vinyl alcohol) (PVA) ($M_w = 124{,}000$ g/mol), and poly(acrylamide) (PAAm) ($M_w = 10{,}000$ g/mol 50 wt% solution in water) were obtained from Aldrich.

The concentrations of these polymers used in the complexation experiments were 0.1 base mole/L. Glacial acetic acid, phosphoric acid, and boric acid were used to prepare Britton-Robinson (B-R) buffers and $Cr(NO_3)_3{\cdot}9H_2O$, $FeCl_3{\cdot}6H_2O$, and VCl_3 and were obtained from Merck.

The 0.1 mol/L stock solution of Fe^{3+} was prepared by dissolving $FeCl_3{\cdot}6H_2O$ in HCl solution to prevent precipitation. The 0.1 mol/L stock solutions of Cr^{3+} and V^{3+}were prepared by dissolving $Cr(NO_3)_3{\cdot}9H_2O$ and VCl_3 in distilled water. $1{\times}10^{-2}$ to $1{\times}10^{-5}$ mol/L working solutions were prepared by daily dilution.

B-R buffer solution was prepared in such a way that 2.3 mL glacial acetic acid, 2.7 mL phosphoric acid, and 2.4720 g boric acid dissolved in water to 1.0 L; 50.0 mL portions of this solution were taken and the pH was adjusted to 4.0 by addition of the appropriate amount of 2.0 mol/L NaOH. For the preparation of acetate buffer solution, 57.2 mL glacial acetic acid was diluted to 1.0 L and 50-mL portions of this solution was adjusted to pH = 4.0 by adding proper amount of 2.0 mol/L NaOH.

Procedure Ten milliliters of buffer solution (pH = 4) containing $5.0{\times}10^{-5}$ mol/L of Fe^{3+}, Cr^{3+}, or V^{3+} in the polarographic cell was deaerated by a stream of nitrogen gas (99.999%) for 3.0 min. Polarograms of Fe^{3+}, Cr^{3+}, and V^{3+} were taken by scanning the potential from +0.15 to −0.45 V, −0.5 to −1.1 V, and −0.7 to −1.3 V, respectively. After addition of polymer solutions onto those trivalent metal ions in the same polarographic cell, the polarograms were recorded by applying the above potential sweeps. All the potentials were measured against the reference of saturated calomel electrode (SCE).

Results and discussions

A total of 10.0 mL acetic acid-acetate buffer (pH = 4.0) in the polarographic cell was deaerated through the passage of pure nitrogen gas for about 5 min. Polarograms of ferric ion solutions were taken through the scanning of the potential from +150 mV to about −450 mV at a scan rate of 5 mV/s. In this solution $5{\times}10^{-5}$ mol/L Fe^{3+} showed a peak at about 0.0 mV which corresponds to its reduction to Fe^{2+}. When polymer solutions were added to this solution the reduction potential shifted towards more negative potentials. The solutions with varying polymer ligand (monomeric unit)/metal ions molar ratios were prepared and shifting in peak potentials were measured. When the PVA/Fe^{3+} molar ratio is increased from 0 to 250, reduction peak broadened and the peak potential of Fe^{3+} shifted from 0 to about −300 mV. The magnitude of this shift in peak potential is related to the stability of the complex between Fe^{3+} and PVA. In the same manner, in 10.0 mL B-R buffer solution of Cr^{3+} shows a reduction peak which corresponds to its Cr^{2+} (at about −700 mV) reduction during the potential scan from −500 mV to −1100 mV. The peak potential for chromium shifted to more negative potentials with increasing the PAAm concentration. When the PAAm/Cr^{3+} molar ratios were increased from 0 to 100, the peak potential of Cr^{3+} shifted from −700 mV to −930 mV (Fig. 1). The shifting in peak potentials for V^{3+} during the potential scanning from −700 mV to −1300 mV were observed from −1000 mV to −1150 mV when the PEO/V^{3+} molar ratios were increased from 0 to 75. Similarly, when the

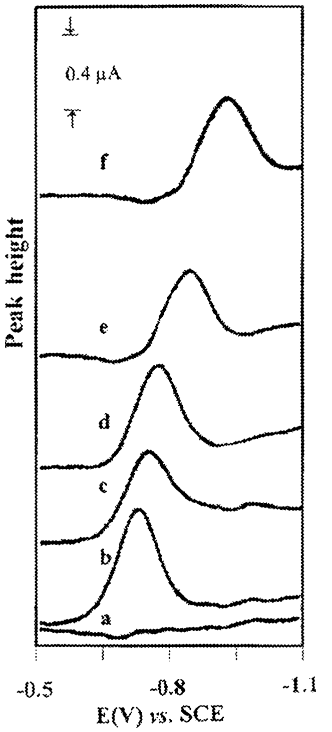

Fig. 1 Determination of the complex formation constant for Cr^{3+}/PAAm complex by differential pulse polarography: *trace a*) 10.0 mL pH = 4.0 B-R buffer solution; *trace b*) 5.0x10^{-5} mol/L Cr^{3+}; *trace c*) 1.25x10^{-3} mol/L PAAm; *trace d*) 2.50x10^{-3} mol/L PAAm; *trace e*) 3.75x10^{-3} mol/L PAAm; *trace f*) 5.00x10^{-3} mol/L PAAm. Drop time: 1.0 s. Pulse amplitude: 50 mV. Pulse duration: 50 ms. Sweep rate: 5 mV/s

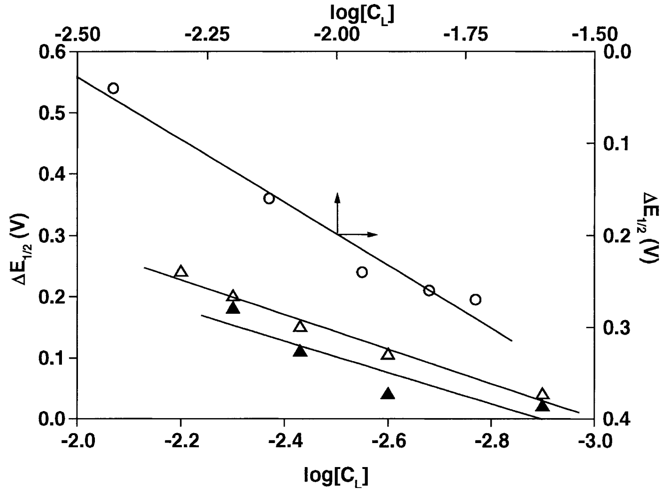

Fig. 2 Plot of $\Delta E_{1/2}$ vs log[C_L] for polymer/M^{3+} complexes. (*open circles*) Fe^{3+}-PVA, (*open triangles*) V^{3+}-PEO, (*filled triangles*) Cr^{3+}-PAAm

PVP/Cr^{3+} molar ratios were increased from 0 to 50, the peak potentials for chromium shifted from −750 mV to −950 mV. It must be mentioned that primary cause for the slight decrease in the peak current intensities results from the decrease of the diffusion coefficient of the trivalent metal ions with increasing polymer concentration because of coordination to slowly diffusing macromolecule [7].

From the data obtained, a plot of $\Delta E_{1/2}$ vs log C_L has been drawn (Fig. 2). From the intercept of the straight line with the $\Delta E_{1/2}$ axis, logK_f and then K_f values for polymer/metal ions complexes were calculated (Eq. 1). The complex formation constants for Fe^{3+}, Cr^{3+}, and V^{3+} with water soluble polymers of PVP, PAAm, PVA, and PEO are given in Table 1. As shown in Table 1, all the water soluble polymers used in this work form relatively stable complexes with Fe^{3+} ions and to a lesser extent with Cr^{3+} and V^{3+}, respectively. We calculated K_f values of the order of 10^{15}–10^{11} for Fe^{3+}, 10^{12}–10^{9} for Cr^{3+}, and 10^{14}–10^{8} for V^{3+} with the relative standard derivations between 5.5 and 12.3%. This behavior could be attributed to the metal ion charge/radius ratio [9]. The charge/radius ratio for the metal ions used in this work, increases in order $V^{3+} < Cr^{3+} < Fe^{3+}$ and the stability of the metal complexes increases with increasing of the metal ion charge/radius ratio. Since Fe^{3+} has the smallest ionic radius than the other ions [10], it forms stronger interaction with polymeric ligands. On the other hand, Fe^{3+} ion has a higher electronegativity than Cr^{3+} and V^{3+}. This behavior should result in more stable complexes between Fe^{3+} and electron donor groups of polymeric ligands.

Other methods for the determination of the complex constants of some metal ions with the selected polymers usually include spectrophotometric or potentiometric techniques. The stability constants for the complexes of

Table 1 Complex formation constants of Fe^{3+}, Cr^{3+}, and V^{3+} with some water soluble polymers (Average ± Standard Derivation, *n* = 3)

Polymers	K_f			RSD[a](%)		
	Fe^{3+}	Cr^{3+}	V^{3+}	Fe^{3+}	Cr^{3+}	V^{3+}
PVA	(1.02 ± 0.11)x10^{15}	(4.20 ± 0.19)x10^{12}	(2.30 ± 0.26)x10^{8}	10.2	4.5	11.3
PEO	(8.30 ± 0.55)x10^{14}	(5.68 ± 0.32)x10^{10}	(2.11 ± 0.25)x10^{14}	6.6	5.6	11.8
PAAm	(4.15 ± 0.33)x10^{13}	(3.79 ± 0.21)x10^{12}	(5.03 ± 0.62)x10^{10}	7.9	5.5	12.3
PVP	(6.00 ± 0.34)x10^{11}	(2.98 ± 0.27)x10^{9}	(7.25 ± 0.66)x10^{8}	5.7	9.1	9.1

n = number of experiments

[a] Relative standard derivation (reproducibility)

poly(acrylic acid) with some metal ions were reported by using potentiometric titration method and K_f values for Zn^{2+}, Ni^{2+}, Co^{2+}, VO^{2+}, and Cu^{2+} were between 2.24×10^9 and 1.58×10^{11} [11]. The K_f values for poly(*N*-vinylimidazole)-trivalent metal ion systems using UV-vis spectroscopy for V^{3+}, Cr^{3+}, and Fe^{3+} were 1.17×10^9, 2.42×10^9, and 2.69×10^9, respectively [2]. The stability constants for some polymeric chelating agents such as poly(glycidyl methacrylate-iminodiacetic acid), poly(glycidyl methacrylate-iminodiacetic acid-*co*-methyl acrylate), and poly(glycidyl methacrylate-iminodiacetic acid-*co*-acrylamide) with Ni^{2+}, Zn^{2+}, and Co^{2+} were 1.35×10^8, 1.94×10^8, and 1.51×10^9, respectively, by using potentiometric and spectrophotometric methods [12].

Since the removal and recovery of metal ions by using polymeric materials from industrial wastewater have been receiving increasing attention in all industrial branches because of a combination of economic and environmental factors, the stability of the complexation between heavy metals and polymeric ligands must be determined by using more reliable or precise techniques rather than conventional methods such as spectrophotometric techniques. Analytical tools used in many works for K_f determination usually include spectrophotometric techniques and the concentration of the species may be higher than present method. On the other hand, the potential shifts of metal ions and their complexes could be determined directly without any interference effects.

References

1. Lin H, Kimura M, Hanabusa K, Shirai H, Ueno N, Mori Y (2002) J Appl Polym Sci 85:1378–1386
2. Pekel N, Savas H, Güven O (2002) Colloid Polym Sci 280:46–51
3. Howard AG (1998) Aquatic environmental chemistry. Oxford University Press, New York, p 35
4. Lingane JJ (1941) Chem Rev 29:1
5. Nishide H, Oki N, Tsuchida E (1982) Eur Polym J 18:799–802
6. Kramer C, Dunsch L (1988) Electrochim Acta 44:819–829
7. Leroy D, Martinot L, Jérôme C, Jérôme R (2001) Polymer 42:4589
8. Bard AJ, Faulkner LR (1980) Electrochemical methods. Wiley, New York
9. Vogel AIA (1961) Textbook of quantitative inorganic analysis. Longman, London, p 892
10. Huheey JE (ed) (1993) Principles of structure and reactivity. Inorganic chemistry. Harper Collins, London
11. Roma-Luciow R, Sarraf L, Morcellet M (2001) Eur Polym J 37:1741–1745
12. Chen CY, Chen CY (2002) J Apply Polym Sci 86:1986–1994