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Electrooxidation Behaviour of Zinc O,O,O',O'-Tetrabutyl *bis*(phosphorodithioate) on a Platinum Disk Microelectrode

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The electrochemical oxidation behaviour of zinc O,O,O',O'-tetrabutyl *bis*(phosphorodithioate) (ZBPD) on a Pt disk microelectrode in N,N-dimethyl formamide solution was investigated by cyclic voltammetry and steady-state voltammetry methods. The influences of temperature, scan rate and ZBPD concentration on the electrochemical characteristics of ZBPD were also discussed. Results showed that the electrooxidation of ZBPD in DMF solution was an irreversible process with one electron transferred, which was controlled by diffusion. The steady-state limiting current of ZBPD in DMF solution was increased with the temperature increasing, which was due to the enhancement of diffusion of ZBPD in DMF solution at higher temperature. The diffusion coefficient was obtained for each temperature. In terms of the Arrhenius equation, the activation energy of diffusion of ZBPD in DMF solution was calculated to be 13.76 kJ mol^{-1}.

Key Words: Zinc O,O,O',O'-tetrabutyl *bis*(phosphorodithioate), Electrooxidation, Diffusion coefficient, Activation energy.

INTRODUCTION

Zinc dialkyldithiophosphates (ZDDP) are widely used in the automotive industry as an antioxidant additive in engine lubricant formulations[1,2]. The structure of a ZDDP compound is shown in Fig. 1. A plethora of investigations reported in the literature have aimed to elucidate the structure of ZDDP and its nature of antioxidant activity[3,4]. A number of studies have also aimed to determine their content in the lubricant oil[5-7]. Despite the large amount of research which has been undertaken, the mechanistic action of ZDDP compounds in their capacity as antioxidant agents remains poorly defined[8-10]. To study the electrooxidation characteristics and mechanism of ZDDP is of great importance for reasonably allocating the amount of additives in lubricating oil and prolonging the service life of lubricating oil and machinery equipments. In this paper, the electrooxidation behaviours of zinc O,O,O',O'-tetrabutyl *bis*(phosphorodithioate) (ZBPD) were studied in N,N-dimethyl formamide solution. The experimental results showed that ZBPD can be oxidized on Pt disk microelectrode in DMF solution. The number of electrons transferred in ZBPD electrooxidation reaction, the diffusion coefficients (D) at various temperatures and the diffusion activation energy (E_a) were determined.

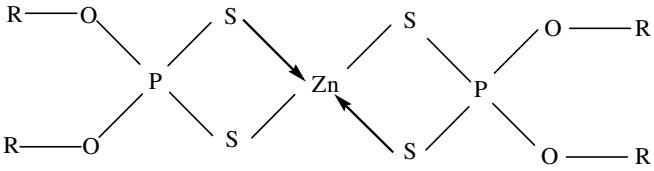

Fig. 1. Chemical structure of ZDDP

EXPERIMENTAL

All chemicals were of analytical grade. The electrolytic solution was prepared by dissolving ZBPD in DMF solution. The supporting electrolyte was 0.2 mol L^{-1} $LiClO_4$. All electrochemical experiments were performanced on μAut71078 Autolab electrochemical workstation (Metrohm Autolab B. V., The Netherlands). A three-electrode electrochemical cell was used for all experiments. A Pt disk microelectrode of disk radius 30 μm was used as a working electrode. A platinum sheet and an Ag/Ag^+ (0.01 mol L^{-1} $AgNO_3$ in DMF) electrode were served as the counter electrode and the reference electrode, respectively. All electrode potentials are reported with respect to the Ag/Ag^+ electrode.

The working electrode was polished to mirror with 0.05 μm Al_2O_3 aqueous slurry. After being polished, the microelectrode was cleaned for 2 min, respectively, by ultrasonic cleaner in HNO_3 (1:1), NaOH (0.2 mol L^{-1}), absolute alcohol and

acetone ordinal. Finally, the microelectrode was checked by recording the cyclic voltammogram of ferrocyanide in 0.1 M KCl aqueous solution.

RESULTS AND DISCUSSION

Cyclic voltammetric behaviour of ZBPD: The electrochemical oxidation behaviour of ZBPD on Pt disk microelectrode was investigated by cyclic voltammetry in DMF solution. Fig. 2 illustrated the cyclic voltammograms of Pt disk microelectrode in the absence (a) and presence (b) of 4.0 mmol L^{-1} ZBPD in DMF solution containing 0.2 mol L^{-1} $LiClO_4$. It can be seen that no redox peak was observed in the absence of ZBPD on Pt disk microelectrode, when ZBPD was added, a well-defined oxidation peak was observed with the oxidation potential of 0.46 V. This phenomenon should be attributed to the oxidation of ZBPD. However, no corresponding reduction peak was observed in the following reverse scan from 1.4 to 0 V, indicating that the oxidation of ZBPD was a totally irreversible electrode process under the above experimental conditions[11].

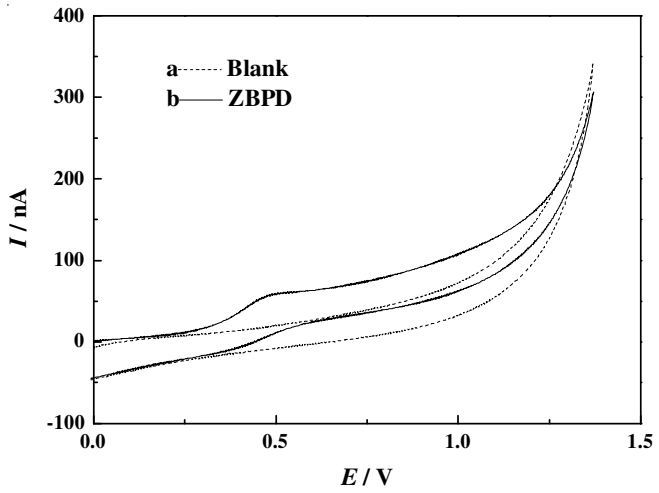

Fig. 2. Cyclic voltammograms of Pt disk microelectrode in 0.2 mol L^{-1} $LiClO_4$ + DMF solution in the absence (a) and presence (b) of 4.0 mmol L^{-1} ZBPD at a scan rate of 200 mV s^{-1}

The influence of temperature on the electrochemical oxidation behaviour of ZBPD was investigated in our study. The cyclic voltammograms for the electrooxidation of ZBPD at various temperatures at the scan rate of 0.2 V s^{-1} were shown in Fig. 3. It was observed that the peak current increased as the temperature increasing, indicating the enhancement of diffusion of ZBPD in DMF solution at higher temperatures. The linearity equation between peak current and temperature was defined as:

$$I_p = 3.696\times10^{-10}T - 6.95268\times10^{-8} \quad R = 0.9994 \qquad (1)$$

From eqn. 1 the temperature coefficient of peak current was calculated to be 0.91 %/K, which was less than 2 %/K. This phenomenon indicated that the electrooxidation process of ZBPD on Pt disk microelectrode was not controlled by the electrochemical process[12], for the reaction controlled by electrochemical process had higher temperature coefficient, when the temperature increased, the active energy would decreased rapidly.

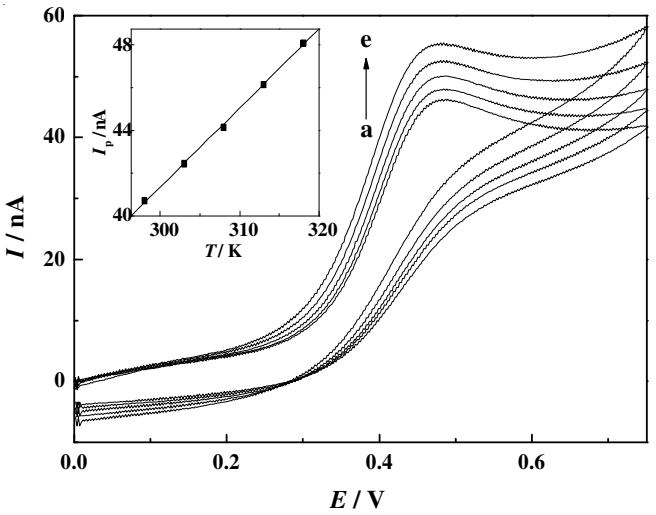

Fig. 3. Cyclic voltammograms of 4.0 mmol L^{-1} ZBPD on Pt disk microelectrode at various temperatures. T/K: a. 298, b. 303, c. 308, d. 313, e. 318. Inset: Variation of peak current of ZBPD *vs.* temperatures. Scan rate: 200 mV s^{-1}

Fig. 4 illustrated the influence of scan rate on the electrochemical oxidation behaviour of ZBPD in DMF solution. It was clearly shown that there was a good linear relationship between the oxidation peak current and the square root of scan rate. The regression equation can be expressed as:

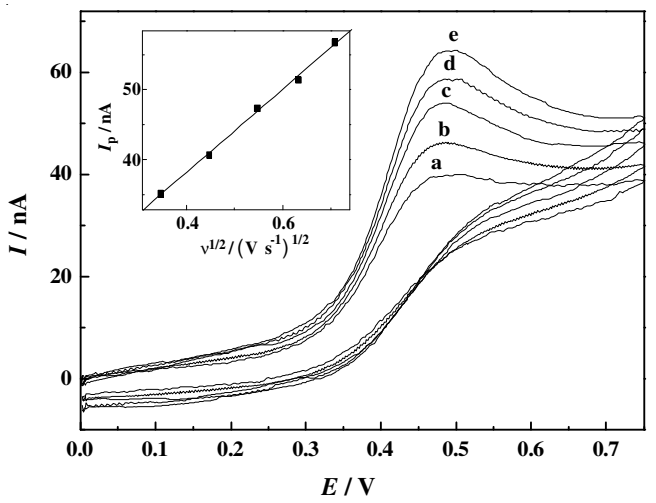

Fig. 4. Cyclic voltammograms of 4.0 mmol L^{-1} ZBPD on Pt disk microelectrode at various scan rates. Scan rates/(mV s^{-1}): a. 120, b. 200, c. 300, d. 400, e. 500. Inset: Variation of peak current of ZBPD, *vs.* square root of scan rate

$$I_p = 5.92932\times10^{-8}v^{1/2} + 1.44801\times10^{-8}, \quad R = 0.99869 \qquad (2)$$

This indicated that the electrode oxidation process was controlled by diffusion.

The influence of ZBPD concentration on its electrochemical oxidation behaviour was studied. The voltammograms at various concentrations of ZBPD were shown in Fig. 5. As can be seen in Fig. 5, the peak current was increased with increasing the concentration of ZBPD, C. We plot I_p *versus* C, the regression equation was:

$$I_p = 1.052\times10^{-8}C - 2.96\times10^{-9}, \quad R = 0.99945 \qquad (3)$$

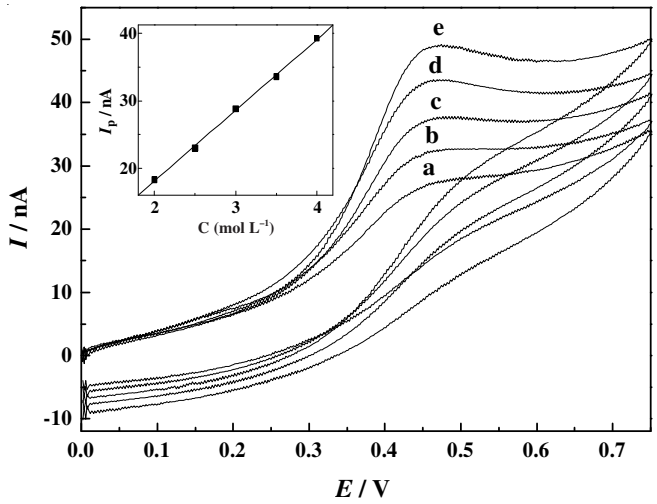

Fig. 5. Cyclic voltammograms of ZBPD on Pt disk microelectrode at various ZBPD concentrations. C (mmol L^{-1}): a. 2.0, b. 2.5, c. 3.0, d. 3.5, e. 4.0. Inset: Variation of peak current of ZBPD *vs*. ZBPD concentration. Scan rate: 200 mV s^{-1}

It can be seen that I_p was proportional to C. This was because with the increase of the substrate concentration, the concentration of diffusion layer and bulk solution increased, the reaction speed got faster, so the peak current increased.

Mechanism studies: As shown in Fig. 4, the oxidation peak potential, E_p, increased with the increase of the logarithm of the potential scan rate, lg ν. As shown in Fig. 6, when the potential scan rate ranged from 0.12 to 0.5 V s^{-1}, the plot of E_p *versus* lg ν was linear, the linearity relationship was:

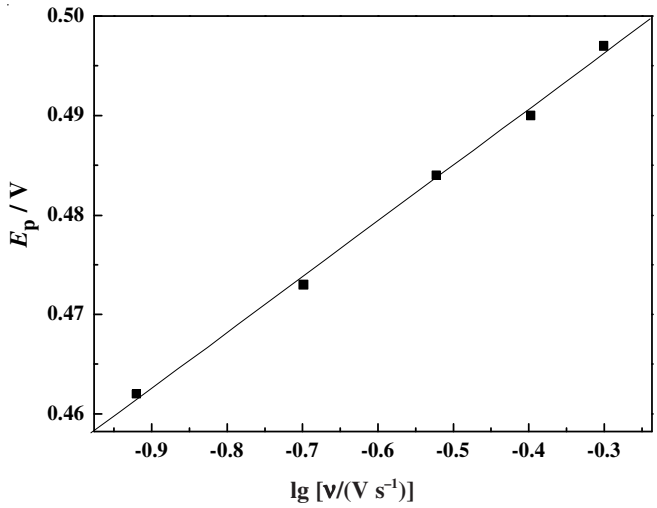

Fig. 6. Variation of E_p of 4.0 mmol L^{-1} ZBPD in DMF solution, *vs*. lg ν

$$E_p = 0.05613 \lg \nu + 0.5131, \; R = 0.99846 \quad (4)$$

For an irreversible process, E_p can be expressed by the following equation[13,14]:

$$E_p = E^0 + \frac{RT}{\alpha nF}\left[\ln\left(\frac{D^{1/2}}{k_s}\right) + \ln\left(\frac{\alpha nF\nu}{RT}\right)^{1/2} + 0.78\right] \quad (5)$$

where E^0 is the formal standard potential, α is the electron transfer coefficient, n is the number of electrons transferred, F is the Faradic constant, R is the gas constant, D is the diffusion coefficient of ZBPD, T is the absolute temperature, and k_s is the standard heterogeneous reaction rate constant. The number of electrons transferred can be obtained according to the slope of the straight line of E_p against lg ν:

$$\frac{0.5 \times 2.303RT}{\alpha nF} = 0.05613 \quad (6)$$

Therefore, αn was calculated to be 0.53. Generally, α was assumed to be 0.5 in totally irreversible electrode process[15]. So n was calculated to be 1.06 ≈ 1.

On the basis of the results obtained, it may be concluded that the electrooxidation of ZBPD in DMF solution was an irreversible process with one electron transferred. In the light of the number of transferred electron obtained in this work and the reference[9], the possible oxidation mechanism of ZBPD was expressed as shown in **Scheme-I**.

$$[(C_4H_9O)_2PS_2]_2Zn \longrightarrow (C_4H_9O)_2PS_2^- + [(C_4H_9O)_2PS_2]Zn^+$$

$$(C_4H_9O)_2PS_2^- \longrightarrow (C_4H_9O)_2PS_2^{\bullet} + e^-$$

$$(C_4H_9O)_2PS_2^{\bullet} + (C_4H_9O)_2PS_2^{\bullet} \longrightarrow [(C_4H_9O)_2PS_2]_2$$

Scheme-I: Possible mechanism of ZBPD oxidation on Pt disk microelectrode

Measurements of diffusion coefficients and the activation energy of diffusion: The diffusion coefficient is one of the most important parameters for the electrode reaction controlled by diffusion. Herein, steady-state voltammetry was used to investigate the diffusion coefficient of ZBPD. Fig. 7 showed steady-state voltammograms of 4.0 mM ZBPD in DMF solution at various temperatures. As can be seen in Fig. 7, the steady-state limiting current was increased as the temperature increasing, this was because with the increase of the temperature, the diffusion coefficient of ZBPD in DMF solution was increased. The diffusion coefficients of ZBPD in DMF solution at various temperatures can be calculated according to the formula[16] as follows:

$$i_{ss} = 4nFDCr \quad (7)$$

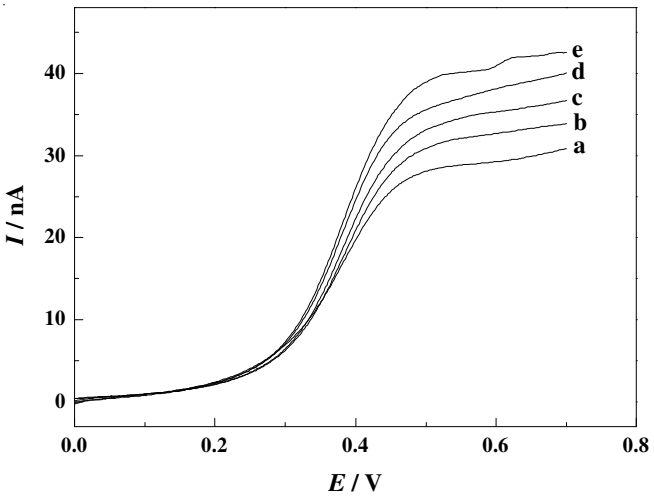

Fig. 7. Steady-state voltammetric responses of ZBPD at various temperatures in DMF solution. Scan rate: 0.5 mV s^{-1}

where i_{ss} is the steady-state limiting current, r is the radius of electrode. According to eqn. 7, the diffusion coefficients of ZBPD at various temperatures were calculated in Table-1.

TABLE-1
VALUES OF D OF ZBPD AT VARIOUS TEMPERATURES IN DMF SOLUTION

T (K)	i_{ss} (10^{-8} A)	D (10^{-6} $cm^2 s^{-1}$)
298	2.79	6.02
303	3.12	6.80
308	3.37	7.28
313	3.67	7.92
318	3.98	8.59

The relationship between D and temperature can be expressed by the Arrhenius equation[17] as follows:

$$\ln D = \ln D_0 - \frac{E_a}{RT} \quad (8)$$

where E_a is the active energy of diffusion, D_0 is the diffusion coefficient of ZBPD at infinite temperature.

Plotting ln D *versus* the inverse of temperature, a straight line was obtained (Fig. 8), the equation was:

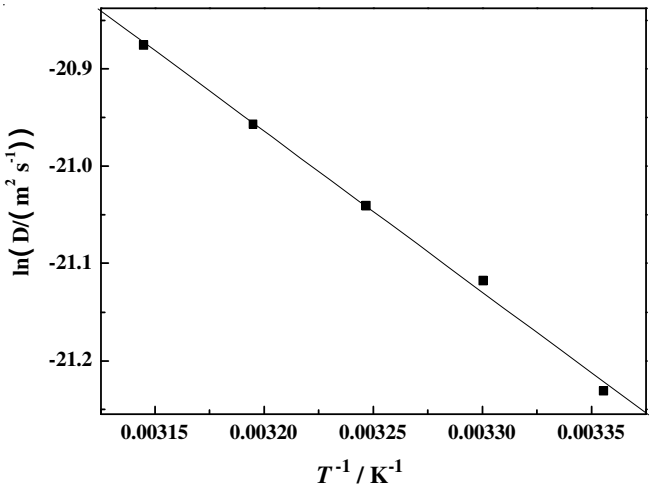

Fig. 8. Variation of ln D of ZBPD in DMF solution, *vs*. 1/T

$$\ln D = -15.66877 - 1654.74012\frac{1}{T},\ R = 0.99842 \quad (9)$$

The value of E_a was calculated as 13.76 kJ mol^{-1}.

Conclusion

In DMF solution, an irreversible electrochemical oxidative wave occurred by the oxidation of ZBPD was observed. The electrooxidation process was controlled by diffusion. The number of the electron transferred in the electrochemical oxidation reaction was determined as one. The steady-state limiting current of ZBPD in DMF solution was increased with the temperature increasing, which was due to the enhancement of diffusion of ZBPD in DMF solution at higher temperature. The diffusion coefficient was obtained for each temperature. In terms of the Arrhenius equation, the activation energy of diffusion of ZBPD in DMF solution was calculated to be 13.76 kJ mol^{-1}.

ACKNOWLEDGEMENTS

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REFERENCES

1. A.M. Barnes, K.D. Bartle and V.R.A. Thibon, *Tribol. Int.*, **34**, 389 (2001).
2. K.L. Windahl and T. Cardwell, *J. Chromatogr. A*, **765**, 181 (1997).
3. F.U. Shah, S. Glavatskih and O.N. Antzutkin, *ACS Appl. Mater. Int.*, **1**, 2835 (2009).
4. M. Becchi, F. Perret, B. Carraze and J.F. Beziau, *J. Chromatogr. A*, **905**, 207 (2001).
5. T.J. Cardwell, R. Colton, N. Lambropoulos, J.C. Traeger and P.J. Marriot, *Anal. Chim. Acta*, **280**, 239 (1993).
6. V.R.A. Thibon, K.D. Bartle, D.J. Abbott and K.A. McCormack, *J. Microcol. Sep.*, **11**, 71 (1999).
7. N. Lambropoulos, T.J. Cardwell, D. Caridi and P.J. Marriott, *J. Chromatogr. A*, **749**, 87 (1996).
8. J.L. Paddy, N.C.J. Lee, D.N. Waters and W. Trott, *Tribol. Trans.*, **33**, 15 (1990).
9. E.A. Stezeryanskii, K.I. Litovchenko and V.S. Kublanovsky, *J. Electroanal. Chem.*, **390**, 143 (1995).
10. R.L. Blankespoor, *Inorg. Chem.*, **24**, 1126 (1985).
11. S. Chitravathi, B.E. Kumara Swamy, G.P. Mamatha and B.N. Chandrashekar, *J. Mol. Liq.*, **172**, 130 (2012).
12. H. Wang, X.H. Ye, L.M. Chen, J.X. Lu and M.Y. He, *Chem. J. Chin. Univ.,* **26**, 326 (2005).
13. J.Y. Li and Y.M. Chi, *Pestic. Biochem. Phys.*, **93**, 101 (2009).
14. J.X. Zhang, B. Yin and Z.X. Zhang, *Acta Chim. Sin.*, **53**, 1124 (1995).
15. H.S. Yin, Y.L. Zhou, R.X. Han, Y.Y. Qiu, S.Y. Ai and L.S. Zhu, *J. Solid State Electr.*, **16**, 75 (2012).
16. K. Caban, M. Donten and Z. Stojek, *J. Phys. Chem. B*, **108**, 1153 (2004).
17. J.Z. Yang, Y. Jin, W. Pan and S.L. Zang, *Chem. J. Chin. Univ.*, **26**, 1146 (2005).