

An Electrochemical Investigation of the Redox Properties of Murexide in Aqueous and Non-Aqueous Media

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Abstract: Knowledge of solvent effects on the redox properties of Murexide (Mu) is important for understanding its role as an electron acceptor in analytical and inorganic chemistry. In the present study, an investigation of the electrochemical behavior of the compound by both Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) in both aqueous and non-aqueous solutions was undertaken. It is suggested that, the reaction mechanism proceeds according to an Erev CE-rev-route. This reaction mechanism is confirmed by the CV behavior for barbituric acid, which is essentially represent a main part of murexide, under the same conditions. In DMSO, the one-electron reduction potential peak of murexide was found to shift positively by 223 mV to the value of the corresponding wave obtained in DMF under the same conditions. The shift is most readily explained by the presence of murexide aggregates in DMF. The one-electron oxidation potential position is relatively unaffected by aggregation. The data has also revealed that murexide decomposes in the level of radical anion at the N = C bond into two approximately equal units. In aqueous sodium perchlorate (NaClO₄) solutions, it is suggested that the decomposition of murexide is relatively slow, leading to nearly a reversible 1e-transfer process (E-mechanism). In both KNO₃ and KCl solutions, the one-electron transfer step of murexide was found to be an adsorption wave. The Electrochemical Impedance (EIS) response of murexide is either low-frequency Warburg impedance or a capacitive semicircle behavior at high frequencies, depending on the medium.

Key words: Murexide-cyclic voltammetry (CV)-electrochemical impedance spectroscopy (EIS)-redox

INTRODUCTION

Murexide is the ammonium salt of purpuric acid and it is of interest because it was probably the first metal ion indicator to be employed in the EDTA titration. The dye color changes are probably due to the displacement of protons from the imido groups; since there are four such groups. Murexide forms complexes with many metal ions: only those with Cu, Ni, Co, Ca and the lanthanoids are sufficiently stable to find application in analysis. Aqueous solutions of murexide are unstable and must be prepared each day^[1].

The murexide (5,5'-nitrilodebarbituric acid, mono ammonium salt) in addition to its classical use as a metallochromic indicator, it has been employed as an efficient scavenger for superoxide and hydroxyl radicals^[2] and recently as a chromogenic agent^[3].

The electrochemical reduction mechanism of murexide complex with dysprosium has been studied by means of cyclic voltammetry and UV-vis spectroelectrochemistry at a gold minigrad optically transparent thin-layer electrode (OTTLE) cell. The

electrode reaction rate constant was estimated and the formal potential and the electron transfer number at different pH-values during the electrochemical process were measured^[4].

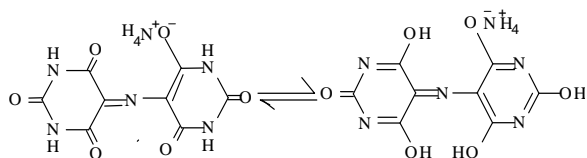
Murexide underwent reduction by rat liver cytosolic fraction or a hypoxanthine-xanthine oxidase system to produce a free radical metabolite. Reduction of murexide by the freshly prepared cytosolic fraction depended upon the presence of ascorbic acid^[5].

In all these treatments, little or no attention is given to the electrochemical behavior of murexide. Therefore, the interest was to use the cyclic voltammetric technique to shed some light on the effect of solvent on the electrochemical behavior of the compound in both aprotic and aqueous media.

MATERIALS AND METHODS

Reagent-grade N, N-Dimethylformamide (DMF) and Dimethyl Sulfoxide (DMSO) were further purified and dried according to a previous recommended method^[6].

Tetrabutylammonium hexafluorophosphate (TBAPF₆) obtained from FLUKA was recrystallized twice from pure ethanol and vacuum dried at 120°C. For sample preparation and purification for electrochemical measurements in super dry media, special type of cell was used which already described elsewhere^[7]. In this cell, three electrodes are used; the working is either a Platinum Disk (Pt) or a metrohm EA 290 Hanging Mercury Drop Electrode (HMDE). A platinum wire is used as an auxiliary electrode. The reference electrode used is an Ag/AgCl where its potential is calibrated for each experiment against the reversible oxidation peak of ferrocene. Aqueous electrolytes have been prepared using also reagent-grade chemicals and were diluted to proper concentrations with bidistilled water. The Saturated Calomel Electrode (SCE) was used in aqueous media as the reference electrode. An EG and G Princeton Applied Research 273A Potentiostat/Galvanostat coupled with an 5208 lock in amplifier were used to perform the desired signals.



RESULTS AND DISCUSSION

CV behavior of murexide: The main features of the cyclic voltammogram for murexide in DMF containing 0.2 M TBAPF₆ on the Pt-disk electrode are an irreversible peak at $E_{pc} = -0.750$ V followed by a small peak at -1.0 V and a reversible process at more negative potentials, $E_{pc} = -1.448$ V vs. Ag/AgCl. The main difference between the response in DMF and DMSO is that the potential position of the 1e-charge transfer process. In DMF, the wave was found to shift positively by 223 mV to the value of the corresponding process in DMSO (~ -0.973 V). The shift is most explained by the presence of murexide aggregates in DMF^[8]. In DMF also, the first peak remains irreversible at all sweep rates less than 20 V/s even if the scan is reversed at -1.2 V (i.e. before the second reversible peak) and its current function ($i_{pc}/v^{1/2}C$) does not vary significantly with potential scan rate.

On increasing the potential scan rate, the small peak at -1.0 V observed in DMF is totally disappeared and the currents of the couple anodic peak at -1.445 V become gradually smaller. It is suggested that the reduction mechanism proposed in this case is $E_{rev}CE_{rev}$ -

route. It is also assumed that the first wave corresponds to the reduction of murexide through a reversible 1e-transfer process followed by a N-C bond-rupture, leading to two approximately identical parts. Two

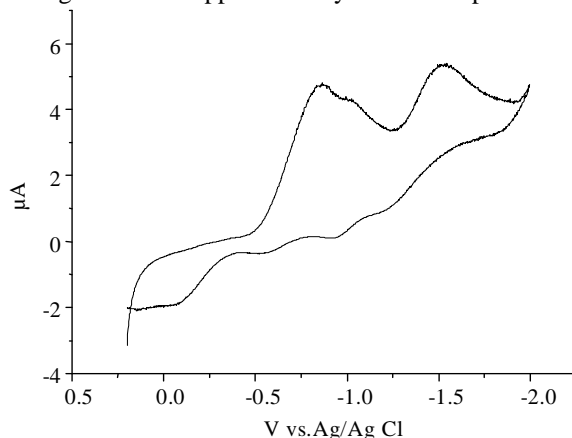


Fig. 1: CV diagram of 2.0 mM of murexide in DMF/TBAPF₆ at 298 K on the Pt-disk electrode ($v = 0.05$ v/s)

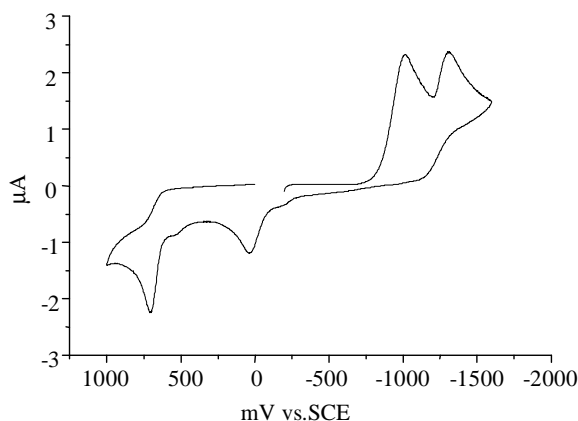


Fig. 2: CV of 1.32 mM murexide in DMSO/0.2 M TBAPF₆ on the Pt-Electrode at 298 K and scan rate of 0.1 V/s

further pieces of evidence confirm strongly the foregoing reaction mechanism. Firstly, the cyclic voltammograms for barbituric acid under the same conditions which were obtained in all media where measurements for murexide were carried out and under the same conditions. Secondly, if the potential scan rate for the electroreduction of murexide is increased to 1V/s, fully reversible wave at $E_{pc} = -0.194$ V is obtained and the small anodic peak at ~ -0.018 V which is corresponding to the oxidation of the product of the follow-up chemical reaction is virtually disappeared.

Fig.3a and Fig.3b represent examples for correlation between the electroreduction of both murexide and barbituric acid respectively. Barbituric acid must represent an essential part of murexide and is expected

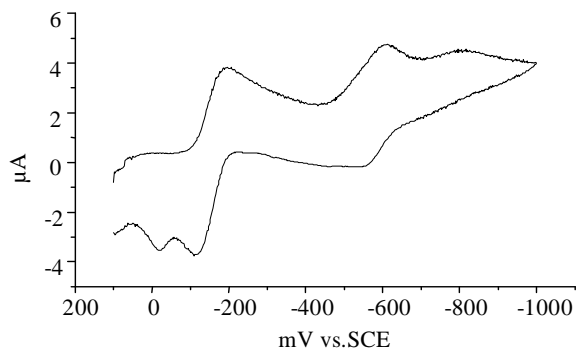


Fig. 3a: CV of 6.6 mM murexide in 0.2 M NaClO₄ on the [HDME] at 298 K and scan rate = 0.2 V/s

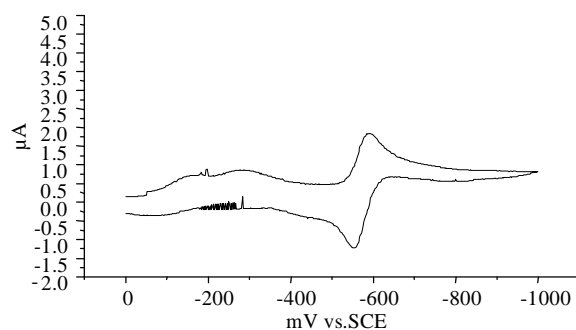


Fig. 3b: 5.0 mM DEBA in 0.2 M NaClO₄ on the [HDME] at 298 K and scan rate = 0.2 V/s

to be a main of the decomposition products of the molecule.

From the variation of I_{pa}/I_{pc} for murexide/murexide radical anion couple at the faster sweep rates, it is possible to estimate the values, 4.0 s^{-1} and 6.0 s^{-1} for the homogeneous rate-constant for the N-C bond-rupture of murexide in DMF and DMSO respectively. On the other hand, the electroreduction voltammogram of murexide in aqueous NaClO₄ is obviously different and consists mainly of two consecutive reversible waves in addition to a small oxidation peak at $\sim 0.0 \text{ V}$ (Fig. 3a). In Both KNO₃ and KCl solutions, at relatively low concentrations of murexide, the voltammogram consists of an adsorption wave at the potential-position of the first wave. Fig. 4 shows the electrochemical behavior of 2.64 mM of murexide in KNO₃ solution at the [HMDE]. The cyclic voltammogram for murexide exhibits another reversible peak similar to that obtained in DMF or DMSO at -1.445 V . It is suggested that this

wave represents the electroreduction of the known electrochemically stable structure of quinone functionalities part, which is similar to structure II resulting from decomposing murexide through the following-up chemical reaction and/or the medium. The voltammogram for barbituric acid, which is assumed to be half of the product after decomposing murexide, shows a well-defined $1e^-$ reversible process at $E_{pc} = -0.588 \text{ V}$ in NaClO₄ (Fig.3b), which is corresponding to the foregoing suggestion.

The CV-response of murexide in DMF in the presence of low concentration of bidistilled water (less than 2%), shows that water increases the currents of both the cathodic and the anodic currents of the first electron reduction-wave. In addition to the increase of its chemical reversibility, appearance of a postpeak at -1.07 V is observed. This small wave is suggested to correspond to the reduction of the adsorbed species of murexide. The response of murexide in the presence of small amounts of water, reveals that the redox reactions of the molecule are also proton dependant.

In aqueous media (KNO₃ and KCl) and at the beginning of measurements, the reduction behavior of low-concentrations of murexide is a simply an adsorption peak followed by a reversible electron transfer process. The peak-separation ΔE for this wave is slightly less than 59 mV and the i_{pa}/i_{pc} is also slightly greater than unity, which are indicative of a weak adsorption of the reduction product of murexide^[9].

The cyclic voltammogram of the adsorption wave obtained in Fig. 4. was checked for symmetry around the peak potential using diagnostic criteria suggested for adsorption behavior^[9]. At concentrations of murexide as low as 0.4 mM , the CV diagram exhibits an ideal symmetrical shape. On the other hand, if the concentration of murexide exceeds 2.0 mM in KNO₃ and 0.8 mM in KCl, the symmetry of the peak is nearly disappeared. At relatively higher concentrations of murexide, the current function at $v = 0.1 \text{ V/s}$ deviates from the constant value expected for diffusion peak uncomplicated by adsorption. This can be attributed to that the adsorbed molecules constitute a constant flow of matter and charge, whereas the number of the diffusing molecules through the electric double layer is potential scan-rate dependent (i.e. time dependent).

The CV-adsorption behavior of the compound in 0.3 M KNO_3 solutions at the [HMDE]. On plotting the current function ($i_p/C_o^* \cdot v^{1/2}$) vs. $\log v$, where C_o^* = the concentration of murexide and v is the potential scan rate, an increase in the sweep rate led to an increase in the current-function value. This behavior would be expected for a weak adsorption process. For an ideal CV-reversible adsorption peak, the peak width at half-

height of its current is $90.6/n$ mV at 298 K^[10]. The calculated peak-width value for the adsorption peak located in the forward scan of 1.88 mM murexide in 0.3 M KNO₃ (Fig. 4) is found 101 mV, which agree well

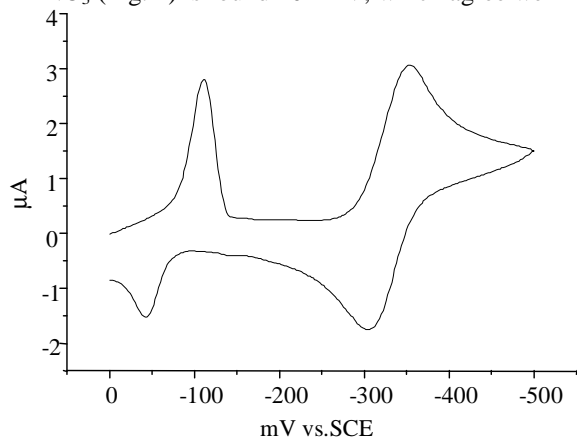


Fig. 4: CV for 2.64 mM of murexide in 0.2 M KNO₄ on [HMDE] at 298 K, scan rate = 0.05 V/s

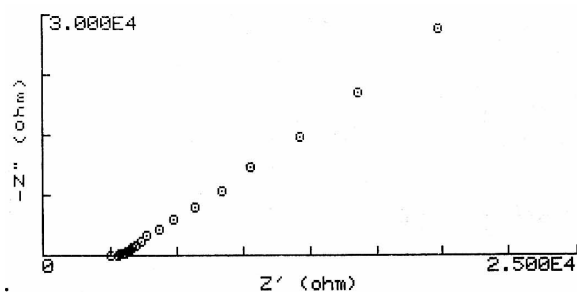


Fig. 5: Complex impedance plane plot (Nyquist) of the prewave of 3.43 mM of murexide in DMF/0.2 M TBAPF₆ on the Pt-electrode at 25°C

with the reversible theoretical value of $1e$ -transfer process. The amount of adsorbed murexide on the [HMDE] is determined from the area of the cathodic peak which is expressed as surface concentration through the equation $A(ad) = nFA\Gamma$, where $A(ad)$ is the peak area, which in this case is 94.28 nC, A is the electrode surface-area and Γ is the surface excess.

Impedance spectroscopic behavior of murexid: Figure 5 presents the Nyquist plot of the first reduction-wave at -0.374 V for 2.0 mM of murexide in DMF/0.2 M TBAPF₆ at the CV-peak potential on the Pt-disc electrode at 298 K. The data demonstrates over the whole frequency range used, a linear impedance locus with an angle of nearly 45° to the real axis with a very small resolved semicircle. The results are indicative of a partially diffusion-controlled process at the electrode-

electrolyte interface. It is also suggested that the reversibility of the process is combined with some adsorption of the reactant and/or the reduction product on the electrode surface. The physical model

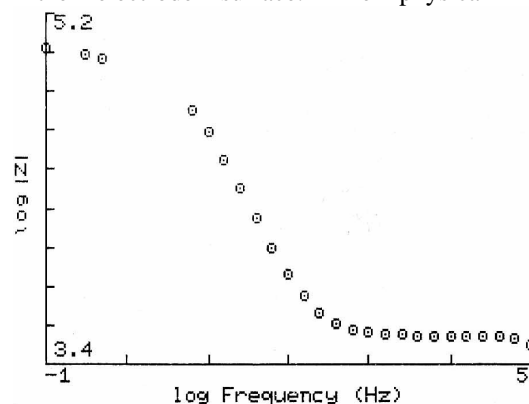


Fig. 6: The Bode magnitude plot of Complex impedance plane of 3.43 mM of murexide in DMF/0.2 M TBAPF₆ on the Pt-electrode at 25°C

appropriate to this case can be the simple equivalent Randle's electrical circuit^[11], which gives an evidence for the expected low-frequency Warburg response. Fig. 6 shows a typical Bode-magnitude plot for the same foregoing data of the peak at -0.374 V.

Changing the solvent from DMF to DMSO and keeping the same conditions, the Nyquist plot is a semicircle at high frequencies with a small straight linear behavior at sufficiently low frequencies. A behavior appears dominated by nondiffusional component, indicating that kinetics of the charge transfer step must be considered. Moreover, the data reveals nearly no evidence for adsorption processes in case of DMSO.

On the other hand, the EIS behavior of murexide in aqueous solutions (0.2 M of each of NaClO₄, KNO₃ and KCl) on the hanging mercury drop electrode [HMDE] is quite different than that obtained in DMSO or DMF. The response obviously consists of either one semicircle with a significant evidence for an adsorption contribution or two semicircles beside each other. In case of only one semicircle, adsorption behavior can be observed at very low frequencies especially with those measurements carried out in KCl, where adsorption-phenomena is relatively significant. Another response for the impedance was the observation of two semicircles, a high-frequency semicircle (on the left) which is concluded to ascribe to bulk electrolyte properties and a low frequency one (on the right) which corresponds to the electrode polarization phenomena.

The data, as concluded, are characteristic for a purely capacitive process. An ideal admittance plot for the electroreduction of 3.43 mM of murexide in 0.2 M NaClO₄ on the [HMDE] at 298 K is presented in Fig. 7.

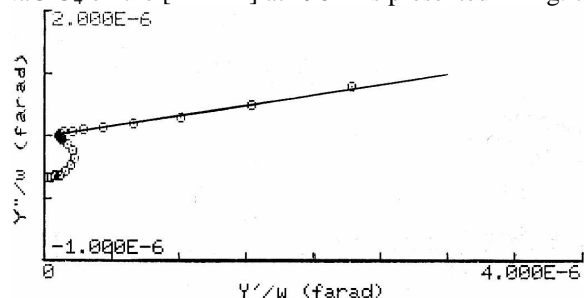


Fig. 7: An admittance plot of 3.43 mM of murexide in 0.2 M NaClO₄ on the [HMDE] at 25 °C

Table 1: Selected impedance Spectroscopic data for the electroreduction of murexide (Mu) in aqueous and non-aqueous solutions on both the [HMDE] and the Pt-electrode respectively at 25°C

System	R _Ω -Ω	R _{ct} Ω	C _{dl} -Farad
1-Mu/DMF			
1st* at -0.374 V	5652	21.40	8.30×10 ⁻⁶
2nd**at -0.650 V	5623	11.40	3.90×10 ⁻⁶
3rd** at -1.335 V	5510	20.20	2.96×10 ⁻⁶
2-Mu/DMSO			
1st* at -1.060 V	6310	36.0	1.58×10 ⁻⁶
2nd** at -1.310 V	6310	79.4	1.43×10 ⁻⁶
3-Mu/NaClO₄			
1st* at -0.200 V	69	773	7.40×10 ⁻⁶
2nd** at -0.614 V	69	146.6	4.65×10 ⁻⁶
4-Mu/KCl			
1st* at -0.105 V	100	501.2	2.0×10 ⁻⁵
2nd** at-0.330 V	100	1000	1.0×10 ⁻⁵
3rd** at-1.300 V	100	5012	2.0×10 ⁻⁶

*data for murexide reduction-wave, **data for product of the following-up chemical reaction, ***Data for an adsorption wave of nurexide

The figure gives a clearer picture of murexide admittance behavior and permits a convenient procedure for the determination of the system capacitance.

Table 1 provides a detailed compilation of the EIS parameters which resulted from application of these data treatment procedures. In aqueous solution, the values of the double-layer capacitance for the first charge transfer process fall in the range of 1*10⁻⁶ Farad, whereas those corresponding to the second charge transfer step are smaller by a factor of about 1.5. In DMF the C_{dl}- values are larger than the corresponding values in aqueous medium by a factor of about 30-50. The table also includes the charge transfer resistance, which is of similar significance. The R_{ct}- values, in aqueous perchlorate solution, are clearly larger than the

corresponding values in aprotic medium by a factor of at least ≈ 30, revealing the diffusion controlling character of the charge transfer processes in DMF as observed from CV results.

CONCLUSION

It is obvious from the data presented here that protic media clearly represent the best conditions for the mechanistic study of murexide. It is obviously that reversible behavior for the molecule is obtained more significant in aqueous than in non-aqueous solutions especially at the beginning of measurements. The difference can be accounted for by the greater basicity of DMF and DMSO compared to approximately neutral aqueous solutions used where murexide-decomposing is slower in the latter solutions. In KNO₃, the one-electron transfer peak-potential of murexide was found to shift positively by about 180 mV than the corresponding wave in NaClO₄ solution. It suggested that, adsorption of murexide and/or its reduction product have a significant effects on its redox potentials in both protic and aprotic solvents.

Minimizing the rate of the follow-up chemical reaction enhances the sensitivity of the measurements. It is also stated that, aqueous NaClO₄ is more convenient than KNO₃ and KCl solutions for both CV and EIS investigations of murexide.

As observed and suggested in this investigation, both murexide and its product of electron transfer are weakly adsorbed on the electrode surface especially the [HMDE]and the significance of adsorption is medium-dependent and is observed to follow the sequence:



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