ELECTROCHEMICAL STUDIES OF NITROPRUSSIDE ION IN AQUE-OUS-METHANOL SOLUTIONS

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ABSTRACT

The electrochemical behaviour of nitroprusside ion in potassium chloride aqueous-methanol solutions was studied by both d.c. and rapid a.c. polarography. In the concentration range from 0 to 70 % (v / v) methanol, the half-wave potentials of the three reduction waves were shifted to more negative values. The free energy of reduction was calculated and compared with the acceptor number of the mixed solvent. The free energy of reduction of $[Fe(CN)_5NO]^{-2}$ to $[Fe(CN)_5NO]^{-3}$ in the mixed solvent is directly proportional to Gutmann's acceptor number of the media.

The effect of potassium chloride concentration on the half-wave potential, the thickness of diffuse layer and the values of the rate constant for the third wave of sodium nitroprusside was discussed.

INTRODUCTION

Polarographic reduction of nitroprusside ion was investigated earlier[1,2]. In previous work the reduction mechanism and application of nitroprusside ion as an analytical reagent was investigated[3-8]. The aim of the present work is to study the effect of aqueous-methanol mixture on the behaviour of sodium nitroprusside. Also the effect of changing the concentration of potassium chloride which acts as supporting electrolyte on the $E_{1/2}$ of the third reduction wave of nitroprrusside ion was investigated.

EXPERIMENTAL

Polarograms of the examined system were obtained using Metrohm Polarecord E506 and Polarography Stand E505. The capillary characteristics were m = 1.414 mg s⁻¹ and t = 4.8 s. in 0.1M KCl at height 80 cm Hg. A saturated calomel electrode was used as a reference elec-

trode. For rapid a.c. polarography the same instrument was used with the following conditions, drop time 1 s. and a.c. amplitude of the applied alternating potential 6 mV at f = 50 Hz.

All the chemicals used were of Analar grade and were dissolved in double distilled water. Potassium chloride was used as supporting electrolyte with constant ionic strength (0.5 M). Aqueous freshly prepared stock solution (10^{-2}M) of sodium nitroprusside (BDH) was prepared by dissolving the appropriate amount in double distilled water. The measurements were carried out at $25 \pm 0\ 5°C$.

RESULTS AND DISCUSSION

The polarographic reduction of 0.5 mM sodium nitroprusside in 0.5M KCl consists of three reduction waves[3] (Fig. 1). These waves correspond to the reduction of $[Fe(CN)_5NO]^{2-}$ to $[Fe(CN)_5NO]^{3-}$ (first wave), $[Fe(CN)_5NO]^{3-}$ to $[Fe(CN)_5NO]^{-4}$ (second wave) and $[Fe(CN)_5NO]^{4-}$ to $[Fe(CN)_5NHOH]^{2-}$ (third wave). On adding different percentage of methanol from 0 to 70 % (v / v) the $E_{1/2}$ values shift to more negative potential. Also, a decrease of the limiting diffusion current from its original value was observed. Typical polarograms were obtained in case of rapid a.c. polarography.

The reversibility of the electrode reaction at the electrode for the three reduction waves in absence and presence of different percentage of methanol was tested by log-plot method, for the d.c. and a.c. polarography using the following equations, respectively[9].

$$E = E_{1/2} + \frac{RT}{nF}\ \ln\ [(1_d - I)/I] \tag{1}$$

$$E = E_{1/2} + \frac{RT}{nF}\ \ln\ \left[\ \left(\frac{I_p}{I}\right)^{1/2} \pm [(I_p - I)/I]^{1/2}\right] \tag{2}$$

where I_d is the limiting diffusion current, I_p is the peak current, I is the current at any potential E, n is the number of electrons consumed along each wave and R, T, F and $E_{1/2}$ have their usual meanings.

On plotting log $I_d - I/I$ vs. E for the three waves straight lines were obtained with slope values amounting to 59.1 ± 0.5 mV for the first and second waves and 141.0 ± 2 **mV** for the third wave.

The plot of log $[(I_p/I)^{1/2} \pm [(I_p - I)/I]^{1/2}]$ against E gives a straight line with a slope of 118.9 ± 0.3 mV for the first and second peaks. The analysis of the third peak has not been studied due to the flatting of the peaks especially at low percentage of methanol (Fig. 1).

The above results indicate that the reduction process of sodium nitroprusside in aqueous and aqueous-methanol mixtures up to 70 % (v / v) are reversible for the first two waves. Furthermore the difference between the half wave potential $(E_{1/2})$ and the peak potential (E_p) together with the halfwidth of the peak (Table 1) indicates that the reduction process proceeds reversibly along the first and second waves. On the other hand, the third wave is completely irreversible as confirmed from the low values of the peak current.

On increasing the percentage of methanol, the limiting current of the first wave gradually decreases up to 70 % (v / v) methanol. For the second and third waves the limiting current gradually decrease up to 50 % (v / v) methanol (maximum viscosity) and thereafter a small increase in the limiting current (Fig. 2) was observed. Table 2 indicates that the diffusion coefficient decreases with the increase of methanol percenttages. This behaviour together with the unconstancy of the produc $I_d \eta^{1/2}$ indicate that the viscosity of the medium is not the main factor in the reduction of the limiting current. The shift in the $E_{1/2}$ potentials to more negative values with increasing the percentage of methanol may be due to the increasing stability of solvated complex species in solution.

The free energies of reduction and their transfer values from 0 % (v / v) methanol as the reference solvent to the mixed solvents under consideration for each wave of sodium nitroprusside ion are calculated by applying the following equation[10,11].

$$\triangle G = - nFE^\circ_{1/2} \tag{3}$$

where $E^\circ_{1/2}$ (vs NHE), $= E_{1/2}$ (vs. SCE) $+ 0.247$. The calculated $\triangle G$ values and their transfer values $\triangle Gt$ from 0 % (v / v) methanol to mixed solvent are given in Table 3.

The shift in the $E_{1/2}$ with the dielectric constant (ε) (Table 3) indicates the considerable effect of the dielectric constant for the complex species reduced along each wave up to 40 % (v / v) methanol. Thus, with lower percentages of methanol, the stability of the solvated complex species increase, as evidenced by the shift in the $E_{1/2}$ to more negative value. This is in accordance with that reported by Tur'yan[12]
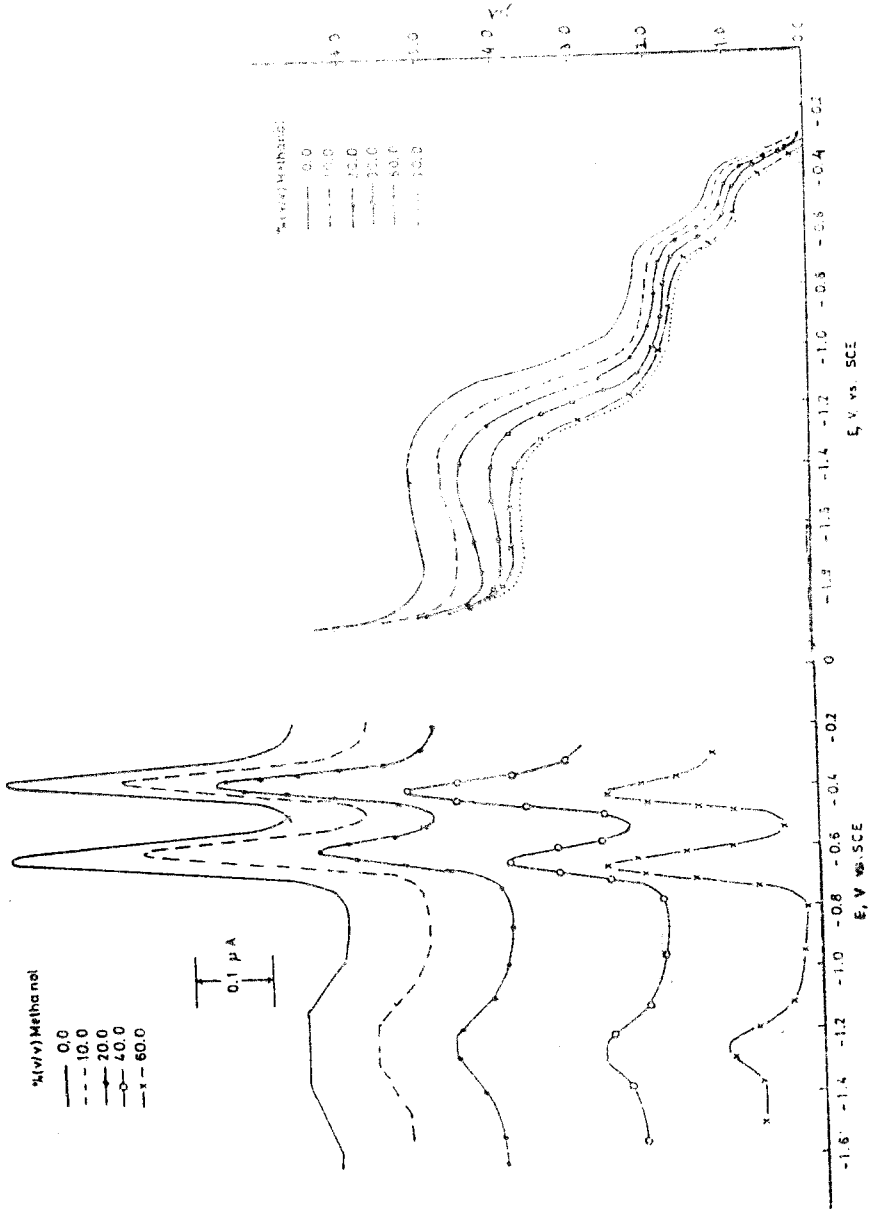
Fig. 1. Effect of methanol concentration on the polarographic waves (dc and rapid ac.) of 0.5
mM sodium nitroprusside in 0.5M potassium chloride supporting electrolye

Table 1. Values of $E_{1/2}$ V vs. SCE, E_p V vs.SCE. half width of peak for 0.5mM sodium nitroprusside at different percentage of methanol.

%(v/v) methanol	1st.		2nd.		3rd.		Half width of peak		
	$E_{1/2}$	E_p	$E_{1/2}$	E_p	$E_{1/2}$ d	E_p	1st.	2nd.	3rd.
	V. vs. SCE						mV		
0.0	0.35	0.35	0.6	0.6	1.20	1.20	90	95	300
10	0.36	0.36	0.61	0.59	1.11	1.20	90	90	280
20	0.37	0.37	0.62	0.59	1.15	1.22	90	90	220
30	0.38	0.38	0.64	0.61	1.19	1.24	90	90	180
40	0.39	0.39	0.65	0.64	1.22	1.26	90	90	180
50	0.4	0.4	0.66	0.65	1.23	1.26	90	90	170
60	0.41	0.41	0.67	0.66	1.22	1.26	90	90	160
70	0.42	0.42	0.67	0.67	1.22	1.26	90	90	150

for the effect of methanol and ethanol on the stability of different complexes.

The acceptor number of different solvents explains the different behaviours in reaction including charge transfer or electroreduction processes. The plot of Gutmann's[13-14] acceptor number (AN) against $\triangle G$ value (Fig. 3) for the three waves of nitroprusside ion at different percentage of methanol indicate a decrease of the free energy with increasing AN value according to the following equation[13].

$$\triangle G = b \, D \, (1 / AN) \qquad (4)$$

where b is constant and D is the diffusion coefficient. The decrease of the free energy for the second and third waves can be attributed to the increase of accepting ability of the media to high charged reduced species or protons hindering the reduction process.

The ill-defined limiting current region of the third wave, implied the study of the polarographic behaviour of 0.5 mM nitroprusside in different concentrations of potassium chloride solution (Fig. 4). It is shown that the $E_{1/2}$ values of the third reduction wave, corresponding to the reduction of $[Fe(CN)_5NO]^{4-}$ complex species, shifted to less negative potentials with increasing of potassium chloride concentrations. Meanwhile, the $E_{1/2}$'s for the first and second wave were not affected. The limiting diffusion current of the three reduction waves remain almost constant at different electrolyte concentration.

This abnormal phenomenon of the third wave may be attributed to one or more of the followings: (i) the formation of ion pairs[15] like Na $[Fe(CN)_5NO]^{3-}$ which is reduced at less negative potentials, (ii) accu-
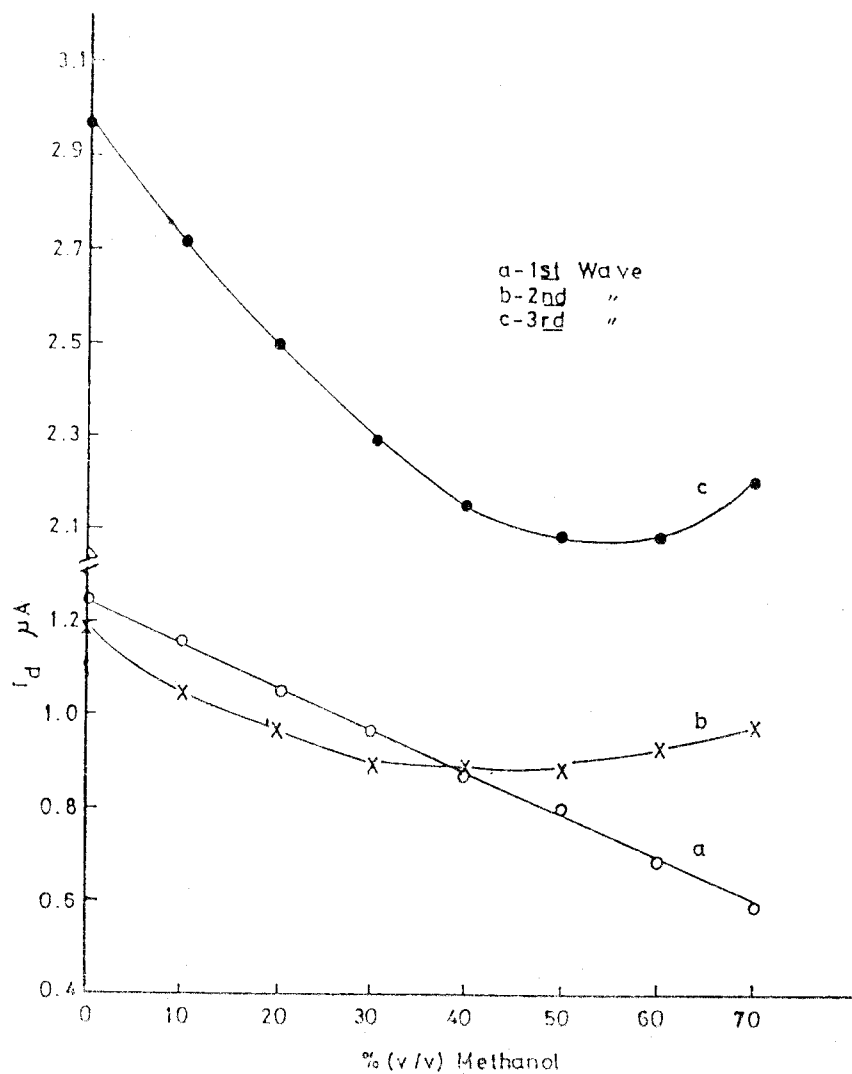
Fig. 2. Effect of methanol percentages on the limiting current of 0.5 mM sodium nitroprusside in 0.5M potassium chloride.

mulation of the positively charged ions at the electrode surface at more negative potentials. This due to the reduction in the potential of Helmholtz layer which facilates the approach of the reducible anions from the electrode surface[16], (iii) the decrease in the thickness of diffuse layer with the increase of supporting electrolyte concentrations[17].

Table 2. Effect of methanol on the limiting current and diffusion coefficient 0.5 mM Sodium nitroprusside.

%(v/v) meth.	i_d μA			η	$i_d \eta^{1/2}$			$D \times 10^5$ cm²/s		
	1st.	2nd.	3rd.		1st.	2nd.	3rd.	1st.	2nd.	3rd.
0.0	1.24	1.18	2.96	0.8904	1.17	1.11	2.79	6.193	5.608	8.822
10	1.16	1.05	2.72	1.1234	1.23	1.11	2.88	5.419	4.440	7.449
20	1.05	0.97	2.50	1.3313	1.21	1.12	2.88	4.440	3.780	6.293
30	0.96	0.90	2.28	1.5372	1.19	1.12	2.83	3.712	3.262	5.234
40	0.88	0.80	2.16	1.6283	1.12	1.15	2.76	3.119	3.262	4.698
50	0.80	0.88	2.08	1.6190	1.02	1.12	2.65	2.578	3.119	4.356
60	0.69	0.92	2.10	1.5243	0.85	1.14	2.59	1.918	3.409	4.440
70	0.60	0.98	2.20	1.3219	0.69	1.12	2.53	1.450	3.868	4.873

Table 3. Values of dielectric constant, Gutmann acceptor number, $E_{1/2}$ V. vs. SCE, free energy and free energy of transfer from water to mixed methanol media.

% (v/v) methanol	ε	$-E_{2/2}$ V. vs. SCE			AN of methanol	$\triangle G$ KJ mole^{-1}			$\triangle G_{tr}$ KJ mole^{-1}		
		1st	2nd	3rd		1st	2nd	3rd	1st	2nd	3rd
0.0	—	0.35	0.60	1.07	—	9.940	34.06	158.84	0.0	0.00	0.00
10	75.1	0.36	0.61	1.11	54.2	10.915	35.03	166.56	0.97	0.97	7.72
20	71.0	0.37	0.62	1.15	53.3	11.870	35.99	174.28	1.93	1.93	15.44
30	67.1	0.38	0.64	1.19	52.2	12.83	37.92	182.00	2.89	3.86	23.16
40	64.6	0.39	0.65	1.22	51.4	13.80	38.89	187.79	3.86	4.83	28.95
50	59.0	0.40	0.66	1.23	49.7	14.76	39.85	189.72	4.82	5.79	30.88
60	54.6	0.41	0.67	1.22	48.3	15.73	40.82	187.79	5.79	6.76	28.95
70	49.7	0.42	0.67	1.22	46.7	16.69	40.82	187.79	6.75	6.76	28.95

The thickness of diffuse layer becomes very small in high electrolyte concentrations and increases by dilution. The thickness of diffuse layer T_d is given by the following relation[18]:

$$T_d = \sqrt{\frac{1000 \, \varepsilon \, kT}{8\pi e^2 N \, \mu}} \tag{5}$$

where ε is the dielectric constant of the solvent, e is the electronic charge, k the Boltzmann constant, N the Avogadro's number and μ is the ionic strength.

The effect in varying electrolyte concentration on the height of the third wave indicates that the reaction rate[14] is strongly affected by the double layer structure. Thus, the variation of the rate constant for the reduction of $[Fe(CN)_5NO]^{4-}$ ion (Table 4) with increasing potassium chloride concentration and the ill-defined limiting current region
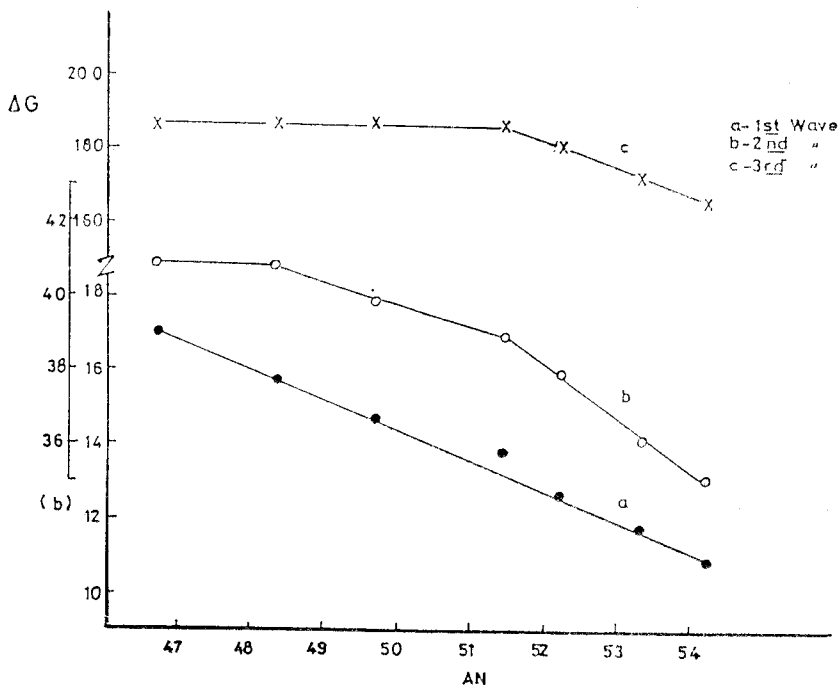
Fig. 3. Variation of free energy of reduction with Gutmann's acceptor number for 0.5 / ml sodium; nitroprusside in 0.5 M KCI

can be taken as a good evidence for the effect of double layer structure. The shift in the half-wave potential ($E_{1/2}$) to less negative values of third wave and the decrease in the free energy changes (Table 4) with increasing KCl concentrations can be explained by the formation of less stable complex species.
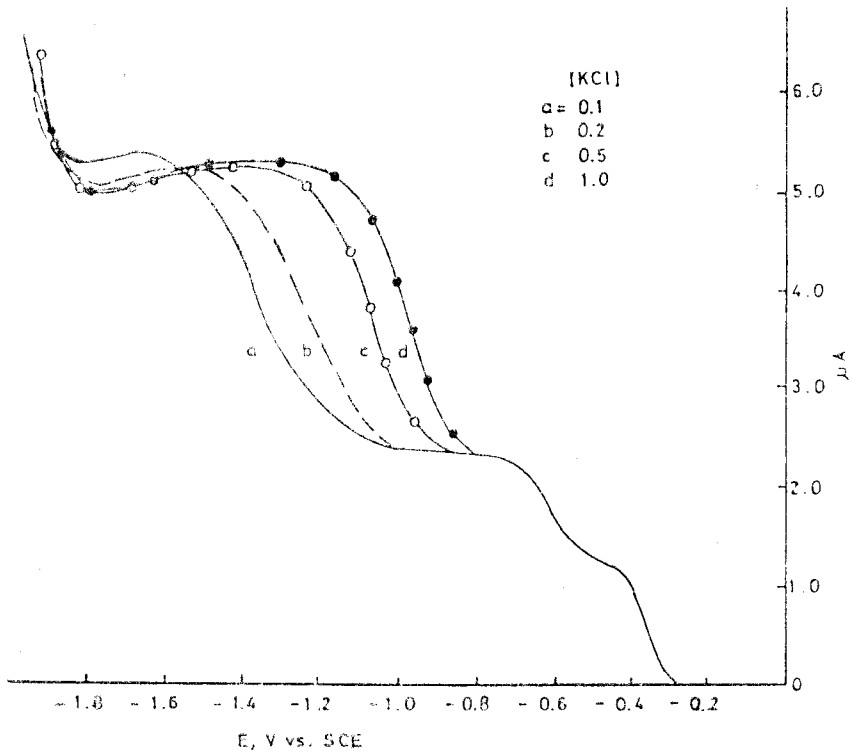
Fig. 4. Effect of potassium chloride concentration of the reduction waves of 0.5mM sodium nitroprusside.

Table 4. Values of $E_{1/2}$; free energies of reduction, rate constant, limiting current and ionic strength at different potassium chloride concentrations.

[KCl] mol / l	i_d μA	$-E^{1/2}$ V. vs.SCE	$\triangle G$ KJ mole^{-1}	k cm.s^{-1}	$\sqrt{\mu}$
0.0	3.08	1.35	212.88	6.36×10^{-4}	0.316
0.2	2.90	1.20	183.93	3.38×10^{-4}	0.447
0.5	2.96	1.07	158.84	7.05×10^{-5}	0.707
1.0	2.90	0.98	141.47	2.75×10^{-7}	1.000

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