EFFECT OF SOLVENTS ON THE POLAROGRAPHIC CHARACTERISTICS OF 2-NITROBENZIDINE

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The effect of various alchols such as methanol, ethanol, ethylene glycol, propylene glycol and glycerol on the polarographic characteristics of 2-nitrobenzidine in unbuffered alchol-water mixtures has been investigated. The results are interpretated in the light of dielectric constant and viscosity of the medium.

In unbuffered solution, although the pH at the electrode-solution interface is more than the pH at the bulk of the solution [1], it may be pointed out that the electrochemical behaviour of some inorganic cations and organic molecules has been investigated in unbuffered aqueous-solvent mixtures [2-4]. Experiments were carried out on 2-nitrobenzidine (2-NB) in unbuffered solutions using different solvents at different compositions of solvent-water mixtures with a view to understand the effect of the nature of the solvents on the polarographic characteristics of 2-NB. The solvents choosen for this study included glycerol, ethylene glycol, methanol, propylene glycol and ethanol.

EXPERIMENTAL

2-NB was prepared as described earlier [5] and its purity tested by mp (141°C) and TLC. All the solvents used were purified by the standard methods. Potassium chloride (G.R.) was used as the supporting electrolyte without further purification.

The polarographic measuremens made in the present work using a three electrode assembly were similar to those described previously [6]. The dropping mercury electrode (dme) used in 0.1 M aqueous potassium chloride supporting electrolyte at 55 cm height of the mercury column (height uncorrected for back pressure) had the following capillary characteristics under open circuit conditions m = 0.8814 mg/sec. ; t = 7.0s.

All the measurements were carried out at 30°C.

RESULTS AND DISCUSSION

2-NB gives a single wave at various compositions of different alchols. The polarographic data obtained for 2-NB (0.5 mM) in unbuffered solutions containing different alchols at various compostions are presented in Table 1. The diffusion controlled nature of the limiting currents (i_l) and irreversible nature of the wave for 2-NB reduction in different unbuffered alchol-water mixtures at various compsitions is confirmed on the basis of the usual criteria [1].

It is found that the $E_{1/2}$ is shifted to more negative values as the alchol content is increased (Table 1) excepting in the case of glycerol. This may be due to (i) the residual liquid-junction potential between the reference electrode (SCE) and the experimental solution and/or (ii) the adsorption of solvent molecules at the electrode-solution interface resulting in the inhibition of electron-trasfer processes [7 & 8]. A rigorous quantitative evaluation of the effect of solution composition on $E_{1/2}$ is impossible because of the fact that the change in liquid-junction potential is not known [9]. However, it may be pointed out in a qualitative way that in any organic solvent-water mixture, the shift of $E_{1/2}$ to more negative values with increase in organic solvent content parallels the decrease in the proton activity due to medium effect which indicated an increased basicity of the medium [10,11]. It is observed from Table 1 that at a given concentration of alcohol, the $E_{1/2}$ of 2-NB shifts cathodically in the order: glycerol < ethylene glycol < methanol < propylene glycol < ethanol. This shift may be ascribed to the increased basicity of the alcohol-water mixtures in the above order. The differences in basicity of the solvent-water mixtures can be explained in terms of structural theory of solvation proposed by Feakins et al [12]. When the composition of alcohol is increased, the decreased proton activity of the medium as well as the adsorption of alcohol molecules caused a shift in $E_{1/2}$ to more negative values thus making the reduction process difficult. In the case of glycerol-water mixtures, the $E_{1/2}$ shift to more positive values when the glycerol content is increased (Table 1) and this is attributed to the high dissociating factor of glycerol [13].

For any particular solvent chosen in the present work, it is found that the limiting currents, i_l generally decrease with increase in composition of the organic solvent (Table 1). The decrease in i_l values may be attributed to the decrease in the magnitude of the diffusion-coefficients of 2-NB as a result of an increase in the viscosity of the medium [14]. If viscosity is the only factor affecting D then $i_l \eta^{1/2}$ should be constant.

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TABLE 1

POLRAGRAPHIC DATA FOR 2-NB (5.0×10^{-4} M) REDUCTION IN UNBUFFERED SOLUTIONS CONTAINING VARIOUS SOLVENTS AT DIFFERENT COMPOSITIONS

Solvent % v/v	Solvent	η* Centi Poise	ϵ **	$-E_{1/2}$ mV vs SCE	i /μA	$i_l \eta^{1/2}$	$-(E_{3/4} - E_{1/4})$ mV	Slope of Log plot mV
	Glycerol	1.84	68.76	720	4.2	5.70	80	50
	Ethylene glycol	1.39	68.40	730	4.7	5.54	80	50
20	Methanol	1.18	61.24	750	5.0	5.43	80	50
	Propylene glycol	1.60	71.90	780	4.6	5.82	90	50
	Ethanol	1.55	56.49	825	4.4	5.48	60	40
	Glycerol	3.79	62.03	690	2.6	5.06	80	50
	Ethylene glycol	2.32	61.08	745	3.3	5.03	60	40
40	Methanol	1.31	51.53	770	4.8	5.49	80	50
	Propylene glycol	2.90	62.65	790	3.3	5.62	80	50
	Ethanol	2.02	44.67	870	4.0	5.69	60	30
	Glycerol	10.31	52.27	680	1.5	4.82	80	40
	Ethylene glycol	4.03	50.64	780	2.3	4.62	80	40
60	Methanol	1.31	41.46	880	4.8	5.49	80	50
	Propylene glycol	5.60	41.15	895	2.5	5.92	110	50
	Ethanol	1.93	33.89	950	4.0	5.56	60	40
	Glycerol	55.34	57.06	-	-	-	-	-
	Ethylene glycol	7.58	56.30	860	2.0	5.51	80	40
80	Methanol	1.09	46.46	960	5.3	5.53	50	50
	Propylene glycol	12.50	41.15	965	2.0	7.07	80	40
	Ethanol	1.53	39.14	1050	4.2	5.20	80	40

* Viscosities are taken from references [16] ** Dielectric constants are taken from references [17]

Difference in solvation would be an additional factor affecting the diffusion coefficients and if this is dominent, the constancy of $i_l \eta^{1/2}$ would be affected.

It is seen from the results of the present study (Table 1) that the product $i_l \eta^{1/2}$ for 2-NB in the presence of various alcohols at different compositions remains constant within the limits of experimental error

In general, the change in solvation caused by changing the dielectric constant largely affects the $E_{1/2}$ in a linear manner, shifting $E_{1/2}$ to more positive values as the dielectric constant is decreased [2,3]. The applicability of such a linear relationship is found to be rather limited [2]. In the present work it is seen from Table 1 that there is no systematic change in $E_{1/2}$ values with dielectric constant. This may be attributed to a variety of factors such as the chemical properties of the depolarizer and of the alcohols, the steric effect of the alchol molecules and the viscosity of the medium [2,15].

ACKNOWLEDGEMENT

One of the authors (SA) is grateful to the Department of Atomic Energy, Bombay for the financial assistance.

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