Polarography of Substituted Phenyl naphthyl azo Compounds in Water - SDS - n-Pentanol Microemulsion

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In microemulsion, a state of zero interfacial tension prevails between organic and water phases and generally remain ever dispersed [1]. Inversion of microemulsion from W/O to O/W is achieved by small addition(s) of water and vigorous agitation when isotropic solution first becomes viscoelastic and anisotropic changes to isotropic. Microemulsion, in brief, is a special case of solubilization in which micelles assume spherical form.

Most organic and inorganic substances dissolve readily in micro- emulsions. These are prepared by solubilization of a vegetable oil in water (or ionic media). A mixture of 1:4 mass ratio of sodium dodecyl sulphate (SDS) and n-pentanol has a profound co-solving tendency of non-polar and polar compounds and has been used to prepare microemulsions. Polarographic investigations and analytical determination of components is thus possible in such microemulsions. In this communication, polarography of azo compounds (including some commerical products - some water soluble and others oil soluble) in such a microemulsion is described.

EXPERIMENTAL

Measurements were made at dme in a Novak Cell in conjunction with universal pen recording polarograph OH-105 (Hungary). Temperature was maintained at 24±1°C. Capillary characteristics were 1.97 $mg^{2/3}s^{-1/2}$ when short circuited in aqueous medium. Potentials refer to modified SCE ($Hg/Hg_2Cl_2/LiCl$ saturated with ethylenediamine). All solutions were deaerated with N_2. A crison micro-pH 2001 potentiometer with combined electrode (Calomel - glass) was used for pH measurements. A propeller mixer - Lightinin - was used in conjuction with a variac to control speed of mixing.

Reagents

The azo compounds used in this study are listed in Table 1.

Compound I was prepared [2] by diazotization of nitrosobenzene with naphthylamine while orange-I (II) was synthesised by coupling sodium salt of 2-naphthol with diazo sulphonic acid [2]. III, IV, V, VI, VII, VII and IX are food colour dyes with FD & C certificate and were obtained from ICI and Dyechem Mfg. Co. All compounds were recrystallized from 50% alcohol, dried over BaO and subjected to spectrophotometry, chromatography and elemental analysis (found 98.9 - 99.3% pure). Sodium dodecyl sulphate, n-pentanol, NaCl, H_3BO_3 and $Na_2B_4O_7$ are of AR grade (from Sigma). Double distilled water was used. Pure but commercial grade corn oil from Mazola (Best Foods Div., CPC International, NJ) and olive oil from Coosure (Jaen, Japan) were used.

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Table 1

Azo compounds used in this study

No	Name	Chemical name	Substituent
I	-	1-phenylazo-2-naphthalene	nil
II	Orange-I	1-phenylazo-2-naphthol	4'-OH
III	Oil red OX	1-Xyleneazo-2-naphthol	2'-OH, 2-CH_3, 5-CH_3
IV	Yellow AB	1-phenylazo-2-naphthylamine	2'-NH_2
V	Yellow OB	1-tolylazo-2-naphthylamine	2'-NH_2, 2-CH_3
VI	Orange SS	1-tolylazo-2-naphthol	2'-OH, 2CH_3
VII	Sunset Yellow FCF	Disodium salt of 1-p-sulphophenylazo-2-naphthol-6-sulphonic acid	2'-OH, 4-SO_3Na 6'-SOH_3Na.
VIII	Ponceau 3R	Disodium salt of 1-pseudocumylazo naphthol-3,6-disulphonic acid	2'-OH, 2,4,5-CH_3 3,6'SO_3Na.
IX	Ponceau SX	Disodium salt of 5-sulpho-2,4-xylylazo-2-naphthol-4-sulphonic acid	2'-OH, 2,4-CH_3 5,7-SO_3Na.

Microemulsion Preparation

Water - (or aqueous ionic solution) along with SDS - n-pentanol aqueous blend (in a fixed mass ratio) and a vegetable oil was taken in 50 ml (screwed) glass tubes. After each addition, tubes were vigorously shaken for 15 min. and left to stand for 5 min.

The SDS - n-pentanol aqueous blends of following compositions were used for preparing microemulsion: 18% SDS, 72% n-pentanol and 10% aqueous solution of reagents (5% NaCl, 1% H_3BO_3 and 4% $Na_2B_4O_7$; sqq: 5% NaCl, 2% H_3BO_3 and 4% $Na_2B_4O_7$ .....etc.). Microemulsion containing 17% SDS, 68% n-pentanol, 15% NaCl, $Na_2B_4O_7$, H_3BO_3 was also employed. A microemulsion of 18% SDS, 72% n-pentanol and 10% water was used for diluting mixtures. The former one with 10% aqueous layer was found to be W/O as determined by electrical conductivity [3]. The latter one inverts to a tranasparent O/W microemulsion.

Polarograms were taken in microemulsion prepared with 2% V/V 2M HCl; 0%, 2.5 .....20% V/V corn oil (or olive oil) and 0.01 - 0.1mM dye solution prepared in microemulsion of SDS, n-pentanol, 5% H_2O and 5% vegetable oil.

RESULTS AND DISCUSSION

A study of water-SDS-n-pentanol phase diagram depicted the existence of a monophase region for wide range of mass fractions of compounds. Particularly,in 1:4 mass ratio of SDS to n-pentanol,water can solve between 10% to 78%. It was established [4] that 20% sunflower oil and 80% of 1:4 SDS to n-pentanol could dissolve substantial amount of detonized water; the boundaries of microemulsion with corn oil were found to range between 8%-28% water. Microemulsion with olive oil were

found to solve 6%-32% water - higher than corn oil.

However, a range of 10-12% aqueous ionic medium with ionic strength < 0.5 M was selected because monophase was undoubtedly stable within this range. It has been reported [4] that they form perfectly spherical droplets having diameter of dispersion ca 1400 A with excellent translucency; further, they remained dispersed throughout the investigations. Microemulsion could dissolve all reagents given above including 2 M NaOH, 2 M HCl. Microemulsion showed no untoward reaction on mixing 0.1-1.0 ml of dye solutions. The colour changes with pH (7.8-10.3) immediately on mixing or long standing were marginal. The dyes in microemulsion showed that currents were proportionally higher with increase in temperature (as expected) indicating stability of microemulsion with temperature.

Often aggragation is described as tight packing produced by surface film bonding. Increase in concentration of ions decreased thickness of the diffused layer; aggregation [5] was encouraged. Low concentration stabilizes lyophobic dye molecule by lowering attaractive part of potential by electrochemical double layer which could make it retain its monomeric form. Preliminary experiments showed that mainly monomer dye is present at concentration $\leq 10^{-2}$ mm [5].

Table 2

Polarographic Characteristics

Comp. No of the Dye	conc (mM)	$i \times 10^2$ (μA)		$D \times 10^6$ (cm^2/sec)		Slope of log plot		$1/n^*.D^{1/2} \times 10^3$ I	
		W/O	O/W	W/O	O/W	W/O	O/W	W/O	O/W
I	0.011	7.6	7.1	3.03	2.59	37.4	36.4	2.02	2.15
II	0.01	6.3	7.1	2.31	3.1	38.4	33.3	2.00	1.99
III	0.0098	6.9	5.1	3.06	1.66	38.9	33.3	2.00	2.01
IV	0.0096	7.2	5.5	3.17	1.88	40.7	33.4	2.10	2.10
V	0.012	7.4	5.8	3.46	2.08	40.9	33.1	1.99	1.97
VI	0.01	7.3	5.6	3.28	2.02	40.3	33.2	2.01	1.96
VII	0.0099	5.9	7.1	2.07	3.17	34.4	40.1	2.07	2.02
VIII	0.0095	5.8	7.2	2.08	3.17	34.5	38.5	2.07	2.12
IX	0.0097	5.7	7.3	2.08	3.31	34.9	39.4	2.05	2.10

* calculated value: Both in W/O & O/W, n varied between 1.77 to 2.32 under controlled potential coulometry;
n is taken as 2 and D calculated from Stokes - Einstein law

Diffusion Controlled Reduction

The slopes of log plots were > 29.5 mV (Table 2) in all cases studied showing polarograms were irreversible. Linear dependance of i_d on $m^{2/3}t^{1/6}$ (±1.2%) for the reduction of 1-phenylazo-2-naphthalene (compound I) and its derivatives confirms diffusion controlled nature of the reduction. Wave heights change with the type of microemulsion (Table 2). The wave height was found to be 15±3% higher in W/O compared with O/W microemulsion(s) in case of oil soluble dyes - oil red OX (III), yellow AB (IV), yellow OB (V) and orange SS (VI); water soluble dyes - orange-I (II), sunset yellow FCF (VII), ponceau 3R (VIII) and ponceau SX (IX) have higher corrent (15±3%) in W/O Microemulsion(s). Droptime decreases shorply in W/O microemulsion from 4.85 to 2.25 near $E_{1/2}$ values; This could account for 10-12% variation in current [6] after considering changes in concentration.

The effect of back pressure acting on the small drop electrode, reduced gravitational pull, non-homogenization of solution near drop surface compared to bulk, density gradient resulting in convective mixing (contemplating irregularities near the plateau of the polarogram at high dye concentration) and non-reversible reduction of dyes vis-a-vis validity of Ilkovic equation makes one not to expect the observed current to be proportional to the concentration of dyes.

The low internal-phase-ratio of water in W/O microemulsion has been proved to undergo quantitative interfacial area increase with ionic emulsifier content when changing to O/W microemulsion thereby resulting in increase of viscosity. To account for this inversion, the product $i_d.\eta^{1/2}$ has been found to be constant upto about 9-10% increase of water in W/O microemulsion. Schwabe [7] depicted in a linear expression that $i_d . \eta^{1/2}$ relationship

Table 3

Substituent Constant, E°_s and $\Sigma\sigma$ Values

$-E_{1/2}$ in W/O is 730 mV (measured with glass and modified calomel ($LiCl/CH_3OH$) electrodes potentiometrically using pH - meter: Toshniwaal CL 46

Comp. No	$-E_{1/2}$ in O/W V *vs* SCE pH8.7	$-E^\circ_s$ (V) Aqu	W/O	O/W	$\Delta E_{1/2}$ V	ρ	Σσ
I	0.48	0.43	0.38	0.48	-	-	-
II	0.51	0.44	0.42	0.46	-0.03	0.16	-0.19
III	0.54	0.49	0.45	0.55	-0.06	0.16	-0.38
IV	0.50	0.46	0.42	0.50	-0.02	0.16	-0.12
V	0.52	0.57	0.40	0.49	-0.04	0.16	-0.24
VI	0.53	0.48	-	-	-0.05	0.16	-0.31
VII	0.44	0.40	0.36	0.50	+0.04	0.16	+0.24
VIII	0.52	0.47	0.42	0.51	-0.04	0.16	-0.24
IX	0.49	0.43	0.42	0.49	+0.01	0.16	+0.06

is obeyed in aqueous medium upto 0.2 mole fraction of non-aqueous addition. When extended to microemulsion systems, the relationship showed reasonable accuracy in the entire range of all the dyes (0.01 to 0.1 mM) studied.

The E°_{c} evaluated by potential mediator method [8] in aqueous medium did not compare well with the values obtained in the presence of W/O or O/W microemulsions (Table 3). Same is the case of calculated slopes of log plots (vide Table 2). Calcualations [8,9] confirm the irreversible nature of reduction waves. The slope of the plot log $[i/(i_d-i)]$ vs E for an irreversible wave differs from the thermodynamic value for a reversible wave because of slowness of redox equilibrium. Certain amount of activation energy is associated with the irreversible reaction which, in general, is specific for a reaction kind and solvents. Attempts are being made to quantify and scrutinize the results so obtained by rigorous treatment of a slow electrode process [6].

Hammett substitution constant is calculated and the values of $\Sigma\sigma$ have been reported (Table 3) which compare well with the closely related dye [9] molecules.

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