Kinetic and Electrolytic Conductivity of C.I. Acid Orange 15 and C.I. Acid Red 97 dyes in Different Media

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Abstract: The electrolytic conductivities for C.I. Acid Orange 15 and C.I. Acid Red 97 have been studied. The electrolytic conductivities have been analyzed by Deby HUckel-Onsager theory, The degree of ionization, α, Van't Hoffs factor, i, and thickness of ionic atmosphere, X^{-1}. were calculated. Each value diminishes with increasing dye concentration. The dye anion transport number, t, mobility's, μ were also computed at infinite dilution. The results provide evidence for the presence of interionic attraction and association. Furthermore the kinetics of two acid dyes has been studied using spectrophotometric and conductimetric methods. The former study was carried out at 28°C at different percentage of solvents. The results revealed that the reaction rate was govemed by a pseudo-first order. [Journal of American Science 2010;6(12):393-399]. (ISSN: 1545-1003).

Keywords : C.I. Acid Orange 15, C.I. Acid Red 97, solvents, electrolytic conductivity, spectrophotometry, kinetics.

1. Introduction

Since the environmental pollutions are increasing day-by-day, the need to reduce the imparities particularly in wastewaters of textile industry is important.

Effluents from the dyeing industry contain highly colored species, such wastes are not only aesthetically displeasing but also hinder light penetration and may in consequence disturbiological processes in water bodies. Dyes are toxic to some organisms and hence harmful to aquatic animals. The expanded uses of azo dyes have shown that some of them are highly carcinogenic. Therefore, removal of dyes before disposal of wastewater is necessary [1,2].

Acid dyes are so called as normally applied from acidic dye liquor. The good sunlight resistance of acid dyes wool textile materials is due to the electron stability of the acid dyes chromophore. This enables the acid dye molecule to resist the photochemical degradation which the ultraviolet rays of sunlight might cause [3]. Some of the dyes were found to have a remarkable mutaganicity, bearing similarities with some antibiotics [4].

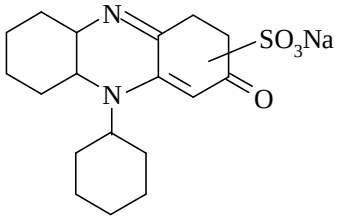
Also azo dye is an interesting and commercially important class compounds that are used for many years as acid-base and redox indicators, stains for bacteriological and histological investigations[5]. Conductivity measurements arc recommended for studying the behavior of dyes in aqueous solution, thus the variation of conductance with concentration in dilute solution provide powerful support for the presence of interionic attraction[6-9]. The mobility of dyes were investigated because its importance in nature and inverious technologies such as adsorption and measurement the drift velocity which can be used to obtain an expression for the ionic current density flowing through a solutions[10]. Mobility has proved to be an important property for providing an insight into the size, fractional coefficients [11] and it is successfully utilized for the control of precipitation.

Kinetic and calorimetric studies have been carried out to determine rate constants for the hydrolysis for some acid dyes at different media. The hydrolysis reactions were carried out in hemogenous media using acetone, dioxane the calorimetric data have been obtained using a sensitive rating-period calorimeter. The results indicate that, irrespective of whether the rate constants k are dependent on percentage of solvents. Taking into consideration both the kinetic and condutimetric data, it is suggested that, for the hydrolysis reaction [4].

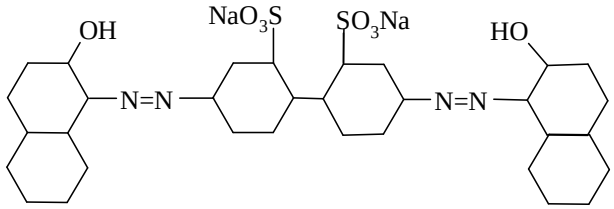
2. Experimental

Reagents

C.I. Acid Orange 15 and C.I. Acid Red 97 were provided by CIBA-GEIGY (Seitzerland), purified by recrystalization twice from 30% ethanol-water mixture and then dried under vacuum at 30°C. Solutions of different concentrations of the dye were prepared by dilution with triply distilled water from stock dye solution (1.0 x 10^{-2}M).



Mol. wt: 375.65 g/mol C.I. Acid Orange 15



Mol. wt.: 698:.04 g/mol, C.I. Acid Red 97, Fig. (1)

The organic solvents used were dioxiane and acetone being of analytical grade.

Apparatus and techniques

A perkin-Elmer lambda 3A. double beam spectrophotometer digital was used. It is a reading and recording instrument operating at the wave length range 190-900 nm (made in Germany).

The conductivity-meter type jenway 4010/REVC (made in United Kingdom) laboratory model with digital, supplied with dipping type conductivity cell with platinized electrodes was used. The cell constant 1.02 and the instrument were provided with a direct reading scale expressed in Siemens (ohm^{-1}).

The equivalent conductance and physical parameters such as, mobility, transport number and thickness of ionic atmosphere were described according to Robinson and Yadav[12].

Calculation:

In spectrophotometer measurements the kinetic study was carried out by mixing with the dye solution appropriate quantities with solvents. The absorbance was then recorded at the maximum wavelength ($\lambda_{max.}$ 410nm for C.I. Acid Orange 15 and $\lambda_{max.}$ 520 nm for C.I. Acid Red 97) every 2 mints till attaining equilibrium (constant reading) over a period of 120 mints. All the measurements were performed at 28°C (room temperature). The solubility of dye under different conditions was checked during 48 hours. The variation of the dye concentration with time at different percentage of solvents with varying polarity was found to fit a straight line of a pseudo-first order rate constant. From slope of these plots, the rate constant of the hydrolysis reaction was calculated using the relation[13].

$$k = \frac{1}{t} \ln \frac{a}{a-x} \qquad (1)$$

Where “k” is rate constant, “x” is the amount of the reactant used up after time “t” and “a” is the initial concentration of the reactant.

The conductimetric measurements the kinetic study of hydrolysis were carried out under the above conditions using time t_1 and t_2, for time intervals, L_1 and L_2 for the respective conductance, one for equation the (1) relation[13].

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{a - L_1}{a - L_2} \qquad (2)$$

If (t_2-t_1) is a constant time interval, then

$$\frac{a - L_1}{a - L_2} = C \qquad (3)$$

where C is constant, rearranging eq. (3) are gets.

$L_1 = CL_2 - a(C-1)$ (4)

Thus, if L_1 is plotted against L_2, a straight line should be obtained with slope C. The logarithm of this value multiplied by 2.303/Δt gives k.

3. Results and Discussion:

I- Conductimetric study[14]

1-Specific Conductance

The specific conductance of aqueous solution for the mono sulphonic azo dye, C.I Acid Orange 15 at various concentration ranging from 1.0 - 9.0 x 10^{-4}g.eq.dm^{-3} and disulphonic azo dye C.I Acid Red 97 covering the concentration range 1.0-9.0x10^{-4} g.eq. dm^{-3} at different percentage of solvents were measured and collected in Figs *(2,3)*. The values of the specific conductance for C.I. Acid Red 97 were high, which may be attributed to the presence of the disulphonic groups attached to the dye with high charge and the presence of more counter ions surrounded the ionisable groups. The plot of the specific conductance, as a function of the concentration for the two dyes at different percentage of solvents Figs (2,3) indicate that in very dilute solutions, specific conductance, increases sharply with increasing dye concentration. "This behaviour may be attributed to the ionization of dyes into sodium ion and dye anions.

$$RNa \longrightarrow R' + Na^+ \qquad (5)$$

$$R(Na)_2 \longrightarrow R' + 2Na^+ \qquad (6)$$

Due to the mutual affinity of ions of different signs surrounding the dye anion. A slight increase in, specific conductance, for monosulphonic and disulphonic azo dyes re-spectively may be attributed to an increase in entropy which arises from the melting of ice-berg" structure around the polar molecules.

Experimental data show that the specific conductance; decreases as the percentage of solvents increase Figs (2,3). This may be explained in terms of the increase in the effective degree of ionization with different percentage of solvents, or it may lower the restricting potential

for migration on raising the percentage of solvents. The specific conductance values can be represented by excellent straight line over the entire different percentage of solvents for each concentration

2-Equivalent conductance, A

The equivalent conductance; A for the investigated dyes in aqueous solutions at different percentage of solvents Figs (4,5) diminishes with increasing dye concentration which either due to the influence of the ionic atmosphere salvation of ions or decrease in mobility and partial dissociation of dyes[15]. The relation between equivalent conductance and square root of concentration is shown in Figs (4,5).

This behaviour may be due to the increase in viscosity [16] and degree of dye aggregates or hindering in the movement of the contour ions. Estimation of, A (equivalent conductance at infinite dilution) where a definite charged ion depends only on its nature and the inter ionic effect disappears. These done by extrapolation to zero concentration The .values of A at different percentage of solvents for the two dyes are to be found in Tables (1,2). These values increase with increasing percentage of solvents represents a high mobility of ions due to the increase in thermal energy and breaking of high number of hydrogen bond. The vibrational, rotational and translation energy also vary with percentage of solvents [17]. The limiting equivalent conductance of an ionic dye molecule λ_o^- is obtained by subtracting the limiting equivalent conductance of sodium ion, λ_o^+ at different percentage of solvents from the conductance at infinite dilution. The acquired values of λ_o at different percentage of solvents are given in Tables (1,2)

3-Van't Hoffs factors i, and thickens of ionic atmosphere,X^{-1}.

Van't Hoffs factors, i Tables (3,4) were computed from the relation i =α (v-l)+l where v is the number of ions and α degree of ionization at different concentrations and different percentage of solvents were estimated as discussed previously. The data in Tables (3,4) indicate those values of Van't Hoffs factors, i decrease with increasing dye concentration indicating incomplete ionization and repulsion between ionic species. This may be due to the decrease in thickness of ionic atmosphere, X^{-1} (Deby length).

To confirm this explanation calculation of, X^{-1} was obtained. The results in Tables (3,4) denoted that the values of X^{-1} decreases as the concentration of the dye increases, which confirms that dye molecules interact with each other and prefer to be in the aggregate form[18].

4- Mobility of dye anion and transport number.

Mobility μ_o is a most important characteristic of ions reflecting their specific participation in electrical conductance of an electrolyte. The mobility's of anionic dye molecule μo at different % of solvents were obtained from the relation μo = λo/zF. Tables (1,2) indicate that mobilities of C.I Acid Orange 15 anions are higher than C.I Red 97 since it has smaller molecular weight than the latter. Further, the lower mobility of C.I Acid Red 97 may be due to the presence of donor and acceptor function groups [19]. This is attributed to the disaggregation and change in the intermolecular bonding. The value of the transport numbers were calculating according to Yadav[12] and recorded in Tables (1,2). The fraction of the total current carried by dye anion is higher than the sodium ion and the values are almost equal at all solvents.

II- Spectrophotometric studies

1- Effect of concentration

The UV-visible spectra of solutions for C.I. Acid Orange 15 and C.I. Acid Red 97 in water were recorded at 28°C within the wavelength range 600 to 350 nm at different concentrations ($1.0\text{-}9.0\times10^{-4}$g.eq. dm^{-3}). The spectra showed increase in absorbance on increasing the dye concentrations.

2- Effect of solvent

The spectra of C.I. Acid Orange 15 and C.I. Acid Red 97 in presence of solvents of varying polarities of dioxane (2.7), aetone (17.9). they dye exhibit similar band in the blue region in absence and presence of solvents. A slight-red shift was notices with different solvents polarity, which may be due to solute-solvent interactions.

3- Kinetic study

The kinetic data of the hydrolysis of dye in presence solvents, fitted pseudo-first order behaviour. This was accomplished by a computer program designed for linear and non linear least squares method, correlation coefficient (r=0.99- 1). The rate constant of hydrolysis k_{abs}., calculated from the slopes of straight lines are recorded in Table (5, 6) results revealed an increase in the rate constant with the increase of the water content of a given solvent system. This may be probably due to the increase of the free hydroxyl ion concentration. Since, it is known that the proton in water has the structure H^+ $(H_2O)_4$ may be left free OH^- in the medium[20].

Table (1): The equivalent conductance, A the limiting equivalent conductance λ_o, dye anion mobility, transport number t, and thickness of ionic atmosphere X^{-1} at infinite dilution in absence and presence of different percentage of solvents for C.I. Acid Orange 15.

Mole% of solvents	A $\Omega^{-1}cm^2\ mol^{-1}$	λ_o $\Omega^{-1}cm^2\ mol^{-1}$	μ_o $cmV^{-1}S^{-1}10^3$	X_o^{-1} $m10^5$	t_o^-	t_o^+
H_2o	265.810	185.810	1.925	2.401	0.699	0.301
Aceton						
10	252.232	178.646	1.851	2.383	0.709	0.291
30	241.016	172.513	1.788	2.364	0.716	0.284
50	220.132	160.732	1.666	2.344	0.723	0.277
Dioxane						
10	208.304	150.845	1.563	2.326	0.724	0.276
30	182.210	132.145	1.370	2.292	0.725	0.275
50	170.740	126.240	1.308	2.286	0.731	0.269

Table (2): The equivalent conductance, A, the limiting equivalent conductance λ_o, dye anion mobility, transport number t, and thickness of ionic atmosphere X^{-1} at infinite dilution in absence and presence of different percentage of solvents for C.I. Acid Red 97.

Mole% of solvents	A $\Omega^{-1}cm^2\ mol^{-1}$	λ_o $\Omega^{-1}cm^2\ mol^{-1}$	μ_o $cmV^{-1}S^{-1}10^3$	X_o^{-1} $m10^5$	t_o^-	t_o^+
H_2o	233.306	169.982	1.644	2.090	0.721	0.279
Acetone						
10	222.400	154.22	1.572	2.000	0.746	0.254
30	210.106	136.17	1.390	1.965	0.763	0.237
50	192.720	129.70	1.227	1.818	0.790	0.210
Dioxane						
10	200.64	146.82	1.368	1.870	0.768	0.232
30	185.951	120.21	1.165	1.724	0.792	0.208
50	164.310	109.73	1.090	1.560	0.801	0.199

Table (3) : Vant Hoff's factors i, and thickness of ionic atmosphere X^{-1} for C.I, Acid Orange 15 at different concentrations of dye and different percentage of solvents.

$C\times10^{-4}$	H_2O		Acetone						Dioxane					
			10%		30%		50%		10%		30%		50%	
	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$
1.0	3.109	8.517	2.790	8.324	2.462	8.211	2.211	2.104	2.091	8.00	1.860	7.856	1.800	7.520
2.0	2.798	7.726	2.624	7.460	2.319	7.270	2.100	7.109	1.940	7.00	1.814	6.801	1.770	6.407
3.0	2.520	7.094	2.602	7.00	2.278	6.814	2.000	6.640	1.876	6.424	1.793	6.260	1.735	6.000
4.0	2.280	6.520	2.314	6.314	2.260	6.100	1.856	6.000	1.800	5.851	1.740	5.514	1.700	5.126
5.0	2.240	6.100	2.201	5.926	7.961	5.720	1.773	5.416	1.716	5.226	1.700	5.090	1.656	5.001
6.0	2.009	5.456	2.010	5.120	1.972	5.010	1.951	4.801	1.900	4.511	1.863	4.210	1.772	4.010
7.0	1.840	4.981	1.792	4.811	1.716	4.514	1.660	4.322	1.612	4.106	1.470	4.00	1.401	3.892
8.0	1.730	4.611	1.715	4.210	1.600	4.026	1.542	3.815	1.502	3.460	1.426	3.172	1.373	3.060
9.0	1.640	4.300	1.610	4.001	1.541	3.810	1.470	3.414	1.414	3.001	1.380	2.817	1.306	2.516

Table (4) : Vant Hoff's factors i, and thickness of ionic atmosphere X^{-1} for C.I, Acid Red 97 at different concentrations of dye and different percentage of solvents .

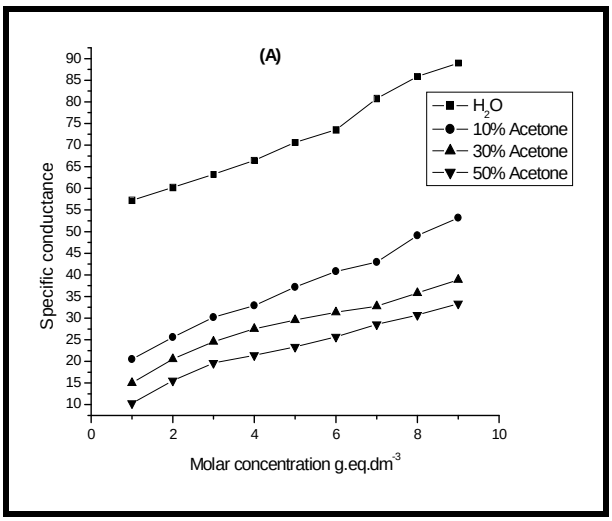
$C\times10^{-4}$	H_2o		Acetone						Dioxane					
			10%		30%		50%		10%		30%		50%	
	I	X^{-1} $m10^5$	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$	i	X^{-1} $m10^5$
1.0	2.926	8.290	2.407	8.010	2.190	7.826	2.000	7.561	1.846	7.280	1.605	7.100	1.314	6.740
2.0	2.773	6.114	2.226	6.002	2.001	5.910	1.810	5.200	1.690	5.050	1.470	4.672	1.276	4.421
3.0	2.590	6.000	2.185	5.860	1.824	5.614	1.562	4.736	1.442	4.329	1.236	4.103	1.090	3.919
4.0	2.260	5.842	2.000	5.460	1.673	5.110	1.336	4.401	1.227	4.100	1.009	3.808	0.985	3.617
5.0	2.090	5.316	1.896	5.096	1.404	4.367	1.227	4.004	1.101	3.870	0.974	3.526	0.874	3.270
6.0	1.960	5.070	1.636	4.854	1.286	4.109	1.090	3.860	0.919	3.566	0.860	3.229	0.800	3.009
7.0	1.814	4.690	1.470	4.246	1.109	3.816	0.960	3.472	0.896	3.219	0.801	3.001	0.764	2.860
8.0	1.653	4.185	1.196	4.60	1.000	3.360	0.924	3.099	0.800	2.809	0.762	2.624	0.716	2.472
9.0	1.375	4.001	0.986	3.870	0.886	3.118	0.817	2.822	0.750	2.636	0.709	2.339	0.640	2.126

Table (5): Rate constant for C.I. Acid Orange 15 in different percentage of solvents at 28°C.

Mole % of solvents	$K\ min^{-1} \times 10^4$	
	Cound.	Spectral
H_2O	18.264	20.201
Acetone		
10	11.060	15.731
30	9.725	12.000
50	7.851	9.246
Dioxane		
10	15.606	19.926
30	12.501	16.011
50	10267	13.000

Table (6): Rate constant for C.I. Red 97 in different percentage of solvents at 28°C.

Mole % of solvents	$K\ min^{-1} \times 10^4$	
	Cound.	Spectral
H_2O	23.650	27.443
Acetone		
10	16.781	20.185
30	13.446	16.704
50	10.219	13.227
Dioxane		
10	19.849	24.368
30	16.908	19.806
50	13.753	15.630



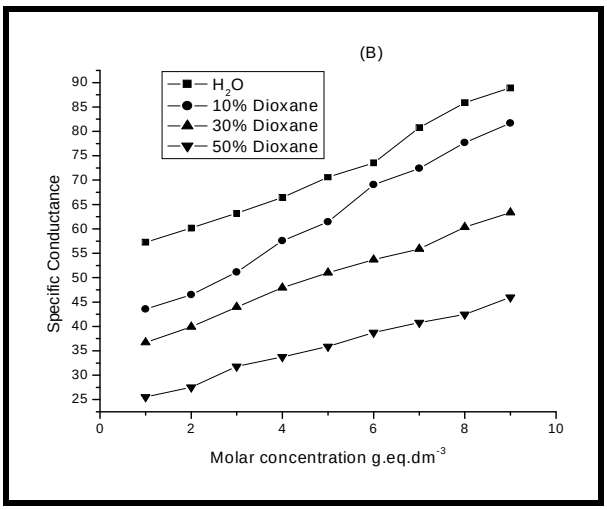


Fig (2a,b): The relation between specific conductance and the molar concentration of C.I. Acid orange 15 in absence and presence of solvents

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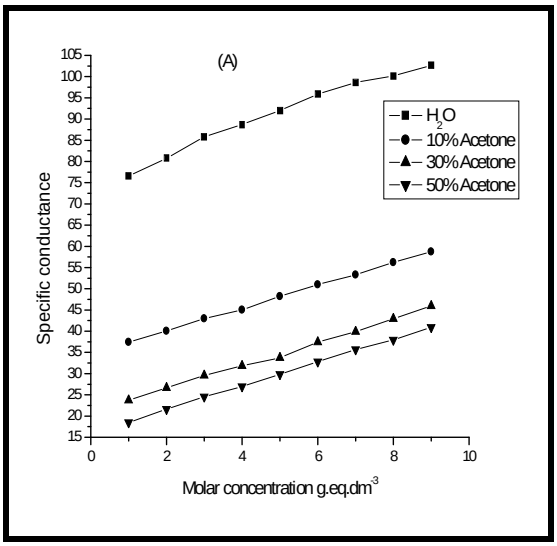


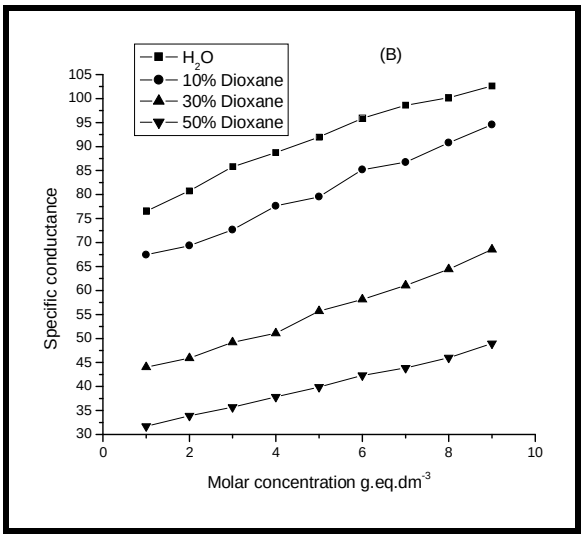
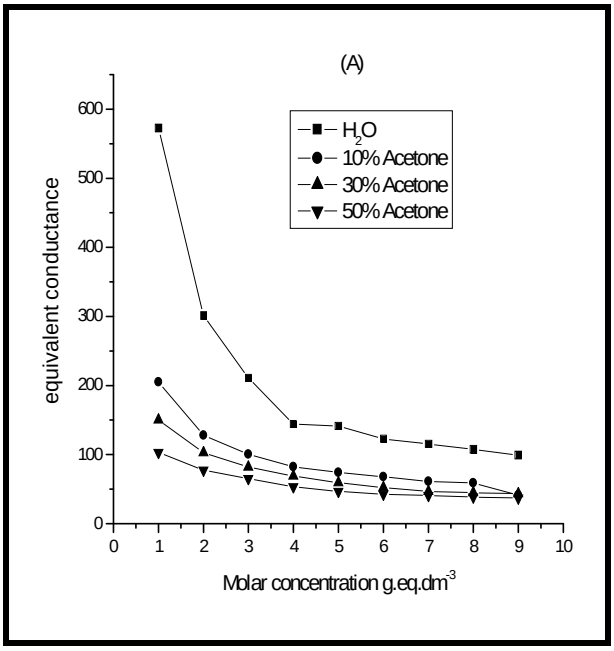


Fig (3a,b,): The relation between specific conductance and the molar concentration of C.I. Acid Red 97 in absence and presence of solvents



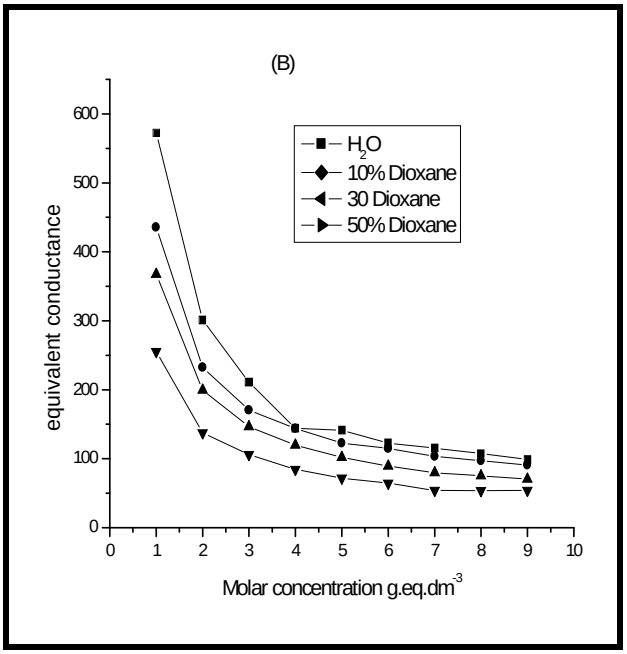
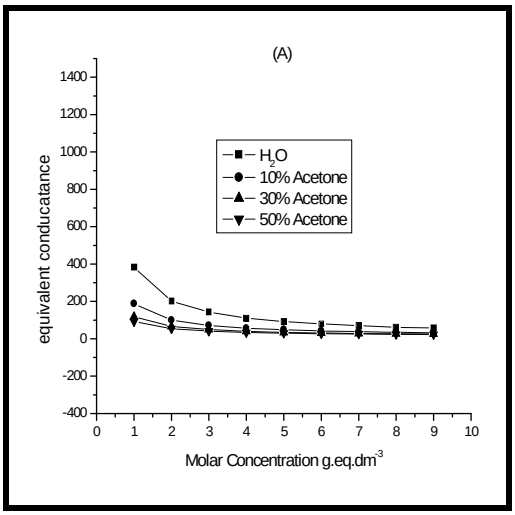


Fig (4a,b): The relation between equivalent conductance and the molar concentration of C.I, Acid Orange 15 in absence and presence of solvents.



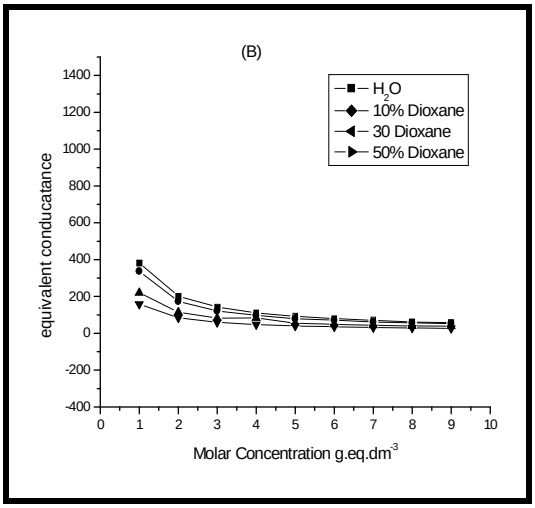


Fig (5a,b) : The relation between equivalent conductance and the molar concentration of C.I., Acid Red 97 in absence and presence of solvents.

4.Conclusions

- The specific conductance increase with concentration of dye increase and decrease in presence of solvent.
- The equivalent conductance decrease with concentration of dye increase and decrease in presence of solvents.
- The dye anion mobility and transport number decrease on solvents than H_2O and in monosulphonic large than disulphonic.
- The Van Hoff's factors i, and thickness of ionic atmosphere decrease on solvents than H_2O and in monosulphonic large than disulphonic .
- The rate constant obeys pesudo first-order reaction in kinetic and conductimentric.

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