COMPLEX PLANE POLAROGRAPHIC BEHAVIOUR OF LEAD(II): PART 2- MONO-, DI- AND TRI-ETHANOLAMMONIUM PERCHLORATE SOLUTIONS

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A detailed investigation of d.c. and complex plane polarographic behaviour of lead ion in mono-, di- and tri-ethanolammonium perchlorate solutions have been made. θ_m and σ_m values have been obtained by various extrapolation methods. In all these three cases it is found that there is no reactant adsorption. The values of θ_m indicate that the reduction is reversible in all these systems. But θ_m increases from mono- to tri-ethanolammonium perchlorate solution, indicating a decrease in the reversibility of the process. The d.c. polarographic method is insensitive to this subtle change in reversibility.

In a previous paper[1] detailed investigations regarding the complex plane polarographic behaviour of lead ion in sodium perchlorate, potassium nitrate and potassium chloride solutions have been presented. Although there is no reactant adsorption in sodium perchlorate solutions, it was felt that there might be some adsorption effects when sodium is replaced by ethanolammonium ion (mono-, di- and tri-) due to the presence of the ethanolic hydroxyl groups. Preliminary experiments indicated that there are no adsorption effects as indicated by the depolarizer concentration independence of double layer capacity. Although the d.c. polarograms had practically the same characteristics, subtle differences were noticed in the complex plane polarographic behaviour of lead (II) in mono-, di- and triethanolammonium perchlorate solutions. Hence, in this paper a detailed investigation of d.c. and complex plane polarographic behaviour of lead (II) in the three ethanolammonium ion solutions is presented.

EXPERIMENTAL

The details of d.c. and complex plane polarographic methods used have been described previously [1,2,3,4]. The apparatus is essentially the same as described by Sluyters et al [5]. The values of m for the capillaries used are 1.861 mg/sec in 1 M MEAP, 1.654 mg/sec in 1 M DEAP and 1.746 mg/sec in 1 M TEAP. The drop time is adjusted for 4 seconds a drop in 1 M potassium chloride solution. All experiments have been conducted at a temperature of $30 \pm 0.1°C$. The list of symbols is given in an earlier paper [1].

RESULTS

Complex plane and d.c. polarographic studies of lead ion have been confined to 1 M MEAP solutions only. In the case of di- and triethanolammonium salt solutions, where θ_m values are higher, investigations could be conducted not only in 1 M solutions but also in 0.5 M or 0.1 M solutions.

D.C. Polarography

The analysis of the d.c. polarograms have been given in Table 1. It is clear that d.c. polarography does not show any difference in the behaviour of lead ion in these base solutions.

Complex plane polarography

Typical complex plane polarograms in MEAP, DEAP and TEAP solutions are given in Fig. 1. In all cases the complex plane peaks are well defined. The potential corresponding to the peak potential is the same as the potential of the minimum in the q vs. potential curve. Typical results are given in Table 2. At the peak potential, frequency variation curves and concentration variation curves have been made. The frequency variation curves are straight lines in the lower frequency range with a slope of about 45° indicating that the curves are reversible.

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TABLE 1

D.C. POLAROGRAPHIC CHARACTERISTICS LEAD(II)

Base solution	Concentration M	$E_{1/2}$ (vs SCE) (Volts)	Slope of log plot (mV)	D.C.C
MEAP	1.0	-0.378	30	3.764
DEAP	1.0	-0.378	30	3.616
	0.5	-0.378	30	3.746
	0.1	-0.378	30	3.893
TEAP	1.0	-0.378	30	3.43
	0.5	-0.378	30	3.67

TABLE 2

DOUBLE LAYER CAPACITY (μ F/cm^2) AND SERIES RESISTANCE (ohm cm^2) VALUES FOR LEAD(II) IN MEAP, DEAP AND TEAP SOLUTIONS

Peak Potential and Potential of q minimum was -0.378 V in all cases

Supporting electrolyte	C_p by analysis of: C_p vs $1/\omega$	Y''_{el} vs Y'_{el}	Y''_{el}/ω vs Y'_{el}/ω	Y''_{el} vs $[Pb^{++}]$	$R\Omega$ (ohm cm^2)
1 M MEAP	26	26	25	26	1.66
1 M DEAP	24	24	24	24	1.93
0.5 M DEAP	26	26	26	26	2.81
0.1 M DEAP	28	28	28	28	8.20
1 M TEAP	22	21	22	21	2.20
0.5 TEAP	24	23	22	22	2.85

The series resistance is determined by using the following extrapolation methods. (i) Z'' vs. Z` plots, (ii) R_E vs. $1/\omega$ plots and (iii) R_E vs. $1/\omega^2$ plots as $\omega \to \infty$. A few typical plots are given in Fig. 2. It is gratifying that the $R\Omega$ values obtained by different techniques are in good agreement with each other. The mean values of $R\Omega$ are included in Table 2. The double layer capacity in presence of the depolarizer has been determined by different methods such as capacity in parallel (C_p) vs. $1/\omega$ plots, Y''_{el} vs Y'_{el} plot, Y''_{el}/ω vs Y'_{el}/ω plots and Y''_{el} vs depolarizer concentration plots. It may however be mentioned that the last three methods do not actually help in obtaining enhanced double layer capacity at a particular concentration of the depolarizer if there is adsorption. Typical plots are given in Fig.3 and the results are presented in Table 2. It is obvious that the double layer capacity is independent of the concentration of the depolarizer indicating that there is no reactant adsorption $E_{1/2}$ in these systems. It is found that $E_m = E_{1/2}$ in these base solutions indicating that $\alpha = 0.5$ in all these cases.

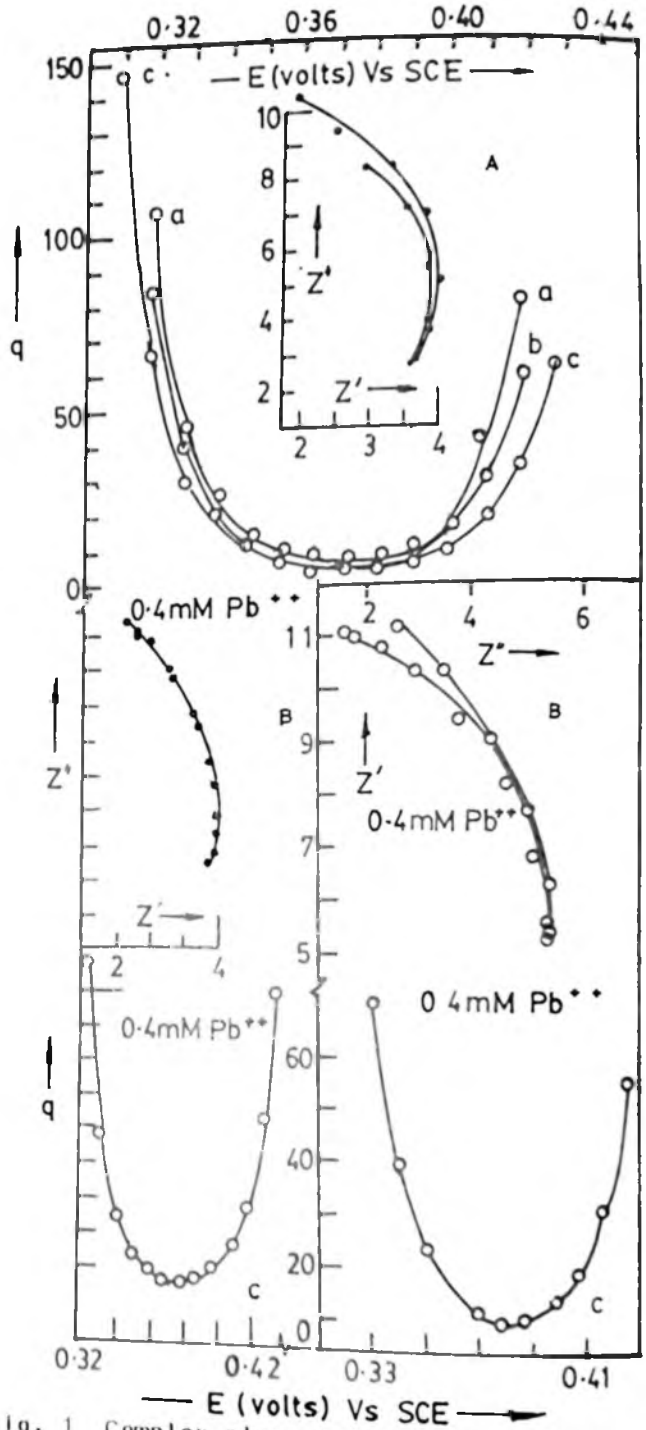


Fig. 1 Complex plane polarograms and corresponding q vs E plots for lead (II) in (A) 1 M MEAP (B) DEAP (C) 1 M TEAP

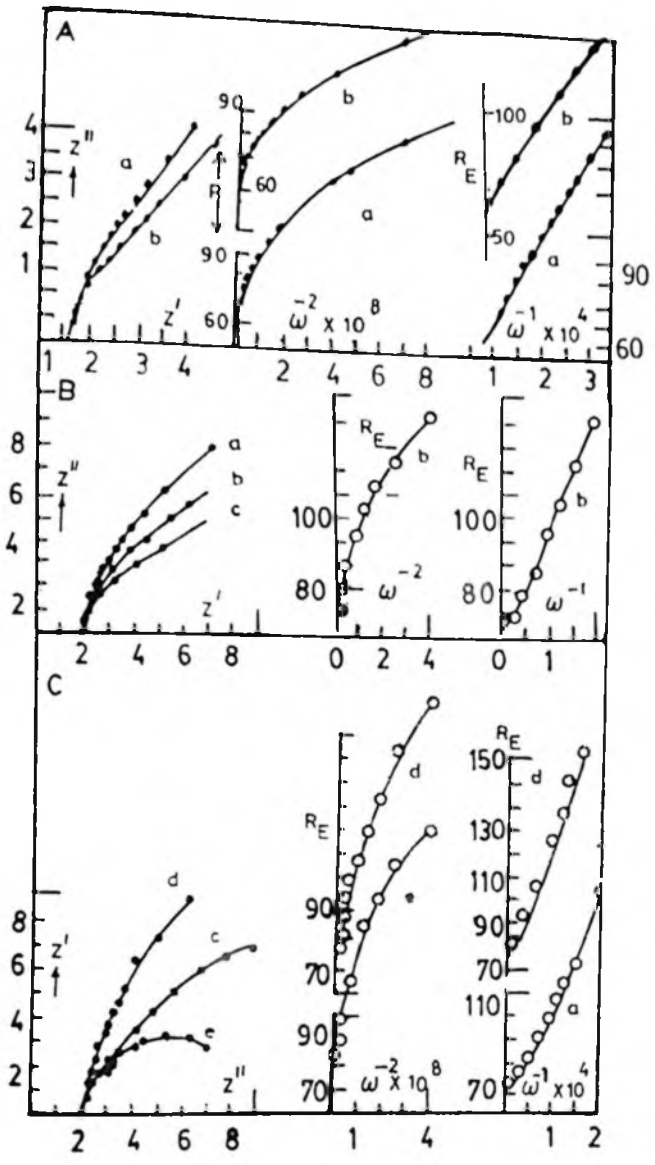


Fig. 2 Frequency variation, R_E vs ω^{-1} plots and R_E vs ω^{-2} plots for lead (II) in (A) 1 M MEAP (B) 1 M DEAP (C) 1 M TEAP (a) 0.2 mM; (b) 0.3 mM; (c) 0.4 mM; (d) 0.5 mM; (e) 0.8 mM

Determination of θ_m and σ_m : Since there are no adsorption effects, the results are analysed using Randles circuit. Attempts were made to obtain θ_m and σ_m values by extrapolation methods. It was found that in the case of q vs. $1/\omega$ and $1/q$ vs. $1/\omega$ plots for obtaining θ_m and $1/\theta_m$, the extrapolations were uncertain. $\sqrt{\omega}/Y'_{el}$ vs $\sqrt{\omega}$ plot which gives the value of $2\sigma_m$ was quite satisfactory. Similarly Z'_f , Z''_f vs. $1/\sqrt{\omega}$ plots for obtaining both θ_m and σ_m were also found to be satisfactory. Typical curves are given in Fig. 4 and 5 and the results are presented in Table 3.

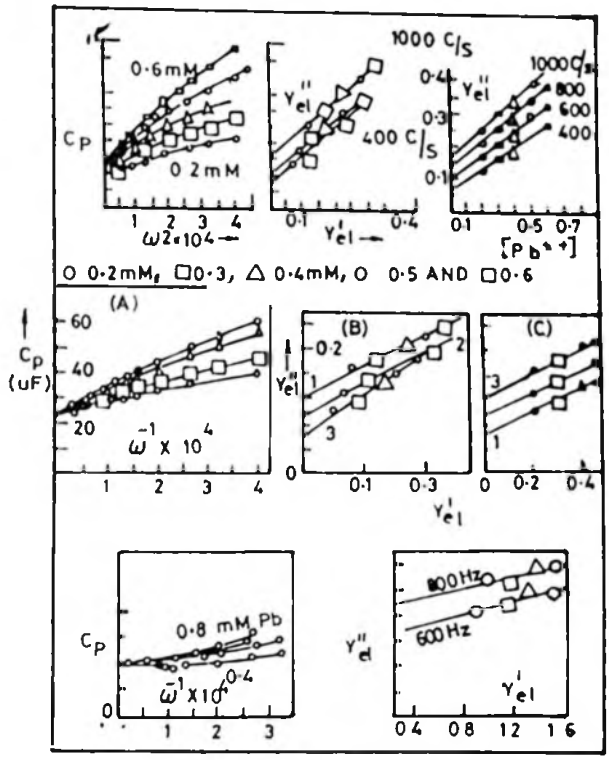


Fig. 3 Calculation of double layer capacity by the methods (A) C_P vs plots (B) Y''_{el} vs Y'_{el} plots and (C) Y''_{el}/ω vs. Y'_{el}/ω plots for lead (II) in (a) 1 M TEAP (b) 1 M DEAP (c) 1 M TEAP

Phase sensitive a.c. polarograms: Phase sensitive a.c. polarograms Y'_{el} vs. potential (in phase) and Y''_{el} vs. potential (quadrature curves) have been made by calculating Y'_{el} and Y''_{el} from the complex plane polarographic data using the following equations.

$$Y'_{el} = \frac{(Z' - R\Omega)}{(Z' - R\Omega)^2 + (Z'')^2} ;$$

$$Y''_{el} = \frac{Z''}{(Z' - R\Omega)^2 + (Z'')^2}$$

The plots are given in Fig.6. The plots are well formed indicating reversibility of the reduction process.

DISCUSSION

Theoretical θ vs potential and q vs potential curves

Timmer and other have given the theoretical θ vs potential and q vs potential curves for a certain set of parameters. It may however be pointed out that these curves vary in their shape with different set of parameters. Hence

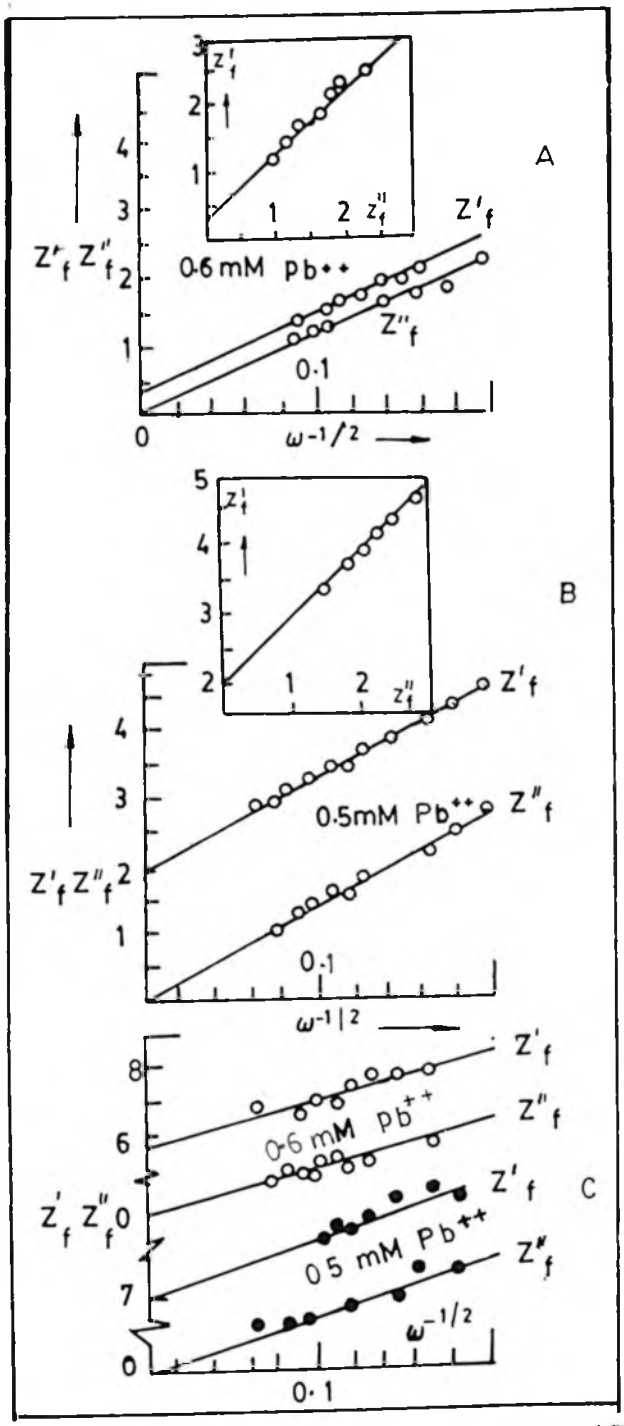


Fig. 4 Calculation of θ and σ by Z'_f vs $1/\sqrt{\omega}$ plot, Z''_f vs $1/\sqrt{\omega}$ and Z'_f vs $-Z''_f$ plots for lead (II) in (A) 1 M MEAP (B) 1 M DEAP (C) 1 M TEAP open circles refer to 0.6 mM Pb^{++}, filled circles to 0.5 mM Pb^{++}

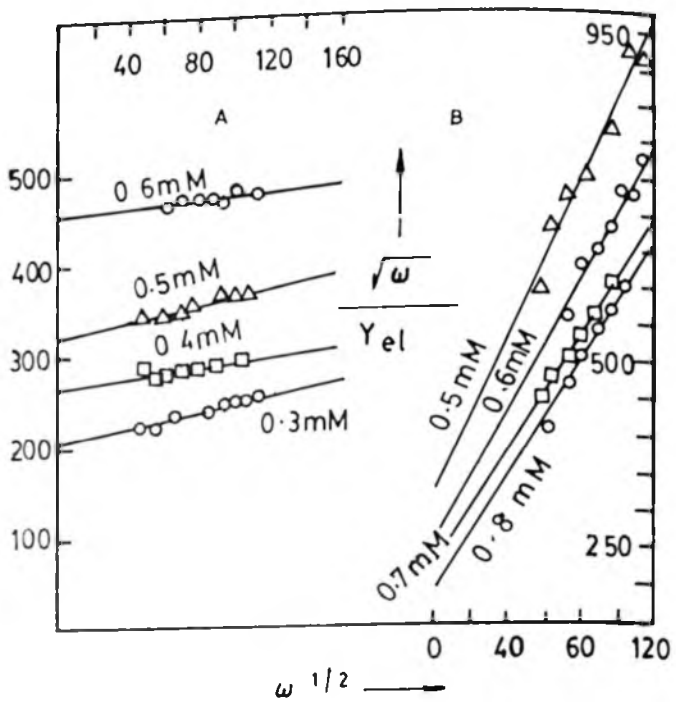


Fig. 5 Determination of σ by $\sqrt{\omega}/Y'_{el}$ vs $\sqrt{\omega}$ plots
(A) 1 M MEAP (B) 1 M TEAP

in the present work these curves have been made for the parameters corresponding to the three systems discussed in this paper. The parameters are presented in Table 4. q and θ are calculated as in ref 1. The k_{sh} values used for computing θ and σ values to get the theoretical curves are 10^{-3}, 10^{-2}, 10^{-1}, 2 x 10^{-1}, 5 x 10^{-1}, 7 x 10^{-1}, 1 and 10 cm sec^{-1}

Examination of the three sets of curves A, B and C in Figs. 7 and 8 indicate how very different they are even though the only parameter that has been changed is diffusion coefficient of lead ion. It is noticed that in the θ vs potential plots, the limiting value of θ follows the order $(\theta_m)_{tri} -> (\theta_m)_{di} > (\theta_m)_{mono}-$. When the rate constant is of the order of 10^{-3} cm/sec, the θ vs potential plot is an L shaped curve without any minimum in MEAP solutions. In DEAP solutions, the minimum has just formed while in TEAP solution, the minimum is fairly well formed. It may be pointed out that the values of θ calculated in the vicinity of the peak potential lie very close to the theoretical curves for all these three base solutions.

q vs potential curves in all the ethanolammonium ion solutions are similar but the value of the potential of q_{min} follows the order mono-< di-< tri-. It is interesting to note that there is a qualitative difference in the nature of q vs potential curves for the rate constant 10^{-3} cm/sec. In MEA ion solution the

TABLE 3

θ_m(ohm cm^2), σ_m(ohm cm^2 sec$^{-1/2}$) AND RATE CONSTANT VALUES OBTAINED FOR LEAD(II) IN DIFFERENT SUPPORTING ELECTROLYTES USING DIFFERENT EXTRAPOLATION TECHNIQUES

Supporting electrolyte	Parameter	Z'_f, Z''_f vs $\omega^{-1/2}$	Z'_f vs Z''_f	$\sqrt{\omega}/Y'_{el}$ vs $\sqrt{\omega}$	Mean value	Rate constants (cm/sec)	
						From Eqn.7	From Eqn.8
1 M MEAP	θ_m C	0.215	0.201	-	0.208	0.745	0.6518
	σ_m C	68.20	-	65.47	66.84		
1 M DEAP	θ_m C	0.95	0.915	-	0.933	0.1726	0.1464
	σ_m C	72.25	-	72.00	72.12		
0.5 M DEAP	θ_m C	0.62			0.62	0.2585	0.2196
	σ_m C	71.50	-	-	71.50		
0.1 M DEAP	θ_m C	0.457			0.457	0.3395	0.2973
	σ_m C	67.0	-	-	67.00		
1 M TEAP	θ_m C	3.63	4.0	-	3.815	0.04494	0.0367
	σ_m C	81.88	-	81.80	81.84		
0.5 M TEAP	θ_m C	1.50			1.50	0.1068	0.09173
	σ_m C	71.00	-	-	71.00		

TABLE 4

EXPERIMENTAL PARAMETERS CORRESPONDING TO LEAD(II) IN 1 M MEAP, 1 M DEAP AND 1 M TEAP SOLUTIONS

R = 8.314 J/Mole/degree F = 96500 coulombs
T = 303°K, f = 600 C/sec α and β = 0.5
D_R = 14.1 x 10^{-6} cm^2/sec C_R = 0 mM

Parameter	1 M MEAP	1 M DEAP	1 M TEAP
D_O (cm^2/sec)x10^6	7.91	6.01	5.06
C_O (mM)	0.6	0.6	0.4
C_R (mM)	0.0	0.0	0.0
t(sec)	3.4	3.9	4.3

curve is symmetrical. In DEA ion solution the curve has slightly become unsymmetrical. In TEA ion solution, the curve is even more unsymmetrical and there is a tendency for splitting. Since all the parameters other than diffusion coefficients are the same, it can only be said that this is a mathematical necessity. However, in the peak potential region the experimental q vs potential curves for lead(II) in monoethanolammonium ion solution lies close to the theoretical q vs. potential curve computed for the rate constant 0.7 cm/sec and for lead (II) in diethanol-

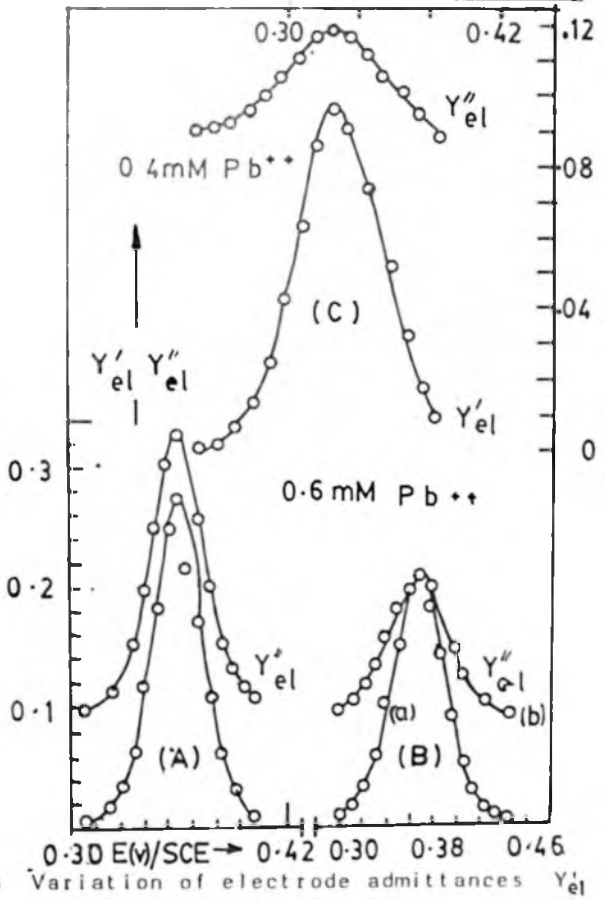


Fig. 6 Variation of electrode admittances Y'_{el} and Y''_{el} with d.c. potential for the solutions of lead (II) in (A) 1 M MEAP (B) 1 M DEAP and (C) 1 M TEAP

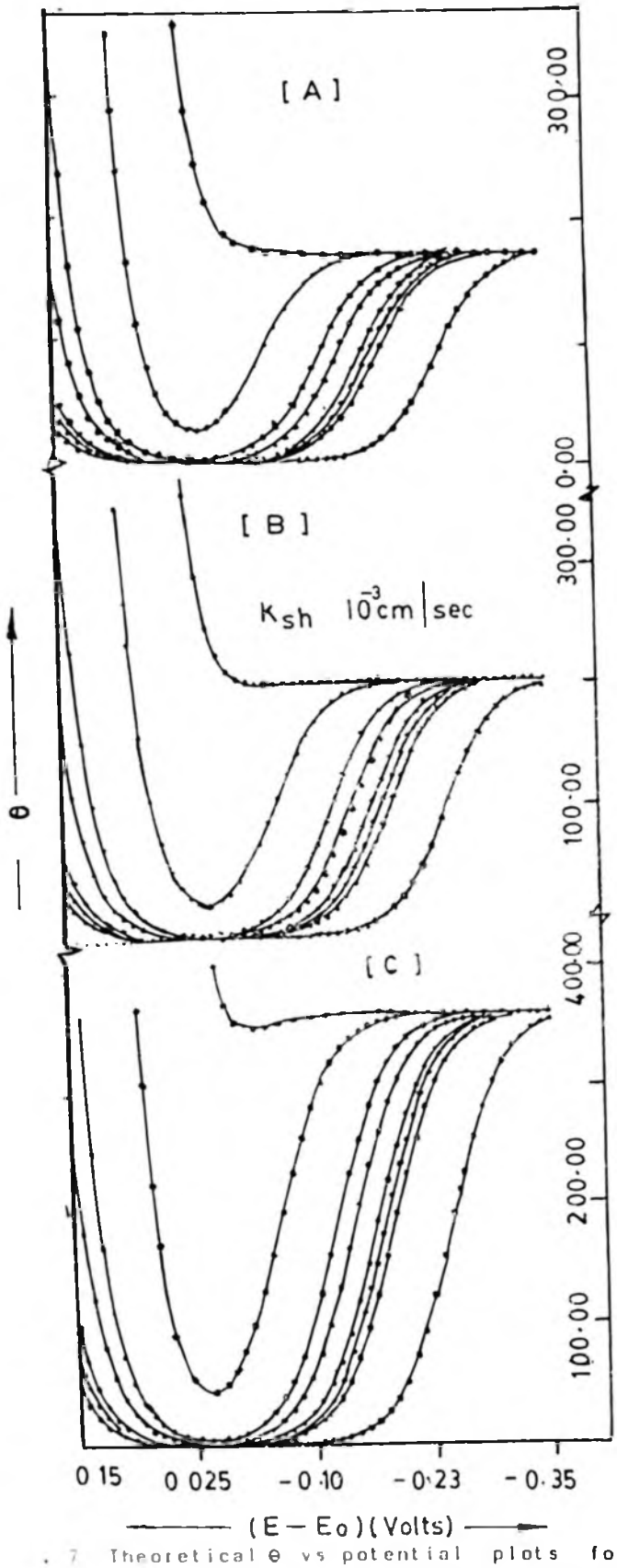


Fig. 7 Theoretical θ vs potential plots for lead (II) in (A) 1 M MEAP (B) 1 M DEAP (C) 1 M TEAP k_{sh} values used for computing θ are 10^{-3}, 10^{-2}, 10^{-1}, 2 x 10^{-1}, $5x10^{-1}$, $7x10^{-1}$, 1 and 10 cm/sec

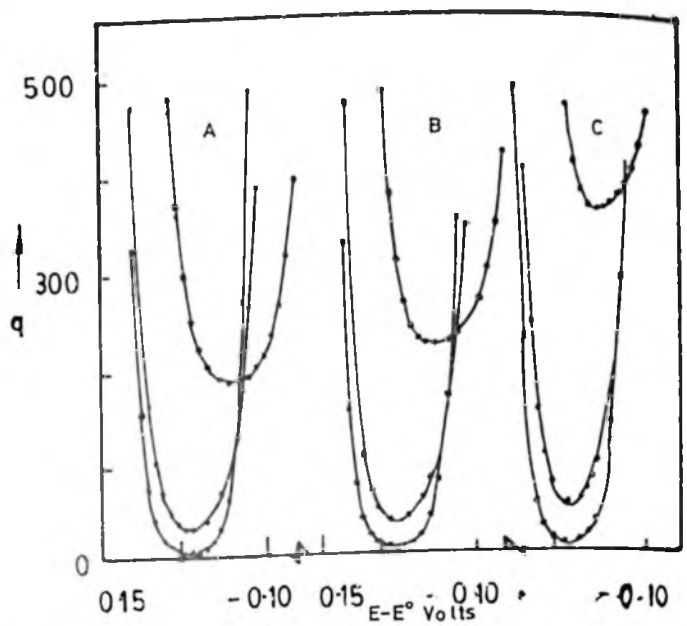


Fig. 8 Theoretical q vs potential plots for lead (II) in (A) 1 M MEAP (B) 1 M DEAP (C) 1 M TEAP

ammonium ion solution, the experimental curve lies on the theoretical curve computed for rate constant 0.2 cm/sec and for lead (II) in triethanolammonium ion solution, the experimental curve lies in the theoretical plots computed for rate constants 0.01 and 0.1 cm/sec. This observation indicates that there is close agreement between the experimental and theoretical curves. Further it indicates that the lead(II) triethanolammonium ion system is less reversible than lead (II) mono- and diethanolammonium perchlorate systems.

Double Layer Capacity and Concentration of Depolarizer

As already mentioned previously, the results presented in Table 2 indicate that the double layer capacity is independent of the concentration of depolarizer in all the three ethanolammonium ion solutions. Further the double layer capacity value is practically the same as that of the blank. It can therefore be concluded that there is no reactant adsorption in these systems.

Phase Sensitive a.c. Polarograms

The height and shape of Y'_{el} vs potential curves (in phase a.c polarogram) and Y''_{el} vs potential curves (quadrature a.c. polarogram) depend solely on the faradaic resistive and capacitative components namely R_s and $1/\omega C_s$.

Since there is no complication of reactant adsorption (which normally contributes to the capacitative part) in the systems being studied in this paper, it can be resolved that the shape and size of these curves are decided by the value of θ to a greater extent. In other words, the theoretical a.c. polarograms computed with parameters corresponding to these systems can be utilized for knowing the degree of reversibility of electrode process in these different systems. Theoretical phase sensitive a.c. polarograms for different rate constants (k_{sh} from 10^{-3} to 10 cm/sec) for the parameters corresponding to these three base solutions (Table 4) are calculated using y'_{el} and y''_{el} as in ref (eq. 3 and 4).

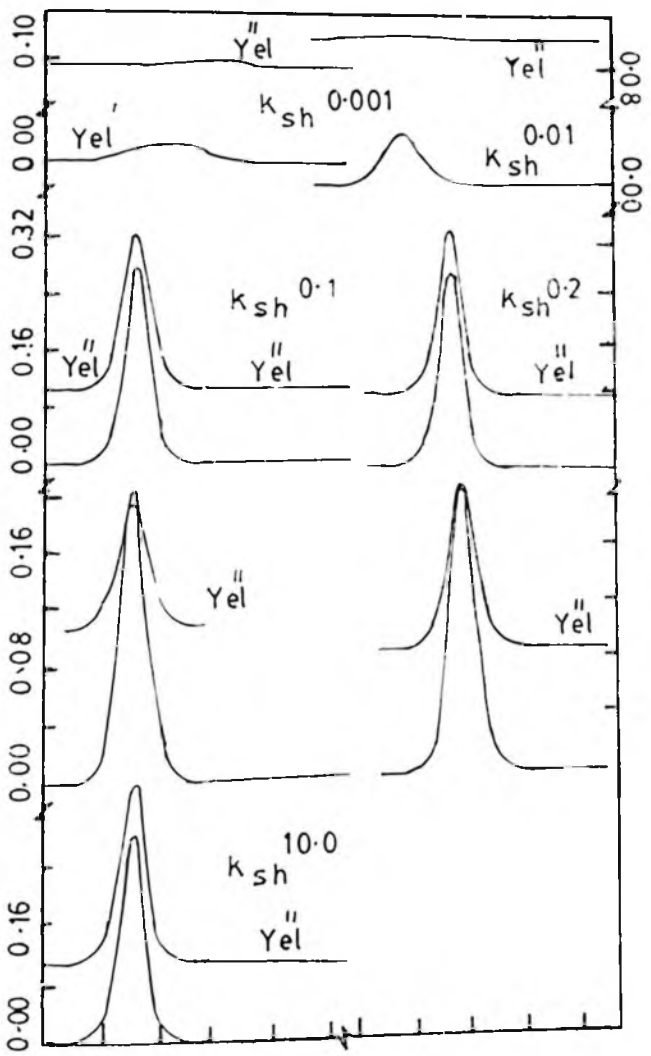


Fig.9 Theoretical phase sensitive a.c polarograms for 0.6 mM lead (II) in 1 M MEAP (for different assumed values of rate constant k_{sh})

The value of C_d used is that of the blank at the peak potential since there is no reactant adsorption. The same value of C_d is used for the entire potential range of the a.c. polarograms since the C_d does not vary very much in the small potential region of the a.c. polarogram. The theoretical curves are given in Fig.9-11.

The experimental curves are given in Fig.6. It is gratifying that there is very good agreement between the theoretical and experimental curves.

Rate constants and σ_m values

The rate constants are calculated using the equations 7 and 8 in reference 1. The results are given in Table 3.

The agreement between the values obtained from the various equations is quite satisfactory. It is noticed that with increase in the concentration of the supporting electrolyte, the

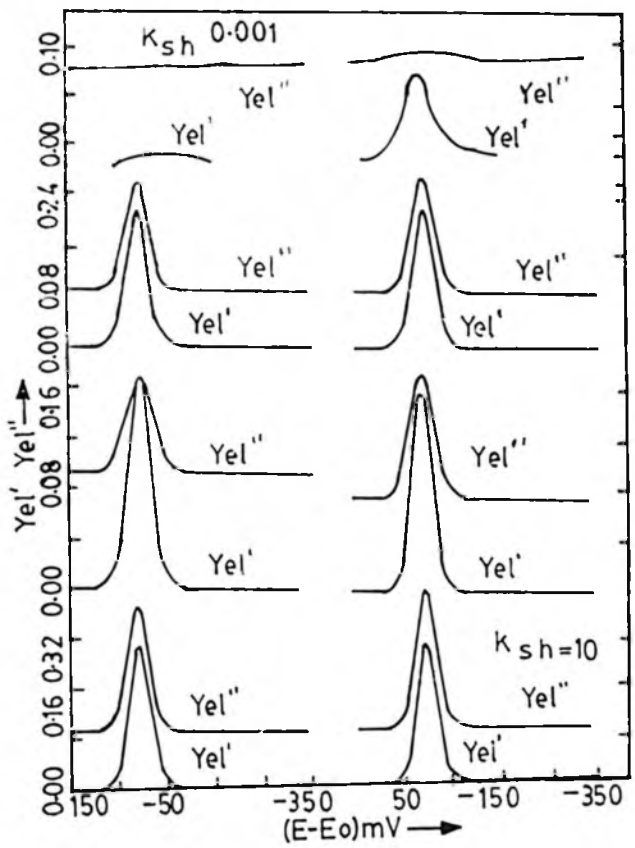


Fig. 10 Theoretical phase sensitive a.c. polargrams for lead (II) in 1 M DEAP (for different assumed values of rate constants k_{sh})

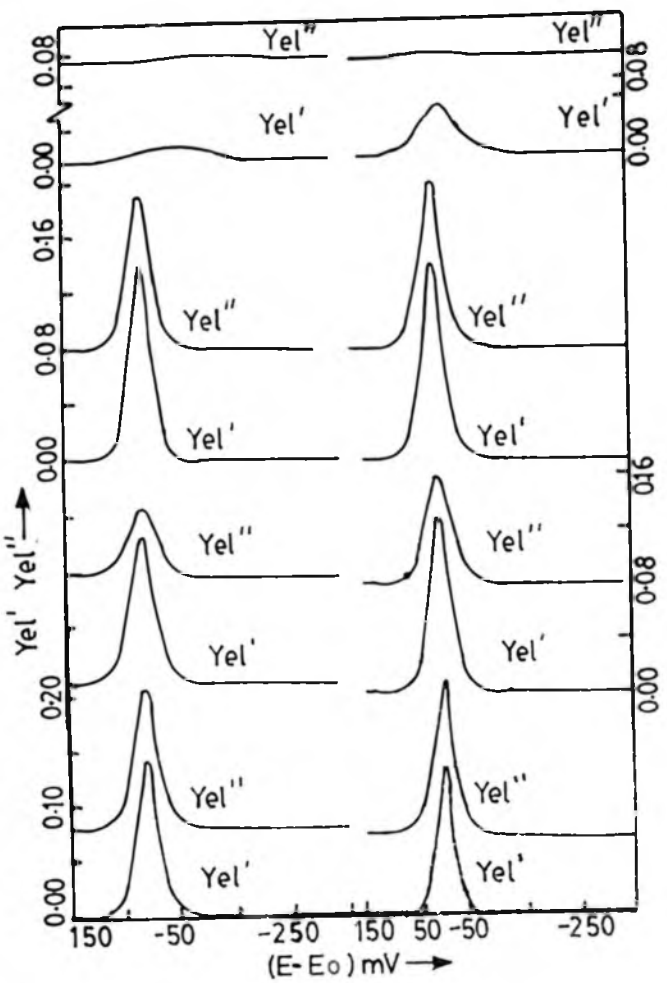


Fig.11 Theoretical phase sensitive a.c polarograms for lead (II)- Triethanolammonium perchlorate solutions for different assumed values of rate constants

rate constant decreases. However, no attempt has been made to apply Frumkin correction since the rate constants are sufficiently high. An interesting feature that has been noticed is the decrease in the value of the rate constant as one proceeds from mono- to tri- ethanolammonium perchlorate. This is evidently due to steric effects on the account of the increase in the number of ethanolic groups. σ_m value is also found to increase with the increase in the number of ethanolic groups indicating the decrease in the value of the diffusion coefficient of the lead ion. Similar conclusion regarding the diffusion coefficient is arrived at since the value of diffusion current constant decreases as we proceed from mono- to triethnolammonium ion solution at constant ionic strength.

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