COMPLEX PLANE POLAROGRAPHIC BEHAVIOUR OF LEAD (II): PART I-SODIUM PERCHLORATE, POTASSIUM NITRATE AND POTASSIUM CHLORIDE SOLUTIONS

A. Selvaraj* and R.S. Subrahmanya**

Department of Inorganic and Physical Chemistry, Indian Institute of Science
Bangalore 560 012, INDIA
** Assistant Professor, GVN College, Kovilpatti - 627 702.*
*** 907/48, 'Janaki Nilaya' Gokul I Stage, I Phase, 6th Cross Road,*
Near Ganesha Temple, Bangalore - 560 054.

A detailed investigation of d.c. and complex plane polarographic behaviour of lead ion has shown that there is no reactant adsorption in $NaClO_4$ solutions as indicated by the non-dependence of double layer capacity on depolarizer concentration. In KCl solutions strong reactant adsorption has been noticed. It is rather surprising that reactant adsorption is observed even in KNO_3 solutions. Phase sensitive a.c. polarograms have been derived from the experimental data which very clearly indicate reactant adsorption. By suitable extrapolation methods θ_m and σ_m have been obtained and rate constants have been calculated.

It is well recognised that lead ion is specifically adsorbed in potassium chloride solutions [1]. However, in the course of the present investigations, it has been noticed that the phase angle for the reduction of lead ion is greater than 45° in potassium nitrate solutions and less than 45° in sodium perchlorate solutions indicating specific adsorption of lead ion even in potassium nitrate solutions which has not been noticed by previous workers. It was therefore thought desirable to make a comparative study of the complex plane polarographic behaviour of lead ion in all these base electrolytes. In the present paper a detailed account of analysis of impedance data in cases of specific adsorption of lead ion including obtaining of phase sensitive a.c polarograms and rate constants have been presented. Since d.c. polarographic measurements are fundamental, d.c. polarograms have been taken in all the base solutions.

EXPERIMENTAL

The d.c. and complex plane polarographic methods employed are the same as described previously [2]. The complex plane polarographic set up (bridge) similar to the one described by Sluyters et al [3] was fabricated and standardised in this laboratory [4]. A low noise amplifier was used in the detector circuit. The impedance balance was made at the end of drop-life. Pool-condenser-saturated calomel electrode developed by Breyer, Gutman and Hacobian [5] was used. From the experimental data, Z' and Z" were calculated using the relations $Z' = A.R_E$ and $Z'' = A/2\pi fC_E$ where A is the surface area of the mercury drop and R_E and C_E are experimentally measured resistance and capacitance of the system at a given frequency, f. In the same test solution d.c. polarogram was taken first using a manual set up and then complex plane polarographic measurements were made. iR drop and residual current corrections have been incorporated. For purposes of clarity and comparison, the sign conventions used by Sluyters-Rehbach and Sluyters [6] have been employed in writing rate equations. However the equations are written such that α refers to cathodic and β to anodic transfer coefficients.

The value of m for capillary in d.c. and complex plane polarographic studies are 1.957 in 1 M perchlorate, 1.659 in 1 M nitrate and 1.959 in 1 M chloride respectively, the drop time being 4s/drop in 1 M KCl solution. All potentials reported are with respect to Calomel Electrode (SCE). All experiments have been conducted at 30 ± 0.1° C.

RESULTS

D.C. Polarography

The characteristics of the polarogram of lead (II) are almost the same in all the three base solutions. Analysis of these polarograms indicates that the log plots are straight lines with a slope of about 0.030 V indicating

0013 466 x 31 (36) 213-223

reversibility of the process in all these base solutions. In base solutions containing 1 M $NaClO_4$, 0.9 M KNO_3 + 0.1 M HNO_3 and 1 M KCl + 0.01 M HCl, the half-wave potential values are -0.378 V, -0.408V and -0.437 V while the d.c.c values are 4.27, 3.90 and 4.38 respectively.

Complex Plane Polarography

To have low impedance in measurements, experiments have to be conducted using a fairly high concentration of the indifferent electrolyte in the solution. Hence experiments were limited to 1 M solutions.

Lead-Perchlorate System

Complex plane polarograms and frequency variation curves: Experiments have been made using various concentrations of lead ion (0.1 mM to 0.5 mM). The peak potentials are obtained from the well-defined complex plane polarograms and are confirmed by the q vs potential curves. At the peak potential, frequency variation curves have been made. The frequency variation curves are straight lines with about 45° slope in the lower frequency range indicating the reversibility of the process. Typical complex plane polarograms and q vs potential plots are given in Fig. 1. The typical frequency variation plots are given in Fig. 2

Calculation of series resitance ($R\Omega$): In the present system since the value of activation polarization resistance (θ), is very small as indicated by the preliminary experiments, the success of obtaining θ depends upon the accuracy with which the series resistance could be estimated and corrected for by subtracting it from resistance part of C.P. polarogram. In the present work, the series resistance is obtained by (i) extrapolation of Z" vs Z' plots to infinite frequency, (ii) extrapolation of (R_E) at various frequencies to infinite frequency using R_E vs ω^{-1} and R_E vs ω^{-2} plots. A few typical plots are given in Fig 2. It is gratifying that the $R\Omega$ values obtained by different methods agree with each other. Typical values are included in Table 1.

Determination of double layer capacity: The determination of the double layer capacity in presence of depolarizer is important to draw conclusions regarding the adsorption of the depolarizer and also to obtain the components of the fardaic impedance namely θ and σ. Two types of methods are used for deterrmining the double layer capacity. The first type is based on the impedence measurements with single concentration of the depolarizer at different

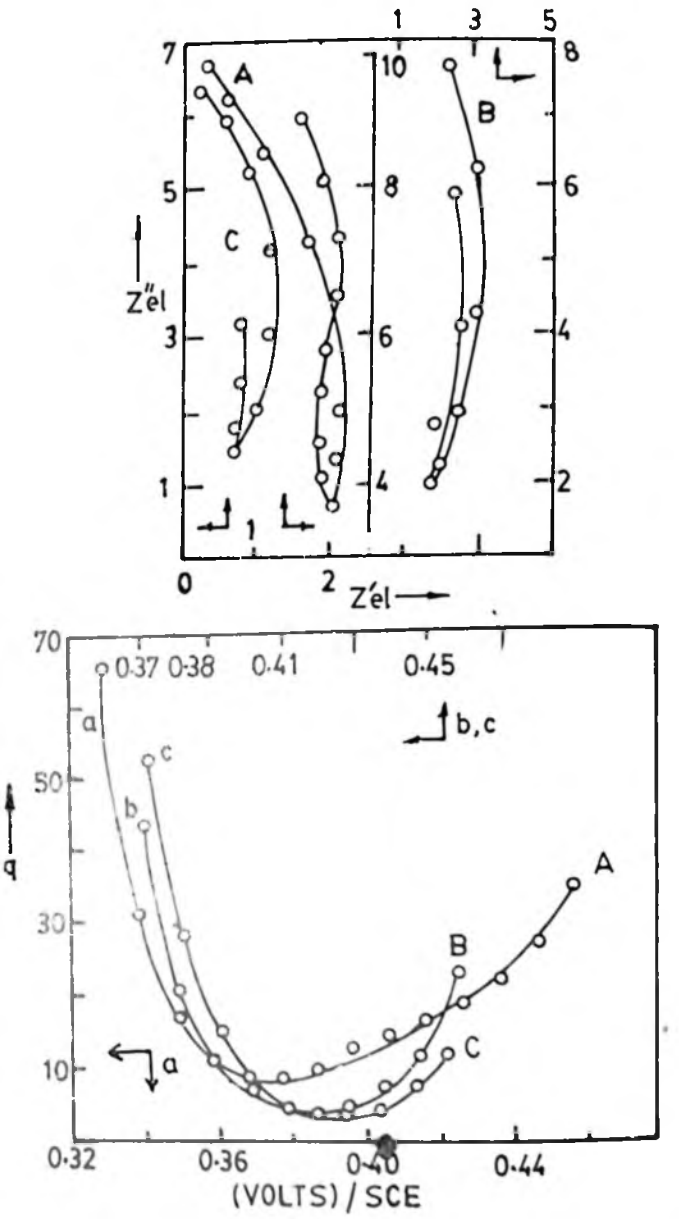


Fig. 1 Complex plane polarograms and corresponding q vs potential plots for lead (II) in (A) 1 M $NaClO_4$ 0.3 mM Pb^{++} (B) 0.9 M KNO_3 - 0.1 M HNO_3 0.5 mM Pb^{++} (C) 1 M KCl - 0.01 M HCl 0.5 mM Pb^{++}

frequencies, i.e., parallel capacity vs $1/\omega$ plots as $1/\omega \longrightarrow 0$. In the second type, impedence measurements made with different concentrations of the depolarizer at fixed frequency are analysed employing the following graphical methods.

(a) $Y''_{el} = Y'_{el}/(p + 1) + \omega C_d$, So plots of either Y''_{el} vs Y'_{el} or Y''_{el}/ω vs Y'_{el}/ω can be used to obtained ωC_d or C_d as intercept and $1/(p + 1)$ as slope.

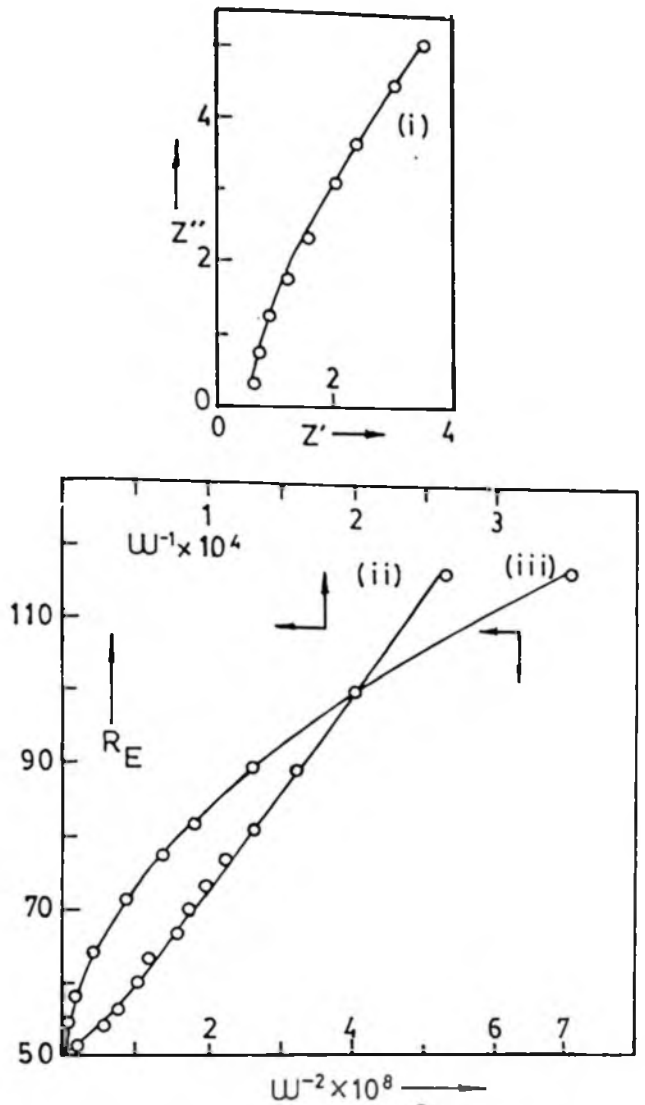


Fig. 2 Determination of R Ω by (i) Z" vs Z' (ii) R_E vs ω^{-1} and (iii) R_E vs ω^{-2} plots for lead (II) in 1 M $NaClO_4$

(b) Since $Y'_{el} = (\omega^{1/2}/\sigma)[1/(p^2 + p + 2)] + \omega C_d$, plot of Y''_{el} vs depolarizer concentration [α $(1/\sigma)$] extrapolated to zero concentration gives ωC_d as intercept.

Some typical plots employing all the four graphical techniques are given in Fig. 3. Both types of techniques given the same value for the double layer capacity indicating that there is no reactant adsorption (Table 1).

Determination of α : The value of α is determined by using the relationship

$$E_m = E_{1/2} + (RT/nF) \ln (\beta/1-\beta) \quad ...(1)$$

It is found that in this system E_m is practically the same as $E_{1/2}$ leading to the conclusion that α = 0.5.

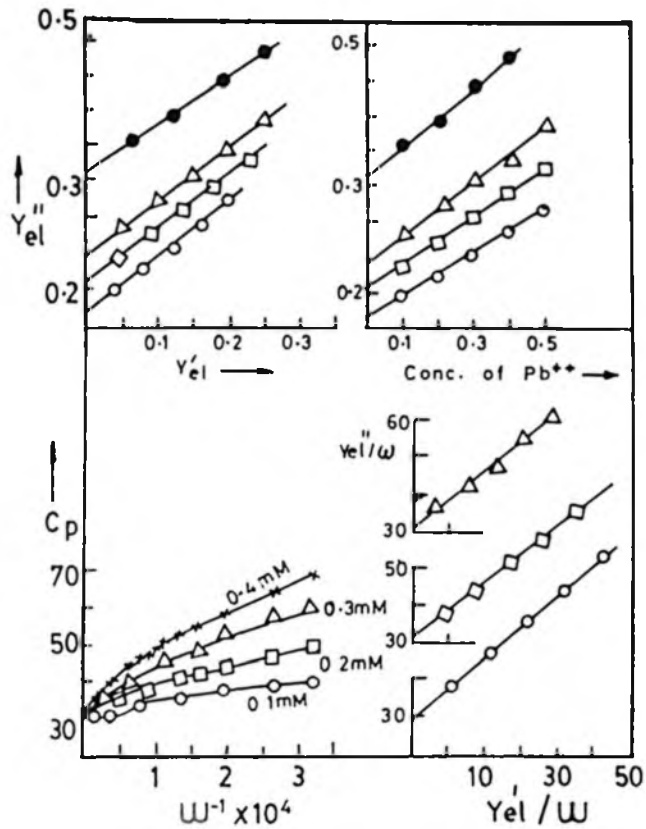


Fig. 3 Determination of double layer capacity by different methods for lead (II) 1 M sodium perchloride. o - 600 c/s; □ - 800 c/s; △ - 600 c/s; ● - 1600 c/s

Calculation of θ_m *and* σ_m : The value of θ_m is quite small. So the analysis of data is rather difficult. So it is checked by different extrapolation methods.

(1) Extrapolation methods based on equation

$$q = \theta + \frac{\sigma}{\sqrt{\omega}} + \frac{\sigma^2}{\omega(\theta + \sqrt{\omega})}$$

(a) Plots of q vs $1/\omega$ and $1/q$ vs $1/\omega$ as $\omega \longrightarrow \infty$ give the values of θ and $1/\theta$ as intercepts. Rearranging the above equation after multiplying both sides by $\sqrt{\omega}$ and noting that $p' = \theta/\sigma$ and $q = 1/Y'_{el}$, it can be written as

$$\frac{\sqrt{\omega}}{Y'_{el}} = \left[\sigma\left[P'\sqrt{\omega} + 1 + \frac{1}{P'\sqrt{\omega} + 1}\right]\right] \quad ..(2)$$

The plot of $\sqrt{\omega}/Y'_{el}$ vs $\sqrt{\omega}$ as $\omega \longrightarrow 0$ gives the value of 2σ as the intercept. Typical plots are given in Fig. 4. The values of θ_m and σ_m are found to be 0.32 ohm cm^2 and 75 ohm $cm^2/sec^{1/2}$ respectively.

TABLE 1

DOUBLE LAYER CAPACITY ($\mu F/cm^2$) VALUES AND SERIES RESISTANCE VALUES FOR Pb (II) - IN SODIUM PERCHLORATE, POTASSIUM NITRATE AND PATASSIUM CHLORIDE SUPPORTING ELECTROLYTES

Electrolyte	Pb^{++} (mM)	C_p vs ω^{-1}	y''_{el} vs y'_{el}	y''_{el}/ω vs y'_{el}/ω	y''_{el} vs $[Pb^{++}]$	Blank C_d value	p at 600 c/s	Series resistance. R_Ω (ohms)
1 M $NaClO_4$	0.1	31.0						
	0.2	31.0						
	0.3	31.0	31.0	32.0	31.0	31	0.25	1.50
	0.4	31.0						
	0.5	31.0						
0.9 M KNO_3	0.3	39.0						
0.1 M HNO_3	0.4	42.0	27.5	27.5	-	27	Deviation from theoretical plot	1.40
	0.5	46.0						
	0.6	55.0						
1 M KCl	0.2	50.0						
0.01 M HCl	0.3	55.0					Deviation from theo-	
	0.4	65.0	40.0	40.0		40	retical plot	1.20
	0.5	75.0						

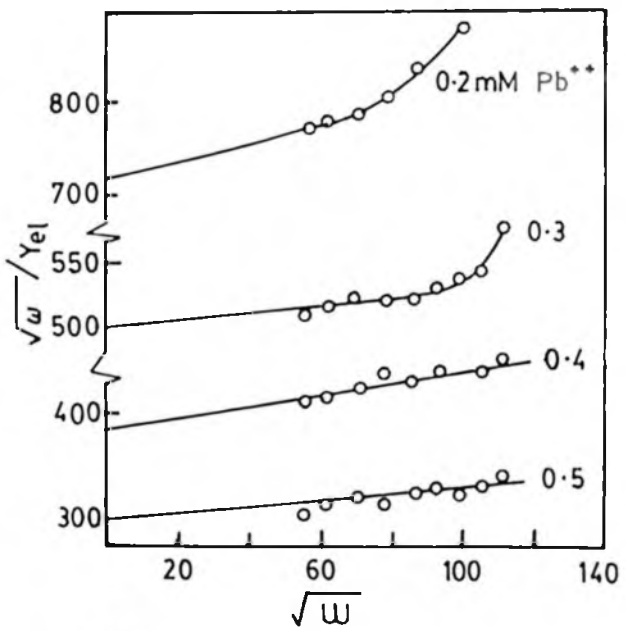


Fig. 4 $\sqrt{\omega}/y'_{el}$ vs y'_{el} plot for lead(II) in 1 M $NaClO_4$

(b) Since the double layer capacity and p values are known as already indicated above, σ can be calculated using equation

$$Y''_{el} = (\sqrt{\omega}/\sigma)\ (1/p^2 + p + 1) + \omega C_d$$

Since $p/\sqrt{\omega} = \theta_m/\sigma_m$, one can obtain θ_m also. The values of θ_m and σ_m obtained by this method are given in Table 2.

(2) Methods based on calculation of faradaic impedence Z'_f and Z''_f

The faradaic impedance values Z'_f and Z''_f can be calculated from Z' and Z" employing the following equations.

$$Z' - R_\Omega = Z'_{el} \quad ; \quad Z''_{el} = Z''$$

$$Y'_{el} = Z'_{el}/(Z'^2_{el} + Z''^2_{el}) = Y'_f$$

$$Y''_{el} = Z'_{el}/(Z'^2_{el} + Z''^2_{el}) = Y''_f + \omega C_d$$

$$Z'_f = Y'_f/(Y'^2_f + Y''^2_f) \text{ and}$$

$$Z''_f = Y''_f/(Y'^2_f + Y''^2_f)$$

Since $Z'_f = \theta + \sigma/\sqrt{\omega}$ and $Z''_f = \sigma/\sqrt{\omega}$, it may be pointed out the plot of Z'_f vs $1/\sqrt{\omega}$ gives the value of θ as intercept and δ as the slope while the plot of Z''_f vs $1/\sqrt{\omega}$ passes through the origin and gives σ as slope. It is clear that these two plots are parallel. Thus both θ and σ can be obtained. These plots are analogous to Randles plots.

Typical plot is given in Fig. 6. The mean values of θ_m and σ_m are 0.32 and 75.0 repective-

TABLE 2

KINETIC PARAMETERS FOR LEAD(II) IN DIFFERENT SUPPORTING ELECTROLYTES

Electrolyte	Parameters (average)	q vs $1/\omega$	$1/q$ vs $1/\omega$	Z_f', Z_f'' vs $\sqrt{\omega}$	$\sqrt{\omega}/Y'$ vs $\sqrt{\omega}$	Z_f' vs Z_f''	From the value of p
1 M $NaClO_4$	$\theta_m C$	0.32	0.32	0.32	-	0.32	0.32
	$\sigma_m C$	-	-	75.0	75.0	-	75.0
0.9 M KNO_3 + 0.1 M HNO_3	$\theta_m C$	Extrapolation		0.48	-	0.48	Deviation from theoretical plot
	$\sigma_m C$	uncertain		62.0	70.0	-	
1.0 M KCl + 0.01 M HCl	$\theta_m C$	Extrapolation		0.14	-		Deviation from theoretical plot
	$\sigma_m C$	uncertain		52.5	52.5	-	

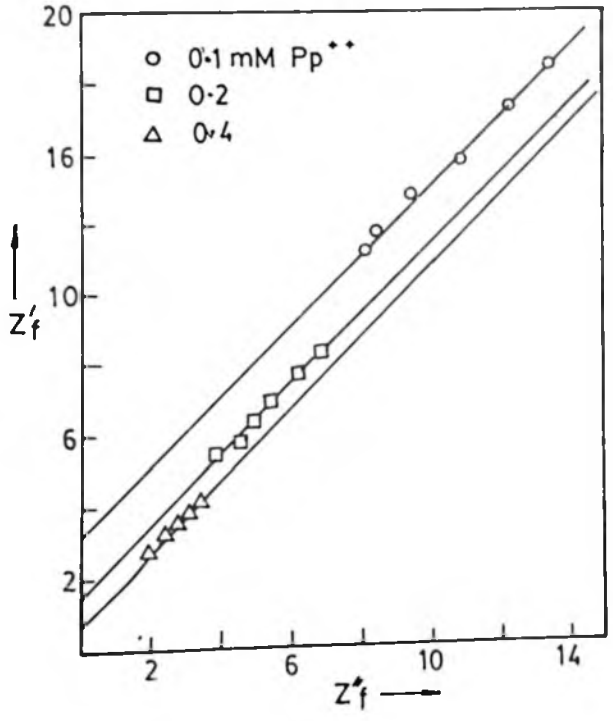


Fig. 5 Representation of faradaic impedances in the complex plane for different concentrations of lead (II) in 1 M $NaClO_4$

ly (Table 2). The intercept of the plot Z_f' vs Z_f'' gives the value of θ (Fig. 5). The mean value of θ C_m from this plot is also given in Table 2.

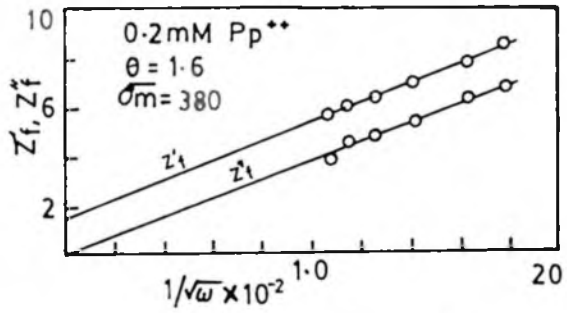


Fig. 6 Z_f' vs $\omega^{1/2}$ and Z_f'' vs $\omega^{1/2}$ plots of lead (II) in 1 M sodium perchlorate solution

0.2 mM Pb	θ_m 1.6	σ_m 380
0.3 mM	1.1	250
0.4	0.8	185
0.5	0.7	150

Phase sensitive a.c. polarograms: Phase sensitive a.c. polarograms can be expected to show the phenomenon of reactant adsorption in a striking way. The phase sensitive a.c. polarograms (both inphase and quadrature are theoretically obtained using data given in Table 3 and compared with experimentally computed polarograms. If there is reactant adsorption, the experimental quadrature a.c. polarograms will be higher than theoretical and peaky in nature. If there is no adsorption, the two coincide. However, the distinction is not so clear in the case of inphase a.c. polarograms. The phase sensitive polarograms also give a graphical picture of the reversibility of the electrode process.

TABLE 3

EXPERIMENTAL PARAMETERS CORRESPONDING TO LEAD (II) IN DIFFERENT SUPPORTING ELECTROLYTES

T = 303 K n = 2 in all cases, f = 600 c/s, σ and β are found to be 0.5 in all cases, R = 8.314 J/degree/mole, F = 96500 coulombs

Parameter	1 M perchlorate	1 M nitrate	1 M chloride
t sec	3.4	4.4	3.4
C_o mM	0.3	0.5	0.5
C_R mM	0.0	0.0	0.0
D_o $cm^2/sec \times 10^6$	6.50	5.94	6.67
D_R $cm^2/sec \times 10^6$	14.1	14.1	14.1
k_{sh} cm / sec	0.513	0.318	0.98

The Y'_{el} and Y''_{el} values required to make the theoretical polarograms are calculated using the following relations.

$$Y'_{el} = \frac{\theta + \sigma/\sqrt{\omega}}{(\theta + \sigma/\sqrt{\omega})^2 + \sigma^2/\omega} \qquad \ldots(3)$$

$$Y'' = \frac{\sigma/\sqrt{\omega}}{(\theta + \sigma/\sqrt{\omega}) + \sigma^2/\omega} + \omega C_d \qquad \ldots(4)$$

where θ and σ are given by the relations for the solution containing only the oxidant

$$q = \theta + \sigma/\sqrt{\omega} + [\sigma^2/(\omega\theta) + \sigma/\sqrt{\omega}]$$

$$\theta = [RT/n^2 F^2 k_{sh}] b \qquad \ldots(5)$$

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \left[\frac{\exp(\beta\phi)}{\sqrt{D_R}} + \frac{\exp(-\sigma\phi)}{\sqrt{D_O}} \right] x\ b \qquad \ldots(6)$$

$$\text{where } b = \frac{a_O + (a_R/a_O)\exp(\beta\phi) + \exp(\sigma\phi)}{a\ \exp(-\sigma\phi)[\sigma + (1/a_R)\exp(\beta\phi)]C_O}$$

with $a_O = (7 D_O/3\pi t)^{1/2} (1/k_{sh})$
and $a_R = (7 D_R/3\pi t)^{1/2} (1/k_{sh})$

The value of double layer capacity C_d used is that of the blank at the peak potential since the double layer opacity does not vary much over the small potential range of a.c. polarograms. The computation is made for the rate constant 0.513 cm/sec observed in the sodium perchlorate system. The other parameters are given in Table 3. The theoretical and experimental curves (Fig. 7) agree well indicating that there is no reactant adsorption in this system.

Lead(II) - Potassium Nitrate and Lead(II) - Potassium Chloride Systems

Experiments have been made in 1 M nitrate and chloride solutions and using different concentrations of lead ion (0.2 mM to 0.6 mM).

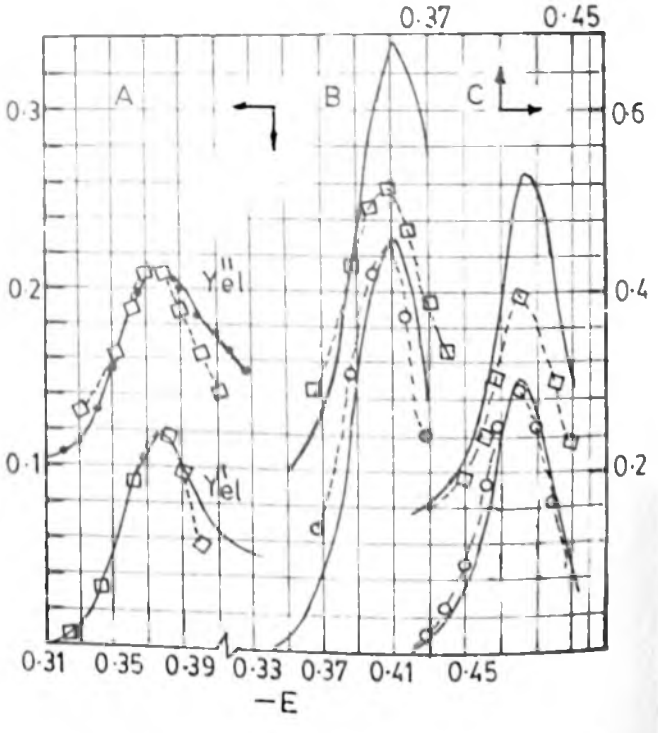


Fig. 7 Phase sensitive a.c. polarograms for lead (II) in (A) 1 M $NaClO_4$ (B) 0.9 M KNO_3 + 0.1 M HNO_3 and (C) 1 M KCl + 0.01 M HCl - Experimental.. Theoretical Y'_{el} Y''_{el} . Lower curves in phase; Upper curves are quadrature component.

Complex plane polarography: Typical complex plane polarograms, and q vs potential curves are given in Fig. 1. The minimum in the q vs potential curve is practically the same as the peak potential. The frequency variation curves are given in Fig.8. The frequency variation curves are straight lines with a slope of 45° in the lower frequency range indicating the reversibility of the process.

The series resistance required in the analysis of the results has been computed by all the three methods described above and the agreement between them is satisfactory. The mean value in the case of lead(II) - potassium nitrate system is 1.40 ohms and in the case of lead(II) - potassium chloride system is 1.20 ohms.

The double layer capacity in the presence of the depolarizer has been determined employing fixed and variable depolarizer concentration methods using (i) capacity in parallel vs ω^{-1} plots, (ii) Y''_{el} vs Y'_{el} plots, (iii) Y''_{el}/ω and Y'_{el}/ω plots. Typical plots are given in Fig. 9. The capacity in parallel vs $1/\omega$ plots give different intercepts for different concentrations of the depolarizer in both the media. The Y''_{el} vs Y'_{el} and Y''_{el}/ω vs Y'_{el}/ω plots depend upon different metal ion concentrations in one and the same plot and hence are not applicable for these systems. The double layer capacity values obtained for different concentrations of the depolarizer is given in Table 1. It is extremely interesting to note that the behaviour of lead ion in potassium chloride and nitrate solutions is different from that in sodium perchlorate solutions.

Since the peak potential is very nearly the same as the half-wave potential both in nitrate and chloride solutions, it follows that α = 0.5 (using equation 1)

Phase sensitive a.c. polarograms: Theoretical phase sensitive a.c. polarograms have been obtained as already described using the parameters given in Table 3. The double layer capacity used was that of the blank at the peak potential. Results in Fig.7 shows that the quadrature components of the experimental a.c. polarograms lie above the theoretical ones for both lead(II)-potassium nitrate and lead(II)-potassium chloride solutions indicating reactant adsorption in these systems. It

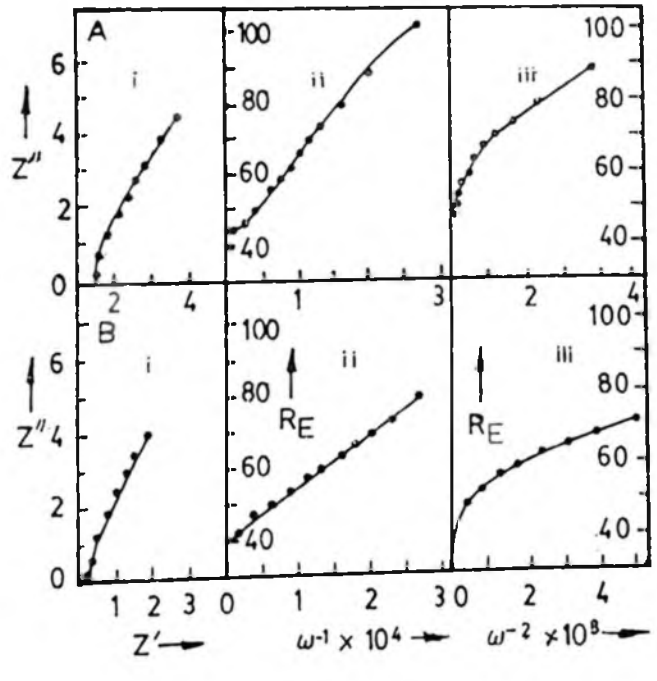


Fig. 8 Determination of RΩ by (i) Z'' vs Z' (ii) R_E vs ω^{-1} and (iii) R_E vs ω^{-2} plots for lead (II) in (A) 0.9 M KNO_3 - 0.1 M HNO_3 (B) 1 M KCl - 0.01 M HCl

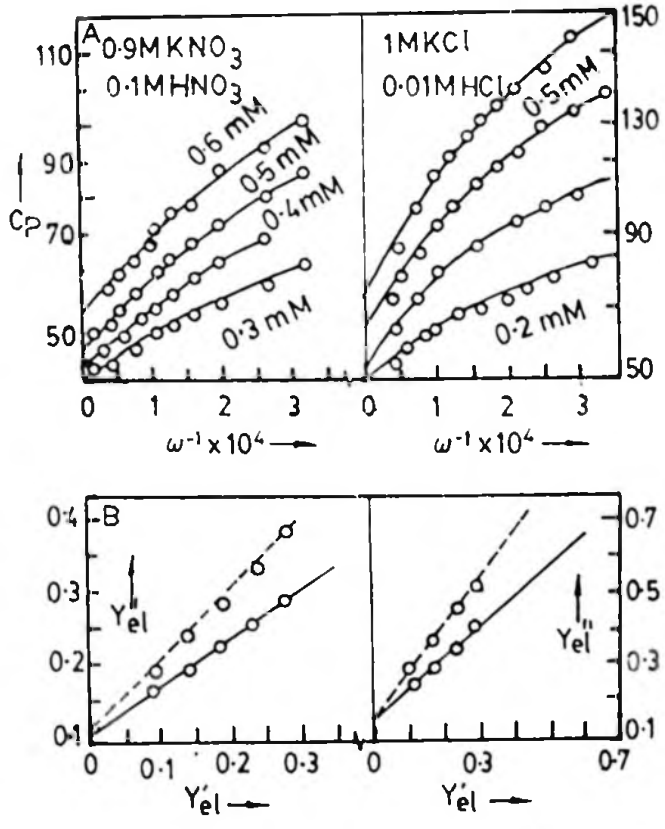


Fig.9 (A)Capacity in parallel vs ω^{-1} plots for lead (II) in above solutions (B) Y''_{el} vs Y'_{el} plots for lead (II) in above solutions---Experimental,—Theoretical

may, however, be pointed out that the experimental inphase a.c. polarograms are only slightly lying above the theoretical ones.

DISCUSSION

Treatment of Data

Lead-potassium chloride system has been very extensively studied by Sluyters and co-workers [1]. They have tried to apply the treatment developed by Randles [9], Senda and Delahay [10], Delahay [11]. Baticle and Perdue [12] and finally Reinmuth [13]. They have not been able to conclude even regarding the value of charge transfer resistance (0 or 1.5 Ω). They have said that Randles circuit is not applicalbe but in a later paper mentioned that Randles circuit may be applicable with enhanced double layer capacity even in cases of strong adsorption.

In the case of fully reversible process, $\sqrt{\omega}/Y'_{el}$ does not vary with frequency. In the case of irreversible process, the value increases. In the cases of reactant adsorption, the value decreases. This effect is noticeable when there is very strong reactant adsorption even when the process is slightly irreversible. The result recorded in the case of lead(II)-potassium chloride system show decrease in the value of $\sqrt{\omega}/Y'_{el}$ with frequency indicating strong reactant adsorption.

Since the value of θ_m is very small, extrapolation methods that have been employed in lead(II)-sodium perchlorate system(q vs $1/\omega$ and $1/q$ vs $1/\omega$ plots) were not quite successful in lead(II)-KCl systems. Attempts were next made to find whether Randles type of method could be fitted into this system. Since the double layer capacity depends upon the concentration of the depolarizer, the experimentally determined enchanced double layer cpacity has been used in this analysis. Typical Z'_f vs $1/\sqrt{\omega}$ and Z''_f vs $1/\sqrt{\omega}$ plots are given in Fig. 10. Analysis of the data presented in this paper very clearly indicates that Randles type of circuit with the enhanced double layer capacity as determined by experiment applies very well to this system. The results are presented in Table 2.

In the case of lead(II)-potassium nitrate system $\sqrt{\omega}/Y'_{el}$ values very slightly increase at various values of frequency. This could be interpreted as due to the very nearly reversible nature of the process. But the results recorded indicate that the double layer capacity is dependent on the concentration of the

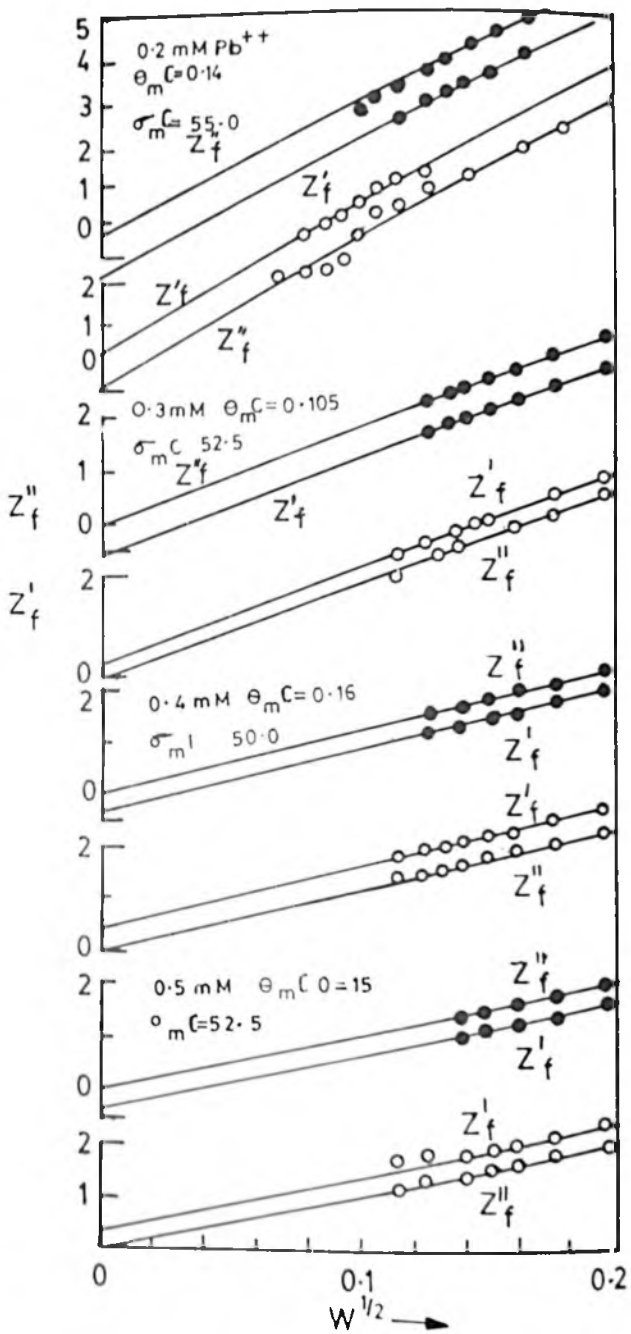


Fig. 10 Z'_f vs $1/\omega$ and Z''_f vs $1/\omega$ plots for lead (II) in 1 M KCl - 0.1 HCl solutions. o - with blank double layer capacity; • - with double layer capacity from extrapolation.

depolarizer indicating reactant adsorption. Analysis of the data employing Randles type of circuit using experimentally determined enhanced double layer capacity values gives a value of 0.48 ohm cm for θ_m indicating slight

irreversibility (Fig.13). The slight increase of $\sqrt{\omega}/Y'_{el}$ values with frequency despite adsorption is obviously due to the balancing of the two opposite effects namely reactant adsorption and degree of irreversibility. It may be concluded that this system represents a weak adsorption case while lead(II)-potassium chloride represents a strong adsorption case because $\sqrt{\omega}/Y'_{el}$ decreases despite slight irreversibility displayed by this system (Fig.11 & 12). From the analysis of the data obtained for lead(II) sodium perchlorate solutions wherein the double layer capacity has been found to be independent of the concentration of the depolarizer, it can be concluded that there is no reactant adsorption and normal Randles type of circuit applies to the system.

Y''_{el} vs Y'_{el} plots

It has been noticed in sodium perchlorate system where there is no reactant adsorption, the experimental values of Y''_{el} and Y'_{el} fall on theoretical plots of y''_{el} . But in potassium chloride and potassium nitrate solutions, the experimental values lie above theoretical curves obtained using blank double layer capacity (Fig. 9). The difference between the experimental and theoretical values decrease with decrease in the concentration of depolarizer. When extrapolated to zero metal concentration, they cut at the same point on the Y''_{el} axis as expected by theory. Hence these plots can be used for detecting reactant adsorption.

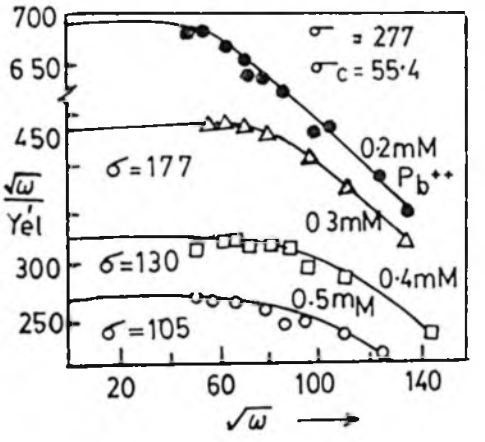


Fig. 11 $\sqrt{\omega}/Y'_{el}$ vs $\sqrt{\omega}$ plots for lead (II) in 1 M KCl - 0.01 M HCl solutions

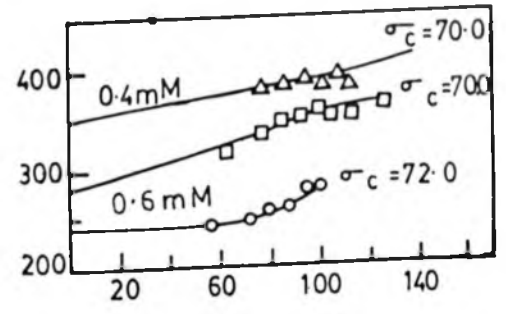


Fig. 12 $\sqrt{\omega}/Y'_{el}$ vs $\sqrt{\omega}$ plots for lead (II) in 1 M KNO_3 solutions

Z'_f vs $1/\sqrt{\omega}$ and Z''_f vs $1/\sqrt{\omega}$ plots

In cases where there is no specific adsorption, these plots are parallel to each other with Z'_f vs $1/\sqrt{\omega}$ plot lying above Z''_f vs $1/\sqrt{\omega}$ plot passing through the origin. When there is specific adsorption, Z'_f vs $1/\sqrt{\omega}$ plot lies below Z''_f vs $1/\sqrt{\omega}$ plot if the double layer

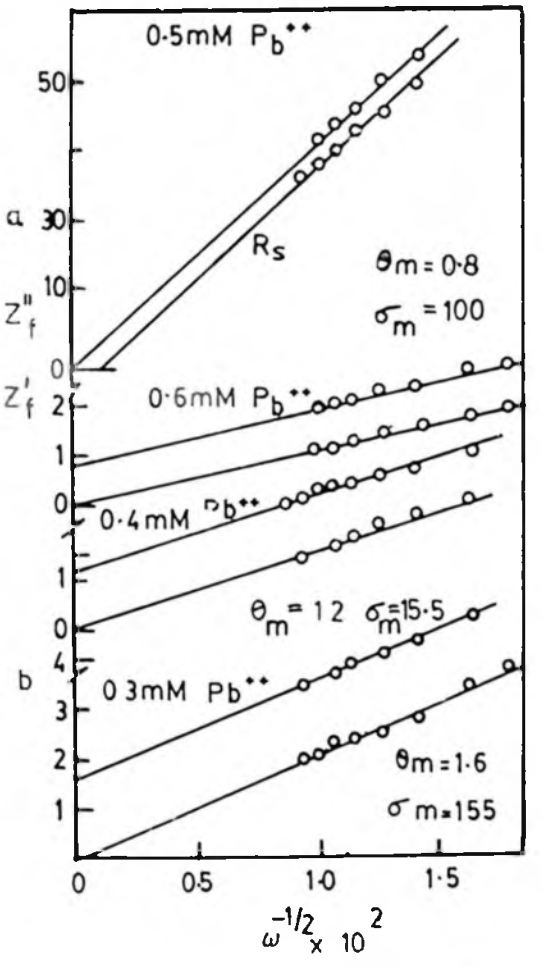


Fig. 13 Faradaic impedances vs $1/\sqrt{\omega}$ for lead (II) in 0.9 M KNO_3 + 0.1 M HNO_3 (a) with double layer capacity of the blank (b) double layer cpacity in presence of the depolarizer

TABLE 4

RATE CONSTANTS FOR Pb (II) IN DIFFERENT SUPPORTING ELECTROLYTES AT THE PEAK POTENTIAL

Electrolyte	$\theta_m C$ average	$\sigma_m C$ average	k_{sh} (cm/sec) Eqn.7	k_{sh} (cm/sec) Eqn.8
1 M $NaClO_4$	0.32	75.0	0.5129	0.4242
0.9 M KNO_3 + 0.1 M HNO_3	0.48	65.0	0.3184	0.2831
1 M KCl + 0.01 M HCl	0.14	52.5	0.9809	0.9677

capacity of the blank is used for the computation of Z_f''. If on the other hand, the enhanced double layer capacity as obtained from the extrapolation method (C_p vs $1/\omega$ plot as $\omega \longrightarrow 0$) is used, the correct behaviour of the curves is obtained and the values of θ_m and σ_m are derived. This is the case with both lead (II)-KNO_3 and lead (II)-KCl systems Figs.10 and 13.

Determination of Constants

The rate constants have been calculated using the following equations [2] applicable to cases where only the oxidant is present in the solution.

$$\theta_m = \frac{RT\, d^{\frac{1}{2}(1-\beta)}}{n^2 F^2 k_{sh} C_0\, \beta^{\beta}\, (1-\beta)^{1-\beta}} \qquad ..(7)$$

Reversible case

$$C_0\, k_{sh}^2\, \frac{\sqrt{D_0}}{\sqrt{D_R}}\, e^{\beta}\, \left(\frac{\beta nF}{RT}\right) \theta_m - \frac{\sqrt{D_0}}{\sqrt{D_R}}\, \frac{1}{nF}\, k_{sh} - \frac{\sqrt{7D_0}}{\sqrt{3\pi t}}\, \frac{1}{nF}\, e^{\alpha}\, \alpha = 0 \qquad ..(8)$$

General Equation

CONCLUSION

The highlight of this paper is the presentation of a spectrum of systems with varying degrees of reactant adsorption. It starts with sodium perchlorate system where there is practically no reactant adsorption as shown by double layer capacity calculations. It is possible to apply almost all the methods to analyse the data for getting θ_m and δ_m though the system is highly reversible. This is followed by lead(II)-potassium nitrate system which presents weak reactant adsorption which has been detected for the first time in this work. It has been possible to determine θ_m and δ_m values by suitable extrapolation methods. Finally we come across lead(II)-potassium chloride system which shows strong reactant adsorption which many authors feel requires elaborate model to explain the behaviour. The results recorded in this paper show that the results can be explained on the basis of simple Randles circuit employing the enhanced double layer capacity obtained by extrapolation methods.

SYMBOLS

C_d ($\mu F\ cm^{-2}$) Double layer capacity

C_0 (mol cm^{-3}) Concentration of the species 0 in the bulk of the solution

D_0 and D_R ($cm^2\ sec^{-1}$) Diffusion coefficient of the oxidised and reduced species

E (volts) Electrode potential

E_m (volts) Complex plane peak potential

ω (rad/sec) Angular frequency

δ ($\sqrt{Dt}$) Diffusion layer thickness

$R\Omega$ (ohm cm^2) Ohmic resistance

Z', Z'' (ohm cm^2) Components of cell impedance

Z'_{el}, Z''_{el} (ohm cm^2) Components of electrode impedance

Y'_{el}, Y''_{el} ($ohm^{-1}\ cm^2$) Components of electrode admittance

Z'_f, Z''_f (ohm cm^2) Components of faradaic impedance

θ_m (ohm cm^2) Charge transfer resistance at complex plane peak potential

θ (ohm cm^2) Charge transfer resistance

σ (ohm cm^2 sec$^{-1/2}$) Warburg coefficient

σ_m (ohm cm^2 sec$^{-1/2}$) Warburg coefficient at complex plane peak potential.

$\phi = (nF/RT)(E - E_0)$

α Cathodic transfer coefficient
β Anodic transfer coefficient

REFERENCES

1. M. Sluyters-Rehbach B. Timer and J.H. Sluyters, *J. Electroanal. Chem.*, 15 (1967) 343.

2. P. Sridhar and R.S.Subrahmanya, *Indian J. Chem.*, **21A** (1982) 873.

3. M. Sluyters-Rehbach and J.H. Sluyters, *Rec. Trav. Chim.* **82** (1963) 535.

4. R.S. Subrahmanya, A simple set up for taking complex plane polarograms - Unpublished.

5. B.Breyer, I. Gutmann and S. Hacobian, *Australian J. Sci. Res.*, **44** (1951) 595.

6. M. Sluyters-Rehbach and J.H. Sluyters, *Electroanalytical Chemistry*, Edited by A.J. Bard (**Marcel Dekker, New York**), (1970).

7. B. Timmer, M. Sluyters-Rehbach, and J.H. Sluyters, *J. Electroanal. Chem.* (1968) 93.

8. M. Sluyters-Rehbach, J.S.M.C. Breukel, K.A Gijsbertsen, C.A. Wifnhorst and J.H. Sluyters, *J. Electroanal. Chem.*, **38** (1972) 17.

9. Randles, *Discussions Faraday Soc.*, 1 (1947) 11.

10. M. Senda, and P. Delahay, *J. Phys. Chem.*, 65 (1961) 1580.

11. P. Delahay, *J. Phys. Chem.*, **70** (1966) 2067, 2373.

12. A.M. Baticle and J. Perdu, *J. Electroanal. Chem.*, 12 (1966) 15.

13. W.H. Reinmuth, (Private communication to J.H. Sluyters).

Asian Paints' Research and Development are more than surface deep

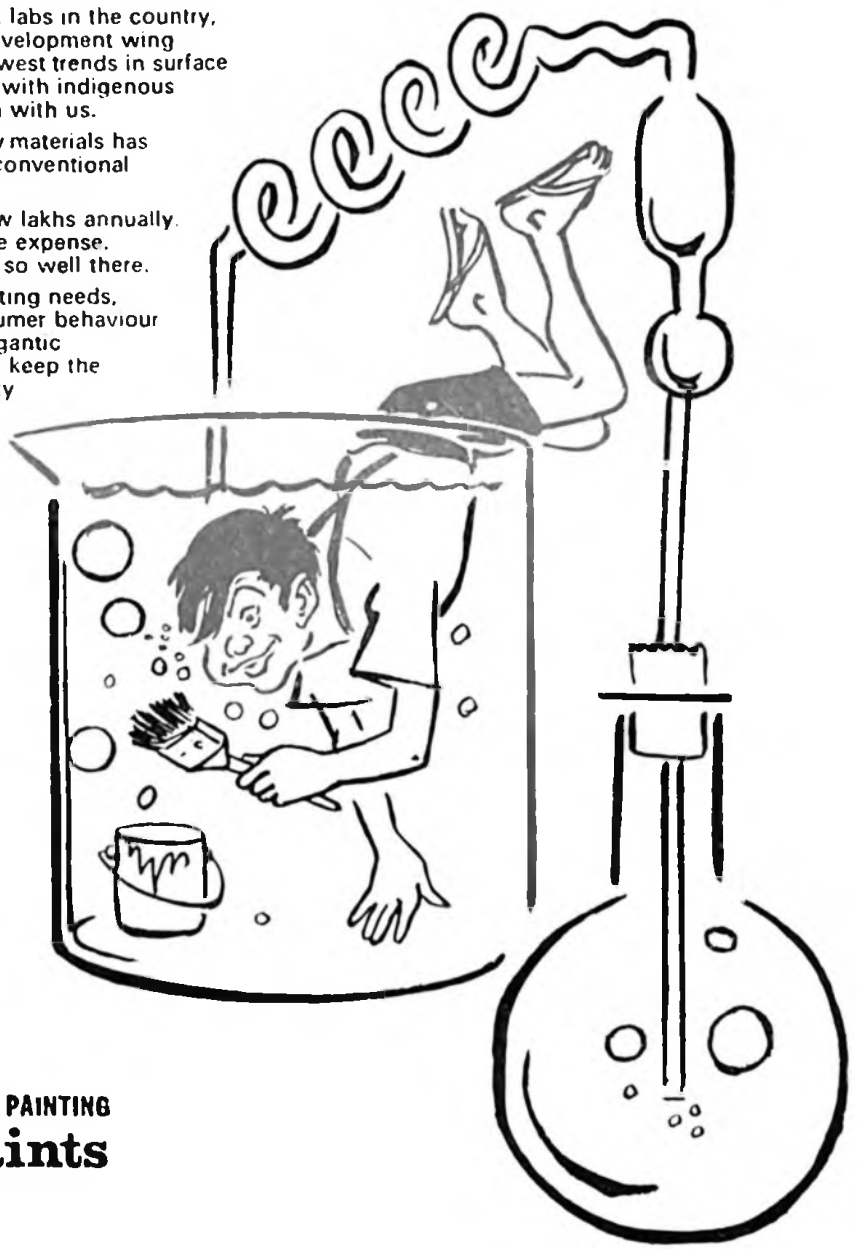
Equipped by one of the finest labs in the country, our technical research and development wing keeps in close touch with newest trends in surface coatings. Import substitution with indigenous materials has been a tradition with us.

Fundamental research on raw materials has resulted in putting to use unconventional materials available in India

This costs the Company a few lakhs annually. But then we don't grudge the expense. Our research boys are doing so well there.

Projecting tomorrow's marketing needs, analysing the trends of consumer behaviour for this country's size, is a gigantic job. Professionals in the field keep the facts at fingertips. EDP facility makes the task easier.

Development of materials for mass markets is our commitment.



ANY SURFACE THAT NEEDS PAINTING NEEDS asian paints