

Polarographic Studies of Praseodymium Europium and Gadolinium Cations and it's Applications in solvent extraction using Some Crown Ethers

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Summary:

In this paper a polarographic behavior of rare earth cations (Pr^{3+} , Eu^{3+} and Gd^{3+}) complexes with crown ethers was studied. The factors that effect of diffusion current was investigated, it was found that 0.1M KCl is the suitable supporting electrolyte with drop time of 1.4 sec. Direct current polarography revealed half wave potential $E_{1/2}$ of -1.496V , -1.507V and -1.524V for (Pr^{3+} , Eu^{3+} and Gd^{3+}) respectively.

A shift in half wave potential of metal ions to negative values by adding the crown compound to the metal ion indicates the complex formation. The extraction of the complexes of Pr (III), Eu (III) and Gd (III) with crown compounds (B_{15}C_5 , 18C_6 , B_218C_6 and B_224C_8) were performed with picric acid in different organic solvents.

The slope analysis methods indicates that Pr^{3+} , Eu^{3+} and Gd^{3+} forms 1:1 complexes with B_{15}C_5 , 18C_6 and B_218C_6 . In addition Pr^{3+} form 1:1 complex with B_224C_8 while other ions forms 1:2 sandwich complexes with B_224C_8 .

The results of the extraction of Pr^{3+} , Eu^{3+} and Gd^{3+} are a good agreement with the results obtained polarographically.

الخلاصة:

طبقت الانظمة البولاروغرافية لدراسة السلوك البولاروغرافي والظروف المثلى لتقدير معقدات ايونات البراسيودميوم Pr^{3+} , اليوربيوم Eu^{3+} و الكادولينيوم Gd^{3+} مع مركبات الايثرات التاجية. تم دراسة العوامل المؤثرة على تيار الانتشار، حيث وجد ان 0.1 مولاري من كلوريد البوتاسيوم هو الاكتروليت الساند المناسب لقياس ايونات Pr^{3+} , Eu^{3+} , Gd^{3+} في هذا النظام كما وجد ان 1.4 ثانيه هو عمر القطرة المناسب الذي يعطي اعلى قيمة لتيار الانتشار. ولأيجاد جهد نصف الموجه وعدد الالكترونات المصاحبة لعمليات الاختزال عند قطب الزئبق المتقاطر استخدمت تقنيه بولاروغرافي التيار المباشر حيث أظهرت النتائج

$$(E_{1/2})_{\text{Eu}^{3+}} = -1.507 \text{ v} , (E_{1/2})_{\text{Pr}^{3+}} = -1.496 \text{ v} , (E_{1/2})_{\text{Gd}^{3+}} = -1.524 \text{ v}$$

تم دراسة استخلاص ايونات (Pr^{3+} , Eu^{3+} , Gd^{3+}) بواسطة مركبات الايثرات التاجية (بنزو-15-كراون-5, 18-كراون-6, ثنائي بنزو-18-كراون-6, ثنائي بنزو-24-كراون-8) المذابه في 1،2-ثنائي كلورو ايثان و التي استخلصت بوجود حامض البكريك. من تحليل قيم الانحدارات تقترح النتائج المستحصلة ان ايونات Pr^{3+} , Eu^{3+} , Gd^{3+} تكون معقدات 1:1 مع بنزو-15-كراون-5, 18-كراون-6 وثنائي بنزو-18-كراون-6, اضافة الى ذلك فان Pr^{3+} يكون معقد 1:1 مع ثنائي بنزو-24-كراون-8, بينما بقية الايونات تكون معقدات ساندويچ 2:1 مع ثنائي بنزو-24-كراون-8. ان قيم ثوابت الاستقرار لمعقدات اللانثانات مع مركبات الايثرات التاجية تعكس بوضوح مدى تطابق الايون الموجب وحجم الحلقة التاجية و بالتالي درجة الترابط بينها.

Introduction:

Polarographic, organic electrochemistry, use of electrochemistry in investigation of kinetic, equilibrium and mechanisms of organic reactions, electroreduction of hydrazones and oximes, and lignin adsorbent and as a raw material in the future (1). Janos and Vaclav Synek used humic substances (HS) and other substance of similar nature, such as salicylates or phthalates influence strongly a polarographic behavior of europium at a mercury drop electrode. An addition of these substances into the supporting electrolyte causes an enhancement of the differential pulse polarographic (DPP) peak of Eu and an anodic shift of the maximum peak potential(2).

M.Riri et al. has been study a formation of colorless gadolinium complexes between gadolinium ions, ligands and proton, of some organic acids in aqueous solution. In this work the researchers present the results of investigations on the interaction of gadolinium ion Gd^{3+} with malic acid in dilute aqueous solution for pH values between 5.5 and 7.5 (3).

Freiser et al. described a polarographic behavior of the chelating extractants, 1- phenyl- 3-methyl-4-trifluoro acetyl-5- pyrazolone and 1- phenyl- 3-methyl-4-benzoyl-5- pyrazolone with La (III), Gd (III) and Yb (III) in 1, 2- dichloroethane- aqueous system(4).

Derivative spectrophotometer has been used for simultaneous determination of La (III), Gd (III) in their mixtures with Arsenazo (III) (5).

Nezhadali et al. studied the complexation reaction between Pb^{2+} , Tl^{+} and Cd^{2+} ions and microcyclic ligands, 18-crown-6 and dibenzo-18-crown -6 in DMSO, nitromethane and dimethylformamide- nitromethane binary system by square wave polarography (SWP) technique(6).

The solvent extraction of sodium perrhenate by 3m-crown-m ethers (m=5, 6) and their mono-benzo-derivatives into 1,2- dichloroethane (7) .

In this study the Polarographic behavior of Pr (III), Eu (III) and Gd (III) complexes with crown ethers were investigated according to the shifts in half wave potential.

Experimental

Apparatus:

Metrohm polarecord E 506 equipped with polarography stands E 505.

PH meter- expandable ion analyzer EA940 (Orion research).

Dropping mercury Electrodes (DME) Metrohm EA1019/1.

Saturated calomel electrodes (SCE) type Metrohm 6.0701.1 has a large surface area.

Chemicals and solutions:

- Stock solutions:-
 - $7.1 \times 10^{-3} M$ Pr (III) was prepared by dissolving 1.171 gm of Pr_2O_3 (supplied from Riedel-de Haen Company, purity 99.5%) in 10 ml conc. HCl and diluted to one liter.
 - $6.58 \times 10^{-3} M$ Eu (III) was prepared by dissolving 1.158 gm Eu_2O_3 (supplied from Ferak Company, purity 99%) in 50% v/v HCl and diluted to one liter.
 - $6.37 \times 10^{-3} M$ Gd (III) was prepared by dissolving 1.152 gm Gd_2O_3 (supplied from Fluka AG Company, purity 99.9%) in 50% v/v HCl and diluted to one liter.
- Supporting electrolytes were prepared in concentration ranged from 0.0001M to 2.0M ammonium chloride (supplied from Riedel-de Haen Company, purity 99.5%), potassium chloride(supplied from Fluka AG Company, purity 99.5%) and tetramethyl Ammonium iodide(supplied from Fluka AG Company, purity 99%).

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- Crown compounds: 18-Crown-6 (18C6), benzo15-Crown-5 (B15C5), dibenzo- 18-Crown-6 (B₂18C6) and dibenzo- 24-Crown-8 (B₂24C8) were obtained from Fluka AG Company with purity 98%.
- 10 mg/ml picric acid as ion pair (supplied from Merck Company, purity 99%).
- Organic solvents: benzene, 1, 2- dichloroethane (supplied from Fluka AG Company, purity 99%), while toluene, nitrobenzene(supplied from BDH Company, purity 99.5%)and finally chloroform(obtained from Ferak, purity99.4%).

Polarographic measurement at DME:

Direct current polarography (DCP) was used:

Dropping time, 1.4 sec.

Scan rates, 2.0 mv/sec.

Current range, (0.06-5.00) μ A/mm.

Differential pulse polarography (DPP):

Dropping time, (0.4-2.0) sec.

Pulse amplitude, 80 mv.

Scan rates, 2.0 mv/sec.

Current range, (0.06-5.00) μ A/mm.

Results and Discussion:

Three types of supporting electrolytes "potassium Chloride, ammonium Chloride and tetramethyl-ammonium iodide" have been used for reduction of Pr (III), Eu (III) and Gd (III). The limiting current decreases most rapidly with the first addition of the supporting electrolyte until it finally becomes constant. The data obtained are shown in table (1).

Table (1): Influence of various concentrations of supporting electrolytes on the limiting current. Temp.25°C, t_d : 1.4 sec., Scan rate: 2.86mV/sec., D_p : 80.

Conc. of supporting/M	Limiting current μ A ^(a)								
	Pr (III)			Eu (III)			Gd (III)		
	KCl	NH ₄ Cl ^(b)	(CH ₃) ₄ NI	KCl	NH ₄ Cl ^(b)	(CH ₃) ₄ NI	KCl	NH ₄ Cl ^(b)	(CH ₃) ₄ NI
0	18.81	18.81	18.81	19.91	19.91	19.91	16.84	16.84	16.84
0.0001	16.44	17.30	16.91	17.90	18.29	18.30	15.01	15.22	15.53
0.0002	15.64	15.88	15.70	16.31	17.20	16.84	14.66	14.81	14.92
0.0005	14.23	14.21	14.01	14.86	15.39	15.0	12.97	13.09	13.20
0.001	12.32	12.61	13.23	12.34	14.44	C	11.20	12.00	11.66
0.005	10.69	11.01	11.87	10.26	12.86	C	9.02	10.41	9.86
0.1	8.55	9.63	C	9.05	10.70	C	8.70	9.32	C
1.0	8.52	9.53	C	9.02	10.63	C	8.68	9.20	C
2.0	8.49	9.50	C	9.00	10.30	C	8.67	9.20	C

- Corrected for the residual current.
- Small peak present at $E_{1/2} = -0.976V$ vs. SCE.
- Maximum present and diffusion current not well defined.

In the case of Pr³⁺, Eu³⁺ and Gd³⁺ the reduction of the limiting current is increased by the electrical migration, therefore, the migration current is given by the product of the transference number of the reducible ion and the total limiting current.

$$I_m = T_i + I_t$$

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T_i is the transference number of the reducible ion in the particular solution, which depends on the relative concentration of Pr^{3+} , Eu^{3+} and Gd^{3+} as well as the added electrolyte and to a lesser degree on the charges and mobility's of rare earth cations concerned .

The transference number approaches zero when the supporting electrolyte is present in large excess. The current time relation during the growth of individual group was studied and optimum drop time was for Pr^{3+} , Eu^{3+} and Gd^{3+} is equal to 1.4 sec. which gives maximum value for the diffusions current.

The accuracy and precision for the determination of Pr^{3+} , Eu^{3+} and Gd^{3+} in 0.1M KCl are listed in Table (2).

Table (2): Accuracy and precision of the determination of Pr (III), Eu (III) and Gd (III) in 0.1M KCl. The values listed have been corrected for the residual current. t_d : 1.4 sec. Scan rate : 2.86 mV/sec. D_p : 80.

Ions	Added (mM)	Calculated (mM)	i_d (μA)	i_d/c	Absolute Error	Relative Error %	Recovery %	RSD * %
Pr^{3+}	2.62×10^{-3}	2.56×10^{-3}	0.24	93.7	-6.0×10^{-5}	-2.29	97.70	0.041
	2.1×10^{-2}	2.1×10^{-2}	1.95	93.3	-1.0×10^{-4}	-0.47	99.52	0.270
	3.7×10^{-1}	3.36×10^{-1}	33.61	92.6	-7.0×10^{-3}	-1.89	98.11	0.940
Eu^{3+}	1.40×10^{-3}	1.38×10^{-3}	0.48	348.6	-2.3×10^{-5}	-1.64	98.40	0.050
	2.1×10^{-2}	2.1×10^{-2}	7.35	350.0	0.0	0.00	100.00	0.920
	5.2×10^{-1}	5.15×10^{-1}	18.00	344.5	-5.0×10^{-4}	-0.96	99.03	1.221
Gd^{3+}	1.34×10^{-3}	1.30×10^{-3}	0.13	100.0	-4.0×10^{-5}	-2.98	97.01	0.312
	4.6×10^{-2}	4.5×10^{-2}	4.51	100.2	-1.0×10^{-3}	-2.17	97.80	1.204
	3.1×10^{-1}	3.01×10^{-1}	30.06	99.8	-9.0×10^{-3}	-2.90	97.10	1.022

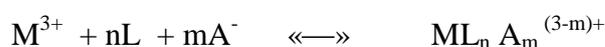
*Mean of six values.

A Plot of $\log i/i_d - i$ vs. E for Pr (III), Eu (III) and Gd (III) gives a slope of values 0.067, 0.072 and 0.073 V respectively, in which the (n) values calculated are approximately equal unity which mean the process irreversible. A typical plot for Pr (III) in 0.1 M KCl at pH = 3.75 , which mean the reduction of the rare earth cations from (III) to (II).

The calculated of $E_{1/2}$ for the Pr (III), Eu (III) and Gd (III) are equal (-1.496, -1.507 and -1.524 V) respectively in 0.1M KCl, shown in figure (1-3).

Before applying the polarographic method to study the complex formation of the Pr (III), Eu(III) and Gd(III) with the crown compounds (B15C5, 18C6 , B₂18C6 and B₂24 C8) the solvent extraction was used to examine the complex formation .

The distribution coefficient of the extraction:



is given by the following equation :

$$D = \frac{\sum [M^{3+}]_{org.} [ML_n A_m^{(3-m)^+}]_{org.}}{\sum [M^{3+}]_{aq.} [M^{3+}]_{aq.} + [ML_n^{3+}]_{org.}}$$

- M^{3+} = Pr , Eu and Gd.
 L = Crown compound.
 A = picrate ion.

Picric acid concentration should effect extraction at constant concentration of crown ethers, and it is reasonable to predict that rare earth ions can form stronger complexes can be easily extracted by crown compounds.

Figure (3) shows the linear relationship between distribution ratio (log D) and crown ether concentrations when the concentration of picric acid constant. The graph gives a straight line with slope equal n, from the values of (n), the structure of extracted species can be elucidated.

The n values obtained from the slopes of the graphs seem to indicate that the extraction species of rare earth ions as $[M^{3+}(\text{crownether})_n(\text{picrate})_m]$ n= 1or 2 m=3 . Pr (III), Eu (III) and Gd (III) ions can forms 1:1 complexes with B15C5, 18 C6 and B₂18C₆ and Pr³⁺ ion can form 1:1 with B₂24C8 while Eu³⁺ and Gd³⁺ forms 1:2 sandwich complexes with B₂24C8.

After optimization conditions were obtained by using picrate ion and crown ether, different organic solvents (8) with a wide rage of dielectric constants were used in order to determine the D factor. This is shown in Table (3). As we noticed the distribution ratio increase with increase of dielectric constant (€) of solvent for Pr (III), Eu (III) and Gd (III).

Table (3): Ratio of distribution ratio with different dielectric constants of organic solvents for an individual extraction of 5×10^{-4} M Pr³⁺, Eu³⁺ and Gd³⁺ with 0.1M of crown ethers.

Solvent	€*	$D_{(Pr)^{3+}}$				$D_{(Eu)^{3+}}$				$D_{(Gd)^{3+}}$			
		B15C5	18C6	B ₂ 18C6	B ₂ 24C8	B15C5	18C6	B ₂ 18C6	B ₂ 24C8	B15C5	18C6	B ₂ 18C6	B ₂ 24C8
Nitrobenzene	35.740	158.48	29.06	36.43	48.90	54.50	6.43	13.79	55.37	47.78	13.40	14.45	23.33
1,2- DCE	10.650	5.37	1.99	5.01	5.24	38.01	1.95	8.77	12.57	30.19	2.00	3.01	4.67
Chloroform	4.800	2.53	2.71	0.94	1.20	4.20	1.98	2.60	4.31	3.31	1.53	0.56	2.31
Toluene	2.380	1.10	0.99	0.68	0.29	3.16	0.26	1.21	0.98	0.25	0.95	1.21	1.20
Benzene	2.284	1.09	1.00	0.93	0.23	0.98	0.32	1.03	0.88	0.19	1.23	0.77	1.01

*from ref(9)

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Therefore, a polarographic method can be applied to study the complex formation. In fact, the half-wave potentials of metal ions are shifts, usually to more negative value by complex formation. From this shift the formula and dissociation constant of the complex can be determined. The shift of the $E_{1/2}$ by complex formation can be given by,

$$(E_{1/2})_c - (E_{1/2})_s = 0.0591/n \log K_d - P 0.0591 /n \log C_x$$

In which the subscripts c and s refer to the complex and metal ions, respectively.

K_d = dissociation constant of metal ion complex.

P = coordination number of metal ion complex.

C_x = concentration of complexing agent at electrode surface.

Values of $\log K_d$ calculated from the equation of the complexes of various kinds of crown ether with Pr (III), Eu (III) and Gd (III) in 1,2-dichloroethane are summarized in Table (4).

Table (4): $\log K_d$ for the complexing reaction of crown ethers with rare earth cations in 1,2-dichloroethane at 25 °C (concentration $4 \times 10^{-4} M$).

Crown ether	Pr ³⁺	Eu ³⁺	Gd ³⁺
B15C5	3.32	3.02	2.45
18C6	3.43	3.98	3.44
B ₂ 18C6	1.96	2.10	1.56
B ₂ 24C8	3.42	4.10	4.41

The values of stability constant for rare earth cations correspond approximately to the relationship between the cavity diameter of rare earth cations and crown ether.

The ion dipole interaction between the donor atom (**10,11**) and the cation declines with decreasing negative charge of the donors and thus complexation ability is reduced (Table 4).

Beside the electrostatic interaction, there is a difference in the values of K_d for the complexes. The order of K_d are $B_218C6 < B15C5 < 18C6 < B_224C8$.

The lower values of B_218C6 and $B15C5$ correspond to the decrease in the electronegativity of the donor groups due to the phenyl groups as well as the flexible rings.

The large values of K_d is due to ion-dipole interaction between the donor atoms and the cations which increases with the increasing negative charge of the donor groups, and thus the complexation ability is more stable (Such as 18C6), and the large values of stability constants between the rare earth cations and B_224C8 , because the number of (**11,12**) donor and flexible B_224C8 (sandwich complex).

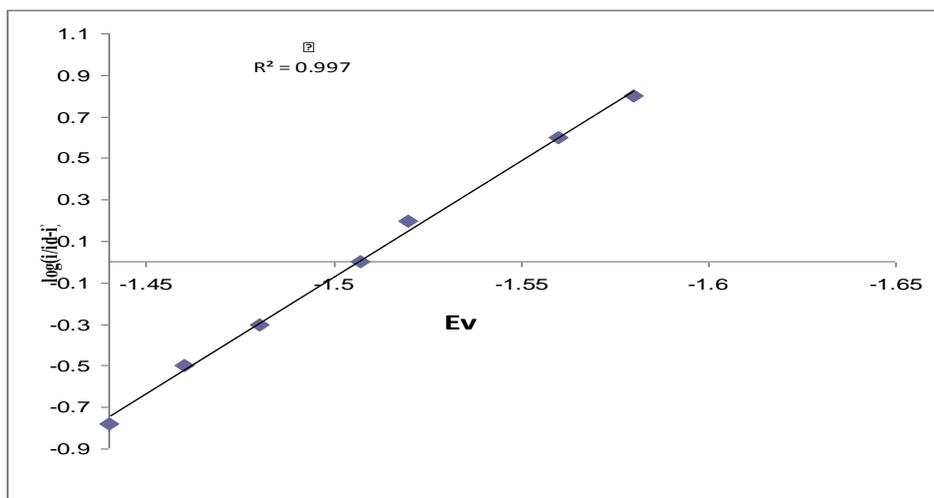


Fig.1 A plot of $E_{d.e}$ versus $\log i/(i_a-i)$ for the reduction of Pr^{+3} test of the equation of the wave of $5 * 10^{-3}M Pr^{+3}$.

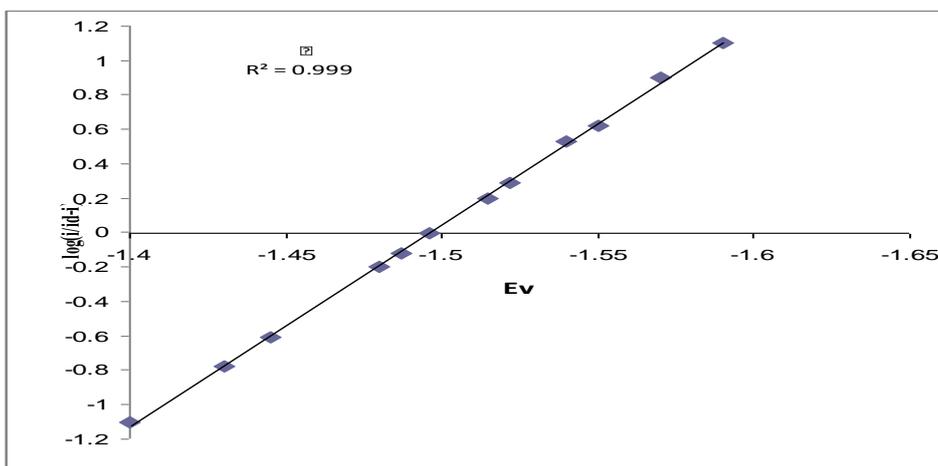


Fig.2 A plot of $E_{d.e}$ versus $\log i/(i_a-i)$ for the reduction of Eu^{+3} test of the equation of the wave of $3 * 10^{-3}M Eu^{+3}$.

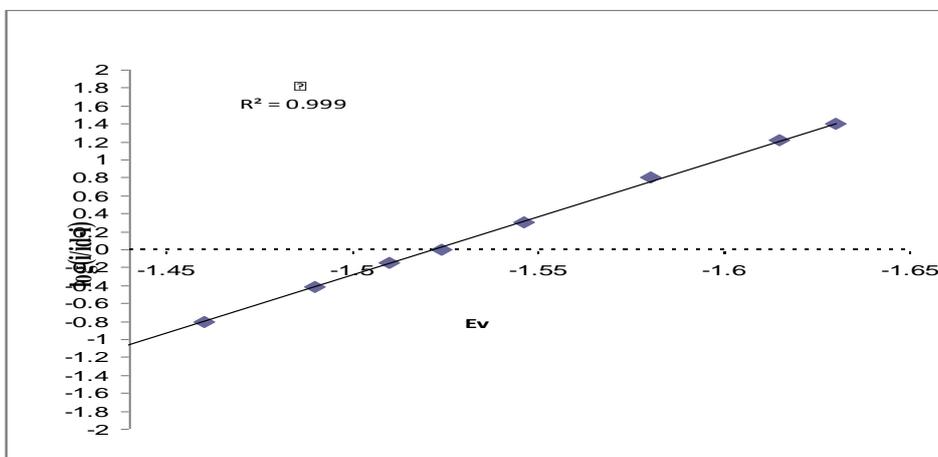


Fig.3 A plot of $E_{d.e}$ versus $\log i/(i_a-i)$ for the reduction of Gd^{+3} test of the equation of the wave of $3 * 10^{-3}M Gd^{+3}$.

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