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Uses of some monomers and polyamides of aminodibenzo-18-crown-6 in solid-liquid extraction of potassium permanganate, dichromate, chromate, thiocyanate and nitrate

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Abstract

Crown ethers are very important compounds in the extraction of alkali, alkaline earth, and transition metal ions that by formation of complexes with these ions .Crown ether polymers may have more ability of extraction compared with their monomers .In addition these polymers may be less poison, expensive, and can be used as catalysts.
This study had been aimed for using of some monomers and polymers contains dibenzo-18-crown-6 in solid – liquid extraction of potassium permanganate, dichromate, chromate and thiocyanate.
The value of E% (D) was found to be increased with time in the case of extraction of KNO_3, $K_2Cr_2O_7$ and KMnO4 for all compounds expect in the case ofDB18C6, cis-DNDB18C6 and trans-DNDB18C6 when were used for KNO3 and KMnO4 extraction. In case of K_2CrO_4, a decrease was observed in the values of E% (D) after 15-30 minutes.

1. Introduction

It was 1967 that Pedersen[1] published the first report on crown compounds, they were obtained unexpectedly .They are very important compounds in the extraction of alkali, alkaline earth, and transition metal ions, that by formation of complexes with these ions. Crown ether polymers may have more ability of extraction compared with their monomers. In addition these polymers may be less poison, expensive, and can be used as catalysts. This study had been aimed for using of some monomers and polymers contains dibenzo-18-crown-6 in solid – liquid extraction of the alkaline metal nitrates.
Crown compounds are, generally described [2] as macrocyclic compounds, having hetero atoms such as O, N, or S as electron donor atoms. Prior to 1971, Pedersen reported on a series of complexes crystals 3, nine kinds on novel crown compounds [4], nine kinds of macrocyclic polyether sulfides [5] having sulpher atoms in addition to oxygen atoms. Pedersen synthesized a number of aromatic and alicyclic crown ethers [3,6],and discovered that they are capable of complexation with salts of various metal cations comprising all of group 1a, almost all of group 1b metal ions,and some of 11b,111a,1Vb metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Au^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, Ce^{3+}, Ti^{2+}, Pb^{2+}) and with NH_4^+, and RNH_3^+ salts. The extraction of picrate ion with alkali metal ions, by some crown ethers was reported [3, 7-11]. The extraction of KMnO4[12], $K_2Cr_2O_7$[13], and K_2CrO_4 [14] by dibenzo-18 crown-6 was reported. Feigenbaum and Michel [15] prepared 4,4'-diaminodibenzo-18-crown-6 . Polyamides were prepared using cis-4,4'-diaminodibenzo-18-crown-6[16,17]. The mobility of Na^+ and Rb^+ in poly (dibenzo-18-crown-6) has been studied[18]. The first example of main chain liquid-crystalline polymers containing dibenzo-18-crown-6 was reported by Percec and Rodenhouse [19]. The EDTA dianhydride was used in the reaction with diazacrown ethers to obtain the water-soluble EDTA-diazacrown ether polymers[20].

2. Experimental

2.1 Chemicals and Techniques

All chemical used are of high purity (98 % or more). The shaking apparatus was Scientific Technical Suppliers Frankfurt W-Germany. UV-Visible Spectrophotometer 4050 LKB Biochrom Ultraspec 11, with two matched quartz cells was used.

2.2 Extraction of Potassium Permanganate

From stock solution of KMnO4 (10^{-2}M), various concentrations were prepared by accurate dilution. A calibration curve was elaborated for $KMnO_4$ determination at 552 nm .For extraction of $KMnO_4$(10^{-4}M) solution, the experiments were performed by shaking the mixture of o.o36 g ofDB18C6 and 10 ml of the extracted solution (10^{-4} M) for 5,10,15,….60 minutes and overnight, then the absorbance of the permanganate solution was measuredat each time, (represent the absorbance of the un-reacted ion).The percentage of the extracted permanganateion was determined by difference between the absorbance of permanganate ion at zero time and that at appropriate time of extraction .Similar procedure was repeated for DNDB18C6(0.045 g),DADB18C6(0.039 g),Schiff-base of DAD18C6(XV) (0.077), polyamide of DADB18C6(V1)(0.1 g),and polyamide of diaza18C6(XX11)(0.1g) .

2.3 Extraction of Potassium Dichromate

A calibration curve for $K_2Cr_2O_7$was built at 320 nm .The same procedure was followed as in potassium permanganate. Solutions of $K_2Cr_2O_7$ were prepared in 3, 5 N sulphuric acid.

2.4 Extraction of Potassium Chromate

Solutions of K_2CrO_4were prepared in (0.05N) potassium hydroxide solution. The absorbance of K_2CrO_4 was measured at 372 nm (Fig. 2.1). For extraction of this compound the same procedure was followed as in potassium permanganate.

2.5Extraction of Potassium Thiocyanate

Stock solution of 0.1 M of KSCN in deionized water was prepared. Other concentrations were prepared by dilution .To each solution 10 ml of ferric chloride was added .The latter was prepared by dissolving (33.3 g) of $FeCl_3.6H_2O$ in 10 ml concentrated HCl, and then diluted to 100ml[21] . The absorbance was obtained at 480 nm. For extraction of KSCN the same procedure was followed as in potassium permanganate, except that the contact time was 60 minutes only.

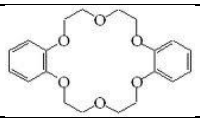
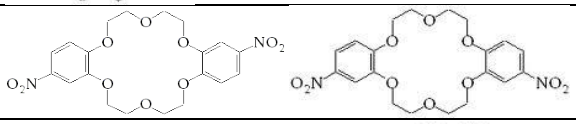
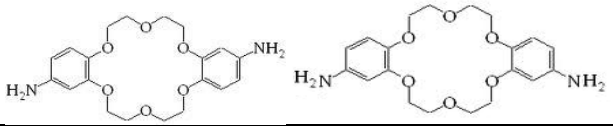
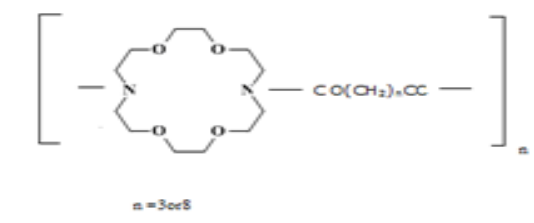
3. Results and Discussion

The structures of the compounds or polymers used in this study are presented in Table 1.

Since the pioneering work of Pedersen [3-5], the monomeric crown compounds have been the object of many extraction investigations. However, little attention has been paid to polymeric crown compounds. For the sake of comparison, studies of various anions have been carried out on the new prepared macrocyclic compounds.

Working curves for the determination of concentrations of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, KSCN and KNO_3, were constructed as in Figures 1-5 respectively.

Table 1 The structures of the compounds and polymers used in the extraction

Compound or Polymer	**Structure**	
DB18C6		
Cis-and trans-DNDB18C6		
Cis and trans-DADB18C6		
Schiff-base of trans-DADB18C6 (XV)	C_6H_{13}Oph-CH=-N-Trans-N=CH-ph-OC_6H_{13}	
Polyamides of DADB18C6	V	[CO-$(CH_2)_3$-CO-NH-Trans*-NH-]$_n$--
	V1	[CO-$(CH_2)_4$-CO-NH-Trans*-NH-]$_n$--
	V11	[CO-$(CH_2)_7$-CO-NH-Trans*-NH-]$_n$--
	V111	[CH-$(CH_2)_8$-CO-NH-Trans*-NH-]$_n$- -
	1X	[CO-$(CH_2)_3$-CO-NH-Cis*-NH-]$_n$--
	X	[CO-$(CH_2)_4$-CO-NH- Cis* -NH-]$_n$--
	X1	[CO-$(CH_2)_8$-CO-NH- Cis* -NH-]$_n$--
Model compounds	1	C_5H_{11}-CO-NH-Trans*-NH- CO- C_5H_{11}
	11	C_7H_{15}-CO-NH-Trans*-NH- CO- C_7H_{15}
	111	C_5H_{11}-CO-NH-Cis*-NH- CO- C_5H_{11}
	1 V	C_7H_{15}-CO-NH-Cis*-NH- CO- C_7H_{15}
Polyamides of Diaza18C6		
	XX1	n=3
	XX1	n=8
Polschiff-base(X1X)	(= N-transDADB18C6-N=CH-ph-OCO$(CH_2)_8$COOph-CH=)$_n$	

Cis* or Trans*=cis or trans-DADB18C6

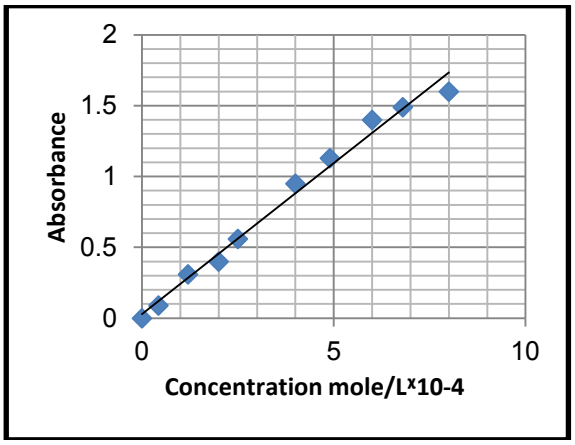


Fig 1 Working Curve of Potassium Permanganate

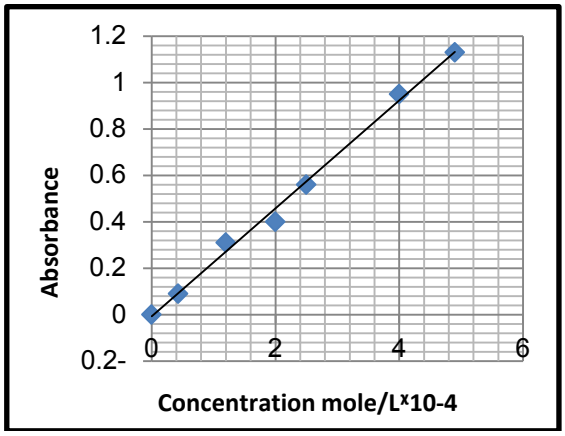


Fig 2 Working Curve of Potassium Dichromate

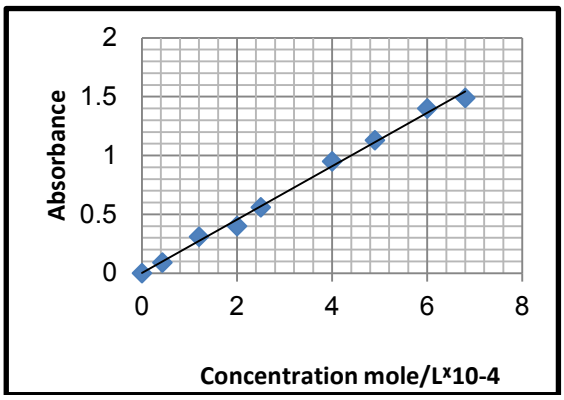


Fig 3 Working Curve of Potassium Chromate

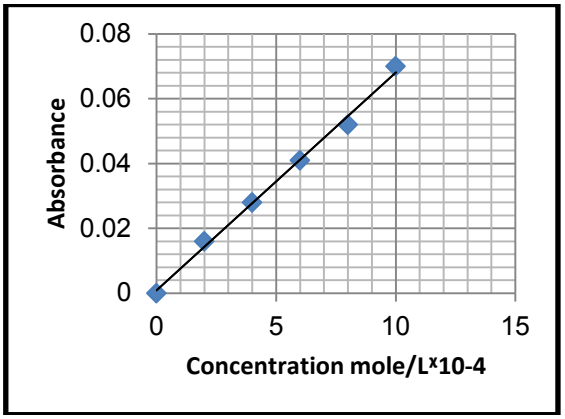


Fig 4 Working Curve of Potassium thiocynate

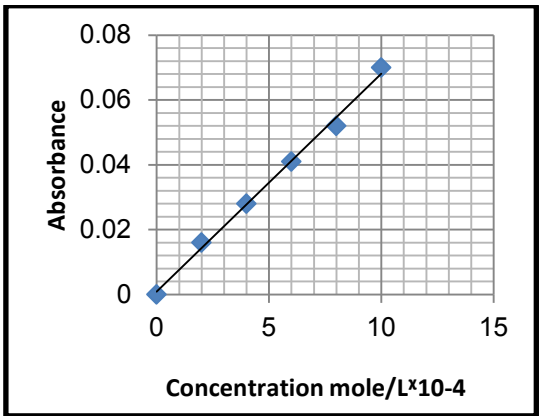


Fig 5 Working Curve of Potassium Nitrate

The results of extraction of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, and KNO_3 by DB18C6, cis-DNDB18C6, trans-DNDB18C6, cis-DADB18C6, trans-DADB18C6, Schiff-base of DADB18C6 (XV), polyamide of DADB18C6 (V1), and polyamide of Diaza18C6 (XX11), are shown in tables (3.2-3.10) respectively.

Table 2 Effect of time on extraction of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, and KNO_3 (10^{-4} M) by DB18C6, (0.036g/10ml)

Time (min)	E%				D			
	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-
5	4.2	10.1	11.7	14.3	12	31	36	46
10	7.1	12.4	17.3	37.1	20	39	57	164
15	8.4	15.7	20.1	44.3	25	51	69	220
20	10.3	16.1	18.7	57.1	31	50	36	370
25	11.7	17.1	15.9	55.7	36	57	52	349
30	12.6	17.5	13.8	55.7	40	58	44	349
35	11.7	18.9	12.6	52.9	36	64	40	311
40	11.2	19.8	11.9	51.4	35	68	37	294
45	10.8	20.3	11.2	51.4	33	70	35	294
50	11.2	20.6	10.0	50.0	35	76	30	277
55	10.8	23.2	9.1	45.7	33	83	27	233
60	10.3	24.0	8.4	42.9	31	89	25	208
1440 Overnight	**31.3**	**70.5**	**8.9**	**57.1**	**1261**	**664**	**27**	**370**

Table 3 Effect of time on extraction of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, and KNO_3 (10^{-4} M) by cis-DNDB18C6, (0.045g/10ml)

Time (min)	E%				D			
	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-
5	1.9	7.8	11.4	27.9	4	18	28	86
10	5.2	8.8	14.9	32.4	12	21	40	1o6
15	6.5	10.1	18.4	35.3	15	25	50	121
20	7.9	10.1	16.3	38.2	19	25	43	137
25	9.4	10.1	15.2	42.7	22	25	39	165
30	11.2	10.1	13.8	41.2	28	25	35	155
35	7.9	10.1	12.1	44.1	22	25	30	175
40	8.4	10.1	11.9	45.6	20	25	29	186
45	7.9	10.1	11.7	47.1	19	25	29	197
50	7.9	12.4	9.1	45.6	19	31	22	186
55	7.2	15.2	7.9	44.1	17	39	19	175
60	7.0	17.1	8.2	42.7	16	45	20	165
1440 Overnight	24.3	32.3	4.9	41.2	71	105	11	155

Table 4 Effect of time on extraction of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, and KNO_3 (10^{-4} M) by trans-DNDB18C6, (0.045g/10ml)

Time (min)	E%				D			
	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-
5	4.7	11.2	13.8	35.7	10	27	35	123
10	6.5	12.4	16.1	42.7	15	31	42	166
15	7.9	13.8	18.9	42.7	19	36	51	166
20	9.8	14.8	17.0	52.9	24	38	45	249
25	11.2	15.7	14.9	44.3	28	41	38	167
30	11.2	16.1	13.3	45.7	28	42	34	181
35	11.7	17.1	11.4	50.0	29	45	28	222
40	11.2	18.9	10.3	51.4	28	51	25	235
45	10.8	21.2	9.1	54.3	26	59	22	263
50	10.8	22.1	8.2	52.9	26	63	19	249
55	10.2	23.0	7.2	50.0	25	66	17	222
60	9.8	24.0	6.3	47.1	24	70	14	198
1440 Overnight	28.5	33.2	5.8	45.7	88	110	13	181

Table 5 Effect of time on extraction of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, and KNO_3 (10^{-4} M) by trans-DNDB18C6, (0.045g/10ml)

Time (min)	E%				D			
	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-
5	4.7	11.2	13.8	35.7	10	27	35	123
10	6.5	12.4	16.1	42.7	15	31	42	166
15	7.9	13.8	18.9	42.7	19	36	51	166
20	9.8	14.8	17.0	52.9	24	38	45	249
25	11.2	15.7	14.9	44.3	28	41	38	167
30	11.2	16.1	13.3	45.7	28	42	34	181
35	11.7	17.1	11.4	50.0	29	45	28	222
40	11.2	18.9	10.3	51.4	28	51	25	235
45	10.8	21.2	9.1	54.3	26	59	22	263
50	10.8	22.1	8.2	52.9	26	63	19	249
55	10.2	23.0	7.2	50.0	25	66	17	222
60	9.8	24.0	6.3	47.1	24	70	14	198
1440 Overnight	28.5	33.2	5.8	45.7	88	110	13	181

Table 6 Effect of time on extraction of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, and KNO_3 (10^{-4} M) by cis-DADB18C6, (0.039g/10ml)

Time (min)	E%				D			
	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-
5	62.2	-	20.5	28.6	421	-	66	102
10	63.1	-	22.1	32.9	438	-	72	125
15	63.1	-	24.7	57.1	438	-	84	341
20	64.0	-	20.1	60.0	456	-	64	384
25	64.5	-	17.3	71.4	465	-	53	641
30	65.0	-	15.9	80.0	475	-	48	1025
35	65.9	-	14.0	81.0	495	-	41	1124
40	66.4	-	13.5	81.4	505	-	40	1124
45	66.8	-	10.7	82.9	516	-	30	1239
50	67.3	-	9.1	82.9	527	-	25	1239
55	67.3	-	7.2	84.3	527	-	19	1357
60	67.8	-	5.6	84.3	538	-	15	1357
1440 Overnight	97.9	-	7.3	87.1	990	-	21	1737

Table 7 Effect of time on extraction of KMnO4, $K_2Cr_2O_7$, K_2CrO_4, and KNO_3 (10^{-4} M) by trans-DADB18C6, (0.039g/10ml)

Time (min)	E%				D			
	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-
5	53.3	-	22.6	40.0	658	-	74	170
10	72.0	-	25.2	52.9	863	-	86	287
15	77.1	-	26.6	58.1	886	-	92	347
20	77.6	-	22.1	61.4	911	-	72	408
25	78.0	-	18.7	74.3	962	-	58	740
30	79.0	-	18.2	85.7	1019	-	56	1538
35	79.9	-	16.6	85.7	1081	-	50	1538
40	80.8	-	15.4	87.1	1115	-	46	1737
45	81.3	-	14.0	87.1	1115	-	41	1737
50	81.9	-	12.4	88.6	1150	-	36	1987
55	81.9	-	11.4	88.6	1150	-	33	1987
60	82.2	-	9.1	90.0	1187	-	25	2307
1440 Overnight	89.7	-	4.8	91.4	2237	-	23	2735

Table 8 Effect of time on extraction of KMnO4, K2Cr2O7, K2CrO4, and KNO3 (10-4 M) by Schiff-base (XV) (0.077g/10ml)

Time (min)	E%				D			
	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-
5	66.4	59.0	13.3	55.7	257	187	20	169
10	61.2	61.3	23.4	57.1	292	206	39	174
15	72.0	62.2	27.8	60.0	335	214	47	195
20	73.4	63.1	25.9	77.1	359	222	45	440
25	76.6	63.5	22.7	58.7	428	227	38	783
30	79.0	63.5	20.7	88.6	490	227	34	1011
35	81.3	64.9	18.5	88.6	567	241	29	1011
40	85.1	65.3	16.5	88.6	742	245	25	1011
45	78.4	65.8	15.8	90.0	904	250	24	1174
50	88.3	66.2	17.0	90.0	1986	255	21	1174
55	89.7	67.1	13.8	90.0	1139	266	20	1174
60	90.7	67.6	12.3	91.4	1266	271	18	1392
1440 Overnight	92.5	84.7	26.1	92.7	1615	721	47	1697

Table 9 Effect of time on extraction of KMnO4, K2Cr2O7, K2CrO4, and KNO3 (10-4 M) by polyamide of diaza18C6 (XX11) (0.1g/10ml)

Time (min)	E%				D			
	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-	MnO_4^-	$Cr_2O_7^{2-}$	CrO_4^{2-}	NO_3^-
5	65.2	14.4	5.9	15.7	187	16	6	18
10	73.7	15.8	8.1	25.7	281	18	8	38
15	77.4	23.4	11.3	30.0	341	30	12	42
20	78.7	24.3	14.0	34.3	370	32	16	52
25	80.1	25.2	18.2	42.9	402	33	22	75
30	81.9	25.7	16.3	45.7	452	34	19	84
35	83.3	27.9	13.6	50.0	497	38	15	100
40	85.1	29.7	10.3	54.3	569	42	11	118
45	86.4	31.5	8.9	57.1	636	46	9	133
50	88.2	32.9	6.7	61.4	750	48	7	159
55	90.1	35.1	5.4	65.7	904	54	5	191
60	91.9	36.9	4.2	68.6	1127	58	5	218
1440 Overnight	95.5	80.6	35.5	71.4	2110	416	54	550

Table 10 Effect of time on extraction of KMnO4, K2Cr2O7, K2CrO4, and KNO3 (10-4 M) by polyamide of DADB18C6 (V1) (0.1g/10ml)

Time (min)	E%				D			
	$MnO4^-$	$Cr_2O_7^{2-}$	CrO_4^{2-}	$NO3^-$	$MnO4^-$	$Cr_2O_7^{2-}$	CrO_4^{2-}	$NO3^-$
5	90.7	68.5	29.3	62.9	970	217	41	169
10	91.6	72.5	33.7	71.4	1088	263	50	250
15	92.2	76.6	36.7	75.7	1188	326	58	311
20	92.5	80.2	36.5	85.7	1237	404	57	600
25	93.0	82.0	36.0	90.0	1326	454	56	900
30	93.9	82.9	35.7	92.9	1546	434	55	1300
35	94.4	85.1	37.7	94.3	1683	572	60	1650
40	94.4	86.5	39.2	94.3	1683	640	64	1650
45	94.4	87.8	40.9	94.3	1683	722	69	1650
50	95.3	88.3	35.5	95.7	2040	753	54	2233
55	96,8	89.6	33.3	95.7	2277	865	49	2233
60	99.6	91.0	29.8	97.1	2277	1010	42	3400
1440 Overnight	99.9	95.5	65.0	98.6	5250	9212	185	6900

An inspection of Tables 2-10 leads to the following observations:

(i) The values of E %(or D) values for the extraction of KNO_3, $K_2Cr_2O_7$, and $KMnO_4$, increase with time for all compounds except in the case of DB18C6 (Table 2), cis-DNDB18C6 (Table 3) and trans-DNDB18C6 (Table 4) when were used for KNO_3, or $KMnO_4$, extraction.

In case of K_2CrO_4 a decrease was observed in the values of E %(or D) after 15-30 minutes.

Table 11 summarize the optimum times of extraction of these ions by the prepared compounds.

In general, long equilibrium periods are required for the extraction of these ions .This can be due to the steric hindrance of the groups attached to the prepared compounds, and the size of anions which are involved in the extraction process. From Tables (2-10) ranges of E% values of these ions (after 15 mintues, 60 minutes and 24 hours of contact) are presented in Table 12.

There have been few reports on E% values of these anions; but from different extraction systems, Jalhoom and AL- Haidary[12] using DB18C6 for extraction of $KMnO_4$ reported that E% =95.2 in chloroform, 99.3 in dichloroethane and 98.1 in nitrobenzene. In separate studies AL- Haidary[13]reported E% ($K_2Cr_2O_7$) =96 in chloroform, 97.7 in dichloroethane, and 98.3 in nitrobenzene, while Fakkri[14] in his study reported E% (K_2CrO_4) =53.1 using the flow injection technique. It is evident that the values of E% obtained by the usage of crown compounds in the solid-liquid extraction system are almost in accordance with those obtained from liquid-liquid extraction systems. Al-Shaify[22] found that the value of E% for extraction of $KMnO_4$ by polyDB18C6 in acidic or basic medium is about 92-100%, while that for extraction of $K_2Cr_2O_4$ in basic medium (50%) and(100%) in acidic medium, which is in good agreement with our results.

(ii) Turning now to the effect of the nature of the anions. Table 14 summarizes the sequences of the extraction of the anions involved in the study under the same conditions, which are abstracted from the data of Table 13.

With regard to change of the anion, most of the compounds show a marked selectivity for the monovalent anions; MnO_4^-, SCN^- and NO_3^- compared to $Cr_2O_7^{2-}$ and CrO_4^{2-}. However, the following factors affect the nature of the anions and could be in part the causes of these sequences;

(1) Softness and hardness of the anion.
(2) Size, charge, density and hydration energy.
(3) Degree of nucleophicity.
(4) Geometry of the anion.

(iii) With respect to the effect of the chemical nature of the synthesized compounds; Fig. 6 has been built for the variation of E% of the anions versus the extracting compounds.

Generally speaking; as can be seen from Fig. 6 the polyamides DADB18C6 (V1) possess better ability for extraction than the polyamides of diaza18C6 (XX11).Cis- and trans-isomers of DNDB18C6 have lower ability than those of other product under study.

Table 11 The Optimum extraction time of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, and KNO_3 by the prepared compounds

Extraction Agent	**Optimum time /min**			
	$MnO4^-$	**$Cr_2O_7^{2-}$**	**CrO_4^{2-}**	**$NO3^-$**
DB18C6	30	60	15	20
Cis- DNDB18C6	30	15	15	45
Trans- DNDB18C6	35	60	15	45
Cis- DADB18C6	60	-	15	55
Trans- DADB18C6	60	-	15	60
Schiff-base(XV)	60	60	15	45
Polyamide(XX11)	60	60	25	60
Polyamide(V1)	60	60	45	60

Table 12 Ranges of E% of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, and KNO_3

Extraction Agent	E%		
	15 min.	60 min.	24 hrs.
DB18C6	8-44	8-43	9-71
Cis- DNDB18C6	6-35	7-43	5-41
Trans- DNDB18C6	8-34	6-47	5-46
Cis- DADB18C6	24-57	5-84	7-87
Trans- DADB18C6	26-58	9-90	8-91
Schiff-base(XV)	27-72	12-91	26-93
Polyamide(XX11)	11-27	64-92	35-95
Polyamide(V1)	36-76	29-97	65-99

Table 13 The Optimum extraction time of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, and KNO_3 by the prepared compounds

Extraction Agent	$MnO4^-$		$Cr_2O_7^{2-}$		CrO_4^{2-}		SCN^-		$NO3^-$	
	E%	D	E%	D	E%	D	E%	D	E%	D
DB18C6	10.3	31	24.0	89	8.4	25	60.6	153	42.9	370
Cis- DNDB18C6	7.0	18	17.1	45	8.2	20	56.1	127	42.7	20
Trans- DNDB18C6	9.8	24	24.0	70	6.3	14	58.5	140	47.1	181
Cis- DADB18C6	67.8	238	-	-	5.6	15	-	-	84.3	1375
Trans- DADB18C6	82.2	1187	-	-	9.1	25	-	-	90.0	2307
Schiff-base(XV)	90.7	1266	67.8	271	12.3	18	86.9	133	91.4	1392
Model (1)	92.0	1160	83.8	506	55.0	122	86.5	643	77.8	350
Model (11)	91.9	1158	80.6	412	64.7	182	84.0	554	84.7	1340
Model (111)	92.4	1194	84.2	525	63.3	177	87.8	717	87.5	700
Model (1V)	91.5	1121	85.4	589	64.7	182	88.4	760	88.9	800
Polyamide(V)	99.1	11500	89.1	852	75.6	309	89.6	861	96.1	2477
Polyamide(V1)	99.7	23100	91.0	1010	29.8	286	93.0	1334	97.1	3400
Polyamide(V11)	98.7	6733	8.0	733	86.1	616	81.3	834	99.6	23100
Polyamide(V111)	100	>10000	87.4	700	65.0	185	90.5	954	98.7	603
Polyamide(1X)	96.1	4277	86.7	640	88.5	810	88.7	783	93.1	1342
Polyamide(X)	98.7	7633	90.1	900	76.7	330	88.7	783	99.4	2388
Polyamide(X1)	100	>10000	91.2	1011	47.9	298	89.9	890	99.8	23115
Polyamide(XX1)	89.2	828	77.2	334	71.4	249	65.5	190	28.1	38
Polyamide(XX11)	91.9	1127	36.9	58	4.2	54	71.5	251	68.9	218
Polyschiff-base(X1X)	94.0	1557	-	-	52.8	111	-	-	58.8	142

Table 14 The sequences of extraction of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, KSCN and KNO_3 for 60 minutes by the prepared compounds

Extraction Agent	sequence of extraction
DB18C6, Cis-,and Trans- DNDB18C6	$SCN^- > NO_3^{-} > Cr_2O_7^{2-} > CrO_4^{2-} > MnO_4^-$
Cis-,and Trans- D◌DB18C6	$NO_3^- > MnO_4^{--} > CrO_4^{2-}$
Schiff-base(XV)	$NO_3^- > MnO_4^{--} > SCN^- > Cr_2O_7^{2-} > CrO_4^{2}$
Model (1)	$MnO_4^{--} > Cr_2O_7^{2-} > SCN^- > NO_3^{-} > CrO_4^{2-}$
Model (11) and(1V) Polyamides(V), (V1)and(V111)	$MnO_4^{--} > NO_3^{-} > SCN^- > Cr_2O_7^{2-} > CrO_4^{2}$
Model (111) andPolyamide (XX11)	$MnO_4^{--} > SCN^- > NO_3^{-} > Cr_2O_7^{2-} > CrO_4^{2-}$
Polyamide (V11)	$NO_3^- > MnO_4^{--} > Cr_2O_7^{2-} > CrO_4^{2-} > SCN^-$
Polyamide (1X)	$NO_3^- > MnO_4^{--} > SCN^{---} > Cr_2O_7^{2-} > CrO_4^{2}$
Polyamide (X)	$NO_3^- > MnO_4^{--} > Cr_2O_7^{2-} > SCN^{---} > CrO_4^{2}$
Polyamide (X1)	$MnO_4^{--} > NO_3^{-} > Cr_2O_7^{2-} > SCN^{---} > CrO_4^{2}$
Polyamide (XX1)	$MnO_4^{--} > Cr_2O_7^{2} > CrO_4^{2--} > SCN^- > NO_3^{--}$
Polyschiff-base(X1X)	$MnO_4^{--} > NO_3^{-} > Cr_2O_7^{2}$

Table 15 Ability of extraction time $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, KSCN and KNO_3 by the prepared compounds and polymers

$MnO4^-$	**$Cr_2O_7^{2-}$**	**CrO_4^{2-}**	**SCN^-**	**$NO3^-$**
Polyamides(V111)&(X1)	Polyamide (X1)	Polyamide (1X)	Polyamide (V1)	Polyamide (X1)
Polyamide (V1)	Polyamide (V1)	Polyamide (V11)	Polyamide (V111)	Polyamide (V11)
Polyamide (V)	Polyamide (X)		Polyamide (X1)	Polyamide (X)
Polyamides(V11)&(X)	Polyamide (V)	Polyamide (X)	Polyamide (V)	Polyamide (V111)
Polyamide (1X)	Polyamide (V11)	Polyamide (V)	Polyamides (1X) &(X)	Polyamide (V1)
Polyschiff-base(X1X)	Polyamide (V111)	Polyamide (X1)	Model(1V)	Polyamide (V)
Model(111)	Polyamide (1X)	Polyamide (XX1)	Model(111)	Polyamide (1X)
Model(1)	Model(1V)	Polyamide (V111)	Schiff-base (XV)	Schiff-base (XV)
Polyamide (XX11) & Model((11)	Model(111)	Model(11) &(1V)	Model(1)	Trans-DADB18C6
Model(1V)	Model(1)	Model(111)	Model(11)	Model(1V)
Polyamide (XX1)	Model(11)	Model(1)	Polyamide (V11)	Model(111)
Schiff-base (XV)	Polyamide (XX1)	Polyschiff-base(X1X)	Polyamide (XX11)	Model(11)
Trans-DADB18C6	Schiff-base (XV)	Polyamide (V1)	Polyamide (XX1)	Model(1)
Cis-DADB18C6	Polyamide (XX11)	Schiff-base (XV)	[DB18C6	Cis-DADB18C6
DB18C6	DB18C6	Trans-DADB18C6	Trans-DNDB18C6	Polyamide (XX11)
Trans-DNDB18C6	Trans-DNDB18C6	DB18C6	Cis-DNDB18C6	Polyschiff-base(X1X)
Cis-DNDB18C6	Cis-DNDB18C6	Trans-DNDB18C6		Trans-DNDB18C6
		Cis-DNDB18C6		DADB18C6 & Cis-DNDB18C6
		Cis-DADB18C6		Polyamide (XX1)
		Polyamide (XX11)		

These findings reveal that introducing substituents in the benzene ring of DB18C6 affect the stability of the complex formed between the crown compound and the extracted species. Introducing $-NH_2$ group, which is a typical electron donor group, increases the basisity of the oxygen via resonance effect. This effect and similar ones which increase the basisity of the cavity could be responsible for the improvements in the exastability of all compounds substituted with such groups. In contrast the substituent effect for the $-NO_2$ group, which is a typical electron acceptor group, is to decrease the basisity of the oxygen atoms. Smid et al [23] reported similar conclusions from the determination of the stability constant values for Na^+ and K^+ complexes of $-NH_2$ and $-NO_2$ derivatives of benzo-15 crown-6 and benzo-18-crown-6 by electroconductivity measurements. Moreover, it is reported that the substituents effect is more important in some cases than the effect of the relation between cation diameter and the cavity size of the crown ring[2].

When two of the oxygen donors in 18C6 are replaced by nitrogen atoms (i.e. diaza18C6 and related compounds in this study), the extrability is less than those of the corresponding crown ethers (Table 3.13) i.e. the polyamide of diaza18C6 (XX11) reflected lower extraction power compared with the polyamides of DADB18C6 (V1).This may be attributed to that the polyamide of diaza18C6 which contains nitrogen atoms, has softer basic properties than oxygen atoms, consequently higher affinity towards cations such some of the transition or heavy metal ions, while crown ethers have affinity for hard cations such as alkali or alkaline – earth metal ions. Also this is to be expected because the ion-dipole interaction between the

Donor atoms and the cations declines with decreasing of the electronegativity of the donor atoms, and thus the complexation ability reduced. Results of this study are in agreements with Frensdorff [8] results, which revealed that complexation ability of crown ethers, are in the order O>N>S.

Extraction ability of the nitrophenyl derivatives is less than that of the substituted one, while that of amino derivatives is much better which could be explained by the different electronic effect of these groups, as is mentioned previously. However, the high extraction abilities of the liquid crystalline polyamides and Schiff-bases could be related to their mesotropic properties. It seems that the planarity, polarizability and molecular axis alignment that are characteristics feature of liquid crystalline molecules plays an important role in increasing their extraction ability .It is well known that liquid-crystalline molecules have been used as stationary phases in gas liquid-chromatography separation due to their features.

Conclusion

1. Generally there was increase in the values of E% (or D) with time for the extraction of potassium permanganate, dichromate and nitrate, while there was decrease in these values in the extraction of potassium chromate by the prepared compounds.

2. Most of the compounds, show a remark selectivity for the monovalent anions MnO_4^-,SCN^- and NO_3^- compared with divalent ones $Cr_2O_7^{2-}$ and CrO_4^{2-}.
3. The sequence of extraction of $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, KSCN and KNO_3 by the prepared compounds is as follows: polyamides of DADB18C6 give higher value of extraction, while the cis-DNDB18C6 gives the lowest value. Polyamide of diaza18C6 has less ability than that of DADB18C6 .The $–NH_2$ group increases the power of extraction of DB18C6, while the $–NO_2$ group decreases this value. The trans- isomer gives higher value of extraction than the cis-isomer.

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