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Solvent Effect upon Ion-pair Extraction of Different Sodium Dyes Using Some Crown Ethers

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Abstract. Liquid-liquid extractive-spectrophotometric studies of sodium ion complexes of 18-crown-6(18C6), dibenzo-18-crown-6(DB18C6), 15-crown-5(15C5), and 12-crown-4(12C4) and anionic dyes [4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (PAR), Eriochrom Black T (EBT), and methyl orange (MOR)] and sodium picrate (PICRAT) as the counter ion are described. The overall extraction equilibrium constants for the 1 : 1 complexes of the above crown ethers with sodium dyes between different organic solvents and water have been determined at 25°C. They were conducted in various solvent-water systems maintaining an identical initial cation concentration in water, $[M_0^+]_w$, and macrocyclic ligand concentration in the organic phase, $[L_0]_{\mathrm{org}}$, so that in all extractions $[M_0^+]_w : [L_0]_{\mathrm{org}}$ ratios were 1 : 1, 1 : 10, 1 : 20, 1 : 50, and 1 : 62.5. An ion association complex formed between the sodium-crown ether complex ion and a dye anion was extracted into the organic solvent, and then the dye concentration of the separated aqueous phase was measured with an ultraviolet-visible spectrophotometer. PAR was the best associated dye with all crown ethers sodium-dyes and the extracted dye occurs as the ion-pair complex. Methylene chloride was found to be better than other extractive solvents used in this study.

Key words: crown ether complex, solvent extraction, ion-pair extraction, anionic dyes, spectrophotometry.

1. Introduction

Crown ethers show a remarkable ability to extract alkali and alkaline earth metal ions selectively [1, 2] as well as other ions such as organic cations and anions [3, 4]. These macrocyclic ligands have been widely used and several reviews [5–10] have been published. The particular role of liquid-liquid alkali cation transfer in membranes has expanded the area of interest. The cation binding selectivity of such molecules and particularly the crown ethers were investigated with different types of macrocyclic structures by several authors and well documented for molecular recognition [11–13]. The determination of sodium by means of ion-selective electrodes [14–16] involving the use of crown ethers has been reported, as has their use as potentiometric titrants [17]. Crown ethers have also been used for chromatographic separations [3, 18]. Photometric or fluorimetric determina-

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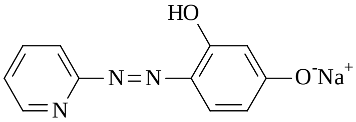
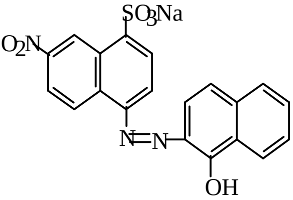
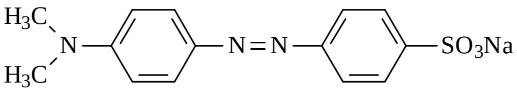


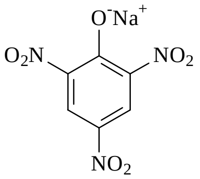
PAR



EBT



MOR



PICRAT

tions, particularly of alkali and alkaline earth metal ions, can be carried out by solvent extraction of the ion-pair formed between the complexed crown ether and a coloured [4, 19–24] or fluorescent [25] counter ion. However, the cation extraction properties of the macrocyclic ethers with different side groups of various types were examined for their extractive abilities [11, 12, 26, 27].

The spectrophotometric methods for solvent extraction of an ion association complex and an anionic dye have commonly been used [21–23, 28, 29]. Since a large anion is easily extracted into low dielectric constant solvents [30], the picrate anion was widely used as the counter ion [2, 26, 31, 32].

This paper describes the extractive-spectrophotometric determination of sodium using crown ethers as complexing agents and anionic dyes as coloured counter ions. The effects of the cavity size and type of the crown compounds and also the size and different functional groups of anionic dyes have been studied. For this purpose, the crown ethers chosen were 18C6, DB18C6, 15C5 and 12C4, and the anionic dyes were 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate **(PAR)** [21], Eriochrom Black T **(EBT)**, methyl orange **(MOR)** and sodium picrate **(PICRAT)** [26, 31, 32].

2. Experimental

2.1. MATERIALS

Commercial macrocyclic ethers (Aldrich) were used without further purification. Anionic dyes, 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate **(PAR)**, Eriochrom Black T **(EBT)**, and methyl orange **(MOR)** were commercial products from Aldrich dried over P_2O_5 for 48 h at 0.1 torr. The sodium picrate **(PICRAT)** was prepared by adding a sodium carbonate solution to an aqueous solution of picric acid; the resulting precipitate of sodium picrate monohydrate was recrystal-

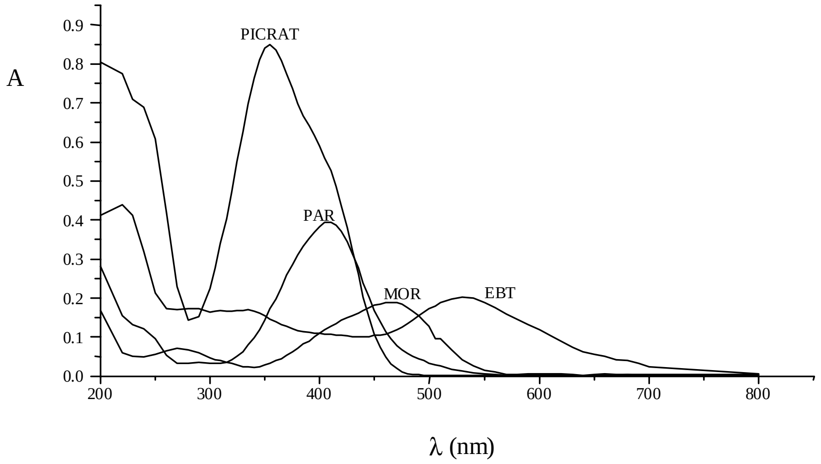


Figure 1. Absorption spectra of PAR, MOR, EBT and PICRAT in water at pH: 6.1–6.7.

lized from water-ethanol (1 : 3) mixture. The picrate salt was dried at 100°C for 24 h. All solvents (dichloromethane, chloroform, carbon tetrachloride, benzene, toluene, and *n*-hexane) used were of analytical-reagent grade.

2.2. EXTRACTION PROCEDURE

The extraction measurements were done in a 100 mL glass thermostated cell compartment with a mechanical stirrer where 25 mL of an aqueous anionic sodium dye solution (4×10^{-5} M) and crown ethers in organic solvents in appropriate concentration were placed and stirred for 30 min at 25°C and subsequently allowed to stand for 30 min to complete the phase separation. The optimum concentration of crown ethers were determined by extracting the sodium salts with 10 mL of various concentrations of crown ethers (4×10^{-5}, 40×10^{-5}, 80×10^{-5}, 200×10^{-5} and 250×10^{-5} M) (Table I). All the extractions were carried out at the natural pH of the aqueous dye solutions which were about 6.1–6.7.

The distribution coefficients ($K_{\mathrm{D,L}}$) of the crown ethers (18C6, 15C5 and 12C4) in the solvents used in the study were determined according to the method given by Takeda and Kato [33].

2.3. DETERMINATION OF THE ANIONIC SODIUM DYES

The concentrations of PAR, EBT, MOR and PICRAT in the aqueous phases were determined spectrophotometrically (Varian Cary model 1E UV-visible spectrophotometer) at 404, 555.05, 466.6, and 356.6 nm, respectively, with appropriate quartz cells 2–50 mm in length. Each absorbance value was the average of three subsequent measurements.

3. Results and Discussion

3.1. EXTRACTION EQUILIBRIA

We just studied in the present work with a common formalism of equations (1–18) [33]. The equilibrium processes taking place during the extraction between an aqueous solution containing the alkali metal cation, $M^+_{(w)}$, and the organic anion, $A^-_{(w)}$, and an organic solution containing crown ethers $L_{(\mathrm{org})}$, can be written as:

$$M^+_{(w)} + A^-_{(w)} + nL_{(W)} \rightleftharpoons ML_nA_{(\mathrm{org})}$$

$$K_{\mathrm{ext}} = \frac{[ML_nA]_{\mathrm{org}}}{[M^+]_w[A^-]_w\{[L]_w\}^n} \quad \text{and} \quad K_D = [ML_nA]_{\mathrm{org}}/[M^+]_w \tag{1}$$

$$L_{(w)} \rightleftharpoons L_{(\mathrm{org})}, \qquad K_{D,L} = [L]_{\mathrm{org}}/[L]_w \tag{2}$$

$$M^+_{(w)} + A^-_{(w)} \rightleftharpoons MA_{(\mathrm{org})}$$

$$K_{MA} = \frac{[MA]_{\mathrm{org}}}{[M^+]_w[A^-]_w} \qquad \text{and} \quad K'_D = [MA]_{\mathrm{org}}/[M^+]_w \tag{3}$$

and

$$H^+_{(w)} + A^-_{(w)} \rightleftharpoons HA_{(\mathrm{org})}, \quad K_{HA} = \frac{[HA]_{\mathrm{org}}}{[H^+]_w[A^-]_w} \tag{4}$$

for the extraction process of an acid, HA, with the anionic dye in the equations above. $[M^+]_w$, $[A^-]_w$ and $[ML_nA]_{\mathrm{org}}$ denote the concentrations of uncomplexed cation and anion in the aqueous phase and the complex ion-pair extracted in the organic phase, respectively. Mass balances for these processes are expressed as:

$$[L_0] = [L]_w + [ML_nA]_{\mathrm{org}} + [L]_{\mathrm{org}} \tag{5}$$

$$[M_0^+] = [M^+]_w + [ML_nA]_{\mathrm{org}} + [MA]_{\mathrm{org}} \tag{6}$$

and

$$[A_0^-] = [M_0^+] = [ML_nA]_{\mathrm{org}} + [MA]_{\mathrm{org}} + [HA]_{\mathrm{org}} \tag{7}$$

where the subscript ($_0$) designates the initial concentrations.

As can be seen from the results of blank experiments without the crown ethers in Tables I–IV,

$$[ML_nA]_{\mathrm{org}} \gg [MA]_{\mathrm{org}} + [HA]_{\mathrm{org}} \tag{8}$$

then,

$$[ML_nA]_{\mathrm{org}} \cong [A_0^-] - [A^-]_w \tag{9}$$

Therefore, for the overall extraction process, the following equation can be written by adding Equation (1) to the reverse of Equation (2),

$$M^+_{(w)} + A^-_{(w)} + nL_{(\mathrm{org})} \rightleftharpoons ML_nA_{(\mathrm{org})} \tag{10}$$

the equilibrium constant of the extraction process can be written as:

$$K_{\mathrm{ext}} = \frac{[ML_nA]_{\mathrm{org}}}{[M^+]_w[A^-]_w\{[L]_{\mathrm{org}}\}^n} \tag{11}$$

and hence,

$$K_{\mathrm{ext}} = \frac{[A_0^-] - [A^-]_w}{\{[A^-]_w\}^2[L]_{\mathrm{org}}} \tag{12}$$

at $n = 1$, which refers to a stoichiometric coefficient for the reaction.

There were two possible cases in our results:

Case (1): When $K_{D,L} \gg 1$ (i.e., for a hydrophobic crown ether such as DB18C6),

$$[L_0] = [MLA]_{\mathrm{org}} + [L]_{\mathrm{org}} \cong [L]_{\mathrm{org}} \quad (\text{if } [L]_{\mathrm{org}} \gg [MLA]_{\mathrm{org}} \text{ holds}) \tag{13}$$

here $K_{D,L}$ denotes a distribution constant of a crown ether between water and organic solvent and is defined as,

$$K_{D,L} = [L]_{\mathrm{org}}/[L]_w \tag{14}$$

hence Equation (12) with $n = 1$ is rewritten as,

$$K_{\mathrm{ext}} = \frac{[A_0^-] - [A^-]_w}{\{[A^-]_w\}^2[L_0]} \tag{15}$$

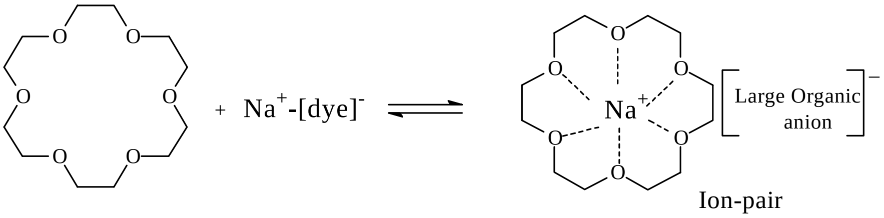
According to Equation (15), K_{ext} values were obtained by determining $[A^-]_w$ spectrophotometrically. The results obtained for DB18C6 are shown in Tables I–IV.

Case (2): When $K_{D,L} \ll 1$ (i.e., for a hydrophilic crown ether such as 12C4,15C5 and 18C6),

$$[L_0] \cong [L]_w = [L]_{\mathrm{org}}/K_{D,L} \quad (\text{if } [L]_w \gg [MLA]_{\mathrm{org}} \tag{16}$$

and, in this case, Equation (12) can be written in a modified form:

$$K_{\mathrm{ext}} = \frac{[A_0^-] - [A^-]_w}{\{[A^-]_w\}^2[L_0]K_{D,L}} \tag{17}$$



I

Therefore, the relationship between K_{ext} and K'_{ext} from Equations (1), (2), (15) and (17) can be written as:

$$K'_{\mathrm{ext}} = K_{\mathrm{ext}} K_{D,L} \tag{18}$$

The K'_{ext} values for hydrophilic crown ethers (18C6, 15C5 and 12C4) are given in Tables I–IV. In calculating the K'_{ext} values in benzene; $[L_0] \cong [L]_w$ was considered because $K_{D,L} = 0$ for this situation.

Three anionic sodium dyes and sodium picrate were examined with various crown ethers and extraction solvents. The general extraction scheme is illustrated in **I** for the case of 18C6. The selection of the optimum counter anion, crown ether and extraction solvent was made with regard to phase separation efficiency, determination sensitivity and accuracy of complexation constants (K_{ext} and K'_{ext}). The results of ion-pair extractions obtained in our experimental conditions of identical cation/ligand concentrations of monovalent Na-PAR, Na-EBT, Na-MOR and Na-PICRAT salts are summarised in Tables I–IV.

A variety of organic solvents has been utilized for the sodium-dyes extraction by crown ether compounds which have different cavity sizes.

The results obtained with PAR in Table I have shown the higher extraction ability in the order of $CHCl_3 > CCl_4 > CH_2Cl_2 > C_7H_8 > C_6H_6 > C_6H_{14}$.

For PAR with 18C6 the various organic solvents yield systematically decreasing values of K'_{ext}, in the order $CH_2Cl_2 > CHCl_3 > C_6H_6 > C_7H_8 > CCl_4$ (Table I).

Dichloromethane was found to be the best solvent for the extraction studies. When the used anionic dyes are extracted as 1 : 1 complexes with crown ethers, the cation-complexing ability of the crown ethers show a selectivity order of 18C6 > DB18C6 > 12C4 > 15C5 [13, 21]. The extraction equilibrium constant values for PAR with DB18C6 decrease in the order of $CH_2Cl_2 > CHCl_3 > C_6H_6 > C_7H_8$. The K'_{ext} values of PAR for the 15C5 and 12C4 compounds for different organic solvents were found in the order of $CH_2Cl_2 > CHCl_3 > C_6H_6 > C_7H_8 > CCl_4 > C_6H_{14}$ and $CHCl_3 > CH_2Cl_2 > C_7H_8 > C_6H_6 > C_6H_{14} > CCl_4$ respectively [21].

In the PAR complexation state, when complexation involves a singly-charged cationic guest, there will be no need for a separate counter ion. A well-studied example of this type involves the large anion-containing sodium-dyes [34]. The sodium ion of PAR is well surrounded by the electron pairs of the crown oxygen atoms as illustrated in **II** [21].

Table I. Equilibrium constants for extractions of PAR with crown ethers in various extraction solvents at 25°C ($^{\theta}$)

Solvent	ϵ^{20}	Crown ether	Log K_{ext}	K_D	Log K'_{ext}	$K_{D,L}$
CH_2Cl_2	9.080	WCr		1.12^{+}		
		DB18C6	12.49 ± 1.64	29.90	–	–
		18C6		31.18	12.61 ± 1.67	0.87
		15C5		1.83	9.62 ± 1.14	2.00
		12C4		5.27	9.94 ± 0.71	1.00
$CHCl_3$	4.806	WCr		1.47^{+}		
		DB18C6	9.62 ± 1.23	2.40	–	–
		18C6		3.17	10.24 ± 1.10	4.14
		15C5		1.85	9.24 ± 1.05	1.17
		12C4		5.09	10.48 ± 0.78	4.38
CCl_4	2.238	WCr		1.37^{+}		
		DB18C6*	–	–		
		18C6		0.17	5.37 ± 0.54	0.04
		15C5		0.17	6.38 ± 1.17	0.04
		12C4		0.45	7.23 ± 0.17	0.83
C_6H_6	2.284	WCr		0.41^{+}		
		DB18C6	8.60 ± 1.02	0.86		
		18C6		1.41	9.02 ± 1.05	0.00
		15C5		1.35	8.00 ± 0.39	0.00
		12C4		2.62	8.03 ± 0.07	0.00
C_7H_8	2.438	WCr		0.62^{+}		
		DB18C6	8.15 ± 0.80	0.69		
		18C6		0.81	6.85 ± 1.01	0.02
		15C5		0.94	7.59 ± 0.74	0.12
		12C4		2.50	8.84 ± 0.40	1.50
C_6H_{14}	1.890	WCr		0.00^{+}		
		DB18C6*	–	–	–	–
		18C6	–	–	–	–
		15C5		0.01	5.79 ± 1.02	0.26
		12C4		0.17	7.30 ± 0.29	2.86

(*) DB18C6 did not dissolve in CCl_4 and C_6H_{14}.

$^{+}$ K'_D values.

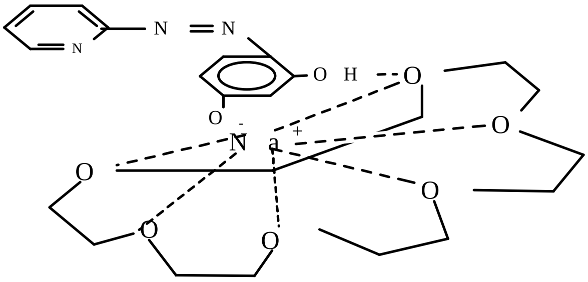
$^{\theta}$ Corr. Coefficient: 0.998.

WCr: Without Crown Ether.

Table II. Equilibrium constants for extractions of MOR with crown ethers in various extraction solvents at 25°C ($^{\theta}$)

Solvent	Crown ether	Log K_{ext}	K_D	Log K'_{ext}	$K_{D,L}$
CH_2Cl_2	WCr		0.02^{+}		
	DB18C6	5.79 ± 0.50	0.02		
	18C6		0.04	6.65 ±0.80	0.87
	15C5		0.03	7.10 ± 1.02	2.00
	12C4		0.06	6.50 ± 0.61	1.00
$CHCl_3$	WCr		0.11^{+}		
	DB18C6	6.51 ± 0.39	0.02		
	18C6		0.04	7.01 ± 0.74	4.14
	15C5		0.02	6.58 ± 1.15	1.17
	12C4		0.02	7.23 ± 0.90	4.38

$^{(+)}$ K'_D values.
($^{\theta}$) Corr. Coefficient: 1.000.
WCr: Without Crown Ether.



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II

Likewise the organic anion of PAR is well hydrogen bonded to the crown ether by the O—H hydrogen on the large organic counter ion. From the model of the PAR-18C6 complex, it is apparent that 18C6 with all oxygen electron pairs pointing inwards, also provides an ideal cavity for the guest molecule. Thus, a solution of this crown in polar solvents, such as dichloromethane and chloroform has given much more dye extraction than other crown compounds and solvents [31, 35, 36].

The results of EBT extractions are in the following orders: the dependence of the extraction ability of EBT on organic solvent without crown compounds decreased in the order of $CCl_4 > CHCl_3 > CH_2Cl_2 > C_6H_6 > C_6H_{14} > C_7H_8$. The equilibrium constant values between EBT and 18C6, DB18C6, 15C5, and 12C4 compounds decrease in the order of $CHCl_3 > CH_2Cl_2 > CCl_4 > C_6H_6 > C_6H_{14} > C_7H_8$; $CHCl_3 > CH_2Cl_2 > C_6H_6$; $CHCl_3 > CH_2Cl_2 > CCl_4 > C_6H_6 > C_6H_{14} > C_7H_8$ and $CHCl_3 > CCl_4 > CH_2Cl_2 > C_6H_6$, respectively.

Table III. Equilibrium constants for extractions of EBT with crown ethers in various extraction solvents at 25°C ($^{\theta}$)

Solvent	Crown Ether	Log K_{ext}	K_D	Log K'_{ext}	$K_{D,L}$
CH_2Cl_2	WCr		0.80^{+}		
	DB18C6	8.72 ± 0.51	0.86		
	18C6		1.07	8.55 ± 0.85	0.87
	15C5		0.56	8.49 ± 0.88	2.00
	12C4		0.56	8.15 ± 0.88	1.00
$CHCl_3$	WCr		0.88^{+}		
	DB18C6	9.37 ± 0.57	1.25		
	18C6		1.75	10.22 ± 1.37	4.14
	15C5		4.96	10.34 ± 1.13	1.17
	12C4		3.93	10.98 ± 1.31	4.38
CCl_4	WCr		5.10^{+}		
	DB18C6∗	–	–		
	18C6		1.75	7.85 ± 1.80	0.04
	15C5		1.78	7.96 ± 1.04	0.04
	12C4		1.69	9.22 ± 1.24	0.83
C_6H_6	WCr		0.14^{+}		
	DB18C6	6.68 ± 0.47	0.10		
	18C6		0.26	7.43 ± 0.63	0.00
	15C5		0.12	7.72 ± 0.92	0.00
	12C4		–	7.82 ± 0.36	0.00
C_7H_8	WCr		0.00^{+}		
	DB18C6	–	–		
	18C6		0.04	5.55 ± 1.50	0.02
	15C5		–	–	–
	12C4		–	–	–
C_6H_{14}	WCr		0.11^{+}		
	DB18C6∗	–	–		
	18C6		0.14	6.22 ± 0.99	0.06
	15C5		0.12	6.92 ± 0.94	0.26
	12C4		–	–	–

∗ DB18C6 did not dissolve in CCl_4 and C_6H_{14}.

$^{(+)}$ K'_D values.

WCr: Without Crown Ether.

($^{\theta}$) Corr. Coefficient: 0.999.

Table IV. Equilibrium constants for extractions of PICRAT with crown ethers in various extraction solvents at 25°C ($^{\theta}$)

Solvent	Crown ether	Log K_{ext}	K_D	Log K'_{ext}	$K_{D,L}$
CH_2Cl_2	WCr		0.02^{+}		
	DB18C6	6.58 ± 0.24	0.02		
	18C6		0.05	6.58 ± 0.70	0.87
	15C5		0.04	6.78 ± 0.59	2.00
	12C4		0.03	6.46 ± 0.74	1.00
$CHCl_3$	WCr		0.01^{+}		
	DB18C6	–	–		
	18C6		0.01	6.77 ± 0.66	4.14
	15C5		0.02	6.45 ± 0.841.17	
	12C4		–	–	
CCl_4	WCr	–	0.01^{+}		
	DB18C6∗	–	–		
	18C6		–	–	–
	15C5		–	–	–
	12C4		–	–	–
C_6H_6	WCr		0.00^{+}		
	DB18C6	–	–		
	18C6		0.00	5.13 ± 0.38	0.00
	15C5		0.01	5.96 ± 1.000.00	
	12C4		0.01	6.85 ± 0.00	0.00
C_7H_8	WCr		0.00^{+}		
	DB18C6	–	–		
	18C6		–	–	–
	15C5			–	–
	12C4		–	–	–
C_6H_{14}	WCr		0.01^{+}		
	DB18C6∗	–	–		
	18C6		–	–	–
	15C5			–	–
	12C4		–	–	–

∗ DB18C6 did not dissolve in CCl_4 and C_6H_{14}.
($^{\theta}$) Corr. Coefficient: 1.000.
$^{(+)}$ K'_D values.
WCr: Without Crown Ether.

The extractions of MOR were only studied for two solvents (CH_2Cl_2 and $CHCl_3$), the order being $CHCl_3 > CH_2Cl_2$. The equilibrium constants values between MOR and 18C6, DB18C6, 15C5, and 12C4 compounds were changed in the order of $CHCl_3 > CH_2Cl_2$; $CHCl_3 > CH_2Cl_2$; $CH_2Cl_2 > CHCl_3$ and $CHCl_3 > CH_2Cl_2$, respectively.

The equilibrium constants values between PICRAT and only solvent (without crown compounds), and 18C6, DB18C6, 15C5, and 12C4 decreased in the order of $CH_2Cl_2 > CHCl_3$, $CCl_4 > C_6H_{14}$; $CHCl_3 > CH_2Cl_2 > C_6H_6$; $CH_2Cl_2 \gg$ other solvents; $CH_2Cl_2 > CHCl_3 > C_6H_6$ and $C_6H_6 > CH_2Cl_2$, respectively. These results demonstrate that the influence of solvent for PICRAT extraction by crown complexing agents have been obtained at a moderate level by dichloromethane [26, 31, 32, 36].

With 4×10^{-5} M concentration of sodium dyes, the crown ether concentrations were varied from 4×10^{-5} to 2.5×10^{-3} M. It is shown in Table V that optimum crown concentrations versus standard anionic dyes concentrations were observed. 12C4 is too small to accommodate Na^+ since its cavity is only about 1.5 Å at best and the ionic diameter of Na^+ is nearly 2 Å [1, 37]. Another, and probably more serious difficulty is that 12C4 can provide only four donor groups and Na^+ prefers a solvation of a sandwich structure of stoichiometry $(crown)_2.Na^+A^-$ [38, 39].

The difference between 12C4 and the other crown ethers is especially obvious since the sodium-dyes with 12C4 are shown to exist as crown separated ion-pairs (sandwich complexes).

In this case, Na^+ is coordinated to eight oxygen atoms, but in the case of 15C5, Na^+ is coordinated to six oxygen atoms, five from the crown and one from water. As might be expected, the extraction complexation constant for 12C4 was found to be higher than for 15C5 in a few solvents and salts.

From the discussion above it was found that PAR is much more associated with crown compounds and the best extracted dye as the ion pair complexes (96%) than corresponding sodium-dyes (decrease in the order of PAR > EBT > MOR > PICRAT) [21–23].

Solvent media effects, and the anion in a salt-ligand system, play a fundamental role in both the stability of the ion-pair complexes, their solubilization and the resulting charge separation in solution [2, 31, 35, 36]. Since the effect of solvent is studied in this paper, justification of the results found should involve consideration of solvent properties and solvent-solute interactions. Three studied solvents are haloalkanes, two solvents are arenes and one is an alkane. The dielectric constants of the organic solvents used in this study are shown in Table I. Several correlations between the solvent properties and extraction efficiency have been obtained by Iwachido and coworkers [40].

Since in real extraction systems some amount of dye is soluble in organic solvent without crown compounds, the values of the solubility in organic solvents are also given in the first lines of Tables I–IV.

Table V. Effect of crown ether concentrations on the maximum extraction of anionic dyes of sodium salts from aqueous solution into organic phase. (These are numerical values of concentrations that are 1 : 1, 1 : 10, 1 : 20, 1 : 50 and 1 : 62.5 ratios ($[M_0^+]_w$: $[L_0]_{\text{org}}$) versus 4 × 10^{-5} M of constant anionic dye concentration). (∗)

Anionic dye	Crown ether	Solvent					
		CH_2Cl_2	$CHCl_3$	CCl_4	C_6H_6	C_7H_8	C_6H_{14}
PAR	DB18C6	80	200	–	200	–	250
	18C6	200	200	80	80	–	200
15C5	4^+	4^+	–	250	80	250	
12C4	250	250	250	250	250	250	
EBT	DB18C6	4^+	4^+	–	200	–	–
18C6	250	40	80	200	80	4^+	
15C5	250	250	250	4^+	–		
12C4	200	4^+	40	250	–	–	
MOR	DB18C6	40	4^+				
18C6	200	250					
15C5	40	80					
12C4	200	250					
PICRAT	DB18C6	250	–	–	–	–	–
18C6							
15C5	200	–	250	–	–		
12C4	250	–	–	–	–	–	

$^{(+)}$ Inital cation concentration $[M_0^+] = [L_0] = [A^-]$ in × 10^5.

(∗) Values are in mol L^{-1} × 10^5.

Though the effect of solvent polarity (Table I) on the extractability of complex ion-pairs was not investigated systematically, a preliminary test has shown that polar solvents, such as dichloromethane and chloroform, give rise to enhanced extractability [2, 32]. This observation is consistent with the results obtained by Frensdorff [41]. The polarity is represented best by Dimroth and Reichardt's solvent polarity parameter [42]. This work has shown that methylene chloride is found to be better than chloroform, carbon tetrachloride, benzene, toluene and n-hexane as an extractive solvent for the above sodium-dyes complexes of 18C6, DB18C6, 15C5, and 12C4 [2, 4, 35].

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