Effect of Solvent upon Competitive Liquid–Liquid Extraction of Alkali Metal Cations by Isomeric Dibenzo-16-crown-5-oxyacetic Acids [#]

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Abstract. The selectivity and efficiency of competitive liquid–liquid extraction of alkali metal cations into organic solvents containing *sym*-(octyl)dibenzo-16-crown-5-oxyacetic acid (**2**) and *sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxyacetic acid (**3**) have been determined. Solvents examined include: dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, toluene, *p*-xylene, chlorobenzene, 1,2-dichlorobenzene, and 1,2,3,4-tetrahydronaphthalene. The Na^+/K^+ and Na^+/Li^+ extraction ratios are highest in chloroform. The extraction selectivity is found to correlate with the diluent parameter (DP) of the organic solvent.

Key words. Lipophilic crown ether carboxylic acids, solvent extraction of alkali metal cations, organic solvent variation in extraction.

Comments by Dr Richard A. Bartsch

Although I never met Charlie Pedersen, his work provided the foundation for our present research effort in metal ion separations with macrocyclic multidentate ligands. Without his discovery of synthetic routes to crown ethers and the initial exploration of metal salt interactions with such molecules, it is unlikely that our program, which uses crown ethers with pendant acidic groups to perform metal ion separations in solvent extraction, liquid membrane, and ion exchange resin systems, would have developed. Thanks to you Charlie for allowing me to have so much fun with my chemistry.

1. Introduction

The potential of crown ethers (macrocyclic polyethers) as the next generation of specific metal ion extracting agents was markedly enhanced by the introduction of crown ethers which bear proton-ionizable groups. Metal ion extraction by such chelating agents does not involve concomitant transfer of the aqueous phase anion into the organic medium. This factor is of immense importance to potential

practical applications in which hard aqueous phase anions (chloride, nitrate, and sulfate) would be involved.

The influence of organic solvent variation upon the selectivity and efficiency of alkali metal cation extraction by 2-[(*sym*-dibenzo-16-crown-5)oxy]decanoic acid (**1**) has been examined [1]. For extractions conducted with lipophilic crown ether carboxylic acid **1** in chloroform, 1,1,1-trichloroethane, benzene, toluene, *p*-xylene and 1,2,3,4-tetrahydronaphthalene, formation of an oily second organic layer was noted for the last three solvents when the aqueous phase pH was ≥ 10. Despite this complication, it was noted that the extraction efficiency and Na^+ selectivity were much higher in chloroform than in other organic solvents.
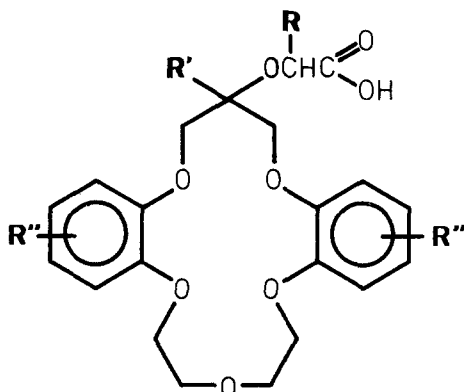
	R	R'	R''
1	C_8H_{17}	H	H
2	H	C_8H_{17}	H
3	H	H	$C(CH_3)_3$

Competitive liquid–liquid extractions of alkali metal cations by *sym*-(octyl)dibenzo-16-crown-5-oxyacetic acid (**2**) and *sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxyacetic acid (**3**) in a wider range of hydrocarbon and chlorinated hydrocarbon solvents have now been conducted. Since the complicating formation of an oily second organic layer at highly alkaline pH was not observed for **2** or **3**, these results provide a better opportunity to determine the influence of organic solvent variation upon the selectivity and efficiency of alkali metal cation extraction by lipophilic crown ether carboxylic acids. Dibenzo-16-crown-5-oxyacetic acids **1**, **2**, and **3** are structural isomers which differ only in the lipophilic group attachment site(s). Therefore, the influence of varying the attachment site for the lipophilic group upon extraction selectivity and efficiency may also be assessed.

2. Experimental

2.1. REAGENTS

The sources of inorganic reagents were the same as reported previously [2]. Syntheses of crown ether carboxylic acids **2** and **3** have been published [3, 4]. Reagent grade chloroform (Fisher) was shaken four times with deionized water to remove the stabilizing ethanol and saturate the chloroform with water. Reagent-grade dichloromethane (Mallinkrodt), carbon tetrachloride (Fisher), 1,2-dichloroethane (MCB), 1,1,1-trichloroethane, 1,2-dichlorobenzene, 1,2,3,4-tetrahydronaphthalene (Aldrich), benzene, chlorobenzene, toluene, and *p*-xylene (Baker) were used.

2.2. APPARATUS AND PROCEDURE

The apparatus and procedure for competitive liquid–liquid extractions of alkali metal cations (0.25M in each) from aqueous solutions of their chlorides and hydroxides into 0.050M solutions of **2** in organic solvents were the same as those reported previously [1].

For the competitive liquid–liquid extraction of alkali metal cations by **3**, a new micro-extraction technique was developed. An aqueous solution of lithium, sodium, potassium, rubidium, and cesium chloride (1.00 mL, 0.25M in each with 0.25M cesium hydroxide added for pH adjustment) and an organic solution of **3** (1.00 mL, 0.050M) in a 5-mL, stoppered centrifuge tube was agitated with a vortex mixer (Scientific Industries, Model K-350-G) for four minutes at room temperature (21–23°C). After centrifuging for four minutes, the equilibrium pH of the aqueous layer was measured with a Fisher Accumet Model 620 pH meter and a Sargent Welch S3001005 ultra-semimicro combination electrode. A 0.50 mL sample of the organic layer was transferred to a 5-mL centrifuge tube and aqueous hydrochloric acid (0.50 mL, 0.20M) was added. The tube was stoppered and the mixture was agitated for four minutes with the vortex mixer to strip the alkali metal cations from the organic phase into the aqueous phase. The tube was centrifuged for four minutes and concentrations of alkali metal cations in the aqueous phase were determined with a Dionex Model 2000i ion chromatograph. The reproducibility of the extraction procedure has been demonstrated previously [1].

3. Results

Results for the competitive liquid–liquid extraction of alkali metal cations (0.25M in each) for aqueous solutions into 0.050M solutions of lipophilic crown ether carboxylic acid **2** in eleven organic solvents are presented in Figure 1. The solvent series includes dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, toluene, *p*-xylene, 1,2,3,4-tetrahydronaphthalene, chlorobenzene, and 1,2-dichlorobenzene. Assuming formation of 1 : 1 crown ether carboxylate–metal ion complexes, the metal ion loading of all organic phases was quantitative when the equilibrium aqueous phase pH was 10. Extraction selectivity orders for the five alkali metal cations as well as the Na^+/K^+ and Na^+/Li^+ concentration ratios in the organic phases are given in Table I.

Organic phase concentrations of alkali metal cations as a function of the equilibrium aqueous phase pH for the isomeric lipophilic crown ether carboxylic acid **3** in eight organic solvents are shown in Figure 2. Organic phase metal ion loadings (82–94%), extraction selectivity orders, and selectivity ratios for Na^+/K^+ and Na^+/Li^+ are presented in Table II. In the absence of lipophilic crown ether carboxylic acid **2** or **3**, extraction of alkali metal cations into the organic phases was undetectable.

4. Discussion

4.1. ALKALI METAL CATION EXTRACTION SELECTIVITY AND EFFICIENCY

As would be predicted from comparison of the polyether cavity size and the diameter of the alkali metal cations [2], lipophilic dibenzo-16-crown-5 carboxylic
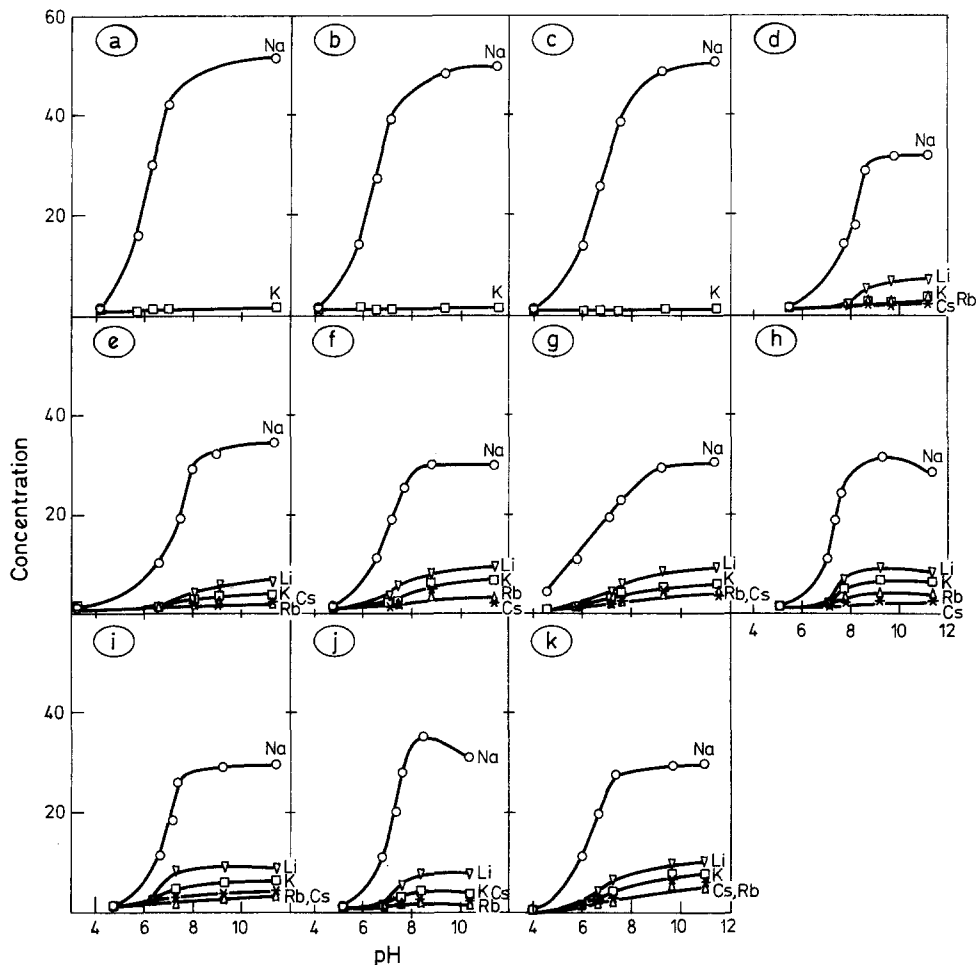
Fig. 1. Concentrations of metal cations ($M \times 10^3$) in the organic phase vs. the equilibrium pH of the aqueous phase for competitive extraction of alkali metal cations (0.25M each) by 0.050M **2** in (a) chloroform, (b) dichloromethane, (c) 1,2-dichloroethane, (d) 1,2-dichlorobenzene, (e) chlorobenzene, (f) 1,1,1-trichloroethane, (g) benzene, (h) toluene, (i) *p*-xylene, (j) 1,2,3,4-tetrahydronaphthalene and (k) carbon tetrachloride.

acids **2** and **3** exhibit competitive extraction selectivity for Na$^+$. However, the degree of selectivity is found to be markedly influenced by the identity of the organic solvent and the positioning of the lipophilic group within the extractant molecule (Figures 1 and 2, Tables I and II).

For competitive solvent extraction of alkali metal cations into chloroform, dichloromethane, and 1,2-dichloroethane by lipophilic crown ether carboxylic acid **2**, the selectivity order was Na$^+ \gg$ K$^+ >$ Li$^+ \geqslant$ Rb$^+$, Cs$^+$ with Na$^+/$K$^+$ ratios at pH = 10 of 71, 47 and 44, respectively (Table I). In contrast, for the remaining eight solvents of carbon tetrachloride, 1,1,1-trichloroethane, chlorobenzene, 1,2-dichlorobenzene, benzene, toluene, *p*-xylene, and 1,2,3,4-tetrahydronaphthalene, the

Table I. Selectivity in competitive extraction of alkali metal cations from aqueous solutions into organic solutions of lipophilic dibenzo-16-crown-5-oxyacetic acid **2** at pH = 10.0

| Solvent	Extraction Selectivity Order	Selectivity Ratio	
		Na^+/K^+	Na^+/Li^+
dichloromethane	$Na^+ \gg K^+ > Li^+, Cs^+ > Rb^+$	47	85
chloroform	$Na^+ \gg K^+ > Li^+ > Rb^+ > Cs^+$	71	77
carbon tetrachloride	$Na^+ > Li^+ > K^+ > Rb^+, Cs^+$	4.4	2.9
1,2-dichloroethane	$Na^+ \gg K^+ > Li^+ > Cs^+ > Rb^+$	44	49
1,1,1-trichloroethane	$Na^+ > Li^+ > K^+ > Rb^+, Cs^+$	4.9	3.7
benzene	$Na^+ > Li^+ > K^+ > Rb^+, Cs^+$	5.2	3.5
toluene	$Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$	5.1	3.4
p-xylene	$Na^+ > Li^+ > K^+ Cs^+ > Rb^+$	5.1	3.4
chlorobenzene	$Na^+ > Li^+ > K^+ > Rb^+, Cs^+$	8.8	4.3
1,2-dichlorobenzene	$Na^+ > Li^+ K^+, Rb^+, Cs^+$	13	5.7
1,2,3,4-tetrahydronaphthalene[a]	$Na^+ > Li^+ > K^+ > Cs^+ > Rb^+$	4.7	3.4

[a] At pH = 10.4.
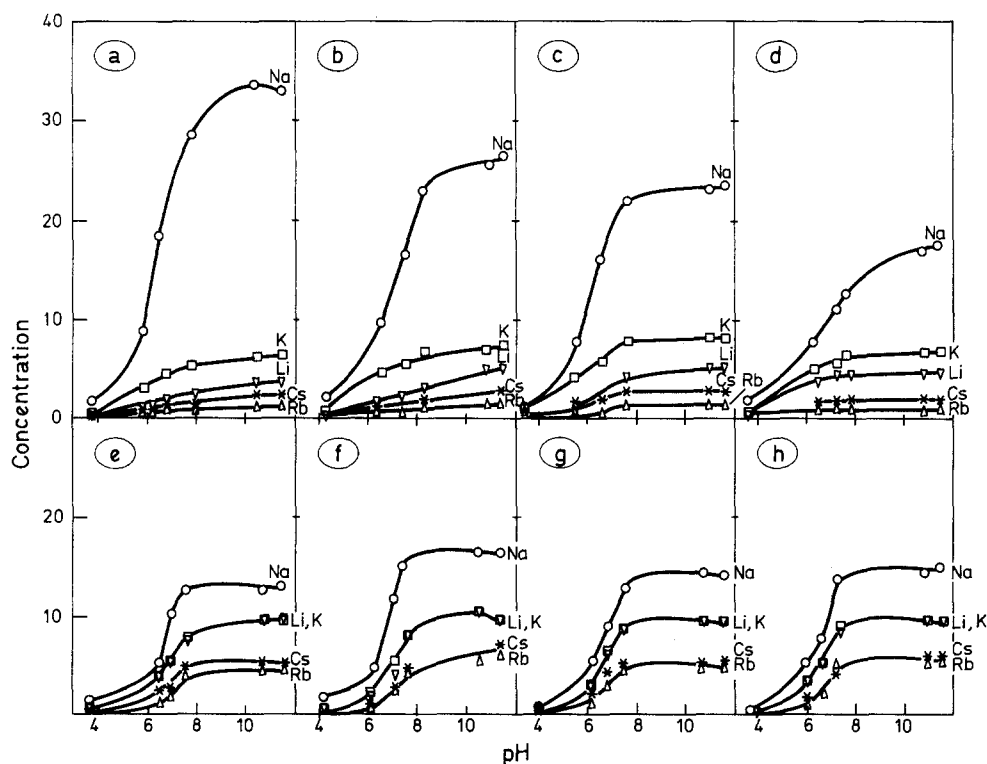
Fig. 2. Concentrations of metal cations ($M \times 10^3$) in the organic phase vs. the equilibrium pH of the aqueous phase for competitive extraction of alkali metal cations (0.25M each) by 0.050M **3** in (a) chloroform, (b) dichloromethane, (c) 1,2-dichloroethane, (d) 1,2-dichlorobenzene, (e) chlorobenzene, (f) benzene, (g) 1,1,1-trichloroethane, and (h) carbon tetrachloride.

Table II. Organic phase loading and selectivity in competitive extraction of alkali metal cations from aqueous solutions into organic solutions of lipophilic dibenzo-16-crown-5-oxyacetic acid **3** at pH = 11.0.

Solvent	Organic Phase Loading, %	Extraction Selectivity Order	Selectivity Ratio	
			Na^+/K^+	Na^+/Li^+
dichloromethane	82	$Na^+ > K^+ > Li^+ > Cs^+ > Rb^+$	3.7	5.5
chloroform	94	$Na^+ > K^+ > Li^+ > Cs^+ > Rb^+$	5.2	8.9
carbon tetrachloride	86	$Na^+ > Li^+, K^+ > Rb^+, Cs^+$	1.6	1.6
1,2-dichloroethane	82	$Na^+ > K^+ > Li^+ > Cs^+ > Rb^+$	3.1	4.0
1,1,1-trichloroethane	85	$Na^+ > Li^+, K^+ > Rb^+, Cs^+$	1.7	1.7
benzene	94	$Na^+ > Li^+, K^+ > Rb^+, Cs^+$	1.7	1.7
chlorobenzene	84	$Na^+ > Li^+, K^+ > Cs^+ > Rb^+$	1.9	1.7
1,2-dichlorobenzene	91	$Na^+ > K^+ > Li^+ > Cs^+ > Rb^+$	1.9	1.7

second best-extracted metal ion changed to Li^+ and the Na^+/Li^+ ratios were much lower (2.9–5.7). For this latter grouping of solvents, 1,2-dichlorobenzene gave the highest Na^+ selectivity and carbon tetrachloride the lowest. Metal ion loading of the organic phases was quantitative for all eleven solvents.

For the lipophilic crown ether carboxylic acid **3**, the extraction selectivity order was $Na^+ > K^+ > Li^+ > Cs^+ > Rb^+$ in chloroform, dichlorometane, 1,2-dichloroethane, and 1,2-dichlorobenzene with Na^+/K^+ ratios of 5.2, 3.7, 3.1, and 1.9, respectively. For the other four solvents of carbon tetrachloride, 1,1,1-trichloroethane, chlorobenzene, and benzene, the extraction selectivity order changed to $Na^+ > Li^+$, $K^+ > Rb^+$, Cs^+ with Na^+/Li^+ ratios of 1.6–1.7. The organic phase metal ion loading varied from 82–96% for **3** (Table II) with no apparent correlation between extraction efficiency and selectivity.

4.2. VARIATION OF THE LIPOPHILIC GROUP ATTACHMENT SITE

Solvent extractions of alkali metal cations into organic solvents by the isomeric lipophilic dibenzo-16-crown-5-oxyacetic acids **1** [1], **2**, and **3** have now been conducted for the common solvents of chloroform, 1,1,1-trichloroethane, and benzene. For each of these three solvents, the extraction selectivity with **2** is much higher than with **1** or **3**. (The Na^+/K^+ ratios for **1**, **2**, and **3** when the equilibrium aqueous phase pH = 10–11 are 8.9 [1], 71, and 5.2, respectively.) Examination of CPK space-filling models reveals that when the lipophilic octyl groups attached to the central carbon of the three-carbon bridge in **2** extends away from the polar polyether ring then the carboxylic acid group is positioned directly over the crown ether cavity. Thus the enhanced extraction selectivity noted for crown ether carboxylic acid **2** may be attributed to pre-organization of the binding site [5, 6, 7].

4.3. EFFECT OF SOLVENT UPON EXTRACTION SELECTIVITY

Rationalization of the extraction selectivities observed for lipophilic crown ether carboxylic acids **2** and **3** should involve considerations of solvent properties and

solvent–solute interactions. Five of the solvents investigated are haloalkanes, two are haloarenes, and four are alkylarenes. Selected physical properties of these eleven organic solvents are presented in Table III. In the first four columns, values for the molar volume [8], viscosity [9], dielectric constant [10], and dipole moment [8] are given. Since some amount of water is also present in the organic solvent during extraction, the solubility of water in the solvent [8] is listed in column five.

The solubility parameter (δ) as well as its hydrogen-bonding component (δ_h) are given in the next two columns. The solubility parameter is the square root of the cohesive energy density of the solvent and contains contributions from three types of interactions [11]. Thus

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

where δ_d, δ_p, and δ_h are dispersion, polar and hydrogen-bonding components, respectively, of the solubility parameter.

The penultimate column contains the value of the normalized parameter of solvent polarity, E_T^N. Reichardt [10] has recommended use of the normalized solubility parameter instead of E_T. The E_T^N value is defined according to Equation 2

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} = \frac{E_T(\text{solvent}) - 30.7}{32.4} \tag{2}$$

using water and tetramethylsilane (TMS) as extreme reference solvents. The last column in Table III contains the diluent parameter, DP [11], of the solvent.

Some researchers have attempted to correlate extraction complex stability with the dielectric constant of the solvent [13] and the ion solution energy [14]. Correlations between solvent properties and extraction efficiency have been obtained by Iwachido, Masayoshi, Naito, and Toei [15]. In that paper, the extractability of potassium picrate from aqueous solutions into solutions of the non-ionizable crown ether 18-crown-6 in 57 organic solvents was investigated. Good correlation between the picrate distribution coefficient and the solubility parameter (δ) was noted. In addition, a good correlation between the picrate distribution coefficient and the solvent polarity parameter (E_T) was observed.

Shmidt [16] has introduced the empirical diluent parameter (DP) as a 'universal constant' for characterizing the diluent in extraction system that obey the relationship

$$\log D = k + (a)(DP) \tag{3}$$

in which D is the distribution coefficient and k and a are constants characteristic of the extraction system. Solvent properties which may be related to DP are those which describe the polarity of the solvent and its cohesiveness. The polarity is best represented by E_T and the cohesiveness of a solvent is best described by δ. In a recent study, Marcus [12] found the best correlation between DP, E_T and δ was

$$DP = -(10.6 \pm 0.93) + (0.241 \pm 0.026)E_T + (0.217 \pm 0.077)\delta \tag{4}$$

For 23 solvents (excluding chloroform) a correlation coefficient of 0.972 was obtained.

Returning now to the matter of selectivity in competitive alkali metal cation solvent extraction by the lipophilic dibenzo-16-crown-5-oxyacetic acids **1**, **2**, and

Table III. Selected properties of organic solvents used in competitive extractions of alkali metal cations by lipophilic dibenzo-16-crown-5-oxyacetic acids 2 and 3.

Solvent	V^a	η^b	ε^c	μ^d	sol.^{e}	δ^f	δ_h^f	E_T^{Ng}	DP^h
dichloromethane	64.5	0.499	8.93	1.14	0.198	9.88	3.0	0.309	–
chloroform	80.7	0.596	4.81(20°)	1.15	0.072(23°)	9.49	2.8	0.259	4.5
carbon tetrachloride	97.1	0.965	2.23	0.00	0.010(24°)	8.55	0.3	0.052	1.6
1,2-dichloroethane	79.4	0.887	10.37	1.86	0.150(20°)	9.78	2.0	0.327	3.5
1,1,1-trichloroethane	100.4	0.903	7.25(20°)	1.57	0.034	8.50	1.0	0.170	–
benzene	89.4	0.603	2.27	0.00	0.063	9.17	1.0	0.111	2.3
toluene	106.8	0.587	2.38	0.31	0.033	8.91	1.0	0.099	1.8
p-xylene	123.9	0.644	2.27(20°)	0.02	–	8.77	1.5	0.074	1.8
chlorobenzene	102.2	0.799	5.62	1.54	0.033	9.68	1.0	0.188	2.4
1,2-dichlorobenzene	113.0	1.324	9.93	2.27	0.309	10.05	1.6	0.225	2.7
1,2,3,4-tetrahydronaphthalene	136.8	2.202	2.77	0.60	–	9.50	1.4	0.093	–

[a] Molar volume in cm^3/mol from Ref. [8].
[b] Viscosity at 20°C in (mN)s/m^2 from Ref. [9].
[c] Dielectric constant at 25°C from Ref. [10].
[d] Dipole moment in Debye units (10^{-18} esu) from Ref. [8].
[e] Water solubility in the organic solvent at 25°C from Ref. [8].
[f] Solubility parameter in (cal/cm^3)$^{1/2}$ with its hydrogen-bonding component from Ref. [11].
[g] Normalized E_T^N values from Ref. [10].
[h] Diluent parameter from Ref. [12].

3, the Na^+/K^+ selectivity ratio for **2** decreases as the organic solvent is varied: chloroform $\gg$ dichloromethane, 1,2-dichloroethane $\gg$ 1,2-dichlorobenzene $>$ chlorobenzene $>$ benzene, toluene, p-xylene $>$ 1,1,1-trichloroethane $>$ 1,2,3,4-tetrahydronaphthalene $>$ carbon tetrachloride (Table II). For **3**, the Na^+/K^+ selectivity ratio decreases as the diluent is varied: chloroform $>$ dichloromethane $>$ 1,2-dichloroethane $>$ chlorobenzene, 1,2-dichlorobenzene $>$ 1,1,1-trichloroethane, benzene $>$ carbon tetrachloride. From data reported [1] for **1**, the Na^+/K^+ selectivity ratio when the equilibrium aqueous phase pH $= 10$ decreases as the solvent is varied: chloroform $>$ 1,2,3,4-tetrahydronaphthalene, toluene $>$ 1,1,1-trichloroethane $>$ benzene $> p$-xylene. Although there is some variation in solvent ordering for the lipophilic dibenzo-16-crown-5-oxyacetic acids **1**, **2**, and **3**, the overall trends are quite similiar for the three structural isomers. Since the range of Na^+/K^+ selectivity ratios and the number of different solvents are larger for **2**, the comparison of extraction selectivity with solvent properties is most appropriate for this lipophilic crown ether carboxylic acid.

Comparison of the Na^+/K^+ selectivity ratios for **2** (Table I) with selected properties of the organic solvents (Table III) reveals no correlation with the molar volume, viscosity, dielectric constant, dipole moment, or water solubility in the organic solvent. The poor correlation of the solubility parameter (δ) with the Na^+/K^+ extraction selectivity ratio is improved when only the hydrogen-bonding component (δ_h) of the solubility parameter is considered. In this case, only the δ_h values for chloroform, xylene and 1,2,3,4-tetrahydronaphthalene fail to show ordering consistent with the observed selectivity. For the comparison between the Na^+/K^+ selectivity ordering and E_T^N values, good correlation is noted except for the E_T^N values of chloroform, xylene, and 1,1,1-trichloroethane.

The best correlation between Na^+/K^+ extraction selectivity and a solvent property is found for Shmidt's empirical diluent parameter (*DP*). Unfortunately, *DP* values have not been determined for dichloromethane, 1,1,1-trichloroethane and 1,2,3,4-tetrahydronaphthalene. However for the remaining eight solvents, the Na^+/K^+ extraction ratio and *DP* values have the same ordering. Particularly important is the correlation between the high Na^+/K^+ extraction selectivity observed for **2** in chloroform with the highest *DP* value for any of the solvents examined.

5. Conclusions

Selectivity in competitive liquid–liquid extraction of alkali metal cations by the lipophilic dibenzo-16-crown-5-oxyacetic acid isomers **1**, **2**, and **3** is strongly influenced by variation of the organic solvent and the lipophilic group attachment site. Pre-organization of the binding site in **2** by appropriate location of the lipophilic group produces excellent Na^+ selectivity with $Na^+/K^+ = 71$ and $Na^+/Li^+ = 77$ for extractions into chloroform. For **2** the Na^+/K^+ extraction selectivity ratio correlates well with the diluent parameter (*DP*) of the organic solvent. The extraction efficiencies observed for lipophilic dibenzo-16-crown-5-oxyacetic acids **2** and **3** are higher than those reported [1] and exhibit no apparent correlation with the organic solvent parameters.

Acknowledgements

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