Available online at www.sciencedirect.com
SCIENCE DIRECT®
Talanta 65 (2005) 819–823
Talanta
www.elsevier.com/locate/talanta

Short communication

Association constants of dibenzo[3*n* + 2]crown-*n* ethers using steady-state fluorescence spectroscopy

Hülya Tuncer[a], Çakıl Erk[b,*]

[a] *Chemistry Department, Fırat University, TR-23169, Elazığ, Turkey*
[b] *Chemistry Department, İstanbul Technical University, Maslak, TR-34469, İstanbul, Turkey*

Received 24 March 2004; received in revised form 7 July 2004; accepted 22 July 2004
Available online 17 September 2004

Abstract

The steady-state fluorescence spectra of cation complexes of fluorophore macrocyclic ethers have been studied for the estimation of 1:1 association constants, and perchlorate salts of Li^+, Na^+, K^+ Rb^+ and Pb^{2+} complexing with dibenzo[23]crown-9, dibenzo[26]crown-10, and *sym*-dibenzo[26]crown-10, were investigated. The fluorescence emission maximum of the free and the various ligand/cation mixtures of complexed crown ethers were measured at room temperature in AN. The concentrations of chromophore crown ether were obtained from nonlinear calibration plots. The 1:1 stoichiometry of association constants (K_{ass}) were calculated using the equation, $1/K_{ass}\,[L_o] = (1 - nP)^n(1 - m)^m/P$ with linear best fit of plots depending on $1/[L_o]$ where $P = P_C/[1 + (m - 1)P_C]$ and P_C is the mole fraction of *n/m* ratio of the complexed ligand. The association constants of cations, K_{ass}, displayed the cation selectivities depending on the cation radii and the macrocyclic ether size, and Pb^+ was found to give the strongest association with such crown ethers.

Keywords: Dibenzocrown ethers; Cation association constant; Fluorescence spectroscopy

1. Introduction

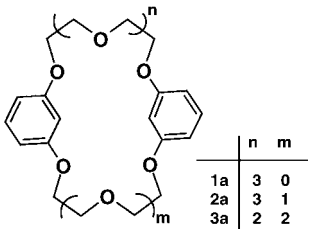
There is a very rapid development in clinical and environmental analytical techniques for qualitative and quantitative estimation of ions that requires to provide real-time monitoring. The methods for specific analysis of small quantities are in significant needs of chemical processes. Currently available methods are either limited to selective probes or large concentrations of analyte solutions. Macrocyclic ethers have been known to complex with the alkali cations selectively [1–3]. The effective chromophores-linked crown ethers have received much attention recently as the optical utility of fluorescence-based chemosensors. Lumophores of various ion choices and selectivities are used in very low concentrations [4–9]. However, conjugation of π electrons of chromophores enhances the sensitivity of the sensor behaviour.

Benzocrown ethers may be less sensitive sensors than the naphthalene derivatives [10–12], and coumarins accordingly display more sensitive chemosensor roles [8–9]. However, the cation binding selectivity is the prime importance of the analytical use of a chemosensor [10–12].

In this work, dibenzo[3*n* + 2]crown-*n* type macrocycles [13–19] involved photo physical effects with fluorophore benzo groups upon cation complex formation. **1a**, **2a** and **3a** were studied for the 1:1 ratio of Li^+, Na^+, K^+, Rb^+, and Pb^{+2} association constants (as shown in Scheme 1) with spectrofluorometry, which is very sensitive technique measuring both emission and excitation intensities of fluoroionophores in concentrations of 10^{-5}–10^{-7} mol L^{-1} [12]. Cation complexing induce the changes in triplet energy relative to excited singlet, $S_1 \rightarrow T_1$ and ground state $T_1 \rightarrow S_0$ and the increased phosphorescence lifetime of luminescent macrocycles gave complexation enhanced quenching fluorescence spectra, CEQFS. If fluorescence lifetime is reduced and

* Corresponding author. Tel.: +90 212 285 3227; fax: +90 212 285 6386.
E-mail address: erk@itu.edu.tr (Ç. Erk).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.07.050



Scheme 1. Raj

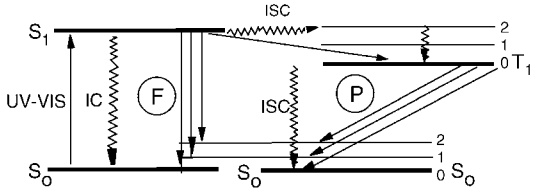


Fig. 1. Fluorescence and phosphorescence transitions.

phosphorescence lifetime is increased complexation enhanced fluorescence spectra, CEFS, is observed (Fig. 1) [6–8].

2. Experimental

The fluorescence spectra were measured with a JASCO Luminescence spectrometer, model 750, in dry acetonitrile, AN, within a fluorophore concentration of 10^{-3}–10^{-5} mol L^{-1} in 10 mm quartz cells. Ligands and metal salts were dried under vacuum and used immediately with the identical cation–ligand concentrations arranged with a micro syringe. The aliquots were inserted into the acetonitrile containing stirred fluorescence cell (3.0 mL) and standard spectrometer software was used for the measurements. The slit widths were 5 nm due to optimised concentrations that gave minimum quenching in the experimental range. The peak emission intensities at 303 nm relative to isoemissive points were taken as unity instead of peak areas where excitation wavelength is 280 nm. The mole fraction, P_c of the complexed macrocycle, is obtained from the fluorescence emission intensities of free and uncomplexed ligand in a complex solution, (Tables 1 and 2, Figs. 2 and 3).

Table 2
The 1:1 metal complexing data of [3n + 2]crown-*n* macrocyclic ethers

No	Cation	ln *K*	log *K*	$-\Delta G$ (kJ M^{-1})	Correlation coefficient R^2	Intercept
1a	Li^+	8.01	3.48	20.09	0.991	+4.25
1a	Na^+	6.71	2.92	16.84	0.999	+1.29
1a	K^+	7.15	3.11	17.93	0.985	+1.65
1a	Rb^+	7.63	3.31	19.14	0.996	+10.14
1a	Pb^{2+}	9.77	4.24	24.49	0.997	−0.32
2a	Li^+	7.13	3.09	17.87	0.997	−0.47
2a	Na^+	5.48	2.38	13.74	0.999	−5.70
2a	K^+	6.23	2.70	15.62	0.999	−3.92
2a	Rb^+	4.74	2.06	11.89	0.988	−1.00
2a	Pb^{2+}	6.53	2.84	16.73	0.998	+0.56
3a	Li^+	7.62	3.31	19.11	0.999	−1.22
3a	Na^+	4.81	2.09	12.07	0.999	−11.42
3a	K^+	7.57	3.29	18.98	0.998	+1.03
3a	Rb^+	6.16	2.67	15.44	0.998	+0.46
3a	Pb^{2+}	6.45	2.80	16.18	0.998	−3.19

The association constants, K_{ass} were calculated according to Eqs. (1)–(10) as we reported recently [10,11]. The macrocyclic ligand, mL, forms a complex, $A^+{}_nL_m$, with a cation nA^+ where P_C is the mole fraction of the cationic complex, $A^+{}_nL_m$. However, experimentally, we used equivalent cation, $[A_o{}^+]$ and macrocyclic ligand, $[L_o]$ concentrations so that, $[A_o{}^+] = [L_o]$.

$$nA^+ + mL \leftrightarrow A^+{}_nL_m \quad (1)$$

$$K_{ass} = \frac{[A^+{}_nL_m]}{[A^+]^n[L]^m} \quad (2)$$

$$[A^+] = [A_o{}^+] - n[A^+{}_nL_m] \quad (3)$$

$$[L] = [L_o] - m[A^+{}_nL_m] \quad (4)$$

Table 1
1:1 Complexing data of **1a**/$Pb(ClO_4)_2$ complex in AN at 303 K

$[L_o]$ (mol L^{-1})	Int(free)	[L] (mol L^{-1})	Int(complex)	$P_{complex}$	$[L_o]/1000$	$(1*P)^2/P$
0.00005	80.0	0.000033	59.5	0.3335	30.0	1.3318
0.00008	103.5	0.000044	75.0	0.3749	22.9	1.0422
0.00010	125.1	0.000057	90.0	0.4326	17.6	0.7441
0.00013	142.2	0.000065	98.0	0.4831	15.4	0.5530
0.00015	152.8	0.000071	103.5	0.5037	14.0	0.4888
0.00018	167.7	0.000081	111.0	0.5386	12.4	0.3951
0.00020	177.5	0.000087	116.0	0.5657	11.5	0.3334
0.00023	184.1	0.000093	120.0	0.5860	10.8	0.2924
0.00025	189.7	0.000098	124.0	0.6003	10.2	0.2660
0.00028	194.9	0.000103	127.0	0.6213	9.8	0.2307
0.00030	198.4	0.000106	129.0	0.6361	9.5	0.2081
0.00033	204.6	0.000111	133.0	0.6517	9.0	0.1861
0.00035	207.4	0.000116	136.0	0.6741	8.6	0.1575
0.00038	209.7	0.000119	138.0	0.6781	8.4	0.1528
0.00040	213.1	0.000121	139.5	0.6964	8.2	0.1324
0.00043	215.9	0.000124	141.0	0.7100	8.1	0.1184

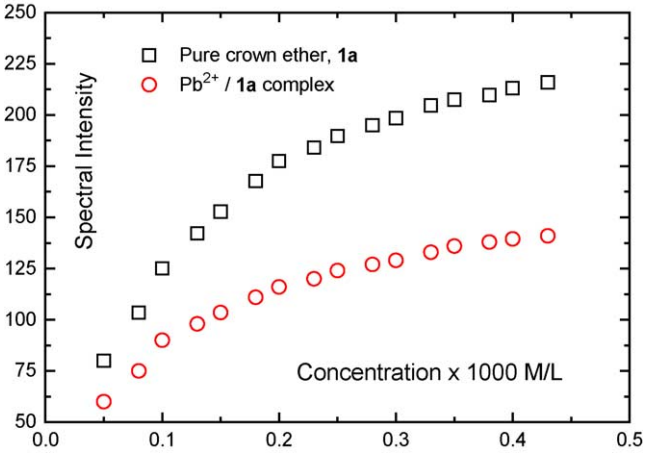


Fig. 2. Fluorescence intensities of **1a** and **1a**/$Pb(ClO_4)_2$ CEQFS of a complex depending on the concentration in AN, λ_{max} = 303 nm at 303 K, excitation λ_{max} = 280 nm, (see Table 2).

$$K_{ass} = \frac{[A^+{}_nL_m]}{([A_o{}^+] - n[A^+{}_nL_m])^n([L_o] - m[A^+{}_nL_m])^m} \quad (5)$$

$$P_C = \frac{[A^+{}_nL_m]}{[L] + [A^+{}_nL_m]} \quad \text{and}$$

$$P_C = \frac{[A^+{}_nL_m]}{[A^+] - n[A^+{}_nL_m] + [A^+{}_nL_m]} \quad (6)$$

$$P_C = \frac{[A^+{}_nL_m]}{[A^+] - (n-1)[A^+{}_nL_m]} \quad (7)$$

However, $P = P_c/[1 + (m - 1)P_c]$ is used for calculation of association constants, K_{ass}

$$K_{ass}[L_o]^{n+m-1} = \frac{P}{(1-nP)^n(1-mP)^m} \quad (8)$$

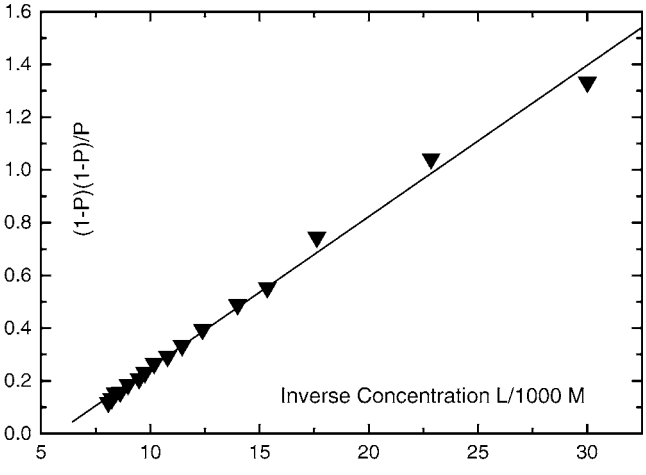


Fig. 3. The plot of 1:1, (*n*:*m*), complex of **1a**/$Pb(ClO_4)_2$ according to Eq. (10), Table 1.

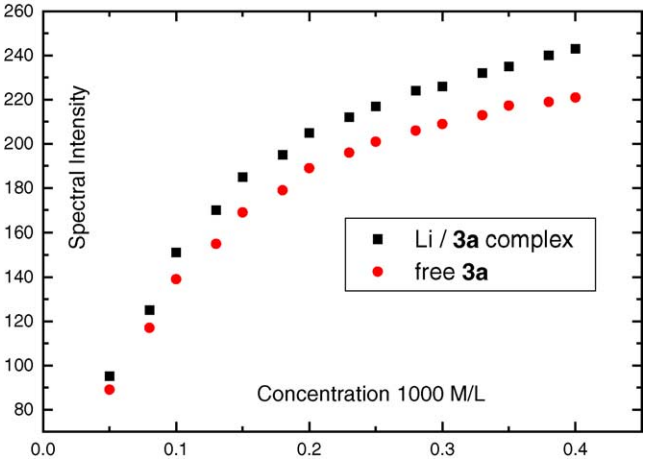


Fig. 4. Fluorescence intensities of **3a** and **3a**/$LiClO_4$.CEFS of a complex depending on the concentration in AN, λ_{max} = 303 nm at 303 K, excitation λ_{max} = 280 nm.

$$\frac{1}{(K_{ass}[L_o]^{n+m-1})} = \frac{(1-nP)^n(1-mP)^m}{P} \quad (9)$$

$$\frac{1}{(K_{ass}[L_o])} = \frac{(1-nP)(1-mP)}{P} \quad \text{if } n = m = 1 \quad (10)$$

Therefore, the inverse of $[L_o]$ versus calculated values of $(1 - mP)^2/P$ give the 1/1 (*n*/*m*) of K_{ass} from inverse of the slope (Figs. 4 and 5) [21–25].

3. Results and discussion

There are numerous techniques to study the cation complexing of neutral ligands [1–3]. Spectrofluorometry is a very sensitive and selective technique as an analytical tool that measures both emission and excitation intensities of a fluorescent molecule which is usually influenced by different cations via the electronic interactions [4–12]. Morita et al. have presented the fluorescence non-radiative and radiative deactivation rates of dibenzo[18]crown-6 alkali complexes at vari-

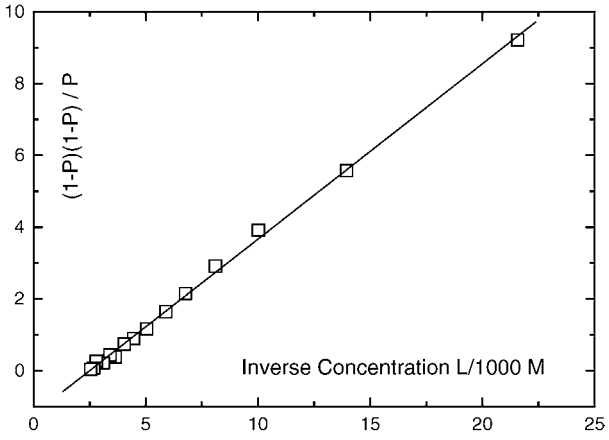


Fig. 5. The plot of 1:1, (*n*:*m*), complex of **3a**/$LiClO_4$ according to Eq. (10).

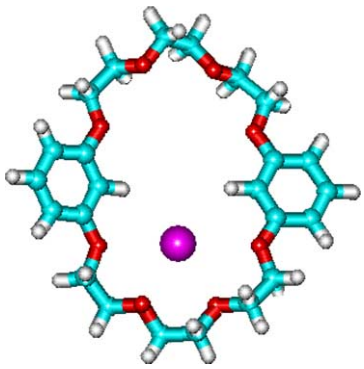


Fig. 6. The illustration of 1:1 ratio of a metal complex of **3a**.

ous temperatures showing the strong K^+/benzo[18]crown-6 complex evidencing utility of the fluorescence spectroscopy for ion binding [4].

The generic question is how to transduce a cation binding even into a fluorescent event, $S_1 \rightarrow S_0$. Radiative (fluorescence and phosphorescence, $T_1 \rightarrow S_0$) transfers and non-radiative (intersystem crossing, ISC, $S_1 \rightarrow T_1$, and internal conversion, IC) transfers are taken place, (see Fig. 1).

Scablonski diagram displays that the mechanisms of the fluorescence lifetimes are changed if the quenching of the excited states is involved due to the incorporating donor and following the different photo physical routes that may involve, likewise, the energy transfer, internal charge transfer, electron transfer, intersystem crossing, ISC, as well as the heavy atom effect [6–8].

However, in most cases, fluorescence emission spectra are less affected due to cation ejection during excited state. Accordingly, the phosphorescence displayed from $\pi \rightarrow \pi^*$ triplet state is observed from the length of lifetimes when the cation fits into the crown cavity. The emission component of $\pi \rightarrow \pi^*$ origin is significantly quenched if oxygen lone pairs, which were held by a cation like, K^+ or Na^+, are de-conjugated from the rest of the π electron system. We have previously reported the synthesis and metal selectivity of crown ethers with lumophore moieties using steady-state fluorescence spectroscopy with the same method [9–12].

The cation selectivity of dibenzo[3*n* + 2]crown-*n* has been studied not very much in details [13–20]. However, we now report some of their association constants of large crown ethers using steady-state fluorescence spectroscopy with Eqs. (1)–(10) [21]. Recently, we have successfully estimated the association constants using ion selective electrodes, ISE, in water, dioxane/water and THF/water solutions using Eqs. (1)–(10) [22–26].

However, the present work particularly deals with bis-*m*-phenyl ended glycols like crown ethers of complicated structures due to their conformational behaviour to encapsulate the different size of cations, (Fig. 6) [21]. The reliability of the analytical tool with the linear regression technique enabled us to determine the association constants precisely, Eqs. (1)–(10) [9–11]. However, quenching of the both free and complexed iono-chromophore due to increased concentration in solutions is a difficult analytical problem even for the 10^{-5}–10^{-7} mol L^{-1} range, Figs. 2 and 3. The quantitative measurements of steady-state fluorescence emission with various concentrations usually give the nonlinear plots due to quenching of fluorescence intensity upon the increased concentrations. The calibration plots are not linearly concentration depended, Figs. 2 and 3, therefore, the determination of free and complexed macrocyclic ligand concentrations obtained from non-linear calibration plots should be used with a linear regression method for the calculation of cation association constants (Eqs. (1)–(10), Figs. 4 and 5).

Presented results primarily showed the flexible cation complexing role of dibenzo[3*n* + 2]crown-*n* [7–20]. They mostly possessed the strong complexes with different radii of metals despite of the large cyclic structures and hindering hydrogen in the aromatic ring, (Fig. 6, Table 1). Mostly, strongest complexed metal in this work is Pb^{2+} that has been also reported for common benzo[3n]crown-*n* molecules [3]. However, strong Li^+ complexing depends on the size of macrocyclic structure due to cation coordination ability towards such macrocycles, likewise, **1a** complex, (Fig. 6), which also displays the essential role of such type of macrocycles for cation binding selectivity. However, Na^+ forms moderate but selective complexes interestingly with the large cavities of macrocycles and exhibited good cation radii-macrocyclic size relationship, (see Fig. 6). The observed K^+ and Rb^+ stabilities of large radii of cations showed the flexibility of such molecules upon complexing [18,21]. The di(*m*-dioxo)benzo groups, as shown in Scheme 1, interestingly regulate cation binding in solutions.

Acknowledgements

The authors acknowledged the support of the work by TUBİTAK with a project, TBAG-2026.

References

[1] J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.
[2] F. Vögtle, Supramolecular Chemistry, Wiley, Chichester, 1991.
[3] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruenning, Chem. Rev. 91 (1991) 1721.
[4] H. Shizuka, K. Takada, T. Morita, J. Phys. Chem. 84 (1980) 994.
[5] O.S. Wolfbeis, H. Offenbacher Monath für Chem. 115 (1984) 647.
[6] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1515) (1997) (references cited).
[7] J. Bourson, B. Valeur, J. Phys. Chem. 93 (1998) 3871.
[8] B. Valeur, I. Leray, Coord. Chem. Rev. 205 (2000) 3.
[9] A. Göçmen, M. Bulut, Ç. Erk, Pure Appl. Chem. 65 (1993) 447.
[10] A. Göçmen, Ç. Erk, J. Incl. Phenom. 26 (1996) 67.
[11] A. Göçmen, Ç. Erk, Talanta 53 (2000) 37.
[12] Ç. Erk, Ind. Eng. Chem. Res. 39 (2000) 3582.
[13] J.F. Stoddart, Pure Appl. Chem. 60 (1988) 467 (references cited).
[14] Y. Delaviz, H.W. Gibson, Macromolecules (1992) 4859.

[15] E. Weber, H.J. Köhler, K. Panneerselvam, K.K. Chacko, Perkin Trans. 1 (1990) 1599.
[16] Thomas J.D.R., Analyst (1991) 1211.
[17] E. Luboch, S. Fonari, A. Yu, V.K. Simonov, J. Belski, F. Biernat, Russian Chem. Bull. 44 (1995) 2353.
[18] G.W. Buchanan, M. Lefort, A. Moghimi, C. Bensimon, J. Mol. Struct. 415 (1997) 267.
[19] H. Tuncer, Ç. Erk, Talanta 59 (2003) 303.
[20] H. Tuncer, Ç. Erk, Supramol. Chem. 11 (2002) 49.
[21] G. Yapar, Ç. Erk, J. Incl. Phenom. 42 (2002) 145 (references cited).
[22] A. Göçmen, Ç. Erk, Fresenius J. Anal. Chem. 347 (1993) 472.
[23] Ç. Erk, Ü. Çakır, B. Çiçek, Mikrochim. Acta 132 (1999) 79.
[24] Ç. Erk, Ü. Çakır, B. Çiçek, J. Prakt. Chem. 341 (6) (1999) 584.
[25] Ü. Çakır, H.İ. Uğraş, Ç. Erk, Supramol. Chem. 16 (2004) 193.
[26] G. Yıldız, G. Yapar, Ç. Erk, Talanta (2004). in press.