Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **23:** 41–51, 1995.

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A Competitive Polarographic Study of Complexation of Ammonium, Anilinium, Hydrazinium and Pyridinium Ions with Some Macrocyclic Ligands in Binary Ethanol–Water Mixtures Using a Pb(II)/Pb(Hg) Couple as an Electrochemical Probe

MOHAMMAD REZA GANJALI
Department of Chemistry, Tehran University, Tehran, Iran.

and

MOJTABA SHAMSIPUR*
Department of Chemistry, Razi University, Kermanshah, Iran.

(Received: 9 May 1995; in final form: 23 August 1995)

Abstract. The formation of ammonium, anilinium, hydrazinium and pyridinium ion complexes with the crown ethers 18-crown-6 (18C6) and 1,10-diaza-18-crown-6 (C22) and the cryptand C222 in different binary ethanol–water mixtures has been studied by a competitive polarographic method using a Pb^{2+}/Pb(Hg) couple as a sensitive electro-chemical probe. Lead ion was found to form very stable complexes with the ligands used, in all solvent mixtures studied; Pb^{2+}–C222 cryptate revealed a pronounced 'cryptate effect' compared to the corresponding complexes with the monocyclic crown ethers used. In all solvent mixtures studied, the stability of the resulting 1 : 1 complexes between the protonated amines and macrocyclic ligands used vary in the order C22 > C222 > 18C6. The observed selectivity order of each macrocyclic ligand used for different protonated amines is discussed based on the chemical and structural features of the host–guest partners in solution. In all cases studied there is an inverse linear relationship between the complex formation constants and the mole fraction of water in the mixed solvent.

Key words. Protonated amines, macrocyclic ligands, complexation, mixed solvent, polarography.

1. Introduction

Macrocyclic [1] and macrobicyclic polyethers [2] have been extensively used as interesting model compounds for the study of molecular effect on membrane permeability [3–6], due to their many similarities to cyclic antibiotics and biological transport agents. Because of the fundamental role of ammonium ion in different biological processes [7,8], the interaction between organic and biogenic ammonium

* Author for correspondence.

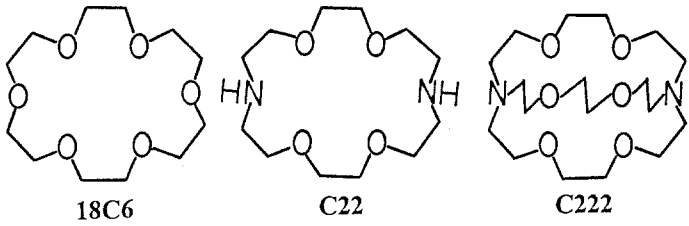

Fig. 1. Structures of the ligands.

ions and macrocyclic ligands has received considerable attention during the past two decades [9–18].

We recently reported the thermodynamics of ammonium ion complexation with several crown ethers and cryptands in some nonaqueous solvents [17,18]. In the present paper, the $Pb^{2+}/Pb(Hg)$ couple was employed as a suitable electrochemical probe to study the complexation of ammonium, anilinium, hydrazinium and pyridinium ions with 18-crown-6 (18C6), 1,10-diaza-18-crown-6 (C22) and cryptand C222 (Figure 1) in binary ethanol–water mixtures at 25 °C by a competitive polarographic method [19,20].

2. Experimental

All chemicals used were of the highest purity available from Merck Chemical Company. Perchlorate salts of ammonium, anilinium, hydrazinium and pyridinium ions were prepared from the 1 : 1 interaction of perchloric acid with ammonia, aniline, hydrazine and pyridine, respectively. The resulting perchlorate salts were recrystallized three times from triply distilled deionized water and vacuum dried over P_2O_5 for 72 h. Macrocyclic ligands 18C6, C22 and C222 were purified and dried using previously reported methods [21,22]. Reagent grade tetrabutylammonium perchlorate (TBAP) was used without further purification except for drying over P_2O_5 *in vacuo* for 72 h. Absolute ethanol (EtOH) and triply distilled deionized water were used for the preparation of the solvent mixtures by volume.

The polarographic measurements were carried out with a dropping mercury electrode (DME) in a three-electrode arrangement. A Pt wire with a considerably larger surface area than that of the DME was used as the auxiliary electrode. A saturated aqueous calomel reference electrode (SCE) was used, having a bridge containing the base electrolyte of the electrolyzed solution. The base electrolyte was 0.025 M in TBAP. All solutions were deaerated for 10 min with pure argon and an inert atmosphere was maintained over the solutions during the reaction. In order to keep the amines used completely in their protonated forms, the pH of all solutions prepared was kept at a value of about 3.0.

The polarographic measurements were made with a POLARECORD E-506 Metrohm Herisau instrument. The usual instrumental parameters were: constant drop time 0.50 s; mercury height, 50 cm; scan rate, 5.0 mV s^{-1}; pulse duration,

0.020 s, pulse magnitude, 25 mV. All experiments were carried out at 25.0 ± 0.1 °C.

Determination of the formation constants of Pb^{2+}-macrocycle complexes was based on the measurement of the shifts in $E_{1/2}$ (half-wave potential) or E_p (peak potential) brought about by addition of an increasing amount of the ligands [23]. In the EtOH–water mixtures used, the reversible amalgam-forming reduction of the complexes results in a shift of the $E_{1/2}$ or E_p to more negative values in accordance with the Lingane equation [24]:

$$\Delta E_p = E_p^{Pb-macrocycle} - E_p^{Pb} = -(RT/2F)(\ln K_f^{Pb} + m \ln[\text{macrocycle}]_t \quad (1)$$

where $E_p^{Pb-macrocycle}$ and E_p^{Pb} are the peak potentials of the complexed and free metal ions, respectively, m is the stoichiometry of the complex (i.e. macrocycle/cation ratio), K_f^{Pb} is the complex formation constant and $[\text{macrocycle}]_t$ is the analytical concentration of the macrocycle. In all experiments, the concentrations of TBAP (0.025 M) and Pb^{2+} ion (0.25 mM) were kept constant and the concentration of ligand added varied (2.5–7.5 mM).

Addition of the protonated amine (10–30 mM), M^+, to 0.025 M TBAP solutions containing Pb^{2+} (0.25 mM) and macrocyclic ligand (2.5–7.5 mM) shifts the reversible cathodic peak potential of the Pb^{2+}-macrocycle complex to more positive values in such a way that $-E_p^{Pb} < -E_p^{Pb-macrocycle-M} < -E_p^{Pb-macrocycle}$. Sample polarograms are shown in Figures 2 and 3. The formation constant of M^+-macrocycle complexes can then be evaluated from the measurement of such positive shifts in the E_p of the corresponding Pb^{2+} complexes upon addition of protonated amines. The procedural details and the equations used are given elsewhere [19,20].

3. Results and Discussion

It was found that the Pb^{2+}/Pb(Hg) couple yields essentially reversible polarograms in a range of solvents including water [25,26] and alcohol [27]. Addition of the macrocyclic ligands used to a 0.25 mM Pb^{2+} solution in different EtOH–water mixtures containing 0.025 M TBAP shifts the dc half-wave potentials ($E_{1/2}$) and differential pulse peak potentials (E_p) for the reduction of complexed lead towards more negative values. In all Pb^{2+}-macrocycle systems studied, the reduction waves of the complexed ion were found to be reversible and diffusion controlled. The logarithmic analysis of the polarograms in dc mode showed a linear dependence of $\log(i_d - i)/i$ vs E_{dc} with the slopes corresponding to a reversible reduction (29 ± 2 mV).

The variation of ΔE_p as a function of $\log [L]_t$ was linear for all Pb^{2+} complexes, indicating the formation of a single complex in solution. The slopes of these straight lines gave a value of $m \cong 1$, which suggests the formation of a 1 : 1 complex in solution. The formation constants of Pb^{2+} complexes were obtained by computer

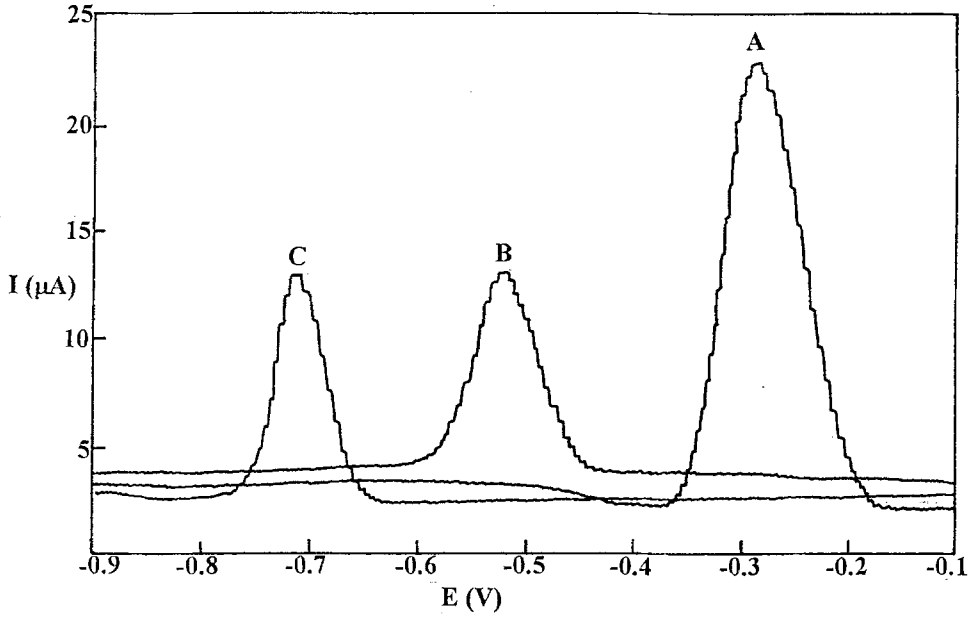

Fig. 2. Effect of NH_2–NH_3^+ ion on differential pulse polarograms of Pb^{2+}–C22 complex in 0.025 M of TBAP in 90% ethanol solution: (A) Pb^{2+}, 0.25 mM; (B) Pb^{2+}, 0.25 mM + C22, 2.5 mM + NH_2–NH_3^+, 10.0 mM; (C) Pb^{2+}, 0.25 mM + C22, 2.5 mM.

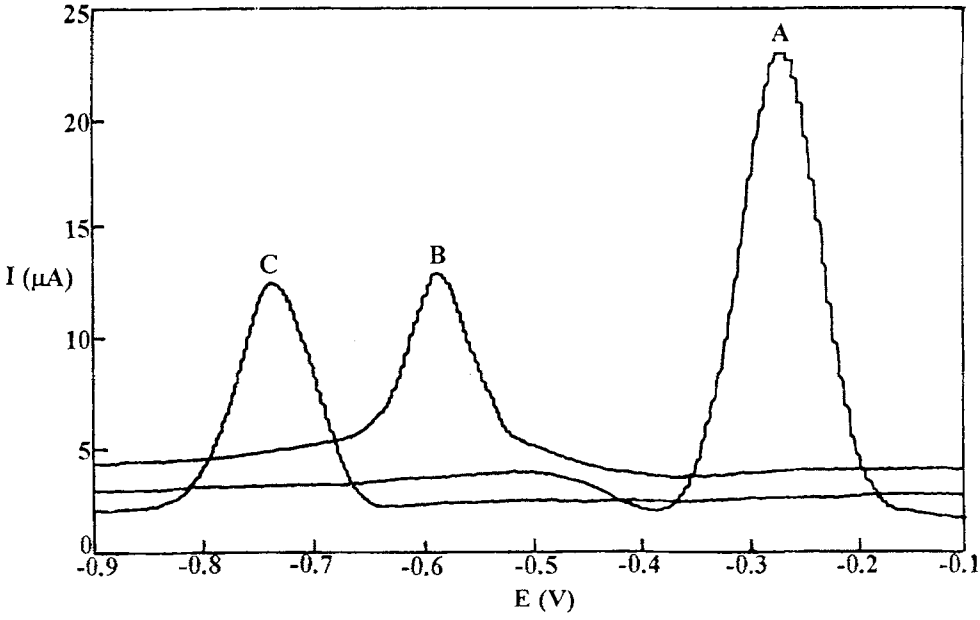

Fig. 3. Effect of $C_5H_5NH^+$ ion on differential pulse polarograms of Pb^{2+}–C22 complex in 0.025 M of TBAP in 70% ethanol solution: (A) Pb^{2+}, 0.25 mM; (B) Pb^{2+}, 0.25 mM + C22, 2.5 mM + $C_5H_5NH^+$, 10.0 mM; (C) Pb^{2+}, 0.25 mM + C22, 2.5 mM.

TABLE I. Formation constants of Pb^{2+} complexes with macrocycles 18C6, C22 and C222 in various ethanol-water mixtures at 25 °C.

Solvent composition, vol.% ethanol in water[a]	log K_f		
	18C6	C22	C222
90	6.86 ± 0.08	11.73 ± 0.09	15.53 ± 0.09
80	6.13 ± 0.07	10.46 ± 0.04	14.63 ± 0.09
70	5.30 ± 0.07	9.66 ± 0.06	13.63 ± 0.08
60	4.80 ± 0.09	8.46 ± 0.06	12.46 ± 0.07
0	4.21[b]	7.01[c]	12.0[d]

[a] These solutions have the following X_{EtOH}: 90% (0.73), 80% (0.55), 70% (0.42), 60% (0.32).
[b] Data from Ref. 26.
[c] Data from Ref. 57.
[d] Data from Ref. 48.

TABLE II. Formation constants of different protonated amines with macrocycles 18C6, C22 and C222 in various ethanol-water mixtures at 25 °C.

Ligand	Solvent composition vol.% ethanol	log K_f			
		$C_6H_5NH_3^+$	$C_5H_5NH^+$	NH_2–NH_3^+	NH_4^+
18C6	90	3.63 ± 0.02	4.39 ± 0.04	3.43 ± 0.04	3.33 ± 0.02
	80	3.50 ± 0.03	4.27 ± 0.03	3.39 ± 0.04	3.22 ± 0.03
	70	3.41 ± 0.02	4.19 ± 0.03	3.33 ± 0.02	3.18 ± 0.02
	60	3.37 ± 0.02	3.99 ± 0.03	3.23 ± 0.03	3.10 ± 0.03
C22	90	6.58 ± 0.05	4.74 ± 0.05	6.00 ± 0.07	3.98 ± 0.02
	80	6.39 ± 0.04	4.70 ± 0.05	5.88 ± 0.05	3.93 ± 0.03
	70	6.20 ± 0.03	4.58 ± 0.04	5.69 ± 0.05	3.86 ± 0.02
	60	6.12 ± 0.02	4.52 ± 0.05	5.45 ± 0.05	3.84 ± 0.02
C222	90	3.6 ± 0.3	4.39 ± 0.02	5.22 ± 0.07	3.39 ± 0.02
	80	3.63 ± 0.02	4.30 ± 0.02	5.10 ± 0.05	3.37 ± 0.02
	70	3.52 ± 0.02	4.21 ± 0.03	4.99 ± 0.02	3.30 ± 0.02
	60	3.49 ± 0.02	4.10 ± 0.03	4.92 ± 0.03	3.23 ± 0.02

fitting of the polarographic data to Equation (1) and the results are presented in Table I. The corresponding reported values in aqueous solution are also included for comparison. The formation constants of various protonated amine complexes with the macrocycles used were determined in different solvent mixtures by the competitive polarographic method described above, using the Pb^{2+}/Pb(Hg) couple as a suitable electrochemical probe. The resulting values are summarized in Table II.

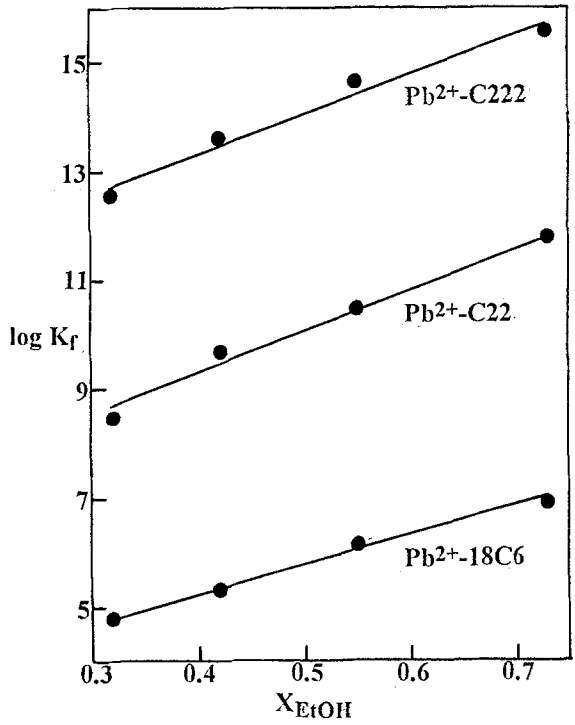

Fig. 4. Variation of the stabilities of different Pb^{2+} ion complexes with X_{EtOH} of the binary mixtures.

The data given in Tables I and II clearly indicate the important influence of the solvent properties in all complexation reactions studied. As can be seen, in all cases, the stability of the complexes decreases significantly with increasing amount of water in the mixed solvent. It is well known that the solvating ability of solvents, as expressed by the Gutmann donicity scale [28], has a great influence on both the thermodynamics [17, 21, 29–32] and kinetics [33–35] of complexation reactions. The solvating ability of EtOH (DN = 19) [28] is much lower than that of water (DN = 33) [36]. It is thus reasonable to expect that the addition of water to EtOH will decrease the extent of interaction between the macrocycle donor atoms and the cations used.

It is interesting to note that, in all complexes studied, log K_f varies linearly with the mole fraction of ethanol (X_{EtOH}) in the mixed solvents (Figures 4 and 5). We have recently observed the same trend for various metal ion complexes with both macrocyclic [37–41] and classical [42–44] ligands in a variety of mixed solvents. It seems reasonable to assume that the preferential hydration of the cations is mainly responsible for such a monotonic dependence of the stability constants on the solvent mixture *composition*.

From Table I, it is obvious that the stability of Pb^{2+} complexes with different macrocycles varies in the order C222 > C22 > 18C6. It should be noted that all

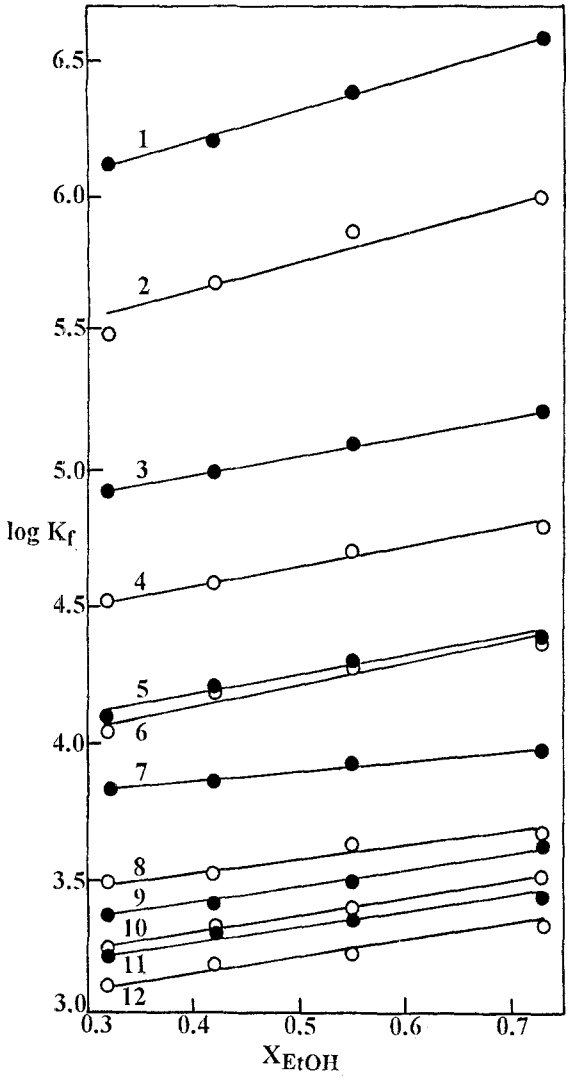

Fig. 5. Variation of the stabilities of different protonated amine-macrocycle complexes with X_{EtOH} of the binary mixtures: (1) $C_6H_5NH_3^+$–C22, (2) NH_2–NH_3^+–C22, (3) NH_2–NH_3^+-C222, (4) $C_5H_5NH^+$–C22, (5) $C_5H_5NH^+$–18C6, (6) $C_5H_5NH^+$–C222, (7) NH_4^+–C22, (8) $C_6H_5NH_3^+$–C222, (9) $C_6H_5NH_3^+$–18C6, (10) NH_2–NH_3^+–18C6 (11) NH_4^+–C222, (12) NH_4^+–18C6.

three ligands used in this study have about the same cavity radii of 14 Å [45] which is well suited to enclose lead ion with an ionic radius of 1.2 Å [46]. However, the substitution of two oxygen atoms by two nitrogens in the 18C6 macrocyclic ring increases the stability of Pb^{2+} ion very significantly [47]. It is also evident that the Pb^{2+}-C222 cryptate shows a rather sharp increase in stability (about four orders of magnitude), in comparison with the Pb^{2+}–C22 complex. It is well known that Pb^{2+}

ion forms a cryptate-type inclusion complex uith C222 [45,48]; consequently, a pronounced 'cryptate effect' is observed, which involves such a large enhancement in complex stability.

The data given in Table II clearly indicate that, in the case of all protonated amines used, the stability of the resulting 1 : 1 complexes vary in the order C22 > C222 > 18C6. Since the theoretical [49,50] and experimental results [51] reveal that in NH_4^+ and R—NH_3^+ ions the positive charge is mainly distributed over the H-atoms (and not located on the nitrogen atom, as implied by the valence bond picture), their binding with macrocyclic crown ethers will result from the electrostatic interaction of the amine hydrogen atoms and the electron donating hetero atoms of the ring. (i.e. N^+—H· · ·heteroatoms). Macrocycles of the 18C6 type are recognized as good receptors for primary ammonium ions through tripod H-bonding [9–18]. It is well known that the tetrahedral R—NH_3^+ cations bind to three of the available six heteroatoms in the 18-membered rings, so that the R-group protrudes upward from the centre of, and perpendicular to, the mean plane of the heteroatoms [8, 11, 16, 17, 52]. However, it has been shown that, when the macrocyclic ring contains a pyridine nitrogen, its interaction with an α-(1-naphthyl) ethylammonium cation involves an appreciable contribution from π–π overlap between the aromatic group of the cation and the pyridine group of the macrocycle [16]. Since N^+—H· · ·N hydrogen bonding is stronger than N^+—H· · ·O [9, 16, 53], it is not surprising to observe a significant increase in the stability of the protonated amine complexes by substitution of two oxygen atoms by two —NH— groups in the 18C6 macrocyclic ring. On the other hand, although the connection of a —$CH_2CH_2OCH_2CH_2OCH_2CH_2$— bridge onto the C22 ring, which results in the formation of a rigid macrobicyclic ligand C222, is expected to enhance the stability of the resulting amine complexes [10, 18], an opposite effect was observed in this work. This could be most probably because the size of cations is too large to penetrate inside the rigid cavity of C222.

From the stability data given in Table II, the selectivity order of each macrocyclic ligand used for different protonated amines in various ethanol–water mixtures can be summarized as follows:

$$C22: C_6H_5NH_3^+ > NH_2—NH_3^+ > C_5H_5NH^+ > NH_4^+;$$

$$C222: NH_2—NH_3^+ > C_5H_5NH^+ > C_6H_5NH_3^+ > NH_4^+;$$

$$18C6: C_5H_5NH^+ > C_6H_5NH^+ > NH_2—NH_3^+ > NH_4^+.$$

There are at least four factors which can make significant contributions to the stability of the protonated amine complexes with macrocyclic ligands: (1) the number of hydrogen bonds available for host-guest interaction; (2) steric hindrance of guest groups; (3) electronic withdrawing or donating effects of guest groups and (4) the extent of ionic solvation of the protonated amines.

As can be seen, among the different protonated amines used, the ammonium ion forms the least stable complexes with the host macrocycles. This is most probably due to the relatively strong solvation of ammonium ion in aqueous and alcohol solutions [54, 55].

In the case of cryptand C222, a successful host-guest interaction requires at least the partial penetration of the protonated amines inside the rigid cavity of the macrocycle [9, 10]. Thus, it seems reasonable to assume that the steric hindrance of the protonated amines is the dominant factor in determining the stability of the resulting C222 cryptates. Since the NH_2—NH_3^+ ion has a lower steric hindrance than C_6H_5—NH_3^+ ion, the formation of a more stable C222 complex with the former cation is not unexpected. It is interesting to note that, despite the existence of only one N—H proton in the structure of $C_5H_5NH^+$ available for H-bonding, it forms a more stable complex with C222 than the C_6H_5—NH_3^+ ion. This is most probably due to the much easier penetration of the former cation inside the C222 cavity than that of the latter one.

On the other hand, in the case of C22 and 18C6–amine complexes, the steric hindrance of the guest groups does not seem to play a dominant role in the complexation processes, since the cation can sit above the plane of the host macrocycles to form H-bonds with some donating atoms of the rings. Thus, due to the stronger electron withdrawing effect of the phenyl group than that of the NH_2— group, the anilinium ion forms more stable complexes with these monocyclic hosts than the hydrazinium ion. As seen from the observed selectivity orders, pyridinium ion has an exceptional behavior in complexation with the 18C6 macrocycle. While the cation with only one available hydrogen atom for H-bonding is expected to form weaker complexes than anilinium and hydrazinium ions with the host molecules (such as that observed in the case of C22), it forms the most stable complex with 18C6, among the four protonated amines used.

The pyridinium ion is a planar cation in which the positive charge is mainly localized on the —NH group [56]. Molecular models show that this cation can partially penetrate inside the cavity of 18-crowns, so that the positive nitrogen atom can presumably have some interactions with all six donating atoms of the ring. Thus, it is not unexpected for pyridinium ion to form the most stable complex with 18C6 among the protonated amines used.

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