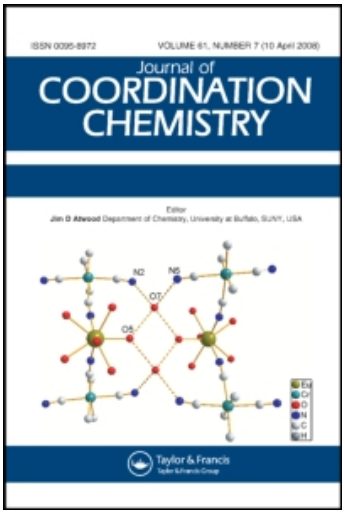


**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Cu(II), Zn(II), AND Pb(II) STABILITY CONSTANTS OF CYCLAM AMPHIPHILES

Dhananjay B. Puranik[a]; Alok Singh[a]; Eddie L. Chang[a]
[a] Center for Bio/Molecular Science and Engineering, Washington, D.C.

**To cite this Article** Puranik, Dhananjay B. , Singh, Alok and Chang, Eddie L.(1996) 'Cu(II), Zn(II), AND Pb(II) STABILITY CONSTANTS OF CYCLAM AMPHIPHILES', Journal of Coordination Chemistry, 39: 3, 321 — 331
**To link to this Article: DOI:** 10.1080/00958979608024340
**URL:** http://dx.doi.org/10.1080/00958979608024340

*J. Coord. Chem.*, 1996, Vol. 39, pp. 321–331
Reprints available directly from the publisher
Photocopying permitted by license only



# Cu(II), Zn(II), AND Pb(II) STABILITY CONSTANTS OF CYCLAM AMPHIPHILES

DHANANJAY B. PURANIK, ALOK SINGH and EDDIE L. CHANG*

*Center for Bio/Molecular Science and Engineering, Code 6900, Naval Research Laboratory, Washington, D.C. 20375-5348*

*(Received 19 January 1996; Revised 22 April 1996; In final form 17 June 1996)*



1-Hexadecyl-1,4,8,11-tetraazacyclotetradecane (hexadecyl cyclam) and 1-(3,7,11,15-tetramethyl) hexadecyl-1,4,8,11-tetraazacyclotetradecane (tetramethylhexadecyl cyclam) have been synthesized and their deprotonation and ligand-metal formation constants, K, determined for Cu(II), Zn(II) and Pb(II). The coupling of a long hydrocarbon chain to a ring nitrogen decreased the general ability of the cyclam ring to complex with metal ions. The greatest effect appeared to be for Cu(II) decreasing from a pK of 27 for cyclam to about 17. The titrations were fitted by HYPERQUAD and the concentrations of the intermediate complexes obtained as a function of pH. Metal-ligand complexes $LMH_2^{4+}$, $LMH_{2+}$ and $LM_{2+}$ can co-exist through a wide pH range. We have also calculated a composite metal-binding constant, K′, to reflect more accurately the overall ability of these ligands to bind a metal at any particular pH. K′, which is 14.6 for (hexadecyl cyclam)-Cu(II), is constructed from the concentrations of all the metal-chelated species at pH = 7. Generally, K′ is much lower than K.

*Keywords*: copper(II); zinc(II); lead(II); cyclam; amphiphiles

Cyclic amine 'chelates' are among the strongest metal chelators known.[1] The high metal-affinity of these azamacrocyclic molecules is, in part, attributed to the 'macrocyclic effect', as first described by Cabbiness and Margerum.[2] The high metal-affinity and selectivities of cyclic amines make them attractive as systems for metal sensors,[3–4] as redox systems[5] and for water remediation as ion flotation collectors.[6]

The transformation of cyclam into an amphiphile is useful for applications in remediation of water, as well as in non-aqueous media-although such modifications affect the properties that make cyclam potentially useful. Modification of the ring size of the macrocyclic ligands alters the 'selectivity' of ring complexation for different metals.[7–12] In contrast, coupling of short, saturated hydrocarbons

* Author for correspondence.

to the ring carbons of cyclam does not appear to alter significantly either its metal chelating or metal-selectivity properties.[1,6] However, less is known concerning the effect of attachment through the ring-nitrogens. In particular, no studies have been done on the effect long N-hydrocarbon chains have on the deprotonation and metal-binding constants of cyclam.[4–6] In this report, we describe the synthesis of 1-hexadecyl-1, 4, 8, 11-tetraazacyclotetradecane (hexadecyl cyclam, HDC)[5] and 1(-3, 7, 11, 15 tetramethyl)-1, 4, 8, 11-tetraazacyclotetradecane (tetramethyl hexadecyl cyclam, TMHDC), and their metal-binding properties for the series of metal ions: Cu(II), Zn(II) and Pb(II). HDC and TMHDC were selected as model compounds for their ability both to bind divalent cations with a high affinity and to sequester hydrophobic solute molecules. TMHDC, in addition, will potentially have a higher buoyancy than HDC, due to the presence of the methyl groups, which should be advantageous for ion-flotation applications.



## METHODS

### Materials

The fluorophore, prodan (6-propionyl-2-dimethylaminonaphthalene), was purchased from Molecular Probes, Inc. (Eugene, OR) and used without further purification.

### Synthesis of N-hexadecyl cyclam (HDC)

HDC was prepared according to the literature.[5,13] In summary, a chromium-cyclam complex was prepared following published procedures. The complex was then neutralized with sodium carbonate followed by reaction with a slight excess of hexadecyl bromide. Demetallation with successive acid-base treatment yielded the desired product. $^{1}$H-NMR ($CDCl_3$): 2.89, 3.00, 3.12, 3.25 (all multiplets, 20 H), 1.94 (m, 2H), 1.35(m, 2H), 1.12(m, 26H), 0.74(t,3H);[13] CMR($CDCl_{13}$): 14.1, 22.6, 29.2, 29.3, 29.4, 29.6, 31.8, 47.8, 49.6, 50.6, 51.1, 52.5, 53.8, 54.2; HRMS (electrospray technique) $[M+Na]^+$ 447, $[M+K]^+$ 463.

### Preparation of the intermediate 3.7.11.15-tetramethylhexadecanol

Palladium on charcoal (5% Pd-C, 1.0 g) was added to a solution of phytol (20 g, 67.4 mmol) in 100 mL methamol. The solution was then shaken under a hydrogen atmosphere overnight in a Parr Hydrogenator. The suspension was filtered and the residual Pd charcoal was washed with 100 mL methamol and dried over sodium

sulfate. The evaporation of the solvent gave 15 g (75%) of a clear, colorless, viscous liquid. $^1$H NMR ($CDCl_3$) 0.84–0.9 (m, 15H), 1.1–1.4 (overlapping m, 24 H), 3.67 (m, 2 H); $^{13}$CMR $CDCl_3$ 11.0, 19.6, 19.7, 22.6, 22.7, 24.3, 24.5, 24.8, 28.0, 29.5, 32.8, 37.3, 37.4, 39.5, 61.2 ppm. IR 2955, 2865, 1482, 1378, 1261, 1168 and 1092 cm$^{-1}$.

### Preparation of the intermediate 3.7.11.15-Tetramethylhexadecylbromide

3, 7, 11, 15-Tetramethylhexadecanol (4.0 g, 11.4 mmol) was stirred with $PBr_3$, (0.43 ml, 1.23 g, 4.54 mmol overnight. The oil was dissolved in $CHCl_3$, washed with water (1x), 5% $NaHCO_3$ (1x) and dried over $CaCl_2$. Evaporation gave 2.8 g (79%) of the bromide as a clear colorless oil. $^1$H NMR ($CDCl_3$) 0.84–0.9 (m, 15H), 1.1–1.4 (overlapping m, 24 H), 3.42 (m, 2 H), $^{13}$CMR $CDCl_3$ 11.4, 18.9, 19.0, 19.2, 19.7, 19.8, 22.6, 22.7, 24.2, 22.4, 24.8, 28, 31, 32, 32.7, 34, 38, 39.5, 40 ppm. IR 3368, 2962, 2924, 2871, 1469, 1384, 1068 cm$^{-1}$.



### Preparation of 3.7.11.15-tetramethylhexadecyl cyclam (TMHDC)

TMHDC was prepared from the bromide derivative according to the literature procedure.[13] For $^1$H NMR ($CDCl_3$) 0.7 (m, 15H), 1.1–1.4 (overlapping m, 24 H), 1.59–2.56 (m, 20 H). $^{13}$CMR $CDCl_3$ 11.0, 18.8, 19.4, 22.3, 22.4, 24.1, 24.4, 25.4, 27.6, 29.1, 31.0, 32.2, 34.0, 36.1, 37.0, 39.0, 47.0, 47.2, 48.4, 49.0, 49.1, 49.8, 50.5, 53.0, 53.1, 53.5. HRMS (electrospray technique) $[M+Na]^+$ 503, $[M+K]^+$ 519.

The proton and carbon NMR spectra observed for the compounds are consistent with those expected.

The protonated amine surfactants HDC·4HCl and TMHDC·4HCl were prepared by dissolving the surfactant in 95% ethanol followed by the addition of conc. HCl. The precipitate was then separated and re-treated with conc. HCl. HCl was then removed and the precipitate dried under high vacuum for 4–5 days. The Metal salts employed were KCl, $KNO_3$, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $Pb(NO_3)_2$ and $Hg(NO_3)_2$ which were used directly without purification. Major IR (KBr) peaks of HDC·4HCl were: 3500(vs), 2938(s), 1622(m), 1450(s) cm$^{-1}$ and major IR (KBr) peaks of TMHDC·4HCl were: 3447(vs), 2924(s), 1653(m), 1457(s) cm$^{-1}$.

### Titration of HDC and TMHDC

50 mL of either $1.0 \times 10^{-3}$ M HDC·4HCl or $1.0 \times 10^{-3}$ M TMHDC·4HCl were titrated against NaOH to obtain metal-free titration curves. Titrations of the ligands in the presence of metal ions were performed with ligand:metal ratios of either 1:11 or 1:1. The mixtures were allowed to stand overnight before titration.

Each titration used freshly prepared carbonate-free 0.1 M NaOH solution, standardized against potassium hydrogen phthalate. Titrations were performed with an Orion 920A digital pH meter with the electrode standardized against pH 7.00 and 4.01 buffer standards prior to each titration. Excess salts of 0.10M KCl for Cu and Zn and 0.10M $KNO_3$ for Pb were employed for the titrations.

## Fluorometry and light-scattering measurements of the critical micelle concentration (c.m.c.)

The c.m.c. was determined by monitoring the fluorescence of prodan as a function of surfactant concentration. 1 mM HDC samples were prepared with a stock aqueous solution of prodan (10 μM) at pH 10.1 (KOH). In order to keep the fluorophore concentration constant, serial dilutions were performed with 10 μM (pH 10.1) prodan aqueous solution. Fluorescence of prodan was measured with an SLM 8000 fluorometer (SLM-Aminco, Urbana, IL). Excitation was at 360 nm and the emission spectra taken from 370 to 600 nm. The ratio of fluorescence values at 522 nm to 440 nm, which compares the signals arising from polar and hydrophobic environments,[14–15] was plotted as a function of concentration. The intersection of the falling and relatively constant slopes of the curve were used to estimate the c.m.c.[16]

Light-scattering was used to determine the c.m.c. of HDC, as a function of concentration and pH. Total scattered light at 90° was measured with a Coulter N4MD sub-micron particle analyzer (Coulter, Hialeah, FL). The counts per second (cps) were plotted against concentration and the method of intersection of 2 slopes was used to define the c.m.c. For the onset of aggregation as a function of pH (or **a** the number of equivalents of base added), 1 mM HDC was titrated as described in the previous section and the scattered light at 90° measured as a function of pH.

## Computer calculation of the stability constants

An analytical method was first used to estimate the initial deprotonation and Cu-stability constants of HDC.[12, 17–18] Using this analytical approach, we found values for the four deprotonation constants of HDC. A more detailed analysis of the solution species' concentrations was then obtained by using the above analytical results as initial input for HYPERQUAD, a suite of programs designed for analyzing chemical equilibria. A description of HYPERQUAD and its antecedents can be found in the literature.[19] By fitting the titration curves computationally, we were able to estimate the extent of protonated and hydroxide complexes in solution and their individual influences on the titration results.

## RESULTS

The c.m.c. of HDC, as a function of concentration at pH 10.1, was measured by fluorescence and light-scattering measurements and found to be 0.17 and 0.20 ± 0.02 mM, respectively. As a function of pH, the 'critical micellar pH' was found to be at pH 8.5 ± 0.5 for 1.0 mM HDC solution (data not shown).

Titration curves for HDC alone, and with Cu(II), and similar curves for TMHDC with Zn, are shown in Figures 1a and 2a. The most prevalent species for each metal-ligand titration, as determined by HYPERQUAD, are plotted in Figures 1b and 2b.

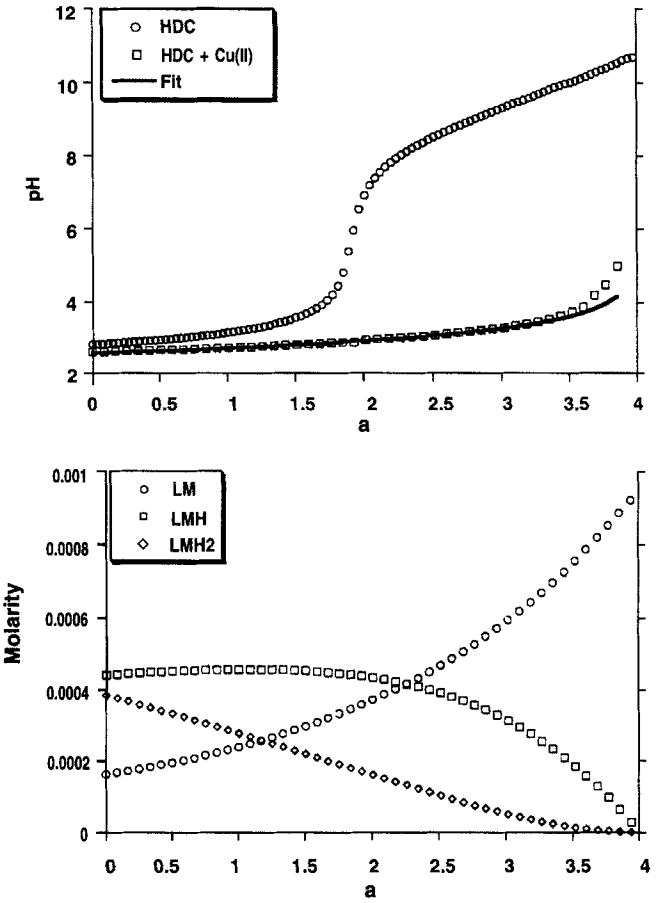


FIGURE 1 Titration curves for (the protonated) HDC and HDC: Cu(II) at 10:1 ratio. 1a: For HDC, 50 mL of 1.00 mM HDC·4HCl in 1M KCl, titrated with 0.971NaOH; for HDC·4HCl + Cu(II), 25 mL of 0.0247 M HDC·4HCl and 0.275 M $CuSO_4$ in 1M KCl with 0.1035 M NaOH. Line fit is from HYPERQUAD. 1b: The most significant species concentrations, as determined from HYPERQUAD, for the HDC·4HCl + Cu(II) titration curve.

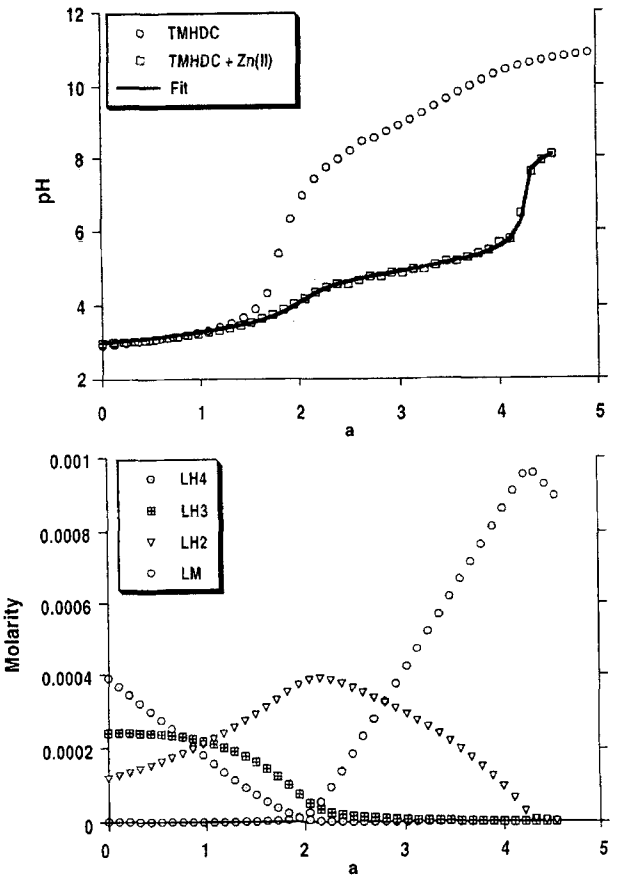


FIGURE 2 Titration curves for (the protonated) TMHDC and TMHDC with 1:1 Zn(II) added. 2a: For TMHDC, 20 mL of 1.00 mM TMHDC·4HCl with 0.120 M NaOH; for TMHDC·4HCl + Zn(II), 20 mL of 0.0204 M ligand and 0.0204 M $ZnSO_4$ in 1 M KCl with 0.1036 M NaOH. Line fit is from HYPERQUAD. 2b: The most significant species concentrations, as determined from HYPERQUAD, for the TMHDC·4HCl + Zn(II) titration curve.

The $pK_1$ through $pK_4$ values of HDC are 10.3, 8.8, 3.5 and 3.0, respectively, while those for TMHDC are 9.7, 8.1, 3.4 and 2.1, respectively. A summary of the deprotonation and metal-formation constants for both HDC and TMHDC are shown in Table I along with the literature values for cyclam. The 'composite formation-constant, rd, K', for a particular ligand and metal combination, was obtained by summing concentration of each species' at each titration point (see Discussion). Two examples of K's, plotted as a function of pH, are given in Figures 3 for HDC with Cu and for TMHDC with Zn. Table I lists the composite binding-constnts, at pH 7, for both ligands and all three metals.

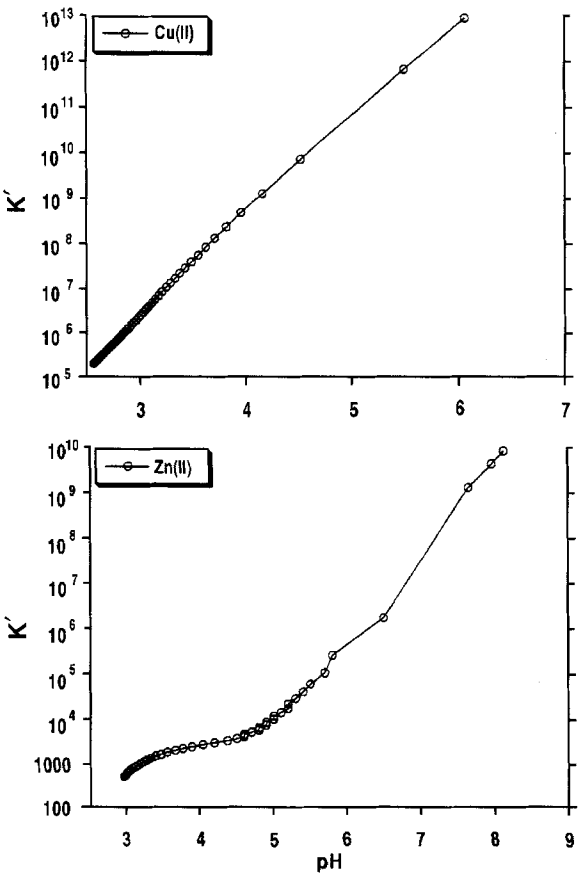


FIGURE 3 Plots of K′ as a function of pH. See text for definitions. 3a: K′ for HDC·4HCl + Cu(II). The data joints are connected for ease ofr visualization. K′ at pH 7 is determined by extrapolation. 3b: K′ for TMHDC·4HCl + Zn(II). K′ at pH 7 is determined by interpolation.

TABLE I Summary of deprotonation, formation and composite constants for HDC and TMHDC

| | *Cyclam*[a] | *HDC* | *TMHDC* |
|---|---|---|---|
| $pK_1$ | 11.6 | 10.3 | 9.7 |
| $pK_2$ | 9.6 | 8.8 | 8.1 |
| $pK_3$ | 3.6 | 3.5 | 3.4 |
| $pK_4$ | 2.6 | 3.0 | 2.1 |
| $pK_{Cu}$ | 27.2 | 20 | 17.2 |
| $pK_{Zn}$ | 15.5 | 11.1 | 12.9 |
| $pK_{pb}$ | 10.8 | 9.1 | 10 |
| [b]log $K'_{Cu}$ | 14.6 | 14.8 | |
| log $K'_{Zn}$ | 8.3 | 7.5 | |
| log $K'_{Pb}$ | 4.1 | 7.1 | |

[a]Cyclam values taken from Bianchi, *et al.* (1991) [b]log K′ values are for pH 7.

## DISCUSSION

The coupling of a long hydrocarbon chain to cyclam affects both its aqueous solubility as well as its metal-binding capacity. The polar ring in conjunction with the hydrophobic hexadecyl or tetramethylhexadecyl chains make HDC and TMHDC into surfactant-like molecules. Since surfactants aggregate above their c.m.c., it was necessary to know the c.m.c. for the cyclam surfactant before titration. However, due to the presence of four amines in the cyclam ring, the c.m.c. for cyclam derivatives will be influenced by both pH and ligand concentration. We have checked this dependence for HDC (see Results). As a function of concentration at pH 10.1, the c.m.c. for HDC, as estimated from both fluorescence and light-scattering measurements, are 0.17 and 0.20 ± 0.02 mM, respectively. As a function of pH, the 'critical micelle pH' was found to be pH 8.5 ± 0.5 for a 1 m MHDC solution. For comparison, the c.m.c. values for hexadecyltrimethylammonium chloride is 1.4 mM,[16] which is much higher than these cyclam derivatives. However, it is expected that the presence of carbons in the cyclam ring will lower the c.m.c. with respect to that of the ammonium analog — as is the case for hexadecylpyridinium chloride with a c.m.c. of approximately 0.2 mM.

The c.m.c. values for HDC were used as a general guide to estimate where the titration may include aggregate structures; these regions were avoided in the initial estimates of the binding constants. The dependence of the titration curves on possible structure formation were also tested by performing titrations in excess Triton X-100 (up to 40:1 Triton:HDC°4HCl). The curves were essentially identical to titrations without the detergent present, suggesting that micellar formation did not appear to affect significantly the titrations. As a precaution, however, attention was focused primarily in the acidic to neutral portion of the titration curves when deriving the metal stability constants.

The deprotonation constants for HDC and TMHDC are defined as follows: 1 and step-wise complexations to the bare, or protonated ligand, are given by: 23 where L and $M^{2+}$ are ligand and metal, respectively. The net charges have been left off the subscripts of the formation constants for convenience.

The titration curves of the ligands, *per se*, appear similar to the titration of a simple acid with base because the four deprotonation constants are divided into two distinct groups. The immediate lowering of the Cu(II)/HDC titration curve, compared to the titration of HDC alone, (Figure 1a) is a consequence of Cu(II) binding to HDC, even before addition of any base. This is seen in more detail from the HYPERQUAD results (Figure 1b) that show the most important species at the initial titration point are $LCu^{2+}$, $LCuH^{3+}$ and $LCuH^{4+}_2$. Generally, these types of complexes are expected to dominate, at the expense of proton-ligand species, for a ligand with strong affinity for the divalent cation.

$$LH_n^{n+} \rightleftharpoons LH_{n-1}^{(n-1)} + H^+ \qquad K_n \; n = 1, 2, 3, 4 \tag{1}$$

$$L + M^{2+} \rightleftharpoons LM^{2+} \qquad K \tag{2}$$

$$\begin{aligned} LH + M^{2+} &\rightleftharpoons LMH^{3+} \qquad KLHM \\ \bullet &\rightleftharpoons \bullet \qquad \bullet \\ \bullet &\rightleftharpoons \bullet \qquad \bullet \\ LH_n^+ + M^{2+} &\rightleftharpoons LMH_n^{(n+2)+} \qquad K_{LH_nM} \end{aligned} \tag{3}$$

The amount of complex $LCu^{2+}$, which is the species associated with the Cu-formation constant, increases monotonically with added base, at the expense of the other two species, but does not dominate until more than two equivalents, **a**, of base are added. The Cu(II)/HDC titration, performed at a 1:11 ligand to metal ratio, was not carried out beyond pH 6 and Cu(II) hydroxide complexes were not found to be important for the fit. For other titrations, where the ligand:metal ratio was 1:1 and the titrations end at a higher pH, metal-hydroxide complexes — although included in the calculations — were still found to be negligible up to four equivalents.

For a metal that binds less strongly to the ligands than Cu(II), such as Zn(II), the interaction of the cyclic amine with the aqueous metal ions is much weaker. The ligand does not bind metal ion until **a** is almost 2, or when the first two protons have been mostly neutralized by base (Figure 2a). This is shown explicitly in Figure 2b, where $LZn^{2+}$ appears only after 2 equivalents.

The titration results of HDC and TMHDC show that $pK_1$ and $pK_2$ of the N-alkyl cyclams have become more acidic than cyclam ($pK_1$ through $pK_4$ of 12.6, 10.4, 1.9 and 0.8, respectively),[20] while $pK_1$ and $pK_4$ are relatively unchanged. A summary of the deprotonation and metal-formation constants for both HDC and TMHDC are shown in Table I along with the literature values for cyclam. The addition of a long chain to a ring-nitrogen creates a more acidic tertiary amine in HDC[21–22] producing a marked decrease in copper chelation ($pK_{Cu}$ = 20.2) compared to cyclam ($pK_{Cu}$ = 27.2).[10] The weaker copper-ion complexation, reflecting a lowered ability to bind the metal ion, has been predicted qualitatively from studies of the interaction of Ni(II) with monomethylated cyclams.[23] This decrease was attributed to steric repulsion which affects both coordinating capability and nitrogen basicity. While a singly-methylated cyclam copper binding-constant is not available for direct comparison, the differences in the Cu(II) binding-constant for the analog compounds 1,4,7,10-tetraazacyclododecane ($pK_{Cu}$ = 24.0) and its N-N′-dimethylated derivative ($pK_{Cu}$ = 17.9)[1] show that modification of ring nitrogens will significantly affect Cu(II) affinity. The Cu(II) formation constants of HDC and TMHDC lie between that of the parent cyclam and a tetramethylated cyclam ($pK_{Cu}$ = 18.3), suggesting that the macrocyclic effect can be considerably altered either by attaching several short chains to the ring nitrogens, or by the

presence of just one long hydrocarbon chain. Howover, consideration of the direct effect of N-coupling on ring structure may not entirely explain the weakening effect, since the Cu(II) formation constant of TMHDC — essentially a more hydrophobic molecule — is less than that of HDC.

While the metal-binding constants of HDC and TMHDC are directly obtained from the step-wise complexation reactions, the apparent, or overall, metal-binding capability of these compounds is a more complicated property than can be described by any one formation constant. That is, metal complexes are formed, not only between the bare ligand and metal ion, but also with protonated-ligand species. Thus, it is the sum of all the metal complexes, which co-exist in solution, that determine the overall ability of HDC and TMHDC to sequester divalent cations. Furthermore, since all the complexes are pH dependent, the apparent binding, which is a composite of all these concentrations is also a sensitive function of pH. In order to quantitate this overall binding constant, Bjerrum (1957)[24] proposed a 'composite constant', K′, at a particular pH, to be the sum of all possible ligand-proton-metal complexes at that pH. K′ is obtained by replacing L with L′ and $LM^{2+}$, respectively, in equation (2) where 4 to yield a composite 'formation-constant' 5. Not all values of n will be important (high enough concentration) for each titration. Graphs of K′ *vs.* pH calculated for each titration point (*i.e.*, for each pH value) can be generated from data provided by HYPERQUAD. Of particular interest is K′ around pH 7.0, where most potential applications of these compounds take place. The K′ (pH 7) values are given in Table I. It is seen that K′ (pH 7) is lower than K, because concentrations of ions such as $LMH^{3+}$ and $LMH_2^{4+}$ (which have lower formation constants) contribute significantly to the overall concentration of complexed metal at neutral pH (Figure 3). This is important from a practical point of view.

In summary, we have synthesized two surfactant derivatives of cyclam and examined the effect of ring N-coupling to long chain hydrocarbons on the ability of these compounds to bind metal ions. The compounds were designed to exhibit simultaneous abilities to bind divalent-cations tightly, to sequester hydrophobic solute molecules and to have buoyancy in aqueous solutions. We have found that both HDC and TMHDC still possess a high affinity for metal ions, even while acquiring surfactant properties. The decrease in binding constant is greatest for $Cu^{2+}$ and becomes less for the larger divalent cations. The complex titration-curves were best fit with a rich mixture of ionic species. The ability to calculate the concentrations of these species has enabled us to use the concept of a composite binding-constant, K′, to estimated the apparent metal-binding capabilities of HDC and TMHDC over a large pH range. Since most ligands are Lewis bases, utilization of the composite constant can give insight into the pH-sensitive nature of the apparent ability of ligands to bind metals under 'different' conditions.

$$L' = \sum_{n=0}^{4} LH_n{}^{n+} \quad LM'^{2+} = \sum_{n=0}^{4} LMH_n{}^{(n+2)+} \tag{4}$$

to yield a composite "formation–constant"

$$K' = \frac{\sum_{n=0}^{4} LMH_n{}^{(n+2)+}}{(\sum_{n=0}^{4} LH_n{}^{n+})(M^{2+})} \tag{5}$$

***Acknowledgments***

This project was funded from the Environmentally Sound Ships Program of the Office of Naval Research.



***References***

[1] A. Bianchi, M. Micheloni and P. Paoletti, *Coordination Chemistry Reviews,* **110**, 17 (1991).
[2] D.K. Cabbiness and D.W. Margerum, *J. Am. Chem. Soc.,* **91**, 6540 (1969).
[3] M. Shimomura and T. Kunitake, *J. Am. Chem. Soc.,* **104**, 1757 (1982).
[4] A. Singh, L.I. Tsao, M. Markowitz and B.P. Gaber, *Langmuir,* **8**, 1570 (1992).
[5] G. De Santis, M. DiCasa, M. Mariani, B. Seghi and L. Fabbrizzi, *J. Am. Chem. Soc.,* **111**, 2422 (1989).
[6] K. Yamada, Y. Koide, H. Yamanokuchi, M. Ohmura and H. Shosenji, *Bull. Chem. Soc. Jpn.,* **62**, 2867 (1989).
[7] F.P. Hinz, and D.W. Margerum, *Inorg. Chem.* **13**, 2941 (1974).
[8] M. Kodama and E. Kimura, *J. Chem. Soc. Dalton Trans.*, 116 (1976).
[9] M. Kodama and E. Kimura, *J.C.S. Dalton Trans.*, 2335 (1976).
[10] M. Kodama and E. Kimura, *J.C.S. Dalton Trans.*, 1473 (1977).
[11] M. Kodama and E. Kimura, *J.C.S. Dalton Trans.*, 1169 (1977).
[12] M. Kodama and E. Kimura, *J. Chem. Soc. Dalton Trans.*, 1081 (1978).
[13] J.J. Yaouanc, B.N. Le, G.G. Le, J.C. Clement, H. Handel and A.H. des, *J. Chem. Soc. Chem. Comm.*, 206 (1991).
[14] G. Weber and J.J. Farris, *Biochemistry,* **18**, 3075 (1979).
[15] P.L.-G. Chong, *Biochemistry,* **27**, 399 (1988).
[16] P. Mukerjee and K.J. Mysels, *Critical Micelle Concentrations of Aqueous Surfactant Systems*, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S. Government Printing Office, Washington, DC, 1970), vol. NSRDS-NBS 36.
[17] G. Schwarzenbach, A. Willi and R.O. Bach, *Helvetica Chim. Acta,* **30**, 1303 (1947).
[18] G. Schwarzenbach and H. Ackermann, *Helvetica Chim. Acta,* **31**, 1029 (1948).
[19] A. Sabatini, A. Vacca, and P. Gans, *Coordination Chemistry Review,* **120**, 389 (1992).
[20] N.F. Curtis, *J. Chem. Soc.*, 2644 (1964).
[21] H.C. Brown, *J. Am Chem. Soc.,* **67**, 378 (1945).
[22] H.C. Brown, *J. Am Chem. Soc.,* **67**, 1452 (1945).
[23] M. Ciampolini, L. Fabbrizzi, M. Licchelli, A. Perotti,, F. Pezzini and A. Poggi, *Inorg. Chem.,* **25**, 4131 (1986).
[24] J. Bjerrum, G. Schwarzenbach and L.G. Sill én, *Stability Constants Pt. I* (The Chemical Society, London, 1957).