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Influence of electronic and steric effects on stability constants and electrochemical reversibility of divalent ion complexes with glycine and sarcosine
A glass electrode potentiometric, sampled direct current polarographic, virtual potentiometric, and molecular modelling study

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Abstract

Cd^{II} complexes with glycine (gly) and sarcosine (sar) were studied by glass electrode potentiometry, direct current polarography, virtual potentiometry, and molecular modelling. The electrochemically reversible Cd^{II}–glycine–OH labile system was best described by a model consisting of M(HL), ML, ML_2, ML_3, ML(OH) and $ML_2(OH)$ ($M = Cd^{II}$, L = gly) with the overall stability constants, as log β, determined to be 10.30 ± 0.05, 4.21 ± 0.03, 7.30 ± 0.05, 9.84 ± 0.04, 8.9 ± 0.1, and 10.75 ± 0.10, respectively. In case of the electrochemically quasi-reversible Cd^{II}–sarcosine–OH labile system, only ML, ML_2 and ML_3 ($M = Cd^{II}$, L = sar) were found and their stability constants, as log β, were determined to be 3.80 ± 0.03, 6.91 ± 0.07, and 8.9 ± 0.4, respectively. Stability constants for the ML complexes, the prime focus of this work, were thus established with an uncertainty smaller than 0.05 log units. The observed departure from electrochemical reversibility for the Cd–sarcosine–OH system was attributed mainly to the decrease in the transfer coefficient α. The MM2 force field, supplemented by additional parameters, reproduced the reported crystal structures of diaqua-bis(glycinato-O,N)nickel(II) and *fac*-tri(glycinato)-nickelate(II) very well. These parameters were used to predict structures of all possible isomers of (i) $[Ni(H_2O)_4(gly)]^+$ and $[Ni(H_2O)_4(sar)]^+$; and (ii) $[Ni(H_2O)_3(IDA)]$ and $[Ni(H_2O)_3(MIDA)]$ (IDA = iminodiacetic acid, MIDA = *N*-methyl iminodiacetic acid) by molecular mechanics/simulated annealing methods. The change in strain energy, ΔU_{str}, that accompanies the substitution of one ligand by another ($ML + L' \rightarrow ML' + L$), was computed and a strain energy $\Delta U_{str} = +0.28\,kcal\,mol^{-1}$ for the reaction $[Ni(H_2O)_4(gly)]^+ + sar \rightarrow [Ni(H_2O)_4(sar)]^+ + gly$ was found. This predicts the monoglycine complex to be marginally more stable. By contrast, for the reaction $[Ni(H_2O)_3IDA] + MIDA \rightarrow [Ni(H_2O)_3MIDA] + IDA$, $\Delta U_{str} = -0.64\,kcal\,mol^{-1}$, and the monoMIDA complex is predicted to be more stable. This correlates well with (i) stability constants for Cd–gly and Cd–sar reported here; and (ii) known stability constants of ML complex for glycine, sarcosine, IDA, and MIDA.

Keywords: Glycine; Sarcosine; Iminodiacetic acid; *N*-Methyl iminodiacetic acid; Stability constants; Molecular modelling; Polarography; Potentiometry; Cadmium; Nickel; Virtual potential

1. Introduction

The effectiveness with which a metal ion is coordinated by a ligand, L, in aqueous solution may be assessed by determining the equilibrium constant described by, for example, an overall stability constant log β_{MpLqHr}. The magnitude of such equilibrium constants depends, *inter alia,* on the electronic and steric properties of the ligand. A typical inductive electronic effect is observed in case of divalent metal complexes of iminodiacetic acid (IDA) and its methyl derivative, *N*-methyl iminodiacetic acid (MIDA). Available data [1] indicate that MIDA forms stronger complexes with divalent metal ions with ionic radius

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between 0.57 (Cu^{II}) and 1.19 Å (Pb^{II}) [2]. Clearly, in the case of MIDA, the inductive electronic effect overrides steric effects. By contrast, reported stability constants for Cu^{II}, Ni^{II} and Zn^{II} with glycine and sarcosine (*N*-methylglycine) [1], show an opposite trend and the stability constants for sarcosine are a fraction of a log unit smaller. This implies that steric effects are more significant in the case of sarcosine than the inductive effect. Unfortunately, the absence of data for larger metal ions, such as Cd^{II} and Pb^{II}, precludes a generalisation to be made concerning the influence on the stability constant of the addition of the methyl group to glycine to form sarcosine.

Glass electrode potentiometry (GEP) is the most versatile and most frequently employed analytical technique in the study of metal ion complexes [3]. However, due to its intrinsic limitations and significant difficulties in the final data interpretation, several studies of the complexation of cadmium with glycine resulted in two somewhat different stability constants, (as log K_1) 4.18 and 4.28. These two values are recommended by two authoritative compilations, namely that by Martell [1] and that from IUPAC [4]. There is no recommended value for any complex of Cd^{II} with sarcosine [1] as the only two literature reports referenced by Martell do not meet that compilation's criteria. In the case of lead, IUPAC [4] does not recommend any value for log K_1 for Pb^{II}–glycine due to a large uncertainty and spread in data reported from several analytical techniques, including GEP and polarography. No data are available for stability constants of lead with sarcosine [1]. It is clear that the study of large metal ion complexes with glycine and sarcosine has presented significant difficulties; hence either the reported data has large uncertainty or relevant data are not available at all.

The analysis of existing data suggests that stability constants of interest in this work will differ by about 0.5 log units and hence they should ideally be established to the nearest 0.05 log unit. It is expected that the sole use of GEP as the analytical method is unlikely to lead to reliable values of stability constants because metal–ligand complexes may be formed in regions of pH where the response of a glass electrode is problematic due to extended hydrolysis and subsequent precipitation of metal hydroxides. Polarography has an advantage in that it allows working at a low total metal ion concentration ($[M_T]$) and large total ligand to total metal ion concentration ratios ($[L_T]$:$[M_T]$). This often makes it possible to postpone or minimise the extent of hydrolysis and opens up a wider pH-window for investigation of $M_pL_qH_r$ complexes.

A rigorous approach to the study of metal complexes by polarography was developed and successfully tested recently in our laboratories on metal–ligand systems showing different homogeneous kinetics (from dynamic to inert) [5–8]. A single mathematical expression allows a study of the formation of several complexes simultaneously in a solution with protonated, hydrolysed, or polynuclear complexes [7] being formed as major or minor components of the solution composition. Any known metal complex and competing equilibria are accounted for by including them in mass-balance equations written for the assumed overall metal–ligand model. The above are fundamental differences between the DeFord and Hume method [9,10] and our method of describing speciation. In addition, we make extensive use of overall polarographic complex formation curves (experimental and theoretical) [11,12] and non-linear curve fitting operations in order to arrive at stability constants.

A challenge one is faced with in this study is the expected small difference (a fraction of a log unit) between stability constants of divalent metal ions with glycine and sarcosine. The difficulties and the expected accuracy can be estimated from the extensively studied Cd–glycine–OH system. There are two recommended values of log K_1 and these values differ only by 0.1 log unit [1,4]. In order to arrive at reliable stability constants one must (i) acquire many experimental data points of the highest quality (regardless of the analytical technique employed) within a narrow pH-range prior to hydrolysis or precipitation of $M(OH)_2(s)$; (ii) as accurately as possible correct for the departure from electrochemical reversibility in case of polarographic studies; (iii) employ non-linear regression techniques in refinement and optimisation operations involving mass-balance equations; (iv) make use of more than a single analytical technique; and (v) if possible, perform refinement and optimisation operations simultaneously on data coming from different analytical techniques.

The aim of this work was to (i) develop and test non-linear regression equations, based on the Ružić method [13], for fitting electrochemically non-reversible polarograms in order to compute the reversible half-wave potential required in refinement operations; (ii) test the applicability of the virtual potential (VP) approach [14–17] in the refinement of stability constants from computed reversible potentials; (iii) determine stability constants for the Cd^{II}–glycine–OH system in order to rigorously verify the procedures proposed in this work; (iv) establish a reliable model and determine the stability constants for the Cd^{II}–sarcosine–OH system by use of two experimental techniques, namely GEP and sampled direct current polarography (DCP) with the aid of VP-based methodology; (v) propose rigorous polarographic data treatment procedures that could be reliably applied by non-electrochemists; and (vi) explore the steric effects in metal–ligand interactions by use of molecular mechanics (MM) methods. Molecular mechanics methods are especially useful in exploring steric effects, and they have been extensively used as adjuncts to more traditional methods of studying the structure of coordination complexes [18,19]. The ligands investigated in this work are shown in Fig. 1.

2. Experimental

2.1. Chemicals

The ligands glycine (99% pure) and sarcosine (99% pure) were purchased from Aldrich (Milwaukee, USA). All ligands were used as received in their solid forms as free acids. Cadmium nitrate tetrahydrate (analytical grade, 99% pure) was obtained from Aldrich. All other reagents used were of analytical grade and obtained from Saarchem (Muldersdrift, South Africa). De-ionised water (18 MΩ) was obtained by passing distilled water through a Milli-Q-water-purification system (Millipore, Bedford, MA, USA). A 0.05 M stock solution of cadmium nitrate was prepared in de-ionised water and adjusted to ionic strength