

Polarographic Study of Composition and Stability Constants of Pb(II) N-(2-Acetamido) Imino Diacetate Complexes

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Summary. The complexation of Pb(II) by N-(2-acetamido) imino diacetate (*ADA*) has been studied polarographically (dc and ac polarographic techniques). Ac polarographic studies have been particularly helpful in deciding the reversibility of the reduction of both simple and complexed metal ions and for confirmation of the overall stability constants. A weighted least squares numerical technique has been applied for the calculation of the overall stability constants using both dc and ac techniques. The reduction of Pb(II) in N-(2-acetamido) iminodiacetate solutions has been found to be reversible and diffusion controlled, involving a two electron transfer process. Potential vs. concentration data at $\mu = 0.1 \text{ mol dm}^{-3}$ (KNO_3) are interpreted on the basis of the formation of two complex species PbADA and Pb(ADA)^{2-} in the *pH* range 6.85–8.50. The logarithms of the stability constants (calculated from ac measurements) of these complexes are 8.73 ± 0.12 , 10.86 ± 0.18 at 25°C, 8.31 ± 0.28 , 10.31 ± 0.09 at 35°C and 7.61 ± 0.20 , 10.10 ± 0.11 at 45°C, respectively. The thermodynamic parameters ΔG , ΔH and ΔS have been calculated at 35°C.

Keywords. Pb(II) N-(2-acetamido) imino diacetate complexes; Stability constants; Polarography.

Polarographische Untersuchung von Zusammensetzung und Stabilitätskonstanten von Pb(II) N-(2-Acetamido)iminodiacetat-Komplexen

Zusammenfassung. Es wurde die Komplexierung von Pb(II) mit N-(2-Acetamido)iminodiacetat (*ADA*) polarographisch mittels DC- und AC-Techniken untersucht. Insbesondere AC-Polarographie ergab eine klare Entscheidung bezüglich der Reversibilität der Reduktion von einfachen und komplexierten Metallionen und für die Bestätigung der Stabilitätskonstanten. Zur Bestimmung der Gesamtstabilitätskonstanten wurde eine gewichtete mittlere Fehlerquadrat-Methode auf Basis von DC- und AC-Messungen herangezogen. Die Reduktion von Pb(II) in N-(2-Acetamido)iminodiacetat-Lösung stellte sich als ein reversibler und diffusionskontrollierter Zweielektronen-Transferprozess heraus. Die Abhängigkeit des Potentials von der Konzentration bei $\mu = 0.1 \text{ mol dm}^{-3}$ (KNO_3) läßt sich mit der Bildung von zwei Komplex-Spezies PbADA und Pb(ADA)^{2-} im *pH*-Bereich 6.85–8.50 erklären. Die Logarithmen der Stabilitätskonstanten dieser Komplexe (aus AC-Messungen) sind 8.73 ± 0.12 und 10.86 ± 0.18 bei 25°C, 8.31 ± 0.28 und 10.31 ± 0.09 bei 35°C bzw. 7.61 ± 0.20 und 10.10 ± 0.11 bei 45°C. Die thermodynamischen Parameter ΔG , ΔH und ΔS wurden für eine Temperatur von 35°C berechnet.

Introduction

N-(2-Acetamido) iminodiacetic acid (*ADA*) was prepared by Schwarzenbach and co-workers [1]. The choice of alternative buffers has increased with the commercial

availability of zwitterionic amino acids, mainly N-substituted taurines or N-substituted glycines prepared by Good and co-workers [2]. Organic buffers suitable for use in biochemistry now include N-(2-acetamido) imino diacetic acid (*ADA*). Zwitterionic buffers—comparable to amino acids—show significant advantages over conventional buffers: insignificant penetration through biological membranes, maximum buffer capacity at a physiological *pH* range of 6.0–8.50 and no enzyme substrate or enzyme inhibitor properties. Metalbinding abilities of some of the newer buffers were determined by Schwarzenbach [1] and Good [2]. Complex formation between some cations and some N-substituted iminodiacetic acid were studied by several authors [3–15]. In the present investigation, the complexation of N-(2-acetamido) iminodiacetic acid with Pb(II) has been studied polarographically (dc and ac techniques) to determine the composition and stability constants of the complex ions formed. The values of the thermodynamic parameters ΔG , ΔH and ΔS have also been calculated and are reported in this paper.

The preparation of new metal ion buffers required for standardization of a Pb(II) ion selective electrode are now in progress and the results obtained in this paper will be the subject of further publication in continuation to the author's work in this field [16–17].

Experimental Part

$\text{NH}_2\text{-CO-CH}_2\text{-N(CH}_2\text{COOH)}_2$ was analytical grade (BDH) with purity not less than 98% and was used without further purification. Since the solubility of the free acid N-(2-acetamido) imino diacetic is very small, the mono-potassium salt was prepared by titration with standard carbonate-free potassium hydroxide solution. All other chemicals were reagent grade commercial products.

All test solutions were $6 \cdot 10^{-4} \text{ mol dm}^{-3}$ in Pb(II) ion, added as Pb(II) nitrate. The solutions were made in conductivity water. The desired amount of mono-potassium salt of *ADA* stock solution was added and the *pH* was adjusted by addition of nitric acid or potassium hydroxide. The total ionic strength was made to be 0.1 mol dm^{-3} by addition of potassium nitrate. 0.001% triton-X-100 was added as maximum suppressor.

The (ac, dc) polarographic measurements were carried out with a Tacussel PRG3 apparatus equipped with three Tacussel RMO6 electrodes and a thermostated cell. A saturated calomel electrode served as the reference electrode. The dropping mercury working electrode (DME) had the following characteristics: $m = 1.625 \text{ mg s}^{-1}$ and $t = 4.8 \text{ s/drop}$ in $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$.

Before polarography, solutions were deaerated by passage of purified nitrogen. The gas was purified by allowing it to pass through the following solutions:

(a) A vanadous solution (prepared as recommended by Meites [18]) was placed in a tall cylinder provided with a coarse-porosity sintered pyrex gas dispersion disc. The cylinder contained also about 25 g heavily-amalgamated zinc which served mainly to reduce the oxidized vanadium formed by reaction of the vanadous solution with oxygen (contaminating the inert gas).

(b) A copper sulphate solution, prepared from a BDH product.

(c) A 0.1 mol dm^{-3} silver nitrate solution, prepared from a BDH product.

(d) 1% sodium plumbite solution, obtained by adding a solution of sodium hydroxide dropwise to another of pure lead nitrate.

(e) Twice distilled water.

The adjustment of the *pH* of the solutions was made using an Orion (M 601 A) digital *pH*-meter with a combined glass-calomel electrode.

Results and Discussion

In the absence of dissolved oxygen, Pb(II) produces a single well-defined reduction wave in $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$. In the absence of a maxima suppressor, a maximum

appears, which is suppressed by the addition of 0.001% triton-X-100. The plot of i_d vs. \sqrt{h} (square root of the effective height of the mercury column) and i_d vs. C [C =concentration of Pb(II)] is linear, indicating the diffusion-controlled nature of the reduction wave. The values of slopes from log plots (i.e. plot of $\log i/i_d - i$ vs. E) agreed with the theoretical values for a two electron transfer. The half wave potential shifted toward more negative values with increasing ADA concentration indicating complex formation. Logarithmic analysis of the dc and ac polarograms shows a linear relationship of $\log(i/i_d - i)$ and $E_{d, c}$, and of $\log \left[(i_p/i)^{1/2} + \left(\frac{i_p - i}{i} \right)^{1/2} \right]$

and E_p , respectively, with slopes corresponding to a reversible reduction involving the transfer of two electrons.

The effect of pH on the complex formation (c. f. Figs. 1, 2) indicated that the measurements could be made at a pH range of 6.85–8.50. The half wave potential remains constant at this pH range. These results indicate that the complex is stable in the pH range 6.85–8.50. Also, at higher pH 's ($pH > 8.50$), hydroxo-complexes of the types $Pb(OH)(ADA)^-$ and $Pb(OH)(ADA)_2^{3-}$ may be present in the solution. A plot of $E_{1/2}$ as a function of $\log [ADA]$ showed a curvature indicating the formation of more than one complex.

The mathematical treatment of polarographic data for the determination of the formation constants of successive mononuclear complexes has been described in detail by Deford and Hume [19] who applied the graphical solution method of

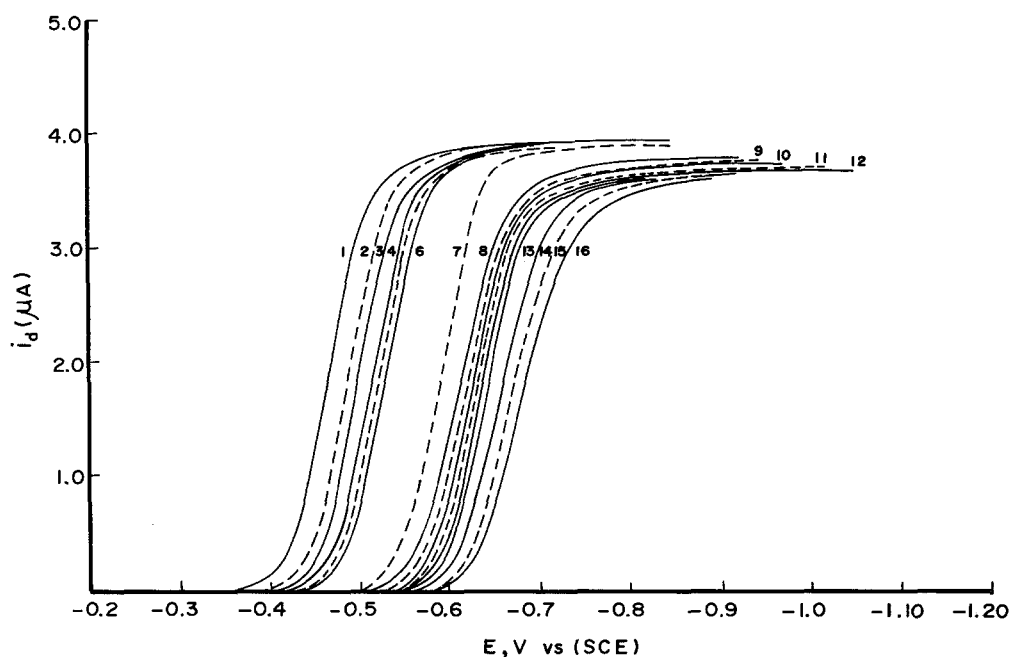


Fig. 1. Effect of pH on the polarograms of the Pb(II)-ADA system $[Pb(II)] = 6.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $[ADA] = 5.5 \cdot 10^{-2} \text{ mol dm}^{-3}$. (1) pH 2.98, (2) pH 3.16, (3) pH 3.68, (4) pH 4.39, (5) pH 5.33, (6) pH 6.05, (7) pH 6.49, (8) pH 6.80, (9) pH 7.12, (10) pH 7.50, (11) pH 8.07, (12) pH 8.50, (13) pH 9.00, (14) pH 9.93, (15) pH 10.70, (16) pH 11.52

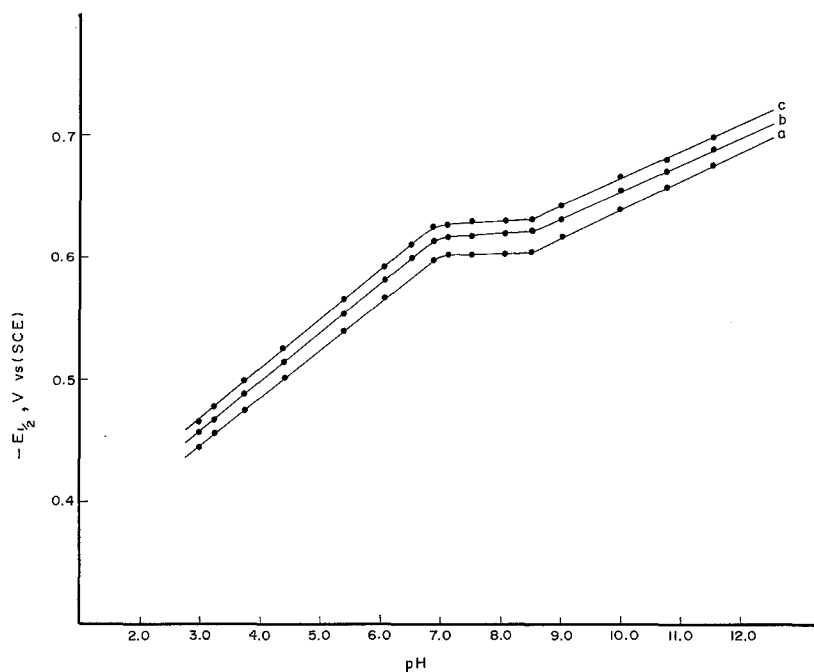


Fig. 2. Effect of pH on the half wave potential at various concentration of ADA. (a) $2.0 \cdot 10^{-2} \text{ mol dm}^{-3}$, (b) $4.16 \cdot 10^{-2} \text{ mol dm}^{-3}$, (c) $5.5 \cdot 10^{-2} \text{ mol dm}^{-3}$

Leden [20] to the problem. This method is based on the following equations defining the successive $F_i(x)$ functions.

$$10^{F_0(x)} = \left(\frac{0.435 n \mathcal{J}}{RT} \Delta E_{1/2} - \log \frac{I_s}{I_c} \right) = 1 + \beta_1 [x] + \beta_2 [x]^2 + \quad (1)$$

$$F_1(x) = \frac{F_0(x) - 1}{[x]} = \beta_1 + \beta_2 [x] + \quad (2)$$

$$F_2(x) = \frac{F_1(x) - \beta_1}{[x]} = \beta_2 + \beta_3 [x] + \quad (3)$$

where β_j is the overall successive formation constants, $[x]$ is the free ligand concentration, $n \mathcal{J} / RT$ the usual coefficient in the Nernst equations. In deriving the above functions, the total ligand concentration was approximated for the free ligand concentration. For systems involving complexes of high stability constants such an approximation may be unreliable. Thus, the ligand number, \bar{n} , was first found, assuming at this stage that $[x] \simeq C_x$, from a plot of $\log F_0[x]$ against $\log [x]$ since the following relation holds [21]:

$$\bar{n} = \frac{d \log F_0(x)}{d \log (x)}$$

providing a value of free ligand concentration nearer to the true value.

Evaluation of successive formation constants of mononuclear complexes from the above relationships can be done graphically. Such a graphical approach offers a useful method and has been widely accepted for studies of relatively weak complexes of mononuclear species which give reversible polarographic waves at the dropping mercury electrode (DME). Some plottings of F_i values, however, do not fit a smooth curve, especially in the low concentration region of the ligand which is most important for the extrapolation. Thus, the intercept is apt to suffer from inevitable deviations which will result in larger deviations from the higher order constants. Ambiguities in the evaluation of successive formation constants of mononuclear complexes $PbADA$ and $Pb(ADA)^{2-}$ from polarographic data with small 95% confidence intervals have been avoided by using a weighted least squares numerical technique [22]. The fundamental relationships,

$$1 + X_i\beta_1 + X_i^2\beta_2 + \dots + X_i^N\beta_N = F_{0i} \quad (4)$$

are a series of observation equations, which are solved for β_j 's by the method of least squares. This is possible, however, only if the weights of F_{0i} can be estimated from experimental data, as X_i is again assumed to have no error. The equation for F_{0i} is rewritten as

$$F_{0i} = \exp\left(\frac{n\mathcal{F}}{RT}\Delta E_{\frac{1}{2}i} + \ln \frac{I_{ds}}{I_{dci}}\right) \quad (5)$$

where $E_{\frac{1}{2}i}$ shows the difference between two half-wave potentials $E_{\frac{1}{2}s}$ and $E_{\frac{1}{2}ci}$, with the variances of these three being based only on the precision of the potential measurement in the relation

$$\sigma E_{\frac{1}{2}s}^2 + \sigma E_{\frac{1}{2}ci}^2 = \sigma \Delta E_{\frac{1}{2}i}^2 \approx 2\sigma E_{\frac{1}{2}s}^2 \approx 2\sigma E_{\frac{1}{2}ci}^2 (\equiv 2\sigma E_{\frac{1}{2}}^2) \quad (6)$$

The relative weights W_i' of F_{0i} , which are only needed for the computation, will be derived by applying the law of propagation of errors to Eq. (5) as

$$\frac{1}{W_i'} \alpha \sigma F_{0i}^2 \approx \left(\frac{\delta F_{0i}}{\delta \Delta E_{\frac{1}{2}i}}\right)^2 \sigma \Delta E_{\frac{1}{2}i}^2 = F_{0i}^2 \sigma \Delta E_{\frac{1}{2}i}^2 \quad (7)$$

and changed to

$$W_i' = \frac{1}{F_{0i}^2} \quad (8)$$

Thus, a group of appropriate observation equations, all of which have the weight 1, are finally attained by multiplying $(W_i')^{1/2} = 1/F_{0i}$ in Eq. (4) as

$$\frac{[X]_i}{F_{0i}}\beta_1 + \frac{[X]_i^2}{F_{0i}}\beta_2 + \dots + \frac{[X]_i^N}{F_{0i}}\beta_N = 1 - \frac{1}{F_{0i}} \quad (9)$$

If only 1:1 and 1:2 Pb to ADA complexes are formed the equation can be written in the following form:

$$\frac{[X]_i}{F_{0i}}\beta_1 + \frac{[X]_i^2}{F_{0i}}\beta_2 = 1 - \frac{1}{F_{0i}} \quad (10)$$

Eq. (5) was rearranged into an equation of the form $y = mx + c$
i.e.

$$\frac{F_{0i} - 1}{[X]_i} = [X]_i \beta_2 + \beta_1. \quad (11)$$

The most probable values of the successive formation constants, as well as their precisions, were determined directly by applying the method of least squares. Series of currents and $E_{1/2}$ potentials of appropriate polarographic waves (dc and ac) at several levels of concentration of the ligand with a constant one of the metal ion were measured. The $E_{1/2}$ mean values from three measurements were determined graphically from the polarographic data. $E_{1/2}$ is then calculated by non-linear least squares calculations [22]. The data given in Table 1 were used in the computer programs.

Table 1. Polarographic characteristics for the Pb(II)-ADA system at pH 7.12, $\mu = 0.1 \text{ mol dm}^{-3}$ (KNO_3) and $T = 25^\circ\text{C}$

$10^2 [\text{L}]$ (mol dm^{-3})	$E_{1/2}$, V vs. (SCE)	E_p , V vs. (SCE)	$10^{-7} F_0 (X)^a$
1.10	0.1992	0.1982	0.551
1.62	0.2186	0.2175	2.546
2.15	0.2213	0.2204	3.113
2.65	0.2296	0.2287	5.968
3.14	0.2335	0.2326	8.088
3.60	0.2367	0.2357	10.367
4.05	0.2395	0.2386	12.867
4.40	0.2414	0.2403	14.996
5.26	0.2457	0.2448	20.916

^a Calculated using ac polarographic measurements. Characteristics of the reduction of Pb(II) in $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$:
 $-E_{1/2} = 0.408 \text{ V}$, $i_d = 4.240 \mu\text{A}$

Table 2. Stability constants and thermodynamic functions^a at 35°C

Com- position	log β			ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 ($\text{JK}^{-1} \text{mol}^{-1}$)
	25°C	35°C	45°C			
1:1	8.70 ± 0.30^b	8.34 ± 0.17^b	7.64 ± 0.20^b	-49.03 ± 0.28	103.64 ± 0.30	177.22
	8.73 ± 0.12^c	8.31 ± 0.28^c	7.61 ± 0.20^c			
1:2	10.82 ± 0.15^b	10.35 ± 0.27^b	10.13 ± 0.18^b	-60.83 ± 0.19	96.37 ± 0.20	115.33
	10.86 ± 0.18^c	10.31 ± 0.19^c	10.10 ± 0.11^c			

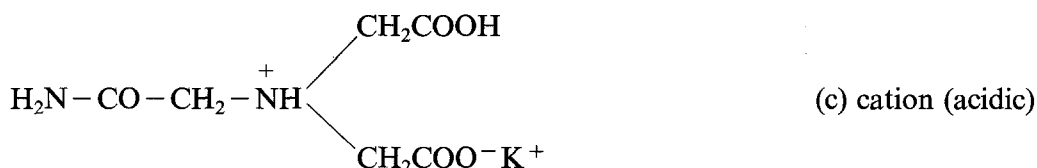
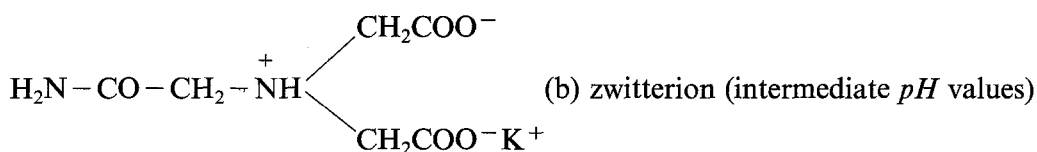
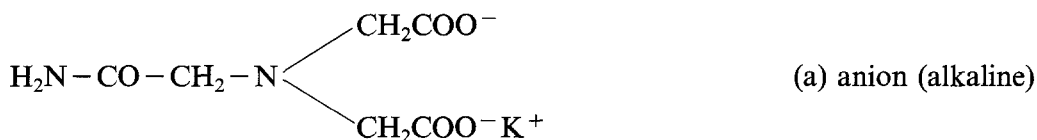
^a Calculated using ac polarography

^b dc polarography

^c ac polarography

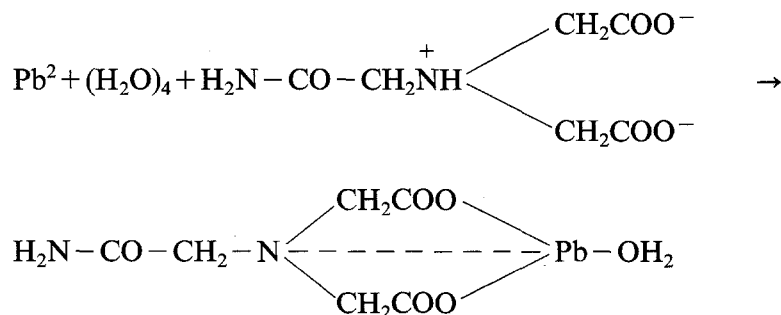
Bond [23, 24] and others [25, 26] have shown that for reversible electrode reactions ac polarographic measurements may be used with good accuracy to obtain information on the nature and stability of a complexed ion which is electroactive at the DME. For a reversible electrode reaction monitored by ac polarography, the peak potential E_p is equal to the reversible dc half-wave potential $E_{1/2}$ and therefore the same method can be applied to estimate the consecutive overall stability constants. The same treatment has been applied with good accuracy by the author in previous papers [16, 17, 27, 28]. The formation constants determined with this treatment should be "concentration constants" at the same composition of neutral electrolyte because of uncertainties in activity coefficients [29]. The data obtained in the present work at 25°C for $\log \beta_1 = 8.70 \pm 0.30$, $\log \beta_2 = 10.82 \pm 0.15$ agree with the literature data [1] ($\log \beta_1 = 8.40$, $\log \beta_2 = 10.64$). Thermodynamic parameters ΔG , ΔH and ΔS with statistically determined uncertainty have been calculated using known equations [30] and are given in Table 2.

The potassium salt of N-(2-acetamido) imino diacetic acid, with different pK_a values at different temperatures (25, 35, 45°C) [31], in aqueous solutions gives rise to an equilibrium between its protonated forms, neutral and N-(2-acetamido) imino diacetate ion, governed by the acidity constants. The equilibria may expressed as follows:

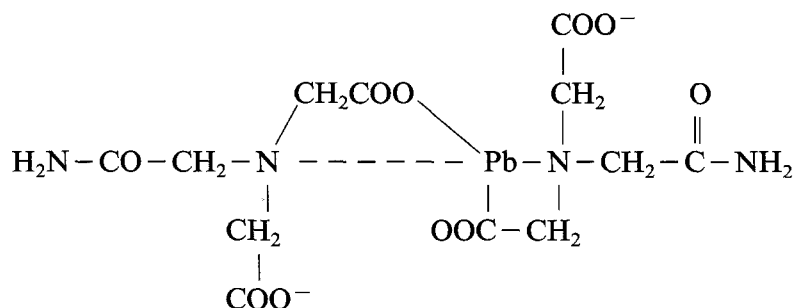
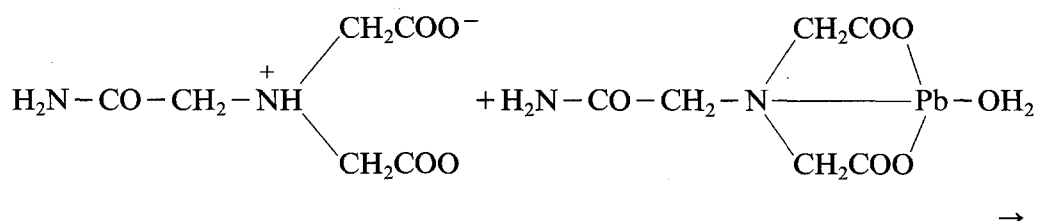


In highly acidic solutions only cations are present, e. g. (c) and in highly alkaline solutions only anions, e. g. (a). At intermediate pH values (6.85 – 8.50) the majority of molecules are present in zwitter-ionic form (b) [32]. Thus, the complexes of Pb(II) with the zwitter-ion form will predominate in that pH range. At a sufficiently high pH , the complexes with N-(2-acetamido) imino diacetate ion will predominate, since its concentration will be significant and the corresponding stability constants

are much higher than those of the possible species co-ordinated with the zwitterionic form. Thus, the formation of (1:1) and (1:2) complexes at the pH range 6.85–8.50 may be represented by



and



Our results prove that Pb(II) may form 1:1 or 1:2 metal to ADA^{2-} complexes at physiological pH values.

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