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Comparative Measurements of Calcium Stability Constants of Some Dicarboxylic Acids by Titrimetry with pH Glass and Calcium Ion-Selective Electrodes

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Calcium ion-selective electrodes based on the ionophore ETH1001 have been used to obtain free calcium ion levels, and hence by data fitting, metal−ligand stability constants in the presence of phthalate, maleate, malonate, oxalate, diglyconate, and tartrate under the conditions of a background ionic strength of 0.1 mol dm^{-3} NaCl and (25 ± 0.5) °C. The dissociation constants for the acids and the stability constants for calcium ion-ligand complexes, for comparison with the calcium ion-selective results, were separately determined with pH electrodes under the same conditions.

Introduction

A limited amount work with divalent metal ion-selective electrodes (ISEs) has been carried out for the determination of metal ion activities[1−4] to estimate association processes and to calculate association constants in aqueous solutions at various ionic strengths and temperatures. The present work describes the use of a calcium ion-selective electrode based on the ionophore ETH1001, in the determination of stability constants of calcium with the carboxylate ligands: oxalate, maleate, malonate, tartarate, diglycolic, and phthalate. To confirm the results obtained using a calcium ISE, a pH glass electrode was also used.

The method adopted for both was to vary the pH of a solution containing fixed concentrations of calcium and ligand. The effect of pH on the response of the calcium electrode is therefore of great importance. Previous studies[5] have shown that calcium ISE based on the ionophore chosen for this work, ETH1001, was Nernstian and selective over pH in the range of 3 to 10.

The effect of pH on an ETH1001-based calcium ISE has been investigated using either the separate solution or the mixed solution methods and also a NMR spectroscopic method.[5] The performance of the Ca ISE was carefully checked in the present work, and it was found to be highly selective to calcium ion over hydrogen ion with good electrode performance. There were no significant impurities present in the NMR spectrum of the ligand.[5] Therefore, it was concluded that the Ca ISE could confidently be used in potentiometric acid−base titrations and compared with those obtained with the glass electrode.

Experimental Section

All solutions were prepared using distilled water; 1.0 mol dm^{-3} NaCl was used to adjust the ionic strength to 0.1 mol dm^{-3}. Phthalic, tartaric, oxalic, maleic, and malonic acids were obtained from BDH (Analar), and diglycolic acid was from Fluka. All were used without further purification. NaCl and KCl, were obtained from Fisher. $CaCl_2$ was BDH volumetric reagent (1.0 mol dm^{-3}). HCl and NaOH solutions were prepared from BDH Convol ampules. The purity of the ligands and NaOH solutions was determined using the Molspin titration system.[6] Potassium hydrogen phthalate (KHP) (Analar) was used for the calibration of glass electrode at pH 4.008. For the preparation of the membranes for calcium ISEs, the following chemicals (Fluka) were used: 1 mass % calcium ionophore (ETH1001), 33 mass % poly(vinyl chloride) high molecular weight (PVC), 66 mass % 2-nitrophenyloctyl ether (*o*-NPOE), and potassium tetrakis(4-chlorophenyl)borate (KTpClPB) in a mole ratio of 0.5 relative to the ligand. THF (BDH) was used for dissolving the membrane components; it was dried over CaH_2 and freshly distilled before use. The membranes were cast and used to cut disks to fit the Philips electrode IS-561 body. Both before and after measurements, the glass electrode was calibrated with 0.05 mol dm^{-3} KHP and the calcium ISE with a series of $CaCl_2$ solutions (10^{-1} to 10^{-5} mol dm^{-3} at 25.0 ± 0.5 °C). The data obtained were analyzed by SUPERQUAD.[7]

Table 1. Acid Dissociation Constants (pK_a) $I = 0.1$ mol dm^{-3} NaCl at (25 ± 0.5) °C[a]

acid	pK_{a1}	pK_{a2}	reference
phthalic	3.10 ± 0.03	5.08 ± 0.01	this work
	2.82	5.09	8
maleic	1.85 ± 0.01	5.91 ± 0.01	this work
	1.77	6.02	8
diglyconic	2.91 ± 0.05	3.99 ± 0.01	this work
	2.86	3.98	8
	2.78	3.95	10
oxalic	1.60 ± 0.09	3.88 ± 0.02	this work
		4.00	10
malonic	2.92 ± 0.02	5.40 ± 0.01	this work
	2.70	5.36	8
	2.75	5.45	11
tartaric	2.90 ± 0.04	3.99 ± 0.04	this work
	2.86	4.01	8

[a] Errors shown are standard deviations.

Results and Discussion

Acid dissociation constants are shown in Table 1 with their structural formulas in Scheme 1. The values for

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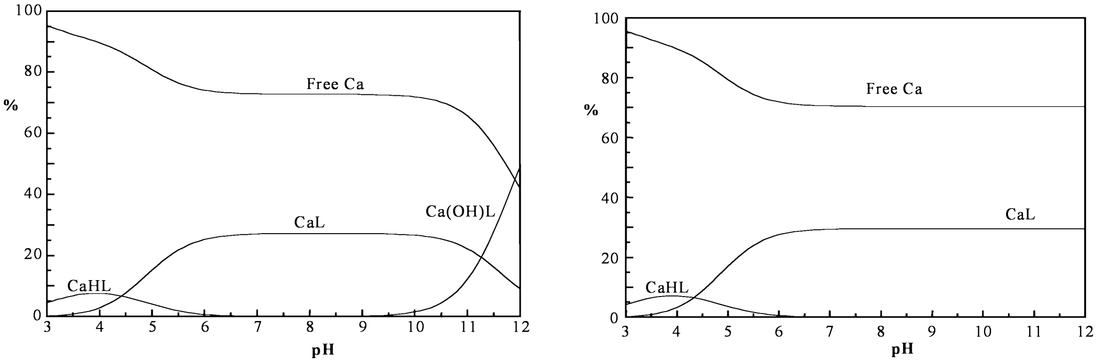
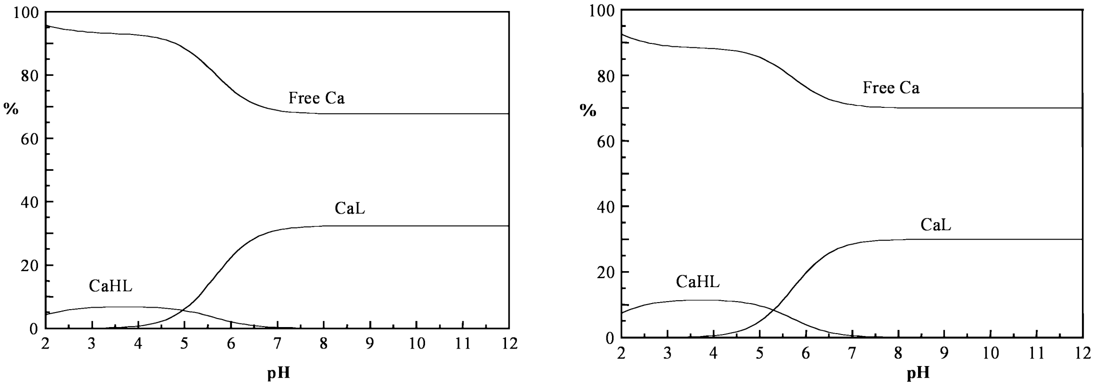
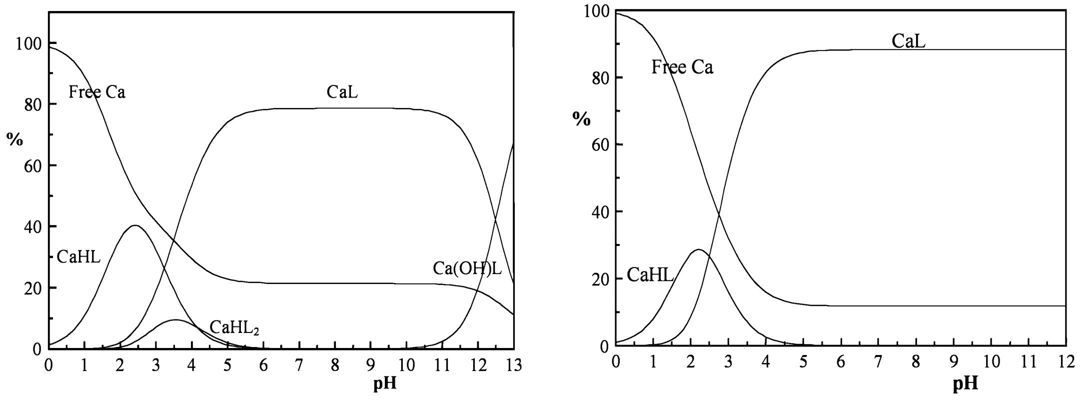


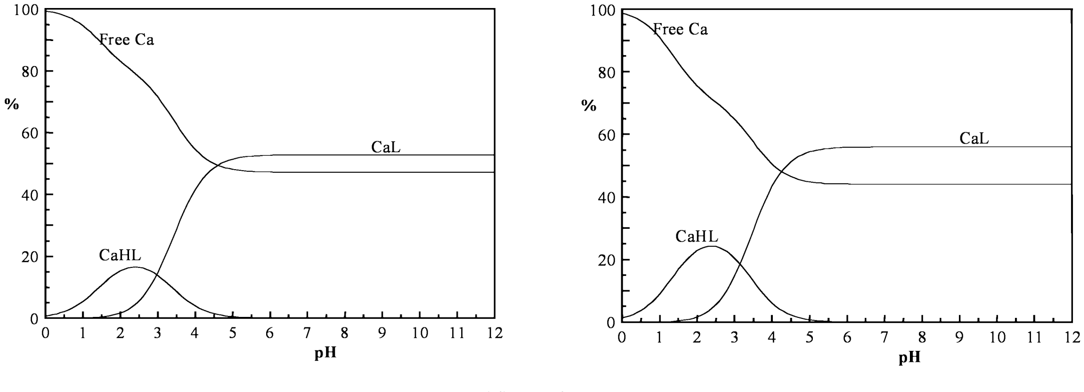
(a) phthalate



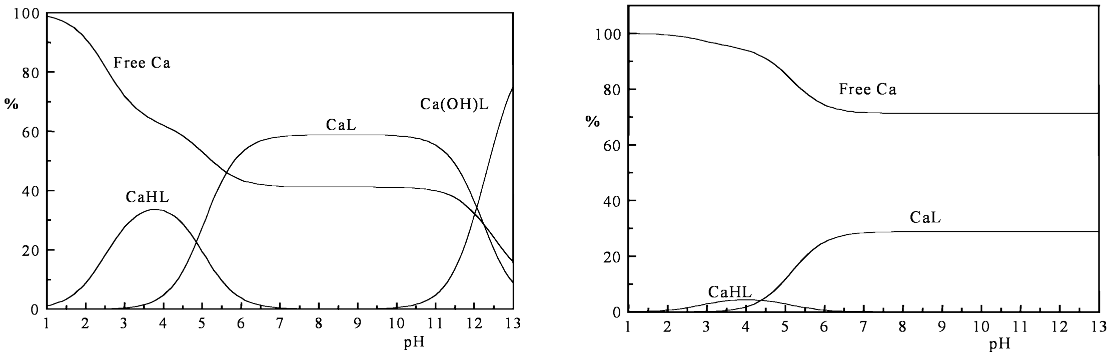
(b) maleate



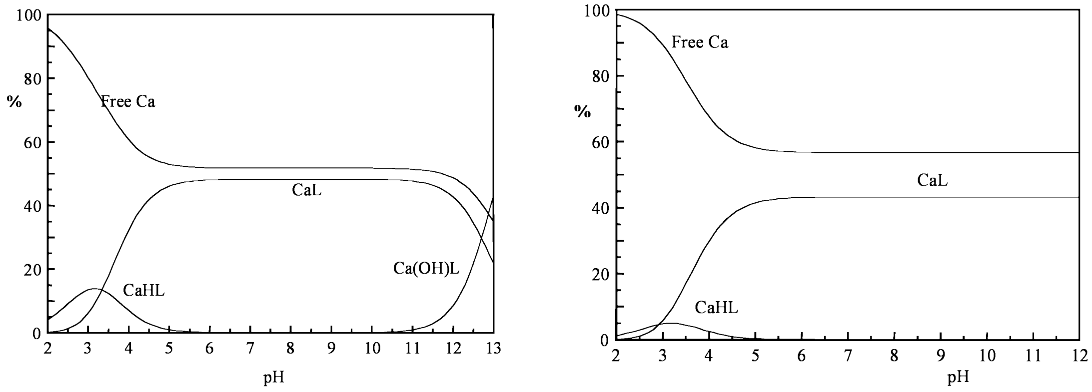
(c) diglyconate



(d) oxalate



(e) malonate



(f) tartrate

Figure 1. Species distribution curves for complexes: (a) Ca-phthalate; (b) Ca-maleate; (c) Ca-diglyconate; (d) Ca-oxalate; (e) Ca-malonate; (f) Ca-tartrate. All species were obtained in I = 0.1 mol dm^{-3} NaCl and at (25 ± 0.5) °C. The ratio [Ca]/[L] was 1.

Scheme 1. Structural Formulas and Names of Acids

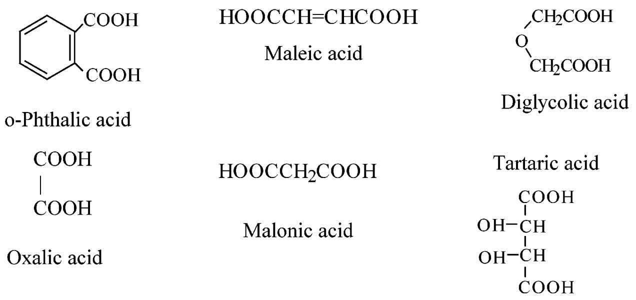


Table 2. Stability Constants for Ca-Ligand Complexes, I = 0.1 mol dm^{-3} NaCl at (25 ± 0.5) °C[a]

ligand	$M_pH_qL_r$	lg β (GE)	lg β (Ca-ISE)	reference
phthalate	1 0 1	2.01 ± 0.05	2.08 ± 0.10	this work
	1 1 1	6.44 ± 0.13	6.41 ± 0.15	
	1 −1 1	−9.25 ± 0.01		
	1 0 1	1.71		8
	1 1 1	5.70		8
maleate	1 0 1	1.85 ± 0.04	1.79 ± 0.01	this work
	1 1 1	6.82 ± 0.03	7.08 ± 0.01	
	1 0 1	1.76, 2.43	2.00	8, 14, 2
	1 1 1	6.67		8
diglyconate	1 0 1	3.24 ± 0.01	3.44 ± 0.03	this work
	1 1 1	6.46 ± 0.02	6.30 ± 0.05	
	1 1 2	9.38 ± 0.01		
	1 −1 1	−9.26 ± 0.01		
	1 0 1	3.46, 3.54		8, 10
	1 1 1	6.38, 6.56		8, 10
oxalate	1 0 1	2.38 ± 0.06	2.46 ± 0.014	this work
	1 1 1	5.35 ± 0.05	5.61 ± 0.05	
	1 −1 1	-		
	1 0 1	4.85	2.54	11, 2
malonate	1 0 1	2.54 ± 0.01	1.75 ± 0.01	this work
	1 1 1	7.39 ± 0.01	6.14 ± 0.03	
	1 −1 1	−9.52 ± 0.01		
	1 0 1	2.49, 1.85	1.83, 1.52	2, 3, 12, 13
tartrate	1 0 1	2.26 ± 0.02	2.13 ± 0.01	this work
	1 1 1	5.49 ± 0.05	5.05 ± 0.01	
	1 −1 1	−10.45± 0.04		
	1 0 1	2.10, 2.98		8, 11
	1 1 1	5.02, 6.03		8, 11

[a] The general formula of the complex is $M_pH_qL_r$. Errors shown are standard deviations.

dissociation constants for phthalate, tartrate, maleate, and malonate are similar to those given by Daniele et al.,[8] and diglycolate values are similar to those of De Robertis et al.[3] Small discrepancies in the values are due to differences in the background electrolyte and ionic strength chosen. The value of pK_{a2} of oxalic acid (3.88) is slightly smaller than given by Daniele et al.[9] (4.00). The other problem is that pK_{a1} and pK_{a2} values for oxalate are very close (1.60 and 3.88) and to determine such very close protonation constants can large give errors. The purity of the ligand is very important as a small impurity can lead to a very large error in the determination of protonation constants. In preliminary work, it was found that if a small amount of HCO_3^- was added to the test solution it resulted in a large error in pK_a values, so the test solution was isolated from the atmosphere.

Stability constants (Table 2) were obtained for Ca complexes of ligands at I = 0.1 mol dm^{-3} NaCl ionic strength (at 25 ± 0.5 °C) using a glass electrode (GE) and Ca ISE. For the Ca-phthalate system, the GE results are very close to Ca ISE results (GE lg β_{101} = 2.01 and lg β_{111} = 6.44; Ca ISE 2.08 and 6.40), but Daniele's reported values[8] (1.71 and 5.70) are smaller. For Ca-diglycolate complexes, GE values for CaL and CaHL species are similar to those by ISE. The present GE values are good agreement with those of Field et al.[10] and Daniele et al.[8] However, for $CaHL_2$ a value of lg $\beta_{112} = 9.38$ was determinable with GE but could not be obtained with the CaISE. For the Ca-malonate system, lg β_{101} and lg β_{111} values by GE for CaL and CaHL species are bigger than those by ISE. However, the ISE values are close to those of Daniele et al.[8] with GE, and there is good agreement between the present value and literature value. The present the GE value for lg β_{101} is 2.54, and Stock and Davies[12] found 2.49. However, although Campi's value[13] (1.85) is smaller than the present GE value, it is similar to the ISE value. The present GE value is larger than that of Daniele et al.[8] (1.64) perhaps because of the lower ionic strength. De Robertis et al.[3] found 1.83 using ISE in good agreement with the present ISE value. With Ca-maleate complex system, there is good agreement between the GE and ISE values for CaL and CaHL species. Also the present values (1.85 and 6.82) are close to the literature values (1.76, 6.67)[8] but in disagreement with that of Topp and Davies[14] (2.43) for CaL, but closer to the ISE value (2.00) of Craggs et al.[2]

In the Ca-tartrate complex system, the GE values are slightly bigger than the ISE values but are very good agreement with the values of Daniele et al.[8] obtained with the GE. Heinz[11] determined stability constants of 2.98 and 6.03 for CaL and CaHL complexes at $I = 0.1$ mol dm^{-3} that are bigger than the present value but a background electrolyte not used. Craggs et al.[2] studied the Ca-oxalate system at several ionic strengths with ISE and found stability constants for CaL complexes of 2.70, 2.54, and 1.99, respectively, at (0.05, 0.1, and 0.15) mol dm^{-3} NaCl ionic strength. The present result (2.46) for $I = 0.1$ mol dm^{-3} agrees with that of Craggs et al.[2]

Calcium Ion-Ligand Complexes. Figure 1 shows distribution diagrams calcium complexes with left-hand side obtained with the glass electrode and right-hand side with the calcium ISE. Figure 1a shows the results for Ca-phthalate complexes. In the glass electrode method (GE), ML, MHL, M(OH)L, and free Ca species are found. Above pH 9.5 calcium is hydrolyzed, and a M(OH)L complex is formed. With the Ca ISE method, the species distribution curves are similar to those with the GE, but a M(OH)L species was not found because the free calcium ion concentration is below the limit of detection of the CaISE.

Ca-maleate system has the same speciation (Figure 1b) as phthalate with ML the dominant species above pH 4.0. The ISE method gave a result similar to the glass (GE).

In the Ca-diglyconate system (Figure 1c), ML (65 %) and MHL (25 %) were obtained with the GE. The ISE method result is similar, but the level of MHL is smaller than that with the GE. Similar behavior is seen with the Ca-oxalate (Figure 1d) and Ca-tartrate (Figure 1e) systems, and the species distribution curves are very similar with both GE and ISE. In the Ca-malonate complex system (Figure 1f), the main species is CaL which is formed above pH 3. It exists at 60 % in the GE results but only at 25 % in the ISE results. With the GE results, CaHL rises to 30 % between pH 1 to 7 but by ISE the same species is found at only 5 %.

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