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Calcium and inorganic carbon speciation in Spanish Mediterranean brackish waters

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SUMMARY

The concentrations of free ions and major inorganic complexes of calcium and inorganic carbon (i.e. free Ca^{2+}, free HCO_3^-, free CO^{2-}_3, H_2CO_3, $CaSO^0_4$, $CaCO^0_3$, $CaHCO^+_3$, $NaHCO^0_3$, $MgHCO^+_3$, $NaCO^-_3$ and $MgCO^0_3$) have been calculated according to an ion-pair model, on the basis of their relative abundance in total concentrations, in Spanish Mediterranean brackish waters. Calcium complexes amount to 25% of total calcium, whereas bicarbonate and carbonate complexes reach 10 and 47% of total alkalinity respectively. $NaHCO^0_3$ and $MgHCO^+_3$ expressed as percentages of total alkalinity, and $NaCO^-_3$, $MgCO^0_3$ and free CO^{2-}_3 expressed as percentages of total carbonate are dependent on ionic strength. $NaCO^-_3$, $MgCO^0_3$ referred to total carbonate and free HCO_3^-, and free CO^{2-}_3 as percentages of total alkalinity are strongly dependent on pH. Inorganic carbon complexes amount to an important fraction of total alkalinity when I (ionic strength)> 0.05 and pH> 8.5, when I> 0.10 and pH> 8.3, and when I> 0.20 and pH> 8.1. Calcium complexes cannot be expressed as single function of pH or ionic strength. Their maximum percentages appear at high pH values and moderate or high ionic strength, when $CaSO^0_4$ and $CaCO^0_3$ coexist at significant levels.

KEYWORDS: ion-pairs, alkalinity, calcium, coastal waters.

RESUMEN

Especiación de calcio y carbono inorgánico en aguas salobres del litoral mediterráneo español. Se han calculado las concentraciones de iones libres y de los principales complejos inorgánicos de calcio y de carbono inorgánico (es decir, Ca^{2+} libre, HCO_3^- libre, CO^{2-}_3 libre, H_2CO_3, $CaSO^0_4$, $CaCO^0_3$, $CaHCO^+_3$, $NaHCO^0_3$, $MgHCO^+_3$, $NaCO^-_3$ y $MgCO^0_3$) según un modelo de pares iónicos, sobre la base de su importancia relativa en las concentraciones totales, en aguas salobres del litoral mediterráneo español. Los complejos de calcio suponen el 25% del calcio total, mientras que los complejos de bicarbonato y carbonato alcanzan, respectivamente, el 10 y el 47% de la alcalinidad total. $NaHCO^0_3$, $MgHCO^+_3$, expresados como porcentajes de la alcalinidad total, y $NaCO^-_3$, $MgCO^0_3$ y CO^{2-}_3 libre, expresados como porcentajes de los carbonatos totales, dependen de la fuerza iónica. $NaCO^-_3$ y $MgCO^0_3$ referidos a carbonato total y HCO_3^- libre, y CO^{2-}_3 libre, como porcentajes de la alcalinidad total dependen mucho del pH. Los complejos de carbono inorgánico suponen una fracción importante de la alcalinidad total cuando I (fuerza iónica) > 0,05 y pH > 8,5, cuando I > 0,10 y pH >8,3 y cuando I > 0,20 y pH > 8,1. Los complejos de calcio no pueden expresarse como una función sencilla del pH o de la fuerza iónica. Sus porcentajes máximos aparecen a valores altos de pH y a fuerza iónica moderada o alta, situaciones en las que $CaSO^0_4$ y $CaCO^0_3$ coexisten a niveles significativos.

PALABRAS CLAVE: pares iónicos, alcalinidad, calcio, aguas costeras.

INTRODUCTION

The dissolution and dissociation of weakly acidic gases and the weathering and sedimentation of rocks play a major controlling role in the geochemical cycle of major elements. Ion-pair formation, in comparison, plays a minor role. However, the chemical behaviour of an element depends on its form; for example, because the total soluble concentration of elements can be increased by complexation, ion-pairs are relevant for elements participating in geochemical processes such as precipitation-dissolution (Garrels *et al.*, 1961) or adsorption-desorption (O'Connor & Kester, 1975). On the other hand, the rate at which an element participates in a chemical process is also affected by ionic interaction (Pytkowicz, 1965, 1973; Stumm & Lee, 1961; Millero, 1990).

In freshwater systems, ion-pair complexes are relatively irrelevant in the speciation of major components (see Table I) and can be neglected (Stumm & Morgan, 1981), although in some cases "intermediate" ligands such as CO^{2-}_3 can form a significant amount of complexed forms with calcium and magnesium (Millero, 1975; Turner *et al.*, 1981). In marine waters, ion-pair formation has been extensively considered (rewiev in Kester *et al.*, 1975; Stumm & Morgan, 1981). Because the ionic composition of seawater is constant, the chemical characteristics of the major constituents can be treated by general interaction models, which are an alternative to speciation models (Whitfield, 1973; Morel, 1983). Similarly, the apparent dissociation constants of carbonic acid for seawater have been described (Hansson, 1973; Mehrback *et al.*, 1973). In some cases, the equilibrium data obtained for seawater can be applied to estuarine waters (Pytkowicz *et al.*, 1975). However, the total activity coefficients (or the apparent equilibrium constants which can be deduced) are not useful for brackish or highly mineralized waters, which composition differs from that of dilute seawater (Morel, 1983).

The speciation of calcium, carbonate and bicarbonate in seawater has been described by several authors (see Table I). Calcium and inorganic carbon are significantly associated with other ions as ion-pair complexes, which play an important role in other chemical processes such as calcite precipitation (Garrels *et al.*, 1961; Schindler, 1967; Pytkowicz, 1973). However, few data exist about brackish waters, where calcite precipitation is also a frequent phenomenon.

TABLE I. Percentages of major species of calcium and inorganic carbon compiled from the literature. *Porcentajes de las principales especies de calcio y carbono inorgánico, compilados de la bibliografía.* 1: Atkinson *et al.*, 1973; 2: Hanor, 1969; 3: Pytkowicz & Hawley, 1974; 4: Garrels & Thompson, 1962; 5: Millero, 1975; 6: Dyrssen & Wedborg, 1974; 7: Kester & Pytkowicz, 1969.

	Seawater	Reference	Freshwater	Reference
Free HCO_3^-	63 - 81	1,2,3,4	99,23	5
$NaHCO^0_3$	8 - 20	1,2,3,4	0.04	5
$MgHCO^+_3$	6 - 19	1,2,3,4	0.21	5
$CaHCO^+_3$	1 - 4	1,2,3,4	0.52	5
CO^{2-}_3	8 - 10	1,2,3,4	31.03	5
$NaCO^-_3$	3 -19	1,2,3,4	0.03	5
$MgCO^0_3$	44 - 67	1,2,3,4	6.50	5
$CaCO^0_3$	21 - 38	1,2,3,4	62.44	5
Free Ca^{2+}	85 - 92	1,2,3,4,6,7	96.89	5
$CaSO^0_4$	8 - 13	1,2,3,4,6,7	1.45	5
$CaHCO^+_3$	0.1 - 1	1,2,3,4,6,7	1.32	5
$CaCO^0_3$	0.1 - 0.9	1,2,3,4,6,7	0.33	5

Because the forms of inorganic carbon depend on pH, the free concentrations of metals and hence their effects on carbonate speciation would also be affected by the pH through carbonate complexation. Nevertheless, ion-pair formation depends not only on ionic strength, but also on the concentrations of each one of the major components, so to describe the relationships between the ratio free/total ion and environmental variables such as pH or ionic strength, it is necesary to recognize the specific types of complexed species in the system (Kester *et al.*, 1975).

The study of the chemical composition of different brackish waters located off the Spanish Mediterranean coast provided the base-line data to study general trends of calcium and carbonate speciation in this kind of water (López & Tomàs, 1989; López, 1990). Two aspects made the study of chemical speciation in these lagoons especially interesting. Firstly, they are located in calcareous watersheds presenting high concentrations of calcium and total alkalinity, which are not clearly related to salinity or seawater input (López, 1990). These components appear supersaturated or near the equilibrium with respect to calcium carbonate (López, 1993). Secondly, the lagoons present a wide range of pH and ionic strength, two factors that influence inorganic speciation.

The study of relationships between percentages of complexed forms of calcium and inorganic carbon and the main factors controlling chemical speciation, ionic strength and pH, can provide the general trends determining ion-pair formation, and also evaluate the relative contribution of complexation in the chemistry of calcareous brackish waters.

METHODS

Water analyses were carried out according to standard methods: Cl^- was analyzed by titration with silver nitrate and potassium bichromate (APHA, 1975); alkalinity by acidimetric titration with sulphuric acid (Golterman, 1969) and SO_4^{2-} by the method described by Fritz & Yamamura (1955). Cations were determined by atomic spectrophotometry (APHA, 1975). All samples were analyzed in the same way: the water was diluted when its concentration was higher than the upper limit of the method. The accuracy of the analyses were evaluated by the determination of percentage error in cation/anion balance by means of the equation:

% error = (Σ cation eq - Σ anion eq)/(Σ cation eq + S anion eq)x100

Samples exceeding 5% error were rejected.

The concentrations of free and complexed ions were deduced from dissociation constants for carbonic acid and the stability constants for the main ion pairs (Table II). Constants were corrected for ionic strength by using Davies' equation:

$\log f = -Az^2((\sqrt{I}/(\sqrt{I}+1))-0.2I)$ (Stumm & Morgan, 1981)

where $I = 1/2\sum m_i z$; A is temperature dependent (Drever, 1982)(0.25 at 25 °C); z_i is the charge of ion i; m_i is the molality of ion i.

TABLE II. Logarithms of the equilibrium constants for carbonic acid system and the stability constants for the main ion-pairs at infinite dilution and 25 °C, compiled from the literature. *Logaritmos de las constantes de equilibrio para el sistema del ácido carbónico y constantes de estabilidad para los principales pares de iones a dilución infinita y a 25° C, compilados de la bibliografía.* 1: Stumm & Morgan, 1981; 2: Golterman & Meyer, 1985; 3: Morel, 1983.

		Reference
K_1 H_2CO	-6.35	1
K_2 H_2CO_3	$-10.625 + 0.0145T - 1.089T^2$	2
$NaHCO^0_3$	-0.25	3
$MgHCO^+_3$	+1.16	3
$CaHCO^+_3$	+1.26	3
$NaCO^-_3$	-9.06	3
$MgCO^0_3$	-6.93	3
$CaCO^0_3$	-7.13	3
$CaSO^0_4$	+2.31	3
KSO^-_4	+0.96	3
$NaSO^-_4$	+1.06	3
$MgSO^0_4$	+2.36	3

Calculations consisted of the simultaneous solution of 18 equations with 18 unknowns. They were made iteratively assuming first that the ions were not significantly complexed (Morel, 1983).

RESULTS

Inorganic carbon

Inorganic carbon was present in the waters studied as three free forms, H_2CO_3, HCO^-_3 and

CO^{2-}_3, and six ion-pair complexes: $NaHCO^0_3$, $CaHCO^+_3$, $MgHCO^+_3$, $NaCO^-_3$, $CaCO^0_3$ and $MgCO^0_3$. In Table III, maximum, minimum and mean values are given for each form.

TABLE III. Inorganic speciation of calcium and carbon in Spanish Mediterranean brackish waters (n=90). Max. maximum; Min, minimum; Mean, mean values; SD, standard deviation. *Especiación inorgánica de calcio y carbono en aguas salobres del litoral mediterráneo español (n=90). Max., valores máximos; Min., valores mínimos; Mean., valores medios; SD, desviación típica.*

Percentage of total Ca^{2+}	Max.	Min.	Mean	SD
free Ca^{2+}	93.46	74.63	84.15	4.62
$CaSO^0_4$	22.92	2.45	12.55	4.17
$CaHCO^+_3$	4.04	0.30	1.97	0.80
$CaCO^0_3$	11.65	0.05	1.63	2.16
Percentage of total alkalinity				
Free HCO_3^-	93.55	34.45	82.90	10.51
$NaHCO^0_3$	5.65	0.03	1.22	1.10
$CaHCO^+_3$	5.79	0.20	2.20	1.23
$MgHCO^+_3$	6.11	0.16	2.17	1.26
Free CO^{2-}_3	17.50	0.04	2.13	3.15
$NaCO^-_3$	6.03	0.01	0.74	1.12
$CaCO^0_3$	9.87	0.10	1.58	2.04
$MgCO^0_3$	33.28	0.07	4.15	6.10
Percentage of total carbonate				
Free CO^{2-}_3	44.51	12.49	25.01	6.68
$NaCO^-_3$	22.65	0.20	7.23	4.61
$CaCO^0_3$	54.03	4.18	24.33	11.41
$MgCO^0_3$	68.61	10.63	43.43	11.51

Free HCO^-_3 was always the most abundant species (from 34,4 to 93.5% of total alkalinity), but its percentage was strongly influenced by pH, reaching the maximum values at moderate pH (8.3) (Fig.1, Table IV). Free CO^{2-}_3 and H_2CO_3 percentages were also strongly dependent on pH: H_2CO_3 was a significant fraction of total inorganic carbon (from 1 to 19%) at pH from 6.9 to 8.1; at pH above 8.0, free CO^{2-}_3 was significant (1-17%) (Fig.1). Regression equations for free CO^{2-}_3 showed highly significant coefficients with pH and non significant coefficients with ionic strength. For free HCO^-_3, regression coefficient with pH was lower, but still significant, also showing a weak dependence on ionic strength (Table IV).

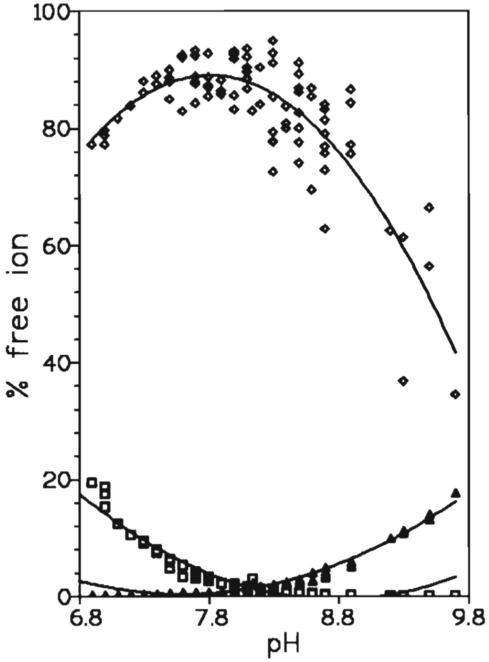

FIGURE 1. Relationship between free HCO_3^- (circles), free CO^{2-}_3 (triangles) and H_2CO_3 (squares) expressed as percentages of total inorganic carbon and pH. *Relación entre HCO_3^- libre (círculos), CO^{2-}_3 libre (triángulos) y H_2CO_3 (cuadrados), expresados como porcentaje de carbono inorgánico total y pH.*

Bicarbonate complexes (i.e. $NaHCO^0_3$, $CaHCO^+_3$, and $MgHCO^+_3$) were usually a small fraction of total alkalinity (less than 7%). They were dependent on ionic strength, especially $NaHCO^0_3$ and $MgHCO^+_3$ (Fig. 2, Table IV). At low ionic strength $CaHCO^+_3$ was the main bicarbonate complex, whereas at medium and high ionic strength $MgHCO^+_3$ and $NaHCO^0_3$ predominated. Only $CaHCO^+_3$ showed a weak regression coefficient with pH (Table IV).

TABLE IV. Equations of the regression lines ($y = A_2x^2 + A_1x + A_0$) between pH, ionic strength and percentages of calcium and inorganic carbon species. Parameters of the regression lines are given only when regression coefficients are significant ($r>0.40$, $n=90$). *Ecuaciones de las rectas de regresión* ($y = A_2x^2 + A_1x + A_0$) *entre pH, fuerza iónica y porcentajes de especies de calcio y carbono inorgánico. Los parámetros de las rectas de regresión se dan sólo cuando los coeficientes de regresión son significativos* ($r>0.40$, $n=90$).

	vs pH				vs logI			
	r	A_0	A_1	A_2	r	A_0	A_1	A_2
Percentage of total calcium								
Free Ca^{2+}	0.54	-20.00	29.37					
$CaSO^0_4$								
$CaHCO^+_3$					0.65	0.76	-0.86	-1.77
$CaCO^0_3$		0.80	66.32	-18.55	1.30			
Percentage of total alkalinity								
Free HCO_3^-	0.84	-730	209	-13.4	0.37			
$NaHCO^0_3$	0.29				0.93	6.30	7.25	2.14
$CaHCO^+_3$	0.41	-50	13	-0.8	0.49	4.61	3.02	0.68
$MgHCO^+_3$	0.31				0.89	6.67	5.67	1.30
Free CO^{2-}_3	0.98	209	-55	3.6	0.15			
$NaCO^-_3$	0.70	26	-8	0.5	0.49	3.50	3.99	1.19
$CaCO^0_3$	0.79	77	-21	1.4	0.21			
$MgCO^0_3$	0.88	307	-82	5.5	0.23			
Percentage of total carbonates								
Free CO^{2-}_3	0.23				0.80	8.9	-15.7	-1.1
$NaCO^-_3$	0.30				0.86	23.4	20.5	4.8
$CaCO^0_3$	0.41	-51.9	26.3	-2.07	0.41	25.9	15.7	11.2
$MgCO^0_3$	0.26				0.56	41.7	-20.4	-14.9

Carbonate complexes (i.e. $NaCO^-_3$, $CaCO^0_3$ and $MgCO^0_3$) presented a wide range of variation (Table III). Their abundance relative to total alkalinity was clearly related to pH (Table IV, Fig. 3), varying from less than 0.1% at the lowest pH to 6, 9 and 33% for $NaCO^-_3$, $CaCO^0_3$ and $MgCO^0_3$ respectively at the highest pH. Carbonate ion-pairs were the main fraction of total carbonate, free CO^{2-}_3 usually being less than 25% of total carbonate. When percentages of carbonate species were related to total carbonate, $NaCO^-_3$ and $MgCO^0_3$ showed highly significant coefficients of regression with ionic strength, but not with pH (Fig. 4). $CaCO^0_3$ was the main fraction at low ionic strength, its percentage decreasing when ionic strength increased, although it showed great variability. $MgCO^0_3$ and especially $NaCO^-_3$ rose with ionic strength, $MgCO^0_3$ becoming the main fraction from $I > 0.05$. At high pH, $MgCO^0_3$ reached a percentage of total alkalinity similar to those of free HCO^-_3 (33.28% and 36.72% respectively).

In Figure 5, the sum of bicarbonate complexes (A) and the sum of carbonate complexes (B) is plotted against ionic strength, grouping the samples with equal pH. Bicarbonate complexes were dependent on ionic strength, but did not show important differences when pH varied, although the maximum values were observed at pH 8.3. Carbonate complexes were influenced by both pH and ionic strength. Its percentage rose with ionic strength, but, the slopes of regression lines also increased with pH. As a whole, at pH <7.7, bicarbonate complexes were the only complexed forms, their percentage increasing to 10% of total alkalinity at i=0.26. At medium pH (7.9-8.3), carbonate and bicarbonate complexes coexisted and total complexed forms attained 20% of total alkalinity at

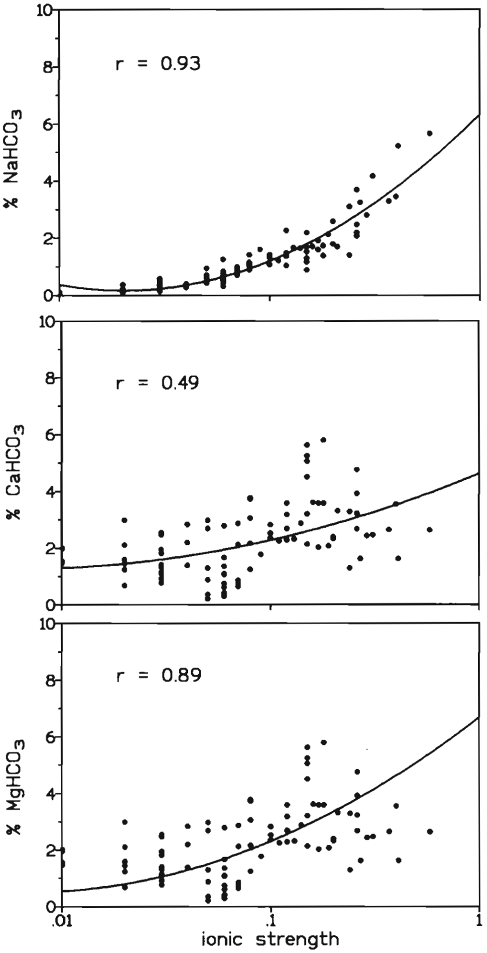

FIGURE 2. Relationships between $NaHCO^0_3$, $CaHCO^+_3$ and $MgHCO^+_3$ expressed as percentages of total alkalinity and ionic strength. *Relaciones entre $NaHCO^0_3$, $CaHCO^+_3$ y $MgHCO^+_3$ expresados como porcentajes de la alcalinidad total y fuerza iónica.*

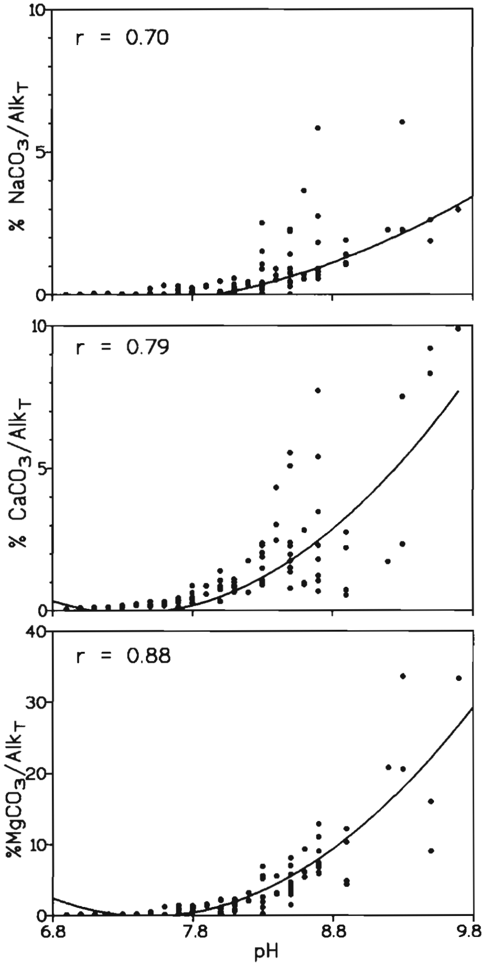

FIGURE 3. Relationships between $NaCO^-_3$, $CaCO^0_3$, and $MgCO^0_3$ expressed as percentages of total alkalinity and pH. *Relaciones entre $NaCO^-_3$, $CaCO^0_3$ y $MgCO^0_3$ expresados como porcentajes de la alcalinidad total y pH.*

i>0.40. For the highest pH (>8.5), carbonate species became dominant, reaching 50% of total alkalinity at i=0.26.

Calcium

Calcium was present as free ion (74.6-93.4% of total calcium; Table III), showing weak coefficients of regression with pH (Table IV).

The most abundant calcium complex was always $CaSO^0_4$, which attained 22.9% of total metal (Table III). Its percentage was not related with pH or ionic strength (Table IV). $CaCO^0_3$ was strongly dependent on pH (Table IV, Fig. 6), reaching 10 % of total calcium at pH>9. It was not related to ionic strength. $CaHCO^+_3$ usually presented low percentages (<5%), being mainly influenced by ionic strength

(Table IV). In the pH range from 8 to 8.5, $CaCO^0_3$, $CaSO^0_4$ and $CaHCO^+_3$ coexisted at percentages greater than 1%. At lower pH, $CaHCO^+_3$ and $CaSO^0_4$ were the only significant complexes, and at pH>8.5 $CaCO^0_3$ became more abundant, $CaHCO^+_3$ shifting and reaching values similar to those of $CaSO^0_4$ (Fig. 6).

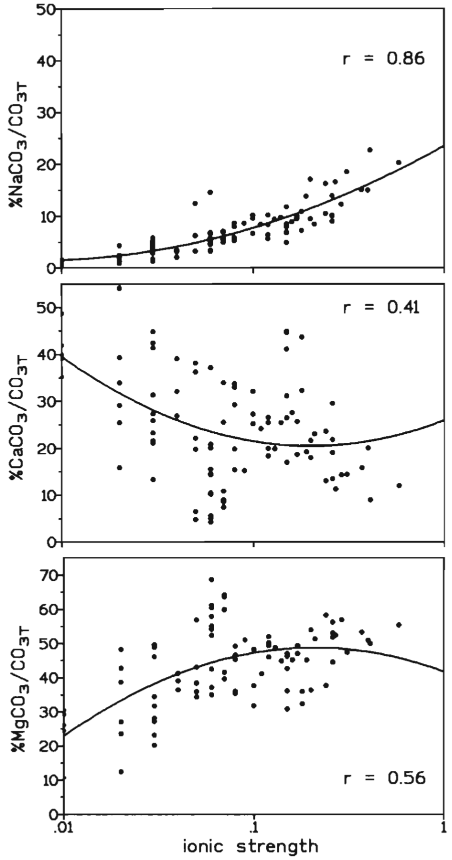

FIGURE 4. Relationships between $NaCO^-_3$, $CaCO^0_3$, and $MgCO^0_3$ expressed as percentages of total carbonates and ionic strength. *Relaciones entre* $NaCO^-_3$*,* $CaCO^0_3$ *y* $MgCO^0_3$ *expresados como porcentajes de carbonatos totales y fuerza iónica.*

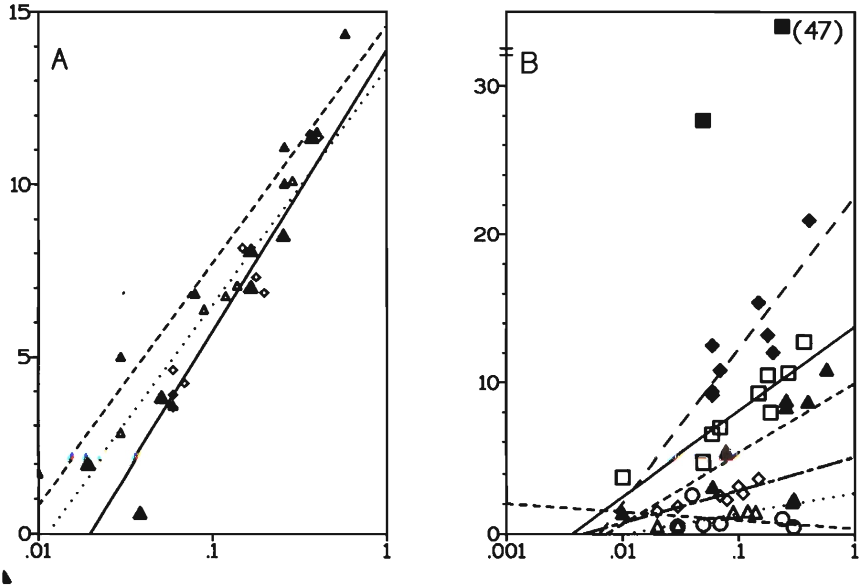

FIGURE 5. Regression plots of sum of bicarbonate complexes (A) and carbonate complexes (B) versus ionic strength. Data are grouped by pH. Circles: pH = 7.5; open triangles: pH = 7.7; open diamonds: pH = 8.1; full triangles: pH = 8.3; open squares: pH = 8.5; full diamonds: pH = 8.7; full squares: pH = 9.3. *Gráficos de regresión de la suma de complejos de bicarbonato (A) y complejos de carbonato (B) frente a fuerza iónica. Los datos se agrupan en función del pH. Círculos: pH = 7,5; triángulos vacíos; pH = 7,7; rombos vacíos: pH = 8,1; triángulos llenos: pH = 8,3; cuadrados vacíos: pH = 8,5; rombos llenos: pH = 8,7; cuadrados llenos: pH = 9,3.*

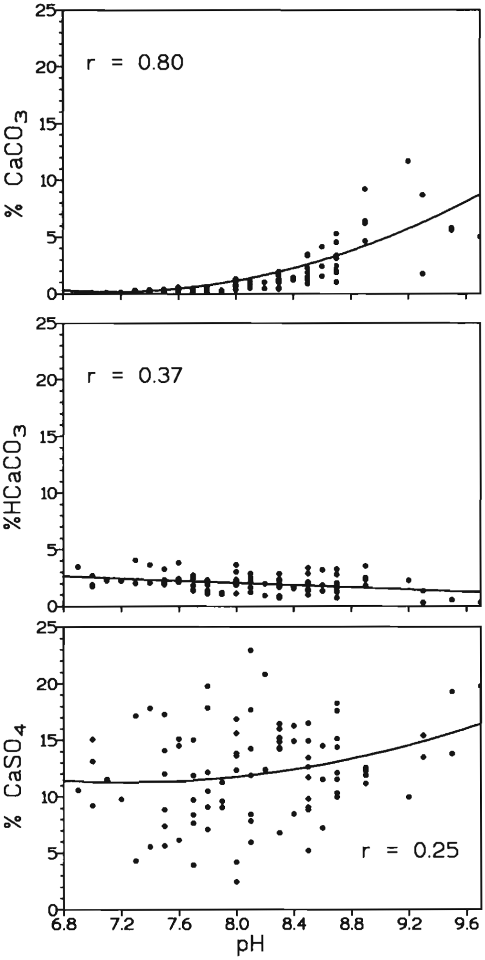

FIGURE 6. Relationships between $CaCO^0_3$, $CaSO^0_4$ and $CaHCO^+_3$ expressed as percentages of total calcium and pH. *Relaciones entre* $CaCO^0_3$, $CaSO^0_4$ *y* $CaHCO^+_3$ *expresados como porcentajes de calcio total y pH.*

DISCUSSION

Ion-pair formation is a complicated process, which depends not only on ionic strength, but also on specific chemical composition. Mediterranean brackish waters have a chemical composition which clearly differs from diluted seawater, showing great variability, especially in calcium and alkalinity concentrations (López & Tomàs, 1989; López 1990). Percentages of free ions deduced for these waters showed important differences with respect to the values reported for marine and estuarine waters (Kester, 1975; Stumm & Morgan, 1981). In spite of the variability of data, some ionic species can be expressed as a function of two major descriptors: ionic strength and pH. $NaHCO^0_3$ and $MgHCO^+_3$ were related to ionic strength and could be expressed as a single function of this. Because seawater has a higher ionic strength than that found in the waters studied (0.7 in seawater, <0.6 in studied lagoons), the values observed were always lower than those reported in the literature for seawater: from 8 to 10% for $NaHCO^0_3$ and from 7 to 19% for $MgHCO^+_3$ (review in Stumm & Morgan, 1981). In contrast, the percentages observed were higher than those reported by Millero (1975) for river water, which has lower ionic strength. $CaHCO^+_3$ was not related to ionic strength and the values observed were similar to those of seawater. In fact, in brackish waters ionic strength is mainly due to seawater input, which, in turn, is highly correlated with Na and Mg concentrations (López, 1990). In this case, specific (chemical composition) and non-specific (ionic strength) interactions were dependent on the same factor, which can be expressed by ionic strength determining the observed relationship between $NaHCO^0_3$ and $MgHCO^+_3$ and ionic strength. Calcium concentration, on the other hand, presents weak dependence on seawater input (López, 1990), so $CaHCO^+_3$ percentages showed weak correlation with ionic strength.

Percentages of free CO^{2-}_3 and H_2CO_3 were strongly dependent on pH and they can be expressed as a single function of this. As seawater pH is near 8.2 and the range observed in the waters studied was from 6.9 to 9.6, percentages observed differed greatly from those of seawater.

Carbonate complexes were influenced by pH when they were referred to total alkalinity, whereas $NaCO^-_3$ and $MgCO^0_3$ depended on ionic strength when they were expressed as percentages of total carbonates. These values were similar to those of seawater: 43-67% for $MgCO^0_3$ and 16-19% for $NaCO^-_3$ (Stumm & Morgan, 1981). Because the concentration of CO^- is pH dependent, a correlation between carbonate complexes and pH can be expected (Morel, 1983). Dependence of $NaCO^-_3$ and $MgCO^0_3$ as fraction of total carbonates on the ionic strength could have a similar explanation to that indicated for $NaHCO^0_3$ and $MgHCO^+_3$ percentages.

As a whole, complexed forms of inorganic carbon were a significant fraction of total alkalinity when i>0.05 and pH>8.5; when i>0.10 and pH>8.1 and when i>0.20 and pH>8.1. In these ranges, bicarbonate and especially carbonate complexes greatly influenced total inorganic carbon concentrations, so they can be taken into account in order to successfully describe their chemical behavior.

Calcium species could not be expressed as single equations of pH or ionic strength. In fact, only $CaCO^0_3$ percentage could be clearly related to pH, reaching values much greater than those reported for seawater (0.2%). Because the stability constant of calcium carbonate is much higher than the constant of the hydrogen carbonate equilibria, protonated and unprotonated calcium complexes were present in about the same amounts at pH 8, in spite of the high value of the ratio HCO^-_3/CO^{2-}_3. However, when pH increased, the ratio HCO^-_3/CO^{2-}_3 decreased rapidly and $CaCO^0_3$ reached values similar to those of $CaSO^0_4$ (Ahrland, 1975). $CaSO^0_4$ and $CaHCO^+_3$ observed were also greater than seawater values: 8 to 10% and 0.3 to 1% respectively (Stumm & Morgan, 1981), which could be related to the high concentrations of calcium and sulphate observed in Mediterranean brackish waters (López & Tomàs, 1989; López, 1990). Although calcium is an a-type cation with a low polarising power and its speciation is dominated by the free ion in both sea and freshwater (Turner *et al.*, 1981), sometimes it reached a significant fraction of total metals in the waters studied, especially at high pH values and moderate or high ionic strength when $CaSO^0_4$ and $CaCO^0_3$ could be present at high levels.

Calcium and inorganic carbon speciation thus played an important role in the chemical equilibrium of calcareous brackish waters, modifying concentrations of reactive species in different proportion to that in seawater. Complexed forms must be taken into account in order to describe chemical relations in which calcium and/or inorganic carbon participate.

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