

# Ion Pairs in Karst Waters

by  
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A method of calculating the concentrations and activities of the  $\text{CaCO}_3^0$ ,  $\text{CaHCO}_3^+$ ,  $\text{CaSO}_4^0$ ,  $\text{MgCO}_3^0$ ,  $\text{MgHCO}_3^+$ ,  $\text{MgSO}_4^0$ ,  $\text{NaCO}_3^-$ ,  $\text{NaHCO}_3^0$  and  $\text{NaSO}_4^-$  ion pairs, which are formed in karst waters with ionic strength between  $2.5-8.1 \times 10^{-3}$  mole/l and pH between 6.90-8.60 is presented. On this basis it has been observed that in such waters, 3.7%, on an average, from the total concentration of calcium, 3.8% from magnesium, 0.2% from sodium and 14.2% from sulphate are associated in ion pairs. The influence of ionic strength, pH and  $\text{SO}_4^{2-}$  ions concentration upon the degree of ion association is discussed. The results have been obtained by calculation on 56 water samples from the karst areas situated in the middle basin of the Cerna River (Banat), and the Sebeş Mountains, as well as from the Zăton-Bulba hydrokarstic basin (South Carpathians).

## INTRODUCTION

It is known that the cations and anions of natural waters have, under certain conditions, the tendency to associate forming either ion pairs or complexes. At a ion pair the chemical bond between the two ions with opposite charge is essentially electrostatic, the cation keeping the dipoles of water which hydrate it. As far as complexes are concerned, the covalent forces of the bond prevail and the anion penetrates into the hydration shell of the cation eliminating one or more molecules of water. There are, of course, some thermodynamics criteria of differentiation between ion pairs and complexes (Petrucci, 1971). The major cations from natural waters ( $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) are forming ion pairs with the  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  anions. The metallic ions ( $\text{Zn}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$  etc.) which are usually minor constituents of the natural waters, are forming complexes with the same ligands.

Although the ion pair concept has been known for a long time, it was used for the first time in the study of natural waters by Garrels et al. (1961). Garrels and Thompson (1962), used this concept in constructing the chemical model for sea water. The authors demonstrate that the presence of these chemical species in water cannot be ignored when the solubility of the minerals must be estimated. The ion pair concept has afterwards been used for some other categories of natural waters: Truesdell and Blair (1969) for brines, Nakayama (1968) and Hassett and Jurinak (1971) for soil water, Langmuir (1971) and Thrailkill (1972) for underground waters and streams. At the same time a great number of papers are dedicated to the study of ion pairs properties: Hostetler (1963), Jacobson and Langmuir (1974), Reardon and Langmuir (1974 and 1976), Reardon (1975), and others. The programmes of calculating ion and ion pair concentrations and activities from different kinds of waters are made by Van Breemen (1973) and O'Connor and Cadena (1975), and by Thrailkill (1972 and 1976) and Wilcock (1976) for karst waters. In speology, Picknett (1973) and Picknett et al. (1976) have established the solubility

product of the calcium carbonate and some other constants regarding the presence of the  $\text{CaCO}_3^0$  and  $\text{CaHCO}_3^+$  ion pairs.

In this study we have tried to establish the share of ion pairs in karst waters (springs and streams) and certain elements which influence the ion associations. A method of calculating the activities and concentrations of different chemical species dissolved in water has been used. The 56 water samples were taken from three karst areas situated in the South Carpathians: 26 samples from the karst area situated in the middle basin of the Cerna River between Țăsna and Arșasca, 20 samples from the karst of the Sebeș Mountains and 10 samples from the Zăton-Bulba hydrokarstic basin.

## CALCULATION PROCEDURE

The analytical part consisted in determining in situ the temperature and water pH. The error in pH determination was  $\pm 0.05$  pH units. In the laboratory  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^-$ ,  $\text{Cl}^-$  and the total alkalinity were analysed, immediately after samples collection. Small concentrations of sodium (3.5 mg/l on an average) and potassium (1.2 mg/l) have been found in all the analysed water samples. Under these circumstances it has been agreed that potassium should be expressed as sodium, the errors introduced in the subsequent calculations being minor. It has also been assumed that the total water alkalinity is carbonate alkalinity.

The programme of calculation has determined the concentration and activities of the following dissolved chemical species:  $\text{Ca}^{++}$ ,  $\text{CaCO}_3^0$ ,  $\text{CaHCO}_3^+$ ,  $\text{CaSO}_4^0$ ,  $\text{Mg}^{++}$ ,  $\text{MgCO}_3^0$ ,  $\text{MgHCO}_3^+$ ,  $\text{MgSO}_4^0$ ,  $\text{Na}^+$ ,  $\text{NaCO}_3^-$ ,  $\text{NaHCO}_3^0$ ,  $\text{NaSO}_4^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{--}$ ,  $\text{SO}_4^{--}$ ,  $\text{Cl}^-$ ,  $\text{H}^+$ , and  $\text{OH}^-$ .

The equations of mass balance for the respective ions are of the following kind:

$$\text{Total Ca} = m\text{Ca}_{\text{free}}^{++} + m\text{CaCO}_3^0 + m\text{CaHCO}_3^+ + m\text{CaSO}_4^0,$$

where by  $\text{Ca}_{\text{free}}^{++}$  we denote unassociated calcium ions. In the initial stage of calculation the free ionic concentrations have been considered equal with the total concentrations, and the concentrations of the ion pairs have been considered null.

The process of calculation can be divided into five stages of work:

1. The calculation of the water ionic strength on the basis of analytical results.
2. The calculation of the activity coefficients of individual ions and ion pairs.
3. The determination of the activities of free ions and ion pairs.
4. Recalculation of the concentrations of all species.
5. The calculation of a new ionic strength and the repetition of the 2-4 steps until a difference has been obtained between the previous ionic strength and the final ionic strength not exceeding  $\pm 5 \times 10^{-6}$  mole/l. With the final ionic strength established, all the activities and concentrations are calculated at the end.

The checking of the accuracy of the method of calculation is realized by calculating the charge balance. There have been necessary 4-6 cycles of calculation, obtaining charge imbalance between 0.01 and 0.39%.

The ionic strength ( $\mu$ ) of the waters has been calculated with the well-known relation :

$$\mu = \frac{1}{2} \sum m_i \cdot z_i^2,$$

where  $m_i$  represents the concentration of the chemical species and  $z_i$  its charge.

The activity coefficients ( $f$ ) of the individual ions have been calculated with the Debye-Hückel relation :

$$-\log f_i = \frac{A \cdot z_i^2 \sqrt{\mu}}{1 + a \cdot B \cdot \sqrt{\mu}}.$$

The values of the constants  $A$ ,  $B$  and  $a$  have been taken from Garrels and Christ (1965). The activity coefficients of the  $\text{CaCO}_3^0$ ,  $\text{MgSO}_4^0$ ,  $\text{NaHCO}_3^0$  ion pairs have been considered equal with the unit. The activity coefficients of the  $\text{CaHCO}_3^+$ ,  $\text{MgHCO}_3^+$ ,  $\text{NaCO}_3^-$  and  $\text{NaSO}_4^-$  ion pairs are the same with the activity coefficient of  $\text{HCO}_3^-$  ion. The activity coefficients of the  $\text{CaSO}_4^0$  and  $\text{MgCO}_3^0$  species have been calculated regarding the ionic strength after the relation given by Reardon and Langmuir (1976) :

$$\log f_i = -C \cdot \mu,$$

where  $C$  is a constant which has the values of  $0.45 \pm 0.15$  for  $\text{CaSO}_4^0$  and  $0.63 \pm 0.1$  for  $\text{MgCO}_3^0$  at  $25^\circ\text{C}$  and the ionic strength smaller than  $0.05$  moles  $\text{l}^{-1}$

Table 1

Values of equilibrium constants used in calculations

Reaction	pK						Reference*
	0°C	5°C	10°C	15°C	20°C	25°C	
$\text{CaCO}_3$ (calcite) $\rightarrow \text{Ca}^{++} + \text{CO}_3^{--}$	8.39	8.40	8.41	8.42	8.45	8.47	1
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$	1.114	1.194	1.269	1.341	1.406	1.463	2
$\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{H}_2\text{CO}_3^*$	6.578	6.517	6.465	6.421	6.383	6.352	2
$\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{--}$	10.625	10.557	10.490	10.430	10.377	10.330	3
$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	14.943	14.734	14.535	14.396	14.167	13.996	4
$\text{CaCO}_3^0 \rightarrow \text{Ca}^{++} + \text{CO}_3^{--}$	3.01	3.02	3.04	3.07	3.11	3.15	5
$\text{CaHCO}_3^+ \rightarrow \text{Ca}^{++} + \text{HCO}_3^-$	0.68	0.75	0.82	0.88	0.95	1.02	1
$\text{CaSO}_4^0 \rightarrow \text{Ca}^{++} + \text{SO}_4^{--}$	2.20	2.22	2.24	2.27	2.29	2.31	6
$\text{MgCO}_3^0 \rightarrow \text{Mg}^{++} + \text{CO}_3^{--}$	2.76	2.77	2.79	2.81	2.84	2.88	5
$\text{MgHCO}_3^+ \rightarrow \text{Mg}^{++} + \text{HCO}_3^-$	0.95	0.95	0.95	0.95	0.95	0.95	7
$\text{MgSO}_4^0 \rightarrow \text{Mg}^{++} + \text{SO}_4^{--}$	2.03	2.10	2.16	2.23	2.29	2.36	6
$\text{NaCO}_3^- \rightarrow \text{Na}^+ + \text{CO}_3^{--}$	1.27	1.27	1.27	1.27	1.27	1.27	4
$\text{NaHCO}_3^0 \rightarrow \text{Na}^+ + \text{HCO}_3^-$	-0.25	-0.25	-0.25	-0.25	-0.25	-0.25	4
$\text{NaSO}_4^- \rightarrow \text{Na}^+ + \text{SO}_4^{--}$	0.65	0.66	0.68	0.69	0.71	0.72	8

\* References : (1) Jacobson and Langmuir (1974); (2) Harned and Davis (1943); (3) Harned and Scholes (1941); (4) Garrels and Christ (1965); (5) Reardon and Langmuir (1974); (6) Langmuir (1971); (7) Hostetler (1963); (8) Thrailkill (1972)

The passing from the activities ( $a_i$ ) to the concentrations and conversely has been realized with the relation:

$$a_i = m_i \cdot f_i.$$

The equilibrium constants used in the calculation method are of the following type:

$$K_{\text{CaCO}_3^0} = \frac{a_{\text{Ca}^{++}} \cdot a_{\text{CO}_3^{--}}}{a_{\text{CaCO}_3^0}}$$

Their values are written in Table 1. These values have been interpolated in the calculation for the temperatures of the water samples. The same method has been used for the constants in the Debye—Hückel relation.

Molar concentrations have been used instead of molal concentrations because the differences between them are negligible at such small ionic strength.

## RESULTS AND DISCUSSION

The main chemical characteristic of the water samples collected from the three karstic areas are represented in Figs. 1 and 2. Their ionic strength varies between  $2.5 \times 10^{-3}$  and  $8.1 \times 10^{-3}$  moles  $l^{-1}$  and pH between 6.90—8.60 units. The common features of all these waters are their small concentrations of  $\text{Mg}^{++}$  and  $\text{Cl}^-$ . The average concentrations are of 2.8 mg/l for  $\text{Mg}^{++}$  and 3.5 mg/l for  $\text{Cl}^-$ . The waters from the middle basin of the Cerna river generally have concentrations of magnesium and chloride below these average values.

The existence of three main factors should be noticed which participate in increasing the degree of ion association in waters. These factors are: the ionic strength, pH, and the concentration of the sulphate ions in water.

Table 2 shows the percentage of free ions found in karst waters in comparison with that in sea water. It can be easily noticed that the ionic strength of sea water is more than the ionic strength of the karst waters

Table 2  
The percentage of free ions in karst waters and sea water

Ions	Karst waters				Sea water
	This study		Picknett (1973) <sup>(a)</sup>		Garrels and Christ (1965) <sup>(b)</sup>
	range	average	range	average	average
$\text{Ca}^{++}$	94.05—98.61	96.3	94.9—97.0	95.9	91
$\text{Mg}^{++}$	95.07—98.13	96.2	—	—	87
$\text{Na}^+$	99.70—99.88	99.8	—	—	99
$\text{K}^+$	—	—	—	—	99
$\text{SO}_4^{--}$	81.59—88.76	85.8	—	—	54
$\text{Cl}^-$	100	100	—	—	100

(a) The values are calculated on saturated solutions of calcium carbonate with a content of  $\text{Ca}^{++}$  of 0.001 moles  $l^{-1}$ .

(b) Sea water with chlorinity of 19 ‰ at 25°C, pH of 8.15 and ionic strength 0.7 moles  $l^{-1}$ .

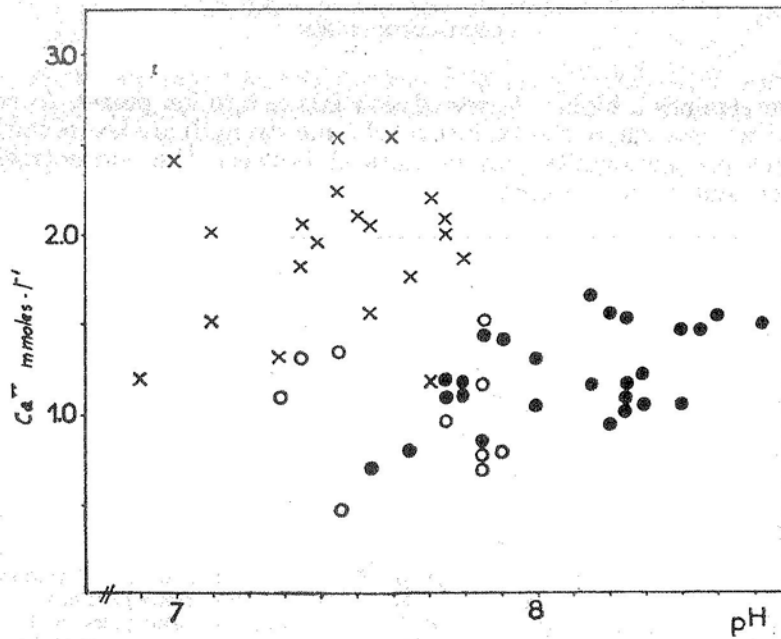


Fig. 1. — Variation of the calcium concentrations and of pH with the studied waters

(●) Sebeş Mountains, (×) Cerna river middle basin, (○) Zăton-Bulba hydrocarstic area.

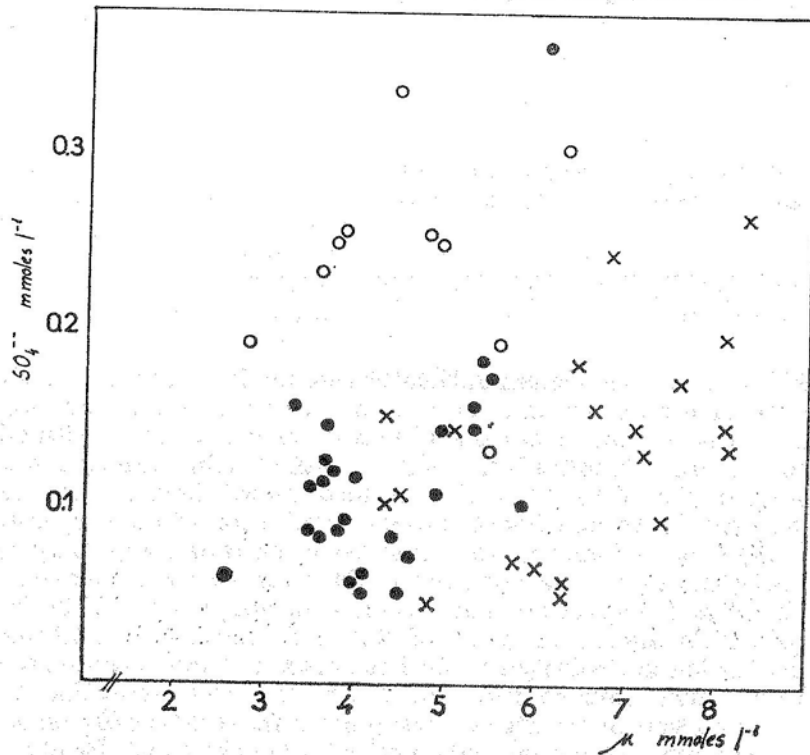


Fig. 2. — Variation of the sulphate concentrations and of ionic strength with the studied waters

(●) Sebeş Mountains, Cerna river middle basin, (○) Zăton-Bulba area.

and it determines a higher degree of association into ion pairs. As regards the karst waters, where the variations of ionic strength are less remarkable, the direct proportionality can be noticed between the concentration of ion pairs and ionic strength.

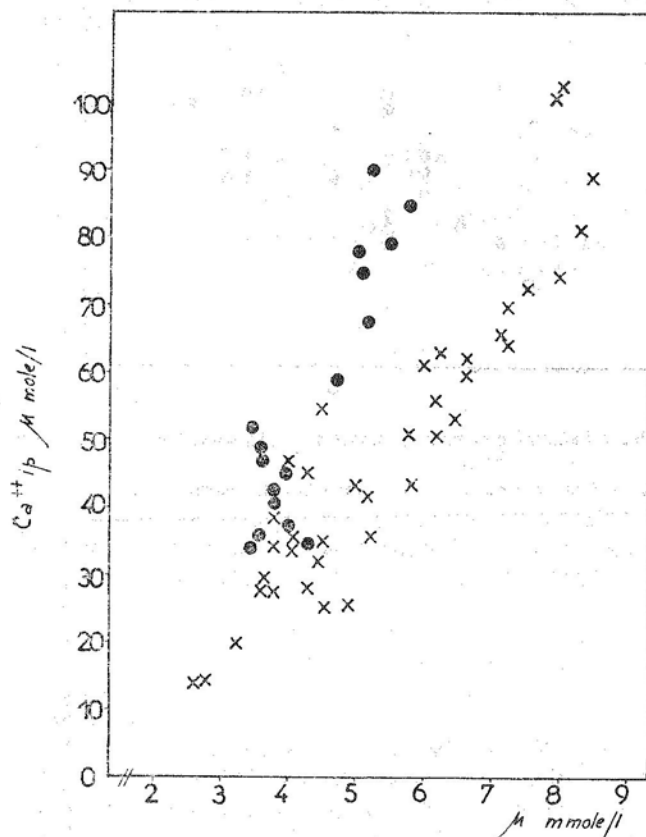


Fig. 3. — Variation of the concentrations of calcium ion pairs with the ionic strength

(●) pH above 8.00, (x) pH under 8.00.

Fig. 3 shows the concentrations of calcium ion pairs in terms of the respective ionic strength and the role of water pH in forming ion pairs. It is shown that for the same value of ionic strength in waters with alkaline pH, the ion pair concentration is higher than in acid waters. The increasing concentration of  $\text{CO}_3^{2-}$  in alkaline medium will influence the increase of ion pair concentration. Fig. 4 shows the variation of the concentrations of the  $\text{CaCO}_3^0$  pairs found in the analysed samples also regarding pH. An asymptotic tendency of the curve to the pH values over 8.50 can be noticed.

The third condition which determines the obstruction of the free ions in ion pairs is the big concentration of  $\text{SO}_4^{2-}$ . Taking into account the inter-reactions ion-ion in electrolytes solutions, in an aqueous medium, the ionic association is more important for the 2 : 2 valent electrolytes than for 2 : 1 or 1 : 1 valent electrolytes. This is a result of the fact that the big ionic charge influence the ion associations into ion pairs (Bockris and Reddy, 1970). If we plot the activities of the  $\text{CaSO}_4^0$  and  $\text{CaHO}_3^+$  pairs depending on the

activity of the free  $\text{SO}_4^{--}$  and  $\text{HCO}_3^-$  ions respectively (Fig. 5), we notice that the sulphate ion has a stronger tendency of association than the bicarbonate ion. We can explain in the same way why a small part of the total sodium participates in forming ion pairs in comparison with alkaline earth ions.

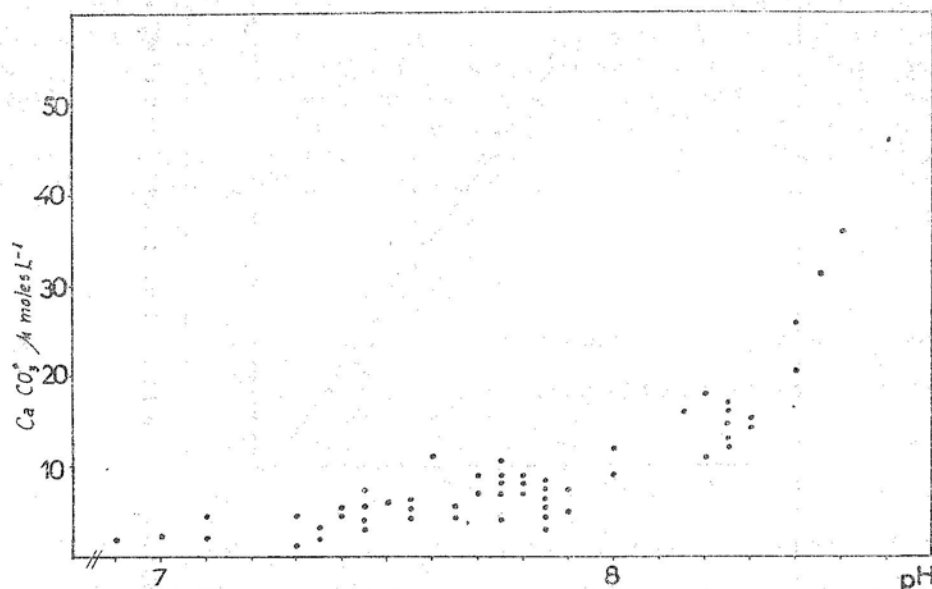


Fig. 4. — Variation of  $\text{CaCO}_3$  concentrations with pH.

The interdependence of the main factors which makes possible the ion association can be illustrated by comparing the results of the calculations obtained in the three karstic areas the samples came from. Table 3 presents the average values of the sums of percentage concentrations for all the ion pairs. If we refer only to the calcium ion pairs we can draw two conclusions: (1) although  $\mu$  is smaller by 35% in the Cerna river basin than in the Sebeş Mountains, the pH values, which are more alkaline in the first area, makes possible a much higher degree of association; (2) The same role of pH can be also taken by a high concentration of sulphate.

Table 3

The average of the percentage of ion pairs in the three studied karstic areas

	The Cerna river basin	Sebeş Mountains	Zăton-Bulba
$\mu$ m moles $\text{l}^{-1}$	4.7506	7.2469	4.8108
pH	8.20	7.50	7.50
$\text{SO}_4^{--}$ mg/l	12.7	16.8	24.7
$\text{Ca}_{\text{ip}}$ %	3.85	3.45	3.87
$\text{Mg}_{\text{ip}}$ %	3.59	3.93	3.88
$\text{Na}_{\text{ip}}$ %	0.21	0.26	0.21
$\text{SO}_{\text{dip}}$ %	12.53	16.78	12.46

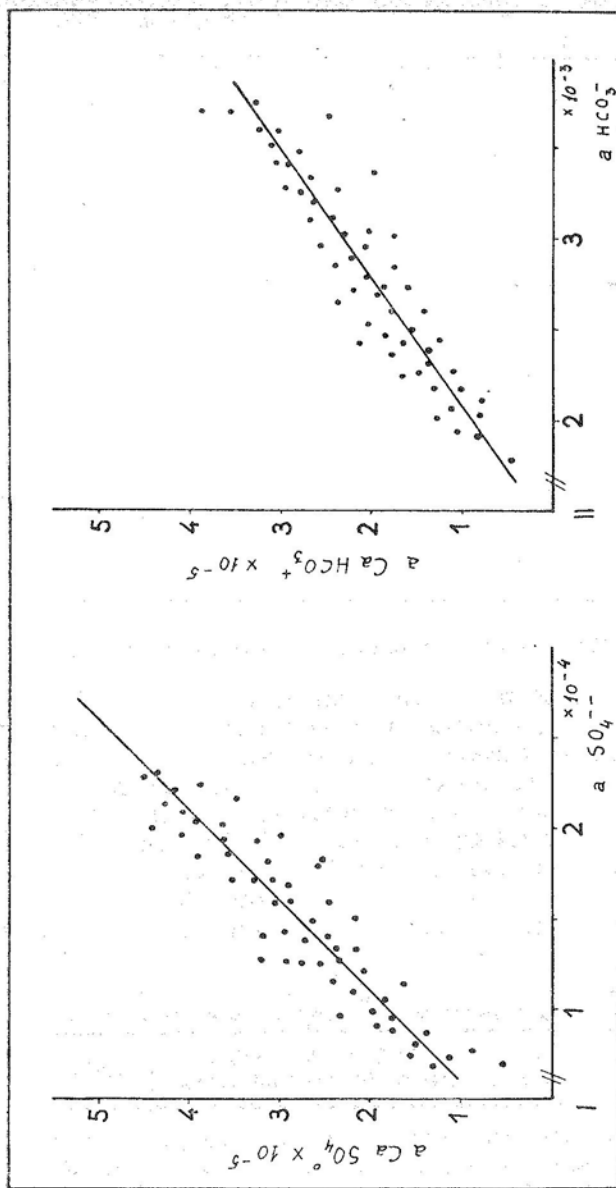


Fig. 5. — Correlation between the activity of  $CaSO_4^0$  and  $SO_4^{2-}$  — (I), and the activity of  $CaHCO_3^+$  and  $HCO_3^-$  (II).



**Conclusions.** The analytical determinations on the 56 water samples collected from the three karstic areas situated in the South Carpathians have proved the existence of ionic strength between 2.5 and 8.1 moles  $l^{-1}$  and the values of the pH between 6.90–8.60. By applying a method of calculation with iteration, it has been found that in this kind of waters about 96 % of the calcium concentration analytically determined are free ions. The rest is blocked in ion pairs of the  $CaCO_3^0$ ,  $CaHOC_3^+$ ,  $CaSO_4^0$  type. The proportion of unassociated magnesium is also about 96 %, of free sodium of 99.8 % and of the sulphate ion of 86 %. We can generally find a higher degree of ion pair formation at higher ionic strength, strong alkaline pH and big concentrations of sulphate ions.

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