

The Effect of Magnesium on the Solar Evaporation Process

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ABSTRACT

The small size and dipositive charge of the magnesium ion results in extensive hydration of the ion and formation of ion-pairs in aqueous solution. Measurements of density, refractive index and viscosity of the magnesium ion in solutions of MgSO_4 and MgCl_2 dissolved in NaCl brines demonstrate the effect of the MgSO_4 ion-pair and magnesium ion hydration. These measurements serve to illustrate the effect of magnesium content on the evaporation behavior of saline brines and the influence of the magnesium content on the specific gravity of those brines. It has been demonstrated that the magnesium content of saline brines affects the solubility of gypsum by ion-pair formation. The significance of these various effects on the solar evaporation process for seawater will be discussed.

INTRODUCTION

The effect of magnesium content on the evaporation rate of concentrated seawater brines has been shown by deFlers (1967) to be very close to that predicted by Raoult's Law. In view of our knowledge of the behavior of concentrated electrolyte solutions this is a surprising and entirely unexpected result.

Modern theories of the activities of aqueous solutions of polyvalent electrolytes generally lead to expected behavior which deviates widely from that predicted by Raoult's Law which is based upon the assumption of ideal solution behavior. It is, therefore, informative to consider the types of ion-ion and ion-solvent interactions of the magnesium ion in concentrated solutions of electrolytes in order to shed some light on the effect of the magnesium ion on the evaporation of water from concentrated brines.

It is generally accepted that one can represent the physical properties of seawater by a substitute solution which is 0.5 normal in NaCl and 0.05 normal in MgSO_4 . For the purposes of laboratory investigations we have adopted this simplified approach to the study of natural brines in order to minimize spurious phenomena which might mask the behavior of magnesium salts in concentrated brines.

In our laboratory we are conducting a systematic program of studying the physical and chemical properties of

solutions of MgCl_2 and MgSO_4 in sodium chloride solutions of varying composition. As the basis of our studies we are measuring various solution properties of MgCl_2 and MgSO_4 up to a concentration of 1.5 molal in 5, 10 and 15 percent by weight of NaCl in water. In this presentation, we discuss measurements of viscosity, refractive index and density of these solutions as manifestations of the interactions of the magnesium ion in solution. We also show that the presence of magnesium in brines influences the solubility of gypsum through the phenomenon of ion-pairing.

Because of its small size and dipositive charge, the magnesium ion is strongly hydrated in aqueous solution. This hydration of an ion results from the interaction between an ion and the dipolar water molecule. Although different methods lead to different estimates of the number of water molecules associated with particular ions, results are usually self-consistent for any given method (Horne, 1969). Consequently, by one method, the sodium ion has a hydration number of 2-4 while the magnesium ion yields a value in the range of 10-12 molecules of water per magnesium ion. Clearly, then, the magnesium ion with its high degree of hydration exerts a significant effect on the escaping tendency of water molecules from solution and consequently would diminish the evaporation rate of an aqueous solution to an extent exceeding that predicted by Raoult's Law.

A second property of the magnesium ion which influences the evaporation of water from brines is its tendency to form ion-pairs with other anions in brines. The predominant and strongest of such ion-pairs results from the interaction of Mg^{+2} and SO_4^{-2} to form the solution species, MgSO_4^0 .

Ion-pairs result from coulombic attraction between the anion and cation involved. The net effect is the formation of an ion-pair such as MgSO_4^0 with a reduction in net charge. Because of the resulting reduction of net charge, the number of water molecules associated with the individual ions is reduced. For instance, it is estimated that 35–40% of the water is lost from the hydration atmospheres of Ca^{+2} and SO_4^{-2} when the ion-pair, CaSO_4^0 , is formed (Millero, et al., 1977). This general behavior has also been observed for MgSO_4^0 , (Padova, 1964).

The effect of ion-pairing, then, is to exert an influence counter to the effect of ionic hydration on the evaporation tendency of concentrated brines. When an ion-pair forms in aqueous solution, the net interaction between ions and solvent molecules is diminished and hydration of the involved ions is lowered resulting in a higher vapor pressure than would be observed in the absence of this effect. Further, the formation of ion-pairs reduces the number of individual solute particles in solution which, according to Raoult's Law should result in an increase in the vapor pressure of the solution.

We are faced, then, with the presence of two effects, each exerting an opposite influence on the vapor pressure of water in concentrated brines. We shall now proceed to some experimental studies designed to demonstrate the influence of hydration and ion-pairing on the properties of brine systems. Through this process we hope to gain a better understanding of the structure of brine systems and, hence, a better understanding of their behavior.

EXPERIMENTAL STUDIES:

Molal volume. Very precise measurement of the density of salt solutions permits the calculation of the apparent molal volume, ϕ_v , of the salt in that solution. The apparent molal volume of a solute is defined as the contribution of that substance to the total volume of the solvent-solute system and may be either positive or negative depending upon molecular and ionic interactions. Franks and Smith (1967) have made density measurements of magnesium sulfate solutions at low concentration. Their data show the effect of the magnesium ion hydration which results in "electrostriction" of water molecules at low concentration. Negative values of the apparent molal volume approach -7.1 cm^3 per mole for magnesium sulfate. This negative value showing the collapse of the water structure is due to attraction of the polar water molecules by the magnesium ion.

At slightly higher concentrations the apparent molal volume of magnesium sulfate shows a positive deviation from

the limiting values at low concentration. This deviation is due to the formation of MgSO_4^0 , an ion-pair, which because of charge neutralization reduces the degree of hydration of the magnesium ion. As magnesium sulfate concentration increases, the relative concentration of magnesium sulfate ion-pairs increases and, thus, the electrostriction effect is lessened.

We have measured the apparent molal volumes of MgCl_2 and MgSO_4 in 5, 10 and 15% solutions of NaCl. The results of these measurements are shown in Figure 1. The distinguishing characteristic of these results is that the values of ϕ_v are lower for MgSO_4 than MgCl_2 in the same solvent systems and ϕ_v for each salt decreases with increasing NaCl concentration in the solution. Further, the plots of ϕ_v vs. \sqrt{m} show that, in all cases, the apparent molal volume of the magnesium salts decrease as their concentration increases which is opposite from the behavior of these salts in dilute aqueous solutions.

The most likely explanation for the observed solution behavior is that ionic interaction is the cause for the decrease of ϕ_v . Solutions of MgSO_4 show the greatest reduction in this parameter which is enhanced by increasing NaCl content. The formation of MgSO_4^0 and NaSO_4^- ion-pairs in concentrated solutions of relatively low water content probably exerts a greater effect on volume reduction than does electrostriction. It is very likely that in these solutions relatively little water of hydration is excluded from the atmosphere of the magnesium ion when an ion-pair is formed.

That the reduction in ϕ_v for MgCl_2 is less pronounced than for MgSO_4 is not unexpected. It is uncertain whether MgCl^+ ion-pairs are formed although conductance measurements have been interpreted to mean that this ionic species is formed (Horne and Frysinger, 1963).

We conclude, then, that in concentrated brines there is extensive ion-pairing and less hydration of the magnesium ion than is found in more dilute solutions. The combined effect of these phenomena is, consequently, manifested in the observations of deFlers and his co-workers that the evaporation rates of brines may be adequately represented by Raoult's Law.

Molal refraction. The apparent molal refraction, R_{app} , of a solute of molecular weight M , is defined by the condition that the total refraction, R , of a solution containing one mole of solute is the sum of R_{app} and the refraction which the amount (W_0 grams) of solvent present in this solution would have in the pure state. Hence, the molal refraction, R , is designated by

$$R = R_{app} + r_0 W_0$$

where r_0 is the specific refraction of the solvent.

Using a differential refractometer, we have measured the refractive indexes of solutions of MgCl_2 and MgSO_4 of varying concentration in 5, 10 and 15% NaCl solution.

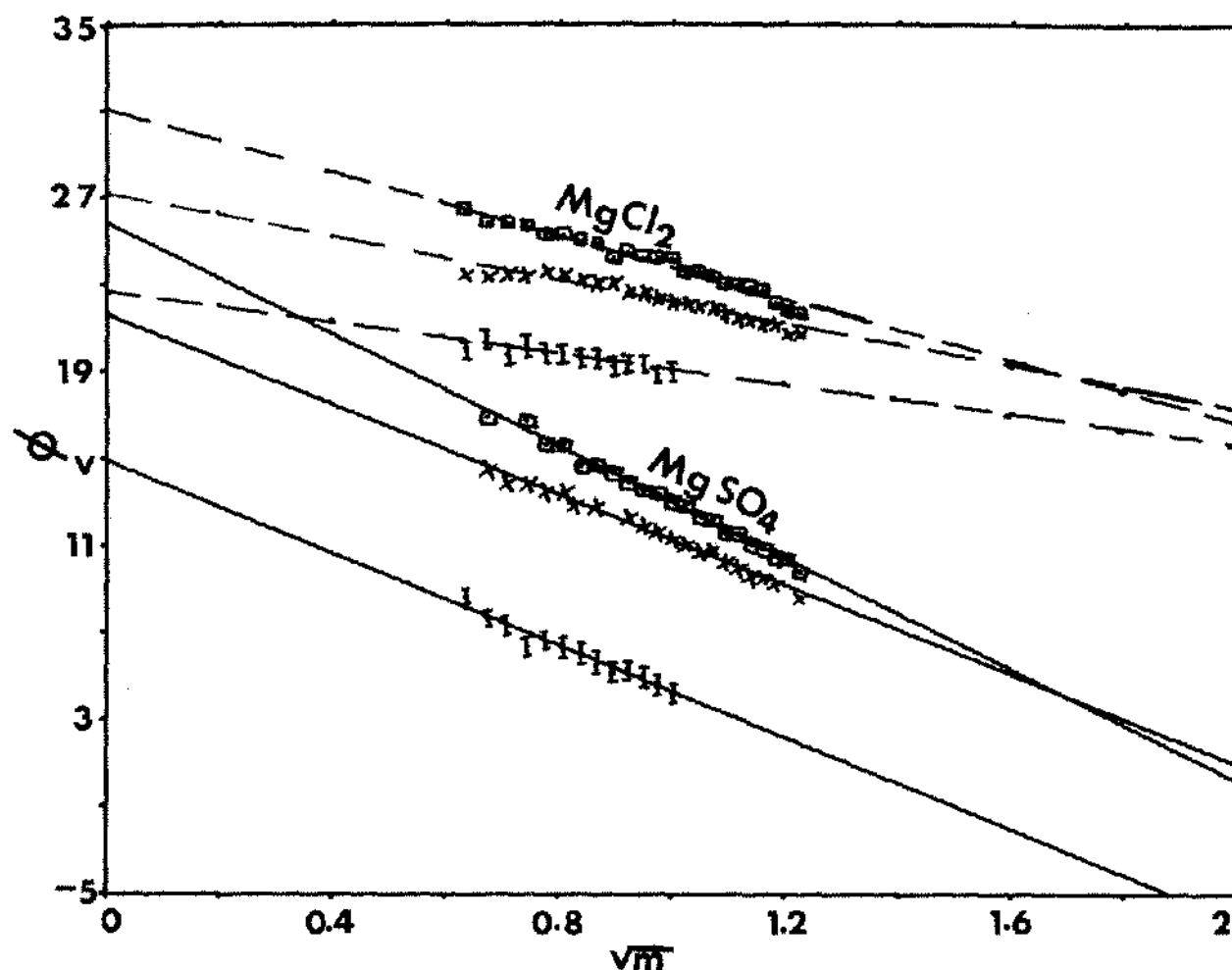


Figure 1. Partial volume of MgSO_4 and MgCl_2 in 5% (\square), 10% (\times) and 15% ($\bar{\mid}$) NaCl.

Using these refractive index values and density data derived from the study in another part of this paper we have calculated R_{app} , the apparent molal refraction, of MgCl_2 and MgSO_4 as a function of concentration and NaCl concentration.

The values of R_{app} were calculated using the equation

$$R_{\text{app}} = \left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \cdot \frac{1000 + mM_1}{m} \right) - \left(\frac{n_0^2 - 1}{n_0^2 + 2} \cdot \frac{1}{d_0} \cdot \frac{1000}{m} \right)$$

where n and n_0 are the refractive index of solution and solvent, respectively, d and d_0 the density of solution and solvent, m the molality (in moles/kg solvent) of MgCl_2 or MgSO_4 and M_1 the molecular weight of the solute. In all cases the NaCl solution is treated as the solvent.

In Figure 2 we have plotted the apparent molal refractive

index vs the square root of the molality is a function of concentration for MgCl_2 and MgSO_4 in solutions of NaCl.

According to Fajans (1941), the molar refraction of an electrolyte decreases as the degree of ion association increases. Consequently, we would expect to observe decreases in R_{app} as the extent of ion-pair formation increases in the systems reported here. Referring to Figure 2 we note that the change in R_{app} with concentration is greater for MgSO_4 than MgCl_2 in accord with an expected greater degree of ion-pair formation for MgSO_4 than MgCl_2 . Further, values of R_{app} decrease as the concentration of NaCl in the solvent increases, a result explained by formation of NaSO_4^\pm ion-pairs in the MgSO_4 solutions and possible formation of MgCl^+ ion-pairs in the MgCl_2 solutions.

Measurements of refractive index, thus, support the conclusion drawn from density measurements that there is extensive ion-pairing in concentrated seawater brines. In fact, we can conclude that ion-pairing increases as concentration increases.

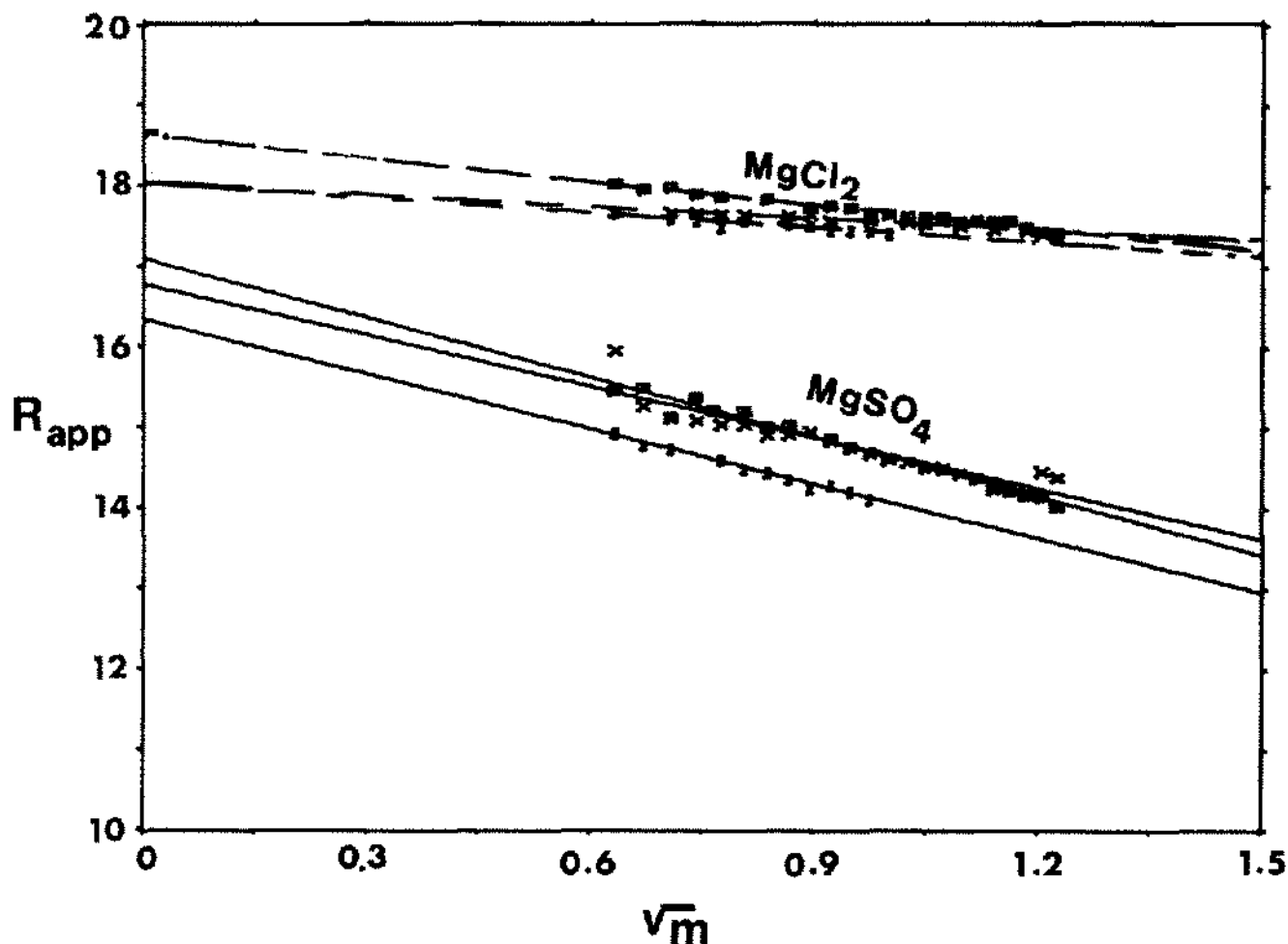


Figure 2. Apparent molal refraction of MgSO_4 and MgCl_2 in 5% (\square), 10% (\times) and 15% (\circ) NaCl.

Viscosity. The presence of electrolytes in water causes an increase in the viscosity of the system. The viscosity of electrolyte solutions reflects the effect of ions on fluid structure and the interactions occurring between the various ionic species in solution.

The dependence of the viscosities of solutions of electrolytes can be represented by the Jones-Dole equation (1929)

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{C} + Bc$$

where η and η_0 are the viscosities of solution and solvent, respectively and C is the electrolyte concentration in moles per liter. We define the relative viscosity of a solution as

$$\eta_{\text{rel}} = \eta/\eta_0$$

which is directly applicable to the Jones-Dole equation. The factors A and B are constants characteristic of the solute.

The viscosity B -coefficients has been shown to be indicative of the water structure altering properties of ions (Horne, 1969). Positive B -coefficients are characteristic of ions and electrolytes designated as water structure makers and those solutes showing negative B -coefficients are designated as structure breakers. The ionic B -coefficients are additive. We find that in water MgSO_4 is a very powerful structure maker and MgCl_2 somewhat less so. The difference between these electrolytes indicating that the SO_4^{2-} B -coefficient is positive and for Cl^- is negative.

As a consequence of this interpretation, we can relate the sign and magnitude of the viscosity B -coefficient to the degree of hydration of ions. Water associated with the hydration atmosphere of an ion is more highly structured than water in the main portion of the solution.

The Jones-Dole equation can be rearranged in the form

$$\frac{\eta_{\text{rel}} - 1}{\sqrt{C}} = A + B\sqrt{C}$$

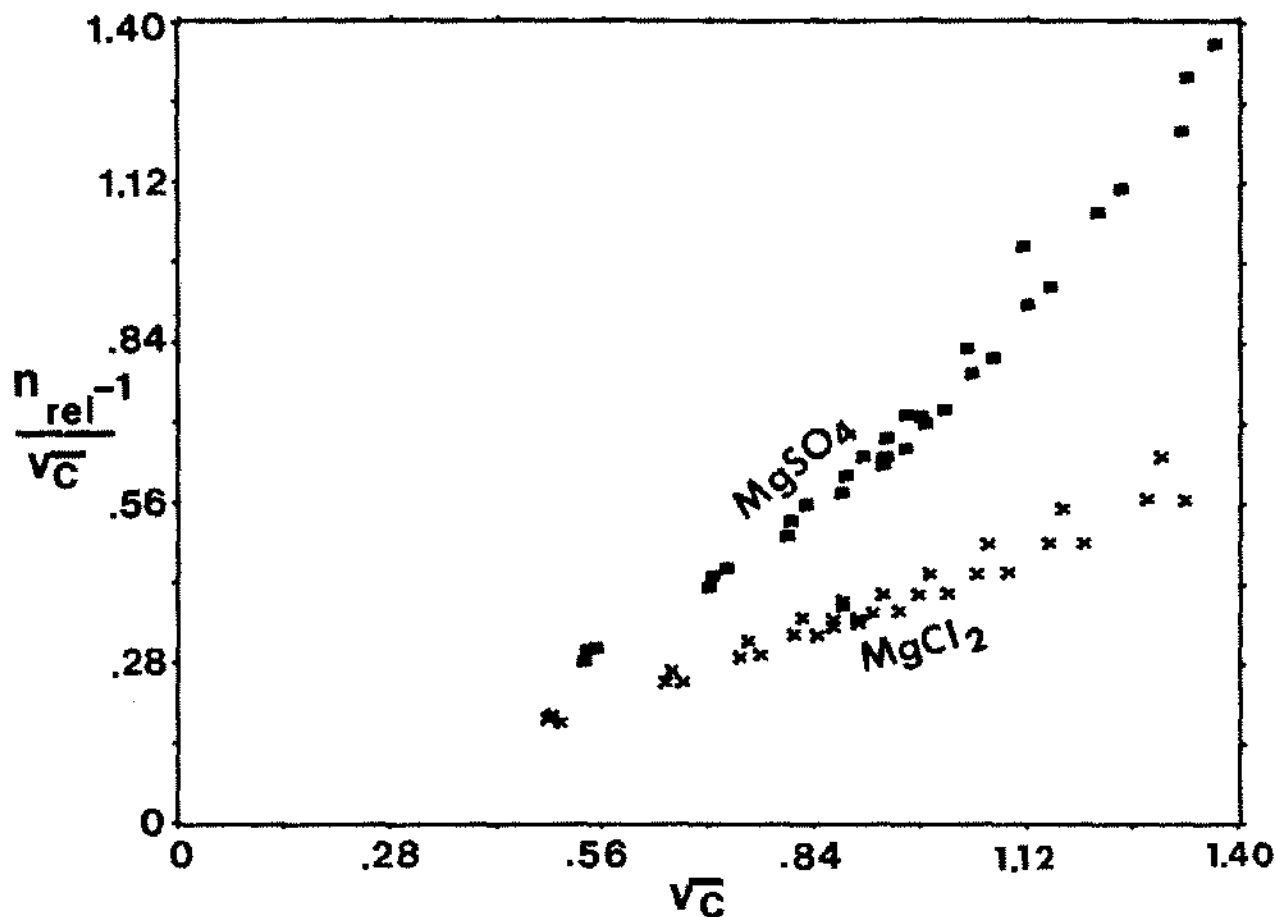


Figure 3. Jones-Dole plot for MgSO_4 and MgCl_2 in 5%, 10% and 15% NaCl.

so that by plotting the left-hand side of this equation versus the square root of solute concentration we should obtain a linear plot with a slope equal to the B-coefficient.

In Figure 3 are Jones-Dole plots for MgSO_4 and MgCl_2 in 5, 10 and 15% NaCl solutions. We have not indicated on this graph which points apply to a particular NaCl composition because scattering of our data points results in overlapping. The general shape of the curves, however shows, two general effects. The slopes in the low concentration range show that the B-coefficient of MgSO_4 is greater than that of MgCl_2 .

In Table 1 are tabulated the values of the B-coefficients of these solutions determined from our measurements and, for comparison, the B-coefficients of MgSO_4 and MgCl_2 in water (Horne, 1969).

The values of these B-coefficients for our study were calculated, in the case of MgSO_4 from the linear portion of the curve and do not reflect the pronounced curvature at higher concentrations for the curve in Figure 3.

It is not likely that the pronounced increase of the B-coefficients in NaCl solutions can be attributed to water

TABLE 1
Viscosity B-coefficients of MgSO_4 and MgCl_2 in 5, 10 and 15% NaCl Solutions and in Water at 25°C

Solvent	MgSO_4	MgCl_2
H_2O	0.594	0.378
5% NaCl	0.94	0.45
10% NaCl	0.94	0.50
15% NaCl	0.96	0.44

structure making. This effect is most likely a result of ion-pairing which results in more bulky solution species which tend to increase viscosity. The ion-pairing effect is supported by the fact that B-coefficient increase is greater for MgSO_4 than MgCl_2 and by the upward curvature of the Jones-Dole curve at high concentrations of MgSO_4 , a region of more extensive ion-pair formation.

Consequently, as in the case of refractive index and density measurements, viscosity studies show a substantial degree of ion-pair formation in concentrated brine systems.

Solubility of gypsum. In a recent study (Rands, et al.,

1979) it has been shown that the solubility of gypsum in concentrated brine solutions is increased by the presence of magnesium in those solutions. This phenomenon is explained on the basis of the tendency for the formation of MgSO_4^0 ion-pairs.

The equilibrium expression for the solubility of gypsum may be represented by



The equilibrium constant for the solubility of gypsum is

$$K = (\text{Ca}^{+2})(\text{SO}_4^{-2})$$

where the species in brackets represent the concentration of calcium and sulfate ions in solution.

Magnesium ions interact with sulfate ions to form the ion-pair, MgSO_4^0 . The formation of this solution species

effectively removes a portion of the sulfate ions in solution by a complexation phenomenon. This reduction in sulfate ion in solution causes the gypsum solubility equilibrium to shift toward the direction of increased solubility according to the Principle of le Chatelier.

In Figure 4 are shown the results of the study designed to show the effect of magnesium on the solubility of gypsum in concentrated brines. The solubility of gypsum in solutions of sodium chloride and magnesium chloride of varying magnesium/sodium ratios and at three different ionic strengths was determined. The concentration of gypsum has been plotted as a function of $R_{\text{Mg/Na}}$, the ratio of concentrations of magnesium to sodium. This figure shows that, at constant ionic strength, the solubility of gypsum increases as the concentration of magnesium is increased.

This experiment provides evidence for the formation of MgSO_4^0 ion-pairs in concentrated brines up to a molality exceeding 4.0 in NaCl which is about 20% by weight solids.

SUMMARY

Experimental studies outlined in this study verify the conclusion of investigators such as deFlers (1967), Jain and his co-workers (1967) and Rands and Hendricks (1975) that the magnesium content of seawater brines does not suppress the evaporation rate to the extent expected from normal hydration behavior of the magnesium ion. Extensive formation of MgSO_4^0 ion-pairs in concentrated brines leads to a partial reduction in the extent of hydration of the magnesium ion and tends to result in evaporation behavior approximating that predicted by Raoult's Law.

Although the interpretation of measurements of the physical properties of concentrated salt solutions cannot be made on a quantitative basis, general trends in various physical properties may be used to provide a profitable qualitative picture of the structure of such systems.

DISCUSSION

H.H. Emons.

Comments. 1) Our NMR investigations show a coordination of 6 H_2O molecules around the Mg^{+2} ion from the concentrated solution of electrolytes up to the hydrate melting. The influences are consequently in the fluid or cluster phase.

2) Conductimetrics naturally include all associations of ions, not only the neutral ion pairs; nevertheless the main influence may come from them.

3) Structure-producing and structure-breaking effects are highly dependent on the medium. With KCl, RbCl or CsCl the mutual effects are more distinctive than for NaCl.

Answers. 1) In our studies the most concentrated solutions contain Mg^{+2} ions and H_2O molecules at a numerical ratio of 30 water to 1 magnesium. Professor Emons is quite correct, then, in his statement that the influences which we have presented result

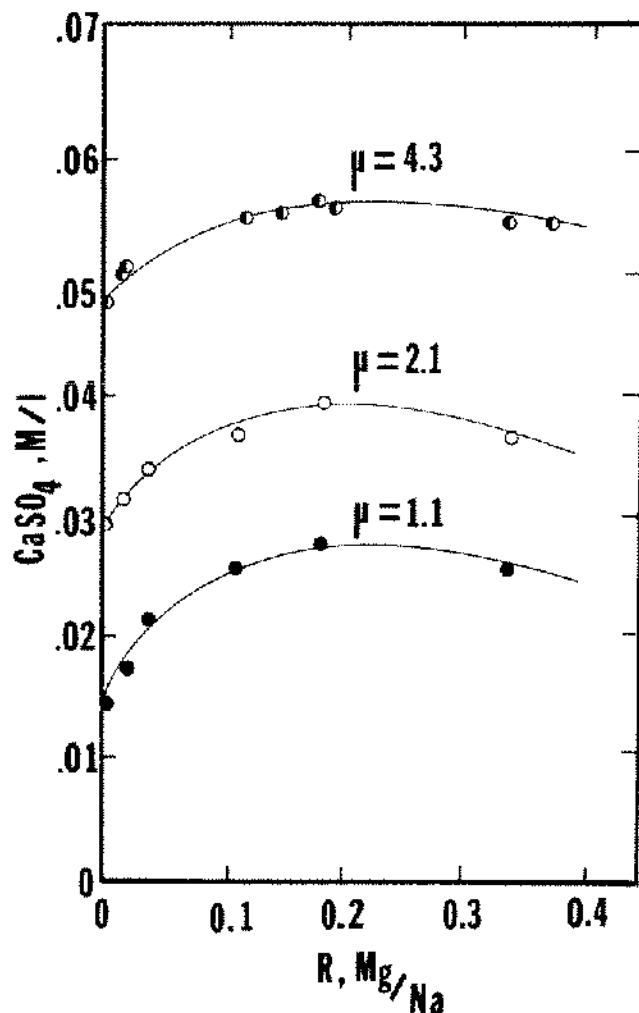


Figure 4. Solubility as a function of Mg/Na ratio at various ionic strengths.

from disruption of the water molecules in the cluster region. There is a sufficient quantity of excess water molecules in these solutions that it is not unreasonable to suppose that the cluster region is formed around the Mg^{++} ion.

2) This is an observation of Professor Emons with which I concur.

3) Our experiments were designed to note the effects of $MgCl_2$ and $MgSO_4$ on the structuring effects in solution.

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