ILL: 8330579

Call Number: ** QE515 C43

Location:

DateReq: 7/9/2002

Date Rec: 7/10/2002

Borrower: MFL

☐ Yes ☐ No ☐ Conditional

Maxcost: $15.00

LenderString: *CFS,CSF,CSH,CDS,CLO

Title: Chemical geology.

Author:

Edition:

Imprint: Amsterdam ; New York : Elsevier, 1966-

Article: Frantz. "Ion-pairing in aqueous MgSo4 solutions..."

Vol: 116 **No.:** **Pages:** 181-188 **Date:** 1994

Borrowing Notes: MLML is a part of the California State University System.

Fax:

```
ILL: 8330579      :Borrower: MFL      :ReqDate: 20020709 :NeedBefore: 20020808
:Status: IN PROCESS 20020709          :RecDate:          :RenewalReq:
:OCLC: 1553973    :Source: OCLCWEB    :DueDate:          :NewDueDate:
:Lender: *CFS,CSF,CSH,CDS,CLO
:CALLNO:      :TITLE:   Chemical geology.   :IMPRINT: Amsterdam ; New York :
Elsevier, 1966-   :ARTICLE: Frantz. "Ion-pairing in aqueous MgSo4 solutions..."
:VOL: 116    :NO:          :DATE: 1994                 :PAGES: 181-188
:VERIFIED: OCLC ISSN:  0009-2541 [Format: Serial]   :SHIP TO:  CSU Moss Landing
Marine Labs/Library/8272 Moss Landing Road/Moss  Landing, CA 95039   :BILL TO:  Same
address   :SHIP VIA: ARIEL PREFERRED. 192.190.45.28  :MAXCOST: $15.00    :COPYRT
COMPLIANCE: CCL   :FAX: (831)632-4403/Ariel 192.190.45.28   :E-MAIL:
parker@mlml.calstate.edu   :BORROWING NOTES: MLML is a part of the California State
University System.   :AFFILIATION: IAMSLIC, LVIS, California State University
:LENDING CHARGES:                 :SHIPPED:          :SHIP INSURANCE:
:LENDING RESTRICTIONS:    :LENDING NOTES:    :RETURN TO:    :RETURN VIA:
```

ELSEVIER

Chemical Geology 116 (1994) 181–188

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

Ion-pairing in aqueous $MgSO_4$ solutions along an isochore to 500°C and 11 kbar using Raman spectroscopy in conjunction with the diamond-anvil cell

J.D. Frantz[a], J. Dubessy[b], B.O. Mysen[a,α]

[a]*Geophysical Laboratory (CIW), 5251 Broad Branch road N.W., Washington, DC 20015-1305, USA*
[b]*Cregu (GDR CNRS 0077), BP-23, F-54501 Vandœuvre-les-Nancy Cedex, France*

Received December 12, 1993; revision accepted March 15, 1994

Abstract

A high-temperature diamond-anvil cell is used in conjunction with a micro-Raman spectrometer in the study of aqueous fluids containing 0.5 *m* $MgSO_4$ along an isochore from room conditions to 500°C and 11 kbar. Gaskets lined with platinum are used to contain the chemically-reactive fluid. Ion-pairing of $MgSO_4$ is shown to increase with increasing pressure along an isochore with a density of ~ 1 g cm^{-3}. Mass-action constants for the reaction $Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4$ range from $3.5 \cdot 10^1$ at 20°C, 1 bar to $1.25 \cdot 10^4$ at 500°C, 11.4 kbar. The results agree favorably with those obtained through electrical conductance measurements by V.G. Ritzert and E.U. Franck. The relative abundances of the species are shown as a function of temperature and pressure along the isochore.

1. Introduction

As fluids are the fundamental agents responsible for heat- and mass-transfer in the Earth's crust and mantle, experimental investigation and modeling of high-temperature, high-pressure fluids is vital towards understanding some of the processes controlling the Earth's evolution. The properties of aqueous electrolytic solutions are highly influenced by competing processes of solvation and ion–ion interaction. At room temperature and pressure, solvation of individual ions by surrounding water dipoles greatly inhibits ion–ion interactions. Under hydrothermal conditions, however, ion–ion interactions become increasingly important. Electrical conductance measurements of aqueous solutions performed at high temperatures and pressures have demonstrated that the degree of formation of molecular species or ion pairs increases with increasing temperature and decreasing density (Franck, 1956; Quist and Marshall, 1968; Frantz and Marshall, 1982). Salts such as NaCl, KCl and $CaCl_2$, and strong acids such as HCl become weak electrolytes under hydrothermal conditions. This behavior parallels changes in the structure of water itself. The network connectivity with local tetrahedral symmetry exhibited by water at ambient temperature and pressure disappears with increasing temperature and decreasing density (Frantz et al., 1993). Accordingly, the dielectric constant and viscosity of water decrease dramat-

[EW]
[α]Also member of NSF-sponsored Center for High-Pressure Research (CHiPR).

0009-2541/94/$07.00 © 1994 Elsevier Science B.V. All rights reserved
SSDI 0009-2541(94)00039-B

ically with increasing temperature (Dudziak and Franck, 1966; Uematsu and Franck, 1980). In the case of both water and dissolved electrolytes, the changes summarized above are primarily the result of the susceptibility of the relatively weak ion–water dipole and water dipole–water dipole bonds to increasing thermal agitation in response to increasing temperature.

Experimental determination of association constants for dissolved electrolytes at elevated temperatures and pressures has proven exceedingly difficult. Electrical conductance techniques (Marshall and Frantz, 1987) have provided association constants for the relatively simple alkali and alkaline-earth chloride complexes in aqueous solutions, but have proven to be unsatisfactory for the investigation of more complicated solutes involving transition elements and corrosive solutions. Spectroscopic investigations have provided additional information. Aqueous complexes have been studied by both UV–visible absorption spectroscopy and Raman spectroscopy depending on the degree of covalency of the bond between the cation and ligand. UV–visible absorption spectroscopy was used for the characterization of the symmetry of transition elements such as Co and Ni (Lüdemann and Franck, 1967, 1968) and more recently by Susak and Crerar (1985). Non-transition elements were studied by UV absorption spectroscopy (Seward, 1984) and Raman spectroscopy (Irish et al., 1963; Schulz, 1974). Farges et al. (1993) investigated gold chloride solutions using extended X-ray absorption fine-structure spectroscopy (EXAFS) and Sharpes et al. (1993) used nuclear magnetic resonance (NMR) spectroscopy to investigate ligand exchange mechanisms in solutions containing Au, Zn and Cd. One of the fundamental limitations which has plagued spectroscopic investigations has been reaction between electrolytic solutions and the optical cells necessary for high-temperature, high-pressure studies. The development of a high-temperature diamond-anvil cell (Bassett et al., 1994) and techniques for using these cells as isochoric systems in the study of hydrothermal systems (Shen et al., 1993) holds great promise in extending these investigations.

In the following study, the diamond-anvil cell is used in the high-temperature, high-pressure investigation of a 0.5 *m* $MgSO_4$ solution. Davis and Oliver (1973) suggested the existence of $MgSO_4$ contact ion pairs based on the Raman and ultrasonic absorption studies of Atkinson and Petrucci (1966). Ritzert and Franck (1968) computed association constants to 350°C for the magnesium sulfate ion pair using electrical conductance data. Marshall (1967) computed dissociation constants along the liquid–vapor curve to 200°C. As both magnesium and sulfate are major components in fluids associated with mid-oceanic spreading centers, the purpose of this research was to document the presence of these ion pairs and obtain an association constant describing its relative abundance under hydrothermal conditions.

2. Experimental methods

Use of a high-temperature diamond cell designed for hydrothermal studies in conjunction with a platinum-lined gasket serves as a chemically-inert optical cell suitable for the study of electrolytic solutions along isochores at elevated temperatures and pressures. The cell, purchased from W.A. Bassett is described in Bassett et al. (1994). The cell utilizes two low-fluorescence diamonds with 1-mm culet faces which are heated by molybdenum-wound furnaces surrounding each diamond. Temperature is measured with two Chromal®–Alumel® thermocouples cemented on each of the diamonds. Temperature calibration (±2°C) was achieved using the melting point of crystalline sodium chloride. Pressure was determined from the measured homogenization temperature of the bubble contained in the sample chamber in conjunction with the measured experimental temperature and isochoric data for electrolytic solutions given in Zhang and Frantz (1987) [see Shen et al. (1993) and Bassett et al. (1994) for additional details]. A 500-μm-thick stainless-steel gasket lined with a platinum ring having a wall thickness of 100 μm was used to contain the sample (Fig. 1). The inner diameter of the gas-

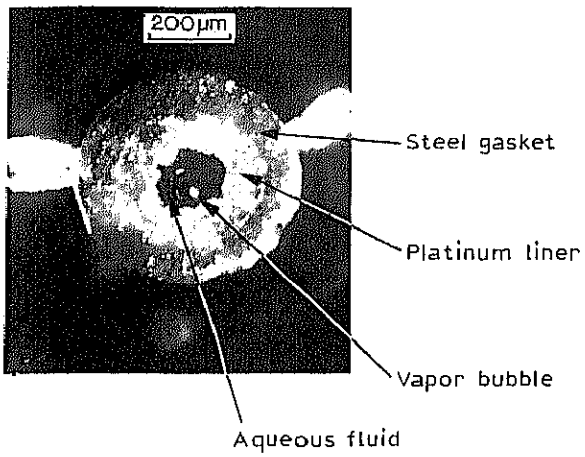

Fig. 1. Photomicrograph through the diamond-anvil cell showing fluid sample containing the aqueous fluid, a vapor bubble, the platinum liner and the stainless-steel gasket.

ket was 200 μm. The indentation pressure on the gasket due to the diamond anvils was 30–40 kbar with the distance between the diamond faces being ~300 μm. A 0.5 *m* $MgSO_4$ solution was loaded into the cell under a binocular microscope with a 1-μl syringe. The solution was prepared from reagent hydrous $MgSO_4$ and triple-distilled water passed over charcoal. Sample volume was adjusted to allow for the presence of a vapor bubble (Fig. 1). The magnesium sulfate concentration of the loaded solution is determined by freezing point depression measurements of ice in presence of liquid and vapor. No significant evaporation appeared to take place during the loading procedure. The homogenization temperature was 50°C (±1°C). Isochoric behavior of the sample chamber was documented both by the reproducibility of the homogenization temperature before and after the experiment and by the observation that interference fringes did not moved only slightly during heating and cooling.

The Raman spectra were recorded with a *XY* Raman spectrometer (Dilor®) equipped with an OMA*4* CCD (EGG®) detector cooled at liquid nitrogen temperature. Slit widths were 200 μm large giving a spectral resolution of 0.6 cm^{-1}. The exciting radiation (λ=488.5 nm) was provided by a SpectraPhysics® Ar^+ laser focused on the sample using a Leitz® objective (UT*40* with a 0.34 numerical aperture). Accumulation times ranged from 10 to 100 s. After subtracting experimental background, the resulting spectra were corrected for temperature- and frequency-dependent scattering intensity (Long, 1977). Spectral deconvolution (Mysen et al., 1982; Seifert et al., 1982) was carried out with the method of least squares with the algorithm described by Davidon (1966).

3. Experimental results

The Raman spectra taken at 50°C intervals to 500°C are presented in Fig. 2. Pressures (noted in parentheses next to the experimental temperatures) were computed by assuming that the *PVT*

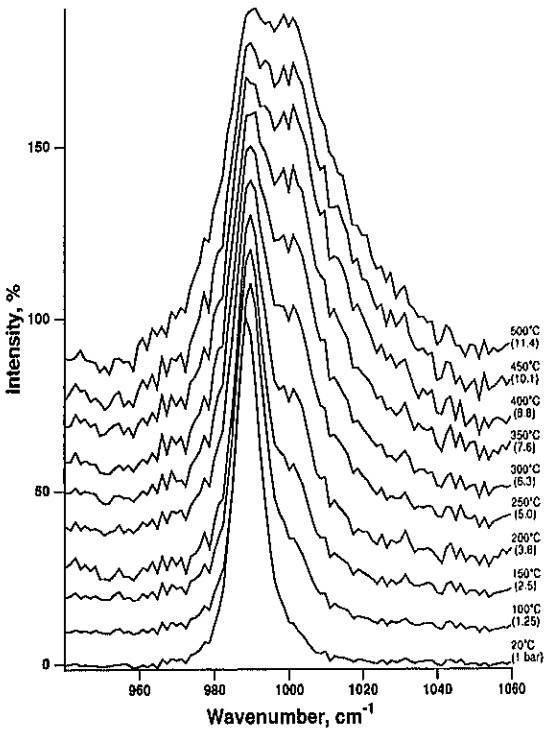

Fig. 2. Raman spectra of 0.5 *m* $MgSO_4$ solutions at temperatures and pressures ranging from 20°C and 1 bar to 500°C and 11.4 kbar. All spectra are normalized to 100% of their respective maximum intensities. Temperatures and pressures are listed at right of spectra; pressures are denoted by *parentheses*. An offset has been added to each spectrum.