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WATER RESEARCH PROGRAM

BIENNIAL PROGRESS REPORT

FOR THE PERIOD

MARCH 15, 1966 TO MARCH 15, 1968

PROPERTIES OF SOLUTIONS

for the

OFFICE OF SALINE WATER

U.S. Department of the Interior

MASTER

OAK RIDGE NATIONAL LABORATORY

OPERATED BY UNION CARBIDE CORPORATION • FOR THE U.S. ATOMIC ENERGY COMMISSION

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WATER RESEARCH PROGRAM BIENNIAL PROGRESS REPORT

For the Period March 15, 1966, to March 15, 1968

PROPERTIES OF SOLUTION

Compiled by Richard J. Raridon, and George E. Moore

K. A. Kraus, Program Director

For the
OFFICE OF SALINE WATER
U.S. DEPARTMENT OF THE INTERIOR
OSW-AEC INTERAGENCY AGREEMENT 14-01-0001-937

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MAY 1973

OAK RIDGE NATIONAL LABORATORY
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*Paper published in open literature.

†Work cosponsored by the U.S. Atomic Energy Commission.

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*Paper published in open literature.

†Work cosponsored by the U.S. Atomic Energy Commission.

Preface

The Water Research Program at the Oak Ridge National Laboratory, sponsored by the Office of Saline Water, U.S. Department of the Interior, was authorized in March 1962 under an interagency agreement (14-01-0001-937) between the Department of the Interior and the Atomic Energy Commission. Results of the work carried out under this program have been reported on a regular basis to the Office of Saline Water, and completed portions of the work were published in the open literature. A biennial report covering the activities under the program for the period March 15, 1962, to March 15, 1964, was issued in a single volume as Office of Saline Water Research and Development Progress Report No. 302 (ORNL-CF-67-8-55). For the second biennium, March 15, 1964, to March 15, 1966, work was divided into three categories, "Properties of Solutions," "Reaction and Transport Phenomena at Surfaces and Corrosion Studies," and "Separations Processes." The report for "Properties of Solutions" was issued as U.S. Office of Saline Water Research and Development Progress Report No. 685 (ORNL-CF-70-6-30). The present report on "Properties of Solutions" covers March 15, 1966, to March 15, 1968.

In order to retain maximum coherence in subject matter, a sharp time distinction has not been drawn. That is, in some cases articles which appeared in the open literature after March 1968 but which cover work that was done mainly in the third biennium have been included in this volume, and, conversely, some work started during this period but developed mainly in the fourth biennium is only briefly mentioned in this report.

In the interest of economy and completeness of presentation, work that was reported in the open literature is given as a direct reproduction of the corresponding journal articles. We are grateful to the various publishers (American Chemical Society, Tennessee Academy of Science, and John Wiley and Sons, Inc.) for permission to reprint the complete texts of these articles. A notation of the source appears at the head of each reprinted article. Part of the work reported here was cosponsored

by the U.S. Atomic Energy Commission; such support is acknowledged in the individual articles and in the index.

The desalination program at the Oak Ridge National Laboratory has two branches: the Water Research Program directed by K. A. Kraus during the period of this report, and the Nuclear Desalination Program directed by R. P. Hammond. This report is concerned with the Water Research Program, Properties of Solutions, coordinated during the period by Richard J. Raridon.

Introduction

The investigations in the field "Properties of Solutions" were undertaken to provide information on the thermodynamic and transport properties of aqueous and nonaqueous electrolyte systems. The specific studies were selected primarily because of their direct pertinence to desalination problems, and many are continuations of studies initiated earlier. Various standard physical-chemical techniques were employed, including solubility measurements, distribution coefficient measurements, dielectric constant measurements, emf measurements, isopiestic techniques, and diffusion coefficient measurements.

Knowledge of the properties of aqueous electrolyte solutions under a variety of conditions is basic to the understanding of all desalination methods. Information on electrolyte solutions in mixed solvents (water-organic) has provided valuable insight into the salt-rejecting properties of membranes used in the hyperfiltration process. High-temperature phase studies have focused on precipitation or scaling problems which might occur on treatment of natural waters.

This report is divided into three parts dealing with (1) properties of aqueous systems, (2) properties of water-organic systems, and (3) high-temperature phase studies.

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1. Thermodynamic and Transport Properties in Aqueous Solutions

Summary

The thermodynamic properties of aqueous solutions are fundamental to desalination. For example, they fix the minimum energy requirements, they determine the boiling point elevation in distillation, the freezing point depression in freezing, and how much of the applied pressure is effective as driving force in hyperfiltration. The Water Research Program has been active since its inception in developing fundamental information pertinent to desalination.

During this biennium, computed boiling point elevations of seawater and its concentrates were revised in view of new data on osmotic coefficients, presented in the previous biennial report.¹ Osmotic coefficients of solutions containing sodium, magnesium, sulfate, and chloride over a wide range of compositions were measured. From these results and the computational methods developed to analyze them, free energies of most natural waters can be estimated adequately for practical purposes. A preliminary report is given.

Cation-sensitive glass electrodes have been of considerable interest on this program, both for obtaining thermodynamic information and for potential analytical applications. Reported here are measurements of KCl activities in aqueous solutions as a function of temperature, and the emf response of electrodes in seawater composition.

Of the kinetic processes which affect desalination, perhaps the most fundamental is diffusion of ions. These rates are crucial in the polarization occurring in separations, such as the buildup of rejected solute at the interface between feed and hyperfiltration membranes. A quick way

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1. Water Research Program Biennial Progress Report for Period March 15, 1964 to March 15, 1966, Properties of Solutions, R. J. Raridon and K. A. Kraus, U.S. Office of Saline Water Research and Development Report 685 (July 1971); previously issued as ORNL-CF-70-6-30 (October 1970).

of measuring self-diffusion coefficients--from the rate at which tracer diffuses out of a calibrated porous frit into a circulating non-radioactive stream--was developed in previous years. Several recent applications are reported here.

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1.1 THE ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION AS MEASURED WITH A CATION-SENSITIVE GLASS ELECTRODE¹

M. H. Lietzke and R. W. Stoughton

INTRODUCTION

Glass electrodes which respond to monovalent cations such as Na⁺ and K⁺ are now commercially available. Such electrodes have been used to measure the activity coefficient of NaCl in various media (1, 2, 3). In the present work the activity coefficient of KCl in aqueous solution has been measured in the range 0.01 *m* to 2.5 *m* at temperatures from 15° to 55° using a cation-sensitive glass electrode. The study was undertaken to determine how well the activity coefficients so measured would agree with those measured by other methods.

EXPERIMENTAL

The glass electrodes used were Beckman cationic 39137 electrodes, while the reference electrodes were Ag,AgCl electrodes of the thermal type. The reference electrodes were shorted together and allowed to equilibrate in KCl solution prior to use.

A vibrating reed electrometer, in conjunction with a Rubicon K-2 potentiometer and a Brown recorder, was used for measurement of the emf of the cell. The precision of individual measurements was of the order of a few hundredths of a millivolt, but reproducibility between experiments was sometimes no better than a millivolt. Equilibrium was attained in a few hours with solutions of low concentration and in 6-8 hours with the solutions of high concentration.

The solutions were prepared by weight from reagent grade KCl and triply distilled water. The emf cell was immersed in a constant temperature bath controlled to a few hundredths of a degree. The entire bath and electrode assembly were surrounded by an aluminum shield to minimize external effects on the emf readings.

RESULTS AND DISCUSSION

The fundamental equation relating the measured emf *E* of the cell, the "standard potential" *E*[°] of the electrode couple, and the activity *a* of the KCl in solution is

$$E = E^{\circ} - \frac{RT}{F} \ln a. \quad (1)$$

Since *a*_{KCl} may be expressed as *m*_{K⁺} *γ*_{K⁺} *m*_{Cl⁻} *γ*_{Cl⁻}, where *γ*_{K⁺} and *γ*_{Cl⁻} are the activity coefficients of the K⁺ and the Cl⁻ ions and the *m*'s are molalities, eq. (1) may be written

$$E = E^{\circ} - \frac{2RT}{F} \ln m - \frac{2RT}{F} \ln \gamma_{\pm}, \quad (2)$$

where $\gamma_{\pm} = \sqrt{\gamma_{K^+} \gamma_{Cl^-}}$ is the mean ionic activity coefficient of the KCl. It is assumed that the concen-

tration dependence of $\ln \gamma_{\pm}$ is given by an extended Debye-Huckel equation of the type

$$\ln \gamma_{\pm} = -\frac{S_T \sqrt{m}}{1 + A \sqrt{m}} + B m + C m^2, \quad (3)$$

then substitution of eq. (3) into eq. (2) gives eq. (4)

$$E = E^{\circ} - \frac{2RT}{F} \ln m - \frac{2RT}{F} \left[-\frac{S_T \sqrt{m}}{1 + A \sqrt{m}} + B m + C m^2 \right] \quad (4)$$

in which the temperature dependence of the *B* and *C* coefficients may be expressed as

$$B = b_1 + \frac{b_2}{T} \quad (5a)$$

and

$$C = c_1 + \frac{c_2}{T}. \quad (5b)$$

The form of eqs. (5a) and (5b) is consistent with the assumption that $\Delta C_p = 0$ for the KCl in solution over the temperature range studied.

Since the *E*[°] values of many cell combinations vary quadratically with temperature, we may further assume that

$$E^{\circ} = a_1 + a_2 T + a_3 T^2 \quad (6)$$

In treating the data the individual emf values (measured with a given electrode combination) at each temperature and concentration were averaged. The averaged values for each electrode combination were then fitted by the method of least squares to eq. (4), with the temperature dependence of *B*, *C*, and *E*[°] given by eqs. (5a), (5b), and (6) and with the appropriate Debye-Huckel limiting slope *S_T* used at each temperature. In carrying out the calculations all the data (at all temperatures and concentrations) were used simultaneously in determining the values of *a*₁, *a*₂, *a*₃, *b*₁, *b*₂, *c*₁, and *c*₂ for each electrode combination separately.

Three different glass electrode-reference electrode combinations were used in this study. It was found that, whereas each electrode pair had a different *E*[°] value, all three pairs gave essentially the same activity coefficient values for the KCl solutions. The average maximum deviation between the *E*[°]–*E* values for all concentrations and temperatures for all three electrodes was 1.6 mv, while the average deviation was 1.0 mv. Since the activity coefficient values obtained with the three different glass electrodes were not significantly different, only the values obtained with one electrode will be presented here.

In carrying out the calculations it was found that when the value of *A* in eq. (4) was taken as 1.45 the best overall fit of the data was obtained, i.e., that the average deviations between the observed and calculated values were the smallest. The activity coefficient values

¹ Research sponsored by The Office of Saline Water, U. S. Department of the Interior under Union Carbide Corporation's contract with the U. S. Atomic Energy Commission.

computed with $A = 1.45$ are shown in column 4 of Table I. Also included in the table are values of the

TABLE I

THE ACTIVITY COEFFICIENT OF KCl

t°C	m _{KCl}	E	γ^1_{KCl}	γ^2_{KCl}	γ^3_{KCl}
15	0.01	-.0456 +17	.904	.903	
	.1	-.1507 + 3	.776	.769	
	.5	-.2217 + 1	.653	.650	
	1.0	-.2524 + 6	.601	.601	
	2.5	-.2946	.571	.562	
25	0.01	.0370 -13	.903	.901	
	.1	-.1471 -13	.772	.769	.769
	.5	-.2208 -12	.649	.651	.649
	1.0	-.2524 -11	.598	.606	.603
	2.5	-.2969 -11	.573	.572	.567
40	0.01	-.0305 + 9	.900	.900	
	.1	-.1447 - 4	.767	.765	
	.5	-.2231 + 9	.643	.646	
	1.0	-.2564 +14	.592	.603	
	2.5	-.3046 +21	.574	.575	
55	0.01	-.0218 +14	.897		
	.1	-.1399 -13	.761		
	.5	-.2230 + 4	.639		
	1.0	-.2557 - 5	.586		
	2.5	+.3055 -10	.572		

¹ Present work (glass electrode)

² Harned and Cook (amalgam cell)

³ Based on data of Robinson and Sinclair

activity coefficients obtained with amalgam cells (4) and with the isopiestic method (5). The values given in column 6 of Table I have been recomputed from the original isopiestic data using a newer technique (6) than that used in the original paper. As can be seen the activity coefficient values obtained with the cation-sensitive glass electrodes agree in most cases to within 1% with the values obtained by the other methods.

As a further check on the reproducibility of the glass electrode measurements the smoothest values of the activity coefficients and the E° values were substituted into eq. (2) at each concentration and temperature to back-calculate the emf values. The deviations between the observed values and the calculated values are shown in column 3 of Table I immediately below the observed emf values. A positive deviation indicates that the observed value is numerically higher than the calculated value. The greatest deviation is 2.1 mv at 40° in the 2.5 m solution.

Measurements were also made at 5° in all the above solutions and in .001 m KCl solutions from 5° to 55°. However, the observed values were more erratic than those reported and the resulting activity coefficients were 15 to 40% different from those in the literature.

Recently the activity coefficient of KCl was measured from 0° to 50°C in the concentration range .05 to 4.0 m using an amalgam cell.⁷ When these values are extrapolated to 55°, then excellent agreement is observed with the values reported in this paper. The greatest deviation (2.3%) is at 1.0 m where it appears that our value is more consistent.

The authors wish to express their sincere appreciation to Walter J. Stevens, Jr., and Richard Shea for performing the experimental measurements.

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1.2 ACTIVITY COEFFICIENTS OF SALTS IN MIXED ELECTROLYTES²

G. Scatchard, R. M. Rush, Y. C. Wu, and J. S. Johnson

Preliminary measurements have been made of solute activities in aqueous solutions containing two electrolytes. Pairs of salts include all possible combinations of NaCl, Na₂SO₄, MgCl₂, and MgSO₄. A model sea-salt solution, satisfactory for determination of solvent activities in that it avoids complications from precipitation of low-solubility components, can be formulated by replacing Ca(II) with additional Mg(II). The composition can be further simplified for present purposes by like substitution of Na⁺ for K⁺, Cl⁻ for Br⁻, and HCO₃⁻, etc.

A good first approximation of the properties of any (electrically neutral) mixture of these ions may be obtained from measurements on solutions of the four single salts by use of the extended Brønsted principle. A second approximation may be obtained by including measurements on solutions of the four pairs of mixtures with a common ion. Each of these approximations was tried for these systems.

Isopiestic techniques were used on all systems studied. In addition, measurements were made with cation-sensitive glass electrodes in the system NaCl-MgSO₄-H₂O. Some emf measurements in this system were reported previously.³ A comparison of the emf and isopiestic results at 25° for the NaCl-MgSO₄-H₂O system is shown in Fig. 1.2.1. The activity coefficients obtained from emf measurements agree closely with those computed from isopiestic measurements at high NaCl ionic fractions, but are somewhat higher than the isopiestic values at low NaCl ionic fractions, perhaps because of a small sensitivity of the glass electrode to magnesium ions.

Preliminary results on the four systems with common ions show approximately the linear relationship between $\log \gamma_{12}$ and I_2 expressed in

2. Work cosponsored by the U.S. Atomic Energy Commission.

3. See Ref. 1, Section 2.2.

ORNL-DWG 67-11535A

FIG. 1.2.1. ACTIVITY COEFFICIENTS OF NaCl IN NaCl-MgSO₄-H₂O SOLUTIONS. Symbols represent emf measurements; solid lines, isopiestic.

Harned's Rule:⁴

$$\log \gamma_{12} = \log \gamma_{10} - \alpha_{12} I_2$$

where γ_{12} is the mean ionic activity coefficient of solute 1 in a three-component solution also containing solute 2; γ_{10} is the activity coefficient of component 1 at the total ionic strength, I , in the absence of component 2; α_{12} is a constant at a given ionic strength; and I_2 is the contribution to the ionic strength of component 2.

4. H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, ACS Monograph Series, 3rd Ed., Reinhold Publishing Corp., New York, 1958, Chapter 14.

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1.3 CORRELATION OF SEA SALT CONCENTRATION WITH THE EMF RESPONSE OF A CATION-SENSITIVE GLASS ELECTRODE¹

M. H. Lietzke, Richard Shea, and R. W. Stoughton

ABSTRACT

A cationic glass electrode has been used to monitor the total concentration of sea salts in both natural and synthetic sea salt solutions from 0.01 to 5.0 times natural and to 2.0 times "standard" synthetic sea water. The results have been interpreted in terms of sodium chloride activity coefficients which deviate less from unity than those in pure sodium chloride solutions.

INTRODUCTION

Some processes for desalting sea water concentrate the sea salts without changing their relative concentration (e.g., freezing or distillation) while removing essentially pure H_2O . Other procedures (e.g., hyperfiltration methods) effectively concentrate the salts together in one stream while diluting them in the other. For such processes an analytical tool for measuring "on line" total salt concentration may be useful.

Glass electrodes responding to the alkali ions Na^+ and K^+ and to the alkaline earth ion Ca^{++} have been commercially available for some time. The activity coefficient of KCl has recently been measured as a function of concentration (0.01 to 2.5 *m*) and temperature (10° to 55° C) (1, 2) and that of NaCl has been measured as a function of concentration (to 6 *m*) and medium (3, 4, 5) by the use of such electrodes. Since sea water is a somewhat adulterated NaCl solution and since some cationic glass electrodes are highly sensitive to sodium ion concentration, a study of cationic glass electrode response to total sea salt concentration (using both natural and synthetic sea salt solutions) was carried out at 25° C.

EXPERIMENTAL

Natural sea water was obtained from the Atlantic Ocean at Daytona Beach, Florida. It was concentrated by evaporation up to a maximum of about five times natural concentration. Eight new concentrations 0.01,

0.03, 0.1, 0.3, 2.0, 3.0, 4.0, and 5.0 times the concentration of natural sea water were prepared by dilution with water. The small amount of precipitate which came out of solution during the concentration step was removed and not taken into account. Each of the new solutions as well as the natural sea water was analyzed for chloride gravimetrically by AgCl precipitation. It was assumed that the relative concentrations of ions were the same as those given by Spiegler (6) for "standard" sea water but that the total concentration of sea salts near shore may have been increased by evaporation. By means of this assumption and the chloride analyses, the ionic strength and the sodium and chloride molalities of the solutions were calculated.

The synthetic sea water was a mixture of NaCl, KCl, $MgCl_2$ and Na_2SO_4 . Three solutions were prepared on a weight basis: one containing 5.022 *m* NaCl and 0.1208 *m* KCl, a second containing 0.7152 *m* Na_2SO_4 and a third containing 1.606 *m* $MgCl_2$. These solutions were mixed with water on a weight basis to give a concentration five times that of our "standard" synthetic sea water, the latter containing

0.4756 *m* Na^+
0.0101 *m* K^+
0.0645 *m* Mg^{++}
0.5577 *m* Cl^-
0.02856 *m* SO_4^{--}

The solution containing five times "standard" concentration was diluted to approximately 2.0, 1.0, 0.3, 0.1, 0.03, and 0.01 times "standard" on an accurate weight basis, so that concentrations were known relatively precisely.

The glass electrodes used were Beckman cationic 39137 electrodes, while the reference electrodes were Ag, AgCl electrodes of the thermal type. The reference electrodes were shorted together and allowed to equilibrate in sea salt solutions prior to use. The solutions used for the emf measurements were maintained at

¹ Research sponsored by The Office of Saline Water, U.S. Department of the Interior under Union Carbide Corporation's contract with the U.S. Atomic Energy Commission.

saturation with respect to AgCl by adding additional solid AgCl.

A vibrating reed electrometer, in conjunction with a Rubicon K-2 potentiometer and a Brown recorder, was used for measurement of the emf of the cell. The emf cell was immersed in a constant temperature bath controlled at 25° C to within a few hundredths of a degree. The entire bath and electrode assembly were surrounded by an aluminum shield to minimize external effects on the emf readings. The precision of individual measurements was of the order of a few hundredths of a millivolt; but reproducibility between experiments was sometimes no better than a millivolt. Reproducibility was generally poorer for relative concentrations above 1.0 times natural or "standard" synthetic sea water. Equilibrium was attained within a few hours; in some cases within 15 minutes.

Since the "standard potential" of a glass electrode has no readily interpretable meaning and changes with time, values of $\Delta E = E_1 - E$ were recorded, where E_1 and E were measured on the same day. Here E_1 is the emf measured with the natural sea water or the approximately 1.0 times "standard" artificial sea water, and E is the emf measured in any other concentration. Usually two different values of ΔE (for the same concentration) were within 0.5 mv, but sometimes deviations of more than a millivolt were observed. Two runs were made at each concentration, each run involving three different glass electrodes measured separately against the Ag-AgCl electrode.

RESULTS AND DISCUSSION

In each run at each concentration the three different ΔE values were averaged. The two different average ΔE values at each concentration were then averaged with equal weights if both runs appeared to be equally precise; if not, a higher weight was given to the average value of the run of higher precision. The results are given in Table I, while Fig. 1 shows a plot of ΔE for natural sea salt solutions against the logarithm of the ionic strength. The data fall nearly on a straight line ($\Delta E = 0.0155 + 0.1126 \log I$) and are reproducible; the data for synthetic sea salt solutions also fall very near this same line. Hence we conclude that a cationic glass electrode can be used to monitor the total concentration of sea salts in a desalination process. In such a process, however, it would probably be necessary to keep the reference electrode in its own separate compartment and have it bridged into the salt solution containing the glass electrode by means of a fritted KCl bridge.

An attempt has been made to interpret the deviations of the ΔE vs $\log I$ plot from a straight line in terms of changes in activity coefficients. The electrode used is not sensitive to divalent cations, but is sensitive to monovalent ions including H^+ . An equation of the Nernst type, which has been used for such glass electrodes (7, 8), is given as Equation (1).

$$\Delta E = E_1 - E = \frac{RT}{F} \ln \frac{[a_{Na} + k_K a_K + k_{Ag} a_{Ag} + k_H a_H] a_{Cl}]_1}{[a_{Na} + k_K a_K + k_{Ag} a_{Ag} + k_H a_H] a_{Cl}]_2} \quad (1)$$

TABLE I
AVERAGE ΔE VALUES IN VOLTS VS CONCENTRATION OF
SEA SALT SOLUTIONS

Approx. rel. conc.	$(E_1 - E)$	I	$m_{Na} +$	$m_{Cl} -$
Natural Sea Salt Solutions				
0.01	-0.2250	0.007253	0.004873	0.005680
.03	-.1716	.02188	.01470	.01713
.1	-.1130	.07303	.04906	.05719
.3	-.0607	.2195	.1475	.1719
1.0*	0	.7494	.5034	.5868
2.0	+ .0353	1.477	.9923	1.157
3.0	+ .0555	2.285	1.535	1.789
5.0	+ .0883	3.904	2.623	3.057

*"Standard" sea water (6) shows $m_{Na} = 0.4756$, $m_{Cl} = 0.5544$ and $I = 0.7078$.

Synthetic Sea Salt Solutions				
0.01	-0.2190	0.007753	0.005172	0.006100
.03	-0.1730	.02123	.01416	.01670
.1	-0.1118	.07190	.04796	.05658
.3	-0.0595	.2126	.1418	.1673
1.0	0	.7091	.4730	.5580
2.0	+0.0330	1.418	.9462	1.1161

Figure 1. Emf response of cationic glass electrode to concentration of natural sea salt solutions.

Here the a 's represent the activities of the various ions, the k 's are empirically determined constants, while R , T , and F have their usual significance.

Since the pH of the solutions was near 7, the concentration of H^+ was always some five orders of magnitude smaller than that of Na^+ , under which conditions the effect of H^+ is known to be small. A similar argument should hold for the Ag^+ concentration. The concentration of K^+ is not negligible (m_K being about

2% of m_{Na}) and k_K was found to be in the range of 6 to 9 for three glass electrodes (7). However, to a first approximation the activity of K^+ should vary proportionally to that of Na^+ and thence the ratios of the two cationic expressions should be approximately equal to $a_{Na}/(a_{Na})_1$. Thus Equation (1) becomes

$$\Delta E \approx \frac{RT}{F} \ln \frac{m_{Na} m_{Cl} \gamma^2}{(m_{Na} m_{Cl} \gamma^2)_1} \quad (2)$$

As is customary in the treatment of activity coefficient (or osmotic coefficient) data (see e.g., refs. 9, 10) the logarithm of the mean activity coefficient was assumed to be represented by a Debye-Huckel expression plus a (quadratic) power series in ionic strength:

$$\ln \gamma = -\frac{S\sqrt{I}}{1+A\sqrt{I}} + BI + CI^2 \quad (3)$$

where S is the Debye-Huckel limiting slope and A , B , and C are adjustable parameters.

Equation (3) was inserted into equation (2) for both $\ln \gamma$ and $\ln \gamma_1$. The parameters B and C were then evaluated by the method of least squares for a range of values of A (1.0, 1.25, 1.5, 1.75 and 2.0) by using the values of ΔE , I , m_{Na+} and m_{Cl-} shown in Table I. Although the activity coefficients calculated from the parameters of fit obtained with $A = 1.5$, 1.75 and 2.0 were probably all within experimental error (i.e., they were within 1% of each other), the variance of fit was smallest for both the natural and synthetic sea salt solutions when $A = 2.0$. These values of the parameters are shown in Table II. The B and C parameters

TABLE II
PARAMETERS OF EQUATION (3) FOR
SEA SALT SOLUTIONS

	Natural	Synthetic
$A =$	2.00	2.00
$B =$	0.13404	0.23072
$C =$	-0.011735	-0.066470

are very strongly correlated, i.e., if one is changed by a substantial amount a new value of the other one can be obtained which will give an almost equally good fit. Thus although the curves for activity coefficients in natural and synthetic sea salt solutions (Fig. 2) lie close together the values of the parameters (obtained by the method of least squares) are appreciably different.

Figure 2. Approximate logarithm of activity coefficient of NaCl vs square root of ionic strength in sea salt conditions.

A plot of $\log \gamma$ for natural sea salt solutions vs the square root of ionic strength is shown in Figure 2. The corresponding curve for pure NaCl and the Debye-Huckel limiting slope for a 1-1 electrolyte are also shown for comparison. Apparently γ_{NaCl} in a sea salt mixture deviates from unity by a somewhat smaller amount than it does in pure NaCl solutions.

Values of $\log \gamma_{NaCl}$ in synthetic sea water are also shown in Fig. 2. These activity coefficients are larger than those in natural sea salt solutions, with a maximum difference of about 3.5%. The difference between the measurements in natural and synthetic sea salt solutions may be due to the difference in the two media or to the presence of a small amount of bromide in natural sea salt, as well as perhaps some experimental error.

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1.4 THERMODYNAMIC PROPERTIES OF SEA SALT SOLUTIONS

R. W. Stoughton and M. H. Lietzke

Thermodynamic properties of sea salt solutions have been recalculated in view of re-evaluations of the properties of NaCl solutions as a function of temperature and an experimental comparison of the osmotic coefficients of NaCl and sea salt solutions at 25°C. Boiling point elevations (BPE's) were evaluated in the ranges 2 to 28 wt. % salts and 25° to 260°C.; theoretical minimum energies of recovery of water from sea water, in the ranges of 0 to 100% recovery and 25° to 200°C.; and osmotic pressures, in the ranges 1 to 25 wt. % solids and 25° to 100°C. The new values show greatest deviations from the previous calculations at high concentrations and low temperatures. The largest change is a 12% increase in BPE at 25°C. and 28 wt. % solids. In general, where there is a change, the new values are higher; the values of BPE at the highest concentrations and temperature are exceptions—e.g., a 2% decrease at 28 wt. % solids at 260°C.

IN PREVIOUS WORK (15, 16) vapor pressures of sea salt solutions were calculated from 25° to 175°C. and from 1 to 28 wt. % solids by using the following extended Debye-Hückel equation and parameters obtained from measured osmotic coefficients of sodium chloride solutions.

$$\phi = 1 - \frac{S}{A^3 I} \left\{ \left[1 + A(I)^{1/2} \right] - 2 \ln \left[1 + A(I)^{1/2} \right] - \frac{1}{1 + A(I)^{1/2}} \right\} + BI' + CI'^2 \quad (1)$$

In Equation 1, S is the appropriate Debye-Hückel limiting slope for either a single electrolyte or an electrolyte mixture, A is the Debye-Hückel parameter (here set equal to 1.5), I is the ionic strength, I' is a concentration term discussed below, while B and C are adjustable parameters. The latter parameters for NaCl solutions were evaluated to 270°C. (15, 16) from osmotic or activity coefficients from the literature up to 4m to 100° (11) and up to 3m from 100° to 270°C. (4).

In applying Equation 1 to sea salt solutions, the values of B and C for NaCl solutions were used with three different concentration terms for I' :

$$I' = \frac{1}{2} \sum m_i Z_i^2 = I \quad (2a)$$

$$= \frac{1}{2} \sum m_i |Z_i| \quad (2b)$$

$$= \frac{1}{2} \sum m_i \quad (2c)$$

where m_i is the molality and Z_i the charge of any ionic constituent. (For a 1-to-1 electrolyte all three expressions are equal to the molality.)

The calculated vapor pressures were compared with the measured values of Arons and Kientzler (1) at 25° and 35°C. and those of Higashi, Nakamura, and Hara (8) from 25° to 175°C. and to 28 wt. % solids. The agreement was best when Equation 2c was used and poorest when 2a was used. Vapor pressure measurements of Forrest and Worthley (2) from 25° to 100°C. gave better agreement with Equation 2a than with 2b or 2c, although the scatter of the various experimental values (1, 2, 8) was much greater than the difference between the values calculated using Equations 2a and 2c; even at 28 wt. % solids the scatter was greater by at least a factor of two than the difference between the two sets of calculated values. Because the measurements of Arons and Kientzler (1) appeared to be the most precise ones available, the authors concluded (15, 16) that Equation 2c gave best results for the thermodynamic properties of sea salt solutions.

Recently, Rush and Johnson (12) have measured osmotic coefficients of synthetic sea salt solutions in the ionic

strength range 0.6 to 7.0 at 25°C. by using NaCl as a standard and the osmotic coefficients of reference (11) for the standard. These were compared with values of ϕ calculated by using Equations 2a and 2c and Equation 1 with the addition of a cubic term DI'^3 in which the B , C , and D parameters were evaluated from osmotic coefficients at 25°C. only. Throughout the whole concentration range, Equation 2a gave best agreement, showing a maximum deviation of 0.003. By contrast, Equation 2c showed a deviation of 0.001 at the lowest and about 0.1 at the highest concentration.

The authors believe the measurements of Rush and Johnson are the best available and, hence, now conclude that Equation 2a should be used to calculate the thermodynamic properties of sea salt solutions, at least at and near room temperature. The authors, therefore, recommend that, unless and until good experimental measurements suggest otherwise, Equation 2a be used at all temperatures—i.e., it is best to set $I' = I = \frac{1}{2} \sum m_i Z_i^2$ at all temperatures.

The current change in recommendation for the concentration term to be used for I does not change the authors' previous conclusion (15) concerning the use of NaCl solutions for a stand-in for sea salt solutions—i.e., where NaCl solutions are used for a stand-in for sea salt solutions, a solution of the same total concentration of ions is preferable to one of the same ionic strength. The reason is that in thermodynamic calculations the most important concentration term is the coefficient of ϕ in the definition of the osmotic coefficient:

$$\left(\sum m_i\right)\phi = -\frac{1000}{W} \ln a_1 \quad (3)$$

Table I. Parameters of Fit of ϕ_{NaCl} vs. T

$B_1 = -330.332$	$C_1 = 32.6806$
$B_2 = 6.31446$	$C_2 = -0.553679$
$B_3 = -0.909395$	$C_3 = 0.0790215$

Figure 1. Osmotic coefficients of NaCl as a function of temperature from 25° to 250° C.

where a_1 and W are the activity and molecular weight of water. The authors' current change in recommendation does not affect this concentration term.

ACCURACY OF EXISTING NaCl OSMOTIC COEFFICIENTS

The test of the applicability of Equations 2a, 2b, and 2c to calculations of osmotic coefficients of sea salt solutions ϕ_{ss} is approximately independent of the accuracy of the osmotic coefficients of NaCl providing the same values of ϕ_{NaCl} are used for the standard in isopiestic measurements and for the evaluation of the B and C (and D) parameters of Equation 1. However, the accuracy of the calculated values of ϕ_{ss} is essentially the same as the accuracy of

the values of ϕ_{NaCl} at 25°C. (being not more than about 0.003 of a unit different at any concentration).

Lanier (9) has shown that different investigators have reported activity coefficients of NaCl at 25°C. which differ by 1.5% at 3m and 2% at 6m. The corresponding difference in osmotic coefficients is a little less than this. Hence there is an uncertainty of at least 1% even at 25°C. at the higher concentrations.

The authors have re-evaluated the B and C parameters of Equation 1 by the method of least squares on the assumption that their variation with absolute temperature T was the same as that given in Equation 4 for B

$$B = \frac{B_1}{T} + B_2 + B_3 \ln T \quad (4)$$

At 15° and 35°C. the authors used osmotic coefficients at 0.5, 1.0, 2.0, 3.0, and 4.0m which had been calculated (10) from activity coefficients presented by Harned and Owen (7). At 60°, 80°, and 100°C. the authors used osmotic coefficients at the same concentrations, while at 25°C. the value at 5m was included also—all from reference (11). Between 125° and 250°C. (inclusive) at every 25° interval the results of reference (4) were used, plus some additional and some corrected experimental values (3). Unit weights were assigned to all values except those at 25°C.; at 25° statistical weights of 3.0 were assigned in the least squares fit since these were the result of a critical evaluation of measurements from different sources. The resulting values of the B and C parameters are given in Table I.

Figure 1 shows a typical plot of ϕ_{NaCl} vs. temperature at 2.0 and 3.0m. Figure 2 shows the deviations of calculated from experimental values at 0.5, 1.0, 2.0, 3.0, and 4.0m. At lower temperatures, the deviations are within those between different experimental measurements. The region of most consistency appears to be that of 60° to 100°C. where the observed values were those calculated by Smith and Hirtle (14) to give best reasonable agreement with the boiling point elevation measurements of Smith and Hirtle (13, 14) between 60° and 100°C. and the e.m.f.

Figure 2. Deviations between observed and calculated osmotic coefficients of NaCl

measurements of Harned, Cook, and Nims (5, 6) between 0° and 40° C.

Additional fits were made by using different weights, by fixing the values of the parameters at 25° C. to be consistent with the 25° data, and by using seven temperature-dependent parameters—i.e., by adding a term B, T . None of these gave a fit to the measured values which was significantly better than that using the par-

The current calculations assume no precipitation of CaSO_4 . Corrections for precipitation should be made as indicated previously (15)—i.e., the same percentage variation—if so desired.

The new values all show the greatest deviations from the previous calculations (15) at low temperatures and high concentrations (100% recovery in the case of the free energy of recovery). The largest change is a 12% increase

Table II. Calculated Boiling Point Elevations for Sea Salt Solutions, ° C.

T, ° C.	p_0 , Atm.	Wt. % Sea Salt									
		2.0	3.45*	4.0	6.0	8.0	12.0	16.0	20.0	25.0	28.0
25	0.031	0.177	0.312	0.366	0.570	0.795	1.324	1.991	2.858	4.36	5.58
30	0.042	0.184	0.325	0.380	0.594	0.829	1.381	2.077	2.977	4.52	5.77
40	0.073	0.198	0.350	0.410	0.642	0.898	1.497	2.250	3.216	4.86	6.16
50	0.122	0.214	0.377	0.442	0.692	0.969	1.616	2.426	3.458	5.19	6.56
60	0.197	0.229	0.405	0.474	0.744	1.041	1.737	2.604	3.704	5.53	6.96
70	0.309	0.245	0.433	0.508	0.797	1.115	1.860	2.786	3.952	5.88	7.36
80	0.469	0.262	0.463	0.542	0.851	1.191	1.986	2.969	4.202	6.22	7.77
90	0.694	0.279	0.493	0.578	0.907	1.269	2.113	3.155	4.454	6.57	8.18
100	1.003	0.296	0.524	0.615	0.964	1.348	2.242	3.342	4.708	6.92	8.60
110	1.418	0.315	0.556	0.652	1.022	1.429	2.374	3.532	4.963	7.27	9.01
120	1.965	0.334	0.590	0.691	1.082	1.512	2.508	3.723	5.22	7.62	9.43
130	2.673	0.354	0.624	0.731	1.144	1.597	2.643	3.917	5.48	7.98	9.86
140	3.577	0.375	0.660	0.773	1.208	1.684	2.782	4.113	5.74	8.34	10.28
150	4.711	0.396	0.697	0.816	1.274	1.774	2.923	4.311	6.00	8.70	10.71
160	6.119	0.418	0.735	0.861	1.341	1.866	3.066	4.511	6.27	9.06	11.15
180	9.931	0.466	0.817	0.955	1.484	2.057	3.361	4.920	6.81	9.79	12.03
200	15.407	0.519	0.906	1.058	1.637	2.261	3.670	5.342	7.36	10.54	12.94
220	22.993	0.577	1.003	1.170	1.802	2.480	3.995	5.777	7.92	11.30	13.87
240	33.184	0.642	1.111	1.293	1.983	2.715	4.338	6.231	8.49	12.08	14.84
260	46.520	0.716	1.232	1.431	2.181	2.971	4.703	6.700	9.08	12.88	15.83

*Standard sea water.

ameters of Table I. They all appeared to fit the data well within the apparent uncertainties.

Thus at least at 25° C., the uncertainties in the calculated values of the thermodynamic properties of sea salt solutions result from the uncertainties in the measured values of NaCl solutions.

RECALCULATED BPE's, MINIMUM ENERGIES OF RECOVERY, AND OSMOTIC PRESSURES

The authors have recalculated the boiling point elevations (BPE's) of sea salt solutions, the minimum energies of recovery of water from standard sea water, and the osmotic pressures of sea salt solutions over wide ranges of temperature using the current recommendation (Equation 2a), and the new NaCl parameters (Table I). These are presented, respectively, in Tables II, III, and IV.

The minimum energies of recovery are expressed in the dimensionless form $\Delta G_{\text{rec}}/RT$ in Table III. In this form (rather than as ΔG_{rec}) their variation with temperature over the range 25° to 200° C. is reduced from some 45% to about 10%.

Table III. $\Delta G_{\text{rec}}/RT$ for Recovery from Standard Sea Water

3.45 Wt. % Salts

T, ° C.	Recovery, %				
	0	25	50	75	100
25	0.0185	0.0214	0.0260	0.0356	0.081
50	0.0186	0.0215	0.0261	0.0359	0.082
75	0.0185	0.0214	0.0261	0.0358	0.081
100	0.0183	0.0212	0.0258	0.0354	0.080
125	0.0181	0.0209	0.0254	0.0348	0.079
150	0.0178	0.0205	0.0250	0.0341	0.078
175	0.0174	0.0201	0.0244	0.0331	0.076
200	0.0170	0.0195	0.0236	0.0320	0.074

$$RT = 0.12831 T \text{ kw.h. per 1000 kg. water}$$

$$= 1.9866 T \text{ cal. per mole water}$$

$$= 82.057 T \text{ cc.-atm. per mole water}$$

where T is in ° K.

Table IV. Osmotic Pressures of Sea Salt Solutions, Atm.

T, ° C.	Wt. % Salts								
	1.00	2.00	3.45*	5.00	7.50	10.00	15.00	20.00	25.00
25	7.11	14.29	25.15	37.49	59.30	83.97	144.93	228.59	348
40	7.42	14.93	26.34	39.35	62.41	88.53	152.81	239.86	362
60	7.80	15.70	27.74	41.51	65.98	93.69	161.53	252.06	376
80	8.13	16.37	28.94	43.32	68.89	97.82	168.27	261.17	386
100	8.42	16.94	29.92	44.79	71.17	100.97	173.16	267.47	393

*3.45 wt. % solids is taken as the value for standard sea water.

in BPE at 25°C. at 28 wt. % solids. The largest change at 12 wt. % solids and below is a 4% increase in BPE at 25°C. In general, where there is a change the new values are higher. The BPE values at the highest concentrations and temperatures are exceptions to this general observation; a 2% decrease occurs at 28 wt. % solids at 260°C.

ANALYTICAL EXPRESSIONS for BOILING POINT ELEVATIONS

Attempts were made to get an analytical expression for the BPE's vs. concentration and temperature given in Table II so that intermediate values could be calculated directly without resorting either to graphical interpolation or to the elaborate iteration procedure used in the original calculations (15). The authors' general approach to the problem was to express the BPE's as BPE_{ideal} , or some approximation thereof, times a function of temperature and concentration. The ideal BPE is given by Equation 5.

$$BPE_{ideal} = (RT^2 \sum m_i) / \Delta H_{vap}, \quad (5)$$

where R is the molal gas constant and ΔH_{vap} is the heat of vaporization of a kilogram of water. In this equation, the mole fraction of solute in Raoult's law has been replaced by the mole ratio of solute to solvent. Equation 5 may be expressed in terms of the absolute temperature T and the ionic strength I as follows.

$$BPE_{ideal} (^{\circ}C.) = 0.24048 T^2 I / (93,467.7 - 6,189,790/T - 96,584.9 T), \quad (6)$$

where

$$I = 0.19819 \times \text{wt. \%} / (1 - 0.01 \times \text{wt. \%}) \quad (7)$$

Equation 6 may be used as a rough approximation. The BPE values obtained are good to within about 10% at concentrations below about 16 wt. % and temperatures below about 125°C. At 260°C. the values obtained are about 30% low at all concentrations to about 20 wt. %. The ideal BPE's (Equation 6) showed in general a greater deviation from the more accurately calculated ones (15) than did those based on Raoult's law and the authors' previous equation (15) for the vapor pressure of water as a function of temperature, particularly at the higher temperatures. However, the latter calculations involved an iteration to evaluate the BPE such that the vapor pressure of the solution at temperature $T + BPE$ was equal to the vapor pressure of pure water at temperature T .

Because of the peculiar way in which the calculated BPE's (15) deviated from the ideal values, it was difficult to get a suitable analytical expression by the method of least squares. When only a few parameters—e.g., five or six—were used, the agreement was not as good as desired. Equation 8 is the equation of best fit that was obtained with six parameters.

$$BPE = BPE_{ideal} \times (0.205648 + 3.49091 \times 10^{-3} T + 0.150005 I - 2.86240 \times 10^{-4} I T - 4.61964 \times 10^{-6} T^2 + 2.78176 \times 10^{-3} I^2) \quad (8)$$

In the range 0 to 20 wt. % solids the maximum deviation (4%) of Equation 8 from the accurate values is at 2 wt. % at both 25° and 260°C. For weight per cents between 3.45 (standard sea water) and 20 for temperatures between 30° and 240°C., the maximum deviations are about 2.5%.

When seven to ten parameters were used to get better agreement, convergence difficulties were encountered. Equation 9 was obtained by a combination of adjusting the temperature dependence of ΔH_{vap} and of evaluating a few parameters, fixing these, and then evaluating additional ones.

$$BPE = [565.757/T - 9.81559 + 1.54739 \times \ln T - (337.178/T - 6.41981 + 0.922753 \times \ln T) I + (32.681/T - 0.55368 + 0.079022 \times \ln T) I^2] \times I / (266,919.6/T^2 - 379.669/T + 0.334169) \quad (9)$$

Equation 9 shows deviations from the more accurate calculation of about 1% or less in the ranges 3.45 to 20 wt. % and 30° to 250°C. At 2 wt. % and at 25°C., many of the deviations are about 2%. Thus, this equation reproduces the BPE's to well within the accuracy to which they are known, except at the lowest concentration and at the lowest temperature.

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1.5 SELF-DIFFUSION COEFFICIENTS OF SODIUM ION IN NaCl SOLUTIONS AS A FUNCTION OF TEMPERATURE AND CONCENTRATION⁵

H. O. Phillips, S. B. Sachs,⁶ and K. A. Kraus

The radiometric porous-frit method⁷ was used to measure the self-diffusion coefficient, D_{Na} , of Na^+ in aqueous solutions over the concentration range from $M_{NaCl} = 0.05$ to 5.0. The results are given in Table 1.5.1. This method involves calibration of the frit with a solution in which the diffusion coefficient is known. In this study, the literature value of Mills⁸ at $M_{NaCl} = 1.0$ was used. The values measured at the other concentrations agree within 2% with the values of Mills over the range he studied, showing further evidence of the reliability of the porous-frit method. Also given in Table 1.5.1 are the diffusion-viscosity products which show little variation with concentration except for a slight increase in the more concentrated solutions.

TABLE 1.5.1
SELF-DIFFUSION COEFFICIENTS OF Na^+ IN NaCl SOLUTIONS AT 25°

M_{NaCl}	$D \times 10^5 (cm^2/sec)$		$D\eta \times 10^7$ ^b
	This study	Mills ^a	
0.05	1.29		1.16
0.10	1.27	1.30 ^c	1.14
0.50	1.26	1.28 ^c	1.17
1.00	1.234 ^d	1.234 ^d	1.20
2.00	1.13	1.13 ^c	1.23
3.00	1.04	1.03	1.27
4.00	0.95	0.93	1.33
5.00	0.78		1.30

a. See Ref. 8.

b. η indicates viscosity (poise).

c. Interpolated values.

d. Data normalized at this concentration.

5. Work cosponsored by the U.S. Atomic Energy Commission.
6. Visiting scientist from the Weizmann Institute, Rehovot, Israel.
7. F. Nelson, J. Polym. Sci. 40, 563 (1959); F. Nelson and K. A. Kraus, Production and Use of Short-Lived Isotopes from Reactors, vol. 1, pp. 191-213, IAEA, Vienna, 1962; A. E. Marcinkowsky, F. Nelson, and K. A. Kraus, J. Phys. Chem. 69, 303 (1965).
8. R. Mills, J. Amer. Chem. Soc. 77, 6116 (1955).

A preliminary study has been made to investigate the feasibility of using the radiometric porous-frit method to measure diffusion coefficients at temperatures other than 25°C. A difficulty arises from the lack of available diffusion coefficient data at other temperatures to use for calibration. The following study was carried out to see if it is possible to calibrate a frit at one temperature and then use the same calibration for diffusion studies at other temperatures.

Measurements were made of half-times ($t_{1/2}$) for Na^+ ion removal from a gold frit in 0.05, 0.10, and 1.0 M NaCl solutions at several temperatures in the range 15° to 85°C. The half-times changed by about a factor of 4 over this temperature range. Self-diffusion coefficients are inversely proportional to $t_{1/2}$ values, the proportionality constant being the frit calibration factor. To estimate constancy of this factor the $t_{1/2}$ values as a function of temperature were compared with limiting conductance data⁹ since these can also be related to diffusion coefficients. The comparison is shown in Fig. 1.5.1. The ordinate gives the ratio of solution viscosity to $t_{1/2}$ and also the viscosity-conductance product, both quantities normalized at 25°. The variation of the two quantities with temperature is very similar, indicating that it is satisfactory to use a single frit constant to determine diffusion coefficients at temperatures other than the one at which the frit was calibrated.

1.6 SELF-DIFFUSION COEFFICIENTS OF Na^+ IN SODIUM PHOSPHATE SOLUTIONS¹⁰

H. O. Phillips and K. A. Kraus

Self-diffusion coefficients of Na^+ have been determined by the radiometric porous-frit method in sodium phosphate solutions at 25°. Measurements were made at several salt concentrations, up to 0.4 M for

9. R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2nd Ed., Academic Press, New York, 1959.

10. Work cosponsored by the U.S. Atomic Energy Commission.

FIG. 1.5.1 TEMPERATURE DEPENDENCE OF SELF-DIFFUSION COEFFICIENTS AND LIMITING CONDUCTANCES OF Na^+ IN AQUEOUS SOLUTIONS.

Na_3PO_4 and up to 0.6 M for H_2NaPO_4 and HNa_2PO_4 . Preliminary results are given in Table 1.6.1. Viscosity increases with increasing salt concentration while D_{Na} decreases. The diffusion-viscosity products do not change appreciably with salt used or their concentration.

1.7 TRACER DIFFUSION COEFFICIENTS OF Cu(II) AND La(III) IN HCl AND HClO_4 SOLUTIONS AT 25°C ¹¹

A. E. Marcinkowsky and H. O. Phillips

The radiometric porous-frit method was used to measure tracer diffusion coefficients of Cu(II) and La(III) in HCl and HClO_4 solutions at 25°C up to concentrations of 10 M. Preliminary results are given in Table 1.7.1. In the HCl system, D_{La} decreases slowly as the acid concentration increases while D_{Cu} is nearly constant up to 4 M HCl . In contrast, D_{La} in HClO_4 solutions remains nearly constant up to 3 M HClO_4 . Beyond this concentration there is a rapid decrease with increasing concentration for both D_{La} and D_{Cu} . A similar study on Zn(II) was reported in the previous biennial report.¹

Also listed in Table 1.7.1 are the diffusion-viscosity products for each system measured. There is little difference between the two acids except at the highest concentrations.

11. Work cosponsored by the U.S. Atomic Energy Commission.

TABLE 1.6.1

SELF-DIFFUSION COEFFICIENTS OF Na^+ IN SODIUM PHOSPHATE SOLUTIONS AT 25°C

Salt Solution	Conc. (M)	$\eta \times 10^2$ (P) ^a	$D \times 10^5$ (cm ² /sec)	$D\eta \times 10^7$
H_2NaPO_4	0.05	0.908	1.23	1.12
	0.10	0.926	1.22	1.13
	0.30	0.975	1.16	1.13
	0.60	1.050	1.06	1.12
HNa_2PO_4	0.05	0.919	1.19	1.09
	0.15	0.976	1.13	1.10
	0.30	1.070	1.01	1.08
	0.60	1.301	0.89	1.16
Na_3PO_4	0.033	0.922	1.15	1.06
	0.10	0.981	1.07	1.05
	0.20	1.076	0.98	1.05
	0.40	1.287	0.85	1.09

a. Viscosities measured in this laboratory by J. Csurny.

TABLE 1.7.1

TRACER DIFFUSION COEFFICIENTS AND DIFFUSION-VISCOSITY PRODUCTS OF
Cu(II) AND La(III) IN HCl AND HClO₄ SOLUTIONS AT 25°C

Conc. (M)	$D \times 10^5$ (cm ² /sec)		$(D\eta/\eta_0)^a \times 10^5$ (cm ² /sec)	
	Cu(II)	La(III)	Cu(II)	La(III)
HCl Solution				
0.0	0.713 ^b	0.618 ^b	0.713	0.618
0.25	.71		.72	
1.00	.71	.59	.76	.62
1.94	.71	.58	.79	.65
3.01	.70	.57	.83	.68
4.16	.70	.53	.88	.67
6.06	.67	.49	.94	.69
8.01	.62	.43	.99	.69
10.0	.57	.39	1.04	.72
HClO ₄ Solution				
0.245	.74		.74	
1.10	.76	.62	.76	.63
1.86	.75	.62	.78	.64
3.04	.73	.61	.81	.68
3.96	.69	.57	.84	.69
6.12	.57	.45	.92	.72
7.76		.33		.70
9.76	.28	.20	.90	.65

a. η_0 is the viscosity of water at 25°C.

b. Calculated from limiting conductance values using the Nernst Equation.

2. Thermodynamic and Transport Properties in Water-Organic Systems

Summary

In previous biennia, interesting correlations were found between properties of membranes and of chemically similar organic-water solutions ("model solutions"). Measurements of activity coefficients of salts have been particularly helpful in rationalizing equilibrium properties of membranes pertinent to their hyperfiltration behavior. For a neutral membrane, activity coefficient ratios of a solute between membrane and solution determine the distribution coefficient of the salt. Measurements of the activity coefficients of salts in solvents containing water plus acetylated glycols correlated well with properties of cellulose acetate membranes--salt activity coefficients in the water-organic solutions increased with increasing degree of acetylation and with decreasing water content.¹ Quantitative correlation with distribution coefficients of membranes, measured at Gulf General Atomic, was about as close as one could expect.² Measurements with aliphatic and aromatic polyamide-water solvents³ suggested that membranes of these substances might have favorable desalination properties, a prediction confirmed by later developments.

In general, the model solution studies indicated that low water contents should be conducive to high salt rejections. Results with poly(vinylpyrrolidone) film membranes, for example, follow this trend.⁴ Membranes dynamically formed from poly(vinylpyrrolidone) have shown low salt rejection. Since the high solubility of this polymer indicates strong

1. K. A. Kraus, R. J. Raridon, and W. H. Baldwin, J. Amer. Chem. Soc. **86**, 2571 (1964).
2. J. S. Johnson, Jr., L. Dresner, and K. A. Kraus, Chapt. 8 in Principles of Desalination, K. S. Spiegler, ed., Academic Press, New York (1966).
3. C. F. Coleman, J. Phys. Chem. **69**, 1377 (1965).
4. R. L. Riley, C. R. Lyons, and U. Merten, Desalination **8**, 177 (1970).

water-organic interactions, the dynamic membranes probably are of high water content, and thus are consistent with the observations with film membranes. The importance of casting procedures and subsequent membrane treatments thus appears to be primarily in determining the thickness and integrity of the salt-rejecting layer and its water content.

During this biennium, several additional water-organic systems were investigated. One of particular interest involved pyridine, since advantage could be taken of its weak-electrolyte properties to study it both as a neutral material and as an electrolyte. Effect of molecular weight and branching on NaCl activity coefficients was investigated with a number of polyalcohol-ethers. Alkyl sulfoxides and quaternary amine salts also received attention.

Self-diffusion of ions in water-organic solutions was studied by the porous-frit method discussed in Section 1. Correlations of kinetic properties between solutions and membranes are not as straightforward as of equilibrium properties. With low-molecular-weight glycols, the product of the diffusion coefficient of Na^+ in water-organic solutions and the viscosity of the solution is to a rough approximation independent of water content. With polymeric organic components, the correlation disappears. With polymeric organic components, both in water-organic solutions and in membranes, diffusion coefficients, D , are a strong function of water content, f_w . Over a large composition range, $\log D$ decreases linearly with $\log f_w$.⁵ The slope ($d \log D / d \log f_w$) is greater (more negative) for membranes than for most water-organic solutions. With a series of cellulosic membranes whose permeabilities indicated a wide range of pore sizes, the pore sizes were shown to be unimportant in comparison with the water content in determining diffusion coefficients.

In supporting work, dielectric constants of water solutions of amides were measured, and photopolymerization procedures utilizing uranyl ions were developed.

5. K. A. Kraus, H. O. Phillips, and A. E. Marcinkowsky, U.S. Office of Saline Water Research and Development Report 685 (1971), p. 77.

[Reprinted from the Journal of Physical Chemistry **72**, 925 (1968)]

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2.1 PROPERTIES OF ORGANIC-WATER MIXTURES. VI. ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE IN SATURATED WATER-PYRIDINE MIXTURES AT 5 AND 25°¹

Richard J. Raridon, Willis H. Baldwin, and Kurt A. Kraus

The solubility of NaCl in mixtures of pyridine and water was determined at 5 and 25° by packed-column techniques. Miscibility limits of pyridine and water in saturated NaCl solutions were established as a function of temperature. The pyridine-water system, saturated with NaCl, was found to have a lower consolute temperature of 11° with a broad minimum from 20 to 40 wt % pyridine. From the solubility data, activity coefficient ratios, Γ^* , of NaCl were computed. The values of Γ^* at 5°, where the system is completely miscible, and at 25°, where a miscibility gap from 6 to 63 wt % pyridine is present, did not differ appreciably. Comparison is made of activity coefficient ratios with salt rejection by hyperfiltration membranes containing poly(4-vinylpyridine).

As part of the study of water desalination by hyperfiltration (separation of salts from water by filtration through suitable membranes under pressure) thermodynamic and transport data for a variety of organic-water mixtures have been measured. Previous papers^{2,3} dealt with the comparison of activity coefficients of several salts, including NaCl, in water-organic mixtures at saturation. Several of these solvent systems showed miscibility gaps with salts present. When using model

solution systems for predicting properties of membranes, one wonders about the direct applicability of

(1) (a) Research sponsored by The Office of Saline Water, U. S. Department of the Interior under a Union Carbide Corp. contract with the U. S. Atomic Energy Commission; (b) previous paper in series: A. E. Marcinkowsky, H. O. Phillips, and K. A. Kraus, *J. Phys. Chem.*, **69**, 3968 (1965).

(2) K. A. Kraus, R. J. Raridon, and W. H. Baldwin, *J. Am. Chem. Soc.*, **86**, 2571 (1964).

(3) C. F. Coleman, *J. Phys. Chem.*, **69**, 1377 (1965).

the values of the activity coefficients, $\gamma_{\pm}^*$, of salts obtained in homogeneous systems to these intrinsically two-phase systems. Estimation of $\gamma_{\pm}^*$ for partially miscible systems and suitable interpolations seem satisfactory if one can assume that the presence of a miscibility gap has little influence on the activity coefficients of the salt, although, of course, activities of the water and organic components can be very different for miscible and immiscible systems.

The present paper deals with a test of this assumption with the pyridine-water system. There is a large miscibility gap in this system at 25° when saturated with NaCl. However, at low temperatures (<11°), the pyridine-water system saturated with NaCl is completely miscible and activity coefficients can be measured by the solubility method in the same solvent system but under conditions of both miscibility and immiscibility.

Experimental Section

1. *Method.* The solubilities were measured using the packed-column techniques previously described.^{2,4} These techniques are particularly well suited for measurements at other than ambient temperatures. Analyses were by titration with silver nitrate, using chromate as indicator, except for measurements at pyridine contents of 95% or greater where a Buchler-Cotlove chloridometer was used to obtain the desired accuracy. It was necessary to evaporate the pyridine from the collected samples because of interference with the titration.

For the miscibility studies, weighed amounts of pyridine and water were added to a 5-ml flask. Sufficient NaCl was added to saturate the mixture. The flask was placed in a water bath and the mixture agitated with a magnetic stirrer. The temperature was gradually changed and visual observation was used to determine the maximum temperature for miscibility in the presence of solid NaCl.

2. *Materials.* Reagent grade NaCl was used, with a stated maximum impurity of 0.025%. It was dried for 24 hr at 400° to remove traces of moisture. The pyridine was purified by standard distillation techniques. It was analyzed by Karl Fischer titration and was found to contain 0.07% water.

Results and Discussion

1. *Miscibility Limits.* Pyridine and water, which are miscible in all proportions, are salted out by NaCl.⁵ In the present study, we found that the miscibility gap at 25° extends from ca. 6 wt % pyridine to ca. 63 wt % pyridine when saturated with NaCl. The gap is smaller at lower temperatures and disappears entirely below ca. 11°. Measurements of maximum temperature for miscibility at saturation with NaCl were made at selected pyridine-water compositions in the presence of solid NaCl. Readings made as the temperature was

Figure 1. Effect of temperature on the miscibility of pyridine-water mixtures saturated with NaCl.

increased and then decreased, generally agreed to within 0.5°. The results are shown in Figure 1. The miscibility curve is asymmetrical, with a broad minimum extending from 20 to 40 wt % pyridine, at which the maximum miscibility temperature is 11°. The curve rises rapidly at high water contents, with the maximum miscibility temperature being over 100° at 4.5 wt % pyridine. There is a gradual increase in maximum temperature with increasing pyridine content between 40 and 65 wt % pyridine, beyond which there is a rapid rise in the maximum temperature.

2. *Solubility of NaCl.* The solubility of NaCl was measured at 5° over the entire range of pyridine-water compositions and at 25° in the organic-rich end of the phase diagram (above 63 wt % pyridine). The results are given in Table I. The solubilities at 5° are somewhat lower (at the same solvent composition) than those at 25°, except at 95 wt % pyridine, where the solubility of NaCl at 5° seems slightly higher than at 25°.

Table I: Solubility of NaCl in Pyridine-Water Mixtures at 5 and 25°

Wt % pyridine	Solubility in mixed solvent, g/kg		Activity coefficient ratios, Γ^*	
	5°	25°	5°	25°
0.0	357	360	1.00	1.00
25.0	225	...	1.19	...
50.0	113	...	1.58	...
65.0	50.5	53.2	2.47	2.37
75.0	18.3	20.6	4.88	4.37
85.0	3.43	3.95	15.6	13.6
90.0	1.13	1.14	31.6	31.6
95.0	0.18	0.15	99	120
99.9		<0.001		

(4) K. A. Kraus, H. O. Phillips, and F. Nelson, "Radioisotopes in the Physical Sciences and Industry, Sept 1960," Vol. III, IAEA, Vienna, 1962.

(5) P. M. Ginnings, B. Webb, and E. Hinohara, *J. Am. Chem. Soc.*, 55, 4898 (1933).

3. *Activity Coefficients of NaCl.* The results at different temperatures can be compared in terms of an activity coefficient ratio, $\Gamma^* = \gamma_{\pm}^*/\gamma_{\pm}$ where the activity coefficient in the mixed solvent, $\gamma_{\pm}^*$, is computed on the same basis as that in water ($\gamma_{\pm}$), namely, by using the same standard state as in water and expressing concentrations in moles per kilogram of water. Γ^* thus measures the relative selectivity of the medium for salt and water; it is a useful quantity for evaluation of model solutions for hyperfiltration membranes.⁶

If s_{aq} is the solubility in pure water and s_o is the solubility in the water-organic mixture, both expressed in moles per kilogram of solvent, and f_w is the fractional water content of the pyridine-water mixture (kilogram of water per kilogram of solvent), Γ^* is given by

$$\Gamma^* \equiv \gamma_{\pm}^*/\gamma_{\pm} = s_{aq}f_w/s_o \quad (1)$$

Γ^* is approximately the same as $\gamma_{\pm}^*$ for NaCl since, by coincidence, at saturation $\gamma_{\pm NaCl} \approx 1$.

Values of Γ^* obtained in the present study are listed in Table I. The variation of Γ^* with temperature is less than the variation of solubility, since NaCl is slightly less soluble at the lower temperature. The miscibility gap at 25° seems to have no substantial effect on the activity coefficient ratios in the miscible region of the solvent system at 25°.

Although activity coefficients are evaluated here at saturation (activity $a_{NaCl} = 38.4$) rather than infinite dilution, correlation with dielectric constants ϵ seems of interest. Dielectric constants of pyridine-water mixtures were measured (see Table II) at 25° with a cell and bridge arrangement essentially identical with that used by Fuoss and coworkers.⁷ Values of ϵ for the mixtures at 5° were calculated assuming a linear variation of $\log \epsilon$ with temperature, as is the case with water and pure pyridine over this temperature range.⁸ For pyridine, $d \log \epsilon/dT = -0.00182$ and for water $d \log \epsilon/dT = -0.00204$; for intermediate compositions the slopes were assumed to vary linearly with water content.

Table II: Dielectric Constants of Pyridine-Water Mixtures

Wt % pyridine	Dielectric constant	
	25°	5° ^b
0	78.5	86.2 ^a
25	64.0	70.1
50	49.5	54.1
65	40.4 ^a	44.1
75	33.9	37.0
85	26.4 ^a	28.8
90	22.3	24.3
95	18.0 ^a	19.6
100	13.2	14.4 ^a

^a Interpolated values. ^b Values for mixtures calculated from 25° values by extrapolation using temperature coefficients given in text.

Figure 2. Activity coefficients of NaCl at saturation in pyridine-water mixtures.

In Figure 2, $\log \Gamma^* - \log X_1$ (X_1 is the mole fraction of water in the mixture) is plotted vs. $(\epsilon_1/\epsilon_{13}) - 1$, where ϵ_1 and ϵ_{13} are the dielectric constants of water and of the water-pyridine mixture, respectively. The plot is linear, except for a slight curvature near the origin. Qualitatively a linear variation of $(\log \Gamma^* - \log X_1)$ with $((\epsilon_1/\epsilon_{13}) - 1)$ is perhaps expected. Lanier⁹ used a similar plot, suggested by Scatchard,¹⁰ to compare activity coefficients (at infinite dilution of salt) in different water-organic systems. Lanier employed an emf method to measure NaCl activities as a function of concentration and then extrapolated to get $\gamma_{\pm}^*$ at infinite dilution. He found that the quantity $(\log \gamma_{\pm}^* - \log X_1)$ vs. the same reciprocal function of the dielectric constant (ρ in ref 9 corresponds to ϵ_{13}/ϵ_1) gives plots that are roughly linear, but with different slopes for different water-organic mixtures. Apparently similar linear variations hold at saturation. The curvature near the origin occurs at high water contents and high solubilities where, in addition to the Debye-Hückel function, terms linear in concentration become increasingly important for representing activity coefficients.

4. *Some Implications for Hyperfiltration.* In hyperfiltration (removal of salts from solution by pressure filtration through suitable membranes) limiting salt rejection R_{∞} at sufficiently high fluxes of water is related to a distribution coefficient D^* at the entrance interface by⁶

$$1 - R_{\infty} = \beta D^* \quad (2)$$

(6) J. S. Johnson, L. Dresner, and K. A. Kraus in "Principles of Desalination," K. S. Spiegler, Ed., Academic Press Inc., New York, N. Y., 1966.

(7) J. E. Lind, Jr., and R. M. Fuoss, *J. Phys. Chem.*, **65**, 999 (1961).

(8) F. Buckley and A. A. Maryott, "Tables of Dielectric Dispersion Data for Pure Liquids and Dilute Solutions," National Bureau of Standards Circular No. 589, U. S. Government Printing Office, Washington, D. C., 1958.

(9) R. D. Lanier, *J. Phys. Chem.*, **69**, 3992 (1965).

(10) G. Scatchard, *ibid.*, **68**, 1056 (1964).

Here β is a coupling coefficient which is presumed to be usually between 0 and 1. Thus, a low value of D^* is equivalent to good limiting salt rejection and for $\beta = 1$, $R_\infty = 1 - D^*$. The distribution coefficient (for uncharged membranes) in turn is related to the activity coefficient ratio by $D^* = 1/\Gamma^*$. Present observations support the view that the miscibility gap, which by necessity exists in a membrane-water system, does not seriously affect prediction of D^* from the values of Γ^* obtained from a suitable model water-organic system. Hence one predicts that pyridine-containing membranes should have good salt-rejecting properties at sufficiently low water content and dielectric constant. Predicted asymptotic rejections R_∞ for $\beta = 1$ for a "pyridine membrane" are given as a function of f_w in Figure 3 and as a function of $(\epsilon_1/\epsilon_{13}) - 1$ in Figure 4. We presume that the dielectric constant variable is more directly applicable to membranes which, in general, will also contain other groups. Since for neutral membranes $\beta \leq 1$, the values of R_∞ given should be lower limits. Also, at a given water content Γ^* and hence R_∞ are usually less at saturation than at lower activities a .

We have attempted to prepare hyperfiltration membranes from various pyridine derivatives but with only limited success. Membranes prepared by grafting poly(4-vinylpyridine) to cellulose membranes (Schleicher and Schuell 06, 07, and 08) yielded salt rejections of 20–45% (0.5 M NaCl) and fluxes of 1–4 gal/day ft² at 1500–2000 psi pressure.

In attempts to cast poly(4-vinylpyridine) from various solvents, a membrane prepared from a methanol-glycerol solvent mixture (0.5 g of polymer in 5 ml of methanol and 1 ml of glycerol) gave 70% salt rejection (0.5 M NaCl); flux was only 1.5 gal/day ft² at 2500 psi pressure. However, considering the thickness of this neutral membrane (43 μ , measured wet), its flux seems high. A cellulose acetate membrane of the same thickness should have a flux of 0.14 gal/day ft² if Reid and Breton's permeability data¹¹ are used.¹²

The water content of this membrane was 48.8%, as determined by "wet" and dry weighings. Using the values of Γ^* for pyridine (Figure 3) at this composition, one predicts that $(1 - R_\infty) \leq 0.62$ or $R_\infty \geq 0.38$. As already mentioned, there are several reasons why one expects R_{obsd} to be larger than the computed limiting value of R_∞ . (Effects which might cause R_{obsd} to be less than R_∞ are concentration polarization and too low a pressure to reach R_∞ . We presume that these effects should be negligible here.) The observed rejection was obtained at $M = 0.5$, rather than at saturation; D^* should be less (or Γ^* larger) at $M = 0.5$ than at saturation.⁹ The calculations refer to pyridine; a substituted pyridine (e.g., methylpyridine) with a presumably lower dielectric constant and hence probably higher values of Γ^* should be a better model. Finally, the calculations assume $\beta = 1$; values of $\beta < 1$ for this system are not

Figure 3. Computed salt rejection for pyridine system (saturated NaCl, $\beta = 1$).

Figure 4. Computed salt rejection for pyridine system (saturated NaCl, $\beta = 1$).

unexpected. We thus consider the agreement between computed and observed rejections satisfactory and conclude that this membrane probably was reasonably homogeneous and free of pinholes.

Use of the dynamic technique¹³ gave poly(4-vinylpyridine) membranes with somewhat better rejections and fluxes. Thus chloride rejection of 90% was observed with sea water at fluxes of 3 gal/day ft² at 1500 psi pressure. Presumably, this membrane had a somewhat lower water content and was much thinner than the cast membrane. Hopefully, still thinner membranes will eventually be prepared which permit fuller exploitation of the attractive intrinsic salt-rejecting properties of these pyridine-based materials.

Acknowledgment. We are greatly indebted to J. S.

(11) C. E. Reid and E. J. Breton, *J. Appl. Polymer Sci.*, **1**, 133 (1959).

(12) R. J. Raridon, L. Dresner, and K. A. Kraus, *Desalination*, **1**, 210 (1966).

(13) K. A. Kraus, A. J. Shor, and J. S. Johnson, Proceedings of the Second European Symposium on Fresh Water from the Sea, Athens, 1967; *Desalination*, **2**, 243 (1967).

Johnson for permission to quote the hyperfiltration results and for many helpful discussions. We are also indebted to M. D. Danford, C. G. Westmoreland, J. Curny, and Neva Harrison for technical assistance.

2.2 ACTIVITY COEFFICIENTS OF NaCl IN SATURATED ORGANIC-WATER MIXTURES

R. J. Raridon and K. A. Kraus

The solubility of NaCl was measured at 25° in water mixtures of a number of diols and ethers containing 4 to 9 carbon atoms. Activity coefficient ratios were calculated for mixtures containing 5% and 15% water, as part of the continuing study of the effects of functional groups, molecular weights, and branching on the water miscibility of organic compounds and the activity coefficients of salts in water mixtures of these compounds.

If $\underline{s}_{aq}$ is the solubility in pure water and $\underline{s}_o$ the solubility in the water-organic mixture, both expressed in moles per kilogram of solvent, and $\underline{f}_w$ is the fractional water content of the solvent (kg of H₂O per kg of solvent), Γ^* , the activity coefficient ratio is given by

$$\Gamma^* = \gamma_{\pm}^*/\gamma_{\pm} = \underline{s}_{aq}\underline{f}_w/\underline{s}_o,$$

where the activity coefficient in the mixed solvent, $\gamma_{\pm}^*$, is computed on the same basis as that in water ($\gamma_{\pm}$), namely, by using the same standard state as in water and expressing concentrations in moles per kilogram of water.

Table 2.2.1 lists the compounds studied and the values of Γ^* . As found previously, Γ^* for NaCl generally increases with increasing molecular weight in a homologous series, and decreases with increased branching of isomers. However, if the branching involves the functional groups, such as -OH, Γ^* may increase with increased branching, as evidenced by 1,6-hexanediol ($\Gamma^* = 3.8$) and 2,5-hexanediol ($\Gamma^* = 7.1$).

TABLE 2.2.1

ACTIVITY COEFFICIENT RATIOS OF NaCl IN ORGANIC-WATER MIXTURES AT 25°

<u>Compound</u>	<u>$\Gamma^*(5\% \text{ H}_2\text{O})$</u>	<u>$\Gamma^*(15\% \text{ H}_2\text{O})$</u>
Propylene glycol monomethyl ether $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OCH}_3$	7.0	3.6
1,5-Pentanediol $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	6.7	4.5
1,6-Hexanediol $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	too viscous	3.8
2,5-Hexanediol $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{CH}(\text{OH})\text{CH}_3$	26	7.1
2-Methyl-2-ethyl propanediol $\text{HOCH}_2\text{C}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$	too viscous	2.0
2-Methyl-2,4-pentanediol $\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	18	two-phase system
Tetrahydropyran-2-methanol $\text{OC}_4\text{H}_8\text{CHCH}_2\text{OH}$	2.4	1.9
1,2,6-Hexanetriol $\text{HOCH}_2\text{CH}(\text{OH})\text{C}_4\text{H}_8\text{OH}$	0.9	1.4
Dipropylene glycol monomethyl ether $\text{HOC}_3\text{H}_6\text{OC}_3\text{H}_6\text{OCH}_3$	4.7	3.2
Butoxyethoxypropanol $\text{C}_4\text{H}_9\text{OC}_2\text{H}_4\text{OCH}_2\text{CH}(\text{OH})\text{CH}_3$	22	two-phase system

2.3 ACTIVITY COEFFICIENTS OF K_2SO_4 IN AQUEOUS SOLUTIONS OF PYRIDINE AND PYRIDINIUM SULFATE⁶

H. E. Hellwege,⁷ R. J. Raridon, and K. A. Kraus

In Section 2.1, activity coefficients of NaCl in pyridine-water solutions saturated in the salt were correlated with hyperfiltration of NaCl by poly(vinylpyridine) membranes. Pyridine is a weak electrolyte, and an interesting aspect of membranes based on polymers of it is the option of varying their character from neutral to ion-exchange by changing the pH of the contacting solution. Analogous model solutions can be prepared by acid additions to pyridine-water systems, to convert part of the pyridine to the pyridinium ion. It seemed of interest to study a 2:1 electrolyte. With sodium sulfate there would be complications arising from the fact that the solid would be a hydrate. Consequently, potassium sulfate was adopted as the solute for these studies.

K_2SO_4 in pyridine-water solutions: Solubilities of K_2SO_4 in pyridine-water, measured by packed-column techniques,⁸ are listed in Table 2.3.1. To facilitate analyses, the salt was spiked with ^{42}K tracer. Values of the activity coefficient ratio,

$$\Gamma^* = \frac{\gamma_{\pm}^*}{\gamma_{\pm}} = \frac{s_{aq} f_w}{s_o}, \quad 2.3.1$$

of K_2SO_4 in a saturated solution in the mixed solvent to that in water are presented in Fig. 2.3.1. As in Section 2.1, the asterisk on Γ indicates that the concentration scale is moles salt/kg water in both the mixed solvent and water; s_{aq} indicates solubility in water; s_o solubility in moles/kg of mixed solvent; f_w weight fraction of water in the mixed solvent; $\gamma_{\pm}$, the mean ionic activity coefficient, the asterisk on $\gamma_{\pm}$ signifying the water-organic solution. The standard state is the same for both media, selection being to make the salt activity coefficient unity at infinite dilution of the salt in water.

6. Cosponsored by the U.S. Atomic Energy Commission.

7. 1967 Summer Research Participant (Oak Ridge Associated Universities) from Rollins College, Winter Park, Florida.

8. K. A. Kraus, R. J. Raridon, and W. H. Baldwin, J. Amer. Chem. Soc., **86**, 2571 (1964).

TABLE 2.3.1

SOLUBILITY OF K_2SO_4 IN PYRIDINE (P)- H_2O AT 25° .

<u>Wt. % H_2O</u>	<u>Wt. % P</u>	<u>Solubility, K_2SO_4 gm/kg of solvent^a</u>
100.0	0.0	120.4
91.0	9.0	73.2
86.3	13.7	58.1
75.0	25.0	30.5
50.0	50.0	2.9
43.0	57.0	1.0
35.0	65.0	0.21
25.0	75.0	0.018
20.0	80.0	0.0070
15.0	85.0	0.0031
10.0	90.0	0.0013

a. Solvent is pyridine plus water.

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FIG. 2.3.1 ACTIVITY COEFFICIENTS OF K_2SO_4 AND $NaCl$ IN PYRIDINE-WATER MIXTURES AT $25^\circ C$. Points indicated by X taken from J. J. Fox and A. J. H. Gauge, J. Chem. Soc. 27, 377 (1910).

The activity coefficient ratio Γ^* rises very rapidly with increasing organic content (decreasing dielectric constant), becoming larger than 10^4 at >90% organic content. Comparison of solubilities, on the basis of activity coefficients computed from them, with literature values⁹ is satisfactory, at least below 50% organic. At higher organic contents, low solubilities make measurements by conventional analytical techniques difficult, and we suspect our measurements, by tracer techniques, are more accurate. As expected, values of Γ^* are much higher for K_2SO_4 at 25° than for NaCl at 5°C (miscibility gaps in the NaCl system preclude a comparison at 25°C).

K_2SO_4 in pyridine-water- H_2SO_4 solvent: Solubilities of K_2SO_4 in pyridine-water solutions, in which the pyridine is converted to varying extent to the salt form by H_2SO_4 addition, are given in Table 2.3.2. Values are arranged in order of percent neutralization of the pyridine. By inspection, it can be seen that for a given fraction neutralized, solubility, as expected, increases with increasing water content; further, for a given water fraction, activity coefficients override the common ion effect and solubility increases with increasing neutralization.

These trends are illustrated in terms of Γ^* in Fig. 2.3.2. The equation for computation of Γ^* in this case is

$$\Gamma^* = \frac{\gamma_{\pm}^*}{\gamma_{\pm}} = \frac{\frac{s_{aq} f_w}{s_o}}{\left[1 + \frac{m^* (PH)_2SO_4 f_w}{s_o} \right]^{-1/3}} \quad 2.3.2$$

since

$$\begin{aligned} a_{K_2SO_4} &= m_K^2 m_{SO_4} \gamma_{\pm}^3 = 4s_{aq}^3 \gamma_{\pm}^3 = (m_K^*)^2 m_{SO_4}^* (\gamma_{\pm}^*)^3 \\ &= (2s_o/f_w)^2 [(s_o/f_w) + m^* (PH)_2SO_4] (\gamma_{\pm}^*)^3, \end{aligned}$$

where $(PH)_2SO_4$ represents pyridinium sulfate. Values of Γ^* decrease with increasing percent neutralization and increasing water content.

Note that as before the starred symbols refer to terms whose concentration is expressed in moles/kg of water and subscript "o" refers to moles per kg of solvent, here defined as the sum of water, pyridine and

9. J. J. Fox and A. J. H. Gauge, J. Chem. Soc. 97, 377 (1910).

TABLE 2.3.2

SOLUBILITY OF K_2SO_4 PYRIDINE (P)- H_2SO_4 - H_2O AT 25° .

Wt. % H_2O	Wt. % P	Wt. % H_2SO_4	% P Neutralized	Solubility, K_2SO_4 gm/kg of $H_2O + P + H_2SO_4$
22.64	76.83	0.53	1.12	0.036
32.43	66.81	0.76	1.84	0.242
22.64	76.15	1.21	2.57	0.059
50.00	48.83	1.17	3.87	3.67
32.43	65.83	1.74	4.26	0.367
50.00	47.32	2.68	9.14	4.10
32.43	63.85	3.62	9.16	0.641
50.00	44.27	5.73	20.9	5.29
43.09	43.44	13.47	50.0	3.33
50.00	38.16	11.84	50.0	5.63
60.41	30.22	9.37	50.0	14.3
24.28	46.74	28.98	100.0	0.80
29.98	43.22	26.80	100.0	1.29
32.43	41.71	25.86	100.0	1.66
37.00	38.89	24.11	100.0	2.57
50.00	30.86	19.14	100.0	8.51
75.01	15.43	9.56	100.0	46.8

FIG. 2.3.2 ACTIVITY COEFFICIENT RATIO OF K_2SO_4 IN PYRIDINE- H_2O - H_2SO_4 SYSTEMS AT $25^\circ C$,

sulfuric acid; i.e., including water, pyridine, and pyridinium sulfate.

The rapid decrease at low percentage neutralization is qualitatively consistent with what might be expected from Debye-Hückel effects, since the square root of ionic strength changes most rapidly with pyridinium sulfate concentration at low concentrations. The steeper decline at lower water content is consistent with the lower dielectric constant and consequent larger magnitude of the Debye-Hückel limiting slope.

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2.4 SOLUBILITIES AND ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE AND POTASSIUM CHLORIDE IN ORGANIC-WATER MIXTURES. METHYL(2-ETHYLHEXYL)SULFOXIDE AND SEVERAL QUATERNARY AMMONIUM CHLORIDES AND CARBOXYLATES CONTAINING WATER

C. F. Coleman

Organic-phase activity coefficients $\gamma_{\pm}^*$ or ratios $\Gamma = \gamma_{\pm}^*/\gamma_{\pm}$, which measure the selectivity of an organic liquid for extracting water in preference to salt, were determined for inorganic salts in a series of quaternary ammonium salts and in methyl(2-ethylhexyl)sulfoxide (MEHSO). Results support the previous generalization (from esters and amides) that the selectivity is controlled mainly by the water content of the organic-rich phase, but the selectivities with the present compounds are relatively low. In the absence of inorganic salts, saturation mole ratios of water to quaternary salt at 25°C. ranged from 2 to 15 (up to 28 wt. % of water), increasing with decreasing molecular weight and with decreasing symmetry. Saturated MEHSO contained 57 wt. % of water at 25°C., with only 1.7 wt. % of MEHSO in the water-rich phase; mutual solubility increased to a lower consolute point at 8°C. and 86 wt. % of water.

AS a part of a water research program directed toward a better understanding of selective hyperfiltration membrane behavior, the selectivity of a dialkylsulfoxide and of a series of quaternary ammonium salts for water over inorganic salts was examined by measuring the activity coefficients of sodium and potassium chlorides, via solubilities and liquid-liquid distributions. The principal objective was to test extension of the generalities previously observed for both esters (2) and amides (1) to still different types of organic compounds. The quaternary ammonium salts were varied in regard to both structure and equivalent concentration, in the hope of finding either unusually high selectivity for water over salt, or reversal to a useful selectivity for salt over water. The results do support the previous generalization that the selectivity for water over salt is controlled mainly by the water content of the organic-rich phase, and they show some consistent dependence of

water capacity on structure. However, the selectivities for water over salt were relatively low, and no instance of selectivity for salt over water was found.

The sulfoxide was examined because in the course of a study of metal-ion extractions by a series of dialkylsulfoxides (3), this one compound, the unsymmetrical methyl(2-ethylhexyl)sulfoxide ($C_8H_{17}SO-CH_3$, MEHSO), was observed to dissolve a considerable amount of water although not itself very soluble in water.

EXPERIMENTAL

Solubility of water in the quaternary ammonium salts was measured in liquid-liquid equilibrations with inorganic salt absent, present at tracer concentration, or present at saturation. Solubility of the inorganic salt in the organic

phases was also measured (by means of radioactive tracer) in the latter liquid-liquid equilibrations. When the water content of the organic phases was limited to less than saturation, the inorganic salt solubility was measured by saturation in slow flow through a salt-packed column. Quaternary ammonium salt solubilities in the water-rich phases were determined in separate equilibrations with consecutive increments of the organic salt until a visible excess (<0.01 ml.) remained undissolved. Details of these methods were reported (1). MEHSO-in-water and water-in-MEHSO solubilities were determined by measuring cloud-point temperatures.

Tracers ^{24}Na and ^{42}K were obtained first from the ORNL Radioisotopes Division and later were prepared by special irradiation. The quaternary ammonium cations and the carboxylate anions are identified in Tables I and II. Aliquat 336 and Aliquat 204 were obtained from General Mills, Inc., the other quaternary ammonium chlorides and the pivalic and ethylbutyric acids from Eastman Organic Chemicals, the abietic acid from Arizona Chemical Co., and the neodecanoic acid from Enjay Chemical Co. The two ester-acids were prepared at ORNL by alcoholysis of the acid anhydrides. Aliquat 336 chloride in petroleum ether was scrubbed with about 50 volumes of 0.01M HCl solution and then with water to remove any significant water-soluble fraction, then was recovered in a rotary vacuum evaporator. Its equivalent weight and selectivity performance were not significantly changed. The other reagents were used as received. The quaternary ammonium carboxylates QA were prepared by dissolving the calculated amounts of QCl and KA separately in petroleum ether (or benzene), mixing the solutions to precipitate KCl, and evaporating. Approximately 2% excess QCl was used to ensure that there would be no excess of A^+ . Preliminary tests showed that replacement of up to 5 wt. % of QA by QCl had little effect on the uptake of tracer-tagged sodium ion, while, as expected, a slight excess of A^+ increased it significantly. MEHSO was prepared both from reaction of methyl iodide with 2-ethylhexyl mercaptan and of methyl mercaptan with 2-ethylhexyl iodide to produce methyl(2-ethylhexyl)sulfide, followed by oxidation of the sulfide in glacial acetic acid with 30% hydrogen peroxide. The products were recovered by vacuum distillation with a small Vigreux column, b.p. 135°C . at 12 mm. Di-*n*-butylsulfide was prepared similarly.

RESULTS AND DISCUSSION

The miscibility curve of MEHSO and water (Figure 1) confirms the highly one-sided solubility behavior previously suggested (3). At 25°C . there is 57 wt. % or 0.93 mole fraction water in MEHSO (mol. wt. 175.3), but only 1.7 wt. % or 0.002 mole fraction MEHSO in water. In comparison, the symmetrical analog di-*n*-butylsulfide, of slightly lower molecular weight (162.3) and considerable solubility in water (6 wt. %), dissolves only 5 wt. % water. Thus, the unsymmetrical structure of MEHSO is an important factor in the skewed miscibility gap. This is reminiscent of the pair of isomeric amides noted previously (1): Dimethylauramide dissolved 17.4 wt. % water, while its isomer dipropyloctanamide dissolved only 2.35 wt. %.

Equilibrium Compositions. The initial conditions and equilibrium phase compositions are shown in Tables I and II. In each test, the organic phase was saturated with water, with salt (in the presence of limited amounts of water), or with both simultaneously. The water contents of MEHSO at different water activities are compared in Figure 2. Pure water is taken as the reference state for both phases, so that a_1 is the same in both phases at equilibrium. Values of a_1 for the various (binary) salt solutions are from tabulations of Robinson and Stokes (4). The MEHSO contents of the aqueous phases are so small

Table I. Quaternary Ammonium Salts (QA) and Dialkylsulfide (MEHSO) Saturated with Water; Distribution of NaCl and KCl at Tracer Concentrations; 25°C .

Initial ^a M Cpd.	Wt. % Cpd. in Aq. Phase	Wt. % Water in Org.- Rich Phase	Γ_{NaCl}	Γ_{KCl}
MEHSO: METHYL(2-ETHYLHEXYL)SULFOXIDE				
5.3	1.7	57	1.6	1.4
0.5	<0.2	4.3	170	120
0.1	<0.1	0.8	90	60
Q336-CL: METHYLTRIALKYLAMMONIUM ^b CHLORIDE				
● 1.9	0.04	22.1	1.8	1.5
■ 1.0	0.02	8.3	3.1	2.4
⊗ 0.4	<0.01	2.9	12.5	
Q336-HS: METHYLTRIALKYLAMMONIUM ^b HEPTADECYL SUCCINATE ^c				
○ 1.1	<0.01	16.9	2.2	2.0
⊗ 0.5		7.4	7.0	
Q336-HM: METHYLTRIALKYLAMMONIUM ^b HEPTADECYL MALEATE ^c				
● 1.1	<0.01	14.3	3.5	
⊗ 0.4		4.9	27	
Q336-AB: METHYLTRIALKYLAMMONIUM ^b ABIETATE ^d				
○ 1.1	<0.01	14.7	3.0	
⊗ 0.5		6.3	18	
HEPT ₄ -CL: TETRA- <i>n</i> -HEPTYLAMMONIUM CHLORIDE				
■ 1.9	0.05	10.8	4.4	
HEPT ₄ -HS: TETRA- <i>n</i> -HEPTYLAMMONIUM HEPTADECYL SUCCINATE ^c				
□ 1.0	<0.01	8.4	10.4	
Q204-CL: DIMETHYLDILAURYLAMMONIUM CHLORIDE				
▲ 2.0	0.05	28.4	1.3	
Q204-HS: DIMETHYLDILAURYLAMMONIUM HEPTADECYL SUCCINATE ^c				
⋈ 0.7	<0.01	14.0	2.8	
16 ME ₃ -HS: <i>n</i> -HEXADECYLTRIMETHYLAMMONIUM HEPTADECYL SUCCINATE ^c				
⋈ 0.5	<0.01	12.0	2.5	
OCT ₃ PR-HS: <i>n</i> -PROPYLTRI- <i>n</i> -OCTYLAMMONIUM HEPTADECYL SUCCINATE ^c				
⋈ 0.5	<0.01	4.4	10	

^aThe marginal symbols identify the points plotted in Figure 3. X-marked symbols (●, etc.) indicate dilution with diethylbenzene to the molarity shown. ^bAliquat 336 contains a random mixture of *n*-alkyls, principally octyl and decyl plus some hexyl and lauryl. ^cMonomer of dicarboxylic acid with 3,9-diethyltridecanol-5. ^dMixture of abietic acid (90%) with some other closely similar resin acids.

(maximum, 0.002 mole fraction in water) that with at least approximate conformity to Raoult's law the effects on a_1 are negligible. Of the esters (2) and amides (1) previously reported, only two extracted enough salt (MgCl_2) for it to be a significant component in the organic-rich phase and to increase the extraction of water; in all of the other tests the values of a_1 vs. X_1 fell along a single smooth curve for each organic reagent, such as indicated by the dashed line in Figure 2. In contrast, MEHSO extracted a significant amount of every salt tested, and along with it, more water than would be proportional to a_1 , so that the points are not aligned. This effect appears to be greatest with magnesium chloride and least with potassium chloride. Analogy with the amides (1) suggest that the effect should decrease and disappear with sulfoxides of higher molecular weight. It did disappear for sodium chloride and potassium chloride when the MEHSO was diluted with diethylbenzene (Table II), which is analogous to increasing the molecular weight of the sulfoxide.

Table II. Quaternary Ammonium Salts (QA) and Dialkylsulfoxide (MEHSO) Saturated with Salt or with Both Salt and Water; 25° C.

Organic-Rich Phase					Organic-Rich Phase					
Initial ^a M Cpd.	Contacting ^a Phase	Wt. % water	Wt. % salt	Γ salt	Initial ^a M Cpd.	Contacting ^a Phase	Wt. % water	Wt. % salt	Γ salt	
MEHSO: METHYL(2-ETHYLHEXYLSULFOXIDE)					Q336-CL: METHYLTRIALKYLAMMONIUM ^b CHLORIDE					
5.3	Sat. NaCl	22	5.1	1.56			3.4	0.002	10.0	
	Dry NaCl	11.3	0.9	4.2			2.9	0.001	11.8	
		5.5	0.03	70			2.5	<0.001	14	
		3.9	0.010	145			2.0		20	
		2.7	0.005	180			1.2 ^c		42	
		1.8	0.004	155	● 0.4	Sat. NaCl	2.8	0.005	8.8	
	Sat. KCl	23	3.8	2.2		Sat. KCl	2.8	0.003	10.9	
	Sat. LiCl	32	30	1.08	Q336-HS: METHYLTRIALKYLAMMONIUM ^b HEPTADECYL SUCCINATE ^c					
	Sat. BaCl ₂	37	10	1.13	○ 1.1	Sat. NaCl	15.7	2.33	2.4	
	Sat. SrCl ₂	33	18	1.11		Dry NaCl	5.0	0.151	12	
Sat. MgCl ₂	41	26	1.06		Sat. KCl	16.3	1.62	3.6		
0.5	Sat. NaCl	1.6	0.003	180	⊗ 0.5	Sat. NaCl	6.7	0.35	6.5	
	Dry NaCl	0.9	0.002	135		Dry NaCl	2.2	0.003	230	
		0.6	0.002	100	Q336-HM: METHYLTRIALKYLAMMONIUM ^b HEPTADECYL MALEATE ^c					
		0.2	<0.001	75	● 1.1	Sat. NaCl	12.6	1.38	3.3	
	Sat. KCl	1.3	0.003	210		Dry NaCl	3.2	0.015	80	
	Dry KCl	0.9	0.002	150	⊗ 0.4	Sat. NaCl	4.4	0.065	25	
		0.5	0.001	100		Dry NaCl	1.7	0.001	500	
		0.2	<0.001	80	Q336-AB: METHYLTRIALKYLAMMONIUM ^b ABIETATE ^d					
	Sat. NaCl	0.2	0.002	50	● 1.1	Sat. NaCl	12.5	1.49	3.0	
	Dry NaCl	0.2	0.001	55		Dry NaCl	3.9	0.049	30	
0.1	Sat. KCl	0.3	0.001	65	⊗ 0.5	Sat. NaCl	5.4	0.115	17	
	Dry KCl	0.2	0.001	40		Dry NaCl	1.2	<0.001	600	
	Q336-CL: METHYLTRIALKYLAMMONIUM ^b CHLORIDE					Q336-NEOD: METHYLTRIALKYLAMMONIUM ^b NEODECANATE ^e				
	● 1.9	Sat. NaCl	15.0	1.12	1.45	● 1.4	Sat. NaCl	23.0	5.4	1.53
		Dry NaCl	8.5	0.21	2.1		Dry NaCl	2.7	0.028	35
			5.2	0.030	3.3	Q336-ETBU: METHYLTRIALKYLAMMONIUM ^b ETHYLBUTYRATE ^f				
			4.0	0.004	6.5	⊖ 1.5	Sat. NaCl	24.9	6.1	1.47
			3.5	0.002	7.4		Dry NaCl	3.7	0.066	21
			2.6	<0.001	11.5	Q336-PIV: METHYLTRIALKYLAMMONIUM ^b PIVALATE ^f				
			2.4		13	● 1.6	Sat. NaCl	26.9	7.6	1.28
		2.0		18		Dry NaCl	4.1	0.115	13	
		0.6		105	HEPT ₄ -CL: TETRA- <i>n</i> -HEPTYLAMMONIUM CHLORIDE					
	Sat. KCl	17.3	0.48	2.5	■ 1.0	Sat. NaCl	7.7	0.027	5.1	
	Dry KCl	9.6	0.093	3.0		Dry NaCl	5.0	0.004	8.0	
		6.4	0.025	3.9			1.8	<0.001	150	
		5.1	0.081	5.3	HEPT ₄ -HS: TETRA- <i>n</i> -HEPTYLAMMONIUM HEPTADECYL SUCCINATE ^c					
		4.1	0.024	7.8	□ 1.0	Sat. NaCl	7.1	0.26	9.8	
		3.4	0.012	8.9		Dry NaCl	4.6	0.082	20	
		3.0	<0.001	10.3			1.5	0.001	400	
		2.8		13	Q204-CL: DIMETHYLDILAURYLAMMONIUM CHLORIDE					
		0.9		55	▲ 2.0	Sat. NaCl	23.6	4.0	1.15	
1.0	Sat. NaCl	7.2	0.164	2.6		Dry NaCl	7.4	0.134	2.0	
	Dry NaCl	4.4	0.013	5.5			0.9	<0.001	26	
		2.7	0.001	11.2	Q204-HS: DIMETHYLDILAURYLAMMONIUM HEPTADECYL SUCCINATE ^c					
		2.0	<0.001	19	⊗ 0.7	Sat. NaCl	12.0	1.56	2.8	
		1.7		25		Dry NaCl	3.2	0.058	22	
		1.3		35			1.6	0.003	175	
		1.2		40	OCT ₃ -PR-HS: <i>n</i> -PROPYLTRI- <i>n</i> -OCTYLAMMONIUM HEPTADECYL SUCCINATE ^c					
		1.0		65	⊗ 0.5	Sat. NaCl	3.0	0.084	13	
		0.4		110		Dry NaCl	1.0	0.002	200	
		Sat. KCl	8.0	0.105	3.2					
	Dry KCl	4.8	0.010	6.2						

^a See Table I. ^b "Sat. NaCl": saturated NaCl solution plus excess crystals; "Dry NaCl": NaCl crystals, with limited water content in the organic phase and no free aqueous phase. Wt. % organic cpd. in equilibrium aqueous phases: MEHSO: satd. BaCl₂, <0.4; satd. LiCl, <0.3; satd. SrCl₂, MgCl₂, <0.2; satd. NaCl, KCl, <0.1. Quaternary ammonium salts: <0.01 in each. ^c Pivalic acid = tri-*n*-butylammonium pivalate.

^a See Table I. "Sat. NaCl": saturated NaCl solution plus excess crystals; "Dry NaCl": NaCl crystals, with limited water content in the organic phase and no free aqueous phase. Wt. % organic cpd. in equilibrium aqueous phases: MEHSO: satd. BaCl₂, <0.4; satd. LiCl, <0.3; satd. SrCl₂, MgCl₂, <0.2; satd. NaCl, KCl, <0.1. Quaternary ammonium salts: <0.01 in each. ^b Pivalic acid = trimethylacetic acid; neodecanoic acid = dimethyl-*n*-hexylacetic acid; ethylbutyric acid = diethylacetic acid.

Figure 1. Miscibility curve of water-MEHSO from cloud-point temperatures

● Mixtures determined by weight
○ Mixtures determined by volume

Figure 3. Variation of NaCl and KCl activity coefficients with water contents of quaternary ammonium chlorides (filled symbols) and carboxylates (open and shaded symbols)

X-marked symbols indicate dilution with diethylbenzene; individual symbols are identified in Tables I and II

Figure 2. Activity of water in the two-phase water-MEHSO system, 25°C. For the equilibria with saturated salts, the mole fraction of water is calculated as $m_{H_2O}/(m_{H_2O} + m_{MEHSO} + 3m_{BaCl_2})$, etc. If the salts are assumed to exist as ion clusters instead of dissociating, the corresponding mole fractions of water are higher, respectively, 0.86, 0.69, 0.70, 0.83, 0.84, and 0.66 for $BaCl_2$ to $LiCl$

In the absence of inorganic salt, saturation mole ratios of water to quaternary salt ranged from around 2 to nearly 15 over the range of compounds tested. They increased with decreasing molecular weight of the quaternary ammonium salts and, at similar molecular weights, increased with increasing number of methyl groups around the quaternary nitrogen.

Salt Activity Coefficients. As previously (1), concentrations in each phase are expressed as moles of component per kilogram of water (m), even when water is itself only a minor component, and the activities in all phases are referred to the same standard state as in pure aqueous salt solution, providing the useful relation between activity coefficients and selectivity for water over salt

$$\Gamma = \gamma_{\pm}^*/\gamma_{\pm} = m/m^* = D(\text{water})/D(\text{salt}) \quad (1)$$

The activity coefficient ratio Γ is unity when water and inorganic salt are extracted equally well—i.e., when they are in the same ratio in both phases. Values of Γ greater than one represent preferential extraction of water; conversely, fractional values would represent preferential extraction of salt. In Equation 1, D is the distribution coefficient of the component indicated: $D(\text{salt}) = [\text{tracer}$

counts per milliliter of organic phase] per [tracer counts per milliliter of aqueous phase]. For quaternary ammonium salts QA where $A \neq Cl$ (no common ion), at saturation with—e.g., NaCl, the mean activity coefficient

$$\gamma_{\pm}^* = (\gamma_{\pm} m_{NaCl})/m_{NaCl}^* \quad (2)$$

At tracer salt concentration

$$\Gamma = D(\text{water})/D(\text{NaCl}) \quad (3)$$

and $\gamma_{\pm}^* \approx \Gamma$ since $\gamma_{\pm} \approx 1$. For QCl (chloride common ion), at saturation with NaCl

$$\gamma_{\pm}^* = (\gamma_{\pm} m_{NaCl})/m_{NaCl}^*[1 + m_{QCl}^*/m_{NaCl}^*]^{1/2} \quad (4)$$

and at tracer NaCl concentration

$$\Gamma \approx [D(\text{water}) m_{NaCl}/D(\text{Na}) m_{QCl}^*]^{1/2} \quad (5)$$

Here m_{NaCl} must be estimated from the specific activity of the tracer solution, typically around 2×10^{-6} for $^{24}\text{NaCl}$, and 5×10^{-4} for ^{42}KCl .

In the foregoing, the slight amount of the quaternary ammonium compound dissolved in the water-rich phase is assumed to have no significant effect on $\gamma_{\pm}$. If the effects of the larger but still small amounts of dissolved MEHSO on $\gamma_{\pm}$ in the water-rich phases are also negligible, then $\gamma_{\pm}^* \approx 0.588 \Gamma$ for saturated potassium chloride, and $\gamma_{\pm}^* \approx \Gamma$ for saturated sodium chloride and for both salts at tracer concentrations in MEHSO. However, to avoid depending on that assumption, only the ratios Γ are reported for MEHSO.

As with the amides (1), the activity coefficients and activity coefficient ratios of the inorganic salts depend mainly on the water content of the organic phase, whether or not saturated with water. Dilution of a given reagent with a hydrocarbon has little effect on $\gamma_{\pm}^*$ or Γ , other than indirectly by the resulting decrease of the maximum water content. At a given water content for each quaternary ammonium salt, $\gamma_{\pm}^*$ is higher with the carboxylates than with the chloride. Between individual quaternary ammonium salts, $\gamma_{\pm}^*$ decreases slightly with increasing number of methyl groups. The shapes of the $\gamma_{\pm}^*$ vs. water content curves (Figure 3) are similar to those with dialkylamides (1), but they drop more sharply, and approach unity at lower water contents (at <5% vs. >10%) than did the amides. However, there is no suggestion of crossing the $\gamma_{\pm}^* = 1$ axis into a region of selective extraction of salt. The selectivity for water over salt by MEHSO almost disappeared at water contents above 30%, Γ being only slightly above unity. The maximum values of Γ , near 2% water, are around 200, much lower than the maxima obtained with several other compounds—e.g., 300 to 3000 for NaCl in several amides (1). It may be more appropriate,

however, to consider these as rather high values of Γ for a compound having such a high water capacity as MEHSO does, suggesting that some homologs might show better combinations of salt rejection and water capacity.

ACKNOWLEDGMENT

It is a pleasure to thank J. P. Eubanks for extensive technical assistance, W. J. Ross for preparation of radio-tracers, and W. J. McDowell and G. N. Case for a sample of di-*n*-butylsulfoxide and for aid in preparing MEHSO.

NOMENCLATURE

- a_1 = activity coefficient of water (mole fraction scale, reference state pure water)
 A^- = anion of quaternary ammonium salt
 $D(s)$ = distribution coefficients $[s]_{org}/[s]_{aq}$ of the substance s
 m_s = moles of the substance s per kilogram of water
 Q^+ = quaternary ammonium cation
 X_1 = mole fraction of water

- $\gamma_{\pm}$ = mean activity coefficient of an inorganic salt (molality scale, reference state infinite dilution)
 Γ = activity coefficient ratio $\gamma_{\pm}^*/\gamma_{\pm}$
 $*$ = refers to components in the organic-rich phase

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2.5 PROPERTIES OF ORGANIC-WATER MIXTURES. VIII.
DIELECTRIC CONSTANTS OF N,N-DIALKYLAMIDES CONTAINING WATER¹

C. F. Coleman

Dielectric constants of a series of amides at varying water contents were measured to test correlation with the previously reported activity coefficients ($\gamma_{\pm}$) of sodium and potassium chlorides in these same

Figure 1. Dielectric constants of N,N-dialkylamide-water mixtures; $\square$, dipropylacetamide; $\diamond$, dipropylpropionamide; $\circ$, dibutylacetamide; $\circ$ with $\times$, dibutylacetamide saturated with NaCl; $\circ$ with $\times$ and ϕ , 50.3 vol. % dibutylacetamide-49.7 vol. % diethylbenzene; $\triangle$, diisobutylpropionamide; $\triangle$, dibutylpropionamide; $\times$, diethyldecylamide; ϕ , tetrathylphthalamide; $\times$, diethylbenzene.

Figure 2. Dielectric constants at zero water content vs. molarity of amido nitrogen; symbols as defined in Figure 1.

amides.² Of these amides, dipropylacetamide is miscible in all proportions with water at 25°, and its dielectric constant was measured over the entire range. The plot against volume per cent water (Figure 1) is smooth and nearly linear. The curves for the other amides (up to saturation except for tetrathylphthalamide) parallel the dipropylacetamide curve. Dilution of dibutylacetamide by 50% with diethylbenzene decreased the dielectric constant by about 50%. The dielectric constant found for diethylbenzene (2.35) is close to the literature value for benzene (2.27).³

(1) Research sponsored by the Office of Saline Water, U. S. Department of the Interior, under Union Carbide Corporation's contract with the U. S. Atomic Energy Commission. Preceding paper in series: A. E. Marcinkowsky, H. O. Phillips, and K. A. Kraus, "VII. Self-Diffusion Coefficients of Na⁺ in Ethylene Glycol-Water and Glycerine-Water Mixtures," *J. Phys. Chem.*, in press.

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If the amido groups provide the main contribution to the inductive capacity in the absence of water, and if the volume occupied per amido-group is about the same in each compound, the dielectric constants extrapolated to zero water content should be proportional to the moles of amido nitrogen per liter. Figure 2 shows that this is approximately true for the monoamides, including the dibutylacetamide diluted with hydrocarbon. The much lower value for tetraethylphthalamide probably reflects internal cancellation of the dipoles of the two amido groups.

Lanier⁴ reported a theoretically based correlation of salt activity coefficients $\gamma_{\pm}^*$ with dielectric constants that approaches linearity and shows different slopes in mixtures of different organic compounds with water, where $\gamma_{\pm}^*$ is the value of $\gamma_{\pm}$ extrapolated to infinite dilution of the salt at each composition of the organic-aqueous mixture.

In the measurement of activity coefficients² in the amides examined here, the water-amide ratio as well as the salt concentration was different in each test, precluding direct extrapolation of $\gamma_{\pm}^*$ to infinite dilution of the salt. Instead, values of $\gamma_{\pm}^*$ were estimated by calculating the ratio $\gamma_{\pm}^*/\gamma_{\pm}$ from the Debye-Hückel equation

$$-\log \gamma_{\pm} = Az_+z_- \sqrt{I}/(1 + aB\sqrt{I})$$

A and B were adjusted for the dielectric constant of each mixture, and a was taken arbitrarily as 2.5×10^{-8} . The resulting curves for sodium chloride (Figure 3) lie in the same general direction as does Lanier's curve for sodium chloride in dimethylformamide (DMF, included in Figure 3), but they are concave upward, instead of downward as were most of Lanier's curves. The curvatures are compatible with smooth extension to the point (0,0) for pure water, which is the limiting member of each series. The results for potassium chloride are similar.

Experimental Section

The amides were described previously.² Capacitances were measured with the equipment (except the cell) described by McDowell and Allen,⁵ a General Radio Type 716-CS1 bridge plus Type 722-NQ precision capacitor, permitting direct reading of up to 2300 μmf . All measurements were made at 1 Mc/sec. The cell, following a design used by Fuoss,⁶ was made of stainless steel and Teflon, plus a thin glass disk to provide a wettable surface under the Teflon. It was calibrated with 1,2-dichloroethane, ϵ 10.36 at 25° (ref 3), and gave satisfactory measurements on known compounds (see Table I). The cyclohexane (spectral grade) was dried in a molecular sieve column; the dichloroethane and acetonitrile were dried with calcium

Figure 3. Correlation of NaCl activity coefficients with dielectric constants of amides containing water; symbols as defined in Figure 1; X_1 = mole fraction of water; ϵ_1 and ϵ_{13} = respective dielectric constant of water and of aqueous-organic mixture; DMF, dimethylformamide; the function $(\epsilon_1/\epsilon_{13}) - 1$ is identical with the function $(1 - \rho)/\rho$, $\rho = \epsilon_{13}/\epsilon_1$ used in ref 4.

Table I

Compound	Dielectric constant at 25°	
	Meas'd (10° cps)	Lit. ^a (static)
Cyclohexane	2.02	2.015
Methanol	32.66	32.63
Nitrobenzene	34.8	34.82
Acetonitrile	35.9	36.0
Water	78.5	78.54

sulfate and then distilled, the methanol was rectified in a 4-ft Podbielniak column, and the nitrobenzene was fractionally crystallized.

Acknowledgment. It is a pleasure to thank J. P. Eubanks for extensive technical assistance.

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2.6 PROPERTIES OF ORGANIC-WATER MIXTURES. VII. SELF-DIFFUSION COEFFICIENTS OF Na^+ IN ETHYLENE GLYCOL-WATER AND GLYCEROL-WATER MIXTURES AT 25°¹

Arthur E. Marcinkowsky, Harold O. Phillips, and Kurt A. Kraus

Self-diffusion coefficients, $\mathcal{D}_{\text{Na}}$, of Na^+ were measured for water mixtures of ethylene glycol and of glycerol at 25° ($m_{\text{NaCl}} = 0.1$) by the radiometric porous-frit method. The diffusion coefficients decrease more rapidly in glycerol than in glycol solutions, qualitatively, as expected from the viscosities of the systems. The diffusion-viscosity product, $\mathcal{D}\eta/\eta_0$, for the ethylene glycol system is essentially independent of solvent composition. In the glycerol system, however, $\mathcal{D}\eta/\eta_0$ rises in the organic-rich region. In contrast, $\mathcal{D}\eta/\eta_0$ for water mixtures of methanol, ethanol, and 1-propanol was earlier found to decrease in the same region. The self-diffusion-composition curves for the ethylene glycol and glycerol systems are similar to the corresponding NaCl limiting equivalent conductance-composition curves.

In a previous paper,² it was shown that the radiometric frit method can be used for self-diffusion studies in water-organic-electrolyte systems. The self-diffusion coefficients, $\mathcal{D}_{\text{Na}}$, of Na^+ in water mixtures of methanol (MeOH), ethanol (EtOH), and 1-propanol (PrOH) at a constant salt concentration of $m_{\text{NaCl}} = 0.1$ (mol of NaCl/kg of solvent) and at 25° were reported.

The purpose of this paper is to report on the sodium ion self-diffusion coefficient ($\mathcal{D}_{\text{Na}}$) measurements at a constant salt concentration $m_{\text{NaCl}} = 0.1$ for the water mixtures of ethylene glycol (EG) and glycerol (G) at 25°. The $\mathcal{D}_{\text{Na}}$ results expressed as a self-diffusion coefficient-viscosity product, $\mathcal{D}^\pm = \mathcal{D}\eta/\eta_0$ (η is the viscosity of the solution, and η_0 is the viscosity of water), for both the EG and G systems are compared with the corresponding limiting equivalent conductance-composition data (Walden products) for NaCl reported by Accascina and coworkers.^{3,4}

Experimental Section

1. Method. Self-diffusion coefficients were measured by the radiometric porous-frit method described earlier.⁵ Briefly, porous frits are loaded with a solution containing radioactive tracer, and the same solution not containing tracer is pumped past it. The resulting (diffusional) decay of tracer is measured as a function of flow rate; diffusion coefficients are calculated from the decay rates when these are independent of flow rate. All diffusion coefficients reported here were obtained from such a plateau. Porous gold frits with about 50% void volume and approximate dimensions of $1.2 \times 0.7 \times 0.07$ cm, prepared and calibrated as described earlier,⁵ were used. The temperature for all calibrations and for the EG-H₂O measurements was maintained at $25 \pm 0.1^\circ$, and at $25 \pm 0.2^\circ$ for the

G-H₂O measurements. Distribution coefficient measurements showed that the gold frits did not adsorb sodium ions significantly from the mixtures.

2. Tracers. Two different radiotracers were used: ^{24}Na ($T_{1/2} = 15.05$ hr) was obtained from the radioisotopes division of ORNL, and ^{22}Na ($T_{1/2} = 2.58$ years) was obtained from the Nuclear Science and Engineering Corp. Examination of the γ -energy spectra showed no detectable impurities in either tracer and no purifications were carried out. The ^{24}Na tracer was always of high specific activity and had stated radiochemical purity greater than 99%. To avoid impurity buildup, use of ^{24}Na tracer was discontinued after approximately 5 half-lives had elapsed.

3. Materials. Reagent grade NaCl was used without further purification. The ethylene glycol and glycerol were purified by vacuum distillation.⁶ The EG- and G-H₂O mixtures were prepared on a weight basis. In addition, each solution was separately analyzed for water content by Karl Fischer titration. The titrated water contents agreed within 0.5% of the

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calculated compositions. We report the solvent compositions in terms of weight per cent and volume per cent. The latter were calculated from the weights, w_1 , of water and, w_2 , of organic component as: vol % organic = $100/[(w_1\rho_2/w_2\rho_1) + 1]$ where ρ_1 and ρ_2 are the densities of water and organic component, respectively. The densities at 25° used in the calculations are 1.1099⁷ and 1.2480⁸ for ethylene glycol and glycerol, respectively. The solution viscosities were measured with Cannon-Ubbelohde⁹ viscometers.

Results and Discussion

1. *Results.* The self-diffusion coefficients of the sodium ion in H₂O-EG and H₂O-G at $m_{\text{NaCl}} = 0.1$ and the viscosities of the NaCl solutions are given in Tables I and II. The self-diffusion coefficient of Na⁺ is highest in the aqueous solution (1.28×10^{-5} cm² sec⁻¹)² and decreases with increasing organic content of the solvent. At comparable solvent compositions, the $\mathcal{D}_{\text{Na}}$ curve decreases more rapidly in the G- system than in the EG- system, qualitatively, as expected from the viscosities of the systems.

Table I: Self-Diffusion Coefficients of Na⁺ in NaCl-Ethylene Glycol-Water Mixtures at 25° ($m_{\text{NaCl}} = 0.1$)

Wt % EG	Vol % EG	η/η_0	$10^5 \mathcal{D}$, cm ² sec ⁻¹	$10^5 \mathcal{D}\eta/\eta_0$, cm ² sec ⁻¹
0.0	0.0	1.01	12.8	1.29
25.4	23.4	1.89	8.09	1.53
50.0	47.3	3.65	4.38	1.60
74.8	72.7	7.80	2.19	1.71
85.0	83.6	11.26	1.54	1.73
95.0	94.5	16.57	1.07	1.77
100.0	100.0	20.26	0.83	1.69
100.0	100.0	20.26	0.82	1.66 ^a

^a Measurement made with ²²Na.

Table II: Self-Diffusion Coefficients of Na⁺ in NaCl-Glycerol-Water Mixtures at 25° ($m_{\text{NaCl}} = 0.1$)

Wt % G	Vol % G	η/η_0	$10^5 \mathcal{D}$, cm ² sec ⁻¹	$10^5 \mathcal{D}\eta/\eta_0$, cm ² sec ⁻¹
14.7	12.1	1.49	9.71	1.45
25.0	20.9	2.06	7.79	1.61
34.8	29.9	2.87	6.08	1.75
48.9	43.4	5.32	3.39	1.80
50.0	44.2	5.74	3.14	1.80
58.7	53.2	9.06	2.29	2.07
72.7	68.0	25.3	1.03	2.61
75.0	70.4	32.2	0.796	2.56
77.4	73.2	39.6	0.751	2.97
80.0	76.0	53.2	0.558 ^a	2.97
82.2	78.6	66.3	0.451	2.99
85.0	81.8	94.6	0.339 ^a	3.21
90.0	87.7	194.6	0.168 ^a	3.27
95.0	93.8	424.0	0.088 ^a	3.73

^a Measurements made with ²²Na.

Figure 1. Comparison of self-diffusion coefficient-viscosity products: open symbols, diffusion data ($m_{\text{NaCl}} = 0.1$); filled symbols, calculated from limiting conductances.

The viscosities of ethylene glycol and glycerol are 16.84³ and 945,⁴ respectively. A solution 95 wt % G ($m_{\text{NaCl}} = 0.1$) with $\eta/\eta_0 = 424$ is the most viscous system that we have studied. Our reproducibility at the higher viscosities is not as great as that at the lower viscosities and uncertainties in the self-diffusion coefficients seem to be of the order of 5%. A correction for tracer decay⁵ was applied whenever $(\mathcal{D}_{\text{uncor}} - \mathcal{D}_{\text{cor}})/\mathcal{D}_{\text{cor}}$ was above 0.5%. The maximum correction was 2.1%. For the viscous glycerol-water systems, 75 wt % glycerol and above, the long-lived ²²Na tracer was used to avoid this correction.

The self-diffusion coefficient-viscosity products, including the data² for the MeOH system, plotted as a function of volume per cent organic, are shown in Figure 1. Up to an organic content of about 40 vol %, the three curves remain similar but not identical. At 40 vol %, the values of $\mathcal{D}^\pm$ are 1.40 , 1.55 , and 1.75×10^{-5} cm² sec⁻¹ for the methanol-, ethylene glycol-, and glycerol- systems, respectively. Above 40 vol % organic, $\mathcal{D}^\pm$ for the methanol system decreases, it remains constant for the ethylene glycol system, and increases for the glycerol system. At 95 vol % organic, the values of $\mathcal{D}^\pm$ are 0.76 , 1.75 , and 3.8×10^{-5} cm² sec⁻¹, while the corresponding $\mathcal{D}_{\text{Na}}$ values are 0.93×10^{-5} , 1.03×10^{-6} , and 0.73×10^{-7} cm² sec⁻¹ for the MeOH-, EG-, and G- systems, respectively. Thus the values of $\mathcal{D}_{\text{Na}}$ for the MeOH and G systems differ by a factor slightly greater than 100, whereas the $\mathcal{D}^\pm$ values, when the solution viscosity is taken into account, differ by a factor of only 5.

If the viscosity is raised to a fractional power k before multiplying by the self-diffusion coefficient (i.e., $\mathcal{D}(\eta/\eta_0)^k$), the best correlation is found when k is 0.7, the preferred exponent of others.¹⁰ A plot of $\mathcal{D}(\eta/\eta_0)^{0.7}$ vs. volume per cent alcohol describes the

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data for the MeOH-, EtOH-, PrOH-,² and the EG- and G- systems to within $\pm 20\%$.

2. *Comparison of Self-Diffusion and Conductance.* According to the Onsager limiting theory¹¹ for 1:1 electrolytes at constant temperature, the diffusion coefficient $\mathcal{D}_M$ of an ion M depends on the square root of the salt concentration (c) in mol/l., the ionic conductance, λ^0 , of both cation and anion, and on the dielectric constant of the solvent medium, ϵ . The relation is given by the equation

$$\mathcal{D}_M = \frac{RT\lambda_M^0}{|z|F^2} \left[1 - \frac{0.544 \times 10^8}{\epsilon^{1/2}} \zeta \sqrt{c} \right] \quad (1)$$

where

$$\zeta = 1 - \sqrt{(3\lambda_K^0 + \lambda_M^0)/(4(\lambda_K^0 + \lambda_M^0))}$$

λ_M^0 is the limiting ionic conductance of the ion M ($\text{cm}^2 \text{ ohm}^{-1} \text{ equiv}^{-1}$); λ_K^0 is the limiting ionic conductance of the counterion K; R is the gas constant ($\text{J deg}^{-1} \text{ mol}^{-1}$); T is absolute temperature; F is the Faraday (international coulombs g-equiv⁻¹). At infinite dilution, eq 1 reduces to the well-known Nernst equation¹⁰

$$\mathcal{D}_M^0 = \frac{RT\lambda_M^0}{|z|F^2} = 2.663 \times 10^{-7} \frac{\lambda_M^0}{|z|} \text{ cm}^2 \text{ sec}^{-1} \quad (2)$$

where $\mathcal{D}_M^0$ is the self-diffusion coefficient of the ion M at infinite dilution and $|z|$ is the absolute value of the charge of the ion.

Using the Nernst and Onsager theories, ionic or self-diffusion coefficients at infinite dilution and at 0.1 m for the water-methanol system were found to correlate well.² A similar comparison between diffusion and con-

ductance data for the EG- and G- systems is not possible because the single ion mobilities as a function of solvent composition are lacking. It is, however, possible to compare the values of $\mathcal{D}_{Na}$ in a semiquantitative manner with the corresponding limiting equivalent conductances, Λ_{NaCl}^0 , which are known for both the EG- and G- systems.^{3,4}

For comparison, we shall set the transport number, t_{Na}^0 , of the sodium ion at infinite dilution, in the various water-organic mixtures, equal to 0.3962, its value in water. This is equivalent to setting $\lambda_{Na}^0 = 0.3962 \times \Lambda_{NaCl}^0$ at all solvent compositions.

The filled symbols in Figure 1 for the MeOH-, EG-, and G- systems represent the self-diffusion coefficient-viscosity products, $\mathcal{D}^0\eta/\eta_0$, calculated in this manner from the limiting conductances. For the EG- and G- systems, the Λ_{NaCl}^0 values used are those reported by Accascina and coworkers^{3,4} and for the MeOH-system, the data of Shedlovsky reported by Harned and Owen¹² are used. Agreement between the calculated self-diffusion coefficients and the experimental results is surprisingly good. Presumably the expected decrease of the self-diffusion coefficient with concentration is compensated by a similar increase of the sodium ion transport number in the organic-water mixtures.

Acknowledgment. It is a pleasure to thank G. Scatchard, R. M. Fuoss, R. A. Robinson, and F. Nelson for a number of helpful discussions.

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2.7 SELF-DIFFUSION COEFFICIENTS OF Na^+ IN POLY(ETHYLENE GLYCOL)-WATER MIXTURES¹⁰

H. O. Phillips, A. E. Marcinkowsky, S. B. Sachs,¹¹ and K. A. Kraus

Preliminary studies indicate that the radiometric porous-frit method for measuring self-diffusion coefficients of ions in organic-water mixtures (see Section 2.6) can be extended to include high-molecular-weight polymers. Although care had to be taken to ensure proper equilibration of the frit, measurements of $\mathcal{D}_{\text{Na}}$ were made in water mixtures of poly(ethylene glycol) [PEG] of molecular weight 20,000. As the organic fraction of the solution increased, $\mathcal{D}_{\text{Na}}$ decreased rapidly, from $1.28 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ in water to $0.39 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ in 0.31 volume fraction PEG. The salt concentration was 0.1 M NaCl.

There appears to be little correlation between diffusion coefficients and viscosities for the PEG solutions. While the diffusion-viscosity product changed only slightly with solution composition for ethylene glycol, the product increases rapidly as PEG content increases. In 0.31 volume fraction PEG, the product is over 200 times greater than that for water. There is a better correlation between $\mathcal{D}_{\text{Na}}$ and volume fraction (f_v) of water. A plot of the logarithm of $\mathcal{D}$ vs. the logarithm of f_v yields a straight line with a slope of ~ 3.2 . This can be compared to a slope of 2.1 for glycerol-water mixtures.

10. Work cosponsored by the U.S. Atomic Energy Commission.

11. Visiting scientist from the Weizmann Institute, Rehovot, Israel.

2.8 MEASUREMENT OF MEMBRANE PERMEABILITIES

H. O. Phillips and K. A. Kraus

Water permeabilities have been measured for a number of the membranes used in the self-diffusion coefficient studies. In general, permeability decreased with increasing pressure, often a factor of two or more as the pressure was increased from 300 to 1500 psig. From the measured permeabilities $P(\text{cm hr}^{-1} \text{ atm}^{-1})$ at 300 psig, intrinsic permeabilities $P_I(\text{cm}^2 \text{ hr}^{-1} \text{ atm}^{-1})$ were calculated ($P_I = P\ell$ where ℓ is the thickness of the membrane in cm). The range of intrinsic permeabilities was greater than 10^4 . However, there was much less variation in the self-diffusion coefficients in the different membranes. The values of the coefficients, D , appear to be a function only of the volume fraction, f_v , of water in the membrane. This is shown in Fig. 2.8.1 where D divided by f_v^5 , is plotted vs P_I . The data are best represented by a horizontal line.

FIG. 2.8.1 RATIO OF DIFFUSION COEFFICIENTS OF Na^+ TO FIFTH POWER OF VOLUME FRACTION OF WATER IN MEMBRANES AS A FUNCTION OF INTRINSIC PERMEABILITY.

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2.9 PHOTOPOLYMERIZATION OF HYDROXYPROPYL ACRYLATE AND TETRAETHYLENE GLYCOL DIMETHACRYLATE INITIATED BY URANYL ION

Cecil E. Higgins and Willis H. Baldwin

Synopsis

Uranyl nitrate, acetate, sulfate, and dibutyl phosphate were used in solution for the photoinitiation of homopolymerization and copolymerization of hydroxypropyl acrylate and tetraethylene glycol dimethacrylate. Solvents used included water, water-ethylene glycol mixtures, and dimethylformamide. Polymer yields in excess of 90% can readily be obtained by exposing solutions containing $0.014M$ UO_2^{2+} to light from a tungsten bulb for 1 hr. The rigidity of the polymers varied directly, the affinity for water inversely, with the concentration of tetraethylene glycol dimethacrylate in the monomer mixture. Poly(hydroxypropyl acrylate) contained 52% water and poly(tetraethylene glycol dimethacrylate) 34% water, at equilibrium.

Hydrophilic homopolymers and copolymers from glycol and polyglycol esters of acrylic and methacrylic acids have been prepared by Wichterle,¹ Wichterle and Lím,² Wichterle, Bartl, and Rosenberg,³ and Refojo and Yasuda.⁴ The polymerizations were usually initiated with persulfate or benzoyl peroxide.

The uranyl ion is a frequently used initiator for room-temperature photo-induced polymerizations of vinyl compounds.⁶⁻²³ Economical photopolymerization processes might well be developed with uranium that has been depleted of ^{235}U . In our work reported here uranyl salts were tested as photoinitiators of the homopolymerization and copolymerization of hydroxypropyl acrylate (H) and tetraethylene glycol dimethacrylate (T) monomers. The monomers were obtained from Monomer-Polymer Laboratories, The Borden Chemical Co., Philadelphia, Pennsylvania. Uranyl nitrate hexahydrate (UNH) was used most often as the initiator, but the acetate, sulfate, and dibutyl phosphate compounds were also used. The uranyl dibutyl phosphate was made in earlier work.²⁴

The polymerization was shown to be photo-induced with uranyl ion as initiator by tests in the presence and in the absence of light. Monomer H solution (1:1 by volume with dimethylformamide), $0.01M$ in UO_2^{2+} , did not react in 20 hr. in the dark but polymerized in a few minutes in light. Photopolymerization without uranyl ion initiation occurred only with monomer T and much more slowly than when UO_2^{2+} was present.

Solutions to be exposed to light from a tungsten bulb were prepared by dissolving a monomer solution of known composition in an equal volume of solvent, usually dimethylformamide but sometimes water or water-ethylene glycol, containing a known concentration of uranyl ion as initiator. The initiator solutions were freshly prepared just before each polymerization experiment. Weighed monomer solutions (100% H, H containing 5 and 20 wt.-% T as crosslinking agent, and 100% T) were dissolved in an equal volume of solvent containing various amounts of uranyl ion. The weights were again recorded so that the fractional weight of monomers

TABLE I
Water Content of Water-Soaked Polymers from Hydroxypropyl Acrylate and Tetra-ethylene Glycol Dimethacrylate Mixtures Photopolymerized with 0.014M Uranyl Ion as Initiator^a

Monomer compn., %	Irrad. time, hr.	Polym. yield, %	Water cont., ^b %
All H	1	89	50.8
"	24	94	52.4
"	24 ^c		53.0
95 H-5 T	1	92	45.1
80 H-20 T	1	94	35.9
"	1	90	35.9
All T	0.5	91	34.2
"	1	100	33.5
"	1 ^d	97	31.9
"	1 ^e	96	34.2
"	24	98	34.2
"	24 ^d	99	33.0
"	72 ^e	96	34.5

^a All monomer solutions were dissolved in an equal volume of dimethylformamide 0.028M in uranyl nitrate except those indicated by footnotes c, d, and e.

^b Polymer was soaked in water at 19–22°C. for 8–19 days, blotted, and dried *in vacuo* at 76–100°C.; water content, wt.-% based on weight of wet (blotted) polymer.

^c Monomer was dissolved in an equal volume of water containing 0.028 moles of uranyl sulfate per liter.

^d Monomer was dissolved in an equal volume of dimethylformamide solution containing 0.028 moles of uranyl dibutyl phosphate per liter.

^e Monomer was dissolved in an equal volume of dimethylformamide solution containing 0.028 moles of uranyl acetate per liter.

would be known for determination of polymer yield. The solutions were then drawn up into tared 4 mm. Pyrex tubes to a height of 15–16 cm., after which rubber tubes at the top were closed off with hemostats.

Light was furnished by a 150 w. tungsten filament bulb 15 cm. away from the mid-height of the liquid. Exposure time varied from as little as 0.5 hr., with 0.014M UO_2^{2+} , to as long as 8 days, with 0.00014M UO_2^{2+} .

Reaction was rapid at 0.014M UO_2^{2+} . At this concentration the T polymerized fastest to form a clear hard gel in 15 min.

Both polymer yield and amount of water contained in polymer that had been soaked in water were obtained by weight measurements. After the light irradiation treatment the tube was reweighed, and the contents were removed. The cylinder of homopolymer from T in dimethylformamide and any other cylinders from monomer in water or water-ethylene glycol could be easily forced by pressure from a rubber bulb into the water wash container. The polymers from H and H-T solutions in dimethylformamide could be removed only by breaking the glass tube. Some fractures formed in the more rigid, crosslinked polymer cylinders, but these had no effect on the determination of polymer yield and apparently none on the water content at equilibrium.

Solvent was removed by soaking the polymer in distilled water, changed daily, for several days. From the weight of a segment of the cylinder, rolled on Whatman #50 filter paper, to blot the surface water, it appeared that the dimethylformamide was completely removed, and the polymer was at equilibrium with the water within 3 days. Assays were made after a minimum of 8 days' water soaking at 19–22°C. The polymers were

TABLE II
Photopolymer Yield at Various Uranyl Ion Concentrations and Water Content of Water-Soaked Polymers

UNH concn., ^b moles/l.	Irrad. time, hr.	Polym. yield, %				Water cont., ^a %			
		H	H, T ^c	H, T ^d	T	H	H, T ^c	H, T ^d	T
0.014	0.5				91				34.2
"	1	89.4	91.6	89.8, 93.6	100	50.8	45.1	35.9, 35.9	33.5
"	24	93.8			98	52.4			34.2
0.0014	3	31.5	50.9	59.0	89.5		45.2	34.6	30.9
"	24	80.8	89.0	86.2		52.4	45.8	36.1	
0.00014	14				67				31.0
"	20	0	0	52.0				35.2	
"	192	36				51.4			

^a Weight per cent of blotted polymer.

^b In irradiated solution of equal volumes of dimethylformamide and monomer solution.

^c H/T ratio, 95:5.

^d H/T ratio, 80:20.

blotted and weighed in stoppered weighing tubes. Drying to constant weight was done in an Abderhalden dryer at a pressure of 2 mm. Hg. The time required was 4-6 hr. at 100°C. and up to 16 hr. at 76°C. Polymer yield was obtained from the ratio of dried polymer weight to that of the starting monomer. Water content was based on the weight of the water-saturated polymer.

In Table I is shown the influence of crosslinking compound T in the polymer on the water content of the swollen material. The water content decreased from 52% in H polymer saturated with water at 22°C. to 36% with 20% crosslinker in the starting monomer solution. T homopolymer contained essentially the same amount of water (34%). Our values agree favorably with those of Refojo and Yasuda⁴ in the crosslinking range common to both investigations.

Polymer yields were high in all cases in which the photoinitiator ion (UO_2^{2+}) concentration in the irradiated solution was 0.014M. The lowest yield was 89% when H was exposed to light for 1 hr. The T polymers from exposures of 1 hr. and longer averaged 98% in yield. Under the conditions shown in Table I no difference in yield or in behavior toward water was found when the anion was varied.

Photopolymerization characteristics as a function of uranyl ion concentration are shown in Table II. The major effect of decreasing the concentration by one-tenth and one one-hundredth was to increase the time for polymerization and to lower the yield. At 0.00014M UNH 8 days were required for a 36% yield of H homopolymer, compared to 32% yield in 3 hr. with 0.0014M UNH and 89.4% yield in 1 hr. with 0.014M UNH. Regardless of yield, however, the water content was essentially the same for polymers derived from the same starting monomer composition but at different initiator strengths.

The appearance of the polymers depended on the solvent for the monomers. Polymers formed in dimethylformamide were clear; those formed in water or water-ethylene glycol were an opaque white. T homopolymer turned white on immersion in water. The clear homopolymers and copolymers stayed clear in water, except when the temperature rose; the polymers were expelling water, and they cleared again at equilibrium. All polymers were clear when dried.

As the percentage of T crosslinker was increased, the polymers became more rigid. H homopolymer saturated with water was very pliable and sticky. H polymers crosslinked with T were less pliable and were easily broken. T homopolymer was stiff and harder to break. Drying toughened the polymers.

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3. Solubility and Thermodynamic Relationships at High Temperatures

Summary

An important limitation which must be met in design of desalination units is the possible formation of undesirable precipitates, on heat transfer surfaces or on membranes, for example. Solubilities of such salts as CaSO_4 and CaCO_3 are therefore of great pertinence from a practical point of view, as well as of interest because of implications for fundamental chemistry of aqueous solutions. The Water Research Program has from its inception included phase studies. Results for several new systems, as well as extensions of previous work, are reported for this biennium.

Values for the dissociation quotients of magnesium sulfate were obtained from the differences in the solubility of calcium sulfate and its hydrates in sodium chloride and in sea-salt solutions at temperatures from 30° to 200° and at ionic strengths from very low to 6 m.

The solubilities of calcium sulfate dihydrate (gypsum) at 60° and 95° and anhydrous calcium sulfate (anhydrite) from 100° to 200° have been determined in synthetic sea-salt solutions over a range of concentrations.

Measurements have been made of the solubility of calcium sulfate in the system $\text{Na}_2\text{SO}_4\text{-NaNO}_3\text{-H}_2\text{O}$ at constant ionic strengths from 0.25 to 6 and at temperatures from near zero to 350° .

The solubility of calcium sulfate dihydrate was measured in a number of 1-1 electrolytes in the temperature range 0 to 80° . The salts included LiCl , KCl , LiNO_3 , NaNO_3 , and KNO_3 .

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3.1 AQUEOUS SYSTEMS AT HIGH TEMPERATURE. XX. THE DISSOCIATION CONSTANT AND THERMODYNAMIC FUNCTIONS FOR MAGNESIUM SULFATE TO 200°^{1,2}

William L. Marshall

Values for the dissociation quotients of magnesium sulfate were obtained from the differences in the solubility of calcium sulfate and its hydrates in sodium chloride and in sea salt solutions at temperatures from 30 to 200° and at ionic strengths from very low to 6 *m*. These quotients were extrapolated to zero ionic strength by means of an extended Debye-Hückel expression to obtain the dissociation constants. The pK_d° values obtained varied from 2.5 at 30° to 4.0 at 200° and compared favorably (within 0.1 pK_d° unit) with the best literature values to 40°, the highest temperature of previous work. The constants show that magnesium and sulfate ions associate strongly with rising temperature like the previously observed but weaker association behavior of 1-1 electrolytes at very high temperatures (400-800°). By the use of the van't Hoff isochore, values of the thermodynamic quantities, ΔG° , ΔH° , ΔS° , and ΔC_p° were obtained. These values varied from 2.66 to 8.66 kcal mole⁻¹ for ΔG° , -4.08 to -11.0 kcal mole⁻¹ for ΔH° , and -24.7 to -41.5 cal mole⁻¹ deg⁻¹ for ΔS° from 0 to 200°, respectively, with an average value for ΔC_p° of -25 cal mole⁻¹ deg⁻¹.

Introduction

Experimental data on the dissociation behavior of 2-2 electrolytes at temperatures above ~50° are virtually nonexistent. This lack of information arises from the comparative difficulty of experimental measurements in aqueous solutions at high temperatures, especially above 100°, and the fact that in a virgin field the simpler (1-1 salts) systems usually are investigated first.³ Nevertheless, the dissociation behavior of 2-2 salts at high temperatures, and the attainment of activity coefficients, is of much interest in understanding the basic behavior of aqueous electrolytes.

At this laboratory, extensive measurements of the solubility of calcium sulfate (and its hydrates) have been made in solutions of mixed electrolytes containing molal ratios of salt components in sea water (herein called sea salt solutions) and in sodium chloride-water solutions^{4,5} at temperatures to 200° and at ionic strengths from ~0.05 to 6 *m*.

In sea water, the predominantly dissolved constituents are chloride (0.554 *m*), sodium (0.476 *m*), magnesium (0.0542 *m*), sulfate (0.0286 *m*), potassium

(0.0127 *m*), and calcium (0.0103 *m*); all other components combined contribute less than 0.004 *m*. Therefore, the effect of the remaining components on the solubility behavior of calcium sulfate should be very small. The chief differences in solubility behavior in sea salt solutions over those in sodium chloride solutions can then be attributed to the presence of magnesium, to a molal ratio SO_4/Ca equal to 2.66 instead of unity, and to the substitution of a small amount of potassium

(1) Work sponsored jointly by the U. S. Atomic Energy Commission and the Office of Saline Water, U. S. Department of the Interior, and performed at the Oak Ridge National Laboratory, which is operated by the Union Carbide Corp. Presented before the Division of Water, Air and Waste Chemistry at the 151st National Meeting of the American Chemical Society, Miami Beach, Fla., April 9-14, 1967.

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for sodium. An investigation at this laboratory on the solubility of CaSO_4 in Na_2SO_4 - NaCl - H_2O solutions⁶ has shown that solution molal ratios of 2.66 at constant ionic strengths have little effect ($\sim +2.5\%$) on the solubility product ($m_{\text{Ca}})(m_{\text{SO}_4})$. A substitution of KCl for NaCl to the extent of that in sea water, estimated from work performed also at this laboratory,⁸ showed little change ($\sim +1.5\%$ at an ionic strength of $3m$) in the solubility product for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 25° .

Therefore, with the assumption that the increase in solubility in a sea salt solution over that in a NaCl - H_2O solution of the same (formal) ionic strength is due predominantly to the formation of a neutral MgSO_4^0 species, an estimate of a dissociation quotient, K_d , for magnesium sulfate can be obtained. By means of

Debye-Hückel treatment, the dissociation quotients can be extrapolated to zero ionic strength to obtain the dissociation constant, K_d^0 , at each temperature, from which the thermodynamic functions can be calculated.

Mathematical Procedure

An expression for the dissociation quotient (K_d), assumed herein to be a constant at constant ionic strength, for magnesium sulfate according to the equilibrium of eq 1 can be written as

$$K_d = \frac{[\text{Mg}^{2+}][\text{SO}_4^{2-}]}{[\text{MgSO}_4^0]} \quad (2)$$

Let s = solubility of calcium sulfate, m = sulfate in excess of stoichiometric CaSO_4 , n = total magnesium, and x = $[\text{MgSO}_4^0]$ (all values in molalities). Then the solubility product for the equilibrium at ionic strength I

in the solution containing magnesium salts can be written

$$K_{sp} = (s)(s + m - x) \quad (4)$$

The expression for K_d becomes

$$K_d = \frac{(n - x)(s + m - x)}{(x)} \quad (5)$$

and upon substitution for x from eq 4

$$K_d = \frac{[n - m - s + (K_{sp}/s)](K_{sp}/s)}{[m + s - (K_{sp}/s)]} \quad (6)$$

The solubility product constant for calcium sulfate (or one of its hydrates) is equal to

$$K_{sp}^0 = K_{sp} \gamma_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}} \quad (7)$$

where $(\gamma_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}})^{1/2}$ is the mean activity coefficient of CaSO_4 . The equations are given elsewhere,⁴ together with all needed constants, to express the values of K_{sp} for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$, or CaSO_4 in NaCl - H_2O solutions as a function of ionic strength and temperature

$$\log K_{sp} = \log K_{sp}^0 +$$

$$8S \frac{\sqrt{I}}{(1 + A_{sp}\sqrt{I})} + BI - CI^2 \quad (8)$$

where A_{sp} , B , and C are constants at each temperature and $8S$ is the Debye-Hückel limiting slope for a 2-2 electrolyte. The formal ionic strength, $I' = 1/2(mz^2)$, is corrected for the presence of MgSO_4^0 to give the true ionic strength, I .

$$I = I' - 4x \quad (9)$$

With an initial estimate of I equal to I' , eq 8 was used to obtain an initial value of K_{sp} . This value was used with eq 4 and 6 to obtain initial values of x and K_d . The value of x was substituted into eq 9 to obtain a better value for I and the procedure repeated until successive values of K_d differed by less than 0.1%.

The above procedure was repeated for all experimental solubilities given elsewhere,² which include our own results in sea salt solutions and those of Hara, *et al.*,⁷ Langelier, *et al.*,⁸ Posnjak,⁹ and Shaffer.¹⁰ Since the iteration method would be successful only if solubilities were greater in sea salt than in the analogous sodium chloride solutions, the method sometimes failed or gave highly uncertain results at 30 - 60° at low ionic strengths where the solubility differences approached or were within the experimental precision of the measurements; these values were not included in Figure 1 discussed in the next section.

Results

General. The dissociation constant for magnesium sulfate can be expressed by

$$K_d^0 = K_d \frac{\gamma_{\text{Mg}^{2+}} \gamma_{\text{SO}_4^{2-}}}{\gamma_{\text{MgSO}_4^0}} \quad (10)$$

where $\gamma_{\text{Mg}^{2+}}$, $\gamma_{\text{SO}_4^{2-}}$, and $\gamma_{\text{MgSO}_4^0}$ are the activity coefficients of the respective species. If we assume that

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Figure 1. Variation of the dissociation quotient of magnesium sulfate with ionic strength (I) and temperature.

γ_{MgSO_4} is unity and independent of ionic strength, the other two activity coefficients can be expressed by an extended Debye-Hückel expression for the mean activity coefficient, $(\gamma_{\text{Mg}^{2+}}\gamma_{\text{SO}_4^{2-}})^{1/2} = \gamma_{\pm(\text{MgSO}_4)}$; thus

$$\log \gamma_{\pm(\text{MgSO}_4)} = -4S \frac{\sqrt{I}}{1 + A\sqrt{I}} \quad (11)$$

where A contains the ion-size parameter and S and I are already defined.

By substituting eq 11 for $\log \gamma_{\pm(\text{MgSO}_4)}$ into eq 10, the following relationship is obtained

$$\log K_d = \log K_d^0 + 8S\sqrt{I}/(1 + A\sqrt{I}) \quad (12)$$

which is similar to that for the solubility product of CaSO_4 (eq 8) but without the BI and CI^2 terms. This equation was used to describe the behavior of K_d at the several temperatures from 30 to 200° (with the exception of the few at 30 and 60° mentioned in the previous section). This description is shown in Figure 1 where the slopes drawn are the limiting Debye-Hückel slopes. In contrast to the behavior of the mean activity coefficient of CaSO_4 (from the solubility product behavior), a value of A equal to unity instead of 1.5–1.6 gave essentially the best fits. A least-square treatment was used but with elimination of some points, including those of Langelier at 100° and the divergent values at 175 and 200° at very high ionic strengths. The standard error in K_d^0 (the intercept at zero ionic

strength) for the several temperatures varied from about ± 0.05 to $\pm 0.12 \text{ p}K_d^0$ units (base 10). Although the scatter of calculated points appears great, each value of K_d was obtained from a relatively small difference between the solubility product in sea salt and that in sodium chloride solution shown in Figure 1 of ref 2. Agreement of the calculations from the several sets of data is good. A comment on the slight deviation of calculated values from those of Langelier, *et al.*,⁸ is given elsewhere.² The deviations at high ionic strengths at 175 and 200° could be eliminated mathematically by the addition of BI and CI^2 terms to eq 12, although this was not done.

Comparison with Low-Temperature Results. The values of $\log K_d^0$, obtained from the intercepts (at $I = 0$) on Figure 1, are plotted against $1/T(^{\circ}\text{K})$ in Figure 2. Included in this figure are all published values of $\log K_d^0$ that could be found over the temperature range 0–200°;^{11–22} the highest temperature of previously published values was 40°. The presently calculated value of K_d^0 at 30°, although having a large uncertainty, agrees well with the relatively recent values of Nancollas¹³ and also with those of Jones and Monk,¹⁶ the only previous studies made as a function of temperature (0–40° and 20–35°, respectively). A very recent result of Atkinson and Petrucci¹¹ at 25° falls slightly below the other values but appears to be in good agreement for the ultrasonics method used, which is applied chiefly to obtain rate constants. With the comparisons shown in Figure 2, it is felt that the dissociation constants presented herein are reasonably reliable to 200°. Their change with temperature shows that magnesium and sulfate ions associate strongly with rising temperature. The 1–1 electrolytes previously studied associate similarly with rising temperature but to a much less extent at comparable solution densities.³ This difference in degree of association

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Figure 2. The dissociation constant of magnesium sulfate from 0 to 200°.

can be related directly to the differences in charge of divalent and monovalent ions.

Thermodynamic Functions

By using the van't Hoff isochore and an assumed linear dependency of ΔC_p° on temperature over the 0–200° range, the present values of $\log K_d^\circ$ and those of Nancollas,¹³ Jones and Monk,¹⁶ Brown and Prue,¹⁵ and Kenttämää¹⁴ were fitted by a method of least squares as described previously⁴ to yield the following equation for $\log K_d^\circ$ as a function of temperature (°K).

$$\log K_d^\circ = -158.540 + 62.160 \log T + (4180.6/T) - 0.046298T \quad (13)$$

From the treatment of eq 13 by the usual methods,⁴ thermodynamic functions for the standard changes in free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°), and heat capacity (ΔC_p°) were obtained from 0 to 200°. The values are given in Table I. At 25° the values of ΔG° , ΔH° , and ΔS° in this table compare reasonably well with those of Nancollas¹³ of 3.22, –4.55, and –26.1 and of Jones and Monk¹⁶ of 3.2, –5.7, and –31, respectively.

When a constant value for ΔC_p° was assumed, eq 14 was obtained

$$\log K_d^\circ = 30.953 - 12.4547 \log T - (750.2/T) \quad (14)$$

which yielded an average value of ΔC_p° of –25 cal mole^{–1} deg^{–1} from 0 to 200°. Calculated values for ΔG° , ΔH° , and ΔS° from this equation were very little different from those given in Table I. Equation 13, however, gave a somewhat better fit to the data and

Table I: Standard Thermodynamic Quantities for the Equilibrium $\text{MgSO}_4(\text{aq}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ (at $I = 0$)

T , °C	$-\log K_d^\circ$ ^a	ΔG° , kcal/mole	ΔH° , kcal/mole	ΔS° , cal/mole deg	ΔC_p° , cal/mole deg
0	2.129	2.661	–4.08	–24.7	+7.8
25	2.399	3.273	–4.01	–24.4	–2.8
50	2.631	3.890	–4.22	–25.1	–13.4
75	2.846	4.53	–4.68	–26.5	–24
100	3.057	5.22	–5.41	–28.5	–35
125	3.274	5.96	–6.41	–31.1	–45
150	3.501	6.78	–7.67	–34.1	–56
175	3.743	7.67	–9.20	–37.6	–66
200	4.002	8.66	–11.0	–41.5	–77
250 ^b	4.58	10.9	–15.4	–50.3	–98
300 ^b	5.23	13.7	–20.8	–60.2	–119
350 ^b	5.96	17.0	–27.3	–71.0	–140
370 ^b	6.27	18.5	–30.2	–75.6	–149

^a Use of eq 13 for all values. ^b Use of eq 13 for extrapolation; no experimentally attained values beyond 200°.

provided estimates for ΔC_p° as a function of temperature.

Another equation for $\log K_d^\circ$ was obtained by assuming that ΔC_p° varied as a quadratic function of temperature. This equation

$$\log K_d^\circ = 4091.991 - 1762.800 \log T - (87514.4/T) + 2.191689T - 0.001038956T^2 \quad (15)$$

indeed provided a maximum value of ΔC_p° at approximately 80° in accordance with maxima for ΔC_p° observed for other ionization reactions.²³ Nevertheless, both calculated thermodynamic quantities, ΔH° and ΔS° , although close to the values given in Table I, showed both maxima and minima between 0 and 200°. When all thermodynamic quantities were calculated to 350° by using eq 15, they approached unreasonably very low or very high values. Therefore, the four-constant eq 13 is believed to provide the best description to 200°, with estimates to 350°, of this equilibrium within the precision of the available values for K_d° .

Assigned Entropy and Heat Capacities for MgSO_4° at 0–200°. Criss and Cobble have assigned values for the entropy²⁴ and average heat capacity²⁵ of ions at temperatures from 25 to 200° by means of a correspondence principle and the use of experimentally derived assignments at low temperatures (based on a specific assign-

(23) Th. Ackermann and F. Schreiner, *Z. Elektrochem.*, **62**, 1143 (1958).

(24) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5385 (1964).

(25) C. M. Criss and J. W. Cobble, *ibid.*, **86**, 5390 (1964).

ment of -5.0 eu at 25° for the hydrogen ion).²⁴ From Table I, average values for $\Delta\bar{C}_p]_{25}^t$ and also values for ΔS_t° can be obtained at $25, 60, 100, 150$, and 200° for use with Criss and Cobble's estimates of ionic quantities at these temperatures. From eq 1 for the dissociation equilibrium, the (assigned) entropy of the neutral species, MgSO_4° , is equal to $[S_t^\circ(\text{Mg}^{2+}) + S_t^\circ(\text{SO}_4^{2-})]$ (from Criss and Cobble) minus ΔS_t° (from Table I) where t refers to the temperature. The average heat capacities for MgSO_4° are obtained by a similar relationship. The calculated values for the two quantities are given in Table II. They show that the entropy of MgSO_4° is relatively small and, surprisingly, changes very little with temperature. The average heat capacity, $\bar{C}_p]_{25}^t$, of MgSO_4° rises with increasing temperature.

Table II: The Entropy and Average Heat Capacity of $[\text{MgSO}_4^\circ]$

T , $^\circ\text{C}$	S_t° , cal/mole deg	$\bar{C}_p]_{25}^t$, cal/mole deg
25	-1.6	-50
60	-5.1	-39 ^a
100	-6.1	-25
150	-5.3	-10
200	-4.5 ^b	-2

^a From smoothed Criss and Cobble values²⁵ at 60° for $\bar{C}_p]_{25}^{60}$ for Mg^{2+} and SO_4^{2-} . ^b Calculated using smoothed value for SO_4^{2-} and extrapolated value for Mg^{2+} from Criss and Cobble²⁴ to 150° .

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3.2 AQUEOUS SYSTEMS AT HIGH TEMPERATURE. SOLUBILITY TO 200°C OF CALCIUM SULFATE AND ITS HYDRATES IN SEA WATER AND SALINE WATER CONCENTRATES, AND TEMPERATURE-CONCENTRATION LIMITS

William L. Marshall and Ruth Slusher

The solubilities of calcium sulfate dihydrate (gypsum) at 60° and 95° C. and anhydrous calcium sulfate (anhydrite) at 100° to 200° C. have been determined in synthetic sea salt solutions at concentrations from zero to about ten times that of sea water. The values extend previous studies to include approximately the entire range of sea salt concentrations from 30° to 200° C. The formal solubility products at low concentrations were essentially the same at temperatures up to 100° C. as those previously determined in sodium chloride-water solutions of the same ionic strength, but about 70% higher at 200° C. With dissociation quotients for magnesium sulfate obtained from the comparative solubilities in sea salt and sodium chloride solutions, representative calculations for several natural waters, including sea water, were made of concentration and temperature limits to avoid precipitation of calcium sulfate or its hydrates. With the method used, limits of saturation can be estimated for saline waters in general.

IN THE DESIGN of distillation plants for purifying water, knowledge of temperature and concentration limits for avoiding scale formation by calcium sulfate, a common constituent of natural waters, is essential. Many somewhat restrictive methods based on experimental data have been presented for obtaining limits of saturation to avoid precipitation of this solid or its hydrates, particularly calcium sulfate dihydrate (gypsum) (2, 4, 5, 6, 11, 16, 20, 24, 28). In the present work, by using solubilities in NaCl-H₂O solutions given and referenced elsewhere (15, 16) and in sea water concentrates (2, 7, 8, 11, 22, 25) and the new solubilities in synthetic sea salt solutions from 60° to 200° C. presented here, a procedure believed to be of more general applicability has been developed. This (computer) procedure allows the rapid estimation of concentration and temperature limits for avoiding precipitation of CaSO₄ or its hydrates from saline waters in general, including those waters from which calcium (and/or magnesium) initially has been depleted.

EXPERIMENTAL

A concentrated stock (sea salt) solution (~5 molal total salt) was prepared that contained molal salt ratios of a synthetic sea water composition given by Spiegler (27) (Table III) but excluding stoichiometric CaSO₄. (In this paper, the term "sea salt" refers to this composition but with any amount of concentration or dilution with respect to water. The term "sea water concentrate" sometimes is used interchangeably, and refers also to solutions more dilute or more concentrated than sea water.) The salts used for the preparation of the stock solution, all of reagent grade purity, were NaCl, KCl, Na₂SO₄, MgCl₂·6H₂O, MgSO₄, and NaBr. Before weighing, the salts, except MgSO₄, were dried at 100° to 110° C. for 4 to 24 hours. The formula, MgCl₂·6H₂O, was verified by dehydrating a weighed sample at 200° C. to determine the loss of 6H₂O within 1%. Magnesium sulfate hydrate was dehydrated to MgSO₄ by drying at 400° C. for 24 hours.

The stock solution was quantitatively diluted with deionized water to give the many solutions of different concentrations in which the solubility of gypsum

(CaSO₄·2H₂O) or anhydrite (CaSO₄), formed from gypsum within the solubility vessel, was determined. The washing of the reagent grade gypsum used in the solubility determinations, the addition of 2 cc. of 30% H₂O₂ (which decomposes to O₂ at high temperature) to 40 cc. of solution to prevent corrosion of the titanium alloy vessel, and the methods of equilibrating and sampling from the high pressure vessels have been described in detail (14, 15, 16). As in previous studies, solubilities of anhydrite at 100° and 125° C. were obtained by making runs first at 150° C. or higher to convert gypsum or hemihydrate (CaSO₄·½H₂O) rapidly to anhydrite.

The solubility values at 60° C. were obtained by rocking bottles containing the solid-liquid mixtures in a constant temperature bath (± 0.3° C.) and withdrawing solution samples (through a porous glass tip sampling tube) for analysis after periods of time varying from 16 to 48 hours. Attainment of equilibrium was substantiated by agreement of analyses (to ± 1%) of samples obtained after 5 to 48 hours.

Since both calcium and magnesium were present, it was difficult to use a potentiometric titration for calcium [the end point potentials for the titration of calcium and magnesium with (ethylenedinitrilo)tetraacetic acid (EDTA) as a complexing titrant are relatively close]. Therefore, a titration with a standardized EDTA solution and Mallinckrodt analytical reagent hydroxynaphthol blue as a colorimetric indicator was used as in the procedure of Patton and Reeder (21). The method was substantiated by analyses of known solutions in approximately the same ranges of calcium and additional salt concentrations.

The total salt concentration was obtained and verified by evaporating a weighed sample to dryness at 100° C. and weighing the total solid, knowing the dilution factor of the solution, and removing all metallic cations with a Dowex 50 cation exchange resin and titrating the eluent for total acid. The total sulfate concentration was obtained from the analysis for dissolved calcium sulfate, the total salt concentration, and the exact molal ratios of the salts in the diluted stock solution. The formal solubility product, $K'_{sp} = [m_{Ca}][m_{SO_4}]$, and the formal ionic strength, $I' = \frac{1}{2} \sum m_i z_i^2$, where m_i is the formal molality of ion i and

Table I. Negative Logarithm of Solubility Product Constants for Anhydrite (A), Hemihydrate (B), and Gypsum (G), and Several Other Constants for Evaluating Solubility Products at 0–300° C.

Temp., ° C.	–Log K_{sp}^o (A)	–Log K_{sp}^o (H)	–Log K_{sp}^o (G)	A_{sp}	B_G	C_G	Debye-Hückel Slope ^a (for Molalities for 1–1 Electrolyte)
0	3.818	3.682	4.466	1.450	0.0880	0.0234	0.4875
25	4.192	3.734	4.373	1.500	0.0194	0.0134	0.5080
50	4.539	3.933	4.409	1.544	0.0000	0.0108	0.5337
75	4.884	4.236	4.514	1.575	0.0000	0.0068	0.5645
100	5.240	4.614	4.650	1.594	0.0000	0.0020	0.6006
125	5.617	5.044	4.792	1.600	0.0000	0.0000	0.6422
150	6.020	5.512	4.920	1.600	0.0000	0.0000	0.6900
175	6.453	6.007	5.025	1.600	0.0000	0.0000	0.7451
200	6.017	6.520	5.008	1.600	0.0000	0.0000	0.8097
250	7.941	7.576	5.130	1.600	0.0000	0.0000	0.9848
300	9.093	8.648	4.996	1.600	0.0000	0.0000	1.2870

^a Debye-Hückel slopes for molar units multiplied by square root of density of water to convert for use with molal units.

z_i equals the charge on that ion, could then be obtained. For these values, m_{Ca} and m_{SO_4} represent the total molality of calcium and sulfate.

All samples were analyzed on a volume basis and were converted to molalities by using the densities at 25° C. of sodium chloride solutions of comparable salt concentration (10). Since sodium chloride is the predominant constituent of sea water, it was believed that this procedure was acceptable within the precision of the solubility determinations.

SOLUBILITY RELATIONSHIPS IN NaCl-H₂O SOLUTIONS

Solubilities of CaSO₄ and its hydrates in dilute and concentrated NaCl-H₂O solutions at temperatures from 0° to 200° C., determined at this laboratory, have been published with references to earlier work (15, 16). A recent paper by Ostroff and Metler (20) presents additional solubilities of CaSO₄·2H₂O in NaCl-H₂O solutions, 28° to 70° C., in very good agreement with both experimental and calculated (to ±1.5% at all ionic strengths) values (15, 16). A study by Madgin and Swales, not compared previously but also in good agreement, contains solubilities of CaSO₄·2H₂O and CaSO₄ in NaCl-H₂O solutions at 25° and 35° C. (12). Previous work (15, 16) showed that the solubility of gypsum, hemihydrate, and anhydrite could be described at a particular temperature by the following equation (Debye-Hückel type with added terms),

$$\log K_{sp} = \log K_{sp}^o + 8S(I)^{1/2} / [1 + A_{sp}(I)^{1/2}] + BI - CI^2 \quad (1)$$

where I is the (true) ionic strength of the solution defined in the experimental section in terms of the formal rather than the true ionic molalities, K_{sp} is the ionic (practical) solubility product, $[m_{Ca^{2+}}][m_{SO_4^{2-}}]$, S is the theoretical limiting Debye-Hückel slope for a 1–1 electrolyte multiplied by the square root of the density of water to convert it for use with molal units, K_{sp}^o is the solubility product constant at $I = 0$, and A_{sp} , B , and C are adjustable parameters. Values of A_{sp} , B_G , and C_G (subscripts G, H, and A are used here to designate application to gypsum, hemihydrate, and anhydrite, respectively) at several temperatures for gypsum are given elsewhere (15). Also given (15) is an equation for the variation with temperature (T , ° Kelvin) of K_{sp}^o for gypsum, included as follows:

$$\log K_{sp}^o (\text{gypsum}) = 390.9619 - 152.6246 \log T - 12545.62/T + 0.0818493 T \quad (2)$$

In place of the equation for anhydrite given previously (15), an equation for K_{sp}^o (anhydrite) that fitted the results somewhat better at temperatures from 100° to 200° C. (but

Table II. Experimental Values Obtained from the Solubility of Calcium Sulfate Dihydrate and Calcium Sulfate in Seawater Concentrates and Diluents, 30–200° C.

Source ^a	I ^b	–Log K _{sp} ^c	–Log [Ca(m)] ^d	Source ^a	I ^b	–Log K _{sp} ^c	–Log [Ca(m)] ^d
T = 30°C. (CaSO ₄ · 2H ₂ O) ^e							
	0.0599	3.631	1.862	1	0.0314	4.757	2.400
2	0.443	2.992	1.557	1	0.0314	4.740	2.391
2	0.791	2.783	1.487	1	0.0314	4.717	2.378
2	1.506	2.373	1.440	1	0.0828	4.462	2.294
2	2.202	2.471	1.438	1	0.0840	4.387	2.260
2	2.613	2.433	1.446	1	0.0901	4.434	2.285
2	3.64	2.403	1.507	1	0.1817	4.161	2.191
2	4.00	2.411	1.541	1	0.352	3.971	2.166
3	0.598	2.883	1.519	1	0.352	3.943	2.146
3	1.866	2.489	1.418	1	0.675	3.699	2.104
3	3.94	2.416	1.540	1	0.683	3.674	2.087
3	6.68	2.559	1.849	1	0.683	3.658	2.075
4	0.708	2.810	1.491	1	1.998	3.284	2.076
4	2.111	2.488	1.442	1	1.998	3.299	2.028
4	4.20	2.432	1.573	1	3.37	3.131	2.124
				1	5.69	3.056	2.260
				1	6.10	3.114	2.345
				3	0.570	3.690	2.058
				3	1.697	3.288	2.026
				3	1.697	3.244	1.988
				3	3.42	3.081	2.084
				3	3.58	3.114	2.132
T = 60°C. (CaSO ₄ · 2H ₂ O)							
1	0.0599	3.636	1.865				
1	0.0599	3.635	1.864				
1	0.0805	3.559	1.785				
1	0.0816	3.548	1.779				
1	0.1370	3.394	1.714				
1	0.1388	3.381	1.708				
1	0.762	2.770	1.474	1	0.0065	5.562	2.828
1	0.771	2.767	1.474	1	0.0067	5.547	2.776
1	0.432	2.983	1.550	1	0.0246	5.244	2.661
1	2.111	2.451	1.414	1	0.0261	5.131	2.600
1	2.111	2.444	1.409	1	0.0717	4.900	2.550
3	0.598	2.866	1.509	1	0.1708	4.561	2.457
3	1.866	2.480	1.412	1	0.1705	4.481	2.397
3	3.94	2.387	1.516	1	0.332	4.294	2.396
3	6.68	2.485	1.780	1	0.344	4.264	2.381
4	0.708	2.804	1.488	1	0.635	3.951	2.291
4	2.111	2.450	1.413	1	0.651	3.921	2.273
4	4.20	2.367	1.518	1	1.305	3.614	2.226
				1	1.948	3.450	2.110
				1	1.970	3.427	2.201
				1	2.690	3.310	2.207
				1	3.32	3.244	2.225
				1	3.32	3.225	2.208
				1	5.89	3.125	2.342
				1	0.556	3.943	2.448
				3	1.697	3.514	2.227
				3	1.720	3.456	2.179
				3	1.720	3.426	2.162
				3	3.81	3.237	2.273
				3	6.68	3.131	2.400
T = 95°C. (CaSO ₄ · 2H ₂ O)							
1	0.0513	3.780	1.937				
1	0.0513	3.772	1.933				
1	0.0627	3.658	1.830				
1	0.0696	3.706	1.859				
1	0.1300	3.475	1.757				
1	0.1300	3.475	1.757				
1	0.422	3.055	1.591				
1	0.427	3.046	1.587				
1	0.762	2.815	1.503				
1	2.111	2.417	1.390				
1	2.141	2.338	1.336				
1	2.42	2.246	1.366				
1	5.89	2.378	1.636				
1	5.89	2.301	1.568				
3	0.598	2.907	1.534	1	0.0037	5.991	2.996
3	1.866	2.498	1.424	1	0.0040	5.914	2.957
3	3.94	2.402	1.523	1	0.214	5.611	2.866
3	6.68	2.400	1.701	1	0.214	5.516	2.809
				1	0.214	5.311	2.807
				1	0.706	5.164	2.722
				1	0.727	5.244	2.782
				1	0.705	4.775	2.610
				1	0.328	4.572	2.617
				1	0.332	4.509	2.568
				1	0.651	4.174	2.489
				1	0.659	4.184	2.501
				1	0.675	4.190	2.515
				1	1.970	3.609	2.369
				1	1.970	3.595	2.356
				1	3.37	3.377	2.358
				1	3.42	3.432	2.417
				1	5.79	3.222	2.429
				1	5.79	3.149	2.358
				3	0.563	4.229	2.490
				3	1.866	3.699	2.433
				3	3.94	3.398	2.442
T = 100°C. (CaSO ₄)							
1	0.0201	4.580	2.337				
1	0.0401	4.413	2.222				
1	0.2008	3.917	2.047				
1	0.355	3.710	1.990				
1	0.379	3.684	1.978				
1	0.683	3.450	1.918				
1	0.717	3.432	1.915				
1	1.998	3.070	1.889				
1	2.265	3.057	1.917				
1	2.811	2.987	1.928				
1	3.32	2.959	1.960				
1	5.53	2.963	1.985				
1	5.89	2.991	2.212				
5	0.841	3.201	1.778				
5	1.092	3.143	1.789				
5	1.411	3.036	1.767				
5	1.675	3.032	1.807				
5	1.743	3.009	1.799				
5	1.917	3.000	1.818				
5	2.082	3.000	1.843				
5	2.202	3.000	1.860				
3	0.584	3.415	1.864				
3	1.866	2.983	1.797				
3	3.87	2.896	1.959				
3	3.87	2.879	1.943				
3	6.68	2.848	2.124				
T = 125°C. (CaSO ₄)							
1	0.0129	4.971	2.532				
1	0.0138	4.932	2.466				
1	0.0138	4.917	2.461				
1	0.0214	4.770	2.407				
T = 150°C. (CaSO ₄)							
1	0.0065	5.562	2.828				
1	0.0067	5.547	2.776				
1	0.0246	5.244	2.661				
1	0.0261	5.131	2.600				
1	0.0717	4.900	2.550				
1	0.1708	4.561	2.457				
1	0.1705	4.481	2.397				
1	0.332	4.294	2.396				
1	0.344	4.264	2.381				
1	0.635	3.951	2.291				
1	0.651	3.921	2.272				
1	1.305	3.614	2.226				
1	1.948	3.450	2.110				
1	1.970	3.427	2.201				
1	2.690	3.310	2.207				
1	3.32	3.244	2.225				
1	3.32	3.225	2.208				
1	5.89	3.125	2.342				
1	0.556	3.943	2.448				
3	1.697	3.514	2.227				
3	1.720	3.456	2.179				
3	1.720	3.426	2.162				
3	3.81	3.237	2.273				
3	6.68	3.131	2.400				

essentially the same at lower temperatures) was obtained and used in this work,

$$\log K'_{sp}(\text{anhydrite}) = -215.509 + 85.685 \log T + 6075.2/T - 0.070707 T \quad (3)$$

From the solubilities of hemihydrate (16, 23, 24, 26) (25° to 125°C.), most of them in H₂O, and those referenced by Smith (26) (90° to 125°C.), we have estimated the values of K'_{sp} for hemihydrate as a function of temperature (°K.) from 0° to 200°C., and have obtained the following equation similar to that for gypsum and anhydrite (15) to describe its behavior,

$$\log K'_{sp}(\text{hemihydrate}) = 154.527 - 54.958 \log T - 6640.0/T \quad (4)$$

The A_{sp} parameter at each temperature was assumed the same for expressing the behavior of each of the three

salts, since it should not be a function of the hydration state of the saturating solid. From the previous relationships (15), it was shown that $B_A = B_G - 0.020$ and $C_A = C_G + 0.0030$. The difference, $(B_G I - C_G I^2) - (B_A I - C_A I^2)$, is attributable to the hydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and corresponds to $2 \log a_{\text{H}_2\text{O}}$, where $a_{\text{H}_2\text{O}}$ is the activity of H₂O in the solution phase. By analogy, Equations 5 and 6 for B_H and C_H were derived:

$$B_H = B_A + 0.25 (B_G - B_A) \quad (5)$$

$$C_H = C_A + 0.25 (C_G - C_A) \quad (6)$$

The BI and CI^2 terms of Equation 1 are important only at very high ionic strengths (above 2 molal) and at low temperatures; they become very small or drop out entirely at temperatures above about 50° to 100°C. For convenience, some values for the several constants, calculated with Equations 2 to 4, and parameters are given in Table I.

Figure 1. Solubility products, K'_{sp} , vs. $[I']^{1/2}/(1 + A_{sp}[I']^{1/2})$ of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 in sea water concentrates compared with their behavior in NaCl-H₂O solutions from 30° to 200°C.

With the use of the above equations and constants at the several temperatures the solubility of gypsum in NaCl-H₂O from 0° to 110° C. is believed to be described to within about $\pm 3\%$ (15), and for hemihydrate and anhydrite to 200° C., within about $\pm 6\%$.

SOLUBILITY PRODUCTS IN SEA WATER CONCENTRATES

The experimentally determined solubility products, K'_{sp} , of anhydrite at 100° to 200° C. in synthetic sea water concentrates and diluents, expressed as $-\log K'_{sp}$ and obtained as described above, are given in Table II. Included also are the experimentally determined negative logarithms of the molal concentration of calcium (the solubility value). The logarithm of the total sulfate concentration is equal to the difference, $\log K'_{sp} - \log [m_{Ca}]$. The values for K'_{sp} are plotted in Figure 1 as $\log K'_{sp}$ vs. $(I')^{1/2}/[1 + A_{sp}(I')^{1/2}]$ where the A_{sp} values are the same as those used earlier for CaSO₄ in NaCl solutions (15) and are included in Table I. Values in H₂O are given elsewhere (15, 16). The solid lines on Figure 1 correspond to the behavior of K_{sp} derived from the previously determined solubilities in NaCl-H₂O solutions. Although at 100° C. there are no solubility measurements of anhydrite in NaCl-H₂O solutions, the solid line is consistent with extrapolated solubility products from both lower and higher temperatures [K_{sp}° (anhydrite) is calculated with Equation 3], and is believed to represent closely the equilibrium solubility behavior. Thus, our own values at 100° C. in sea salt solutions are believed to represent equilibrium values (they were obtained by approaching 100° C. from higher temperatures) while those values of Langelier *et al.* at 100° C., obtained by approaching 100° C. from lower temperatures, appear to be somewhat high.

Included also in Figure 1 and Table II are those values of K'_{sp} in sea water concentrates at 30° C. calculated from the solubilities of Posnjak (22), at 30° and 60° C. obtained from some very recent measurements of Shaffer (25), at 100° C. given by Langelier *et al.* (11) in molal units, and

at the several temperatures calculated from the solubilities of Hara *et al.* (8). Values of K'_{sp} from the results of both Posnjak and Hara *et al.* were obtained by multiplying the analyzed saturation concentration of calcium [Tables I and II of Posnjak (22); solubilities of Posnjak's Table II, incorrectly listed as grams per 100 grams of H₂O, are in grams per 100 grams of solution; Tables II and III of Hara *et al.* (8)], converted to molal units, by the molality of total sulfate ($m_{CaSO_4} + m_{\text{excess sulfate}}$). Posnjak's series of synthetic concentrates before saturation with CaSO₄·2H₂O did not contain calcium. Therefore, total sulfate was calculated from his values by adding the concentration of sulfate in the stock concentrate to that obtained by analysis for saturation calcium (= CaSO₄). To obtain total sulfate from the measurements of Hara *et al.* (which in the stock concentrates contained analyzed small amounts of calcium), the molal excess of sulfate over that of calcium in the stock concentrate [evaluated from Table II (7)] was added to the analyzed total calcium after saturation; this amount corresponded to total sulfate after saturation. The methods of conversion are stated in detail, since the data of Hara are misinterpreted elsewhere (2), but interpreted correctly later (25). The agreement of the present results with previously published solubilities is good (except at 100° C.) and is within the range of scatter of the individual solubility measurements.

The solubility products of gypsum in synthetic sea water concentrates at 30° and 60° C. are essentially identical with those in NaCl-H₂O solutions when compared at the same ionic strength, except at the highest ionic strengths. At 100° to 200° C. the solubility products of anhydrite are greater in sea salt than in sodium chloride solutions, and at a constant temperature the logarithmic difference, $\log (K'_{sp}/K_{sp})$, is approximately constant over a very wide range of ionic strength. This difference (Figure 2) is a function of both K_{sp}° and the dissociation constant(s) of any associated species present in the sea salt solutions. Thus, values in Figure 2 could be used for correcting differences in solubility in the solution compositions (sea

Table III. Molal Compositions of Several Representative Saline Waters

Component	Saline Water Code ^a						
	A	B	C	D	E	F	G
Sodium	0.4738	0.1463	0.2190	0.0147	0.00401	0.02756	0.0459
Calcium	0.01034	0.00915	0.01490	0.00513	0.00551	0.01150	0.01878
Magnesium	0.0542	0.0309	0.00672	0.00222	0.00420	0.00813	0.01539
Potassium	0.01007	0.0025	0.00065	0.00046	...	0.000229	0.06574
Iron	...	...	...	0.000023	...	...	...
Manganese	...	...	...	...	...	...	...
Chloride	0.5544	0.1529	0.2303	0.00235	0.00054	0.0371	0.1156
Sulfate	0.02856	0.03238	0.01575	0.01262	0.00893	0.01107	0.03097
Bicarbonate	0.00241	0.0028	0.00341	0.00286	0.00534	0.00605	0.00250
Carbonate	...	0.0004	...	...	...	...	...
Bromide	0.00084	0.0140 ^b	...	...	...	...	...
Fluoride	...	...	0.00004	0.00013	...	...	...
Nitrate	...	...	0.000035	...	...	0.00084	...
Silicon dioxide	...	...	0.00022	0.00023	...	0.00053	0.00023
Boron	...	...	0.000060	0.00017	...	0.00020	...
I' (original) ^c	0.7080	0.2979	0.3018	0.0501	0.0422	0.0975	0.2452
R (original) ^c	2.763	3.539	1.057	2.461	1.622	0.959	1.649
I' (revised) ^d	0.7092	0.2993	0.3035	0.0515	0.0449	0.1003	0.2464
R (revised) ^d	2.878	3.692	1.171	2.741	2.105	1.220	1.716

^aA. Standard sea water (27) based on chlorinity of 19.00 grams per kg. of solution. B. Caspian Sea, analysis of water obtained near Baku, U. S. Geol. Survey analysis (29). C. Deep well, Roswell, N. M., Jan. 14, 1965 (1). D. West well, Miller, S. D., depth 1245 feet, sampled Oct. 31, 1955 (U. S. Geol. Survey analysis) (18). E. Deep well No. 5, Webster, S. D. (17). F. Irrigation well, Buckeye Irrigation Co., Buckeye, Ariz., sampled April 23, 1955 (U. S. Geol.

Survey analysis) (18). G. Pecos River below Grandfalls, Tex., sampled April 1951; U. S. Geol. Survey Water Supply Paper 1199 (18).

^bBromide added arbitrarily to achieve electroneutrality; could be any other monovalent ion. ^cIonic strength (I') and molal ratio $SO_4^{2-}/Ca^{2+}(R)$, of original saline water. ^dIonic strength (I') and molal ratio $SO_4^{2-}/Ca^{2+}(R)$ after removal of CO_3^{2-} and HCO_3^- by addition of H_2SO_4 .

Figure 2. Correction for $K_{sp}(\text{CaSO}_4)$ to obtain apparent solubility product, K'_{sp} , in sea water concentrates

salt solutions) and for the solid phase from which they were obtained but not in other saline water compositions.

As a sea salt solution approaches infinite dilution (solubility of CaSO_4 or its hydrates approaches that in water), the value of K'_{sp} must approach K_{sp} ; Figure 1 shows this convergence occurring only at total salt concentrations below about 0.04 molal. Figure 3 shows schematically how the curve must approach the same Debye Hückel limiting slope and solubility product in water upon dilution of either sea salt or NaCl solutions.

CALCULATION OF SOLUBILITY LIMITS

Assumptions: Dissociation Constant of Magnesium Sulfate. The increase in solubility in sea salt solutions over that in sodium chloride solutions can be attributed essentially to the formation of a neutral species, MgSO_4^0 , which removes part of the concentration of sulfate ion and thereby allows the solubility of CaSO_4 (or its hydrates) to increase in order to satisfy its solubility product, K_{sp} . The existence of neutral CaSO_4^0 was not expected to interfere appreciably with this assumption (except in extreme cases mentioned below), since its concentration (in solutions saturated with CaSO_4) should be nearly independent of ionic strength and is incorporated into the values of K_{sd} used in this study (13, 15).

From the solubility results in sea salt solutions given in this paper and from those solubilities in sodium chloride solutions, values for the dissociation quotient, K_d , of the equilibrium,

and constant, K_d , at $I = 0$ were calculated and are presented elsewhere (13), where $\log K_d$ was estimated by the following Debye-Hückel equation,

$$\log K_d = \log K_d^0 + 8S(I)^{1/2} / [1 + (I)^{1/2}] \quad (8)$$

and $\log K_d^0$ varied with temperature according to the equation,

$$\log K_d^0 = -158.540 + 62.160 \log T + \frac{4810.6}{T} - 0.046298T \quad (9)$$

[4810.6 given incorrectly as 4180.6 elsewhere (13)].

Calculated vs. Observed Solubilities, 25° to 200° C. By using the several equations for solubility products of calcium sulfate and its hydrates and the dissociation quotients of magnesium sulfate, with their respective constants (Table

Figure 3. Schematic behavior of apparent solubility product, K'_{sp} , of CaSO_4 in magnesium containing saline waters

I), solubilities were calculated for direct comparisons with saturated solution compositions given in Table II and with other published, experimentally observed values in mixed electrolyte systems (4, 5, 12, 20). The formal ionic strengths were corrected slightly for the calculated amount of neutral species, MgSO_4^0 . The entire procedure was similar to that for obtaining concentration factors, described below, except that I' in Equation 11 was kept always equal to the initial, formal ionic strength. CF in Equation 12 then represented the molal solubility ratio, calculated to an observed, rather than a concentration factor, where formal ionic strength changes with concentration. When I' was corrected for this change the differences usually were less than 0.1 to 0.2% for ratios (calculated to observed) between 0.9 and 1.1, and were never greater than 0.7% for those of 0.6 to 0.9 and 1.1 to 1.4.

Figure 4 compares the calculated with observed solubilities from 25° to 95° C. in sea water solutions for all the (observed) results presented in Table II. Included also are comparisons with observed solubilities in mixed electrolytes obtained by several investigators (5, 12, 20). Comparisons with observed solubilities in $\text{NaCl-H}_2\text{O}$ other than those in Figure 4 have been given (15).

The use of a dissociation constant for CaSO_4^0 , roughly estimated from data up to 200° C. (15), may well account for the positive deviations from those values of Ostroff and Metler (Figure 4) where $m_{\text{MgCl}_2}/m_{\text{NaCl}}$ equals 0.5 to infinity, and also for the negative deviations from those of Madgin and Swales containing similarly high values (0.5 to infinity) of $m_{\text{Na}_2\text{SO}_4}/m_{\text{NaCl}}$. The presence of some neutral CaSO_4^0 in solution would yield calculated deviations in the directions shown for these two extreme types of solutions. From a solubility study in progress (30), we hope to obtain sufficiently accurate values for the dissociation constant and quotients of CaSO_4^0 that can be applied as a refinement to these calculations for the extreme deviations.

In Figure 5 are shown the comparative calculations for sea salt solutions at temperatures from 100° to 200° C. The drop in the calculated values at 175° and 200° C. at ionic strengths above 1 molal can be attributed to the deviation from the relationship of Equation 8 in calculated

Figure 4. Representative comparison of calculated and observed solubilities of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 in sea salt solutions and other mixed electrolytes at 25° to 95° C.

dissociation quotients of magnesium sulfate at these high ionic strengths (13). Additional terms could be added to Equation 8 to account for this deviation but, with the lack of any other solubility data to substantiate their inclusions, this was not done.

Comparisons of calculated with observed solubilities of Clampett and Fowler (4) for $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ at temperatures from 100° to 150° C. (not included in Figure 5) were not within reasonable agreement. Their values do not agree with those of Langelier *et al.* (11) at 100° C. for $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ nor with our own values (16) at 125° C. except in water and unconcentrated sea water. In view of the extrapolated, reasonable agreement between our own values (at

125° C.) and those of Langelier *et al.* (at 100° C.), we suspect an error in the measurements of Clampett and Fowler for the concentrated solutions.

The method of calculation and the assumptions used thus appear satisfactory for calculating solubilities in saline waters in general at temperatures from 25° to 200° C.; but for maximum reliability, it should be applied to waters containing a predominance of a 1-1 electrolyte.

Calculation of Concentration Factors. It can be shown that (13)

$$[\text{MgSO}_4] = (\Sigma [\text{Mg}]) K_{sp} / (K_d [\text{Ca}^{2+}] + K_{sp}) \quad (10)$$

Figure 5. Representative comparison of calculated and observed solubilities of CaSO_4 (anhydrite) in sea salt solutions at 100° to 200°C .

$$I = I' \cdot 4[\text{MgSO}_4] \quad (11)$$

from which

$$CF = \{(K_{sp} + [\text{Ca}^{2+}] \cdot [\text{MgSO}_4]) / FP_1\}^{1/2} \quad (12)$$

In Equations 8 to 12, T is in degrees Kelvin, I and I' are the true and formal (molal) ionic strengths, respectively, FP_1 is the formal product $[m(\text{total calcium}) \cdot m(\text{total sulfate})]$ in the initial (unconcentrated) saline water, $\Sigma[\text{Mg}]$, $[\text{Ca}^{2+}]$, and $[\text{MgSO}_4]$ are the molal concentrations of total magnesium, calcium ion, and MgSO_4 , respectively, and CF is the concentration factor on a molal basis $[= I' (\text{concentrate}) / I' (\text{original solution})]$.

By first using I' (initial), $\Sigma[\text{Ca}]$ (initial) for $[\text{Ca}^{2+}]$, and $\Sigma[\text{Mg}]$ (initial), preliminary values of K_{sp} , K_d , $[\text{MgSO}_4]$, I , and CF were calculated. By iterative calculations a final value of CF (and thus of I' for the concentrate) was obtained that differed less than 0.5% from the previously calculated value. Equations 1 to 6 and 8 to 12 were used for the calculations.

Use of Computer Program for Obtaining Concentration Factors. A computer program was written to perform the above calculations. After values of the Debye-Hückel slopes and the A_{sp} , B_G , and C_G parameters from Table I are included in the "Read In" data for each of a series of temperatures, only the original, formal ionic strength, I' ; the analytical molalities of calcium and of magnesium, and the molal

COMPUTER PROGRAM

Computer Program for Calculating Concentration Factors (CF) to Avoid Precipitation of CaSO_4 and Its Hydrates from Saline Waters. [Program written in FORTRAN IV

The READ Values:

NST = No. of separate temperatures for evaluation; maximum value of subscript, I .
 TEMP = temperature ($^{\circ}\text{C}$).
 DHS = limiting Debye-Hückel slope $[x (\text{density of } \text{H}_2\text{O})^{1/2}]$ for 1-1 electrolyte.
 $A = A_{\text{sp}}$ parameter.
 $B = B_G$ parameter (for gypsum only) for solubility product calculations for gypsum.
 $C = C_G$ parameter (for gypsum only) for solubility product calculations for gypsum. (Above quantities are read in once for $I = 1$ to NST for evaluation of all saline water compositions.)
 TITLE = title for the particular saline water composition.
 $A11$ = molal ionic strength of the saline water.
 $CAL1$ = molal concentration of calcium in the saline water.
 R = molal ratio, SO_4/Ca in the saline water.
 $TMG1$ = total molality of magnesium in saline water. (Calculations are repeated for each additional TITLE card and different values of $A11$, $CAL1$, R , and $TMG1$.)

(International Business Machines Co.). For interpretation and use, a basic knowledge of the FORTRAN languages is necessary.]

The WRITE Values:

A. TITLE, $A11$, $CAL1$, R , $TMG1$, the A parameter used for the variation of $K_s(\text{MgSO}_4)$.
 B. For each solid: TEMP, concentration factors (CF) on molal, molar, and weight fraction bases, ionic strengths at saturation, K_{sp} 's and number of iterative calculations (NIT) to obtain values of CF.
 C. Some particular constants used to obtain values of CF: DHS, $K_3(\text{MgSO}_4)$, A_{sp} parameters for K_{sp} variations with ionic strength, and A , B , and C parameters for anhydrite, hemihydrate, and gypsum.

An Alternate Equation to Substitute into Program for Specific Use with Sea water:

$$WF1/A11 = 0.04790 - 0.002194 * A11 + 0.00006900 * A11^{**2} \quad (= \text{wt. fraction/ionic strength})$$

FORTRAN IV Computer Program for Calculating Temperature-Solubility Limits of Calcium Sulfate and Its Hydrates in Saline Waters and Their Concentrations

C CALCN, TEMP-SOLY LIMITS(CASO4+HYDRATES IN SALINE WATERS), MARSHALL (1967)
 C W. L. MARSHALL (1967)-OAK RIDGE NATL. LAB., TENN., U.S.A.

C PROGRAM IN FORTRAN IV LANGUAGE (READ IN TAPE 5, READ OUT TAPE 6), (1967)

DDIMENSION TITLE (10), DHS(100), TEMP(100), TA(100), A(100), B(100,3),
 IC(100,3), JJ(100,3), XKDISO(100), SOLPO(100,3), AIF(100,3),
 2CFML(100,3), CFMR(100,3), CFWF(100,3)

READ (5,1)NST

1 FORMAT (110)

READ (5,2) (TEMP(I), DHS(I), A(I), B(I,3), C(I,3), I=1, NST)

2 FORMAT (5E10.0)

DO 21 I=1, NST

B(I,1)=C(I,3)-0.020

C(I,1)=C(I,3)+0.0030

B(I,2)=B(I,1)+0.25*(B(I,3)-B(I,1))

C(I,2)=C(I,1)+0.25*(C(I,3)-C(I,1))

TA(I)=TEMP(I)+273.16

OSOLPO(I,1)=10.**(215.509+85.685*ALOG10(TA(I)))

1+6075.2/TA(I)-0.070707*TA(I))

SOLPO(I,2)=10.**(154.527-54.958*ALOG10(TA(I))-6640.0/TA(I))

OSOLPO(I,3)=10.**(390.9619-152.6246*ALOG10(TA(I)))

1-12545.6/TA(I)+0.0818493*TA(I))

210XKD150(I)=10.**(158.540+62.160*ALOG10(TA(I)))

1+4810.4/TA(I)-0.046298*TA(I))

22 READ (5,3) TITLE, A11, CAL1, R, TMG1

3 FORMAT (10A4, 4E10.0)

SOLP1=R*CAL1**2

WF1=A11*(0.05838-0.003260*A11+0.00012489*A11**2)

FMRI=A11*(0.9970-0.01883*A11)

DO 25 K=1,3

DO 25 I=1, NST

ASSMG=0.0

CFML(I,K)=1.

DO 23 J=1, 100

CAL=CAL1*CFML(I,K)

IMC=TMG1*CFML(I,K)

A=A11*CFML(I,K)-4.*ASSMG

OSOLP=SOLPO(I,K)*10.**(8.*DHS(I)*SQRT(A/1)+(1.+A(I)*SQRT(A11))

1-B(I,K)*A1-C(I,K)*A1**2)

XKDIS=XKDISO(I)*10.**(8.*DHS(I)*SQRT(A11)/(1.+SQRT(A11)))

ASSMG=TMG*SOLP/(XKDIS*CAL+SOLP)

X=SQRT((SOLP+ASSMG*CAL)/SOLP1)

IF(ABS(X-CFML(I,K))/X-.001)24,24,23

23 CFML(I,K)=X

24 JJ(I,K)=J

AIF(I,K)=CFML(I,K)*A11

OCFWF(I,K)=AIF(I,K)*(0.05838-0.003260*AIF(I,K)+0.00012489*

1AIF(I,K)**2)/WF1

25 CFMR(I,K)=AIF(I,K)*(0.9970-0.01883*AIF(I,K))/FMRI

WRITE(6,4)TITLE

4 FORMAT(11H,10A4)

WRITE(6,5)A11

5 FORMAT(27H01ONIC STR OF SALINE WATER=E12.4)

WRITE(6,6)CAL1

6 FORMAT(20H INITIAL CONC'N OF CALCIUM=E12.4)

WRITE(6,7)R

7 FORMAT(20H MOLAL RATIO SO_4/Ca =E12.4)

WRITE(6,8)TMG1

8 FORMAT(20H INITIAL CONC'N OF MAGNESIUM=E12.4)

WRITE(6,9)

9 FORMAT(20H A PAR FOR KD155(MGSO4)=1.0)

WRITE(6,10)

100FORMAT(65H0CONCN FACTORS FOR CASO4(ANHYDRITE), CF=CONCN(SATD)/CONCN

1(INITIAL))

WRITE(6,11)

110FORMAT(112H0 TEMP(C) CF(MOLAL) CF(MOLAR) CF(WT

IFRAC) ION STR(MOLAL-SATD) SOLY PD(ZERO) NO ITER)

OWRITE(6,12)(TEMP(I), CFML(I,1), CFMR(I,1), CFWF(I,1), AIF(I,1),

1SOLPO(I,1), JJ(I,1), I=1, NST)

12 FORMAT(11H ,F6.0,3E18.3,112)

WRITE(6,13)

130 FORMAT(60H0CONCN FACTORS FOR HEMIHYDRATE, CF=CONCN(SATD)/CONCN(INIT

IAL))

WRITE(6,11)

OWRITE(6,12)(TEMP(I), CFML(I,2), CFMR(I,2), CFWF(I,2), AIF(I,2),

1SOLPO(I,2), JJ(I,2), I=1, NST)

WRITE(6,14)

140FORMAT(65H0CONCN FACTORS FOR CASO4 DIHYDRATE, CF=CONCN(SATD)/CONCN

1(INITIAL))

WRITE(6,11)

OWRITE(6,12)(TEMP(I), CFML(I,3), CFMR(I,3), CFWF(I,3), AIF(I,3),

1SOLPO(I,3), JJ(I,3), I=1, NST)

WRITE(6,15)

15 FORMAT(52H0PARTICULAR CONSTANTS USED IN THE ABOVE CALCULATIONS)

WRITE(6,16)

160FORMAT(119H0 TEMP(C) D H SLOPE R-DIS(U)(MUSUJ4) A PARA

1 B(ANHYD) B(HEMI) B(GYPS) C(ANHYD) C(HEMI) C(GYPS))

OWRITE(6,17)(TEMP(I), DHS(I), XKDISO(I), A(I), B(I,1), B(I,2), B(I,3),

1C(I,1), C(I,2), C(I,3), I=1, NST)

17 FORMAT(11H ,F6.0,F13.4,E20.3,F13.3,6F11.4)

GO TO 22

END

ratio (R), sulfate/calcium, are needed for calculating separately the temperature-concentration limits for anhydrite, hemihydrate, and gypsum. The program contains the equations for the temperature variation of the solubility product constants of anhydrite, hemihydrate, and gypsum, of the dissociation constants of magnesium sulfate, and the conversion expression for the B and C parameters for anhydrite and hemihydrate. The calculation is based on the assumption that natural waters will behave generally like sea water, and the neutral species, MgSO_4 , will be the predominant species contributing to the increase in solubility over that in sodium chloride solutions (of the same, formal ionic strength).

Equations are included in the program for the variation of molarity/molality and weight fraction/molality ratios with molal ionic strength of sodium chloride solutions; molarities were obtained from densities given elsewhere (10). With these equations, the CF values were estimated also with molar (at 25°C.) and weight fraction units based on the variations (with ionic strength) of density and weight fraction of NaCl , the predominant salt constituent in most natural waters. All three values of CF approach unity for the original water but diverge by as much as 10% at CF values of 5 to 6. [As an option for substitution, an equation for the variation of weight fraction/molality vs. molality specifically for sea water is included with the program. This equation gives $CF(\text{weight fraction})$ values only slightly different from those obtained with the equation for $\text{NaCl-H}_2\text{O}$ solutions.]

Calculations for Representative Saline Waters. For representative calculations, a "standard composition" for sea water (27) was selected together with those for several other natural waters. The reported analyses were converted to molal units, and are given in Table III together with each source and reference. The (molal) ionic strengths (I') of the original waters were obtained and are included in Table III. In distillation practices, a stoichiometric amount of H_2SO_4 is usually added to replace and allow removal of bicarbonate and carbonate ions. With this substitution, a revised set of values for I' and R is given in Table III. For addition of HCl to remove carbonate and bicarbonate, R does not change from the original value. I' changes slightly if carbonate, in addition to bicarbonate, is present.

Figure 6 shows the calculations for sea water. The concentration factor, CF , represented by $I'_{\text{soln}}/I'_{\text{orig.}}$, which corresponds to the molal or molar (at 25°C.) ionic strength or the weight fraction of the salt solution saturated with CaSO_4 (or one of its hydrates) divided by the corresponding molality (or molarity or weight fraction, respectively) of the unconcentrated saline water, is plotted against temperature. A calculated molar CF value of 3.3 for hemihydrate at 102°C. (the approximate boiling point of sea water of this CF at 1 atm.) compares well with 3.2 obtained with Marineland, Calif., sea water by Glater, Ssutu, and McCutchan (6) by a boiling concentration method (at sea level). The small difference could be due to slight differences between our standard composition (Table III) and their Marineland water. At temperatures below 95°C. and at moderately low ionic strengths, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), although metastable above about 40° to 60°C., is the usual precipitating phase, and therefore the boundary curve for this solid (below 95°C.) is the most important (5, 15, 23, 24, 25). [Controversy still exists over the true transition temperature of conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to CaSO_4 . Recently, two papers have appeared, one of which (Zen) estimates the transition temperature in water to be $46^\circ \pm 25^\circ\text{C}$. (31) and the other (Ostroff) decides that gypsum will not convert to anhydrite at temperatures below 97°C. (19). The curve for the solubility product constant (K'_{sp}) of anhydrite obtained with our Equation 3 intersects that for gypsum obtained with Equation 2 at about 41°C. and is based on our own and other measurements for gypsum

Figure 6. Calculated limits of solution stability to avoid precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), and anhydrite (CaSO_4) from sea water concentrates

I' , Molal ionic strength of sea water
Ca, Mg, Original molalities of Ca and Mg
 R , Molal ratio, SO_4/Ca

and the solubility measurements of Hill (9) and later of Bock (3) and of Power *et al.* (24) for anhydrite. The difficulty in obtaining complete agreement on this transition temperature lies in the sluggishness of the transition to anhydrite below about 90°C. Above 95°C., the transient solubility of metastable $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ (hemihydrate) (23, 24) and the equilibrium solubility of CaSO_4 (anhydrite) (16) are the significant equilibria; these curves (above 95°C.) therefore become the more useful.

Some concentration factors were obtained by plotting experimental values of $(K'_{\text{sp}})^{1/2}$ against I' and determining the intersection with a straight line representing the formal ion product in solution concentrates [like the method used by Langelier *et al.* (11)]. These experimentally derived values are compared to calculated values in Table IV. The agreement is good.

In Figure 7, concentration factors for anhydrite, hemihydrate, and gypsum are given for the several representative natural waters listed in Table III, where carbonate and bicarbonate are not removed. It is believed that they approach the solubility behavior reasonably closely in view

Table IV. Comparison of Some Calculated Concentration Factors (CF) on a Molal Basis with Smoothed, Experimentally Observed Values for Sea Salt Solutions

$t, ^\circ\text{C.}$	CF		Saturating Solid Phase
	Exptl.	Calcd.	
30	3.53	3.48	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
60	3.56	3.51	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
100	1.20	1.24	CaSO_4
125	0.74	0.78	CaSO_4
150	0.47	0.48	CaSO_4
175	0.25	0.27	CaSO_4
200	0.15	0.16	CaSO_4

Figure 7. Calculated limits of solution stability to avoid precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), and anhydrite (CaSO_4) from representative saline waters

I'_i . Molal ionic strength of original water
 I'_s . Molal ionic strength of concentrate
 Ca , Mg . Original molalities of Ca and Mg
 R . Molal ratio, SO_4/Ca

of the good agreement in sea salt and other mixed electrolyte solutions (Figures 4 and 5).

The composition for the Pecos River (Grandfalls, Tex.) represented in Figure 7 appears to be saturated or nearly saturated with gypsum at 25°C . For this water, the concentration factor for anhydrite falls below 1.0 at a temperature much below 100°C . Therefore, a rather large amount of calcium must be removed to prevent precipitation of anhydrite at a temperature somewhat above 100°C , or to increase the concentration factors for gypsum at lower temperatures. In contrast, sea water is considerably undersaturated with respect to gypsum (a metastable phase above 30° to 60°C .) at temperatures at least above 160°C .

REMOVAL OF CALCIUM AND MAGNESIUM FROM SALINE WATERS

Temperature and Concentration Limits. If calcium (and/or magnesium) is removed from a saline water and replaced by an equivalent amount of sodium—for example, by an ion exchange process—then either the temperature limits (at a concentration factor of 1.0) or concentration factors at a particular temperature can be calculated easily with the computer program. In Figure 8, the calculated saturation limits for gypsum at 90°C ., expressed as concentration

factors, are plotted against the percentage depletion of calcium (by substitution of sodium) only and of both calcium and magnesium for several of the representative saline waters. In Figure 9, the temperature limits for precipitation of anhydrite from the several waters are plotted against the percentage removal of calcium (and also with simultaneous and equivalent removal of magnesium). When magnesium is depleted simultaneously, the rise is less than with calcium alone because of the removal of the complexing agent, magnesium.

CONCLUSIONS

The examples shown in Figures 6 to 9 are representative calculations. While we believe that the analyses for the several natural waters were reliable at the time of sampling, the compositions may vary with time and particular location (excluding a near-constancy for sea water). For rapid evaluations of other saline waters, the computer program can be used, together with constants given in Table I. This procedure should prove very valuable where the input water composition of a desalination plant varies with time; rapid evaluation could allow immediate adjustment in operating conditions.

Figure 8. Effect at 90°C. of calcium and magnesium depletion on allowable concentration of representative saline waters before precipitation of gypsum
 I_0 . Molal ionic strength of original water
 I . Molal ionic strength of concentrate

Figure 9. Effect of calcium and magnesium depletion on temperature of precipitation of anhydrite from representative saline waters
 Unconcentrated

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3.3 APPARENT INVARIANCE OF ACTIVITY COEFFICIENTS OF CALCIUM SULFATE AT CONSTANT IONIC STRENGTH AND TEMPERATURE IN THE SYSTEM $\text{CaSO}_4\text{-Na}_2\text{SO}_4\text{-NaNO}_3\text{-H}_2\text{O}$ TO THE CRITICAL TEMPERATURE OF WATER. ASSOCIATION EQUILIBRIA^{1,2}

LeRoy B. Yeatts and William L. Marshall

To obtain and interpret activity coefficient behavior over wide ranges of temperature and concentration, measurements were made of the solubility of calcium sulfate in mixed aqueous solutions of sodium nitrate and sodium sulfate at ionic strengths (I) from 0.25 to 6 m and at temperatures from 0 to 350°. With the assumption of ion association, the activity coefficients of the neutral molecule (CaSO_4^0) and of the ions were found to remain constant, at all temperatures, as the molality of sodium sulfate was varied widely at constant I . When I was varied, the logarithms of the activity coefficients of CaSO_4^0 appeared to be linear functions of $I^{1/2}$ rather than of I as is usually considered for neutral molecules. The logarithms of the mean ionic activity coefficients adhered well to an extended Debye-Hückel expression over the ranges of temperature and ionic strength. From the interpretation given, the equilibrium constants and thermodynamic functions were obtained for the formation of the neutral molecule and for the dissociation equilibria.

Introduction

The question of the existence of ion association for particular electrolytes in aqueous solutions is still debated.³ For example, association constants for several 1-1 electrolytes, KNO_3 , AgNO_3 , and TiCl_3 , in water solution at 25° are estimated from conductance measurements to be 0.58, 0.51, and 3.1, respectively,³ indicating an appreciable fraction of ion pairs at finite concentrations. Yet 1-1 salts in general are usually considered to be very strongly or completely ionized at 25° and Debye-Hückel theory used to predict their thermodynamic behavior. Furthermore, in treating the behavior of activity coefficients in mixed-electrolyte solutions, usually the change in formal (stoichiometric) activity coefficients is related to a change in composition of mixed electrolytes at constant ionic strength.⁴ With this approach the potential existence of ion pairs, a physically significant entity, is concealed in the formal coefficient. It was therefore the purpose of this study to make solubility measurements of a suitable salt, calcium sulfate, in a mixed-electrolyte system over a wide range of temperature to determine whether an assumption of ion association might account for the major change in formal activity coefficient with change in composition of mixed electrolytes. This finding would provide further support for ion association and also additional clues to the general behavior of electrolyte solutions over wide ranges of temperature and ionic strength.

The extent of association of calcium sulfate in water at 25° was calculated by Money and Davies⁵ from the

conductivity data of both MacGregory⁶ and Harkins and Paine.⁷ They obtained a value for the dissociation constant of $10^{-2.28}$, assuming first that the conductivity of a completely ionized 2-2 electrolyte is given by an extended form of Onsager's equation and, second, that all deviations from this extended equation are due to ion association. An electrode for measuring calcium ion activity was used with saturated CaSO_4 solutions by Nakayama and Rasnick⁸ to determine a dissociation constant of $10^{-2.27}$ at 25°. The activity coefficient of the undissociated CaSO_4 was required for the calculation of K_d and was assumed to be unity. Bell and

(1) The research was sponsored jointly by the U. S. Atomic Energy Commission and the Office of Saline Water, U. S. Department of the Interior, and was performed at the Oak Ridge National Laboratory under contract with Union Carbide Corp. Presented before the Division of Physical Chemistry at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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George⁹ in 1953 estimated the dissociation constants at 0, 25, and 40° to be $10^{-2.22}$, $10^{-2.31}$, and $10^{-2.39}$, respectively. These values were obtained indirectly from measurements of the solubility of calcium iodate in potassium sulfate solutions, with the assumption that all deviations from the Davies equation could be attributed to incomplete ionization and again that the activity coefficients of uncharged ion pairs are equal to unity. Recently, estimates of the dissociation constants for CaSO_4 were extended to 200° by solubility measurements at this laboratory.¹⁰ These approximate values ranged from $10^{-1.8 \pm 0.4}$ at 0° to $10^{-3.5 \pm 0.6}$ at 200° and could account for the small deviations from an extended Debye-Hückel expression. The use of theoretical equations by Helgeson¹¹ for the dissociation reaction at 25° gives values for thermodynamic quantities which are in reasonable agreement with those of Bell and George.⁹

Some of the basic concepts that were applied in this present study are indicated in papers by Ramette¹² and Meites, Pode, and Thomas.¹³ The present measurements were made generally in the four-component, mixed-electrolyte system $\text{CaSO}_4\text{-Na}_2\text{SO}_4\text{-NaNO}_3\text{-H}_2\text{O}$ at constant ionic strengths of 0.25, 0.5, 1, 2, and 6 at temperatures of 0.5, 25, 150, 250, and 350°. Sodium sulfate was used to vary the sulfate ion concentration and sodium nitrate was added to adjust the ionic strength of the solutions to the desired constant value. Several studies¹⁴ between 25 and 100° have been made in the past of the solubilities of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the presence of soluble sulfates, but no effort was made to maintain constant ionic strength.

Experimental Section

Stock solutions of 6 M NaNO_3 and 1 M Na_2SO_4 were prepared from weighed quantities of dried reagent grade chemicals and demineralized water. These solutions were diluted quantitatively to the desired concentration for each experiment. Reagent grade $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was suspended in boiling demineralized water, was stirred constantly for about 1 hr to remove soluble impurities, and then was filtered. The recovered material was treated again in this manner and the final product was dried near 100°. An excess of this solid was equilibrated with aqueous solutions of NaNO_3 , Na_2SO_4 , or mixtures of the two at constant ionic strength for a given experiment. Polyethylene bottles were the containing vessels for the 0.5 ± 0.1 and $25.0 \pm 0.1^\circ$ experiments; these with their contents were rocked in a constant-temperature water bath for 18–22 hr before sampling. Pressure vessels made from a titanium alloy contained the mixtures for the experiments at 150 ± 1 , 250 ± 1 , and $350 \pm 1^\circ$. The equilibration times before sampling were generally 65 hr at 150°, followed by additional 20-hr periods at both 250 and 350°. A longer equilibration time was used at 150° to assure complete conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the

solid added, to CaSO_4 , the stable solid at the high temperature. The volume of starting materials was sufficient to permit sampling at all three temperatures before reloading of the vessels was required. Solutions at each temperature were filtered through porous Teflon disks,¹⁵ during sample withdrawal, at the temperature of the experiment. The total calcium concentration of each solution sample was determined from a semimicro potentiometric titration with standard EDTA solution. The density and the total weight of solids per unit volume of each solution were determined after equilibration. The former was used to convert molarity to molality and the latter served as a means of checking the prior dilution of standard solutions.

More detailed descriptions of the experimental equipment and procedures have been presented previously.^{10, 15–17}

Results and Discussion

General. Our results for the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in water are $0.0132 \pm 0.0002 m$ (average deviation) at 0.5° and $0.0154 \pm 0.0001 m$ (average deviation) at 25°, in agreement with previously determined values.¹⁰ The experimentally determined molal solubilities of CaSO_4 or its dihydrate in aqueous $\text{Na}_2\text{SO}_4\text{-NaNO}_3$ solutions from 0.5 to 350° are presented in Table I. A plot of the solubilities of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in aqueous NaNO_3 solutions at 25° against the molality of NaNO_3 provides a smooth curve with previous data.¹⁸ The recent solubility measurements in NaNO_3 at 300° by Templeton and Rodgers¹⁹ are in reasonable agreement with our results at ionic strengths of 0.5 and 1, but at $I = 2$, their result is about 25% higher than would be anticipated from a plot of solubility vs. temperature using our data. Comparisons of the solubilities of the dihydrate in the presence of NaNO_3 (Table I) show that the solubility at 0.5° is less than at 25° up to an ionic strength near 1, at which point the

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for which the equilibrium quotient expression is

$$Q_d = [\text{Ca}^{2+}][\text{SO}_4^{2-}]/[\text{CaSO}_4^0] \text{ (molal units)} \quad (4)$$

The ionic solubility product quotient is then defined as

$$Q_{isp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = Q_d Q_u \quad (5)$$

With these assumptions the molal solubility of calcium sulfate, s , at constant temperature and ionic strength is given by

$$s = [\text{CaSO}_4^0] + [\text{Ca}^{2+}] \quad (6)$$

Since $[\text{CaSO}_4^0] = Q_u$ and $[\text{Ca}^{2+}] = Q_{isp}/[\text{SO}_4^{2-}]$, then

$$s = Q_u + (Q_{isp}/[\text{SO}_4^{2-}]) \quad (7)$$

The total calcium sulfate and the sodium sulfate molalities are found experimentally. The molality of SO_4^{2-} ions is determined in the following manner

$$[\text{SO}_4^{2-}] = (\text{total sulfate}) -$$

$$[\text{CaSO}_4^0] = [\text{SO}_4]_{\text{total}} - Q_u \quad (8)$$

where

$$[\text{SO}_4]_{\text{total}} = s + [\text{Na}_2\text{SO}_4] \quad (9)$$

A more useful form initially of eq 7 is

$$s = Q_u + [Q_{isp}/([\text{SO}_4]_{\text{total}} - Q_u)] \quad (10)$$

indicating that successive approximations of the value for Q_u are necessary to establish the molality of SO_4^{2-} ion. The ionic strength is defined throughout this paper as

I (molal units) =

$$m_{\text{NaNO}_3} + 3m_{\text{Na}_2\text{SO}_4} + 4(s - m_{\text{CaSO}_4^0}) \quad (11)$$

Implicit in these arguments are the complete ionization of NaNO_3 and Na_2SO_4 at all ionic strengths and invariant or nearly invariant activity coefficients at constant ionic strength. If these assumptions are correct, a plot of s vs. $1/[\text{SO}_4^{2-}]$, at constant temperature and ionic strength, should produce a straight line, according to eq 7, with a slope equal to Q_{isp} (or $Q_d Q_u$) and an intercept equal to Q_u (or $[\text{CaSO}_4^0]$).

The data in Table I were treated by a method of nonlinear least squares²² to produce values of Q_{isp} , Q_u , and Q_d ; these are expressed as logarithms and are presented in Table II. The results for 25, 250, and 350° are plotted according to eq 7 in Figures 1-3 and show the general linear behavior observed at all five temperatures. (The open and filled circles in the figures are used only to distinguish between data at different ionic strengths.) The data at 0.5 and 150° with the corresponding values of Q_u from Table II also provide straight lines. All plots show a similar ionic strength effect on solubility at constant temperature. In Figures 1-3 a dashed curve was drawn to indicate

Figure 1. The solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in Na_2SO_4 - NaNO_3 - H_2O at 25° and several constant ionic strengths.

Figure 2. The solubility of CaSO_4 in Na_2SO_4 - NaNO_3 - H_2O at 250° and several constant ionic strengths.

$a_{\text{H}_2\text{O}}^3$, which in molal units would still equal $(55.51)^3$. An allowance for a variation in the activity of water over the range of electrolyte compositions at constant I was unnecessary to describe the system within the precision of the measurements. The authors also consider it misleading to mix units in an equilibrium constant expression, as is frequently done, by multiplying the activity of water on the mole fraction scale together with the molality of CaSO_4^0 and its activity coefficient. These remarks apply also to our considerations of Q_{isp} and K_{isp} for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

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solubility in $\text{NaNO}_3\text{-H}_2\text{O}$ as a function of I , again at constant temperature; there is no added Na_2SO_4 in these solutions so that it represents the three-component system $\text{CaSO}_4\text{-NaNO}_3\text{-H}_2\text{O}$. Similar experimental conditions prevailed at the other temperatures (see Table I). The data at 0.5 and 25° contain some results at zero molality of NaNO_3 or results for the system $\text{CaSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$.

Table II: Experimentally Obtained Equilibrium Quotients at Several Ionic Strengths from 0.5 to 350°

Temp. ^a °C	I	$-\log Q_{\text{isp}}$	$-\log Q_u$	$-\log Q_d$
0.5	0.229	3.416	2.49	0.93
	0.503	3.063	2.52	0.54
	1.02	2.726	2.47	0.26
	2.14	2.376	2.56 (2.37) ^b	0.01
	6.02	2.210	2.17	0.04
25	0.236	3.365	2.33	1.03
	0.504	3.055	2.30	0.76
	1.01	2.765	2.24	0.52
	2.10	2.478	2.22	0.26
	6.00	2.269	2.14 (2.04) ^b	0.23
150	0.250	4.540	3.10	1.44
	0.506	4.195	3.19	1.00
	1.07	3.891	2.92	0.97
	2.19	3.537	2.88	0.66
	5.82	3.196	2.66	0.54
250	0.244	5.836	3.95	1.89
	0.498	5.417	3.68 (3.87) ^b	1.55
	1.06	4.802	3.71	1.09
	2.21	4.248	3.47	0.78
	5.82	3.473	2.89	0.58
350	0.263	7.086	4.91	2.18
	0.542	6.291	4.62	1.67
	1.14	5.567	3.80 (4.24) ^b	1.33
	2.30	4.643	3.65	0.99
	6.08	3.521	2.69	0.83

^a The saturating solid is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 0.5 and 25° and CaSO_4 at 150–350°. ^b The value obtained from the plot of $\log Q_u$ vs. $I^{1/2}$ (Figure 5).

The only deviations from the linear relationship, within the precision of the measurements, are found at 350° for the lower ionic strengths of 0.26 and 0.54 (see Figure 3). Without additional information, it is difficult to account for these deviations, although they may be related to significant hydrolysis of Ca^{2+} at the highest temperature. The fact that eq 7 applies to the experimental data substantiates the assumption of constant activity coefficients at constant ionic strength with varying $\text{Na}_2\text{SO}_4/\text{NaNO}_3$ ratio. This is more readily apparent by writing eq 7 in the equivalent form

$$s = (K_u/\gamma_{\text{CaSO}_4^0}) + [K_{\text{isp}}/([\text{SO}_4^{2-}]\gamma_{\text{Ca}^{2+}}\gamma_{\text{SO}_4^{2-}})] \quad (12)$$

where K_u and K_{isp} are the equilibrium constants (or equilibrium quotients at $I = 0$ expressed by eq 2 and 5,

Figure 3. The solubility of CaSO_4 in $\text{Na}_2\text{SO}_4\text{-NaNO}_3\text{-H}_2\text{O}$ at 350° and several constant ionic strengths.

respectively) and $\gamma_{\text{CaSO}_4^0}$, $\gamma_{\text{Ca}^{2+}}$, and $\gamma_{\text{SO}_4^{2-}}$ are the activity coefficients for the corresponding species in solution. The above description, however, does not explain differences in solubility of CaSO_4 in other 1-1 and mixed-electrolyte solutions at very high, constant ionic strengths, as our recent unpublished results show. Some additional interpretation therefore is still needed to account fully for the general solubility behavior under these conditions.

The description of the data by eq 7, within experimental error, constitutes a valid argument against the formation of significant amounts of either CaNO_3^+ or NaSO_4^- . If both of these ion pairs form, the solubility of calcium sulfate, s , would no longer be given by eq 10 but would be given by the equation

$$s = [\text{CaSO}_4^0] + [\text{Ca}^{2+}] + [\text{CaNO}_3^+] = \frac{Q_u}{[\text{SO}_4]_{\text{total}} - Q_u - [\text{NaSO}_4^-]} + [\text{CaNO}_3^+] \quad (13)$$

where $[\text{SO}_4^{2-}] = [\text{SO}_4]_{\text{total}} - Q_u - [\text{NaSO}_4^-]$. If it is assumed that no NaSO_4^- forms when the concentration of added Na_2SO_4 is low, eq 13 indicates that an upward curvature of the lines (Figures 1-3) is expected, resulting from the formation of increasingly higher concentrations of CaNO_3^+ as the NO_3^- concentration increases. If CaNO_3^+ does not form at the lower concentrations of NaNO_3 , then an upward curvature of the lines should appear as the concentration of added Na_2SO_4 increases, opposite to the previous case, resulting from the increased solubility of CaSO_4 due to the formation of increasingly greater amounts of NaSO_4^- . If both ion pairs, CaNO_3^+ and NaSO_4^- , form in conjunction with CaSO_4^0 , then the last two terms in eq 13 must change with mixed-electrolyte composition

such that a straight line with slope Q_{isp} is still obtained. This is necessary to satisfy the results of the plots in Figures 1-3. While it is true that CaNO_3^+ and NaSO_4^- may play a significant role only where the molalities of Ca^{2+} , Na^+ , NO_3^- , and SO_4^{2-} are highest, the stringent condition placed on eq 13 for linearity must be met at all five experimental temperatures. We suggest that linearity under these conditions is highly improbable and prefer to present the simpler model which satisfactorily describes the experimental results. (Within experimental uncertainty, lower limits of 1350 and 14,000 for the dissociation quotients of CaNO_3^+ and NaSO_4^- , respectively, were calculated at $I = 6$ and at 25°).

Both the slope (Q_{isp}) and the intercept (Q_u or $[\text{CaSO}_4^0]$) of the lines are seen to increase with an increase in ionic strength at constant temperature (see Figure 1), following the same general relationship as does the solubility. The ratio slope/intercept, which is the dissociation quotient, Q_a , and is independent of the extent of hydration of the solid phase, also increases with an increase in I at constant temperature. The fraction of CaSO_4 in the form of ion pairs, Q_u/s , in aqueous NaNO_3 (no added Na_2SO_4) at constant I increases slightly in going from 0.5 to 25° where the solid phase is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Where CaSO_4 is the saturating solid (100 – 350°), this fraction decreases gradually with increasing temperature. At constant temperature, the degree of association decreases as the ionic strength increases up to about $I = 3$, from which point it remains essentially constant. The fraction associated decreases from approximately 0.14 to 0.07 at 0.5° , 0.18 to 0.10 at 25° , 0.12 to 0.07 at 150° , and 0.09 to 0.05 at 250° , at $I = 0.25$ and 3 – 6 , respectively. Only two data points are available at 350° with no added Na_2SO_4 ; therefore, no range is reported. Comparable results¹⁹ for CaSO_4 dissociation at 250° have been found in the system CaSO_4 – NaCl – H_2O .

Thermodynamic Considerations. (a) Solid Neutral Species Equilibrium. A relationship between the logarithm of the activity coefficient for the neutral species and the ionic strength, at constant temperature, was obtained by starting arbitrarily with an equation analogous to the Debye-Hückel expression

$$\log \gamma_{\text{CaSO}_4^0} = -S^*I^{1/2}/(1 + A_u I^{1/2}) \quad (14)$$

where S^* and A_u are constants. In terms of the equilibrium involved (eq 1), the form is

$$\log Q_u = \log K_u + [S^*I^{1/2}/(1 + A_u I^{1/2})] \quad (15)$$

The unsmoothed results for Q_u and I were treated by the method of least squares to obtain simultaneously values for K_u , S^* , and A_u . The values for A_u varied randomly with temperature. Therefore, the average value, within the standard error, of 0 over all temperatures was adopted. Equation 15 was then reduced to eq 16

$$\log Q_u = \log K_u + S^*I^n \quad (16)$$

the least-squares process was repeated, and the values for K_u , S^* , and the exponent n were computed. The average value over all temperatures for n was 0.5 . The results for S^* are plotted in Figure 4 as a function of temperature to obtain smoothed values. Finally, $\log K_u$ was calculated with eq 16 by the method of least squares from the raw values for $\log Q_u$ at each ionic strength, using $n = 0.5$ and smoothed S^* values. (The values for Q_u from the solubility measurements at 0.5° and $I = 2.14$, at 25° and $I = 6.00$, at 250° and $I = 0.498$, and at 350° and $I = 1.14$ were not used in these calculations, since they were inconsistent randomly with the other results.) The results are shown in Figure 5, where $\log Q_u$ is plotted as a function of $I^{1/2}$. The intercept and the slope of the line for each temperature correspond to the calculated values of $\log K_u$ and S^* , respectively. The activity coefficients for the neutral species CaSO_4^0 are equal to K_u/Q_u . This ratio decreases sharply with increasing ionic strength at all temperatures and especially at the higher temperatures. Hence, the experimental results show a pronounced ionic strength effect upon the activity coefficient of the ion pair CaSO_4^0 . In many instances where measurements are lacking, activity coefficients of neutral species are arbitrarily set equal to unity,^{8–10} or their logarithms are allowed to vary linearly with ionic strength, with a calculation or estimate of the slope.

Theoretical equations have been derived by Scatchard and Kirkwood,²³ Kirkwood,²⁴ and Bateman,²⁵ *et al.*, which predict the logarithm of the activity coefficient for a neutral species or a dipolar ion, in the limit,

Figure 4. The comparison to 350° between the limiting slopes for a 1-1 electrolyte and the observed slopes for associated CaSO_4 .

(23) G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297 (1932).

(24) J. G. Kirkwood, *Chem. Rev.*, **24**, 233 (1939).

(25) L. C. Bateman, *et al.*, *J. Chem. Soc.*, 979 (1940).

Figure 5. The relationship between the ionic strength and the molality of associated CaSO_4 from 0.5 to 350°.

to have a dependence on the ionic strength to the first power. The measurements of Cohn²⁶ and his coworkers on amino acids, proteins, and peptides, along with the considerations of Randall and Failey²⁷ on the solubility of H_2 , O_2 , N_2 , N_2O , CO_2 , H_2S , NH_3 , C_2H_2 , and I_2 in salt solutions, confirm the form of the limiting law, with the initial term linear in the ionic strength. Above an ionic strength of 0.05–0.1, a polynomial expression is required to relate this dependence. The treatment of our data, given above, establishes empirically, within experimental error, a square-root dependence over a wide range of ionic strength and temperature. A fit to a polynomial expression of equal accuracy was not made since it would require the use of more numerous coefficients. Other investigators^{28,29} find that their results for $\log$ (solubility) or $\log$ (activity) are best described by $I^{1/2}$ at still lower ionic strengths.

The ion pair CaSO_4^0 can be pictured as an unsymmetrical molecule with a dipole moment such that the limiting slope of $\log \gamma_{\text{CaSO}_4^0}$ changes with temperature, in a qualitative manner, as does the Debye-Hückel limiting slope for a 1-1 electrolyte (see Figure 4). Figure 6 shows that the limiting slope for the neutral species CaSO_4^0 (molar units) varies with $1/(DT)^2$. The theoretical considerations of neutral molecules by Kirkwood²⁴ and Bateman, *et al.*,²⁵ agree with this observation. In contrast, the limiting slope for ions varies with $1/(DT)^{1/2}$ (Figure 6).

In order to calculate the values for the various thermodynamic functions describing the solubility equilibrium for anhydrous CaSO_4 (see eq 1), the assumption

Figure 6. The dependence of the limiting slope for CaSO_4^0 upon the product of the dielectric constant and temperature (°K).

Figure 7. The equilibrium constants for CaSO_4 from 0.5 to 350°.

was made that the change in standard molal heat capacity, ΔC_p^0 , is a linear function of temperature.

(26) E. J. Cohn, *Chem. Rev.*, **19**, 241 (1936); E. J. Cohn, *et al.*, *J. Amer. Chem. Soc.*, **58**, 2365 (1936); E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids, and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943, pp 236–303.

(27) M. Randall and C. F. Failey, *Chem. Rev.*, **4**, 271, 285 (1927).

(28) N. R. Joseph, *J. Biol. Chem.*, **116**, 353 (1936).

(29) A. H. Palmer, *ibid.*, **104**, 359 (1932).

Table III: Thermodynamic Functions for the Equilibrium $\text{CaSO}_4(\text{s}) \rightleftharpoons \text{CaSO}_4^0(\text{aq})$

Temp, °C	K_u, m	ΔG° , kcal mol ⁻¹	ΔH° , kcal mol ⁻¹	ΔS° , cal mol ⁻¹ deg ⁻¹	ΔC_p° , ^b cal mol ⁻¹ deg ⁻¹
0	1.08×10^{-3}	2.46	-4.05	-23.8	8.88
25	5.85×10^{-3}	3.05	-3.95	-23.5	-0.37
50	3.47×10^{-3}	3.64	-4.07	-23.9	-9.63
100	1.37×10^{-3}	4.89	-5.02	-26.5	-28.1
150	5.42×10^{-4}	6.32	-6.89	-31.2	-46.7
200	1.94×10^{-4}	8.03	-9.68	-37.4	-65.2
250	6.10×10^{-5}	10.1	-13.4	-44.9	-83.7
300	1.65×10^{-5}	12.5	-18.0	-53.3	-102
350	3.84×10^{-6}	15.4	-23.6	-62.7	-121

^a The solid phase is anhydrous CaSO_4 ; when $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the solid phase, $K_u = 2.49 \times 10^{-3}$ and 3.83×10^{-3} at 0 and 25°, respectively. ^b ΔC_p° as a linear function of temperature.

With the temperature in degrees Kelvin, this leads to

$$\log K_u = -142.051 + 55.3676 \log T + (4435.6/T) - 0.0404600T \quad (17)$$

which defines the curve in Figure 7, where $\log K_u$ is plotted against the reciprocal of the absolute temperature. Estimates were made of K_u at 0.5 and 25° for anhydrous CaSO_4 from the experimentally determined values of K_u for the dihydrate by noting the relative difference in K_{sp}^0 's which were obtained previously at this laboratory^{10,20} for the two solids. The curve was determined by the method of nonlinear least squares mentioned earlier and describes the results well from 0.5 to 350°. Use of the van't Hoff expression with eq 17 relates the standard enthalpy change to the temperature (°K) by

$$\Delta H^\circ (\text{cal mol}^{-1}) = -20290 + 110.01T - 0.185104T^2 \quad (18)$$

The results for K_u and ΔH° were used to calculate ΔG° and ΔS° for the reaction from the usual thermodynamic equations. All calculated values are listed in Table III. There is no apparent explanation for the shallow maxima through which the values for ΔH° and ΔS° pass near 25°. Considering the change in heat capacity to be independent of temperature eliminated the maxima but created a greater variance of fit between data and curve.

(b) *Solid-Ion Equilibrium.* The net equilibrium for the dissolution of CaSO_4 to form ions is

which can be expressed by

$$K_{isp} = Q_{isp} \gamma_{\pm}^2 \quad (20)$$

where $\gamma_{\pm}$ is the mean ionic activity coefficient. Upon using an extended form of the Debye-Hückel expres-

sion for the mean ionic activity coefficient, this equation converts to

$$\log Q_{isp} = \log K_{isp} + [8SI^{1/2}/(1 + A_{isp}I^{1/2})] \quad (21)$$

where S is the limiting Debye-Hückel slope in molal units for a 1-1 electrolyte (0.4875, 0.5080, 0.6899, 0.9848, and 1.984 at 0.5, 25, 150, 250, and 350°, respectively), I is the ionic strength in molal units, and A_{isp} is a constant varying only with temperature. The experimental values for $\log Q_{isp}$ and I reported in Table II, along with the theoretical slope (S), were used in eq 21 to obtain preliminary values of $\log K_{isp}$ and A_{isp} at each temperature by the method of least squares. The calculated values for A_{isp} were smoothed with respect to temperature, and a revised value of $\log K_{isp}$ then was calculated. In Figure 8, $\log Q_{isp}$ is plotted against $I^{1/2}/(1 + A_{isp}I^{1/2})$ and straight lines result over the range of ionic strength from 0.25 to 6 at 0.5, 25, and 150°. At 250 and 350° there are deviations from the straight-line relationship above ionic strengths 1.5-2. The smoothed values of A_{isp} are presented in the figure; the intercept of the line for each temperature is equal to $\log K_{isp}$, the ionic solubility product constant for that temperature. The logarithm of the ionic activity coefficient at a given ionic strength and a particular temperature is given by $1/2(\log K_{isp} - \log Q_{isp})$.

In Figure 7 the variation of $\log K_{isp}$ for anhydrous CaSO_4 is plotted vs. $1/T$ (°K). Again, the experimentally derived values for K_{isp} at 0.5 and 25° were for the saturating solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Therefore, estimates of K_{isp} for CaSO_4 at these temperatures were made by the method described above for obtaining the corresponding K_u 's. In addition, the apparently low calculated result at 350° was not included in the computation of the curve representing the best least-squares fit of the data. The analogous discrepancy occurred at 350° in the determination of K_{sp}° for $\text{Ca}(\text{OH})_2$, so that now there is reason to suspect that the solubilities of these compounds are decreasing more sharply than expected as the temperature rises from 300° to the critical temperature of water, 374°.

Table IV: Thermodynamic Functions for the Net Equilibrium $\text{CaSO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

Temp, °C	K_{isp}, m^2	ΔG° , kcal mol ⁻¹	ΔH° , kcal mol ⁻¹	ΔS° , cal mol ⁻¹ deg ⁻¹	ΔC_p° , ^b cal mol ⁻¹ deg ⁻¹
0	1.24×10^{-4}	4.88	-5.05	-36.4	-23.8
25	5.41×10^{-5}	5.82	-5.80	-39.0	-35.7
50	2.38×10^{-5}	6.83	-6.84	-42.3	-47.6
100	4.35×10^{-6}	9.15	-9.82	-50.8	-71.5
150	6.72×10^{-7}	12.0	-14.0	-61.3	-95.3
200	8.48×10^{-8}	15.3	-19.3	-73.2	-119
250	8.69×10^{-9}	19.3	-25.9	-86.4	-143
300	7.27×10^{-10}	24.0	-33.6	-101	-167
350	5.04×10^{-11}	29.4	-42.6	-115	-191

^a The solid phase is anhydrous CaSO_4 ; when $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the solid phase, $K_{\text{isp}} = 2.87 \times 10^{-5}$ and 3.03×10^{-5} at 0 and 25°, respectively. ^b ΔC_p° as a linear function of temperature. ^c $K_{\text{isp}} = 1.88 \times 10^{-12}$ from the experimental data at 350° (see the text).

Figure 8. The variation of the ionic solubility product for CaSO_4 with the ionic strength function from 0.5 to 350°.

The values for the thermodynamic functions of this equilibrium when anhydrous CaSO_4 is the solid phase were determined, again assuming that ΔC_p° is a linear function of temperature. Hence

$$\log K_{\text{isp}} = -133.207 + 53.5472 \log T + (3569.6/T) - 0.0520925T \quad (22)$$

and the standard enthalpy change-temperature correlation is given by

$$\Delta H^\circ (\text{cal mol}^{-1}) = -16,331 + 106.39T - 0.238323T^2 \quad (23)$$

Calculated values for the thermodynamic functions at several temperatures are given in Table IV. Again, it was found that considering ΔC_p° for the reaction as a constant independent of temperature was not satis-

factory. The mean heat capacities ($\overline{\Delta C_p^\circ}$) for the reaction at 25, 25–100, 25–150, and 25–200° from this investigation are -36, -54, -66, and -88 cal deg⁻¹ mol⁻¹, respectively. Corresponding values for ΔC_p° of -85, -74, -70, and -74 cal deg⁻¹ mol⁻¹ were calculated from Criss and Cobble's³⁰ average ionic heat capacities along with Kelley's³¹ expression for the heat capacity of solid anhydrous CaSO_4 . The latter values remain essentially constant with rising temperature, and a relatively good agreement with our results exists at the higher temperatures.

(c) *Dissociation Equilibrium.* The equilibrium quotients for the dissociation of the neutral molecule into ions (eq 3) were obtained from eq 5. The experimental, unsmoothed results in Table II for $\log Q_{\text{isp}}$ and $\log Q_u$ were used, with the exception of four values for $\log Q_u$ that were taken from the straight lines in Figure 5. To evaluate K_d at each temperature from the experimental information, the following identities were applied

$$\log Q_d = \log Q_{\text{isp}} - \log Q_u = \log K_{\text{isp}} + [8SI^{1/2}/(1 + A_{\text{isp}}I^{1/2})] - \log K_u - S^*I^{1/2} \quad (24)$$

leading to

$$\log Q_d + S^*I^{1/2} = \log K_d + [8SI^{1/2}/(1 + A_{\text{isp}}I^{1/2})] \quad (25)$$

The function $\log Q_d + S^*I^{1/2}$ is plotted against $I^{1/2}/(1 + A_{\text{isp}}I^{1/2})$ in Figure 9. The linear relationship using the theoretical limiting slope (S) is seen to hold well except at 250°, where the dashed curve shows the deviation from linearity. This curvature may be due to experimental error, since both the 150 and 350° results lie reasonably close to the lines calculated by the method of least squares. However, the intercept value, $\log K_d$,

(30) C. M. Criss and J. W. Cobble, *J. Amer. Chem. Soc.*, **86**, 5390 (1964).

(31) K. K. Kelley, U. S. Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960, p 46.

Table V: Thermodynamic Functions for the Dissociation Equilibrium $\text{CaSO}_4(\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

Temp, °C	K_d, m	ΔG° , kcal mol ⁻¹	ΔH° , kcal mol ⁻¹	ΔS° , cal mol ⁻¹ deg ⁻¹	ΔC_p° , cal mol ⁻¹ deg ⁻¹
0	1.17×10^{-2}	2.41	-1.11	-12.9	-31.1
25	9.29×10^{-3}	2.77	-1.93	-15.8	-34.0
50	6.83×10^{-3}	3.20	-2.81	-18.6	-36.9
100	3.13×10^{-3}	4.27	-4.80	-24.3	-42.6
150	1.23×10^{-3}	5.63	-7.07	-30.0	-48.4
200	4.35×10^{-4}	7.28	-9.63	-35.7	-54.1
250	1.42×10^{-4}	9.21	-12.5	-41.5	-59.9
300	4.40×10^{-5}	11.4	-15.6	-47.2	-65.6
350	1.30×10^{-5}	13.9	-19.0	-52.9	-71.4

^a ΔC_p° as a linear function of temperature.

Figure 9. The relationship between the dissociation quotient for CaSO_4 and the ionic strength from 0.5 to 350°.

at 250° does not appear to be especially erroneous, since on Figure 7 it falls close to the smooth curve with the results at lower temperatures, and this curve has a logical symmetry with the other curves shown. Extrapolation above 250° is used in Figure 7 for the same reason given earlier for the $\log K_{1sp}$ curve, since the two are related.

With ΔC_p° as a linear function of temperature, the dependence of the equilibrium constant for eq 3 upon temperature is

$$\log K_d = 3.53483 + 0.180124 \log T - (674.13/T) - 0.0125832T \quad (26)$$

independent both of the presence or form of solid CaSO_4 (hydrate or anhydrous). Calculated values for $\text{p}K_d$ at 0, 25, and 40° are 1.93, 2.03, and 2.11, respectively, which are 0.28 pK unit less at each temperature than those estimated by Bell and George.⁹ The 25° value of Money and Davies⁵ is 2.28 and that of Nakayama and Rasnick⁸ is 2.27 for $\text{p}K_d$. In all three of these cases where $\text{p}K_d = 2.29 \pm 0.02$ at 25°, it was assumed that the activity coefficient for the neutral CaSO_4^0 species was unity. The relationship

$$K_d = Q_d \gamma_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}} / \gamma_{\text{CaSO}_4^0} \quad (27)$$

with the fact that we find $\gamma_{\text{CaSO}_4^0}$ decreasing sharply from unity with increasing I indicates one reason for the earlier values of K_d being smaller and the values for $\text{p}K_d$ being larger than is the actual case. The present determination of values for $\gamma_{\text{CaSO}_4^0}$ should have produced a more reliable value for K_d . Within the limits of the stated precision, estimates of this constant made previously at this laboratory¹⁰ at 0, 25, 100, and 200° agree with the present ones. The standard enthalpy change is given by

$$\Delta H^\circ (\text{cal mol}^{-1}) = 3084 + 0.360T - 0.057568T^2 \quad (28)$$

Calculated values for ΔH° , ΔG° , and ΔS° at several temperatures are given in Table V. Bell and George reported values at 25° for ΔG° , ΔH° , and ΔS° of 3.15 ± 0.03 kcal mol⁻¹, -1.65 ± 0.20 kcal mol⁻¹, and -16.1 ± 0.8 cal deg⁻¹ mol⁻¹, respectively. At temperatures above 100°, there is reasonably good agreement between our results for $\log K_d$ and the extrapolated ones by Helgeson.¹¹

3.4 SOLUBILITY OF CALCIUM SULFATE DIHYDRATE IN 1-1 ELECTROLYTES AS A FUNCTION OF TEMPERATURE AND IONIC STRENGTH

W. L. Marshall and R. Slusher

Preliminary measurements have been made of the solubility of calcium sulfate dihydrate (gypsum) in a number of 1-1 electrolytes for the temperature range 0 to 80°C. Data were obtained at ionic strength 3 and 6 (molal units) for LiCl, LiNO₃, and NaNO₃ and, because of limited solubilities, at ionic strength 3 only for KCl and KNO₃. Similar data for NaCl were published earlier.¹

Table 3.4.1 gives the results for these six salts at an ionic strength of 3. They show moderate differences.

At high ionic strengths, solubilities in the various media are influenced by differences in the mean activity coefficients of calcium sulfate, by large differences in the activity of water, and by possible phase changes (e.g., double-salt formation).

TABLE 3.4.1
MOLAL SOLUBILITIES OF CaSO₄·2H₂O IN
1-1 ELECTROLYTES AT IONIC STRENGTH 3

Supporting Electrolyte	Temperature (°C)		
	0	25	80
LiCl	0.037	0.046	0.055
NaCl	.055	.058	.060
KCl	.090	.101	.107
LiNO ₃	.063	.070	.073
NaNO ₃	.072	.074	.069
KNO ₃	-	.157	.078

1. W. L. Marshall and R. Slusher, J. Phys. Chem. **70**, 4015 (1966).