WATER RESEARCH PROGRAM

BIENNIAL PROGRESS REPORT
FOR THE PERIOD
MARCH 15, 1968 TO MARCH 15, 1970

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, 1968, to March 15, 1970

PROPERTIES OF SOLUTIONS

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

AUGUST 1973

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OAK RIDGE NATIONAL LABORATORY
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*Paper published in open literature.

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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 U.S. 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 302 (ORNL-CF-67-8-55). For subsequent biennia, the work was divided into a number of categories and is being reported in ORNL memoranda, some of which have also been issued as Office of Saline Water Research and Development Progress Reports, as follows:

Second Biennium, March 15, 1964 to March 15, 1966

Properties of Solutions: OSW R&D Progress Report 685 (July 1971),
ORNL-CF-70-6-30 (October 1970)

Reactions and Transport Phenomena at Surfaces. Corrosion Studies:
ORNL-TM-4097 (in preparation)

Separations Processes: OSW R&D Progress Report 508 (February 1970),
ORNL-CF-69-5-41 (September 1969)

Third Biennium, March 15, 1966 to March 15, 1968

Properties of Solutions: ORNL-TM-4096 (May 1973)

Reactions and Transport Phenomena at Surfaces: ORNL-TM-4099 (March 1973)

Separations Processes: ORNL-TM-4000 (November 1972)

Fourth Biennium, March 15, 1968 to March 15, 1970

Properties of Solutions: ORNL-TM-4212 (this report)

Reactions and Transport Phenomena at Surfaces (to November 1, 1970):
ORNL-TM-4145 (May 1973)

Separations Processes: ORNL-TM-4001 (February 1973)

Fifth Biennium, March 15, 1970 to close of contract:

Properties of Solutions: ORNL-TM-4213 (in preparation)

Separations Processes: ORNL-TM-4236 (in preparation)

In addition, reports are planned covering Corrosion Studies.

The present report covers the work performed during the fourth biennium (the period March 15, 1968 to March 15, 1970) on the Properties of Solutions. 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 1970 but which cover work that was done mainly in the fourth biennium have been included in this volume, and, conversely, some work started during this period but developed mainly in the fifth 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 American Chemical Society 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.

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.

SUMMARY

Most natural waters that are potential feeds for desalination contain more than one solute, and the chemistry of mixed electrolytes is therefore fundamental to desalting. The ORNL Water Research Program has had a continuing interest in thermodynamic and other properties of aqueous solutions (Section 1), specifically the determination of free energies of multi-component aqueous solutions containing ions frequently found in natural waters. In addition to such studies in entirely aqueous medium, thermodynamic data for a variety of organic-water mixtures have been collected to provide insight into the mechanism by which hyperfiltration membranes reject salt (Section 2). All these studies in addition to the primary, practical objective, also expand our knowledge concerning the fundamental nature of solutions.

The objectives of many of the studies in Section 1 were the same: to determine the osmotic coefficients from a limited number of measurements and from these to determine the excess free energy and the activity coefficients in electrolyte mixtures. From this information, important practical quantities, such as boiling point elevation, freezing point depression, and minimum energies of desalting may be obtained. The free-energy relationships in the six binary salt mixtures made up from NaCl, Na₂SO₄, MgSO₄, and MgCl₂ in aqueous solution were investigated; isopiestic measurements on the four systems involving a common ion are reported in Section 1.2, and the results of isopiestic measurements on the two binary salt systems without a common ion are described in Section 1.3. Both these sections treat the solutes as neutral electrolytes, whereas the ion-component approach (initially considered in Section 1.1) is shown to develop more tractable mathematical expressions in Section 1.4.

Section 2 chiefly summarizes solubility data for a number of inorganic salts in aqueous solutions of a number of organic solvents. From such solubility data for NaCl, the activity coefficients of NaCl at saturation in aqueous solutions of a variety of organic solvents were computed (Sections 2.1 and 2.2). Section 2.3 summarizes the results of a miscibility study in the system pyridine-sulfuric acid-water, a corollary to the study of activity coefficients of salts in pyridine-water-acid mixtures.

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1. THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS

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1.1 THE EXCESS FREE ENERGY AND RELATED PROPERTIES OF SOLUTIONS CONTAINING ELECTROLYTES

George Scatchard

Contribution from the Department of Chemistry and the Laboratory of Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, and the Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Abstract: Analytical expressions are developed for the excess free energy of solutions containing any number of electrolytes of any valence types, and those properties which may be derived from it by differentiation; such as the osmotic coefficient, the activity coefficients of the components, and the excess enthalpy. Approximations are discussed, such as Brønsted's principle of specific interactions of ions, Harned's rule, Young's rule, the cross-square rule, and Guggenheim's recent hypothesis. The use of ions as components and of equivalent concentrations is found very useful.

Recently there has been a renewed interest in mixed electrolyte solutions, much of it inspired by the desalination of sea water. From 1934 to 1964 there have been eight studies from the MIT laboratory of the osmotic coefficient of dilute aqueous solutions with more than two components.¹⁻⁸

References 1-4 include measurements of freezing point depressions, ref 6 and 8 include measurements of isotonic (isopiestic) equilibrium, and ref 5 and 7 include no new experimental work. Reference 1 deals with two nonelectrolyte solutes, ref 2 and 4 concern mixtures of one electrolyte with one or two nonelectrolytes, and the rest deal with electrolyte solutions. I have also been coauthor of two papers from the Oak Ridge National Laboratory^{9,10} on mixed electrolytes and consultant for several others. The practical objectives all were the same: to determine the osmotic coefficients from a limited number of measurements and to determine from these measurements the Gibbs free energy and the activity coefficients in electrolyte mixtures from those of solutions of single solutes, or some-

what better with the addition of mixtures with a common ion. The approaches have varied somewhat over the years, however, and it seems worthwhile to present a consistent approach to the whole field and to discuss more fully solutions of electrolytes of different valence types.

The use of ions as components, with the restriction that the total charge is zero, gives an excellent contrast to the earlier treatments. We did use this convention in ref 6, but the description was very terse and without explanation. It also contained an excessive number of misprints.

Solutions of Nonelectrolytes

Reference 1 inaugurated the policies of starting such studies with the total Gibbs free energy and of expressing the excess free energy of nonelectrolyte solutions as an integral power series in the molalities of the solutes. This is analogous to the virial expansion of $pV/RT\sum n_i$ for a gas or gas mixture in terms of the volume concentrations of the components. The corresponding expansion in terms of mole fractions is analogous to the more complicated virial expansion for a gas in terms of the partial pressures.

We take the pure solvent as the standard state of unit activity for itself and as the reference state of unit activity coefficient for each solute, and we write

$$G^e/RT = G/RT - \sum_j n_j (G_j^0/RT - 1 + \ln m_j) = W \sum_{jk} b_{jk} m_j m_k + W \sum_{jkl} d_{jkl} m_j m_k m_l + \dots \quad (1)$$

$$= W(\sum_i m_i)^2 \sum_{jk} b_{jk} x_j x_k + \frac{W(\sum_i m_i)^3 \sum_{jkl} d_{jkl} x_j x_k x_l}{W(\sum_i m_i)^3 \sum_{jkl} d_{jkl} x_j x_k x_l} + \dots \quad (2)$$

(1) G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **56**, 1486 (1934).

(2) G. Scatchard and S. S. Prentiss, *ibid.*, **56**, 2314 (1934).

(3) G. Scatchard and S. S. Prentiss, *ibid.*, **56**, 2320 (1934).

(4) G. Scatchard and M. A. Benedict, *ibid.*, **58**, 837 (1936).

(5) G. Scatchard, *Chem. Rev.*, **19**, 309 (1936).

(6) G. Scatchard and R. G. Breckenridge, *J. Phys. Chem.*, **58**, 596 (1954); **59**, 1234 (1955).

(7) G. Scatchard, *J. Am. Chem. Soc.*, **83**, 2636 (1961).

(8) R. L. Yoest, Ph.D. Thesis, Massachusetts Institute of Technology, 1964.

(9) J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, **63**, 787 (1959).

(10) R. M. Rush and G. Scatchard, *ibid.*, **65**, 2240 (1961).

in which G is the Gibbs free energy of the system, G^e is the excess free energy defined by eq 1, m_j is the molality of solute j , n_j/W , G_j° is its "standard molal free energy," n_j is the number of moles of j , W is the number of kilograms of solvent, and b_{jk} , d_{jkl} , etc. are coefficients which, like G_j° , are functions of T and p and of the nature of the solvent, but not of the composition of the solute. The use of G^e/RT has the advantage that it is dimensionless.

In the first decade of this century, before G. N. Lewis, J. N. Brønsted, and N. Bjerrum began their studies of ion activities, there was much interest in nonelectrolyte mixtures. The theories ranged from van Laar's use of the van der Waals equation¹¹ to Dolezalek's purely chemical theory.¹² van Laar extended the van der Waals theory by making the excluded volume, b , a function of the solvation. He used only two parameters per mole, b and a . Dolezalek, on the other hand, attributed all deviation from ideality to chemical action; each irregularity in the curve demanded a new chemical species with a new constant.

It was realized that positive deviations from ideality were usually roughly proportional to m , and that negative deviations were roughly proportional to $m/(1 + bm)$. There was much interest in salting-out, which was attributed to the removal of solvent by solvation of the salt.

Reference 1 treats ethanol, glycine, and their mixtures. G^e/RT of ethanol is slightly negative and that of glycine is much more negative. To Dolezalek this would mean that glycine is largely associated and ethanol slightly associated. G^e/RT of their 1:2 and 2:1 mixtures, however, is positive, meaning solvation to Dolezalek. In ref 2, it is shown that ethanol is salted out by sodium chloride, but glycine is salted in. This would offer quite a problem to Dolezalek. The physical picture is that ethanol decreases the dielectric constant of water but glycine increases it. From ref 4, we find that dioxane gives almost ideal solutions with water but is salted out about three times as much as ethanol. Reference 3 deals with the reciprocal salt pair: $\text{KNO}_3\text{-LiCl}$.

Electrolyte Solutions. The Non-Debye-Hückel Term

There are two important differences between solutions containing only nonelectrolytes and those containing one or more electrolytes, both due to the charges on the ions. The first is that there cannot be a solution of a single solute because each equivalent of cation must be balanced by an equivalent of anion. The second is that the free energy per mole of solute, the osmotic coefficient, and the logarithms of the activity coefficients contain terms in the square root of the ionic strength which cannot be represented by integral power series in the concentrations. We will split G^e for an electrolyte solution into the Debye-Hückel term, G^{DH} , and the remainder G^n . We will consider G^{DH} in the next section.

If the neutral molecules are chosen as solute components, a series of arbitrary decisions is necessary.

The first is for a mixture of two salts of different valence types with a common ion. It is seldom recognized because any chemist would choose the ions-as-solutes answer: that in sodium and magnesium chloride, for example, the number of equivalents of NaCl is equal to that of sodium ion, and the number of equivalents of MgCl_2 is equal to that of magnesium ion.

The next decision arises when there are two cations and two anions. The "reasonable choice" suggested in ref 7 is not a useful one, because it does not extrapolate correctly for mixtures with a common ion. If the Rubicon is crossed, however, and the ions are chosen as components, all further decisions fall into line.

If the ions are taken as components with the restriction that $\sum_i n_i z_i = 0$, it is necessary to distinguish between neutral solutes, cations, and anions. We will denote solutes in general with the subscripts i, j, k, l as in eq 1 and 2, which are also applicable to electrolyte solutions. We will use the subscripts a, b, c, d for cations, e, f, g, h for anions, and p, q, r, s for neutral molecules.

It is most convenient to express the quantity and concentration of an ion in equivalents: $n_i' = n_i \delta_i$, $m_i' = m_i \delta_i$, where δ_i is the absolute value of the valence, $\delta_i = |z_i|$. At any stage we may reconvert to concentrations, or convert to ionic strengths by use of the corresponding relation $m_i' = 2I_i/\delta_i$. We write the equivalent fraction $x_j' = m_j'/(\sum_i m_i'/2)$, so that in a solution of a single electrolyte, a_f , x_a' and x_f' are each unity. It is useful to separate the sums into those for cations only, for anions only, and for the different mixtures.

The non-Debye-Hückel free energy, G^n , in dilute solution is given by

$$(G^n/RTW)_2 = \sum_i \sum_k m_j' m_k' b_{jk} \quad (3)$$

In a solution of a single electrolyte, a_f , $m_a' = m_f'$

$$\sum_i \sum_k m_j' m_k' b_{jk} = m_a' m_f' (2b_{af} + b_{aa} + b_{ff}) \quad (4)$$

In general, since $\sum m_a' = \sum m_f'$, $\sum m_a' m_f' = \sum m_a' m_b' = \sum m_f' m_g'$, $(2b_{ii} - b_{ii} - b_{ii}) = 0$, and

$$\begin{aligned} (G^n/RTW)_2 &= \sum_i \sum_k m_j' m_k' b_{jk} = \sum_a \sum_f m_a' m_f' (2b_{af} + \\ &\quad b_{aa} + b_{ff}) + \sum_a \sum_b m_a' m_b' (2b_{ab} - b_{aa} - b_{bb}) + \\ &\quad \sum_f \sum_g m_f' m_g' (2b_{fg} - b_{ff} - b_{gg}) = \sum_i \sum_k m_j' m_k' B_{jk} = \\ &\quad (\sum_i m_i'/2)^2 \sum_j \sum_k B_{jk} x_j' x_k' \quad (5) \end{aligned}$$

with

$$B_{jk} = (2b_{jk} - b_{jj} - b_{kk}) \quad (6a)$$

if $z_j z_k > 0$ and

$$B_{jk} = (2b_{jk} + b_{jj} + b_{kk}) \quad (6b)$$

if $z_j z_k < 0$.

$$\begin{aligned} (G^n/RTW)_3 &= \sum_i \sum_k \sum_l m_j' m_k' m_l' d_{jkl} = \\ &\quad (\sum_i m_i'/2)^3 [\sum_a \sum_f (D_{aaf} x_a'^2 x_f' + D_{aff} x_a' x_f'^2) + \\ &\quad \sum_a \sum_b (D_{aab} x_a'^2 x_b' + D_{abb} x_a' x_b'^2) + \\ &\quad \sum_f \sum_g (D_{ffg} x_f'^2 x_g' + D_{fgg} x_f' x_g'^2) + \\ &\quad \sum_a \sum_b \sum_f 2 D_{abf} x_a' x_b' x_f' + \sum_a \sum_f \sum_g 2 D_{afg} x_a' x_f' x_g'] \quad (7) \end{aligned}$$

$$(G^n/RTW)_1 = \sum_i \sum_j \sum_k m_i' m_j' m_k' m_l' i_{ijkl} \quad (8)$$

(11) J. J. van Laar, *Z. Physik. Chem.*, **72**, 723 (1910); **83**, 599 (1913).

(12) F. Dolezalek, *ibid.*, **64**, 727 (1908).

The Debye-Hückel Free Energy

The Debye-Hückel equation assumes that all the ions have the same size. We will assume this as a first approximation, but we will follow our longtime customs^{6,13} of using the ionic strength in moles per kilogram of solvent and of assuming that $ka/\sqrt{I} = a'$ is independent of temperature and pressure.

Then the Debye-Hückel free energy may be expressed as

$$G^{\text{DH}}/RT = WS \sum_i I_i X/a' \quad (9)$$

in which S is the Debye-Hückel slope for $\ln \gamma_{\pm}$ of a univalent electrolyte, a function of T and p , $I_i = m_i' \partial_i' / 2$, $x = \kappa a$, and

$$X = [x^2 - 2x + 2 \ln(1+x)]/x^2 = 2[(x/3) - (x^2/4) + (x^3/5) - (x^4/6) + \dots] \quad (10)$$

We assume that for a single electrolyte, the deviations from this equation may be represented by an integral power series in I , or in m' , which becomes part of the series discussed in the preceding section.

We have been moderately successful in describing the properties of solutions of simple ions with $a' = 1.5$. However, there is a large amount of evidence that more accurate expressions are given by assigning different values of a' to different electrolytes (equation in ref 7). For a mixture we take

$$G^{\text{DH}}/RT = WS \sum_a^+ \sum_t^- m_a' m_t' (\partial_a / \sum_g^- m_g' + \partial_t / \sum_b^+ m_b') X_{at}/a_{at}' \quad (11)$$

This equation depends upon the assumptions that $a_{at}' = (2a_{at} + a_{aa} + a_{tt})\kappa/4I^{1/2}$ and that $a_{ab}' = (2a_{ab} - a_{aa} - a_{bb})\kappa/4I^{1/2} = 0$. This latter assumption is not necessarily contradictory to the "primitive model" treatment of Mayer¹⁴ and Friedman¹⁵ which includes much more than the electrostatic terms. It is discussed in detail in ref 7. We assume only that deviations from eq 11 may be included in the integral power series in the concentrations.

If H^e is the excess enthalpy and V^e is the excess volume, $H^e/RT = -(\partial G^e/RT) \partial \ln t$ and $pV^e/RT = (\partial G^e/RT) \partial \ln p$. The assumptions used in our laboratory since 1942¹⁰ that each a_{at}' is independent of the temperature and pressure lead to expressions for H^e/RT and pV^e/RT of the same forms as those for G^e/RT with S and each b or b' replaced by its appropriate derivative. The differentiations may be carried further to give the heat capacity, the compressibility, or mixed quantities involving both temperature and pressure differentiation.

At constant temperature $\partial(G^e/RT)/\partial n_i = \ln \gamma_i$, and $\partial(G^e/RT)/\partial n_s = \partial \ln \gamma_s = -(\sum_i n_i/n_s)\phi$.

Approximate Rules

Most of the rules which follow have been given the names of men, though in no case has the man himself used this name.

Lewis Ionic Strength Rule. The boldest, and I think the oldest, approximation of G^e/RT or of one of its derivatives is that of Lewis¹⁶ that the activity coefficient of an ion depends only on the ionic strength. There is no record in his published papers that there was any theory behind this assumption. Lewis was so impressed by the successes of the rule that the activity coefficient of an ion depends only on the ionic strength that he felt that it must be universal. However, Brønsted¹⁷ showed that it requires that the activity coefficient be the same for all ions of the same valence type. With the perspective of almost half a century we can see that Brønsted proved that the ionic strength rule holds for one ion when it holds for all ions.

Brønsted's Principle of the Specific Interaction of Ions. In the same papers Brønsted presented the thesis that the electrostatic repulsion between ions of the same sign keeps them so far apart that the short-range attraction forces between them are zero. He assumed, however, that the forces due to solvation of the ions are unaffected. Since he limited his principle to 0.1 N solutions, it applies obviously to dilute solutions only. The confusion caused by an error in Brønsted's derivation is discussed fully in ref 6. We will treat Brønsted's principle as a special case of Harned's rule.

Harned's rule¹⁸ states that, in a mixture of two electrolytes with a common ion at constant ionic strength, each $\ln \gamma_i$ is a linear function of the ionic strength fraction. In the special case of Brønsted's principle, the slope is the same for the two coions, and $\ln \gamma_{af(bf)} = \ln \gamma_{bf(af)}$ if $\ln \gamma_{af(bf)}$ is the logarithm of the activity of af in bf , etc.

$$(G^n/RTW)_2 = \frac{B_{af}n_a'n_t' + B_{bf}n_b'n_t' + B_{ab}n_a'n_b'}{W^2} \quad (12)$$

$$\frac{\partial(G^n/RTW)}{\partial n_a'} + \frac{\partial(G^n/RTW)}{\partial n_t'} = \frac{B_{af}(n_a' + n_t') + B_{bf}n_b' + B_{ab}n_b'}{W} \quad (13)$$

$$= \frac{n_t'}{W}[B_{af}(2-y) + B_{bf}y + B_{ab}y] \quad (14)$$

$$= \frac{n_t'}{W}[2B_{af} + (B_{bf} - B_{af} + B_{ab})y] \quad (15)$$

if $y = n_b'/n_t'$, so

$$\frac{d}{dy} \left[\frac{\partial(G^n/RTW)}{\partial n_a'} + \frac{\partial(G^n/RTW)}{\partial n_t'} \right] = \frac{n_t'}{W}(B_{bf} - B_{af} + B_{ab}) \quad (16)$$

However, the Debye-Hückel activities are independent of the composition at constant ionic strength.

A very large majority of the measurements of ion activities are for the determination of single ion activities with a saturated potassium chloride bridge. Most

(13) G. Scatchard and L. F. Epstein, *Chem. Rev.*, **30**, 211 (1942).

(14) J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1950).

(15) H. L. Friedman, *ibid.*, **32**, 1351 (1960); "Ionic Solution Theory," Interscience Publishers, New York, N. Y., 1962.

(16) G. N. Lewis and M. Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921); "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

(17) J. N. Brønsted, *J. Am. Chem. Soc.*, **44**, 877, 938 (1922); **45**, 289 (1923).

(18) H. S. Harned and B. B. Owen, "Electrolytic Solutions," McGraw-Hill Book Co., Inc., New York, N. Y., 1943.

physical chemists have always disliked such measurements for two reasons. They believe that the measurements are inexact and that the activity of a single ion cannot be determined. It is true that the inaccurate measurements are possible and many such are made every day. On the other hand, it is possible to make the error in the liquid junction smaller than that in the electrodes just as in a concentration cell with transference. To determine single ion activities, it is sufficient to have an operational definition for one cell, say the hydrogen-hydrogen ion electrode *vs.* the saturated potassium chloride bridge. I calculated this potential¹⁹ with the MacInnes assumption that the liquid junction potential of the cell $\text{KCl (1 } m)|\text{KCl (satd)}$ is zero.²⁰ Then the potential in millivolts for the cell $\text{HCl (1 } m)|\text{KCl (satd)}$ is $+0.09$ at $0.2\ m$, -0.01 at $0.5\ m$, -0.15 at $0.6\ m$, -3.2 at $0.8\ m$, and -5.00 at $1\ m$. It must be remembered, however, that the assumptions underlying these calculations are very different from the previous ones.

Reference 3 contains the only published measurements I know on osmotic coefficients of a reciprocal salt pair. An objection has been raised²¹ that the experimental results are not given in ref 3. I believe that publication of the parameters for a set of equations with deviations from these equations is the best way to present such results. Figure 6 in ref 3 shows that of 93 measurements with $I = 0.01$ or above on the single salts, 79 deviate less than 0.001 and 14 deviate between 0.001 and 0.002. Of 145 measurements on mixtures in the same concentration range, which depend also on the two-ion series, 134 deviate less than 0.001, 9 between 0.001 and 0.002, and 2 between 0.002 and 0.003. The equations used are not very convenient, however. They are of the form

$$\phi = 1 + 0.5M^{1/2}\sum J A_J' + M\sum_{JK} x_J x_K (B_{JK}' + 1.5C_{JK}'M^{1/2}) + M^2\sum_{JKL} x_J x_K x_L (2D_{JKL}' + 2.5E_{JKL}'M^{1/2}) \quad (17)$$

in which $M = 2I$ for 1:1 electrolytes. Then in our terms

$$\alpha_J = 0.5(2I)^{1/2}A_J' + (2I)B_{JJ}' + 1.5(2I)^{3/2}C_{JJ}' + 2(2I)D_{JJ}' + 2.5(2I)^{5/2}E_{JJ}' \quad (18)$$

$$\beta_{JK} = (2I)(2B_{JK}' - B_{JJ}' - B_{KK}') + 1.5(2I)^{3/2}(2C_{JK}' - C_{JJ}' - C_{KK}') + 2(2I)^2(D_{JK}' + D_{JKK}' - D_{JJ}' - D_{KKK}') + 2.5(2I)^{5/2}(E_{JK}' + E_{JKK}' - E_{JJ}' - E_{KKK}') \quad (19)$$

For the $\text{KNO}_3\text{-KCl-LiNO}_3\text{-LiCl}$ system, $(2B_{JK}' - B_{JJ}' - B_{KK}')$ and $(2C_{JK}' - C_{JJ}' - C_{KK}')$ are zero. Most readers will probably be satisfied, however, with the plots of $(\alpha_J - \alpha_K)/I$ and β_{JK}/I in Figures 1-3 of ref 7. The freezing point constant is 0.001 too small. This leads to nearly constant errors of $+0.001$ in α and in β above $0.01\ m$.

Young and his students^{22,23} have made many measurements of the heat of mixing at constant ionic strength of many 1:1 electrolytes, and Wood and his students²⁴⁻²⁶ have extended the measurements to 2:1 and 1:2 electrolytes. These have the advantages over free-energy measurements that the ideal term is zero and that they measure directly the term corresponding to $B_{JK}y_Jy_K$, which we will call $B_{JK}^{(H)}y_Jy_K$.

From the measurements of his students, Young has arrived empirically at two important relations.

Young's rule states that the heat of mixing at constant ionic strength two 1:1 electrolytes with a common ion, af and bf, is independent of the common ion, f. It must hold for $(H^n/RT)_2$ and it holds for $(H^n/RT)_3$ if $d_{aaf} + d_{bbf} = 0$.

The cross-square rule states that for a reciprocal salt pair of 1:1 salts, af, bf, ag, bg, the heat of mixing 0.5 mole of af and ag, of bf and bg, of af and bf, and of ag and bg is the same as that of mixing 0.5 mole of af and bg and of ag and bf. In reply to Böttger at the Faraday Society Discussion,²² Young said that the holding of Young's rule is a necessary but not a sufficient condition for the holding of the cross-square rule. No additional condition is necessary for the terms proportional to $(H^n/RT)_2$ and to $(H^n/RT)_3$.

Wood and Anderson²⁵ have calculated the terms in G^e/RT proportional to the first and second powers of the ionic strength. They say that triplet formation should lead to terms proportional to $I^{3/2}$, but they do not use this erroneous statement. They also copy the erroneous conclusion of ref 7 concerning the ionic strength fractions, but this has no effect because they apply it only to cases of the same valence type so that the ionic strength fraction is a constant times the ion-component fraction. The statement that the interactions of three ions of like charge lead to asymmetry is also erroneous.

Guggenheim's Recent Hypothesis.^{21,27} Guggenheim starts with the hypothesis that up to $2\ m$ the differences in B for most uniunivalent electrolytes are proportional to I and takes NaCl as standard. This hypothesis was examined in Figure 8 of ref 3 under the name "the Åkerlöf-Thomas Hypothesis" and found to hold better at higher concentrations than at lower ones. Then he states that up to $2\ m$ the deviations from Brønsted's principle, our B 's, are small and proportional to I . He also rediscovered Young's rule. In Figures 1 and 2 of ref 7, the terms for B/I are small, but the constant term and that proportional to $I^{1/2}$ are zero, and at $I = 1$, $(B_{af} - B_{bg})$ is about as large as $(B_{af} + B_{bg})/2$, and $(B_{ag} - B_{bf})$ is about as large as $(B_{ag} + B_{bf})/2$. For the isopiestic results at 25° , only those in Figure 4 of ref 7 extend below $2\ m$. They are nearly linear from 1 to $4\ m$, but the slope is far from zero.

(22) T. F. Young, Y. C. Wu, and A. A. Krawetz, *Discussions Faraday Soc.*, **24**, 37, 77, 80 (1957).

(23) Y. C. Wu, M. B. Smith, and T. F. Young, *J. Phys. Chem.*, **69**, 1868, 1873 (1965).

(24) R. H. Wood and R. W. Smith, *ibid.*, **69**, 2974 (1965).

(25) R. H. Wood and H. L. Anderson, *ibid.*, **70**, 992 (1966).

(26) R. H. Wood and H. L. Anderson, *ibid.*, **70**, 1877 (1966).

(27) E. A. Guggenheim, *Trans. Faraday Soc.*, **62**, 3446 (1966).

(19) G. Scatchard, *J. Am. Chem. Soc.*, **47**, 696 (1925).

(20) D. A. MacInnes, *ibid.*, **41**, 1086 (1919).

(21) E. A. Guggenheim, "Applications of Statistical Mechanics," Clarendon Press, Oxford, 1966.

The worst difficulty with these papers for me is the statement that these conclusions are thermodynamic coming from one with such a high, and well-deserved, reputation for knowledge of thermodynamics as Guggenheim.

Our Later Work. Johnson²⁸ and Rush²⁹ have corrected the errors in ref 7 and have measured the osmotic coefficients of mixtures of NaClO_4 , LiClO_4 , and HClO_4 up to very high concentrations.

Yoest⁸ measured the osmotic coefficients of a reciprocal salt pair, CuCl_2 - NaClO_4 , with one bivalent cation, one univalent cation, and two univalent anions, with a very large spread in the osmotic coefficients of the two component systems.

Johnson, Scatchard, and Kraus⁹ studied the system BaCl_2 - HCl in the ultracentrifuge and applied eq 15 of ref 7 to the interpretation of the results. Rush and Scatchard¹⁰ corrected the equation of Young and Smith²⁹ for a mixture of electrolytes of different va-

lence types to complete the application of eq 15 of ref 7 in ref 9.

Acknowledgment. It is impossible to thank here all the people who have helped in the development of the ideas of this paper. The list should certainly include every coauthor listed here. Above all, however, I should acknowledge Peter J. W. Debye. The charging process in his development of the interionic attraction theory first taught me the advantage of excess free energy over the activity coefficients of the components, and since I first met him in 1925 he has given me valuable lessons in physico-chemical research and in his philosophy, "Ich bin Physiker weil es mir Spass macht."

This work was supported by the U. S. Atomic Energy Commission, under Contract No. AT(30-1)-905 under Union Carbide Corporation's contract with the U. S. Atomic Energy Commission and by the Office of Saline Water, U. S. Department of the Interior.

(28) J. S. Johnson and R. M. Rush, *J. Phys. Chem.*, **72**, 767 (1968).

(29) T. F. Young and M. B. Smith, *ibid.*, **58**, 716 (1954).

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1.1.1 ERRATA: THE EXCESS FREE ENERGY AND RELATED PROPERTIES OF SOLUTIONS CONTAINING ELECTROLYTES

George Scatchard¹

The Excess Free Energy and Related Properties of Solutions Containing Electrolytes [*J. Am. Chem. Soc.*, **90**, 3124 (1968)]. By GEORGE SCATCHARD, Department of Chemistry and Laboratory of Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and the Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

In eq 5, the last line should be $(\sum_i m_i'/2)^2 \sum_j \sum_k B_{jk} x_j x_k$.

Equation 8 should be $(G^E/RTW)_i = \sum_j \sum_k \sum_l m_i' m_j' m_k' f_{ijkl}$.

In the sixth line below, $ka/\sqrt{I} = a'$ should be $ka/\sqrt{I} = a'$.

Equation 11 should be $G^{DH}/RT = WS\sum_a + \sum_i -m_a' m_i' (\partial_a + \partial_i) X_{at}/2a_{at}' m'$.

In footnote 17, 289 should be 2898.

In eq 13 "d" is omitted in the denominator of the second derivative.

In the twelfth line below eq 19, "and 1:2" should be omitted.

On page 3127, the paragraph beginning **Young's rule** should read as follows: Young's rule states that the free energy, the heat, and the volume changes of mixing at constant ionic strength of two 1:1 electrolytes with a common ion af and bf (or af and ag) is independent of the common ion, f (or a). It must hold for G^{DH}/RT and for $(G^E/RT)_2$, and it holds for $(G^E/RT)_3$ if $(2D_{abg} -$

$D_{aag} - D_{bbg}) = (2D_{abf} - D_{aaf} - D_{bbf})$.

I had forgotten that H. E. Wirth, R. E. Lindstrom, and J. N. Johnson [*J. Phys. Chem.*, **67**, 2339 (1963)] had defined Young's rule as the special case in which the changes are zero, which is equivalent to Brønsted's Principle of the Specific Interaction of Ions or our extension of it.³ They also applied it to mixtures without a common ion for which the earlier treatment is much superior.

On page 3127 in the first paragraph on the cross-square rule the quotation from Young should read "a sufficient but not a necessary condition." The last sentence of that paragraph should be deleted and replaced by, "It holds for $(G^E/RT)_2$ and $(G^E/RT)_3$ and it holds for $(G^E/RT)_4$ if $4f_{abfg} - 2(f_{abff} + f_{abgg} + f_{aafg} + f_{bbfg}) + (f_{aaff} + f_{bbff} + f_{aagg} + f_{bbgg}) = 0$."

On page 3127, column 2, line 5, add "It is true that there is no asymmetry without interactions between three ions of the same sign."

The authors of ref 28 should be R. M. Rush and J. S. Johnson, Jr.

The last sentence of the paper should read: "This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-905 and 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."

1. Professor of Physical Chemistry, Emeritus, Massachusetts Institute of Technology; Consultant, Oak Ridge National Laboratory.

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1.2 OSMOTIC AND ACTIVITY COEFFICIENTS FOR BINARY MIXTURES OF SODIUM CHLORIDE, SODIUM SULFATE, MAGNESIUM SULFATE, AND MAGNESIUM CHLORIDE IN WATER AT 25°.

I. ISOPIESTIC MEASUREMENTS ON THE FOUR SYSTEMS WITH COMMON IONS¹

Y. C. Wu, R. M. Rush, and G. Scatchard²

Isopiestic measurements are presented for the systems NaCl-Na₂SO₄-H₂O, Na₂SO₄-MgSO₄-H₂O, MgSO₄-MgCl₂-H₂O, and MgCl₂-NaCl-H₂O. Parameters obtained from these results are used to derive the activity coefficients in the mixtures. The deviations from Harned's rule are less than 3% in the activity coefficient up to an ionic strength of 6.

The purpose of the investigation reported in this series of papers is to explore the free energy relationships in the six binary salt mixtures made up from NaCl, Na₂SO₄, MgSO₄, and MgCl₂ in aqueous solution. In this first paper we present the results of isopiestic measurements on the systems involving a common ion: NaCl-Na₂SO₄-H₂O, Na₂SO₄-MgSO₄-H₂O, MgSO₄-MgCl₂-H₂O, and MgCl₂-NaCl-H₂O.

Experimental Section

Materials. A saturated solution of NaCl was prepared from reagent grade crystals dried at 200° for 2 days. The concentration was determined by density measurement, and the molality was calculated from Wirth's empirical equation.³ The result thus obtained agreed with the value given in Seidell⁴ to within 0.1%.

Stock solutions of Na₂SO₄, MgSO₄, and MgCl₂ were prepared from reagent grade chemicals. These solutions were analyzed by displacement of hydrogen ion from a hydrogen-form cation-exchange resin and weight titration of the resulting acid. In addition, the MgSO₄ stock solution was analyzed by the precipitation and weighing of BaSO₄. The two results agreed to within 0.1%.⁵

The mixed solutions were prepared by weight from these stock solutions. Distilled water was used in the preparation of all solutions.

Apparatus and Procedure. The apparatus and procedure were the same as described by Rush and Johnson.⁶ For each set of equilibrations, there were two dishes containing the same solution, except as noted in the tables. Where there were duplicate dishes, the maximum difference in molality between the duplicate dishes was 0.2% except for the most dilute set of solutions ($\nu m\phi = 0.5934$) for the system MgSO₄-MgCl₂-H₂O, where the difference was as much as 1%. The reference solution was NaCl in all cases, and the osmotic coefficients for this salt were taken from Robin-

son and Stokes.⁷ The temperature was maintained at 25.0°.

Results

The results of the measurements are given in Tables I-IV. Here we have tabulated $\nu m\phi$ and the osmotic coefficients for the two- and three-component mixtures for each of the equilibrations (ν is the number of moles of ions per mole of solute, m is the concentration in moles per kilogram of water, and ϕ is the osmotic coefficient; for the three-component mixtures νm is the sum of the values of νm for the two salts). The compositions of the mixtures are given as ionic strength fractions, $y_A = I_A/I$, where I is the total ionic strength on the molality scale and I_A is the ionic strength of component A, and as osmolality fractions, $z_A = \nu_A m_A / (\nu_A m_A + \nu_B m_B)$. Where there were duplicate dishes, the results given are averages.

The ranges of ionic strengths for the mixtures reported here are as follows: NaCl-Na₂SO₄, 1.1-9.4; Na₂SO₄-MgSO₄, 1.5-8.8; MgSO₄-MgCl₂, 0.8-6.8; and MgCl₂-NaCl, 1.1-5.9. The equations and coefficients presented in this paper should not be used for calculations at ionic strengths higher than those given above.

(1) Research jointly sponsored by the Office of Saline Water, U. S. Department of the Interior, and the U. S. Atomic Energy Commission under contract with Union Carbide Corp.

(2) Professor of Physical Chemistry, Emeritus, Massachusetts Institute of Technology; Consultant, Oak Ridge National Laboratory.

(3) H. E. Wirth, R. E. Lindstrom, and J. N. Johnson, *J. Phys. Chem.*, **67**, 2339 (1963).

(4) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, 3rd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1953, p 1217.

(5) We are indebted to Dr. H. Kubota for the gravimetric analysis and to Mrs. D. C. Michelson for the cation-exchange analyses.

(6) R. M. Rush and J. S. Johnson, *J. Chem. Eng. Data*, **11**, 590 (1966).

(7) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., revised, Butterworth and Co. Ltd., London, 1965.

Table I: Osmotic Coefficients for the System NaCl-Na₂SO₄-H₂O^a

$\nu m\phi$	$z_{\text{Na}_2\text{SO}_4}$				
	0	0.1430	0.2951	0.6164	1
$\nu m\phi$	$y_{\text{Na}_2\text{SO}_4}$				
	0	0.2502	0.4557	0.7852	1
10.822	1.1644	1.1175	1.0686	0.9446	0.8115
4.5685	0.9999	0.9561	0.9093	0.7852	0.6407
2.8891	0.9569	0.9181	0.8762	0.7637	0.6281
2.1449	0.9406	0.9048	0.8668	0.7643	0.6409
1.6992	0.9324	0.8994	0.8643	0.7699	0.6575

^a Duplicate dishes for all measurements except those for pure Na₂SO₄.

Table II: Osmotic Coefficients for the System Na₂SO₄-MgSO₄-H₂O^a

$\nu m\phi$	z_{MgSO_4}					ϕ_{NaCl}
	0	0.2582	0.5133	0.7564	1	
	y_{MgSO_4}					
	0	0.4104	0.6784	0.8613	1	
3.5602	0.6282	0.6466	0.6749	0.7083	0.7435	0.9738
2.2199	0.6395	0.6233	0.6158	0.6161	0.6204	0.9420
1.4777	0.6691	0.6316	0.6000	0.5765	0.5575	0.9287
1.0851	0.6936	0.6464	0.6022	0.5643	0.5307	0.9227
0.7715	0.7214	0.6661	0.6127	0.5640	0.5181	0.9204

^a Single dish for all measurements except those for pure NaCl.

Table III: Osmotic Coefficients for the System MgSO₄-MgCl₂-H₂O

$\nu m\phi$	z_{MgCl_2}					ϕ_{NaCl}
	0	0.3950	0.6605	0.8582	1	
	y_{MgCl_2}					
	0	0.2461	0.4932	0.7516	1	
4.0434	0.7801	0.9476	1.0481	1.1185	1.1672	0.9862
1.9742	0.5980	0.7708	...	0.9459	0.9942	0.9374
1.2381	0.5397	0.7122	0.8135	0.8827	0.9299	0.9249
0.8086	0.5189	0.6851	0.7819	0.8478	0.8931	0.9205
0.5934	0.5220	0.6784	0.7695	0.8345	0.8768	0.9212

Table IV: Osmotic Coefficients for the System MgCl₂-NaCl-H₂O^a

$\nu m\phi$	z_{NaCl}			
	0.4263	0.6802	0.7784	1
$\nu m\phi$	y_{NaCl}			
	0.2709	0.5153	0.6371	1
10.822	1.4351	1.3145	1.2092	1.1044
4.5685	1.1201	1.0668	1.0471	0.9999
2.8891	1.0229	0.9937	0.9831	0.9569
2.1449	0.9785	0.9622	0.9556	0.9406
1.6992	0.9527	0.9443	0.9410	0.9324

^a Single dish for all measurements except those for pure NaCl.

with the further restriction that for NaCl-Na₂SO₄ calculations should not be carried beyond $I = 6$, the limit for the two-component data for NaCl. Extrapolations to lower values than those given above are less likely to be in error because the equations include a Debye-Hückel term.

The data for the two-component systems may be compared with the values given by Robinson and Stokes⁷ for these salts. The average deviation without regard to sign between our osmotic coefficients and those obtained from the data tabulated by Robinson and Stokes are as follows: Na₂SO₄, 0.006; MgSO₄, 0.006; and MgCl₂, 0.002.

In the treatment of the experimental data we utilize the equations developed by Scatchard.⁸ In this treatment the excess free energy, G^e , is expressed as a sum of contributions calculated from the limiting two-component solutions (A terms, solute indicated by single subscript) and contributions involving concentration of two solute components (a series of B terms, the solutes indicated by a double subscript). The equation is as follows (ref 8, eq 13) where R is the

$$G^e/RT = (n_A^* + n_B^*)[A_A + (A_B - A_A)y_B +$$

$$B_{AB}^{(0)}y_B(1 - y_B) + B_{AB}^{(1)}y_B(1 - y_B)(1 - 2y_B)] \quad (1)$$

gas constant, T the temperature in degrees absolute, and $n_J^* = n_J^{1/2} \sum_i \nu_{iJ} z_i^2$ (where n_J is the number of moles of solute J , ν_{iJ} is the number of moles of ion i in 1 mol of component J , and z_i is the valence of ion i).

If eq 1 is differentiated with respect to the amount of solvent, the following expression for the osmotic coefficient, ϕ , is obtained (ref 8, eq 14)

$$\phi = 1 + \frac{I}{\nu_A m_A + \nu_B m_B} [\alpha_A + (\alpha_B - \alpha_A)y_B +$$

$$\beta_{AB}^{(0)}y_B(1 - y_B) + \beta_{AB}^{(1)}y_B(1 - y_B)(1 - 2y_B)] \quad (2)$$

where

$$\alpha_J = \partial A_J / \partial \ln I; \quad \beta_{JK}^{(i)} = \partial B_{JK}^{(i)} / \partial \ln I$$

If eq 1 is differentiated with respect to the number of moles of a given solute, the following equations for the activity coefficients of components A and B are obtained (ref 8, eq 15)

$$\ln \gamma_{\pm A} = \frac{I_A}{\nu_A m_A} [A_A + \alpha_A + (\alpha_B - \alpha_A)y_B +$$

$$\beta_{AB}^{(0)}y_B + (B_{AB}^{(0)} - \beta_{AB}^{(0)})y_B^2 + \beta_{AB}^{(1)}y_B + 3(B_{AB}^{(1)} - \beta_{AB}^{(1)})y_B^2 - 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)})y_B^3] \quad (3)$$

$$\ln \gamma_{\pm B} = \frac{I_B}{\nu_B m_B} [A_B + \alpha_B + (\alpha_A - \alpha_B)y_A +$$

$$\beta_{AB}^{(0)}y_A + (B_{AB}^{(0)} - \beta_{AB}^{(0)})y_A^2 - \beta_{AB}^{(1)}y_A - 3(B_{AB}^{(1)} - \beta_{AB}^{(1)})y_A^2 + 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)})y_A^3] \quad (4)$$

In the equations given above the contributions from the limiting two-component systems are given

as a Debye-Hückel term plus a power series in I

$$\alpha_J = \frac{2S}{a_J^3 I} \left[1 + a_J I^{1/2} - \frac{1}{1 + a_J I^{1/2}} - 2 \ln(1 + a_J I^{1/2}) \right] + a_J^{(1)} I + a_J^{(2)} I^2 + a_J^{(3)} I^3 \quad (5)$$

$$A_J + \alpha_J = \frac{2SI^{1/2}}{1 + a_J I^{1/2}} + 2a_J^{(1)} I + \frac{3}{2} a_J^{(2)} I^2 + \frac{4}{3} a_J^{(3)} I^3 \quad (6)$$

where a_J is the distance of closest approach parameter for component J and $S = -1.17202$ for aqueous solutions at 25°. The B and β terms are expanded as

$$\beta_{AB}^{(0)} = b_{AB}^{(0,1)} I + b_{AB}^{(0,2)} I^2 + b_{AB}^{(0,3)} I^3 \quad (7)$$

$$\beta_{AB}^{(1)} = b_{AB}^{(1,2)} I^2 + b_{AB}^{(1,3)} I^3 \quad (8)$$

$$B_{AB}^{(0)} = b_{AB}^{(0,1)} I + \frac{1}{2} b_{AB}^{(0,2)} I^2 + \frac{1}{3} b_{AB}^{(0,3)} I^3 \quad (9)$$

$$B_{AB}^{(1)} = \frac{1}{2} b_{AB}^{(1,2)} I^2 + \frac{1}{3} b_{AB}^{(1,3)} I^3 \quad (10)$$

It should be noted that our $b_{AB}^{(j,k)}$ are Scatchard's $\beta_{AB}^{(j,k)}/I^k$.

The above equations (especially eq 3 and 4) may appear quite formidable with regard to hand calculation. However, the following relationships should be noted

$$A_J + \alpha_J = \frac{\nu_J m_J}{I_J} \ln \gamma_{\pm J(J)} \quad (11)$$

$$\alpha_J = \frac{\nu_J m_J}{I_J} (\phi_J - 1) \quad (12)$$

where $\gamma_{\pm J(J)}$ is the activity coefficient of component J in pure J and ϕ_J is the osmotic coefficient of pure J both taken at the ionic strength of the mixture in question. It is thus possible to calculate the contributions of the pure components to $\ln \gamma_{\pm}$ with eq 3 and 4 using either the analytical expressions for $A + \alpha$ and α given by eq 5 and 6 and the coefficients of Table V or eq 11 and 12 and tabular data on the pure components such as those given by Robinson and Stokes.⁷ The latter alternative greatly simplifies hand calculations. Equations 3 and 4 are further simplified, since, for the systems considered here, $\beta_{AB}^{(1)}$ and $B_{AB}^{(1)}$ are zero.

Table V: Parameters for the Two-Component Systems^a

	NaCl	Na ₂ SO ₄	MgSO ₄	MgCl ₂
a	1.45397	1.24072	1.37486	1.60067
$a^{(1)}$	0.04472	-0.06580	-0.02712	0.06633
$a^{(2)}$	0.018616	0.007263	0.004213	0.009003
$a^{(3)}$	-0.0010724	-0.0001945	-0.0000950	-0.0002545

^a Adapted from ref 9.

For the limiting two-component systems we use the parameters given by Lietzke and Stoughton⁹ (derived from the data of Robinson and Stokes⁷) and shown in Table V. (It should be noted that the power-series coefficients given by Lietzke and Stoughton, B , C , and D , are multiplied by the factor $-2/z_+ z_-$ to obtain the coefficients $a_J^{(i)}$.)

The b coefficients of eq 7 and 8 were obtained from the observed osmotic coefficients of the mixtures by the method of least squares. The values thus obtained are given in Table VI along with the standard deviation, $\sigma = [\sum d^2/(n - k)]^{1/2}$, where d is the deviation, n the number of observations, k the number of variable parameters, and the summation is over all observations. For each system fits were obtained using combinations of parameters other than those shown in the table. The sets of parameters given in Table VI are those with the least number of parameters which do not represent a significant increase in the standard deviation (σ). It was not necessary to include either the term $b_{AB}^{(1,2)}$ or $b_{AB}^{(1,3)}$ for any of the systems reported here.

Table VI: Parameters for the Three-Component Systems

	NaCl(A)- Na ₂ SO ₄ (B)	Na ₂ SO ₄ (A)- MgSO ₄ (B)	MgSO ₄ (A)- MgCl ₂ (B)	MgCl ₂ (A)- NaCl(B)
$b_{AB}^{(0,1)}$	-0.05821	0.03178	-0.03681	0.0654
$b_{AB}^{(0,2)}$	...	-0.003055	...	-0.0176
$b_{AB}^{(0,3)}$	0.000439	...	...	0.00191
σ (in ϕ)	0.0010	0.0010	0.0009	0.0014

The experimental values can thus be represented by eq 2 with the a parameters of Table V and the b parameters of Table VI. The same parameters may be used to calculate the activity coefficient of either component by eq 3 or 4.

The variation of activity coefficients with composition at several ionic strengths for the systems studied is shown in Figures 1-8. The lines representing our results were calculated using eq 3 and 4 and the parameters given in Tables V and VI. Where available, the results of other investigators are also shown.

Discussion

Several authors have reported measurements of the activity coefficient of NaCl in the system NaCl-Na₂SO₄-H₂O. Lanier¹⁰ reported measurements with a cation-sensitive glass electrode at ionic strengths of 1, 3, and 6. Butler, Hsu, and Synnott¹¹ reported results at ionic strengths 1 and 3 using a sodium amalgam

(9) M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.*, **66**, 508 (1962).

(10) R. D. Lanier, *ibid.*, **69**, 3992 (1965).

(11) J. N. Butler, P. T. Hsu, and J. C. Synnott, *ibid.*, **71**, 910 (1967).

Figure 1. Activity coefficients of NaCl in Na_2SO_4 : —, this work; ····, Gieskes;¹² O, Lanier;¹⁰ Δ, Butler;¹¹ ♦, estimate from two-component data.

Figure 2. Activity coefficients of NaCl in MgCl_2 : —, this work; ---, Platford;¹⁴ O, Lanier;¹⁰ Δ, Butler;¹³ ♦, estimate from two-component data.

electrode. Gieskes¹² used a sodium-sensitive glass electrode and reports results at an ionic strength of 0.7 (the approximate composition of seawater). The results of these measurements along with our own are shown in Figure 1. These results are all in reasonably good agreement and indicate that $\log \gamma_{\pm\text{NaCl}}$ is essentially a linear function of $y_{\text{Na}_2\text{SO}_4}$. Our results are somewhat closer to those of Butler, *et al.*,¹¹ than to those of Lanier,¹⁰ although the differences are only of the order of 1 mV.

Figure 3. Activity coefficients of Na_2SO_4 in NaCl: ♦, estimate from two-component data.

Figure 4. Activity coefficients of Na_2SO_4 in MgSO_4 : ♦, estimate from two-component data.

Similar studies of the activity coefficient of NaCl in the system $\text{MgCl}_2\text{--NaCl--H}_2\text{O}$ have been reported. Lanier¹⁰ gave results obtained at ionic strengths 1, 3, and 6 with a cation-sensitive glass electrode. Butler and Huston¹³ reported results obtained with a sodium amalgam electrode at ionic strengths from 0.5 to 6.0. Platford¹⁴ has obtained activity coefficients for both solutes in this system. These were calculated by the McKay-Perring method from isopiestic measurements. The results of these measurements along with our own are shown in Figures 2 and 7. They are all in reasonably good agreement, except for the results of Butler and Huston for NaCl in MgCl_2 at an ionic strength of 6.

(12) J. M. T. M. Gieskes, *Z. Phys. Chem. (Frankfurt am Main)*, **50**, 78 (1966).

(13) J. N. Butler and R. Huston, *J. Phys. Chem.*, **71**, 4479 (1967).

(14) R. F. Platford, *ibid.*, **72**, 4053 (1968).

Figure 5. Activity coefficients of MgSO_4 in Na_2SO_4 :
◆, estimate from two-component data.

Figure 6. Activity coefficients of MgSO_4 in MgCl_2 :
◆, estimate from two-component data.

Table VII: Values of the Parameters Q_{AB} and Q_{BA}

I	Q_{AB}	Q_{BA}
$\text{NaCl(A)}-\text{Na}_2\text{SO}_4(\text{B})$		
1	-0.045	0.041
2	-0.045	0.039
3	-0.045	0.040
4	-0.045	0.042
5	-0.045	0.043
6	-0.045	0.044
$\text{Na}_2\text{SO}_4(\text{A})-\text{MgSO}_4(\text{B})$		
1	0.037	-0.022
2	0.032	-0.014
3	0.029	-0.010
4	0.026	-0.008
5	0.024	-0.006
6	0.022	-0.005
$\text{MgSO}_4(\text{A})-\text{MgCl}_2(\text{B})$		
1	0.077	-0.071
2	0.071	-0.067
3	0.070	-0.067
4	0.071	-0.067
5	0.072	-0.068
6	0.074	-0.069
$\text{MgCl}_2(\text{A})-\text{NaCl}(\text{B})$		
1	0.012	0.019
2	0.015	0.014
3	0.016	0.011
4	0.017	0.009
5	0.017	0.008
6	0.017	0.007

Their results differ from the others by about 10% in $\gamma_{\pm}$.

Equations 3 and 4 provide a means of estimating the

Figure 7. Activity coefficients of MgCl_2 in NaCl : —, this work; ---, Platford;¹⁴ ◆, estimate from two-component data.

activity coefficients in mixtures from the data on the limiting two-component systems. The A and α terms are derived from the two-component systems, and limiting the equations to these terms provides such an estimate. It has been shown that estimates of this type are good to within 7% in $\gamma_{\pm}$ up to $I = 5$ for several 1:1 perchlorate mixtures.¹⁵ Estimates for the systems studied in this investigation are shown in Figures 1-8. At $I = 1$, the error introduced by these

(15) R. M. Rush and J. S. Johnson, *J. Phys. Chem.*, **72**, 767 (1968).

Figure 8. Activity coefficients of MgCl_2 in MgSO_4 :
◆, estimate from two-component data.

estimates varies from 3 to 8% in $\gamma_{\pm}$. At $I = 6$, however, the error varies from 11 to 56%.

In general, the systems investigated here follow well the linear relationship between $\log \gamma_{\pm A}$ and y_B as ex-

pressed in Harned's rule.¹⁶ In Table VII values are given for the quantities

$$Q_{AB} = [\log (\gamma_{\pm A(B)} / \gamma_{\pm A(A)})] / I$$

and

$$Q_{BA} = [\log (\gamma_{\pm B(A)} / \gamma_{\pm B(B)})] / I$$

where $\gamma_{\pm A(B)}$ is the activity coefficient of component A in a pure solution of component B ($y_B = 1$) and $\gamma_{\pm A(A)}$ is the activity coefficient of component A in a pure solution of component A ($y_B = 0$), with analogous definitions for the quantities involved in Q_{BA} . These quantities thus represent a straight-line approximation for the variation of $\log \gamma_{\pm}$ with y using the end points to define the straight line. This approximation is exact only for the system $\text{MgSO}_4\text{--MgCl}_2\text{--H}_2\text{O}$. The deviations from the straight line are all 1% in $\gamma_{\pm}$ or less except for $\log \gamma_{\pm \text{MgSO}_4}$ in Na_2SO_4 , where the deviation is 3% at $I = 6$.

Acknowledgment. We express our appreciation to J. S. Johnson, K. A. Kraus, and R. J. Raridon for helpful discussions.

(16) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 14.

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1.3 OSMOTIC AND ACTIVITY COEFFICIENTS FOR BINARY MIXTURES OF SODIUM CHLORIDE, SODIUM SULFATE, MAGNESIUM SULFATE, AND MAGNESIUM CHLORIDE IN WATER AT 25°.

II. ISOPIESTIC AND ELECTROMOTIVE FORCE MEASUREMENTS ON THE TWO SYSTEMS WITHOUT COMMON IONS¹

Y. C. Wu, R. M. Rush,² and G. Scatchard³

Isopiestic measurements are presented for the systems $\text{NaCl-MgSO}_4\text{-H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\text{-MgCl}_2\text{-H}_2\text{O}$. Emf measurements with a Na-sensitive glass electrode vs. a Ag-AgCl electrode are presented for the same systems. Parameters obtained from the isopiestic results are used to derive the activity coefficients in the mixtures. The deviations from Harned's rule are less than 2% in the activity coefficient up to an ionic strength of 6. Values of the excess free energy of mixing are given for the binary aqueous mixtures involving NaCl, Na_2SO_4 , MgSO_4 , and MgCl_2 . The cross-square rule, shown to be valid for heats of mixing, is applicable to the free-energy changes for these mixtures.

The purpose of the investigation reported in this series of papers is to explore the free-energy relationships in the six binary salt mixtures made up from NaCl, Na_2SO_4 , MgSO_4 , and MgCl_2 in aqueous solution. In the first paper⁴ we presented the results of isopiestic measurements on the four systems involving a common ion. In this paper we present the results of isopiestic measurements on the systems without a common ion: $\text{NaCl-MgSO}_4\text{-H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\text{-MgCl}_2\text{-H}_2\text{O}$. The results of emf measurements with a Na-sensitive glass electrode on these systems are also given.

The results reported here complete the free-energy measurements for the six binary mixtures noted above. The excess free energies for the six systems are calculated. These calculations indicate that the cross-square relationship first proposed by Young and co-workers⁵ for the heats of mixing of 1:1 electrolytes is also applicable to the excess free energies of mixing for the systems studied here.

Experimental Section

Materials. The stock solutions of the single salts were the same as those used in the previous investigation.⁴ The mixed solutions were prepared by weight from these stock solutions. Distilled water was used in the preparation of all solutions.

Isopiestic Experiments. The apparatus and procedure were the same as described by Rush and Johnson.⁶ For each set of equilibrations, there were two dishes containing the same solution except as noted in the tables. Where there were duplicate dishes, the maximum difference in molality at equilibrium between

the duplicate dishes was 0.2%. The reference solution was NaCl in all cases, and the osmotic coefficients for this salt were taken from Robinson and Stokes.⁷ The temperature was maintained at 25.0°.

Emf Experiments. The apparatus and procedure were similar to those described by Lanier.⁸

The glass electrodes used were Beckman Instruments cationic glass electrodes (39137). Only those which exhibited long stability and quick response were used. In general, the drift was not more than 0.1 mV/hr, and the time to reach equilibrium was less than 15 min.

The Ag-AgCl electrodes were prepared by the method described by Greyson.⁹ A sheet of 1 mm thick AgCl crystal obtained from Harshaw Chemical Co. was cut to approximately 3 × 5 mm. A piece of No. 18 silver wire 15 cm long was sealed to the AgCl crystal by

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(3) Professor of Physical Chemistry, Emeritus, Massachusetts Institute of Technology; Consultant, Oak Ridge National Laboratory.

(4) Y. C. Wu, R. M. Rush, and G. Scatchard, *J. Phys. Chem.*, **72**, 4048 (1968).

(5) T. F. Young, Y. C. Wu, and A. A. Krawetz, *Discussions Faraday Soc.*, **24**, 37, 77, 80 (1957).

(6) R. M. Rush and J. S. Johnson, *J. Chem. Eng. Data*, **11**, 590 (1966).

(7) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, revised, Butterworth and Co. Ltd., London, 1965.

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

(9) J. Greyson, *J. Electrochem. Soc.*, **109**, 745 (1962).

heating the wire to red heat and then pressing it into one end of the crystal. The electrode was washed with concentrated NH_4OH , HNO_3 , and water. It was then plated in 0.1 *m* HCl with a Pt anode for a few minutes at about 1 mA. Six electrodes were prepared at one time and were measured against each other. Of those that differed from each other by less than 0.1 mV, one was used in the measurements and the rest were stored in 0.1 *m* HCl.

The emf of a NaCl reference solution was measured both before and after the measurement of the test solution using the same pair of electrodes. The difference was usually 0.2 mV or less. If the change was greater than 0.5 mV, the electrodes were examined and tested and the experiment repeated. The solutions were measured while in a water bath maintained at $25.00 \pm 0.02^\circ$.

The activity coefficients of NaCl in the mixtures were calculated from the equation

$$\log \gamma_{\pm} = \frac{E' - E_R}{118.3} + \log a_{\pm R} - 1/2 \log m_{\text{Na}} m_{\text{Cl}} \quad (1)$$

where E' and E_R are the observed emf's in millivolts of the test and reference solutions, respectively (E_R is the average of the measurements made before and after the measurement of E); $a_{\pm R}$ is the mean activity of the reference solution; and m_{Na} and m_{Cl} are the molalities of the sodium and chloride ions, respectively, in the test solution.

The accuracy of the procedure was tested with a series of standard NaCl solutions in the range 1.0–6.16 *m*. The deviations from the results calculated from the activity coefficients given by Robinson and Stokes⁷ were less than 0.4 mV.

Results

Isopiestic Data. The results of the isopiestic measurements are given in Tables I and II. Here we have tabulated $\nu m\phi$ and the osmotic coefficients for the two- and three-component systems for each of the equilibrations (ν is the number of moles of ions per mole of solute, m is the concentration in moles per kilogram of water, and ϕ is the osmotic coefficient; for the three-component mixtures νm is the sum of the values of νm

Table I: Osmotic Coefficients for the System $\text{NaCl-MgSO}_4\text{-H}_2\text{O}$

$\nu m\phi$	$\nu m\text{MgSO}_4$				
	0	0.0779	0.1993	0.4249	1
$\nu m\phi$	$\nu m\text{NaCl}$				
	0	0.2526	0.4990	0.7472	1
7.3064	1.0729	1.0740	1.0739	1.0693	1.0619
4.0910	0.9874	0.9739	0.9517	0.9059	0.7908
2.5410	0.9487	0.9285	0.8955	0.8284	0.6490
1.7464	0.9332	0.9115	0.8735	0.7961	0.5790
1.3186	0.9261	0.9038	0.8636	0.7819	0.5455
1.0203	0.9220	0.8967	0.8552	0.7726	0.5260

Table II: Osmotic Coefficients for the System $\text{Na}_2\text{SO}_4\text{-MgCl}_2\text{-H}_2\text{O}^a$

$\nu m\phi$	$\nu m\text{MgCl}_2$			ϕ_{NaCl}
	0	0.2438	0.5486	0.7747
7.3064		0.8885		1.2626
4.0910		0.7832		1.0664
2.5410		0.7485		0.9633
1.7464		0.7449		0.9124
1.3186		0.7489		0.8853
1.0203		0.7533		0.8658
3.5602	0.6282		0.9317	0.9738
2.2199	0.6395		0.8686	0.9420
1.4777	0.6691		0.8392	0.9287
1.0851	0.6936		0.8262	0.9227
0.7715	0.7214		0.8203	0.9204

^a Single dish for all measurements except those for pure NaCl and Na_2SO_4 .

for the two salts). The compositions of the mixtures are given as ionic strength fractions $y_A = I_A/I$, where I is the total ionic strength on the molality scale and I_A is the ionic strength of component A, and as osmolality fractions $z_A = \nu_A m_A / (\nu_A m_A + \nu_B m_B)$. Where there were duplicate dishes, the results given are averages.

The ranges of ionic strengths for the mixtures reported here are 0.7–7.8 for NaCl– MgSO_4 and 0.9–8.2 for Na_2SO_4 – MgCl_2 . The equations and coefficients presented in this paper should not be used for calculations at ionic strengths higher than those given above with the further restriction that for NaCl– MgSO_4 mixtures calculations should not be carried beyond $I = 6$, the limit for the two-component data for NaCl. Extrapolations to lower values than those given above are less likely to be in error because the equations include a Debye–Hückel term.

The treatment of the experimental data was the same as that used in the previous paper⁴ which utilized the equations developed by Scatchard.¹⁰ These equations are given below. In these equations a_j is the distance-of-closest-approach parameter for component J and $S = -1.17202$ for aqueous solutions at 25° .

$$\phi = 1 + \frac{I}{\nu_A m_A + \nu_B m_B} [\alpha_A + (\alpha_B - \alpha_A)y_B + \beta_{AB}^{(0)}y_B(1 - y_B) + \beta_{AB}^{(1)}y_B(1 - y_B)(1 - 2y_B)] \quad (2)$$

$$\alpha_j = \frac{2S}{a_j^3 I} \left[1 + a_j I^{1/2} - \frac{1}{1 + a_j I^{1/2}} - 2 \ln(1 + a_j I^{1/2}) \right] + a_j^{(1)} I + a_j^{(2)} I^2 + a_j^{(3)} I^3 \quad (3)$$

$$\beta_{AB}^{(0)} = b_{AB}^{(0,1)} I + b_{AB}^{(0,2)} I^2 + b_{AB}^{(0,3)} I^3 \quad (4)$$

$$\beta_{AB}^{(1)} = b_{AB}^{(1,2)} I^2 + b_{AB}^{(1,3)} I^3 \quad (5)$$

(10) G. Scatchard, *J. Amer. Chem. Soc.*, **83**, 2636 (1961).

$$\ln \gamma_{\pm A} = \frac{I_A}{\nu_A m_A} [A_A + \alpha_A + (\alpha_B - \alpha_A)y_B + \beta_{AB}^{(0)} + (B_{AB}^{(0)} - \beta_{AB}^{(0)})y_B^2 + \beta_{AB}^{(1)}y_B + 3(B_{AB}^{(1)} - \beta_{AB}^{(1)})y_B^2 - 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)})y_B^3] \quad (6)$$

$$\ln \gamma_{\pm B} = \frac{I_B}{\nu_B m_B} [A_B + \alpha_B + (\alpha_A - \alpha_B)y_A + \beta_{AB}^{(0)}y_A + (B_{AB}^{(0)} - \beta_{AB}^{(0)})y_A^2 - \beta_{AB}^{(1)}y_A - 3(B_{AB}^{(1)} - \beta_{AB}^{(1)})y_A^2 + 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)})y_A^3] \quad (7)$$

$$A_J + \alpha_J = \frac{2SI^{1/2}}{1 + a_J I^{1/2}} + 2a_J^{(1)}I + \frac{3}{2}a_J^{(2)}I^2 + \frac{4}{3}a_J^{(3)}I^3 \quad (8)$$

$$B_{AB}^{(0)} = b_{AB}^{(0,1)}I + \frac{1}{2}b_{AB}^{(0,2)}I^2 + \frac{1}{3}b_{AB}^{(0,3)}I^3 \quad (9)$$

$$B_{AB}^{(1)} = \frac{1}{2}b_{AB}^{(1,2)}I^2 + \frac{1}{3}b_{AB}^{(1,3)}I^3 \quad (10)$$

For the limiting two-component systems we use the parameters given by Lietzke and Stoughton¹¹ (derived from the data of Robinson and Stokes⁷) and shown in Table III. (It should be noted that the power series coefficients given by Lietzke and Stoughton, B , C , and D , are multiplied by the factor $-2/z_+z_-$ to obtain the coefficients $a_J^{(i)}$.)

The b coefficients of eq 4 and 5 were obtained from the observed osmotic coefficients of the mixtures by the method of least squares. The values thus obtained are given in Table IV along with the standard deviation $\sigma = [\sum d^2/(n - k)]^{1/2}$, where d is the deviation, n the number of observations, k the number of variable parameters, and the summation is over all observations. For both systems, fits were obtained using combinations of

Table III: Parameters for the Two-Component Systems^a

	NaCl	Na ₂ SO ₄	MgSO ₄	MgCl ₂
a	1.45397	1.24072	1.37486	1.60067
$a^{(1)}$	0.04472	-0.06580	-0.02712	0.06633
$a^{(2)}$	0.018616	0.007263	0.004213	0.009003
$a^{(3)}$	-0.0010724	-0.0001945	-0.0000950	-0.0002545

^a Adapted from ref 11.

Table IV: Parameters for the Three-Component Systems

	NaCl (A)- MgSO ₄ (B)	Na ₂ SO ₄ (A)- MgCl ₂ (B)
$b_{AB}^{(0,1)}$	...	...
$b_{AB}^{(0,2)}$	-0.00798	-0.00657
$b_{AB}^{(0,3)}$	0.000855	0.000231
σ (in ϕ)	0.0012	0.0022

Figure 1. Activity coefficients of NaCl in MgSO₄: —, this work, isopiestic; O, this work, emf; Δ, this work, emf (Lanier); •, Gieskes (ref 12); +, Platford, isopiestic (ref 13); ×, Platford, emf (ref 13); ♦, estimate from two-component data.

parameters other than those shown in the table. The sets of parameters given in Table IV are those with the least number of parameters which do not represent a significant increase in the standard deviation (σ). It was not necessary to include the terms $b_{AB}^{(0,1)}$, $b_{AB}^{(1,2)}$, or $b_{AB}^{(1,3)}$ for the systems reported here (these terms were set equal to zero for the determination of the other terms).

(11) M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.*, **66**, 508 (1962).

The experimental values can thus be represented by eq 2 with a parameters of Table III and the b parameters of Table IV. The same parameters may be used to calculate the activity coefficient of either component by eq 6 or 7.

Figure 2. Activity coefficients of MgSO_4 in NaCl : —, this work; +, Platford, isopiestic (ref 13); ♦, estimate from two-component data.

Figure 3. Activity coefficients of Na_2SO_4 in MgCl_2 : ♦, estimate from two-component data.

The variation of activity coefficients with composition at several ionic strengths for the systems studied is shown in Figures 1-4. The lines representing our

Figure 4. Activity coefficients of MgCl_2 in Na_2SO_4 : ♦, estimate from two-component data.

Figure 5. Activity coefficients of NaCl in the system Na_2SO_4 - MgCl_2 - H_2O : ■, values from other three-component data.

isopiestic results were calculated using eq 6 and 7 and the parameters given in Tables III and IV. Where available, the results of other investigators are also shown (where necessary, these results were adjusted to correspond to the values we used for $\log \gamma_{\pm}$ for the pure salt).

Emf. The results of the emf measurements are shown in Figures 1 and 5. Values of $\log \gamma_{\pm}$ were calculated from the observed emf's using eq 1. These values were adjusted so that the values for the pure NaCl solutions are consistent with the parameters of Table III.

Discussion

The values of $\log \gamma_{\pm \text{NaCl}}$ from our isopiestic and emf results for the system NaCl-MgSO₄-H₂O are compared in Figure 1. The results of several other investigators are included in this figure. Gieskes¹² used a Na-sensitive glass electrode *vs.* a Ag-AgCl electrode and reported results at an ionic strength of 0.7 (the approximate concentration of sea water). The values shown in Figure 1 are the uncorrected (stoichiometric) values (labeled "MgSO₄") taken from Figure 5 of Gieskes' paper. Platford¹³ reported results at ionic strengths of 0.72 and 0.432. He presented results using both the isopiestic technique and emf measurements using a sodium amalgam electrode *vs.* a Ag-AgCl electrode.

The emf measurements are, in general, in good agreement with the isopiestic results. However, at low NaCl fractions, the emf results at all concentrations show an upward curvature that is not observed in the results derived from our isopiestic measurements. The deviations are of the order of several millivolts and appear to be real and reproducible. Lanier⁸ observed this same upward curvature in mixtures of NaCl with various other salts. He suggested as explanations for this effect the sensitivity of the glass electrode to the divalent ion in cases where the second salt contained a divalent ion and to difficulties with the Ag-AgCl electrode in cases where the second salt was not a chloride. For the NaCl-MgSO₄ mixtures both of these effects could appear and seem to be the most likely explanations for the observed deviations.

Comparison of the isopiestic and emf results for the system Na₂SO₄-MgCl₂-H₂O is more difficult since the emf measurements give the quantity $\log \gamma_{\pm \text{NaCl}}$. With NaCl as a component the system becomes a four-component one except at the two ends and the midpoint. It is possible to calculate from the isopiestic results values of $\log \gamma_{\pm \text{NaCl}}$ at these three points, and these values are shown in Figure 5 with square symbols. The values at $y_{\text{MgCl}_2} = 0$ were calculated from the NaCl-Na₂SO₄-H₂O parameters with $y_{\text{NaCl}} = 0$; for $y_{\text{MgCl}_2} = 1$, the values were calculated from the parameters for MgCl₂-NaCl-H₂O with $y_{\text{NaCl}} = 0$; and for $y_{\text{MgCl}_2} = 0.5$ the parameters for NaCl-MgSO₄-H₂O were used with $y_{\text{MgSO}_4} = 0.6667$. The results of these cal-

Table V: Values of the Parameters Q_{AB} and Q_{BA}

<i>I</i>	Q_{AB}	Q_{BA}
NaCl (A)-MgSO ₄ (B)		
1	-0.022	0.080
2	-0.024	0.083
3	-0.026	0.088
4	-0.028	0.092
5	-0.029	0.095
6	-0.030	0.097
Na ₂ SO ₄ (A)-MgCl ₂ (B)		
1	0.078	-0.080
2	0.068	-0.073
3	0.064	-0.072
4	0.061	-0.072
5	0.059	-0.072
6	0.058	-0.073

culations are in good agreement with the observed (emf) values. (One observed point is not shown in Figure 5. It deviated from the trend of the other points at the same concentration by about 10 mV and was discarded as a wild point.)

Equations 6 and 7 provide a means of estimating the activity coefficients in mixtures from the data on the limiting two-component systems. The A and α terms are derived from the two-component systems and limiting the equations to these terms (*i.e.*, with all b coefficients equal to zero) provides such an estimate. Such estimates for the systems studied in this investigation are shown in Figures 1-4. At $I = 1$, the error introduced by these estimates is less than 1% in $\gamma_{\pm}$; at $I = 6$, the error varies from 4 to 18%.

In general, the systems investigated here follow closely the linear relationship between $\log \gamma_{\pm A}$ and y_B as expressed in Harned's rule.¹⁴ In Table V values are given for the quantities

$$Q_{AB} = [\log (\gamma_{\pm A(B)} / \gamma_{\pm A(A)})] / I$$

and

$$Q_{BA} = [\log (\gamma_{\pm B(A)} / \gamma_{\pm B(B)})] / I$$

where $\gamma_{\pm A(B)}$ is the activity coefficient of component A in a pure solution of component B ($y_B = 1$) and $\gamma_{\pm A(A)}$ is the activity coefficient of component A in a pure solution of component A ($y_B = 0$) with analogous definitions for the quantities involved in Q_{BA} . These quantities thus represent a straight-line approximation for the variation of $\log \gamma_{\pm}$ with y using the end points to define the straight line. The deviations from the straight line are 2% or less in $\gamma_{\pm}$ in all cases.

(12) J. M. T. M. Gieskes, *Z. Phys. Chem.* (Frankfurt am Main), **50**, 78 (1966).

(13) R. F. Platford, *Can. J. Chem.*, **45**, 821 (1967).

(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 14.

Further Results for the System NaCl-Na₂SO₄-H₂O

Recently Synnott and Butler¹⁵ published activity coefficients of Na₂SO₄ in the system NaCl-Na₂SO₄-H₂O at $I = 1$. These measurements were made with a lead amalgam-lead sulfate electrode *vs.* a Na-sensitive glass electrode. Their results are in good agreement with our values obtained by the isopiestic method,⁴ the maximum deviation being equivalent to about 0.5 mV. Their results confirm our conclusion that Harned's rule is closely followed for Na₂SO₄ under these conditions. Recent isopiestic measurements of Platford,¹⁶ analyzed by the procedure used here, give activity coefficients of NaCl and Na₂SO₄ in very good agreement with values obtained from isopiestic results reported in our previous paper;⁴ the maximum differences between $\log \gamma_{\pm}$ of either NaCl or Na₂SO₄ between the two sets, found for trace concentrations of the electrolyte in question, is 0.002 for $I = 1$, 0.005 for $I = 3$, and 0.012 for $I = 6$.

From the slope of $\log \gamma_{\pm \text{Na}_2\text{SO}_4}$ *vs.* $y_{\text{Na}_2\text{SO}_4}$, Synnott and Butler derived -0.035 for Harned's α_{21} . Earlier,¹⁷ from measurements of $\gamma_{\pm \text{NaCl}}$ in NaCl-Na₂SO₄ solutions and literature values of $\phi_{\text{Na}_2\text{SO}_4}$, they obtained $\alpha_{21} = -0.043$ at $I = 1$; Lanier⁸ by the same procedure, obtained -0.014 . If Harned's rule is obeyed by Na₂SO₄ in NaCl-Na₂SO₄ solutions, $\alpha_{21} = -Q_{\text{BA}}$; the value of α_{21} implied by the isopiestic results is thus -0.041 (Table VII, ref 4).

These values appear quite different. The scatter, however, perhaps reflects the severe strain in the data involved in the procedure of calculating α_{21} from $\gamma_{\pm \text{NaCl}}$ more than inaccuracy of the data; the agreement of $\gamma_{\pm \text{NaCl}}$ for NaCl-Na₂SO₄ solutions in ref 8 with the isopiestic results is not as good as for NaCl-MgCl₂, reported in ref 4, nor as good as for NaCl-MgSO₄, reported in this paper; but it is nevertheless fairly good. (It is of interest that values of $\log \gamma_{\pm \text{NaCl}}$ reported by Platford,¹⁶ which were calculated by the MacKay-Perring technique, appear to agree better with Lanier's values⁸ than with the activity coefficients computed by the techniques of this paper.) Computation of α_{21} from α_{12} magnifies apparent errors greatly when α_{21} , as here, is not greatly different from zero. An error of 0.013 (corresponding to about 1.5 mV) in $\log \gamma_{\pm \text{NaCl}}$ between $y = 0$ and $y = 1$ would, for example, account for the difference between α_{21} of -0.014 and -0.035 .

Excess Free Energy

The osmotic and activity coefficients are measures of the excess free energy of the systems studied. It is thus appropriate to look at the free energy relationships among the three-component systems studied in the present investigation. The systems reported in this and the previous paper⁴ consist of the six binary salt mixtures of NaCl, Na₂SO₄, MgSO₄, and MgCl₂ in aqueous solution. To our knowledge, this is the first such investigation involving mixtures of salts of differ-

Figure 6. Variation of the parameter $B_{AB}^{(0)}/I$ as a function of I .

ent valence types, except for that of Yoest¹⁸ on mixtures of NaCl, NaClO₄, CuCl₂, and Cu(ClO₄)₂. Some years ago Scatchard and Prentiss¹⁹ studied binary mixtures of KNO₃, KCl, LiCl, and LiNO₃ in aqueous solution. They measured the freezing point depression in these mixtures and gave parameters for the calculation of the osmotic coefficients and the excess free energies. They showed that the osmotic coefficients of the two mixtures without a common ion could be calculated from measurements on the single salts and on mixtures with a common ion. They thus established the validity of the cross-square rule (see below) for the excess free energies of mixing for mixtures of these 1:1 electrolytes. Recently, Covington, Lilley, and Robinson²⁰ have shown the validity of the cross-square rule for the excess free energies of mixing for pairs involving NaCl, KCl, NaBr, and KBr in aqueous solutions.

The excess free energy, G^e , is the total free energy of the solution less that of the components in their standard state and less the ideal free energy represented by the concentration terms. In the treatment used here the equation for the excess free energy is (ref 10, eq 13)

$$G^e/RT = (n_A^* + n_B^*)[A_A y_A + A_B y_B + R_{AB}^{(0)} y_A y_B + R_{AB}^{(1)} y_A y_B (y_A - y_B)] \quad (11)$$

where R is the gas constant, T the temperature in degrees absolute, and $n_J^* = n_J(1/2 \sum_i \nu_{iJ} z_i^2)$ (n_J is the number of moles of solute J , ν_{iJ} is the number of moles of ion i in 1 mol of component J , and z_i is the valence of ion i).

It is convenient to consider the change in excess free energy per kilogram of water on forming a three-

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(20) A. K. Covington, T. H. Lilley, and R. A. Robinson, *J. Phys. Chem.*, **72**, 2759 (1968).

Table VI: Excess Free Energies of Mixing, Calories per Kilogram of Water, at $y_A = y_B = 0.5$

	<i>I</i>					
	1	2	3	4	5	6
NaCl-Na ₂ SO ₄	-9	-34	-76	-132	-202	-282
MgCl ₂ -MgSO ₄	-5	-22	-49	-87	-136	-196
Na ₂ SO ₄ -MgSO ₄	4	17	36	61	89	121
NaCl-MgCl ₂	8	30	60	96	138	190
$\Sigma \square$	-2	-9	-29	-62	-111	-167
NaCl-MgSO ₄	-1	-4	-12	-27	-48	-73
Na ₂ SO ₄ -MgCl ₂	-1	-4	-12	-28	-54	-90
$\Sigma \times$	-2	-8	-24	-55	-102	-163
$\Sigma \square - \Sigma \times$	0	-1	-5	-7	-9	-4

component mixture from the limiting two-component solutions at the same ionic strength.

$$\Delta_m G^e = RTI[B_{AB}^{(0)}y_A y_B + B_{AB}^{(1)}y_A y_B(y_A - y_B)] \quad (12)$$

It should be noted that $B_{AB}^{(0)}/I$ and $B_{AB}^{(1)}/I$ correspond to the terms g_0 and $-g_1$ in the treatment given by Friedman.²¹

Values of $\Delta_m G^e$ for mixtures containing equal ionic strength fractions ($y_A = y_B = 0.5$) of the two solutes are given in Table VI. These values were calculated from eq 12 and the b coefficients of Table IV and of Table VI of the previous paper.⁴ Values of the quantity $B_{AB}^{(0)}/I$ for the same systems are shown in Figure 6.

The extensive investigations of Young and co-workers^{5,22} and Wood and coworkers^{23,24} have indicated two general relationships for the heats of mixing of aqueous electrolyte solutions: (1) for two electrolytes with a common ion, the heat of mixing is independent of the common ion; (2) for a system of reciprocal salt pairs, the sum of the heats of mixing for the four pairs with common ions equals the sum for the two pairs without a common ion (cross-square rule). For the excess free energies of mixing for the six salt pairs of the present investigation (involving mixtures of 1:1, 1:2,

and 2:2 electrolytes), the results in Table VI indicate that relationship 1 is only qualitatively true and that the cross-square rule (relationship 2) is obeyed.

It is possible to calculate the excess free energy, osmotic coefficient, and mean activity coefficient of any electrolyte in any mixture of ions approximately from the parameters for the two-component mixtures, and more exactly from these plus the parameters for the three-component mixtures with a common ion, by the ion-component treatment of Scatchard.²⁵ We plan to illustrate this for the four-ion system investigated here and for sea water solutions in the third paper of this series.

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1.4 OSMOTIC AND ACTIVITY COEFFICIENTS FOR BINARY MIXTURES OF SODIUM CHLORIDE, SODIUM SULFATE, MAGNESIUM SULFATE, AND MAGNESIUM CHLORIDE IN WATER AT 25°.

III. TREATMENT WITH THE IONS AS COMPONENTS¹

G. Scatchard, R. M. Rush,² and J. S. Johnson

Equations for the excess free energy, osmotic coefficient, and activity coefficients are derived from the ion-component treatment of Scatchard (1968). Applications of these equations to the reciprocal salt system Na-Mg-Cl-SO₄ and to synthetic sea-water solutions are discussed. These are compared with the earlier neutral-electrolyte treatment of Scatchard (1961). The ion-component treatment provides a better estimate of the osmotic and activity coefficients when only data on the two-ion (single-salt) systems are available, provides as good a fit to the three-ion (common-ion) data, and provides a means of calculating values for the four-ion (noncommon-ion) systems using only parameters derived from the three-ion data.

The treatment of electrolyte solutions with the ions as components³ (with the restriction, of course, of electroneutrality) promises to be considerably more powerful than the treatment with neutral electrolytes as solutes⁴ used in papers I and II of this series.^{5,6} The equations of ref 3 are not, however, convenient for computation. In this paper, we develop more tractable expressions with the ion-component approach and illustrate their application to several solutions containing more than one electrolyte solute.

Equations

In ref 3, the excess free energy, G^e , of a solution was divided into a Debye-Hückel contribution, $(G^e)^{DH}$, and

a non-Debye-Hückel part, $(G^e)^n$

$$\begin{aligned} G^e/RT &= (G/RT) - (n_0 \bar{G}^{\circ}_0/RT) - \sum_i n_i [(\bar{G}^{\circ}_i/RT) - 1 + \ln m_i] = (G^e/RT)^{DH} + (G^e/RT)^n \quad (1) \end{aligned}$$

G is the total Gibbs free energy of the system; $n_0 \bar{G}^{\circ}_0$,

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Table I: Free Energy Equations

$$\begin{aligned}
\text{(a)} \quad \left(\frac{G^e}{RTW} \right) &= \left(\frac{G^e}{RTW} \right)^{\text{DH}} + \left(\frac{G^e}{RTW} \right)^{\text{nI}} + \left(\frac{G^e}{RTW} \right)^{\text{nII}} \\
\text{(b)} \quad \left(\frac{G^e}{RTW} \right)^{\text{DH}} &= mS \sum_a^+ \sum_f^- x_a x_f (z_a + z_f) \frac{x_{af}}{a_{af}'} \\
\text{(c)} \quad x_{af} &= \frac{a_{af}'^2 I - 2a_{af}' \sqrt{I} + 2 \ln(1 + a_{af}' \sqrt{I})}{a_{af}'^2 I} \\
\text{(d)} \quad \left(\frac{G^e}{RTW} \right)^{\text{nI}} &= \sum_a^+ \sum_f^- x_a x_f \left(B_{af}^{(1)} m'^2 + \frac{1}{2} B_{af}^{(2)} m'^3 + \frac{1}{3} B_{af}^{(3)} m'^4 + \dots \right) \\
\text{(e)} \quad \left(\frac{G^e}{RTW} \right)^{\text{nII}} &= \sum_a^+ \sum_b^+ \sum_f^- x_a x_b x_f \left(B_{abf}^{(0,1)} m'^2 + \frac{1}{2} B_{abf}^{(0,2)} m'^3 + \frac{1}{3} B_{abf}^{(0,3)} m'^4 \right) \\
&\quad + x_a x_b x_f (x_a - x_b) \left(\frac{1}{2} B_{aab}^{(1,2)} m'^3 + \frac{1}{3} B_{aab}^{(1,3)} m'^4 \right) + x_a x_b x_f (x_a - x_b)^2 \frac{1}{3} B_{aab}^{(2,3)} m'^4 \\
&\quad + \sum_a^+ \sum_f^- \sum_g^- x_a x_f x_g \left(B_{afg}^{(0,1)} m'^2 + \frac{1}{2} B_{afg}^{(0,2)} m'^3 + \frac{1}{3} B_{afg}^{(0,3)} m'^4 \right) \\
&\quad + x_a x_f x_g (x_f - x_g) \left(\frac{1}{2} B_{ffg}^{(1,2)} m'^3 + \frac{1}{3} B_{ffg}^{(1,3)} m'^4 \right) + x_a x_f x_g (x_f - x_g)^2 \frac{1}{3} B_{ffg}^{(2,3)} m'^4 \\
&\quad + \sum_a^+ \sum_b^+ \sum_f^- \sum_g^- x_a x_b x_f x_g \frac{1}{3} B_{abfg}^{(2,3)} m'^4
\end{aligned}$$

the free energy of the solvent; n_j , the number of moles of solute j ; G_j^0 , the "standard molal free energy" of j ; m_j , the molality of j ($m_j = n_j/W$, where W is the number of kilograms of solvent); R , the gas constant; and T , the absolute temperature.

Since we are interested in equations expressing free energies in terms of ions, we use equivalent concentrations

$$m_i' = m_i z_i = 2I_i/z_i = x_i m' \quad (2)$$

z_i being the absolute value of the charge on ion i (a script z was used for z_i in ref 3), and I_i is the contribution of i to the ionic strength (I) of the solution. Equation 2 also defines the equivalent fraction of i , x_i , the total equivalent concentration of the solution being

$$m' = \sum_i m_i' / 2 \quad (3)$$

It should be noted that $\sum_i x_i = 2$ and that the total equivalent fraction for ions of each charge sign is 1. Lower case subscripts will be used for ions; $a, b, c, \dots$ designate cations, and $f, g, h, \dots$, anions. Equations in this pattern can be developed for solutions having more than one nonelectrolyte component, but we restrict ourselves here to those containing one neutral solvent and one or more electrolyte solutes.

The bulk of the electrostatic contribution (which is the total contribution at infinite dilution) to G^e is probably accounted for in a Debye-Hückel term (Table I,

eq b and c). In these equations S is the Debye-Hückel limiting slope for $\ln \gamma_{\pm}$ of a univalent electrolyte at infinite dilution ($S = -1.17202$ for an aqueous solution at 25° and 1 atm); $a_{af}'\sqrt{I}$ is the Debye κ times the "distance of closest approach" d . Unless a' values are the same for all solute components, eq b (Table I) is somewhat different for finite concentrations from the Debye-Hückel expression used in ref 4. In both cases, residual electrostatic effects are lumped into the non-Debye-Hückel terms.

The non-Debye-Hückel contribution to G^e is expressed as a series of interaction terms involving products of m'_i .

$$\begin{aligned}
(G^e/RTW)^n &= \sum_i \sum_j b_{ij} m'_i m'_j + \\
&\quad \sum_i \sum_j \sum_k d_{ijk} m'_i m'_j m'_k + \\
&\quad \sum_i \sum_j \sum_k \sum_l f_{ijkl} m'_i m'_j m'_k m'_l + \\
&\quad \dots = m'^2 \sum_i \sum_j b_{ij} x_i x_j + \\
&\quad m'^3 \sum_i \sum_j \sum_k d_{ijk} x_i x_j x_k + \\
&\quad m'^4 \sum_i \sum_j \sum_k \sum_l f_{ijkl} x_i x_j x_k x_l + \dots \quad (4)
\end{aligned}$$

(3) G. Scatchard, *J. Amer. Chem. Soc.*, **90**, 3124 (1968); **91**, 2410 (1969). See also G. Scatchard and R. G. Breckenridge, *J. Phys. Chem.*, **58**, 596 (1954); **59**, 1234 (1955).

(4) G. Scatchard, *J. Amer. Chem. Soc.*, **83**, 2636 (1961).

(5) Y. C. Wu, R. M. Rush, and G. Scatchard, *J. Phys. Chem.*, **72**, 4048 (1968); **73**, 4433 (1969).

(6) Y. C. Wu, R. M. Rush, and G. Scatchard, *ibid.*, **73**, 2047, 4434 (1969).

Table II: Definition of B Coefficients

$$B_{af}^{(1)} = b_{aa} + 2 b_{af} + b_{ff}$$

$$B_{af}^{(2)} = 2(d_{aaa} + 3 d_{aaf} + 3 d_{aff} + d_{fff})$$

$$B_{af}^{(3)} = 3(f_{aaaa} + 4 f_{aaaf} + 6 f_{aaff} + 4 f_{afff} + f_{ffff})$$

9 similar terms involving ag, bf, and bg

$$B_{ab}^{(0,1)} = 2 b_{ab} - b_{aa} - b_{bb}$$

$$B_{abf}^{(0,2)} = 2 \left[\frac{3}{2} (d_{aab} + d_{abb} - d_{aaa} - d_{bbb}) + 3(2 d_{abf} - d_{aaf} - d_{bbf}) \right]$$

$$B_{abf}^{(0,3)} = 3 \left[6(f_{aabf} + f_{abbf} - f_{aaaf} - f_{bbbf}) + 3(2 f_{abff} - f_{aaff} - f_{bbff}) \right. \\ \left. + (f_{aaab} + f_{abbb} - f_{aaaa} - f_{bbbb}) + \frac{3}{4} (2 f_{aabb} - f_{aaaa} - f_{bbbb}) \right] \\ + 3[3(2 f_{abff} - f_{aaff} - f_{bbff})]^*$$

$$B_{aab}^{(1,2)} = 2 \left[\frac{1}{2} (3 d_{aab} - 3 d_{abb} - d_{aaa} + d_{bbb}) \right]$$

$$B_{aabf}^{(1,3)} = 3 [2 f_{aaab} - 2 f_{abbb} - f_{aaaa} + f_{bbbb} + 2(3 f_{aabf} - 3 f_{abff} - f_{aaaf} + f_{bbbf})]$$

$$B_{aaab}^{(2,3)} = 3 \left[f_{aaab} + f_{abbb} - f_{aaaa} - f_{bbbb} - \frac{3}{4} (2 f_{aabb} - f_{aaaa} - f_{bbbb}) \right]$$

6 additional terms involving a common anion by substituting f for a, g for b, and a for f

3 additional terms with common cation by substituting g for f

3 additional terms with common anion by substituting b for a

$$B_{abfg}^{(2,3)} = 3[24 f_{abfg} - 6 f_{abff} - 6 f_{abgg} - 6 f_{aafg} - 6 f_{bbfg}]$$

In expanding eq 4, terms are included for i less than, equal to, and greater than j , and $d_{ijk} = d_{jik} = d_{kij} = d_{kji}$, etc. For example, for a solution containing only ions i and j , $\sum_i \sum_j b_{ij} m'_i m'_j = 2b_{ii} m'^2_i + b_{jj} m'^2_j$. The coefficients b_{ij} , d_{ijk} , and f_{ijkl} are coefficients which, like G^E , are functions of temperature and pressure and of the nature of the solvent but not of the composition.

These coefficients cannot be determined independently. However, they can be arranged into groups each of which is measurable. Of the grouped coefficients thus obtained, those which probably make the most important contributions to the excess free energy of solutions containing many types of ions can be determined by measurements on simpler systems.

This was illustrated in ref 3 with the products of concentrations of only two ions. Since $\sum_a x_a = \sum_i x_i = 1$, the contribution to $(G^E/RTW)^n$ is

$$m'^2 \left[\sum_a \sum_i x_a x_i (2b_{ai} + b_{aa} + b_{ii}) + \sum_a \sum_b x_a x_b (2b_{ab} - b_{aa} - b_{bb}) + \sum_i \sum_g x_i x_g (2b_{ig} - b_{ii} - b_{gg}) \right] = \\ m'^2 \left[\sum_a \sum_i x_a x_i B_{ai}^{(1)} + \sum_a \sum_b x_a x_b B_{ab}^{(0,1)} + \sum_i \sum_g x_i x_g B_{ig}^{(0,1)} \right] \quad (5)$$

The first term in brackets can be evaluated from data on two-component solutions of electrolyte af, and the other two can be evaluated from solutions of two electrolytes with a common ion, e.g., af and bf, and af and ag. In eq 5 and the equations in Tables I, III, and IV, for double summations involving the same types of ions only terms for $b > a$ (or $g > f$) are included. For example, in a solution containing cations a, b, and c and anion f the terms which would appear in the first summation of eq 5, Table I, are $x_a x_b x_f$, $x_a x_c x_f$, and $x_b x_c x_f$.

Table III: Osmotic Coefficient Equations

$$(a) \quad \phi - 1 = (\phi - 1)^{DH} + (\phi - 1)^{nI} + (\phi - 1)^{nII}$$

$$(b) \quad (\phi - 1)^{DH} = \frac{S}{\sum_i x_i/z_i} \sum_a \sum_f x_a x_f (z_a + z_f) \frac{Z_{af}}{a_{af}}$$

$$(c) \quad Z_{af} = \frac{\partial X_{af}}{\partial \ln I} = \frac{1 + a'_{af} \sqrt{I} - [1/(1 + a'_{af} \sqrt{I})] - 2 \ln(1 + a'_{af} \sqrt{I})}{a_{af}^2 I}$$

$$(d) \quad (\phi - 1)^{nI} = \frac{1}{\sum_i x_i/z_i} \sum_a \sum_f x_a x_f (B_{af}^{(1)} m' + B_{af}^{(2)} m'^2 + B_{af}^{(3)} m'^3 + \dots)$$

$$(e) \quad (\phi - 1)^{nII} = \frac{1}{\sum_i x_i/z_i} \left[\sum_a \sum_b \sum_f x_a x_b x_f (B_{abf}^{(0,1)} m' + B_{abf}^{(0,2)} m'^2 + B_{abf}^{(0,3)} m'^3) \right. \\ + x_a x_b x_f (x_a - x_b) (B_{aab}^{(1,2)} m'^2 + B_{aab}^{(1,3)} m'^3) + x_a x_b x_f (x_a - x_b)^2 B_{aaab}^{(2,3)} m'^3 \\ + \sum_a \sum_f \sum_g x_a x_f x_g (B_{afg}^{(0,1)} m' + B_{afg}^{(0,2)} m'^2 + B_{afg}^{(0,3)} m'^3) \\ \left. + x_a x_f x_g (x_f - x_g) (B_{ffg}^{(1,2)} m'^2 + B_{ffg}^{(1,3)} m'^3) + x_a x_f x_g (x_f - x_g)^2 B_{fffg}^{(2,3)} m'^3 \right]$$

(f) for a solution containing only ions a, b, f, and g:

$$(\phi - 1)^{nII} = \frac{1}{\sum_i x_i/z_i} \left\{ x_a x_b x_f [B_{abf}^{(0,1)} m' + B_{abf}^{(0,2)} m'^2 + B_{abf}^{(0,3)} m'^3] + x_a x_b x_f (x_a - x_b) \right. \\ \times [B_{aab}^{(1,2)} m'^2 + B_{aab}^{(1,3)} m'^3] + x_a x_b x_f (x_a - x_b)^2 B_{aaab}^{(2,3)} m'^3 \\ + x_a x_b x_g [B_{abg}^{(0,1)} m' + B_{abg}^{(0,2)} m'^2 + B_{abg}^{(0,3)} m'^3] + x_a x_b x_g (x_a - x_b) [B_{aab}^{(1,2)} m'^2 + B_{aab}^{(1,3)} m'^3] \\ + x_a x_b x_g (x_a - x_b)^2 B_{aaab}^{(2,3)} m'^3 \\ + x_a x_f x_g [B_{afg}^{(0,1)} m' + B_{afg}^{(0,2)} m'^2 + B_{afg}^{(0,3)} m'^3] + x_a x_f x_g (x_f - x_g) [B_{ffg}^{(1,2)} m'^2 + B_{ffg}^{(1,3)} m'^3] \\ + x_a x_f x_g (x_f - x_g)^2 B_{fffg}^{(2,3)} m'^3 \\ + x_b x_f x_g [B_{bfg}^{(0,1)} m' + B_{bfg}^{(0,2)} m'^2 + B_{bfg}^{(0,3)} m'^3] + x_b x_f x_g (x_f - x_g) [B_{ffg}^{(1,2)} m'^2 + B_{ffg}^{(1,3)} m'^3] \\ \left. + x_b x_f x_g (x_f - x_g)^2 B_{fffg}^{(2,3)} m'^3 \right\}$$

Similar resolutions of the higher terms can be made, with the use as necessary of the relations

$$1 = x + (1 - x) =$$

$$x^2 + 2x(1 - x) + (1 - x)^2 \quad (6)$$

Equation 4 can thus be resolved into two components of $(G^\circ)^n$, $(G^\circ/RTW)^{nI}$ (Table I, eq d) which, along with $(G^\circ/RTW)^{DH}$ can be evaluated from measurements on two-ion (two-component or single-salt) solutions, and

$(G^\circ/RTW)^{nII}$ (Table I, eq e) obtained from three-ion (common-ion) solutions. Table II relates the upper case coefficients of eq d and e of Table I with the lower case ones of eq 4.

The superscripts on the B coefficients indicate the power to which the concentration is raised in the appropriate term in the osmotic coefficient equation (Table III, eq d). In the case of double superscripts, the first superscript indicates the power to which the

Table IV: Activity Coefficient Equations

$$\begin{aligned}
\text{(a)} \quad (\ln \gamma_{\pm})_{pq} &= (\ln \gamma_{\pm})_{pq}^{\text{DH}} + (\ln \gamma_{\pm})_{pq}^{\text{NI}} + (\ln \gamma_{\pm})_{pq}^{\text{NII}} \\
\text{(b)} \quad (\ln \gamma_{\pm})_{pq}^{\text{DH}} &= z_p z_q S \left[\sum_a^+ x_a \cdot \frac{(z_a + z_q)}{(z_p + z_q)} \cdot \frac{X_{aq}}{a'_{aq}} + \sum_f^- x_f \cdot \frac{(z_p + z_f)}{(z_p + z_q)} \cdot \frac{X_{pf}}{a'_{pf}} - \sum_a^+ \sum_f^- x_a x_f \cdot \frac{(z_a + z_f)}{(z_p + z_q)} \cdot \frac{X_{af}}{a'_{af}} \right. \\
&\quad \left. + \frac{1}{\sum_i x_i z_i} \sum_a^+ \sum_f^- x_a x_f (z_a + z_f) \frac{Z_{af}}{a'_{af}} \right] \\
\text{(c)} \quad (\ln \gamma_{\pm})_{pq}^{\text{NI}} &= \frac{1}{(1/z_p) + (1/z_q)} \left[\sum_a^+ x_a \left(B_{aq}^{(1)} m' + \frac{1}{2} B_{aq}^{(2)} m'^2 + \frac{1}{3} B_{aq}^{(3)} m'^3 \right) + \sum_f^- x_f \left(B_{pf}^{(1)} m' + \frac{1}{2} B_{pf}^{(2)} m'^2 + \frac{1}{3} B_{pf}^{(3)} m'^3 \right) \right. \\
&\quad \left. + \sum_a^+ \sum_f^- x_a x_f \left(\frac{1}{2} B_{af}^{(2)} m'^2 + \frac{2}{3} B_{af}^{(3)} m'^3 \right) \right] \\
\text{(d)} \quad (\ln \gamma_{\pm})_{pq}^{\text{NII}} &= \frac{1}{(1/z_p) + (1/z_q)} \left[\sum_a^+ R_{ap}^{(0,1)} m'_a + \frac{1}{2} R_{aup}^{(1,2)} (m'_a{}^2 - 2 m'_a m'_p) + \frac{1}{3} R_{auup}^{(2,3)} (m'_a{}^3 - 4 m'_a{}^2 m'_p + 3 m'_a m'_p{}^2) \right. \\
&\quad + \sum_f^- B_{fq}^{(0,1)} m'_f + \frac{1}{2} B_{ffq}^{(1,2)} (m'_f{}^2 - 2 m'_f m'_q) + \frac{1}{3} B_{fffq}^{(2,3)} (m'_f{}^3 - 4 m'_f{}^2 m'_q + 3 m'_f m'_q{}^2) \\
&\quad + \sum_a^+ \sum_f^- \frac{1}{2} B_{apf}^{(0,2)} m'_a m'_f + \frac{1}{3} B_{apf}^{(0,3)} m'_a m'_f m' + \frac{1}{3} B_{aapf}^{(1,3)} (m'_a{}^2 m'_f - 2 m'_a m'_p m'_f) \\
&\quad + \sum_a^+ \sum_b^- \frac{1}{2} B_{abq}^{(0,2)} m'_a m'_b + \frac{1}{3} B_{abq}^{(0,3)} m'_a m'_b m' + \frac{1}{3} B_{aabbq}^{(1,3)} (m'_a{}^2 m'_b - m'_a m'_b{}^2) + \sum_a^+ \sum_b^- \sum_f^- \frac{1}{3} B_{abf}^{(0,3)} m'_a m'_b m'_f \\
&\quad + \sum_a^+ \sum_f^- \frac{1}{2} B_{afq}^{(0,2)} m'_a m'_f + \frac{1}{3} B_{afq}^{(0,3)} m'_a m'_f m' + \frac{1}{3} B_{affq}^{(1,3)} (m'_a m'_f{}^2 - 2 m'_a m'_f m'_q) \\
&\quad \left. + \sum_f^- \sum_g^- \frac{1}{2} B_{pfg}^{(0,2)} m'_f m'_g + \frac{1}{3} B_{pfg}^{(0,3)} m'_f m'_g m' + \frac{1}{3} B_{pffg}^{(1,3)} (m'_f{}^2 m'_g - m'_f m'_g{}^2) + \sum_a^+ \sum_f^- \sum_g^- \frac{1}{3} B_{afg}^{(0,3)} m'_a m'_f m'_g \right]
\end{aligned}$$

equivalent fraction difference is raised in the appropriate term in the osmotic coefficient equation (except for $B_{abfg}^{(2,3)}$). The second superscript indicates the power of the concentration in the same manner as the single superscript (Table III, eq e).

With some terms there is an approximation involved in using coefficients evaluated from simple systems in computations for more complicated ones. For example, in a three-ion system, a, b, and f, $x_t = 1$, and coefficients multiplied by $x_a x_b$, by $x_a x_b x_t$, and by $x_a x_b x_t^2$ cannot be distinguished. No approximation will be involved in the contribution of the terms including the first two to a solution containing a, b, f, and g. Although terms corresponding to interactions of a and b cannot be distinguished from terms for a, b, and f, the coefficient for a and b will presumably be the same as for an a, b, and g solution, and since $x_t + x_g = 1$, the total contribution to excess free energy will be correctly evaluated. However, with coefficients of $x_a x_b x_t^2$ or $x_a x_b x_g^2$, there is an approximation from the in-

ability to resolve the coefficients, since in the four-ion system, x_t and x_g are not unity. In Table II, in the expression for $B_{abf}^{(0,3)}$, the grouping of lower case coefficients in the bracket indicated by an asterisk should be multiplied by $x_a x_b x_t^2$. Here we shall multiply by $x_a x_b x_t$ and by the analogous products for $B_{abg}^{(0,3)}$, $B_{afg}^{(0,3)}$, and $B_{bfg}^{(0,3)}$.

The coefficient $B_{abfg}^{(2,3)}$ is included in Tables I and II only for completeness of correspondence between eq 4 and the equations with B coefficients. We believe it will usually be too small to make an appreciable contribution to the excess free energy, and we make no attempt to evaluate it.

Experimental data are usually in the form of measurements of solvent activity, in terms of osmotic coefficients, ϕ , or of mean activity coefficients of the solutes, $\gamma_{\pm}$. Expressions for these quantities are obtained by differentiation of the equations for excess free energy

$$\left(\frac{\partial(G^e/RTWI)}{\partial \ln W} \right)_K = -2 \sum_i x_i z_i (\phi - 1) \quad (7)$$

Table V: Activity Coefficient Equations

For component af in a solution containing ions a, b, f, and g:

$$\begin{aligned}
 (a) \quad (\ln \gamma_{\pm}^{\text{DH}})_{af} &= z_a z_f S \left\{ (x_a + x_f - x_a x_f) \frac{X_{af}}{a_{af}} + x_b x_g \left[\frac{(z_a + z_g)}{(z_a + z_f)} \cdot \frac{X_{ag}}{a_{ag}} + \frac{(z_b + z_f)}{(z_a + z_f)} \cdot \frac{X_{bf}}{a_{bf}} - \frac{(z_b + z_g)}{(z_a + z_f)} \cdot \frac{X_{bg}}{a_{bg}} \right] \right. \\
 &\quad \left. + \frac{1}{x_a z_a + x_b z_b + x_f z_f + x_g z_g} \left[x_a x_f (z_a + z_f) \frac{Z_{af}}{a_{af}} + x_a x_g (z_a + z_g) \frac{Z_{ag}}{a_{ag}} + x_b x_f (z_b + z_f) \frac{Z_{bf}}{a_{bf}} + x_b x_g (z_b + z_g) \frac{Z_{bg}}{a_{bg}} \right] \right\} \\
 (b) \quad (\ln \gamma_{\pm}^{\text{NI}})_{af} &= \frac{1}{(1/z_a) + (1/z_f)} \left[B_{af}^{(1)} (m'_a + m'_f) + \frac{1}{2} B_{af}^{(2)} (m'_a m'_f + m'_f m'_f + m'_b m'_f) + \frac{1}{3} B_{af}^{(3)} (m'_a m'^2 + m'_f m'^2 + 2 m'_a m'_f m') \right. \\
 &\quad + B_{bf}^{(1)} m'_b + \frac{1}{2} B_{bf}^{(2)} (m'_b m'_f + m'_b m'_f) + \frac{1}{3} B_{bf}^{(3)} (m'_b m'^2 + 2 m'_b m'_f m') \\
 &\quad + B_{ag}^{(1)} m'_g + \frac{1}{2} B_{ag}^{(2)} (m'_g m'_f + m'_a m'_g) + \frac{1}{3} B_{ag}^{(3)} (m'_g m'^2 + 2 m'_a m'_g m') \\
 &\quad \left. + \frac{1}{2} B_{bg}^{(1)} m'_b m'_g + \frac{2}{3} B_{bg}^{(3)} m'_b m'_g m' \right] \\
 (c) \quad (\ln \gamma_{\pm}^{\text{NII}})_{af} &= \frac{1}{(1/z_a) + (1/z_f)} \left[B_{ab}^{(0,1)} m'_b + \frac{1}{2} B_{abf}^{(0,2)} (m'_b m'_f + m'_a m'_b) + \frac{1}{3} B_{abf}^{(0,3)} (m'_b m'_f m' + m'_a m'_b m' + m'_a m'_b m'_f) + \frac{1}{2} B_{abg}^{(0,2)} m'_b m'_g \right. \\
 &\quad + \frac{1}{3} B_{abg}^{(0,3)} (m'_b m'_g m' + m'_a m'_b m'_g) + \frac{1}{2} B_{aaf}^{(1,2)} (2 m'_a m'_b - m_b'^2) + \frac{1}{3} B_{aaf}^{(1,3)} (2 m'_a m'_b m'_f + m_a'^2 m'_b - m_b'^2 m'_f - m'_a m_b'^2) \\
 &\quad + \frac{1}{3} B_{aag}^{(1,3)} (2 m'_a m'_b m'_g - m_b'^2 m'_g) + \frac{1}{3} B_{aag}^{(2,3)} (3 m_a'^2 m'_b - 4 m'_a m_b'^2 + m_b'^3) \\
 &\quad + B_{fag}^{(0,1)} m'_g + \frac{1}{2} B_{fag}^{(0,2)} (m'_f m'_g + m'_a m'_g) + \frac{1}{3} B_{fag}^{(0,3)} (m'_f m'_g m' + m'_a m'_g m' + m'_a m'_f m'_g) + \frac{1}{2} B_{bfg}^{(0,2)} m'_b m'_g \\
 &\quad + \frac{1}{3} B_{bfg}^{(0,3)} (m'_b m'_g m' + m'_b m'_f m'_g) + \frac{1}{2} B_{ffg}^{(1,2)} (2 m'_f m'_g - m_g'^2) + \frac{1}{3} B_{ffg}^{(1,3)} (m_f'^2 m'_g + 2 m'_a m'_f m'_g - m_f'^2 m_g'^2 - m'_a m_g'^2) \\
 &\quad \left. + \frac{1}{3} B_{bffg}^{(1,3)} (2 m'_b m'_f m'_g - m_b'^2 m_g'^2) + \frac{1}{3} B_{fffg}^{(2,3)} (3 m_f'^2 m'_g - 4 m'_f m_g'^2 + m_g'^3) \right]
 \end{aligned}$$

and

$$\left(\frac{\partial(G^e/RTW)}{\partial m'_J} \right)_{w,K \neq J} = \left(\frac{1}{z_p} - \frac{1}{z_q} \right) \ln \gamma_{\pm J} \quad (8)$$

J being an electrolyte made up of p and q ions, with $m'_J = m'_{p(J)} = m'_{q(J)}$. Differentiation of equations for G^e with respect to temperature and pressure yield expressions for heats and volumes.

We list in Tables III and IV the equations for osmotic coefficient and $\ln \gamma_{\pm}$, including those terms which involve B 's obtainable from two-ion and three-ion solutions. For convenience, we give also in Tables III and V the equations for the systems of particular interest here, these containing only four ions, a, b, f, and g. In eq d, Table IV, in summations involving terms subscripted with p (or q), terms in which a (or f) are replaced by p (or q) are not included; e.g., there are no terms $B_{ppf}^{(0,2)}$ (or $B_{aqq}^{(0,2)}$).

The fit for a given set of osmotic coefficient data can be made within the experimental error for both the neutral-electrolyte and the ion-component treatment if enough parameters are used. For this reason the good-

ness of fit obtainable is not a very useful basis for comparison of the two approaches. However, the ability to estimate ϕ and $\ln \gamma_{\pm}$ for three-ion solutions from data on two-ion solutions is a meaningful criterion. For a solution containing four ions, a further test for the ion-component approach is how well osmotic coefficients can be calculated from two-ion and three-ion data; it is not obvious how to do this with the other approach.

Application

The System Na-Mg-Cl-SO₄. In the previous papers in this series,^{5,6} we have presented the results of isopiestic measurements on the six aqueous binary salt mixtures possible using NaCl, Na₂SO₄, MgSO₄, and MgCl₂. In these papers the results for each salt mixture were analyzed by the neutral-electrolyte treatment⁴ in which the components were considered to be the neutral salts and water. The concentration was expressed as the ionic strength, I , and the solute composition as the ionic strength fraction, y .

We have now analyzed these data by the ion-component treatment³ considering the system to be com-

posed of water and Na^+ (a), Mg^{2+} (b), Cl^- (f), and SO_4^{2-} (g). In this procedure the two-ion parameters involving ions of unlike sign ($B_{af}^{(1)}$, $B_{bg}^{(2)}$, etc.) were derived from the a parameters previously used^{5,6} which were, in turn, derived from the compilation of Lietzke and Stoughton.⁷ The values of these parameters are given in Table VI. The three-ion parameters (those

Table VI: B Parameters for the System Na (a)-Mg (b)-Cl (f)- SO_4 (g)

$a'_{af} = 1.45397$	$B_{ab}^{(0,1)} = 0.0630$
$B_{af}^{(1)} = 0.04472$	$B_{abf}^{(0,2)} = -0.0228$
$B_{af}^{(2)} = 0.018616$	$B_{abf}^{(0,3)} = 0.00221$
$B_{af}^{(3)} = 0.0010724$	$B_{aab}^{(1,2)} = 0$
$a'_{ag} = 1.24072$	$B_{aabf}^{(1,3)} = -0.00068$
$B_{ag}^{(1)} = -0.14805$	$B_{aabf}^{(2,3)} = 0$
$B_{ag}^{(2)} = 0.024513$	$B_{abg}^{(0,2)} = -0.0066$
$B_{ag}^{(3)} = -0.0009847$	$B_{abg}^{(0,3)} = -0.00147$
$a'_{bf} = 1.60067$	$B_{aabg}^{(1,3)} = 0$
$B_{bf}^{(1)} = 0.14924$	$B_{bf}^{(0,1)} = -0.0243$
$B_{bf}^{(2)} = 0.030385$	$B_{bf}^{(0,2)} = 0.01105$
$B_{bf}^{(3)} = -0.0012884$	$B_{bf}^{(0,3)} = -0.00079$
$a'_{bg} = 1.37486$	$B_{bff}^{(1,2)} = -0.00246$
$B_{bg}^{(1)} = -0.10848$	$B_{bff}^{(1,3)} = 0$
$B_{bg}^{(2)} = 0.033704$	$B_{bff}^{(2,3)} = 0$
$B_{bg}^{(3)} = -0.001520$	$B_{bfg}^{(0,2)} = 0$
	$B_{bfg}^{(0,3)} = 0.00031$
	$B_{bffg}^{(1,3)} = 0$

involving three-ion interactions, $B_{abf}^{(0,2)}$, $B_{aabf}^{(1,3)}$, etc., as well as those involving the interaction of two ions of like sign, $B_{ab}^{(0,1)}$, $B_{fffg}^{(2,3)}$, etc.) were evaluated by a least-squares procedure using eq f of Table III and the osmotic coefficients for the four systems involving a common ion.⁵ The values for these parameters are also given in Table VI. The experimental data for the common-ion mixtures can thus be described by eq f of Table III and the parameters of Table VI. The standard deviation of this fit is 0.0012 in ϕ .

A comparison of the ion-component treatment with the neutral-electrolyte treatment used previously is given in Table VII in terms of the ability to fit the common-ion data. (The standard deviation given in this table differs slightly from the definition previously used; it was chosen so as to avoid ambiguity regarding the number of variable parameters.) The first two columns of figures compare the two treatments when only the two-ion (single-salt) parameters are used. These figures indicate that, given only the two-ion data, the ion-component treatment provides a better approximation for the osmotic coefficient than the neutral-electrolyte treatment.

The third and fourth columns of Table VII compare the two treatments when terms characteristic of the mixtures [cross terms, $(G^e/RTW)^{n11}$] are included. The results indicate that the quality of the fit is about the same for the two treatments. It should be noted, however, that for the neutral-electrolyte treatment each

Table VII: Standard Deviation for Fits to the Data for the System Na-Mg-Cl- SO_4

$$S = \sqrt{\frac{\sum (\phi_{\text{obsd}} - \phi_{\text{calcd}})^2}{\text{no. of observations}}}$$

	Two-ion terms		All terms	
	N.E. ^a	I.C. ^b	N.E. ^a	I.C. ^b
NaCl-Na ₂ SO ₄	0.0219	0.0054	0.0009	0.0009
Na ₂ SO ₄ -MgSO ₄	0.0191	0.0121	0.0010	0.0013
MgSO ₄ -MgCl ₂	0.0339	0.0066	0.0008	0.0012
MgCl ₂ -NaCl	0.0145	0.0056	0.0013	0.0009
NaCl-MgSO ₄	0.0097	0.0037	0.0012 ^c	0.0016 ^d
Na ₂ SO ₄ -MgCl ₂	0.0191	0.0074	0.0021 ^c	0.0042 ^d

^a N.E., neutral-electrolyte treatment. ^b I.C., ion-component treatment. ^c Cross-term parameters from direct fit to experimental osmotic coefficients. ^d Cross-term parameters from fit to three-ion osmotic coefficients.

mixture is treated independently, while for the ion-component treatment the data for all four common-ion mixtures are taken together and some of the parameters are affected by the data from more than one mixture (e.g., the parameter $B_{ab}^{(0,1)}$ must satisfy the data for both the NaCl-MgCl₂ and the Na₂SO₄-MgSO₄ mixtures).

For the two four-ion (noncommon-ion) mixtures in Table VII the results computed from two-ion data are also much better with the ion-component approach than with the neutral-electrolyte treatment. The results with cross terms included are much the same for the two methods. This is shown in more detail by the deviation plots in Figure 1. Here the fits using only the two-ion data are decidedly better for the ion-component treatment. When the mixture terms are included, the standard deviations in Table VII suggest a better fit by the neutral-electrolyte treatment. It should be noted again, however, that the neutral-electrolyte treatment involves a direct fit to the data for the mixture in question with parameters characteristic of that mixture. With the ion-component treatment the only parameters used are those derived from the three-ion data and do not depend on any measurements on the four-ion mixtures. The deviation plots in Figure 1 indicate that the fit is only slightly worse with the ion-component treatment. In addition, five points for the Na₂SO₄-MgCl₂ mixtures at $y_{\text{MgCl}_2} = 0.5$ show a consistent deviation. This consistent deviation is more apparent for the ion-component treatment and contributes to the larger standard deviations in Table VII. We suspect that there may have been experimental or computational errors in these measurements; however, we have been unable to identify such errors and have concluded that disregarding these points would not be justified. The deviation of these points from the bulk of the data would not be so apparent with the neutral-electrolyte

(7) M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.*, **66**, 506 (1962).

Table VIII: Trace log $\gamma_{\pm}$ (NaCl) in Mixtures with Na_2SO_4 , MgCl_2 , and MgSO_4 ($y_{\text{NaCl}} = 0$)

	I	Two-ion terms		All terms		Platford ^c	N.E., ^a all terms
		N.E. ^a	I.C. ^b	N.E. ^a	I.C. ^b	McKay-Perring	
NaCl- Na_2SO_4	1	-0.2151	-0.2258	-0.2278	-0.2287	-0.250	-0.229
	3	-0.2432	-0.2765	-0.2803	-0.2816	-0.308	-0.283
	6	-0.2055	-0.2726	-0.2744	-0.2738	-0.314	-0.280
NaCl- MgCl_2	1	-0.1757	-0.1718	-0.1633	-0.1638	-0.176	-0.166
	3	-0.1416	-0.1303	-0.1124	-0.1112	-0.120	-0.113
	6	-0.0098	0.0146	0.0367	0.0431	0.037	0.049
NaCl- MgSO_4	1	-0.2030	-0.2057	-0.2038	-0.2017		
	3	-0.2181	-0.2310	-0.2242	-0.2197		
	6	-0.1687	-0.1977	-0.1865	-0.1788		

^a N.E., neutral-electrolyte treatment. ^b I.C., ion-component treatment. ^c NaCl- Na_2SO_4 , ref 8; NaCl- MgCl_2 , ref 9.

Figure 1. Deviation plots for four-ion data. Neutral-electrolyte treatment (left) and ion-component treatment (right). Ionic strength fractions for second component: Δ , 0.25; $\bullet$, 0.5; and $\blacksquare$, 0.75.

treatment, since the direct fit to the data used in this approach adjusts the parameters to compensate partially for these deviations.

The activity coefficients provide an additional means of comparing the treatments, although there are fewer direct measurements of this quantity for comparison, and the reliability of available data is more questionable, than with osmotic coefficients. Comparison of log $\gamma_{\pm}$

computed in different ways from osmotic coefficient data are also of interest, both to indicate the uncertainty of activity coefficients obtained in this way and to indicate the extent to which they can be estimated from two-ion data alone, and from two-ion plus three-ion data. Equations for the calculation of log $\gamma_{\pm}$ for the general case are given in Table IV and for the specific case of component *a* (NaCl) in a mixture of *a* (Na^+), *b* (Mg^{2+}), *f* (Cl^-), and *g* (SO_4^{2-}) ions in Table V.

A convenient comparison of results obtained by different methods of computing log $\gamma_{\pm}$ from osmotic coefficients is given by values of "trace" log $\gamma_{\pm}$, shown in Table VIII. In this case the figures given are for log $\gamma_{\pm}$ of NaCl in the mixture indicated where the fraction of NaCl is zero. These represent an extrapolated value and can be obtained from the neutral-electrolyte equations with the ionic strength fraction of NaCl equal to zero and from the ion-component equations (Table V) with the appropriate equivalent fractions equal to zero. Again we have compared the neutral-electrolyte and the ion-component treatments with only the two-ion terms and with the cross terms. It should again be noted that the figures in the column "all terms, I.C." were calculated from the parameters derived from all of the three-ion data and in the case of NaCl- MgSO_4 do not involve any direct measurements on this mixture.

The results using only the two-ion terms indicate that, except for the NaCl- MgSO_4 mixtures for which agreement is good for either approach, the ion-component treatment gives values closer to those given by the complete equation than the neutral-electrolyte treatment. When the mixture terms are included the two treatments are in good agreement, the maximum difference being 0.008 in log $\gamma_{\pm}$.

We have also included in Table VIII values from the isopiestic measurements of Platford on the systems NaCl- Na_2SO_4 ⁸ and NaCl- MgCl_2 .⁹ In these cases Platford calculated activity coefficients by the McKay-

(8) R. F. Platford, *J. Chem. Eng. Data*, **13**, 46 (1968).

(9) R. F. Platford, *J. Phys. Chem.*, **72**, 4053 (1968).

Figure 2. Activity coefficients of NaCl in NaCl-MgCl₂ mixtures: — — —, neutral-electrolyte treatment, two-ion parameters; — — —, ion-component treatment, two-ion parameters; — · —, neutral-electrolyte treatment, direct fit; — — —, ion-component treatment, three-ion parameters; ●, emf measurements (ref 10).

Figure 3. Activity coefficients of NaCl in NaCl-MgSO₄ mixtures: — — —, neutral-electrolyte treatment, two-ion parameters; — — —, ion-component treatment, two-ion parameters; — · —, neutral-electrolyte treatment, direct fit; — — —, ion-component treatment, three-ion parameters; ●, emf measurements (ref 6).

Perring method, and these results are compared with computations by the neutral-electrolyte method. These results when treated by the neutral-electrolyte method are in good agreement with our results. The differences for the McKay-Perring treatment are prob-

Figure 4. Activity coefficients of NaCl in Na₂SO₄-MgCl₂ mixtures: — — —, ion-component treatment, two-ion parameters; — — —, ion-component treatment, three-ion parameters; ●, emf measurements (ref 6).

ably due in large part to the method of extrapolation to zero concentration used with that method.⁹

A comparison of the various treatments with experimental emf measurements is given in Figures 2-4. The experimental results for the NaCl-MgSO₄ and Na₂SO₄-MgCl₂ mixtures are taken from our previous publications⁴ and those for NaCl-MgCl₂ from the work of Lanier.¹⁰ A discussion of these results relative to the neutral electrolyte treatment has been given in the previous papers in this series.^{5,6} The results for NaCl-MgCl₂ (Figure 2) and NaCl-MgSO₄ (Figure 3) show clearly the increased power of the ion-component treatment when using only two-ion data. In these cases the two treatments give about the same quality of fit to the experimental data when the terms characteristic of the mixtures are included. The ion-component treatment, however, does reproduce more closely the upward curvature of the experimental data at low NaCl fractions. This agreement raises questions concerning our earlier tentative conclusion^{6,10} that the curvature arises from nonideality of the electrodes.

Values of $\log \gamma_{\pm}(\text{NaCl})$ in the system Na₂SO₄-MgCl₂ can be calculated only at the end points and the midpoint by the neutral-electrolyte treatment.⁶ Using the ion-component treatment, values for any point can be calculated and the results at $I = 3$ are shown in Figure 4. Here curves are calculated using only the two-ion parameters and using these plus the three-ion

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

parameters. The agreement is satisfactory at least for the three-ion case. It should be reemphasized that the solid line in Figure 4 was calculated using parameters derived from the three-ion (common-ion) data and does not depend on any direct measurements on the $\text{Na}_2\text{SO}_4\text{-MgCl}_2$ mixtures.

In summary, the following points have been established for the mixtures comprising this system. (1) The ion-component treatment provides a better estimate of the osmotic coefficient or the activity coefficient than the neutral-electrolyte treatment when only data from the two-ion (single-salt) systems are available. (2) For three-ion (common-ion) systems the ion-component treatment provides as good a fit as the neutral-electrolyte treatment. (3) The ion-component treatment provides an entirely adequate means of calculating the osmotic and activity coefficients for the four-ion systems using only the results obtained from the three-ion mixtures.

Synthetic Sea-Water Solutions. We have previously reported¹¹ the osmotic coefficients for synthetic sea-water solutions measured by the isopiestic technique. These solutions were prepared with NaCl, KCl, MgCl_2 , and Na_2SO_4 so as to have the relative composition of sea water. These data when fitted to an equation with a Debye-Hückel term and a power series in ionic strength gave a standard deviation of 0.0003 in ϕ . A comparison of the experimental data with values calculated from an equation derived from data on pure NaCl solutions at the same ionic strength gave a standard deviation of 0.0040.

By combining the KCl with the NaCl, these solutions can be considered as the four-ion system discussed above. Using the parameters of Table VI it is then possible to calculate the osmotic coefficients by the ion-component method. The resulting standard deviations are 0.0048 using only the two-ion terms and 0.0020 using both the two-ion and three-ion terms. The ion-component treatment using only the two-ion terms does not give quite as good a fit as the NaCl equation, but inclusion of the three-ion terms provides a somewhat better fit to the data.

Discussion

Young and coworkers have enunciated a number of empirical rules for changes of excess thermodynamic quantities on the mixing of electrolyte solutions. Usually, these rules have been initially stated and tested for heats and volumes of mixing, but possible applications to excess free energy were clearly in Young's mind,^{12,13} and it is of interest to discuss the connections between the rules and the equations of this paper.

These rules are usually stated for mixings carried out at constant ionic strength, and concentration enters the expressions for $(G^e/RTW)^{\text{DH}}$ as I and $(G^e/RTW)^{\text{NI}}$ as m' . This causes no difficulty if all electrolytes are (1-1)

and have a common ion, as they were in the original applications of the rules, since $m' = I$. However, with electrolyte groups which include ions of different valence, as $\text{Na}^+\text{-Mg}^{2+}\text{-Cl}^-\text{-SO}_4^{2-}$ does, there are differences in the contributions from parameters evaluated from the single-salt solutions between mixed and unmixed solutions; these differences do not drop out as simply as, for example, they did in the discussion of the cross-square rule by the neutral-electrolyte approach.⁶ Since the ion-component method gives at least as good a fit to osmotic coefficient data, mixing rules can be tested for free energies as well by it as by the neutral-electrolyte method. To be able to discuss the rules in terms of coefficients from $(G^e/RTW)^{\text{NI}}$ only, however, we shall limit our attention to 1-1 electrolytes.

For a mixture with a common ion, the first rule is in its simplified form implicit in Brønsted's principle of specific interaction of ions.¹⁴ It states that $(G^e/RTW)^{\text{NI}}$ is very small. Brønsted's reasoning was that electrostatic repulsion prevents two ions of the same sign from approaching closely. An even more powerful reason is illustrated by the terms proportional to the concentration. That in $(\phi - 1)_{\text{af}}^{\text{NI}}$ is $(2b_{\text{af}} + b_{\text{aa}} + b_{\text{ff}})$; that in $(\phi - 1)_{\text{abf}}^{\text{NI}}$ is $(2b_{\text{ab}} - b_{\text{aa}} - b_{\text{bb}})$. Other upper case coefficients in $(G^e/RTW)^{\text{NI}}$ are likewise seen (Table II) to be differences of an equal number of positive and negative lower-case interaction coefficients which might be expected to be similar in magnitude. Guggenheim¹⁵ extended Brønsted's relation to reciprocal salt pairs. Scatchard and Prentiss¹⁶ applied the relations to the reciprocal salt pair $\text{KNO}_3\text{-LiCl}$. The rule was stated in connection with measurements of volumes and heats of mixing by Young¹² and extended by Young and Smith¹⁷ to mixtures without a common ion. A deviation from the simple rule analogous to the $B^{(0,1)}$ terms in these equations was also given (see also ref 18). If there is no common ion, statement of the rule only in terms $(G^e/RTW)^{\text{NI}}$ is approximate even for 1-1 electrolytes, since there are contributions from $(G^e/RTW)^{\text{DH}}$ and $(G^e/RTW)^{\text{NI}}$ in the mixed solutions not in the equations for the unmixed solutions. For example, if we mix af and bg, the excess free energy for the mixture includes contributions from the single-salt equations for ag and bf.

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Young's second rule^{13,19} is that the heat of mixing for two electrolytes having a common ion is independent of the common ion. The corresponding rule for free energy would imply that $(\phi - 1)^{n11}$ is independent of the common ion. The rule should hold if only $B_{ab}^{(0,1)}$ ($B_{fg}^{(0,1)}$ if common cation) and other coefficients with only a and b subscripts contribute to $(\phi - 1)^{n11}$, but not necessarily if other terms of higher power in concentration are important.

Young's third rule,¹³ better known as the cross-square rule, states that for a group of electrolytes of the same valence type af, bf, ag, bg, the free energy of mixing 1 mol of af with 1 mol of bg plus that of mixing 1 mol of ag with 1 mol of bf is equal to that of mixing 1 mol of af with 1 mol of bf plus that of mixing 1 mol of ag with 1 mol of bg plus that of mixing 1 mol of bf with 1 mol of bg plus that of mixing 1 mol of ag with 1 mol of af. With our equations, it holds if $B_{abfg}^{(2,7)}$ is zero.

A recent paper²⁰ based on the treatment of Friedman gives terms which appear to be similar to the low-order

concentration terms in the ion-component treatment presented above. In applying these equations²¹ the interaction parameters are determined separately for each ionic strength and vary with ionic strength. Some of the apparent complexities of our treatments arise from the fact that the equations for these treatments include both the variation with the fraction of each solute and with the overall solute concentration.

Since the earlier treatment¹¹ of sea-water compositions as slightly perturbed NaCl solutions was satisfactory at room temperature, the ion-component approach does not result in a great improvement. It is possible, however, that the ion-component treatment will be useful at higher temperatures, for which data now exist.²²

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1.5 VISCOSITY OF MIXTURES OF ELECTROLYTE SOLUTIONS¹Y. C. Wu²

The relative viscosity of binary electrolyte solutions is generally discussed in terms of the equation of Jones and Dole³

$$\eta/\eta_0 = 1 + a\sqrt{I} + bI \quad (1)$$

where η is the viscosity of the solution, η_0 is that of the solvent, and I is the ionic strength in molar concentration units. (This equation is most often written in terms of the molar concentration c rather than ionic strength. The form used here is more convenient in discussing mixtures and in comparison with other limiting laws. For 1:1 electrolytes the two concentrations scales are the same.) The coefficient a has been identified as the slope of the limiting law of Falkenhagen.⁴ The coefficient b has been shown to have the property of additivity⁵ and has been discussed by several authorities on electrolyte solutions.⁶

Onsager and Fuoss⁷ developed equations for the ionic contribution to the viscosity of multicomponent systems, η^* , which lead to a limiting law of the form

$$\eta^* \equiv \eta - \eta_0 = a'\sqrt{I} \quad (2)$$

The limiting slopes in eq 1 and 2 are related by $a' = a\eta_0$.

It has been suggested that the additivity rule for the b coefficient of eq 1 can be extended to multicomponent mixtures.^{6a} There appear to be no explicit tests of this rule.

In this communication, the viscosities of the systems LiCl-NaCl-H₂O, LiCl-KCl-H₂O, and NaCl-MgCl₂-H₂O at 25° and in the concentration range 0.01 to 1 ionic strength are reported. These results are compared by means of eq 1 with the a coefficients of the Onsager-Fuoss theory and the b coefficients obtained from the additivity rule.

Experimental Section

Stock solutions of LiCl, NaCl, KCl, and MgCl₂ were prepared from reagent grade chemicals which had been recrystallized and dried. The concentrations were verified by titration with AgNO₃. Dilutions and mixtures were made from these stock solutions.

Viscosities were measured with Cannon-Ubbelohde semimicroviscometers with efflux times of about 400 sec. The kinetic energy correction for this type of viscometer⁸ is very small and was neglected for the systems studied here. The relative viscosity was determined from the densities and efflux times; the viscosity of water at 25° was taken as 0.8903 cP.^{6b} The densities were measured with 5-ml pycnometers. The efflux time was measured to 0.1 sec with an electric timer. The over-all reproducibility and accuracy is $\pm 0.1\%$.

Results and Discussion

Viscosity measurements were made on solutions of LiCl, NaCl, and KCl and equimolar mixtures of LiCl-NaCl and LiCl-KCl. In addition, measurements were made on an NaCl-MgCl₂ mixture (88.06 mol % NaCl) having the Na:Mg ratio of sea water.⁹ The results are shown in Table I.

Table I: Viscosities (cP) at 25°

I	KCl	LiCl-KCl 1:1	LiCl	LiCl-NaCl 1:1	NaCl
0.01		0.8912	0.8921	0.8918	0.8915
0.05		0.8944	0.8978	0.8964	0.8951
0.0625	0.8898	0.8951	0.8986		
0.10		0.8976	0.9045	0.9017	0.8991
0.125	0.8900	0.8988	0.9066		
0.25	0.8903	0.9078	0.9246		
0.50	0.8883	0.9214	0.9565	0.9400	0.9294
1.00	0.8875	0.9540	1.0250	0.9997	0.9664

I	NaCl-MgCl ₂ 88.06 mol % NaCl
0.07034	0.8978
0.1407	0.9041
0.3517	0.9240
0.7034	0.9540
1.0551	0.9934
1.4068	1.0284

The Onsager-Fuoss theory⁷ provides a means of calculating the coefficient a' of eq 2 and thus the limiting slope, a , of eq 1. The electrostatic contribution to the viscosity may be written as (ref 7, eq 3.7.2)

(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.

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$$\eta^* = A'(P - Q_n)\sqrt{I} = a'\sqrt{I} \quad (3)$$

where

$$A' = 0.362\sqrt{2}(1/DT)^{1/2}$$

$$P = \sum_i x_i z_i / \lambda_i$$

$$Q_n = 4[R] \sum_{n=0}^{\infty} b_n S^{(n)}$$

and x_i is the ionic fraction $c_i z_i^2 / \sum c_i z_i^2$, z_i the absolute value of the valence, and λ_i the ionic equivalent conductance for ion i ; D is the dielectric constant for the solvent, T is the absolute temperature, b_n are the binomial coefficients, $[R]$ and $S^{(n)}$ are matrices whose elements are functions of ionic fractions and ionic mobilities, n is the number of recursions, and $A' = 0.00335$ for aqueous solutions at 25° with the viscosity in poise units. Values for P , Q_n , and a' calculated by eq 3 are given in Table II along with the resulting value of a for eq 1.

Table II: Parameters of Eq 3

	P	Q_3	$a' \times 10^3$	a
KCl	0.01336	0.00000	4.47	0.00502
LiCl-KCl (1:1)	0.01641	0.00098	5.17	0.00580
LiCl	0.01947	0.00143	6.03	0.00678
LiCl-NaCl (1:1)	0.01800	0.00100	5.68	0.00638
NaCl	0.01653	0.00049	5.37	0.00603
NaCl-MgCl ₂ ^a	0.01665	0.00044	5.43	0.00610
MgCl ₂	0.01693	0.00032	5.56	0.00624

^a 88.06 mol % NaCl.

It can be seen from Table II that the P term is the main contribution to η^* and that it is dependent on the mixing ratio. The Q_n term is a small correction, but causes the limiting slope for mixtures to diverge from a linear combination of that of their components.

It has been shown⁶ that the b coefficient of eq 1 for binary electrolyte solutions is an additive property of the constituent ions. It seemed reasonable that values of b for mixtures of electrolytes could be obtained from the values for the individual components; thus for a mixture of two electrolytes

$$b = y_A b_A + y_B b_B \quad (4)$$

where y_J is the ionic strength fraction and b_J the linear coefficient of eq 1 for component J . Values of b for the pure salts and the mixtures are given in Table III. In this table, values for the pure salts were obtained from the ionic values^{6b} and values for the mixtures were obtained from those for the pure salts combined according to eq 4. Since most of the b coefficients in the literature are on the molar scale, it is necessary to divide these coefficients by a valence factor (1 for 1:1

Figure 1. Viscosities of pure salt solutions.

Figure 2. Viscosities of electrolyte mixtures.

Table III: Values of the b Coefficient^a

KCl	-0.014
LiCl-KCl (1:1)	0.0645
LiCl	0.143
LiCl-NaCl (1:1)	0.111
NaCl	0.079
NaCl-MgCl ₂ ^b	0.092
MgCl ₂	0.371

^a Ionic b coefficients (molar scale) used: Li⁺, 0.150; Na⁺, 0.086; K⁺, -0.007; Mg²⁺, 0.385; Cl⁻, -0.007. ^b 88.06 mol % NaCl; b coefficient converted to ionic strength scale.

electrolytes and 3 for 2:1 electrolytes) to convert them to ionic strength units for use in eq 4.

The experimental results are shown in Figures 1 and 2

as plots of $[(\eta/\eta_0) - 1]/\sqrt{I}$ vs. $\sqrt{I}$. The solid lines represent eq 1 with values of a from the Onsager-Fuoss theory (Table II) and values of b from the additivity rule (Table III). The agreement between the calculated curves and the experimental points is satisfactory, at least up to $I = 1$.

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2. THERMODYNAMIC PROPERTIES OF WATER-ORGANIC SYSTEMS

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2.1 PROPERTIES OF ORGANIC-WATER MIXTURES. X. ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE AT SATURATION IN WATER MIXTURES OF POLYGLYCOLS AND POLYGLYCOL ETHERS AT 50°¹

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

The solubility of NaCl in water mixtures of a number of organic solvents was determined at 50° by packed-column techniques. The solvents included ethylene glycol (EG) and polyethylene glycols (PEG) to molecular weight 1000, monomethyl ethers of EG and PEG to mol wt 750, and dimethyl ethers of EG and PEG to mol wt 1230. From the solubility data, activity coefficient ratios Γ^* of NaCl were computed and compared as a function of molecular weight and functional end groups. As expected, the influence of the end groups on Γ^* becomes less as the molecular weight increases. A value for Γ^* of ca. 20 is predicted at 50° for infinite chains of ethoxy groups (or films) containing 5% water. Implications for hyperfiltration membranes are discussed.

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 papers²⁻⁵ dealt with the comparison of activity coefficients of several salts, including NaCl, in organic-water mixtures at saturation. The present paper deals with the effect of chain length and functional end groups on the activity coefficient of NaCl in water mixtures of organic compounds in three homologous series, namely, ethylene glycol and polyethylene glycols; methoxyethanol (methyl cellosolve) and methoxypolyethylene glycols; and ethylene glycol dimethyl ether and methylated products of polyethylene glycol.

Experimental Section

Packed-Column Method. The packed-column technique for measuring solubilities has been described previously.^{2,6} It involves passage of a solution through a small column filled with salt and analysis of the effluent. Most of the columns were 6 mm i.d. and the salt beds were 6 to 8 cm high. The columns were thermostated by circulation of water through a jacket surrounding them. Normally, gravity flow yielded adequate flow rates; for the more viscous solutions, however, a small external pressure was applied. For each solvent mixture at least two samples were collected and in many cases flow rates were varied to establish that sufficient contact time had been allowed.

The effluent samples were weighed and analyzed. The salt concentration was established by chloride titration with silver nitrate, using chromate as indicator. Titration precision was usually better than 0.1%.

Materials. (a) *Salt.* Reagent grade NaCl was used,

with a maximum stated impurity of 0.025%. It was dried at 400° for 24 hr to remove traces of moisture.

(b) *Solutions.* Mixtures of the organic solvents and water were prepared by weight. Some of the dimethyl ethers are not completely miscible with water, particularly in the presence of NaCl, and only mixtures containing small amounts of water could be used.

Organic Compounds. Ethylene glycol was distilled, retaining the middle 60%. Samples of polyethylene glycols were used as received—Union Carbide Carbowax 200, 300, 400, 600, and 1000. The numbers (manufacturer's designations) indicate the average molecular weight ($\pm 5\%$) of the polymers. Ethylene glycol monomethyl ether was distilled, retaining the middle 70%. The hydroxyl content was found to be 22.2%, compared to 22.4% calculated. Diethylene glycol monomethyl ether was dissolved in 2 volumes of chloroform, extracted 5 times with 0.1 volume of water each time. The product from fractionation of the chloroform layer was found to contain, by reaction with acetic anhydride, 14.5% hydroxyl (14.2% calculated) and, by reaction with periodate, 0.2% ethylene glycol. Carbowax 350 and 750 (methoxypolyethylene glycols) were used as received. Dimethyl ethers of ethylene glycol, diethylene glycol, triethylene glycol, and tetra-

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ethylene glycol (Ansul ethers 121, 141, 161, and 181) were fractionated before use and found to contain less than 0.4% hydroxyl.

Polyethylene glycols (obtained from Wyandotte Chemical Co., designated Pluracol E200, E400, E600, and E1000) were methylated with dimethyl sulfate according to the method of Haworth.⁷ A sample of the polyethylene glycol (0.25 mol) was placed in a 3-necked flask fitted with two dropping funnels and a mechanical stirrer. The flask was placed in a water bath that had been heated to 70°. During the course of 1 hr, reagents were added, with stirring: from one funnel 500 ml (3.75 moles) of 30% sodium hydroxide and from the other funnel 190 g (1.5 moles) of dimethyl sulfate. The addition of the sodium hydroxide was started first and maintained at a more rapid rate to keep the solution in the flask alkaline. When the addition had been completed the temperature of the water bath was raised to 100° and held there for 0.5 hr. The mixture was allowed to cool and to stand overnight. Eight hundred ml of distilled water was added to the reaction mixture and the aqueous solution was extracted 5 times with chloroform, a fresh 250-ml portion being used each time. Each chloroform extract was equilibrated with 100 ml of distilled water; the same 100-ml portion of water being used for all of the chloroform extracts. The combined chloroform solutions were evaporated first at atmospheric pressure, and finally at oil pump pressure (1 Torr). The yield of product was 96% of that calculated and the product contained 0.2% hydroxyl.

The molecular weights of the methylated products of E200, E400, and E600 were determined cryoscopically to be 260, 580, and 850, respectively, using cyclohexane as the solvent. The mol wt of the methylated product of E1000 was measured to be 1230 by vapor-phase osmometry, using chloroform as the solvent. The values obtained are estimated to be accurate to $\pm 10\%$.

Results

Solubility of NaCl. The solubility of NaCl was measured at 50° in aqueous mixtures of 18 different organic compounds which are members of three homologous series, as shown in Table I. The results are given in Table II in terms of grams of NaCl dissolved in 1 kilogram of mixed solvent. In some cases measurements were made over the entire range of organic-water composition. For other compounds measurements were made only at high organic content (5–10% water) which is the region of primary interest in this study. For a few compounds, *e.g.*, EGDME, limited miscibility with water determined the range of composition studied. Measurements were made at 50° ($\pm 0.02^\circ$) so that mixtures of PEG 1000 containing 5 and 10% water and PEGDME 1230 containing 5% water, which are solid at 25°, could be included.

Table I: Organic Compounds Studied

Glycols—HO(CH₂CH₂O)_nH	
Ethylene glycol (EG)	
Polyethylene glycol (PEG)—mol wt 200, 300, 400, 600, and 1000	
Monomethyl ethers of glycols—CH₃O(CH₂CH₂O)_nH	
Ethylene glycol monomethyl ether (EGMME) (methyl cellosolve)	
Diethylene glycol monomethyl ether (DEGMME) (methyl carbitol)	
Polyethylene glycol monomethyl ether (PEGMME)—mol wt 350 and 750	
Dimethyl ethers of glycols—CH₃O(CH₂CH₂O)_nCH₃	
Ethylene glycol dimethyl ether (EGDME)	
Diethylene glycol dimethyl ether (DEGDME)	
Triethylene glycol dimethyl ether (TEGDME)	
Tetraethylene glycol dimethyl ether (TetEGDME)	
Polyethylene glycol dimethyl ether (PEGDME)—mol wt 260, 580, 850, 1230	

The solubility of NaCl in ethylene glycol–water mixtures can be compared with previous results at 25°. The solubility is slightly higher (1–2%) at 50° for solvent mixtures containing at least 15% water, essentially the same for 5% water, and slightly less (2%) at 50° for the pure EG.

For the glycols and monomethyl ethers, the solubility of NaCl at a given water content decreases as mol wt increases as has been observed previously with alcohols (methyl, ethyl, etc.) at 25°. However, for the dimethyl ethers, the solubility of NaCl increases with increasing molecular weight. The replacement of an –OH group with a –OCH₃ group for any given chain length causes a decrease in the solubility of NaCl. However, for the dimethyl ethers, lengthening the chain with additional –CH₂CH₂O– groups tends to offset the effect of two –OCH₃ groups and results in an increase in solubility for NaCl. There is also an increase in miscibility with water with increasing molecular weight for the diethers.

Activity Coefficients of NaCl. The results for the different compounds 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.^{4,9}

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Table II: Solubility of NaCl in Organic-Water Mixtures at 50°

Compd	Wt % organic	Solubility, g/kg of solvent	Compd	Wt % organic	Solubility, g/kg of solvent
EG	25.30	266.8	PEGMME 350	25.01	242.8
	50.24	184.7		50.01	139.0
	74.83	113.6		75.00	50.0
	85.26	91.9		84.99	23.2
	95.06	75.6		90.00	12.4
	100.0	68.4		95.00	3.96
PEG 200	89.87	43.0	PEGMME 750	25.01	248.0
	95.02	32.2		49.98	137.5
PEG 300	89.99	30.7		74.97	47.0
	95.03	19.8		85.00	19.5
PEG 400	24.07	250.5		90.00	9.16
	49.92	150.0		95.00	2.14
	74.90	63.4	EGDME	95.01	0.13
	84.98	36.0		90.00	2.32
	90.01	24.6	DEGME	94.73	0.22
	94.74	13.4		90.00	3.12
	100.0	4.57	TEGDME	04.08	0.31
PEG 600	90.00	17.0		90.00	3.32
	95.00	7.00	TetEGDME	94.95	0.32
PEG 1000	24.94	248.8		94.97	0.55
	50.07	140.6	PEGDME 260	94.99	0.66
	74.96	51.6		94.87	0.65
	85.05	23.0	PEGDME 1230	25.01	246.6
	89.99	11.9		50.02	135.0
	95.01	3.19		74.93	43.8
EGMME	95.03	11.3		84.92	15.5
DEGMME	90.00	16.65		95.00	0.64
	95.16	7.94			

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 kg of solvent, and f_w is the fractional water content of the solvent (kg of H_2O per kg of solvent), Γ^* is given by

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

The solubility of NaCl in pure water, s_{aq} , was taken to be 366.7 g/kg of H_2O at 50°.⁸

The values of Γ^* for different glycols as a function of water content are shown in Figure 1. At any given water content Γ^* increases with increasing mol wt, although the change is small for $f_w > 0.5$. Maxima are observed for EG and PEG 400 and are implied for PEG 200 and 300 for $f_w > 0.10$. Since Γ^* must approach zero as f_w goes to zero, maxima are also implied for PEG 600 and 1000, for $f_w < 0.05$ (95 to 100% organic). Although measurements were not made for PEG 200, 300, and 600 for $f_w > 0.10$, Γ^* values, and hence solubilities, could be estimated for this range with a fair degree of accuracy, at least better than 10%.

Figure 2 shows similar data for the monoethers and diethers. Except for EGMME and DEGMME, the maximum values of Γ^* lie between $f_w = 0$ and 0.05.

The Γ^* values at 5% water for all the compounds are replotted in Figure 3 as a function of molecular weight. A reasonably smooth curve can be drawn through the points for each series. The three curves are far apart at low mol wt but seem to converge to a single point as the mol wt approaches infinity. At high mol wt the end groups become less important relative to the long chains of $-CH_2CH_2O-$ groups. One would therefore predict that an infinitely long chain (or film) composed of $-CH_2CH_2O-$ groups and containing 5% water would have a value for Γ^* (if it could be measured) of ca. 20. Similar extrapolations at 10% and 15% water yield Γ^* values of 6 and 3.5, respectively. These extrapolated values are plotted in Figure 4, together with three curves from Figures 1 and 2 for comparison. At $f_w > 0.15$, the curve for the infinite polymer should be approximated by the curve for PEGDME 1230. Thus one could estimate the activity coefficient of NaCl at saturation for any given water content in an infinite polymer of the type $R(CH_2CH_2O)_nR$.

Knowledge of activity coefficients allows calculation of minimum asymptotic salt rejection R_{∞} by hyperfiltration membranes. The limiting rejection R_{∞} of a membrane at sufficiently high fluxes of water through

Figure 1. Activity coefficient ratios of NaCl at saturation in aqueous solutions of ethylene glycol and polyglycols at 50°.

Figure 3. Activity coefficient ratios at 50° of NaCl at saturation in solutions of polyglycols and polyglycol ethers containing 5% water.

Figure 2. Activity coefficient ratios of NaCl at saturation in aqueous solutions of some glycol monomethyl and dimethyl ethers at 50°.

Figure 4. Estimation of NaCl activity coefficient ratio at 50° for polyethers.

it is related to a distribution coefficient D^* at the entrance interface by⁹

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

Here β is a coupling coefficient which is usually presumed to be between 0 and 1; the minimum value of R_{∞} occurs for $\beta = 1$. The distribution coefficient (for uncharged membranes) is related to the activity coefficient ratio by $D^* = 1/\Gamma^*$. Hence

$$R_{\infty}(\beta = 1) = 1 - 1/\Gamma^* \quad (3)$$

Polyether membranes containing 25% water ($\Gamma^* \approx 2$) would thus have $R_{\infty}(\beta = 1) = 0.5$, or a minimum asymptotic salt rejection of 50%. At lower water contents minimum asymptotic rejection would be considerably higher.

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2.2 PROPERTIES OF ORGANIC-WATER MIXTURES. XII. ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE AT SATURATION IN AQUEOUS SOLUTIONS OF SOME OXY-OXA COMPOUNDS AT 25°C

Richard J. Raridon and Kurt A. Kraus

The solubility of NaCl in aqueous solutions of a number of organic solvents was determined at 25°C by packed column techniques. The solvents were primarily low-molecular-weight diols, cellosolves, or carbitols. From the solubility data, activity coefficients $\gamma_{\pm}$ of NaCl can be computed. For solutions containing 5% water, $\log \gamma_{\pm}$, as a first approximation, varies linearly with the number of carbon atoms in a given series.

As part of the continuing 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 collected. Previous papers (1, 3) dealt with the comparison of activity coefficients of several salts, including NaCl, in aqueous organic solutions at saturation. The present paper summarizes a large number of solubility measurements at 25°C for NaCl in 21 different organic compounds as a function of water content. The compounds are primarily low-molecular-weight diols, cellosolves, or carbitols. They can be classified under the types $R''OR'OH$ or $R''OR'OROH$ where R and R' range from $-C_2H_4-$ to $-C_6H_{12}-$, and R'' ranges from $-H$ to $-C_4H_9$.

EXPERIMENTAL

Packed Column Method. The packed column technique for measuring solubilities has been described previously (3). It involves passage of a solution through a small column filled with salt plus analysis of the effluent. Columns of 0.6-cm diameter were filled to a height of 6 to 8 cm with fine grained (ca. 50 mesh) NaCl; gravity flow rates were ca. 1 cm/min which, according to earlier studies, and confirmed in occasional cross-checks here, were easily within the range demanded by the 0.1% analytical precision and corresponding approach to equilibrium.

The effluent samples were weighed and analyzed. The salt concentration was established by chloride titration with silver nitrate, using chromate as indicator.

Materials. *Salt.* Reagent grade NaCl was used, with a stated maximum impurity of 0.025%. It was dried at 400°C for 24 hr to remove traces of moisture.

Organic Compounds. All of the compounds used were commercial materials that were further purified by crystallization, distribution, and fractional distillation where appropriate. The middle portions from the distillation step (bp range $< 1^\circ$) were reserved for this study. They were checked to be essentially water-free. Mixtures with water were prepared by weight to give generally five different water contents, 5, 15, 25, 50, and 75%.

RESULTS AND DISCUSSION

Solubility Measurements. The solubility of NaCl was measured at 25°C in aqueous solutions of 21 different organic compounds. The results are given in Table I in terms of grams of NaCl dissolved in 1 kg of mixed solvent. In most cases, measurements were made over the entire range of organic-water composition. For a few compounds, however, limited miscibility in the presence of NaCl determined the range of composition studied. Water-free measurements could not be made in three of the compounds that are solids at 25°C: but-2-yne-1,4-diol, 2,2-dimethylpropane-1,3-diol, and 2-methyl-2-ethylpropane-1,3-diol.

Table I. Solubility of NaCl in Organic-Water Mixtures at 25° C

No.	Compound	Solubility,			No.	Compound	Solubility,				
		Wt % organic	g/kg solvent	$\gamma_{\pm}$			Wt % organic	g/kg solvent	$\gamma_{\pm}$		
1	Butane-1,3-diol, $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{OH}$	25.51	222.0	1.21	12	2-Methoxy,1-(2'-hydroxy-ethoxy)ethane, (methyl carbitol), $\text{CH}_3\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$	24.98	233.5	1.16		
		50.09	113.1	1.60			50.02	129.2	1.40		
		75.04	32.6	2.77			75.00	49.6	1.82		
		85.01	14.1	3.84			84.89	27.1	2.02		
		95.02	4.82	3.74			95.16	10.1	1.74		
100.0	2.73		100.0	4.04							
2	Butane-1,4-diol, $\text{CH}_2(\text{OH})\text{C}_3\text{H}_6\text{OH}$	24.99	231	1.18	13	2-Methoxypropane-1-ol, $\text{CH}_3\text{OC}_3\text{H}_7\text{OH}$	25.00	222.0	1.22		
		50.01	119.8	1.51			50.01	120.1	1.51		
		74.96	33.9	2.67			74.98	36.3	2.50		
		84.89	15.0	3.65			84.98	14.9	3.65		
		94.82	5.04	3.72			95.07	2.56	6.97		
100.0	2.69		100.0	0.05							
3	But-2-ene-1,4-diol, $\text{CH}_2(\text{OH})\text{CH}=\text{CHCH}_2\text{OH}$	25.00	238.8	1.14	14	2-Methoxy,1-(2'-hydroxy-propoxy)propane, $\text{CH}_3\text{OC}_3\text{H}_7\text{OC}_3\text{H}_7\text{OH}$	25.00	226.2	1.20		
		50.00	132.8	1.36			49.91	123.4	1.47		
		75.00	47.2	1.92			75.04	39.7	2.28		
		85.00	23.7	2.29			85.06	16.8	3.22		
		94.98	9.91	1.83			95.04	3.85	4.67		
100.0	6.02		100.0	1.09							
4	2-Butoxyethane-1-ol (butyl cellosolve), $\text{C}_4\text{H}_9\text{OC}_2\text{H}_4\text{OH}$	30.39	°		15	2-Methyl-2-ethylpropane-1,3-diol, $\text{CH}_2(\text{OH})\text{C}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$	49.93	°			
		60.36	°				75.06	°			
		90.05	9.42	3.82			85.00	27.2	2.00		
		91.99	6.01	4.82			90.04	12.2	2.96		
		94.06	3.36	6.40			100.0	°			
		95.92	1.73	8.58							
		97.95	0.76	9.76							
100.0	0.29										
5	2-Butoxy,1-(2'-hydroxy-propoxy)ethane, $\text{C}_4\text{H}_9\text{OC}_2\text{H}_4\text{OC}_3\text{H}_7\text{OH}$	75.01	°		16	2-Methylpentane-2,4-diol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CH}_3$	50.01	°			
		84.99	°				74.97	°			
		95.06	0.835	21.4			90.00	3.78	9.58		
		100.0	0.067				95.01	1.00	18.1		
				100.0	0.23						
6	But-2-yne-1,4-diol, $\text{CH}_2(\text{OH})\text{C}\equiv\text{CCH}_2\text{OH}$	25.00	244.5	1.11	17	Bis(2-hydroxyethyl)ether, $\text{CH}_2(\text{OH})\text{CH}_2\text{OC}_2\text{H}_4\text{OH}$	24.79	253.1	1.08		
		49.99	143.7	1.26			50.07	160.6	1.12		
		77.51	59.5	1.49			75.04	88.4	1.02		
		100.0	°				84.89	68.8	0.79		
7	2,2-Dimethylpropane-1,3-diol, $\text{CH}_2(\text{OH})\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}$	25.10	228.3	1.19		95.09	51.9	0.34			
		49.94	129.3	1.40	100.0	45.4					
		75.02	42.4	2.13							
		85.82	18.6	2.76							
		100.0	°								
8	2-Ethoxyethane-1-ol (cellosolve), $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{OH}$	25.10	219.9	1.23	18	Bis(1-methyl-2-hydroxy-ethyl)ether, $\text{CH}_2(\text{OH})\text{CH}(\text{CH}_3)\text{OCH}(\text{CH}_3)\text{CH}_2\text{OH}$	25.45	229.1	1.18		
		50.60	116.4	1.54			50.10	127.3	1.42		
		75.08	38.0	2.37			75.06	48.8	1.85		
		85.23	16.6	3.21			85.05	27.4	1.97		
		95.03	4.39	4.10			95.04	12.3	1.46		
		100.0	1.24				100.0	6.09			
9	2-Ethoxy,1-(2'-hydroxyethoxy)-ethane (carbitol), $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$	24.98	227.6	1.19	19	Pentane-1,5-diol, $\text{CH}_2(\text{OH})\text{C}_4\text{H}_9\text{OH}$	25.10	230.2	1.18		
		50.01	118.9	1.52			50.30	121.7	1.48		
		75.01	38.0	2.38			74.92	34.7	2.62		
		84.86	17.2	3.19			85.06	12.0	4.51		
		94.07	4.62	3.94			94.84	2.68	6.97		
		100.0	1.33				100.0	1.02			
10	Hexane-2,5-diol, $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{CH}(\text{OH})\text{CH}_3$	25.01	222.0	1.22	20	Propane-1,2-diol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$	25.06	237.3	1.14		
		50.04	117.8	1.54			50.13	141.7	1.27		
		75.02	29.2	3.10			75.03	68.8	1.31		
		85.00	7.65	7.10			85.08	48.7	1.11		
		94.97	0.70	26.0			95.02	34.4	0.52		
		100.0	0.12				100.0	28.8			
11	2-Methoxyethane-1-ol, $\text{CH}_3\text{OC}_2\text{H}_4\text{OH}$	25.10	229.2	1.18	21	Propane-1,3-diol, $\text{CH}_2(\text{OH})\text{C}_2\text{H}_4\text{OH}$	25.00	224.2	1.21		
		50.63	125.6	1.42			49.94	122.3	1.48		
		75.08	51.8	1.74			74.85	47.6	1.91		
		85.34	30.6	1.73			85.00	26.8	2.03		
		95.03	15.2	1.18			94.99	14.9	1.22		
100.0	8.41		100.0	11.3							

° Immiscible mixture when saturated with NaCl. ° Solid at 25° C.

Figure 1. Activity coefficients of sodium chloride at saturation in solutions of some oxy-oxa compounds containing 5% water N_{CH} = no. of carbon-hydrogen bonds, N_O = no. of oxygen atoms, compounds identified in Table I

The solubility of NaCl in 5% water mixtures of 2-methoxyethane-1-ol and 2-methoxy,1-(2'-hydroxyethoxy)ethane can be compared with previous results at 50°C (1). In both cases the solubilities are about 25% higher at 25°C.

For the straight-chain compounds, the solubility of NaCl at a given water content decreases as mol wt increases, as had been previously observed with glycols (1), glycol monomethyl ethers (1), and alcohols (4). Branching has a measurable effect on solubility but, as might be expected, the effect becomes less pronounced as the chain length increases. For example, at water contents less than 15%, the solubilities of NaCl in the propane diols differ by a factor of two or more; for the butane diols, the solubilities are nearly the same over the entire composition range. Comparison of the results for the 5-carbon diols (pentane-1,5-diol and 2,2-dimethylpropane-1,3-diol) shows that branching not involving functional groups can also result in a higher NaCl solubility at low water contents.

The effect of unsaturation on the solubility of NaCl can be seen for the 4-carbon diols. The solubility at any water content increases as the unsaturation increases, being highest in water mixtures of but-2-yn-1,4-diol.

It is interesting to note that in two pairs of isomers involving a diol and a monoether, the solubility of NaCl is nearly the same in each at any given water content—i.e., for propane-1,3-diol and 2-methoxyethane-1-ol and for butane-1,4-diol and 2-ethoxyethane-1-ol.

Activity Coefficients of NaCl. The results for the different compounds can also be compared in terms of an activity coefficient $\gamma_{\pm}^*$, which 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 mol/kg of water. The $\gamma_{\pm}^*$ is a measure of the relative selectivity of the medium for salt and water; it is a useful quantity

for evaluation of model solutions for hyperfiltration membranes (1, 2).

If s_{aq} is the solubility in pure water and s_o is the solubility in the water-organic mixture, both expressed in mol/kg of solvent, and f_w is the fractional water content of the solvent (kg of H_2O /kg of solvent), $\gamma_{\pm}^*$ is given by (3):

$$\gamma_{\pm}^* = s_{aq} f_w \gamma_{\pm} / s_o$$

The solubility of NaCl in pure water, s_{aq} , was taken to be 360 g/kg of H_2O at 25°C (4), and $\gamma_{\pm} = 1.006$ (3).

The values of $\gamma_{\pm}^*$ in 5% water mixtures are shown in Figure 1 as a function of N_{CH}/N_O where N_{CH} is the number of carbon-hydrogen bonds and N_O is the number of oxygen atoms present in the molecule. The value for ethylene glycol (3) is also included. The logarithm of the activity coefficients for these two series ($R''ONROH$ and $R''OR'OROH$) increases roughly linearly with this ratio. The equation for the dashed line in Figure 1 is

$$\log \gamma_{\pm}^* = -1.8 + 0.53 N_{CH}/N_O$$

Activity coefficients in some of the higher members of the polymer series of polyethylene glycols and their monomethyl ethers (1) also fall near this straight line. The activity coefficients in the dimethyl ethers and the highest molecular-weight members of the other two polymer series, however, are far above those predicted from Figure 1. Thus, although the relationship could be used to approximate activity coefficients for other members of the series studied here, it should not be used for widely differing series.

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NOMENCLATURE

- f_w = wt fraction H_2O in water-organic mixture
- N_{CH} = number of hydrogen atoms attached to carbon atoms in molecule (C-H bonds)
- N_O = number of oxygen atoms in molecule
- s_{aq} = solubility of NaCl in water (mol/kg water)
- s_o = solubility of NaCl in water-organic mixture (mol/kg solvent)
- $\gamma_{\pm}$ = mean activity coefficient of NaCl in water
- $\gamma_{\pm}^*$ = mean activity coefficient of NaCl in water-organic mixture (for concentrations expressed as mol/kg water)

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2.3 MISCIBILITY IN THE SYSTEM PYRIDINE-SULFURIC ACID-WATER

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

During the study of the activity coefficients of salts in pyridine (P)-water-acid mixtures, we observed that the preparation of some (P)-H₂SO₄-H₂O mixtures resulted in two-phase systems. We undertook a brief study to determine the phase diagram of this system. The experimental method was similar to that used previously for the glycerol triacetate-water-salt systems.¹ A mixture of two components [(P)-H₂SO₄ or (P)-H₂O] was prepared by weight in a flask, and then the third component was added drop-wise while the mixture was stirred in a water bath kept at 25°C. The sulfuric acid contained a few percent water. Whenever the number or type of phases changed, the flask was reweighed. The results are shown in Fig. 2.3.1, where each hash mark indicates a 10% change by weight. Although most of the figure is occupied by one liquid phase, there is a region where two liquid phases are present, one of them being primarily (P)-H₂O. Another portion is occupied by a liquid phase and a solid phase, the solid material being stoichiometrically (P)₂(H₂SO₄), pyridinium sulfate. There is also a small region where three phases are present, two liquid phases and solid pyridinium sulfate.

There may be some significance to the positions of the peaks for the two-phase regions shown [43%(P)-14% H₂SO₄-43% H₂O and 38% (P)-50% H₂SO₄-12% H₂O]. The (P)-H₂SO₄ ratios for these two points correspond nearly stoichiometrically to (P)₄(H₂SO₄) and (P)(H₂SO₄).

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FIG. 2.3.1 MISCIBILITY IN THE SYSTEM PYRIDINE-H₂SO₄-H₂O AT 25°C.

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