Determination of the Mean Activity Coefficients of Mixed Aqueous Sulfuric Acid-Sulfate Solutions

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Isopiestic measurements of the activities of water at 298 K were extended to the aqueous solution system sulfuric acid-sulfate (including nickel sulfate, zinc sulfate and copper sulfate). The mean activity coefficients of sulfuric acid and sulfate of these solutions were calculated by the McKay-Perring method. The authors compared the calculated values of the mean activity coefficients of sulfuric acid in aqueous sulfuric acid solutions containing sodium sulfate, lithium sulfate, magnesium sulfate and zinc sulfate as determined by McKay-Perring method to those previously determined by *emf* measurements. It was found that the calculated mean activity coefficients of sulfuric acid in concentrated mixed solutions based on water activity data estimated from Zdanovskii rule coincided well with those experimentally determined. In dilute mixed solutions, however, the difference between the calculated mean activity coefficients of sulfuric acid and those experimentally determined become appreciable even after the corrections due to deviations from the Zdanovskii rule were made.

1 Introduction

In the authors' laboratory, the activities of sulfuric acid in aqueous sulfuric acid solutions containing sulfates of alkali or alkali earth metals were determined by measuring the *emf* of a cell consisting of platinum-platinum black electrode, lead dioxide-lead sulfate electrode and test solution¹⁾. Also the activities of water in these solutions were measured by an isopiestic method²⁾. Furthermore, the authors calculated the activities of solutes based on the Gibbs-Duhem relationship by using the activity data of sulfuric acid and water determined by themselves as reported elsewhere³⁾.

During the course of this study a difficulty emerged in the employment of the electromotive force measurement technique for determining the activity of sulfuric acid in aqueous sulfuric acid solutions containing sulfates of common metals such as zinc, nickel, copper and others.

McKay and Perring studied methods of calculating the mean activity coefficients of mixed aqueous electrolytes from water vapor pressures, and derived thermodynamic equations⁴⁾. According to those authors, one of those equations is particularly suitable for application to iso-

piestic experiments. Based on this, the activities of sulfuric acid in aqueous sulfuric acid-sulfate solutions can be calculated by using the data of the activity of water in the solutions being studied.

In this study, the applicability of the McKay-Perring method for the determination of the mean activity coefficients of solutes in sulfuric acid-sulfate solutions was examined by comparing the calculated mean activity coefficients of sulfuric acid in the aqueous sulfuric acid solutions containing sodium sulfate, lithium sulfate or magnesium sulfate to those determined by *emf* measurements. It was found through this comparison that reasonable similarity between calculated activity coefficients and those experimentally determined was obtainable; agreement increased with solution concentration. Based on this finding, the mean activity coefficients of sulfuric acid in aqueous solutions of sulfuric acid-sulfate (including zinc sulfate, nickel sulfate and copper sulfate) were calculated by the McKay-Perring method, using activity data on water as determined by the isopiestic method detailed in the present study.

2 Experimental Procedures

Activities of water in aqueous sulfuric acid-sulfate solutions were determined by using an isopiestic method.

The apparatus and the experimental proce-

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dures used are as detailed in a previous paper²⁾. All measurements of solution vapor equilibrium were made at 298 K. Reagent grade chemicals and de-ionized water with the specific resistivity of $5 \times 10^6 \Omega \cdot \text{cm}$ were used in this study.

3 Experimental Results

By determining the composition of solutions equilibrated with water vapor, the activities of water in aqueous solutions containing involatile solutes could be readily estimated. The activities of water, $a(w)$, in aqueous sulfuric acid-sulfate (including zinc sulfate, nickel sulfate and copper sulfate) solutions were determined on this basis.

Figure 1 shows the equi $a(w)$ lines of the aqueous sulfuric acid-zinc sulfate solutions determined at 298 K in this work. The dotted line shown in the same figure were determined from the Zdanovskii rule⁹⁾.

In the previous work in which the activities of water in aqueous sulfuric acid solutions containing sulfates of alkali or alkali earth metals were determined, the authors noted that the empirical Zdanovskii rule, originally developed for aqueous solutions, was also applicable in providing a rough determination of the activity of water in the aqueous solutions of sulfuric

acid-sulfate. As can be seen in Fig. 1, the activity of water decreases with an increase in the concentration of either sulfuric acid or zinc sulfate. The measured deviation of $a(w)$ from the empirical Zdanovskii rule for this particular solution system was small, showing a slight deviation towards the lower side. A similar deviation was noted for solution of nickel sulfate and copper sulfate. It may be concluded, therefore, that the solution system sulfuric acid-zinc sulfate can be accurately estimated by using the values of $a(w)$ of the solution systems water-sulfuric acid and water-zinc sulfate.

Similar isopiestic experiments were made for the aqueous solutions of sulfuric acid-nickel sulfate and sulfuric acid-copper sulfate. A part of these experimental results are depicted in the form of an equi $a(w)$ diagram as shown in Fig. 2. For comparison purposes, the equi $a(w)$ lines for the aqueous sulfuric acid solutions of sodium sulfate, lithium sulfate and magnesium sulfate are illustrated on the same figure. In contrast to this, the equi $a(w)$ lines of aqueous sulfuric acid solutions containing sulfates of alkali or alkali earth metals deviated towards upper side.

Fig. 1 Equi $a(w)$ lines of the aqueous solutions H_2SO_4 - ZnSO_4 determined by an isopiestic method at 298 K

(dotted lines show the calculated lines from the Zdanovskii rule)

Fig. 2 Comparison of equi $a(w)$ lines of the aqueous H_2SO_4 - MSO_4 solutions of different metal sulfates

4 Calculation of Mean Activity Coefficients of Sulfuric Acid in the Aqueous Solutions of Sulfuric Acid-Sulfate

McKay and Perring derived the equations which permit the exact calculation of the mean activity coefficients of solutes in mixed solutions using vapor pressures⁴. A modified form of one of those equations which is particularly suitable for application to isopiestic experiments may be written as equation (1)

$$0.018 \nu_1 \ln \frac{\gamma_{\pm,1} \cdot m^*}{\Gamma_{\pm,1} \cdot M_1} = - \int_0^{\ln a(w)} \left\{ \frac{1}{m^{*2}} \cdot \left(\frac{\partial m^*}{\partial \ln x_2} \right) + \frac{1}{m^*} - \frac{1}{M_1} \right\} d \ln a(w) \quad (1)$$

$$m^* = m_1 + (\nu_2/\nu_1)m_2 \\ x_2 = (\nu_2/\nu_1)m_2/m^*$$

where suffixes 1 and 2 denote sulfuric acid and sulfate, respectively. m and $\gamma_{\pm}$ are the molarity of a solute and its mean activity coefficients, respectively, in the mixed solutions. M and $\Gamma_{\pm}$ are the values of m and $\gamma_{\pm}$, respectively, in a pure solution containing the solute, whose $a(w)$ value is the same as the mixed solution and ν denotes the number of ions formed by complete dissociation of one molecule of the solute.

Figure 3 schematically shows an equi $a(w)$ diagram. In order to calculate the mean activity coefficient of sulfuric acid in a mixed aqueous solution of sulfuric acid and sulfate from equation (1), it is necessary to integrate from A to O under a constant m_2/m_1 ratio, where A corresponds to the composition of the mixed solu-

Fig. 3 The direction of integration by McKay-Perring method based on the equi $a(w)$ diagram

tion being studied. If we express the integrand in equation (1) by I , equation (2) is obtained.

$$I = \frac{1}{m^{*2}} \left(\frac{\partial m^*}{\partial \ln x_2} \right) + \frac{1}{m^*} - \frac{1}{M_1} \quad (2)$$

When the equi $a(w)$ lines of a mixed solution system obey the Zdanovskii rule, the calculation of equation (1) is simplified as the integrand I equals zero.

$$m_1/M_1 + m_2/M_2 = 1 \quad (3)$$

Equation (1) in this case can be simplified to be

$$\gamma_{\pm,1} = \Gamma_{\pm,1} \frac{M_1 \nu_1}{m(\nu_1 y_1 + \nu_2 y_2)} \quad (4)$$

where y denotes the ratio of molality of solute to the total molality m of solutes.

The activity of water in mixed solutions often deviates from the Zdanovskii rule. For such solution systems, the use of a corrected isopiestic relationship as originally proposed by Kirgintsev and Lukyanov⁶ is effective. This relationship is given by equation (5).

$$y_1/M_1 + Y_2/M_2 + b y_1 y_2 = 1/(m_1 + m_2) \quad (5)$$

where b is a parameter relating to the deviation from the Zdanovskii linearity. Generally speaking, however, b itself is a function of $a(w)$ and is only available when the value of $a(w)$ for the ternary system has been previously determined.

A re-arrangement of equation (5) yields equation (6).

$$m_1/M_1 + m_2/M_2 + b m_1 m_2/m = 1 \quad (6)$$

In this case, the integrand in equation (1) is expressed as

$$I = b y_2^2 \quad (7)$$

Mikhailov⁷ rationalized equation (5) and assumed a linear relationship between b and $a(w)$.

$$b = A + B a(w) \quad (8)$$

where A and B are constants.

If the relationship between b and $a(w)$ in equation (8) holds, we can calculate $\gamma_{\pm,1}$ according to equation (9).

$$\gamma_{\pm,1} = \Gamma_{\pm,1} \frac{M_1 \nu_1}{m(\nu_1 y_1 + \nu_2 y_2)} e^{\Delta} \quad (9)$$

in which

$$\Delta = - \frac{1}{0.018 \nu_1} y_2^2 \cdot [A \ln a(w) + B \{a(w) - 1\}]$$

Therefore, as the constants A and B are known, we can calculate.

Fig. 4 Linear relationship observed between b and $a(w)$ values of the aqueous solutions of H_2SO_4 - MSO_4 at 298 K

Figure 4 depicts the relationship between b and $a(w)$ in the mixed solution systems studied in this work. As shown in this figure, a satisfactory linear relationship can be seen for all solutions. The values of b for the aqueous sulfuric acid containing sulfate of alkali or alkali earth metal appear to be negative, while those for the solutions containing zinc sulfate, nickel sulfate and copper sulfate are positive. The results shown in Fig. 4 indicate that it is reasonable to calculate the mean activity coefficients of sulfuric acid in the mixed solutions of sulfuric acid-sulfate by using equation (9).

As mentioned before, two of the present authors and their collaborators previously determined the mean activity coefficients of sulfuric acid in mixed aqueous solutions of sulfuric acid-sulfate (including magnesium sulfate, sodium sulfate and lithium sulfate) by electromotive force measurements. Using this data we can compare the calculated mean activity coefficients based upon the McKay-Perring method with those determined experimentally for the mixed solutions of these solution systems.

Figure 5 shows $\gamma_{\pm}(\text{H}_2\text{SO}_4)$ of $0.1 \text{ mol} \cdot \text{kg}^{-1}$ H_2SO_4 solutions as a function of the molality of sulfate at 298 K. In these figures the blank circles indicate the experimentally determined mean activity coefficients of sulfuric acid; solid

Fig. 5 Comparison of the mean activity coefficients of H_2SO_4 in the aqueous $0.1 \text{ mol} \cdot \text{kg}^{-1}$ H_2SO_4 solutions containing MgSO_4 , Na_2SO_4 or Li_2SO_4 with those determined by *emf* measurements

(Blank circle: determined by *emf* technique, solid line: calculated based on the corrected Zdanovskii rule, dotted line: calculated based on Zdanovskii rule)

lines correspond to the calculated mean activity coefficients according to the corrected Zdanovskii rule, while the dotted lines show the calculated values applying the Zdanovskii rule. The mean activity coefficients of sulfuric acid in the aqueous sulfuric acid-magnesium sulfate solution as calculated by applying the Zdanovskii rule perfectly coincide with those calculated based on the corrected Zdanovskii rule. The deviation between the calculated values and experimental values ranged from 11 to 13 %.

In the case of the aqueous solution of sulfuric acid-sodium sulfate or sulfuric acid-lithium sulfate, the calculated mean activity coefficients based on the corrected Zdanovskii rule deviate less significantly from the experimental results than those calculated by assuming the Zdanovskii rule. Those results showed a deviation from the experimental value at $1.0 \text{ mol} \cdot \text{kg}^{-1}$ MSO_4 of 24 % for the former, while the latter was found to be about 37 % for sulfuric acid-sodium sulfate. The deviation was found to be 21 % and 13 %, respectively for sulfuric acid-lithium sulfate.

Fig. 6 Comparison of the mean activity coefficients of H_2SO_4 in the aqueous $1.0 \text{ mol}\cdot\text{kg}^{-1}$ H_2SO_4 solutions containing MgSO_4 , Na_2SO_4 or Li_2SO_4 with those determined by *emf* measurements (See Fig. 5)

Similar comparisons were made for the aqueous $1 \text{ mol}\cdot\text{kg}^{-1}$ H_2SO_4 solutions containing magnesium sulfate, sodium sulfate or lithium sulfate. The calculated results are shown together with those results experimentally determined. In concentrated sulfuric acid solutions, the deviation of calculated mean activity coefficients of sulfuric acid was far smaller than that in dilute sulfuric acid solution as clearly shown in this figure, although a slight deviation can be seen in the aqueous solution system sulfuric acid-lithium sulfate. However, the deviation of the mean activity coefficients as calculated from those experimentally determined was found to be less than 0.5 % for all concentrated solutions examined. Thus, the application of the McKay-Perring method to the calculation of the mean activity coefficients of sulfuric acid in concentrated aqueous sulfuric acid-metal sulfate solutions promises to provide a more reliable estimation than in dilute solutions.

Figure 7 depicts the mean activity coefficients of sulfuric acid in the aqueous sulfuric acid-zinc sulfate from equation (9) by using *b* values

Fig. 7 Calculated mean activity coefficients of H_2SO_4 in the aqueous solutions of H_2SO_4 - ZnSO_4

determined from the equi $\alpha(w)$ lines shown in Fig. 1. In dilute sulfuric acid solutions, the values of $\gamma_{\pm}(\text{H}_2\text{SO}_4)$ tend to greatly decrease with the addition of zinc sulfate approaching an almost constant value at about 0.12 around $1.0 \text{ mol}\cdot\text{kg}^{-1}$ ZnSO_4 . By contrast, the change in $\gamma_{\pm}(\text{H}_2\text{SO}_4)$ was not significant with the addition of zinc sulfate in concentrated sulfuric acid solutions. These results may be attributed to the formation of bisulfate ions with the addition of zinc sulfate.

The calculated mean activity coefficients of sulfuric acid in the aqueous sulfuric acid-zinc sulfate were compared to those determined by *emf* measurements of a cell consisting of glass electrode, lead dioxide-lead sulfate electrode and test solution containing sulfuric acid and zinc sulfate. The results are shown in Fig. 8. It is noted in this figure that the calculated values agree well with those experimentally determined in concentrated sulfuric acid-zinc sulfate solutions, showing less than 1 % deviation. In dilute solutions, the deviations between calculated and experimentally determined values become larger, exhibiting the deviation of 8 % in maximum. Thus, we can assume that the McKay-Perring method is also applicable to calculate the mean activity coefficients

Fig. 8 Comparison of the mean activity coefficients of H_2SO_4 in the aqueous H_2SO_4 - ZnSO_4 with those determined by *emf* measurements (Blank circle : determined by *emf* technique, solid line : calculated based on Zdanovskii rule)

Fig. 9 Comparison of the mean activity coefficients of H_2SO_4 in the 0.1 and 1.0 $\text{mol}\cdot\text{kg}^{-1}$ H_2SO_4 solutions containing ZnSO_4 , NiSO_4 or CuSO_4 at different concentrations

of sulfuric acid in the aqueous sulfuric acid solutions containing common metal sulfates.

Similar calculations were made for the aqueous solutions of sulfuric acid-nickel sulfate and sulfuric acid-copper sulfate. Figure 9 shows comparative calculated values of mean activity coefficients of sulfuric acid in both 0.1 and 1.0 $\text{mol}\cdot\text{kg}^{-1}$ H_2SO_4 solutions as a function of MSO_4 concentration for ZnSO_4 , NiSO_4 and CuSO_4 . No distinct differences were observed among these sulfates.

By applying the McKay-Perring method, we can also calculate the mean activity coefficient of zinc sulfate in the aqueous solution of sulfuric acid-zinc sulfate by using the value of $a(w)$ for the aqueous solution being studied. Figure 10 illustrates the mean activity coefficients of zinc sulfate in the aqueous sulfuric acid-zinc sulfate from equation (9). In dilute zinc sulfate solutions, the values of $\gamma_{\pm}(\text{ZnSO}_4)$ tend to greatly decrease with the addition of sulfuric acid. By contrast, the change in mean activity coefficients of zinc sulfate was not significant with the addition of sulfuric acid in concentrated zinc sulfate solutions.

Similar calculations were made for the aqueous solutions of sulfuric acid-nickel sulfate and sulfuric acid-copper sulfate. Figure 11 shows comparative calculated values of mean activity

Fig. 10 Calculated mean activity coefficients of MSO_4 in the aqueous solutions of H_2SO_4 - ZnSO_4

Fig. 11 Comparison of the mean activity coefficients of MSO_4 in the 0.1 and 1.0 $\text{mol} \cdot \text{kg}^{-1}$ H_2SO_4 solutions containing ZnSO_4 , NiSO_4 , or CuSO_4 at different concentrations

coefficients of MSO_4 in both 0.1 and 1.0 $\text{mol} \cdot \text{kg}^{-1}$ MSO_4 solutions as a function of sulfuric acid concentration for zinc sulfate, nickel sulfate and copper sulfate. No significant differences were observed among these sulfates studied.

5 Conclusions

The activities of water in the aqueous sulfuric acid solutions containing zinc sulfate, nickel sulfate and copper sulfate at 298 K were determined by means of an isopiestic method.

The application of a thermodynamic equation, derived by McKay and Perring, was examined by comparing mean activity coefficients of sulfuric acid in the mixed sulfuric acid-sulfate

(including magnesium sulfate, sodium sulfate, lithium sulfate and zinc sulfate) calculated by this method with those determined by *emf* measurements. It was found that the McKay-Perring method was applicable to concentrated H_2SO_4 - MSO_4 solutions with high accuracy.

The mean activity coefficients of sulfuric acid and metal sulfate (including zinc sulfate, nickel sulfate and copper sulfate) in the aqueous sulfuric acid-metal sulfate solutions, whose activity could not be determined by *emf* measurements, were calculated by the McKay-Perring method. The mean activity coefficients of sulfuric acid in dilute sulfuric acid solutions greatly decreased with the addition of metal sulfate, while those in concentrated solutions stayed almost constant. Also the mean activity coefficients of MSO_4 in dilute MSO_4 solutions greatly decreased with the addition of sulfuric acid, while those in concentrated solutions stayed almost constant. No distinct differences were observed among the sulfates studied.

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