Isopiestic Determination of the Osmotic Coefficients of Aqueous H_2SO_4 at 25 °C

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The osmotic coefficients of aqueous H_2SO_4 have been measured from 0.35 to 4.36 mol kg^{-1} at 25 °C with the isopiestic method, using NaCl as the reference solution. Previously published results from this laboratory extend this concentration range down to 0.14 mol kg^{-1}. The purpose was to refine the osmotic coefficients of this important isopiestic standard. These new data are compared to published thermodynamic data for H_2SO_4 solutions, and some published low-concentration isopiestic data were found to be inaccurate. An assessment is made as to which published data are more reliable, and recommendations are made as to which should be given greater weight in future evaluations.

Introduction

Solutions of NaCl, KCl, H_2SO_4, and $CaCl_2$ are the most important standards for isopiestic measurements involving aqueous solutions. NaCl and KCl are obvious choices since they are obtainable in very high purity, they are easy to work with, and their solutions can be accurately analyzed for concentration. In addition, high-quality thermodynamic data are available for them from a wide variety of measurements. However, NaCl and KCl are usable only for water activities greater than 0.75 at 25 °C owing to solubility limitations.

Stokes (*1*) suggested that $CaCl_2$ solutions would be suitable as isopiestic standards at higher concentrations. There are very few reliable vapor pressure measurements for $CaCl_2$ solutions, and emf measurements are mainly restricted to lower concentrations. Therefore, the osmotic coefficients of $CaCl_2$ solutions are mainly known by isopiestic measurements, and above 3.0 mol kg^{-1} are based almost entirely on H_2SO_4 as the standard. Thus, data for H_2SO_4 solutions take on added importance for isopiestic measurements since H_2SO_4 is used both as a standard in its own right and to determine $CaCl_2$ activity values.

We previously reviewed available thermodynamic data for H_2SO_4 and $CaCl_2$ solutions at 25 °C (*2*, *3*). During those reviews it became clear that there were concentration regions where their activity data are not as well characterized as is commonly assumed. We therefore undertook a program to improve this situation.

Stokes (*1*) reported isopiestic data for $CaCl_2$ solutions relative to a NaCl standard from 0.09 to 2.98 mol kg^{-1}, and relative to H_2SO_4 from 2.95 to 10.77 mol kg^{-1}. We redetermined the H_2SO_4–$CaCl_2$ isopiestic ratio for 2.63–8.83 mol kg^{-1} $CaCl_2$ (*4*). During the course of investigating other electrolytes (*5*, *6*), we determined the KCl–$CaCl_2$ isopiestic ratio from 0.48 to 2.25 mol kg^{-1} $CaCl_2$, the NaCl–$CaCl_2$ ratio from 1.49 to 2.98 mol kg^{-1}, and the H_2SO_4–$CaCl_2$ ratio for 1.49 to 3.96 mol kg^{-1} $CaCl_2$. Similarly, Robinson and Covington (*7*) and Robinson and Bower (*8*) reported data for $CaCl_2$ from 0.37 to 2.85 mol kg^{-1} relative to KCl and NaCl standards. These various isopiestic studies are in very good agreement, with maximum differences of 0.3–0.4% over the entire concentration range. Thus, average osmotic coefficients for $CaCl_2$ are known to at least 0.2% *relative to the other isopiestic standards*.

For H_2SO_4 solutions at high concentrations there are several accurate vapor pressure studies (*9*, *10*) and an isopiestic comparison to NaOH (*11*) to determine its osmotic coefficients. At lower concentrations most evaluations have given high weight to older isopiestic data relative to KCl (*12*, *14*) and NaCl (*12*, *13*, *15*) standards. There are four isopiestic studies for H_2SO_4 in this region: Scatchard et al. (*12*) from 0.09 to 4.37 mol kg^{-1}, Sheffer et al. (*13*) from 0.02 to 4.35 mol kg^{-1}, Robinson's 1939 study (*14*) for 0.19–3.14 mol kg^{-1}, and Robinson's later study (*15*) for 2.08–4.35 mol kg^{-1} H_2SO_4.

Robinson's 1945 data (*15*) and Scatchard et al.'s (*12*) are in good agreement with each other. Robinson's 1939 data (*14*) are in reasonable agreement with these other two studies but are so badly scattered at higher concentrations as to be of less value in characterizing H_2SO_4. Sheffer et al.'s (*13*) osmotic coefficients, in contrast, are lower than the other studies by 0.3–1.0%. According to Olynyk and Gordon (*16*), the osmotic coefficients of H_2SO_4 were redetermined in Ferguson's laboratory and the new values were in "substantial agreement with Scatchard, Hamer, and Wood's measurements" but not with their earlier study (*13*). Unfortunately, this redetermination does not seem to have been published.

During our $MgCl_2$ study (*6*) we redetermined the NaCl–H_2SO_4 isopiestic ratio for 2.09–4.36 mol kg^{-1} H_2SO_4. These new data are in good agreement with Robinson (*15*) and Scatchard et al. (*12*), and these three studies accurately characterize H_2SO_4 from 2.1 to 4.36 mol kg^{-1}.

No such check was possible at lower concentrations since two of the published isopiestic studies (*13*, *14*) in this region are suspect as mentioned above, and Scatchard et al.'s isopiestic data (*12*) below 0.4 mol kg^{-1} are quite scattered owing to the short equilibration times used. In addition, Scatchard et al.'s data (*12*) between 0.6 and 0.9 mol kg^{-1} are rather lumpy and have a peculiar concentration dependence, so they may be in error at these lower concentrations. We determined the KCl–H_2SO_4 isopiestic ratio for 0.14–0.17 mol kg^{-1} H_2SO_4 (*17*) and our results fall generally lower than Scatchard et al. (*12*). Staples (*18*) did a comparison of isopiestic with emf data, and similarly concluded that most published isopiestic data below 0.4 mol kg^{-1} were too high.

We have, therefore, redetermined the NaCl–H_2SO_4 isopiestic ratio from 0.35–4.36 mol kg^{-1} to resolve these remaining discrepancies and to characterize H_2SO_4 more accurately. This completes our effort to refine the major isopiestic standards by isopiestic intercomparison.

Experimental Section

Experimental details are nearly identical with those reported elsewhere (*5*, *6*). Isopiestic equilibrations were performed at 25.00 ± 0.005 °C (IPTS-68) using NaCl solutions as reference solutions. One-month equilibration times were used below 0.4 mol kg^{-1}, three-week equilibrations around 0.5 mol kg^{-1}, two to three weeks between 0.6 and 1.1 mol kg^{-1}, and five-day or longer equilibrations at higher concentrations. Duplicate samples of NaCl and H_2SO_4 were used and, in all cases but one, the molalities of each electrolyte at equilibrium agreed to ±0.09% or better. For that other experiment (0.793 61 mol

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Table I. Isopiestic Molalities of Aqueous NaCl and H_2SO_4 at 25 °C

[NaCl], *m*	[H_2SO_4], *m*	$\Phi(H_2SO_4)$	[NaCl], *m*	[H_2SO_4], *m*	$\Phi(H_2SO_4)$
0.37490	0.346 19	0.6638	2.1988	1.7886	0.8148
0.40408	0.372 71	0.6646	2.2554	1.8285	0.8202
0.53125	0.486 10	0.6709	2.4673	1.9780	0.8401
0.55031	0.503 43	0.6713	2.6591	2.1108	0.8585
0.66790	0.605 86	0.6790	2.9907	2.3366	0.8906
0.67552	0.612 47	0.6795	3.4464	2.6413	0.9350
0.77959	0.701 34	0.6870	3.6157	2.7521	0.9519
0.78409	0.705 16	0.6873	3.6769	2.7926	0.9578
0.89066	0.793 61	0.6964	4.3465	3.2236	1.0252
0.89723	0.799 34	0.6966	4.5164	3.3335	1.0417
1.0222	0.902 20	0.7067	4.6809	3.4379	1.0583
1.0825	0.950 40	0.7122	4.7575	3.4872	1.0658
1.1713	1.021 8	0.7196	4.8641	3.5536	1.0768
1.2399	1.075 1	0.7263	4.8701	3.5573	1.0774
1.2937	1.118 5	0.7302	4.9600	3.6148	1.0862
1.3077	1.128 2	0.7322	5.0649	3.6827	1.0962
1.4405	1.230 1	0.7446	5.1505	3.7353	1.1052
1.4677	1.251 4	0.7468	5.4227	3.9047	1.1328
1.6517	1.390 1	0.7637	5.6553	4.0512	1.1557
1.7759	1.481 5	0.7757	5.9465	4.2265	1.1863
1.9699	1.624 0	0.7934	6.1630	4.3615	1.2075
2.1239	1.735 5	0.8076	6.1661	4.3599	1.2088

kg^{-1} H_2SO_4) the deviations were ±0.11%. All weights were corrected to vacuum.

The highest NaCl concentration is about 0.1% above the previously determined solubility (*6*). NaCl exhibits very little tendency to supersaturate under isothermal conditions. NaCl stock no. 2 and H_2SO_4 stock were used for these measurements; their preparation and analyses have been described in detail elsewhere (*6*). Molecular masses used were 98.074 g mol^{-1} for H_2SO_4 and 58.443 g mol^{-1} for NaCl.

Previous measurements in this laboratory (*6*), for 2.09–4.36 mol kg^{-1} H_2SO_4, involved the same H_2SO_4 stock solution but a different NaCl stock solution. The present measurements are in complete agreement with the earlier values between 2.09 and 3.5 mol kg^{-1}, but differences of 0.15% occur at higher concentrations.

Isopiestic samples were equilibrated in the same set of tantalum metal cups used for most of our previous experiments (*4–6*, *17*, *19*). Tantalum metal was chosen because it is one of the most inert of all metals owing to a protective and "self-healing" surface film of Ta_2O_5. Tantalum metal is completely resistant to attack by H_2SO_4 solutions below about 175 °C (*20*), although free SO_3 will react with it.

Results

Table I contains the isopiestic equilibrium molalities of NaCl and H_2SO_4 solutions and the osmotic coefficients of H_2SO_4. The osmotic coefficients of H_2SO_4 solutions were calculated with the equation

$$\Phi = \nu^* m^* \Phi^* / \nu m \qquad (1)$$

where $\nu = 3$ is the number of ions formed by the complete dissociation of one molecule of H_2SO_4 and m is the H_2SO_4 molality. Corresponding quantities for the NaCl reference solutions are indicated with asterisks ($\nu^* = 2$). Osmotic coefficients of the NaCl reference solutions were calculated by using Hamer and Wu's equation (*21*). Osmotic coefficients are directly related to water activities by

$$\Phi = -1000 \ln a_1/(\nu m M_1) \qquad (2)$$

where a_1 is the water activity and $M_1 = 18.0152$ g mol^{-1} is the molecular mass of water.

Table I contains 44 new isopiestic points for H_2SO_4 relative to a NaCl standard. Together with previously reported values using NaCl and KCl standards (*6*, *17*), a total of 64 new points have been measured for H_2SO_4 solutions between 0.14 and 4.36 mol kg^{-1}. This represents a thorough reinvestigation of that system.

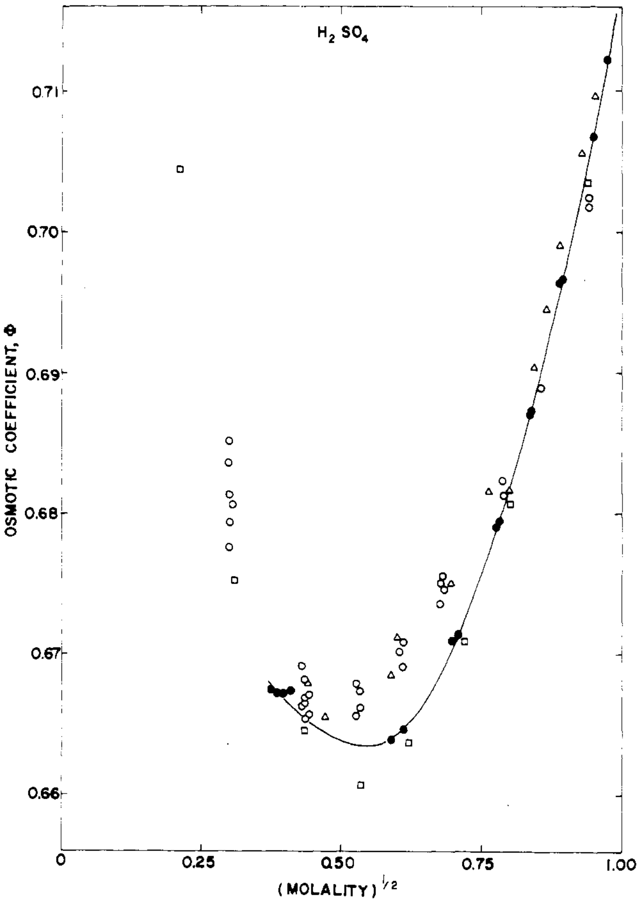

Figure 1. Comparison of H_2SO_4 isopiestic data below 1.0 mol kg^{-1}: (●) Rard and Miller (*6*, *17*) and present results; (○) Scatchard et al. (*12*); (△) Robinson (*14*); (□) Sheffer et al. (*13*).

Isopiestic data from this laboratory are in excellent agreement with the results of Scatchard et al. (*12*) above 1.0 mol kg^{-1}, with all but two of their osmotic coefficients being within 0.002 of ours. One of their points is 0.003 high, whereas their highest concentration (in equilibrium with saturated NaCl) is low by 0.01 in Φ. Robinson's 1945 data (*15*) are similarly in good agreement, with all but one of his points being within 0.003 of ours. Robinson's somewhat scattered 1939 data (*14*) are also

Table II. Corrections to the H_2SO_4 Osmotic Coefficients of Rard, Habenschuss, and Spedding (2)

m	$\Delta\Phi^a$	m	$\Delta\Phi^a$
0.1	≈−0.0050	2.0	+0.0004
0.2	−0.0002	2.2	−0.0005
0.3	−0.0014	2.4	−0.0011
0.4	−0.0034	2.6	−0.0016
0.5	−0.0038	2.8	−0.0017
0.6	−0.0036	3.0	−0.0019
0.7	−0.0034	3.2	−0.0023
0.8	−0.0030	3.4	−0.0028
0.9	−0.0025	3.6	−0.0024
1.0	−0.0012	3.8	−0.0015
1.2	+0.0009	4.0	−0.0005
1.4	+0.0016	4.2	+0.0016
1.6	+0.0015	4.36	+0.0030
1.8	+0.0010		

[a] These correction factors are known to about 0.0005 above 0.9 mol kg^{-1}, but uncertainties become larger at lower concentrations. These $\Delta\Phi$ values should be added to the recommended Φ results of ref 2.

in reasonable agreement but tend to be slightly high. Sheffer et al.'s data (*13*) are systematically low at all concentrations as was mentioned above.

Below 1.0 mol kg^{-1} differences between the various isopiestic studies are quite significant, and some previous studies have fairly large scatter below 0.5 mol kg^{-1}. Figure 1 illustrates the available low-concentration isopiestic data. Scatchard et al.'s data (*12*) are higher than our results except around 0.9 mol kg^{-1} where they are low. The solid curve in Figure 1 was drawn with the assistance of a plot of $(1 - \Phi)m^{1/4}$ vs. $m^{1/2}$. This deviation function varies little with concentration between 0.14 and 1.0 mol kg^{-1} and allows accurate interpolation to be made.

Scatchard et al.'s data (*12*) below 0.5 mol kg^{-1} exhibit increasing scatter as the concentrations decrease (1.2% at 0.09 mol kg^{-1}), and they are systematically high. Scatchard et al. used 2–3-day isopiestic equilibrations at these low concentrations. Our present data at low concentrations are much smoother and were based on 21–31-day equilibrations. Up to 8 weeks was allowed at the lowest concentrations (*17*). All of the problems with Scatchard et al.'s measurements at lower concentrations can be attributed to not allowing sufficient time to reach thermodynamic equilibrium. Some of the scatter in Robinson's 1939 data may be due to this cause also, but equilibration times for that work were not given (*14*). Errors in the low-concentration data from these two studies (*12*, *14*) are in the same direction but are smaller in magnitude than suggested by Staples (*18*).

These differences in Φ are significant relative to the accuracy and precision attainable with isopiestic measurements. However, fairly large differences in Φ at low concentrations correspond to very small water activity differences. For example, a difference of 0.5% in Φ corresponds to a difference in a_1 of only 0.002% at 0.1 mol kg^{-1} and 0.009% at 0.5 mol kg^{-1}.

Discussion

It is not our intention at this time to perform a complete reevaluation of the osmotic coefficients of aqueous H_2SO_4 solutions. The present data help to resolve discrepancies below 4.36 mol kg^{-1}. However, data at higher concentrations are uncertain by about ±0.004–0.005 in Φ, so some additional accurate vapor pressure measurements would be very desirable.

Equation 7 of Rard et al. (*2*) for Φ should still be adequate for most applications. However, if maximum accuracy is desired, then the correction values in Table II should be applied to this equation. These correction factors are based on including our new experimental data and on giving reduced weight to less reliable values (*13*, *14*) including Scatchard et al.'s results below 1.0 mol kg^{-1} (*12*).

In addition to isopiestic data for H_2SO_4 solutions relative to NaCl and KCl standards, the $CaCl_2$–H_2SO_4 isopiestic ratio has been investigated several times (*1*, *4*, *6*). These data in principle could be used to make data for H_2SO_4 and $CaCl_2$ solutions mutually consistent. However, the more reliable data for $CaCl_2$ above 3 mol kg^{-1} are isopiestic relative to H_2SO_4 standards, and little benefit would be gained by reversing the calculations.

At high concentrations most evaluations for H_2SO_4 give high weight to the vapor pressure measurements of Shankman and Gordon (*9*) and Hornung and Giauque (*10*), and to Stokes' (*11*) isopiestic data relative to NaOH. These still seem to be the best results for high concentrations. Vapor pressure measurements of Grollman and Frazer (*22*), Collins (*23*), and Jones (*24*) are of somewhat lower precision but should be given some consideration. Tarasenkov's (*25*), McHaffie's (*26*), and Hepburn's (*27*) vapor pressures are very scattered and should be given little or no weight.

Freezing point depression data can also be used to determine the osmotic coefficients of H_2SO_4 solutions at low concentrations. Randall and Scott (*28*) have compared most of the freezing point results. Because of discrepancies and scatter, it is difficult to tell whether any of them are reliable.

Electromotive force measurements have been used numerous times to measure activity coefficients of H_2SO_4 solutions. Several recent sets of data seem to be quite accurate (29–31). Some of the earlier emf data (*32*, *33*) are reliable to about 1 mV but are of lower precision than the more recent data. Staples (*18*) has considered these data in detail.

Recent emf data tie in fairly well with isopiestic data. However, very accurate solute activities are needed for a meaningful Gibbs–Duhem integration to compare these results to isopiestic data. This requires a very reliable extrapolation of emf data to infinite dilution, and it is difficult to do since H_2SO_4 is an associated electrolyte. Detailed calculations using the bisulfate ion dissociation constant, such as those of Wirth (*34*) and Pitzer et al. (*35*), could resolve these difficulties. It should be noted that Wirth's calculations (*34*) also indicated that available low-concentration isopiestic data (*12*, *14*) were too high (although not as high as claimed by Staples (*18*)), and this agrees with our experimental results.

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Registry No. Sulfuric acid, 7664-93-9.

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Excess Volumes of Binary Mixtures of *n*-Heptane with Hexane Isomers†

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Dilatometric measurements of excess volumes are described for binary mixtures of *n*-heptane with the five isomeric hexanes at 298.15 K. The results are compared with those of other investigators and are correlated with previously reported excess enthalpies by means of the Flory theory of mixtures.

Currently our laboratory is studying the variations in the excess thermodynamic properties of binary mixtures which result from isomeric changes in one of the components. Recently we reported (*1*) molar excess enthalpies for binary mixtures of *n*-heptane with the five isomeric hexanes: *n*-hexane (n-C6), 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB). As an extension of that work, we have measured molar excess volumes at 298.15 K for the same set of mixtures.

Experimental Section

The samples of *n*-heptane and the hexane isomers were the same as used in our calorimetric work (*1*). Molar excess volumes V_m^E were measured at 298.15 K and atmospheric pressure in the successive dilution micrometer syringe dilatometer described by Tanaka et al. (*2*). The errors of V_m^E and of the *n*-heptane mole fraction x are estimated to be less than $0.0003 + 0.001|V_m^E|$ cm^3 mol^{-1} and 5×10^{-5}, respectively.

Results and Discussion

The experimental values of V_m^E are listed in Table I. The method of least squares with all points assigned unit weight was used to fit the form

$$V_m^E = x(1-x)\sum_{j=1}^{n} v_j(1-2x)^{j-1} \qquad (1)$$

to each set of results. Values of the coefficients v_j and the standard deviations σ for these representations are summarized in Table II. Plots of the experimental results and of their representations by eq 1 are given in Figure 1.

Densities of binary mixtures of *n*-heptane with n-C6 at 293.15 K were reported by Loiseleur et al. (*3*). These lead to negative values of the molar excess volume (−0.08 cm^3 mol^{-1} for an equimolar mixture) which are larger in magnitude than our results (−0.0280 cm^3 mol^{-1} for an equimolar mixture), and it is unlikely that the differences can be attributed to the difference in the temperatures of the two studies. More recently, V_m^E at 298.15 K has been reported for mixtures of *n*-heptane with n-C6 (*4*) and with 2,3-DMB (*5*). Deviations between the results of these previous investigations and our findings are shown in Figure 2. There is agreement within ~0.001 cm^3 mol^{-1} between our results for the n-C6 system and those of Goates et al. (*4*). However, the latter show more scatter and tend to be higher (i.e., less negative) than our results for $x < 0.5$ and lower (i.e., more negative) than our results for $x > 0.5$. Larger deviations are evident between the two sets of results for the 2,3-DMB system. The data of Grolier and Faradjzadeh (*5*) are more skewed toward low x values, and for $x = 0.3$ are ~0.004 cm^3 mol^{-1} higher than our findings.

The magnitudes of V_m^E for the five systems in Figure 1 decrease in the following order:

$$\text{2,2-DMB} > \text{2-MP} > \text{2,3-DMB} > \text{n-C6} > \text{3-MP} \qquad (2)$$

This differs from the order of the excess enthalpy curves (*1*) and is closer to, although not identical with, the order of the V_m^E curves for mixtures of 1-hexanol with the hexane isomers (*6*). In the latter case, we noted that V_m^E (0.5) for equimolar mixtures varied nearly linearly with the solubility parameter of the isomer (coefficient of correlation $r = 0.977$). Since then we have examined correlations between the values of $V_m^E(0.5)$ and several other physical properties or configurational parameters of the isomers. These include the internal pressure, molar energy of vaporization, isothermal compressibility, number of gauche conformations, and third-order connectivity. The best correlation is shown in Figure 3, where there is a nearly linear variation of $V_m^E(0.5)$ with the isothermal compressibility κ_T of the pure hexane isomer for both the present *n*-heptane mixtures and the previous 1-hexanol mixtures (*6*) with $r = 0.994$ and 0.995, respectively.

The negative excess volumes and positive excess enthalpies (*1*) of *n*-heptane–hexane isomer mixtures are in disagreement

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