

# Diffusion Coefficient and Solubility of Isobutene and *trans*-2-Butene in Aqueous Sulfuric Acid Solutions

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The diffusion coefficient and the physical solubility of isobutene and *trans*-2-butene in aqueous sulfuric acid solutions cannot be determined experimentally due to the occurrence of fast chemical reactions. In the present contribution these physicochemical parameters are estimated. For the solubility an isobutane–isobutene analogy is applied for the range 0–100% H<sub>2</sub>SO<sub>4</sub>. A correlation technique, initially proposed by Rudakov et al.,<sup>11</sup> was used for describing the experimental data at low acid concentrations and for estimation purposes for more concentrated solutions. Diffusion coefficients for inert gases in electrolyte solutions were measured using a modified diaphragm cell. It was found for CO<sub>2</sub> and N<sub>2</sub>O in KCl solutions that the diffusion coefficient is not a function of the ionic strength of the electrolyte solution and therefore not a function of the activity coefficient of the diffusing component. It appears that the correlation  $D\eta^{0.6} = \text{constant}$  holds up to 80 mass % sulfuric acid, as is the case for several other aqueous electrolyte solutions. Diffusion coefficients for butenes in sulfuric acid solutions (up to 96 mass %) are estimated from CO<sub>2</sub> coefficients in these solutions.

## 1. Introduction

The absorption of butenes in sulfuric acid solutions occurs in large scale processes; especially the removal of isobutene from C<sub>4</sub>-streams produced by a naphtha cracker via selective hydration and the production of *sec*-butanol from linear butenes are important industrial applications. For designing and modeling of these processes, physicochemical properties are required.

Therefore, considerable attention has been paid to the mechanism and kinetics of the protonation reactions of olefins in (strong) acid solutions. However, the reaction kinetics found in the literature were not consistent and until recently<sup>1</sup> no data were available for sulfuric acid solutions of 70 mass % and higher. This latter regime is of interest for, for example, the Koch reaction of isobutene to pivalic acid.<sup>2</sup> For an experimental determination of the reaction kinetics of the butene protonation reaction, the physicochemical properties such as the solubility and diffusion coefficient of the butenes in the sulfuric acid solution were required.

Since the protonation of butenes in moderate to strong acidic solutions is fast to extremely fast, these physicochemical properties cannot be measured directly. To obtain a reasonably accurate estimation of the diffusion coefficient and the solubility of the reacting species in the reactive liquid phase, it is proposed to use an analogy. The usefulness of this type of analogy is probably best demonstrated by the frequently used CO<sub>2</sub>–N<sub>2</sub>O analogy for amine treating processes.<sup>3–5</sup>

For the selection of an inert component which resembles isobutene best, thermodynamic properties such as molar volume, critical properties, solubility parameters, and so forth of a number of compounds were compared. Judging by these properties (see Table 1), isobutane seems to resemble isobutene quite well.

The major difference between these components is found in the dipole moment, which is directly reflected in the

Table 1. Properties of Isobutene and Isobutane<sup>6,7</sup>

	isobutene	isobutane
molar mass/g·mol <sup>-1</sup>	56.107	58.123
melting point/K	132.81	113.54
boiling point/K	266.25	261.43
<i>T</i> <sub>crit</sub> /K	417.90	408.14
<i>P</i> <sub>crit</sub> /MPa	3.999	3.648
acentric factor	0.194	0.183
dipole moment/D	0.5	0.1
2nd virial coefficient (298 K)/m <sup>3</sup> ·mol <sup>-1</sup>	−6.5 × 10 <sup>-4</sup>	−6.5 × 10 <sup>-4</sup>
solubility in water (298 K, 1 bar)/mol·m <sup>-3</sup>	6.0	0.8
diffusion coefficient in water/m <sup>2</sup> ·s <sup>-1</sup>	10.4 × 10 <sup>-10</sup>	9.9 × 10 <sup>-10</sup>
solubility parameter/J <sup>1/2</sup> ·m <sup>-3/2</sup>	1.4954 × 10 <sup>4</sup>	1.4027 × 10 <sup>4</sup>

difference in the solubility in polar solvents such as water. Another, more polar, inert gaseous component which resembles isobutene equally as well as isobutane does was however not found.

Both the solubility and the diffusion coefficient of isobutene and *trans*-2-butene in aqueous sulfuric acid solutions will be estimated by comparing with experimental data for isobutane and other gases, determined in this work and taken from the literature.

## 2. Experimental Section

A diaphragm cell has been used frequently to determine diffusion coefficients. In this technique two well mixed phases are separated by a porous, nonselective membrane, which is filled by the phase in which the diffusion coefficient is to be determined. In this case, where the diffusion coefficients of gas-phase components into a liquid phase will be determined, the membrane pores are filled with liquid. The liquid inside the membrane will be stagnant at not too high stirring rates in the liquid bulk. By determining (in this case) the gas absorption flux, the diffusion coefficient of the absorbed gas-phase component in the liquid phase can be calculated when the bulk phase compositions are known, using the well-known film theory. The gas–liquid diaphragm cells used in the literature often require relatively long measurement times (1–2 days)<sup>8</sup>

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before a pressure drop in the gas phase could be determined sufficiently accurately. This problem has been overcome in the present study by using two gas-phase chambers connected via a differential pressure indicator. One chamber is kept at a fixed reference pressure ( $P_0$ ), and the gas is absorbed from the other one. From mole balances for both the gas phase and the liquid phase (and applying the ideal gas law) the diffusion coefficient  $D_i$  can be evaluated from pressure  $P_i(t)$  versus time  $t$  data; see eqs 1–5.

Overall Balance:

$$V_g \frac{P_{i,0}}{RT} + V_L C_{L,0} = V_g \frac{P_i(t)}{RT} + V_L C_L(t) \quad (1)$$

Gas Phase:

$$\frac{V_g}{RT} \frac{dP_i(t)}{dt} = -k_L A \left( m \frac{P_i(t)}{RT} - C_L(t) \right) \quad (2)$$

Initial Conditions:

$$t = 0: \quad P_i = P_{i,0}, \quad C_L = C_{L,0} = 0 \quad (2-a)$$

For isobutane and isobutylene the Redlich–Kwong–Soave equation of state was used instead of the ideal gas law for evaluating the pressure drop in terms of molar fluxes. In eq 2  $V_g$  and  $V_L$  represent the gas chamber and liquid chamber volume, respectively,  $T$  is the temperature,  $R$  is the universal gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ),  $m$  is the distribution coefficient for the gas-phase component between the gas and liquid phases ( $m = C_L/C_g$  at equilibrium), and  $A$  is the membrane surface area. The parameters  $P_{i,0}$  and  $C_{L,0}$  represent the values of  $P_i(t)$  and  $C_L(t)$  at the start of the experiment, that is, at  $t = 0$ . The  $k_L$  value represents the liquid side mass transfer coefficient according to the film theory:

$$k_L = \frac{D_i}{\delta} \quad (3)$$

The characteristic effective film thickness  $\delta$  is now determined by the dimensions of the membrane  $d_m$ , its porosity  $\epsilon$ , and the tortuosity of the pores  $\tau$ , respectively. Since these values are constant, but not known beforehand, a (configuration dependent) membrane calibration factor  $f$  can be defined and can be determined experimentally:

$$k_L A = \frac{D_i}{d_m} A \frac{\epsilon}{\tau} = D_i f \quad (4)$$

The membrane parameter  $f$  can be measured by calibration experiments with known gas–liquid absorption systems. In this work the absorption of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  in water was used for this purpose. From eqs 1 and 2 the apparent  $k_L A$  value can be determined from experiments using eq 5, and with this the calibration factor  $f$  is calculated according to eq 4. When the membrane is calibrated (and the value of  $f$  is known), the diffusion coefficient can be determined for other gas-phase components.

$$\ln \left[ \frac{P_i(t) (V_g + mV_L) - V_g P_{i,0}}{mV_L} \right] = -k_L A \left( \frac{1}{V_L} + \frac{m}{V_g} \right) t \quad (5)$$

### 3. Estimation of Solubility of Gas-Phase Components in Electrolyte Solutions

The solubility of a gas-phase component  $i$  in aqueous solutions usually decreases on addition of electrolytes

(“salting out”). This decrease, corresponding with an increase in the activity coefficient of component  $i$  in the liquid phase, can often be described for aqueous solutions using the classical Sechenow equation (see eq 6-a) and summing the contributions of the different ions present to the ionic strength (as in the Debye–Hückel Limiting Law).

Based on Ionic Strength  $I$ :

$$^{10}\log \left( \frac{He}{He^\circ} \right) = \sum_i K_i I_i \quad (6-a)$$

Based on Ion Concentration  $c_i$ :

$$^{10}\log \left( \frac{He}{He^\circ} \right) = \sum_i K_i c_i \quad (6-b)$$

Weisenberger and Schumpe<sup>9</sup> proposed an alternative estimation method (see eq 6-b), based on the ion concentrations. At slightly more concentrated solutions (roughly above 0.5 M) more sophisticated activity models for electrolyte solutions are to be preferred (see e.g. Clegg et al.<sup>10</sup> for a model, claimed to be valid up to 6 mol kg<sup>-1</sup> solutions). At even higher (sulfuric acid) electrolyte concentrations, these models are no longer valid and even “salting in” may occur. Since there are no activity models available for the regime of interest for the Koch synthesis (>70 mass %  $\text{H}_2\text{SO}_4$ ), a more empirical approach has to be used.

For concentrated sulfuric acid solutions the gas-phase solubility of a small number of inert components has been reviewed by Rudakov et al.<sup>11</sup> This overview indicated that these solubility curves at increasing acid content are nonlinear and show a minimum. The position of the minimum depends on the gas; a fair correlation of the position of the minimum and of the ratio of the solubilities in pure  $\text{H}_2\text{O}$  and pure  $\text{H}_2\text{SO}_4$  with the molar volume of the solute  $V_n$  was observed. The method proposed<sup>11</sup> is in fact a Sechenow technique, describing a “salting out” effect in an “ideal” (or “regular”) solution of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ . For the solubility of a gaseous solute  $j$  in an (homogeneous) mixture of  $N$  solvents, expressed through the Henry coefficient  $He_{\text{mix},j}$ , the following addition rule can be applied:

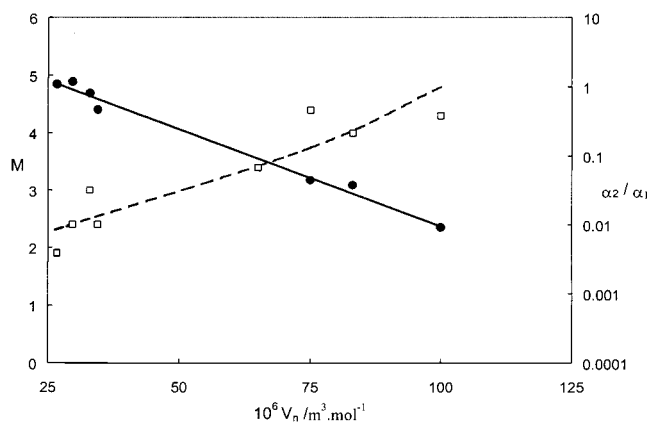
$$\ln(He_{\text{mix},j}) = \sum_{i=1 \dots N} x_i \ln(He_{i,j}) \quad (7)$$

in which  $x_i$  represents the mole fraction of solvent  $i$  in the solution and  $He_{i,j}$  the Henry coefficient of component  $j$  in solvent  $i$ . According to this method, the deviation of the actual solubility parameter  $\alpha$  (with  $\alpha$  being the reciprocal of  $m$ :  $\alpha = m^{-1}$ ) from the solubility in a “regular solution”,  $\alpha_{\text{RS}}$ , of  $\text{H}_2\text{O}$  (1) and  $\text{H}_2\text{SO}_4$  (2) is related to the total ionic concentration  $c$ , according to eq 8. In eq 8  $B$  is the proportionality constant.

$$\Delta \log(\alpha) = \log(\alpha) - \log(\alpha_{\text{RS}}) = \log(\alpha) - x_1 \log(\alpha_1) - x_2 \log(\alpha_2) = Bc \quad (8)$$

The total ionic concentration  $c$  required is unfortunately not well-known for the concentrated solutions considered. By using the result of McDevit and Long<sup>12</sup> that ionic salting out is proportional to the excess molar volume ( $V^E$ ) of the medium, an alternative, and much more convenient correlation, can be made:

$$\Delta \log(\alpha) = \log(\alpha) - \log(\alpha_{\text{RS}}) = L \left( \frac{V^E}{V} \right) \quad (9)$$



**Figure 1.** Correlation of  $M$  and  $\alpha_2/\alpha_1$  for various gases with molar volume in solution  $V_n$  for  $\text{H}_2\text{O}$  (1) and  $\text{H}_2\text{SO}_4$  (2):  $\square$ ,  $M$ ;  $\bullet$ ,  $\alpha_2/\alpha_1$  (ref 11).

with  $V^E$  being defined by

$$V^E = V - x_1 V_2 - x_2 V_2 \quad (10)$$

In this equation  $V$  represents the molar volume for the mixture and  $V_1$  and  $V_2$  represent the molar volumes for component 1 ( $\text{H}_2\text{O}$ ) and component 2 ( $\text{H}_2\text{SO}_4$ ), respectively.  $L$  is a dimensionless parameter depending on the nonelectrolyte. The parameter  $L$  can be calculated according to eq 11.

$$L = \frac{V_n}{2.3RTM\beta} \quad (11)$$

with  $\beta$  the compressibility factor of the solution, approximated by the following mixing rule using the compressibilities for the solvents 1 and 2:

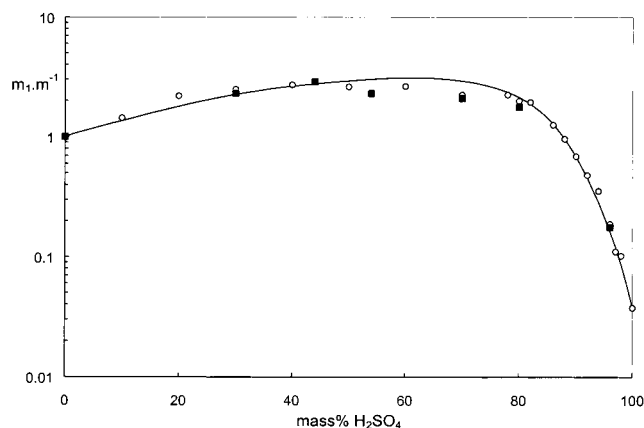
$$\beta = x_1\beta_1 + x_2\beta_2 \quad (12)$$

In eq 11  $M$  is a solute dependent, dimensionless correlation parameter. For  $\beta_{\text{H}_2\text{O}}$  and  $\beta_{\text{H}_2\text{SO}_4}$  the values proposed by Rudakov et al.<sup>11</sup> were taken. The  $M$  value can be determined by data fitting for inert components (which was done for isobutane, isopentane, cyclopentane, methane, hydrogen, and helium), but in the case of reactive gases its value needs to be estimated. A fair correlation of  $M$  with the molar volume of the inert gaseous solutes in solution  $V_n$  was obtained for the above-mentioned set of gases, see Figure 1.

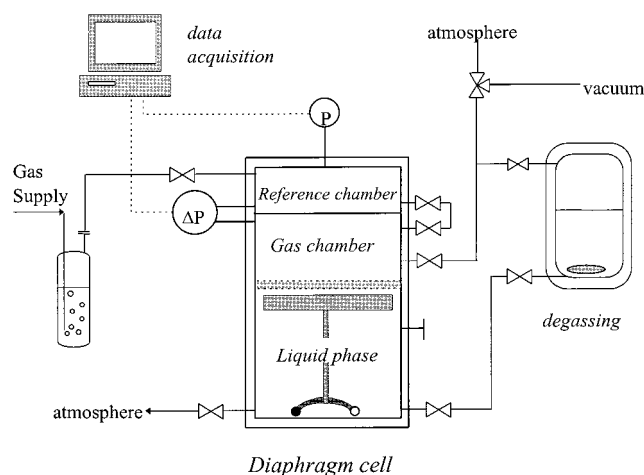
The method describes the set of data reasonably well, as is illustrated by Figure 2. In this figure the experimental data taken from the literature<sup>11</sup> and additional data points measured (see Table 5 for numerical values) are presented, as well as the solubility estimated by the above-mentioned method. Within the range 50–80 mass %  $\text{H}_2\text{SO}_4$  the deviations between model prediction and experimental determined data points are relatively large but still within 30% (which is relatively accurate if one considers that the protonation reaction rate constant varies over several decades in the range of acid concentrations).<sup>1</sup> The general trend is reasonably well described. This technique will be used for estimating the isobutene and *trans*-2-butene solubilities in aqueous sulfuric acid solutions.

## 4. Experimental Section

**4.1. Diffusion Coefficients.** Diffusion coefficients of isobutane, isobutene, and carbon dioxide in water and aqueous sulfuric acid solutions were determined using a



**Figure 2.** Solubility of isobutane in water  $m_1$  relative to the solubility of isobutane in aqueous sulfuric acid solutions  $m_r$ :  $\blacksquare$ , this work;  $\circ$ , Rudakov et al.;<sup>11</sup> —, estimation method.



**Figure 3.** Diaphragm cell setup.

**Table 2. Characteristics of the Diaphragm Cell**

liquid phase	volume	$V_L/\text{cm}^3$	282.5
gas phase	lower chamber	$V_g/\text{cm}^3$	187.5
	upper chamber	$V_{rel}/\text{cm}^3$	170.5
diaphragm	material		sintered glass spheres
	pore size (type P2)	$d_p/10^{-6}\text{ m}$	10–20
	porosity	$\epsilon$	0.45
	thickness	$d_m/10^{-3}\text{ m}$	4.0
	diameter	$d/10^{-3}\text{ m}$	60
operating range	upper chamber	$P_0/\text{Pa}$	$\leq 10^5$
pressure	differential pressure		various: 0– $10^2$ to 0– $10^5\text{ Pa}$
	temperature	$T/\text{K}$	280–313
	stirrer speed	rpm	20–60

diaphragm diffusion cell. The cell is depicted in Figure 3, and the characteristics of the cell are given in Table 2.

The cell contains two gas-phase chambers, separated by a glass wall. The diaphragm cell is completely thermostated. The pressure indicator of the upper gas chamber operates within the range 0–1000 mbar, having an uncertainty of 1 mbar. This pressure is the reference pressure during the measurements. The lower gas-phase chamber is separated from the liquid phase by a nonpermselective, liquid filled membrane, made of sintered glass. Various differential pressure indicators (Druck, 600DP series) were used. A typical example is a differential pressure indicator operating within the range 0–12 mbar ( $\pm 1\%$  of full scale).

**4.2. Calibration of the Diaphragms Used.** Carbon dioxide and nitrous oxide diffusion coefficient measurements were performed at 298 K to calibrate the diaphragm.



The diaphragm was characterized by determining experimentally the ratio  $f = A\epsilon/(\tau d_m)$  for different stirrer speeds. It was found that this ratio  $f$  was independent of stirrer speed within the range 20–60 rpm. Moreover, the same value ( $0.47 \pm 0.01$  m) was found for the CO<sub>2</sub> into water and for the N<sub>2</sub>O into water experiments.

Because of the use of differential pressure indicators, the relatively long measurement times, a major disadvantage of the diaphragm cell technique, could be substantially reduced. Typically, a single experiment took 1 h. This time could be optimized by choosing differential pressure indicators operating in an appropriate differential pressure range. Some experimental restrictions were found when isobutane was absorbed in sulfuric acid solutions. The extremely low solubility ( $<1$  mol/m<sup>3</sup> at 1 bar partial pressure of isobutane), especially at moderately high acid concentrations, resulted in scatter in the estimated diffusion coefficients, and no accurate determination was possible. These deviations could be caused by diffusion of isobutane through the short ( $10^{-2}$  m) Viton tubes to the differential pressure indicator and/or small fluctuations in the thermostat bath temperature. It was found for this particular setup that the gas–liquid distribution coefficient  $m$  should exceed 0.05 for reliable operation of this diaphragm cell and standard deviations in the diffusion coefficients not exceeding 5%.

**4.3. Solubility Measurements.** Solubilities of the gases in the sulfuric acid solutions were determined by gas absorption experiments in a thermostated glass reactor of total volume 1130 mL. The cell is equipped with a Hastelloy C-22 gas-inducing Medimex stirrer. Physical equilibrium between gas and liquid phases was usually reached in 20–30 s. This rapid equilibration enables the use of the solubility determination method for *trans*-2-butene up to 60 mass % H<sub>2</sub>SO<sub>4</sub> solutions. The temperature was controlled using a Tamson T1000 thermostat bath (accuracy:  $\pm 0.1$  K). The liquid-phase volumes used were in general 500 mL. The pressure drop was registered using a pressure indicator (Druck PTX-620, range  $(0-1.5) \times 10^5$  Pa ( $\pm 10^2$  Pa)). The cell was operated batchwise with respect to both the liquid phase and the gas phase. Prior to filling the gas space with the gas to be absorbed, the liquid was degassed by applying vacuum while stirring. Gases were purchased from Hoek Loos and were not further purified; isobutane (99.95%), isobutene (99.7%), and CO<sub>2</sub> (99.9%) were absorbed in aqueous sulfuric acid solutions prepared from 95–97 mass % pro analysis grade H<sub>2</sub>SO<sub>4</sub> (purchased from Merck). Acid concentration was determined by titration. Uncertainties of the solubilities were generally less than 1% for  $m$  values of 0.01 and higher. In the case of low solubilities the inaccuracy increased to 5–10%, which was encountered for isobutane in moderately strong sulfuric acid solutions (40–60 mass %).

## 5. Results

**5.1. Diffusion Coefficients.** To check whether the ionic strength of the liquid phase influences the apparent diffusion coefficients, experiments with potassium chloride solutions were performed. Aqueous potassium chloride solutions were selected, since the addition of KCl to water does not change the viscosity of the solution significantly (less than 2% increase, up to 3 M KCl<sup>13</sup>). With KCl the effects of ionic strength and solution viscosity could be separated.

For CO<sub>2</sub> and N<sub>2</sub>O in aqueous KCl solutions it was found that the diffusion coefficient did not change (within experimental accuracy of  $\pm 5\%$ ) for the range 0–3 M KCl

**Table 3. Diffusion Coefficients  $D$  and Distribution Coefficients  $m$**

[KCl]/M	$m$	exp no.	st dev	$10^9 D/\text{m}^2\cdot\text{s}^{-1}$	exp no.	st dev
(a) CO <sub>2</sub> in KCl Solutions at 293 K						
0.00	0.911	3	0.003	1.73	2	0.005
0.10	0.872	6	0.019	1.76	4	0.04
0.80	0.784	6	0.006	1.75	3	0.03
2.00	0.681	3	0.003	1.68	3	0.02
3.00	0.610	3	0.003	1.76	2	0.04
(b) N <sub>2</sub> O in KCl Solutions at 293 K						
0.00	0.675	5	0.01	1.63	2	0.005
1.00	0.530	3	0.004	1.63	3	0.06
2.00	0.430	3	0.003	1.64	2	0.07
3.00	0.369	3	0.001	1.63	2	0.005

**Table 4. Distribution Coefficients  $m$  and Diffusion Coefficients  $D$  of CO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub> Solutions at 298 K**

[H <sub>2</sub> SO <sub>4</sub> ]/mass %	$m_{\text{CO}_2}$	exp no.	st dev	$10^9 D_{\text{CO}_2}/\text{m}^2\cdot\text{s}^{-1}$	exp no.	st dev
0	0.84	3	0.003	1.93	2	0.005
54	0.71	2	0.002	0.71	1	
70	0.67	2	0.003	0.42	2	0.005
80	0.63	2	0.003	0.34	2	0.04
85				0.13	2	0.01
90				0.15	2	0.05
96	0.94	2	0.02	0.19	1	

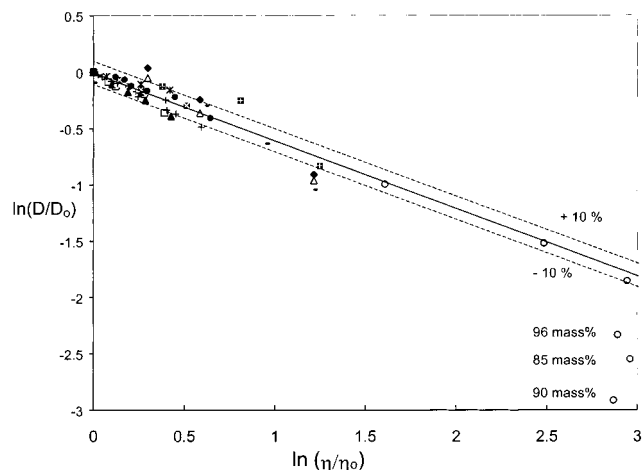
(Table 3). Therefore, the ionic strength of the liquid phase (or the activity coefficient of the diffusing gas) does not seem to have any influence on the apparent Fick diffusion coefficient.

Due to its extremely low solubility, the diffusion coefficient of isobutane could not be measured at all sulfuric acid concentrations. Gubbins et al.<sup>8</sup> suggested that the ratio of the diffusion coefficient in the aqueous solution to the diffusion coefficient in water would be the same for any pair of inert, sparingly soluble gases, because of the low (mole) fraction of the gas-phase component in a saturated liquid phase. This would justify the use of another inert gas for the estimation of the diffusion coefficient for isobutene and *trans*-2-butene in sulfuric acid solutions. With this assumption, carbon dioxide was selected to be used for estimating the diffusion coefficient of isobutene in aqueous sulfuric acid solutions. The experimental results for the CO<sub>2</sub>–aqueous sulfuric acid system are given in Table 4.

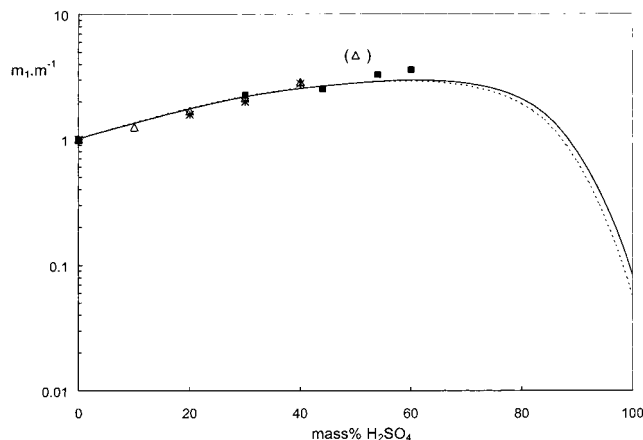
For the various gas-phase components available, diffusion coefficient data for aqueous electrolyte solutions were summarized in Figure 5. This figure shows that the data are reasonably well correlated by  $(D\eta)^{0.6} = \text{constant}$ . The relationship  $(D\eta)^{0.6} = \text{constant}$  was also found for the diffusion coefficients of several amines in aqueous amine solutions.<sup>13</sup>

Figure 4 shows that aqueous sulfuric acid solutions behave like other (less viscous) aqueous electrolyte solutions. The proposed correlation apparently holds for aqueous sulfuric acid solutions up to about 80 mass % and having a relative viscosity of nearly 20. The experimental values at (85, 90, and 96) mass % deviate from the correlation. This latter observation is probably due to the fact that water is no longer in excess in sulfuric acid solutions exceeding 84.5 mass % and the structure of the solution may change drastically in these regions.

**5.2. Solubility.** The solubility of isobutene and *trans*-2-butene in aqueous sulfuric acid solutions was estimated with the method described before. Using Figure 1, the parameter  $M$  for isobutene and *trans*-2-butene was estimated to be 3.4 for both gases. For estimating  $\alpha(\text{H}_2\text{SO}_4)$  again, Figure 1 was used;  $\alpha(\text{H}_2\text{O})$  can be measured directly



**Figure 4.** Correlation of literature data<sup>5,8,17</sup> on gas diffusion in aqueous electrolyte solutions and data obtained for CO<sub>2</sub> diffusion in H<sub>2</sub>SO<sub>4</sub> solutions (ref 1 and this work) at 298 K:  $\blacktriangle$ , CO<sub>2</sub> in NaCl (aq);  $\square$ , CO<sub>2</sub> in NaNO<sub>3</sub> (aq) + CO<sub>2</sub> in Na<sub>2</sub>SO<sub>4</sub> (aq);  $\times$  in a box, CO<sub>2</sub> in MgCl<sub>2</sub> (aq);  $*$ , CO<sub>2</sub> in Mg(NO<sub>3</sub>)<sub>2</sub>;  $\bullet$ , CO<sub>2</sub> in MgSO<sub>4</sub> (aq) + N<sub>2</sub>O in K<sub>2</sub>CO<sub>3</sub> (aq);  $-$ , H<sub>2</sub> in MgCl<sub>2</sub> (aq);  $\circ$ , CO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub>;  $\triangle$ , H<sub>2</sub> in MgSO<sub>4</sub> (aq);  $+$  in a box, CH<sub>4</sub> in MgCl<sub>2</sub> (aq);  $\blacklozenge$ , CH<sub>4</sub> in MgSO<sub>4</sub> (aq);  $-$ , fit  $\ln(D/D_0)$ .



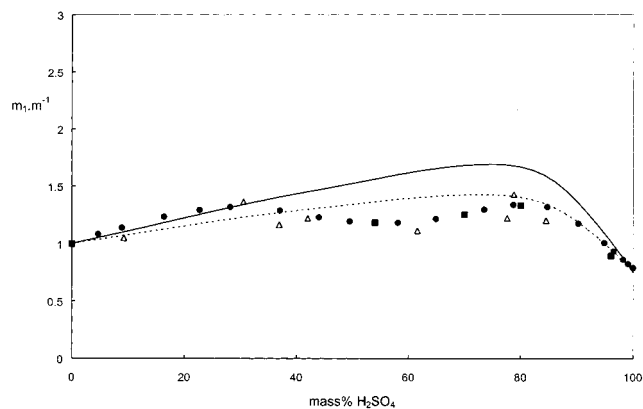
**Figure 5.** For isobutene and for *trans*-2-butene the solubility in water  $m_1$  relative to the solubility in aqueous sulfuric acid solutions  $m$  at 298 K. *trans*-2-Butene:  $\blacksquare$ , this work;  $\triangle$ , Sankholkar, Sharma;<sup>15</sup>  $---$ , estimation method. Isobutene:  $*$ , Gehlawat, Sharma;<sup>16</sup>  $-$ , estimation method.

**Table 5. Distribution Coefficients  $m$  of *trans*-2-Butene (1) and Isobutane (2) in H<sub>2</sub>SO<sub>4</sub> Solutions at 298 K**

[H <sub>2</sub> SO <sub>4</sub> ]/mass %	$m_1$	exp no.	st dev	$m_2$	exp no.	st dev
0	0.152	3	0.0010	0.023	3	0.0002
30	0.067	3	0.0005	0.010	3	0.0001
44	0.060	3	0.0003	0.008	3	0.0004
54	0.046	3	0.0004	0.010	3	0.0003
60	0.042	3	0.0004			
70				0.011	3	0.0003
80				0.013	3	0.0002
96				0.13	3	0.0009

or found in the literature. With these, the relative solubilities at different acid strengths have been calculated and are presented in Figure 5, together with experimental data from the literature<sup>15,16</sup> and experimental data from this work (see Table 5).

Due to the estimation method based on partial molar volume in aqueous solutions, the relative solubilities of *trans*-2-butene and isobutene in aqueous sulfuric acid solutions differ only slightly.



**Figure 6.** Solubility of carbon dioxide in water  $m_1$  relative to the solubility of carbon dioxide in aqueous sulfuric acid solutions  $m$ :  $\blacksquare$ , this work;  $\bullet$ , Markham, Kobe;<sup>17</sup>  $\triangle$ , Shchennikova et al.;<sup>18</sup>  $-$ , estimation method;  $---$ , estimation method fitted to experimental data.

In the low acid regime the protonation reaction is slow, and the physical solubility can be determined experimentally from gas absorption experiments if the liquid phase is saturated relatively fast. From Figure 5 it may be concluded that the estimation method works reasonably well for, at least, *trans*-2-butene up to 60 mass % sulfuric acid solutions. The solubility data point at 50 mass % taken from Sankholkar and Sharma<sup>15</sup> may have been disturbed by consumption due to chemical reaction.

Extrapolation of the method to gases differing drastically in properties from those of the calibration set is not recommended. For carbon dioxide, which is used in the diffusion coefficient estimation, the solubilities were determined experimentally and by the estimation method mentioned above. The results, presented in Figure 6, clearly show that the estimation method used is an oversimplification, although the results are very good up to 30 mass % sulfuric acid. The data by Markham and Kobe (1941)<sup>17</sup> and the data of Shchennikova et al. (1957)<sup>18</sup> were retrieved from the IUPAC Solubility Data Series.<sup>19</sup> The local minimum in the curve at approximately 60 mass % H<sub>2</sub>SO<sub>4</sub>, which can also be seen in Figure 2, is not predicted by the model; this would require, for example, the introduction of a third component to the regular solution. Nevertheless, the order of magnitude of the solubility remains predicted fairly well. By adapting the  $M$ , value a slightly better overall description of the experimental data can be obtained, as is shown in Figure 6.

When the above results and methods are used for interpretation of isobutene and *trans*-2-butene absorption fluxes in aqueous sulfuric acid solutions in order to retrieve kinetic data,<sup>1</sup> it is found that a significant part of the observed discrepancy in these kinetic data as found in the literature could be resolved.

## 6. Conclusion

The diaphragm cell with the differential pressure concept was found to be convenient for a quick determination of diffusion coefficients, while maintaining a reasonable accuracy of  $\pm 3\%$ . Since it was found that the diffusion coefficient of a gaseous component (here: CO<sub>2</sub>) in an inert electrolyte solution (here: KCl) is not influenced by the ionic strength of this solution, but apparently only by solution viscosity, a fairly good estimation of the diffusion coefficient in aqueous electrolyte solutions is obtained by using eq 13:

$$(D\eta)^{0.6} = \text{constant}$$

(for a particular gas, at a certain temperature) (13)

The (order of magnitude of the) physical solubilities of isobutene and *trans*-2-butene in aqueous sulfuric acid solutions at different sulfuric acid strengths can be estimated fairly well by using a method initially proposed by Rudakov et al.,<sup>11</sup> although deviations up to 50% cannot be excluded (especially within the range 60–80 mass %). The application of the above developed estimation methods for the diffusion coefficients and solubilities of isobutene and *trans*-2-butene leads to a consistent set of kinetic rate data for the protonation of these components in aqueous sulfuric acid solutions up to 96 mass %.

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