Solubility of Isobutene in Sulfuric Acid–*tert*-Butanol–Water Mixtures

Wolf-Dieter Deckwer
Institut für Technische Chemie, Technische Universität Berlin, 1 Berlin 12, West Germany

The solubility of isobutene in sulfuric acid–*tert*-butanol–water mixtures is measured, including the region of concentrations of industrial significance. The presence of *tert*-butanol causes a nonlinear increase in solubility. The solubility is also determined in solutions of $(NH_4)_2SO_4$ and aqueous H_2SO_4. Each system satisfies Setchenow's equation, but the additivity of the constant could not be confirmed. The presented data for the acid–alcohol mixtures are useful in designing isobutene absorbers.

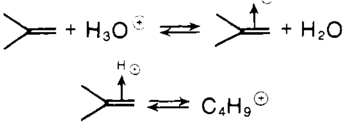
The access and availability of accurate solubility data of gases in liquids are very important in designing reliable gas absorbers. The saturation solubility modifies the driving concentration difference, and it can easily be shown that the performance of gas absorbers depends to a great degree on the solubility.

Industrial absorption processes are frequently accompanied by chemical reactions in the liquid phase to increase the mass transfer rates and the absorption capacitance of the liquid phase. In such reacting systems, reliable and accurate data of the physical solubility of gases are not easy to obtain. In particular, if the reaction rate in the liquid phase is fast, the solubility can only be estimated by more or less empirical correlations, as, for instance, the Setchenow relation for electrolytic solutions. These correlations may lead to considerable errors at higher concentrations of electrolytes, and it is seldom possible to take into account the variation of the liquid phase due to the generation of reaction products which may strongly modify the absorption properties of the liquid phase.

An example of such a reacting system is the separation of isobutene from C_4-olefins which is carried out by extraction or absorption with sulfuric acid. This process is of considerable industrial importance since at special operating conditions, isobutene of high purity can be recovered from the acid solution (*2, 6, 17*), which is preferentially used for producing butyl rubber.

Reaction Scheme

From studies of olefin hydration at low and moderate acid concentrations, Taft et al. (*11, 12, 16*) proposed a reaction mechanism. The main steps can be assumed as follows:



$$C_4H_9^{\oplus} + H_2O \rightleftharpoons C_4H_9OH_2^{\oplus} \qquad (3)$$

$$C_4H_9OH_2^{\oplus} + H_2O \rightleftharpoons C_4H_9OH + H_3O^{\oplus} \qquad (4)$$

The formation of the carbonium ion, Equation 2, is the rate determining step. The other steps involved are fast equilibrium reactions. At higher acid concentrations one has to consider additionally the possibility of the formation of sulfates which hydrolyze to *tert*-butanol:

$$C_4H_8 + H_2SO_4 \longrightarrow C_4H_9OSO_3H \qquad (5)$$

$$C_4H_9OSO_3H + H_2O \longrightarrow C_4H_9OH + H_2SO_4 \qquad (6)$$

Valet et al. (*17*) assumed that the isobutene exists in the liquid phase as sulfuric acid ester at acid concentrations of 40–50 wt %. However, this assumption appears not to be justified since Robey (*13*) pointed out that even at 80 wt % H_2SO_4, the fraction of *n*-butenes bounded as sulfate is not more than 30–40 wt %. Therefore, it seems reasonable that at acid concentrations below 60 wt %, the reaction mechanism proposed by Taft et al. (Equations 1–4) is rather significant. A further indication is that the rate constants determined at low and high acid concentrations follow Hammett's acidity function (*9*). This can be expected only for a reaction mechanism presented by Equations 1–4. On the other hand, it is not possible to extract *tert*-butanol from isobutene-loaded sulfuric acids (40–60 wt %). This was explained by Robey (*13*) and Pelofsky (*8*) who assume that the alcohol exists in the form of an alcoxonium ion (Equations 3 and 4) in acid solutions.

From the reaction rate data for sulfuric acid available from the literature (*5, 9*), one might expect that the absorption takes place in the fact reaction regime of mass transfer theory (*1, 3*); therefore, no unreacted isobutene should be found in the liquid phase. However, the high isobutene loadings applied in industry (1–1.5 g-mol isobutene/g-mol H_2SO_4), corresponding to appreciable amounts of *tert*-butanol in the liquid phase, may decrease the reaction rate but increase the physical solubility of isobutene. When studying the sulfuric acid catalyzed absorption and reaction of isobutene in several bubble columns at 30 °C (*4, 9, 10*), it was possible to proof the existence of unreacted isobutene in the liquid phase (*10*). This observation obviously indicates that the process occurs in the slow reaction regime. Therefore, it was thought that the solubility of isobutene in aqueous mixtures of sulfuric acid and *tert*-butanol can be measured, if the absorption rate is high enough to provide for complete saturation. This paper reports results of these measurements which cover the range of concentrations where the absorption rate in bubble columns was found to be highest. Also, measurements were carried out in ammonium sulfate solutions and in mixtures with *tert*-butanol to examine the usefulness and efficiency of Setchenow's relation. The data may be valuable for design purposes of isobutene absorbers.

Experimental

The experimental setup is schematically shown in Figure 1. Isobutene taken from a cylinder was saturated with vapor using the same liquid mixture as that wherein the solubility should be measured. The isobutene flow was measured with a calibrated rotameter and introduced through a glass sintered plate downward to the liquid in the vessel which was held at constant temperature. It was found best to gas the liquid by means of a sintered plate directed downward; thus, liquid samples could be withdrawn quickly from the vessel by a short tube (diam 3 mm) without entrainment of any gas. The flow through the tube did not take more than 0.1–0.2 s; thus, the error due to the reaction may be small but depends on the sulfuric acid concentration, of course. The liquid was fed directly into a flask with a known amount of cooled isobutene free water, thus avoiding any contact with gas. When using acid solutions, the reaction was stopped by feeding the sample stream into a prepared NaOH solution. The flask was completely filled and immediately closed with a lamella of silicone rubber and a threaded cock.

When using acid solutions, the reaction of isobutene takes place; hence, at steady state conditions the concentration of isobutene depends on the rate of absorption and reaction. Therefore, to know for certain that the isobutene concentration found is not a steady state concentration but the physical solubility runs were carried out at different isobutene throughputs, thus varying the rate of absorption. Results of these measurements are given in Figure 2 for two liquid-phase compositions. At gas flow rates above 100 l./h, the amount of isobutene found is constant. The gas throughput used in all measurements with acid solutions was above 150 l./h; thus, saturation with isobutene was always guaranteed. It should be pointed out, however, that complete saturation can be obtained easily as the absorption rate can be enhanced by increasing the gas flow. A more serious difficulty is the fast sampling and stopping of the reaction. Also, gassing over a period of 5 min is sufficient to establish saturation. The amount of *tert*-butanol accumulated in the liquid phase during this time could be neglected.

The diluted liquid samples were analyzed on their isobutene content by gas chromatography using a Perkin-Elmer F 20 chromatograph with a 3-m column packed with 10% Carbowax 20 M on Chromosorb W (60/80 mesh). Isobutene saturated water was used as standard. The integrated peak areas were proportional to the amount of isobutene. The solubility of isobutene in water at 30 °C was determined by titration (*7*) and is $4.5 \cdot 10^{-6}$ g-mol/cm^3, which agrees well with ref. *11*.

The major part of the measurements was carried out at 30 °C. The data were corrected with the vapor pressure by use of aqueous sulfuric acid data. The solubilities given in this paper refer to a partial pressure of isobutene of 760 torr.

One may argue that the isobutene analyzed by the applied technique may be formed by reverse reactions due to Taft's mechanism. However, this appears improbable as the reverse reaction, i.e., the formation of isobutene from isobutene-loaded sulfuric acids, occurs only at higher temperatures (about 100 °C) and short heating times. For instance, isobutene cannot be desorbed from isobutene-loaded acid at 30 °C. This fact was quite recently confirmed by Sankholkar and Sharma (*14*). On the other hand, heating of isobutene-loaded sulfuric acids to 50 °C yields oligomers only. Oligomers are also obtained when heating mixtures of *tert*-butanol and sulfuric acid. From these findings, the isobutene measured by this analytical procedure presents the physically dissolved isobutene and probably the isobutene bounded as a π-complex. However, the concentration of this π-complex may be very small except at high sulfuric acid concentrations.

Investigation of Setchenow's Equation

The solubility in aqueous solutions of electrolytes can be estimated by the relation:

$$\log \frac{c_o}{c} = hI \tag{7}$$

which was originally proposed by Setchenow (*15*). In Equation 7 c_o is the solubility in water, and c is the solubility in the electrolyte solution of ionic strength I. The concentrations c_o and c refer to a gas partial pressure of 760 torr. Partial pressure and concentration are connected by Henry's law:

$$p = Hc \tag{8}$$

van Krevelen and Hoftijzer (*18*) showed that the constant h is additively composed from the contributions of the ions and the gas:

$$h = h_+ + h_- + h_G \tag{9}$$

Data of h_+, h_-, and h_G for various ions and gases are summarized by Danckwerts (*3*).

The measured solubilities of isobutene in aqueous solutions of $(NH_4)_2SO_4$ satisfy the Setchenow equation up to values of 12 for the ionic strength, as shown in Figure 3. From the slope of the straight line and the contributions of the NH_4^+ and the SO_4^{2-} ions given in ref. *3*, the value of h_G for isobutene can be evaluated. h_G is 0.081, which appears rather high compared with values for other gases reported in ref. *3*.

In Figure 4 the solubilities of isobutene in aqueous sulfuric acid are shown. The plot of log c_o/c vs. I gives again a

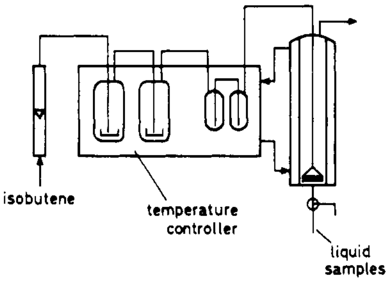


Figure 1. Experimental setup

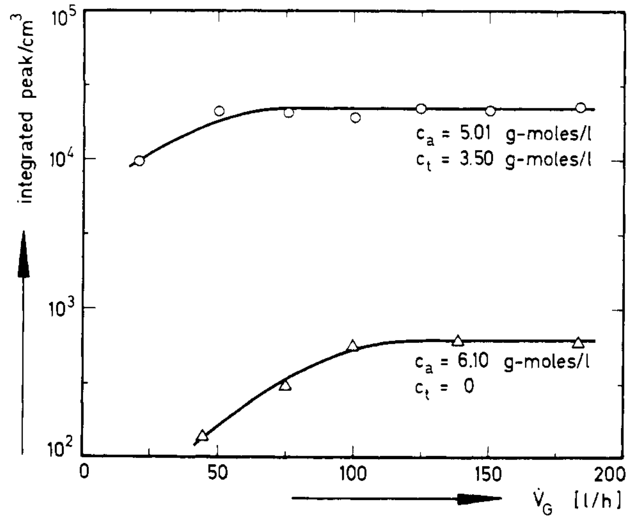


Figure 2. Amount of isobutene (integrated peak/cm^3 of sample) as function of gas flow rate

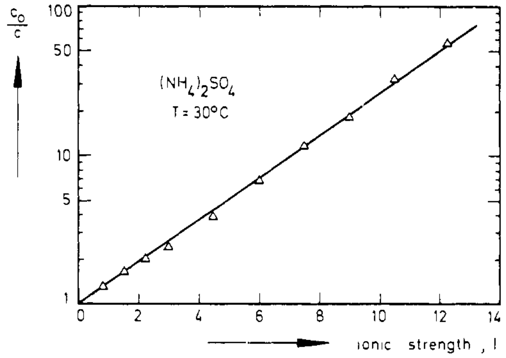


Figure 3. Dependence of isobutene solubility on ionic strength of ammonium sulfate

straight line up to values of the ionic strength of 12 (32 wt %). However, the calculated value of h_G is much smaller (0.014) which means that the solubility of isobutene in H_2SO_4 is higher than one might expect from the data obtained from solutions of $(NH_4)_2SO_4$. Therefore, Equation 7 can be applied in principle up to a certain ionic strength, but the additivity of the constant h (Equation 9) is not fulfilled for the systems studied in this work.

From Figure 4, the solubility runs through a minimum. A small but distinct increase of the solubility at higher concentration of sulfuric acid was also found in the measurements with mixtures of *tert*-butanol and H_2SO_4. A possible explanation for this observation, as well as the increased solubility in comparison with the prediction from the data of $(NH_4)_2SO_4$ solutions, may be the formation of a π-complex between isobutene and protons in the acid solution. The fast formation of such a π-complex is the first step in the hydration scheme of isobutene to *tert*-butanol (Equation 1). The π-complex is assumed to be in equilibrium with solved isobutene and may possibly be responsible for the increased solubility of isobutene in sulfuric acid solution.

Solubility of Isobutene in Liquid Mixtures with *tert*-butanol

Table I presents solubilities of isobutene in aqueous solutions of $(NH_4)_2SO_4$ with various amounts of *tert*-butanol. Up to a *tert*-butanol concentration of 1 g-mol/l., Equation 7 is satisfied; yet, increasing values of h are found for increasing c_t, as the presence of *tert*-butanol may modify the value of the ionic strength. From Table I, the solubility increases more strongly at higher concentrations of *tert*-butanol. Only a few data could be obtained at $c_t > 1$ g-mol/l. because of salting out of $(NH_4)_2SO_4$.

In Figure 5 the solubilities of isobutene at 30 °C are given for H_2SO_4–*tert*-butanol–water mixtures. As the solubilities vary from about 0.4 to $140 \cdot 10^{-6}$ g-mol/cm^3, a logarithmic scale is used in Figure 5. Additional data for different concentrations of *tert*-butanol are compiled in Table II. Figure 5 shows that up to a concentration of 30 wt %, the sulfuric acid has little effect on the solubility of isobutene, particularly at *tert*-butanol concentrations above 2 g-mol/l. At higher acid concentrations the solubility runs through a minimum. A possible explanation for this increase at high acid concentrations was given above. Higher acid concentrations than shown in Figure 5 could not be used since in the presence of *tert*-butanol, the formation of oligomers of isobutene takes place.

The course of the solubility as shown in Figure 5 is mathematically difficult to describe. Therefore, a correlation is presented only for the range of 30–55 wt % sulfuric acid and 2–5 g-mol/l. *tert*-butanol, which is important in industrial applications. The correlation is evaluated for log H (cf. Equation 8), though the error of the solubility measurements is not logarithmically distributed. However, when using log H, the regression analysis yields a much simpler expression which may be more appropriate for practical purposes. The resulting regression equation based on 38 experiments with replications was determined by a stepwise regression:

$$\log H = b_0 + b_1 c_a + b_2 c_t + b_3 c_a^2 \qquad (10)$$

Table I. Solubilities of Isobutene (10^6 c in g-mol/cm^3) at 30 °C for Aqueous Solutions of $(NH_4)_2SO_4$ and *tert*-Butanol

c_t, g-mol/l.	Concn of $(NH_4)_2SO_4$, g-mol/l. 0	0.25	0.5	0.75	1.0
0	4.50	3.63	2.88	2.27	1.81
0.3	4.63	3.97	3.29	2.69	2.23
0.6	4.76	4.26	3.51	2.97	2.46
1.0	4.98	4.41	3.77	3.34	2.69
1.5	5.41	5.27	4.53	4.36	. . .
1.8	6.81	6.28	6.33	. . .	. . .
2.1	8.34	8.31	. . .	. . .	. . .
2.5	13.42	. . .	. . .	. . .	. . .

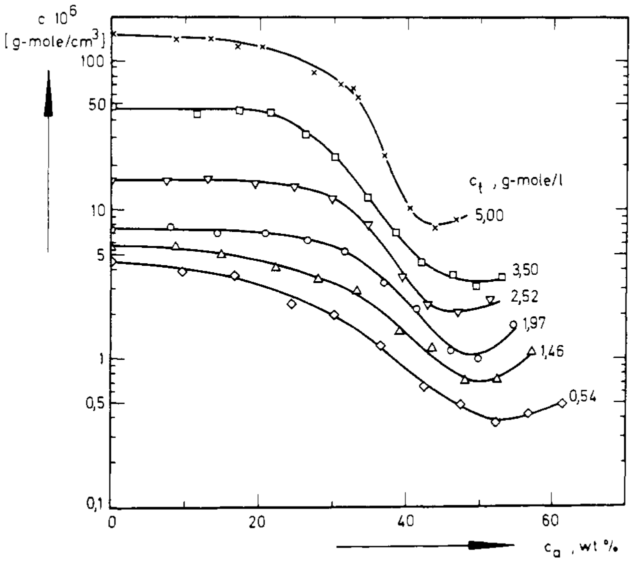


Figure 5. Solubility of isobutene vs. sulfuric acid concentration (concentration of *tert*-butanol as parameter)

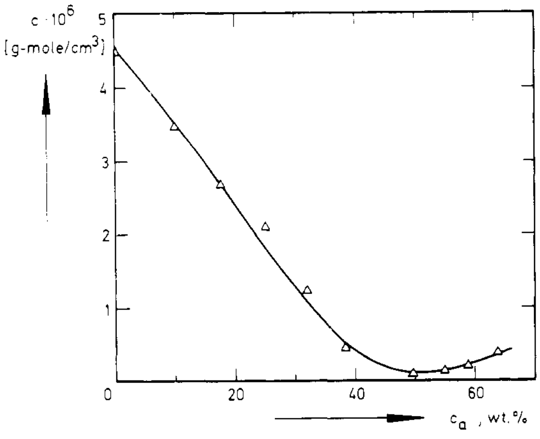


Figure 4. Solubility of isobutene in sulfuric acid

Table II. Solubilities of Isobutene in H_2SO_4–*tert*-Butanol–Water Mixtures at 30 °C

c_t = 1.02 g-mol/l. c_a, wt %	c_t = 1.02 g-mol/l. 10^6 c, g-mol/cm^3	c_t = 3.01 g-mol/l. c_a, wt %	c_t = 3.01 g-mol/l. 10^6 c, g-mol/cm^3	c_t = 4.0 g-mol/l. c_a, wt %	c_t = 4.0 g-mol/l. 10^6 c, g-mol/cm^3
9.04	4.99	12.3	27.6	16.0	76.3
15.4	4.19	18.4	27.0	20.0	73.6
23.3	3.32	23.4	24.5	24.5	74.2
29.2	2.54	28.0	24.2	28.5	41.4
34.8	2.27	32.7	12.9	32.3	37.4
40.5	1.14	37.2	8.60	36.8	16.6
45.6	0.83	40.8	3.41	39.0	9.63
50.0	0.53	44.5	3.23	43.1	5.80
54.3	0.58	49.0	2.99	49.5	5.05
59.3	0.66	51.6	3.24	52.1	6.98

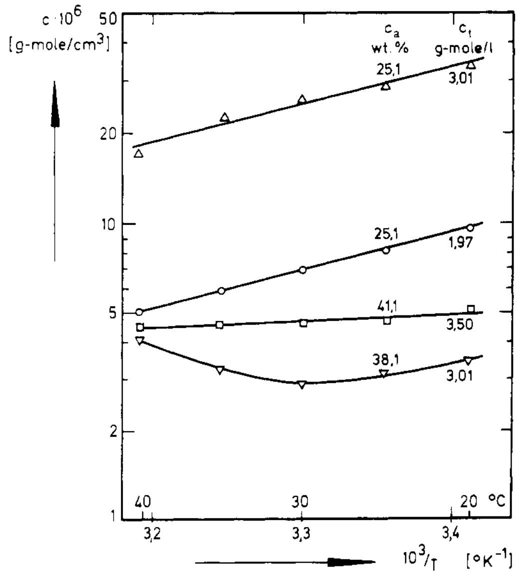


Figure 6. Temperature dependence of solubility of isobutene in various mixtures of acid and *tert*-butanol

(c_t in g-mol/l.; c_a in wt %; H in torr cm³/g-mol). The regression coefficients obtained and their individual confidence intervals to a 95% confidence coefficient are:

$$\begin{aligned} b_0 &= 2.514 \pm 0.841 \\ b_1 &= 0.276 \pm 0.057 \\ b_2 &= -0.338 \pm 0.034 \\ b_3 &= -0.0027 \pm 0.00065 \end{aligned} \qquad (11)$$

The residual variation concerning the logarithmic values of H is $s = 0.105$. By applying the F-test for "lack of fit", it was proved that the selected model satisfactorily represents the experimental data.

Temperature Dependence

For several mixtures of acid, *tert*-butanol, and water, the solubility was measured temperature dependent. Some examples are given in Figure 6. No uniform behavior was observed. At a concentration of approximately 40 wt % sulfuric acid and 3–3.5 g-mol/l. *tert*-butanol, the solubility appears to be only weakly dependent on the temperature.

Acknowledgment

Thanks are due to G. Zoll for carrying out the measurements and to H.-J. Warnecke for providing the regression program.

Literature Cited

(1) Astarita, G., "Mass Transfer with Chemical Reaction", Amsterdam, London, New York, 1967.
(2) Bauman, C. P., Smith, R. M., *Pet. Refiner,* **33,** 156 (1954).
(3) Danckwerts, P. V., "Gas-Liquid Reactions", McGraw-Hill, New York, N.Y., 1970.
(4) Deckwer, W.-D., Allenbach, U., to be published.
(5) Gehlawat, J. K., Sharma, M. M., *Chem. Eng. Sci.,* **23,** 1173 (1968).
(6) Kröper, H., Schlömer, K., Weitz, H. M., *Hydrocarbon Process.,* **48** (9), 195 (1969).
(7) Lucas, H. J., Eberz, W. F., *J. Am. Chem. Soc.,* **56,** 460 (1934).
(8) Pelofsky, A. H., *Ind. Eng. Chem. Process Des. Dev.,* **11,** 187 (1972).
(9) Popovic, M., Deckwer, W.-D., *Chem. Eng. Sci.,* **30,** 913 (1975).
(10) Popovic, M., Deckwer, W.-D., paper presented at 5th CHISA Congress, Prague, Czechoslovakia, August 25–29, 1975.
(11) Purlee, E. L., Taft, R. W., de Fazio, C. A., *J. Am. Chem. Soc.,* **77,** 837 (1955).
(12) Purlee, E. L., Taft, R. W., *ibid.,* **78,** 5807 (1956).
(13) Robey, R. F., *Ind. Eng. Chem.,* **33,** 1076 (1941).
(14) Sankholkar, D. S., Sharma, M. M., *Chem. Eng. Sci.,* **30,** 729 (1975).
(15) Setchenow, M., *Ann. Chim. Phys.,* **25,** 226 (1892).
(16) Taft, R. W., *J. Am. Chem. Soc.,* **74,** 5372 (1952).
(17) Valet, A. M., Micheaux, J. P., Bellec, J. J., *Pet. Refiner,* **41,** 119 (1962).
(18) van Krevelen, D. W., Hoftijzer, P. J., Chimie et Industrie, No. Special du XXIe Congres International de Chimie Industrielle, Bruxelles, Belgium, 1948.

Received for review March 24, 1975. Accepted December 1, 1975.

Densities and Viscosities of Binary Systems Toluene–Acetone and 4-Methyl-2-Pentanone–Acetic Acid at 20, 25, 35, and 45 °C

M. Hafez and S. Hartland*
Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology, Zürich 8006, Switzerland

Densities and viscosities of the binary miscible liquid systems toluene–acetone and 4-methyl-2-pentanone–acetic acid are measured at 20, 25, 35, and 45 °C. The results compare well with the theories proposed by Hildebrand and Kosanovich.

The evaluation and prediction of the transport properties of binary miscible liquid systems as functions of composition and temperature are of theoretical and practical importance, but very little data are available.

A general statistical mechanical theory has been proposed by Bearman and Kirkwood (*3*) and Bearman (*4*) to predict the transport properties. Based on the thermodynamics of irreversible processes, Albright (*1*) also proposed an equation to relate the intradiffusion of components of a solution to the viscosity of the solution. These and other statistical and thermodynamic approaches have not yet been successfully reduced to numerical results. Hildebrand (*6*) and Hildebrand and Lamoreaux (*7*) proposed general equations for the viscosity and diffusivity of pure liquids, and Cullilan and Kosanovich (*5*) extended the equations for viscosity to mixtures and showed it to be valid for reduced temperatures ≥0.46. Hildebrand's equation for the single components is:

$$\phi = B\left(\frac{V - V_0}{V_0}\right) \qquad (1)$$

where ϕ is the fluidity ($1/\eta$), V is the molecular volume (M/ρ), V_0 is the ultimate molecular volume when viscous flow ceas-