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Determination of Density, Viscosity, and Surface Tension for the System Isobutene–Sulfuric Acid–*tert*-Butyl Alcohol–Water

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The density, viscosity, and surface tension of the system isobutene–sulfuric acid–*tert*-butyl alcohol–water were measured in the range of concentrations including those of industrial significance. For each property, regression functions depending on c_{A_0} and c_t are presented. The data can be valuable for the design of isobutene absorbers.

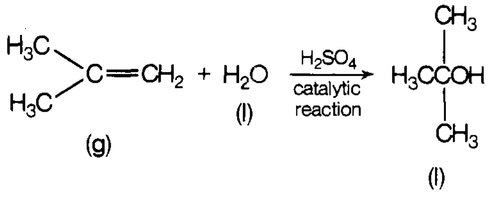
The separation of isobutene from a gaseous mixture of C_4-hydrocarbons is an important industrial process. It is based on the high chemical reactivity of isobutene to form *tert*-butyl alcohol when selectively absorbed in sulfuric acid solutions up to 45 wt % (*7*).

A lot of experimental studies have been published referring to the kinetics of the reaction (*2*), to the effect of *tert*-butyl alcohol on the solubility of isobutene (*1*), and on the absorption rate in a bubble column (*8*). Yet it is necessary to get a detailed knowledge of the physical parameters of the system like density, viscosity, and surface tension, because these variables directly influence the values of gas holdup and the product of mass transfer coefficient and specific interfacial area in bubble columns (*3–5*).

It is the aim of this paper to present measured data of density, viscosity, and surface tension as a function of the sulfuric acid and *tert*-butyl alcohol concentration. The dependences are investigated under conditions similar to those found in the bubble column reactor. The data may be valuable for designing isobutene absorbers.

Experimental Section

The absorption–reaction that occurs is:



$$\underset{(g)}{(H_3C)_2C{=}CH_2} + \underset{(l)}{H_2O} \xrightarrow[\text{catalytic reaction}]{H_2SO_4} \underset{(l)}{H_3C\overset{CH_3}{\underset{CH_3}{C}}OH}$$

Because of 1 to 1 correspondence between water and *tert*-butyl alcohol and of a large difference in the molecular weights, the molar volume increases by 78.3 ml at 30.0 °C, the density of *tert*-butyl alcohol being 0.77 g cm^{-3}. Thus the initial acid is diluted as well as the alcohol. To simulate the course of the reaction in the bubble column, an experimental design was proposed with the variables: initial acid concentration varying from 3 to 10 g-mol l.$^{-1}$ and number of moles of isobutene n_i reacted lying between 0 and 10 mol.

The actual concentration of acid c_A and the number of moles of *tert*-butyl alcohol n_t can be calculated by the equations

$$c_A = c_{A_0}\frac{1000}{1000 + n_i 78.3} \qquad (1)$$

$$n_t = n_i\frac{1000}{1000 + n_i 78.3} \qquad (2)$$

The volume contraction, occurring when highly concentrated acid solutions are used, and the heat released during the dilution of sulfuric acid solutions with water were taken into account during the preparation of the solutions. The density of the sulfuric acid–*tert*-butyl alcohol–water mixture was measured at 30.0 °C with the digital densimeter DMA 50 (manufactured by Anton Paar K.G., sold by Heraeus, Germany). The solution was filled into a U-shaped Duran 20 glass tube, representing a mechanical oscillator. The method assumes a quadratic relation

$$\rho = AT^2 + B \qquad (3)$$

between the density of the fluid and the period of the oscillator, where A and B are empirical constants to be determined with the help of two liquids with known densities.

The kinematic viscosity ν was measured with the Ubbelohde viscosimeter (Schott) at 30.0 °C. Considering the Hagenbach correction term, ν is given by

$$\nu = kt - \frac{2.5}{t} \qquad (4)$$

where k is a capillary constant and t means the flow time between two calibration marks. The dynamic viscosity η is then $\eta = \nu\rho$.

The surface tension σ of the solution against air and isobutene was measured at 30.0 °C with a tensiometer (MGW Lauda, Germany), that allowed σ to be recorded automatically as a function of time. For the measurement of σ against isobutene

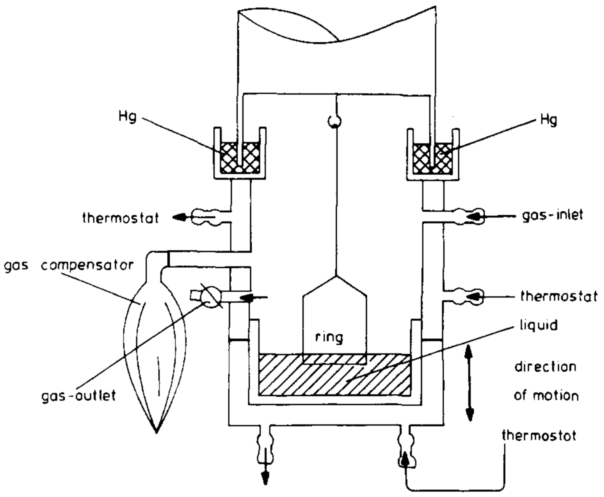


Figure 1. Apparatus for the measurement of surface tension.

an apparatus was devised as shown in Figure 1. In order to compensate the variation of the gas volume in the cell by moving the lower part of the apparatus, a compensator was added to the equipment. The lower and upper part were sealed up with mercury.

The device of Lauda is based on a classical ring method.

All the measurements were carried out at 30.0 °C, because this temperature is the optimum reaction temperature (*7*).

Discussion

Figure 2 shows the density ρ as a function of the actual concentration of *tert*-butyl alcohol with the initial acid concentration c_{A_0} as parameter. The nearly linear dependence can be described by the following regression function with an average percentage error of ±0.2%.

$$\rho = b_0 + b_1 c_{A_0} + b_2 c_t + b_3 c_{A_0} c_t \qquad (5)$$

$$b_0 = 1.029 \pm 0.008$$

$$b_1 = 0.05 \pm 0.0008$$

$$b_2 = -0.02 \pm 0.001$$

$$b_3 = -0.0037 \pm 0.002$$

This function was determined so precisely that it can be used for quantitative analysis of *tert*-butyl alcohol. By application of the F-test for this model and the models proposed below it was proved that the selected function is most adequate for the problem and contains significant parameters only.

In Figure 3 the relatively strong increase of the dynamic viscosity η plotted as a function of c_t is illustrated. This dependence can be linearized on a semilog plot of log η vs. c_t as per Figure 4. The regression function gives an average percentage error of ±2.4% for log η:

$$\log \eta = b_0 + b_1 c_{A_0} + b_2 c_t + b_3 c_{A_0} c_t \qquad (6)$$

$$b_0 = -0.079 \pm 0.003$$

$$b_1 = 0.079 \pm 0.004$$

$$b_2 = 0.080 \pm 0.008$$

$$b_3 = 0.0043 \pm 0.001$$

Investigations of the temperature dependence of the viscosity do not reveal any influence of *tert*-butyl alcohol in the aqueous mixture on the energy of viscous flow.

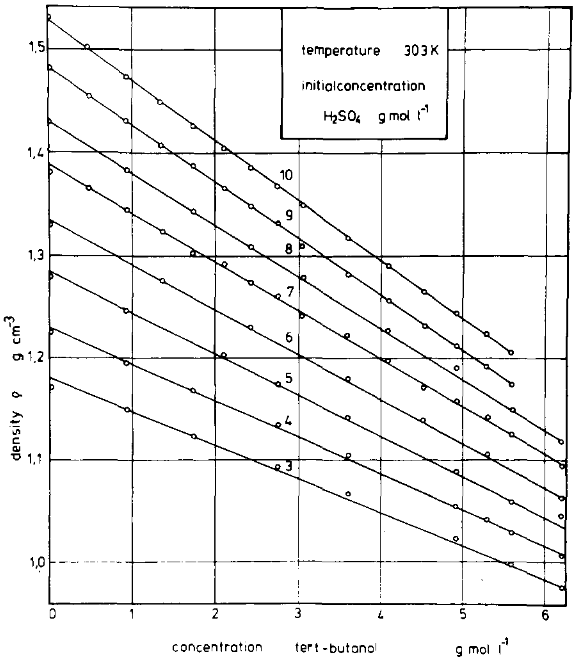


Figure 2. Density as a function of the concentration of *tert*-butyl alcohol.

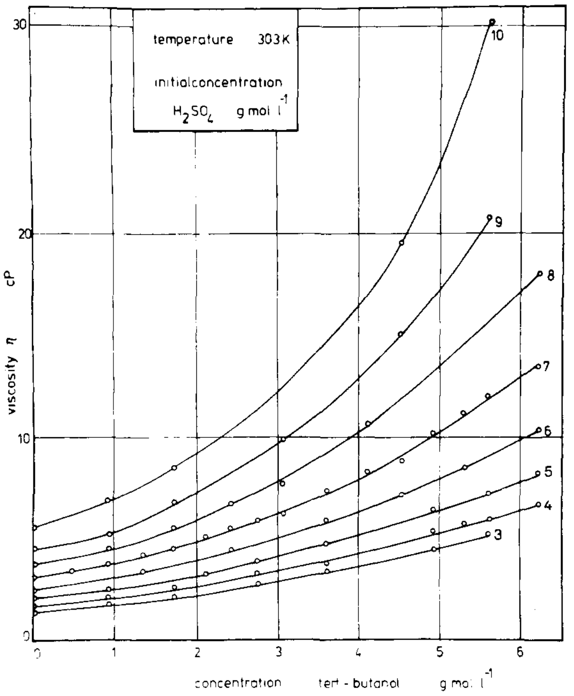


Figure 3. Viscosity vs. *tert*-butyl alcohol concentration.

The surface tensions of the solutions were measured in contact with air and isobutene. In normal cases the influence of the gas or vapor is negligible, if the pressure is not too high (*9*). Yet here it is not only the chemical reaction taking place that affects the surface tension, but also the absorbed isobutene. The result is that for pure *tert*-butyl alcohol in contact with air a value of σ = 19.6 dyn cm^{-1} is obtained at 30.0 °C. If it is in contact with isobutene, the surface tension decreases to the value of σ = 17.7 dyn cm^{-1}.

Figure 5 gives the quantitative dependences of the surface tension of the reaction mixture as a function of the alcohol

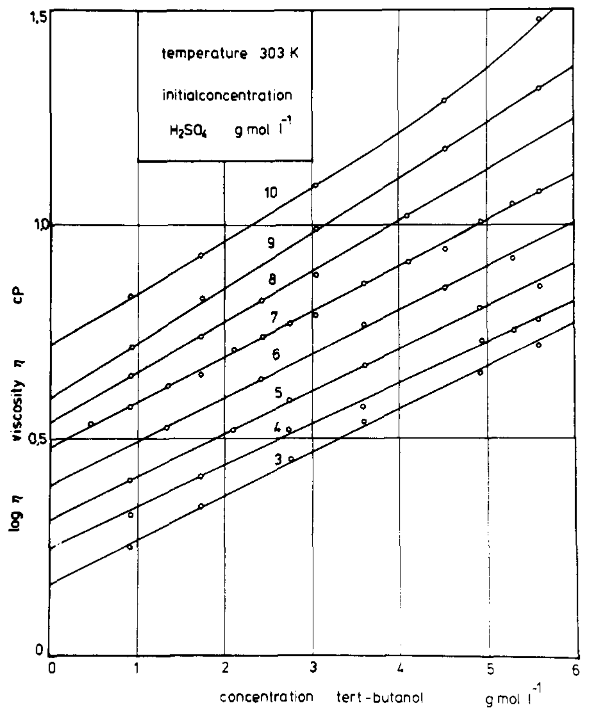


Figure 4. Logarithm of viscosity as a function of *tert*-butyl alcohol concentration.

concentration with the sulfuric acid concentration c_{A_0} as a parameter. The broken lines show the influence of the gas the solution is in contact with.

The curves can be described by

$$\sigma = b_1 c_t^{b_2} \exp(b_3 c_{A_0})$$

(average percentage error: ±5%). The values of the regression coefficients are: against air for $0.25 < c_t < 5.5$ g-mol l.$^{-1}$

$$b_1 = 32.3 \pm 2.1$$
$$b_2 = -0.185 \pm 0.015 \qquad (7)$$
$$b_3 = 0.023 \pm 0.009$$

against isobutene for $0.25 < c_t < 5.5$ g-mol l.$^{-1}$

$$b_1 = 31.29 \pm 2.5$$
$$b_2 = -0.186 \pm 0.02 \qquad (8)$$
$$b_3 = 0.015 \pm 0.01$$

The question whether there is any excess concentration of *tert*-butyl in the surface area can be answered by applying the Gibbs adsorption equation for our system in analogy to Wolf (*9*) and Graeser (*6*) who have studied only butanol-water mixtures. The equation of Gibbs gives a positive value of the excess concentration which fulfills the necessary condition for the enrichment of the alcohol.

The sufficient criterion, that the absolute value of $d\sigma/dc_t$ is greater than the differential quotient resulting from a linear relationship, is just satisfied, too. Thus the surface activity of *tert*-butyl alcohol is established thermodynamically.

This statement is in good agreement with the findings of Zieminski et al. (*10*) who investigated among other dispersions the system air-different alcohols-water. It was shown that the surface activity increases progressively with the length of the carbon chain of the alcohol. While the normal, iso-, and *tert*-butyl alcohols exhibit a relatively small enrichment in the surface area, the effect of the higher alcohols in the range of *n*-amyl to *n*-octyl alcohol turns out to be considerably greater.

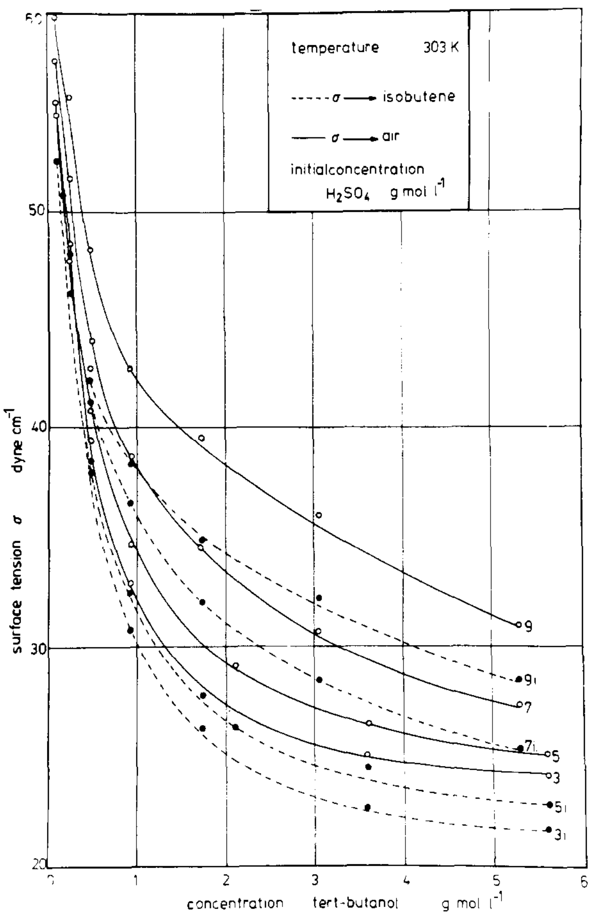


Figure 5. Dependence of the surface tension on the *tert*-butyl alcohol concentration.

The regression functions (*5–8*) form the basis for describing the physical properties of the system isobutene-sulfuric acid-*tert*-butyl alcohol-water. With the aid of these equations pertinent hydrodynamic and mass transfer design parameters for bubble columns can be calculated for specific operating conditions.

This paper represents the very basic information necessary to project a complicated three component reaction system described above and therefore justifies a careful consideration.

Acknowledgment

The authors wish to thank Professor Dr. H. Kölbel for having initiated this study.

Glossary

A,B	constants (eq 3)
b_0,b_1,b_2,b_3	regression coefficients
c_{A_0}	initial concentration of sulfuric acid, g-mol l.$^{-1}$
c_A	actual concentration of sulfuric acid, g-mol l.$^{-1}$
c_t	actual concentration of *tert*-butyl alcohol, g-mol l.$^{-1}$
k	capillary constant (eq 4)
n_i	number of moles of isobutene, used by reaction, g-mol
n_t	number of moles of *tert*-butyl alcohol, g-mol
t	time, s
T	period of the oscillator, s
ρ	density, g cm^{-3}
η	dynamic viscosity, cP
ν	kinematic viscosity, cSt
σ	surface tension, dyn cm^{-1}

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Phase Equilibria in Ternary Systems of Hexamethyldisiloxane–Butylamines–Water

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Liquid–liquid phase equilibria have been studied in systems comprising hexamethyldisiloxane, water, and *n*-butylamine, isobutylamine, or *tert*-butylamine. Tie lines of two-phase conjugated systems have been determined by employing the Mertslin method, as well as partition coefficients of the amines between the aqueous and hexamethyldisiloxane phases.

Results of our further studies have been reported on deriving some equilibrium relationships in three ternary systems comprising hexamethyldisiloxane (HMDS), water, and *n*-butyl-, isobutyl-, or *tert*-butylamine. Although HMDS has been found to be more resistant to hydrolysis (*3, 10*) than an earlier reported tetraisopropoxysilane (*6–9*), it has been, however, shown to undergo hydrolysis to some extent, especially in alkaline media. For this reason, studies on equilibrium relationships in systems involving HMDS, water, and basic components, seem to be especially useful in evaluation of the suitability of HMDS as a solvent in extraction and chromatography.

Experimental Section

Materials. HMDS was a commercial product boiling at 99.5–100.5 °C, d^{20}_4 0.7636, N^{20}_D 1.3774. Isomeric butylamines were also commercial products and had physical constants shown in Table I.

Table I. Physical Constants of the Amines Used

Amine	Boiling range (°C)	d^{20}_4	n^{20}_D
n-Butyl	77–78	0.7414	1.4009
Isobutyl	68–70	0.7346	1.3970
tert-Butyl	44–45	0.7002	1.3789

Procedure. The solubility of HMDS in aqueous solutions of amines was determined by employing the Bancroft's method (*1, 2*) and that developed by Nikurashina and Mertslin (*5*). The HMDS/amine ratios used for the preparation of solutions, as well as a limiting amount of water soluble in the individual ternary systems at 20 ± 1 °C have been listed in Table II.

The results have been presented graphically in Figures 1–3 in the form of solubility curves.

Tie lines were determined by analyzing phases of the individual ternary systems over heterogeneous regions. To do this, the refraction index (n^{20}_D) of lower phases was measured. Relationships between the refraction index and amine concentration have been shown in Figures 4–6.

During determination of tie lines use was made of a characteristic property of the conjugated phases, according to which each tie line is the locus of points of a constant composition of the conjugated phases.

The concentration of components of the individual phases was read out after plotting tie lines using a graphoanalytical method developed by Nikurashin et al. (*5*). Partition coefficients of the amines between a polar and nonpolar phase were calculated based on composition of the conjugated phases.

Results

Based on results shown in Table II, solubility curves were plotted which separate a homogeneous and a two-phase region in the ternary systems (Figures 1–3).

A relationship between the refraction index and the concentration of an amine in lower phases of heterogeneous systems is shown in Figures 4–6.

Table II. Concentration of Components Determining the Solubility Curve (weight %)

No.	HMDS	n-$C_4H_9NH_2$	H_2O	HMDS	t-$C_4H_9NH_2$	H_2O	HMDS	i-$C_4H_9NH_2$	H_2O
1	1.80	18.02	80.18	0.9	20.98	78.12	1.12	14.45	84.43
2	3.95	34.50	61.55	2.01	34.94	63.05	1.52	26.57	71.90
3	8.64	47.56	43.80	6.05	49.95	44.00	4.52	37.26	58.22
4	13.17	50.87	35.96	14.66	53.77	31.93	9.21	47.90	42.89
5	22.86	51.75	25.39	24.01	51.39	24.60	13.81	50.66	35.53
6	32.99	48.04	19.00	34.05	46.85	19.10	23.30	49.88	26.82
7	42.67	41.65	15.68	44.50	40.81	14.69	33.31	45.83	20.87
8	53.90	34.89	11.21	55.66	34.04	10.30	44.04	40.40	15.57
9	65.03	27.06	7.92	67.66	26.58	5.76	55.00	33.63	11.37
10	77.23	18.75	4.03	76.77	18.26	4.99	68.53	26.94	4.53
11	88.68	9.57	1.76	90.31	9.20	0.49	79.34	18.18	2.48
12	—	—	—	—	—	—	90.19	9.19	0.62