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Solubilities and Enthalpies of Absorption of Isobutene into *tert*-Butyl Alcohol–Water Mixtures

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The solubilities of isobutene in *tert*-butyl alcohol–water mixtures were determined for alcohol concentrations up to 2.95 kmol/m^3 and temperatures up to 333 K. The temperature coefficient of the solubility (at constant alcohol concentration) allows determination of the absorption enthalpy and entropy changes.

Introduction

Direct hydration of isobutene to *tert*-butyl alcohol can be carried out in a slurry of catalyst particles or in a trickle-bed reactor. Also, residual isobutene in effluent gas streams can be absorbed with *tert*-butyl alcohol solutions. Reliable data on the solubilities and the heat effects associated with absorption are essential for the design of these processes.

The solubility of isobutene in pure water is well characterized (*1–3*). Particularly the data of Kazanskii et al. (*3*), covering a wide temperature range (0–70 °C), show two temperature intervals with different solution enthalpies. Because isobutene has been traditionally absorbed into aqueous H_2SO_4, data on its solubility in H_2SO_4–*tert*-butyl alcohol–water mixtures are also available (*4*, *5*). Thus, Deckwer (*4*) correlated the solubilities of isobutene in aqueous *tert*-butyl alcohol with and without H_2SO_4 at 30 °C. Without H_2SO_4, the solubility is enhanced exponentially by the presence of the alcohol. This is in agreement with the theory of gas solubility in mixed solvents (*6*). Deckwer correlation is most useful because it covers a range of alcohol concentrations up to 37 wt % but it is given only at 30 °C.

The purpose of this work was to determine experimentally the solubilities of isobutene in aqueous *tert*-butyl alcohol for the concentration and temperature ranges of interest in multiphase catalytic reactors, and hence in the absence of dissolved acid. Subsequent analysis of the temperature coefficient of the solubility allows us to determine the enthalpy and entropy changes for the absorption process thus saving burdensome calorimetric determinations.

Experimental Section

Apparatus. Solubility measurements were made in the apparatus shown in Figure 1. The essential part is the glass reservoir for liquid mixtures, 5, where isobutene is bubbled at atmospheric pressure. The reservoir is contained in a thermostated bath, 6, which holds the temperature within ±0.2 °C. Excessive carryover of vapor is prevented by the reflux condenser 7, operated at 2 °C. The liquid mixture is recycled by means of a pump, 4, through the rotameter, 2, to ensure good mixing and to allow for sampling at septum 3. By use of gas-chromatographic syringes, liquid samples could be directly analyzed. All recycle lines were insulated. In order to reproduce saturation times, the gas flow rate through the reservoir was held constant at 3 cm^3/s (760 mmHg, 25 °C) in all measurements.

Table I. Solubility Data and Partial Pressures of Isobutene at a Total Pressure of 101.3 kPa

C_A, kmol/m^3	*T*, K			
	303	313	323	333
Isobutene Solubilities × 10^3, kmol/m^3				
0	4.66		2.68	
	(4.66)^a	(3.55)	(2.69)	(1.93)
0.51	5.28	4.04	3.19	2.31
1.04	5.50	4.18	3.23	2.60
2.10	9.02	7.71	6.09	5.06
2.95	33.0	28.4	26.5	20.3
Isobutene Partial Pressures, kPa				
0	97	94	89	81
0.51	95	92	85	76
1.04	94	91	83	72
2.10	93	88	80	67
2.95	93	88	79	66
Henry's Law Constants, 10^{-5}*H*, kPa				
0	11.4	14.6	18.6	23.1
0.51	9.75	12.2	14.4	17.6
1.04	9.00	11.4	13.4	14.5
2.10	5.09	5.62	6.44	6.57
2.95	1.30	1.43	1.38	1.50

^{a} Pure water from Kazanskii et al. (*3*).

tert-Butyl alcohol–water mixtures were prepared by directly weighing the alcohol into previously tared 1-L flasks. Hence, approximate molar concentrations and densities were known. Later, effective molar concentrations of alcohol in the equilibrated liquid mixtures were measured by gas chromatography. After a mixture was placed in the reservoir, temperature was adjusted and the flow of gas was started. Saturation took in our case about 30 min as determined with pure water. Thirty additional minutes were left to ensure equilibrium. After this time, the analyses of dissolved isobutene and alcohol concentration were made.

Analytical Procedures. *tert*-Butyl alcohol concentrations were determined by gas chromatography (Varian 1400 apparatus provided with a flame ionization detector) using a column of 15% Carbowax 20M on 80/100 mesh Chromosorb W at 85 °C. Isopropyl alcohol was used as internal standard. Dissolved isobutene in the equilibrated mixtures was measured by using the same chromatograph and conditions as for *tert*-butyl alcohol except that an isobutene-saturated solution was used as external standard. Ten to twelve replicate 2-μL injections of equilibrated liquid withdrawn from 3 (Figure 1) were made. By use of gas-tight syringes, the method was accurate within ±2.2%. To calibrate the peaks of the external standard, synthetic gas mixtures of isobutene–N_2, with equivalent amounts of isobutene, were prepared in a gas-mixing facility.

Chemicals. Isobutene from Phillips Chemical Co., with a stated purity of 99 mol %, was used without further purification. *tert*-Butyl and isopropyl alcohols were reagent grade, ACS certified, from Mallinckrodt Chemical Co. Deionized plus distilled water from laboratory facilities was used.

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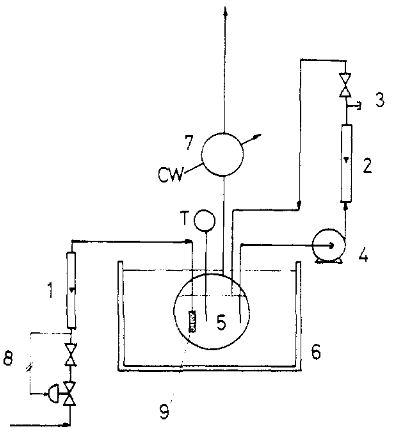

Figure 1. Apparatus: 1, gas rotameter; 2, liquid rotameter; 3, sampling septum; 4, pump; 5, reservoir; 6, thermostated bath; 7, reflux condenser; 8, gas-flow controller; 9, porous glass sparger.

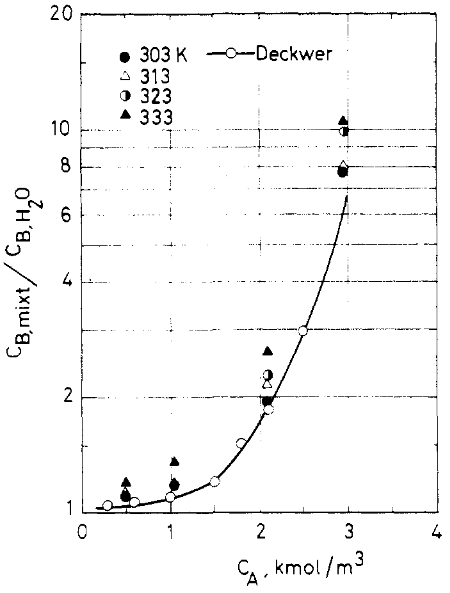

Figure 2. Solubility enhancement relative to pure water at 101.3 kPa total pressure.

Results and Discussion

The measured solubilities are given in Table I showing the ranges of temperature and alcohol concentration of our study. As seen, the values for pure water (C_A = 0) compare well with those found by Kazanskii et al. (*3*). Generally, solubility increases with alcohol concentration and decreases with temperature at constant C_A, as expected. In Figure 2 the solubility enhancement factors relative to pure water at corresponding temperatures are given. Experimental data points and the correlation of Deckwer at 303 K (*4*) are also compared. Although our data are close to the line, large deviations (40–75%) for high C_A and T are observed.

The solubilities of Figure 2 correspond to variable partial pressures of isobutene. They were thus reduced to the same basis by using the Henry's law constant defined as

$$H = \lim_{(x \to 0)} (f/x) = p/x \qquad (1)$$

Because $x = 10^{-3}$–10^{-4}, the above approximation is reasonable. The partial pressures of the butene are calculated by the difference between the total pressure and the vapor pressure of the solvent, as it is usually done for sparingly soluble gases (*7*). Liquid–vapor (L/V) equilibrium data for the system *tert*-butyl alcohol–water are plentiful (*8*, *9*), allowing us to calculate the activity coefficients of the components and the vapor pressure of the solution. Isothermal L/V equilibrium data at 298 and 353 K from Gmehling et al. (*9*) were taken to calculate A_{12} and A_{21} for use in the Wilson equation (*10*) for the activity coefficients.

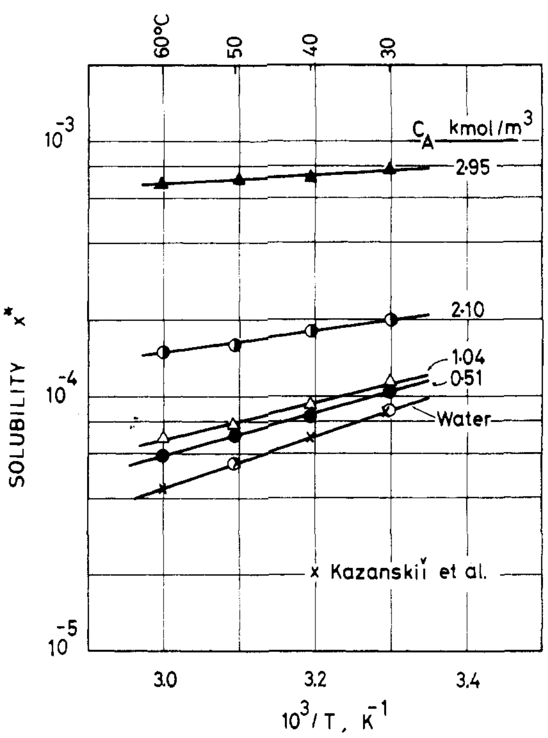

Figure 3. Temperature dependence of solubilities at constant *tert*-butyl alcohol concentration.

With the above approximations and using appropriate values for liquid densities, the partial pressures of isobutene and the Henry's law constants calculated from eq 1 are given in Table I.

Correlation of Data. From thermodynamic principles (*11*), it is shown that neglecting the effect of total pressure on H and using the approximation of eq 1, we have

$$\frac{d \ln x^*}{d(1/T)} = -\frac{\Delta \bar{h}^\circ}{R} \qquad (2)$$

$$\frac{d \ln x^*}{d \ln T} + \ln x^* = \frac{\Delta \bar{s}^\circ}{R} \qquad (3)$$

where x^* is the isobutene mole fraction in the liquid in equilibrium with isobutene gas at a partial pressure of 101.3 kPa. $\Delta \bar{h}^\circ$ is the standard partial molar enthalpy of solution from an ideal gas into a diluted liquid and $\Delta \bar{s}^\circ$ is the standard partial molar entropy of solution into a hypothetical liquid solute (x = 1) (*11*, *12*). Integration of eq 2 for constant $\Delta \bar{h}^\circ$, gives

$$\ln x^* = B + A/T \qquad (4)$$

where the integration constants A and B are found by combining eq 2, 3, 4. They are

$$A = -\Delta \bar{h}^\circ/R \qquad (5)$$

$$B = \Delta \bar{s}^\circ/R \qquad (6)$$

Equation 4 is useful for correlating solubility data. Thus, a semilog plot of x^* vs. $1/T$, at constant C_A, should give a straight line whose slope and intercept provide values of $\Delta \bar{h}^\circ$ and $\Delta \bar{s}^\circ$ from eq 5 and 6, respectively. These can be further correlated with alcohol concentrations. The results are shown in Figure 3. Linear least-squares fits give correlation coefficients better than 0.98, usually about 0.99 except for C_A = 2.95 kmol/m^3 for which data are more scattered. The linear dependence of Figure 3 gives support to our prior assumption

Table II. Partial Molar Enthalpies and Entropies for Isobutene Absorption (T = 303-333 K)

C_A, kmol/m^3	$\Delta\bar{h}°$, J/mol	$\Delta\bar{s}°$, J/(mol K)
0	−19 550	−142
0.51	−16 280	−130
1.04	−13 520	−120
2.10	−7 620	−96
2.95	−3 220	−70

of constant $\Delta\bar{h}°$ over the temperature range of this study.

The values of the standard partial molar quantities calculated from A and B by linear regression are given in Table II. As seen, the absorption of isobutene is an exothermic process, consistent with the observation of a decrease of solubility with increasing temperature. Partial enthalpies and entropies are seen to increase markedly with alcohol concentrations, a fact that can be interpreted in terms of the mixing effects due to the presence of the alcohol, as follows (*13*). The partial molar enthalpy change for solution can be written as

$$\Delta\bar{h}° = \Delta\bar{h}_c + \Delta\bar{h}_{mix}$$

where $\Delta\bar{h}_c$ is the enthalpy of condensation of pure isobutene and $\Delta\bar{h}_{mix}$ is the molar enthalpy of mixing. The fact that the values of $\Delta\bar{h}°$ increase so much (see Table II) is due to an increasingly positive value of $\Delta\bar{h}_{mix}$, since $\Delta\bar{h}_c$ is approximately constant. For $\Delta\bar{h}_c$ = −20 550 J/mol given by Perry (*14*), the enthalpies of mixing would change from a very small value, +1000 J/mol in pure water, to about +17 330 J/mol, in the alcohol-rich solvent. As explained by Prausnitz (*13*), the effect of the alcohol in the mixture would be to increase the cohesive energy density of the liquid solution relative to that of the pure liquid butene. This would give increasingly positive enthalpies of mixing.

For practical applications, eq 4 is most useful for representing solubility data as a function of temperature and alcohol concentration. We found that a linear regression of A vs. C_A gives a very good fit (correlation coefficient = −0.999) while B vs. C_A could also be well-fitted by using a least-squares parabola. With these values of A and B, ln x^* vs. T and C_A represents the experimental data closely (see below).

Conclusions

In summary, isobutene solubilities in *tert*-butyl alcohol-water mixtures at 101.3 kPa partial pressure can be correlated with temperature and alcohol concentration with the following equations:

$$x^* = \exp(B + A/T) \qquad (7)$$

$$B = -16.975 + 2.101C_A + 0.259C_A^2 \qquad (8)$$

$$A = 2322 - 662.4C_A \qquad (9)$$

for $303 \leq T \leq 333$ K and $0 \leq C_A \leq 2.95$ kmol/m^3.

Molar enthalpies of absorption of isobutene into the solvent mixtures are given by

$$\Delta\bar{h}° = -8.314A \text{ J/mol}$$

where A is given by eq 9. With the above equations, estimated solubilities relative to measured values deviate ±12% on average.

Glossary

A_{ij}	exponential arguments of Wilson equation for the *tert*-butyl alcohol (1)-water (2) binary solution, J/mol
C_A	*tert*-butyl alcohol concentration in the liquid, kmol/m^3
f	isobutene fugacity in the vapor, Pa
$\Delta\bar{h}°$	standard partial molar enthalpy change of absorption, J/mol
$\Delta\bar{h}_c$	molar enthalpy of condensation of pure isobutene, J/mol
$\Delta\bar{h}_{mix}$	standard enthalpy of mixing of isobutene, J/mol
H	Henry's law constant, eq 1, Pa
p	partial pressure of isobutene, Pa
R	ideal gas law constant, R = 8.314 J/(mol K)
$\Delta\bar{s}°$	standard partial molar entropy change of absorption, J/(mol K)
T	temperature, K
x	isobutene mole fraction in the liquid
x^*	as above, in equilibrium with isobutene at a partial pressure of 101.3 kPa

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Registry No. Isobutene, 115-11-7; *tert*-butanol, 75-65-0.

Literature Cited

(1) Purlee, E. L.; Taft, R. W.; de Fazio, C. A. *J. Am. Chem. Soc.* **1955**, *77*, 837–840.
(2) McAuliffe, C. *J. Phys. Chem.* **1966**, *70*, 1267–1275.
(3) Kazanskii, V. S.; Entelis, S. G.; Chirkov, N. M. *Z. Fiz. Khim.* **1959**, 33, 1409–1413.
(4) Deckwer, W.-D. *J. Chem. Eng. Data* **1976**, *21*, 176–179.
(5) Friedrich, A.; Warnecke, H.; Langeman, H. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 401–403.
(6) O'Connell, J. P.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* **1964**, *3*, 347–351.
(7) Sada, E.; Kito, S.; Ito, Y.; *Ind. Eng. Chem. Fundam.* **1975**, *14*, 232–237.
(8) Hirâta, M.; Ohe, S.; Nagahama, K. *Computer Aided Data Book for Vapor-liquid Equilibria*; Kodansha-Elsevier: Tokyo, 1975.
(9) Gmehling, J.; Onken, V.; Arlt, W. *Vapor-liquid Equilibrium Data Collection*; DECHEMA Chemistry Series: DECHEMA: Frankfurt, 1975.
(10) Smith, J. M.; Van Ness, H. C. *Introduction to Chemical Engineering Thermodynamics*, 3rd ed.; McGraw-Hill: New York, 1975.
(11) Denbigh, K. G. *The Principles of Chemical Equilibrium*, 4th ed.; Cambridge University: Cambridge, U.K., 1981.
(12) Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1–9.
(13) Prausnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall: New York, 1969.
(14) Perry-Chilton *Chemical Engineer's Handbook*, 5th ed.; McGraw-Hill: New York, 1973.

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