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Solubility Studies of Isobutene in Tertiary Butyl Alcohol + Water Mixtures

C. M. Zhang, A. A. Adesina, and M. S. Wainwright*

School of Chemical Engineering & Industrial Chemistry, University of New South Wales,
Sydney, NSW 2052, Australia

The solubility of isobutene in water + tertiary butyl alcohol (the systematic name is 2-methyl-2-propanol) mixtures has been investigated as part of a major study of tertiary butyl alcohol synthesis from isobutene hydration using catalytic distillation. The experimental conditions covered much wider ranges of concentrations (0 to 7.9 kmol·m^{-3}) and temperatures (303 K to 353 K) than those in previous studies in order to provide a useful empirical correlation for the catalytic reactor design purposes. The data revealed that the isobutene solubility increased exponentially with tertiary butyl alcohol concentration and decreased exponentially with temperature. Excellent correlations were obtained for both isobutene solubility and the Henry's law constants for isobutene dissolving in water + tertiary butyl alcohol mixtures as a function of tertiary butyl alcohol concentration and temperature. The parameter consistency and the difference of the empirical equilibrium concentration model and the empirical Henry's law constant model are discussed.

Introduction

Tertiary butyl alcohol (TBA), the common name for 2-methyl-2-propanol, can be used as a substitute for the lead-containing additive in order to boost the octane rating of gasoline. Unlike methyl tertiary butyl ether (MTBE),[1] it is not carcinogenic, and it may, indeed, be cheaper to produce than MTBE, since water replaces methanol (as the coreactant with isobutene) in the synthesis of TBA. Even so, like MTBE production, the reaction of isobutene hydration is also equilibrium-limited,[2−4] and the product yield may be improved via simultaneous reaction with separation. The isobutene solubility in water and TBA mixtures becomes very important for the investigation of isobutene hydration via catalytic distillation.

The absorption of isobutene in water is strongly influenced by the presence of the product, TBA. This significantly affects the liquid-phase reaction kinetics and hence the distillation processes. Previous studies by Leung et al.[5] and other authors[6−8] have focused on the solubility of isobutene in the presence of low TBA concentrations (<3 kmol·m^{-3}), and so their models are limited. Absorption of isobutene in aqueous H_2SO_4 solutions has also been investigated by Gehlawat and Sharma[9] while Deckwer[10,11] provided an empirical correlation, which indicated the exponential dependency of isobutene solubility on liquid-phase TBA concentration. Many of the previous solubility studies[5−8] were carried out at relatively low TBA concentrations and temperatures where catalytic distillation is not feasible. In a catalytic distillation column, the reaction temperatures and TBA concentrations are significantly higher, and the system is more complex. For this reason, the relationship between gas-phase isobutene partial pressure and the liquid-phase isobutene concentration in highly concentrated aqueous TBA solutions is necessary in order to assess the performance of the catalytic distillation process. This study therefore investigates the solubility and the Henry's law constants for a wider range of TBA solutions and temperatures than previously reported in the literature.[5]

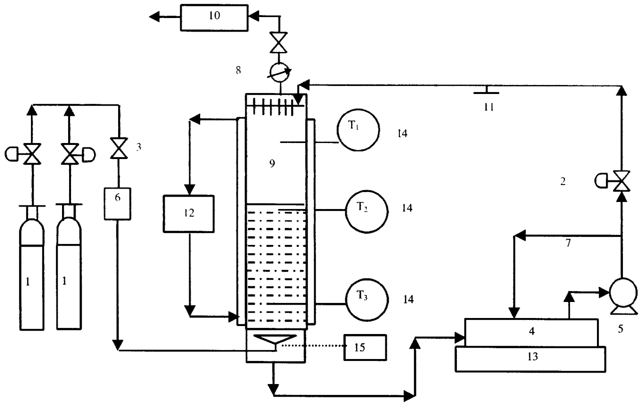

Figure 1. Apparatus for isobutene solubility measurement: 1, isobutene and nitrogen cylinders; 2, mass flow controllers; 3, valves; 4, liquid reservoir; 5, pump; 6, mixture; 7, liquid bypass; 8, condenser; 9, reactor; 10, online gas chromatograph; 11, sample port; 12, oil bath; 13, temperature controller; 14, thermocouples; 15, porous gas distributor.

Experimental Section

Materials. High-purity (>99%) isobutene was obtained from Matheson (Sydney) and used without further purification. TBA and 1-propanol were analytical research grade reagents from Aldrich while deionized Milli-Q water was used to prepare all solutions.

Apparatus. Solubility measurements were conducted in a reactor column, which was used for reaction kinetics and catalytic distillation studies and is depicted in Figure 1. The mixing vessel was a 1 L glass cylinder (inner diameter = 45 mm) fitted with a 100 μm sintered glass frit at the bottom and an outside jacket through which heated silicone oil flowed to maintain the temperature of the column

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* To whom correspondence should be addressed. Fax No.: 61-2-93858008. E-mail address: m.wainwright@unsw.edu.au.

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within ±0.5 K (95% confidence). Isobutene (or an isobutene + N_2 mixture when determining Henry's law constants) was fed upward through the porous glass plate into a column with recirculating liquid (water or water + TBA mixtures). The gas flow rate was kept at 3×10^{-6} m^3 s^{-1} using mass flow controllers to ensure smooth bubble formation (fine bubbles) and dispersion. Deckwer et al.[10,11] have indicated that the best mass transfer rates may be obtained in a bubble column with a sintered plate glass distributor. In particular, liquid recirculation through a jet at about 5×10^{-6} m^3 s^{-1} provided sufficiently low (<1) gas-to-liquid flow rate ratios to guarantee liquid saturation with isobutene. Liquid samples (1 mL aliquots) were withdrawn through a septum in the liquid recirculation line for analysis by gas chromatography to determine the concentrations of isobutene and TBA. Excess carryover of vapor in the tube was prevented using an overhead condenser (273 K) fitted to the vessel prior to venting the gas.

Henry's law constants were obtained by experiments at the total pressure 101.3 kPa and the total gas flow rate 3×10^{-6} m^3 s^{-1} by varying the ratios of isobutene and nitrogen to adjust the isobutene partial pressures. The slopes of plots of the partial pressure of isobutene in the gas phase versus the equilibrium isobutene concentration measured in the liquid phase determined the Henry's law constant.

Analysis. Liquid sample analyses for concentrations of isobutene in the liquid phase were performed on a Shimadzu gas chromatograph (model 8A) with a flame ionization detector. Separation of isobutene, TBA, and 1-propanol (the internal standard) was performed using a 3 m × 6 mm o.d. stainless steel column packed with 15% Carbowax Chromosorb-AW (80−100 mesh) operating at 383 K.

The calibration curve for determining the isobutene concentration using gas chromatography was prepared by injecting known volumes of a standard equilibrium isobutene + water mixture which was obtained by saturation at 298 K and 101.3 kPa using a calibrated liquid syringe. The curve was extended for high concentrations of isobutene by injecting pure isobutene with a calibrated gastight syringe. Repeated analyses of isobutene concentrations in the liquid phase over several samples at one operating condition confirmed the attainment of equilibrium. An internal standard curve for measuring the TBA concentrations was obtained by preparing different mole ratios of TBA to 1-propanol (the internal standard) gravimetrically.

Results and Discussion

Flow Hydrodynamics. The solubility measurements were conducted in the same tubular vessel that was used for the catalytic distillation studies and were made in a countercurrent bubble column mode. It was necessary to ensure that the liquid recirculation rate (5×10^{-6} m^3 s^{-1}) and the gas distribution through the sintered glass frit provided a suitable flow regime for the solubility measurements. The experimental measurements were conducted so that the gas flow ($u_s = 0.19$ cm s^{-1}) was continuous and well dispersed in the liquid. Furthermore, the liquid flow was in the turbulent flow regime, since the liquid Reynolds number $N_{Re,L} = 10\,600$ was more than the turbulent threshold value of 4000.

For liquid mixtures of water and TBA, there are only small changes for density and viscosity, which means the $N_{Re,L}$ is still much greater than the turbulent threshold value of 4000; therefore, the liquid flow regime was turbulent in all experimental runs.

Table 1. Solubility of Pure Isobutene in Aqueous TBA Solutions at Different Temperatures and a Total Pressure of 101.3 kPa

C_{TBA}	T	$10^{-3}C_{iB,L}$	C_{TBA}	T	$10^{-3}C_{iB,L}$
kmol·m^{-3}	K	kmol·m^{-3}	kmol·m^{-3}	K	kmol·m^{-3}
0	303	4.76	4.9	323	241
0	323	2.22	4.9	333	140
0	343	1.334	4.9	343	95
2.9	303	28.6	4.9	353	57
2.9	323	16.5	7.9	303	2220
2.9	333	10.2	7.9	323	1120
2.9	343	8.9	7.9	333	814
2.9	353	8.0	7.9	343	582
4.9	303	500	7.9	353	291

To verify that the column was operated homogeneously, the equilibrium isobutene concentrations were obtained at different positions of the tube. The liquid samples were withdrawn from several axial and radial positions when measuring the solubility of isobutene in pure water at 303 K. Repeated measurements at five separate points in the column gave a value of $(4.67 \pm 0.11) \times 10^{-3}$ kmol·m^{-3} (95% confidence) for isobutene solubility in water compared with the literature value[5] of 4.66×10^{-3} kmol·m^{-3}. This result shows that isobutene gas was well dispersed in the water + TBA liquid phase in this apparatus. The experimental results and estimated values using a literature correlation[12] confirm the adequacy of the apparatus to measure the isobutene equilibrium solubility in aqueous TBA solutions.

Equilibrium Concentrations Using Pure Isobutene Gas. Experiments to measure equilibrium isobutene concentrations in the liquid phase were carried out using pure isobutene gas with varying compositions of water + TBA mixtures at different temperatures to cover a range of conditions not previously reported in the literature[5] but relevant to the catalytic distillation process. As may be seen from Table 1, the presence of TBA enhanced the solubility of isobutene, as expected, and the solubility decreased with increasing temperature.

Since previous isobutene solubility data obtained in solutions with low TBA concentrations at less than 3 kmol·m^{-3} exhibited an exponential type dependency,[5−8] the isothermal data for isobutene solubility in this study were also fitted to an exponential model. This model covers a wide range of TBA concentrations (C_{TBA}) and may be expressed as

$$C_{iB,L}/C_{iB,L}{}^{\circ} = A \exp(-b/C_{TBA}) \qquad (1)$$

where $C_{iB,L}{}^{\circ}$ is the isobutene concentration in the liquid phase at a standard conditions (pure water, $T = 298$ K, $P = 101.3$ kPa), b is a constant with the units kmol·m^{-3}, and A is the constant at the isothermal conditions.

The data in Table 1 were fitted to eq 1, and the value of b obtained was 19.4 kmol·m^{-3}. To accommodate the temperature dependency of the solubility data, eq 1 is rewritten as

$$C_{iB,L}/C_{iB,L}{}^{\circ} = A_0 \exp(-\Delta H/RT) \exp(-b/C_{TBA}) \qquad (2)$$

where A_0 is a constant, T is the absolute temperature, and ΔH is only an apparent enthalpy for isobutene absorption from the empirical eq 2, because we have not accounted for the vapor pressures of water or TBA to correct for the actual isobutene partial pressures in the water + TBA mixtures at a total pressure of 101.3 kPa. The correction will be discussed later in the paper. Equation 2 is simply a generalized model for practical use for absorption of pure

Table 2. Henry's Law Constants for Isobutene−Water−TBA Mixtures

C_{TBA}	T	10^2H	C_{TBA}	T	10^2H
$kmol \cdot m^{-3}$	K	$kPa \cdot m^3 \cdot kmol^{-1}$	$kmol \cdot m^{-3}$	K	$kPa \cdot m^3 \cdot kmol^{-1}$
0	303	207	4.9	303	1.95
0	323	392	4.9	323	3.32
0	343	543	4.9	343	4.72
2.9	303	32.5	7.9	303	0.493
2.9	323	48.1	7.9	323	0.732
2.9	343	63.3	7.9	343	0.852

isobutene in water + TBA mixtures at atmospheric pressure for a range of temperatures. Nonlinear regression analysis of the data according to eq 2 provided $\Delta H = -35.3$ $kJ \cdot mol^{-1}$.

The increase in isobutene solubility in the presence of TBA may be explained in terms of increased polarity of the water + TBA mixture due to hydrogen bonding between water and TBA molecules. TBA, due to its relatively higher electron-donating capacity, will induce weak water dissociation, and the presence of an electron-poor hydrogen atom will facilitate greater absorption of electron-rich isobutene molecules as they arrive in solution.

Henry's Law Constants. Henry's law constants were obtained from the slope of the plot of gas-phase isobutene partial pressure (P_{iB}) versus the isobutene activity $a_{iB,L}$ in the liquid phase. The isobutene partial pressure can be obtained using eq 3:

$$P_{iB,g} = (101.3 - (P_w + P_{TBA}))/(1 + N) \qquad (3)$$

In eq 3, P_w and P_{TBA} are the water and TBA saturation pressures in the gas phase, which were calculated using standard saturation pressures and the fraction of the activities of water and TBA. The activities of water and TBA were calculated using the Wilson equation.[13] N is the flow ratio of nitrogen to isobutene.

The isobutene mole fractions in the water and TBA mixtures are in the range 10^{-2} to 10^{-4}, so the activity coefficients of isobutene in the liquid phase for all experimental runs can be assumed to be one. Therefore, the experimental value of $C_{iB,L}$ can be substituted for the activity $a_{iB,L}$ in Henry's law, eq 4:

$$H = P_{iB,g}/a_{iB,L} = P_{iB,g}/C_{iB,L} \qquad (4)$$

The equilibrium liquid-phase isobutene concentrations in the system were determined by experiments varying the N_2 to isobutene ratios in the gas phase at the same temperatures and the TBA concentrations. The isobutene partial pressures ($P_{iB,g}$) were obtained using eq 3. The Henry's law constants for different aqueous TBA mixtures and different temperatures were obtained by $P_{iB,g}$ versus $C_{iB,L}$. The values of the Henry's law constants are presented in Table 2.

The value of the Henry's law constant obtained in pure water at 303 K is 20.7×10^3 $kPa \cdot m^{-3} \cdot kmol^{-1}$ (Table 2), which is close to the published value[14] 21×10^3 $kPa \cdot m^{-3} \cdot kmol^{-1}$.

It is obvious from Table 2 that both the temperature and the aqueous-phase TBA concentration affect Henry's law constants, and indeed, they are a function of both variables. To model the nonlinear dependency of H on TBA concentration and temperature, and keep consistent with eq 2, a similar exponential model has been used to deal with the experimental data of the Henry's law constants:

$$H/H_0 = A_0{}' \exp(\Delta H'/RT) \exp(b'/C_{TBA}) \qquad (5)$$

Table 3. Ratios of Isobutene Concentration in the Liquid Phase to Isobutene Concentration in the Gas Phase at Different Temperatures and the TBA Concentrations (from Table 1) Accounting for Gas-Phase Water and TBA Concentrations Using the Wilson Equation[13]

C_{TBA}	T		C_{TBA}	T	
$kmol \cdot m^{-3}$	K	$C_{iB,L}/C_{iB,g}$	$kmol \cdot m^{-3}$	K	$C_{iB,L}/C_{iB,g}$
2.9	303	0.821	4.9	343	5.99
2.9	323	0.599	4.9	353	2.55
2.9	333	0.452	7.9	303	64.8
2.9	343	0.544	7.9	323	38.0
2.9	353	0.364	7.9	333	34.5
4.9	303	14.5	7.9	343	34.1
4.9	323	8.25	7.9	353	12.6
4.9	333	6.14			

where $\Delta H'$ is the enthalpy of isobutene absorption, H_0 is the Henry's law constant at the standard conditions (pure water, $T = 298$ K), b' is a constant with the units $kmol \cdot m^{-3}$, and A_0 is a constant.

Parameter estimation based on eq 5 and Table 2 provided $b' = 19.5$ $kmol \cdot m^{-3}$, which closely compares to the value of $b = 19.4$ $kmol \cdot m^{-3}$ obtained for pure isobutene solubility from eq 1. The enthalpy of isobutene absorption, $\Delta H' = -17$ $kJ \cdot mol^{-1}$, is close to the literature value[14] of -20 $kJ \cdot mol^{-1}$, because we have now taken into account the liquid-phase vapor pressures and nonideal mixtures of water and TBA.

Further Discussion of Equilibrium Concentrations Using Pure Isobutene Gas. Equation 2 is very useful in practical applications, such as reactor design. However, the ΔH value of -35 $kJ \cdot mol^{-1}$ in eq 2 is much greater than the value of -20 $kJ \cdot mol^{-1}$ previously reported in the literature.[14]

As was pointed out earlier, the isobutene gas-phase concentration used in eq 2 was not the actual isobutene partial pressure, because the solvent (water + TBA) vapor pressures are significant and increase with increasing temperature at the total pressure of 101.3 kPa, as discussed in reference to estimation of the Henry's law constants. To check the consistency of the temperature dependency, it is necessary to correct the isobutene partial pressures at the different temperatures and the TBA concentrations at the total pressure of 101.3 kPa. By using the actual gas-phase concentrations ($C_{iB,g}$) that have been adjusted using the Wilson equation[13] to account for the gas-phase concentrations of TBA and water, we can determine the true values of the ratio of liquid- and gas-phase isobutene concentrations ($C_{iB,L}/C_{iB,g}$) using the data from Table 1. The results shown in Table 3 were then modeled according to eq 6:

$$C_{iB,L}/C_{iB,g} = A_0{}'' \exp(-\Delta H''/RT) \exp(-b''/C_{TBA}) \qquad (6)$$

The values of b'' and $\Delta H''$ obtained from Table 3 using eq 6 are $b'' = 19.4$ $kmol \cdot m^{-3}$ and $\Delta H'' = -20.7$ $kJ \cdot mol^{-1}$, respectively. The isobutene absorption enthalpy is very close to the standard value of -20 $kJ \cdot mol^{-1}$ previously reported in the literature.[14]

We contend that the empirical eq 2 is very useful in practical engineering applications, but we recognize that the isobutene absorption enthalpy (ΔH) is only an apparent value. Equation 6 is strictly correct but is less easily used, since the partial pressure of isobutene in the gas phase must be calculated in order to account for the vapor pressure exerted by the liquid phase.

Model Validations. Figures 2−4 are plots of predicted versus measured values of $C_{iB,L}$, H, and $C_{iB,L}/C_{iB,g}$, respec-

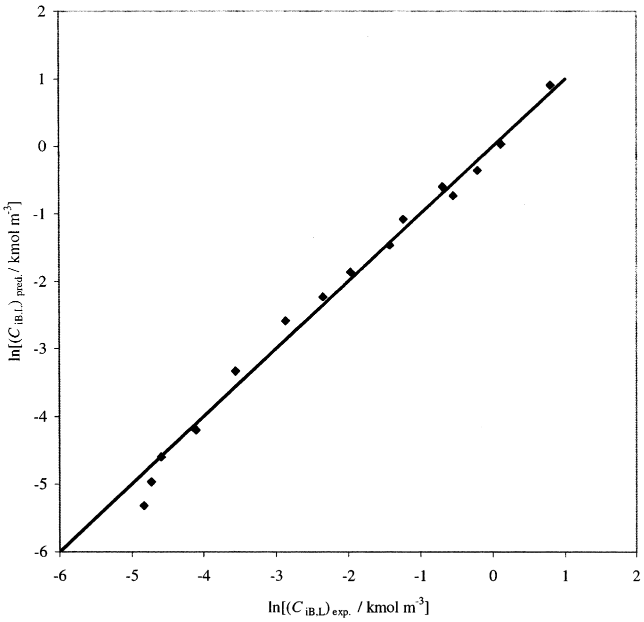

Figure 2. Comparison of the experimental and calculated values of equilibrium isobutene concentration for wider ranges of TBA concentrations and temperatures.

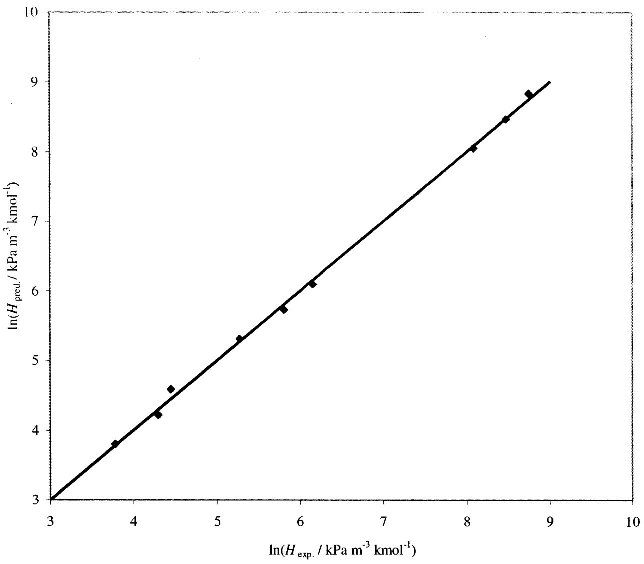

Figure 3. Comparison of the experimental and calculated values of the Henry's law constants for different water−TBA mixtures and temperatures.

tively. The plots have been made on a logarithmic basis to represent the large range of values for the wide range of experimental conditions studied. The linear regression constants (R^2 values) are all in excess of 0.98, indicating that the respective models accurately represent the data.

Conclusions

The present study has been carried out to investigate the equilibrium isobutene concentrations and the Henry's law constants over a wide range of conditions (aqueous TBA concentration and temperature) that apply in catalytic reactor studies of the hydration of isobutene.

The experimental data showed that the presence of TBA significantly increased the equilibrium isobutene concentration and that the equilibrium isobutene concentration decreased exponentially with temperature, as expected. The data were fitted to nonlinear equations to provide excellent correlations for the estimation of isobutene solubility in wider ranges of TBA concentrations and temperatures than previously reported. One equation (eq 2) is very useful in practical engineering applications, while the other (eq 6) is more strictly correct but less easily applied.

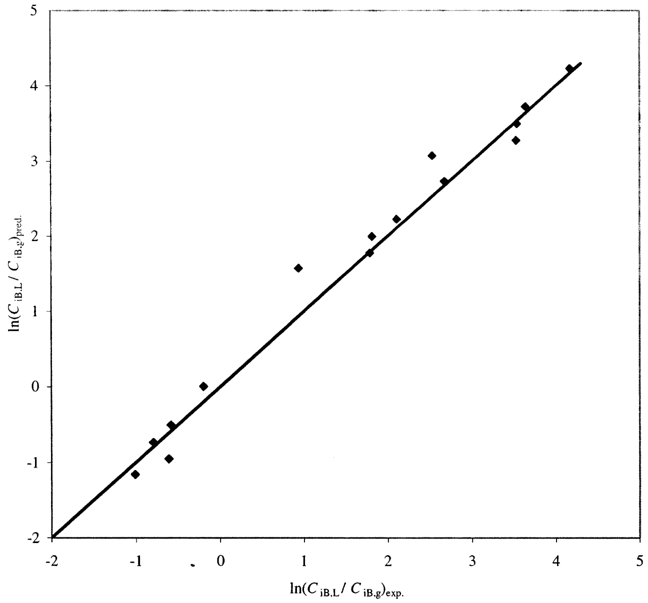

Figure 4. Comparison of the experimental and calculated values of ($C_{iB,L}/C_{iB,g}$) for different TBA mixtures and temperatures.

Henry's law constants were also determined from the experimental data, and they were shown to be comparable to those of earlier studies and cover wider ranges of experimental conditions than those previously reported.

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