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Solubility of Sulfur Dioxide in Water–Acetonitrile Solutions

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The solubilities of sulfur dioxide in water–acetonitrile solutions were determined at 25 and 50 °C and total pressure of 101.3 kPa. The solubilities are expressed in grams of sulfur dioxide dissolved/100 g of solute gas-free solution. At 25 °C two phases are observed when the overall composition lies between 20 and 80 wt % acetonitrile. The composition of each phase remains constant but the fraction of each phase is altered as the overall composition changes. Above 40 °C only one phase is observed for the entire composition range.

Introduction

The solubility of sulfur dioxide in water and other pure solvents has been investigated by many researchers; however, data on sulfur dioxide solubility in aqueous–nonaqueous solvent mixtures are very limited. Of particular interest is the system water–acetonitrile which has been proposed as a leaching and stabilizing medium in the hydrometallurgical processing of metallic minerals using sulfur dioxide (*1–3*).

In this paper, the solubility of sulfur dioxide in water–acetonitrile mixtures is examined at 25 and 50 °C over the complete composition range using both iodometric titration and chromatographic analytical techniques. A rather unexpected result was observed for the system which is the separation of two phases, a phenomenon which persisted in the range 20–80 wt % acetonitrile. An examination of the interaction of H_2O and SO_2 and CH_3CN and SO_2 using UV spectra was undertaken in an attempt to explain this phase separation.

Experimental Section

Materials. All chemicals were of reagent grade and were used directly without further purification. Acetonitrile was supplied by J. T. Baker. Sulfur dioxide (anhydrous) was obtained from Union Carbide Canada, Ltd. Aqueous solutions were made from distilled water free of carbon dioxide.

Sulfur Dioxide Solubility Experiments. The solubility of sulfur dioxide in water–acetonitrile solutions and the phase equilibria phenomena were studied in a 50-mL buret equipped with a water jacket. The circulating water was controlled to ±0.1 °C. Sulfur dioxide was bubbled at a slow flow rate approximately 60 mL-/min with the gas flow being from bottom to top of the buret. The gas exited through a spiral condenser in order to avoid excessive loss of acetonitrile. The sulfur dioxide concentration after saturation was measured by titrating excess iodine with standard thiosulfate solution using starch as the indicator. The presence of acetonitrile in the analytical solution was determined not to interfere with the titration.

Phase Separation Experiments. In cases where there was a separation of two liquid phases upon sulfur dioxide saturation, the composition of each phase was determined by a gas chromatography technique using the internal normalization method. The GC measurements were made with a Hewlett-Packard F&M Scientific 700 laboratory chromatograph. The columns were stainless tubes 0.91 m long and 0.04 cm i.d. packed with 50–80 mesh Porapak Q. The carrier gas was helium (91.5% He–8.5% H_2) flowing at the rate of 30 mL/min. The temperatures of the injection port, the column oven, and the thermal conductivity detector were maintained at 165, 135, and 175 °C, respectively. Samples were injected by using either 10- or 25-μL Hamilton microsyringes through a silicone rubber septum contained in the injection block. The sample sizes were 2 μL for the water-rich phase and 5 μL for the acetonitrile-rich phase. The identity of each component was checked by injecting pure samples and comparing the retention times. The chromatograms were recorded by using a standard millivolt recorder equipped with a disk integrator.

Spectrophotometric Experiments. In order to investigate the SO_2–CH_3CN and SO_2–H_2O interactions, we examined ultraviolet spectra of solutions of SO_2 in acetonitrile and SO_2 in water by using a Beckman DK spectrophotometer with two matched 1.0-cm cells. The wavelength region investigated was 250–300 nm. The temperature of the cells was controlled by using a thermostated cell holder. Stock solutions of SO_2 in distilled water and in pure acetonitrile (0.02–0.03 mol of SO_2/L) were prepared. The SO_2 content was verified by iodometry. From these stock solutions known solutions of SO_2–H_2O and SO_2–CH_3CN were prepared and their UV spectra measured. The range of solutions examined were as follows: SO_2–H_2O, $5 \times 10^{-4} - 1 \times 10^{-3}$ mol of SO_2/L; SO_2–CH_3CN, 3×10^{-3}-5×10^{-3} mol of SO_2/L.

Results and Discussion

Sulfur Dioxide Solubility and Phase Separation at 25 °C. The solubility of sulfur dioxide in a number of water–acetonitrile mixtures at 25 °C and the total pressure of 101.3 kPa is summarized in Table I. Investigating this system over the range of pure water to pure acetonitrile produced a somewhat unusual result. As indicated in the table when the acetonitrile content was between 20 and 80 wt %, the sulfur dioxide saturated mixture was composed of two liquid phases. The upper layer (measured density of 0.975 g/mL) was the acetonitrile-rich phase and the lower layer (measured density 1.005 g/mL) was the water-rich phase. The notable feature of these data is the fact

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Table I. Solubility of Sulfur Dioxide in Acetonitrile-Water Mixtures at 25 °C and 101.3 kPa Total Pressure

liquid components		SO_2 solubility,[b] g/100 g			phase fraction	
CH_3CN, wt %	H_2O, wt %	single phase	CH_3CN rich phase	H_2O rich phase	CH_3CN rich phase	H_2O rich phase
0	100	8.24				
5	95	8.37				
10	90	9.03				
15	85	10.0				
20	80	2 phases	[a]	[a]		
30	70	2 phases	59.4	12.4	0.25	0.74
40	60	2 phases	59.4	12.4	0.45	0.55
50	50	2 phases	59.4	12.4	0.60	0.40
60	40	2 phases	59.4	12.4	0.74	0.25
70	30	2 phases	59.4	12.4	0.87	0.13
80	20	2 phases	[a]	[a]		
90	10	73.8				
95	5	78.7				
100	0	84.6				

[a] Phase separation ill-defined leading to poor reproducibility. [b] SO_2 solubility data expressed as g of SO_2/100 g of solute gas-free solution.

Table II. Composition of Acetonitrile-Rich and Water-Rich Phases at 25 °C and 101.3 kPa Total Pressure

component	CH_3CN rich phase, wt %	H_2O rich phase, wt %
H_2O	12.9	73.0
SO_2	37.3	11.0
CH_3CN	49.8	16.0

that the sulfur dioxide solubility in each phase remains constant; however, the fraction of each phase varies as the liquid component proportions are altered. As noted in Table I the phase separation is indicated to exist in the range 20–80 wt % acetonitrile. Solubility data are not provided at these limiting compositions because the measurements were not reproducible due to a somewhat diffuse phase separation. Table II gives the composition of both phases on a weight percent basis.

The separation of two liquid phases in the acetonitrile–water–sulfur dioxide system could be considered on the basis of the formation of a charge-transfer complex between sulfur dioxide and acetonitrile. Sulfur dioxide previously has been reported to interact strongly with polar molecules (*4–6*). The UV spectrum in Figure 1 for the SO_2–CH_3CN interaction is quite similar to that observed for the 1:1 donor–acceptor complex of trimethylamine and SO_2 (*4*) whereas that of the SO_2–H_2O interaction agrees with that previously reported (*6*). The complex formed between SO_2 and CH_3CN may have a certain solubility limit in either water or acetonitrile and thus appears as a second phase.

This phase separation phenomenon appears to be rather unusual since other systems such as CH_3OH–H_2O–SO_2, CH_3OH–CH_3CN–SO_2, and C_2H_5OH–H_2O–SO_2 have shown only one liquid phase under equilibrium conditions at room temperature (*7*). It should be noted, however, that mixtures of water and a number of organic liquids form two liquid phases when subjected to high-pressure ethylene. This "salting out" effect with a supercritical gas has been reported by Elgin and Weinstock (*8*).

Sulfur Dioxide Solubility at 50 °C. The two-phase system observed at 25 °C was not observed above 40 °C. One-phase solubility data of sulfur dioxide in water–acetonitrile mixtures at 50 °C are summarized in Table III. The data indicate that the sulfur dioxide solubility is very much lower than at 25 °C. This effect seems to be reflected in the disappearance of the two-phase system observed at lower temperature since lower sulfur dioxide content could be interpreted as lower concentration of the charge-transfer complex. Figure 1 does, however, indicate that an interaction is still present at 50 °C.

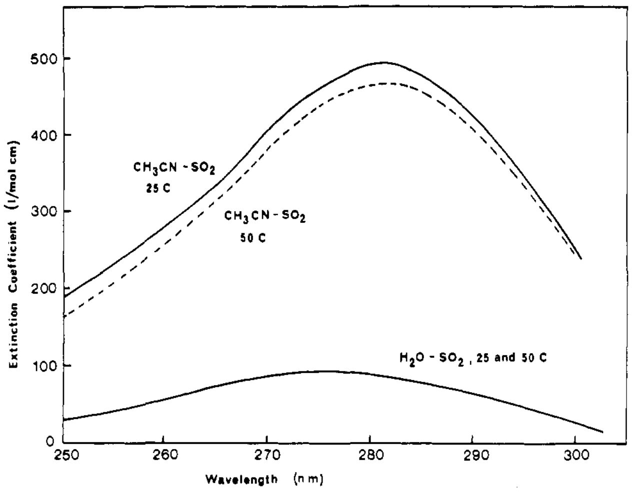

Figure 1. UV spectra of acetonitrile–sulfur dioxide and water–sulfur dioxide mixtures at 25 and 50 °C.

Table III Solubility of Sulfur Dioxide in Acetonitrile-Water Mixtures at 50 °C and 101.3 kPa Total Pressure

CH_3CN, wt %	H_2O, wt %	SO_2 solubility, g/100 g
0	100	3.77
10	90	3.95
20	80	5.08
30	70	6.85
40	60	8.33
50	50	11.09
60	40	13.75
70	30	15.60
80	20	18.67
90	10	23.10
100	0	25.64

Comparison of observed solubility values with those recorded in the literature can only be done for water–sulfur dioxide solutions since solubility data for sulfur dioxide in acetonitrile or water–acetonitrile do not appear to be available. Sulfur dioxide solubility in water has been investigated repeatedly under various conditions with various techniques. A comprehensive evaluation of the values reported has been provided by Plummer (*9*). At 25 °C the most reliable solubility of sulfur dioxide in water at 101.3 kPa partial pressure ranges from 8.9 to 9.1 g of SO_2/100 g of solute gas-free solution (*5, 7, 10*) compared to our observed value of 8.5 g of SO_2/100 g of solute gas-free solution (adjusted to 101.3 kPa partial pressure of SO_2). At 50 °C the accepted sulfur dioxide solubility ranges from 4.3 to 4.5 g of SO_2/100 g of solute gas-free solution (*5, 10*) compared to our observed value of 4.3 g of SO_2/100 g of solute gas-free solution (adjusted to 101.3 kPa partial pressure of SO_2).

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