Summary

The accuracy of a new Tronac isothermal titration calorimeter with an open reaction vessel has been verified for nonvolatile systems by duplicating the accepted value for the ionization of water within 0.38%. Despite an attempt to develop a process model which would accurately correct for the effect of the vapor space in the reaction vessel, the results for the cyclohexane-*n*-hexane system at 25°C were about 2.7% below the accepted midpoint value (52.9 cal mol^{-1}) for this standard system. For the benzene-cyclohexane system at 35°C, the error owing to the vapor space amounted to less than 1% in the measured midpoint value of 187 cal mol^{-1}.

New H^E data for the three xylene-xylene binaries at 25°C closely reproduced the values reported previously by Lam et al. (*2*). Other new data for the three ethylbenzene-xylene binaries at 25°C and for two ethylbenzene-xylene binaries at 70°C are presented. Because of the low volatility of these systems, these data are believed to be quite accurate despite the presence of the vapor space in the reaction vessel.

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Received for review April 9, 1973. Accepted November 28, 1973.

Vapor-Liquid Equilibrium Data for System Tri-*n*-butyl Phosphate and Sulfur Dioxide

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Equilibrium concentrations of sulfur dioxide over solutions in tri-*n*-butyl phosphate were measured in the vapor concentration range of 10–650 mm Hg and a temperature range of 6–70°C. The data were correlated by using a Henry's law model for the vapor-liquid equilibrium and postulating a one-to-one complex in the liquid phase. Spectroscopic evidence of an atomic interaction of the sulfur dioxide and phosphoryl oxygen of the phosphate is presented. The resulting equations correlated the observed data with an average error of under 3%, indicating that this model was useful for interpolation of the data within the experimental range. These equations were used to construct a table of equilibrium data over the range of variables investigated and to compare sulfur dioxide partial pressures over TBP to those over water.

The recent increase in public awareness of ecological problems resulting from man-made wastes being inadequately treated before their return to the environment has placed an increased pressure on industry to limit its output of possible pollutants. In the area of air pollution the major pollutant in many industries is sulfur dioxide. One common method for the removal of sulfur dioxide is absorption. Unfortunately, sulfur dioxide has a low solubility in most inexpensive absorbants, and most solvents in which sulfur dioxide is reasonably soluble are either expensive or difficult to work with.

Tri-*n*-butyl phosphate (TBP) is a nontoxic, noncorrosive chemical commercially available in large quantities at moderate cost. It has a high boiling point, (289°C) and at moderate temperatures the vapor pressure is relatively low (about 0.1 mm Hg at 60°C). Many researchers have suggested the use of TBP as an absorbant for sulfur-containing gases such as hydrogen sulfide and sulfur dioxide (*3, 4, 6–8*). To help evaluate TBP as an absorbant for sulfur dioxide, a program to measure the vapor-liquid phase equilibrium of this system was undertaken.

This paper reports phase equilibrium data for the TBP–sulfur dioxide system over the range 6–70°C and for partial vapor pressures of sulfur dioxide from 10 to 650 mm Hg. A model that assumes a one-to-one complex of the TBP and sulfur dioxide is used to correlate this data, and infrared spectroscopic evidence of an interaction of the sulfur dioxide with the phosphoryl oxygen of the TBP will be presented. This model was used to calculate equilibrium data over the range studied and has been compared with similar data for the system sulfur dioxide–water (*12*).

Experimental

The TBP used in this study was BDH reagent grade and by standard Karl Fischer analysis, it contained 0.099 wt % water. The sulfur dioxide was obtained from Matheson of Canada Ltd., and was 99.9% pure.

The phases were equilibrated in a cylindrical flask (volume 125 cc) constructed of glass. The volume of liquid was usually about 25 cc. This flask was constructed so that sulfur dioxide could be added through a sparger, and gas sampling could be done with the flask completely immersed in the water bath. During equilibration the flask was open to the atmosphere through a fine capillary tube about 10 cm long with a bulb (volume about 2 cc) near the lower end. Experiments were done at an atmospheric pressure of 757 mm Hg (±3 mm Hg). The experimental procedure was as follows:

A known weight of TBP was placed in the flask, and the flask closed and placed in a water bath (±0.1°C). After thermal equilibration the flask was dried and weighed at a fixed time after removal from the bath. All later weighings were done by using this procedure. The

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flask was placed in the bath, and an appropriate amount of sulfur dioxide was added through the sparger. The gas sparger was purged with air, sealed with a short piece of tubing, and the system left to equilibrate for 2–12 hr.

After this time a 1-ml sample of the gas was taken with a gas-tight syringe; this sample was injected into a Carle Model 7004 gas chromatograph which used a thermistor detector. The column was a 6-ft long stainless-steel column, ⅛ in. in diameter packed with Poropak Q (50–80 mesh) run at 100°C. Helium was used as the carrier gas at a flow rate of 17.4 cc/min. The output was recorded on a millivolt recorder, and areas were measured with a planimeter. The flask was removed from the water bath, dried, and weighed. The weight of sulfur dioxide in the liquid phase was then calculated by difference after applying suitable corrections for temperature and weight of sulfur dioxide in the vapor phase.

Repeated vapor composition measurements for the same liquid composition taken over a period of 12 hr showed no significant change (i.e., the slope of a linear regression performed on vapor composition vs. time was not significantly different from 0). These measurements suggested an error of less than 2% in vapor composition measurement. Repeated weighings by using the procedure outlined above showed a variation of under 0.002 gram. Preliminary experiments with freshly distilled TBP in a nitrogen and sulfur dioxide atmosphere did not give results significantly different than those in air.

The spectroscopic work was done on a Beckman IR-9 spectrophotometer with NaCl cells nominally 0.025 mm thick. The solvents used were spectroscopic grade *n*-hexane and carbon tetrachloride obtained from Fisher Scientific Co.

Results and Discussion

The experimental results for the sulfur dioxide–TBP system are presented in Table I.

To correlate the data, it was assumed that Henry's law related the partial pressure of sulfur dioxide in the vapor phase to the mole fraction of sulfur dioxide in the liquid phase. Thus,

$$P_{SO_2} = Hx_{SO_2} \qquad (1)$$

In the liquid phase, the association equilibrium

$$TBP + SO_2 \rightleftharpoons TBP{\cdot}SO_2$$

was assumed. For this equilibrium, we can write:

$$K' = \frac{x_{TBP\cdot SO_2}}{x_{TBP}x_{SO_2}} \; \frac{\gamma_{TBP}}{\gamma_{TBP}\gamma_{SO_2}} \qquad (2)$$

By assuming the ratio of activity coefficients constant,

$$K = \frac{x_{TBP\cdot SO_2}}{x_{TBP}x_{SO_2}} \qquad (3)$$

the liquid phase could be considered "ideal." By use of Equation 1 and the method suggested by Prausnitz (11) for solutions with complex formation, this model was fitted to the observed data. (The one-parameter model suggested by Prausnitz did not adequately describe the data, the best fit having a root mean square error of over 15%.) The variation of *H* and *K* with temperature is given by the equations:

$$\ln(H) = -3218.0/T \quad +18.382 \qquad (4)$$

$$\ln(K) = 944.4/T \quad -0.733 \qquad (5)$$

This model predicted the observed vapor-liquid equilibrium data with an average error of 2.8% and a root mean square error of 3.5%. The close fit of the experimental data by this model does not confirm it, and there is reason to suppose that the TBP dimerizes (10) and that the ester oxygens as well as the phosphoryl oxygen can form addition compounds with the sulfur dioxide (1). Hence, the model serves mainly as a convenience for correlation.

Table I. Experimental Values of Partial Vapor Pressure of Sulfur Dioxide over Tri-*n*-butyl Phosphate Solutions

Temp, °C	Total g SO_2/100 g TBP	SO_2 partial press, mm Hg	Temp, °C	Total g SO_2/100 g TBP	SO_2 partial press, mm Hg
6.0	2.39	6.9	54.1	0.62	13.6
	2.91	8.7		1.06	23.7
	3.89	12.4		1.55	37.2
	5.84	19.3		2.22	54.4
	8.07	30.4		2.85	69.6
	10.45	43.7		4.27	115.
	13.15	64.0		4.29	115.
	14.26	72.8		4.86	139.
	17.31	105.		6.11	176.
	21.56	162.		7.33	226.
	25.38	219.		9.95	320.
	31.16	299.		11.60	405.
	37.71	394.		11.92	429.
	42.56	492.		12.20	449.
				13.20	480.
17.0	6.08	33.8		13.67	511.
	7.30	44.9		14.58	590.
	8.71	57.8		16.10	677.
	10.16	73.9			
	11.92	94.6	69.5	0.56	21.7
	14.58	130.		1.37	58.7
	17.64	179.		3.15	142.
	22.03	267.		4.49	200.
	26.63	362.		5.48	262.
	32.79	534.		6.30	331.
	38.09	661.		7.10	365.
				8.50	430.
33.8	0.73	7.4		10.28	587.
	1.06	11.0		11.48	663.
	1.67	17.6			
	2.88	31.6			
	3.45	38.8			
	3.88	44.4			
	4.67	55.1			
	5.75	70.8			
	7.85	105.			
	11.31	177.			
	14.78	269.			
	16.55	326.			
	20.09	458.			
	20.78	486.			
	22.79	570.			

Table II contains calculated values of equilibrium data over the experimental range and compares some of these values to similar fitted data reported by Rabe and Harris for the sulfur dioxide–water system (12). As is apparent, the partial pressure over TBP for a given weight fraction sulfur dioxide and temperature is about an order of magnitude lower than that for water.

In an effort to confirm the presence of the TBP–SO_2 complex, several samples of TBP, sulfur dioxide, and TBP with sulfur dioxide in different concentrations were scanned on a Beckman IR-9 infrared spectrophotometer with spectroscopic *n*-hexane and carbon tetrachloride as solvents. The results were similar in both solvents. The region of prime interest was 900–1500 cm^{-1}. Figure 1 presents some typical spectra which include a small sec-

Table II. Calculated Values of Partial Pressure of SO_2 over TBP Solutions and Selected Data for Water-SO_2 (*12*), mm Hg

Total g SO_2/100 g TBP	Temp, °C										
	10		15	20	30		40	50	60		70
	TBP	H_2O	TBP	TBP	TBP	H_2O	TBP	TBP	TBP	H_2O	TBP
0.5	...	17.0	...	...	...	37.1	...	...	14.1	96.8	20.2
1.0	...	39.5	...	...	...	83.7	13.2	19.7	28.8	212.	41.0
1.5	...	63.6	...	...	13.1	132.	20.2	30.1	43.9	331.	62.5
2.0	...	88.5	...	11.3	17.8	183.	27.4	40.8	59.5	453.	84.7
2.5	...	114.	11.3	14.4	22.7	234.	34.8	52.0	75.6	576.	108.
3.0	10.7	139.	13.8	17.6	27.7	285.	42.5	63.5	92.3	700.	131.
4.0	14.9	192.	19.1	24.3	38.4	389.	58.9	87.7	128.	...	181.
5.0	19.4	245.	24.9	31.7	49.9	496.	76.4	114.	165.	...	234.
6.0	24.3	299.	31.2	39.6	62.4	602.	95.3	142.	206.	...	291.
7.0	29.6	353.	38.0	48.2	75.8	710.	116.	172.	249.	...	352.
8.0	35.4	407.	45.3	57.5	90.3	818.	138.	204.	295.	...	417.
9.0	41.7	462.	53.4	67.7	106.	...	161.	239.	345.	...	487.
10.0	48.6	517.	62.1	78.7	123.	...	187.	276.	398.	...	561.
12.0	64.4	628.	82.1	104.	162.	...	244.	359.	516.	...	...
14.0	83.2	740.	106.	133.	207.	...	311.	455.	650.	...	...
16.0	106.	852.	134.	168.	259.	...	386.	562.	...	...	...
18.0	132.	...	166.	208.	318.	...	472.	...	...	...	...
20.0	162.	...	203.	253.	384.	...	566.	...	...	...	...
22.0	195.	...	244.	303.	455.	...	...	...	...	...	...
24.0	231.	...	288.	355.	530.	...	...	...	...	...	...
26.0	268.	...	333.	409.	606.	...	...	...	...	...	...
30.0	342.	...	421.	516.	...	...	...	...	...	...	...
33.0	394.	...	484.	500.	...	...	...	...	...	...	...
36.0	441.	...	541.	...	...	...	...	...	...	...	...
40.0	498.	...	609.	...	...	...	...	...	...	...	...
45.0	558.	...	...	...	...	...	...	...	...	...	...
50.0	608.	...	...	...	...	...	...	...	...	...	...

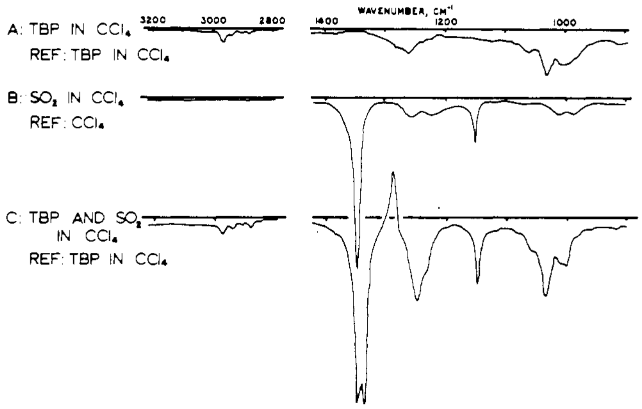

Figure 1. Ir spectra of TBP and SO_2 solutions

tion between 2800 and 3200 cm^{-1}. This region includes the CH_2 and CH_3 stretch frequencies for the *n*-butyl groups on the ester, hence, its intensity is indicative of how well the TBP concentrations were matched. Since the two cells used were of a slightly different thickness, it was not possible to match both concentrations of TBP and solvent; thus, in regions where both absorb moderately strongly (around 1275 cm^{-1} and particularly around 1000 cm^{-1}), only rough qualitative conclusions could be obtained. The concentration of TBP for these spectra was about 8% by volume.

The doublet band at 1340 cm^{-1} was due to the asymmetric stretch of the sulfur dioxide. Without TBP present, a narrow band at 1345 cm^{-1} was obtained, whereas in the presence of TBP, the second peak at 1335 cm^{-1} was found. As the concentration of sulfur dioxide was increased, the peak at 1345 cm^{-1} increased more rapidly than that at 1335 cm^{-1}, which was what would be expected by the postulated model since the relative ratio of complexed sulfur dioxide to free sulfur dioxide decreases with increasing sulfur concentration.

The region between 1200 and 1300 cm^{-1} is the region of the $P = 0$ stretch. This was normally a doublet with maxima occurring at 1268 and 1285 cm^{-1}. It has been suggested (*5*, *10*) that these are due to two rotational isomers of monomeric TBP and a weak band owing to a dimer. As sulfur dioxide was added, the band at 1285 cm^{-1} decreased in intensity, and a new band appeared at 1246 cm^{-1} which increased in intensity. The band at 1268 cm^{-1} seemed unaffected. It is likely that this is the result of the 1285 and 1268 cm^{-1} bands shifting by about 20 cm^{-1}. The 1285 band would shift to 1265 cm^{-1}, thus replacing the 1268 cm^{-1} band which would shift to 1246 cm^{-1}. This shift would be comparable to the shift of 16 cm^{-1} found for the TBP water system by Alcock et al. (*2*) and Miles (*9*).

The symmetric stretch for free sulfur dioxide was found at 1148 cm^{-1}. This did not seem to be affected by the presence of TBP; however, if it had shifted 80 cm^{-1} or more in either direction it would likely be obscured by the $P = 0$ stretch at 1236 cm^{-1} or the $P—O—C$ stretch between 970 and 1070 cm^{-1}. The $P—O—C$ stretch displayed anomalous behavior as suggested in Figure 1, A and C. The bands at 2800-3000 cm^{-1} indicate that the TBP concentrations were matched quite well for these two spectra, but there was a distinct change in the intensity (and a slight change in the position 1030-1035 cm^{-1}) of the predominant maximum in this region. Interpretation of this region was further complicated by a medium strength absorption band for the CCl_4 between 960 and 1030 cm^{-1}. The general appearance of this band does seem to imply that its probable cause is a change in the $P—0—C$ stretch frequencies. This would be in contrast to the findings of Miles (*9*) who found this band unaffected by inorganic acids and water in TBP.

If the sulfur dioxide were bonded at the sulfur atom, then it would be expected that the asymmetric stretch would show a larger shift than the symmetric stretch which appears to be the case here. On this basis, it seems reasonable to conclude that there is an interaction between the phosphoryl oxygen on the TBP and the sulfur atom of the sulfur dioxide.

Conclusions

Equations 1 and 3-5 give a good fit for measured vapor-liquid equilibrium data over the range 6-70°C and vapor compositions from 10 to 650 mm Hg in SO_2. Although this model was semiempirical, it was a convenient method of correlating the experimental data. Spectroscopic evidence of an interaction of the sulfur atom of the sulfur dioxide and the phosphoryl oxygen of the TBP was also presented.

Acknowledgment

We are grateful to F. Frantisak (Peabody Engineering Co., Toronto, Canada) for his help in this work.

Nomenclature

H = Henry's law constant, mm Hg
K, K' = liquid-phase equilibrium constants
P = pressure, mm Hg
T = temperature, K
x = liquid-phase mole fraction
γ = liquid-phase activity coefficient

Subscript

i = refers to component i in mixture

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Received for review April 13, 1973. Accepted December 26, 1973. This study was financed by the National Research Council of Canada.

Diffusion Coefficients of *n*-Heptane and *n*-Decane in *n*-Alkanes and *n*-Alcohols at Several Temperatures

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The diffusion coefficients of the solutes *n*-heptane and *n*-decane were measured in the series of alkane solvents *n*-hexane through *n*-decane and in the alcohol solvents *n*-hexanol and *n*-heptanol. Mutual and self diffusivities in most cases were measured at the temperatures of 20°, 25°, 30°, and 40°C. Concentrations of the diffusion species were in the infinitely dilute region. An unsteady-state porous frit technique was used with carbon-14 tagged diffusion species. The diffusion coefficients measured were compared with various liquid diffusivity prediction correlations.

The diffusion coefficients of the solutes *n*-heptane and *n*-decane were measured in the series of alkane solvents *n*-hexane through *n*-decane and in the alcohol solvents *n*-hexanol and *n*-heptanol. Diffusivities in most cases were measured at the temperatures of 20°, 25°, 30°, and 40°C. Concentrations of the diffusion species were in the infinitely dilute region.

The diffusion coefficients measured in this work add new information to the existing literature data for normal alkane diffusivities which in large part have been obtained by Bidlack et al. (*1*), Douglass and McCall (*2*), and McCall et al. (*11*). The diffusion of *n*-alkanes in the normal alcohols hexanol and heptanol, also studied in this work, makes it possible to study the effects of solvent hydrogen bonding. Regularities in these homologous series permit data extension correlations to be proposed. The measured diffusion coefficients are also useful in examining some of the existing liquid diffusivity prediction correlations.

An unsteady-state porous frit technique developed in this laboratory was used to measure the diffusion coefficients. A detailed discussion of this method is given elsewhere (*12*). In this technique, the unsteady-state buildup of a diffusing tagged species from a nonglazed porcelain frit into a thermostated pure solvent bath is monitored. The diffusion coefficient is obtained by a least-squares curve fit of the experimental solvent bath solute concentration vs. time profile to the analytic expression describing this process.

Model of Diffusion in Frit

The unsteady-state porous frit method employs the diffusion of a tagged or otherwise analytically identifiable species from the confines of an enclosed volume, the frit, into a surrounding homogeneous volume, the stirred sol-

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