Table IV
Excess Volume of Mixing Data for the System Ethyl Acetate (1)-Ethanol (2)-2-Ethoxyethanol (3)

mole fraction			V^E mL/mol
ethyl acetate	ethanol	2-ethoxyethanol	exptl
0.7000	0.1000	0.2000	0.1495
0.2998	0.5002	0.2000	0.0076
0.1000	0.7000	0.2000	0.1096
0.4893	0.3150	0.1957	0.1349
0.5000	0.0999	0.4001	0.1311
0.4000	0.1999	0.4001	0.0887
0.2936	0.3148	0.3961	0.0164
0.2193	0.3880	0.3927	0.0252
0.3000	0.0999	0.6001	0.0058
0.2999	0.1999	0.6001	−0.0668
0.0979	0.3148	0.5873	−0.1621
0.3000	0.0999	0.6001	−0.0058
0.1000	0.0999	0.8001	−0.1224
0.1499	0.0501	0.8000	−0.0344
0.2000	0.0500	0.7500	−0.0618
0.0500	0.1000	0.8500	−0.0930
RMSD			0.0003

Values of Constants in Equation 5

$A_{12} = 3.6500$	$A_{13} = 0.4300$	$A_{23} = -1.0900$
$B_{12} = 0.3629$	$B_{13} = -0.6250$	$B_{23} = -0.3620$
$C_{12} = 0.5880$	$C_{13} = 0.1906$	$C_{23} = -0.1330$
	$C^* = -2.9230$	

Excess volume of mixing at 40 °C was calculated from density data. This is given in Table IV. These data are correlated by eq 5. The values of binary and ternary constants are also given

$$V_{123}^E = x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_1x_3[A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2] + x_2x_3[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] + C^*x_1x_2x_3 \quad (5)$$

in Table IV. The least-squares method was applied for calculating the binary and ternary constants.

Glossary

A, B, C	binary constants in eq 1 and 5
C^*	ternary constant
G^E	excess free energy of mixing, cal/mol
G_{123}^E	ternary excess free energy of mixing, cal/mol
H^E	heats of mixing, cal/mol
H_{123}^E	ternary heats of mixing, cal/mol
M	molecular weight
P	system pressure
R	gas constant
RMSD	root mean square deviation, $= [\sum(\nu_{\text{exptl}} - \nu_{\text{calcd}})^2/N]^{1/2}$
N	number of data points
T	absolute temperature, K
V_{123}^E	ternary molar excess volume, mL/mol
x	mole fraction

Greek Letters

ν	kinematic viscosity, cm^2/s
ν_{12}, ν_{23}, ν_{31}	binary constants in eq 2
ν_{123}	ternary constant in eq 2
ν_{mix}	kinematic viscosity of mixture, cm^2/s

Subscripts

1, 2, 3	components one, two, and three
exptl	experimental
calcd	calculated
lit.	literature

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Received for review February 2, 1977. Resubmitted May 4, 1978. Accepted February 18, 1979.

Isothermal Vapor–Liquid Equilibria of Allyl Alcohol–Toluene at 90 °C

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Isothermal vapor–liquid equilibria of allyl alcohol–toluene are presented at 90 °C. The system showed positive deviations from Raoult's law and formed an azeotrope at 720 mmHg total pressure with the composition of allyl alcohol at 64 mol %. The system formed a symmetric solution. The activity coefficient data were correlated by the single-parameter Margules equation log $\gamma_i = 0.65(1 - X_i)^2$.

Anhydrous allyl alcohol is obtained by the azeotropic distillation of the constant boiling mixture of allyl alcohol and water. Allyl alcohol and water are formed as reaction products in the manufacture of the former either from allyl chloride by hydrolysis or from acrolein by oxidation. In an attempt to select a suitable entrainer for the azeotropic distillation, toluene was studied for its suitability as a possible entrainer. Earlier the vapor–liquid equilibrium data of allyl alcohol–toluene at 760 mmHg pressure was reported (*1*, *5*). In this work the isothermal vapor–liquid equilibrium data at 90 °C was determined.

Experimental Section

Chemicals. Toluene of analytical grade supplied by B.D.H. (India), Ltd., was further purified in a laboratory distillation column and the fraction boiling at 110.6 °C was collected and used.

Analytical grade allyl alcohol supplied by B.D.H. (India), Ltd., was distilled in a laboratory packed distillation column and the

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Table I

Physical Properties

		bp, °C		refractive index at 30 °C		
no.	component	lit.[a]	exptl.	lit.[a]	exptl	mol wt
1	allyl alcohol	97.08	97.1	1.4090	1.4090	58.078
2	toluene	110.6	110.6	1.4912	1.4912	92.134

Vapor Pressure Equations[b]

no.	component	equation	vapor pressure at 90 °C, mmHg
1	allyl alcohol	$\log p = 32.6258 - 3451.8/T - 7.94975 \log T$	586.94
2	toluene	$\log p = 6.95334 - 1343.943/(t + 219.377)$	406.73

[a] Reference 8. [b] Reference 3.

Table II. Isothermal Vapor-Liquid Equilibrium Data for the System Allyl Alcohol (1)-Toluene (2) at 90 °C

π, mmHg	x_1	y_1	γ_1	γ_2
407	0.000	0.000	4.45 ± 0.05	1.000
487	0.048	0.195	3.374	1.012
541	0.072	0.292	3.743	1.015
559	0.082	0.345	4.013	0.981
582	0.099	0.364	3.651	1.010
621	0.136	0.416	3.241	1.032
635	0.182	0.455	2.709	1.040
667	0.212	0.465	2.496	1.113
669	0.273	0.503	2.103	1.125
715	0.535	0.592	1.350	1.543
716	0.731	0.687	1.149	2.050
701	0.842	0.763	1.083	2.584
686	0.871	0.823	1.105	2.313
586	1.000	1.000	1.000	4.0 ± 0.5

fraction boiling at 97.1 °C was collected and used.

Equilibrium Still. A vapor recirculatory type still of Jones et al. as modified by Ward (*7*) was used to measure the vapor-liquid equilibrium data at 90 °C. The construction and working of the still were described elsewhere (*6*). The necessary vacuum in the still was maintained with the help of a vacuum pump and regulating the pressure with controlled leak of dry air through a $^1/_8$-in. needle valve.

Analysis. The composition of the equilibrium samples was determined by refractive index. Refractive index measurements were taken at 30 ± 0.1 °C for sodium light with an Abbé precision refractometer capable of reading up to 0.0005. Water from a constant-temperature bath maintained at 30 °C was circulated through the prism of the refractometer. The compositions in mole percent were determined from a standard plot of refractive index vs. composition prepared earlier by using mixtures of known composition. The reproducibility of the results in terms of mole percent was 0.6%.

Results and Discussion

The physical properties of chemicals used along with the vapor pressure equations are given in Table I.

The equilibrium data along with the activity coefficient data are presented in Table II.

The liquid-phase activity coefficient of each component was calculated from the expression

$$\gamma_i = \pi y_i / P^\circ_i x_i$$

The vapor pressure nonideality was not considered, as the total pressure of the system was below atmospheric where ideal behavior for the vapor phase can be assumed (*2*).

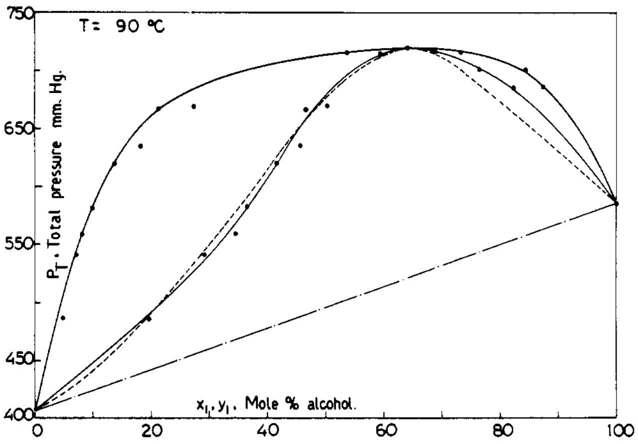

Figure 1. π-x,y diagram: (O) bubble point, (●) dew point, (---) calculated y_1.

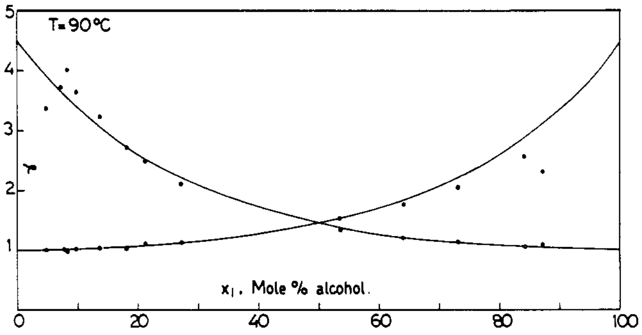

Figure 2. Activity coefficient composition diagram: (O) γ_1 (exptl), (●) γ_2 (exptl), (—) calculated values.

π-x,y plots and the activity coefficient vs. composition diagram are shown in Figures 1 and 2. From the activity coefficient data it could be seen that the system allyl alcohol-toluene showed considerable order of nonideality and showed positive deviations from Raoult's law. The isothermal activity coefficient data of the system were satisfactorily correlated with the single-parameter Margules equations, thus

$$\log \gamma_1 = 0.65 X_2^2$$

$$\log \gamma_2 = 0.65 X_1^2$$

This correlation shows that the system under study formed a symmetric solution. Absolute deviation in y_1 calculated from the Margules equation was 5.6%. This system formed an azeotrope at 720 mmHg total pressure, the composition of allyl alcohol being 64 mol %.

The data were tested for thermodynamic consistency by the Redlich-Kister (*4*) method. At low toluene concentrations the data were not consistent. The deviation in area test was about 10% vs. the less than 2% criterion. However, the data are quite useful.

Glossary

P°	vapor pressure of the pure component, in mmHg
t	temperature, °C
T	absolute temperature, K
x	liquid-phase composition, mole fraction
y	vapor-phase composition, mole fraction

Greek

π	total pressure in mmHg
γ	activity coefficient

Subscripts

i	any component
1	more volatile component

2 less volatile component

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Received for review July 5, 1978. Accepted July 5, 1979.

Solubility of Sulfur Dioxide in Distilled Water and Decarbonated Sea Water

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The solubility of sulfur dioxide in distilled water and decarbonated sea water (salinity 0–40‰) has been measured at a pressure of 1 atm of SO_2 at pH 0.8 over the temperature range 5.8–30 °C. The measurements were made by saturating water with the gas and then analyzing an aliquot of the solution by treating it with hydrogen peroxide and titrating the resultant sulfuric acid with standard sodium hydroxide solution. Values found for the solubility in distilled water agree well with recent published data. The solubility of the gas in sea water decreases slightly with increasing salinity.

Introduction

Suggestions have been made that sulfur dioxide from power plant flue gases could be used for scale prevention and deoxygenation in sea water desaturation plants (*1–3*). In the design of sulfur dioxide absorbers for this purpose it is necessary to have data for the solubility of the gas in sea water. Although many rather discordant values are available for the solubility in pure water (*4–9*) and a few data have been published for aqueous salt solution (*8*, *10*) only one study has been made of the solubility in sea water (*11*). The few data which this study provides are, according to its author, of questionable accuracy—±15%, at best. For this reason it was thought worthwhile to make fresh measurements of the solubility of the gas, covering a wider range of salinities and temperatures. For this purpose a modification of a technique which had been previously used with hydrogen sulfide (*12*) was employed. In this, the acidified sample was sparged with nitrogen to remove oxygen and carbon dioxide. It was then saturated by stirring in a current of sulfur dioxide. Aliquots of the saturated sample were analyzed by allowing them to react with hydrogen peroxide and titrating the resultant sulfuric acid with carbonate-free standard sodium hydroxide. Because there was a tendency to supersaturation at low temperatures, the final equilibration was carried out by stirring the sample very gently for 5 h in a static atmosphere of the gas. The pH values of the saturated solutions were ~0.8.

Experimental Section

Measurement of Physical Parameters and Salinity. Equilibration temperatures were measured by means of mercury in glass thermometers reading to 0.01 °C which had been calibrated by means of a Dymec quartz thermometer that itself had been standardized against a triple point cell. Barometric pressures were measured by using an NPL certified Kew pattern barometer; brass scale corrections were applied.

A Hytech inductive salinometer was used for the measurement of the salinities of samples prior to acidification. Conductivity ratios relative to standard sea water were converted to salinities (g kg^{-1}) by means of the UNESCO conductivity–salinity tables (*13*).

Sulfur Dioxide. The sulfur dioxide used in the present work was of "refrigeration grade" and was supplied by BDH Chemicals Ltd. in 500-g cannisters. Mass spectrometric analysis of the gas showed its purity to exceed the 99.9% specified by the manufacturer.

Sea Water. Surface water (S = ~33‰) from the Irish Sea was filtered through a 0.45-μm filter. Samples of water (10 L) having salinities in the range 10–40‰ were prepared from it by evaporation or dilution with distilled water as appropriate. Acidification to pH 2.8 was carried out by treating 5-L aliquots of the water with 4 mL of 5 M sulfuric acid. After acidification the samples were stored in closely stopped borosilicate glass bottles.

Apparatus. Because supersaturation of sulfur dioxide occurred with ease and because we wished to measure the specific gravity of the saturated solution, it was necessary to modify the saturation vessel which we had used for measurement of the solubility of hydrogen sulfide (*12*). The modified vessel A is shown in Figure 1. It consisted of a water-jacketed glass tube, 40 cm in length and an internal diameter of 5.2 cm. There was a gap of ~2 mm between the inner and outer walls at the bottom to facilitate the use of a magnetic stirrer. At the upper end of the tube were sealed a B24 and a B29 socket and two screwed cap connectors. One of the latter served as a thermometer port, and through the other passed a 9-mm o.d. tube connected to an open ended mercury manometer (R) and a mercury pressure regulator (P). The B29 socket was used to admit a hydrometer which was held upright by a narrow glass tube sealed through the standard cone. The B24 socket was fitted with a cone having sealed through it a gas inlet tube (T) reaching to within 3 cm of the bottom of the saturation vessel. An S13 ball socket at the top of this tube served to connect it to the water sampler and its associated trap N which were the same as those described in our previous paper on the solubility of hydrogen sulfide (see Figure 1 of ref 12).

Procedure

A 650-mL sample of acidified sea water was placed in the saturation vessel, and after being brought to thermal equilibrium it was degassed by bubbling with oxygen-free nitrogen via tube

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