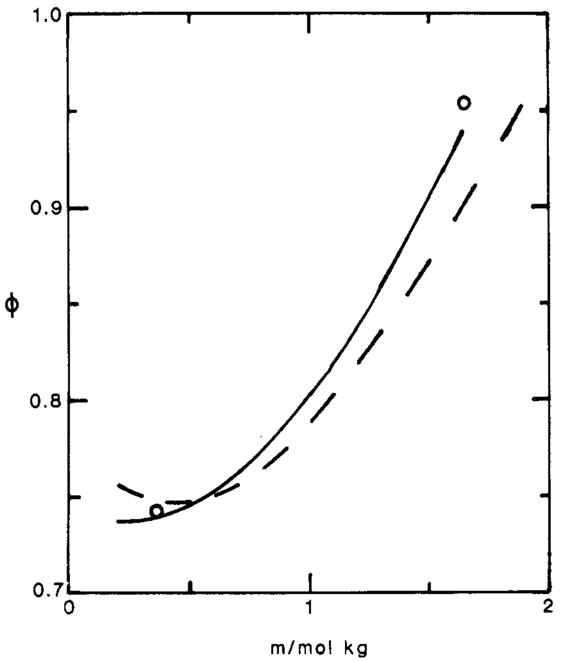

Figure 1. Osmotic coefficient of aqueous $MgCl_2$ at 473.15 K vs. molality: (—) present results; (- - -) Holmes, Baes, and Mesmer (*8*); (O) Liu and Lindsay (*9*).

larger than what is expected from the accuracy of the present calorimetric technique. Similar comparisons on alkali-metal halides normally gave agreement to better than 0.01 in osmotic coefficient at 473.15 K (*2*). The present results agree quite well with the measurements of Lindsay and Liu (*9*).

The present results for Na_2SO_4 can be compared with the measurements of the heat capacity of aqueous Na_2SO_4 of Rogers and Pitzer (*10*). From their measurements of heat capacity as a function of temperature and molality, Rogers and Pitzer calculated the relative apparent molar enthalpy, and this can be compared with the present results. The results are in fair agreement at 423.15 K and 1 mol kg^{-1}. Rogers and Pitzer find L_ϕ = 24.68 kJ mol^{-1}, compared with the present result of 22.49 kJ mol^{-1}. Similarly, at 0.1 mol kg^{-1}, the results are 11.67 and 11.47 kJ mol^{-1}. (A series of measurements on aqueous Na_2SO_4 at 472.95 K (*3*) are not reported here because there appears to have been an error in these measurements. The relative molar enthalpies at 472.95 K do not follow a smooth trend with temperature, they do not agree with the results of Rogers and Pitzer, and they do not agree with a check measurement made in this laboratory at 448.41 K and 17.7 MPa of the heat capacity of a 0.9985 mol kg^{-1} Na_2SO_4 solution; $C_{p,\phi}$ = +2.2 J mol^{-1} K^{-1}. This result is in agreement with the result of Rogers and Pitzer, considering the difference in pressure, and does not agree with our measurements at 472.95 K.) Using the same osmotic coefficients at 298.15 K used by Rogers and Pitzer, we can calculate the osmotic coefficients at 423.15 K and compare with their values. Our results at 0.1, 0.5, and 1.0 mol kg^{-1} are 0.734, 0.648, and 0.604, whereas Rogers and Pitzer get 0.728, 0.630, and 0.597, respectively. This is reasonable agreement.

Acknowledgment

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Solubility of Carbon Monoxide in Alcohols

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The solubility of carbon monoxide in various alcohols at pressures up to 4000 kPa has been measured by using a chromatographic technique to analyze equilibrated gas-in-liquid mixtures from a pressure vessel. Typical dilute-solution behavior was observed with the data fitting a Henry's law relationship. Values of carbon monoxide solubility in methanol, ethanol, 1- and 2-propanol, 2-methyl-1-propanol, 2-methyl-2-propanol, and 1- and 2-butanol are reported at 298 and 323 K.

Introduction

The solubility of carbon monoxide in various alcohols has been determined as part of a study of the base-catalyzed formation of formate esters (*1*).

$$\mathrm{ROH} + \mathrm{CO} = \mathrm{HCOOR} \qquad (1)$$

It has been suggested that the kinetics of these reactions may be controlled by the solubility of the gas in the different alcohols (*2*, *3*) and, in order to test this hypothesis, it is necessary to measure solubilities. The data obtained are also of interest in

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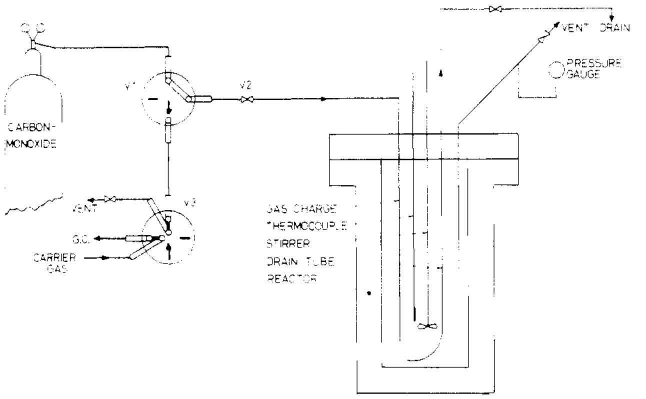

Figure 1. Experimental apparatus.

the context of other liquid-phase reactions of carbon monoxide, which have considerable industrial importance (*4*). Recent research interest in the liquid-phase production of synthetic fuels from synthesis gas (CO/H_2 mixtures) also requires a knowledge of CO solubility (*5–7*). Data are available for carbon monoxide dissolution in various solvents (*8*) but information is limited to measurements at around 100 kPa for alcohols up to C_4 (*9*, *10*). Reaction 1 occurs at pressures up to 6000 kPa and the present experiments were planned with this in mind.

Experimental Section

Experiments were carried out with a 300-cm^3 stainless-steel stirred autoclave rated to 5000 psi and supplied by Autoclave Engineers, Pennsylvania (see Figure 1 for a diagram of the apparatus). The autoclave was fitted with ancillary lines and valves to allow gas charging, sampling of the liquid phase and venting, and draining and cleaning at the conclusion of an experiment.

Temperature control to within ±1 K was achieved by using an electric furnace and a low-power furnace controller. The temperature was measured with a 1-mm o.d., stainless-steel-sheathed, calibrated chromel–alumel thermocouple fitted inside the autoclave and connected to a digital voltmeter. Pressure was measured to within ±10 kPa with a standarized Bourdon-type gauge.

Solubility measurements were conducted by charging 200 cm^3 of the appropriate alcohol into the autoclave which was then pressurized to the desired level from a cylinder of 99.8% carbon monoxide (Matheson C.P. grade). After being stirred for a few minutes for equilibration, the liquid phase was sampled by drawing a fine stream out of the autoclave and through a four-port Valco HPLC valve with an internal volume of 1 μL. The flow was then shut off after the valve, and, after about 30 s was allowed for pressure equilibration between the valve and the autoclave, the 1-μL sample was switched into a stream of hydrogen carrier gas (30 cm^3 min^{-1}) where it vaporized and was carried to a Gow Mac gas chromatograph fitted with a thermal conductivity detector.

Separation of carbon monoxide and the alcohol was achieved with a 6-ft column of Porapak Q maintained at 353–423 K depending on the alcohol.

The relative response of the detector to carbon monoxide and the alcohols was measured beforehand and the values obtained corresponded closely to literature values (*11*). The mole fraction of carbon monoxide was determined by dividing the areas obtained from the integrator by the relative response factors.

Alcohols were obtained from Ajax Chemicals in 99.8% purity.

Results

Preliminary experiments were carried out to confirm that the stirrer speed and the rate of solubility were sufficient to obtain equilibrium in all cases. Reproducible results were obtained after ca. 2 min.

The solubility of carbon monoxide in the different alcohols was measured at 1000, 2000, 3000, and 4000 kPa, at both 298 and 323 K (Table I). The solubility of carbon monoxide was found to increase as the chain length of the alcohol, showing that gas dissolution may be favored by low-polarity solvents. This conclusion is consistent with the observed behavior of carbon monoxide in other solvents (*8*). The high solubility of carbon monoxide in 2-methyl-2-propanol was rather unexpected.

A linear relationship between the pressure of carbon monoxide and the mole fraction dissolved in the liquid phase would be expected if the system behaved as a typical dilute solution (*12*). This relationship is described by Henry's law, which may be written as (*12*)

$$P_{CO} = KX_{CO} \tag{2}$$

where K is the Henry's law coefficient. By use of eq 2, the data in Table I were represented as Henry's law coefficients at 298 and 323 K. Regression analysis showed a 95% confidence fit and the valves obtained are reported in Table II.

It is apparent from Tables I and II that for a particular alcohol there is little difference in carbon monoxide solubility obtained at 298 and 323 K. This result may appear surprising but can be explained by considering the enthalpy change of dissolution as being made up of the heat of liquefaction of the gas, and the heat of mixing of the liquefied gas and solvent (*14*). In most cases, the heat of mixing, though opposite in sign to the former term, is insignificant in comparison, so the overall enthalpy change is estimated in sign and magnitude by the heat of liquefaction.

In our case, however, the heat of mixing is large due to the breaking of hydrogen bonds in solution and may be expected to balance or even exceed the heat of liquefaction, which for carbon monoxide is quite small (6.74 kJ mol^{-1} (*13*)). Hence, the observed effects are not unexpected.

The present study, then, shows that the solubility of carbon monoxide in alcohols is rapid and appears to vary little over the

Table I. Solubility of Carbon Monoxide in Alcohols Expressed as Mole Fraction × 10^2 at 298 and 323 K

	10^2X_{CO}							
	P_{CO} = 1000 kPa		P_{CO} = 2000 kPa		P_{CO} = 3000 kPa		P_{CO} = 4000 kPa	
alcohol	298 K	323 K	298 K	323 K	298 K	323 K	298 K	323 K
methanol	0.32	0.33	0.84	0.83	1.32	1.28	1.78	1.73
ethanol	0.53	0.50	1.11	1.05	1.65	1.64	2.21	2.17
1-propanol	0.67	0.60	1.50	1.43	2.41	2.33	3.23	3.12
2-propanol	0.71	0.69	1.50	1.42	2.26	2.23	3.16	3.23
1-butanol	0.64	0.60	1.54	1.56	2.45	2.39	3.27	3.22
2-methyl-1-propanol	0.64	0.61	1.41	1.39	2.36	2.28	3.09	3.02
2-butanol	0.60	0.60	1.41	1.39	2.18	2.13	2.90	2.86
2-methyl-2-propanol	0.85	0.77	1.93	1.85	3.02	2.89	3.87	3.80

Table II. Henry's Law Coefficients (K) for Solution of Carbon Monoxide in Alcohols at 298 and 323 K

	$10^{-3}K$, kPa	
alcohol	298 K	323 K
methanol	2.06	2.15
ethanol	1.80	1.78
1-propanol	1.16	1.18
2-propanol	1.23	1.18
1-butanol	1.13	1.15
2-methyl-1-propanol	1.20	1.23
2-butanol	1.30	1.33
2-methyl-2-propanol	0.98	1.00

temperature ranges studied. The system obeys Henry's law and the gas appears to be more soluble in low-polarity solvents.

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Discussions with Dr. T. Spurling concerning the solubility of gases in liquids as a function of temperature are acknowledged.

Glossary

P_{CO}	carbon monoxide pressure (kPa)
K	Henry's law constant (kPa)
X_{CO}	mole fraction of carbon monoxide in the liquid phase

Registry No. CO, 630-08-0; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 2-methyl-1-propanol, 78-83-1; 2-butanol, 78-92-2; 2-methyl-2-propanol, 75-65-0; 2-propanol, 67-63-0.

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Excess Volumes of Binary Mixtures of *m*-Xylene + *n*-Alkanes

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Excess volume of the binary mixtures *m*-xylene + *n*-hexane, + *n*-octane, + *n*-decane, + *n*-dodecane, + *n*-tetradecane, and + *n*-hexadecane have been measured at 298.15 K as a function of composition by a dilatometric method.

Introduction

The experimental excess volumes of binary mixtures of *n*-alkanes with *p*-xylene (*1*) and *o*-xylene (*2*) at 298.15 K have been published previously. In this paper the results for the same *n*-alkanes with *m*-xylene at the same temperature are reported. No excess volume data have been found for these systems in the consulted literature.

Experimental Section

The alkanes were the same as those used in earlier works (*3*). The *m*-xylene (Carlo-Erba RPE) was dried with sodium with no further purification. Gas-chromatography analysis and refractive index and density determinations were used as a criterion of purity.

The experimental density at 298.15 K was found to be 0.859 99 g cm^{-3} and the literature value (*4*) is 0.860 00 g cm^{-3}. The experimental refractive index, n_D(303.15 K), was found to be 1.492 15 and the literature value (*4*) is 1.492 00.

Excess Volume Measurements. Excess volumes have been measured as a function of the mole fraction by a semicontinuous dilatometric procedure. The dilatometer is the same used in previous works (*2*) and has been described in detail elsewhere (*1*).

Results

Experimental excess volumes are given in Table I and are plotted in Figure 1.

As in previous works the experimental results were fitted to an equation of the type

$$V^E/[x(1-x)] = \sum A_i(2x-1)^i \qquad (1)$$

where x is the *m*-xylene mole fraction. The coefficients of eq 1 and the standard deviations are given in Table II.

As is shown in Figure 1, the excess volume for *n*-hexane + *m*-xylene is negative. The rest of the *n*-alkanes with *m*-xylene show a positive V^E. This behavior was also observed for the binary mixtures of *n*-alkanes with *p*-xylene (*1*) and *o*-xylene (*2*).

Comparing the behavior of the three xylenes with the different *n*-alkanes, we found that the magnitude of the excess volume increases in the order ortho < para < meta when the alkane is *n*-decane. For *n*-dodecane, *n*-tetradecane, and *n*-hexadecane the order is para < ortho < meta. The systems with a negative excess volume show the order meta < para < ortho for the absolute value of V^E. The behavior shown by *n*-hexane with the three xylenes ($V^E < 0$) is also found for binary mixtures of *n*-pentane with the three xylenes (*5*). Octane with *m*- or *p*-xylene always shows a positive excess volume along the whole mole fraction range being meta > para. However the system *n*-octane + *o*-xylene has a positive V^E for mole fractions smaller than 0.3 becoming negative when the mole fraction of *o*-xylene increases from 0.3 to 1. The magnitude of V^E for this system is always smaller in absolute value

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