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Solubility of Carbon Monoxide in Water–*n*-Butylamine, Ethanol–Cyclohexene, and Water–Dimethylformamide Mixtures

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The solubility of carbon monoxide gas in water–*n*-butylamine, ethanol–cyclohexene, and water–dimethylformamide mixtures was experimentally determined by volumetric method using a 3 × 10^{-4} m^3 autoclave at three temperatures between 373 and 433 K. The solubility measurements have been made at two equilibrium pressures of CO for each set of mixtures at each temperature. The calculated Henry's constants have been correlated by use of the equation $\ln H = a + b/T$ for temperature dependence of CO solubility.

Introduction

Recent years have seen a marked trend in the application of many transition-metal complexes in catalyzed reactions of carbon monoxide to yield valuable chemicals (*1-3*). The predominant factors in these reactions are the feasibility and evaluation of optimum reaction conditions for the chosen catalyst systems to the desired products, and hence studies have been concentrated on these aspects. These reactions involve the interaction between gas and liquid and hence obviously are frequently limited by mass-transfer considerations. Studies on the kinetics of the high-pressure and high-temperature carbonylation reactions in the liquid phase catalyzed by soluble metal complexes necessarily involves knowledge of the solubility of CO in the liquid phase under experimental conditions. This would enable one to evaluate the kinetic rate constants and equilibrium constants involved in the mechanistic study of the reaction.

The CO solubility data that are needed for carbonylation reaction in the systems investigated by us are not known under the reaction conditions (*4*). To offset this, the present study was undertaken to provide data of CO solubility for water–*n*-butylamine, ethanol–cyclohexene, and water–dimethylformamide mixtures.

Experimental Section

The solubility apparatus and the method employed to determine CO solubilities are same as the one described by Chaudhary et al. (*5*). This volumetric method essentially involves the saturation of CO gas in a degassed solvent mixture at the desired partial pressure and temperature in an equilibrium cell (autoclave). A known volume of the saturated liquid is withdrawn after equilibration, and the amount of gas desorbed at room temperature and atmospheric pressure is measured by the volume of water displaced. Carbon monoxide gas of purity >99.96%, obtained from BOC, UK, was used. The solvents *n*-butylamine, ethanol, and dimethylformamide were of AR grade and distilled twice before use. Cyclohexene is prepared in our laboratory by the dehydration of cyclohexanol using concentrated sulfuric acid (*6*), and its purity checked by GLC was 99.8%. The autoclave of 3 × 10^{-4} m^3 volume used as equilibrium cell was procured from Parr Instrument Co., USA.

From a known amount of saturated liquid withdrawn after equilibration from the autoclave, the solubility of CO was calculated from the observed volume of the desorbed gas:

$$S = \frac{V - V_1}{V_1}\left[\frac{P - P_w - h/13.6}{101.3}\right]\frac{273}{T_w} + S_1 \qquad (1)$$

The solubility of CO is determined for the three systems studied at two different CO equilibrium pressures, and the average value after expressing in Henry's coefficient (H) was found to be reproducible within ±2-3% experimental error.

The vapor pressures of the mixtures required for CO partial pressure correction were determined in the same autoclave and used in the solubility calculations. This has the advantage that the value is known from practical measurements and no assumption using any equation need be made. This, we believe, will improve the accuracy of the results. The estimated errors in the present measurements of pressure, volume, and temperature were around ±3 kPa, ±0.1 × 10^{-6} m^3, and ±0.1 K, respectively.

Results and Discussion

The CO solubility data were obtained experimentally for CO–water–*n*-butylamine, CO–ethanol–cyclohexene, and CO–water–dimethylformamide systems in the temperature range 373-433 K at two equilibrium CO pressures (5 × 10^2–25 × 10^2 kPa). The solubilities (S) of CO estimated have been expressed in kmol/m^3. The effect of temperature and mole fraction change of one of the components of the mixtures on CO solubility was determined for the three systems, and these results

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Table I. Solubility Data for CO-*n*-Butylamine-Water

	393 K		413 K		433 K	
mole fracn *n*-butylamine	$10^{-2}P_{CO}$, kPa	10^2S, kmol/m^3	$10^{-2}P_{CO}$, kPa	10^2S, kmol/m^3	$10^{-2}P_{CO}$, kPa	10^2S, kmol/m^3
0	9.61	2.17	8.75	2.12	8.07	2.23
	22.80	5.08	22.27	5.67	19.89	5.34
0.02	10.09	2.32	11.64	2.95	10.09	3.02
	21.75	5.21	20.03	5.23	16.78	5.12
0.49	6.87	6.69	5.84	6.98	3.61	5.36
	20.40	20.10	18.69	22.06	17.32	25.75
1.0	7.38	11.38	7.21	14.11	5.50	11.13
	20.23	31.40	18.86	36.54	16.29	32.78

Table II. Solubility Data for CO-Ethanol-Cyclohexene

	373 K		393 K		413 K	
mole fracn cyclohexene	$10^{-2}P_{CO}$, kPa	10^2S, kmol/m^3	$10^{-2}P_{CO}$, kPa	10^2S, kmol/m^3	$10^{-2}P_{CO}$, kPa	10^2S, kmol/m^3
0	8.75	10.19	7.90	11.12	5.67	10.09
	21.60	25.77	20.23	28.58	16.81	29.82
0.06	5.50	6.67	5.33	7.64	2.93	5.24
	20.57	24.91	20.58	29.41	18.86	33.78
0.43	9.53	12.95	9.46	14.70	10.35	19.02
	20.85	28.25	19.28	30.04	20.04	36.77
1.0	9.27	14.64	9.61	16.84	6.36	12.24
	20.57	32.42	22.40	39.60	20.06	38.69

Table III. Solubility Data for CO-Dimethylformamide-Water

	393 K		413 K		433 K	
mole fracn dimethylformamide	$10^{-2}P_{CO}$, kPa	10^2S, kmol/m^3	$10^{-2}P_{CO}$, kPa	10^2S, kmol/m^3	$10^{-2}P_{CO}$, kPa	10^2S, kmol/m^3
0	9.61	2.17	8.75	2.12	8.07	2.23
	22.80	5.08	22.27	5.67	19.89	5.34
0.3	9.82	2.92	9.34	3.01	9.05	3.13
	19.35	5.77	20.50	6.56	21.36	7.31
0.5	9.20	2.76	8.54	2.89	8.20	2.80
	18.65	6.60	18.31	5.75	17.28	5.70
1.0	10.73	4.85	10.60	5.17	11.15	5.98
	19.80	9.68	19.85	9.77	19.55	9.78

Table IV. Constants of Eq 3 and ΔH Values

system	component mole fracn	a	b	H, kJ/mol
CO-water	0[a]	-9.04	-642.8	0.70
CO-water-*n*-butylamine	0.02[a]	-7.96	-1066.0	1.16
CO-water-*n*-butylamine	0.49[a]	-4.82	-1768.7	1.93
CO-*n*-butylamine	1.0[a]	-5.48	-1141.3	1.24
CO-ethanol	0[b]	-4.84	-1573.5	1.71
CO-ethanol-cyclohexene	0.06[b]	-5.02	-1495.7	1.63
CO-ethanol-cyclohexene	0.43[b]	-5.80	-1162.1	1.27
CO-cyclohexene	1.0[b]	-6.69	-770.3	0.84
CO-water-dimethylformamide	0.3[c]	-5.05	-1483.9	1.62
CO-water-dimethylformamide	0.5[c]	-5.81	-1156.9	1.26
CO-dimethylformamide	1.0[c]	-6.79	-730.1	0.80

[a] *n*-Butylamine. [b] Cyclohexene. [c] Dimethylformamide.

are presented in Tables I-III. Henry's coefficient was calculated according to the relation

$$H = S/P \tag{2}$$

where H = Henry's coefficient (kmol/(m^3·kPa)), S = CO solubility (kmol/m^3), and P = equilibrium pressure of CO (kPa). It was confirmed from our observations that Henry's coefficients calculated at a chosen temperature for two equilibrium CO pressures are the same within the experimental error limit of ±0.5%. This further indicated that the mixtures in which CO solubility is measured was not oversaturated in the range of pressures varied.

To correlate the effect of temperature on CO solubility for utilization of these data at other temperatures, a simple form of the equation can be used:

$$\ln H = a + b/T \tag{3}$$

where H = Henry's constant, T = temperature (K), and a and b are constants.

The values of a and b, which represent intercept and slope, respectively, were obtained for all the systems by use of a least-squares analysis method. The values of ΔH (heat of solution, kJ/mol) were calculated by the value of b. The constants a and b of eq 3 and the heat of solution (ΔH) evaluated for different mole fractions varied for the three systems using averaged values of Henry's coefficients (values of two equilibrium pressures) have been presented in Table IV. We observe that the solubility of CO increases with increase in temperature.

The solubility of CO in pure solvents such as CO-ethanol and CO-water in the temperature range 373-433 K have been reported in the literature (*8*, *9*). Our values on CO solubility in pure solvents are in close agreement with the reported values within the experimental error for CO-ethanol and CO-water solvents. However, comparison of data on CO solubility for solvent mixtures has not been done since it is not available in the literature.

Glossary

S	solubility of CO, m^3/m^3
h	height of the water column in the gas desorption apparatus, m
S_1	solubility of CO at atmospheric pressure and room temperature, m^3/m^3
H	Henry's coefficient of solubility, $kmol/(m^3 \cdot kPa)$
P	barometric pressure, kPa
P_w	vapor pressure of water at T_w, kPa
P_{CO}	partial pressure of CO in the autoclave, kPa
T	temperature in the autoclave, K
T_w	temperature in the gas buret, K
V	volume of water displaced by the desorbed CO gas, m^3
V_1	volume of the liquid sample withdrawn from autoclave, m^3

Registry No. CO, 630-08-0; DMF, 68-12-2; EtOH, 64-17-5; $BuNH_2$, 109-73-9; cyclohexene, 110-83-8.

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Solubilities of Carbon Dioxide in Water and 1 wt % NaCl Solution at Pressures up to 10 MPa and Temperatures from 80 to 200 °C

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Experimental gas solubility data for the CO_2–water and CO_2–1 wt % NaCl solution binary systems are reported. Measurements were made at pressures up to 10 MPa and temperatures from 80 to 200 °C. A thermodynamic model of these systems is also presented. The model employs the Peng–Robinson equation of state to represent the vapor phase and an empirical Henry's law constant correlation for the liquid phase. It is shown that the salting-out effect of the 1 wt % NaCl solution on CO_2 solubility is small. Also described is a new experimental apparatus consisting of a variable-volume equilibrium cell enclosed in a constant temperature controlled oven and the procedure used in conducting the experiments.

Introduction

Carbon dioxide solubility data in water and dilute salt solutions typical of oil-field-produced waters (approximately 1 wt %) are required in the modeling of many enhanced oil and bitumen recovery processes. Applications are also found in geochemical and natural gas systems. In spite of their significance, limited data on the CO_2–water and no data on the CO_2–1 wt % NaCl solution systems are available in the literature.

In the range of temperature and pressure of interest to this study, data for the CO_2–water system were given by Drummond (*1*), Ellis and Golding (*2*), Malinin and Kurovskaya (*3*), and Malinin and Savelyeva (*4*). A summary of the data is provided in Table I. Both Drummond (*1*) and Ellis and Golding (*2*) have reported additional data in the 250–350 °C range. Also, Table I does not include numerous studies that reported solubility measurements at temperatures below 75 °C or at pressure greater than 15 MPa. A summary of these data was provided by Drummond (*1*).

Table I. *PVT* Data for the CO_2-Water System at T = 75-250 °C and P = 1-15 MPa

source	T, °C	P, MPa	no. data pts
Drummond (*1*)	80–250	3–15	34
Ellis and Golding (*2*)	175–250	1.5–9	6
Malinin and Kurovskaya (*3*)	100–150	5	2
Malinin and Savelyeva (*4*)	75	5	1
this work	80–200	2–10	32

The total dissolved solids concentration in a "typical" reservoir produced water is approximately 0.7 wt % (*5*). The solids primarily consist of sodium, potassium, chloride, and bicarbonate ions. On the basis of this, it was decided to perform equilibrium experiments on a synthetic salt solution containing 1 wt % NaCl for which no data exist in the literature. The data available at higher salt concentrations (3–35 wt %) were summarized by Drummond (*1*). At NaCl concentrations greater than 6 wt %, the logarithm of the Henry's law constant, ln (H_g), follows the linear Setschenow relationship with salt concentration. However, it has been shown that the relationship is invalid in the low salt concentration range (*5*).

Thermodynamic models utilizing cubic equations of state are widely used for the modeling of oil and gas phases in petroleum reservoir simulation. However, attempts at modeling the aqueous phase with these equations have concluded that accurate predictions of gas solubility are difficult to obtain (*6*–*8*). Furthermore, the effect of salts in the water cannot be represented by a cubic equation of state. Instead, empirical Henry's law constant correlations have been used to model the aqueous phase with equations of state used for the oil and vapor phases (*9*–*13*).

The effect of the inclusion of NaCl on CO_2 solubility has been modeled empirically by Drummond (*1*) and semiempirically by

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