Table X. Vapor Compositions, Activity Coefficients, and Excess Gibbs Free Energies for the System 1,2-Dichloroethane (1)–1-Hexanol (2) at 700 mmHg

x	y(calcd)	t(calcd), °C	γ_1	γ_2	G^E, J mol^{-1}
0.00	0.0000	154.5	7.9930	1.0000	
0.05	0.7370	118.9	5.1818	1.0148	302
0.10	0.8183	110.5	3.5405	1.0481	518
0.15	0.8479	106.8	2.6905	1.0909	676
0.20	0.8654	104.5	2.1931	1.1398	791
0.25	0.8785	102.6	1.8732	1.1937	871
0.30	0.8897	100.9	1.6534	1.2520	922
0.35	0.8999	99.4	1.4952	1.3146	950
0.40	0.9093	97.9	1.3774	1.3813	956
0.45	0.9184	96.4	1.2877	1.4521	943
0.50	0.9271	95.0	1.2180	1.5273	914
0.55	0.9355	93.6	1.1635	1.6068	871
0.60	0.9436	92.2	1.1205	1.6909	814
0.65	0.9516	90.8	1.0866	1.7796	745
0.70	0.9592	89.4	1.0601	1.8732	665
0.75	0.9667	87.9	1.0396	1.9718	574
0.80	0.9739	86.5	1.0241	2.0756	475
0.85	0.9808	85.1	1.0130	2.1847	367
0.90	0.9875	83.7	1.0055	2.2993	252
0.95	0.9939	82.3	1.0013	2.4197	129
1.00	1.0000	80.9	1.0000	2.5460	

x	mole fraction in liquid phase
y	vapor composition
T	critical temperature
U	molar volume

Greek Letters

γ	activity coefficient
Λ	Wilson parameters

Subscripts

1	1,2-dichloroethane
2	normal alcohols

Registry No. 1,2-Dichloroethane, 107-06-2; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3.

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Solubility of CO in Aqueous Mixtures of Methanol, Acetic Acid, Ethanol, and Propionic Acid[†]

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The solubility of carbon monoxide (CO) in water–methanol, water–acetic acid, water–ethanol, and water–propionic acid has been determined in a temperature range of 298–448 K and a pressure range of 1×10^3–8×10^3 kPa. The values of the enthalpy change of solution and Henry's coefficients have been determined and the solubility data correlated by using the equation ln $H = k_1 + k_2/T + k_3(X)(1/298 - 1/T) + k_4 \ln (1 + X)$. For each system, the values of the constants have been evaluated. The results predicted with this correlation agreed well with the experimental data within 3–4% error.

Introduction

Solubility data for gases in liquids is most essential in studies on gas–liquid and gas–liquid–solid reactions. Several industrial processes involve gas–liquid reactions wherein the liquid-phase composition changes during the course of a reaction. In such cases, determination of solubility of gaseous reactants in liquid mixtures of different compositions becomes essential. The objective of this work was to determine solubility of carbon monoxide (CO) in various liquid mixtures involved in industrial carbonylation processes such as carbonylation of methanol to acetic acid (*1*) and ethanol to propionic acid (*2*). The earlier studies on CO solubility (*3*, *4*) are mainly on binary systems at atmospheric pressure and in a lower temperature range. However, there are no published data available for liquid mixtures encountered in the above processes at higher temperatures and pressures. Therefore, in this work solubility of CO was determined at different temperatures and pressures in liquid mixtures under conditions of practical interest in carbonylation processes. It was also the objective of this work to develop a suitable correlation based on the experimental data.

Experimental Section

The solubility data were obtained by using a technique described by Radhakrishnan et al. (*5*) in which desorbed gas from a saturated sample was measured by using a specially designed apparatus. The details of the apparatus and procedure are described by Radhakrishnan et al. (*5*). Carbon monoxide gas generated in our own laboratory by dehydration of formic acid, and with a purity greater than 99.5%, was used. The solvents used in this work were supplied by BDH Laboratories and freshly distilled before use. The purity of the solvents as evaluated by

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Table I. Vapor Pressure Data of the Solvent Mixtures

no.	component^a	component^a mole fraction	mixture vapor pressure, kPa		
			348 K	398 K	448 K
1		0.0	19.25	312.0	1019.1
2	methanol	0.18	19.25	346.4	1330.1
3	methanol	0.47	53.7	518.7	1605.6
4	methanol	0.80	88.1	518.7	2156.7
5	methanol	1.0	363.7	1517.5	5014.4
6	acetic acid	0.135		70.9	571.3
7	acetic acid	0.38		105.4	709.1
8	acetic acid	1.0		70.9	399.1
9	ethanol	0.135	88.1	346.4	1215.6
10	ethanol	0.38	88.1	346.4	1777.8
11	ethanol	0.75	88.1	380.9	1777.8
12	ethanol	1.0	53.7	415.3	1708.9
13	propionic acid	0.11		4.1	81.0
14	propionic acid	0.325		4.1	81.0
15	propionic acid	1.0		38.5	125.6

[a] Organic component in the mixture.

GC analysis was greater than 99%. The solubility was calculated from the observed volume of gas desorbed from a known quantity of the sample by using

$$A = \left[\frac{V - v}{v}\right]\left[\frac{P - P_w - 9.8h}{101.3}\right] \times \left[\frac{273}{T_w}\right]\left[\frac{P_{CO}}{P_{CO} - \left(\dfrac{P - P_w - 9.8h}{101.3}\right)}\right] \quad (1)$$

In order to ensure the reproducibility of the method used, repeated experiments were carried out which showed that the solubility data can be obtained within 2–3% error. Further experiments were carried out at different temperatures and pressures in a range of 298–448 K and 1 × 10^3–8 × 10^3 kPa pressure, respectively. Similarly, the liquid-phase composition was varied over a wide range.

In order to correct for the vapor pressure of the solvent mixture in the desorption apparatus, the relevant data were calculated by using the correlations described in the literature (*6*) and the Raoult's law. For calculation of the correct partial pressure of CO in the autoclave (P_{CO}), the vapor pressure data of the solvent mixtures determined by independent experiments were used. These data are presented in Table I.

Results and Discussion

The solubility of CO was determined for the following systems: (1) CO–water–methanol, (2) CO–water–ethanol, (3) CO–water–acetic acid, and (4) CO–water–propionic acid. The results calculated by eq 1 were converted into SI units to represent the Henry's solubility constants as kmol/m^3·kPa. The effects of the concentration of liquid-phase components, partial pressure of CO, and temperature were investigated. The results are presented in Tables II–V and discussed below.

Effect of Pressure. The effect of partial pressure of CO on solubility for all the systems was studied in a temperature range of 298–448 K. In all the cases, the solubility was found to be linearly dependent on CO partial pressure.

Effect of Temperature. The effect of temperature on solubility of CO was studied for all the systems described above in a range of 298–448 K. In general, it was observed that the solubility of CO increased with increase in temperature, for all the systems studied. The results are presented in Tables II–V. For each system Henry's constant *H* was calculated from experimental solubility at different pressures (Tables II–V). These

Table II. Solubility Data for CO-Methanol–Water System

	298 K		348 K		398 K		448 K	
methanol mole fraction, *X*	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3
0	2.026	1.607	2.127	1.87	2.198	2.05	2.218	2.19
	4.052	3.17	4.183	3.71	4.254	4.11	4.355	4.46
	6.078	4.82	6.209	5.49	6.260	5.98	6.331	6.47
0.18	2.026	2.41	2.157	2.81	2.279	3.26	2.410	3.66
	4.052	4.78	4.183	5.49	4.305	6.12	4.386	6.69
	6.078	7.23	6.209	8.12	6.331	9.02	6.483	9.91
0.47	2.026	5.89	2.289	7.14	2.623	9.02	2.826	9.99
	4.052	11.61	4.518	14.33	5.065	16.65	5.298	18.53
	6.078	17.32	6.736	20.71	6.979	23.17	7.161	24.91
0.80	1.519	8.84	1.651	10.71	1.772	12.19	1.894	13.70
	3.039	17.86	3.241	20.98	3.373	23.30	3.575	25.53
	5.065	29.91	5.318	34.73	5.520	38.17	5.693	41.20
1.0	1.519	13.62	1.651	15.71	1.772	18.30	1.894	20.31
	3.039	27.45	3.231	31.25	3.423	35.09	3.575	38.39
	5.065	45.76	5.318	51.38	5.520	56.69	5.693	61.6

Table III. Solubility Data for CO–Acetic Acid–Water System

	298 K		348 K		398 K		448 K	
acetic acid mole fraction, *X*	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3
0	2.026	1.607	2.127	1.87	2.198	2.05	2.218	2.19
	4.052	3.17	4.183	3.71	4.254	4.11	4.355	4.46
	6.078	4.82	6.209	5.49	6.260	5.98	6.331	6.47
0.135	2.026	1.92	2.157	2.28	2.279	2.68	2.400	2.95
	4.052	3.88	4.244	4.60	4.355	5.09	4.457	5.54
	6.078	5.89	6.280	6.79	6.452	7.54	6.614	8.21
0.38	2.026	4.02	2.177	8.04	2.299	5.40	2.421	5.94
	4.052	8.12	4.204	9.24	4.355	10.22	4.487	10.94
	6.078	12.19	6.260	16.96	6.473	15.18	6.685	16.29
1.0	2.026	11.87	2.178	13.84	2.329	15.62	2.451	17.05
	4.052	22.36	4.254	25.44	4.396	27.68	4.477	29.42
	6.078	35.80	6.240	39.73	6.412	42.94	6.594	45.98

Table IV. Solubility Data for CO-Ethanol-Water System

	298 K		348 K		398 K		448 K	
ethanol mole fraction, X	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3
0	2.026	1.607	2.127	1.87	2.198	2.05	2.218	2.19
	4.052	3.17	4.183	3.71	4.254	4.11	4.355	4.46
	6.078	4.82	6.209	5.49	6.260	5.98	6.331	6.42
0.135	2.026	2.14	2.238	2.68	2.461	3.30	2.664	3.75
	4.052	4.29	4.254	5.09	4.386	5.85	4.497	6.38
	6.078	6.47	6.290	7.54	6.462	8.62	6.635	9.42
0.38	2.026	4.64	2.228	5.67	2.451	6.79	2.664	8.04
	4.052	9.20	4.244	10.80	4.436	12.19	4.458	13.75
	6.078	13.70	6.311	16.07	6.513	18.03	6.716	20.36
0.75	2.026	10.76	2.228	13.97	2.461	17.19	2.603	20.09
	4.052	21.47	4.224	26.20	4.386	30.58	4.487	34.37
	6.078	32.36	6.280	39.06	6.452	45.09	6.655	51.07
1.0	2.026	16.74	2.228	21.87	2.400	26.87	2.583	32.14
	4.052	33.03	4.254	41.96	4.426	49.77	4.609	56.92
	6.078	49.55	6.280	61.60	6.452	72.54	6.635	82.14

Table V. Solubility Data for CO-Propionic Acid-Water System

	298 K		348 K		398 K		448 K	
propionic acid mole fraction, X	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3	$P_{CO} \times 10^{-3}$, kPa	$S \times 10^2$, kmol/m^3
0.00	2.026	1.607	2.127	1.87	2.198	2.05	2.218	2.19
	4.052	3.17	4.183	3.71	4.254	4.11	4.355	4.46
	6.078	4.82	6.209	5.49	6.260	5.98	6.331	6.42
0.11	2.026	2.10	2.188	2.68	2.299	3.04	2.431	3.44
	4.052	4.29	4.214	5.09	4.325	5.71	4.426	6.25
	6.078	6.43	6.229	7.59	6.351	8.39	6.452	9.11
0.33	2.026	3.75	2.177	4.69	2.299	5.54	2.400	6.16
	4.052	7.95	4.214	9.60	4.335	10.98	4.447	12.05
	6.078	11.16	6.229	13.39	6.351	15.18	6.452	16.61
1.00	2.026	12.05	2.127	15.18	2.228	18.30	2.299	21.87
	4.052	24.11	4.153	29.91	4.254	35.27	4.335	41.52
	6.078	35.71	6.209	45.09	6.351	52.23	6.381	61.16

Table VI. Enthalpy Change of Solution Data Calculated from Experimental Solubilities

no.	system	component[a] mole fraction, X	H,[b] kJ/mol
1	CO-water	0	2.04
2	CO-water-methanol	0.18	1.85
3	CO-water-methanol	0.47	1.51
4	CO-water-methanol	0.80	1.46
5	CO-methanol	1.00	1.36
6	CO-water-acetic acid	0.135	1.89
7	CO-water-acetic acid	0.38	1.44
8	CO-acetic acid	1.00	1.28
9	CO-water-ethanol	0.135	2.11
10	CO-water-ethanol	0.38	2.25
11	CO-water-ethanol	0.75	2.70
12	CO-ethanol	1.00	3.06
13	CO-water-propionic acid	0.11	2.12
14	CO-water-propionic acid	0.325	2.63
15	CO-propionic acid	1.00	3.49

[a] Organic component. [b] Enthalpy change of the solution.

data were plotted as ln H vs. $1/T$ (in accordance with van't Hoff equation).

The slope of this plot is equal to $\Delta H/R$, from which the enthalpy change of solution, ΔH, values were calculated. These data are presented in Table VI for different concentration ranges.

Effect of Liquid-Phase Concentration. The effect of methanol, ethanol, acetic acid, and propionic acid concentration on the solubility of CO in water was investigated at different temperatures and pressures. The results are presented in Tables II–V. It was observed that in the presence of all these components, the solubility of CO increases significantly, being highest for ethanol.

Correlation of Data. It was thought desirable to develop a single correlation for each system to account for changes in liquid-phase composition as well as the temperature. For this purpose, the following form of empirical equation was found to represent the solubility data satisfactorily.

$$\ln H = k_1 + k_2/T + k_3(X)(1/298 - 1/T) + k_4 \ln (1 + X) \quad (2)$$

Solubility data were fitted to eq 2 by using a linear least-squares analysis program and the values of the constants evaluated for each system are presented in Table VII. The results predicted by eq 2 were found to agree with the experimental data within an average error of about 3%.

Table VII. Constants for Eq 2

no.	system	k_1	k_2	k_3	k_4	% error
1	methanol + water	−11.16	−199.6	−25.73	3.543	4.26
2	acetic acid + water	−11.10	−214.4	−60.5	2.972	4.70
3	ethanol + water	−11.11	−211.0	160.2	3.447	3.80
4	propionic acid + water	−10.99	−229.1	185.3	2.91	1.52

Glossary

A	solubiltiy of CO, m^3/m^3
h	height of the water column in the gas desorption apparatus, m
H	Henry's law constant of solubility, kmol/(m^3·kPa)
P	barometric pressure, kPa
P_{CO}	partial pressure of CO in the autoclave, kPa
P_w	vapor pressure of the solvent mixture at temperature T_w, kPa
S	solubility of CO, kmol/m^3
T	temperature in the autoclave, K
T_w	temperature in the gas buret, K
V	volume of the water collected by displacement of CO, m^3
v	volume of the liquid sample taken, m^3

X mole fraction of the organic component in water

Registry No. CO, 630-08-0; methanol, 67-56-1; acetic acid, 64-19-7; ethanol, 64-17-5; propionic acid, 79-09-4.

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Solubility of Aromatic Hydrocarbon Solids in Mixtures of Benzene and Cyclohexane

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The solubilities of five solutes, biphenyl, naphthalene, fluorene, phenanthrene, and acenaphthene, in pure benzene and cyclohexane and in mixtures of benzene and cyclohexane, have been determined. The activity coefficients of the five solutes in cyclohexane are correlated to within an average of 0.6% by Wilson's equation compared to 9.3% by the Scatchard–Hildebrand expression. Similarly for the solutes in benzene, the activity coefficients were correlated to within an average of 0.5% and 1.2%, respectively, by the same two methods. For the ternary mixtures Wilson's method correlates the activity coefficients for the 78 measured data points within 1.4% compared to 2.6% by the Scatchard–Hildebrand expression. As expected, when the solution exhibits a significant deviation from ideal behavior, regular solution theory becomes inadequate and Wilson's equation is proposed as a more appropriate correlation. The solubility data can also be correlated as functions of reduced temperature T_m/T where T_m is the melting point temperature.

Introduction

The correlation of equilibrium solubility behavior of aromatic hydrocarbon solutes in binary mixtures of benzene and cyclohexane by both Scatchard–Hildebrand regular solution theory and Wilson's equation requires four sets of experimental data: solubilities of the aromatic hydrocarbons in pure benzene and pure cyclohexane, VLE data for the benzene–cyclohexane system, necessary to determine the parameters of the chosen activity coefficient model, and solubilities of the aromatic hydrocarbons in the three binary solvent mixtures.

In the present study, the solubilities of the five aromatic hydrocarbons, biphenyl, naphthalene, fluorene, phenanthrene, and acenaphthene have been determined (from around room temperature to near the melting points of the solids) in both pure and mixed solvents for use with the extensive VLE data for the benzene–cyclohexane system that has been compiled by Gmehling et al. (*1*) Experimental activity coefficients of solutes in ternary systems are evaluated by using these data and compared with values predicted from theory.

Experimental Work

Biphenyl and naphthalene were purchased from Eastman Kodak, phenanthrene and fluorene from Eastern Chemical, and acenaphthene from British Drug Houses. All samples, except acenaphthene, were purified further by liquid chromatography on activated alumina by using toluene as eluant. The solids were then recrystallized and toluene removed by evaporation in a vacuum. After recrystallization, fluorene was batch distilled to remove low boiling impurities and acenaphthene was zone refined.

The purified samples were analyzed on a GC mass spectrometer and their melting points determined. The results were as follows: biphenyl 99.67 wt (342.6 K), naphthalene 99.21 wt % (352.8 K), fluorene 97.85 wt % (387.6 K), phenanthrene 98.67 wt % (372.8 K), and acenaphthene 99.2 wt % (366.5 K). The liquid samples of benzene and cyclohexane were "gold label" Aldrich products and were used without further purification.

Mixtures of predetermined composition of single solids with the pure and mixed solvents were made in glass ampules, and sealed while they were frozen in a Dewar bottle containing dry ice. The ampules were then placed in a constant temperature bath, and the temperature at which the last trace of solid disappeared was visually determined, while the bath temperature was increased at a rate of 0.1 K every 1200 s near the expected melting temperature, with the ampules rotated at a speed of 0.25 rps. Measurements were made at least twice for each ampule. The experimental system and techniques were similar to that of McLaughlin and Zainal (*2*, *3*). The solubility data taken in this study are listed in columns 1 and 2 of Tables I–III.

Correlation and Discussion

Equations for the Solubility of Solids. The solubility of a solid in a liquid can be used to evaluate the activity coefficient of the solute component in the solution by eq 1. This equation is valid

$$-\ln X_2 = \frac{\Delta S_2{}^{f}}{R}\left\{\frac{T_m}{T} - 1\right\} - \frac{\Delta C_{p_2}{}^{f}}{R}\left\{\frac{T_m}{T} - 1\right\} + \frac{\Delta C_{p_2}{}^{f}}{R}\ln\frac{T_m}{T} + \ln\gamma_2 \qquad (1)$$

if no phase transition takes place in the solid phase between the system temperature T and the solute melting temperature T_m, and if the Poynting correction is neglected. When a phase transition does take place between T and T_m eq 1 must be modified to include the effect of the transition on solubility at solution temperatures below the transition point. For a first-

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