Solubility of Hydrogen, Carbon Monoxide, and 1-Octene in Various Solvents and Solvent Mixtures

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The solubility of H_2 has been measured as a function of pressure in ethanol + water and various solvents at (298 and 323) K. The results are compared with theoretical predictions for H_2 in different solvents and some mixtures and found to agree within ±10% error, except for acetonitrile. The solubility of CO in 1-octene has also been measured. Liquid−liquid equilibrium for the 1-octene + water + ethanol system was measured at (298 and 323) K, but the predictions of these data by the UNIFAC−UNIQUAC models were not found to be satisfactory, except for higher 1-octene concentrations in water (>6% w/w) for which the predictions were within 10% error.

Introduction

The solubility of gases in liquid media is an important parameter required for the interpretation of rate data in gas−liquid, gas−liquid−liquid, and gas−liquid−solid reactions. For systems involving two immiscible liquids, liquid−liquid equilibrium data are also necessary. In recent years, biphasic hydrogenation and hydroformylation reactions using water soluble catalysts have gained considerable interest, as these systems provide easy separation of the catalyst and products. The solubility and equilibrium data for H_2, CO, and olefin in the liquid medium are necessary to understand such reactions. These data are also useful in studies on a variety of carbonylation and hydroformylation reactions using homogeneous catalysis. Very often a cosolvent such as ethanol, acetone, acetonitrile, etc. is used to solubilize the olefin and other reactants in water (Hablot et al., 1992), and hence the equilibrium data in the presence of cosolvent are also necessary. A large volume of solubility values of H_2 (Young, 1981) and CO (Cargill, 1990) in a variety of solvents is available. Solubility of H_2 in water and ethanol is available at ambient conditions (Linke and Siedell, 1958), but limited data are available at higher temperatures and pressures (Cargill, 1978). The solubility of H_2 in 1-octene has been reported by Sokolov and Polyakov (1977). For CO + water and CO + ethanol, Dake and Chaudhari (1985) have reported solubility data over a wide range of temperature (298 K to 448 K) and pressure (2.2 MPa to 6.3 MPa). The liquid−liquid equilibrium data for 1-octene + water and the effect of ethanol are also not investigated in detail, and limited data are available only at 273 K and 298 K (Nowakowska et al., 1956). In this paper, we report the solubility of H_2 in water, ethanol, 1-octene, acetone, and acetonitrile and ethanol + water mixtures, of CO in 1-octene, and of 1-octene in water and water + ethanol at 298 K and 323 K. The equilibrium data for these systems were also predicted theoretically by thermodynamic relationships and compared with the experimental results.

Experimental Section

The solubility of H_2 and CO was measured in a 5.0×10^{-4} m^3 capacity stirred autoclave (Autoclave Engineers) designed for 39 MPa pressure. The equipment was provided with automatic temperature control and a pressure recording system. The temperature of the liquid in the reactor was controlled within ±1 K. A pressure transducer having a precision of ±1 kPa was used to measure the autoclave pressure. The transducer signal was transmitted to an acquisition card RTI 800 (Analog device) and recorded on-line by a PC. Hydrogen and carbon monoxide gases with purity of 99%, supplied by AGA, were used. The solvents, ethanol, acetone, acetonitrile, and 1-octene with purity greater than 98%, procured from Aldrich, were used as received.

In a typical experiment for the measurement of solubility of H_2 and CO, a known volume (2.5×10^{-4} m^3 to 3.0×10^{-4} m^3) of solvent was introduced into the autoclave and the contents were heated to a desired temperature. After the thermal equilibrium was attained, the void space in the reactor was carefully flushed with the solute gas and pressurized to the level required. The contents were then stirred for about 10 min to equilibrate the liquid phase with the solute gas. In general, it required about 5 min to saturate the liquid phase. The change in the pressure in the autoclave was recorded on-line as a function of time till it remained constant, indicating saturation of the liquid phase. From the initial and final pressure readings, the solubility was calculated in mole fraction as

$$\chi_A = (P_i - P_A)V_g/RTV_L\rho_s \tag{1}$$

where χ_A represents the mole fraction of the solute gas in the liquid phase at the partial pressure of the solute gas prevailing at P_A, P_i and P_A are the initial and final pressure readings in the autoclave, V_g and V_L are the volumes of the gas and liquid phases, respectively, R is the gas constant, T is the temperature, and ρ_s is the molar density of the liquid. Here it is assumed that under the equilibrium conditions the amount of dissolved gas molecules in the liquid phase is negligible compared to the amount of the solvent molecules. Following this procedure, the solubility data were obtained for hydrogen in ethanol, water, acetone, acetonitrile, and ethanol + water mixtures and for CO in 1-octene at 298 K and 323 K. The Henry's law constant, K_H, was calculated as

$$K_H = P_A/\chi_A \tag{2}$$

where P_A represents the partial pressure of the solute gas.

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S0021-9568(96)00024-6 CCC: $12.00

Table 1. Solubility of Hydrogen and Carbon Monoxide in Different Solvents

solvent	solute	T/K	$10^{-3}K_H$/MPa
1-octene	hydrogen	298	0.156
1-octene	hydrogen	323	0.135
ethanol	hydrogen	298	0.513
ethanol	hydrogen	323	0.441
water	hydrogen	298	7.036
water	hydrogen	323	7.456
acetone	hydrogen	298	0.365
acetone	hydrogen	323	0.292
acetonitrile	hydrogen	298	0.545
acetonitrile	hydrogen	323	0.476
1-octene	carbon monoxide	323	0.063

Table 2. Comparison of Observed and Literature Values of Solubility of Hydrogen ($10^4\chi_A$) at 0.101 325 MPa Pressure

solvent	T/K	exptl.	lit.	ref
acetone	298	2.74	2.87	Brunner (1985)
acetone	323	3.43	3.50	Brunner (1985)
acetonitrile	298	1.84	1.78	Brunner (1985)
acetonitrile	323	2.10	2.16	Brunner (1985)
ethanol	298	1.95	2.04	Katayama and Nitta (1976)
water	298	0.14	0.14	Crozier and Yamamoto (1974)

For the measurement of the solubility of 1-octene in water and water + ethanol, a 5 × 10^{-5} m^3 stirred glass vessel with an agitator and temperature control was used. For measurement of equilibrium data, several ternary mixtures of known quantities of 1-octene, ethanol and water were prepared and equilibrated at a desired temperature in a closed system. After 1 h, during which the equilibrium is proved to be attained, stirring was stopped and the contents allowed to separate into two phases at the same temperature. The samples of the two phases were analyzed for 1-octene and ethanol by GC and the exact volumes of the two phases recorded. The water content in the organic phase was analyzed by the Karl-Fischer method using a Mettler DL-18 Karl-Fischer titrator. The GC analysis of 1-octene and ethanol in water was carried out using an HP 5890 GC with a capillary column packed with FFAP and of 20 m length. From the concentration analysis and the initial quantities, the total mass balance in the equilibrated samples was found to be in agreement within ±1%.

Results and Discussion

Solubility Data. The solubility of H_2 in water, ethanol, acetone, acetonitrile, 1-octene, and ethanol + water was measured at 298 K and 323 K in a pressure range of 0.3 MPa to 2.0 MPa. The effect of pressure was found to be linear for all the systems, conforming to Henry's law. The results are presented in Table 1 as Henry's constants (K_H). A comparison of these results with literature data indicated an agreement within 1% to 4% error, as shown in Table 2. Further, the solubility of H_2 in ethanol + water was also determined at different concentrations of ethanol in water at 298 K and 323 K and 0.3 MPa to 2.0 MPa pressure range. These results are presented in Figure 1. The effect of ethanol concentration is very strong, but the temperature effect was found to be very mild. The solubility of CO in 1-octene was determined at 323 K and different pressures, and these results are also presented in Table 1.

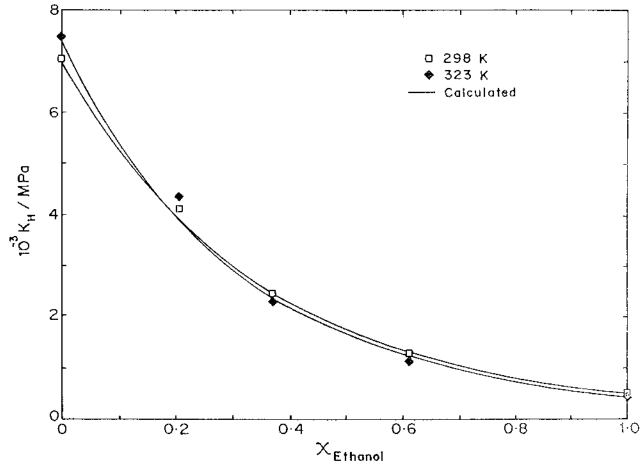

Figure 1. Solubility of hydrogen (K_H) in aqueous ethanol mixtures, comparison of experiments with theory.

The solubility data for H_2 in water, ethanol, and water + ethanol were also compared with theoretical predictions using the correlations proposed by Prausnitz and Shair (1961) and Yen and McKetta (1962). A semi-empirical correlation proposed by these authors for the solubility of gases in pure, nonpolar solvents at atmospheric pressure, based on the theory of regular solutions, is given below:

$$-\ln \chi_A = \ln(f_{As}/f_A) + \phi_s^2 v_A(\delta_s - \delta_A)^2/RT \qquad (3)$$

where χ_A represents the mole fraction of the dissolved solute in the solvent at atmospheric pressure (0.101 325 MPa), f_{As} as f_A are the fugacity of pure gas and hypothetical liquid solute at atmospheric pressure, ϕ_s is the volume fraction of solvent, v_A is the molar volume of gas A, and δ_s and δ_A are the solubility parameters for the solvent and the solute gas, respectively. In eq 3, the volume fraction of the gas can be neglected since the gas H_2 is sparingly soluble in the solvent. The value of ϕ_s can thus be assumed as unity. The parameters v_A and δ_A were obtained from the work of Katayama and Nitta (1976) as 3.73 × 10^{-5} m^3/mol and 7.835 × 10^3 J$^{0.5}$ m$^{-1.5}$, respectively. The parameter f_{As} was calculated from the following equation:

$$f_{As} = -1.50 + 5.90 \times 10^3/(T/\mathrm{K}) - 1.47 \times 10^6/(T/\mathrm{K})^2 + 1.25 \times 10^8/(T/\mathrm{K})^3 \qquad (4)$$

which was developed on the basis of the data reported by Lemcoff (1977) for different temperatures (273 K to 298 K). It is assumed that the extrapolation of the data for 323 K would be applicable. The value of δ_s, the solubility parameter for the solvent, was calculated as

$$\delta_s = (\Delta_{vap}H - RT)/v_s \qquad (5)$$

where $\Delta_{vap}H$ represents the heat of vaporization and v_s the molar volume of the solvent. Equation 5 is valid only for the nonpolar solvents, and Lemcoff (1977) proposed a correction factor to evaluate the value of δ_s for the polar solvents based on the available solubility data for H_2 in various polar solvents. Radhakrishnan et al. (1983) used this method and proposed a new value of the gas solubility parameter depending on the type of solvent. They assumed that for any system, at least one solubility value must be known. The corrected solubility parameter δ_{sc} was calculated as

$$\delta_{sc} = \delta_s/F_c \qquad (6)$$

where F_c, the correction factor is given as

$$F_c = 4.493 \times 10^{-1} + 1.150 \times 10^{-1}[(\delta_s - \delta_A)/\mathrm{J}^{0.5}\ \mathrm{m}^{-1.5}] - 2.187 \times 10^3[(\delta_s - \delta_A)/\mathrm{J}^{0.5}\ \mathrm{m}^{-1.5}]^2 \qquad (7)$$

This relationship was developed using the known solubility

Table 3. Comparison of Experimental and Predicted Values for Hydrogen Solubility ($10^4\chi_A$) at 0.101 325 MPa Pressure

solvent	T/K	exptl.	predicted
acetone	298	2.74	2.94
acetone	323	3.43	3.66
acetonitrile	298	1.84	2.11
acetonitrile	323	2.10	2.67
ethanol	298	1.95	1.99
ethanol	323	2.27	2.53
1-octene	298	6.41	6.62
1-octene	323	7.41	7.98
water	298	0.14	0.14

data at 298 K. The parameter δ_A can be considered the same for polar as well as nonpolar solvents. The solubility values calculated using eq 3 and the above correlations were compared with the experimental data obtained in this work (see Table 3). The theoretical predictions were found to be within a maximum error of ±10% for all the solvents except acetonitrile. For acetonitrile, the error of prediction was 10 to 20% and is not very satisfactory.

For predicting the solubility of a gas in solvent mixtures, the following equation proposed by O'Connell and Prausnitz (1964) was used:

$$\ln \chi_{A,mixt} = \phi_1 \ln \chi_{A,1} + \phi_2 \ln \chi_{A,2} + a_{12}\phi_1\phi_2 \qquad (8)$$

where ϕ_1 and ϕ_2 represent the volume fractions of the two solvents 1 and 2, $\chi_{A,1}$ and $\chi_{A,2}$ are the mole fraction solubilities in the pure solvents 1 and 2, at the pressure of 0.101 325 MPa, respectively, and $\chi_{A,mixt}$ is the mole fraction in the solvent mixture at 0.101 325 MPa. The parameter a_{12} describes the interaction between the two solvents and is given by

$$a_{12} = (\delta_{s,1} - \delta_{s,2})^2(v_{A,1} + v_{A,2})/2RT \qquad (9)$$

For an ideal solution, the interaction parameter a_{12} reduces to zero and the solubility in a mixture is given by the following simplified equation:

$$\ln \chi_{A,mixt} = \phi_1 \ln \chi_{A,1} + \phi_2 \ln \chi_{A,2} \qquad (10)$$

The values of solubilities of H_2 in the ethanol + water mixtures were calculated using eq 10, and the results presented in Figure 1 show an excellent agreement between the observed and predicted values (within <10% error). The correlation given here thus can be useful for extrapolating the data as well as predicting solubilities for other systems.

Liquid–Liquid Equilibrium. The experimental data on the liquid–liquid equilibrium for the 1-octene–ethanol–water system was obtained at 298 K and 323 K for different initial compositions of the mixtures, and the results are presented in Table 4. The data at 298 K were compared (Figure 2) with the previous work (Nowakowska et al., 1956), which agreed within less than ±10% error except for the 1-octene concentration range of 40 to 60% (w/w). In this latter case, the difference was in a range of 15 to 20%. The results were also compared with the theoretical predictions for 323 K using the UNIFAC (Fredenslund et al., 1975) and UNIQUAC (Abrams and Prausnitz, 1975) models, as shown in Figure 3. The predictions agree within ±10% with the experimental data in the region of higher 1-octene concentration in water (>6% w/w), but for lower ethanol concentration, wherein the concentration of 1-octene is also very low, the predictions of UNIFAC and UNIQUAC models are widely different, the error being >50% in some cases. This is due to uncertainty in the interaction parameters used, and perhaps these models can be used to optimize the interaction parameters so that a better prediction of the distribution of the substrate in the two phases can be achieved.

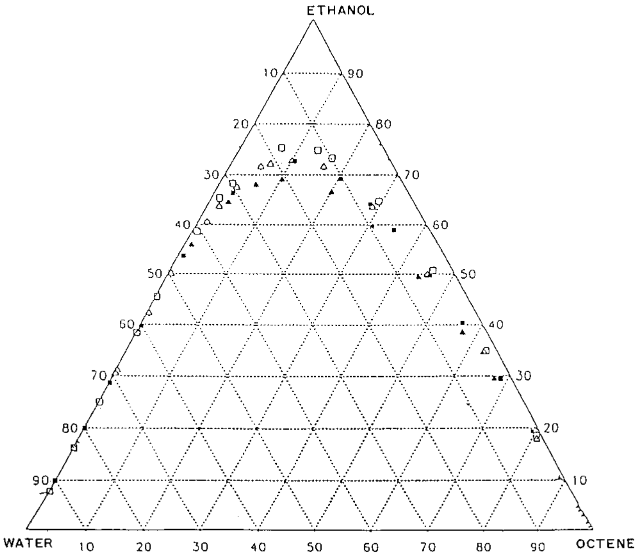

Figure 2. Liquid–liquid equilibrium data of the 1-octene–ethanol–water system, comparison of experiments with literature: (▲) experimental 323 K; (△) Nowakowska et al. (1956) 298 K; (■) experimental 298 K; (□) Nowakowska et al. (1956) 273 K.

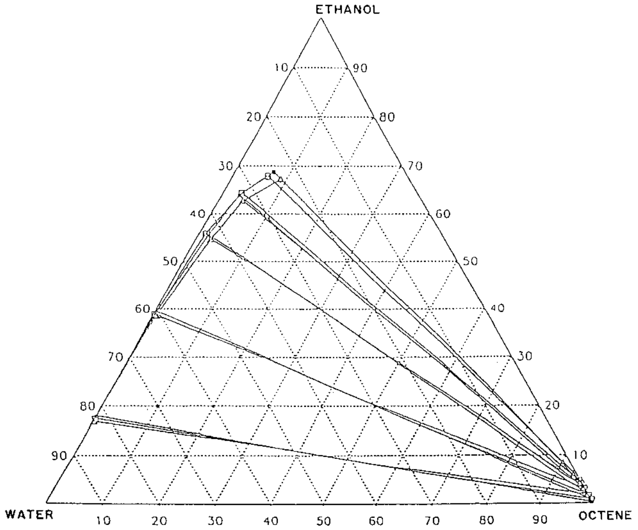

Figure 3. Liquid–liquid equilibrium data of the 1-octene–ethanol–water system at 323 K, comparison of experiments with theory: (■) UNIQUAC; (△) UNIFAC; (□) experimental.

Table 4. Experimental Liquid–Liquid Equilibrium Data for the 1-Octene–Ethanol–Water System at 298 and 323 K

aqueous phase (% w/w)			organic phase (% w/w)		
water	ethanol	1-octene	water	ethanol	1-octene
			298 K		
80.48	19.50	0.02	0.02	0.70	99.28
59.09	40.62	0.29	0.03	0.88	99.09
44.04	55.09	0.87	0.05	2.22	97.73
25.82	68.69	5.49	0.15	3.08	96.77
			323 K		
82.42	17.54	0.04	0.04	0.82	99.14
60.83	38.85	0.32	0.06	1.71	98.23
42.94	55.99	1.11	0.10	3.22	96.68
32.28	64.57	3.15	0.15	4.27	95.58
26.04	67.96	6.00	0.19	4.98	94.83

Conclusions

The solubility of H_2 in various solvents and solvent mixtures and CO in 1-octene are reported at 298 K and 323 K and at different pressures. The data for H_2 in pure solvents and ethanol + water agreed with the theoretical predictions within ±10% maximum error except in acetonitrile as a solvent, for which the error was up to 20%. The liquid−liquid equilibrium data for the 1-octene + ethanol + water system was also obtained at 298 K and 323 K. These data agreed with the predictions of the UNIFAC−UNIQUAC models within ±10% error for higher 1-octene concentrations in water (>6% w/w range) but did not agree for the lower 1-octene concentrations (<6% w/w). Thus, there is a need to further improve the theoretical models and particularly the evaluation of the interaction parameters for systems of practical interest. The data presented here are directly relevant to biphasic hydrogenation and hydroformylation of 1-octene using water soluble catalysts.

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Received for review January 26, 1996. Revised manuscript received May 7, 1996. Accepted August 13, 1996.[⊗]

JE960024E

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1996.