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Solubility of Hydrogen, Carbon Monoxide and 1-Decene in Water, Toluene and Water-*N*-methyl-2-pyrrolidone Biphasic Solvent Mixtures

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The solubility of carbon monoxide and hydrogen has been determined experimentally as a function of their pressure in toluene, water and water-*N*-methyl-2-pyrrolidone (70:30 v/v) mixtures in the 383-403 K temperature range. The value of Henry's constant for hydrogen and carbon monoxide was determined in all three solvent systems. Pressure had a linear influence on all systems, as predicted by Henry's law. Through experimentation, the solubility of 1-decene in the organic and aqueous phase was established. The experimental data for the liquid-liquid equilibrium of 1-decene in a toluene and water-*N*-methyl-2-pyrrolidone mixture has been evaluated in the temperature range of 383-403 K. Temperature has a negligible effect on 1-decene solubility in the aqueous phase, but a significant effect in water-*N*-methyl-2-pyrrolidone (70:30 v/v) combination. The study of the solubility of hydrogen and carbon monoxide in organic and water-*N*-methyl-2-pyrrolidone mixture can be used for the kinetic study.

Keywords: Solubility, Hydrogen, Carbon monoxide, 1-Decene, Water, Toluene, *N*-Methyl-2-pyrrolidone, Biphasic solvent mixtures.

INTRODUCTION

The solubility of gases in liquid media is an important parameter for understanding the kinetics and mass transfer effects of gas-liquid, gas-liquid-liquid and gas-liquid-solid reactions. The study of gas solubility in liquid media also helps in the design and optimization of processes and technologies [1-3]. Liquid-liquid equilibrium data are also required in systems with two immiscible liquids. The simplest method of estimating gas solubility is to apply Henry's law, if the constant is known or it can be determined by using the experimental solubility data. Biphasic reactions (hydrogenation and hydroformylation) using water-soluble catalysts have recently gained significant interest, as these systems provide easy separation of the catalyst and products [4]. Understanding such reactions requires data on the solubility and equilibrium of hydrogen, carbon monoxide and 1-decane in the liquid medium. Additionally, these data are also useful in studies on a variety of reactions involving homogeneous catalysis [5-9]. A cosolvent, such as ethanol, acetone, acetonitrile, *N*-methyl pyrrolidone (NMP), *etc*. is frequently used to solubilize the olefin and other reactants in water; thus, equilibrium data in the presence of cosolvent are also required [10].

A large amount of solubility values of hydrogen and carbon monoxide in several solvents is available in the literature [11, 12]. The solubility of hydrogen in water and ethanol is available at ambient conditions, but there is limited data at higher temperatures and pressures [13,14]. However, neither experimental data nor any theoretical model on the solubility of hydrogen and carbon monoxide in the toluene, water and water-NMP solvent mixture is available in the literature. In the above context, we have investigated the experimental solubilities of hydrogen and carbon monoxide as a function of pressure in toluene, water and a water-NMP solvent mixture relevant to the hydroformylation process. These solvents are preferred because of their high boiling point, thermal stability and inertness to the homogeneous catalyst, olefin, hydrogen, carbon monoxide and reaction products. The liquid-liquid equilibrium data for 1-decene in toluene and water-NMP mixture at 383-403 K are also reported.

EXPERIMENTAL

The solvents, toluene and *N*-methyl-2-pyrrolidone (NMP) were freshly distilled and degassed before use. All operations were carried out using distilled degassed water. Matheson Gas Co., U.S.A. provides carbon monoxide (> 99.8% pure), while Indian Oxygen Ltd., Mumbai, India supplies hydrogen and nitrogen, which are used directly from cylinders. The syn gas with a 1:1 ratio of H_2:CO was prepared by mixing hydrogen and carbon monoxide in a reservoir. All the experiments were conducted in an argon atmosphere.

Experimental procedure: The solubility of CO and H_2 in toluene, water and water-NMP mixture was determined in the temperature range of 383-403 K using a method described by Chaudhari *et al*. [5]. Hydrogen and carbon monoxide solubility were measured in a stirred autoclave having a volume of 5×10^{-5} m^3 and a pressure of 13.5 MPa. The equipment was provided with automatic temperature control and a pressure monitoring system. The liquid temperature in the reactor was precisely controlled within ±1 K. A pressure transducer with a precision of ±1 kPa was used to measure autoclave pressure.

In a typical experiment to measure the solubility of H_2 and CO, a known volume (2.5×10^{-5} m^3) of solvent was added to an autoclave and heated to a specific temperature. After achieving thermal equilibrium, the void space in the reactor was carefully flushed with a solute gas (CO or H_2) and pressurised to the required level (P_i). The contents were then stirred for about 10 min to bring the liquid phase into equilibrium with the solute gas. Saturating the liquid phase typically took about 5 min. The pressure drop in the autoclave was measured over time until it reached a constant value, indicating liquid phase saturation at the final pressure (P_f).

To measure the solubility of 1-decene in toluene and water-NMP mixture, a 5×10^{-5} m^3 stirred glass vessel with an agitator and temperature control was used. To measure equilibrium data, several ternary mixtures of known quantities of 1-decene in toluene and water-NMP mixture, were prepared and equilibrated in a closed system at the desired temperature. After 1 h, when equilibrium was established, stirring was stopped and the contents were allowed to separate into two phases at the same temperature. The samples from the two phases were GC analyzed for 1-decene and toluene, and the exact volumes of each phase were recorded. The water content of the organic phase was determined using the Karl-Fischer method with a Mettler DL-18 Karl-Fischer titrator. The GC analysis of 1-decene was performed on an HP-5 capillary column (30 M × 320 µm × 0.25 µm film thickness with a stationary phase of phenyl methyl siloxane). For this purpose, an HP 6890 gas chromatograph with HP Chemstation software and an autosampler unit was used. The concentration analysis and initial quantities revealed that the total mass balance in the equilibrated samples agreed within (±1%).

RESULTS AND DISCUSSION

The solubility of hydrogen gas in water, toluene and water-NMP mixtures was investigated at temperatures ranging from 383 K to 403 K and pressures ranging from 2-7 MPa. All the pressures are corrected to the vapour pressure of solvents at the corresponding temperature. Here, it is assumed that the number of solvent molecules in the liquid phase is much more than the number of dissolved gas molecules under equilibrium conditions. From the initial and final pressure readings, the solubility was calculated using eqn. 1:

$$\chi_a = \frac{(P_i - P_f)V_g}{RTV_{L\rho s}} \tag{1}$$

where χ_a represents the solubility (kmol m^{-3}) of the solute gas prevailing at P_i and P_f are the initial and final pressure readings in the autoclave (MPa), V_g and V_L (m^3) are the volumes of the gas and liquid phases, respectively, R is the gas constant T is the temperature (K) and ρ_s is the molar density of liquid.

The experimental results are shown in Tables 1-3. Temperature has a significant effect on the solubility of hydrogen gas. The solubility of hydrogen in water, toluene and water-NMP mixtures increases as temperature and pressure increase.

Similarly, the solubility of carbon monoxide gas in water, toluene and a water-NMP mixture was measured at temper-

TABLE-1
SOLUBILITY OF HYDROGEN IN WATER AT 383-403 K

Particulars	383 K			393 K			403 K		
Initial pressure (psi)	469	855	1089	365	675	938	352	660	909
Final pressure (psi)	459	843	1075	351	660	922	336	643	890
Difference (psi)	10	12	14	14	15	16	16	17	19
Solubility (mol)	0.0009	0.0011	0.0013	0.0012	0.0013	0.0014	0.0014	0.0015	0.0016
Solubility (kmol/m^3)	0.0364	0.0436	0.0509	0.0496	0.0532	0.0567	0.0553	0.0588	0.0657

Experimental conditions: T: 383-403 K, P_{H2}: 2.4-7.5 MPa, solvent: water, time: 0.2 h, agitation speed: 20 Hz, total volume: 2.5×10^{-5} m^3

TABLE-2
SOLUBILITY OF HYDROGEN IN TOLUENE AT 383-403 K

Particulars	383 K			393 K			403 K		
Initial pressure (psi)	336	661	842	465	716	859	437	688	829
Final pressure (psi)	323	646	825	448	697	838	417	665	805
Difference (psi)	13	15	17	17	19	21	20	23	24
Solubility (mol)	0.0012	0.0014	0.0015	0.0015	0.0017	0.0019	0.0017	0.0020	0.0021
Solubility (kmol/m^3)	0.0473	0.0546	0.0618	0.0603	0.0673	0.0744	0.0691	0.0795	0.0830

Experimental conditions: T: 383-403 K, P_{H2}: 2.3-5.9 MPa, solvent: toluene, time: 0.2 h, agitation speed: 20 Hz, total volume: 2.5×10^{-5} m^3

TABLE-3
SOLUBILITY OF HYDROGEN IN WATER-NMP (70:30) MIXTURE AT 383-403 K

Particulars	383 K			393 K			403 K		
Initial pressure (psi)	410	800	977	442	677	939	431	676	883
Final pressure (psi)	402	789	964	432	664	923	418	660	865
Difference (psi)	8	11	13	10	13	16	13	16	18
Solubility (mol/25 mL)	0.0007	0.0010	0.0012	0.0009	0.0012	0.0014	0.0011	0.0014	0.0016
Solubility (kmol/m^3)	0.0291	0.0400	0.0473	0.0354	0.0461	0.0567	0.0449	0.0553	0.0622

Experimental conditions: T: 383-403 K, P_{H2}: 2.8-6.7 MPa, solvent: water-NMP (70:30), time: 0.2 h, agitation speed: 20 Hz, total volume: 2.5×10^{-5} m^3

atures ranging from 383 K to 403 K and pressures ranging from 2-7 MPa and the experimental data are presented in Tables 4, 5 and 6, respectively. Temperature has a significant effect on the solubility of carbon monoxide gas. Carbon monoxide solubility increases with increasing temperature and pressure in water, toluene and water-NMP mixtures. The non-polar character of toluene results in much-increased solubility of both these gases in it.

According to Henry's law, the concentration of gas dissolved in a liquid is proportional to its partial pressure above the liquid. The gas solubility was determined for both gases in kmol/m^3 for each gas at a given pressure in MPa. The plot of gas solubility (χ_a) *vs.* gas pressure (P_f) in MPa at different temperatures (383-403 K) provided a straight line, from the slopes of which Henry's constant was determined as acccording to eqn. 2:

$$K_H = \frac{P_f}{\chi_a} \qquad (2)$$

where H is Henry's constant in kmol.m^3/MPa. Fig. 1 shows the plots of Henry's constant for H_2 and CO in toluene, water, and water-NMP mixtures (70:30 v/v) at different temperatures. The extrapolated graph of Henry's constant against H_2 and CO composition provides Henry's constant values at any intermediate solvent-substrate mixture. The values of Henry's constant for H_2 (H_A) and CO (H_B) in toluene, water and water-NMP mixtures (70:30 v/v) are presented in Table-7, for all of the system's pressure effects were found to be linear, obeying Henry's law.

The solubility of 1-decene in aqueous and organic phase was established experimentally. Table-8 shows the experimental data for the liquid-liquid equilibrium of 1-decene in a toluene and water-NMP mixture at a temperature ranging from 393 K to 403 K. The data was found to be compatible with that reported for the solubility of 1-octene in an ethanol-water mixture [5]. In the aqueous phase, temperature has little effect on 1-decene solubility; however, in the water-NMP (70:30 v/v) combination, temperature has a considerable effect. The addition of

TABLE-4
SOLUBILITY OF CARBON MONOXIDE IN WATER AT 383-403 K

Particulars	383 K			393 K			403 K		
Initial pressure (psi)	341	710	892	398	629	780	350	613	868
Final pressure (psi)	332	698	878	384	614	763	334	595	848
Difference (psi)	9	12	14	14	15	17	16	18	20
Solubility (mol)	0.0008	0.0011	0.0013	0.0012	0.0013	0.0015	0.0014	0.0016	0.0017
Solubility (kmol/m^3)	0.0327	0.0436	0.0509	0.0496	0.0532	0.0603	0.0553	0.0622	0.0691

Experimental conditions: T: 383-403 K, P_{CO}: 2.4-6.2 MPa, solvent: water, time: 0.2 h, agitation speed: 20 Hz, total volume: 2.5×10^{-5} m^3

TABLE-5
SOLUBILITY OF CARBON MONOXIDE IN 25 mL TOLUENE AT 383-403 K

Particulars	383 K			393 K			403 K		
Initial pressure (psi)	400	648	805	352	615	832	307	648	769
Final pressure (psi)	382	628	782	330	591	805	283	621	740
Difference (psi)	18	20	23	22	24	27	24	27	29
Solubility (mol/25 mL)	0.0016	0.0018	0.0021	0.0019	0.0021	0.0024	0.0021	0.0023	0.0025
Solubility (kmol/m^3)	0.0655	0.0727	0.0837	0.0780	0.0851	0.0957	0.0830	0.0933	0.1002

Experimental conditions: T: 383-403 K, P_{CO}: 2.4-6.2 MPa, solvent: toluene, time: 0.2 h, agitation speed: 20 Hz, total volume: 2.5×10^{-5} m^3

TABLE-6
SOLUBILITY OF CARBON MONOXIDE IN 25 mL WATER-NMP (70:30) MIXTURE AT 383-403 K

Particulars	383 K			393 K			403 K		
Initial pressure (psi)	428	694	828	317	654	816	303	684	791
Final pressure (psi)	417	680	811	304	638	798	288	665	771
Difference (psi)	11	14	17	13	16	18	15	19	20
Solubility (mol)	0.0010	0.0013	0.0015	0.0012	0.0014	0.0016	0.0013	0.0016	0.0017
Solubility (kmol/m^3)	0.0400	0.0509	0.0618	0.0461	0.0567	0.0638	0.0518	0.0657	0.0691

Experimental conditions: T: 383-403 K, P_{CO}: 2.1-5.7 MPa, solvent: water-NMP (70:30), time: 0.2 h, agitation speed: 20 Hz, total volume: 2.5×10^{-5} m^3

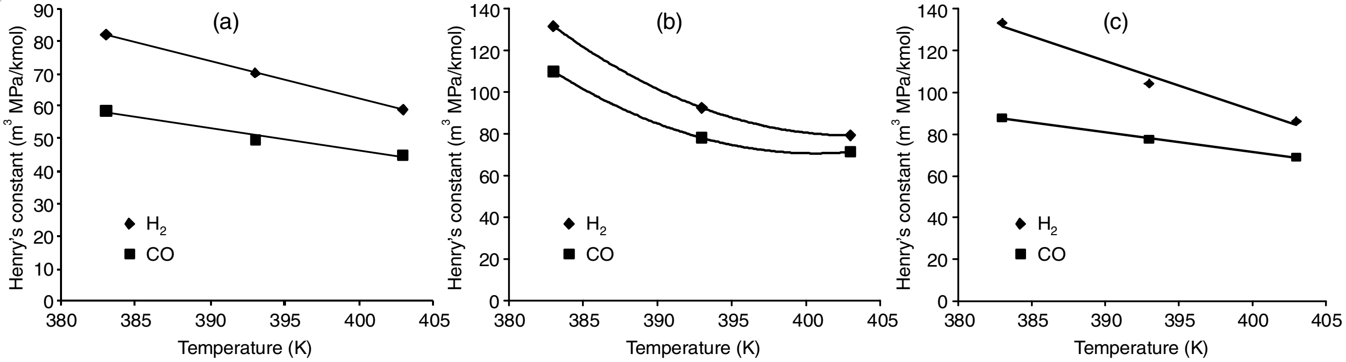

Fig. 1. Henry's constant for H_2 (H_A) and CO (H_B) in (a) toluene, (b) water and (c) water-NMP mixture (70:30 v/v)

TABLE-7
HENRY'S CONSTANT FOR H_2 (H_A) AND CO (H_B) IN TOLUENE, WATER AND WATER-NMP

Solvent	383 K		393 K		403 K	
	H_A (MPa m^3/kmol)	H_B (MPa m^3 /kmol)	H_A (MPa m^3/kmol)	H_B (MPa m^3 /kmol)	H_A (MPa m^3/kmol)	H_B (MPa m^3 /kmol)
Toluene	81.96	58.47	70.42	49.75	58.82	44.84
Water	131.57	109.89	92.59	78.12	79.36	71.42
Water-NMP mixture (70:30 v/v)	133.33	87.71	104.16	77.52	86.20	68.96

NMP to water forms a biphasic solvent system, which can significantly enhance the solubility of non-polar compounds such as hydrocarbons. Indeed, a substantial increase in the solubility of 1-decene in water-NMP mixtures was observed as compared to pure water, indicating the potential utility of water-NMP-toluene as biphasic solvent systems to enhance reaction rates without compromising extraction and separation processes [15]. Henry's constants for hydrogen (H_A) and carbon monoxide (H_B) (Table-7) and partition coefficients for 1-decene (Table-8) were used to evaluate concentrations of H_2 and CO and 1-decene in the aqueous phase, which were necessary for rate analysis [16].

TABLE-8
LIQUID-LIQUID EQUILIBRIUM DATA FOR
1-DECENE-(WATER-NMP)-TOLUENE SYSTEM

Temp. (K)	1-Decene concentration (org) in organic phase (kmol/m^3)	1-Decene concentration (aq.) in aqueous phase (water-NMP) × 10^3 (kmol/m^3)
383	1.057	1.22
393	1.058	1.25
403	1.058	1.34

Conclusion

The solubility of hydrogen and carbon monoxide gases in water, toluene and water-*N*-methyl-2-pyrrolidone (NMP) mixtures was measured at temperatures ranging from 383 K to 403 K and pressures ranging from 2-7 MPa. Present study provides valuable insights into the solubility behaviour of hydrogen, carbon monoxide and 1-decene in water, toluene and water-NMP biphasic solvent mixtures. The liquid-liquid equilibrium data for 1-decene in toluene and water-NMP system were obtained at temperatures ranging from 393 K to 403 K. The results described here are directly applicable to the biphasic hydrogenation and hydroformylation of 1-decene with water-soluble catalysts. The findings emphasize the significance of solvent selection in managing gas and hydrocarbon solubility, as well as the potential of biphasic solvent systems for a wide range of industrial applications.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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