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Vapor–Liquid Equilibria in the Methane–Diethylene Glycol–Water System at 298.15 and 323.15 K

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The water contents of compressed methane gas in equilibrium with water and diethylene glycol–water solutions of 0.156, 0.472, and 0.662 mole fraction water were measured at 298.15 and 323.15 K and pressures of 3, 5, and 8 MPa. The solubilities of methane in the diethylene glycol, water, and diethylene glycol–water solutions were also measured under the same conditions of the water content measurement. The methane solubility data were analyzed with the Krichevsky–Kasarnovsky equation to obtain the Henry constant of methane in the diethylene glycol–water solutions.

Gas dehydration plays an important part in gas purification processes. Diethylene glycol and triethylene glycol are effective gas dehydrating agents. A knowledge of the vapor–liquid equilibria in the gas–glycol–water system is helpful in designing an effective dehydration system. Takahashi et al. (*1*) have reported the vapor–liquid equilibrium data in the carbon dioxide–diethylene glycol–water and carbon dioxide–triethylene glycol–water systems. In this study, we measured the vapor–liquid equilibria in the methane–diethylene glycol–water system at 298.15 and 323.15 K and pressures of 3, 5, and 8 MPa.

Among the binary systems made up of methane, diethylene glycol, and water, the vapor–liquid equilibrium data for the methane–water system have been studied extensively. The solubility of methane in water was measured by Michels et al. (*2*) at temperatures from 298.15 to 423.15 K and at pressures up to 20 MPa, by Culberson and McKetta (*3*) at temperatures from 298 to 444 K and at pressures up to 69 MPa, and by O'Sullivan and Smith (*4*) at temperatures from 323 to 398 K and at pressures up to 61 MPa. The water content in methane was measured by Olds et al. (*5*) at temperatures from 310.7 to 510.8 K and at pressures up to 69 MPa, and by Rigby and Prausnitz (*6*) at temperatures from 298.15 to 373.15 K and at pressures up to 9.3 MPa. The vapor–liquid equilibria in the methane–water system were measured by Gillespie and Wilson (*7*) at temperatures from 323.15 to 588.71 K and at pressures up to 14 MPa. The vapor–liquid equilibria in the diethylene glycol–water system was measured by Jelinek et al. (*8*). Russell et al. (*9*) measured the vapor–liquid equilibria in the natural gas (94% methane)–aqueous diethylene glycol (5 wt % water) system at a temperature of 310.93 K and at pressures up to 13.8 MPa.

Experimental Procedure

The measurements of this study were made in a vapor recirculating static apparatus. The schematic diagram is shown in Figure 1. The equilibrium cell is a 100 cm^3 dual window model constructed by Ruska Instrument Corp. Samples were withdrawn from the equilibrated phases through $^1/_{16}$-in. 316 stainless steel tubing. The bath temperature was controlled to within ±0.02 K with a thermistor controller and measured by the mercury thermometer, which was calibrated by a Leeds-Northrup platinum resistance thermometer with an accuracy 0.01 K. The pressure of the cell was measured with a strain gauge pressure transducer calibrated periodically by a dead weight pressure gauge. The accuracy of the pressure measurement was estimated to be 1 kPa. To promote attainment of equilibrium, the vapor phase was circulated by means of a magnetic recirculation pump. The function of the pump was to withdraw the vapor from the top of the cell and discharge the vapor into the bottom of the cell. After the vapor was recirculated about 2 h, the vapor and liquid phases were allowed to remain stationary to ensure a complete separation of the phases.

The diethylene glycol–water solutions used for the ternary system were prepared by adding water to diethylene glycol until the binary mixture reached a predetermined weight. Weighings were performed on a Sartorius analytical balance capable of precision to at least 0.1 mg. The accuracy of the determination of the composition was within a mole fraction of 0.0002. After the cell was evacuated by a vacuum pump, the solution was fed to the cell. Then methane was bubbled into the solution for 30 min to saturate the solution with methane and discharge other light gases dissolved in the solution. After the degassing procedure, the final composition of the solution was checked by a Karl-Fisher titration apparatus but was found not to change appreciably.

Methane was then added to the cell to adjust the cell pressure. The bath was heated to the desired temperature and the vapor was recirculated by the magnetic pump. Samples of each phases were withdrawn from the cell through $^1/_{16}$-in. tubings, which were heated to prevent a condensation of water and diethylene glycol. After the contents in the sampling line was purged out about 1 cm^3, a sample of 3-5 cm^3 was withdrawn into a sample train and weighed with an accuracy of 0.1 mg.

Sample Analysis

The methane dissolved in the liquid-phase sample was collected in a gas buret with the use of a Toepler pump. The volume of the gas buret was calibrated with mercury to within ±0.01 cm^3. The details of the gas buret and Toepler pump were described by Arai et al. (*10*). The quantity of methane was determined from the pressure, volume, and temperature in the expanded state. The pressure after expansion was

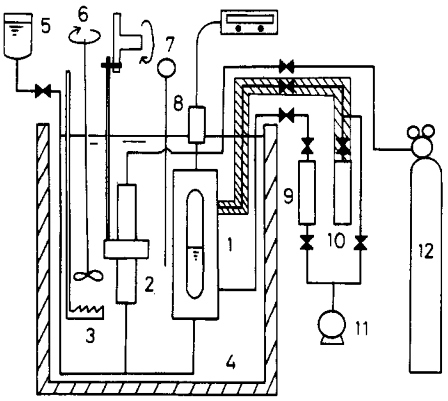

Figure 1. Vapor–liquid equilibrium apparatus: (1) equilibrium cell; (2) magnetic pump; (3) heater; (4) temperature-controlled bath; (5) solution feed tank; (6) stirrer; (7) thermometer; (8) strain gauge pressure transducer; (9) liquid sample train; (10) vapor sample train; (11) vacuum pump; (12) methane cylinder.

Table I. Experimental Data of the Solubility of Methane in Diethylene Glycol–Water Solutions

		methane solubility, mol of CH_4/1000 g of soln				
T, K	P, MPa	1.0[a]	0.662[a]	0.427[a]	0.156[a]	0.0[a]
298.15	3	0.0378	0.0457	0.0657	0.0875	0.0913
	5	0.0600	0.0712	0.106	0.145	0.159
	8	0.0901	0.107	0.158	0.214	0.240
323.15	3	0.0283	0.0392	0.0576	0.0788	0.0865
	5	0.0440	0.0682	0.0991	0.133	0.141
	8	0.0672	0.0937	0.154	0.204	0.224

[a] Mole fraction of water in the solution.

measured by a mercury manometer to within ±0.1 mmHg. The moles of methane were determined from the virial equation of state truncated after the second virial coefficient and the pressure–volume–temperature data. The second virial coefficient data of methane was quoted from Dymond and Smith (*11*). The water content in the vapor-phase sample was determined by a Lockwood-McLorie moisture analyzer with an accuracy of 10 μg as determined by calibration with ethyl ether–water solutions. The moisture analyzer is designed to analyze water content with a precision down to the sub-ppm range and have been described by Bloch and Lifland (*12*). Areas of the resulting chromatographic peaks of the moisture analyzer were determined by the digital integrater. At fixed temperature and pressure, sampling was repeated until three samples taken consecutively gave water contents in agreement to within 1%. It is estimated that all compositions were determined with an accuracy of 5%.

Material

The methane was purchased from Nihon Sanso Co. Ltd., with a stated minimum purity of 99.9 mol %. The distilled water was purchased from Wako Chemical Ltd., with a minimum purity of 99.9 mol %. The reagent-grade diethylene glycol was purchased from Nakarai Chemicals Ltd., with a minimum purity of 99.0 mol %. These chemicals were used without purification. The water content in the diethylene glycol was measured by the Karl-Fisher titration apparatus and was taken into account in the determination of the composition of the diethylene glycol–water solutions.

Table II. Experimental Data of the Water Contents in Compressed Methane Gas in Equilibrium with Diethylene Glycol–Water Solutions

		water content, mg of H_2O/g of CH_4			
T, K	P, MPa	1.0[a]	0.662[a]	0.427[a]	0.156[a]
298.15	3	1.33	0.680	0.410	0.189
	5	0.834	0.424	0.259	0.140
	8	0.484	0.283	0.180	0.101
323.15	3	5.04	2.82	1.72	0.598
	5	3.14	1.78	1.09	0.393
	8	2.37	1.21	0.765	0.267

[a] Mole fraction of water in the solution.

Table III. Henry's Constant for Methane in Diethylene Glycol–Water Solutions

T, K	mole fracn of H_2O in soln	Henry's const, GPa
298.15	1.00	4.12, 4.04[a]
	0.662	1.28
	0.427	0.624
	0.156	0.346
	0.00	0.299
323.15	1.00	5.51, 5.74[a], 5.61[b]
	0.662	1.44
	0.427	0.748
	0.156	0.399
	0.00	0.321

[a] Wilhelm et al. (*15*). [b] Crovetto et al. (*16*) interpolated value.

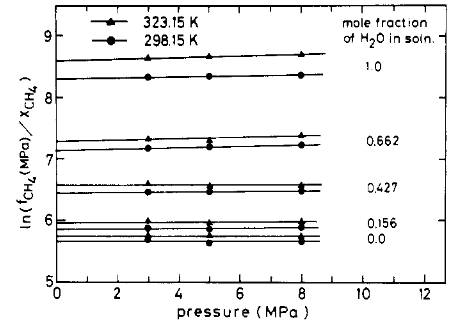

Figure 2. Krichevsky–Kasarnovsky plot for methane–diethylene glycol–water system.

Experimental Results

The experimental data of the solubility of methane in the diethylene glycol–water solutions and those of the water content in compressed methane gas are listed in Tables I and II, respectively. It can be seen from these tables that the water content in compressed methane gas is more affected than the solubility of methane by temperature, pressure, and diethylene glycol concentration. The present data for the water content in methane gas agree well with those of Rigby and Prausnitz (*6*) and Gillespie and Wilson (*7*). The present data for the solubility of methane in water agree with those of Culberson and McKetta (*3*) and Gillespie and Wilson (*7*), while the data of Michels et al. (*2*) deviate from the present data. The Krichevsky–Kasarnovsky equation (*13*) was applied to obtain the Henry constant of methane in the diethylene glycol–water solutions. The fugacity of methane was obtained from the table given by Angus et al. (*14*). The mole fractions of the components in the liquid phase for the ternary system were calculated from the data of the solubility of methane and the feed composition of the diethylene glycol–water solution. It should be a good approximation because the amounts of vaporized water and diethylene glycol are negligible compared with those in the liquid phase. Figure 2 shows the Krichevsky–Kasarnovsky plot for the methane–diethylene glycol–water system. Table III shows the Henry constant data obtained from the Krichevsky–Kasarnovsky plot. The Henry constant of methane in water obtained in this study agreed with those of Wilhelm et al. (*15*) and Crovetto et al. (*16*) within experimental uncertainty. The uncertainty of the Henry constant data of this study is estimated to be 3%.

Registry No. Methane, 74-82-8; diethylene glycol, 111-46-6.

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Solubility of Carbon Monoxide in Aqueous Mixtures of Allyl Alcohol, Diethylamine, and Triethylamine

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The solubility of carbon monoxide (CO) in water–allyl alcohol, water–diethylamine, and water–triethylamine has been determined in a temperature range of 343–403 K and at a equilibrium CO pressure of 3.202 × 10³ kPa. The values of the enthalpy change of solution and Henry's coefficient have been determined. Solubility dependence on temperature and concentration in the liquid phase has been correlated by using the equation ln $H = a + b/T + c(X)(1/303) - (1/T) + d \ln (1 + X)$, and the values of constants have been calculated for each system. The values predicted by using the above equation agreed well with the experimentally determined values within 3–5% error.

Introduction

In any study of the intrinsic kinetics of gas–liquid reactions, data on the solubility of the gas-phase reactant in the liquid medium are essential. In recent years, the study on the gas–liquid reactions involving CO using metal complex catalysts in solution has gained considerable importance (*1–4*). Data on the solubility of CO particularly at higher temperatures and pressures are not available in the literature. The objective of the present work, therefore, was to determine solubility of carbon monoxide (CO) in different solvent mixtures involved in industrial carbonylation process such as carbonylation of allyl alcohol, diethylamine, and triethylamine (*5*). As the data on the solubility of CO in the solvent mixture, which we had studied, were not available in literature at the desired pressures and temperatures, it was decided to determine these solubilities experimentally.

Experimental Section

The solubility of a gas in a liquid at higher pressures and temperatures is generally obtained by taking out a known amount of saturated solution and measuring the dissolved gas in the liquid usually by the volumetric method. This method was used to determine the solubility of CO in aqueous mixtures of allyl alcohol, diethylamine, and triethylamine, as this method has been found to be quite accurate by many investigators (*6*, *7*). The apparatus and procedure to determine the solubility of CO has been described elsewhere (*7*). The carbon monoxide gas used in our studies was obtained from BOC, U.K., and GC analysis shows a purity greater than 99.6%. The solvents used were of A.R. grade and distilled before use. The purities of the solvents were greater than 99.5% as checked by GC. The pressure autoclave (3 × 10⁻⁴ m³) obtained from Parr Instruments Co., USA, was used in the investigations.

The solubility of CO was calculated from the observed volume of gas desorbed from a known amount of liquid withdrawn from the autoclave after equilibration by using the relationship

$$Z = \frac{V - V_1}{V_1}\left[\frac{P - P_w - \frac{h}{13.6}}{101.3}\right]\frac{273}{T_w} \tag{1}$$

As the solubility of the CO measured excludes the solubility of CO at atmospheric pressure, the following equation was used to obtain the actual solubility under the conditions employed to equilibrate the gas with the solvent.

$$S = Z + S_1 \tag{2}$$

In this equation S_1 is the term used for correction.

The reproducibility of the data was also verified by conducting the same experiment twice and the reproducibility was within 2–3% error. The solubility determination of CO was also conducted at a particular chosen pressure using a pressure gauge with the range (0–1.37) × 10⁴ kPa (0–2000 psi) and different temperatures, varying the liquid-phase composition. The errors in the measurements of P, V, T are estimated to be around 3 kPa, 1 × 10⁻⁶ m³, and 0.1 K respectively.

The vapor pressures are calculated from Antoine's equation

$$\ln P_{\text{vap}} = A - \frac{B}{(T + C)} \tag{3}$$

where A, B, and C are Antoine's constants which were taken from the literature (*8*). Since these are predicted values, and previous experience shows that the equation has an accuracy

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