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Experimental Determination of the Solubilities of CO_2 and CH_4 in Diethyl Methylphosphonate

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ABSTRACT: The phase behavior of the binary systems consisting of the organic solvent diethyl methylphosphonate (DEMP) and the gases carbon dioxide (CO_2) and methane (CH_4) is experimentally studied. A synthetic method is used to measure the solubilities. Bubble-point pressures of the system DEMP + CO_2 are reported for CO_2 concentrations ranging from (15.40 to 86.44) mole % and within a temperature range of (283.4 to 338.1) K and compared to the limited experimental data in the literature. Also, bubble-point pressures of the system DEMP + CH_4 are reported for CH_4 concentrations ranging from (5.17 to 15.30) mole % and within a temperature range of (283.2 to 358.5) K, which have never been measured before. The solubilities of CH_4 are much lower than the solubilities of CO_2 in DEMP. Moreover, the temperature has a much larger influence on the CO_2 solubility in DEMP compared to the effect of temperature on the CH_4 solubility.

INTRODUCTION

Solvent selection is an important task to improve and optimize many industrial processes, particularly for chemical process industries where solvents are involved in many process steps, such as the separation of gases, liquids, and solids, reaction processes, washing, and so forth. To evaluate and select the optimal solvent for any specific application, it is possible to rely on chemical information of compounds, such as acid−base properties,[1] hydrogen bonding capabilities, polarity,[2] and so forth. Also, health and safety characteristics must be considered during the solvent selection, and in some cases even heuristic approaches[3] have been used for this purpose. However, this information is only useful to describe general trends, and it is not suitable for obtaining relevant thermodynamic data for solvent separation processes, such as solubilities, selectivities, distribution coefficients, and energy requirements.

The use of predictive equations of state based on group contribution methods,[4] statistical thermodynamics,[5] or quantum mechanics[6] are good alternatives to evaluate and compare thermodynamic properties of different solvents.[7] Group contribution methods, including the unified functional activity coefficient model (UNIFAC)[8] for low pressure systems and the group contribution equation of state (GC-EoS) developed by Skjold-Jørgensen[9] for a wider range of processing conditions, are suitable to predict thermodynamic properties of solvents when their molecular structures share functional groups. Furthermore, if enough group information is available, these methods can be used as designer tools to "build" new and optimal solvents.

Phosphonate-based compounds, which are applied in industrial processes as chelating agents[10] and in pharmaceutical applications as pretreatment drugs for bone-related diseases[11] or as antiviral and as anticarcinogenic agents,[12] are not described by the groups available in the GC-EoS. In addition, the phase equilibria data in literature to obtain the equation of state parameters for the phosphonate group are scarce. As far as the authors know, the vapor pressures of some small alkyl phosphonates[13] and the solubility of DEMP in CO_2[14] are the only phase equilibria data available for these type of molecules. Therefore, the focus of this work is to provide more thermodynamic information on molecules containing the phosphonate group, like the one presented in Figure 1, with the intention to extend the GC-EoS parameters database in the near future. For this purpose, the bubble-point pressures of the systems diethyl methylphosphonate (DEMP) + CO_2 and DEMP + CH_4 are determined in this study by using the synthetic method at temperatures ranging from (283.2 to 358.5) K and pressures up to 11.151 MPa.

EXPERIMENTAL SECTION

Materials. Diethyl methyl phosphonate with a purity of 97 % was obtained from Aldrich Chemical Co and used as received. The CO_2 used in the measurements was supplied by Air Products with a purity of 99.95 %. The CH_4 was supplied by Hoek Loos Netherlands with a purity of 99.995 %.

Procedure. Measurements of the solubilities of CO_2 and CH_4 in DEMP involve bubble-point pressures at different temperatures and compositions. These solubilities were determined using the Cailletet apparatus, which is briefly described here. More detailed information on this setup can be found elsewhere.[15] The Cailletet apparatus can be used to visually determine phase transitions in multicomponent systems by using the synthetic method. A sample of known composition is placed in a thick-walled Pyrex glass tube closed at one side and with the

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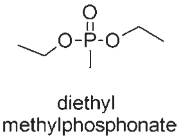

Figure 1. Chemical structure of DEMP.

Table 1. Bubble-Point Pressures for the System (1) DEMP + (2) CO_2. x_2 = Mole Fraction of CO_2 in the Liquid Phase

$x_2 = 0.154$		$x_2 = 0.400$		$x_2 = 0.670$		$x_2 = 0.864$	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
283.4	0.475	283.4	1.427	283.4	2.794	283.3	3.988
288.4	0.535	288.4	1.599	288.4	3.120	288.3	4.453
293.4	0.583	293.3	1.775	293.4	3.470	293.4	4.968
298.2	0.645	298.2	1.945	298.2	3.845	298.1	5.483
303.4	0.703	303.4	2.145	303.3	4.259	303.4	6.099
308.2	0.775	308.1	2.340	308.1	4.686	308.2	6.699
313.5	0.843	313.5	2.566	313.4	5.140	313.4	7.390
313.5	0.849	318.1	2.775	318.6	5.617	318.1	8.055
318.2	0.920	323.5	3.025	323.4	6.161	323.4	8.826
323.5	1.019	328.1	3.245	328.4	6.638	328.2	9.537
328.4	1.065	333.5	3.512	333.5	7.162	333.5	10.378
333.5	1.154	343.5	4.028	343.5	8.262	338.4	11.151
338.1	1.240	348.5	4.288	353.5	9.415		
343.5	1.330	353.4	4.558				
353.5	1.501						

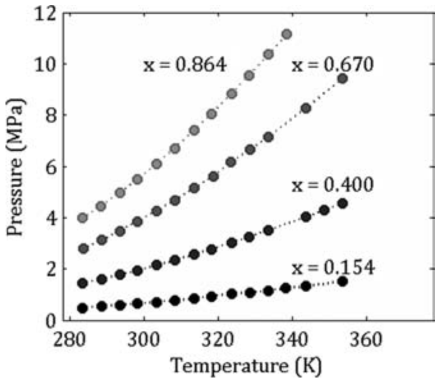

Figure 2. Experimentally determined isopleths in the system DEMP + CO_2. x = mole fraction of CO_2 in the liquid phase.

open end mounted into a stainless steel autoclave. The sample is confined in the top of the tube with mercury, which is also used as a pressure transmitting fluid. A soft iron rod coated with glass is placed within the sample for magnetic stirring, and a dead-weight pressure balance is used to measure the equilibrium pressure. The maximum uncertainty in the pressure measurement in the experimental region of interest is ± 0.005 MPa. In the Cailletet facility the maximum pressure that can be allowed is 15 MPa. The temperature of the experiment is controlled by means of a thermostatic liquid circulating through a glass jacket around the tube. The temperature is measured with a platinum resistance thermometer placed close to the top of the tube, with a maximum uncertainty of ± 0.02 K.

Table 2. Bubble-Point Pressures for the System (1) DEMP + (2) CH_4. x_2 = Mole Fraction of CH_4 in the Liquid Phase

$x_2 = 0.051$		$x_2 = 0.100$		$x_2 = 0.121$		$x_2 = 0.153$	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
283.4	2.810	283.4	5.529	283.2	7.212	283.3	9.830
288.3	2.840	288.4	5.589	288.2	7.262	288.3	9.860
293.4	2.875	293.3	5.639	293.4	7.302	293.4	9.885
298.4	2.901	298.3	5.687	298.4	7.352	298.4	9.915
303.3	2.926	303.4	5.732	303.4	7.383	303.4	9.945
308.4	2.951	308.4	5.774	308.4	7.423	308.4	9.970
313.4	2.976	313.5	5.810	313.4	7.448	313.4	9.991
318.4	2.992	318.4	5.839	318.4	7.478	318.4	10.005
323.4	3.007	323.4	5.868	323.4	7.498	323.4	10.021
328.5	3.026	328.4	5.893	328.2	7.508	328.5	10.026
333.4	3.036	333.5	5.913	333.4	7.518	333.4	10.031
338.4	3.046	338.4	5.929	338.5	7.523	338.4	10.036
343.5	3.062	343.5	5.945	343.4	7.528	343.5	10.036
348.5	3.061	348.4	5.955	348.4	7.523	348.5	10.036
353.5	3.062	353.5	5.966	353.4	7.513	353.4	10.036
358.5	3.067	358.4	5.971	358.4	7.498	358.4	10.031

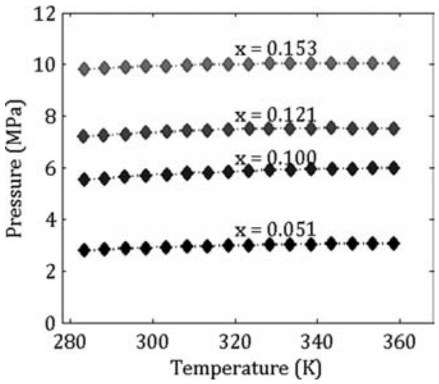

Figure 3. Experimentally determined isopleths in the system DEMP + CH_4. x = mole fraction of CH_4 in the liquid phase.

For the preparation of the sample a known weight of solvent is introduced into the tube and thoroughly degassed with the aid of a high-vacuum pump, while the sample is kept frozen with liquid nitrogen. Several melting and degassing steps of the sample were performed to avoid the presence of any remaining of air that could highly affect the accuracy of the phase equilibrium measurements. Next, a known amount of CO_2 or CH_4 is volumetrically dosed into the tube by pressing the gas with mercury into the tube. Finally, the Cailletet tube is vertically placed into the autoclave with its open end immersed in the mercury present in the autoclave. The maximum uncertainty in the molar concentration of the samples is ± 0.005. Nevertheless, the real error in the molar concentration of the samples is given by the purity of the DEMP and is therefore ± 0.03.

■ RESULTS AND DISCUSSION

The solubility of CO_2 in DEMP at different temperatures and pressures is presented in Table 1, and Figure 2 shows the results graphically. The temperature was varied from (283.4 to 338.1) K

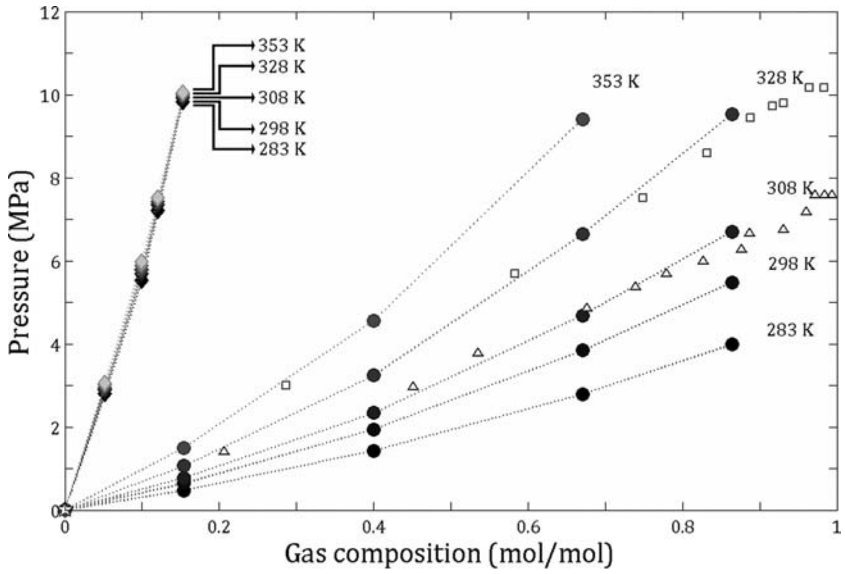

Figure 4. Pressure−composition isotherms for DEMP + CO_2 (●) and DEMP + CH_4 (◆) at (283, 298, 308, 328, and 353) K. Literature data[14] at 308 K (△) and 328 K (□). Literature DEMP vapor pressure[13] (☆).

for four different CO_2 concentrations, and bubble-point pressures were measured. From Figure 2 it is clear that for the isopleths the bubble-point pressures increase with increasing temperature. This means that the solubility of CO_2 in DEMP decreases at higher temperatures, which is a common trend for the solubility of CO_2 in many organic solvents.

Next, the solubility of CH_4 in DEMP at different temperatures and pressures was measured and is presented in Table 2. The bubble-point pressures for four different CH_4 concentrations within the temperature range of (283.2 to 358.5) K are shown in Figure 3. This figure shows that the DEMP + CH_4 system has a completely different solubility behavior compared to the DEMP + CO_2 system. For the DEMP + CH_4 system the bubble-point pressures of the isopleths hardly change (< 0.003 MPa/K) up to higher temperatures. Consequently, the effect of temperature on the bubble-point pressure is almost negligible.

The differences between the two systems can be more easily observed from a pressure−composition diagram, in which the bubble-point pressures are plotted against the mole fraction of CO_2 and/or CH_4 at fixed temperatures as presented in Figure 4. The vapor pressure of pure DEMP[12] and available data for the DEMP + CO_2 system at (308.1 and 328.1) K[13] were also included in this figure. The dashed lines in the figure are only an eye guide.

From Figure 4 it can be observed that bubble-point pressures increase with increasing mole fractions of CO_2 and CH_4 at fixed temperatures. Furthermore, Figure 4 also shows that the solubility of CH_4 in DEMP is significantly lower than the solubility of CO_2 in DEMP. There is a clear difference between the CO_2 solubility data measured in this work and the available data in literature, especially at low CO_2 concentrations: the bubble-point pressures measured in this work exhibit a lower value than the data in literature. This difference could be attributed to the thorough degassing of the samples measured in the present work. From many studies it is known that minor concentrations of dissolved air in the solvent could highly affect the bubble-point pressures, especially for low gas concentrations.[16] Although evidence is missing for our assumption, the observed trend is characteristic for air contamination. Since no experimental data of the system DEMP + CH_4 system have been reported in literature, no comparison could be made.

■ CONCLUSIONS

The solubility of CO_2 and CH_4 in DEMP was measured at temperatures ranging from (283.2 to 358.5) K and pressures up to 11.151 MPa. A different solubility behavior was observed for the DEMP + CO_2 system and the DEMP + CH_4 system within the studied pressure and temperature range. The solubility of CH_4 in DEMP was hardly influenced by temperature changes, while an increase in temperature resulted in lower CO_2 solubilities in the DEMP + CO_2 system. The contribution of this work contributes to the scarce experimental information on the phase behavior of phosphonate-based solvents.

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