Solubility of Diphenyl Carbonate in Pure Alcohols from (283 to 333) K

Dongwei Wei* and Yanhong Pei

Research and Development Center for Petrochemical Technology, Tianjin University, Tianjin 300072, P. R. China

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The solubility of diphenyl carbonate in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol has been measured in the temperature range from (283 to 333) K by a static analytical method. The concentrations of the investigated diphenyl carbonate in saturated solution were analyzed by UV spectrometry. A modified Apelblat eauation was used to correlate the experimental data.

Introduction

Diphenyl carbonate (DPC, $C_{13}H_{10}O_3$, CASRN 102-09-0, Figure 1) is an important chemical intermediate, which has been used extensively for the production of many organic and polymer materials, and it is particularly valuable for the synthesis of polycarbonates since the use of highly toxic phosgene can be avoided.[1,2] The quality of DPC directly impacts the downstream polycarbonate quality, so high-quality DPC is critical for polycarbonate optical media applications. The purification of diphenyl carbonate according to the invention may be performed using crystallization processes.[3,4] To determine the proper solvent and design of an optimized crystallization process, it is necessary to know its solubility in different solvents. In this paper, the solubility of diphenyl carbonate in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol was measured in the temperature range from (283 to 333) K by a static analytical method.

Experimental Section

Chemicals. Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol were purchased from Tianjin Ke-wei Chemical Reagent Co., and all of them were analytical research grade with purity higher than 99.5 mass % with no further purification. Diphenyl carbonate, obtained from Shanghai Shenju Chemical Factory Co., Ltd., was purified by recrystallizing from the solution of ethanol two times. The melting point and purity of DPC determined by differential scanning calorimetry (Mettler DSC30) was 355.95 K, by Carson et al.,[5] to 355 K, and 99.6 mol %.

Apparatus and Procedures. The experimental solubility of DPC in pure alcohol solvents in the temperature range from (283 to 333) K was measured by a static analytical method that was described in our previous work[6] and explained briefly here. The experimental saturated solutions were prepared by excess solute, DPC, in glass vessels containing the solvent. Solubilities were determined by equilibrating the solute with solvent in a water-jacketed vessel with magnetic stirring in a constant-temperature water bath (± 0.05 K) for at least 12 h, followed by a 6 h settling time. The actual temperature in the glass vessel was monitored by a mercury thermometer with an uncertainty of 0.05 K. The fluid between the internal and external glass tube can be exchanged by pressing or relaxing the gas bag at the top of glass tube. Portions of DPC saturated solutions were transferred from the internal glass tube to the volumetric flasks to determine the amounts of samples diluted quantitatively with solvent mixtures using spectrophotometric analysis (SHIMADZU UV-160A). Concentrations of the dilute solutions were determined from absorbance versus concentration calibration curves derived from the measured absorbance of solutions of known mole fractions.

Results and Discussion

UV spectrometry was chosen to determine the concentration of a saturated solution of DPC in the organic solvent. To check the reliability of the experimental method, known masses of DPC were completely dissolved in methanol, and the concentrations of solution were measured by a spectrometer. The average relative uncertainty was 2.5 % ($n = 5$).

The solubilities of DPC in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol with associated standard deviation are listed in Table 1.

According to the solid−liquid-phase equilibrium theory, the relationship between solubility of a solid (1) in a liquid and temperature is described as[7]

$$\ln\left(\frac{1}{\gamma_1 x_1}\right) = \frac{\Delta H_{\mathrm{m},1}}{RT_{\mathrm{t},1}}\left(\frac{T_{\mathrm{t},1}}{T} - 1\right) + \frac{\Delta C_{p,1}}{R}\left(\ln\frac{T_{\mathrm{t},1}}{T} - \frac{T_{\mathrm{t},1}}{T} + 1\right) \tag{1}$$

where x_1 is the solubility and γ_1 the solute activity coefficient. $T_{\mathrm{t},1}$, T, $\Delta H_{\mathrm{m},1}$, and $\Delta C_{p,1}$ are the triple-point temperature, the absolute temperature, the enthalpy of fusion, and the change of the heat capacity of the solute, respectively, and R is the gas constant. For regular solutions, the activity coefficient is given by[8]

$$\ln \gamma_1 = A + \frac{B}{T/\mathrm{K}} \tag{2}$$

where A and B are constants. Introducing γ_1 from eq 2 into eq 1 and subsequent rearrangement results in

$$\ln x_1 = \left[\frac{\Delta H_{\mathrm{m},1}}{RT_{\mathrm{t},1}} - \frac{\Delta C_{p,1}}{R}(1 + \ln T_{\mathrm{t},1}) - A\right] - \left[B + \left(\frac{\Delta H_{\mathrm{m},1}}{RT_{\mathrm{t},1}} - \frac{\Delta C_{p,1}}{R}\right)T_{\mathrm{t},1}\right]\frac{1}{T} + \frac{\Delta C_{p,1}}{R}\ln T \tag{3}$$

Equation 3 can be written as

$$\ln x_1 = a + \frac{b}{T/\mathrm{K}} + c \ln T/\mathrm{K} \tag{4}$$

where a, b, and c are empirical parameters. The c value represents the effect of temperature on the fusion enthalpy, as

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* Corresponding author. E-mail: weidwei@tju.edu.cn.

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Table 1. Mole Fraction Solubility x_1 of DPC in Pure Solvents in the Temperature Range (283 to 333) K

	10^3x_1 (standard deviation) [number of samples]						
T/K	methanol	ethanol	1-propanol	2-propanol	1-butanol	2-butanol	2-methyl- 1-propanol
283	8.601(0.012)[5]	7.325(0.021)[5]	10.08(0.08)[5]	5.055(0.008)[5]	7.308(0.015)[5]	5.685(0.025)[5]	6.555(0.066)[5]
288	10.09(0.09)[5]	8.685(0.020)[5]	10.58(0.21)[5]	7.102(0.055)[5]	9.085(0.043)[5]	6.861(0.031)[5]	7.756(0.035)[5]
293	11.80(0.20)[3]	10.63(0.30)[3]	12.86(0.11)[3]	8.683(0.010)[4]	11.28(0.56)[3]	9.248(0.018)[3]	9.248(0.009)[3]
298	15.32(0.16)[4]	13.41(0.15)[3]	15.50(0.08)[3]	10.50(0.21)[3]	15.50(0.35)[3]	12.23(0.31)[3]	12.12(0.08)[3]
303	19.62(0.33)[3]	18.62(0.22)[3]	20.80(0.55)[3]	15.58(0.10)[3]	22.38(0.46)[3]	17.60(0.21)[5]	15.80(0.43)[3]
308	26.71(0.20)[5]	25.68(0.10)[4]	28.58(0.91)[3]	20.38(0.06)[4]	31.52(0.40)[5]	26.10(0.43)[5]	23.12(0.27)[4]
313	41.67(0.39)[4]	41.38(0.69)[6]	40.20(0.82)[5]	33.08(0.12)[6]	40.55(0.96)[6]	37.00(0.50)[4]	33.54(0.65)[5]
318	70.10(0.24)[4]	70.05(0.82)[8]	61.82(0.40)[8]	51.12(0.55)[8]	68.19(0.40)[7]	61.48(0.79)[6]	54.26(0.40)[7]
323	120.9(0.8)[5]	120.5(0.8)[8]	99.12(0.51)[8]	82.78(0.42)[9]	110.8(1.1)[8]	101.6(0.9)[8]	99.40(0.35)[8]
328		234.9(0.9)[9]	164.8(0.6)[9]	139.6(0.9)[9]	188.9(1.0)[9]	201.8(1.3)[9]	191.0(1.4)[8]
333					364.2(1.4)[9]	430.0(1.0)[9]	425.2(1.3)[9]

Table 2. Optimized Adjustable Parameters of the Modified Apelblat Equation (Equation 4) for DPC Solubility in Various Alcohol Solvents

solvent	a	b	c
methanol	−1783.3	75103	268.04
ethanol	−1866.7	78453	280.68
1-propanol	−1542.8	64817	231.89
2-propanol	−1296.4	52886	195.62
1-butanol	−1366.6	56058	206.12
2-butanol	−1664.6	69033	250.74
2-methyl-1-propanol	−2024.6	85721	304.10

a deviation of heat capacity. The values of a and b reflect the variation in the solution activity coefficient and provide an indication of the effect of solution nonidealities on the solubility of solute.[9] Equation 4 is also called the modified Apelblat equation.[9,10] The experimental data of mole fraction solubility in Table 1 were correlated with eq 4 and were plotted as shown in Figure 2. The values of the three parameters a, b, and c are also listed in Table 2.

From Tables 1 and Figure 2, it was found that the solubilities of DPC in alcohols increase with increase of temperature, but the increment with temperature varies according to different solvents. The molar solubility decreases in the order 1-butanol ≈ 1-propanol > methanol > ethanol > 2-butanol > 2-methanol-1-propanol > 2-propanol at low temperature 298 K and methanol ≈ ethanol > 1-butanol > 2-butanol > 2-methanol-1-propanol ≈ 1-propanol > 2-propanol at high temperature 323 K. The lowest solubility of diphenyl carbonate at 298 K was obtained in 2-propanol giving $x = 1.05 \cdot 10^{-2}$, whereas the highest solubility at 298 K amounted to $x = 1.55 \cdot 10^{-2}$ in 1-propanol and 1-butanol. Thus, the ratio between the highest and lowest solubility is equal to 1.5. All the experimental data were regressed by the modified Apelblat equation for pure alcohol solvents. The experimental solubility and correlation equation in this work can be used as essential models in the manufacturing and purifying processes of diphenyl carbonate in industry.

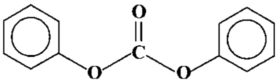

Figure 1. Structure of the diphenyl carbonate molecule.

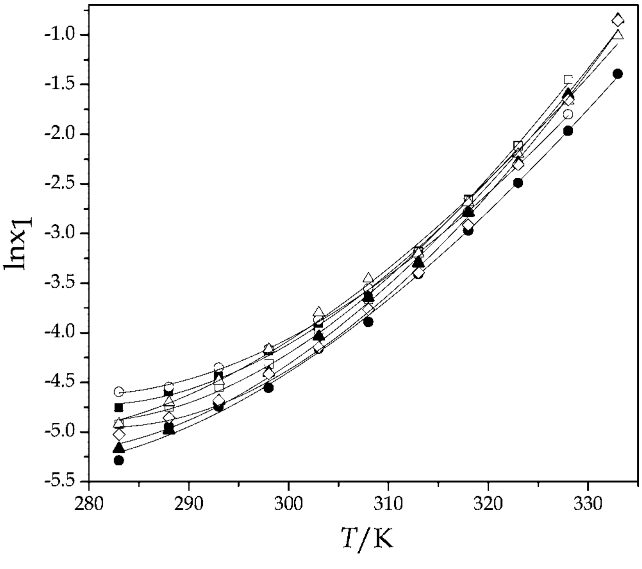

Figure 2. Solubility (x_1) of DPC in various solvents from (283 to 333) K: (a) ■, methanol; □, ethanol; ○, 1-propanol; ●, 2-propanol; (b) Δ, 1-butanol; ▲, 2-butanol; ◇, 2-methyl-1-propanol. The line is the best fit of the experimental data calculated with the modified Apelblat equation.

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