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Propylene Carbonate Cryoscopy

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The melting point and the molal melting point depression constant of propylene carbonate have been determined to be −54.53 ± 0.05 °C and 4.38 ± 0.18 °C m^{-1}, respectively. This melting point differs substantially from the most widely quoted value.

Introduction

The literature reports five estimates of the melting or freezing point of propylene carbonate (PC, 4-methyl-2-dioxolone) ranging from −41 to −73 °C (**1**–**5**), a surprisingly large range for such a value. The most widely quoted value of −49.2 °C (*1*) refers to the freezing point of PC as manufactured, which is ca. 98% pure. This value, which is derived from visual detection of the formation of a solid phase on cooling (*6*), may well reflect an artifact. As manufactured, PC commonly contains a few tenths of a percent of water, and the phase diagram of the PC–water system indicates that for such composition a solid–liquid phase transition occurs a few degrees above the melting point of pure PC (*4*). This suggests that visual detection for the formation of a solid phase on cooling the impure PC may be misconstrued as an indication of the true freezing point, leading to too high an estimate of the freezing point. In addition to this uncertainty in the melting point, the melting point depression constant of PC is unknown. We report here carefully measured values of the melting point and the molal melting point depression constant of highly purified PC.

Experimental Section

After purification by vacuum distillation (*7*), PC contained less than 1 ppm water, which was the only impurity detectable by gas chromatography. All preparative work was performed in a drybox with a moisture content of less than 1 ppm.

The apparatus for determination of the melting point was similar to that described by Anderson (*8*). The temperature probe was a glass-shielded thermistor (Omega No. 44004), whose resistance was monitored with a digital ohmmeter (Data Precision No. 1450) whose calibration is traceable to an NBS standard. The resistance of the Omega thermistor, which was ca. 200 kΩ at −55 °C, could be determined to within 0.3 kΩ, which corresponds to a temperature uncertainty of ±0.02 °C. This thermistor was calibrated over the range of interest against a reference thermistor (Thermometrics No. P85AA392N) which had been calibrated by the manufacturer and whose calibration is certified to be accurate to within ±0.05 °C. A Dewar flask of chloroform maintained at −41 ± 2 °C by a refrigerated immersion coil served as a warming bath.

All cryoscopic measurements were performed under a blanket of dry nitrogen with mechanical stirring. The sample was cooled initially with liquid nitrogen, and, when the temperature dropped below −55 °C, the stirring was interrupted momentarily and several drops of solid–liquid PC seed crystal slurry were added to the supercooled liquid. After the quantity of solid phase had become sufficient that the stirrer action became sluggish, the liquid-nitrogen cooling bath was replaced by the chloroform warming bath. Temperature–time data were then recorded for ca. 1 h during which period the solid phase melted completely and the temperature rose to ca. −46 °C.

Results and Discussion

Initial attempts to measure the freezing point of PC gave poorly reproducible results, a problem which we attribute to the high viscosity of PC just above its freezing point. This reduces the effectiveness of stirring and causes low crystallization velocities, and it may be a principal cause of the well-known tendency of PC to supercool. Because determination of the melting point is not subject to the problem of supercooling and can be performed under conditions which ensure a close approach to equilibrium, it proved to be much more precise.

Temperature–time plots for the melting of PC, such as that shown in Figure 1, were analyzed by the graphical and mathematical method of Taylor and Rossini (*9*) to determine the

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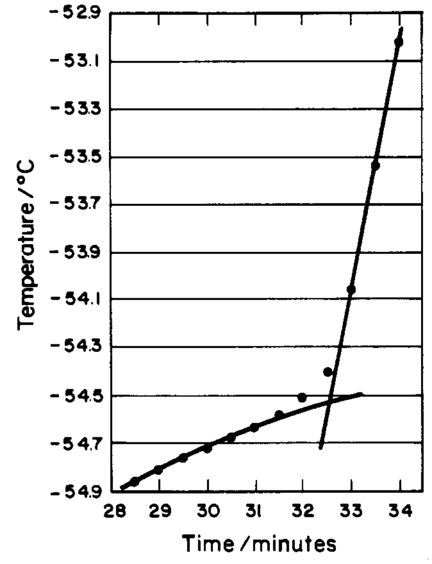

Figure 1. Plot of temperature against time. The melting point is calculated by using the graphical and mathematical analysis of Taylor and Rossini.

melting point. The lack of scatter of the data points in Figure 1 indicates that the precision of the temperature measurements is not a limiting factor in determining the melting point. Eight replicate measurements yields −54.53 °C as the mean melting point of PC with 95% confidence limits of ±0.02 °C. The melting point depression constant was estimated from the melting point of a 0.0985 *m* $LiClO_4$ solution (four measurements) and the melting point of a 0.0978 *m* tetrabutylammonium bromide (TBAB) solution (two measurements). $LiClO_4$ was selected because there is evidence that it behaves as a 1:1 strong electrolyte in PC without significant ion pair formation (*10*). The value of the molal melting point depression constant estimated from the $LiClO_4$ solution is 4.38 ± 0.16 °C m^{-1}, and that estimated from the TBAB solution is 4.25 ± 0.23 °C m^{-1}.

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Isothermal Vapor–Liquid Equilibria for the Ethylene–Carbon Dioxide System at High Pressure

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Isothermal vapor–liquid equilibria (VLE) of the C_2H_4 + CO_2 system were measured at −10.01, 0.01, 10.01, 20.03, and 25.00 °C. The critical properties of the mixture and the azeotropic points at several temperatures were also obtained. The experimental data of this work could be successfully correlated by using the Peng–Robinson equation of state with a binary interaction parameter except for the 25 °C isothermal data.

Introduction

VLE data for the C_2H_4 + CO_2 system are of interest because it forms an azeotropic mixture. Isothermal measurements of the VLE for this system were extensively carried out by Hakuta et al. (*1*), Nagahama et al. (*2*), and Mollerup (*3*) in the temperature range from −50 to 20 °C. Haselden et al. (*4*, *5*) measured dew and bubble points at several compositions.

In the present work, the isothermal vapor–liquid equilibrium data at −10.01, 0.01, 10.01, 20.03, and 25.00 °C were measured and compared carefully with those of other investigators (*1*, *3*–*5*).

The data obtained were correlated by utilizing the Peng and Robinson equation of state (*6*), and it appeared to provide a good representation of the experimental data except for the 25 °C isotherm.

Critical properties and azeotropic points were also determined.

Experimental Section

The measurement of vapor–liquid equilibria were carried out by using a newly constructed apparatus described recently in detail (*7*). The visual type of static apparatus was distinguished by the inclusion of a direct liquid-sampling device to reduce experimental error during sampling and of a magnetically driven agitator by which the vapor phase was dispersed into the liquid phase within the equilibrium cell to attain the equilibrium state.

The cell was placed in a bath containing ethanol as a bath fluid. The temperature of the bath was controlled within ±0.03 °C of the temperature of interest and measured by a calibrated platinum resistance thermometer connected to a digital potentiometer for measurement of its resistance. It was assumed that the bath temperature was identical with that of the equilibrium cell because the bath temperature was held for at least 1 day.

The pressure measurement was carried out by using an Aminco pressure balance. The accuracy of the measurement was believed to be within 0.035 atm. A Bourdon gauge was also employed for reading the pressure rapidly.

The equilibrium liquid of ~8 μL was sampled through a specially designed device mounted directly into the cell wall, which had a construction similar to that of Fredenslund et al. (*3*, *8*). On the other hand, a small portion of vapor was released into an evacuated chamber. At least three samples of liquid and vapor, respectively, were analyzed by gas chromatography. A 3-m column packed with activated charcoal (40/60

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