Some Thermodynamic Properties of Systems Containing Propylene Carbonate and Ethylene Carbonate

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The saturated vapor pressures and the enthalpies of vaporization of propylene carbonate and of ethylene carbonate were measured at various temperatures. The densities of the propylene carbonate + water and propylene carbonate + ethanol systems were measured at 25 °C. The solubility phase diagram of the propylene carbonate + water system and the liquid-liquid phase diagram of the ethanol + propylene carbonate + water system were determined at 25 °C.

Propylene carbonate and ethylene carbonate are widely used extractive solvents in the chemical industry. They dissolve a variety of organic compounds and inorganic salts. The purpose of this investigation was to study the possibility of recovering ethanol from aqueous solutions by using propylene carbonate as an extractive solvent.

Experimental Section

Propylene carbonate and ethylene carbonate, products of the Jefferson Chemical Co., Inc., were purified by repeated low-pressure distillation. The physical properties of the purified products were in good agreement with the literature values (given in parentheses). Propylene carbonate: $d^{25}{}_4$ 1.2004 g cm^{-3} (1.190-1.203 g cm^{-3}); bp 241.9 °C (241.7-242 °C); mp -50.2 °C (48-50 °C) (*1-4*). Ethylene carbonate: $d^{40}{}_4$ 1.3216 g cm^{-3} (1.32-1.33 g cm^{-3}); bp 248.2 °C (248 °C); mp 39.8 °C (39-40 °C) (*2-4*). Fisher spectrograde absolute ethanol was further purified by refluxing it under a condenser for 12 h in the presence of a small amount of LiH in a dry nitrogen atmosphere. Carl Fisher titration showed less than 0.03 wt % of water in the final product.

Double-stem pycnometers, of approximately 25 cm^3, were used for density measurements; buoyancy corrections were applied in the density evaluation. The error caused by evaporation of the solution during the measurement is negligible. The accuracy of the density measurement is estimated to be better than 1×10^{-4} g cm^{-3}.

The saturated vapor pressures were measured by a dynamic method, using two ebulliometers connected in parallel to a pressure-controlling system (*5*). One of the ebulliometers contained deionized, doubly distilled water and the other contained the organic liquid. The corresponding pressure of the system was determined from the boiling point of water (*6*), with an accuracy of better than $\pm 1 \times 10^{-4}$ atm. The boiling points of water and the organic substances, respectively, were measured with a 25-Ω platinum resistance thermometer in a Mueller bridge circuit (Leeds and Northrup) with an accuracy of better than ±0.01 °C.

The enthalpy of vaporization was obtained from measuring the amount of liquid evaporated by a known amount of electrical energy. The reproducibility of the measurement, tested with spectrograde cyclohexane, was ±0.1 kJ mol^{-1}.

The three-component liquid-liquid phase diagram, at 25 °C, was obtained by titrating homogeneous water + ethanol and propylene carbonate + ethanol solutions of different compositions with propylene carbonate and water, respectively. The turbidity point was found to be reproducible within one very small drop (0.015 cm^3). The accuracy of the measurement is estimated to be better than ±0.3 wt %.

Table I. Saturated Vapor Pressure of Ethylene Carbonate and Propylene Carbonate at Various Temperatures

ethylene carbonate		propylene carbonate	
temp, °C	press., atm	temp, °C	press., atm
95.21	0.004 436	95.42	0.006 605
98.76	0.005 296	97.74	0.007 224
100.25	0.005 788	98.52	0.007 434
109.37	0.009 242	99.99	0.008 237
111.25	0.010 18	102.65	0.009 408
115.37	0.012 36	105.32	0.010 52
117.29	0.013 82	108.37	0.012 37
120.35	0.015 54	111.22	0.014 14
124.44	0.018 98	115.38	0.017 13
129.32	0.023 58	118.42	0.019 64
135.72	0.030 68	122.51	0.023 58
138.54	0.034 64	125.62	0.027 03
144.32	0.043 76	129.35	0.031 44
149.51	0.053 58	133.42	0.037 26
152.77	0.060 33	137.54	0.044 04
153.88	0.063 49	141.46	0.051 33
162.82	0.086 16	145.92	0.060 86
165.95	0.097 54	153.68	0.080 95
170.32	0.113 7	158.92	0.097 50
173.56	0.126 6	162.54	0.110 3
175.86	0.136 2	164.56	0.118 2
		168.82	0.136 2
		171.34	0.147 9
		175.86	0.171 0
		182.45	0.210 0
		185.95	0.233 3
		188.92	0.255 0

The solubility phase diagram of the water + propylene carbonate system was obtained by titrating water samples with propylene carbonate and propylene carbonate samples with water at various temperatures. The reproducibility of the measurement was very good, and the error is estimated to be less than 0.3 wt %.

Results

The vapor pressures of the two carbonates as functions of temperature are summarized in Table I.

The experimental data listed in Table I were fitted by the least-squares method to an Antoine equation of the form $\ln P/\text{atm} = -A/(C + t/°\text{C}) + B$. The values of the constants are as follows: $A = 4194.365$, $B = 9.75917$, and $C = 181.076$ for ethylene carbonate; and $A = 4130.044$, $B = 9.66899$, and $C = 185.312$ for propylene carbonate. The Antoine equation, with these constants, reproduces the experimental data well within the limits of experimental error ($\pm 1 \times 10^{-4}$ atm). The measurements are in agreement with the results of Petrov and Sandler (*7*). Inconsistencies in the vapor pressure measurements appeared for both components in the range of higher temperatures. The samples exposed to temperatures higher than 200 °C exhibited slight changes in vapor pressure when measured again at lower temperatures. We attributed the discrepancy to a slight decomposition of the carbonates at higher temperatures.

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Table II. Enthalpy of Vaporization of Ethylene Carbonate and Propylene Carbonate at Several Temperatures

	ΔH_{vap}, kJ mol^{-1}	
temp, °C	ethylene carbonate	propylene carbonate
150	56.3	55.2
160	55.0	54.1
170	54.0	53.0
180	53.3	52.3
190	52.6	51.6
200	52.2	50.9

Table III. Densities of the Propylene Carbonate + Water and Ethylene Carbonate + Ethanol Systems at 25 °C

propylene carbonate + water		propylene carbonate + ethanol	
wt %	$d^{25}{}_4$, g cm^{-3}	wt %	$d^{25}{}_4$, g cm^{-3}
0.0000	0.9986	0.0000	0.7851
0.0147	1.0001	0.0925	0.8123
0.0297	1.0030	0.1792	0.8386
0.0449	1.0062	0.2608	0.8660
0.0593	1.0094	0.3343	0.8911
0.0731	1.0124	0.4083	0.9186
0.1039	1.0192	0.4774	0.9445
0.1323	1.0249	0.5421	0.9702
0.1466	1.0277	0.6044	0.9966
0.1761	1.0338	0.6609	1.0219
0.9288	1.1838	0.7169	1.0478
0.9475	1.1878	0.7701	1.0739
0.9579	1.1900	0.8199	1.0985
0.9687	1.1927	0.9136	1.1494
0.9792	1.1950	0.9579	1.1751
0.9897	1.1976	1.0000	1.2004
1.0000	1.2004		

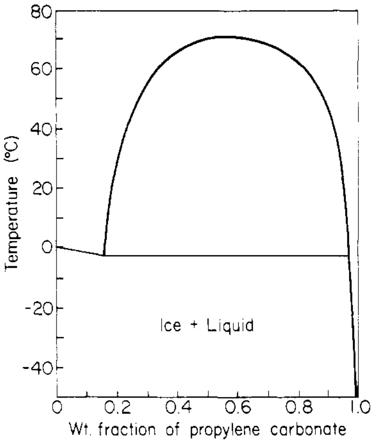

Figure 1. Phase diagram of the propylene carbonate + water system.

The enthalpies of vaporization for the two carbonates at several temperatures are listed in Table II.

The densities of the propylene carbonate + water and propylene carbonate + ethanol systems, at 25 °C, are summarized in Table III.

The propylene carbonate + water system exhibits limiting solubility. The solubility vs. temperature data are shown in Table IV and Figure 1.

The following conclusions can be derived from the solubility data: (a) A small amount of propylene carbonate lowers the freezing point of water. (b) Water affects the freezing point of propylene carbonate substantially. (c) The solubility of propylene carbonate in the water layer increases to a greater extent with temperature than does the solubility of water in the propylene carbonate layer. Complete miscibility is reached at 71 °C.

Table IV. Solubility of the Propylene Carbonate + Water System as a Function of Temperature

t, °C	wt fraction of propylene carbonate	*t*, °C	wt fraction of propylene carbonate
0.0	0.0000	62.6	0.7976
−0.9	0.0513	40.1	0.8934
−1.8	0.1011	7.5	0.9494
27.1	0.2046	−28.1	0.9876
67.2	0.3941	−50.2	1.0000
71.0	0.5958		

Table V. Solubility Data for the Ethanol + Water + Propylene Carbonate System at 25 °C and 1 atm

propylene carbonate, wt %	ethanol, wt %	water, wt %	propylene carbonate, wt %	ethanol, wt %	water, wt %
17.8	0.0	82.2	57.4	10.1	32.5
21.5	4.8	73.7	61.5	9.2	29.3
30.4	7.5	62.1	72.8	6.3	20.9
35.1	8.6	56.3	79.6	4.1	11.3
46.2	11.3	42.5	93.1	0.0	6.9
48.8	11.2	40.0			

Table VI. Composition of the Two Equilibrium Phases for the System Ethanol + Water + Propylene Carbonate at 25 °C and 1 atm

water phase, wt %			propylene carbonate phase, wt %		
PC[a]	E[b]	W[c]	PC[a]	E[b]	W[c]
18.2	5.1	76.7	91.1	1.2	7.7
29.5	8.2	62.3	79.1	8.8	12.1

[a] Propylene carbonate. [b] Ethanol. [c] Water.

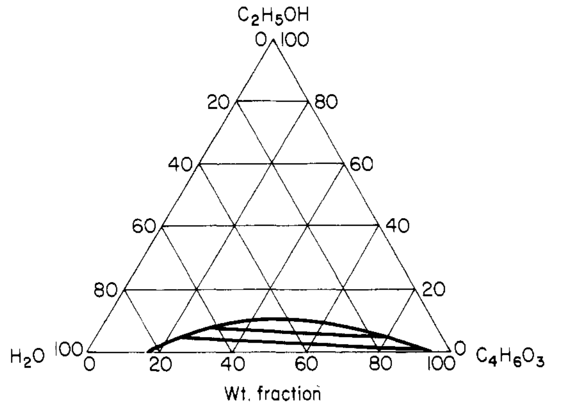

Figure 2. Liquid-liquid phase diagram of the ethanol + water + propylene carbonate system at 25 °C.

The liquid-liquid solubility data and the solubility phase diagram for the ethanol + propylene carbonate + water system, at 25 °C, are shown in Tables V and VI and in Figure 2, respectively. The solubility of water in propylene carbonate, as well as the solubility of propylene carbonate in water, is increased in the presence of ethanol. Complete miscibility is reached with approximately 11 wt % of ethanol at 25 °C. Measurements not listed here prove that the propylene carbonate + water + ethanol system exhibits complete miscibility at approximately 50 °C.

From the data collected in this work, the recovery of ethanol from aqueous solutions with propylene carbonate as an extractive solvent is not very promising.

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Liquid–Liquid Equilibria for Three Ternary and Six Quaternary Systems Containing Sulfolane, *n*-Heptane, Toluene, 2-Propanol, and Water at 303.15 K

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Liquid–liquid phase equilibrium data have been measured for the ternary systems *n*-heptane–toluene–sulfolane, toluene–sulfolane–water, and *n*-heptane–2-propanol–sulfolane at 303.15 K by gas-chromatoraphic analysis of the tie-line material. Limited data have also been obtained for six quaternary systems. Four of these are for *n*-heptane–toluene–sulfolane–water with water/sulfolane content ranging from 2 to 10 mass %, and two are for *n*-heptane–toluene–sulfolane–2-propanol with 2-propanol/sulfolane content of 10 and 20 mass %.

Sulfolane is widely used as a solvent for the extraction of aromatic hydrocarbons from refinery process streams, but published quantitative phase equilibrium data are scarce. In an earlier paper (*1*) we reported vapor–liquid equilibria for several binary sulfolane-containing systems as part of a project to investigate vapor–liquid and liquid–liquid phase relationships of the type encountered in liquid extraction processes. This paper is concerned with liquid–liquid equilibria for the ternary systems *n*-heptane–toluene–sulfolane, toluene–sulfolane–water, and *n*-heptane–2-propanol–sulfolane at 303.15 K. The results of studies on the effect of the addition of small quantities of water and 2-propanol as solvent modifiers upon the system *n*-heptane–toluene–sulfolane at 303.15 K are also reported here. These were carried out to ascertain the variation of both the solvent selectivity and the hydrocarbon solubility with various quantities of solvent modifier. In the present case, water acts as an antisolvent, increasing the size of the two-phase envelope. Conversely, 2-propanol decreases the size of the two-phase envelope and may be described as a prosolvent.

Experimental Section

Materials. Toluene and 2-propanol were BDH high-purity "Aristar" grade reagents. These were dried with activated type 5A molecular sieves but otherwise used as supplied. The toluene was certified by the manufacturers to be of a minimum purity of 99.95 mass % and the 2-propanol to have a maximum water content of 0.1 mass %, with all other impurities to be below 0.001 mass %. This water content was reduced to below 0.01 mass %, as confirmed by gas chromatography.

The *n*-heptane was laboratory reagent grade obtained from Fisons Ltd. This was passed through a silica gel column (to remove aromatics) and then distilled at atmospheric pressure (25-plate, 25-mm i.d. Oldershaw column, 5:1 reflux ratio). The *n*-heptane boiling over 0.1 K was collected and stored over molecular sieves.

Anhydrous sulfolane supplied by the Shell Chemical Co. was dried with molecular sieves and then twice vacuum distilled from phosphorous pentoxide at a pressure below 1 mmHg to yield a colorless, odorless product. To minimize the contact of this deliquescent reagent with moist air, we kept the product in stoppered bottles in a desiccator.

Water was freshly distilled before use. Physical properties of these materials were listed in an earlier paper (*1*).

Equilibrium Measurements. The liquid–liquid equilibrium measurements were made by using a 250-cm^3 cylindrical glass vessel of U-shaped cross section. The top was closed, using a PTFE gasket, by a 6-mm thick stainless-steel plate carrying a stainless-steel stirrer, a thermistor pocket, a closable sampling point, and a tube for the entry of dry nitrogen. The whole was immersed in a water thermostat controlled at 303.15 ± 0.05 K. A thermistor (ITT type F23D) was used to measure temperature in conjunction with an automatic digital bridge (Solartron type EX1732). The thermistor was calibrated against a short-range (5 K) precision mercury thermometer (IPTS 68) certified by the National Physical Laboratory.

The cell was purged with dry nitrogen before being charged. The mixture was stirred for at least 2 h and then allowed to settle. Samples (5 cm^3) of the two phases were withdrawn for analysis by glass syringes equipped with stainless-steel hypodermic needles and then stored in sealed glass containers at a temperature of 303.65 ± 0.5 K in an air bath to await analysis. Sampling techniques, designed to eliminate the possibility of contamination, are given in detail by Clayton (*2*).

Analysis. A Pye-Unicam Series 104 gas chromatograph, equipped with a thermal conductivity detector, was used in conjunction with a Honeywell linear amplifier and integrator. The glass columns were 0.9 m × 3 m i.d., charged with 10 mass % Apiezon L on Chromosorb W, and the carrier gas was helium. For some of the water-containing samples a packing of Porapak Q was used. The calibration and calculation procedure followed that given by Smith and Bowden (*3*). The precision of the measurements was considered to be ±0.003 in mass fraction for the ternary systems and ±0.001 in mass fraction for the *n*-heptane–sulfolane binary system. The accuracy in the quaternary systems was considered to be inferior to that for the ternary systems, owing to the difficulty of obtaining complete resolution of the sulfolane/modifier peaks.

Results and Discussion

Ternary Systems. Tie-line data for the three systems are reported in Tables I–III, as both mass and mole fractions. The mutual solubilities of the partially miscible binary systems *n*-