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Vapor Pressure and Liquid Heat Capacity of Alkylene Carbonates

Yury Chernyak* and John H. Clements

Huntsman Corporation, 7114 North Lamar Boulevard, Austin, Texas 78752

New experimental data on vapor pressure (T = 397 to 523 K) and liquid heat capacity, C_p, (T = 283 to 393 K) of ethylene carbonate, propylene carbonate, butylene carbonate, and glycerine carbonate were developed using ebulliometery and differential scanning calorimetry techniques. These vapor pressure and liquid heat capacity data were combined with selected literature data and correlated using Wagner, Clapeyron, and polynomial-type equations.

Introduction

In recent years, alkylene carbonates, the so-called "cyclic acid esters", have been the subject of considerable interest among academic as well as industrial researchers. In particular, ethylene carbonate (EC) and propylene carbonate (PC) have been commercially available for over 40 years.[1] In that time, EC and PC have found utility in numerous applications as both reactive intermediates and inert solvents. Although a wide variety of alkylene carbonates have since been synthesized and characterized, only two are commercially manufactured in significant quantities in addition to EC and PC. They are butylene carbonate (BC) and glycerine carbonate (GC). Their structures are given in Figure 1. Typically, alkylene carbonates are prepared via the insertion of carbon dioxide into the corresponding alkylene oxides. EC, PC, and BC are commercially manufactured in this manner[1] (Figure 2a). However, due to the high cost and unavailability of glycidol, GC is commercially prepared via the transesterification of glycerine with an alkylene carbonate such as EC or a linear carbonate such as dimethyl carbonate[1] (Figure 2b).

Although the vapor pressure of EC and PC at low temperatures has been previously reported,[2−4] no such data appear in the literature for BC or GC. Only a few sources cite liquid heat capacity (C_p) for EC and PC,[5,6] and no liquid heat capacity data exist for BC and GC. For these reasons, the objective of this study is to expand the range of available experimental data on vapor pressure and liquid heat capacity for EC and PC and to develop data for BC and GC.

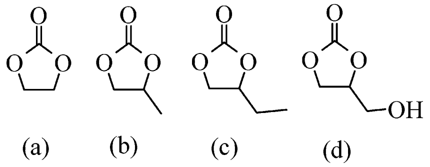

Figure 1. Chemical structures: (a) ethylene carbonate; (b) propylene carbonate; (c) butylene carbonate; (d) glycerine carbonate.

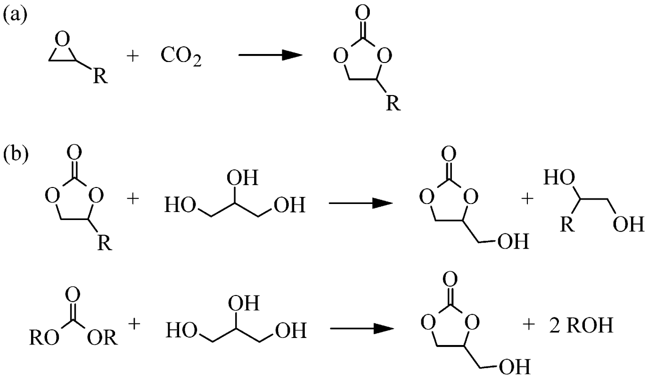

Figure 2. Alkylene carbonate synthesis: (a) preparation of EC, PC, and BC by carbon dioxide insertion; (b) preparation of GC by the transesterification of glycerine.

Experimental Section

Materials. Samples of EC, PC, and BC were obtained from Huntsman (JEFFSOL grade, Conroe, TX) and used without further purification. Purity analysis of EC, PC, and BC was performed using a 5890 Hewlett-Packard gas chromatograph equipped with a 30-m carbowax column and flame ionization detector. Purity above 99.9 mass % was observed for all EC and PC samples used throughout this study. Water and the corresponding glycol (ethylene glycol or 1,2-propylene glycol) were found to be the primary impurities, present in concentrations below 0.02 mass % and 0.05 mass %, respectively. The purity of all BC samples was above 99.7 mass % with 1,2-butylene glycol and water concentrations below 0.1 mass % each. GC was obtained from Huntsman (JEFFSOL grade) and was further purified by three consecutive wipe-film evaporations at temperature (405 to 420) K, pressure (0.3 to 1.0) mmHg, and feed rate (2 to 5) g·min^{-1}. The resulting purified distillate was analyzed by high-performance liquid chromatography using a Waters model 510 HPLC pump equipped with a Waters Ultrahydrogel 120 column, Rainin refractive index detection, and water mobile phase. GC purity of 98.9 mass % was obtained by the above analysis method. The major impurity was glycerin, found at the concentration of 0.5 mass %. This GC sample was used to measure heat capacity. For vapor pressure measurements, a small amount of citric acid (0.5 mass %) was added to the sample to prevent its decomposition at elevated temperatures.

Vapor Pressure. Vapor pressure measurements were performed using a Washburn-type ebulliometer (Figure 3). Details of the design have been described elsewhere.[7,8] Similar to the original Washburn design, the ebulliometer consists of two chambers. The lower chamber is filled with

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* Author to whom correspondence should be addressed (e-mail yury_chernyak@huntsman.com).

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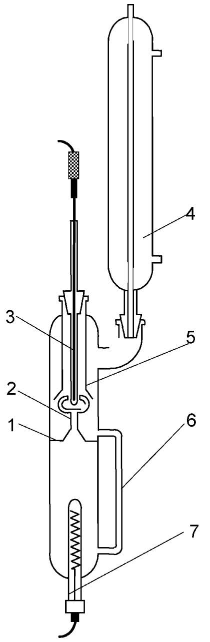

Figure 3. Schematic diagram of the ebulliometer: (1) separation between upper and lower section of the ebulliometer; (2) Washburn pump; (3) Minco 100-ohm platinum RTD probe; (4) condenser; (5) glass shield; (6) side tubing; (7) heating element.

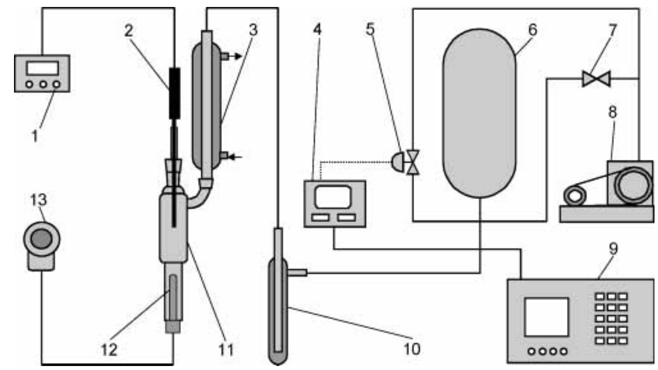

Figure 4. Schematic diagram of the vapor pressure apparatus: (1) Minco RTB8078 resistance thermometer bridge; (2) Minco 100-ohm platinum RTD probe; (3) water-cooled condenser; (4) Mano-Watch MW-1 pressure controller; (5) solenoid valve; (6) ballast volume; (7) valve; (8) vacuum pump; (9) Ruska DDR 6000 pressure gauge; (10) vacuum trap; (11) ebulliometer; (12) heating element; (13) variable transformer.

liquid, which is heated to its boiling point via an electric heating element. Surface tension, uneven heat distribution, and too few centers of vapor bubble formation result in unavoidable superheating of the liquid near the heating element. As a result, boiling point measurements are taken in the upper chamber of the ebulliometer. Vapors produced during the boiling process carry the liquid into the upper chamber by way of a Washburn pump, which consists of a funnel at the bottom and forked tubes at the top. The tubes are slightly bent and converge at a central point occupied by an RTD temperature probe within a glass housing. As boiling liquid rises up the Washburn pump, and the RTD probe is washed by a stream of liquid emerging from the tube openings. The liquid returns to the lower chamber by way of side tubing connecting the two chambers. A glass shield surrounds the RTD probe, preventing contact with liquid flowing downward from the vapor condenser.

A schematic of the complete apparatus is shown in Figure 4. Eighty milliliters of the liquid sample to be tested was placed in the lower chamber of the ebulliometer (11). A vacuum was then applied to bring the system to the desired pressure, which was controlled by a Mano-Watch MW-1 external pressure regulator (4) and solenoid valve (5). After a stable pressure had been achieved, heat was applied until boiling commenced. The heating system consisted of an electrical heater (12) and a variable autotransformer (13) for manual control of heat input. Once a steady boiling process was established, pressure and temperature readings were measured using a Ruska DDR 6000 pressure gauge (9) to an accuracy of 0.03 kPa and a Minco RTB8078 resistance thermometer bridge (1) with 100-ohm platinum RTD (2) to an accuracy of 0.01 ohm (or 0.025 K). Aluminum foil was used to minimize unwanted heat loss by radiation (employed at temperatures >373 K) and to provide more uniform heat distribution inside the ebulliometer. Despite the high accuracy of the instruments used, the overall uncertainty of experimental vapor pressure data depends to some extent on the material under investigation, for example, its liquid viscosity, surface tension, and temperature range. The estimated uncertainty of the vapor pressure data reported herein was found to be better than 5% at pressures below 1 kPa, 2% in the range from 1 to 10 kPa, and 1% at pressures over 10 kPa.

Liquid Heat Capacity (C_p). Heat capacity measurements were carried out using a Netzsch DSC-404C differential scanning calorimeter (DSC). The ratio method was used for all measurements. The experimental procedure employed consisted of three consecutive measurements of the DSC signal (J/mV); (i) empty measuring cell (J_0), (ii) measuring cell containing the reference material (J_R), and (iii) measuring cell containing the test liquid (J_X). The heat capacity of the test liquid $C_{p,\mathrm{X}}$ was determined then using the formula

$$C_{p,X} = \frac{m_\mathrm{R}}{m_\mathrm{X}}\left(\frac{J_\mathrm{X} - J_0}{J_\mathrm{R} - J_0}\right)C_{p,\mathrm{R}} \tag{1}$$

where $C_{p,\mathrm{X}}$ and m_X are heat capacity and mass of the test liquid, respectively, and $C_{p,\mathrm{R}}$ and m_R are heat capacity and mass of the reference material (sapphire), respectively.

Measurements were conducted using ~20 mg of test liquid in a sealed aluminum cell. The amount of material was such that ≥80% of the cell's volume was occupied. To ensure no weight change of the sample during the measurements, the cell was weighed before and after each run. A heating rate of 20 $\mathrm{K \cdot min^{-1}}$ was used throughout this work, which may seem high compared to that commonly used by other researchers, (0.1 to 5.0) $\mathrm{K \cdot min^{-1}}$. However, our measurements were performed using a Netzsch DSC-404C, which operates under the heat flux principle as opposed to instrumentation that utilizes power compensation (e.g., Perkin-Elmer or Tain-Calvet models). Unlike the power compensation DSC, which monitors the heat flowing in and out of the sample, the heat flux DSC tracks the temperature difference between the sample and reference cells. Using such an instrument, the influence of the heating rate on the measurement of heat capacity is not obvious. Previous DSC measurements in our laboratory of liquids with known heat capacity indicated that higher heating rates produced more accurate results. This fact was confirmed in several independent test runs by Netzsch researchers,[9,10] which can also be specific for the particular instrument used in this study. Also, it was observed that more accurate data were achieved when the DSC signals of the reference material (J_R) and the sample (J_X) were of comparable intensities, that is, when the term in parentheses in eq 1 was near unity. Although this phenomenon

Table 1. Vapor Pressure of Alkylene Carbonates

P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K
Ethylene Carbonate							
15.19	451.58	19.94	460.15	44.69	487.10	63.34	500.01
17.52	456.04	24.23	466.22	53.59	493.67	73.45	505.50
Propylene Carbonate							
24.21	459.85	40.81	478.35	66.33	496.95	86.64	508.15
28.46	465.35	45.44	482.25	70.45	499.45	89.87	509.75
31.24	468.45	49.16	485.05	73.46	501.25	92.66	511.15
34.04	471.75	57.38	491.25	78.67	504.05	97.17	513.25
38.09	475.85	61.83	494.25	83.64	506.65		
Butylene Carbonate							
1.90	397.25	7.57	432.03	23.89	467.68	59.91	501.76
2.44	402.93	9.43	438.31	29.14	474.59	70.54	508.33
3.23	409.65	12.03	445.57	35.77	481.93	83.68	515.54
4.45	417.69	15.39	453.20	42.38	488.30	99.08	522.74
5.80	424.67	19.28	460.53	50.52	495.04		
Glycerine Carbonate							
0.26	429.91	0.36	435.94	0.68	449.41		
0.30	432.47	0.41	438.90	0.78	452.48		
0.33	434.39	0.62	447.48	0.90	455.61		

has no concrete theoretical grounding, several different explanations supporting our observations have been proposed in the literature.[11] In an effort to match the intensity of the J_X signal to that of J_R, the sample mass was varied from (15 to 25) mg depending on the material. The effect of pressure buildup and material loss, which accompanies vaporization of the liquid inside the test pan with increasing temperature, is known.[11,12] Taking into account the very low vapor pressure of the samples over the temperature range studied, the combined contribution of these factors to errors in C_p was not expected to exceed 0.1% and was therefore neglected. The overall uncertainty of measured heat capacities was estimated to be within 2.5% for all measurements.

Results

Vapor Pressure. Table 1 summarizes the experimental vapor pressure data obtained. The four-parameter Wagner equation[13] was used to correlate experimental data of EC, PC, and BC:

$$\ln\left(\frac{P}{P_c}\right) = \frac{T_c}{T}\left(A\left(1 - \frac{T}{T_c}\right) + B\left(1 - \frac{T}{T_c}\right)^{1.5} + C\left(1 - \frac{T}{T_c}\right)^{3} + D\left(1 - \frac{T}{T_c}\right)^{6}\right) \quad (2)$$

In eq s P is pressure in bar, T is temperature in K, P_c is critical pressure in bar, T_c is critical temperature in K, and A, B, C, and D are coefficients.

No experimental information on critical properties of alkylene carbonates was available in the open literature. To determine the critical parameters required in eq 2, experimental vapor pressures were regressed using the Antoine equation.[14] Regressed Antoine parameters were then used to calculate the boiling temperature of the alkylene carbonates. Finally, the calculated boiling temperatures were used to predict critical temperature and pressure according to the Joback method.[14] The estimated critical properties are given in Table 2. Our choice of the Wagner model for EC, PC, and BC was based on the exceptional ability of this equation to fit experimental data over a wide temperature range even in cases when critical parameters were obtained by prediction. However, the extrapolative capabilities of the reported model parameters are questionable. Therefore, we do not recommend this model for vapor pressure calculations beyond the range of the experimental data used in regression. Wagner coefficients for EC, PC, and BC and standard deviations are summarized in Table 2.

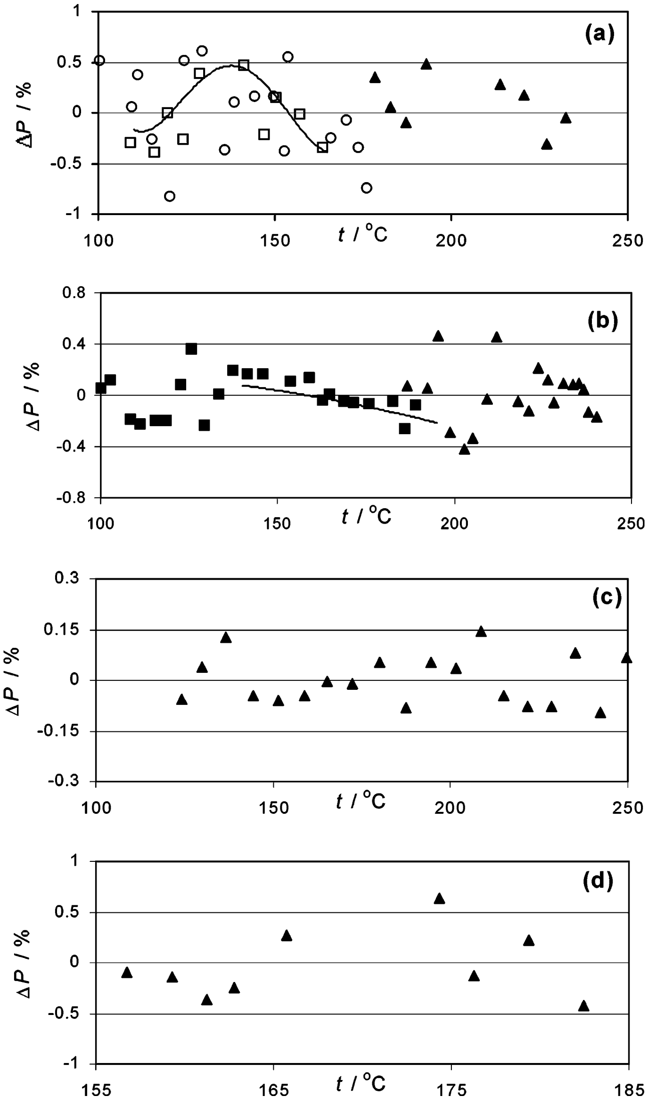

Figure 5. Percentage deviations [100($P_{exptl} - P_{calcd}$)/P_{calcd}] of vapor pressure data from eqs 2 and 3: (a) ethylene carbonate; (b) propylene carbonate; (c) butylene carbonate; (d) glycerine carbonate. ▲, this work; ○, Hong et al.[2]; □, Petrov and Sandler[3]; ■, Jones and Aikens;[4] - - -, Stephenson and Malanowski.[15]

Table 2. Predicted Critical Properties, Equations 2−4 Parameters, and Standard Deviations, *s*

property/ coefficient	ethylene carbonate	propylene carbonate	butylene carbonate	glycerine carbonate
Critical Properties				
T_c/K	805.0	782.6	778.5	
P_c/bar	61.4	50.7	44.4	
Coefficients of Equations 2 (EC, PC, and BC) and 3 (GC)				
A	1.9256	−9.7095	−5.6078	15.788
B	−1.9858	5.1640	−4.8868	9339.5
C	2.1452	−7.1776	6.7442	
D	−35.3071	0	−23.7328	
s/kPa	0.054	0.076	0.037	0.023
Coefficients of Equation 4				
a_1	1.426	0.995	1.034	1.391
a_2	0	2.21×10^{-3}	2.20×10^{-3}	1.41×10^{-3}
a_3	2.51×10^{-6}	0	0	0
s/(J·g^{-1}·K^{-1})	1.46×10^{-2}	5.1×10^{-3}	5.0×10^{-3}	5.5×10^{-3}

Table 3. Liquid Heat Capacity of Alkylene Carbonates

C_p	T	C_p	T	C_p	T
$\mathrm{J{\cdot}g^{-1}{\cdot}K^{-1}}$	K	$\mathrm{J{\cdot}g^{-1}{\cdot}K^{-1}}$	K	$\mathrm{J{\cdot}g^{-1}{\cdot}K^{-1}}$	K
		Ethylene Carbonate			
1.77	383.15	1.79	393.15		
1.78	388.15	1.80	398.15		
		Propylene Carbonate			
1.67	303.15	1.75	343.15	1.85	383.15
1.69	313.15	1.77	353.15	1.87	393.15
1.71	323.15	1.80	363.15		
1.73	333.15	1.82	373.15		
		Butylene Carbonate[a]			
1.66	283.15	1.74	323.15	1.83	363.15
1.68	293.15	1.77	333.15	1.85	373.15
1.70	303.15	1.79	343.15		
1.72	313.15	1.81	353.15		
		Glycerine Carbonate			
1.79	283.15	1.84	323.15	1.91	363.15
1.81	293.15	1.85	333.15	1.92	373.15
1.82	303.15	1.87	343.15		
1.83	313.15	1.89	353.15		

[a] C_p values for BC are the average of two measurements.

Vapor pressure data of GC were collected in a narrow temperature range from 430 to 455 K (Table 1). The low-temperature limit was due to the capabilities of the experimental setup, whereas thermal decomposition of the sample prevented data collection at higher temperatures. To correlate vapor pressure data of GC the Clapeyron equation was used.

$$\ln(P) = A - \frac{B}{T} \tag{3}$$

Here P is pressure in bar, T is temperature in K, and A and B are coefficients. The regressed values of coefficients A and B and the standard deviations are given in Table 2.

Experimental vapor pressure data obtained for EC and PC in the high-temperature regime were regressed together with the corresponding low-temperature data found in the literature[2–4] such that a Wagner correlation over a wide range of temperatures could be obtained. Because vapor pressure data for BC and GC were not found in the literature, only the experimental data developed herein were used in regression. Deviations of the experimental data from the fit as well as deviations of vapor pressures calculated from the Stephenson and Malanowski[15] Antoine equation are shown in Figure 5. For the most part, vapor pressure deviations from eq 2 were within 0.7% and 0.5% for EC and PC, respectively. The agreement between the Stephenson and Malanowski[15] Antoine equation and eq 2 is within 0.5% for EC and better than 0.3% for PC. Deviations of measured vapor pressures from calculated values were less than 0.15% and 0.6% for BC and GC, respectively, over the entire temperature range investigated.

Liquid Heat Capacity (C_p). Experimental heat capacity data were recorded at 0.5 K intervals over the temperature range studied. For simplicity, only the values at 5 K and 10 K intervals are given in Table 3. Heat capacity data as a function of temperature were fitted to the polynomial equation

$$C_p = \sum_{i=1}^{3} a_i T^{i-1} \tag{4}$$

where C_p is heat capacity in $\mathrm{J{\cdot}g^{-1}{\cdot}K^{-1}}$, T is temperature in K, and a_i are coefficients. Table 2 summarizes coefficients a_i for all investigated carbonates as well as standard deviations of experimental data.

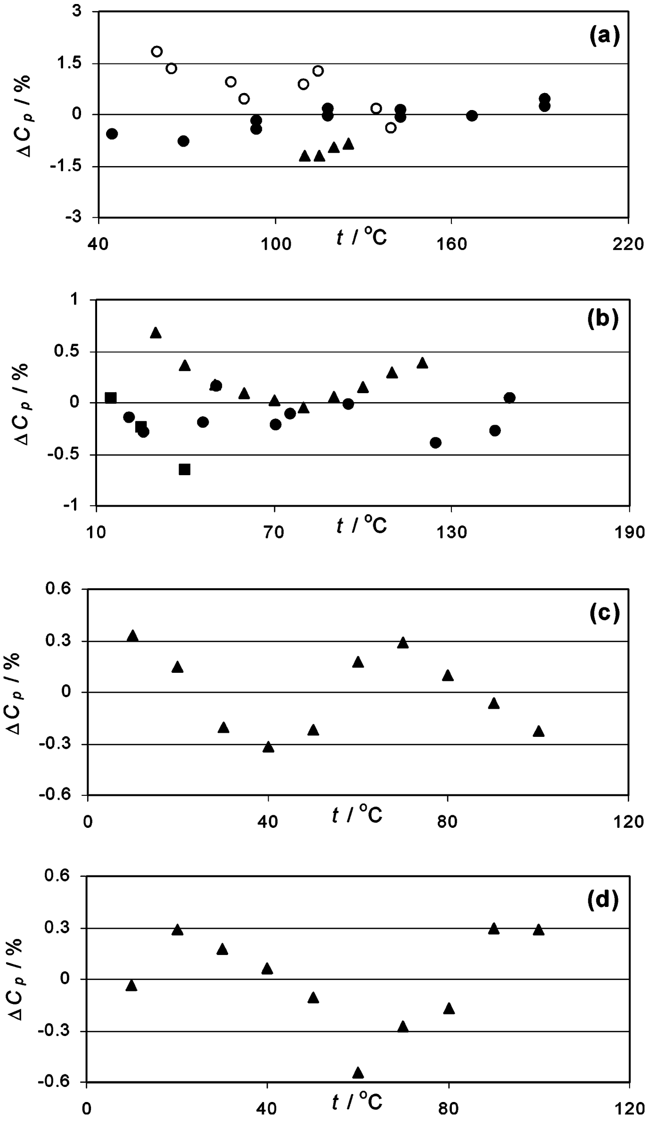

Figure 6. Percentage deviations $[100(C_{p,\mathrm{exptl}} - C_{p,\mathrm{calcd}})/C_{p,\mathrm{calcd}}]$ of liquid heat capacity data from eq 4: (a) ethylene carbonate; (b) propylene carbonate; (c) butylene carbonate; (d) glycerine carbonate. ▲, this work; ○ and ●, Texaco data;[5] ■, Righetti et al.[6]

In the case of EC, heat capacity data generated by Texaco[5] were used in regression along with the experimental data obtained in this work. The Texaco data were developed using a Perkin-Elmer DSC-2 with a reported uncertainty of 2.5%. The heat capacity measurements of EC reported in this work were performed over a limited temperature range mainly for the purpose of validating the Texaco data. The agreement between our data and those developed by Texaco[5] is better than 1.5%, which is within the range of reported experimental uncertainties. Two sets of literature C_p data[5,6] developed for PC were used in regression along with data developed in our laboratory. Better than 1.0% agreement was observed among all three data sets. Because no liquid heat capacity data for BC and GC were found in the literature, only the data developed herein were used to obtain coefficients for eq 4. The deviations of experimental data generated for BC and GC from eq 4 are given in Figure 6. These deviations did not exceed 0.4 and 0.6%, respectively, over the entire temperature interval.

Acknowledgment

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