

Dielectric Constant, Dipole Moment, and Solubility Parameters of Some Cyclic Acid Esters

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Dielectric constant, dipole moment, and solubility parameters are reported for ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), and glycerin carbonate (GC). Dielectric constants have been determined from capacitance measurements using an auto-balancing bridge at 20, 25, and 40 °C. Values of permanent dipole moment of carbonates have been obtained from dielectric constant measurements on dilute solutions of carbonates in benzene and 1,4-dioxane. Hildebrand and Hansen solubility parameters of carbonates have been calculated using several different techniques.

Introduction

Cyclic acid esters or alkylene carbonates (Figure 1) are long-term commercially available solvents used in many industrial applications^{1–3} such as cleaning/degreasing, paint stripping, gas treating, textile dyeing, etc. Electrochemical stability of carbonates made them the solvent of choice for electrolytes of lithium-ion batteries.⁴ Recently, alkylene carbonates found utility as “safe” solvent substitutes in agriculture⁵ and as carrier solvents in therapeutic and cosmetic preparations.⁶ The aim of this work is to develop new information on dielectric constants and dipole moments of alkylene carbonates. These are very critical quantities in determining the extent of molecular interactions and hence responsible for solubility characteristics of the materials. The dissolution of ions is typically enhanced by the high dielectric constant of the solvent, while dipole moment helps to determine the solvent–solute molecules orientation. A product of dipole moment and dielectric constant, also known as electrostatic factor,⁷ is also a useful parameter in analysis of solvent power of materials. Although electrostatic properties of EC and PC have been previously reported, very few data are available for BC, and no data exist for GC. The present study is focused on experimental determination of dielectric constant and dipole moment of alkylene carbonates and on calculation of their Hildebrand and Hansen solubility parameters, which are commonly used in various solvent selection methods.

Dielectric Constant and Dipole Moment

The purity of alkylene carbonates used in this study was above 99.9 mass % for EC and PC, 99.7 mass % for BC, and 98.9 mass % for GC. Details on sample preparation are given in our previous work.⁸ Solvents used in dipole moment measurements were benzene (purity 99.1 mass %, used as received from Fischer) and 1,4-dioxane (HPLC grade, purity 99.9 mass %, used as received from Aldrich).

Measurements of dielectric constant of carbonates were performed using an auto-balancing bridge (Agilent 4284A precision LCR meter) and parallel plate cell (Agilent 16452A liquid test fixture) with 0.3 mm spacer. A static dielectric constant was determined from the capacitance measurements of the tested liquid and air at 1 MHz frequency. Detailed

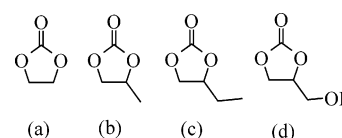


Figure 1. Chemical structures: a, EC; b, PC; c, BC; d, GC.

Table 1. Dielectric Constant of Alkylene Carbonates

<i>T</i> /°C	EC	PC	BC	GC
20		66.6	57.5	111.5
25		65.5	56.1	109.7
40	90.5			

description of the method is given by Smyth.⁹ In our experiment, the cell with the liquid under investigation was thermostated in the NESLAB 201 liquid temperature-controlled bath. The temperature of the bath was measured using a Minco RTB8078 resistance thermometer bridge with 100-Ω platinum RTD to an accuracy of 0.01 °C. Measurements of dielectric constant were performed at 40 °C for EC and at 20 and 25 °C for PC, BC, and GC with uncertainties less than 1.5 %. Experimental values of dielectric constant obtained in the present study are summarized in Table 1. The agreement between our data and literature^{10–15} data for EC, PC, and BC is better than 0.7 %. Dielectric constant of GC was determined in this work for the first time.

Determination of permanent dipole moment from dielectric constant measurements on dilute solutions of a polar compound in a nonpolar solvent is a well-known technique¹⁶ employed in this study. Two different solvents were used in this work. Benzene was used for dipole moment measurements of EC, PC, and BC. 1,4-dioxane was used as a solvent for measurements with GC.

First, molar polarizations of dilute solutions of carbonates, *P*, were determined from the Mosotti–Clausius equation:

$$P = \frac{(\epsilon - 1)M}{(\epsilon + 2)d} \quad (1)$$

where ϵ , *M*, and *d* are dielectric constant, molecular weight, and density, respectively. Dielectric constants (ϵ) of several dilute solutions (concentrations from 0.5 to 5 mol % of carbonate) were measured at 20 °C. *M* and *d* were calculated

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Table 2. Experimental Dielectric Constant and Molar Polarization of Dilute Solutions of Alkylene Carbonates in a Nonpolar Solvent at 20 °C

x_2 (mole fraction)	$d/g \cdot mL^{-1}$	ϵ	P (eq 1)	P_2 (eq 2)
Ethylene Carbonate ($[n_2]_D = 1.4255$; $M_1 = 78.11$; $M_2 = 88.06$)				
0	0.8793	2.227	26.52	-
0.0050	0.8810	2.432	28.67	454.83
0.0075	0.8818	2.505	29.62	439.21
0.0100	0.8827	2.578	30.54	428.17
0.0125	0.8836	2.657	31.50	424.98
0.0150	0.8844	2.737	32.45	421.36
Propylene Carbonate ($[n_2]_D = 1.4203$; $M_1 = 78.11$; $M_2 = 102.09$)				
0	0.8793	2.264	26.34	-
0.0050	0.8808	2.471	29.22	602.57
0.0075	0.8816	2.569	30.50	580.46
0.0100	0.8824	2.689	31.98	590.78
0.0150	0.8839	2.864	34.02	538.38
0.0200	0.8855	3.097	36.51	535.10
0.0250	0.8870	3.297	38.48	511.89
0.0300	0.8886	3.498	40.31	491.90
Butylene Carbonate ($[n_2]_D = 1.4271$; $M_1 = 78.11$; $M_2 = 116.12$)				
0	0.8793	2.297	26.81	-
0.0050	0.8808	2.485	29.44	552.71
0.0075	0.8815	2.572	30.57	529.17
0.0100	0.8823	2.686	32.01	547.47
0.0200	0.8853	3.092	36.60	516.39
0.0300	0.8883	3.457	40.17	472.15
0.0500	0.8943	4.221	46.32	417.14
Glycerin Carbonate ($[n_2]_D = 1.4587$; $M_1 = 88.11$; $M_2 = 118.09$)				
0	1.0340	2.215	24.57	-
0.0053	1.0359	2.421	27.39	556.62
0.0053	1.0359	2.399	27.10	502.06
0.0076	1.0368	2.545	28.96	603.05
0.0079	1.0369	2.463	27.93	450.28
0.0103	1.0377	2.608	29.73	525.97
0.0108	1.0379	2.608	29.73	502.74
0.0129	1.0387	2.718	31.02	525.09
0.0133	1.0388	2.718	31.02	510.02
0.0150	1.0395	2.765	31.56	490.59
0.0150	1.0395	2.766	31.57	491.34

at different compositions as mole fraction average of pure components, which was a valid simplification, confirmed experimentally using limited mixture density measurements.

Then, molar polarization of the solute (carbonate), P_2 , as a function of the concentration was calculated from

$$P_2 = \frac{P - P_1(1 - x)}{x} \quad (2)$$

where x is the mole fraction of the solute in the solution and P_1 is the molar polarization of the solvent.

The value of the molar polarization of the solute in infinite dilution or the total polarization, $[P_2]_0$ was determined by graphical extrapolation of P_2 to zero concentration. Permanent dipole moment of the solute was calculated using Debye equation:

$$\mu = 0.0128\sqrt{T([P_2]_0 - [R_2]_D)} \quad (3)$$

where μ is dipole moment; T is absolute temperature; ($[P_2]_0 - [R_2]_D$) is orientational polarization; and $[R_2]_D$ is solute molar refraction, $[R_2]_D = ([n_2]_D^2 - 1)/([n_2]_D^2 + 2)(M_2/d_2)$. M_2 , d_2 , and $[n_2]_D$ are solute's molecular weight, density, and refractive index, respectively.

Experimental data on dielectric constant and molar polarization of dilute solutions of alkylene carbonates in a nonpolar

Table 3. Total Polarization, $[P_2]_0$, and Dipole Moment, μ , of Alkylene Carbonates

property	EC	PC	BC	GC
total polarization $[P_2]_0$	498.0	620.4	566.7	553.3
dipole moment, μ/D	4.81	5.36	5.10	5.05

Table 4. Hildebrand Solubility Parameters (MPa^{1/2}) of Alkylene Carbonates at 25 °C

EC ^a	PC	BC	GC	source
31.3 ^b and 34.3 ^c	27.6	24.8	34.1	this work
30.1 ^b	27.2			ref 22

^a Cohesion parameter $[(\Delta H - RT)/V]^{1/2}$. ^b ΔH in eq 4 is enthalpy of vaporization. ^c ΔH in Eq 4 is enthalpy of sublimation.

solvent are summarized in Table 2. Values of total polarization, $[P_2]_0$, and dipole moments are given in Table 3. The uncertainty of dipole moment determination in this work was estimated to be less than 5 %.

There is a very good agreement (within 0.1 D) between EC dipole moment values determined in this work and reported in the literature.^{17,18} However, our data on PC (5.36 D) and known literature values (4.94¹⁷ and 4.557¹⁹) are in disagreement with each other. It appears that dipole moment value of PC obtained in this work is slightly higher than it was expected. Dipole moment value reported by Kepma and Lee¹⁷ (4.94 D) is deemed to be more realistic and is recommended until more literature data are reported. Dipole moments of BC and GC were measured for the first time.

Solubility Parameters

Hildebrand solubility parameters of alkylene carbonates were determined at 25 °C directly from Hildebrand and Scott²⁰ equation:

$$\delta = \left(\frac{-U}{V}\right)^{1/2} = \left(\frac{\Delta H_{\text{vap}} - RT}{V}\right)^{1/2} \quad (4)$$

where U is cohesive energy; V is molar volume ($mL \cdot mol^{-1}$); ΔH_{vap} is enthalpy of vaporization ($J \cdot mol^{-1}$); and R is gas constant, $R = 8.314 (J \cdot mol^{-1} \cdot K^{-1})$. Liquid molar volumes (V) of alkylene carbonates at 25 °C used in our calculations were reported earlier.² Enthalpy of vaporization values were estimated from vapor pressure data⁸ using the Watson method.²¹

Ethylene carbonate unlike the other carbonates is a solid at 25 °C. Hildebrand parameter has a liquid-state basis. Therefore, eq 4 does not yield a Hildebrand parameter but rather cohesion parameter.²² Two values of cohesion parameter were calculated for EC in this work. The first value was obtained with the use of extrapolated enthalpy of vaporization $\Delta H_{\text{vap}}(25 \text{ °C})$. The second one was determined via enthalpy of sublimation $\Delta H_{\text{sub}}(25 \text{ °C})$, which was assumed to be a sum of $\Delta H_{\text{vap}}(25 \text{ °C})$ and enthalpy of fusion ΔH_{fus} .²³ Calculated Hildebrand parameters of alkylene carbonates are summarized in Table 4. Our values of Hildebrand solubility parameters for EC and PC agree very well with those reported in the literature.²² Hildebrand parameters for BC and GC have not been previously reported.

Hansen partitioned the cohesive energy density ($-U/V$) for a species into contributions from dispersion forces, dipolar interactions, and hydrogen bonding:

$$\frac{U}{V} = \frac{U_D}{V} + \frac{U_P}{V} + \frac{U_H}{V} \text{ or } \delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (5)$$

where δ_T is the total solubility parameter; and δ_D , δ_P , and δ_H are partial solubility parameters, namely, dispersion, polar, and hydrogen bonding components, respectively.

Table 5. Hansen Solubility Parameters (MPa^{1/2}) of Alkylene Carbonates at 25 °C

method	EC	PC	BC	GC	preferred method
Hansen Dispersive Component, δ_D					
group-contribution method	18.4	17.0	16.9	17.9	+
homograph method	18.0	17.3	16.9	17.9	
Hansen Polar Component, δ_P					
group-contribution method	9.5	7.4	6.2	9.6	+
modified Böttcher (eq 7)	23.1	19.8	15.7	19.5	
modified Beerbower (eq 8)	22.2	21.7	18.9	20.6	
Karim and Bonner (eq 9)	21.3	19.6	16.3	18.6	
Hansen Hydrogen Bonding Component, δ_H					
group-contribution method	12.3	10.8	9.9	18.9	+
eq 10 (from Hildebrand δ , δ_D , and δ_P)	10.4	9.0	9.1	21.5	

All Hansen partial solubility parameters were estimated using van Krevelen and Hoftyzer group contribution method.²⁴ Van Krevelen and Hoftyzer expressed Hansen partial solubility parameters in the following form:

$$\delta_D = \frac{\sum_Z F_D}{V} \quad \delta_P = \frac{\left(\sum_Z F_P^2\right)^{1/2}}{V} \quad \delta_H = \left(-\sum_Z \frac{U_H}{V}\right)^{1/2} \quad (6)$$

where F_D , F_P , and U_H are structural group contributions for dispersion, polar, and hydrogen bonding components, respectively; and V is molar volume.

Several other methods were used to predict partial solubility parameters δ_D , δ_P , and δ_H . The homograph method²² was used to determine dispersion component δ_D , which agrees very well with δ_D calculated by group-contribution method. Böttcher (eq 7) and Beerbower (eq 8) correlations in Hansen and Beerbower modification²⁵ and Karim and Bonner correlation²⁶ (eq 9) were used to determine molar component δ_P of carbonates:

$$\delta_P = \left[\frac{50\,660}{V^2} \frac{\epsilon - 1}{2\epsilon + n_D^2} (n_D^2 + 2)\mu \right]^{1/2} \quad (7)$$

$$\delta_P = \frac{37.433\mu}{V^{1/2}} \quad (8)$$

$$\delta_P = \frac{102.48\mu}{V^{3/4}} \quad (9)$$

where δ_P is the Hansen polar component (MPa^{-1/2}); V is the molar volume (mL·mol⁻¹); ϵ is the dielectric constant; n_D is the index of refraction; and μ is the dipole moment (D).

Values of ϵ , n_D , and μ used in eqs 7 to 9 were taken from this work. Molar volumes (V) were reported earlier.² Equations 7 to 9 predict similar values of polar component (δ_P), but they are significantly higher than those predicted from the group-contribution method. Such difference is not surprising because of group-contribution method's questionable ability to handle ortho -COO- groups discussed by Hansen and Beerbower²⁵ and Hoy.²⁷ To calculate hydrogen bonding component δ_H , the

modified eq 5 was used with total solubility parameter (δ_T) substituted to Hildebrand parameter (δ):

$$\delta_H = \sqrt{\delta^2 - \delta_P^2 - \delta_D^2} \quad (10)$$

Even though δ_T and δ are not identical, such substitution is common and valid for practical purposes.²² The summary on Hansen solubility parameters developed using different theoretical approaches is given in Table 5. Preferred methods of Hansen solubility parameters calculations of carbonates were found to be (i) Van Krevelen and Hoftyzer group-contribution for dispersion component δ_D (eq 6), (ii) modified Böttcher (eq 7) for polar component (δ_P), and (iii) eq 10 for hydrogen bonding component (δ_H).

Literature Cited

- (1) Clements, J. H. *J. Ind. Eng. Chem. Res.* **2003**, *42*, 663–674.
- (2) *JEFFSOL Alkylene Carbonates*; technical bulletin; Huntsman Corporation: Austin, TX, 2001.
- (3) *JEFFSOL Alkylene Carbonates Comparative Solvents Data*; technical bulletin; Huntsman Corporation: Austin, TX, 1999.
- (4) Wakihara, M.; Yamamoto, O. *Lithium Ion Batteries—Fundamentals and Performance*; Kadansha Ltd.: Tokyo, 1998.
- (5) *JEFFSOL AG Carbonates*; technical bulletin; Huntsman Corporation: Austin, TX, 2004.
- (6) Sun, Y.; Liu, J.; Kimbleton, E.; Wang, J. Composition base for topical and cosmetic preparations. U.S. Patent 5,993,787, 1999.
- (7) Dack, M. R. J. The influence of solvents on chemical reactivity. In *Solutions and Solubilities*, Part II; Dack, M. R. J., Ed.; John Wiley & Sons—Interscience: New York, 1976.
- (8) Chernyak, Y.; Clements, J. H. *J. Chem. Eng. Data* **2004**, *49* (5), 1180–1184.
- (9) Smyth, C. P. *Dielectric Behavior and Structure*; McGraw-Hill: New York, 1955.
- (10) Lee, F. M. *Chem. Eng.* **1998**, *105* (12), 112–121.
- (11) Payne, R.; Theodorou, I. E. *J. Phys. Chem.* **1972**, *76* (20), 2892–2900.
- (12) Barthel, J.; Gores, H. J.; Kraml, L. *J. Phys. Chem.* **1996**, *100* (9), 3671–3674.
- (13) Graml, H. M. Dissertation, Regensburg, 1994.
- (14) Wolf, R. R. Dissertation, Regensburg, 1996.
- (15) Ding, M. S. *J. Electrochem. Soc.* **2003**, *150* (4), A455–A462.
- (16) Böttcher, C. J. F. *Theory of Electric Polarization*; Elsevier: New York, 1952.
- (17) Kempa, R.; Lee, W. H. *J. Chem. Soc. (London)* **1936**, 1958.
- (18) Arbuzov, B. A.; Shavsha, T. G. *Doklady Akad. Nauk S.S.S.R.* **1949**, *68*, 1045–1048.
- (19) McClellan, A. L. *Tables of Experimental Dipole Moments*; Raha Enterprises: El Cerrito, CA, 1989.
- (20) Hildebrand, J.; Scott, R. *Regular Solutions*; Prentice Hall: Englewood Cliffs, NJ, 1962.
- (21) Pooling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2000.
- (22) Barton, A. F. M. *Handbook on Solubility Parameters and Other Cohesion Parameters*, 4th ed.; CRC Press: Boca Raton, FL, 1988.
- (23) Vasil'ev, I. A.; Korkhov, A. D. *Zh. Fiz. Khim.* **1973**, *47*, 2710.
- (24) Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*, 2nd ed.; Elsevier: Amsterdam, 1976.
- (25) Hansen, C.; Beerbower, A. Solubility parameters. In *Kirk-Othmer Encyclopedia of Chemical Technology*, Suppl. Vol., 2nd ed.; Standen, A., Ed.; Interscience: New York, 1971; pp 889–910.
- (26) Karim, K. A.; Bonner, D. C. *Polym. Eng. Sci.* **1979**, *19*, 1174.
- (27) Hoy, K. L. *J. Paint Technol.* **1970**, *42*, 76–118.

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