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THE PROPERTIES OF ETHYLENE CARBONATE AND ITS USE IN ELECTROCHEMICAL APPLICATIONS. A Literature Review

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June 1985

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THE PROPERTIES OF ETHYLENE CARBONATE AND ITS USE IN ELECTROCHEMICAL APPLICATIONS

A Literature Review

Paul H. Johnson

June 1985

This report was prepared in partial satisfaction of the requirements for the Masters of Science degree in Chemistry under the supervision of Professor Charles W. Tobias.

This work was supported by the Assistant Secretary of Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

The Properties of Ethylene Carbonate and Its Use in Electrochemical Applications
A Literature Review

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I. Introduction

Ethylene carbonate ($C_3H_4O_3$) is an important industrial solvent and used extensively in the textile and cosmetic industry. Ethylene carbonate (EC) and propylene carbonate (PC) were tested by William Harris (1958) [87] for use as solvents for electrochemical applications. High chemical and electrochemical stability, low toxicity, good ionizing and solvating ability and low volatility make both EC and PC suitable solvents for electrochemical applications. Propylene carbonate has been used extensively in lithium batteries and nonaqueous electrochemical studies. The use of EC in electrochemical technology has been limited, probably due to the fact that EC is a solid at room temperature (fp 36.4 ^{o}C). However, the high freezing point of pure EC should not limit the use of EC as a solvent for electrochemical applications, because the freezing point is easily depressed by combining EC with another solvent or by the addition of salts (freezing point depression constant: 5.39 ^{o}C-kg/mole). A wide range of information on the physical, spectral, solvent and electrochemical properties of EC is available. The intent of this review is to stimulate the use of ethylene carbonate in nonaqueous electrochemistry.

This review covers the literature up to January 1, 1985. Chemical Abstracts was a major citation source. The chemical substance index of the sixth (1957) through tenth collective indices, and volumes 96 through 101 (December 1984) were checked for spectroscopic, physical property, solvent property, chemical

stability and electrochemical application primary source material. The EC systematic name: carbonic acid, cyclic ethylene ester was used in the sixth through eighth collective index (volume 51 through 75), and the name 1,3-dioxolan-2-one after volume 75. References to polymerization, use in textiles and cosmetics, exotic organic reactions, and most patents were not pursued. Journals that were specifically searched for EC material using the subject/keyword index or table of contents include the Journal of Chemical and Engineering Data volume 1 (1956) through volume 29:4 (July 1984), the Journal of Solution Chemistry volume 1 (July 1972) through volume 13:12 (December 1984), the Journal of the Electrochemical Society volume 121 (1974) through volume 131:12 (December 1984), and the Journal of Electroanalytical and Interfacial Electrochemistry volume 101 (1981) through volume 181:2 (December 24, 1984).

The properties of five cyclic carbonate esters, including EC are described in Lee, The Chemistry of Nonaqueous Solvents, volume IV, Lagowski, ed., Academic Press, 1976, pp. 174-188. A technical sales brochure on ethylene carbonate and propylene carbonate available from Texaco Chemical Company[1] contains descriptions of the physical and chemical properties of EC in addition to material not included in this review, such as the commercial application, handling, and toxicity of EC. Several general references on the properties of

[1]Texaco International Sales Corporation, Box 430, Bellaire, Texas, 77401, telephone: 713-666-8000.

nonaqueous solvents are listed in a footnote.[2]

II. Structure of Ethylene Carbonate

A. Molecular Structure of EC and Long-range Structure of Solid EC

Ethylene carbonate is a cyclic carbonate ester. The structure of solid EC was determined by C. Brown (1954)[1] by X-ray crystallography. The molecular structure of EC in the solid is shown in Figure 1. The ring is in the half-chair conformation, and the C-C bond penetrates the plane containing the carbonate group at an angle of 20°.[3] The point group of the molecule is C_2. The solid consists of stacks of EC layers where the dipoles are parallel in a layer and antiparallel to those in adjacent layers. This arrangement is illustrated in Figure 2. The unit cell is monoclinic (a = 8.92 Å, b = 6.25 Å, c = 6.94 Å; B = 100'34") and the space group is C2/c. The EC molecules in a layer appear to be hydrogen bonded into long chains, and the layers held together by dipole-dipole forces [1,108].

Figure 3 is a diagram of a Courtauld model for the molecular structure of EC. This model shows schematically the electron

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[2]General references on nonaqueous solvents include:
Covington, Dickinson, The Physical Chemistry of Organic Solvent Systems, (Plenum Press, 1973);
Popovych, Tomkins, Nonaqueous Solution Chemistry, (Wiley, 1981);
Coetzee, Richie, Solute-Solvent Interactions, (Dekker, 1969);
Burgess, Metal Ions in Solution, (Wiley, 1978);
Janz, Tomkins, Nonaqueous Electrolytes Handbook, (Academic Press, 1972);
Cox, Annual Reports on Progress in Chemistry, 70A, 249(1973);
Jensen, Chemical Review, 78, 1(1978);
Parker, Quarterly Review, 16, 163(1962).

[3]The molecular structure is incorrectly described and pictured in the review by W. Lee (1976) [86].

distribution.

A controversy concerning the molecular structure of EC in the liquid and gas phases was started when C. Angel (1956)[2] reported that based on IR studies, the point group of the EC molecule was C_2 in the solid (i. e. half-chair, in agreement with C. Brown (1954) [1]), but appeared to be C_{2v} (i. e. planar) in the liquid and gas. Subsequent studies addressed this controversy. The conclusions of a microwave study by I. Wang et al. (1965)[4] were that the out-of-plane contribution to the rotational inertia is too large to be due only to the methylene hydrogens, and that the doublets of equal intensity in the microwave spectrum suggest that the ring conformation oscillates between two energetically equivalent conformations with a low energy barrier between the two conformations. This process is illustrated in Figure 4.

Other studies have concluded that the half-chair conformation of the EC molecule in the solid observed by C. Brown (1954) [1] is retained to some extent by the EC molecule in other states. Such is the case with a ^{13}C NMR study [7]. In the structure calculated using a semi-empirical SCF-MO method [3],[4] the C-C bond intersects the carboxylate group plane at an angle of 2.3^{o}, much flatter than the 20° angle observed in solid EC by X-ray crystallography [1]. The proton NMR of EC dissolved in a liquid crystal is consistent with small ring puckering motions of the methylene carbons, rather than

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[4]SCF-MO is Self-consistent field-Molecular orbital

planar with totally eclipsed conformation [77].[5] Photoelectron Spectroscopy (PES) studies indicate that the ring is planar or nearly planar. The dependence of calculated ionization potentials (CNDO method)[6] on the angle that the C-C bond intersects the carboxylate plane indicates that this angle must be less than 20° [5]. Other workers assumed EC was planar, but the ionization potentials calculated for the lone pairs (10.53 eV and 9.69 eV by CNDO/2 and INDO,[7] respectively) were significantly lower than the observed potential (11.47 eV) [17]. A vibronic analysis of the lowest energy PES band concluded that the molecule does not have C_{2v} symmetry in the gas phase [18]. On the other hand, the simplicity of the PES of EC may be due to a molecular high symmetry (i. e. planar C_{2v}) [6].

The general consensus given by the literature is that the molecular structure of ethylene carbonate is half-chair (point group C_2) in all states. In the solid, the EC molecule is frozen into a strongly puckered half-chair conformation, as illustrated in Figure 1. The molecule is nearly planar in solution, the liquid, and the gas, with a rapid fluctuation between two energetically equivalent half-chair conformations, as illustrated in Figure 4.

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[5]In addition, the relative distances between the four hydrogens were calculated.

[6]CNDO is Complete Neglect of Differential Overlap

[7]CNDO/2 is CNDO, Version 2; INDO is Intermediate Neglect of Differential Overlap. The CNDO, INDO and SCF-MO calculations give the molecular orbitals and electronic energies of a molecule for a specified arrangement of the nuclei. For a discussion of these calculations, see: T. Lowry, K. Richardson, Mechanism and Theory in Organic Chemistry, (Harper & Row, 1976).

B. Long-Range Structure in Liquid Ethylene Carbonate

There exists a large body of evidence to support the idea that the long-range structure of solid EC persists in the liquid in the form of a short-range orientation of EC molecules (analogous to the case of ice and water). In the solid, the EC molecules in a layer may be hydrogen bonded into long chains [1,108] and the layers held together by dipole-dipole forces. Many studies conclude that these two types of interactions also exist in the liquid. The greater-than-unity Kirkwood g-factor[8] of ethylene carbonate (g = 1.2 to 1.6 by various reports) is attributed to a parallel alignment of EC dipoles. Such an alignment would exist in a hydrogen-bonded EC aggregate. A compilation of reported Kirkwood g-factors is given in

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[8]The Kirkwood g-factor is an empirical parameter which measures the deviation of the observed bulk dielectric constant from that calculated from the dipole moment of the molecule using the Onsager equation. The Onsager and Kirkwood equations differ by the inclusion of the "g" in the Kirkwood equation:

$$\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} = \frac{4\pi N^2 \mu^2}{9RT\bar{v}} g$$

N is Avogadro's Number and $\bar{v}$ is the molar volume. In the absence of intermolecular interactions, the Kirkwood g-factor is unity. A greater-than-unity g-factor is obtained when intermolecular interactions cause parallel alignment of the molecular dipoles, since this alignment will give the bulk solvent a higher dielectric constant than expected from the dipole moment and the Onsager equation. Antiparallel dipole alignment causes the dielectric constant to be lower than expected and a less-than-unity g-factor is calculated.

For discussion of the Kirkwood g-factor, see:

J. Deutch, Ann Rev Phys Chem, 24, 301(1973)
R. Amey, J Phys Chem, 72:9, 3358(1968)
J. Kirkwood, Faraday Society Trans, 42A, 7(1946)
J. Kirkwood, J Chem Phys, 7, 911(1939).

Table 1.[9]

The influence of the dipole moment on the intermolecular interactions in a pure liquid may account for the correlation between boiling point and dipole moment among chloro-substituted EC molecules [60]. The trend of increasing boiling point with increasing dipole moment is apparent from the data in Table 2.[10] The interactions of the carbonyl oscillators on neighboring EC molecules are credited with causing the Raman anisotropic component of the carbonyl stretch to occur at a higher frequency than the isotropic component. This split is 70 cm^{-1} in the solid [106] and decreases as the temperature increases and EC is diluted [107]. This phenomenon has been attributed to dipole-dipole interactions which exist in the solid and persist in the liquid, but are weakened by dilution and increasing temperature [63]. O. Bonner and S. Kim (1970) [9] concluded from the vapor pressure of EC-benzene mixtures that the EC molecules formed clusters, and that the first association constant is 1.10 and the average value of subsequent association constants is 1.58. A value of 8.3 EC molecules per cluster in pure EC was derived, and the authors concluded that the association is due to dipole-dipole interactions.

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[9]The Kerr constant is another measure of intermolecular association. The molar Kerr constant of EC is 3.505×10^{-10} [122]. At 45 ^{o}C, the Kerr constant of EC relative to nitrobenzene is 0.55 ± 0.03 [111]. The Kerr constant is described in the review by J. Deutch (1973).

[10]From the standpoint of molecular weight, the boiling points of EC derivatives should increase as the chlorine content increases.

The persistence of the long-range structure of the solid after the compound melts, as proposed here for EC, has an extensive literature in the case of water,[11] and has been reported for acetonitrile. The conclusion of an X-ray scattering study of liquid acetonitrile was that a short-range ordering of acetonitrile molecules exists in the liquid. The X-ray data indicate that acetonitrile molecules form 11 Å diameter five-member clusters, where four molecules form a first coordination sphere around a central acetonitrile molecule. On the other hand, dipole-dipole interaction calculations indicate that 13 Å clusters are formed, and each cluster would contain eight molecules.[12] The short-range structure of liquid acetonitrile deduced from X-ray scattering is grossly like that of solid ethylene carbonate: stacked layers of molecules where the dipoles in a layer are parallel and the dipoles in adjacent layers are antiparallel.[13]

It is probable that liquid EC, like acetonitrile (and water), retains a short-range order like that of the solid. The interactions among EC molecules should be stronger than those among acetonitrile molecules, since the dipole moment, donor number and accepter number

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[11] For information of the structure of water, see: F. Wells, Structural Inorganic Chemistry, (Clarendon Press, Oxford, 1975), p. 541.

[12] If an 11 Å diameter cluster contains 5 molecules, a 13 Å diameter cluster should contain 8.3 molecules, based on the ratio of volumes.

[13] The unit cell is orthorhombic, with eight acetonitrile molecules per unit cell and a lattice site occupancy of 95% at 20 °C [145].

are greater for EC than acetonitrile,[14] so this short-range ordering is likely to be even more predominant for EC than acetonitrile.

C. Electronic Structure of Ethylene Carbonate

The electronic structure of EC has been studied using photoelectron spectroscopy (PES) [5,16-20] and IR spectroscopy [135]. The results of several PES studies are summarized in Table 3. CNDO calculations based on the first three ionizations of EC showed strong mixing of the σ-bonding orbitals and the oxygen lone pairs [5]. A PES study of the oxygen lone pairs proposed a carbonyl oxygen charge of 0.32 and 0.38 by CNDO/2 and INDO calculations, respectively [17]. Electron density maps of the orbitals responsible for the first three ionizations are given in Figure 5. A good description of the bonding in EC based on the PES of the three lowest energy ionizations is given in [6]. A particularly thorough PES study measured the first ten ionizations and presented a detailed vibrational analysis of the lowest-energy band [18]. The hybridization of the carbonyl carbon was described based on the IR stretch of the carbonyl and the O-C-O bond angle [135].

The spatial distribution of electrons in the EC molecule is shown schematically in Figure 3.

III. Properties of Pure Ethylene Carbonate

A. Physical and Thermodynamic Properties

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[14]The dipole moment of acetonitrile is 3.92 D, but 4.8 D for EC. The donor number is 14.1 for acetonitrile and 16.4 for EC. The acceptor number is 18.9 for acetonitrile and 19.1 for EC.

Various properties of EC are presented in Tables 4-20. Reliable values of selected properties are listed in Table 4.

The **boiling point** of EC at atmospheric pressure is 238 °C [50,60,139]. The boiling points at various pressures are listed in Table 5. The **freezing point** of EC may not exactly coincide with the melting point since EC is easily supercooled, but the best melting point reported may be 36.37 ± 0.02 °C, obtained using zone refined EC [71]. Several values for the freezing and melting point are listed in Table 6. The **densities** of EC at various temperatures are listed in Table 7. Supercooled EC has a density of 1.3383 g/cc at 25 °C [124]. Over the temperature range of 50-100 °C, the following equation gives the density within ± 0.1%:[15]

$$\rho(t)_{g/cc} = 1.3084 - 0.00111\ (t - 50),\ t \text{ in } {}^{o}C$$

The **viscosity** of EC decreases with an increase in temperature ($\delta\eta/\delta T \simeq -0.034$ cP/°C, 25-55 °C). The viscosity of supercooled EC at 25 °C is 2.547 cP [87]. The viscosity of EC versus temperature is given in Figure 6. Several values of the static and dynamic viscosity are listed in Table 8. A plot of EC **vapor pressure** versus temperature over the range of 130-238 °C is given in Figure 7. C. Hong et al. (1982) [36] reported that over the temperature range of 95-176 °C, the vapor pressure of EC is given by the Antoine equation:

$$\ln P_{atm} = 9.75917 - 4194.365/(181.076 + t) \pm 0.0001,\ t = 95\text{-}176\ {}^{o}C$$

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[15] The equation is accurate below 50 °C, and predicts an EC density of 1.3362 g/cc at 25 °C, 0.16 % lower than the literature value of 1.3382 g/cc [124].

J. Choi and M. Joncich (1971) [62] reported that the logarithm of the vapor pressure of solid EC was linear with 1/T from 273.9 to 296.6 K. Using the three data points from reference [62] and the three lowest temperature data points from reference [36], the logarithm of the vapor pressure was basically linear with 1/T, but was best fit by the equation:

$$\ln P_{mm\ Hg} = 16.9566 - 4258.6\ T^{-1} - 567.74 \times 10^{6}\ T^{-2},\ T = 274\text{-}373\ K$$

The six vapor pressures used to obtain this equation are listed in Table 9.

The **heat of combustion** of EC has been reported and several values are listed in Table 10. Both W. Calhoun (1983) [140] and G. Silvesto and C. Lenchitz (1961) [69] used the Washburn correction[16] and reported similar values: -1165.87 ± 3.74 kJ/mole at 298.15 K and -1171.28 ± 0.63 kJ/mole at 303.14 K. However, J. Choi and M. Joncich (1971) [62] reported a value of -1069.35 kJ/mole, and did not mention using the Washburn correction. In contrast, the Texaco brochure [139] lists -234 kcal/mole and -2662 cal/g (which corresponds to -980.8 kJ/mole).

The **heat of formation** is calculated from the heat of combustion. The standard heat of formation of solid EC was reported by W. Calhoun [140]: -586.30 ± 3.76 kJ/mole. Using the data of Silvesto and Lenchitz (1961) [69], Calhoun calculated a standard heat of formation of -580.86 ± 1.30 kJ/mole. Choi and Joncich [62] reported

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[16] J. Washburn, J Res Natl Bur Std US, 10, 525(1933).

a standard heat of formation of -682.83 kJ/mole for solid EC and -604.30 kJ/mole for EC gas, which gave a standard **heat of sublimation** of 78.53 kJ/mole [62]. Heats of formation are listed in Table 11.

The **heat of fusion** was derived from calorimetric measurements by I. Vasil'ev and A. Korkhov (1973) [141,143] and O. Bonner et al. (1969) [64]. P. Thompson et al. (1971) [71] assumed that the difference between the heat of solution of solid EC in water and liquid EC in water equalled the heat of fusion. R. Kempa and W. Lee (1962) [72] used cooling curves and the method of Plato, but this method may be inaccurate due to the tendency of EC to supercool. Several heat of fusion values are listed in Table 12. A reliable value for the heat of fusion is 13.2 kJ/mole (35.8 cal/g) [71].

The **heats of vaporization** of EC at various temperatures are listed in Table 13. Over the temperature range of 150 to 200 °C, the heat of vaporization is 56.3 to 52.2 kJ/mole. The heat of vaporization at 25 °C should be about 65.2 kJ/mole, given a heat of fusion of 13.295 kJ/mole [141,143] and a heat of sublimation of 78.534 kJ/mole at 25 °C [62],

The **thermodynamic properties** of EC from 52-350 K were reported by I. Vasil'ev and A. Korkhov (1974) [143].[17] Using calorimetry, the **heat capacity** was measured from 52-350 K. The heat capacity was approximately linear over this temperature range (except at the melting point), and the equation:

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[17] Reference [141] is an English summary of reference [143].

$$C_p(T) = 88.9772 + 0.1586\ T\ \text{J-mole}^{-1}\text{K}^{-1},\ T \text{ in } ^{o}\text{K}$$

was used to approximate the heat capacity over the temperature range of 0-52 K.[18] The heat capacity versus temperature for EC and propylene carbonate (PC) are plotted in Figure 7. The **thermodynamic properties:** C_p, S_T, $(H_T - H_o)/T$, **and** $-(G_T - H_o)/T$ at various temperatures are listed in Table 14. The error was estimated to be $\pm$ 1.8 J/mole-K. The EC sample was subjected to fractional fusion and the following results were obtained: The **triple point** is 309.46 K,[19] the melting depression 0.10 degree, and the purity of the sample 99.93 $\pm$ 0.05 % [141]. Several values of the **specific heat** of EC over the temperature range 15-150 ^{o}C were reported in [139] and these are listed in Table 15. The heat capacity at 25 ^{o}C is 117.14 J/mole-K [143].

Formally, EC does not self-ionize and therefore should be an insulator. The **conductivity,** strongly dependent on the types and concentrations of impurities, is a useful indicator of purity. Pure EC should have a specific conductivity in the range of 0.1-1 X $10^{-7}\Omega^{-1}\text{cm}^{-1}$. Various literature values of EC conductivity are listed in Table 16 and Table 22. R. Seward and E. Vieira (1958) [27] put the EC **dielectric constant** data of R. Payne and I. Theodorou (1972) [67] into equation form:

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[18] In addition, they assumed zero residual entropy at absolute zero, and set the enthalpy to be zero at absolute zero.

[19] The pressure at the triple point was not mentioned. However, from the vapor pressure equation reported above, the vapor pressure is 0.0652 mm Hg at 309.46 K.

$$\epsilon(t) = 85.1 - 0.408\ (t - 50)\ \pm 0.5\ \%,\ t = 25\text{-}70\ ^{o}C$$

Other dielectric constant values are listed in Table 17.

Several measured values of the **dipole moment** of EC are listed in Table 18, and these range from 4.78 to 4.93 D. Typically, the dipole moment is calculated from the dielectric properties of a benzene solution of EC. B. Arbousow (1960) [59] calculated the dipole moment of EC for various conformational structures, but these values were lower than the observed moment; the highest calculated was 3.96 D.

The **index of refraction, thermal conductivity and flashpoint** of EC are listed in Table 19.

The **cryoscopic constant** or freezing point depression constant of EC has been extensively investigated and several values are listed in Table 20. The reported values fall into two distinct groups: those with $K_f \simeq 7$ and those with $K_f \simeq 5.4$, and this discrepancy generated considerable discussion in the literature. However, the difference may be due to inaccurate or omitted units, or miscalculations involving solute concentration rather than a difference in real values, since the two group values are neatly related by the density of EC: 1.3 g/cc. It is likely that the molal cryoscopic constant is 5.39 ± 0.12 ^{o}C-kg/mole (5.55 [64], 5.40 [64], 5.32 [71], 5.275 [94]). and the molar cryoscopic constant is 7.00 ± 0.04 ^{o}C-l/mole (6.96 [72], 7.01 [72], 7.03 [70]).

B. Spectra of Ethylene Carbonate

The **infrared (IR) and Raman spectra** of EC have been extensively studied. A complete vibrational assignment is given in B. Fortunato

et al. (1971) [12]. The far-IR (33-1000 cm^{-1}) was studied by J. Durig et al. (1968) [15] and assignments were made to skeletal bending modes. The carbonyl stretch frequency was reported to be 1862.5 cm^{-1} in the vapor phase, 1804 cm^{-1} in the liquid, and 1834 cm^{-1} in the solid [12]. For EC in solution, the carbonyl stretch generally decreases with increasing acceptor number of the solvent (1842 to 1800 cm^{-1}) [109]. The IR and Raman spectra of chloro-EC derivatives were studied by R. Pethrick and A. Wilson (1974) [129]. The carbonyl stretch is split into a doublet by Fermi resonance with the first harmonic of the $-CH_2$ rocking vibration (892cm^{-1}). This Fermi resonance has been studied by isotopic substitution [13] and solvent variation [14]. Many other papers describe the IR or Raman spectra of EC (A few post-1960 papers are: [8,118,61,134]).

The **nuclear magnetic resonances** of all the nuclei in EC have been studied. The proton NMR of EC consists of a single singlet. Reported chemical shifts in CCl_4 are 5.61 ppm [10] and 5.80 ppm [8] relative to TMS.[20] The proton NMR of EC dissolved in a liquid crystal was recorded [77-79]. The ^{13}C spectrum of EC in $CDCl_3$ (15 weight-%) at 25 ^{o}C consisted of two peaks: 156.02 ppm for the carbonyl carbon and 65.10 ppm for the methylene carbon [7]. The J_{C-H} coupling constant was 156.2 Hz. The ^{17}O NMR spectrum of neat EC at 75 ^{o}C obtained using Fourier transform techniques consisted of two singlets. The ether oxygen resonance occurred at 106 ppm and the

[20]Other reported shifts are 4.50 ppm [55] and 4.20 ppm [81], but the reference resonance and solvent were not mentioned.

carbonyl oxygen resonance occurred at 212 ppm, relative to TMS [11].

The **mass spectrum** of EC was studied by P. Brown and C. Djerassi (1968) [21]. The **electron spin resonance** (ESR) of the neutral radical derived from EC in 1 % H_2O_2 by near room temperature abstraction of a methylene hydrogen by photolytically generated hydroxyl radicals has been studied [22]. The absolute value of the hyperfine coupling of the hydrogen of the radical carbon is 14.17 gauss, and 35.30 gauss for the methylene hydrogen. For this neutral radical, the g-value is 2.00302, the pi-electron spin density is 0.788, and the absolute value of McConnell's constant is 18.0 gauss. The **photoelectron spectra** (PES) of EC were described above in the section on electronic structure.

No **ultrasonic absorbance** was detected in the range 15 to 65 MHz [8]. The **microwave spectrum** of EC was studied and the rotational inertia calculated by I. Wang et al. (1965) [4]. The spectrum consists of doublets, which the authors said arise from the oscillation of EC between two molecular conformations (see Figure 4). The rotational constants and moments o* inertia are listed in Table 21.

C. Solvation Power

The ability of a polar molecule to coordinate to another polar molecule or ion can be predicted from three molecular parameters: the dipole moment, the donor number and the acceptor number. The donor number is a measure of the ability of a molecule to coordinate to a cation. The donor number is a measure of the Lewis basicity of a

molecule and is a predictor of the strength of a donor-acceptor complex where the molecule is the donor. The acceptor number is a measure of the ability of the molecule to coordinate to an anion. It is a measure of the Lewis acidity of the molecule and a predictor of the strength of a donor-acceptor complex where the molecule is the acceptor. An estimate for the enthalpy of formation of a donor-acceptor complex is:[21]

$$\Delta H = - [DN \times AN]/100 \text{ in kcal}$$

where DN is the donor number of the donor molecule and AN is the acceptor number of the acceptor molecule. The donor number is defined as the $-\Delta H_{solution}$ of the molecule in 1 mM $SbCl_5$ in dichloroethane in kcal/mole.[22] The donor number of EC determined by this method is 16.3 [82].

Many chemical phenomena involve the formation of a donor-acceptor complex. The complex formed by a donor molecule and $SbCl_5$ (in this case a reference acceptor) provides a basis for the Gutmann donor number scale. A linear relationship often exists between an observable (e. g. NMR shift, IR spectra, enthalpy, conductivity) and the donor number, and this relationship can also be used for determining the donor number. Once the correlation between the observable and the donor number is established using molecules with known donor numbers, that observable can be used to obtain the donor

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[21] V. Gutmann, The Donor-Acceptor Approach to Molecular Interactions, (Plenum Press, New York, 1978), p. 31.

[22] V. Gutmann, loc. cit., p. 19.

number of other molecules. The defining method is not the only reliable method of obtaining the donor number. The analogous situation exists for the acceptor number.

The acceptor number of a solvent equals the ^{31}P chemical shift of Et_3PO in the solvent relative to that in hexane, divided by the chemical shift of $Et_3PO:SbCl_5$ in dichloroethane relative to the ^{31}P resonance of Et_3PO in hexane:[23 24]

$$AN = [\delta - \delta_{hexane}] / [\delta_{SbCl_5} - \delta_{hexane}] \times 100$$

The acceptor number of EC has not been determined by this method. However, the acceptor number often scales with an observable property of the donor-acceptor complex where EC is the acceptor. The carbonyl stretch of perinaphthenone in solution has been studied [83]. In this case, the perinaphthenone is a reference donor, and bonds to the acceptor molecule--the solvent--via the carbonyl group. The carbonyl stretch of perinaphthenone increases with decreasing solvent molecule acceptor number,[25] and was 1643 cm^{-1} in EC, 1641 cm^{-1} in DMSO, and 1645 cm^{-1} in acetonitrile. Thus, the acceptor number of EC should be about 19.1 since DMSO and acetonitrile have acceptor numbers of 19.3 and 18.9, respectively.[26]

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[23] Mayer, Gutmann, Gerger, Monash Chem, 106, 1235(1975).

[24] V. Gutmann, loc. cit., p. 28.

[25] unpublished observation

[26] unpublished result

The dipole moment is a predictor of the strength of the electrostatic interaction between the solvent and an ion. The ion-dipole interaction depends on the charge distribution in the solvent molecule. The dipole of an aprotic solvent molecule is usually only effective in cation solvation because the positive end of the dipole is diffuse and cannot get physically close to the anion. The negative end of the dipole is usually exposed (e. g. the carbonyl oxygen on ethylene carbonate) and can get close to the cation. On the other hand, the positive center of a protic solvent molecule is the acidic proton and this often can get close to an anion. Protic solvents usually solvate anions much more strongly than aprotic solvents. The dipole moment of a molecule is often determined from the dielectric properties of dilute solutions in benzene. The dipole moment of EC is 4.8 D.

There exists a synergistic relationship between solvation by donor-acceptor complex formation and solvation by ion-dipole or dipole-dipole interaction. For example, when a carbonyl donor solvent forms a donor-acceptor complex with a cation, the dipole is aligned such that the ion-dipole interaction also stablizes the complex. Thus the enthalpy of formation of a donor-acceptor complex involves two terms. One is the reduction in electronic energy on complex formation. The electronic states of the donor and acceptor mix (in essence, a charge transfer complex is formed), and the new adduct has a lower electronic energy than the parent molecule. The other term is purely electrostatic, and may simply be an ion-dipole

or dipole-dipole interaction. It may be difficult to separate the electrostatic contribution to the formation energy of a particular donor-acceptor complex from that due to the reduction in electronic energy.

Several studies of EC adducts exist. As described above, quantitative and qualitative information about the donor and acceptor properties of EC can be extracted from studies of EC adducts. Generally, EC is the donor in the adduct [73-76,80,81,84], but EC is the acceptor in one study [83]. An IR study of solid EC adducts with strong Lewis acids $SbCl_5$, $AlCl_3$, $SnCl_4$, $TiCl_4$, and $ZrCl_4$ gave the relative acidity of the Lewis acids to be $SbCl_5 > AlCl_3 > TiCl_4 > SnCl_4 > ZrCl_4$, and concluded that the basicity of EC was between that of acetone and amides [74]. The stoichiometries of the adducts formed, as determined by elemental analysis are: $SbCl_5$:EC, $AlCl_3$:2EC, $SnCl_4$:2EC, $TiCl_4$:4EC, $ZrCl_4$:4EC. Another IR study of EC adducts with $SbCl_5$, $TiCl_4$, BCl_3, and Co^{2+} gave similar results [81]. The proton NMR of EC shifts from 4.20 ppm to 5.42 ppm (versus TMS) in the adduct $SbCl_5$:EC. The melting points and the stoichiometries of some adducts were given: $SbCl_5$:EC (153 ^oC), $TiCl_4$:2EC (116 ^oC), and BCl_3:EC (95 ^oC).

An IR study of the OH stretch in phenol and hexafluoroisopropanol [75] reported the OH frequency shift relative to the alcohol in CCl_4 and the enthalpy of base-alcohol hydrogen bonding for 24 solvents including EC (ΔH = -4.7 and -6.1 for phenol-EC kcal/mole and hexafluoroisopropanol-EC hydrogen bond

formation, respectively). A study of the hydrogen stretching frequency of phenylacetylene and the proton NMR of chloroform relative to that in CCl_4 upon addition of the donor solvent showed that the change in stretch frequency correlated linearly with the change in proton chemical shift [76]. The general trend is a decrease in the stretch frequency of the acetylenic hydrogen and a downfield shift in the proton magnetic resonance with an increase in the donor number of the solvent.[27] The carbonyl stretch of EC in MeOH relative to that in CCl_4 was reported [84]. An NMR study of hydrogen bonding between chloroform and EC concluded that the complex formed was weak [73]. From the effect of millimolar quantities of EC on the conductance of 0.2 mM tributylammonium picrate in orthodichlorobenzene, the formation constant and ΔG for the formation of the hydrogen bonded tributylammonium-EC adduct were obtained [80]. At 25°C, K = 430/M and ΔG = -3.59 kcal/mole. V. Sastri (1972) studied the charge transfer band of various carbonato cobalt coordination complexes, including one with EC, and recorded the UV and IR spectra [147]. The acceptor properties of EC are expressed in a study of the effect of donor molecules on the carbonyl stretch of perinaphthenone [83].

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[27] On forming the donor-phenylacetylene complex, electron density from the donor is probably transferred to an antibonding orbital of the acetylenic ≡C-H bond. This would lower the bond force constant and result in a decrease in stretch frequency. Surprisingly, the acceptor atom--hydrogen in this case--should take a more positive charge density, even though electron density has been transferred to phenylacetylene from the donor. The reduction in electron density on the acetylenic hydrogen would deshield this nucleus and cause a downfield shift in its magnetic resonance. For more information on this phenomenon, see: V. Gutmann, loc. cit., p. 4.

The solvent may affect reaction rates by specific (donor-acceptor) or nonspecific (electrostatic) interactions with the reacting molecules. In the case of mixed solvents, trends in reaction rates may be affected by the effect on solvent-solute interactions wrought by the $solvent_1$-$solvent_2$ interaction. The rate of quarternization of n-butyl bromide with pyridine and 4-picoline increased with the solvent dielectric constant [125]. The rate constants for ligand substitution for several transition metal complexes (Fe(II), Co(III), Cr(III), Pd(II), Pt(IV)) decreased (50 %) as the EC increased (to 40 weight-%) [88]. The protic and aprotic solvents differ greatly in their ability to solvate anions, and fall into two separate groups when indexed by the acceptor number. A study of the effect of solvent on the reaction rate of:

$$n\text{-}BuBr + N_3^- \rightarrow n\text{-}BuN_3 + Br^-$$

concluded that $E^{\ddagger}$ is lower in aprotic dipolar solvents ($\leq$17 kcal) than in protic dipolar solvents ($\geq$ 20 kcal) [130].

VI. Purification of Ethylene Carbonate

Ultra-pure EC is usually obtained by distillation of EC at reduced pressure several times before use. The boiling points of EC at various pressures are listed in Table 5. The major impurities in EC distilled twice over CaO under vacuum at 75 ^{o}C were water (15 ppm), ethylene glycol (10 ppm), and an unidentified organic substance (70 ppm) [40]. Zone refining [94,102] and fractional freezing [34] also effectively purified EC. The conductivity (lower) (see Table 16) and the melting point (higher and sharper) (see Table 6) are two

criteria for assessing the purity of EC. The conductivities and gas chromatograms of EC as-received and after distillation from molecular sieves (after 2 days storage over 4A sieves), lithium metal, CaO, and without additives were presented by G. Pistoia (1971) in [39]. The conductivities are listed in Table 22. The chromatograms were very similar for all distillates.[28]

V. Chemistry of Ethylene Carbonate

A. Thermal Stability of Ethylene Carbonate

The chemical stability of ethylene carbonate was described by W. Harris in 1958 [87] as follows:

> Ethylene carbonate is decomposed slowly at temperatures between 200 and 250 °C in the absence of water or catalysts. Above 125 °C alkalis, and acids to a lesser extent cause rapid decomposition. At 100 °C pure ethylene carbonate is stable in the presence of water, but traces of salts such as sodium chloride accelerate its hydrolysis. At this same temperature, alkalis or strong acid cause rapid hydrolysis. Ethylene carbonate may be distilled rapidly at atmospheric pressure with only slight decomposition. Acidic materials, such as zinc chloride, aluminum chloride, or sulfuric acid at high temperatures will cause appreciable decomposition of ethylene carbonate into carbon dioxide and ethylene oxide.

In his discussion of chemical stability, Harris cites a 1952 ethylene carbonate technical bulletin and a 1956 propylene carbonate technical bulletin published by the Jefferson Chemical Company (now owned by Texaco). A brief description of the chemical stability of EC is

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[28] It should be noted that although the water content of solvents like EC and propylene carbonate can be reduced to a few ppm, the salts used to make electrolyte solutions can be more difficult to dry. For example, G. Pistoia [39] determined the water content of $LiClO_4$ by the Karl Fisher method to be 1.2 % in as-received salt, 0.5 % after 3 days at 150 °C under vacuum, and 0.1 % after fusion under vacuum.

given in the product brochure on ethylene and propylene carbonate available from the Texaco Chemical Company [139]. Much of that description is presented below:

> Ethylene carbonate and propylene carbonate and their aqueous solutions are stable under ordinary storage conditions. If an acid, base or salt is present in the aqueous solutions of these products, decomposition will occur. The decomposition rate increases with temperature. Primary decomposition products are alkylene oxide and carbon dioxide.
>
> Ethylene and propylene carbonate present no unusual hazards of polymerization or explosion. These products have high flash points; however, they can be ignited and must be protected from sources of ignition or static electrical discharge.

Ethylene carbonate should be less stable than propylene carbonate. The methyl group on PC protects the ester linkage from nucleophiles and other reactive groups by blocking the collision of the nucleophile with the carbonato group. The rate constants for acid and alkaline hydrolysis of EC are twice those of PC [54]. However, EC has demonstrated stability in a variety of experimental and technological milieu.

B. Chemical Reactivity of Ethylene Carbonate

Many reactions involving the ester group of EC have been reported. Generally, the reaction mixture must be heated above 100 ^{o}C. However, EC readily reacts with a variety of 1° and 2° aliphatic amines at low temperatures ($<$ 50 ^{o}C) to form carbamates. A detailed study of kinetics of aminolysis of EC by n-butylamine at 50 ^{o}C showed that the reaction is basically second order with K_2 = 0.1-0.41/mole-hr, and catalyzed by water, the final product, and n-butylamine itself [138]. Other amines which react with EC at low temperatures include ethanolamine, diethylamine, $RNHNH_2$, and ammonia

(anhydrous under pressure or in methanol or water) [139]. Diamines, $H_2N(CH_2)_nNH_2$, yield bis-carbamates [121,139]:

$$HOCH_2CH_2CH_2OOCNH(CH_2)_nNHCOOCH_2CH_2CH_2OH$$

The mechanisms of nucleophilic attack in reactions of substituted EC at 60 °C with butylamine, glycine, aniline, ethylene diamine, imidazole and OH^- were studied [55]. Ethylene carbonate reacts with various amine hydrobromides at 150 °C to yield β-hydroxyethylammonium bromides and CO_2. Amine hydroiodides also react with good yields, but amine hydrochlorides give poor yields [137].

Hydroxyalkylation of EC can occur with compounds containing an active hydrogen (e. g. alcohol, mercaptans, phenols, thiophenols, amines, carboxylic acids). The reactions are run at 100-200 °C using a basic catalyst (e. g. K_2CO_3 0.5 weight-%), with the simultaneous production of CO_2 and water [139]. Transesterification can occur in the absence of catalysts at 100-150 °C [139].

The reactivity of EC with various salts at > 150 °C was reported by E. Bergmann and I. Shahak (1966) [116]. 2-Fluoroethanol was prepared by heating EC with KF to 180 °C [116].[29] The following reaction sequence was proposed:

$$EC + KF \rightarrow FCH_2CH_2OCOOK$$

$$FCH_2CH_2OCOOK + H_2O \rightarrow FCH_2CH_2OH + KHCO_3$$

$$2\ KHCO_3 \rightarrow CO_2 + H_2O + K_2CO_3$$

The initial presence of a trace of water was assumed. When equimolar

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[29] Preparation of ^{18}F-fluoroethanol by reaction of EC with $K^{18}F$ was reported by Lemine, Schroader, Reed, J Labelled Cpd Radiopharm, 13-2, 211(1977); Chemical Abstracts # 87:52682q.

quantities of EC and urea or NaOCN were heated to a temperature necessary to initiate CO_2 evolution, oxazolidin-2-one was produced. Reaction of EC with thiourea or KSCN yielded ethylene sulfide, and with aniline, 2-anilinoethanol. Similarly, reaction of EC with LiCl yielded 2-chloroethanol, NaBr yielded 2-bromoethanol, and NaCN yielded 2-cyanoethanol, but NaI gave only ethylene oxide.

Ethylene carbonate reacts with MgX_2 to form the halohydrin $HOCH_2CH_2X$ (I), with R_2Mg to form $RCOOCH_2CH_2OH$ (II), and with RMgX to form a mixture of I and II [123]. The photochemically initiated chlorination of EC proceeds by the replacement of hydrogen by chlorine one hydrogen at a time [119].

Ethylene carbonate was polymerized by heating with the catalysts $Al(acac)_3$ (150 °C) or $Ti(OBu)_4$ (130 °C) to produce the polymer:

$$(-CH_2CH_2OCOOCH_2CH_2O-)_n$$

and n CO_2 from 2n EC. The NMR, IR and solubility of the polymer were reported [128]. Using $TiCl_4$, $(n\text{-}Bu_3Sn)_2O$, or $ZnEt_2/H_2O$ (2:1) as the catalyst produced different polymers. A mechanism for the polymerization was proposed by K. Soga et al. (1977) [115]. No polymerization of pure EC was observed after 93 hours at 140 °C,[30] and many coordination compounds did not catalyze polymerization.[31] S.

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[30] Pure EC did not polymerize when heated up to 250 °C [114].

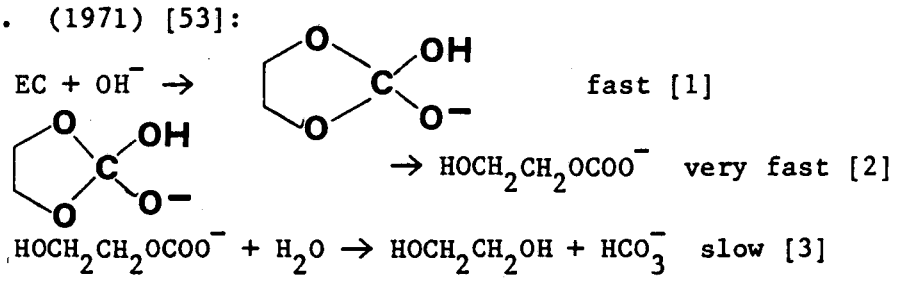
[31] Compounds which did not catalyze EC polymerization include (from reference [128]): $Fe(acac)_3$, $Mn(acac)_3$, $Cr(acac)_2$, $Co(acac)_2$, $Fe(acac)_3$, $Mn(acac)_3$, $Mn(acac)_2$, $MnO_2(acac)_2$, $AlCl_3$, $ZnCl_2$, $Al(O\text{-}iPr)_3$, $Sn(Ph)_3Cl$.

Sakai et al. (1973)[32] reported catalysis of EC polymerization by $(n\text{-}Bu)_3Sn(OCH_3)$ or $(n\text{-}Bu)_2Sn(OCH_2CH_2O)$ at 150 °C to yield:

$$(-CH_2CH_2O)_{1-x} - (CH_2CH_2OCOOCH_2CH_2O-)_x$$

and polymerization catalyzed by some inorganic alkaline compounds at high temperature.

The hydrolysis of EC has been extensively studied. The mechanism of alkaline hydrolysis was proposed by J. Katzhendler et al. (1971) [53]:



Rate constants for reaction [1] were determined using high frequency conductivity measurements, a pH-stat method, and a flow method at various temperatures 0-35 °C [53]. The rate constants for reaction [3] were determined using high frequency conductivity measurements [49][33] and a pH-stat method [57,58] over a temperature range of 15-55 °C. These rate constants and Arrhenius parameters for alkaline hydrolysis are listed in Table 23. The rate of hydrolysis is not affected by added salt (NaCl, NaI, KI [53]; KCl [49]), and is slower in 33 weight-% dioxane-water than in pure water (K_1= 23.0 1/mole-min

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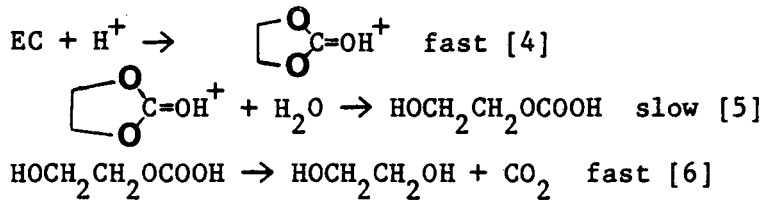
[32] S. Sakai, T. Fujiami, S. Sakurai, M. Suzuki, T. Aono, paper presented at the 30th Meeting of the Chemical Society of Japan, Osaka, 1973.

[33] The rate constants for alkaline hydrolysis reported in [56] were discredited by the authors of [49].

versus 27.5 in pure water at 0 °C [53]).[34]

A mechanism of acid hydrolysis of EC was proposed [48,52]:



The rate constant for reaction [6] was calculated from the pressure changes due to the evolution of CO_2 by I. Levin et al. (1963) [48], and by titration of trapped evolved CO_2 by S. Sarel (1960) [52]. Rate constants and Arrhenius parameters for acid hydrolysis are listed in Table 23. The rate constant for reaction [6] may be similar to that of reaction [3].[35]

A $H_2^{18}O$ tracer study of the mechanism of acid and alkaline hydrolysis of EC was reported [51]. The steric and polar effects of substitution on hydrolysis were studied [54]. The hydrolysis of vinylene carbonate was studied [50]. The rates of hydrolysis of cyclic carbonates were related to the carbonyl stretching frequency [135].

VI. Physical Properties of Ethylene Carbonate Solutions

A. Solutions of Electrolytes

1. Solubilities

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[34] The rate of acid hydrolysis of EC should be faster in dioxane-water than in pure water [48,52].

The solubilities of many salts in EC are listed in Table 24. The solubilities of some salts are much greater in EC that in propylene carbonate. The higher dielectric constant and lower molar volume of EC may account for the higher solubilities. However, the solubilities are substantially lower in EC and PC than in water. Water has a much smaller molar volume, therefore more solvent molecules per unit volume are available to solvate a solute molecule. In addition, the aprotic solvents have low accepter numbers and solvate anions poorly.[36] The higher electrolyte solubilities observed for water are largely due to the ability of water to solvate anions. For comparison, the solvent dielectric constant (ϵ), dipole moment (μ), donor number (DN), acceptor number (AN), molar volume (ml/mole), moles of solvent per 100 grams solvent, and solubilities of KI, NaI, and $CaCl_2$ for EC, PC and water are tabulated below.

solvent	solvent properties						solubility g salt/100g solvent		
	ϵ,	μ,	DN,	AN	ml per mole	mole per 100g	KI,	NaI,	$CaCl_2$
EC(40°C)	89.6,	4.80D,	16.3,	19.1	66.66	1.136	11.16,	37.60,	0.2
PC(40°C)	56.89,	4.98D,	15.1,	18.3	86.25	0.980	3.42,	16.63,	0.06
water (25°C)	78,	1.85D,	18.0,	54.8	18.0	5.549	127.5, (0°C,	184, 25°C,	74.5 20°C)

The solubility of CuF_2 in the solvent 0.84 F $LiClO_4$ in EC at 30

[36]Another advantage of water in ion solvation is second coordination sphere solvation, which is generally negligible in aprotic solvents like EC and PC. See: V. Gutmann. loc. cit., pp. 110-120.

^{o}C was 0.0098 mole/kg solvent [40].[37] The stabilities and solubilities of silver complexes in EC at 40 ^{o}C reported by J. Cabon et al. (1975) [46] are listed in Table 25. The anions involved are $B\phi_4^-$, IO_3^-, Cl^-, Br^-, I^-, SCN^-.

2. Conductivities of Electrolyte Solutions

The limiting equivalent conductances of many salts in EC are listed in Table 26. The limiting ionic conductances of various ions are presented in Table 27. Note that assumptions are made in order to separate the equivalent conductance into ionic components, and this may cause systematic errors in the ionic conductance values. R. Kempa and W. Lee (1961) [105] assumed that the Walden product[38] for Et_4N^+ is 0.294 $cm^2\Omega^{-1}mole^{-1}$-cp. G. Petrella and A. Sacco (1978) [103] assumed that $\Lambda_o(TABB\phi_4)/2 = \lambda_o(TAB^+) = \lambda_o(B\phi_4^-)$ (Coplan-Fuoss assumption).

The specific conductances of a wide variety of EC solutions are listed in Table 28. The specific conductances of saturated solutions of NaI, NaBr, $CaCl_2$, and KI at 40 ^{o}C were reported [87]. The Walden products of 0.1 to 2.2 m Bu_4Picrate in EC at 91 ^{o}C are fairly concentration independent [104]. The equivalent conductances of many salts at 36.8 ^{o}C were reported for a range of concentrations 0.01 to 1 m [94].[39] The specific conductances of various concentrations of

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[37] For data on the solubility of CuF_2 in various concentrations of $LiClO_4$ in EC at 25 ^{o}C and 30 ^{o}C, see [40] and [39], respectively.

[38] The Walden Product is the product of the conductivity and the solution viscosity: $\Lambda \times \eta$.

[39] The equivalent conductances for the most dilute solutions are

KPF_6, KCNS, and $LiClO_4$ in EC at 25 °C were reported [39]. The maximum specific conductivities for these solution [40] are listed in Table 52. The conductivities of various concentrations of zinc iodide in EC at 40 °C were reported [64].

3. Viscosities of Electrolyte Solutions

The viscosities of many ethylene carbonate electrolyte solutions have been measured. The data by P. Thompson et al. [102] shows that electrolyte solutes increase the viscosity and low viscosity nonelectrolyte solutes decrease the viscosity of EC. The densities and relative viscosities for the most concentrated solutions described in reference [102] are listed in Table 29. The viscosities of 0.10 to 2.20 F $Bu_4NPicrate$ in EC at 91°C [104] are listed in Table 30. The viscosities and densities of 1 m solutions of $LiClO_4$, KCNS, and KPF_6 at 30°C are listed in Table 31. Descriptions of the solute-solvent and solvent-solvent interactions were derived from viscosity data using the Jones-Dole equation[40] [102,103]. The authors concluded that EC interacts more strongly with all the ions tested than with other EC molecules.

4. Activity and Osmotic Coefficients of Solutes

Osmotic and activity coefficients for various solutes in EC have been calculated from freezing point depression data [64,94]. The range of solute concentration studied by R. Wood and Q. Craft (1978) [94] (0.1 to 0.7 molal) was higher than that studied by O. Bonner et

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listed in Table 28.

[40] G. Jones, M. Dole, JACS, 51, 2950(1929).

al. (1969) [64] (0.002 to 0.2 molal), and the solution temperatures differed (36.8°C for [94] and 40°C for [64]). The results were discussed in terms of solvent-solvent, solute-solvent, and solute-solute interactions. The osmotic coefficients ranged from 1 to 0.75 and the activity coefficients ranged from 1 to 0.6, generally. At low concentrations [64], the osmotic coefficients of nonelectrolytes (urea, dimethylurea, bisethylene(trimethylammonium iodide)) decrease with increasing concentration more rapidly than in the case of ionic solutes (NaI, KI, CsI); Weak electrolytes (ammonium iodide, tetrapropylammonium iodide) are midway. At higher concentrations (> 0.2 m), the osmotic coefficients of NaI and KI increase with increasing concentration [94]. The osmotic coefficients of $ZnCl_2$ and ZnI_2 are unusually low (0.1 and 0.2, respectively) compared to other solutions (~0.95) [64]. A plot of the osmotic coefficient at 36.8°C versus solute concentration (0 to 0.6 molal) for NaI, KI, CsI and alkylammonium iodides is given in Figure 9.

5. Partial Molal Volumes of Solutes

The partial molal volume of several alkylammonium and alkali metal halides (usually iodide) have been studied [89-91,94,102,136]. D. Agarwal et al. (1976) [90] thoroughly studied many solutes in EC. In the temperature range of 40 to 80°C and concentration range 0.3 to 0.6 molal, the partial molal volume decreased linearly with $\sqrt{c}$ for all tetraalkylammonium iodides except Me_4NI at 40°C (which increased linearly), but for NaI and KI at all temperatures a linear increase was observed. The limiting partial molal volume of NaI and KI peaked

at 50°C (44.55 and 47.80 ml/mole, respectively). The limiting partial molar volumes of $Hept_4NI$ and Hex_4NI increased linearly with temperature, whereas those of Et_4NI, Pr_4NI, Bu_4NI, and Pen_4NI increased monotonically, but with a significant negative second derivative [90].[41] The limiting molal volume was virtually solvent independent for the aprotic nonaqueous solvents studied, although a slight increase with dielectric constant was generally observed [89,91].[42] For tetraalkylammonium iodides, the limiting partial molal volume temperature coefficient was about 0.05 %/°C [89,90]. For NaI and KI, the limiting partial molal volume peaked near 50 °C, then decreased with temperature by about 0.05 %/°C [89,90].

The partial molar volumes of many solutes in dilute EC solutions at 40 °C reported in reference [102] are listed in Table 29.

The limiting ionic partial molal volumes of alkali metal cations and mineral anions (e. g. I^-, NO_3^-) were solvent dependent with no systematic temperature dependence [136]. The limiting ionic partial molal volumes of tetraalkylammonium cations (Me_4N^+ to $Hept_4N^+$) in the nonaqueous solvents studied were practically solvent independent for dipolar nonaqueous solvents[43] and scaled linearly with the cation

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[41] Me_4NI was not soluble enough for inclusion in the study [90].

[42] Solvents used in [89] were dimethylformamide (DMF), dimethylsulfoxide (DMSO), propylene carbonate (PC), ethylene carbonate (EC), formamide (FA), N-methylpropionamide (NMP), N-methylacetamide (NMA). The solvents used in [91] were DMSO, PC, EC, FA, NMP, and NMA.

[43] The solvents used in [136] were water, D_2O, methanol, propylene carbonate, ethylene carbonate, dimethylsulfoxide, formamide, dimethylformamide, and N-methylacetamide.

crystallographic radius over a temperature range of 25 to 70°C. There was a small temperature dependence (~ 0.05%/°C). The limiting ionic partial molal volumes of iodide in EC at 40, 50, 60 and 70 °C were 24.0, 26.1, 26.2 and 25.4 cm^3/mole, respectively [136].

B. Mixtures of Ethylene Carbonate With Nonelectrolytes

1. Solubilities of Nonelectrolytes in EC

The solubilities of several nonelectrolytes in EC at 40 °C are listed in Table 32. The relative solubilities of the components of natural gas[44] at 15, 25 and 35 atmospheres were reported in addition to the solubilities of N_2, CO_2, CH_4, C_2H_6, and C_3H_8 at 1 atmosphere, all at 40 °C [98]. The partial pressures of SO_2 and acetylene were not reported along with the solubilities (26 g and 0.6 g per 100 g EC at 40 °C) [139]. The saturation solubility of EC in water at 25 °C was 88.80 weight-% using an interferometer [23]. However, a 95 weight-% EC was liquid at 25 °C [35]. EC is miscible with water above 40 °C. The saturation solubility of EC in benzene was 78.10 weight-% and 54.46 weight-% in chloroform at 25 °C using an interferometer [23]. Solubility information on many compounds of commercial importance (e. g. camphor, gum shellac, polyacrylonitrile) can be found in [139].

2. Ethylene Carbonate-Water Mixtures

The properties of EC-water mixtures have been extensively studied. Sources of density, dielectric constant, viscosity, and

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[44]Composition of the natural gas: 90 % CO_2, 4.5 % N_2, 3.5 % CH_4, 1 % C_2H_6, 0.5 % C_3H_8, 0.5 % C_4 and C_5 [98].

refractive index data at 25 and 40 °C over a wide range of composition are listed in Table 33. The dielectric constant, density, and viscosity of some EC-water mixtures at 40 and 25 °C are given in [25]. The density, dielectric constant, vapor pressure, and Debye-Huckel constants from 293 to 328 K for 50 weight-% EC in water are given in [31]. In addition, the Kirkwood g-factor, molar polarization, and molar refraction at 40 °C of various EC-water mixtures are given in [45]. The mole fraction, weight fraction, and volume fraction of EC in water for various compositions are compared in [45].

Figure 10 is a plot of the freezing point of EC-water mixtures versus composition made using data from [124]. It is remarkable that the freezing point is virtually independent of composition in the range of 40 to 85 weight-% EC.

Significant differences exist among the three reports on the excess dielectric constant of EC-water mixtures, but in all cases, the magnitude of the excess is small (< 4). R. Payne et al. (1972) [67] reported a positive excess, A. D'Aprano (1974) [35] reported a negative excess, and J. Cabon et al. (1975) [45] reported both (depending of the composition). The excess dielectric constant was greater at 40 °C (-4.3 at $\chi_{EC} = 0.70$) than at 25 °C (-2.2 at $\chi_{EC} = 0.63$) [35].

The excess molar volume exhibited a maximum negative deviation in the water rich region near $\chi_{EC} = 0.2$ at 25 °C. The relative excess molar volume of the EC-water mixture was a minimum at $\chi_{EC} = 0.16$ (-

0.73 %) at 25 °C and at χ_{EC} = 0.08 (-0.5 %) at 40 °C [35]. This was rationalized on the basis of a two-structure model for liquid water. J. Cabon et al. (1975) [45] reported a maximum negative deviation of -0.5 % at χ_{EC} = 0.2 at 40 °C. A maximum positive deviation from additivity was observed for the density, viscosity, and refractive index near χ_{EC} = 0.2 [45]. It should be noted that the free energy of mixing of EC with water (and with benzene and chloroform) was a minimum near χ_{EC} = 0.25 (-980 J/mole) [23].

At 40 °C, the limiting partial molar volume of EC in water is 64.69 and of water in EC, 17.96 cc/mole [45]. The partial molar volume of EC is 66.68 and of water 17.96 for χ_{EC} = 0.2 to 0.9 at 40 °C [45].[45] Density measurements indicate that the limiting partial molar volume of EC in water is 62.3 $\pm$ 0.4 cc/mole at 25 °C (Two calculated values are 63.1 and 62.9) [68]. In the theoretical calculation of the molar volume of solutes in water, terms associated with solute-water interactions were necessary for the presence of carbonyl groups, but not for the presence of ether oxygen [68]. This implies that significant hydrogen bonding exists between water and carbonyl oxygen, but not between water and ether oxygen. Based on the absorbance at 958 nm, EC depolymerizes water [112]. This indicates the presence of significant EC-water interactions, which may induce positive deviations from Raolt's Law and cause EC osmotic and activity coefficients to be below unity in water [112]. The

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[45] At 40 °C, the molar volume of EC is 66.64 ml/mole and that of water is 18.15 [45].

increase in the activity coefficient for transfer of Ag^+ from water to EC-water was attributed to the disruption of the 3-D structure of liquid water by the addition of EC (up to 0.3 χ_{EC}) [47]. This disruption increased the amount of free (not hydrogen-bound) water.

A picture of the EC-water microstructure based on the above facts may be as follows. There exist strong hydrogen-bonding interactions between the carbonyl of EC and water. EC effectively disrupts the 3-D hydrogen-bonded structure of water, increasing the amount of monomeric water. Small amounts of water effectively interfere with the crystallization of EC.

The dissociation of acetic acid in a 50 weight-% EC-water mixture over a temperature range of 20 to 55 °C was studied [29]. The dissociation constants were derived from EMF measurements of the cell:

$$Pt|H_2(g,1\ atm)|HAc(m),NaAc(m),NaCl(m)|AgCl|Ag$$

and the results fit the equation:

$$pK = 442.49/T + 2.2903 + 0.0062735\ T\ ,\ T \text{ in kelvins}$$

The pK at 25 °C was 5.645, compared to 4.756 in pure water.[46] The thermodynamic functions were derived:

ΔH^o = -530 cal/mole,

ΔS^o = -27.6 cal/mole, and

ΔC_p^o = -17 cal/mole-K.

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[46] The pK of acetic acid in other water mixtures at 25 °C were listed in reference [29]: 5.660 in 50 weight-% methanol-water, 5.84 in 50 weight-% ethanol-water, about 6.58 in 50 weight-% dioxane-water, and 5.271 in 50 weight-% glycerol-water.

For the transfer dissociation process:

$$HAc(s) + Ac^-(w) + H^+(w) = HAc(w) + Ac^-(s) + H^+(s)$$

where s and w indicate the mixed solvent and pure water, respectively:

ΔG_t^o = 1212 cal/mole,

ΔH_t^o = -432 cal/mole,

ΔS_t^o = -5.5 cal/mole-K, and

$\Delta C_{p,t}^o$ = 20 cal/mole-K.

On a mole fraction scale, these quantities are (numerically) 912, -432, -4.5 and 20, respectively.[47]

The thermodynamic functions of HCl in 50 weight-% EC-water over a temperature range of 25 to 55 °C were studied [31]. From EMF measurements on the cell:

$$Pt|H_2(g,760\ torr)|HCl(m)\ in\ 50\ weight\text{-}\%\ EC\text{-}water|AgCl|Ag$$

the activity coefficients, partial molar heat capacity, and partial molar enthalpy of HCl in 50 weight-% EC-water and the heat, entropy and heat capacity of transfer of HCl from pure water to the EC-water mixture were derived. The activity coefficient of HCl in the mixture satisfactorily fit the extended Debye-Huckel equation. The relative partial molar enthalpy and relative partial molar heat capacity relative to the infinitely dilute solution were derived, respectively, from the first and second derivative with respect to

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[47] The thermodynamics of dissociation in pure water are described in: H. Harned, R. Ehlers, JACS, 54, 1350(1932); 55, 652(1933); and R. Robinson, R. Stokes, Electrolyte Solutions, 2nd Ed., 1970, app. 12, Table 1.

temperature of the activity coefficient.[48] For the transfer of HCl from pure water to 50 weight-% EC-water at 25 °C are:[49]

ΔG_t^o = 49 cal/mole,

ΔH_t^o = -1530 cal/mole, and

ΔS_t^o = -5.3 cal/mole-K.

The thermodynamics of HCl in EC-water mixtures over a composition range of 0-78 weight-% EC and temperature range 25 to 45 °C were derived from EMF measurements [28] on the cell:

$$Pt|H_2(1\ atm)|HCl(m),EC(\chi),Water(1-\chi)|AgCl|Ag$$

The mean activity coefficient of HCl, which ranged from 0.82 to 0.92, increased with decreasing HCl concentration, increased with increasing EC content, and decreased slightly with increasing temperature. The relative partial molal heat capacity and relative partial molal heat content increased with temperature, and were a minimum near 30 weight-% EC for all temperatures and all HCl concentrations studied (0.01 to 0.05 m). Primary, secondary and total medium effects were discussed.

Where comparisons are possible, there appears to be good agreement among activity coefficient values between [28] and [31], however, the relative partial molar enthalpy and relative partial molar heat capacity results reported in [31] and the relative partial

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[48]The thermodynamics of HCl in pure water were reported by R. Bates, V. Bower, J Res Nat Bur Stand, 53, 283(1954).

[49]The thermodynamics of transfer of HCl from pure water to 50 weight-% methanol-water were mentioned in [31]: ΔG_t^o = 440cal/mole, ΔH_t^o = -312cal/mole, and ΔS_t^o = -2.5cal/mole-K.

molal heat content and heat capacity values listed in [28] are very different.

The solvation of silver halides, iodide, iodine and triiodide in EC-water mixtures at 25 and 40 °C was thoroughly studied, largely by EMF measurements [47]. The solubilities of iodine at 40 °C in several EC-water mixtures and the activity coefficients for transfer of iodine from water to EC-water solvent mixtures, ${}^{w}\Gamma^{s}$, (which are the ratio of the solubility of iodine in in pure water to that in the mixture) are listed in Table 34. The solubility products of AgCl and AgBr (determined by potentiometric titration) and the formation constants for $AgBr_2^-$ and $AgCl_2^-$ are listed in Table 35. The solubility product of AgX decreases with increasing EC content, but the formation constant of the higher halide complexes AgX_2^- increases. Listed in Table 36 are the formal potentials of the iodide-triiodide couple, $E'^{o}(I^-/I_3^-)$, and the triiodide-iodine couple, $E'^{o}(I_3^-/I_2)$, and the formation constant for triiodide (where $I^- + I_2 = I_3^-$) calculated according to the equation: $\log K = [E'^{o}(I_3^-/I_2) - E'^{o}(I^-/I_3^-)]/0.093$. The activity coefficients for the transfer of triiodide and iodide from water to EC-water mixtures were calculated from EMF data. The iodine activity coefficients for transfer according were calculated using the equations:

$$\log {}^{w}\Gamma^{s}(I^-) = [{}^{w}E'^{o}(I^-/I_3^-) - {}^{s}E'^{o}(I^-/I_3^-)]/0.093 + \tfrac{1}{2}\log {}^{w}\Gamma^{s}(I_3^-)$$

$$\log {}^{w}\Gamma^{s}(I_3^-) = [{}^{w}E'^{o}(I_3^-/I_2) - {}^{s}E'^{o}(I_3^-/I_2)]/0.062 + 3/2\ \log {}^{w}\Gamma^{s}(I_2)$$

These activity coefficients for transfer are listed in Table 37.

The activity coefficients for transfer of Ag^+ from water to EC-water were calculated from EMF measurements according to the equation:

$$\log {}^{W}\Gamma^{S}(Ag^+) = [{}^{S}E'^{o}(Ag^+) = {}^{W}E'^{o}(Ag^+)]/c$$

where c is 0.059 at 25 °C and 0.062 at 40 °C. The EMF's and activity coefficients for transfer are listed in Table 38. The activity coefficients for transfer of bromide and chloride were calculated from solubility products and Ag^+ activity coefficients for transfer according to the equation:

$$\log {}^{W}\Gamma^{S}(X^-) = \log K_s{}^{W} - \log K_s{}^{S} - \log {}^{W}\Gamma^{S}(Ag^+)$$

These activity coefficients for transfer are listed in Table 37.

The enthalpy of solution of Bu_4NBr in EC-water mixtures at 45 °C were measured [24]. The ΔH_{soln} decreased sharply from 33.08 KJ/mole in pure EC to a plateau at 22 KJ/mole for χ_{EC} = 0.1 to 0.85, then decreased sharply to 5.89 KJ/mole in pure water. The solubilities of KCN in three EC-water mixtures and pure water at 25 °C were reported [24]: 845 g/l in pure water, 440 g/l in 22 weight-% EC, 320 g/l in 33.3 weight-% EC, and 300 g/l in 45 weight-% EC.

3. Other EC-Cosolvent Mixtures

The physical properties of several EC-cosolvent mixtures have been reported, in addition to those of EC-water as previously noted. These include: the density, dielectric constant and refractive index for EC-dioxane (0-55 weight-% EC) at 25 °C [41]; the density, dielectric constant, viscosity, and specific conductance of EC-acetonitrile (11.7 to 100 weight-% AN) at 25 °C [27]; the density,

dielectric constant, refractive index, viscosity, excess dielectric constant, and excess molar volume of EC-N-methylacetamide and EC-dimethylsulfoxide (0-100 mole-% EC) at 40 °C [34]; the dielectric constant of EC-diphenyl ether (24.7 to 100 weight-% EC) at 50 °C) [125]; and the density, dielectric constant, and viscosity for certain EC mixtures isodielectric with water ($\epsilon \simeq 78$) at 25 °C (EC-methanol, EC-acetone, EC-acetonitrile, and EC-tetramethylsulfolane [26].[50] The physical properties of many mixed solvents are listed in Tables 39-47.

The dielectric constants of mixtures of EC with benzene, methanol, propylene carbonate and water at 40 °C and 25 °C were reported [127]. The excess dielectric constant for these mixtures at 25 °C were calculated and plotted versus composition in [67]. The excess dielectric constant of EC-benzene and EC-propylene carbonate is negative, while that of EC-methanol is positive. The maximum excess occurs at about $\chi_{EC} = 0.55$, and is about -17 for EC-benzene, -3.5 for EC-propylene carbonate, and +4.5 for EC-methanol. The excess of EC-water is small, with a maximum of 1.3 at about $\chi_{EC} = 0.1$. The dielectric properties of EC-propylene carbonate mixtures at 25 °C were reviewed [142]. The viscosities of EC-propylene carbonate mixtures were about 2.5 cp and virtually independent of composition [142].

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[50]The exact compositions were not mentioned in [26], but were obtained by private communication and are given in Table 42.

Fusion and freezing curves for several EC-cosolvent mixtures are available. The shapes of the curves vary considerably and depend on the relative freezing points of the two compounds in the mixture. Figure 10 is a plot of the freezing point of EC-water mixtures versus composition. For EC-water, the freezing point is about 20 °C for 40 to 85 weight-% EC, but varies sharply with composition outside this region. The freezing point of propylene carbonate is initially depressed from -49 to -54 °C for 0 to 9 weight-% EC, then increases almost linearly (small negative second derivative) to 36.4 °C at 100 weight-% EC. The EC-propylene carbonate freezing point curve is given in Figure 11. As shown in Figure 12, a sharp minimum in the fusion point is observed for EC-N-methylacetamide and EC-dimethylsulfoxide mixtures [34]. In both cases, as EC is added, the freezing point decreases almost linearly from that of the pure compound (30.6 °C for N-methylacetamide and 18.5 °C for dimethylsulfoxide), to a minimum of 12.9 °C at $\chi_{EC} = 0.32$ for EC-N-methylacetamide and -7.1 °C at $\chi_{EC} = 0.42$ for EC-dimethylsulfoxide,[51] then increases almost linearly to the freezing point of EC (36.4 °C).

The thermodynamic properties of EC mixtures with water, benzene and chloroform have been reported. The enthalpy of solution of solid or liquid EC in water in the temperature range 298-318 K was reported [71], and the enthalpy, entropy and free energy of solution of solid EC in benzene, chloroform and water at 298 K was reported [23]. At

[51] These values were taken from a plot in [34] since the raw data were not listed in the paper.

infinite dilution, ΔH_s of solid EC was 16.8 $\pm$ 0.5 KJ/mole for water, 14.1 $\pm$ 0.1 for benzene, and 13.4 $\pm$ 0.2 for chloroform at 298 K [23]. For EC in water, an approximate value for ΔH_s at infinite dilution and 298 K is 17.7 KJ/mole [71]. Near the melting point of EC, ΔH_s is 17.8 KJ/mole for solid EC (at 36.29 ^oC) and 5.3 KJ/mole for liquid EC (at 36.68 ^oC). The difference is attributed to the heat of fusion of EC: 13.2 KJ/mole [71] (Reported values for the heat of fusion of EC range from 10 to 13 kJ/mole; see Table 12). The positive ΔH_s for liquid EC in water indicates that the interactions among molecules in pure water and pure EC are on the average greater than those between EC and water [71]. The interaction between EC and benzene is also relatively weak, however, a significant interaction may exist between EC (a donor) and chloroform (an acceptor). The enthalpy of mixing of EC with water, benzene, and chloroform is almost exactly balanced by the entropy of mixing (i. e. the $T\Delta S$ term), so that the free energy of mixing is low: $\Delta G_m \simeq -1$ KJ/mole at $\chi_{EC} \simeq 0.3$ [23]. The vapor pressure, fugacity, and activity coefficient for EC mixtures with water, benzene and chloroform at 298 K show only small positive deviations from additivity, which indicate that the solutions are nearly ideal [23].

The limiting activity coefficients for hexane and benzene in EC at 25, 60 and 100 ^oC were reported [95].[52] Ethylene glycol and EC form an azeotrope, such that complete separation of EC from a mixture

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[52]Limiting activity coefficients in EC for hexane were 90, 51 and 30, and for benzene 3, 2.55 and 2.2 at 25, 60 and 100 ^oC, respectively [95].

would be difficult (even at p > 72 mm Hg, where extrapolation indicated that the azeotrope should not exist) [139].[53] A ternary phase diagram for EC-water-benzene at 25 °C has been published [37].

4. Conductivities of EC-Cosolvent Mixtures

The conductance at 40 and 25 °C of KI (0.005-0.05 F) in a wide range of solvents and solvent mixtures was studied [25]. For each solvent system and temperature, the composition, density (ρ), dielectric constant (ϵ), and viscosity (η) of the solvent, and the limiting equivalent conductance (Λ_o), Walden Product ($\Lambda_o\eta$), and ion pairing constant for KI were tabulated: Table 39 (EC-water and EC-methyl ethyl ketone(MEK) at 40 °C, Table 40 (EC-water and EC-tetramethylsulfoxide(TMS) at 25 °C) and Table 41 (EC-water-TMS at 40 °C). The bulk dielectric constant is the predominant factor in minimizing K_A and maximizing the Walden Product. However, for solvents with similar dielectric constants, K_A is much lower and the Walden Product is much higher if the solvent contains acceptor molecules (e. g. water, methanol).

The conductance of $KClO_4$ (0.002-0.02 F) and KI (0.01-0.05 F) in various isodielectric pure and mixed solvents were studied [26]. The conductance was greatest in water. Ion pairing was lowest in solvents containing molecules with acidic protons (e. g. water, methanol), that is, acceptor molecules which solvate anions well.

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[53]The following EC-ethylene glycol azeotrope distillation data were taken from [139]: Distillation pressure 10 mm Hg, boiling point 88 °C, azeotrope contains 13.9 weight-% EC; 25 mm Hg, 107.5 °C, 7.5 weight-% EC; 50 mm Hg, 122 °C, 2.6 weight-% EC.

The properties of the solvent (composition, ρ, ϵ, η) and conductance parameters (Λ_o, $\Lambda_o\eta$, K_A) are listed in Table 42 for $KClO_4$ and Table 43 for KI.

The conductance of $KClO_4$ (0.001-0.01 F) in EC-acetonitrile mixtures (0-88.7 weight-% EC) at 25 °C was reported by A. D'Aprano (1974) [27]. The properties of the solvent and the conductance parameters are listed in Table 44.

The conductance of $KClO_3$ (0.008-0.06 F) in EC-water mixtures (0-80 weight-% EC) at 25 °C was studied [32]. The solvent properties and the conductance parameters are listed in Table 45. A minimum K_A was observed at 25 weight-% EC. The depolymerization of water caused by the initial addition of EC increased the amount of monomeric water available to solvate ions and led to a reduction in ion association. Ethylene carbonate (AN = 19) is not as effective as water (AN = 55) in solvating anions. Further increase in EC content beyond 25 weight-% resulted in an increase in ion association, despite the increase in bulk dielectric constant, because the ability of the mixture to solvate anions decreased.

The conductances of NaCl (0.001-0.05 F), sodium acetate (0.001-0.02 F), HCl (0.001-0.01 F) and acetic acid (0.001-0.1 F) in EC-water mixtures (56-95 weight-% EC) at 25 and 40 °C were studied [30]. The solvent properties and conductance parameters at 25 °C are listed in Table 46 and at 40 °C in Table 47. The ion association constant increased monotonically with EC content. No minimum in K_A was observed like the case of $KClO_3$ described in reference [32]. A plot

of the Walden product versus 100/ϵ is given in Figure 13. The Walden Products of NaCl and sodium acetate are virtually independent of composition. However, HCl is much more conductive in the water rich region, so the Walden Product of HCl increases with increasing water content.

The properties of EC-propylene carbonate mixtures are reviewed below in the section on EC electrolytes for electrochemical applications.

VII. Commercial Uses of Ethylene Carbonate

Ethylene carbonate is useful as a cryoscopic solvent for molecular weight determination from freezing point depression measurements [70]. A method to determine molecular dipole moments from the dielectric properties of solutions where the solvent is a mixture of EC and dioxane was reported by R. Myers and V. Sun (1966) [41].

The commercial uses of EC are described in the Texaco Chemical Company sales brochure [139]. EC is widely used in many phases of the fiber and textile industry. EC aids textile dyeing and improves fabric finish. EC may be used as the solvent in extrusion or polymerization into fibers of acrylonitrile,[54] or polymerized into fiber-forming polyesters. EC added to some plastics or resins before molding improves the mechanical properties and dye affinity of the

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[54]EC was the solvent for the electropolymerization of acrylonitrile reported by [113].

molded product. EC is used in a photosensitive composition for preparing lithographic plates, and as a component of plasticizers for thin acrylic films. EC can be used as a solvent for separating aromatic amines and as a hydraulic brake fluid. EC (bp 238 °C) was added to alter the relative volatility of isopropyl ether (bp 68.3 °C) and methyl ethyl ketone (bp 79.6 °C) which improved the separation of these two close-boiling compounds by extractive distillation [120].

VIII. Information Relevant to Electrochemical Applications of EC

A. Reference Electrodes in EC

The redox couples Ag/Ag^+ and ferrocene/ferricinium were evaluated for use as reference electrodes in EC at 40 °C [38]. The half-cells used were:

$Ag|0.01\ F\ AgClO_4,\ 0.1\ F\ Et_4NClO_4$

$Pt|0.01$ F ferrocene, 0.01 F ferricinium perchlorate, 0.1 F Et_4NClO_4

Both the silver and ferrocene couples were found to be suitable for reference electrodes. From the EMF of the cell:

$Pt|0.01\ F\ Fc, 0.01\ F\ FcClO_4, 0.1\ F\ LiClO_4||0.1\ F\ LiClO_4, 0.01\ F\ AgClO_4|Ag$

the difference between the formal potential of the Ag/Ag^+ and ferrocene/ferricinium couple was calculated:[55]

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[55]The formal potential of the ferrocene/ferricinium couple in water relative to the normal hydrogen electrode at 25 °C is +0.400 V, as reported by H. Koepp and H. Strehlow, Z Elektrochem, 64, 483(1960). The ferrocene/ferricinium couple is also discussed in The Chemistry of Nonaqueous Solvents, J. Lagowski, editor, (Academic Press, New York, 1966), volume 1, pp. 157-162. The formal potential of the ferrocene/ferricinium couple is generally assumed to be independent of solvent when the couple in used in a reference elec-

$$E'^{o}(Ag) - E'^{o}(ferrocene) = (0.518 \pm 0.010)V$$

Silver [40] and lithium [39] metal have been used as reference electrodes, however, the silver electrode can be adversely affected by certain anions (e.g. halides, SCN^-) and the lithium electrode by electrolyte impurities such as water. Considering the similarities between EC and propylene carbonate, it is quite reasonable to assume that reference electrodes suitable for propylene carbonate will also work well in EC.[56] These include Tl(Hg)/TlX (X: iodide, bromide, chloride), evaluated by F. Baucke and C. Tobias (1969).[57]

B. Electroactivity of Certain Electrolytes and Electrodes

The electroactive range of several 1:1 electrolyte solutions in EC were reported [38,39]. The results are summarized in Table 48. At the platinum electrode, the faradaic reaction at the anodic limit was due to oxidation of the anion rather than oxidation of EC. In the case of alkali metal salts, metal deposition occurred at the cathodic limit. At silver electrodes, anodic dissolution of the metal

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trode. The bases of this assumption are that the solvation forces will be weak and non-specific since both ferrocene and ferricinium have an overall spherical shape and large size (average radius ~2.3 A), and that the molecule and the cation will be equally solvated because the molecule and cation have the same structure and dimensions, and the positive charge of the cation is localized at the interior of the cation.

[56] Two useful reviews of reference electrodes in aprotic organic solvents are:

J. Butler, Reference Electrodes in Aprotic Organic Solvents, Advances in Electrochemistry and Electrochemical Engineering, P. Delahay, C. Tobias, eds, (Interscience, New York, 1970), vol. 7.

J. Jorne, Electrochemical Behavior of the Alkali Metals in Propylene Carbonate, Ph.D. Thesis, University of California, Berkeley, September 1972, Lawrence Berkeley Lab Report LBL-1111, pp. 22-26.

[57] F. Baucke, C. Tobias, JES, 116, 34(1969)

occurred at the anodic limit. When halide anions were present, the anodic limit of the silver electrode was displaced toward more negative potentials. The complex $AgCl_2^-$ is very stable in EC, and the anodic reaction at the electrode in this case is:

$$Ag + 2\ Cl^- = AgCl_2^- + e$$

The silver and platinum electrodes have the same cathodic limits in these electrolytes. The effect of water on the electroactive range at the platinum electrode was also reported. In the case of $LiClO_4$, the cathodic limit was reduced to 2.1 V in the presence of > 0.005 F water. The oxidation of water was noticeable with KPF_6 electrolyte, and limited the anodic range for water concentrations > 0.01 F. The oxidation of water was beyond the anodic potential allowed by the perchlorate anion, however, the anodic limit shifted negatively for water concentrations > 0.1 F.

The polarographic behavior of alkali metal cations were studied in EC, propylene carbonate, water, dimethylsulfoxide, and dimethylformamide [92]. The differences among the half-wave potentials ($E_{1/2}$) were explained as arising from differences in solvation energy. An ion radius correction term for each solvent was derived from the $E_{1/2}$ results by assuming that the effective ion radius used in the Born expression equalled the sum of the cation crystallographic radius and the solvent-specific radius correction term. The radius correction term was 0.86 A for EC at 40 °C, and correlated with the solvent donor number: $R_+ = (0.94 - 0.0093\ (DN))$ Å, and not with the solvent dielectric constant. The half-wave

potentials for alkali metal cations in EC relative to those in water were obtained. The results are summarized in Table 49. The calculated half-wave potentials relative to those in water were based on a Born energy calculation involving the corrected solvent ion radius and included a correction for solvent molality.

The behavior of the lithium metal electrode in EC at 40 °C was studied by L. Heerman and J. Van Baelen (1972) [142]. Micropolarization measurements suggested the presence of a film on lithium in EC. Anodic dissolution of the lithium electrode at 10 mA/cm^2 before micropolarization[58] resulted in a higher exchange current density, i_o, and lower charge transfer resistance, R_t, where:

$$R_t = - \left[\frac{\delta V}{\delta i}\right]_{i \rightarrow 0} = (RT/F)/i_o$$

The electrode behavior with and without pre-treatment are compared in the table below:

electrode condition	R_t, Ω-cm^2	i_o, mA/cm^2	C_{dl}, $\mu F/cm^2$
bright metal	21.4	1.26	1.9
anodic pretreatment at 10 mA/cm^2	8.7	3.11	4.9

From the variation of the exchange current with temperature, the heat of activation was 7.90 kcal/mol, where:

[58]The use of higher anodic currents during pretreatment did not affect the results.

$$\Delta H_o\ddagger = -2.303R \left[\frac{\delta \log i_o}{\delta(1/T)}\right]$$

From the variation of the exchange current with $LiClO_4$ concentration in the range 0.1 to 1.0 F, the charge transfer coefficient, α, was 0.60, where:

$$\alpha = 1 - \left[\frac{\delta \log i_o}{\delta \log c}\right]$$

and c is the concentration of $LiClO_4$.[59] Both pretreated and non-pretreated electrodes gave the same variation in exchange current with temperature and $LiClO_4$ concentration. The addition of 400 ppm water caused the exchange current to drop to as low as 0.03 mA/cm^2 and the double layer capacity to about 0.5 $\mu F/cm^2$. The lithium electrode could be activated by anodic pretreatment in wet electrolyte as well as with anhydrous electrolyte, but the electrode in wet electrolyte returned rapidly to lower activity after interruption of the current. The decomposition of EC on graphite electrodes occurred near +0.6 V versus Li/Li^+ (1.0 F). Analysis of the reaction products after constant current electrolysis showed that the reaction could be:

$$EC + 2e \rightarrow CH_2{=}CH_2 + CO_3^{2-}$$

Since Li_2CO_3 is virtually insoluble in the electrolyte, a carbonate layer could form on the surface of a lithium electrode after exposure of a fresh lithium surface to the EC electrolyte. The presence of

[59] The exchange current at the lithium metal electrode for $LiClO_4$ concentrations greater than 1.0 F were lower than expected from extrapolation of the dilute solution exchange currents, probably due to ion pairing.

trace water could lead to the formation of a hydroxide film on the lithium surface, since the reduction of water occurs at +1.4 V versus Li/Li^+ (1.0 F). However, despite the formation of surface films, the lithium electrode in $LiClO_4$-EC electrolyte behaved as a relatively active and almost reversible electrode.

C. The Mercury-EC Electrolyte Interface

R. Payne (1966) [126] reported that the double layer capacity at the mercury/solution interface for many solvents exhibited capacitance humps analogous to those observed for water (e. g. 0.1 F KPF_6 in EC).[60] The differential capacitance for the mercury/solution interface for many 1:1 electrolytes in EC at 40 °C was studied by W. Fawcett and M. Mackey (1972) [42]. In the absence of specific adsorption, the variation in capacitance with electrode potential was associated with the surface concentration of solvent molecules at the interface and the orientation of the electric dipoles of the interfacial solvent molecules. The capacity increases with solvent surface concentration, and a capacity maximum occurs when an equal number of solvent dipoles point toward the electrode as point toward the bulk solution. Electric dipoles parallel to the interface do not contribute to the double layer capacity. For alkali metal perchlorates at far cathodic potentials, the capacity increased with cation atomic number: $C(Li^+) < C(Na^+) < C(K^+)$. This order was attributed to an increase in solvated ion size. Solvation energy

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[60] A review of models of the structure of solvents at the electrode interphase is: R. Parsons, Electrochimica Acta, 21, 681(1976)

increases with the charge-to-ion radius. Cation solvation is stronger for lithium than for sodium or potassium and the solvation sheath of Li^+ contains more solvent molecules than that of Na^+ or K^+. The larger solvated ion displaces more solvent from the interface, and reduces the solvent surface concentration. In addition, the orientation of solvent molecules by the cation increased the number of interfacial solvent molecules parallel to the electrode. This orientational effect increases with the charge-to-size ratio of the ion (e. g. $K^+ < Na^+ < Li^+$). The capacity for alkylammonium perchlorates at far cathodic potentials decreased with increase in crystallographic cation size: $C(Me_4N^+) > C(Et_4N^+) > C(Bu_4N^+)$. These cations are not specifically solvated by EC. The larger cation displaces more solvent from the interface. Near the point of zero charge, the ordering of capacities is reversed and presumably follows the increase in cation adsorption induced by adsorption of the perchlorate anion. The order of adsorbability of anions on mercury was: $I^- > Br^- > Cl^- > ClO_4^- > BF_4^- > PF_6^-$. As shown in Figure 14, anion adsorption greatly increased the capacitance (see Fig. 1, p. 636 [42]). The anion PF_6^- was found not to specifically adsorb on mercury.

The differential capacity for the mercury-solution interface in EC solutions of KPF_6 with varying concentrations of KI at constant ionic strength was thoroughly studied [43]. One result was that the standard free energy of adsorption of I^- from EC was greater than from protic solvents.

D. EC Electrolytes for Electrochemical Applications

The use of EC as a battery solvent has been investigated. Often, the results using EC were compared to those using propylene carbonate (PC), and in general, the properties and performance of EC electrolytes were superior to those of propylene carbonate. The superior performance was often attributed to the lower viscosity and higher conductivity of the EC electrolytes.[61] G. Pistoia, M. De Rossi, and B. Scrosati (1970) [40] evaluated EC as a nonaqueous battery solvent. They compared the physical properties of EC and PC, the maximum specific conductivities of KCNS, KPF_6, and $LiClO_4$ in EC and PC (see Table 50),[62] and the polarization of lithium anodes and CuF_2 cathodes in EC and PC electrolytes. They concluded that EC does not seem to attack lithium or magnesium. Magnesium was dipped in 0.85 m $LiClO_4$ in EC at 25 °C. After 24 hours, the concentration of Mg^{2+} in the electrolyte was 100 ppm, as determined by polarography. No gas evolution or change in the metal surface was observed for lithium metal dipped in the electrolyte for 7 days. The polarization of a lithium anode (from 0 to 2 volts versus Ag foil) in

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In general, the solvent was purified by distillation under vacuum, the salts were dried by heating under vacuum, and the experiments were performed in a glove box under inert atmosphere. An exception is S. Tobishima and A. Yamaji (1984) [85], who purified EC by heating EC with molecular sieves at 60 °C and estimated the purity to be 99.5 % using gas chromatography, with ethylene glycol as the major impurity.

[62] The existence of a conductivity maximum is not unusual, but not always observed. In propylene carbonate at 25 °C, a maximum is observed near 1.0 F for $LiClO_4$, 1.2 F for KCNS and $AlCl_3$, 1.4 F for NH_4CNS, and 0.7 F for LiBr. But for $LiClO_4$ in tetrahydrofuran, the conductivity increases until solute saturation (data from Fig. 3 and text of reference [142], p. 288).

various electrolytes was basically linear. For 0.85 m $LiClO_4$ in EC (and 1.0 m $LiClO_4$ in PC), the current density was 20 mA/cm^2/volt. For 1.3 m KCNS and 1.0 m KPF_6 in EC, was 10 mA/cm^2/volt was obtained. The polarization of a lithium anode at 10 mA/cm^2 varied somewhat, then stablized after 90 minutes, and was about 0.41 V for 0.85 m $LiClO_4$, 0.53 V for KPF_6, and 0.55 V for 1.3 m KCNS versus Ag foil (measured for 200 minutes). The behavior of a CuF_2 electrode (widely used in primary organic batteries) was poor in both EC and PC electrolytes. The open circuit voltage (OCV) versus Ag foil in 0.85 m $LiClO_4$ was 0.35 to 0.40 V. At a current density of 0.6 mA/cm^2, the CuF_2 electrode potential was negative to Ag foil. After forced discharge, the OCV did not recover and stablized at $\pm$ 0.03 V versus Ag foil. A test battery Li/0.85 m $LiClO_4$ in EC/CuF_2, Cu had an OCV of 3.4 V. The cell voltage dropped rapidly on discharge to about 1.5 V in 3 hours at 1.1 mA/cm^2 and more slowly at lower current densities. The capacity of the cell was limited by cathode utilization (~ 10 %). The battery was somewhat rechargeable, and the chemistry of recharging was discussed.

G. Pistoia (1971) [39] evaluated the use of EC as a solvent for high energy density nonaqueous batteries. A thorough discussion of solvent and salt purification and water content analysis was given (see discussion in **Purification**). The specific conductivities of various solutions of KPF_6, $LiClO_4$, and KCNS in EC at 25 ^oC were given (see Table 28). The variation in specific conductivity with temperature from 25 to 40 ^oC was linear for 13 weight-% KSCN, 18.9

weight-% KPF_6, and 7.7 weight-% $LiClO_4$.[63] The viscosities of 1 m solutions of KPF_6, $LiClO_4$, and KCNS in EC and PC at 30 °C were reported (see Table 31). The behavior of lithium anodes and NiS and CuF_2 cathodes, and discharge curves for Li-CuF_2 and Li-NiS cells using EC or PC electrolytes were reported. The polarization curves of CuF_2, NiS, and lithium electrodes at 30 °C (versus Li/Li^+) were basically linear and generally better in EC than in PC electrolytes. The following electrode current density results were taken from two figures in [39]:

electrode	electrolyte	current density mA/cm^2/volt
Li	1.0 m $LiClO_4$ in EC	40
	in PC	$\leq$40
Li	1.8 m $LiClO_4$ in EC	30
CuF_2	1.0 m $LiClO_4$ in EC	20
	in PC	15
NiS	in EC	15
	in PC	10

Galvanostatic discharge curves for Li-CuF_2 and Li-NiS cells at 30 °C were better for EC electrolytes than PC electrolytes. The following discharge behavior results were taken from two figures in [39]:

[63] The viscosity often decreases linearly with an increase in temperature over the range 25 to 40 °C, so the increase in specific conductivity with temperature is not surprising and is probably primarily due to the viscosity change.

electrode	current density mA/cm^2	1.0 m $LiClO_4$ in solvent	cell voltage over over range of cathode utilization	cathode utilization at 1 V cell voltage
$Li-CuF_2$	1.0	EC	3.2 V; 0-40 %	53 %
		PC	3.2 V; 0-30 %	53 %
	2.4	EC	3.0 V; 0-20 %	36 %
		PC	3.0 V; 0-10 %	36 %
Li-NiS	1.0	EC	1.8 V; 0-40 %	59 %
		PC	1.8 V; 0-20 %	33 %
	2.4	EC	1.8 V; 0-20 %	25 %
		PC	1.8 V; 0-10 %	17 %

The chemistry of both battery systems, and the energy density of the $Li-CuF_2$ battery were discussed.

S. Tobishima and A. Yamaji (1984) [85] investigated the use of mixtures of EC and PC as the solvent for lithium battery electrolytes at ambient temperature (20 to 25 °C). The properties and performance of the electrolyte generally improved with increasing EC content. The only drawback was an increase in the melting point of the electrolyte with increasing EC content. For example: With 2 m $LiClO_4$, when [EC]/[PC] = 6 (χ_{EC} = 0.86), the melting point was 19.2 °C; when [EC]/[PC] = 4 (χ_{EC} = 0.8), the melting point was 12.9 °C; and when [EC]/[PC] = 2 (χ_{EC} = 0.67), the melting point was 3.0 °C. The equivalent ionic conductance, λ_o^+, transference number, t_o^+, and Stoke's radius, r_s^+, for the lithium cation in several $LiClO_4$-EC-PC electrolytes were calculated from concentration cell EMF data. The results are tabulated below.

solvent χ_{EC}	λ_o^+ $\Omega^{-1}cm^2mol^{-1}$	t_o^+	r_s^+ Å
0.75	19.3	0.56	1.71
0.67	15.5	0.48	2.11
0.50	11.1	0.37	2.94
0	8.64	0.32	3.71

The specific conductivity of $LiClO_4$ was a maximum at about 1 F in the range of composition studied (χ_{EC} = 0 - 0.86). The specific conductivities of 1 M $LiClO_4$, 2 M $LiClO_4$, 1 M $LiAsF_6$, and 2 M $LiBF_4$ increased with increasing EC content, but essentially reached plateaus near χ_{EC} = 0.8. This increase is exemplified by the data listed in the table below (from Table 2, reference [85]), where the specific conductivities at χ_{EC} = 0.86 are compared to those in pure PC (χ_{EC} = 0).

solute	specific conductivity in χ_{EC} = 0.86 $\Omega^{-1}cm^{-1}$	% increase in specific cond. over pure PC	anion radius† Å
2 M $LiBF_4$	0.0054	130	2.78
2 M $LiClO_4$	0.0060	40.3	2.83
1 M $LiClO_4$	0.0086	43.3	2.83
1 M $LiAsF_6$	0.0062	17.7	3.26

† Anion radius calculated from Van der Waals radii.

The conductivity enhancement due to combining EC with PC was greatest for the lithium salt with the smallest anion, $LiBF_4$.

What physical phenomena account for the conductivity enhancement obtained by adding EC? In general terms, the specific conductivity (σ) is proportional to the number density of charge carriers (n) and their mobility (μ): $\sigma = n\mu$. A reduction in viscosity is obtained by substituting EC for PC. The mobility of a charge carrier increases as the viscosity of the electrolyte decreases.[64] For example, the viscosity at 30 ^{o}C of 1 m $LiClO_4$ in PC is 8.32 cP, but 7.91 cP in EC--- a 5 % reduction [39]. The observed enhancement is 20 to 130 %, so the viscosity reduction plays a minor role in the conductivity enhancement observed here. The fact that the conductivity enhancement is greater for smaller anions suggests that the enhancement may be due in part to a decrease in ion association arising from the higher dielectric constant and solvating power of EC and EC-PC mixtures over pure PC. A decrease in ion association increases the number density of charge carriers. The Coulomb force between the lithium cation and the anion strengthen as the anion radius decreases, so the relative dissociative effect of the solvent dielectric should be greater for smaller anions. In addition, the anion and cation solvating power of EC is greater than PC (as indicated by the higher donor and acceptor number of EC), and the solvation of the ion is stronger as the ion radius decreases.

The conductivities of nonaqueous electrolyte solutions are often too low for use in electrochemical systems of technological interest

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[64]An increase in conductivity given a reduction in viscosity is expected from Walden's rule: $\Lambda\eta$ = constant. This rule focuses on the contribution of mobility to conductivity.

(e. g. batteries). Nonaqueous electrolyte conductivity can sometimes be increased by using mixtures of solvents to make the electrolyte solution. Typically, a low viscosity cosolvent (e. g. tetrahydrofuran) is mixed with an ionizing solvent (e. g. propylene carbonate). The reduced viscosity results in an increased ion mobility, thus improving the conductivity. Increased conductivity often yields better electrochemical system performance (e. g. higher energy efficiency due to lower iR and i^2R losses). Unfortunately, the low viscosity cosolvent is usually not very effective at solvating ions. Ion pairing often increases as the cosolvent content increases and this lowers the conductivity. One trades increasing the mobility of charge carriers for decreasing the number density of charge carriers.[65]

The results of several mixed solvent conductivity studies involving EC were reviewed by Jasinski [144].[66] The relative specific conductance, relative viscosity, and relative dielectric constant of 1 F KPF_6 in EC-PC mixtures were plotted as a function of weight-% EC. The viscosity decreased 5 %, the dielectric constant increased 140 %

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[65]For a cogent example of this cosolvent conductivity phenomenon involving propylene carbonate, dimethoxyethane, and $NaClO_4$, see:
Y. Matsuda, H. Satake, J Electrochem Soc, 127:4, 877(1980).

[66]A wealth of information on EC and EC-PC electrolytes for electrochemical application exists in hard-to-obtain government reports. A few were reviewed by Jasinski [144], including:
W. Elliott, R. Amlie, Final Report NASA CR-72364, September 1967; and
R. Jasinski, P. Malachesky, B. Burrows, Final Report,
Contract N00019-76-0680, July, 1968.
Also see:
W. Elliot, Report #1, Contract NAS 3-6015 (N 65-11518), September 1964.

and the specific conductivity increased 150 %, almost linearly as the EC content was increased to 90 weight-% (in pure PC, the viscosity was 6.25 cp and the specific conductance was 0.008 $\Omega^{-1}cm^{-1}$).

Lithium charge-discharge testing by S. Tobishima and A. Yamaji (1984) [85] utilized a lithium counter electrode, lithium reference electrode, and platinum working electrode, and galvanostatic control. The charge-discharge efficiency, $E_{ff,10}$, was the average of the ratio of the tenth charge stripped to the charge plated, where the stripping endpoint potential was 0.8 V versus Li/Li^+. In all electrolytes tested, $E_{ff,10}$ was greater for EC-PC mixtures than for PC alone. Typical results are listed below.

solute	$E_{ff,10}$ in χ_{EC} = 0.86	$E_{ff,10}$ in pure PC
1 F $LiClO_4$	87.3 %	65.0 %
2 F $LiBF_4$	75.0 %	68.7 %

current density: 0.5 mA/cm^2; total charge: 0.6 C/cm^2

The best $E_{ff,10}$ was obtained using 1 F $LiClO_4$ in χ_{EC} = 0.8, a current density of 0.5 mA/cm^2, and total charge of 0.6 C/cm^2. For 1 F $LiClO_4$, $E_{ff,10}$ was essentially independent of current density over the range of 0.05 to 5 mA/cm^2. The current at far anodic potentials (5 to 10 V versus Li/Li^+) for 2 M $LiClO_4$ in χ_{EC} = 0.75 was double that in pure PC. The effect of impurities on $E_{ff,10}$ was briefly investigated.[67]

[67] The $E_{ff,10}$ was reduced from 65.0 to 46.6 % by adding 10.0 volume-% ethylene glycol to 1 F $LiClO_4$ in PC. Pre-electrolysis of 1 F $LiClO_4$ in χ_{EC} = 0.75 in a lithium-lithium cell (1 mA/cm^2 for 17.5

EC is a more effective solvent for electrolyte solutions than propylene carbonate, although PC is currently the prefered solvent in lithium primary batteries. One should expect the solvating power of EC to be greater than that of PC, since the dielectric constant, dipole moment, donor number, and acceptor number and number density of molecules (i. e. inverse molar volume) is greater for liquid EC than PC (see table in section **Solubilities**). The solubilities of salts are often greater in EC than in PC [87]. EC solutions are more conductive than PC solutions because ion association is lower in EC [85], and the viscosities of EC solutions are lower than those of PC (see Table 31) [85,144]. Superior electrode and battery performance was obtained using EC electrolytes rather than those based on PC [39]. Ethylene carbonate is a solid at room temperature, but this limitation can be easily overcome by adding a cosolvent (or salt). Electrolytes containing both EC and PC yielded better lithium electrode cycling than those containing only PC [85]. The performance of any electrochemical system using PC should be improved by the addition of EC.

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hours) increased $E_{ff,10}$ from 74.2 to 76.3 %.

THE PROPERTIES OF ETHYLENE CARBONATE AND ITS USE IN ELECTROCHEMICAL APPLICATIONS

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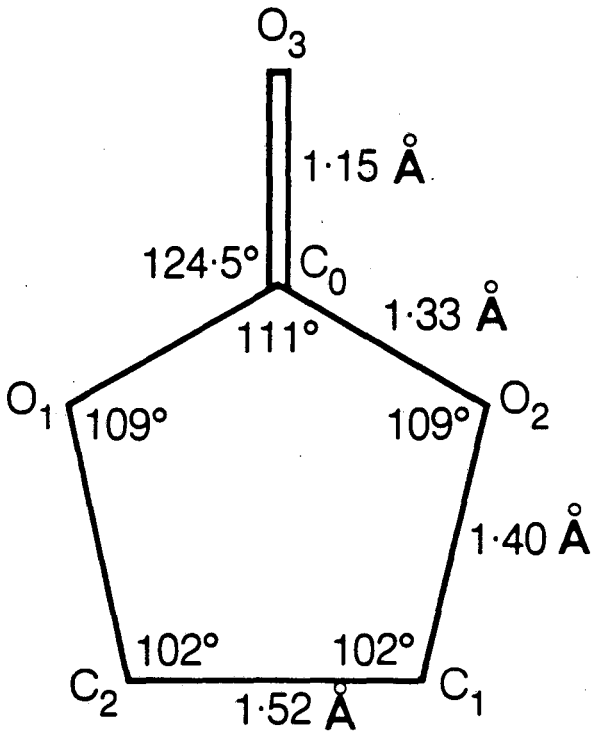
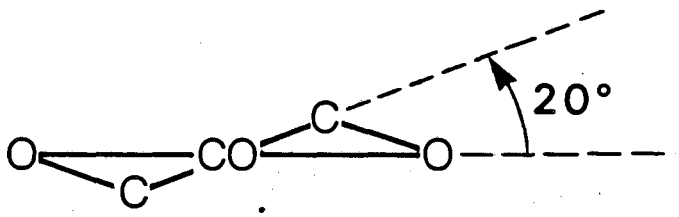
VIII. A. Figures

Figure 1

Molecular Structure of Ethylene Carbonate in the Solid



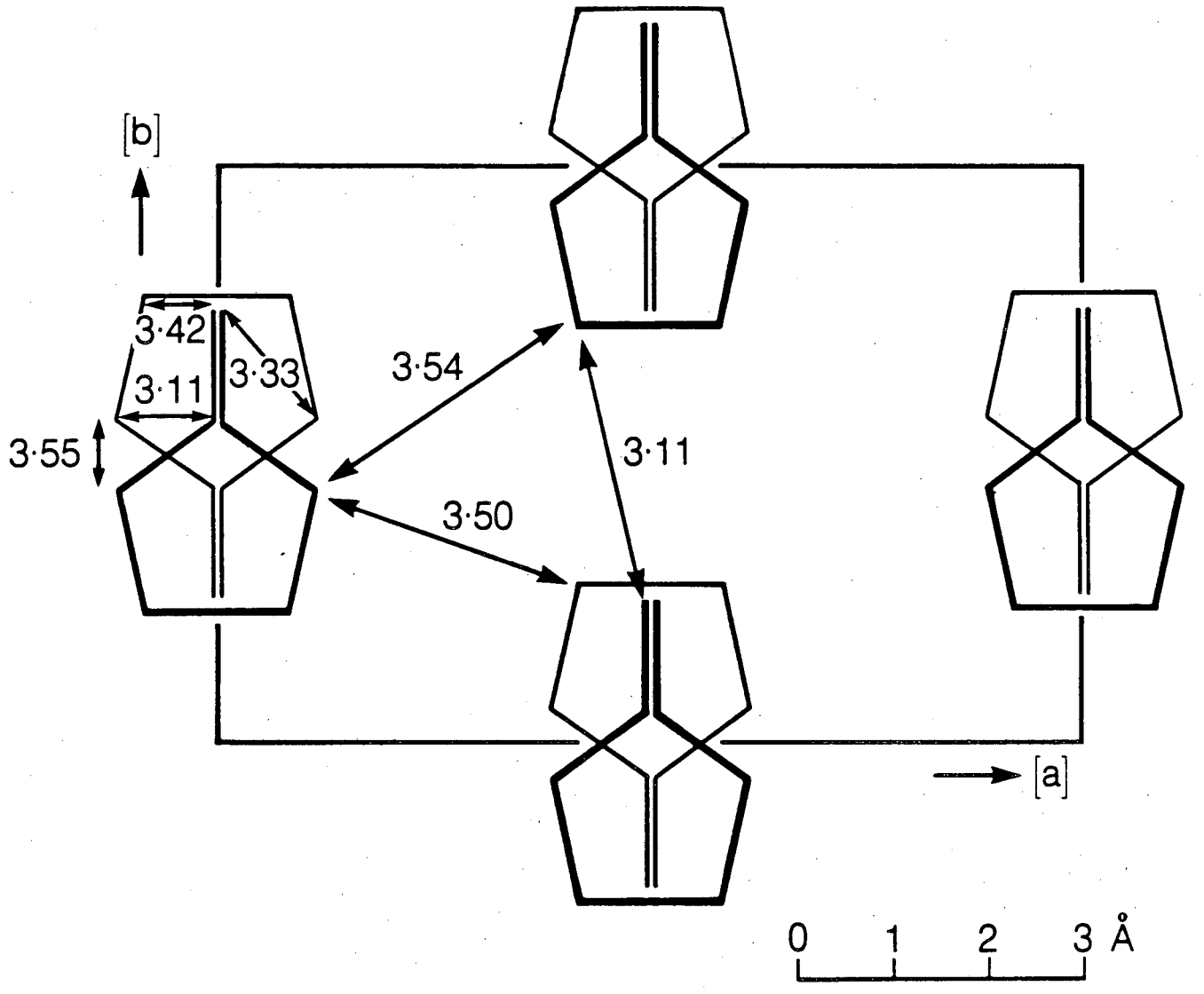


(Hydrogens omitted for clarity)

Figure from reference [1]:
C. J. Brown, Acta Cryst, 7, 92(1954).

XBL 851-8120

Figure 2
Structure of Solid Ethylene Carbonate



Diagrammatic projection of contents of one unit cell on to the (001) face, showing packing and inter-molecular contacts. The thick-lined molecules lie approximately in the plane z = 0·25; the thin-lined in the plane z = 0.75.

Figure from reference [1]:
C. J. Brown, Acta Cryst, 7, 92(1954).

XBL 851-8122

Figure 3

Courtauld Model of Ethylene Carbonate Molecule

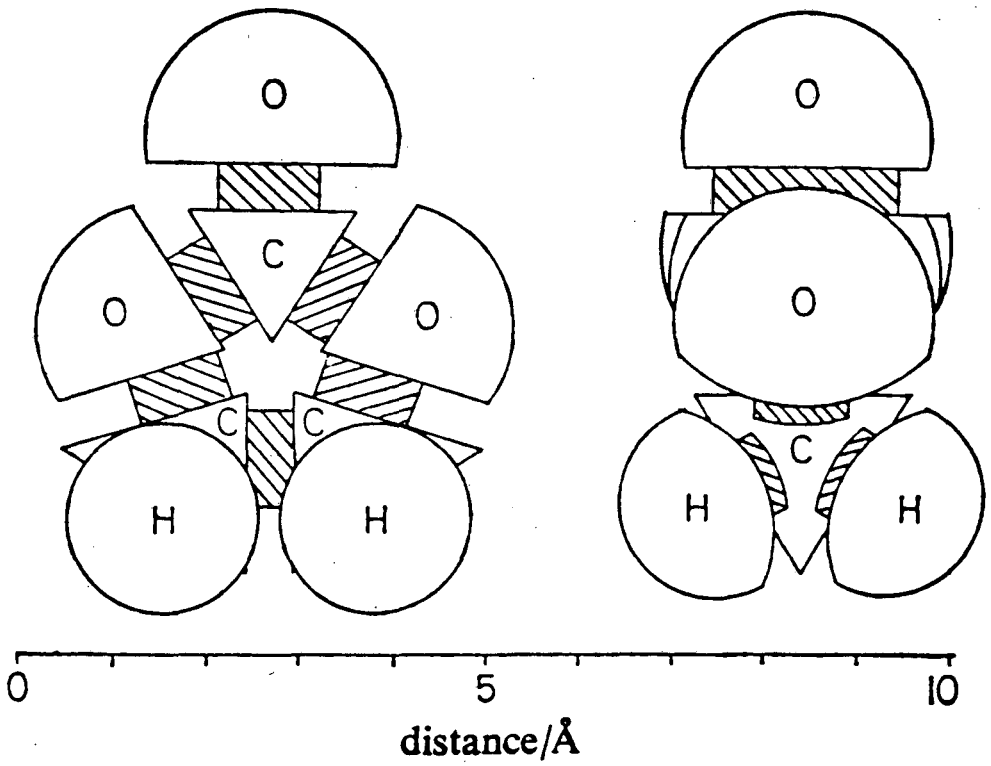
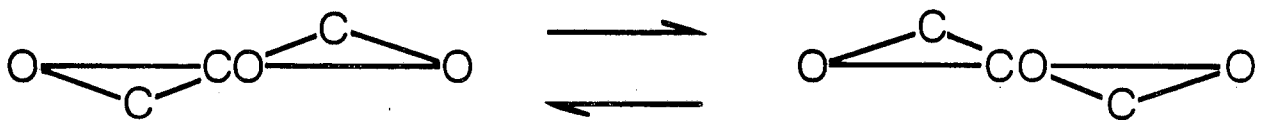


Figure from reference [42]:
W. Fawcett, M. Mackey, J Chem Soc, Faraday Trans I, 69:3, 634(1973).

Figure 4
Oscillation Between Energetically
Equivalent Half-Chair Conformations



(Hydrogens omitted for clarity)

XBL 851-8123

Figure 5

Electron Distributions and Orbital Energies of the Three Highest Occupied Molecular Orbitals of Ethylene Carbonate

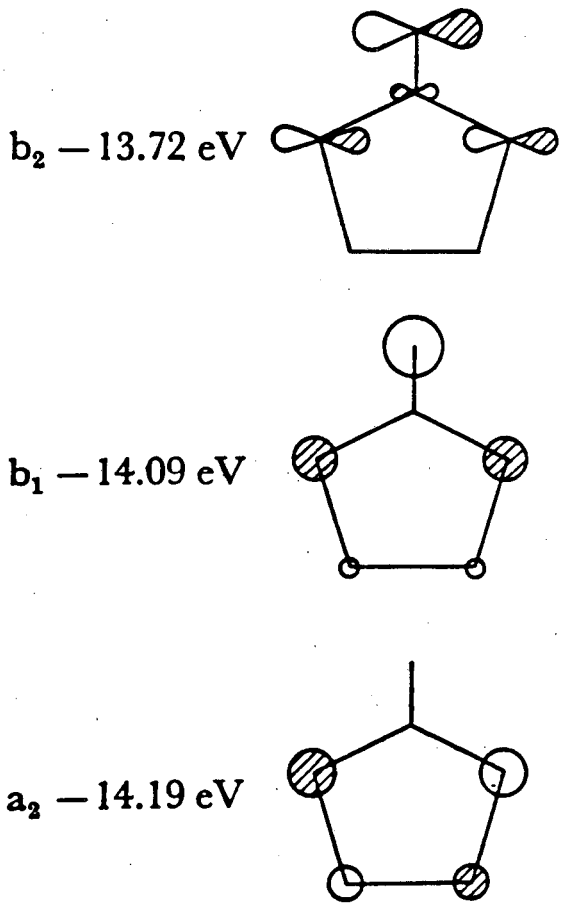


Figure from reference [16]:
M. Jinno, I. Watanabe, Y. Yokoyama, S. Ikeda,
Bull Chem Soc Japan, 50, 597(1977).

Figure 6

Viscosity of Ethylene Carbonate

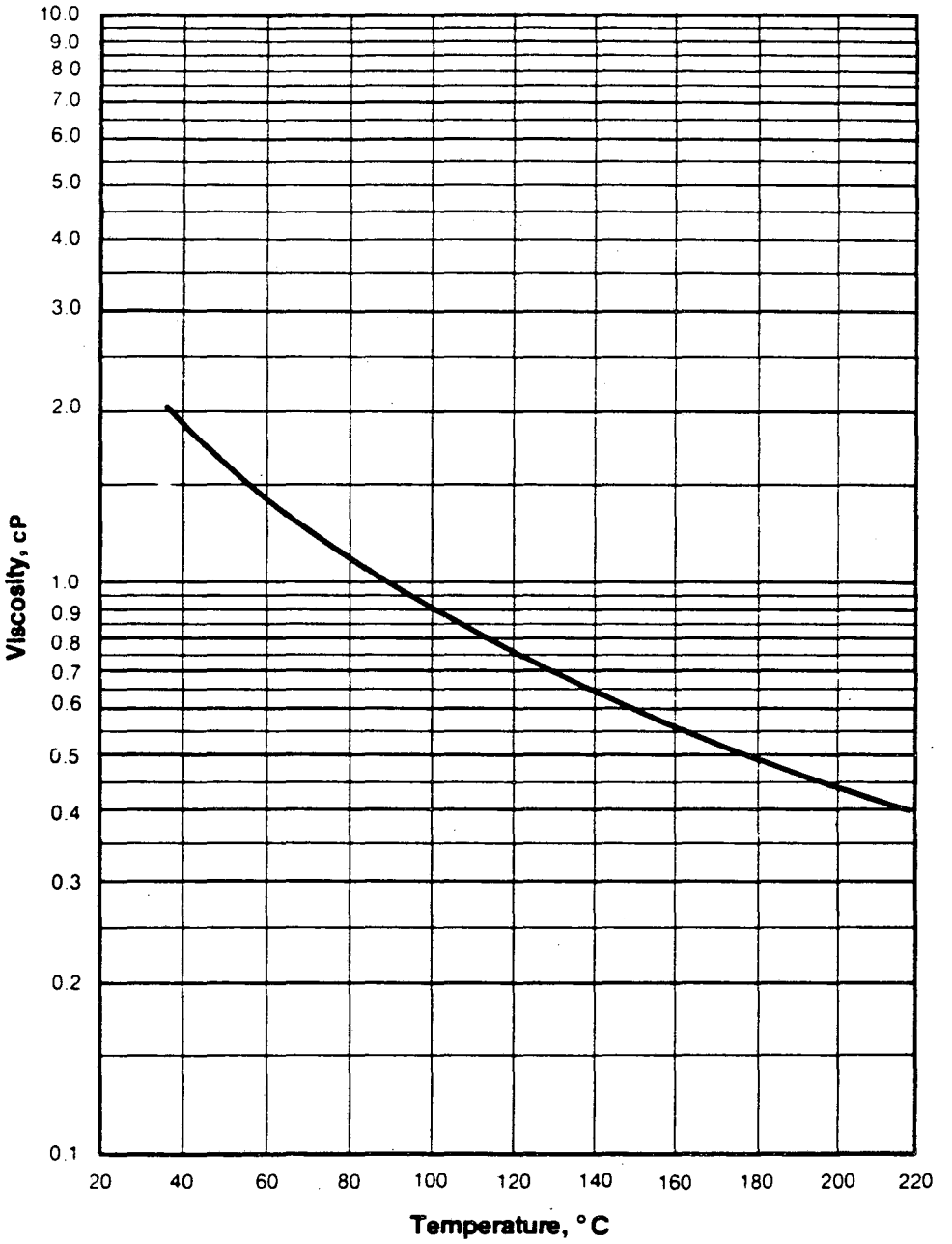


Figure from reference [13]:
Propylene Carbonate, Ethylene Carbonate, Texaco Chemical Company, Box 430,Bellaire, Texas, 77401, 1982.

Figure 7

Vapor Pressure of Ethylene Carbonate

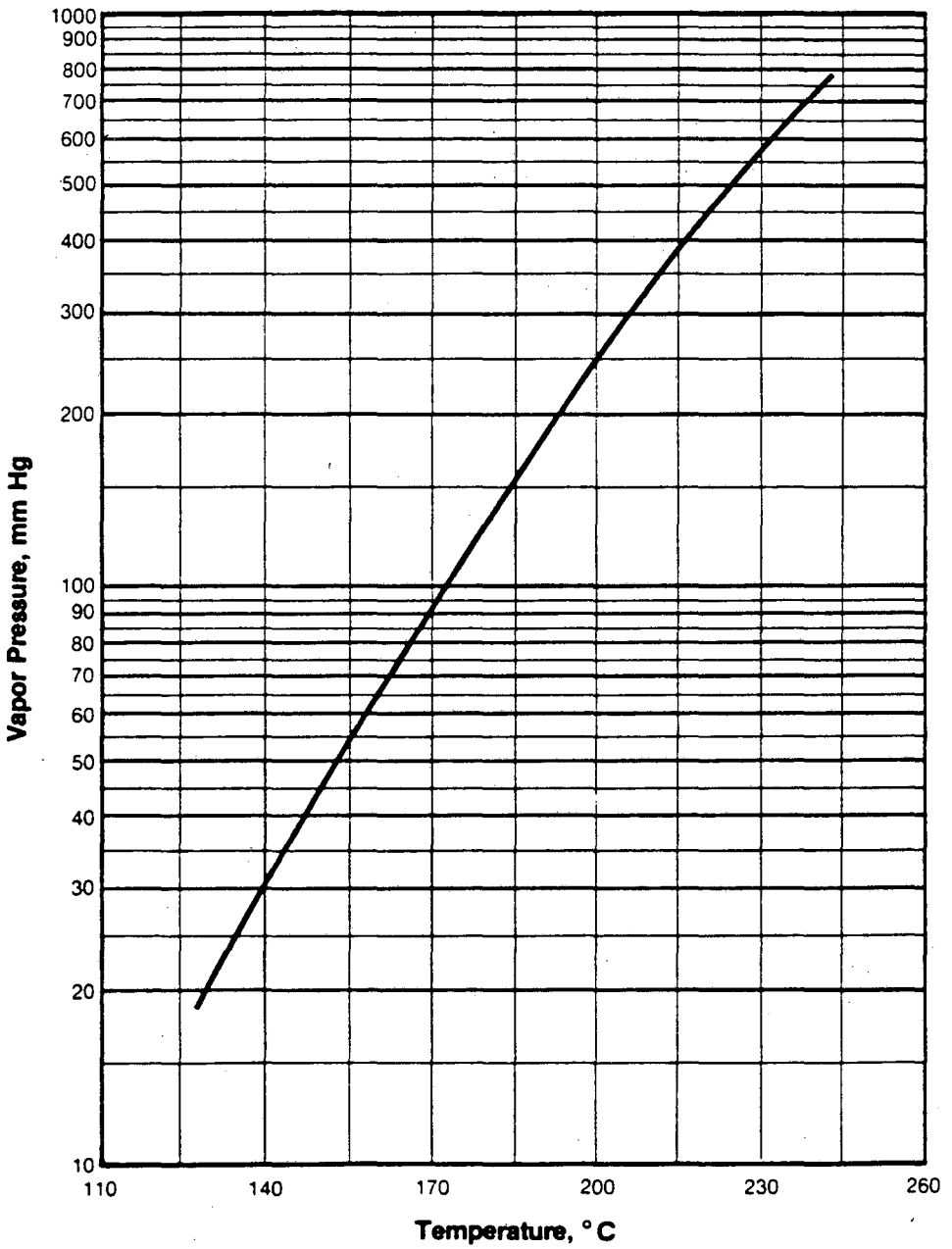
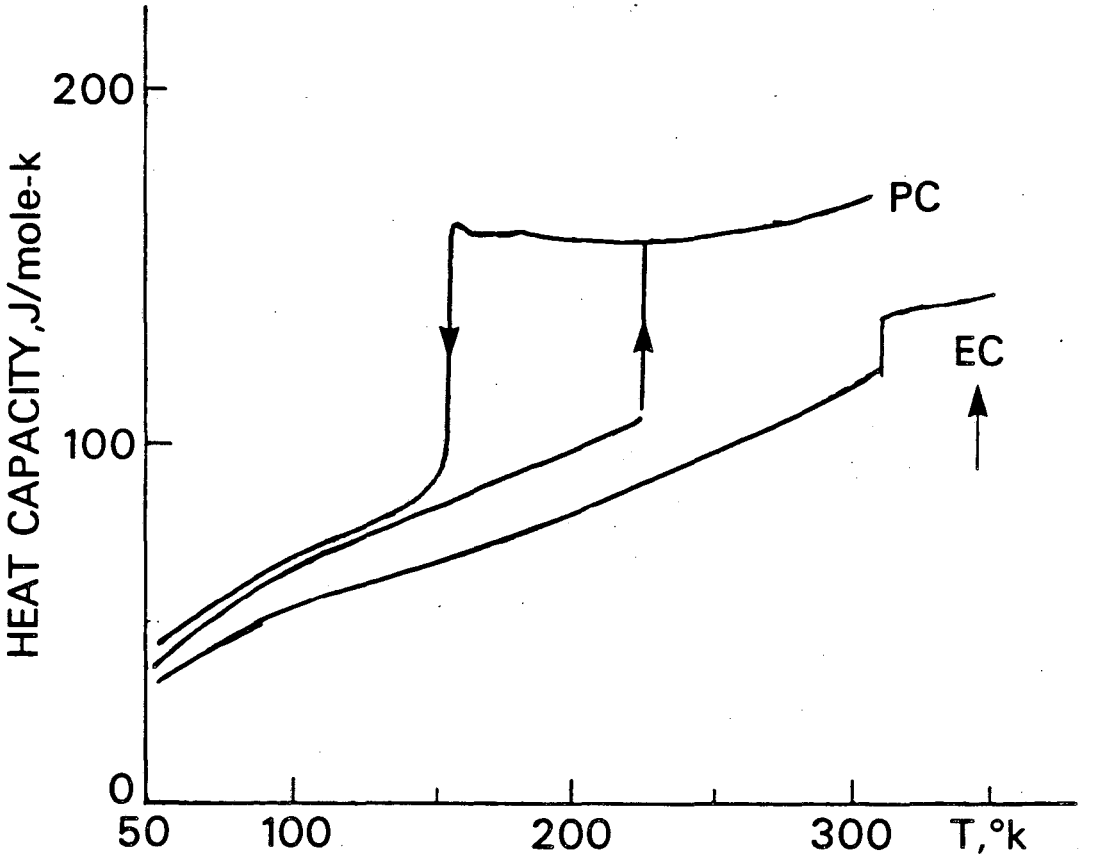


Figure from reference [139]:
Propylene Carbonate, Ethylene Carbonate, Texaco Chemical Company, Box 430, Bellaire, Texas, 77401, 1982.

Figure 8

Heat Capacity of Ethylene Carbonate (EC) and Propylene Carbonate (PC)



Note hysteresis (due to supercooling) in propylene carbonate heat capacity results.

Figure from reference [143]:
I. Vasil'ev, A. Korkhov, Tr Khim Khim Tekhnol, Gorky, Pt I, 103(1974).

Figure 9

Osmotic Coefficients of Various Salts as a Function of Salt Concentration in Ethylene Carbonate at 36.8 °C

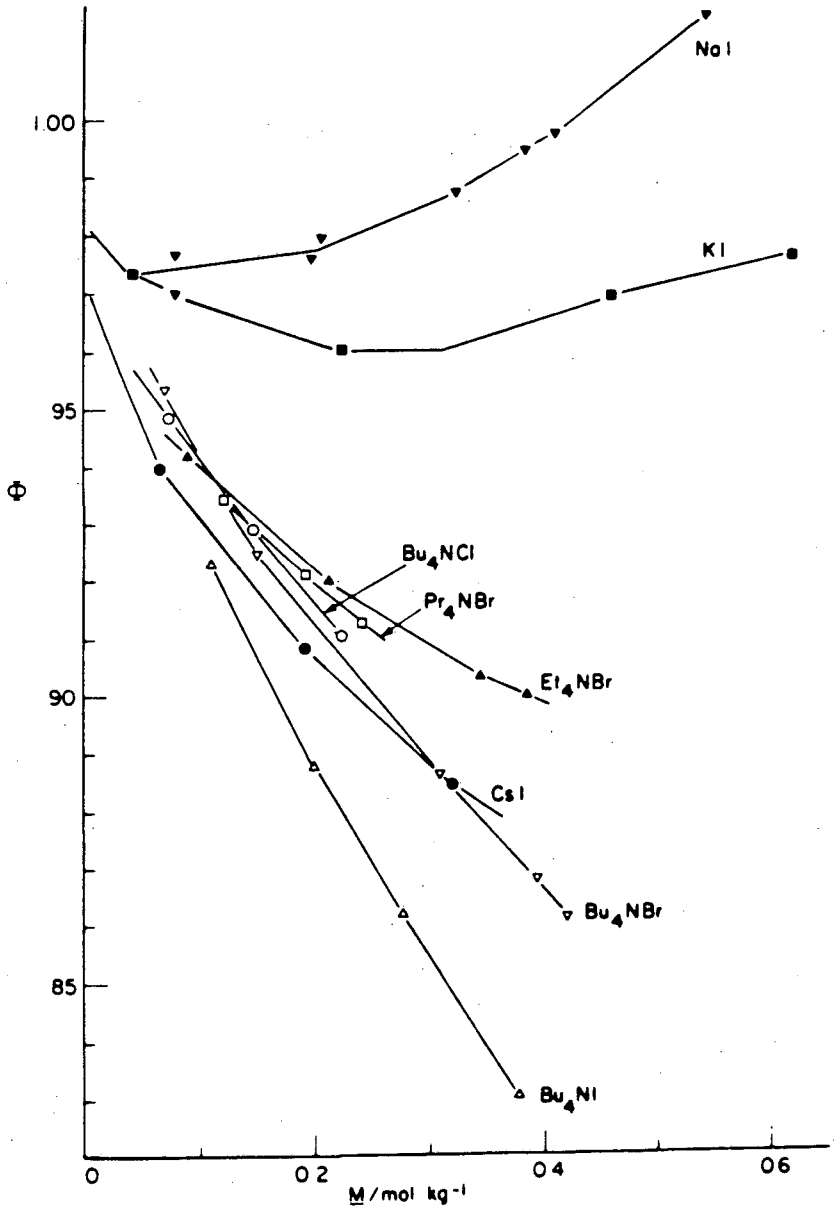
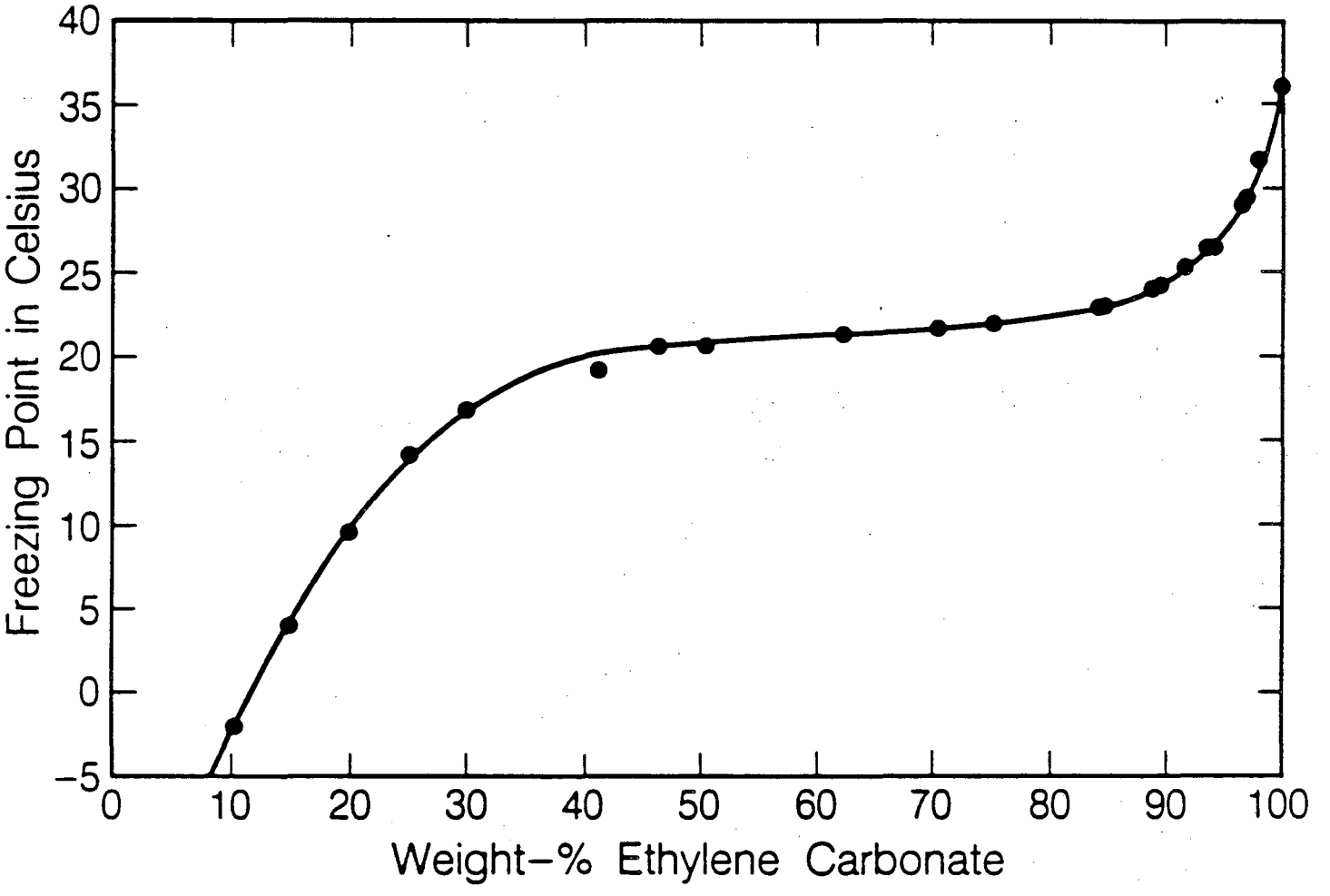


Figure from reference [94]:
R. Wood, Q. Craft, J Solution Chem, 7:11, 799(1978).

Figure 10

Freezing Point of Ethylene Carbonate – Water Mixture vs. Weight–% Ethylene Carbonate



Data from reference [124]:
G. Cunningham, G. Vidulich, R. Kay,
J Chem Eng Data, 12:3, 336(1967).

XBL 851–8121

Figure 11

Freezing Points of Ethylene Carbonate-Propylene Carbonate Mixtures

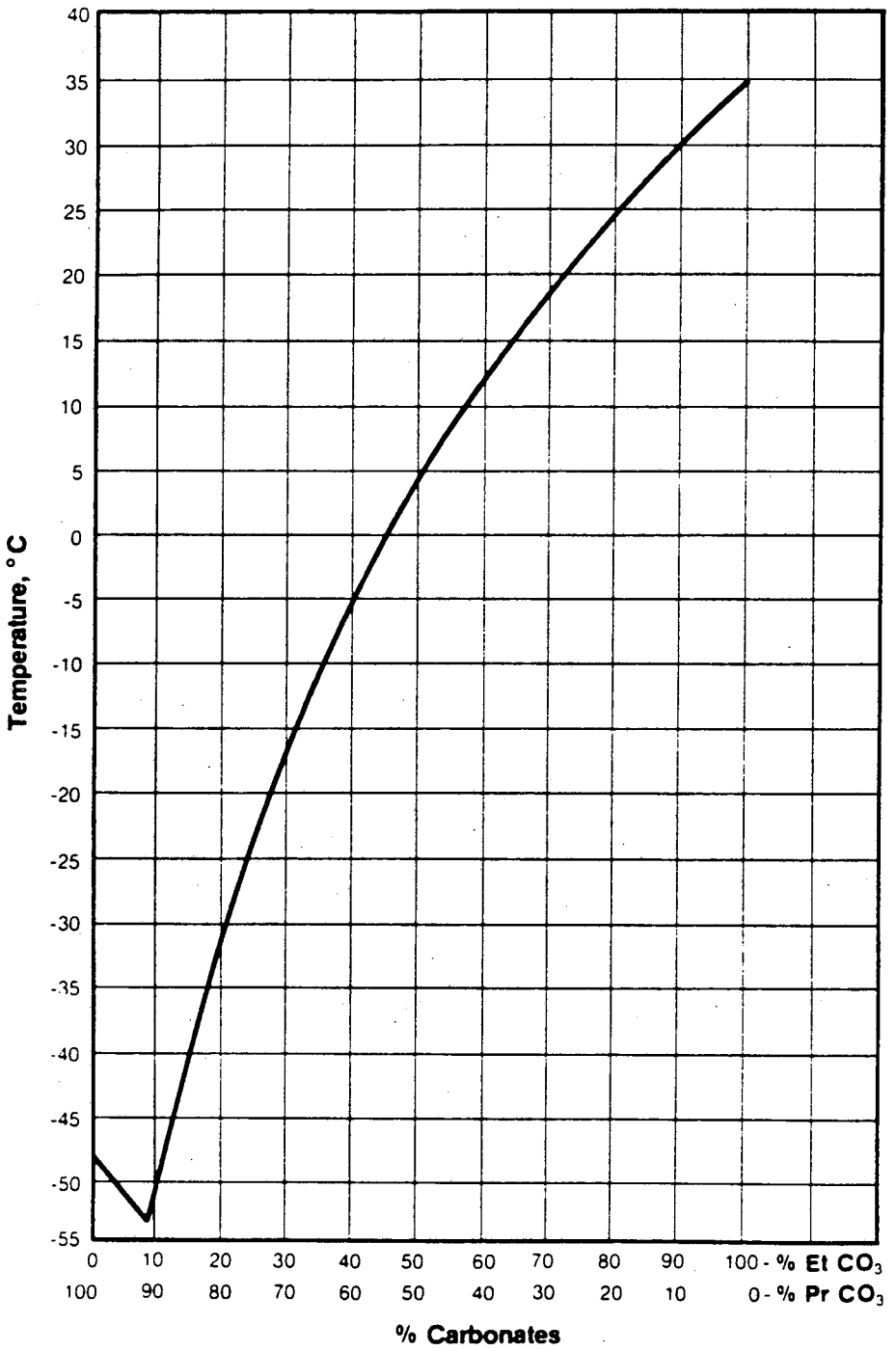


Figure from reference [139]:
Propylene Carbonate, Ethylene Carbonate, Texaco Chemical Company, Box 430, Bellaire, Texas, 77401, 1982.

Figure 12

Fusion Point Curves for Mixtures of Ethylene Carbonate (EC) With N-Methylacetamide (NMA) and Dimethylsulfoxide (DMSO)

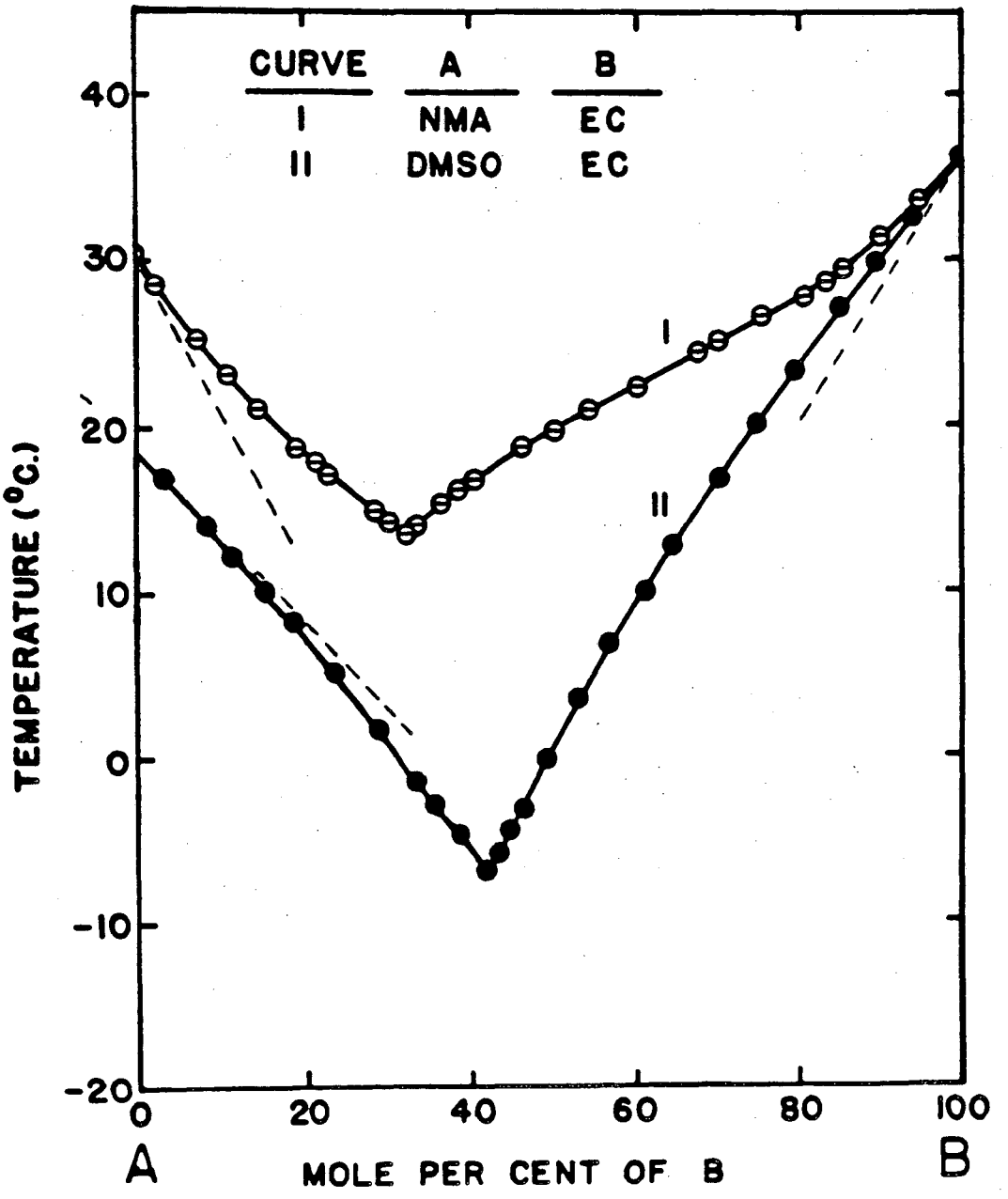
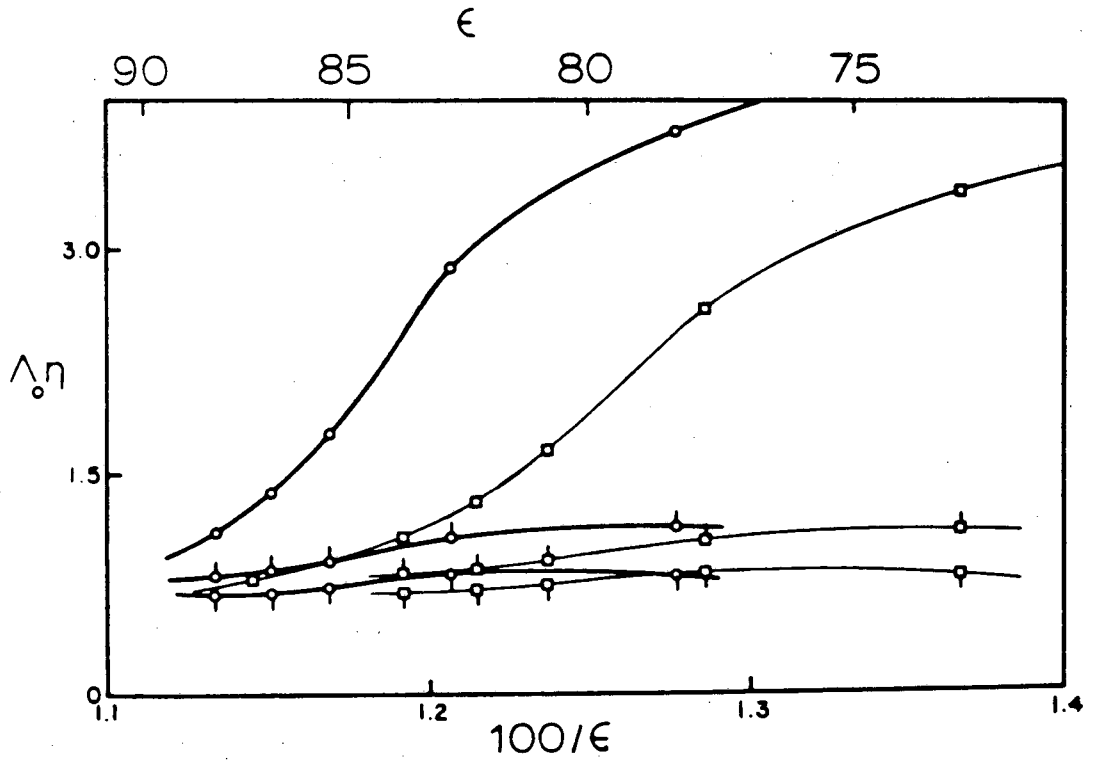


Figure from reference [34]:
P. Sears, T. Stoeckinger, L. Dawson, J Chem Eng Data, 16:2, 220(1971).

Figure 13

Limiting Walden Products as a Function of the Solvent Dielectric Constant For NaCl, HCl and Sodium Acetate in Ethylene Carbonate-Water Mixtures

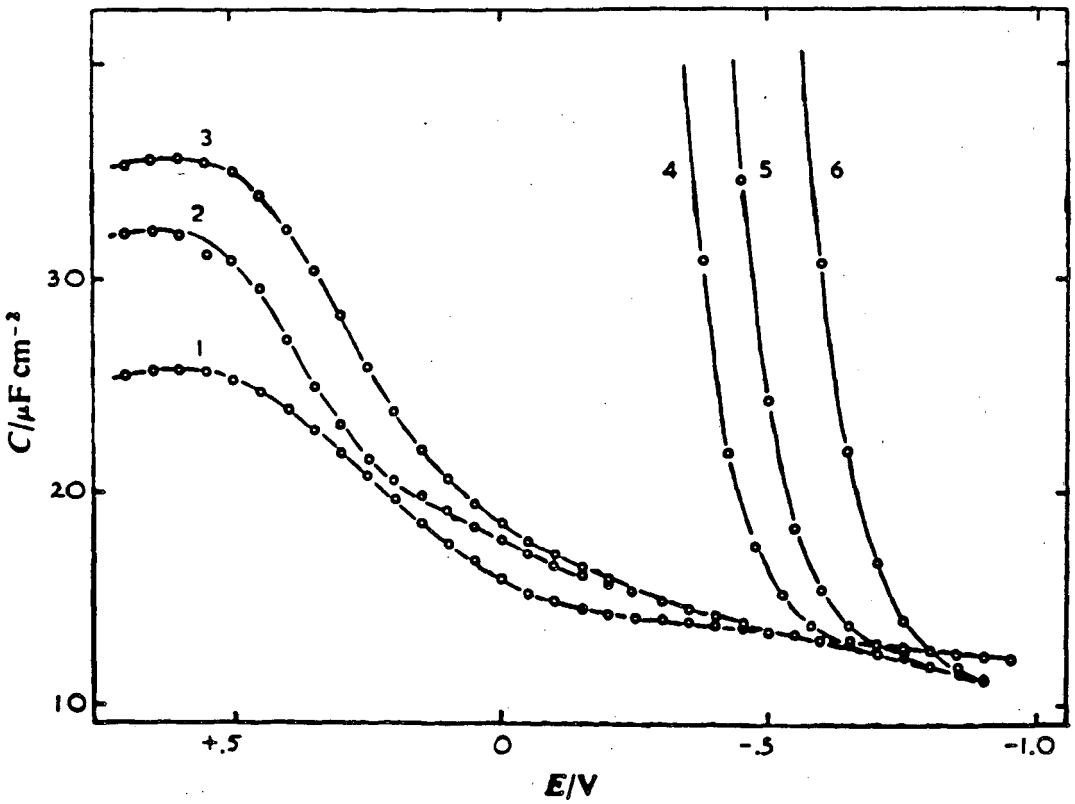


Circles: 25 °C; Squares: 40 °C. Upper flag, NaCl; Lower flag, NaAc; Unflagged, HCl.

Figure from reference [30]:
B. Boerner, R. Bates, J Solution Chem, 7:4, 245(1978).

Figure 14

Differential Capacity of the Mercury/Electrolyte Interface Versus Electrode Potential For Several 0.1 F Ethylene Carbonate Electrolytes at 40 °C



Salt number code: (1) KPF_6, (2) Et_4NBF_4, (3) Et_4NClO_4, (4) Et_4NCl, (5) Et_4NBr, (6) Et_4NI.

All salt concentrations were 0.1 F.

The reference electrode was a nonaqueous saturated calomel and consisted of 0.1 F Et_4NClO_4 in ethylene carbonate saturated with KCl.

Figure from reference [42]:
W. Fawcett, M. Mackey, J Chem Soc, Faraday Trans I, 69:3, 634(1973).

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VIII. B. Tables

Table 1

Kirkwood G-Factor for Ethylene Carbonate

temp., °C	g-factor	reference
40	1.19	144
40	1.6	127
40	1.27	50
40	1.25	105
40	1.43	45
40	1.20	67
50	1.20	67
60	1.19	67
70	1.18	67

Table 2

Boiling Points and Dipole Moments of Chloroethylene Carbonates

molecule	boiling point in °C	dipole moment in debyes
EC	238	4.87
ClEC	212	3.99
Cl_2EC	178	3.60
Cl_4EC	165	2.6

Data from reference [60]: R. Kempa and W. Lee, JCS, 1957, 1936(1957).

Table 3

Photoelectron Spectral Results for First Three Ionizations of Ethylene Carbonate

orbital ionized	ionization potential in eV	cation frequency in cm^{-1}	molecular frequency in cm^{-1}	total # of ionizations reported	reference
$5b_2$ $3b_1$ $2a_2$	11.1 11.3 11.7	1570	1820	6	5
$5b_2$ $2a_2$ $3b_1$	10.70 (A) 10.89 (V) 11.38 (V) 11.45 (V)	1530 910	1765-1790† 1065‡	3	16,20
first ionization	10.70 (A)	1500	1870	1	6
carbonyl lone pair	11.47 (V)			1	17
n π π	10.40 (A) 11.33 (V) 11.56 11.76			10	18,19

(A)=adiabatic; (V)=vertical; †=carbonyl stretch; ‡=skeletal stretch

Table 4

Values of Selected Properties of Ethylene Carbonate

property	value
systematic name	1,3-dioxolan-2-one
chemical formula	$C_3H_4O_3$
abbreviation	EC
GMW	88.06 g/mole
boiling point	238 °C (1 atm)
melting point	36.4 °C
density	1.338 (25 °C)† 1.321 (40 °C)
vapor pressure	0.02439 mm Hg (25 °C) 0.08784 mm Hg (40 °C)
viscosity	2.55 cp (25 °C)† 1.93 cp (40 °C)
dielectric constant	95.3 (extrap.) (25 °C) 89.8 (40 °C)
refractive index	1.4197 (40 °C)
dipole moment	4.80 D (in benzene)
donor number	16.3
acceptor number	19.1
molar volume	66.66 ml/mole (40 °C)
cryoscopic constant	5.39 °C-kg/mole
heat capacity	117.14 KJ/mole (25 °C)
heat of fusion	13.2 KJ/mole
heat of sublimation	78.53 KJ/mole (25 °C)

†supercooled liquid

Table 5

Boiling Point of Ethylene Carbonate

pressure, mm Hg	temperature, °C	reference
0.1	58-63	8
8	110	124
17	126	25,35,125
50	152.5	87
750	236-237	122
760	238	139
atmospheric	238	50
	238	60

Table 6

Freezing/Melting Point of Ethylene Carbonate

transition	temperature, °C	purification method	reference
melting	36.37 ± 0.02	zone refined	71
melting	36.37	zone refined	102
melting	36.49 ± 0.01	triple vacuum distilled	64
melting	36.6	twice vacuum distilled	67
melting	36.2	twice vacuum distilled	40
melting	36.5		90
freezing	36.307-36.326	zone refined	94
freezing	36.4	several vacuum distillations	127
freezing	36.5	fractional freezing	34

Table 7

Density of Liquid Ethylene Carbonate

temperature in °C	density in g/cc	reference
55	1.3107	120
50	1.3093	146
45	1.3155	146
40	1.32160 ± 0.0001	102
40	1.3214	35
40	1.323	87
40	1.32099 ± 0.00004	103
40	1.3208	60
40	1.3218	40
40	1.3208	105
40	1.32140	30
36.8	1.32515 ± 0.00006	94
35	1.3326	120
25‡	1.338	87
25‡	1.3383	124

‡ supercooled

From reference [125], M. Watanabe, R. Fuoss, JACS, 78, 527(1956):

$$\rho = 1.3084 - 0.00111(t-50) \text{ g/cc, t in } ^{o}C$$

Table 8

Viscosity of Ethylene Carbonate

temperature in °C	viscosity in centipoise	viscosity in centistokes	reference
55	1.58		61
40	1.955		87
40	1.925		103
40	1.916		102
40	1.930		40
40	1.850		105
35	2.3		61
30	1.8500		30
25‡	2.547		87
55		1.21	61
40		1.478	87
35		1.73	61
25‡		1.904	87

‡ supercooled

Table 9

Vapor Pressure of Ethylene Carbonate

temperature, °K	vapor pressure, mm Hg	reference
273.9	0.00215	62
286.1	0.00739	62
296.6	0.02172	62
368.36	3.371	36
371.91	4.025	36
373.40	4.399	36

From reference [36]: $\ln (p,atm) = 9.75917-4194.365/(181.076+t)$, t=95-176 °C

Using data in this table:
$\ln P = 16.9566 - 4258.6/T - 567.74/T$, T = 273-373 K (0-100 °C)

See Figure 5 for vapor pressure over range 130-240 °C.

Table 10

Standard Heat of Combustion of Solid Ethylene Carbonate

standard heat of combustion cal/g	kJ/mole	reference
-3179.0 ± 1.7	-1171.3 ± 0.6	69‡
-3164.3 ± 10.1	-1165.87 ± 3.74	140‡
-2902.3	-1069.3	62
-2662	-980.8	139

‡ Results include the Washburn correction;
See Washburn, J Res Natl Bur Std US, 10, 525(1933).

Table 11

Standard Heat of Formation of Ethylene Carbonate

phase	standard heat of formation in kcal/mol	in kJ/mol	reference
solid	-140.13 ± 0.90	-586.30 ± 3.76	140
solid	-138.83 ± 0.31	-580.86 ± 1.30	140
solid	-163.20	-678.64	62
gas	-144.43	-604.30	62

Table 12

Heat of Fusion of Ethylene Carbonate

heat of fusion in kJ/mole	heat of fusion in cal/g	method	reference
13.295	36.084	calorimetry	141,143
13.19 ± 0.07	35.80 ± 0.20	heat of solution	71
12.63	34.3	calorimetry	64
10.06 ± 0.22	27.3 ± 0.6	Method of Plato	72

Table 13

Heat of Vaporization of Ethylene Carbonate

temperature in °C	heat of vaporization in cal/g	heat of vaporization in kJ/mol	reference
25	177.1	65.24	†
150	158	56.3	36
160	149	55.0	36
170	147	54.0	36
180	145	53.3	36
190	143	52.6	36
200	142	52.2	36
248	138	51.0‡	139

† Estimated from the heat of sublimation at 25 °C (78.53 kJ/mole [62]) and the heat of fusion (13.295 kJ/mole [141,143]).

‡ extrapolated from data given in reference [36]

Table 14

Thermodynamic Properties of Ethylene Carbonate

temperature, °K	in J/mole-K C_p	S_T	$(H_T - H_o)/T$	$-(G_T - H_o)/T$
solid				
50	31.94	18.39	12.50	5.89
100	54.18	48.40	28.54	19.86
150	66.80	72.82	39.24	33.58
200	80.57	93.85	47.79	46.06
250	97.92	113.63	56.03	57.60
298.15	117.14	132.54	64.36	68.18
309.49	122.06	137.01	66.39	70.62
liquid				
309.49	138.07	179.91	109.29	70.62
350	144.49	197.34	112.84	84.50

Data from reference [143]:
I. Vasil'ev, A. Korkhov, Tr Khim Khim Tekhnol, Gorky, Pt. I, 103(1974).

Table 15

Specific Heat and Heat Capacity of Ethylene Carbonate

temperature in °C	temperature in °K	specific heat in cal/g	heat capacity in kJ/mole
15	288.15	0.321	118.3
50	323.15	0.363	133.7
100	373.15	0.461	169.9
150	423.15	0.479	176.5

Data from reference [139]:
Propylene Carbonate, Ethylene Carbonate, Texaco Chemical Company, 1982.

Table 16

Specific Conductivity of Liquid Ethylene Carbonate

specific conductivity $10^{-7}\Omega^{-1}cm^{-1}$	temp. °C	purification method	m.p. °C	ref.
10		vacuum distilled	37	23
0.00002-1	45	twice vac. distilled		111
7	40	twice vac. distilled	36.2	40
1	40	triple vac. distilled		103
0.1-1		twice vac. distilled	36.6	67
<1		several vac. distill	36.4	127,104
1.3	40	triple vac. distilled	36.49	64
0.4-0.9	40			105
4.2	40	vacuum distilled		39

Table 17

Dielectric Constant of Liquid Ethylene Carbonate

temperature in °C	dielectric constant	reference
25	95.3‡	127
40	89.6	60
40	90.36	35
40	89.6	111
40	95.3	50
40	89.8	40
40	90.36	30
40	89.78	67
50	85.81	67
60	82.01	67
70	78.51	67

‡ extrapolated

From reference [127], R. Seward, E. Vieira, J Phys Chem, 62, 127(1958):

$\epsilon = 85.1 - 0.408(t-50) \pm 0.5\%$, $t = 25-70$ °C

Table 18

Dipole Moment of Ethylene Carbonate

dipole moment in debyes	temperature in °C	reference
4.87	40	60
4.78	40	50
4.60	25	131
4.93	25	122
4.80		60 †

† From Arbuzov, Shavsha, Doklady Akad Nauk SSSR, 68, 1045(1949).

Table 19

Miscellaneous Properties of Ethylene Carbonate

property	value	ref.
density	11.01 lb/gal	139
flashpoint	305 °F, 152 °C	139
index of refraction	1.4199 at 40 °C	60
index of refraction	1.4195 at 40 °C	34
index of refraction	1.4158 at 50 °C	139
specifc gravity	1.3218 (39/4 °C)	139
thermal conductivity	49.3×10^{-5} cal/(sec-cm^2)(°C/cm) at 41 °C	139
thermal conductivity	0.12 BTU/(hr-ft)(°F/ft) at 41 °C	139

Table 20

Cryoscopic Constant of Ethylene Carbonate

cryoscopic constant reported	infered* units	method	reference
5.55 °C/mole	°K-kg/mole	calorimetry	64
5.40 °C/mole	°K-kg/mole	freezing pt. depression	64
5.5 °C/mole	°K-kg/mole		40
6.96 ± 0.15 °C/mole	°K-1/mole	Method of Plato	72
7.01 ± 0.07 °C/mole	°K-1/mole	freezing pt. depression	72
7.03†	°K-1/mole	freezing pt. depression	70
5.32 ± 0.03 °K-kg/mole	°K-kg/mole	enthalpy of solution	71
5.275 °C/mole	°K-kg/mole		94‡

* The reported cryoscopic constants fall into two groups: one with $K_f \simeq 7$ end the other with $K_f \simeq 5.4$. It is possible that this differece is due to a difference in units rather than a difference in real values, where the molar cryoscopic constant is 7.00 °K-1/mole (i.e. liter of solvent) and the molal cryoscopic constant is 5.39 °K-kg/mole (i.e. kg of solvent), the two quantities being related by the density of EC, 1.3 g/cc.

† Reported as a molar cryoscopic constant

‡ Reference [94], R. Wood and Q. Craft (1978) probably used the heat of fusion reported by I. Vasil'ev and A. Korkhov (1973,1974) [141,143] to calculate a thermodynamic cryoscopic constant using the formula:

$$K_f = RT_f^2/(1000\ l_f)$$

where the heat of fusion of EC was 36.084 cal/g and the freezing point of EC was 309.49 K, yielding a molal cryoscopic constant of 5.275 °K-kg/mole.

Table 21

Ethylene Carbonate Rotational Constants and Moments of Inertia Calculated from Microwave Spectra

quantity	lower frequency set	higher frequency set
A, MHz	8044.3	8045.1
B, MHz	3847.46	3847.95
C, MHz	2718.61	2720.38
I_a, amu-Å	62.824	62.818
I_b, amu-Å	131.353	131.337
I_c, amu-Å	185.895	185.774

The microwave spectrum of EC consists of doublets.

Conversion factor: $I_a = 5.05377 \times 10^5/\text{Å}$, corresponding to a $^{12}C = 12$ atomic scale.

Data from reference [4]:
I. Wang, C. Britt, J. Boggs, JACS, 87:21, 4950(1965).

Table 22

Specific Conductivity of Ethylene Carbonate at 40 °C After Various Purifications

sample	specific conductivity $10^{-7}\Omega^{-1}cm^{-1}$
EC as received	51.7
EC distilled without additives	4.19
EC distilled from molecular sieves	5.91
EC distilled from lithium metal	3.47
EC distilled from CaO	1.51

Data from reference [39]: G. Pistoia, J Electrochem Soc, 118, 153(1971).

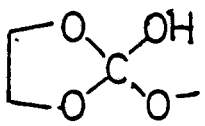
Table 23

Rate constants and Arrhenius Parameters for Intermediate Reactions in Base and Acid Hydrolysis of Ethylene Carbonate at 25 °C

rxn #	temp. °C	rate constant 1/mole-min	ΔH‡ kcal/mole	ΔS‡ cal/mole-K	ΔE‡ kcal/mole	exp. method	ref.
			base	**hydrolysis**			
1	0	28.2				2	53
1	6.40	46.2				2	53
1	10.70	64.2				2	53
1	16.40	94.6				2	53
1	27.60	216				2	53
1	15	89.4				3	53
1	35	405				1	53
3	25	2.160				1	57
3	35	3.800				1	57
3	45	9.450				1	57
3	55	20.0	14.1±1.1	-9.8±3.6		1	57
3	15	0.99				2	49
3	25	2.04				2	49
3	35	4.5	13.1	-15.2		2	49
			acid	**hydrolysis**			
5	52	0.00172				4	48
5	72.8	0.00963		-26.8	17.9	4	48
5	52	0.00099				5	52
5	72	0.0055	18.40	-26.40		5	52

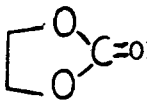
NOTES:

Reaction 1 : EC + OH^- →



Reaction 3: $HOCH_2CH_2OCOO^- + H_2O \rightarrow HOCH_2CH_2OH + HCO_3^-$

Reaction 5:



$+ H_2O \rightarrow HOCH_2CH_2OCOOH$

Index of experimental method used to obtain rate constant:

1. pH-stat method
2. high frequency conductance measurements
3. flow method
4. pressure changes due to CO_2 evolution
5. titration of trapped evolved CO_2

Table 24

Solubilities of Electrolytes in Ethylene Carbonate

salt	solubility in g/100g solvent	temp °C	ref
$LiClO_4$	26.9	40	40
$LiClO_4$	26.6	35	40
$LiClO_4$	26.6	30	40
$LiClO_4$	26.1	25	40
LiCl	0.83	40	40
LiCl	0.74	25	96
NaBr	0.31	40	87
NaI	37.60	40	87
KCl	0.02	25	96
KI	11.16	40	87
KI	11.6	36.8	94
KPF_6	18.8	40	40
KPF_6	18.3	35	40
KPF_6	17.6	30	40
KPF_6	17.0	25	40
KCNS	28.0	40	40
KCNS	27.7	35	40
KCNS	27.4	30	40
KCNS	27.1	25	40
KBF_4	0.04	40	40
RbCl	0.007	25	96
CsI	8.42	36.8	94
$CaCl_2$	0.2	40	87
$FeCl_3$	40.1	25	96
$CoCl_2$	3.13	25	96
$CoCl_2:6\ H_2O$	33	40	139
$Co(NO_3)_2:6\ H_2O$	37	40	139
$NiCl_2$	0.015	25	96
$Ni(NO_3)_2:6H_2O$	74	40	139
$CuCl_2$	0.67	25	96
$ZnCl_2$	33	40	87
$HgCl_2$	49	40	139
$HgCl_2$	22.37	40	96
Me_4NBr	0.09	40	40

Table 25

Stability of Silver Complexes in Ethylene Carbonate at 40°C and Ionic Strength 0.1 M

anion	$\log\beta_{21}$	$\log\beta_{31}$	$\log\beta_{43}$	$\log K_p$	$\log k_s$
$B\phi_4^-$					-13
IO_3^-					-16.1
Cl^-	17.4			-16.9	-17.1
Br^-	18			-17.6	-17.8
I^-	19.7		57.4	-18.4	-18.8
SCN^-	13.8	16.8		-15.5	-14.6

Definitions of constants; Note the special cases involving I^- and SCN^-:

$\beta_{21} = [Ag(anion)_2^-]/[Ag^+][anion]^2$ for 2 anion + Ag^+ = $Ag(anion)_2^-$

$\beta_{31} = [Ag(SCN)_3^{2-}]/[Ag^+][SCN^-]^3$ for 3 SCN^- + Ag^+ = $Ag(SCN)_3^{2-}$

$\beta_{43} = [Ag_3I_4^-]/[Ag^-]^3[I^-]^4$ for $4I^-$ + $3Ag^+$ = $Ag_3I_4^-$

$K_p = [Ag(anion)_2^-][Ag^+]$ for $Ag(anion)_2^-$ + Ag^+ = 2 $Ag(anion)_{(s)}$

$K_p = [Ag_3I_4^-][Ag^+]$ for $Ag_3I_4^-$ + Ag^+ = $4AgI_{(s)}$

$K_s = [anion][Ag^+]$ for anion + Ag^+ = $Ag(anion)_{(s)}$

Data from reference [46]:
J. Cabon, M L'Her, M. Le Demezt, C R Acad Sci Paris Ser C, 280, 819(1975)

Table 26

Limiting Equivalent Conductances of Salts in Ethylene Carbonate

salt	limiting equivalent conductance $cm^2\Omega^{-1}mole^{-1}$	Walden Product $\Lambda_o\eta$	temp °C	ref.
$LiClO_4$	32.85	0.607	40	105
$NaClO_4$	38.84	0.719	40	105
$KClO_4$	41.99	0.776	40	105
$RbClO_4$	42.59	0.788	40	105
$CsClO_4$	43.59	0.807	40	105
Me_4NI	44.81	0.828	40	105
Et_4NI	42.83	0.792	40	105
Et_4NBr	42.48	0.785	40	105
Et_4NClO_4	42.13	0.779	40	105
Bu_4NI	37.41	0.692	40	105
Bu_4NI	34.20		40	103
Bu_4NBr	36.97	0.683	40	105
Bu_4NClO_4	36.52	0.975	40	105
TABI	36.63		40	104
$TABB\phi_4$	21.85		40	103

Table 27

Limiting Ionic Equivalent Conductances in Ethylene Carbonate at 40°C

ion	equivalent conductance $cm^2\Omega^{-1}mole^{-1}$	reference
Li^+	7	105
Li^+	7	105
Li^+	8.04	103
Na^+	13	105
Na^+	14.03	103
K^+	15	105
K^+	17.18	103
Rb^+	17.78	103
Cs^+	17	105
Cs^+	18.78	103
Me_4N^+	17.18	105
Me_4N^+	19.11	103
Et_4N^+	15.8	105
Et_4N^+	17.13	103
Bu_4N^+	10	105
Bu_4N^+	11.71	103
ClO_4^-	26	105
ClO_4^-	24.81	103
Br^-	26.5	105
Br^-	25.26	103
I^-	27	105
I^-	25.70	103

Table 28

Conductivities of Salts in Ethylene Carbonate

salt	concentration	specific conductance Ω^{-1}-cm^{-1}	equivalent conductance cm$^2\Omega^{-1}$mole^{-1}	temp. °C	ref.
$LiClO_4$	0.33 m	0.00607			25
	0.49 m	0.00727		25	39
	0.72 m	0.00787		25	39
	0.85 m, 0.89 F	0.00787		25	40
	0.92 m	0.00780		25	39
	1.36 m	0.00630		25	39
	1.86 m	0.00432		25	39
	2.34 m	0.00273		25	39
	2.82 m	0.00155		25	39
NaI	2.51 m (sat.)	0.011	4.38	40	87
NaI	0.05081 m		31.07	36.8	94
NaBr	0.030 m (sat.)	9.46×10^{-4}	36	40	87
KI	0.671 m (sat.)	0.015	26.8	40	87
KI	0.03735 m		34.55	36.8	94
KCNS	0.93 m	0.01140		25	39
	1.3 m, 1.6 F	0.01184		25	40
	1.35 m	0.01184		25	39
	1.67 m	0.01162		25	39
	2.32 m	0.01068		25	39
	2.60 m	0.01007		25	39
	2.98 m	0.00927		25	39
	3.29 m	0.00850		25	39
	3.63 m	0.00767		25	39
KPF_6	1.0 m, 1.2 F	0.01132		25	40
	1.03 m	0.01132		25	39
CsI	0.01166 m		38.35	36.8	94
$CaCl_2$	0.02 m (sat.)	8.66×10^{-5}		40	87
ZnI_2	0.00447 m		0.00412	40	64
Bu_4NCl	0.04553 m		30.73	36.8	40
Bu_4NBr	0.06165 m		29.14	36.8	94
Bu_4NI	0.03970 m		29.61	36.8	94
Et_4NBr	0.02240 m		36.95	36.8	94
Pr_4NBr	0.05106 m		31.50	36.8	94
$Bu_4NPicrate$	0.10 F		40.0	91	104

Table 29

Densities, Relative Viscosities, and Solute Partial Molar Volumes for Ethylene Carbonate Solutions at 40°C

solute	conc. molal	density g/cc	relative viscosity	solute partial molar volume cm^3/mole
LiI	0.05058	1.32770	1.0440	10.5
NaI	0.11605	1.3363	1.0938	35.2
KI	0.16002	1.33927	1.1086	42.2
CsI	0.10183	1.34035	1.0620	57.5
CsBr	0.01850		1.0112	
Me_4NBr	0.07719	1.32148	1.0310	118.0
Et_4NCl	0.04723	1.31908	1.0169	166.2
Pr_4NBr	0.07247	1.31768	1.0324	242.7
Bu_4NI	0.04217	1.31907	1.0247	325.4
Ph_4AsCl	0.04752	1.32131	1.0365	322.0
Bu_4NBr	0.05080	1.31690	1.0287	314.4
$NaB\phi_4$	0.05181	1.31964	1.0704	288.0
Bu_4NBBu_4	0.01668	1.31658	1.0126	593.5
H_2O	0.39081	1.31885	0.9664	19.0
3,3-diethylpentane	0.10317	1.31670	0.9925	133
pure EC		1.32160		

Data from reference [102]:
P. Thompson, B. Fisher, R. Wood, J Soln Chem, 11:1, 1(1982).

Table 30

Conductances, Viscosities and Walden Products of Solutions of $Bu_4NPicrate$ in Ethylene Carbonate at 91 °C

conc. Formal	equivalent conductance $cm^2\Omega^{-1}mole^{-1}$	viscosity η centipoise	Walden Product
0.10	40.0	1.02	0.408
0.50	25.7	1.38	0.355
1.00	15.6	2.23	0.348
1.50	8.08	4.53	0.366
2.00	2.70	14.5	0.392
2.20	1.47	27.6	0.406

Data from reference [104]:
R. Seward, J Phys Chem, 62, 758(1958).

Table 31

Viscosities and Densities of 1 m Ethylene Carbonate and Propylene Carbonate Solutions at 30°C

salt	ethylene carbonate viscosity cp	ethylene carbonate viscosity cs	ethylene carbonate density g/cc	propylene carbonate viscosity cp	propylene carbonate viscosity cs	propylene carbonate density g/cc
$LiClO_4$	7.91	5.67	1.395	8.32	6.58	1.264
KCNS	5.09	3.72	1.368	4.94	3.99	1.238
KPF_6	4.82	3.36	1.435	4.87	3.78	1.288

Data from reference [39]: G. Pistoia, JES, 118:1, 153(1971).

Table 32

Solubilities of Nonelectrolytes in Ethylene Carbonate at 40 °C

solute	solubility g solute/100 g EC	reference
acetylene	0.6	139
benzene	miscible	139
butyl acetate	miscible	139
chloroform	miscible	139
dichloroethyl ether	miscible	139
ethanol	miscible	139
ethyl acetate	miscible	139
ethylene dichloride	miscible	139
formamide	miscible	139
iodine	0.205 F	47
methanol	miscible	139
methylene dichloride	miscible	139
naphthalene	15	139
nonylphenol	miscible	139
propylene carbonate	miscible	139
sulfur dioxide	26	139
toluene	miscible	139
tricresyl phosphate	miscible	139
urea	1.5	139
water	miscible	139
	solubility † in mole fraction X 1000	
N_2	0.43	98
CO_2	7.03	98
CH_4	0.72	98
C_2H_6	3.48	98
C_3H_8	5.10	98

† Solubility at 1 atm, 40 °C.

Table 33

Sources of EC-Water Mixture Physical Property Data Over a Wide Range of Composition at 25 and 40 °C

property	temp., °C	reference
density	25	30,32,35,124
	40	30,32,35
dielectric constant	25	30,32,35,67,127
	40	30,32,35,45,127
viscosity	25	30,32,124
	40	30,32,45
refractive index	25	124
	40	45

Table 34

Solubility of Iodine in EC-water Mixtures and Activity Coefficients for Transfer of Iodine from Water to EC-Water Mixtures at 40 °C

χ_{EC}	solubility mole/l	$\log {}^{w}\Gamma^{s}(I_2)$
0	0.00210	0
0.05	0.00400	-0.3
0.1	0.0100	-0.7
0.2	0.0300	-1.2
0.3	0.0600	-1.45
0.4	0.0920	-1.65
0.5	0.140	-1.85
0.6	0.165	-1.9
0.7	0.182	-1.95
0.8	0.194	-1.95
0.9	0.198	-2
0.95	0.206	-2
1	0.205	-2

Data from reference [47]:
J. Cabon, M. L'Her, J. Courtot-Coupez, J Electroanal Chem, 64, 219(1975).

Table 35

Solubility Products of AgCl and AgBr and the Formation Constants of $AgCl_2^-$ and $AgBr_2^-$ In EC-Water Mixtures at 40 °C

χ_{EC}	$\log K_s(AgCl)$	$\log K_s(AgBr)$	$\log K_{s2}(AgCl_2^-)$	$\log K_{s2}(AgBr_2^-)$
0	-9	-11.2		
0.1	-9.2	-11.4		
0.2	-9.65	-11.7		
0.3	-10.15	-12.1		
0.4	-10.7	-12.5		
0.5	-11.2	-13.0		
0.6	-11.4	-13.5		
0.7	-11.95	-14.0		
0.8	-13.05	-14.55	-1.25	-1.1
0.9	-14.25	-15.95	-0.8	-0.3
0.95	-15.6	-16.75	-0.4	-0.1
1	-17.15	-17.8	0.5	0.4

Potentials are relative to ferrocene/ferricinium in the same solvent mixture. The potential of the ferrocene/ferricinium couple in water relative to the normal hydrogen electrode at 25 °C is + 0.400 V, as reported by H. Koepp and H. Strehlow, Z Elektrochem, 64, 483(1960).

Data from reference [47]:
J. Cabon, M. L'Her, J. Courtot-Coupez, J Electroanal Chem, 64, 219(1975).

Table 36

Formal Potential of the I^-/I_3^- and I_3^-/I_2 Couples and the Triiodide Formation Constant in Mixtures of Ethylene Carbonate and Water at 40 °C

χ_{EC}	$E'^{o}(I^-/I_3^-)$	$E'^{o}(I_3^-/I_2)$	log K
0	0.159	0.414	2.74
0.1	0.081	0.422	3.65
0.2	0.034	0.417	4.1
0.3	-0.017	0.404	4.5
0.4	-0.038	0.407	4.8
0.5	-0.062	0.410	5.1
0.6	-0.93	0.411	5.4
0.7	-0.120	0.409	5.7
0.8	-0.154	0.400	5.95
0.9	-0.201	0.398	6.45
0.95	-0.214	0.398	6.6
1	-0.222	0.406	6.8

Potentials are relative to ferrocene/ferricinium in the same solvent mixture. The formal potential of the ferrocene/ferricinium couple in water relative to the normal hydrogen electrode at 25 °C is + 0.400, as reported by H. Koepp and H. Strehlow, Z Elektrochem, 64, 483(1960).

Data from reference [47]:
J. Cabon, M. L'Her, J. Courtot-Coupez, J Electroanal Chem, 64, 219(1975).

Table 37

Activity Coefficients for Transfer of Cl^-, Br^-, I^-, and I_3^- From Water to EC-Water Mixtures at 40 °C

χ_{EC}	$\log {}^{W}\Gamma^{S}(Cl^-)$	$\log {}^{W}\Gamma^{S}(Br^-)$	$\log {}^{W}\Gamma^{S}(I^-)$	$\log {}^{W}\Gamma^{S}(I_3^-)$
0	0	0	0	0
0.1	0.8	0.8	0.45	-1.2
0.2	1.45	1.3	0.75	-1.75
0.3	2.1	1.85	1.25	-2.0
0.4	2.6	2.2	1.35	-2.35
0.5	3	2.6	1.5	-2.7
0.6	3.15	3.05	1.75	-2.8
0.7	3.4	3.25	2.1	-2.85
0.8	4.15	3.45	2.45	-2.7
0.9	4.95	4.45	2.95	-2.75
0.95	5.75	4.7	3	-2.75
1	6.35	4.8	3.15	-2.8

Data from reference [47]:
J. Cabon, M. L'Her, J. Courtot-Coupez, J Electroanal Chem, 64, 219(1975).

Table 38

Formal Potential of the Ag/Ag^+ Couple in EC-Water Mixtures and Activity Coefficients for Transfer of Ag^+ from Water to EC-Water Mixtures at 25 °C and/or 40 °C

χ_{EC}	25 °C		40 °C	
	${}^{s}E'^{o}(Ag)$, V	$\log {}^{w}\Gamma^{s}(Ag^+)$	${}^{s}E'^{o}(Ag)$, V	$\log {}^{w}\Gamma^{s}(Ag^+)$
0	0.403	0	0.405	0
0.02	0.396	-0.1	0.394	-0.2
0.05	0.391	-0.2	0.374	-0.5
0.1	0.379	-0.4	0.366	-0.6
0.2	0.357	-0.7	0.354	-0.8
0.3	0.352	-0.8	0.346	-0.95
0.4	0.353	-0.8	0.348	-0.9
0.5	0.358	-0.7	0.354	-0.8
0.6	0.370	-0.5	0.358	-0.75
0.7			0.378	-0.45
0.8			0.398	-0.1
0.9			0.424	0.3
0.95			0.460	0.85
1			0.518	1.8

Potentials are relative to ferrocene/ferricinium in the same solvent. The formal potential of the ferrocene/ferricinium couple in water relative to the normal hydrogen electrode at 25 °C is + 0.400 V, as reported by H. Koepp and H. Strehlow, Z Elektrochem, 64, 483(1960).

Data from reference [47]:
J. Cabon, M. L'Her, J. Courtot-Coupez, J Electroanal Chem, 64, 219(1975).

Table 39

Solvent Properties (ρ, ϵ, η), Conductivity Parameters (Λ_o and Walden Product $\Lambda_o\eta$) and Ion-pairing Constant for KI in Mixed Solvents Containing Ethylene Carbonate at 40 °C

solvent	solvent properties EC content %-weight	mole frac†	ρ g/cc	ϵ	η cP	Λ_o $\Omega^{-1}cm^2mole^{-1}$	Walden Product $\Omega_o\eta$	K_A $mole^{-1}$
Water	0	0	0.9922	73.28	0.654	196.45	1.285	0.53
EC-Water	49.5	0.167	1.1369	77.20	1.005	119.14	1.197	0.52
EC-Water	0.658	0.282	1.1905	79.10	1.160	98.25	1.140	0.63
EC-Water	77.6	0.415	1.2315	80.99	1.300	79.41	1.032	0.96
EC-Water	90.9	0.672	1.2803	85.12	1.570	64.48	1.012	1.37
EC	100	1.000	1.3214	90.36	1.978	75.52	1.139	1.80
EC-MEK	78.9	0.754	1.1662	65.77	1.194	61.38	0.7329	3.22
EC-MEK	47.7	0.428	0.9836	40.23	0.662	91.33	0.6046	10.88
EC-MEK	26.9	0.232	0.8880	28.43	0.479	115.78	0.5546	35.2
MEK	0	0	0.7837	16.85	0.334	164.77	0.5503	444

Data from reference [25]:
A. D'Aprano, J. Komiyama, R. Fuoss, J Soln Chem, 5, 279(1976).
† Mole fraction calculated from %-weight listed in reference [25]

Table 40

Solvent Properties (ρ, ϵ, η), Conductivity Parameters (Λ_o and Walden Product $\Lambda_o\eta$) and Ion-pairing Constant for KI in Mixed Solvents Containing Ethylene Carbonate at 25 °C

solvent	solvent properties EC content %-weight	mole frac†	ρ g/cc	ϵ	η cP	Λ_o $\Omega^{-1}cm^2mole^{-1}$	Walden Product $\Lambda_o\eta$	K_A $mole^{-1}$
Water	0	0	0.9971	78.35	0.890	150.49	1.339	0.69
EC-Water	12.4	0.0282	1.0337	79.52	1.011	130.04	1.315	0.46
EC-Water	27.3	0.0714	1.0786	80.88	1.128	111.64	1.259	0.29
EC-Water	49.3	0.1660	1.1482	82.20	1.388	89.16	1.238	0.28
EC-Water	68.4	0.3070	1.2139	84.23	1.648	71.12	1.117	0.45
EC-Water	80.7	0.4611	1.2594	86.52	1.796	59.45	1.068	0.69
EC-TMS	74.4	0.799	1.3189	78.64	3.47	25.395	0.8812	2.33
EC-TMS	52.7	0.603	1.3035	66.62	4.54	19.946	0.9055	2.93
EC-TMS	17.5	0.225	1.2679	44.73	11.47	10.221	1.172	8.83

Data from reference [25]:
A. D'Aprano, J. Komiyama, R. Fuoss, J Soln Chem, 5, 279(1976).

† Mole fraction calculated from %-weight listed in reference [25]

Table 41

Solvent Properties (ρ, ϵ, η), Conductivity Parameters (Λ_o and Walden Product $\Lambda_o\eta$) and Ion-pairing Constant for KI in EC-TMS-Water Mixtures at 40 °C

solvent properties									
EC content		TMS content		ρ	ϵ	η	Λ_o	Walden Product	K_A
% weight	mole frac†	% weight	mole frac†	g/cc		cP	$\Omega^{-1}cm^2mole^{-1}$	$\Lambda_o\eta$	$mole^{-1}$
7.44	0.0166	2.56	0.00418	1.0251	78.00	0.988	133.19	1.316	0.33
19.4	0.0502	6.43	0.01218	1.0683	77.75	1.146	111.48	1.278	0.31
33.0	0.375	10.93	0.02541	1.1209	77.20	1.388	91.15	1.265	0.34
63.0	0.715	20.84	0.09701	1.2476	76.58	2.129	52.02	1.108	0.89
74.4	0.799	25.6	0.201	1.3189	78.64	3.47	25.395	0.8812	2.33

Data from reference [25]:
A. D'Aprano, J. Komiyama, R. Fuoss, J Soln Chem, 5, 279(1976).

† Mole fraction calculated from %-weight listed in reference [25]

Table 42

Solvent Properties (ρ, ϵ, η), Conductivity Parameters (Λ_o and Walden Product $\Lambda_o\eta$) and Ion-pairing Constant for $KClO_4$ in Mixtures Isodielectric with Water at 25 °C

solvent	solvent properties EC content† %-weight	mole frac‡	ρ g/cc	ϵ	η cP	Λ_o $\Omega^{-1}cm^2mole^{-1}$	Walden Product $\Lambda_o\eta$	K_A $mole^{-1}$
water	0	0	0.9971	78.35	0.890	140.73	1.252	0.98
EC-MeOH	84.58	0.6662	1.2163	78.52	1.364	57.86	0.7892	0.96
EC-ACE	87.04	0.8158	1.2333	78.13	1.610	46.906	0.7552	1.39
EC-AN	84.03	0.7104	1.2097	78.40	1.438	51.92	0.7466	1.42
EC-TMS	74.05	0.7957	1.3181	78.50	3.333	25.167	0.8388	1.40

Data from reference [26]:
A. D'Aprano, I. Donato, E. Caponetti, J Soln Chem, 3, 371(1974).

† The exact EC content was not given in reference [26]. The %-weights were obtained from A. D'Aprano by private communication.

‡ The mole fraction was calculated from the %-weight.

Table 43

Solvent Properties (ρ, ϵ, η), Conductivity Parameters (Λ_o and Walden Product $\Lambda_o\eta$) and Ion-pairing Constant for KI in Mixtures Isodielectric with Water at 25 °C

solvent	solvent properties					Λ_o	Walden Product	K_A
	EC content†		ρ	ϵ	η		$\Lambda_o\eta$	
	%-weight	mole frac‡	g/cc		cP	$\Omega^{-1}cm^2mole^{-1}$		$mole^{-1}$
water	0	0	0.9971	78.35	0.890	150.75	1.342	0.25
EC-TMS	74.05	0.7957	1.3181	78.50	3.333	25.40	0.8466	1.30

Data from reference [26]:
A. D'Aprano, I. Donato, E. Caponetti, J Soln Chem, 3, 371(1974).

† The exact EC content was not given in reference [26]. The %-weights were obtained from A. D'Aprano by private communication.

‡ The mole fraction was calculated from the %-weight.

Table 44

Solvent Properties (ρ, ϵ, η), Conductivity Parameters (Λ_o and Walden Product $\Lambda_o\eta$) and Ion-pairing Constant for $KClO_4$ in Mixtures of Ethylene Carbonate with Acetonitrile at 25 °C

solvent properties EC content %-weight	mole frac†	ρ g/cc	ϵ	η cP	Λ_o $\Omega^{-1}cm^2mole^{-1}$	Walden Product $\Lambda_o\eta$	K_A $mole^{-1}$
0	0	0.7768	36.01	0.341	187.61	0.6398	28.43
11.11	0.0551	0.8176	39.15	0.384	166.92	0.6410	20.09
21.57	0.1136	0.8600	42.52	0.436	148.02	0.6454	14.00
30.76	0.1716	0.9002	45.79	0.494	132.05	0.6523	9.98
39.42	0.1716	0.9405	49.60	0.558	117.87	0.6577	7.38
46.92	0.2328	0.9785	53.18	0.629	105.60	0.6642	5.46
61.20	0.4237	1.0586	61.10	0.821	83.77	0.6878	3.48
70.74	0.5299	1.1172	67.40	1.011	70.10	0.7087	2.23
74.37	0.5750	1.1411	70.03	1.106	65.28	0.7220	2.12
78.48	0.6296	1.1693	73.25	1.228	59.43	0.7298	1.69
80.78	0.6621	1.1854	75.45	1.310	56.20	0.7362	1.60
84.19	0.7128	1.2105	78.52	1.444	51.64	0.7457	1.38
85.98	0.7409	1.2241	80.27	1.522	49.52	0.7537	1.33
88.34	0.7793	1.2433	82.57	1.644	46.34	0.7618	1.26

Data from reference [27]: D'Aprano, J Soln Chem, 3, 363(1974).

† Mole fraction calculated from %-weight given in reference [27]

Table 45

Solvent Properties (ρ, ϵ, η), Conductivity Parameters (Λ_o and Walden Product $\Lambda_o\eta$) and Ion-pairing Constant for $KClO_3$ in Mixtures of Ethylene Carbonate with Water at 25 °C

solvent properties					Λ_o	Walden Product	K_A
EC content %-weight	EC content mole fract†	ρ g/cc	ϵ	η cP	$\Omega^{-1}cm^2mole^{-1}$	$\Lambda_o\eta$	$mole^{-1}$
0	0	0.99707	78.30	0.8903	137.52	1.224	0.70
7.86	0.01717	1.0204	79.14	0.954	127.75	1.219	0.52
10.09	0.02246	1.0269	79.51	0.973	125.00	1.216	0.42
25.14	0.0643	1.0720	80.48	1.108	109.47	1.213	0.27
49.26	0.1658	1.1482	82.20	1.388	87.59	1.216	0.39
73.58	0.3632	1.2328	85.06	1.706	64.84	1.106	1.07
80.65	0.4603	1.2592	86.50	1.792	58.10	1.041	1.44

Data from reference [32]:
A. D'Aprano, M. Goffredi, R. Triolo, Electrochimica Acta, 21, 139(1976).

† Mole fraction calculated from %-weight given in reference [32]

Table 46

Solvent Properties (ρ, ϵ, η), Conductivity Parameters (Λ_o and Walden Product $\Lambda_o\eta$) and Ion-pairing Constant for NaCl, Sodium Acetate, HCl and Acetic Acid in Mixtures of Ethylene Carbonate with Water at 25 °C

solute	solvent properties EC content %-weight†	mole frac	ρ g/cc	ϵ	η cP	Λ_o $\Omega^{-1}cm^2mole^{-1}$	Walden Product $\Lambda_o\eta$	K_A $mole^{-1}$
NaCl	0	0	0.99707	78.30	0.8903			
	54.99	0.2	1.16861	82.86	1.4474	73.15	1.0588	1.06
	76.51	0.4	1.23465	85.55	1.7262	51.765	0.8936	3.30
	83.01	0.5	1.25666	86.89	1.7979	46.477	0.8356	5.53
	88.00	0.6	1.27338	86.89	1.8629	42.880	0.7988	7.93
NaAc	54.49	0.2	1.15780	82.86	1.4474	55.93	0.8095	4.38
	76.51	0.4	1.24365	85.55	1.7262	41.413	0.7149	10.33
	83.01	0.5	1.26634	86.89	1.7979	37.82	0.6800	14.2
	88.00	0.6	1.28549	83.91	1.8629	35.95	0.6697	19.7
HCl	54.99	0.2	1.16861	82.86	1.4474	198.80	2.877	1.35
	76.51	0.4	1.24365	85.55	1.7262	102.06	1.762	2.53
	83.01	0.5	1.26634	86.89	1.7979	75.96	1.366	5.7
	88.00	0.6	1.28549	88.20	1.8629	58.75	1.094	9.7
								$10^{-6}K_A$‡
acetic acid	54.99	0.2	1.16861	82.86	1.4474	181.77	2.631	0.690
	76.51	0.4	1.24365	85.55	1.7262	97.71	1.583	6.41
	83.01	0.5	1.22634	86.89	1.7979	67.30	1.210	20.0
	88.00	0.6	1.28549	88.20	1.8629	51.83	0.9655	98.0

Data from reference [30]: B.Boener, R. Bates, J Soln Chem, 7, 245(1978).

† %-weight computed from mole fraction

‡ K_A taken as the inverse of the dissociation constant reported in [30]

Table 47

Solvent Properties (ρ, ϵ, η), Conductivity Parameters (Λ_o and Walden Product $\Lambda_o\eta$) and Ion-pairing Constant for NaCl, Sodium Acetate, HCl and Acetic Acid in Mixtures of Ethylene Carbonate with Water at 40 °C

solute	solvent properties EC content %-weight†	mole frac	ρ g/cc	ϵ	η cP	Λ_o $\Omega^{-1}cm^2mole^{-1}$	Walden Product $\Lambda_o\eta$	K_A $mole^{-1}$
NaCl	0	0	0.99224	73.15	0.6531			
	54.99	0.2	1.15780	77.75	1.0435	98.69	1.030	1.01
	76.51	0.4	1.23469	80.84	1.2627	71.33	0.9007	3.53
	83.01	0.5	1.25666	82.33	1.3300	63.20	0.8406	6.47
	88.00	0.6	1.27338	83.91	1.3948	58.08	0.8101	8.31
NaAc	54.49	0.2	1.15780	77.75	1.0435	77.05	0.8040	6.15
	76.51	0.4	1.23469	80.84	1.2627	58.15	0.7343	9.98
	83.01	0.5	1.25666	82.33	1.3300	52.81	0.7024	14.26
	88.00	0.6	1.27338	83.91	1.3948	49.21	0.6864	18.2
HCl	54.99	0.2	1.15780	77.75	1.0435	248.26	2.591	0.44
	76.51	0.4	1.23469	80.84	1.2627	130.76	1.651	2.09
	83.01	0.5	1.25666	82.33	1.3300	97.28	1.294	4.79
	88.00	0.6	1.27338	83.91	1.3948	76.41	1.066	8.2
	95.13	0.8	1.30044	87.29	1.5680	49.39	0.7744	49.1
								$10^{-6}K_A$‡
acetic acid	54.99	0.2	1.15780	77.75	1.0435	226.62	2.365	0.781
	76.51	0.4	1.23469	80.84	1.2627	117.58	1.485	7.69
	83.01	0.5	1.25666	82.33	1.3300	86.90	1.156	25.0
	88.00	0.6	1.27338	83.91	1.3948	67.54	0.9420	240

Data from reference [30]: B.Boener, R. Bates, J Soln Chem, 7, 245(1978).

† %-weight computed from mole fraction

‡ K_A taken as the inverse of the dissociation constant reported in [30]

Table 48

Electroactive Range of Several Electrolytes in Ethylene Carbonate at 40 °C

electrolyte	electrode	anodic limit (volts)	cathodic limit (volts)	electroactive range (volts)
$LiClO_4$	Pt	2.5	-3.3	5.8
	Ag	0.4	-3.3	3.7
$NaClO_4$	Pt	2.5	-3.4	5.9
$KClO_4$	Pt	2.5	-3.3	5.8
Et_4NClO_4	Pt	2.5	-2.8	5.3
Bu_4NClO_4	Pt	2.5	-3.7	6.2
Et_4NClO_4	Pt	0.5	-2.8	3.3
	Ag	-0.6	-2.8	2.2
KPF_6	Pt	3.5	-3.3	6.8

NOTES

1) All potentials versus ferrocene/ferricinium:

Pt/0.01 F Fc, 0.01 F $FcClO_4$, 0.1F $LiClO_4$

The formal potential of the ferrocene/ferricinium couple in water relative to the normal hydrogen electrode at 25 °C is + 0.400 V, as reported by H. Koepp and H. Strehlow, Z Elektrochem, 64, 483(1960).

2) The potential limit was reached when the current density reached 1 mA/cm^2.

3) Data from reference [38]:
J. Cabon, M. L'Her, M. Le Demezet, Bull Soc Chim Fr, 5-6, 1020(1975).

Table 49

Redox Potential of Alkali Metal Cations in Ethylene Carbonate at 40 °C Relative to those in Water

cation	E^o relative to that in water EC, calculated	EC, observed	E^o, V Water†
Li^+	0.155	0.122	-3.045
Na^+	0.302	0.269	-2.711
K^+	0.178	0.143	-2.924
Rb^+	0.155	0.122	-2.925
Cs^+	0.153	0.120	-2.923

† E^o for water versus NHE from:
Handbook of Chemistry and Physics, 52nd ed., 1971.

Data from reference [92]:
N. Matsuura, K. Umemoto, M. Waki, Z. Takeuchi, M. Omoto, Bull Chem Soc Japan, 47:4, 806(1974).

Table 50

Maximum Specific Conductivity of Various Salts in Propylene Carbonate and Ethylene Carbonate at 25 °C

salt	propylene carbonate specific conductivity $0.001\Omega^{-1}cm^{-1}$	propylene carbonate salt concentration	ethylene carbonate specific conductivity $0.001\Omega^{-1}cm^{-1}$	ethylene carbonate salt concentration
KCNS	8.9	1.5 F	11.84	1.6 F, 1.3 m
KPF_6	6.8	0.5 F	11.32	1.2 F, 1.0 m
$LiClO_4$	5.6	1.0 F	7.87	0.89 F, 0.85 m

Data from reference [40]:
G. Pistoia, M. Rossi, B. Scrosati, J Electrochem Soc, 117:4, 500(1970).

Table 51

Redox Potential of Alkali Metal Cations in Ethylene Carbonate at 40 °C Relative to those in Water

cation	E^o relative to that in water EC, calculated	EC, observed	E^o, V Water†
Li^+	0.155	0.122	-3.045
Na^+	0.302	0.269	-2.711
K^+	0.178	0.143	-2.924
Rb^+	0.155	0.122	-2.925
Cs^+	0.153	0.120	-2.923

† E^o for water versus NHE from:
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VIII. C. References

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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