JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Electroconductivity of Tetraethylammonium Tetrafluoroborate in Propylene Carbonate at Various Temperatures

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ABSTRACT: Electrical conductivities of tetraethylammonium tetrafluoroborate in propylene carbonate were measured over wide ranges of salt concentration and temperature. The data have been interpreted in terms of ion−solvent and ion−ion interactions using the Lee−Wheaton equation at low concentrations and the semiempirical Castell−Amis equation at high concentrations. The association constants, K_A, and limiting molar conductivities at infinite dilution, Λ_0, have been calculated at (283.15, 291.15, 298.15, and 313.15) K. The results indicate that Et_4NBF_4 is almost unassociated in this solvent medium. The evaluation of Stokes radii, r_S, of the ions at 298.15 K indicates that Et_4N^+ and BF_4^- remain scarcely solvated in the propylene carbonate. The specific conductivity, χ, of Et_4NBF_4 in propylene carbonate was determined in a concentration range of (0.15 to 1.4) $mol \cdot kg^{-1}$ at (253.15, 273.15, 293.15, 313.15, and 333.15) K and was interpreted by the transition state theory. The activation energies for conductivity and for viscous flow are found to be not differing significantly meaning that the two transport processes are closely linked.

INTRODUCTION

A new generation of electrochemical devices for energy storage, that is, capacitors, has recently appeared.[1] They are characterized by a large number of cycles of charge−discharge, long lifetime, and large density of energy, operating independently from a position in space. One of the main ways to increase the energy capacitance of capacitors is the development of new nonaqueous organic electrolytes with a operating voltage above 3 V. The solutions of composite ionophores in propylene carbonate are the most efficient systems.[2] As it is well-known, the conductivity of the electrolyte solution is an important factor in the performance of batteries[3] and, consequently, for capacitors. The study of electrolyte solutions in various solvents like acetonitrile,[4] γ-butyrolactone,[5,6] *N*,*N*-dimethylformamide,[7,8] propylene carbonate,[9] and so forth has been made extensively. However, conductance measurements on tetraethylammonium tetrafluoroborate have not been reported in propylene carbonate. Values of the equivalent or molar conductance of electrolytes at infinite dilution and the ionic association constant can be obtained from conductance data as a function of concentration by using the Lee−Wheaton equation based on a more realistic physical picture than the primitive model. High-concentration studies have been undertaken since concentrated solutions are generally used in organic electrolyte batteries, wet electrolyte capacitors, or electroorganic synthesis.[10] Of particular interest are the ion−solvent and ion−ion interactions which play an important role in determining the magnitudes of ionic mobility. In this paper we present a conductance study of solutions of tetraethylammonium tetrafluoroborate (Et_4NBF_4) in propylene carbonate (PC) in a wide range of concentration and temperature. This work is part of a systematic study on the transport properties of 1−1 electrolytes in dipolar aprotic solvents.[11−15]

EXPERIMENTAL SECTION

Materials. Et_4NBF_4 was prepared as described previously by synthesizing from tetraethylammonium bromide (Russia, pure grade) and fluoboric acid (Russia, pure grade).[11] The salt obtained had been recrystallized from an isopropyl alcohol (Russia, best purity ≥ 99 %) and an acetone (Russia, best purity ≥ 99 %) mixture. The absence of bromide ions in tetraethylammonium tetrafluoroborate was checked by adding several drops of 0.05 M $AgNO_3$ to its aqueous solution. Tetraethylammonium tetrafluoroborate was also tested for the presence of acidic impurities by the titration of its solution with 0.01 M NaOH. The product of a synthesis contained no less than 99.5 % component.[11] This salt was dried under vacuum at temperatures no higher than 50 °C to a constant mass for 48 h, yielding a water content of 0.01 wt % with coulometric Karl Fisher titration,[16] the salt being dissolved in dried propylene carbonate.

Propylene carbonate (Russia, best purity > 99 %) was dried with type 4 Å molecular sieves for around 12 h and then distilled under reduced pressure.[17] The residual water content in PC was less than 0.003 %. The preparation of solutions and measurements of their conductivities were performed without contact with atmosphere. Solutions were prepared by a gravimetric method using a Sartorius-ME215S balance (with a weighing accuracy of $1 \cdot 10^{-5}$ g). All weighing was corrected to vacuum. The solvent and solutions were stored in the drybox.

Conductivity Measurements. Conductance measurements were made with a P-5083 automatic digital bridge (Russia) as a conductivity meter using a conductance cell of the three

Received: March 30, 2011
Accepted: June 10, 2011
Published: June 22, 2011

dx.doi.org/10.1021/je200309v | *J. Chem. Eng. Data* 2011, 56, 3222–3226

Table 1. Specific Electroconductivities, χ, of Et_4NBF_4 in Propylene Carbonate as a Function of Molality, m, and Temperature, T[a]

m	T/K					
	253.15	273.15	293.15	298.15	313.15	333.15
$\text{mol}\cdot\text{kg}^{-1}$	$10^3\ \chi/\text{S}\cdot\text{cm}^{-1}$					
0.15930	1.317	2.390	3.640	3.970	5.160	6.780
0.46100	2.779	5.190	8.120	8.765	11.62	15.35
0.56580	3.133	5.910	9.290	10.11	13.33	17.64
0.72820	3.523	6.760	10.69	11.64	15.43	20.49
0.82340	3. 663	7.120	11.28	12.36	16.35	21.77
0.96660	3.749	7.450	11.86	12.94	17.30	23.14
1.18560	3.593	7.500	12.01	13.22	17.75	23.95
1.42550	-	6.89	11.16	12.66	16.86	23.07

[a] Standard uncertainties $u(\chi(x))$ are $u(\chi(m)) = 0.0004\ \text{S}\cdot\text{cm}^{-1}$, $u(\chi(T)) = 0.001\ \text{S}\cdot\text{cm}^{-1}$, $u(\chi(\text{cell}) = 0.002\ \text{S}\cdot\text{cm}^{-1}$, and the combined expanded uncertainty $u_c(\chi) = 0.003\ \text{S}\cdot\text{cm}^{-1}$ with a 0.95 level of confidence.

electrode type for dilute solutions and cell with two electrodes for concentrated electrolyte solutions. These two hermetic glass (Pyrex) cells with electrodes, made of smooth platinum, were mounted in a lid for immersion in a temperature bath. This thermostatted bath was equipped with a cooling coil which is connected to the cryostat (model MK-70, Russia) by tubing. The double thermostatic control allowed maintaining the temperature of the bath with accuracy better than 0.005 K. The calibration of the conductance cells was based on the conductance of aqueous potassium chloride solutions using the data from the refs 18 and 19 for dilute solutions and for concentrated electrolyte solutions, respectively. To eliminate electrode polarization effects, resistances were measured at five different frequencies in the range of (1 to 10) kHz and extrapolated to infinite frequency. All data were corrected with the specific conductance of the solvent. Taking into account the sources of error (calibration, measurements, purity of materials, temperature, molality), the estimated uncertainty of specific conductance was within ± 0.003 $\text{S}\cdot\text{cm}^{-1}$. The overall relative uncertainties of the electrical conductivities were estimated to be (0.05 to 0.1) %. The specific conductivity values of tetraethylammonium tetrafluoroborate in PC as function of molality, m, (0.15 to 1.4) $\text{mol}\cdot\text{kg}^{-1}$, and temperature, (253.15 to 333.15) K, are presented in Table 1.

RESULTS AND DISCUSSION

Conductivity in the Region of Large Dilutions. The conductance data for Et_4NBF_4 solutions in PC over the concentration range from $(1.3\cdot10^{-3}$ to $40\cdot10^{-3})\ \text{mol}\cdot\text{kg}^{-1}$ were analyzed by means of the Lee–Wheaton conductance equation[20] in the Pethybridze–Taba modified form[21,22] (LWPT). This approach uses the set of equations:[23] the concentration dependence of conductivity (LWPT)

$$\Lambda_i = \alpha\left\{\Lambda^0[1 + C_1\beta k + C_2(\beta k)^2 + C_3(\beta k)^3] - \frac{\rho k}{1+t}\cdot\left[1 + C_4\beta k + C_5(\beta k)^2 + \frac{t}{12}\right]\right\} \qquad (1)$$

Table 2. Limiting Molar Conductivities, Λ^0, and Association Constants, K_A, for Et_4NBF_4 in Propylene Carbonate as a Function of Temperature, T

T	Λ^0	K_A	$\sigma(\Lambda)$[a]
K	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{dm}^3\cdot\text{mol}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
283.15	23.32 ± 0.05	1.76 ± 0.98	0.004
291.15	27.89 ± 0.18	4.0 ± 1.5	0.036
298.15	33.37 ± 0.17	13.6 ± 3.8	0.022
313.15	44.89 ± 0.62	14.4 ± 8.9	0.062

[a] Standard deviations for fitting.

the mass action law association

$$K_A = \frac{(1-\alpha)\gamma_A}{\alpha^2 c\gamma_\pm^2} \qquad (2)$$

and equation for the mean ionic activity coefficient

$$\gamma_\pm = \exp\left(-\frac{qk}{1+kR}\right) \qquad (3)$$

The terms in eq 1 are defined in ref 20. α is the dissociation degree, q is the Bjerrum parameter, γ is the activity coefficient, and R is the closest approach distance. The limiting molar conductivity, Λ^0, and association constant, K_A, were obtained by means of minimizing the function FX with using a nonlinear least-squares method:[7]

$$\text{FX} = \sum_{i=1}^{n}(\Lambda_i^{\text{calc}} - \Lambda_i^{\text{exp}})^2/(n-m) \qquad (4)$$

where Λ_i^{exp} and Λ_i^{calc} are the experimental and calculated values of conductivity, respectively. n is the number of experimental points, and m is the number of fitting parameters ($m = 2$). R has been used as a fixed parameter to be equal to Bjerrum distance $q = e^2/8\pi\varepsilon\varepsilon_0 kT$.[23] According to Fuoss,[24] the experimental data have been chosen to calculate the conductometric parameters (Λ^0, K_A) at such concentrations that did not exceed the quantity $C = 2\varepsilon^3\cdot10^{-7}\ \text{mol}\cdot\text{dm}^{-3}$ (where ε is the dielectric constant of the solvent). The obtained molar conductivities at infinite dilution, Λ^0, together with the corresponding association constants, K_A, are reported in Table 2 over the temperature range (283.15 to 313.15) K. The limiting molar conductance, Λ^0, of the tetraethylammonium tetrafluoroborate increases when temperature increases ($d\Lambda^0/dT > 0$). The association constants, K_A, indicate that the Et_4NBF_4 in PC is essentially unassociated. This is in agreement with earlier findings for large ions such as tetraalkylammonium in PC.[2] Using the $\Lambda^0(Et_4NBF_4)$ value obtained and the value of $\lambda^0(Et_4N^+)$ taken from refs 25 and 26, we estimated the value of limiting molar ionic conductivity for the anion, $\lambda^0(BF_4^-)$ (Table 3). The anion has a higher mobility than the cation indicating relatively poor solvation by PC molecules. The ionic Walden products, $\lambda^0\eta^0$ (where η^0 is the viscosity of the pure solvent), are also included in Table 3. It is usually employed to discuss the ion–solvent interactions. The Stokes law is the theoretical basis of Walden's rule,[27] that allows us to determine the radius of migrating particle. The Stokes radii, r_S, have been evaluated by means of eq 5:[26]

$$r_S = z_i^2F^2/f\pi N_A\lambda^0\eta^0 \qquad (5)$$

Table 3. Limiting Ionic Conductivity, λ^0, Ionic Walden Products, $\lambda^0\eta^0$, Ionic Stokes Radii, r_S, and Crystallographic Radii, r_c, for Et_4N^+ and BF_4^- in Propylene Carbonate at 298.15 K

	λ^0	$\lambda^0\eta^{0a}$	$r_S(f=6)$	$r_S(f=4)$	r_c
ion	$S\cdot cm^2\cdot mol^{-1}$	$S\cdot cm^2\cdot mol^{-1}\cdot P\cdot s$	nm	nm	nm
Et_4N^+	13.2[25] 13.18[26]	0.0334	0.248	0.368	0.337[26]
BF_4^-	20.2	0.0511 0.0486[2]	0.161 0.17[2]	0.240	0.232[25,28]

[a] $\eta^0 = 2.529$ mPa·s.[15]

Table 4. Casteel−Amis Parameters as a Function of Temperature for Concentrated Solutions of Et_4NBF_4 in Propylene Carbonate

T	$10^3\ \chi_{max}$	m_{max}			$10^3\ \sigma(\chi)^a$
K	$S\cdot cm^{-1}$	$mol\cdot kg^{-1}$	a	b	$S\cdot cm^{-1}$
253.15	3.73	0.980	0.796	−0.399	0.002
273.15	7.54	1.093	0.735	−0.412	0.001
293.15	12.50	1.117	0.776	−0.380	0.002
298.15	13.26	1.146	0.781	−0.350	0.002
313.15	17.80	1.166	0.789	−0.340	0.002
333.15	23.90	1.202	0.797	−0.320	0.001

[a] Standard deviations for fitting.

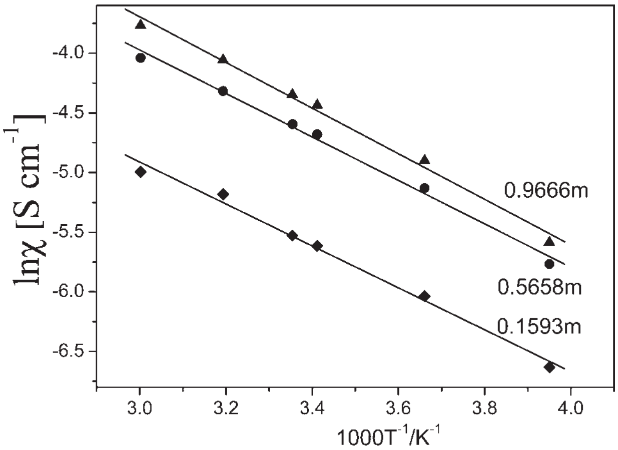

Figure 1. Plot of the temperature dependence of the logarithm of specific conductivity for Et_4NBF_4 in propylene carbonate at several concentrations (m/mol·kg^{-1}).

where F is the Faraday and N_A Avogadro's number and f is a friction factor equal to 4 in the slipping condition and to 6 in the sticking condition. For slipping conditions (f = 4), the radii obtained are greater than the crystallographic ones, r_c, for Et_4N^+ and BF_4^- ions.[25,26,28] On the other hand, for stick conditions (f = 6) the r_S values are less than r_c values. The differences between r_S (f = 4) and r_c are smaller than the differences for stick conditions (f = 6). The Stokes radii, r_S, of both ions are closer to crystallographic radii, r_c, at conditions of the slip. We obtained that the Et_4N^+ and BF_4^- ions are very weakly solvated in PC. These results are agreed to the fact that most anions and large cations (R_4N^+) are poorly solvated by aprotic solvents.[29] Thus, electrostatic interactions are weak in the Et_4NBF_4 − PC, since the large ions such as Et_4N^+ and BF_4^- have the negligible surface charge.

Conductivity in the Region of High Concentration. The isotherms of dependence $\chi = f(m)$ for the Et_4NBF_4 in PC have a traditional appearance. The conductivity rises at lower concentration, passes through a maximum, and decreases after. The specific conductivities of solutions investigated have enough high values due to insignificant solvation of BF_4^- anion and Et_4N^+ cation in propylene carbonate ($\varepsilon = 65.1^{17}$) in the concentrated region.[12] The variations of χ with m can be explained by the competition between the increase in the number of charge carriers and the increase in viscosity (η) leading to the appearance of a maximum on isotherms of χ when $d\eta/dm \gg d\chi/dm$.[27]

The concentration dependence of specific conductivity may be described by empirical relationship of Casteel and Amis:[30]

$$\chi/\chi_{max} = (m/m_{max})^a \exp[b(m - m_{max})^2 - a m_{max}^{-1}(m - m_{max})] \tag{6}$$

where a and b are some constants and m_{max} is a salt concentration corresponding to a maximum in specific conductivity, χ_{max}. The fitted parameters of eq 6 are presented in Table 4. Using eq 6, the optimum composition of electrolyte solutions can be determined at different temperatures. It is necessary to take into account that the maximum on isotherms of χ is displaced into a region of less concentrated salt solutions when temperature decreases.

The conductivity of solutions investigated increases with the rise temperature and depends on the ion mobility and quantity of charge carriers, according to equation:[31]

$$\chi = \sum n_i \cdot q_i \cdot \mu_i \tag{7}$$

where n_i is a number of charged particles, q_i is a charge of the particle, and μ_i is the mobility of the particle. In the temperature range studied the plot of $\ln \chi = f(1/T)$ at different concentrations in salt is linear (correlation coefficient r_{corr} = 0.997) (Figure 1). The variations of the specific conductivity of a liquid electrolyte on temperature are well-described by the Arrhenius-type expression 8:

$$\chi = A_\chi \exp(E^{\neq}/RT) \tag{8}$$

where $E^{\neq}$ is the activation energy for the conductivity and A_x is the pre-exponential term. It is important to note that the activation energy values for the conductivity $E^{\neq}$ vary from (14.3 to 17.6) kJ·mol^{-1} and the variations of the activation energy values for the viscosity $E^{\neq}{}_\eta$ are in the same range of magnitude[11] (14.4 to 16.6 kJ·mol^{-1}) in the Et_4NBF_4-PC system when the salt content increases from (0.15 to 1.42) mol·kg^{-1}.

The dependence of the activation energy for the conductivity on electrolyte concentration can be described by eq 9:[5]

$$E^{\neq} = E^{\neq 0} + x_i E^{\neq el} \tag{9}$$

where x_i is the molar fraction in salt; $E^{\neq 0}$ is the contribution of the pure solvent when Coulombic interaction vanished, and $E^{\neq el}$ is the contribution of the electrolyte to the activation energy for the conductivity. It was shown that the plot of $E^{\neq} = f(x_i)$ is linear in the considered range of temperature (r_{corr} = 0.989). Experimental slope, $E^{\neq el}$, and ordinate, $E^{\neq 0}$, values obtained are

Table 5. Activation Energies Parameters Calculated from eq 9 for 1:1 Electrolytes in Propylene Carbonate

	$E^{\neq 0}$	$E^{\neq \mathrm{el}}$	m	
salt	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{mol \cdot kg^{-1}}$	r_{corr}[a]
Et_4NBF_4	13.8 ± 0.4	28 ± 3	0.15 to 1.42	0.989
Et_4NPF_6[25]	15.2 ± 0.2	34 ± 2	0.26 to 1.20	0.996
$LiBF_4$[34]	15.1 ± 0.3	65 ± 3	0.28 to 2.35	0.996
$LiPF_6$[25]	15.8 ± 0.3	73 ± 4	0.11 to 0.89	0.996
$LiClO_4$[25]	14.6 ± 0.4	81 ± 5	0.27 to 1.26	0.990
$LiAsF_6$[15]	13.5 ± 0.6	87 ± 6	0.19 to 1.39	0.978

[a] Correlation coefficient of eq 9.

reported in Table 5. The contributions of the solvent (PC) and Et_4NBF_4 to the activation energy for the conductivity were found to be commensurate. In the work,[11] a linear relation between the activation energy for the viscous flow and the concentration of Et_4NBF_4 in PC was testified giving the activation energy for the viscosity of pure solvent ($E^{\neq 0}{}_{\eta}$ = 14.5 $\mathrm{kJ \cdot mol^{-1}}$) and the contribution of the salt to the activation energy for the viscous flow ($E^{\neq \mathrm{el}}{}_{\eta}$ = 26.1 $\mathrm{kJ \cdot mol^{-1}}$). It is observed that the energies of activation for the conductivity and the viscosity are comparable. This means that the two transport processes are closely related.

Thus, according to the transition state theory,[32] charge transport in electrolyte solutions and fluidity of the solutions of Et_4NBF_4 in PC is controlled by energy barriers which depend on the solvent and the salt properties. The activation energy of migration of ions is practically defined by the rate of jump of solvent molecule into the neighbor position of equilibrium.[32] The additional numbers of vacancies for jumps of the solvent molecules and the ions introduced are generated owing to destruction of solvent structure as a result of intensification of particles thermal motion with increasing temperature.[11] Propylene carbonate belongs to group of intermediate-structured solvents being placed in the so-called "gray zone" media (a Trouton constant is S_V = 11.63, a Kirkwood dipole orientation factor is g = 1.23[33]).

Table 5 also lists the parameters of conductivity activation energies for the other large size electrolytes in PC. All parameters were calculated by us using conductivity data from the literature[15,25,34] and eqs 8 and 9. It was shown that calculated $E^{\neq 0}$ values are close to the activation energy for the viscosity of pure PC (14.5 $\mathrm{kJ \cdot mol^{-1}}$). The $E^{\neq \mathrm{el}}$ values decrease in the order $LiAsF_6 > LiClO_4 > LiPF_6 > LiBF_4 > Et_4NPF_6 > Et_4NBF_4$ in this solvent medium within the concentration ranges studied. The nature of the cation and the anion has a strong influence on $E^{\neq \mathrm{el}}$. The value of $E^{\neq \mathrm{el}}$ tends to be small with decreasing effective sizes of anions in the order $AsF_6^- > ClO_4^- > PF_6^- > BF_4^-$. This is obviously caused by the variation in electrostatic interaction and the cavity formation effect. Thus, it appears that the Et_4NBF_4-PC system has a relatively low activation energy for the conductivity that may be interesting for its using in capacitors.

CONCLUSION

The mobility of charge particles increases when the fluidity of Et_4NBF_4 solutions in PC rises due to the destruction of solvent structure. The ion-migration mechanism of charge transfer is realized in the Et_4NBF_4 in propylene carbonate in the ranges of concentration and temperature studied. The large sizes of Et_4N^+ and BF_4^- ions, their low charge densities, and the high relative permittivity of PC render these ions to be unassociated and almost unsolvated in this medium. The electrical interionic forces responsible for the variations in conductivity are of the same nature than those acting in viscosity. This is, at least partially, confirmed by the fact that the activation energy values for the two processes remain in the same range of magnitude [(14.3 to 17.6) $\mathrm{kJ \cdot mol^{-1}}$] when the salt content varies from (0.15 to 1.42) $\mathrm{mol \cdot kg^{-1}}$. The Et_4NBF_4-PC system was found to have a relatively low activation energy for the conductivity in comparison with the solutions of other 1−1 electrolytes above-mentioned in propylene carbonate.

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