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CONDUCTIVITY AND INTERPARTICLE INTERACTIONS IN THE SOLUTIONS OF 1-1 ELECTROLYTES IN PROPYLENE CARBONATE IN THE WIDE RANGE OF TEMPERATURES

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Abstract. Results of conductometric investigations of solutions of several 1-1 electrolytes in propylene carbonate in the range of temperatures from 298 to 398 K are presented. Using the expanded Lee-Wheaton equation of electric conductivity, constants of ionic association are defined. It is determined that $LiClO_4$ in propylene carbonate is a non-associated electrolyte. In order to account on the dynamics of ionic solvation, separation into ionic components is made.

Keywords: propylene carbonate, conductivity, association, 1-1 electrolytes.

1. Introduction

Studies of the ion-molecular and ion-ionic interactions, as well as the dynamics of ions in non-aqueous solvents, are of particular interest, primarily for the development of chemical current sources (CCSs) [1, 2]. Propylene carbonate (PC) belongs to the class of ethers widely used as co-solvents for electrolytes in CCSs. This solvent is of particular interest because of its high dielectric permeability ($e^{298} = 64.92$) [3] and molecular dipole moment of the solvent ($m = 4.94$) [4], as well as the wide range of liquid state (from 224.35 to 515 K) [3] and high solubility of lithium salts in it.

In the literature there are quite many works primarily on the concentration-dependent investigations of salts solutions in PC at 298 K (Table 1), but only a few conductometric studies in diluted solutions [3, 5, 6] are known.

In almost all the works, association constants (K_A) of electrolytes in PC at 298.15 K are studied (Table 1), but little attention is given to the limiting molar ionic conductivity (λ_0^i), from which it is possible to obtain information on the dynamics of ionic solvation. Separation into ionic components in the works [3, 7] is made with an assumption that $\lambda_0((i\text{-Am})_4N^+) = \lambda_0((i\text{-Am})_4B^-) = \Lambda_0((i\text{-Am})_4N(i\text{-Am})_4B)/2$. In the works [8, 9, 10], when separating into ionic components, it was assumed that the temperature number of K^+ in $KClO_4$ solutions in PC was determined accurately by R. Zana *et al.* [24]. In the work [6] separation into ionic components is made taking into account the assumption made by B. Krumgalts [25] and discussed earlier, that $\lambda_0\eta_0(Bu_4N^+) = 0.2131$ $S\cdot cm^2\cdot P\cdot mol^{-1}$ remains constant in various organic solvents and at various temperatures.

Proceeding from it, the purpose of the present work was to investigate influence of the temperature, size and nature of the ion on the quantitative characteristics of interparticle interactions, electrical conductivity of ions and ionic association in solutions of 1-1 electrolytes in propylene carbonate in the range of temperatures from 298.15 K to 398.15 K.

2. Experimental

PC after dehydration over anhydrous CaO within several days was subjected to fractional vacuum distillation, collecting the middle fraction. Purity was controlled by specific electrical conductivity, $k_{298.15} = 3.2\cdot 10^{-8}$ $Sm\cdot cm^{-2}$, and moisture presence – by Fisher method of coulometric titration (water content did not exceed 0.003 %). Physical and chemical properties of the solvent at various temperatures were found from the following polynomials described in the work [26]:

$$1/d = 0.81527 + 0.7149 \cdot 10^{-3} \cdot t + 0.459 \cdot 10^{-6} \cdot t^2 \quad (1)$$

$$h = \exp\left(5.3665 - 4.344 \cdot 10^{3} \cdot T^{-1} + 0.87 \cdot 10^{6} \cdot T^{-2}\right) \quad (2)$$

$$e = -33.09 + 36.65 \cdot 10^{3} \cdot T^{-1} - 2.21 \cdot 10^{6} \cdot T^{-2} \quad (3)$$

where d (g·cm^{-3}), h (mPa·s), t (°C), T (K).

Physical and chemical properties of pure propylene carbonate at temperatures from 278.15 to 398.15 K are given in Table 2.

For the measurement of electrical conductivity of solutions, conductometric cells (5 pieces) from molybdenic glass with platinized platinum electrodes were used. The cells were calibrated in the aqueous solutions of potassium chloride [27] and their constants vary from 0.1 to 0.25 cm^{-1}.

Resistance of the solutions was measured with the bridge of alternating current P-5083 and conductometer LCR-821 at the frequency of 1 kHz.

Table 1

Data on the diluted solutions (1·10^{-4}-1·10^{-2} mol/dm^3) of 1-1 electrolytes in propylene carbonate and its mixtures that have been reported in the literature

Solvents	Electrolytes	T, K	Concentration range	Defined parameters	[Ref.]
PC	(Li, Na, K, Rb, Cs, Me_4N, Et_4N, Pr_4N, Bu_4N)ClO_4, NaI, KI, KSCN, Bu_4NI, Bu_4NBr	298		Λ_0, K_A, Λ_0^{ion}	[3]
PC	(Me_4N, Et_4N)PF_6, Me_4NBF_4, $(C_7H_{15})_4NPic$, PyrPic, KPF_6	298	(4–16)·10^{-4} mol/dm^3	λ_0^i, $\lambda_0\eta_0$	[4]
PC	CF_3COOLi, CHF_2COOLi	238–308	(7.3–48)·10^{-4} mol/dm^3	Λ, K_A	[5]
PC	(Na, K, Rb, Cs, Me_4N, Et_4N, Pr_4N, Bu_4N)I, (Et_4N, Ph_4P)Br, Ph_4PCl, $NaBPh_4$, Bu_4NBPh_4	233–318		Λ_0, K_A, Λ_0^{ion}	[6]
PC	LiCl, $LiClO_4$	298	1·10^{-4}–1·10^{-2} mol/dm^3	Λ, Λ_0, λ_0^+, λ_0^-	[7]
PC	$LiClO_4$	298	9.5·10^{-4}–0.4 M	Λ, t^+(Li)	[8]
PC, AN, γ-BL	$LiClO_4$, $LiAsF_6$	298	0.001–0.01 mol/dm^3	Λ, K_A	[9]
PC	(Me_4N, Et_4N, Pr_4N, Bu_4N, Am_4N, K)Pic	298	(12.5–6)·10^{-4} mol/dm^3	Λ_0, K_A, λ_0^i, $\lambda_0\eta$	[10]
PC+1,2-DMM	$LiClO_4$, $LiAsF_6$, *n*-Bu_4NClO_4, n-Bu_4NBPh_4	298	1·10^{-2}–1·10^{-4} mol/dm^3	Λ, λ_0^+, λ_0^-, Λ_0, K_A, K_A^{Bjerum}	[11]
PC, γ-BL, PC+1,2-DME, γ-BL+1,2-DME	$LiAsF_6$, $LiClO_4$, Bu_4NClO_4, Bu_4NCl, Bu_4NBPh_4	298	1·10^{-3}–2·10^{-2} mol/dm^3	Λ, λ_0^{+mix}, λ_0^{-mix}, Λ_0^{mix}, $\lambda_0\eta^{mix}$, K_A	[12]
PC, γ-BL, 1,2-DME, *etc.*	LiX (X=ClO_4, AsF_6, BF_4, Cl, Br, I, NO_3, Pic, BPh_4, SCN)	298		K_A	[13]
PC+ 1,2-DME (1:1)	LiX (X=BF_4, CF_3SO_3, ClO_4, $(CF_3SO_3)_2N$, AsF_6, PF_6, $SO_2(CF_2)_4SO_2N$)	298 248–548		Λ_0, $\Lambda_0\eta$, η κ	[14]
PC	$LiPF_6$, $LiBF_4$, $LiPF_6$·2DG, $LiPF_6$·PMDETA	298	1·10^{-3}–1 M	κ, Λ, Λ_0, $\Lambda_0\eta$, λ_0^+, K_A	[15]
PC	(Li, Na, K, Rb, Cs) ClO_4	298	1·10^{-3}–2·10^{-2} mol/dm^3	Λ_0, K_A, R	[16]
PC	$LiClO_4$, *etc.*	228–298	1 M	Λ	[17]
PC, *etc.*	$LiClO_4$, LiSCN, Bu_4NSCN, Bu_3NHSCN	298	(1.4–19)·10^{-3} mol/dm^3	Λ_0, K_A, $\Lambda_{0(calc)}$	[18]
PC, *etc.*	$LiC_2F_5CO_2$, $LiCF_3CO_2$	298	(0.4–4)·10^{-3} mol/dm^3	Λ_0, K_A, Λ_0^{ion}	[19]
PC	Pr_4NBr, Bu_4NBr, Bu_4NI	223–398		Λ, η	[20]
PC *etc.*	Li(PF_6, BF_4, CF_3SO_3, $(CF_3SO_3)_2N$, $C_4F_9SO_3$)	298		λ_0^i	[21]
PC		298		Λ_0, K_A	[22]
PC, *etc.*	(Li, Na, K, Me_4N, Et_4N, Pr_4N, Bu_4N) ClO_4; Bu_4N (Cl, Br, I); Li (Cl, Br, I)	298		Λ_0, K_A	[23]

Table 2

Physical properties of the pure PC at temperatures from 278 to 398 K (calculated from Eqs. 1-3, 20)

T, K	d, g·cm^{-3}	η, mPa·s	ε	$\tau_D \cdot 10^{11}$, s
278.15	1.2212	4.013	70.11	5.0386
298.15	1.1999	2.592	64.97	4.1526
308.15	1.1893	2.200	62.57	3.6816
318.15	1.1787	1.922	64.97	3.2888
328.15	1.1683	1.722	58.07	2.9906
338.15	1.1578	1.575	55.97	2.6774
358.15	1.1372	1.387	52.01	2.2303
378.15	1.1168	1.289	48.37	1.8941
398.15	1.0967	1.247	45.02	1.6353

For the measurement of resistance of the solutions at the temperatures from 278.15 to 328.15 K, water thermostats were used, and for temperatures from 338.15 to 398.15 K – the oil ones. Accuracy of thermostabilization was 0.02 %.

Solutions of the electrolytes were prepared using the gravimetric method. Salts samples were weighted on the microanalytical scales GR-202 with the accuracy of $2 \cdot 10^{-5}$ g (the mass of the samples ranged within $0.2 \le m_c \le 1.0$ g).

Masses of the solutions were defined (according to the preliminary approximate calculation) by weighing on the scales VLA-200 or analytical scales GR-202 with the accuracy of $2 \cdot 10^{-4}$ g.

Concentration of the initial solutions expressed in moles of dissolved substance per 1 kg of solution ($\tilde{m}$) was defined by Eq. (4):

$$\tilde{m}_i = \frac{m_c \cdot 1000}{M_c \cdot m_p} \tag{4}$$

where m_c (g) and M_c (g/mol) – mass and molar mass of the salt, m_p (g) – mass of initial solution.

Concentrations of the solutions in the series were defined by the ratio:

$$\tilde{m}_i = \frac{\tilde{m}_1 \cdot m_1}{m_i} \tag{5}$$

where $\tilde{m}_i$ and m_i – concentration and mass of the prepared solution; m_1 – sample of the initial solution.

Molar concentration of electrolytes in the solution (c) was defined as:

$$c_i(t) = \tilde{m}_i \cdot d_i(t) \tag{6}$$

where d_i (t) – density of i solution at a particular temperature.

To prevent moisture ingress, solutions were stored in the flasks with double covers with additional sealing with the *Parafilm "M"* tape at the joints of the internal section.

Experimental values of the molar electric conductivity of 1-1 electrolytes in PC in a wide range of temperatures are given in Tables 3–5.

Table 3

Molar conductivities Λ/ S·cm^2·mol^{-1} of 1-1 electrolytes in PC at temperatures 298.15–398.15 K

$\tilde{m} \cdot 10^4$, mol·kg^{-1}	298.15 K	308.15 K	318.15 K	338.15 K	358.15 K	378.15 K	398.15 K
1	2	3	4	5	6	7	8
$LiClO_4$							
3.373	26.18_7	29.55_3	33.03_3	40.34_4	48.92_7	57.63_6	67.04_8
4.912	26.10_7	29.53_4	32.98_3	40.29_4	48.70_5	57.54_9	66.90_5
6.426	26.091	29.465	32.883	40.263	48.692	57.407	66.886
8.281	26.023	29.402	32.787	40.214	48.578	57.296	66.789
10.712	–	29.292	–	40.048	–	–	66.733
13.166	25.976	29.245	32.653	39.990	48.333	56.993	66.496
15.913	25.929	29.181	32.505	39.890	48.277	56.828	66.177
18.865	25.825	29.077	32.460	39.833	48.052	56.592	65.731
22.343	25.788	28.842	32.396	39.770	47.985	56.411	65.667
25.603	25.755	28.970	32.344	39.675	47.847	56.298	65.567
29.444	25.714	28.939	32.302	39.587	47.703	56.144	65.268
31.209	25.755	28.902	32.260	39.572	47.672	56.127	65.266

Table 3 (Continued)

1	2	3	4	5	6	7	8
34.644	25.649	28.824	32.190	39.472	47.543	55.977	65.060
49.831	25.448	28.552	31.908	39.090	47.111	55.444	64.373
69.942	25.250	28.348	31.617	38.612	46.522	54.650	63.429
95.029	25.096	28.141	31.392	38.373	46.116	54.152	62.770
$NaClO_4$							
7.038	27.88_5	–	–	51.59_9	65.17_8	–	95.04_7
10.026	27.72_2	33.40_3	38.87_5	51.33_2	64.92_6	79.58_6	94.95_8
13.164	27.66_4	33.00_3	38.65_7	51.05_5	64.68_1	78.93_9	94.65_4
16.200	27.60_2	32.90_5	38.55_1	50.89_7	64.46_4	78.71_3	94.07_6
20.689	27.53_2	32.85_4	38.49_7	50.82_1	64.38_7	78.67_5	93.83_6
25.431	27.51_0	32.81_2	38.46_2	50.81_1	64.30_6	78.46_8	93.77_9
30.405	27.49_1	32.79_2	38.42_3	50.71_2	64.27_5	78.32_9	93.62_5
36.619	27.39_5	32.65_1	38.27_2	50.66_7	64.11_9	78.15_4	93.34_8
42.286	27.35_1	32.58_7	38.18_8	50.55_2	63.99_3	78.15_5	93.22_6
48.141	27.28_9	32.53_5	38.13_2	50.50_1	63.84_5	78.16_9	93.01_2
55.744	27.24_9	32.50_7	38.09_1	50.36_6	63.65_1	77.78_3	92.96_9
61.212	27.22_2	32.46_1	38.04_4	50.55_1	63.68_6	77.64_0	92.00_2
72.295	27.18_1	32.19_5	37.88_2	50.38_5	62.94_0	77.44_9	91.80_5
Bu_4NClO_4							
2.568	26.93_3	31.98_0	37.34_9	48.73_4	61.57_8	74.96_5	89.12_7
2.953	26.83_5	31.86_1	37.23_2	48.66_8	61.49_8	74.87_8	89.06_0
3.481	26.75_2	31.79_5	37.15_1	48.62_7	61.33_1	74.54_2	88.87_0
4.096	26.74_2	31.75_4	37.10_4	48.52_6	61.17_9	74.44_0	88.72_9
4.640	26.71_6	31.67_3	37.07_8	48.47_5	61.16_3	74.38_8	88.62_6
5.260	26.62_8	31.63_7	36.99_5	48.38_4	60.95_0	74.24_9	88.50_4
5.932	26.58_1	31.58_8	36.91_4	48.32_0	60.87_1	74.17_9	88.40_1
6.669	26.54_0	31.51_6	36.80_0	48.29_7	60.73_9	74.06_9	88.33_3
7.305	26.50_5	31.45_7	36.75_6	48.20_7	60.66_9	73.90_6	88.28_6
7.478	26.49_1	31.41_6	36.73_7	48.15_6	60.62_3	73.82_5	88.12_5
8.369	26.46_8	31.35_1	36.68_4	48.03_9	60.54_4	73.77_9	87.71_6
11.375	26.33_2	31.30_7	36.58_6	47.89_6	60.46_7	73.72_0	87.50_1
15.314	26.20_1	31.14_6	36.38_4	47.60_8	60.23_6	73.23_9	87.14_1
19.310	26.02_1	30.95_4	36.16_7	47.30_3	59.73_6	72.79_9	86.62_8
23.862	25.89_1	30.67_4	35.97_4	47.06_9	59.42_1	72.35_3	85.94_9
29.073	25.72_8	30.56_1	35.72_6	46.70_7	58.97_4	71.75_2	85.29_3
34.983	25.64_9	30.51_5	35.63_9	46.52_8	58.67_2	71.27_2	84.76_5
41.342	25.41_9	30.24_8	35.31_7	46.00_9	58.21_0	70.80_9	84.14_7
47.509	25.34_8	30.16_8	35.21_1	46.97_2	57.99_4	70.66_2	83.88_8
55.495	25.28_2	30.08_6	35.06_6	46.72_8	57.71_3	69.84_8	83.00_7
63.049	25.07_2	29.86_9	34.79_2	45.43_7	57.31_7	69.65_7	82.73_7
70.634	24.89_4	29.63_9	34.56_2	*44.54_7	56.90_9	69.11_9	82.40_1
79.710	24.79_2	29.43_9	34.42_4	44.48_2	56.65_0	68.91_8	81.79_8
Bu_4NBPh_4							
1.250	15.78_5	19.24_6	22.87_6	30.91_0	39.66_4	49.01_8	59.18_9
1.939	15.71_5	19.14_4	22.79_0	30.88_0	39.51_7	49.01_2	59.10_3
2.178	15.64_1	19.07_6	22.71_1	30.81_9	39.50_1	48.77_8	59.00_5
4.228	15.50_3	18.84_3	22.47_9	30.42_0	39.34_8	48.52_8	58.64_6
4.422	15.44_5	18.85_1	22.39_9	30.36_2	39.13_9	48.29_3	58.62_2
4.781	15.35_6	18.69_9	22.26_8	30.17_1	39.06_7	48.10_8	58.40_0
5.592	15.35_3	18.66_1	22.25_8	30.11_7	38.88_6	47.99_7	58.35_8
6.475	15.26_4	18.60_8	22.14_9	29.99_3	38.85_3	47.98_5	57.83_3
13.539	14.96_7	18.14_7	21.55_9	29.26_7	38.65_8	46.73_2	56.61_4
22.025	14.62_8	17.73_2	21.07_8	28.64_4	36.82_0	45.85_5	55.37_7
27.884	14.51_2	17.58_8	20.90_3	28.43_4	36.55_8	45.36_8	54.79_2

Table 3 (Continued)

1	2	3	4	5	6	7	8
33.111	14.39_4	17.34_8	20.74_3	28.18_1	36.29_2	45.13_4	54.63_8
41.552	14.23_6	17.14_7	20.50_8	27.77_2	35.92_8	44.75_1	54.26_4
50.245	14.16_1	16.88_1	20.29_0	27.52_2	35.56_7	44.11_1	53.46_2
61.204	13.92_0	16.68_2	20.06_4	27.22_1	35.18_8	43.63_2	52.94_7
72.036	13.75_1	16.51_0	19.85_5	26.96_4	34.88_5	43.18_7	52.36_3
83.503	13.56_2	16.28_4	19.59_7	26.61_6	34.47_4	42.85_5	52.01_2

Table 4

Molar conductivities L/ S·cm^2·mol^{-1} LiBF$_4$ in propylene carbonate at temperatures 298.15–398.15 K

$m \cdot 10^4$, mol·kg^{-1}	298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	358.15 K	378.15 K	398.15 K
2.850	–	33.02_5	38.87_5	45.20_1	51.70_6	65.33_5	79.02_7	91.76_4
4.332	27.25_9	32.85_4	38.76_8	45.06_8	51.41_8	65.03_3	79.24_5	91.48_6
6.130	27.40_3	32.69_2	38.62_9	44.85_9	51.38_3	64.67_9	–	90.67_9
8.251	27.20_2	32.52_5	38.43_0	44.61_5	50.98_6	64.25_2	77.88_8	89.82_4
10.189	27.19_1	32.42_5	38.41_0	44.54_2	50.95_5	64.23_3	77.20_6	89.28_5
13.295	27.03_7	32.31_6	38.24_6	44.28_6	50.70_9	63.01_8	77.21_0	89.84_7
16.349	26.86_9	32.17_1	37.99_6	44.06_3	50.41_3	62.69_5	76.53_6	89.52_7
23.808	–	31.63_3	37.58_0	43.41_5	48.91_0	61.63_2	75.23_8	88.49_0
28.275	26.22_6	31.44_6	37.01_3	42.95_0	48.54_4	61.10_9	74.36_5	87.60_2
33.215	26.06_9	31.23_3	36.77_9	42.66_2	48.01_6	60.75_9	–	86.93_0
37.850	26.10_1	31.10_3	36.53_6	42.41_8	48.45_9	60.41_9	73.10_9	–
43.455	25.57_8	30.67_1	–	41.81_2	47.37_3	60.04_5	72.43_5	85.64_7
48.826	25.58_7	30.66_6	36.10_1	41.84_3	47.35_0	59.71_2	72.43_1	–
55.023	25.43_4	30.50_9	36.00_4	41.58_6	47.31_1	59.64_2	72.14_0	85.12_9

Table 5

Molar conductivities L/ S·cm^2·mol^{-1} Et$_4$NBF$_4$ in propylene carbonate at temperatures 278.15–398.15 K

$m \cdot 10^4$, mol·kg^{-1}	278.15 K	298.15 K	318.15 K	338.15 K	358.15 K	378.15 K	398.15 K
1.571	19.89_0	30.83_9	43.48_6	57.52_1	72.49_6	88.25_9	104.3_1
2.550	19.87_6	30.76_5	43.43_1	57.32_2	72.35_4	88.51_7	104.3_0
3.608	19.88_1	30.81_6	43.46_9	57.34_5	72.63_1	88.45_0	104.5_2
5.379	19.65_2	30.49_3	43.05_7	56.94_0	71.86_8	87.69_1	103.6_1
6.229	19.59_3	30.41_7	42.95_1	56.68_0	71.72_4	87.00_6	103.4_1
7.889	19.54_1	30.34_0	42.79_4	56.409	71.47_8	86.76_7	103.0_4
9.982	19.44_3	30.21_8	42.59_7	56.25_6	71.17_3	86.45_7	102.8_4
11.708	19.39_7	30.13_2	42.51_4	56.17_9	71.03_7	86.35_2	102.7_0
13.841	19.33_2	30.06_3	42.38_2	55.87_9	70.73_4	85.93_9	102.2_4
16.361	19.27_6	29.93_4	42.23_1	55.77_6	70.48_7	85.62_4	101.6_3
20.769	19.21_1	29.83_9	42.07_0	55.60_4	70.84_2	85.35_2	101.4_4
25.930	19.04_2	29.55_9	41.67_8	55.48_0	69.63_3	84.28_8	100.5_1
32.681	18.89_2	29.38_5	41.38_4	55.41_4	69.96_6	83.81_0	99.97_8
41.371	18.75_4	29.13_4	41.06_4	55.11_2	69.95_4	83.24_5	99.24_3
59.721	18.41_8	28.64_3	40.37_0	53.25_0	67.41_5	81.99_3	97.71_7

3.1. Processing of Experimental Results

To define constant of ionic association (K_A), limiting molar electrical conductivity (Λ_0) and parameter of the closest approach of ions (R) according to the experimental conductometric data (Tables 3-5), the method of processing of experimental data [28] was used. It consists in minimization of the function:

$$Q=\sum_{j=1}^{k}\left[\Lambda_j^{\exp}-\Lambda_j^{th}\left(c_j^{st};X\right)\right]^2\Rightarrow \min . \qquad (7)$$

with a vector of unknown parameters:

$$C = C\,(\Lambda_0, K_A, R) \qquad (8)$$

From the mathematical point of view, the problem of finding of a vector with unknown parameters (8) for a case of symmetric electrolytes with unequal 1st degree of dissociation consists in solving the overflowed system of nonlinear equations: concentration dependence of molar electrical conductivity for a set of k concentrations (9), the law of mass action (10), material balance (11) and expressions for mean ionic coefficients of activity (12):

$$\Lambda_j=c_j\,f(c_j,\Lambda_0,R)/c_j^{st},\ j=\overline{1},\overline{k} \qquad (9)$$

$$K_a=c_j^0/c_j^2y_{+-,j}^2 \qquad (10)$$

$$c_j^0+c_j=c_j^{st} \qquad (11)$$

$$y_{+-,j}=j\,(c_j,R) \qquad (12)$$

where c_j, c_j^0, c_j^{st} – concentration of ions, ionic pairs and stoichiometric concentration of electrolytes, respectively, and for non-associated electrolytes – $c_j^{st}\equiv c_j^i$.

For calculations of electric conductivity we chose the following combination of equations: the second approach of the Debye-Hückel theory (DH2) for coefficients of activity and the Lee-Wheaton equation [29] in the modification of Pethybridge [30] (LWP) for electrical conductivity (Eqs. (13) and (14), respectively) were used.

$$\ln y_\pm=-\frac{1}{2}lk/\left(1+kR\right) \qquad (13)$$

$$\Lambda=\Lambda_0\left[1+C_1(x)\cdot(lk)+C_2(x)\cdot(lk)^2+C_3(x)\cdot(lk)^3\right]- -\frac{rk}{1+x}\left[1+C_4(x)\cdot(lk)+C_5(x)\cdot(lk)^2+x/12\right] \qquad (14)$$

where r = $1.640214\cdot10^{-8}/h_0$, and C_1–C_5 – complex functions of x.

Taking into account that $LiClO_4$ is a non-associated electrolyte, the data on these solutions were processed without considering the ionic association by the method of optimization of parameters $\{\Lambda_0, R\}$, where R – parameter of the closest approach of ions. For all other electrolytes, optimization by two parameters $\{\Lambda_0, K_A\}$ was used, parameter R was fixed as a constant value:

$$R=r^++r^-+nd_s \qquad (15)$$

where r^+ , r^- – radii of cation and anion, respectively, d_s – diameter of a molecule of the solvent; for alkali salts $n = 1$, for tetraalkylammonium salts $n = 0$.

Results of optimisation of 1-1 electrolytes in PC are given in Table 6 (at 298.15 K the literature data for Λ_0 and K_A are cited).

3.2. Discussion

For separation of Λ_0 into ionic components it was suggested that the ratio $l^i_0(Bu_4N^+)/l^i_0(BPh_4^-)$ was constant at all temperatures. It should be noted that this suggestion does not require to assume that $l^i_0h = const$, where h is the solvent density. Thus, Λ_0 values of the studied salts were separated into ionic components in accordance with the following scheme:

$$\begin{tikzcd}
Bu_4NBPh_4 \arrow[r] \arrow[d] & Bu_4N^+ \arrow[r, "Bu_4NClO_4"] & ClO_4^- \arrow[r, "LiClO_4"] \arrow[d, "NaClO_4"] & Li^+ \arrow[r, "LiBF_4"] & BF_4^- \arrow[r, "Et_4NBF_4"] & Et_4N^+ \\
BPh_4^- & & Na^+ & & &
\end{tikzcd}$$

Results are given in Table 7 (for the ions at 298.15 K, the literature values are cited). As the Table shows, limiting molar ionic conductivities obtained indirectly from our data are well agreed with the literature data at 298.15 K.

Recently O. Kalugin *et al.* [31, 32] suggested to use the experimental ionic friction coefficients, $z=|z|eF/l^i_0$, to calculate a new quantitative description of ion-molecular interaction, the product $(g_K{\cdot}g_D)_{ef}$, where g_K and g_D are the modified Kirkwood factor [33] and Debye parameter [34]. According to [33, 34], the effective radius of Hubbard-Onsager dielectric friction theory [35, 36], R_{HO}^{ef} , is related to the experimental friction coefficient $z = = f(r_i/R_{HO}^{ef})$, where r_i is own ionic radius. On the other hand, R_{HO}^{ef} may be expressed as a function of $(g_K{\cdot}g_D)_{ef}$ as [37]:

$$R_{HO}^{ef}=\left\{\frac{\left(zem_V\right)^2}{12\left(4pe_0k_BT\right)^2}\cdot\frac{\left(e_\infty+2\right)^2}{e\left(2e+e_\infty\right)}\cdot\left(g_Kg_D\right)_{ef}\right\}^{1/4} \qquad (16)$$

where m_V, e and $e_¥$ are the molecular dipole moment, dielectric constant of a solvent and dielectric constant at the infinite frequency, respectively.

Eq. (16) allows to obtain the product of two structure-sensitive quantities, g_K and g_D, from the experimental data for the ionic friction coefficient. For a pure solvent, these parameters are given by the well-known formulas [33, 34]:

$$\left(e-e_\infty\right)=\frac{m_V^2g_K}{\left(4pe_0\right)3k_BTa^3}\cdot\frac{e\left(e_\infty+2\right)^2}{2e+e_\infty} \qquad (17)$$

$$t_D=g_D\frac{4pa^3h}{k_BT} \qquad (18)$$

where t_D is the dielectric relaxation time and a is the molecular radius calculated from the molecular volume.

Table 6

Results of conductivity measurements for 1-1 electrolytes in propylene carbonate (Λ_0/ S·cm^{2}mol^{-1}, K_A/dm^{3}mol^{-1}, *R*/nm, s_L/S·cm^2 mol^{-1})

T, K	Λ_0	K_A	*R*	s_L
$LiClO_4$				
298.15	26.87 ± 0.02 26.08(min) [3] – 28.0(max) [18]	0.47(min)[18]– 1.5(max)[13]	2.39 ± 0.04 2.80 ± 0.82 [23]	0.08
308.15	32.26 ± 0.02		2.38 ± 0.04	0.09
318.15	37.80 ± 0.03		2.40 ± 0.04	0.1
338.15	49.65 ± 0.07		1.56 ± 0.11	0.2
358.15	62.08 ± 0.07		1.04 ± 0.07	0.2
378.15	76.35 ± 0.08		0.65 ± 0.06	0.2
398.15	93.01 ± 0.10		0.33 ± 0.07	0.3
$NaClO_4$				
298.15	28.08 ± 0.02 27.29 [23] – 28.30 [31]	4.3 ± 1.8 0 [23] – 1.0 [32]	0.964 1.41 [23]	0.03
308.15	33.60 ± 0.07	6.9 ± 4.6	0.964	0.1
318.15	39.24 ± 0.03	6.9 ± 1.9	0.964	0.1
338.15	51.78 ± 0.08	9.5 ± 3.7	0.964	0.1
358.15	65.68 ± 0.08	15.6 ± 3.2	0.964	0.2
378.15	80.17 ± 0.13	15.6 ± 4.1	0.964	0.2
398.15	96.16 ± 0.27	16.5 ± 7.7	0.964	0.5
Bu_4NClO_4				
298.15	27.40 ± 0.01 27.42 [3] – 28.20 [23]	1.3 ± 0.1 0.2 [12] – 2.2 [3]	0.734 2.54 [23]	0.04
308.15	32.52 ± 0.02	0.9 ± 0.2	0.734	0.06
318.15	38.01 ± 0.02	1.4 ± 0.2	0.734	0.05
338.15	49.70 ± 0.11	1.6 ± 0.8	0.734	0.3
358.15	62.62 ± 0.03	3.2 ± 0.2	0.734	0.1
378.15	76.17 ± 0.04	4.5 ± 0.2	0.734	0.1
398.15	90.62 ± 0.04	5.9 ± 0.2	0.734	0.1
Bu_4NBPh_4				
298.15	17.57 ± 0.02 17.14 [23], 17.15[11], 17.31[12]	4.2 ± 0.4 0.93 [23] –10.2 [12]	0.947 3.98 [23]	0.05
308.15	21.08 ± 0.05	8.5 ± 0.9	0.947	0.1
318.15	24.75 ± 0.04	6.8 ± 0.6	0.947	0.1
338.15	32.92 ± 0.05	7.2 ± 0.5	0.947	0.1
358.15	41.83 ± 0.06	8.1 ± 0.6	0.947	0.2
378.15	51.33 ± 0.09	9.4 ± 0.7	0.947	0.2
398.15	61.60 ± 0.11	10.2 ± 0.7	0.947	0.3
$LiBF_4$				
298.15	28.21 ± 0.07 28.48[15] – 28.83 [22]	8.37 ± 1.25 1.3 [22] –10.1 [15]	0.941	0.2
308.15	33.74 ± 0.04	8.35 ± 0.55	0.941	0.08
318.15	39.85 ± 0.07	9.09± 0.91	0.941	0.1
328.15	46.29 ± 0.07	11.1 ± 0.7	0.941	0.1
338.15	52.95 ± 0.16	14.9 ± 1.6	0.941	0.3
358.15	66.51 ± 0.16	15.7 ± 1.2	0.941	0.3
378.15	80.60 ± 0.17	16.7 ± 1.2	0.941	0.4
398.15	92.96 ± 0.19	19.7 ± 1.24	0.941	0.4
Et_4NBF_4				
278.15	22.18 ± 0.01	2.1 ± 0.2	0.632	0.01
298.15	33.33 ± 0.01 33.96 [22]	1.9 ± 0.2 0 – 3.0 [22]	0.632	0.02
318.15	46.21 ± 0.01	3.1 ± 0.2	0.632	0.03
358.15	75.64 ± 0.03	4.1 ± 0.4	0.632	0.03
378.15	91.32 ± 0.05	5.0± 0.3	0.632	0.09
398.15	107.95 ± 0.07	4.7 ± 0.3	0.632	0.1

Table 7

Values of limiting molar conductivities of ions (λ_0^i) in PC in a wide range of temperatures

T, K	Li^+	Na^+	Et_4N^+	Bu_4N^+	BF_4^-	ClO_4^-	BPh_4^-
298.15	8.512 (7.30 [3]– 8.89 [3,15])	9.722 (9.04–10.71 [12])	13.59 (11.53–13.58 [12])	9.042 (8.48 [12]– 9.39[3])	19.74	18.36 (18.43 [32]– 18.89 [31])	8.528 (8.10 [9])
308.15	10.47	11.82	14.08	10.73	25.03	21.79	10.34
318.15	12.33	13.77	15.15	12.54	31.06	25.47	12.21
338.15	16.35	18.48	17.89	16.40	43.41	33.30	16.53
358.15	21.13	23.73	19.48	20.66	56.16	41.96	21.17
378.15	25.32	29.14	21.78	25.14	69.54	51.03	26.19
398.15	32.30	35.44	27.04	29.90	80.91	60.72	31.70

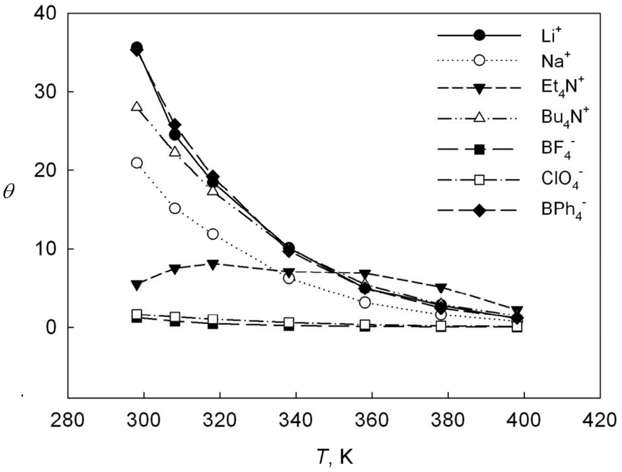

Fig. 1. Dependence of the values q of several ions with the same charge in PC on temperature

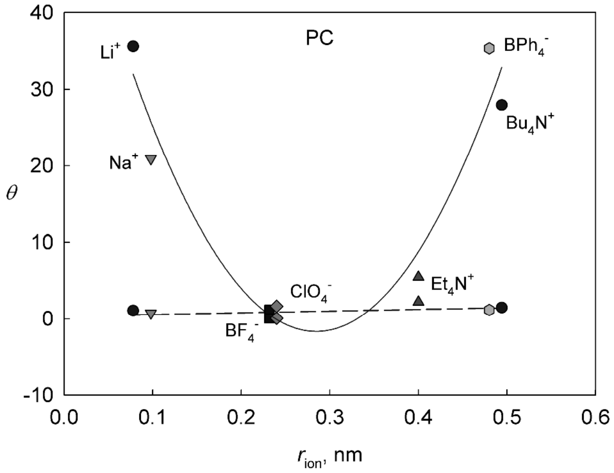

Fig. 2. Dependence of values q of several ions with the same charge in PC on radii of ions at 298 and 398 K

Then, in accordance with Samoilov's approach, the ratio

$$q = \left(g_k g_D\right)^{ef} / \left(g_k g_D\right) \tag{19}$$

was suggested as a measure of ion's influence on the structure and molecular dynamics of a solvent, as the parameter of solvation microdynamics. The value $(g_K g_D)_0$ corresponds to the pure solvent and can be calculated using Eqs. (19, 20) from the physical properties of a solvent. Values $Q > 1$ correspond to structure-making effect of an ion and decrease of molecules activity in its vicinity, and vice versa for $Q < 1$.

The data on the dielectric relaxation time, t_D, taken from [38], is described by:

$$t_D = 5.294 - 0.052 \cdot t + 1.83 \cdot 10^{-4} \cdot t^2. \tag{20}$$

and $e_{¥}$ was calculated from the Clausius-Mosotti equation [39]

$$P = \frac{e_\infty - 1}{e_\infty + 2} \cdot \frac{M}{d} \tag{21}$$

assuming that the deformational polarization P is independent from temperature.

Fig. 1 shows the temperature dependence of q, and Fig. 2 shows the dependence of q for single-charged ions in PC on the ionic radius. The Li^+ ion has rather high values of q, this ion sufficiently slows down the motion of the nearest solvent molecules. As Fig. 1 shows, the values of the parameter q for the lithium ion in PC practically coincide with the values of the parameter q of the BPh_4^- and Bu_4N^+ ions and decrease considerably with the increase of the temperature. It can be connected with the fact that the size of the lithium ion in a solvation shell practically does not differ from the size of ions BPh_4^- and Bu_4N^+. It points to a large positive solvophobic ability of BPh_4^- and Bu_4N^+ in PC, while the values of the parameter q practically do not change with the increase of the temperature for BF_4^-, ClO_4^- and Et_4N^+.

Fig. 2 shows the dependence of the parameter q on the size of the ion at 298.15 and 398.15 K. As Fig. 2 shows, the values of q for Li^+ and Na^+ (at 298.15 K) are much higher than 1, which points to solvophilic solvation of these ions in PC, whereas the values of q for the anions BF_4^-, ClO_4^- and Et_4N^+ are almost equal to 1, which points to the poor solvation of these ions in PC. Meanwhile, the parameters *q* for all ions at 398.15 K are almost equal to 1.

These results can be interpreted as follows. In general, influence of the ions on the nearest solvation dynamics may be represented by two components: solvophilic and solvophobic [40]. The first one is related to the ion's action on the solvent by the electrical field of the ion. Solvophilic solvation, depending on the ionic radius and the solvent structure features (presence of cavities, nature of intermolecular interaction and molecular motion, *etc*.), can be either positive or negative. Solvophobic solvation is observed for the ions of large radii only as an obstacle effect: motion of the solvent molecules becomes slower, because part of the solution space is occupied by the ion itself and is inaccessible for the solvent molecules. Solvophobic solvation increases with the increasing ionic radius and decreases with the increase of the temperature.

The obtained values and dependences of *q* on temperature and radii of ions are confirmed by the data obtained from the spectral characteristics.

Association of the molecules has considerable impact on the properties of liquids and solutions and the kinetics of the processes occurring in them. In the work [41] investigations of the nature of self-association of molecules of liquid propylene carbonate using the method of spectral combinational dispersion of light was performed. The work shows that PC has more stable cyclic dimers as in it both atoms of the carbonyl group participate in the intermolecular interaction, while in a chain-like dimer the interaction occurs only through one of them. As there are more chain dimers in PC, they collapse faster with the increase of temperature. From the work [42] the conclusion is drawn that absorption bands corresponding to the vibrations with the participation of atoms of the C=O bond of the carbonyl group of PC appeared to be the most sensitive to the ion-molecular interaction. Considering that the greatest density of a negative charge in the PC molecule is concentrated on the atom of oxygen of the C=O fragment, it is possible to draw a conclusion that the interaction of the PC molecules with cations of the dissolved salts occurs through an atom of oxygen of the group C=O and is followed by the cleavage of dipole-dipole associates formed in the liquid PC. In a series of cations Na-Li-Mg in PC strengthening of interaction of the corresponding cations with PC molecules is observed, and as a consequence – decrease of frequencies of the absorption bands.

According to the results of spectral studies of both pure solvent and solutions of 1-1 electrolytes in PC, as well as the obtained values and dependences of the parameter *q*, assumption of poor solvation of anions in PC is confirmed.

4. Conclusions

Conductometric investigation of several 1-1 eletrolytes in PC was performed in a wide range of temperatures. The values of limiting molar electrical conductivity (LMEC) Λ_0 and association constants K_A were calculated, which are in good agreement with the data for 298.15 K reported in literature.

The values of LMEC λ_0^i in the wide range of temperatures were obtained for the first time using the indirect method of separation into ionic components. The λ_0^i values are also in good agreement with the data for 298.15 K found in literature.

The assumption about the poor solvation of the ions in PC is confirmed. It was found that Li+ ion in its solvation shell does not concede to the Bu_4N^+ and BPh_4^- ions.

It was confirmed that at high temperatures (> 333 K) all ions virtually have no solvation shells (for Li^+ it is destroyed upon increase of the temperature).

The values of LMEC for the ions can be used for more thorough investigation of the interparticle interactions in solutions.

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ЕЛЕКТРИЧНА ПРОВІДНІСТЬ ТА МІЖЧАСТИНКОВІ ВЗАЄМОДІЇ В РОЗЧИНАХ 1-1 ЕЛЕКТРОЛІТІВ В ПРОПІЛЕНКАРБОНАТІ У ШИРОКОМУ ІНТЕРВАЛІ ТЕМПЕРАТУР

Анотація. *Представлено результати кондуктометричного дослідження розчинів деяких 1-1 електролітів у пропіленкарбонаті в інтервалі температур 298–398 K. З використанням розширеного рівняння електричної провідності Лі-Уітона визначено константи йонної асоціації. Встановлено, що* $LiClO_4$ *в пропіленкарбонаті є неасоційованим електролітом. Для врахування динаміки йонної асоціації проведено поділ на йонні складові електричної провідності в широкому інтервалі температур.*

Ключові слова: *пропіленкарбонат, електрична провідність, асоціація, 1-1 електроліти.*