The Temperature Dependence of the Properties of Electrolyte Solutions. III. Conductance of Various Salts at High Concentrations in Propylene Carbonate at Temperatures from $-45\,^{\circ}C$ to $+25\,^{\circ}C$

J. Barthel, H. J. Gores, and G. Schmeer

Chemisches Institut der Universität Regensburg

Elektrochemie / Lösungen / Transporterscheinungen

Specific conductances of Et_4NPF_6, Pr_4NPF_6, Bu_4NPF_6, $LiPF_6$, KPF_6, $LiClO_4$, and KSCN in propylene carbonate were studied at high concentrations in the temperature range from $+25\,^{\circ}C$ to $-45\,^{\circ}C$. Data are fitted by a least-squares method to a four-parametric empirical equation, yielding the maximum specific conductance κ_{max} and the corresponding concentration μ. Within the frame-work of a hydrodynamic model the Stokes-radii of the ions and the solvent viscosity are found to be the most important conductance-determining parameters, affecting both κ_{max} and μ. Ionic association in solutions with propylene carbonate as the solvent is not of significant importance. Kinetic treatment of conductance yields temperature-dependent activation energies, but at any one temperature equal for all salts at concentration μ.

Die spezifische Leitfähigkeit konzentrierter Lösungen von Et_4NPF_6, Pr_4NPF_6, Bu_4NPF_6, $LiPF_6$, KPF_6, $LiClO_4$ und KSCN in Propylencarbonat wurde im Temperaturbereich zwischen $+25\,^{\circ}C$ und $-45\,^{\circ}C$ untersucht. Die Datenanalyse mittels eines Ausgleichs nach einer vier-parametrigen empirischen Gleichung liefert für jede Temperatur die maximale spezifische Leitfähigkeit κ_{max} mit zugehörigem Konzentrationswert μ. Die Stokes-Radien der Ionen und die Viskosität des Lösungsmittels erweisen sich für ein hydrodynamisches Modell als die wichtigsten leitfähigkeitsbestimmenden Parameter zur Diskussion von κ_{max} und μ. Ionenassoziation spielt in Propylencarbonat als Lösungsmittel keine hervorragende Rolle. Die Behandlung des Transportprozesses im Rahmen eines kinetischen Modells führt zu temperaturabhängigen Aktivierungsenergien, die aber bei jeder Temperatur für alle Salze bei der Konzentration μ gleich sind.

1. Introduction

The conductance of concentrated electrolyte solutions and its temperature dependence are of technological interest, e.g. high energy and low temperature batteries, electrolysis etc. However at present, only a few sets of comprehensive data which are suitable for the discussion of conductance-determining effects are available [cf. [1–3]]. Furthermore, a perusal of the literature shows remarkable deviations in the data.

For example, values of the specific conductance κ of 1 M $LiClO_4$ in propylene carbonate at 25 °C in the literature are $5.6 \cdot 10^{-3}\ \Omega^{-1}\,cm^{-1}$ [1], $4.356 \cdot 10^{-3}\ \Omega^{-1}\,cm^{-1}$ or $4.239 \cdot 10^{-3}\ \Omega^{-1}\,cm^{-1}$ [using the interpolation functions of [4]] and $3.9 \cdot 10^{-3}\ \Omega^{-1}\,cm^{-1}$ [from Fig. 4 in [5]].

Solutions of various electrolytes with PC (propylene carbonate) as the solvent were investigated over a temperature range $-45\,^{\circ}C$ to $+25\,^{\circ}C$ in steps of 10 K from dilute to saturated – or up to concentrations beyond the maximum specific conductance – in order to obtain comprehensive information for a first example of a non-aqueous system which is of technological interest, also.

Ber. Bunsenges. Phys. Chem. *83*, 911–920 (1979) – © Verlag Chemie, D-6940 Weinheim, 1979.
0005-9021/79/0909-0911 $ 02.50/0

2. Experimental

2.1. Materials

Propylene carbonate (Fluka, purum > 99%) was boiled for two hours in the presence of dried CaO to reduce its glycol content to about 20% of the initial value and was then distilled at reduced pressure (~2 Torr). Nitrogen was bubbled through the solvent at 60°C to remove the volatile impurities [6]. The final distillation was carried out in a specially designed column [3] (40 plates, packed with nichrome helices) at reduced pressure (<2 Torr) and at a temperature of the still <130°C to avoid decomposition of the product. Those middle fractions passing over between (85.3 ± 0.1)°C at (1.8 ± 0.3) Torr and (88.7 ± 0.1)°C at (2.7 ± 0.3) Torr were stored after purity control under nitrogen for further use. The distillation temperature agrees well with that known from Refs. [6-8, 26].

Purity control was achieved during the distillation process by continuously measuring the conductance. The stored product ($\kappa = 2 \cdot 10^{-8}\,\Omega^{-1}\,\mathrm{cm}^{-1}$) contained 30-50 ppm of glycol along with further unidentified traces <1 ppm of impurities detectable by gaschromatographic analysis [6] using a Porapak Q column with N_2 carrier gas and flame ionisation detector. In agreement with Fujinaga and Izutsu's observation [9] no UV-absorption was observed between 240 and 340 nm, a steep increase beginning at 200 nm.

$LiClO_4$ (K & K, ≥99.8%), KPF_6 (Schuchhardt, 98-100%), and KSCN (Merck, p. a. ≥99%) were fractionally recrystallised three times from highly purified water ($\kappa \leq 3 \cdot 10^{-7}\,\Omega^{-1}\,\mathrm{cm}^{-1}$), predried for 12 h in vacuum (<1 Torr) at 50°C to 60°C and completely desiccated in a heated desiccator in vacuum at 200°C ($LiClO_4$), 150°C (KPF_6), and 50°C (KSCN). $LiPF_6$ (K & K, 95-99%) was dried in the same way but without the preceding recrystallisation. Bu_4NPF_6 (K & K, >97%) and Pr_4NPF_6 (K & K, >97%) were repeatedly recrystallized from methanol-water mixtures, Et_4NPF_6 (K & K, >97%) from acetone-ether mixtures, and dried in vacuum at 70°C (Et_4NPF_6 and Pr_4NPF_6) or 50°C (Bu_4NPF_6) before storage under vacuum in the presence of sicapent (Merck).

Nitrogen as the protective gas and water for recrystallisation were prepared in the usual way.

2.2. Conductance Measurements

Conductance measurements were made with a set of capillary cells of different cell constants, Fig. 1, immersed in a precise thermostat which could be set exactly to every temperature of the temperature programme (+25°, +15°, +5°, -5°, -15°, -25°, -35°, and -45°C) within 20 min. The reproducibility of temperature and short and long time deviations were $<10^{-3}$ K. For details of the thermostat (see [34]).

The capillary cells, Fig. 1, yield high cell constants as these are required for concentrated solutions. They are provided with bulbs B1 and B2 effecting a replacement of the solution between the electrodes E1 and E2 at every temperature step. To avoid bubbles the cells were filled through inlet C from an appropriate filling device. All operations on the cell and the solutions were made under protective gas. An assembly lid, A, equiped with three conductance cells permits immersion of the cell arrangement into the bath and hermetical sealing.

The calibration of the cells was based on the Jones-Bradshaw standards, 0.1 D and 1.0 D aqueous potassium chloride solutions [10], at 25°C. These values were used at all temperatures of the programme yielding an increasing systematic error with decreasing temperature which is a maximum (+0.025%) at -45°C. For the temperature-dependence of the cell constants of capillary cells see [25].

The conductance cells are connected in one arm of an a. c. bridge built according to present standard of technology guaranteeing a precision of 0.01% [cf. [34]]. Resistances of the solutions were determined at various frequencies, $60 < \frac{f}{\mathrm{Hz}} < 5{,}000$ and extrapolated to $f^{-1} \to 0$ in the usual manner. Taking into account the sources of error (calibration, remaining impurities of the salts, measurements) the specific conductances in Table 1 are certain within 0.1% with the exception of $LiPF_6$ for which impurities may cause higher uncertainty [cf. [1]]. Measurements were carried out according to a method of isologuous sections in a temperature cycle [3, 34] beginning and ending at 25°C.

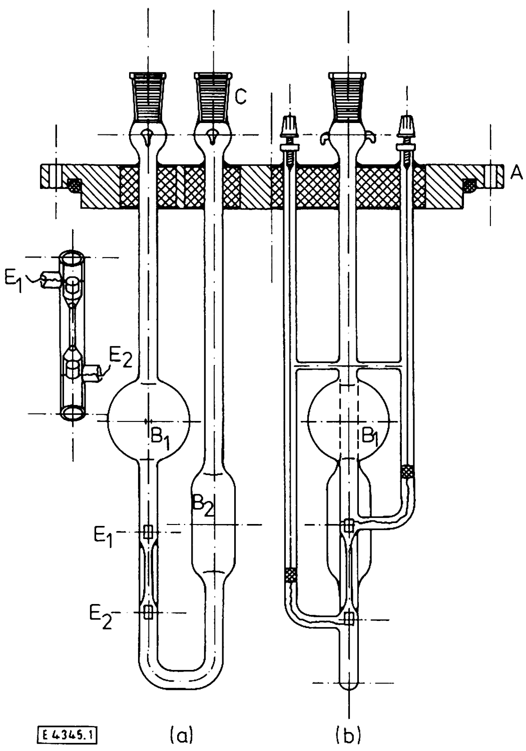

Fig. 1
Capillary cells (a, b) with assembly lid (A) for immersion in the temperature bath. E_1, E_2 Electrodes, C Inlet, B_1, B_2 Bulbs

3. Analysis of Data

Analysis of conductance data of concentrated solutions can actually best be achieved by means of empirical functions. Theoretically based equations like those known for dilute solutions are not so far available. Our experience with different empirical functions has proved that an equation published by Casteel and Amis [11]

$$\frac{\kappa}{\kappa_{\max}} = \left(\frac{m}{\mu}\right)^{a} \exp[b(m-\mu)^2 - a\mu^{-1}(m-\mu)] \tag{1}$$

fits well specific conductances $\kappa[\Omega^{-1}\,\mathrm{cm}^{-1}]$ of all our solutions as a function of molal concentration m [mol/kg of solvent] in a wide concentration range around the point of maximum specific conductance $\kappa_{\max}$ attained at concentration μ [mol/kg solvent]. Equation (1) fulfills the condition $\kappa = \kappa_{\max}$ if $m = \mu$.

The four quantities $\kappa_{\max}$, μ, a, and b are adjusted by a least-squares method, all measuring values contributing with equal weight (in contrast to [11]). Our programme, analoguous to that of DeTar [12], uses the inversion of the coefficient matrix according to Househoulder [13, 14] avoiding deterioration of the matrix condition. Condition numbers of $10^8 - 10^{11}$ obtained from our data were distinctly below the critical limit of 10^{20} proving that our data analysis yields reliable coefficients in spite of a low degree of freedom. Standard deviations of the single values were observed with an order of magnitude of $10^{-6} < \sigma < 10^{-5}$. Convergence was usually found after 4 to 5 iteration steps with a relative accuracy of 10^{-4} for the sum of the squared residuals.

Table 1

Specific conductances $10^3\,\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$ of various electrolytes in propylene carbonate at molal concentrations $m/\mathrm{mol\,kg}^{-1}$ and temperatures $\theta/^\circ\mathrm{C}$

Electrolytes	$\frac{m}{\text{mol /kg}}$ $\frac{\theta}{^\circ C}$	25	15	5	- 5	-15	-25	-35	-45
$LiClO_4$	0.27053	4.1281	3.3481	2.6234	1.9660	1.3868	0.9100	0.5337	0.2678
	0.52147	5.3048	4.2296	3.2435	2.3614	1.6057	0.9972	0.5440	0.2460
	0.68370	5.4056	4.2506	3.2017	2.2797	1.5046	0.8976	0.4631	0.1937
	0.78291	5.3365	4.1604	3.0998	2.1735	1.4073	0.8178	0.4075	0.1628
	1.05740	4.8082	3.6428	2.6188	1.7540	1.0701	0.5733	0.2553	0.0873
	1.26390	4.1937	3.0987	2.1570	1.3865	0.8008	0.3990	0.1612	0.0485
$LiPF_6$	0.116	1.5937	1.2959	1.0209	0.7721	0.5542	0.3712	0.2253	0.1180
	0.213	2.7486	2.2202	1.7376	1.3024	0.9238	0.6090	0.3622	0.1858
	0.412	4.3079	3.4366	2.6452	1.9431	1.3419	0.8545	0.4847	0.2334
	0.607	5.1259	4.0346	3.0515	2.1914	1.4717	0.9019	0.4867	0.2186
	0.891	5.4030	4.1538	3.0511	2.1128	1.3502	0.7778	0.3856	0.1545
KSCN	0.21089	3.9975	3.2460	2.5513	1.9233	1.3743	0.9154	0.5512	0.2884
	0.44662	5.7936	4.6420	3.5868	2.6489	1.8426	1.1856	0.6810	0.3344
	0.72132	6.6929	5.2775	3.9989	2.8799	1.9370	1.1963	0.6489	0.2941
	0.83051	6.8618	5.3742	4.0406	2.8789	1.9134	1.1577	0.6136	0.2689
	1.15538	7.0060	5.3772	3.9352	2.7118	1.7245	0.9841	0.4816	0.1893
	1.41113	6.8838	5.1949	3.7242	2.4989	1.5339	0.8345	0.3822	0.1365
KPF_6	0.11244	2.5793	2.1068	1.6685	1.2666	0.9129	0.6131	0.3735	0.1975
	0.20405	3.9259	3.2001	2.5521	1.9057	1.3615	0.9047	0.5423	0.2804
	0.38994	5.7589	4.6520	3.6280	2.7016	1.8933	1.2241	0.7063	0.3458
	0.57658	6.7103	5.3671	4.1319	3.0232	2.0718	1.2980	0.7184	0.3312
	0.76427	7.1687	5.6673	4.2944	3.0891	2.0663	1.2453	0.6639	0.2884
	0.98268	7.3084	5.6853	4.2197	2.9607	1.9206	1.1173	0.5584	0.2226
Et_4NPF_6	0.26011	5.542	4.513	3.558	2.693	1.933	1.291	0.7810	0.4099
	0.36464	6.964	5.652	4.439	3.343	2.383	1.578	0.9442	0.4876
	0.49597	8.384	6.776	5.294	3.961	2.792	1.835	1.080	0.5478
	0.67278	9.771	7.851	6.090	4.514	3.156	2.037	1.176	0.5776
	0.88208	10.870	8.673	6.671	4.893	3.373	2.138	1.208	0.5766
	1.20960	11.804	9.316	7.070	5.098	3.441	2.119	–1)	–1)
Pr_4NPF_6	0.1450	3.1653	2.5720	2.0235	1.5278	1.0943	0.7303	0.4412	0.2321
	0.2607	4.7943	3.8726	3.0257	2.2645	1.6039	1.0552	0.6262	0.3207
	0.4517	6.5985	5.2721	4.0640	2.9970	2.0801	1.3331	0.7645	0.3736
	0.4806	6.8342	5.4525	4.1974	3.0867	2.1359	1.3632	0.7775	0.3775
	0.7184	7.8895	6.2134	4.7057	3.3885	2.2842	1.4101	0.7691	0.3516
	0.9223	8.3327	6.4888	4.8462	3.4320	–1)	–1)	–1)	–1)
Bu_4NPF_6	0.09139	2.0060	1.6309	1.2855	0.9727	0.6989	0.4685	0.2854	0.1516
	0.1991	3.5884	2.8976	2.2640	1.6957	1.2022	0.7932	0.4729	0.2446
	0.3869	–	–	–	2.3008	1.5992	1.0278	0.5931	0.2939
	0.5106	5.7924	4.5772	3.4862	2.5301	1.7257	1.0843	0.6078	0.2905
	0.9762	6.2551	4.7818	3.4957	2.4153	1.5503	0.9023	0.4607	0.1460
	1.4834	5.5277	4.0718	2.8457	1.8621	–1)	–1)	–1)	–1)

---

1) Solubility limit surpassed.

Table 2
Conductance parameters, Equation (1), and their standard deviations

Electrolyte	$\frac{\Theta}{{}^\circ C}$	$\frac{\sigma_{fit} \cdot 10^5}{\Omega^{-1} cm^{-1}}$	$\frac{\kappa_{max} \cdot 10^3}{\Omega^{-1} cm^{-1}}$	$\frac{\sigma(\kappa_{max}) \cdot 10^5}{\Omega^{-1} cm^{-1}}$	$\frac{\mu}{mol/kg\ solv.}$	$\frac{\sigma(\mu) \cdot 10^2}{mol/kg\ solv.}$	a	σ(a)	$\frac{10\ b}{(mol/kg\ solv)^{-2}}$	$\frac{10\ \sigma(b)}{(mol/kg\ solv)^{-2}}$
$LiClO_4$	25	1.9	5.420	1.2	0.6616	0.75	0.855	0.063	0.8	0.7
	15	1.6	4.279	1.0	0.6237	0.67	0.858	0.065	1.1	0.8
	5	1.3	3.253	1.0	0.5832	0.65	0.862	0.074	1.5	0.9
	- 5	1.0	2.357	0.8	0.5398	0.54	0.868	0.077	1.9	0.9
	-15	0.7	1.604	0.7	0.4947	0.46	0.879	0.091	2.5	1.1
	-25	0.5	1.0084	0.51	0.4447	0.32	0.875	0.095	3.3	1.2
	-35	0.2	0.5681	0.29	0.3938	0.30	0.893	0.10	4.2	1.3
	-45	0.1	0.2747	0.13	0.3410	0.46	0.909	0.11	5.3	1.6
$LiPF_6$	25	2.3	5.409	2.0	0.857	2.9	1.093	0.059	-0.4	1.5
	15	1.9	4.182	1.7	0.800	1.8	1.088	0.060	-0.1	1.6
	5	1.5	3.111	1.4	0.744	1.1	1.090	0.063	-0.1	1.7
	- 5	1.1	2.205	1.1	0.686	0.70	1.094	0.061	0.3	1.6
	-15	0.8	1.469	0.8	0.625	0.67	1.089	0.067	1.0	1.8
	-25	0.5	0.9028	0.4	0.563	0.68	1.093	0.064	1.3	1.8
	-35	0.3	0.4970	0.3	0.500	0.74	1.094	0.071	1.9	2.0
	-45	0.5	0.2344	0.4	0.426	1.9	1.22	0.45	-0.5	10
KPF_6	25	1.7	7.307	1.6	0.971	2.7	0.886	0.023	-1.1	0.05
	15	1.2	5.711	0.9	0.881	1.2	0.887	0.020	-0.9	0.5
	5	0.5	4.294	0.4	0.799	0.4	0.900	0.011	-1.0	0.3
	- 5	0.8	3.092	0.6	0.725	0.4	0.889	0.021	-0.3	0.5
	-15	0.6	2.089	0.4	0.655	0.4	0.891	0.022	-0.02	0.5
	-25	0.4	1.301	0.3	0.582	0.4	0.895	0.025	0.3	0.6
	-35	0.2	0.7258	0.16	0.509	0.4	0.896	0.024	0.8	0.6
	-45	0.15	0.3468	0.11	0.436	0.4	0.893	0.033	1.6	0.9
KSCN	25	0.8	7.003	0.6	1.0968	0.54	0.754	0.012	-0.9	0.1
	15	0.7	5.417	0.5	0.9756	0.36	0.754	0.012	-0.9	0.1
	5	0.3	4.043	0.18	0.8671	0.20	0.753	0.007	-0.8	0.1
	- 5	0.1	2.885	0.07	0.7670	0.10	0.756	0.004	-0.7	0.04
	-15	0.1	1.943	0.07	0.6743	0.13	0.755	0.006	-0.6	0.1
	-25	0.1	1.216	0.09	0.5861	0.16	0.756	0.009	-0.3	0.1
	-35	0.1	0.6851	0.09	0.5048	0.18	0.744	0.015	0.2	0.2
	-45	0.04	0.3348	0.03	0.4261	0.08	0.732	0.011	0.9	0.2
Et_4NPF_6	25	0.4	12.23	5.1 **)	1.795	8.7	0.907	0.008	-0.8	0.1
	15	0.4	9.500	2.3 *)	1.590	4.2	0.908	0.008	-0.8	0.1
	5	0.3	7.125	0.8 *)	1.423	2.0	0.911	0.008	-0.8	0.1
	- 5	0.2	5.102	0.3 *)	1.272	1.2	0.913	0.009	-0.8	0.1
	-15	0.3	3.477	0.2	1.131	0.7	0.897	0.013	-0.7	0.2
	-25	0.1	2.150	0.1	0.997	0.3	0.917	0.011	-0.8	0.1
	-35	0.03	1.208	0.03	0.885	0.3	0.926	0.008	-1.1	0.1
	-45	0.2	0.5811	0.1	0.759	1.2	1.003	0.093	-2.6	1.7
Pr_4NPF_6	25	2.8	8.468	14 **)	1.17	19	0.919	0.047	-1.2	1.1
	15	2.2	6.525	5.7 **)	1.06	10	0.918	0.046	-1.2	1.1
	5	1.7	4.846	2.2 *)	0.956	5.6	0.919	0.047	-1.2	1.1
	- 5	1.3	3.436	1.0	0.860	3.0	0.928	0.050	-1.3	1.2
	-15	0.8	2.284	0.9	0.720	2.7	0.852	0.078	1.5	2.6
	-25	0.5	1.4166	0.5	0.654	1.4	0.861	0.075	1.4	2.5
	-35	0.3	0.7877	0.3	0.580	0.6	0.876	0.071	1.2	2.4
	-45	0.2	0.3768	0.1	0.503	0.6	0.880	0.076	1.2	2.6
Bu_4NPF_6	25	1.8	6.305	1.6	0.840	0.7	0.909	0.016	-1.2	0.2
	15	1.5	4.878	1.3	0.778	0.6	0.910	0.016	-1.2	0.2
	5	1.0	3.639	0.9	0.715	0.5	0.913	0.015	-1.2	0.2
	- 5	2.6	2.582	2.0	0.666	1.5	0.883	0.045	-0.7	0.7
	-15	2.2	1.734	2.6	0.601	2.2	0.893	0.11	-0.9	0.3
	-25	1.1	1.080	1.1	0.536	1.9	0.907	0.087	-1.1	0.3
	-35	0.5	0.6068	0.4	0.475	1.3	0.917	0.064	-1.3	0.2
	-45	0.4	0.2975	0.3	0.408	1.4	0.805	0.11	9.0	3.5

Table 2 summarizes the parameters derived from the measurements in Table 1. Satisfactory accuracy is always observed in cases of sufficiently high electrolyte solubility, i. e. if measurements were possible to a concentration exceeding μ. Otherwise the quality of fit ranges from good [cf. (*) in Table 2] to moderate [cf. (**)].

A feature of Equation (1) must be considered at this point. In spite of a good representation of data around the point (μ, κ_{max}), misrepresentations can occur at very low and high concentrations. The physically necessary condition $\kappa \to 0$ if $m \to 0$ is only fulfilled if $a > 0$, otherwise $\kappa \to \infty$. Table 2 shows that this situation never occurs in our measurements. The limiting tangent $(d\kappa/dm)_0$ is always erroneous. However, the resulting deviations of the fitted curves from the measured values are limited to very small concentrations ($m < 0.02$ mol kg^{-1}). At high concentrations, $m \gg \mu$, finite values of κ are obtained only if $b < 0$, otherwise κ attains a minimum at $m = \dfrac{a}{2b\mu}$ and then increases steadily, in contrast to a real behaviour of κ.

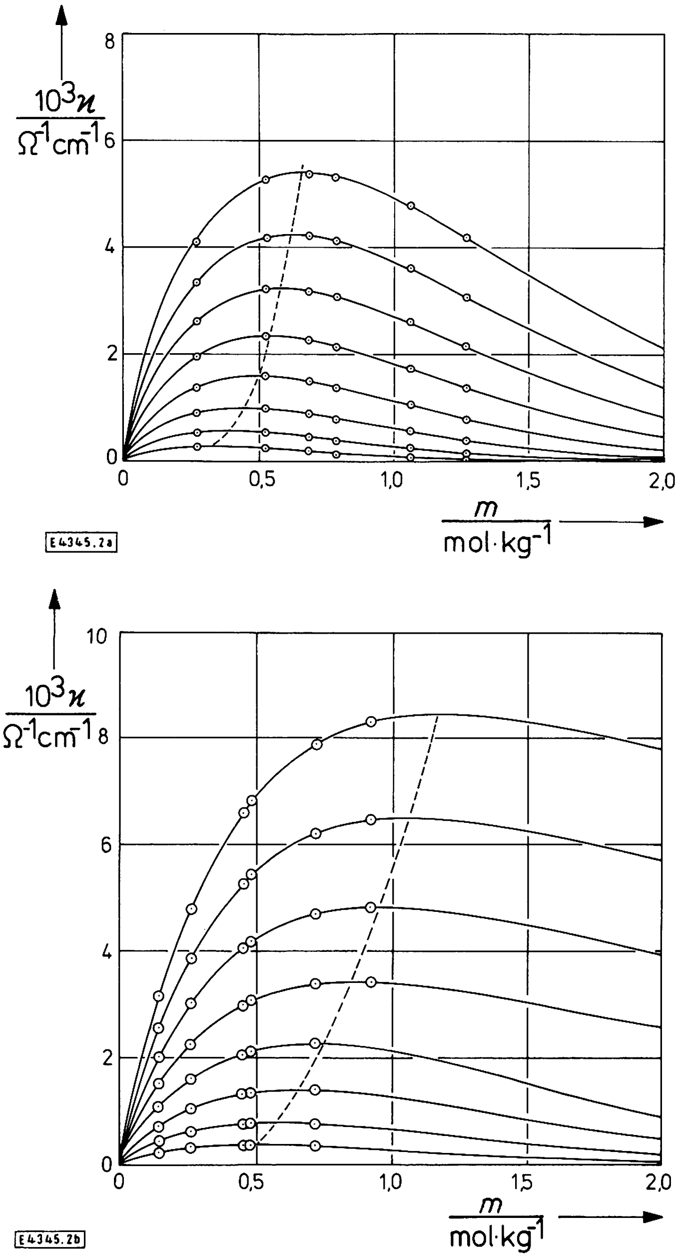

Fig. 2

Specific conductivity $10^3 \cdot \kappa/(\Omega^{-1}\,cm^{-1})$ in propylene carbonate as the solvent at temperatures from +25 °C to −45 °C in steps of 10 K. Solid curves as obtained from computer-plots according to Equation (1). The dotted curves represent the independently determined $\kappa_{max} = \kappa_{max}(\mu)$ functions.

(a) $LiClO_4$ (b) Pr_4NPF_6

Fig. 2a, $LiClO_4$ in PC, gives an example with $a > 0$, $b < 0$ at all temperatures of the programme. The case of $a < 0$ can occur when the coefficients of Equation (1) are determined from measurements at only high concentrations, that of $b > 0$ in the reverse case. The latter situation is often found when the concentration range is limited by the solubility of the electrolyte to concentration $m \approx \mu$. Nevertheless, an acceptable representation of conductance is possible by the inclusion of μ-values extrapolated in a κ-m-T field. As an example, Pr_4NPF_6, Table 2, shows an inversion from negative to positive b-values at a temperature between −15 °C and −5 °C as a result of a solubility-limited concentration range [cf. Table 1 and Fig. 2b]. The shape of $\kappa = \kappa(m)$, Equation (1), at temperatures < −5 °C ($b < 0$) is that observed in Fig. 2a, whereas that at temperatures > −5 °C ($b > 0$) differs distinctly. In sections 4.4 and 4.5 the fundamental expressions governing the functions $\mu = \mu(T)$, $\kappa_{max} = \kappa_{max}(T)$, and $\kappa_{max} = \kappa(\mu)$ are given. So the values μ and κ_{max} can be determined by an extrapolation independent of Equation (1). Figs. 2a and 2b contain these independently obtained functions as dashed lines showing that investigation of the complete κ-m-T field yields compatible information.

It should be mentioned that Casteel and Amis in their original work on Equation (1) [11] found also cases where $b > 0$, e. g. $MgCl_2$ in one of their water-ethanol mixtures. Information on aqueous systems are given in a following paper [15].

4. Discussion

4.1. Maximum Specific Conductance

The maximum of the specific conductance κ_{max} and its interpretation is one of the main interests of investigations on concentrated electrolytes (e. g. [1, 4, 5, 11, 16–20]). The specific conductance $\kappa[\Omega^{-1}\,cm^{-1}]$ is related to the molar conductance

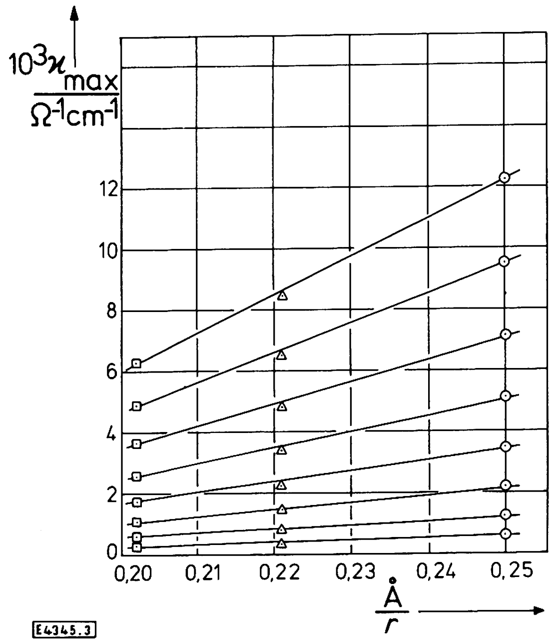

Fig. 3

Functions $10^3 \cdot \kappa_{max} = f(r_{\mp}^{-1})$ for tetraalkylammonium hexafluorophosphates in propylene carbonate as the solvent at temperatures from +25 °C to −45 °C in steps of 10 K.

○ Et_4NPF_6, △ Pr_4NPF_6, □ Bu_4NPF_6

$\Lambda[\Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}]$ and the molar density function $\rho[\mathrm{mol\ cm}^{-3}]$ of the electrolyte compound by the relationship $\kappa = \Lambda \cdot \rho$ yielding the expression

$$d\kappa = \Lambda\, d\rho + \rho\, d\Lambda\,. \qquad (2)$$

Experimental evidence shows that $d\Lambda < 0$ if $d\rho > 0$ and consequently the maximum specific conductance, when $d\kappa = 0$, follows from the competition between the increase $d\rho$ of the ionic density and the lowering $d\Lambda$ of the ionic mobility when the electrolyte concentration increases. Molenat denies that structures change with varying concentration [18] and leaves undecided the question of which factors govern the variation of the ionic mobility. In contrast, Valyashkow and Ivanov [16] stress the competition of ion-solvent and ion-ion interaction, whereas Jasinski [1] favours ion association as the important feature for explaining the maximum of the specific conductance (cf. also [3]).

The comprehensiveness of the data given in Table 1 permits for the first time some insight into these problems for solutions of an aprotic solvent, propylene carbonate.

4.2. Influence of Ionic or Stokes' Radii on Conductance

Fig. 3 shows an approximate linear dependence of $\kappa_{\max}$ on reciprocal radii of the tetraalkylammonium ions. In addition, the ratio $\kappa_{\max}(X_1PF_6)/\kappa_{\max}(X_2PF_6)$ is found to be constant irrespective of temperature, e. g. from Table 2 $\kappa_{\max}(Et_4NPF_6)/\kappa_{\max}(Bu_4NPF_6) = 1.97 \pm 0.02$. Values of μ are also found to vary approximately linear with the cationic radii, r_+^{-1}. This suggests that the data for all the investigated electrolyte solutions could be expressed in the form

$$\frac{\kappa}{m} = C\left(\frac{1}{r_-} + \frac{1}{r_+}\right) \qquad (3)$$

κ/m being an appropriate expression for investigating ion-solvent interactions in the framework of conductance-determining effects, because this expression is correlated to the electrolyte mobility and $\lim_{m\to 0}[\kappa/m] \propto \Lambda^{\infty}$. The quantity C is a function of viscosity, and further parameters which need not to be specified in this context.

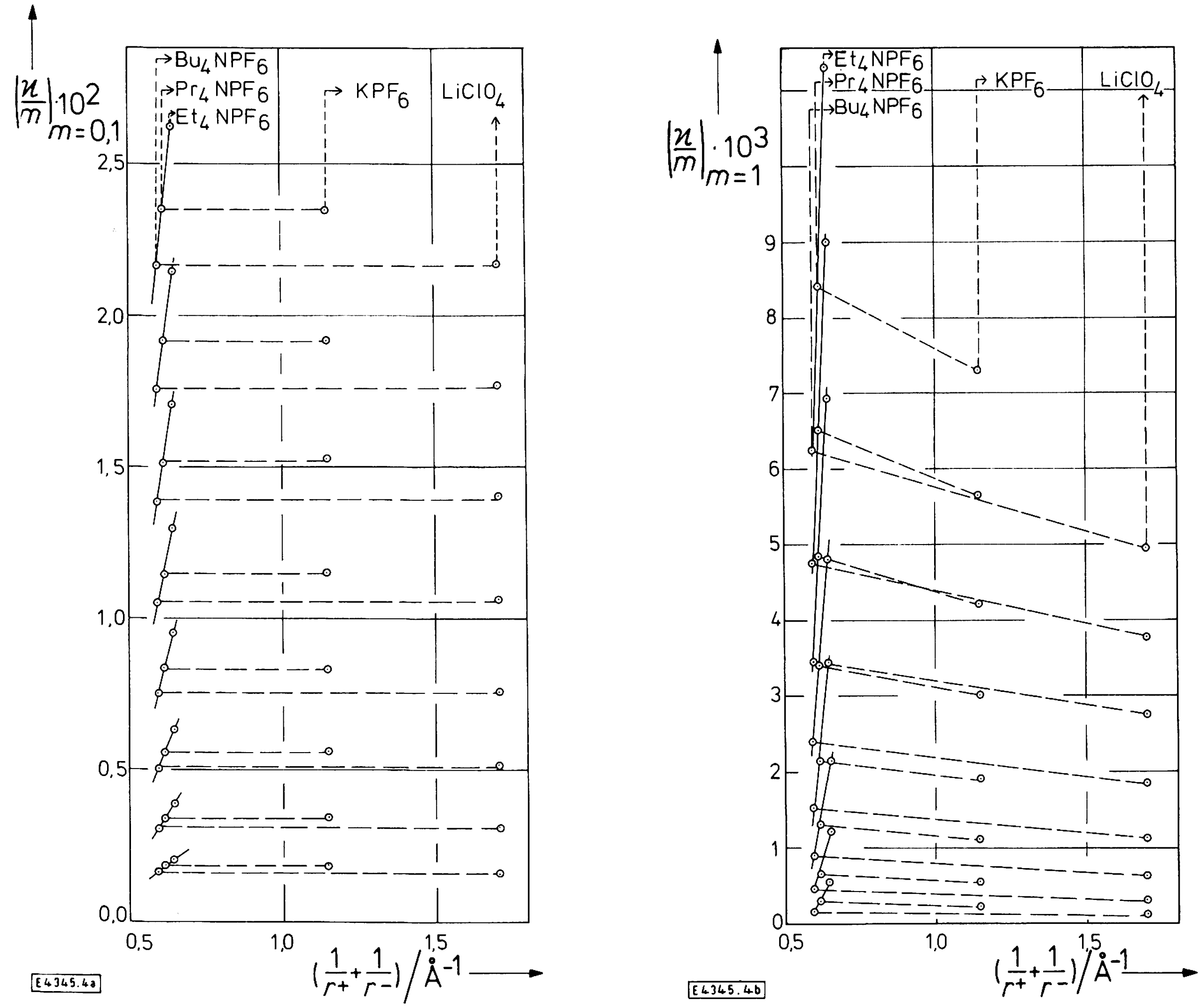

Fig. 4
Representation of $(\kappa/m) = f(r_+^{-1} + r_-^{-1})$ for various salts in propylene carbonate at temperatures from +25 °C to −45 °C in steps of 10 K. The dashed lines join the salts of which Stokes' radii are compared in the text.
(a) $m = 0.1\ \mathrm{mol\,kg}^{-1}$ (b) $m = 1.0\ \mathrm{mol\,kg}^{-1}$

At moderate concentrations, e. g. $m = 0.1\ \mathrm{mol\,kg^{-1}}$ in Fig. 4a, Equation (3) is fulfilled by the experimental data of the three tetraalkylammonium salts, r_- and r_+ being crystallographic radii of ClO_4^- [21], PF_6^- [22], Li^+ [23], and K^+ [24] or ionic radii as given by Robinson and Stokes for the tetraalkylammonium cations [25]. Just like in infinetely dilute solutions we observe $d(\kappa/m)/d(r_+^{-1}) > 0$ for the tetraalkylammonium salts and < 0 for the alkali salts. For sake of comparison $LiPF_6$ was investigated but the impurity of this salt (from decomposition) reduced the reliability of the conductance data. Consequently discussion has to be based on $LiClO_4$ as an example of a lithium salt with an equally hard anion and with $r_{ClO_4^-} \approx r_{PF_6^-}$ [21, 22]. It should be noted that KPF_6 and Pr_4NPF_6 on the one hand and $LiClO_4$ and Bu_4NPF_6 on the other hand yield nearly equal κ/m-values at every temperature. Hence, Stokes' radii (R_+) of the alkali and ionic radii (r_+) of the tetraalkylammonium salts are found to be $R_+(K^+) \approx r_+(Pr_4N^+)$ and $R_+(Li^+) \approx r_+(Bu_4N^+)$ in 0.1 M solutions in agreement with infinitely dilute solutions [26]. Ion-solvent interactions are independent of temperature and as $R(Li^+) > R(K^+)$ are more pronounced for $Li^+ - PC$ than for $K^+ - PC$.

Even at still higher concentrations, e. g. $1.0\ \mathrm{mol\,kg^{-1}}$ in Fig. 4b, the values of κ/m of tetraalkylammonium salts show the same linear dependence on ionic radii r_+^{-1} for tetraalkylammonium salts, however the Stokes' radii $R_+(K^+)$ and $R_+(Li^+)$ are no longer equal to the ionic radii $r_+(Pr_4N^+)$ and $r_+(Bu_4N^+)$, illustrating that for the solvated alkali cations additional conductance determining effects from the interactions in the solvation shells must have occured.

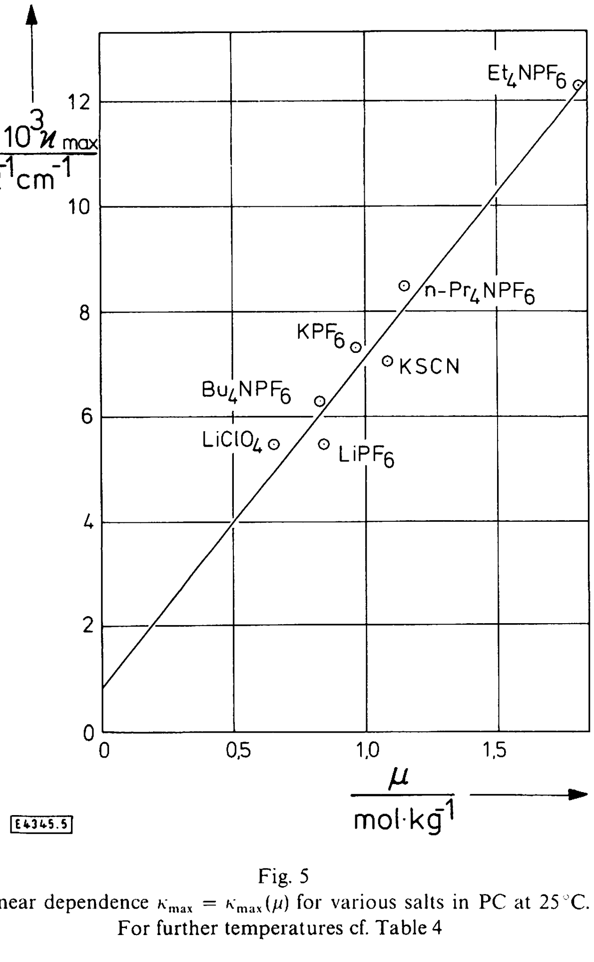

Fig. 5
Linear dependence $\kappa_{max} = \kappa_{max}(\mu)$ for various salts in PC at 25 °C. For further temperatures cf. Table 4

It is interesting to note that κ_{max}/μ is found to be constant for all the salts investigated. Fig. 5 demonstrates this feature with the linear representation

$$(\kappa_{max})_{25\,°C} = (6.3 \pm 0.6)\cdot 10^{-3}\mu + (8 \pm 7)\cdot 10^{-4} \tag{4}$$

illustrating that competition between ion-ion and ion-solvent interactions with increasing salt concentration though changing the environment of the ions in a different way for solvated and unsolvated species leads to comparable states of the different solutions at $m = \mu$.

On the one hand, a specific hindrance such as large ion-solvent interactions, e. g. Li^+, or big ionic radii, e. g. Bu_4N^+, or on the other hand a non-specific hindrance such as increasing viscosity yield low μ-values which are accompanied by low κ_{max}-values according to Equation (4) and vice versa.

The difference in behaviour between moderately and highly concentrated solutions can also be seen from Table 3 in a striking way. The underlying concept is a comparison of Λ^∞ (for Λ^∞-values of $LiClO_4$ and KPF_6 in PC see [30]) and the mobility correlated function (κ/m) by means of the quantity $A(m) = \Lambda^\infty/(\kappa/m)$. For both salts, $LiClO_4$ and KPF_6 the $A(0.1)$-values are independent of temperature. Hence the (κ/m)-values must depend on the temperature in the same way as the Λ^∞-values do, showing that the mobility governing effects at infinite dilution and at $m = 0.1\ \mathrm{mol\,kg^{-1}}$ are the same. In contrast, a significant temperature dependence of $A(m)$ is observed at higher concentrations, e. g. $A(1.0)$. Increasing $A(m)$ values indicate decreasing mobility functions (κ/m). When compared at constant temperature $A(0.1)$ as well as $A(\mu)$ are almost the same for $LiClO_4$ and KPF_6 The values $A(1.0)$ differ distinctly, $A(1.0)_{LiClO_4} > A(1.0)_{KPF_6}$ in accordance with $\mu_{LiClO_4} < \mu_{KPF_6}$. As previously discussed the solutions are in comparable states at $m = \mu$, conductance decreasing effects beginning to exceed the increasing effects at this characteristic concentration.

4.3. Influence of Viscosity

The importance of viscosity as a factor of a non-specific hindrance of transport is illustrated in Table 4. Pursuing the discussion of (κ/m) as a measure of mobility a Walden-analoguous expression

$$B = \eta_0(\kappa_{max}/\mu) \tag{5}$$

is used to show the effect of the solvent viscosity η_0 and its temperature dependence (for η_0 of PC at various temperatures see [31]). The mobility function itself at $m = \mu$, (κ_{max}/μ), generally varies by a factor of 10 between +25 °C and −45 °C, e. g. $LiClO_4$: $8.2\cdot 10^{-3}$ at 25 °C and $0.81\cdot 10^{-3}$ at −45 °C. In contrast, the variation of B is distinctly reduced, e. g. $LiClO_4$: 0.21 at +25 °C and 0.27 at −45 °C.

From the literature it is known that activation energies (temperature coefficients) of viscosity, $E_a(\eta)$, and of equivalent conductance, $E_a(\Lambda)$, or specific conductance, $E_a(\kappa)$, are in the order $E_a(\eta) > E_a(\Lambda) \approx E_a(\kappa)$ [16, 27, 28]. The steeper decrease of fluidity when compared to conductance as functions of temperature is in agreement with the results in Table 4. The quantity ($\kappa_{\max}/\mu$) increases, B decreases with increasing temperature.

Table 3
Values $A(m) = m\Lambda^{\infty}/\kappa(m)$ for $LiClO_4$ and KPF_6 in propylene carbonate over a temperature range $-45 \leq \theta/°C \leq +25$

$\theta/°C$	$LiClO_4$ $A(0.1)$	$A(1.0)$	$A(\mu)$	KPF_6 $A(0.1)$	$A(1.0)$	$A(\mu)$
25	1233	5418	3265	1234	3966	3848
15	1224	5767	3163	1222	4132	3616
5	1217	6267	3063	1205	4376	3427
−5	1215	7023	2965	1202	4722	3263
−15	1224	8202	2879	1198	5245	3131
−25	1217	10157	2779	1198	6084	3004
−35	1238	13719	2690	1202	7500	2889
−45	1263	20945	2603	1216	10164	2783

Table 4
Values $B = 10^3 \eta_0 (\kappa_{\max}/\mu)$ and p-values for various electrolytes in propylene carbonate over a temperature range $-45 \leq \theta/°C \leq +25$

θ/C	Et_4NPF_6	Pr_4NPF_6	Bu_4NPF_6	$LiClO_4$	KPF_6	KSCN
25	0.172	0.182	0.190	0.207	0.190	0.161
15	0.187	0.192	0.196	0.214	0.203	0.173
5	0.200	0.202	0.203	0.222	0.214	0.186
−5	0.212	0.211	0.205	0.231	0.225	0.199
−15	0.225	0.234	0.213	0.239	0.235	0.212
−25	0.237	0.238	0.221	0.249	0.246	0.228
−35	0.245	0.244	0.230	0.259	0.256	0.244
−45	0.259	0.254	0.247	0.273	0.270	0.266
p	0.849	0.873	0.902	0.895	0.886	0.811

A modified B-function, $B^* = \eta_0^p(\kappa_{\max}/\mu)$, used in analogy to a proposal of Robinson and Stokes [25] for dilute solutions, shows a range of variation which is reduced to an almost negligible extent, e. g. $LiClO_4$ ($p = 0.895$) : 0.304 at +25 °C, 0.306 at −45 °C. Values of p for the different salts as determined by a linear logarithmic regression are quoted in Table 4. As in dilute electrolytes p increases with the ionic radii of the tetraalkalyammonium salts.

4.4. Temperature Dependence of κ (m)

Smoothed values of the specific conductances κ, Equation (1), at any concentration m can be calculated with the help of Table 2. From these data isologuous sections have been fitted to an expression of the form

$$\ln \kappa = a + bT^{-1} + cT^{-2} \tag{6}$$

from which activation energies, $E_{m,\theta}$, are given by $E_{m,\theta} = -R(\partial \ln \kappa / \partial (1/T))_{m,\theta}$. Table 5 gives an example.

Table 5
Activation energies $E_{m,\theta}$/kJ mol^{-1} of KPF_6 solutions in propylene carbonate at concentrations m/mol kg^{-1} and temperatures $\theta/°C$

$\theta/°C$	m/mol kg^{-1} 0.1	0.3	0.5	1.0	1.6
25	12.16	12.36	12.73	14.13	16.73
15	14.04	14.50	15.13	17.27	20.73
5	16.05	16.79	17.17	20.63	25.20
−5	18.20	19.25	20.48	24.24	30.01
−15	20.55	21.90	23.46	28.13	35.20
−25	23.09	24.77	26.69	32.24	40.78
−35	25.80	27.88	30.18	36.90	46.84
−45	28.77	31.26	33.98	41.85	53.54

A perusal of Table 5 shows that the underlying kinetic model of electrolyte conductance provides the same information as the hydrodynamic model, section 4.2, in so far as activation energies vary appreciably only at high concentration. $LiClO_4$ shows this fact in an even more pronounced way (at 25 °C: $E_{0.1}$ = 12.22 kJ mol^{-1}; $E_{0.3}$ = 12.56 kJ mol^{-1}; $E_{0.5}$ = 12.95 kJ mol^{-1}; $E_{1.0}$ = 14.88 kJ mol^{-1}; $E_{1.6}$ = 18.45 kJ mol^{-1}) in accordance with its μ-values, since $\mu_{LiClO_4} < \mu_{KPF_6}$. The representations of the data by equations

Table 6
Activation energies E_m/kJ mol^{-1} at fixed concentrations m/mol kg^{-1} as a function of temperature.
$E_m(\theta) = a_0^{(m)} + a_1^{(m)}\theta + a_2^{(m)}\theta^2$

Electrolyte	$m = 0.1$ $a_0^{(m)}$	$a_1^{(m)}$	$10^4 a_2^{(m)}$	$\Delta_{\max}/\%$	$m = 0.5$ $a_0^{(m)}$	$a_1^{(m)}$	$10^4 a_2^{(m)}$	$\Delta_{\max}/\%$	$m = 1.0$ $a_0^{(m)}$	$a_1^{(m)}$	$10^4 a_2^{(m)}$	$\Delta_{\max}/\%$
$LiClO_4$	17.17	−0.2194	8.95	0.3	19.72	−0.2990	11.54	0.7	24.48	−0.4255	17.60	0.4
KPF_6	17.08	−0.2182	9.04	0.3	19.03	−0.2790	11.54	0.3	22.35	−0.3642	15.04	0.4
KSCN	17.05	−0.2040	8.42	0.3	19.21	−0.2584	10.58	0.4	22.24	−0.3317	13.69	0.4
Et_4NPF_6	16.84	−0.2272	9.40	0.3	18.58	−0.2112	8.75	0.2	19.78	−0.2715	10.60	0.3
n-Bu_4NPF_6	17.41	−0.2148	8.93	0.3	20.04	−0.2508	10.38	0.3	22.83	−0.4534	18.53	0.4

Table 7
Activation energies E_θ/kJ mol^{-1} at fixed temperatures $\theta/°C$ as a function of concentrations
$E_\theta(m) = a_0^{(\theta)} + a_1^{(\theta)}m + a_2^{(\theta)}m^2$

Electrolyte	$\theta = 15°C$ $a_0 \pm \sigma(a_0)$	a_1	a_2	$\Delta_{\max}/\%$	$\theta = -5°C$ $a_0 \pm \sigma(a_0)$	a_1	a_2	$\Delta_{\max}/\%$	$\theta = -35°C$ $a_0 \pm \sigma(a_0)$	a_1	a_2	$\Delta_{\max}/\%$
$LiClO_4$	13.82 ± 0.05	2.16	2.53	0.2	17.67 ± 0.09	5.29	3.66	0.4	23.7 ± 1.0	17.0	0.07	2.1
KPF_6	13.81 ± 0.04	1.94	1.50	0.2	17.71 ± 0.10	4.75	1.95	0.1	24.3 ± 0.1	9.4	1.85	1.0
KSCN	13.82 ± 0.05	3.48	0.29	0.3	17.54 ± 0.01	5.58	0.85	0.1	24.85 ± 0.01	9.24	2.81	0.1
Et_4NPF_6	13.39 ± 0.38	3.87	−1.39	0.4	17.70 ± 0.04	3.23	0.21	0.1	25.5 ± 0.5	3.34	1.82	0.4
Bu_4NPF_6	13.52 ± 0.11	8.99	−6.01	0.3	17.86 ± 0.20	6.78	0.40	0.2	25.8 ± 0.4	2.0	13.0	0.8

Table 8
Activation energies $E_\theta(\mu)$/kJ mol^{-1} and their mean values with mean deviations at various temperatures in solutions with propylene carbonate as the solvent

Electrolyte	$\theta = 15\,^\circ C$		$\theta = 5\,^\circ C$		$\theta = -5\,^\circ C$		$\theta = -15\,^\circ C$		$\theta = -25\,^\circ C$		$\theta = -35\,^\circ C$	
	μ	$E_\theta(\mu)$	μ	$E_\theta(\mu)$	μ	$E_\theta(\mu)$	μ	$E_\theta(\mu)$	μ	$E_\theta(\mu)$	μ	$E_\theta(\mu)$
$LiClO_4$	0.624	16.2	0.583	18.9	0.540	21.6	0.495	24.5	0.445	27.1	0.394	30.0
KPF_6	0.881	16.7	0.799	19.3	0.725	22.6	0.655	24.8	0.582	27.5	0.509	30.3
KSCN	0.976	17.5	0.867	19.9	0.767	22.3	0.674	24.7	0.586	27.1	0.505	29.6
Et_4NPF_6	1.590	16.1	1.423	19.5	1.272	22.2	1.131	24.7	0.997	27.2	0.885	29.9
Bu_4NPF_6	0.778	16.9	0.715	19.8	0.666	22.6	0.601	25.0	0.536	27.4	0.475	29.7
$E_\theta(\mu)$	–	16.7	–	19.5	–	22.3	–	24.7	–	27.3	–	29.9
$\Delta E_\theta(\mu)$	–	0.4	–	0.3	–	0.3	–	0.1	–	0.2	–	0.2

Table 9
Parameters, Equation (7), their standard and maximum deviations

Electrolytes	α	$\sigma(\alpha)$	$10^3\beta$	$10^3\sigma(\beta)$	$10^5\gamma$	$10^5\sigma(\gamma)$	$10^3\sigma_{\text{fit}}$	$\frac{\Delta_{\max}}{\%}$
$LiClO_4$	0.5618	0.0003	4.326	0.012	−1.312	0.043	0.6	<0.2
KPF_6	0.7651	0.0023	7.76	0.10	1.17	0.35	4.5	<0.7
KSCN	0.8160	0.0012	10.17	0.05	4.07	0.31	1.9	<0.3
Et_4NPF_6	1.349	0.005	15.80	0.02	6.4	0.8	9.9	<1.2
Pr_4NPF_6	0.8936	0.0007	10.41	0.33	3.7	1.2	15.1	<4
Bu_4NPF_6	0.6913	0.0002	5.99	0.09	−0.65	0.30	4.0	<0.8

of type (6) are satisfactory, the percent deviations always being <0.5%.

From tables of type 5 for all salts, with exception of $LiPF_6$ (see: purity), functions $E_m = f(\theta)$ and $E_\theta = f(m)$ have been established with the help of quadratic least-squares fits for the whole temperature and concentration field. Examples are given in Tables 6 and 7.

Finally, activation energies at $m = \mu$, Table 8, have been calculated with the help of $E_\theta = f(m)$.

In dilute solutions, cf. $E_\theta(m)$ in Table 7 when $m \to 0$, activation energies depend only on the properties of the solvent. This important feature has also been shown meanwhile by direct measurements of the conductance of highly dilute solutions with propylene carbonate [30] and further aprotic and protic solvents [29, 30]. In contrast to acetonitrile or aliphatic alcohols where the activation energies are found to be independent of temperature, $E_\theta(0)$-values of solutions with PC as the solvent are strongly temperature-dependent. This observation is in agreement with the anomalous dependence on temperature of the viscosity of cyclic esters [32].

At high concentrations, cf. Table 6, a sequence of activation energies $LiClO_4 > Bu_4NPF_6 > KPF_6 \approx KSCN > Et_4NPF_6$ is observed which corresponds to the sequence of Fig. 5 based on the hydrodynamic model. At $m = 1.0$ mol kg^{-1}, the maximum specific conductance of Et_4NPF_6 has not yet been attained whereas μ has been passed for KSCN and still further for $LiClO_4$. The variation of activation energy dE_a/dm is a measure of variation of the ionic mobilities.

At concentration $m = \mu$ all salts in propylene carbonate yield identical activation energies at every temperature (cf. Table 8). As a rule, the maximum specific conductance for an electrolyte solution is obtained when the conductance determining effects have established a critical energy barrier which depends almost exclusively on solvent and temperature.

4.5. Temperature Dependence of μ

The fact that interaction forces are the common basis for the quantities $\kappa_{\max}$ and μ, the linear relationship between them, Equation (4), and the temperature dependence of $\kappa_{\max}$ discussed in 4.4 suggests a functional dependence $\mu = u(T)$. This can be empirically represented by a polynominal series expansion

$$\mu = \alpha + \beta\theta + \gamma\theta^2 \tag{7}$$

with θ as the temperature in the Celsius scale.

The coefficients α, β, and γ of Equation (7) were determined by a least-squares fit and are summarized in Table 9 together with their standard deviations σ_α, σ_β, and σ_γ and the standard deviation σ_{fit} of this fit. In addition, the maximum deviation of the experimental quantity from the calculated one, $\Delta_{\max}\mu$ [%], can be found. As μ is the coordinate of a more or less flat maximum or is even sometimes found from an extrapolation the values μ have relatively large limits of error.

It is interesting to remark that Casteel et al. [33] conclude from their measurements at −50 °C that the maximum of specific conductance for Bu_4NBr in PC should be situated at value $\mu \approx 0.34$ mol kg^{-1}. From our values $\mu = \mu(\theta)$, Table 9, a value $\mu = 0.37$ molkg^{-1} can be extrapolated for Bu_4NPF_6, showing as a further example that anions affect the position of μ only to a small extent.

References

[1] R. Jasinski, in: Ch. W. Tobias (Ed.), Advances in Electrochemistry and Electrochemical Engineering, Vol. 8, Wiley, New York 1971.

[2] R. Jasinski, High Energy Batteries, Plenum Press, New York 1967.

[3] J. Barthel, R. Wachter, and H. J. Gores, in: B. E. Conway and J. O'M. Bockris (Eds.), Modern Aspects of Electrochemistry, Vol. 13, Plenum Press, New York 1979.

[4] K. I. Tikhonov, V. A. Ivanova, and B. A. Ravdel', Zh. Prikl. Khim. *50*, 49 (1977).

[5] E. K. Makarenko, É. A. Mendzheritskii, R. B. Sobolev, Yu. M. Povarov, and P. A. Sereda, Elektrokhimiya *10*, 355 (1974).

[6] R. Jasinski and S. Kirkland, Anal. Chem. *39*, 1663 (1967).

[7] R. M. Fuoss and E. Hirsch, J. Am. Chem. Soc. *82*, 1013 (1960).

[8] M. Salomon, J. Phys. Chem. *73*, 3299 (1969).

[9] T. Fujinaga and K. Izutsu, Pure Appl. Chem. *27*, 273 (1971).

[10] G. Jones and B. C. Bradshaw, J. Am. Chem. Soc. *55*, 1780 (1933).

[11] J. F. Casteel and E. S. Amis, J. Chem. Eng. Data *17*, 55 (1972).

[12] D. F. DeTar, Computer Programs for Chemistry, Vol. 4, Academic Press, New York 1972.

[13] A. S. Househoulder, J. Assoc. Comput. Mach. *5*, 339 (1958).

[14] E. Schollmeyer and W. Seidel, Z. Phys. Chem. (Leipzig) *257*, 1103 (1976).

[15] M. C. Vaidya, H. J. Gores, and J. Barthel (in preparation).

[16] V. M. Valyashko and A. A. Ivanov, Zh. Neorg. Khim. *19*, 2078 (1974).

[17] M. A. Klochko, Dokl. Akad. Nauk SSSR *82*, 261 (1952).

[18] J. Molenat, J. Chim. Phys. *66*, 825 (1969).

[19] M. D. Surova and S. I. Zhdanov, Elektrokhimiya *9*, 350 (1973).

[20] A. Than and E. S. Amis, J. Inorg. Nucl. Chem. *31*, 1685 (1969).

[21] A. F. Kapustinskii, Quart. Rev. *10*, 283 (1956).

[22] H. Seifert, Fortschr. Mineral. *15*, 71 (1931).

[23] V. M. Goldschmitt, Ber. Dtsch. Chem. Ges. *60*, 1263 (1927).

[24] L. Pauling, Natur der Chemischen Bindung, Weinheim 1964.

[25] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Academic Press, New York 1959.

[26] M. L. Jansen and H. L. Yeager, J. Phys. Chem. *77*, 3089 (1973).

[27] N. M. Baron and M. U. Shcherba, Zh. Prikl. Khim. *47*, 1855 (1974).

[28] T. V. Rebagy, J. F. Casteel, and P. G. Sears, J. Electrochem. Soc. *121*, 977 (1974).

[29] J. Barthel, F. Feuerlein, R. Neueder, and F. Straßer, J. Solution Chem. (submitted).

[30] J. Barthel, H. J. Gores, and B. Kaukal (in preparation).

[31] J. Barthel, H. J. Gores, and R. Wachter (in preparation).

[32] L. A. Girifalco, J. Chem. Phys. *23*, 2446 (1955).

[33] J. F. Casteel, J. R. Angel, H. B. McNeeley, and P. G. Sears, J. Electrochem. Soc. *122*, 319 (1975).

[34] R. Wachter and J. Barthel, Ber. Bunsenges. Phys. Chem. *83*, 634 (1979).

(Eingegangen am 6. Juni 1979) E 4345