Conductivity Studies of Tetrabutylammonium Salts in 1-propoxy-2-propanol: Ion-association in Dilute solutions

Bernhard Ramsauer, Monika M. Meier, Roland Neueder and Werner Kunz*

Department of Chemistry and Pharmacy, Institute of Physical and Theoretical Chemistry, University of Regensburg, Germany

* Corresponding author: E-mail: werner.kunz @chemie.uni-regensburg.de
Phone: +49 941 943 4044

Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

The molar conductivities Λ of n-tetrabutylammonium bromide, n-tetrabutylammonium nitrate, n-tetrabutylammonium thiocyanate and n-tetrabutylammonium acetate solutions in 1-propoxy-2-propanol (PnP) have been measured. The temperature and concentration range covered is from 248.15 to 313.15 K and 0.18×10^{-3} to 6.4×10^{-3} mol L^{-1}, respectively. Accurate viscosity, density and permittivity data were additionally determined for the pure solvent. Data analysis was performed on the basis of the low concentration Chemical Model (lcCM), including short-range forces. Values for the limiting molar conductivities (Λ^∞) and the association constants K_A are derived. Thermodynamic results on the ion-pair formation process are discussed in terms of coulombic and non-coulombic forces by an appropriate splitting of the Gibbs free energy.

Keywords: Electrolyte conductivity, tetrabutylammonium salts, chemical model, permittivity, viscosity

1. Introduction

A perusal of old and recent literature shows an increasing and persistent interest in physicochemical and transport properties of electrolytes in pure solvents and/or solventmixtures.[1–5] The studied electrolyte systems cover a large number of solvent classes with regard to their permittivity and ability to act as Lewis-acids and bases and a wide variety of electrolytes (ionophores and ionogens). The advantages of solvent mixtures are manifold, namely adjustable physicochemical properties and flexibility in tackling actual technical problems, competing with solid state ionics and aqueous solutions.

Numerous systematic investigations on aqueous as well as non-aqueous electrolyte systems were carried out in our institute over the last three decades and were subject of a series of publications concering the proper evaluation of ion-ion, ion-solvent and solvent-solvent interactions in solution.[1,6–9] Analysis of the temperature and concentration dependence of electrical conductivity was performed within the framework of the low concentration chemical model introduced by Barthel.[10]

1-propoxy-2-propanol (PnP) classified as a solvo-surfactant[11] was studied along with surfactants and hydrotropes in the solubility of hydrophobic dyes in water. In this context the hydrophobic part of the hydrotrope or cosolvent molecules seems to be the major factor influencing the hydrotropic efficiency. Measurements on the surface properties of aqueous PnP solutions strengthen the assumption of PnP being amphiphilic with characteristic properties of organic solvents and classical surfactants.[12] Very recently some work has been done on the phase behavior of binary mixtures containing PnP and alcohols. Isobaric binary boiling diagrams were recorded and correlated with different models and quantum-chemical calculations.[13]

Thermodynamic investigations of solutions containing PnP have been the focus of some research in the last

few years at our institute: Bauduin et. al. determined the temperature-dependent solubility behavior of different propylene glycol ethers in water and the effect of salts on their phase diagrams.[12,14] There is a great number of patents dealing with propylene glycol ethers and their widespread usage, mainly due to their excellent ability to solubilize organic compounds. Despite the wide range of applications of short-chain propylene glycol monoalkyl ethers in industrial as well as commercial areas, thermodynamic data are either constraint to a relatively small temperature range or not known at all.

Electrical conductivity is a very reliable experimental method, which provides a first basis for a detailed analysis of the intermolecular interactions between ion-solvent and ion-ion. In the present work we report the results of reliable electrical conductivity of dilute solutions of *n*-tetrabutylammonium salts, Bu_4NX (X = Br^-, NO_3^-, SCN^- and OAc^-) covering the temperature range from 248.15 to 313.15 K at electrolyte concentrations from 0.18×10^{-3} to 6.4×10^{-3} mol L^{-1}. Many electrical conductance studies of these salts in aqueous and non-aqueous solvent systems have been reported and allow for a direct comparison of the results among different solvents.[15–19] Nevertheless few reliable information is available on their solvation and association behavior in glycol ether solvents. Because there is also a lack of literature information on the properties of PnP over the desired temperature range, we extended our investigations with the measurements of the viscosity, density and permittivity of PnP. The experimental molar conductivities Λ have been analyzed in terms of the chemical model and temperature-dependent limiting molar conductivities Λ^∞ and association constants K_A are derived. Thermodynamic results on the ion-pair formation are discussed in terms of coulombic and non-coulombic forces by an appropriate splitting of the Gibbs free energy.

2. Experimental Section

2. 1. Materials

PnP was purchased from Aldrich with a stated purity of 99% and stored over 3 Å molecular sieve for a few weeks and subsequently fractionally distilled under reduced pressure. The solvents purity was checked by gas chromatography and its water content by Karl-Fischer titration (mci, model CA-02). Purity is better than 99.9% and also head-space analysis showed no increased amount of volatile impurities. The water content was less than 0.009%. The solvent was stored in a specially designed flask under a protective atmosphere of nitrogen and degassed under vacuum prior to all measurements in the same flask. The specific conductivity of the purified solvent was found to be less than 5.8×10^{-7}S m^{-1}.

Potassium chloride (suprapur, Merck, Germany) was recrystallized twice from distilled water and was dried for 2 days under reduced pressure in the presence of P_2O_5 at 200 °C. Bu_4NBr (puriss), Bu_4NSCN (purum) and Bu_4NOAc were purchased from Sigma-Aldrich, Bu_4NNO_3 (puriss) was purchased from Merck. All salts were dried under reduced pressure (p < 10^{-1} mbar) in the presence of P_2O_5 prior to the preceding purification: all salts were heated in diethylether to reflux and acetone was successively added until complete dissolution. The warm solution was filtered to remove any insoluble constituents. The recrystallization procedure was repeated several times until the mother liquor was colorless. The crystallized salts were dried over P_2O_5 under vacuum. The more or less hygroscopic products were stored in a glove box under nitrogen atmosphere until further use.

Stock solutions of dilute electrolytes were prepared by adding weighed amounts of solvent to the weighed amounts of salts under nitrogen atmosphere. Solutions were prepared and stored in specially designed glass-flasks to avoid any contact with air. All weights were corrected to vacuum.

2. 2. Thermostat

The high-precision thermostat used for measurements of electrical conductivity as well as permittivity is described in details elsewhere.[20,21] A desired temperature within a certain temperature program can be set quickly and reproducible within 10^{-3} K. The temperature control for the viscosity and density measurements was performed by a Julabo cryostat (model FP 40) within a precision of 10^{-2} K. Prior to all measurements the accuracy of temperature was verified by a Pt-100 temperature sensor, which was previously calibrated according to the triple-point of water.

2. 3. Permittivity Measurement

Temperature-dependent permittivity measurements on PnP were executed with a low-frequency (1–15 kHz) capacitance bridge (General Radio, model 1616) in conjunction with a conductance-balancing network and a three-terminal dielectric cell designed for high-precision measurements[8] immersed in a thermostat.

The cell constant ($C_0 = C_s / \varepsilon_s$ = 11.1554 pF, 298.15 K) was determined from 248.15 to 313.15 K by measuring the capacitance of the cell filled with pure and dry argon (99.9996%), for which temperature- and pressure-dependent data are available in the literature.[22] The temperature coefficient of the cell constant was 1.8×10^{-4} pF K^{-1}. The permittivity of the sample was calculated from the ratio of the capacitance of the dielectric cell filled with the sample to that of the cell filled with dry argon. Great care was taken in the process of filling the cell with gaseous or degassed liquid samples in an inert atmosphere of argon. Comparisons with well-known permittivity data on ethanol and ethylacetate show an agreement within 0.3%.

2. 4. Viscosity Measurement

The temperature-dependent viscosities of the pure solvent were determined with the help of an Ubbelohde viscometer placed in a dewar flask connected to the Julabo cryomat. The flow time was detected by a control unit using photodiodes and optical fibber bundles for transmission of the signal to the viscometer, which was filled with the test solution under a protective atmosphere of nitrogen. The apparatus and experimental procedure is described in more detail elsewhere.[23] Each measurement was automatically repeated at least twenty times and yielded a reproducibility of the flow time of less than 0.04%. Taking into account the precision of the reference solution data and the reproducibility of measurements on different samples, an accuracy of better than 0.9% is obtained.

Table 1. Permittivity, Viscosity and Density of 1-propoxy-2-propanol.

$\dfrac{T}{K}$	ϵ	$\dfrac{\eta \cdot 10^3}{Pa\ s}$	$\dfrac{d}{kg\ m^{-3}}$
248.15	11.879	22.058	926.959
258.15	11.056	11.985	917.780
268.15	10.333	7.2060	908.611
278.15	9.6913	4.6948	899.434
288.15	9.1279	3.2596	890.228
298.15	8.6235	2.3798	880.973
308.15	8.1734	1.8074	871.648
313.15	7.9580	1.5942	866.953

2. 5. Density Measurements

The densities of the solvent and electrolyte solutions were determined with an accuracy of 4×10^{-5} g cm^{-3} using a vibrational tube densitymeter (Anton Paar equipment, DMA 60, DMA 602 HT). In the concentration range of this study a linear change of density d with increasing salt content was assumed, $d = d_S + Dm$. The temperature-independent density gradient D of all solutions was determined by the method of Kratky et. al.[24] Results of pure solvent properties at different temperatures are given in Table 1. The temperature dependence of the measured quantities can be expressed in terms of the following equations:

$$\epsilon = \frac{a_0}{T^2} + \frac{a_1}{T} + a_2 + a_3 T \tag{1}$$

$$\ln\left(\frac{\eta}{10^{-3}\ Pa\ s}\right) = \frac{a_0}{T^2} + \frac{a_1}{T} + a_2 + a_3 T \tag{2}$$

$$\frac{d}{kg\ m^{-3}} = a_0 + a_1(T - 298.15) + \\ + a_2(T - 298.15)^2 + a_3(T - 298.15)^3 \tag{3}$$

Numerical values of the parameters of Eqs. (1–3) were obtained by least-square method and are given in Table 2. The extended temperature range of the density data represented by Eq. (3) is based on experimental values determined for a different investigation. The density of PnP is also reported in the literature for different temperatures and pressures. A direct comparison of d_{PnP} values obtained from Eq. (3) of the present work with those from Lugo[25] shows close agreement within 0.09%. Densities at three temperatures (298.15, 308.15 and 318.15) K reported by Ku[26] are also consistent with values evaluated by our polynomial (deviation < 0.04%).

2. 6. Electrical Conductivity Measurement

The electrical conductivities of dilute solutions were determined with the help of a three-electrode cell, with an arrangement of three compartments of different cell constants C connected to the same mixing chamber ($C_1 = 0.8760$ m^{-1}, $C_2 = 11.614$ m^{-1}, $C_3 = 2.1280 \times 10^2$ m^{-1}). Measurements in the region of optimal resistance values can be performed with all electrolyte concentrations. The cell was calibrated with dilute aqueous potassium chloride solutions.[27]

The measurements were executed for each temperature program according to the method of isologues sections practised in our laboratory.[28] At the beginning the cell was filled with a weighed amount of previously degassed solvent (approximately 300 mL). After measurement of its conductivity at every temperature of the program (from 248.15 to 313.15 K), needed for the calculation of the solvent corrections, weighed amounts of a stock solution were added in steps with the help of a gas-tight syringe and the temperature program was executed after every addition. A steady atmosphere of dry nitrogen during the filling and measurements prohibits the contact of the solution with air and moisture. Taking into account all sources of errors (temperature, concentration, resistance measurement and cell calibration), the mean error of electrical conductivity is estimated to be less than 0.1%. Table 3 shows the results of the conductance measurements; as usual, all conductance values quoted are the results of extrapolation to infinite frequency from measurements in the frequency interval 480 to 10000 Hz.[32]

Table 2. Values of the parameters of polynomial Eqs. (1–3).

Eq.	Permittivity (1)	Viscosity (2)	Density (3)
T/K	248.15– 313.15	248.15–313.15	248.15–403.15
a_0	$1.215\ 81 \times 10^6$	$2.220\ 23 \times 10^6$	880.973
a_1	–5391.96	–17 131.1	–0.928 662
a_2	18.0014	42.6897	$-3.486\ 96 \times 10^{-4}$
a_3	–0.016 671 6	–0.054 498 6	$-3.366\ 55 \times 10^{-6}$
σ	2.6×10^{-3}	2.8×10^{-5}	0.46

Table 3. Experimental electrical conductivities of Bu$_4$NX (X = Br$^-$, NO$_3^-$, SCN$^-$ and OAc$^-$) in PnP as functions of concentration and temperature form 248.15 to 313.15 K.

$\tilde{m} \times 10^3$ mol kg^{-1}	Molar conductances, Λ/S cm^2 mol^{-1}							
	248.15 K	**258.15 K**	**268.15 K**	**278.15 K**	**288.15 K**	**298.15 K**	**308.15 K**	**313.15 K**
Bu$_4$NBr: M_E = 322.37; d_E = 1.13[29]; $(a_+ + a_-)$ = 0.690[30]; D = 54								
0.4801	0.36133	0.58000	0.84203	1.15338	1.49642	1.84592	2.19167	2.36463
1.0852	0.26201	0.42045	0.61235	0.83416	1.07294	1.32430	1.57361	1.69790
1.7047	0.22098	0.35149	0.51565	0.70055	0.90283	1.11454	1.32450	1.42885
2.4060	0.19520	0.31119	0.45387	0.61891	0.79860	0.98604	1.17190	1.26459
3.1406	0.17722	0.28379	0.41405	0.56535	0.73020	0.90247	1.07317	1.15828
3.9287	0.16423	0.26340	0.38562	0.52733	0.68122	0.84280	1.00292	1.08297
5.0176	0.15312	0.24423	0.35905	0.49113	0.63628	0.78804	0.93901	1.01450
6.3808	0.14269	0.22868	0.33689	0.46249	0.59977	0.74411	0.88790	0.96013
Bu$_4$NNO$_3$: M_E = 304.48; d_E = 0.909[31]; $(a_+ + a_-)$ = 0.714[30]; D = 33								
0.2399	0.60529	0.97600	1.43208	1.96383	2.52104	3.15034	3.74729	4.04153
0.7041	0.40078	0.63907	0.92656	1.26613	1.62612	2.00586	2.38386	2.57309
1.2054	0.32482	0.51574	0.75437	1.02312	1.31657	1.62325	1.92769	2.07998
1.8521	0.27743	0.44044	0.64061	0.87105	1.12187	1.38387	1.64280	1.77259
2.3621	0.25301	0.40389	0.58661	0.79936	1.02884	1.26941	1.50793	1.62736
3.2037	0.22791	0.36237	0.52921	0.72168	0.92983	1.14819	1.36504	1.47400
4.0488	0.21179	0.33602	0.49138	0.67063	0.86518	1.06950	1.27286	1.37493
4.9938	0.19728	0.31508	0.46150	0.63126	0.81557	1.00962	1.20320	1.30048
Bu$_4$NOAc: M_E = 301.51; d_E = 1.0; $(a_+ + a_-)$ = 0.764[30]; D = 21								
0.1986	0.69124	1.05870	1.55098	2.10876	2.71213	3.33023	3.89982	4.17488
0.5359	0.46558	0.74252	1.07435	1.45459	1.83944	2.22465	2.59040	2.77667
0.9315	0.38075	0.60353	0.87278	1.16763	1.47486	1.78206	2.06908	2.20535
1.5362	0.31855	0.50162	0.71864	0.96059	1.21168	1.46077	1.69235	1.80195
2.3354	0.27091	0.42788	0.61299	0.81975	1.03296	1.24348	1.43890	1.53106
3.1197	0.24632	0.38490	0.55225	0.73781	0.92889	1.11757	1.29215	1.37436
4.1365	0.22249	0.34891	0.50080	0.66873	0.84165	1.01212	1.17000	1.24422
5.0978	0.20701	0.32528	0.46676	0.62356	0.78549	0.94417	1.09127	1.16032
7.2484	0.18458	0.29094	0.41837	0.55919	0.70461	0.84778	0.98039	1.04259
Bu$_4$NSCN: M_E = 300.55; d_E = 1.0; $(a_+ + a_-)$ = 0.831[30]; D = 21								
0.3785	0.46851	0.77760	1.14738	1.58448	2.07488	2.58808	3.10643	3.37052
0.9332	0.30882	0.54729	0.80683	1.10456	1.43339	1.78632	2.14233	2.32326
1.6560	0.22983	0.43873	0.64332	0.88464	1.15156	1.43447	1.72044	1.86503
2.6844	0.17642	0.36688	0.54083	0.74538	0.97078	1.21057	1.45245	1.57559
3.4081	0.16448	0.33764	0.49915	0.68940	0.89881	1.12206	1.34762	1.46210
4.6053	0.14097	0.30738	0.45563	0.63031	0.82308	1.02890	1.23749	1.34372
5.6263	0.17940	0.29022	0.43112	0.59724	0.78091	0.97767	1.17739	1.27920
7.1256	0.16774	0.27251	0.40606	0.56421	0.73952	0.92783	1.11939	1.21744

[a] Units: molar mass, M_E, g mol^{-1}; density, d_E, g cm^{-3}; distance parameter, a, nm; density gradient, D, kg^2 m^{-3} mol^{-1}.

The molar concentrations c are obtained from the experimentally given temperatureindependent molonities $\tilde{m}$ with the help of the relationships

$$c = \tilde{m}(d_S + \tilde{m}D) \tag{4}$$

$$\tilde{m}_n = \tilde{m}^* \cdot \frac{\sum_{i=1}^n g_i}{G + \sum_{i=1}^n g_i}, \tag{5}$$

where G is the weighed amount of solvent, $\tilde{m}$ the molonity of stock solution and g_i the mass of stock solution added to the solvent at each step.

3 Data Analysis

The evaluation of measured conductivity data in the framework of the lcCM[33] model is based on the following set of equations:

$$\frac{\Lambda}{\alpha} = \Lambda^\infty - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + \\ + J_1(R)\alpha c - J_2(R)(\alpha c)^{3/2} \tag{6}$$

$$K_A = \frac{1 - \alpha}{\alpha^2 c y_\pm'^2}; \qquad y_\pm' = \exp\left(-\frac{\kappa q}{1 + \kappa R}\right) \tag{7a,b}$$

$$K_A = 4\pi N_A \int_a^R r^2 \exp\left(\frac{2q}{r} - \frac{W^*_{+-}}{kT}\right) dr \qquad (8)$$

Λ and Λ^∞ are the molar conductivities at molarity c and infinite dilution, respectively, $(1-\alpha)$ is the fraction of oppositely charged ions acting as ion pairs, K_A is the equilibrium constant of the ion-pair formation process in case the activity coefficient of the ion pair is approximated by unity in dilute solution. $y'_\pm$ the mean activity coefficient of the free ions. The Debye parameter κ (reciprocal radius of the ion cloud) is given by:

$$\kappa^2 = \frac{N_A e^2}{\epsilon_0 \epsilon k T} \sum (\alpha c_j) z_j^2; \quad q = \frac{e^2 |z_+ z_-|}{8\pi\epsilon_0 \epsilon k T} \qquad (9a,b)$$

q is the Bjerrum parameter, e is the proton charge, ε_0 is the permittivity of vacuum. All other symbols have their usual meaning.

A detailed form of the parameters in Eq. (6) can be found elsewhere.[34] The limiting slope S and parameter E are dependent only on pure solvent properties and the ion charge. J_1 and J_2 show additional dependence on the distance parameter R representing the distance to which oppositely charged ions can approach as freely moving particles in the solution. This distance parameter is also set as the upper limit of association, within which a paired state of oppositely charged ions, the so-called ion pair, suppresses long-range interactions with other ions. The ion pairs are not participating in the charge transport.

Data analysis was carried out with the help of a set of equations (6) (7) (9) by a leastsquares method. The method used, applicable to accurate conductivity data, is a three parameter fit yielding Λ^∞, J_2, and K_A with calculated values of S and E, and a preset distance parameter R. This distance parameter is chosen by chemical evidence, mostly as $R = a + s$, where s is the length of an oriented solvent molecule and a is the sum of the ionic radii of cation and anion. In this study we fixed the distance parameter R at R /nm = a + 0.73. The length of an orientated PnP molecule is estimated by comparison with different molecules of the same class. Data for distance parameters and ionic radii of the ions under investigations are taken from Ref. [30] and given in Table 3.

4 Results and Discussion

The molar conductivities of dilute electrolytic solutions of Bu$_4$NBr, Bu$_4$NNO$_3$, Bu$_4$NOAc and Bu$_4$NSCN in 1-propoxy-2-propanol over the given temperature range are presented in Table 3 and analyzed with the procedure described above. Best values of Λ^∞, K_A and J_2 are obtained by minimizing the standard deviation σ_Λ, which is defined as the difference between the calculated Λ_{fit} and experimental Λ_{exp} conductivity values:

$$\sigma_\Lambda = \sqrt{\sum_{j=1}^{n} [\Lambda_{j,fit} - \Lambda_{j,exp}]^2 / (N_p - 3)} \qquad (10)$$

with N_p being the number of measuring points. No significant changes in σ_Λ could be observed when the values of

Table 4: Limiting molar conductivities Λ^∞, association constants K_A, Walden products ($W = \eta\Lambda^\infty$) and standard deviations (σ_Λ) in the temperature range from 248.15 K to 313.15 K

T	Λ^∞/S cm^2 mol^{-1}				W/10^{-6} S kg m s^{-1} mol^{-1}			
K	**Bu$_4$NBr**	**Bu$_4$NNO$_3$**	**Bu$_4$NOAc**	**Bu$_4$NSCN**	**Bu$_4$NBr**	**Bu$_4$NNO$_3$**	**Bu$_4$NOAc**	**Bu$_4$NSCN**
248.15	1.65 ± 0.06	1.96 ± 0.04	1.41[a]	1.77[a]	3.6	4.3	3.1[a]	3.9[a]
258.15	3.05 ± 0.20	3.69 ± 0.08	2.61 ± 0.01	3.26 ± 0.08	3.7	4.4	3.1	3.9
268.15	4.80 ± 0.14	6.18 ± 0.16	4.21 ± 0.04	5.21 ± 0.25	2.9	4.5	3.0	3.8
278.15	7.70 ± 0.19	9.74 ± 0.17	6.23 ± 0.08	8.34 ± 0.13	3.0	4.6	2.9	3.9
288.15	11.23 ± 0.66	15.05 ± 0.20	9.25 ± 0.05	13.91 ± 0.60	3.7	4.0	3.0	4.5
298.15	14.63 ± 0.53	20.77 ± 0.84	13.34 ± 0.23	18.90 ± 0.72	3.5	4.9	3.2	4.5
308.15	17.19 ± 0.23	25.96 ± 0.88	17.19 ± 0.32	24.22 ± 0.76	3.1	4.7	3.1	4.4
313.15	19.09 ± 0.47	28.04 ± 0.79	18.96 ± 0.20	27.75 ± 0.94	3.0	4.5	3.0	4.4

T	K_A/10^4 L mol^{-1}				σ_Λ/10^{-4}			
K	**Bu4NBr**	**Bu4NNO3**	**Bu4NOAc**	**Bu4NSCN**	**Bu4NBr**	**Bu4NNO3**	**Bu4NOAc**	**Bu4NSCN**
248.15	5.05 ± 0.45	4.26 ± 0.21	1.54 ± 0.06[a]	4.49 ± 0.53[a]	0.001	0.001	0.012	0.026
258.15	6.97 ± 1.02	6.19 ± 0.32	2.46 ± 0.03	5.20 ± 0.30	0.001	0.001	0.001	0.001
268.15	6.03 ± 0.39	8.52 ± 0.50	3.20 ± 0.08	6.28 ± 0.70	0.001	0.001	0.001	0.002
278.15	8.63 ± 0.48	11.72 ± 0.45	3.97 ± 0.13	8.83 ± 0.31	0.001	0.001	0.002	0.001
288.15	15.38 ± 1.95	11.91 ± 0.35	5.72 ± 0.07	15.13 ± 0.14	0.001	0.001	0.001	0.002
298.15	17.33 ± 1.33	22.09 ± 1.91	8.46 ± 0.34	18.24 ± 1.48	0.001	0.003	0.003	0.002
308.15	16.94 ± 0.63	24.61 ± 1.79	10.56 ± 0.45	21.04 ± 1.41	0.001	0.002	0.003	0.002
313.15	18.03 ± 0.96	24.71 ± 1.50	11.30 ± 0.27	23.65 ± 1.68	0.001	0.002	0.002	0.002

[a] calculations were performed with extrapolated values for W providing a constant Λ^∞

the parameters a and R were varied from 6.5 to 7.6 Å and 4.0 to 7.3 Å, respectively in a series of least-square calculations. Thus values for a and R given in the previous section are used.

The derived values of limiting molar conductance Λ^∞ (1%) and K_A (8%) of the investigated salts in PnP are reported in Table 4 together with the standard deviations σ_Λ. Due to the large association constants in PnP the molar conductance increase rapidly at low concentrations (c.f. Fig. 1). This leads to uncertainties in Λ^∞ which are admittedly larger than the corresponding values from conductivity data in usual protic or aprotic solvents.[35–37] For Bu₄NSCN and Bu₄NOAc the results at 248.15 K are based on calculations with fixed Λ^∞ derived from the constant Walden product of the higher temperatures (c.f. Table 4). Representative plots of $\Lambda = f(c^{1/2})$ for the solutions of Bu₄NOAc in PnP between 248.15 and 313.15 K are given in Fig. 1. All other investigated systems show similar concentration dependences.
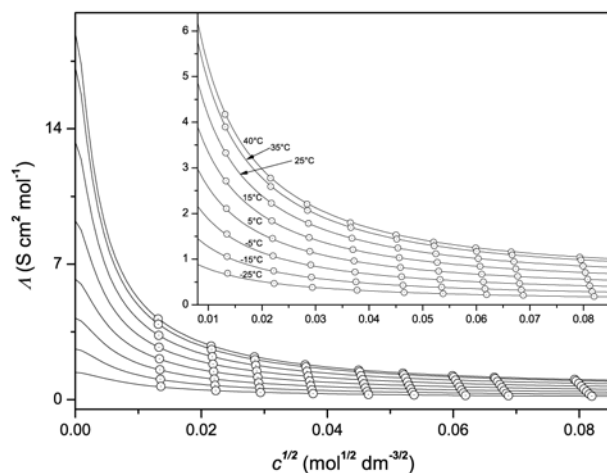
Figure 1. Molar conductivities of solutions of Bu₄NOAc in PnP from 248.15 to 313.15 K in the concentration range 0.0002 < c = mol dm⁻³ < 0.0064. Full lines: lcCM calculations.

4. 1. Association Constants

Due to the relatively low permittivity of PnP, classified according to *Barthel* [10] as a neutral, amphiprotic solvent, the values for the association constants in Table 4 are very high when compared to different alcohols, ketones and esters.[30] Hence all salts are considered to be highly associated in PnP (weak electrolytes). As seen in Table 4, the difference in the association constants of the bromide, nitrate and thiocyanate salts, however, is far less distinct than observed in solvating type solvents like 1,1,1,3,3,3-Hexafluoro-2-propanol[38] and aprotic acetone[39]; for example in acetone, the association constant of NBu₄⁺ salts is 435 for the chloride, 264 for the bromide and 143 for the iodide. Only Bu₄NOAc shows considerable smaller association in the present study.

The solutions show a strong variance of association constant with temperature, an effect much more pronounced in solvents with small ε. The change of K_A with temperature for all salts is described by a positive temperature coefficient $dK_A / dT > 0$. There is no indication for a minimum, which is characteristic for tetraalkylammonium salts in other solvents.[19,40] Inspection of the variation of K_A with the permittivity of the solvent at different temperatures shows a regular behavior, e.g. log K_A increases monotonically with $(\varepsilon T)^{-1}$ due to the decreasing permittivity of PnP with increasing temperature. The small effect of the anion on the association pattern in tetrabutylammonium salts is best seen at temperatures above 0 °C. For a given cation we found the order: OAc⁻ < Br⁻ ≤ SCN⁻ < NO₃⁻ which is not in accordance to the sequence of the anions crystallographic radii Br⁻ < NO₃⁻ < OAc⁻ < SCN⁻. Increasing associations as the crystallographic size of the anions decrease was found elsewhere for electrolyte solutions of tetraalkylammonium salts in nonhydrogen-bonding solvents like acetone, nitrobenzene and acetonitrile.[15,40] The reverse behavior is reported for the same salts in water and some short-chain alcohols.[19,41,42] Despite the higher errors of K_A in PnP solutions, neither trend of size-effect is evident from the presented results. Hence, an attempt is made to deduce some quantitative information on the hydrodynamic (solvated) radii of the ions at infinite dilution, estimated from Waldens product ($W = \eta\Lambda^\infty$), see Table 4. Given that for tetraalkylammonium salts the cations are coordinately saturated, the occurrence of specific solute-solvent interactions is assumed to be restricted to interactions between the anion and the solvent molecules.[43] As a result any change in Λ^∞ amongst the four investigated salts can be assigned to differences in r^-. In doing so an order of increasing W and Λ^∞ is related to a decreasing order of the solvated anions radii.

An inspection of W reveals the following sequence of r^-: NO₃⁻ < SCN⁻ < Br⁻ < OAc⁻. Together with the opposite trend in K_A it permits us to show an increasing association with decreasing radii of the solvated anions. Absolute values for r_i can not be deduced, as transference numbers, necessary to split up into contributions from the cation and anion are missing.

A comparison of the K_A values obtained in the present work with literature values is not possible due to lack of any experimental data. A comparison to dichloromethane, a solvent of almost equal dielectric constant ($\varepsilon^{25°C} = 8.93$)[44] can be made for Bu₄NBr, Bu₄NNO₃ and Bu₄NSCN at 298.15 K[45], which show association constants almost one order of magnitude lower than those in PnP. Since experimental data are not given in the literature, re-evaluation of K_A using Eqs. (6)–(9) could not be executed and it could not be excluded that these differences arise partially from different calculation procedure. Nevertheless the increased association of NBu₄⁺ salts in PnP may be due to different short range forces, such as H-bonding, which produce different competing effects of ion
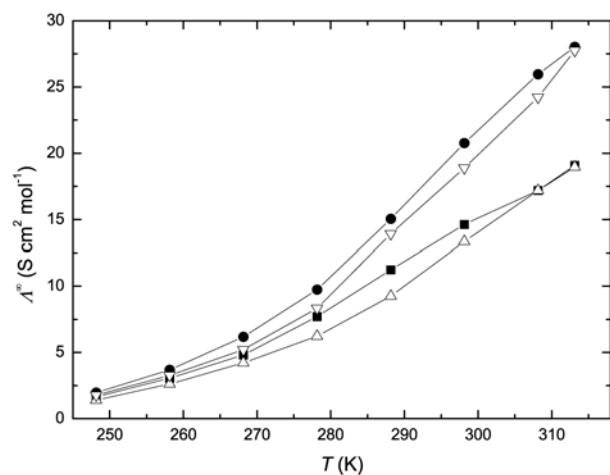
Figure 2. Plot of the limiting molar conductivities Λ^∞ vs. temperature for Bu$_4$NNO$_3$ (●), Bu$_4$NSCN (▽), Bu$_4$NBr (■) and Bu$_4$NOAc (△) in the temperature range from 248.15 to 313.15 K.

solvation and association, apart from purely "electrostatic" behavior.

4. 2. Limiting Molar Conductivities

Table 4 shows the limiting electrolyte conductances obtained from the data in Table 3 with the help of three parameter fits. As expected within the framework of electrolyte theory, the Λ^∞ values of four salts in PnP are not very sensitive to the choice of the distance parameter R (agreement within less than 1% in the range of R given above).

Furthermore, Λ^∞ values increase monotonically with the increase in temperature due to the increase of the mobility of the free ions, as can be seen in Fig. 2. The values of Λ^∞ vary almost inversely with the viscosity of the solvent medium and the Walden product ($\Lambda^\infty\eta$) is nearly constant and independent of the temperature (Table 4). The results indicate that the mobility of the free ions is completely controlled by the bulk viscosity.

The limiting conductivity can be interpreted as a quantity free of ion-ion interactions, which describes the mechanism of ionic migration in the solvent. Thus it permits statements on ion-solvent interactions. The temperature dependence of Λ^∞ can be approximated in the framework of the kinetic theory of conductance[46,47] by the equation

$$\ln \Lambda^\infty + \frac{2}{3}\ln d = -\frac{\Delta H^\ddagger}{RT} + B \qquad (11)$$

which connects the enthalpy of activation of the charge transport $\Delta H^\ddagger$ to the limiting conductance Λ^∞ and the solvent density d. B is the integration constant. Values for $\Delta H^\ddagger$ from the slope of the function at the left-hand side of Eq. (11) versus the inverse temperature are tabulated in Table 5. Within a reasonable limit of error, $\Delta H^\ddagger$ for four

salts are roughly equal, indicating that the energy needed for the rearrangement of ions and solvent molecules during the charge transport process mainly depends on the properties of the solvent. Needless to say that a discussion of the limiting conductance based on the limiting ionic conductances would be more fruitful with regard to the ion-specific solvation, mobility and size.

Table 5. Enthalpy of activation of the charge transport, $\Delta H^\ddagger$, in the temperature range from 248.15 to 313.15 K.

Salt	$\dfrac{\Delta H^\ddagger}{\text{kJ mol}^{-1}}$
Bu$_4$NBr	24.3
Bu$_4$NNO$_3$	25.9
Bu$_4$NOAc	25.3
Bu$_4$NSCN	27.1

This contribution is intended as a first basic study of conductivity phenomena in PnP and further investigations will be necessary to make the split into individual ion contributions.

4. 3. Thermodynamics of the Ion-Pair Process

The temperature-dependent equilibrium constants K_A for the ion association reaction allows the investigation of the thermodynamics of this process. Consequently, the standard Gibbs energy ΔG_A^0 is calculated at all temperatures according to

$$\Delta G_A^0(T) = -RT \ln K_A(T) \qquad (12)$$

The temperature dependence of $\Delta G_A^0(T)$ is expressed with the help of a linear function

$$\Delta G_A^0(T) = A_0 + A_1(298.15 - T) \qquad (13)$$

Discussion of ion-pair equilibria is based on the temperature dependence of $\Delta G_A^0(T)$, leading to the enthalpy ΔH_A^0 and entropy ΔS_A^0, as

$$\Delta S_A^0(T) = -\left(\frac{\partial \Delta G_A^0(T)}{\partial T}\right)_p = A_1 \qquad (14)$$

$$\Delta H_A^0(T) = \Delta G_A^0(T) + T\Delta S_A^0(T) = A_0 + 298.15A_1 \qquad (15)$$

and summarized in Fig. 3. From the ΔG_A^0 values at all temperatures of the program the coefficients A_0 and A_1 were obtained by the usual least squares methods and are given in Table 6. The values of ΔG_A^0 and ΔS_A^0 at 298.15 K are $\Delta G_A^0 = A_0$ and $\Delta S_A^0 = A_1$. The positive ΔH_A^0 values indicate that the process of the ion-pair formation is endothermic in na-

ture and energy consuming. The enthalpic contributions appear not to vary much with temperature. Because of the choice of a linear temperature-dependence of ΔG_A^0 the temperature-dependence of the entropy of ion-pairing is neglected yielding constant ΔS_A^0 values. Based on that fact, presumably the number of the degrees of freedom does not change considerably due to the weak solvation of the ions. Nevertheless, the $T\Delta S_A^0$ term is sufficiently positive to compensate the positive contribution of the ΔH_A^0 term. Consequently, the standard Gibbs free energy is negative and the ion-association process can be recognized as an exergonic process. The increase of the temperature leads to more negative ΔG_A^0 values indicating that the ion-asso-

ciation equilibrium is shifted toward ion-pairs at elevated temperatures.

According to Eq. (8) the Gibbs' energy of association can be split in two parts, one containing contributions of coulombic ion-ion-interactions

$$\exp\left[\frac{-\Delta G_A^{coul}}{RT}\right] = K_A^{coul} = 4\pi N_A \int_a^R r^2 \exp\left[\frac{2q}{r}\right] dr \quad (16)$$

and a non-coulombic part ($\Delta G_A^* = N_A W_{+-}^*$). Analysis of the temperature dependence of the non-coulombic contribution gives values of $\Delta G_A^* < 0$, whilst $\Delta H_A^*, \Delta S_A^* > 0$ and
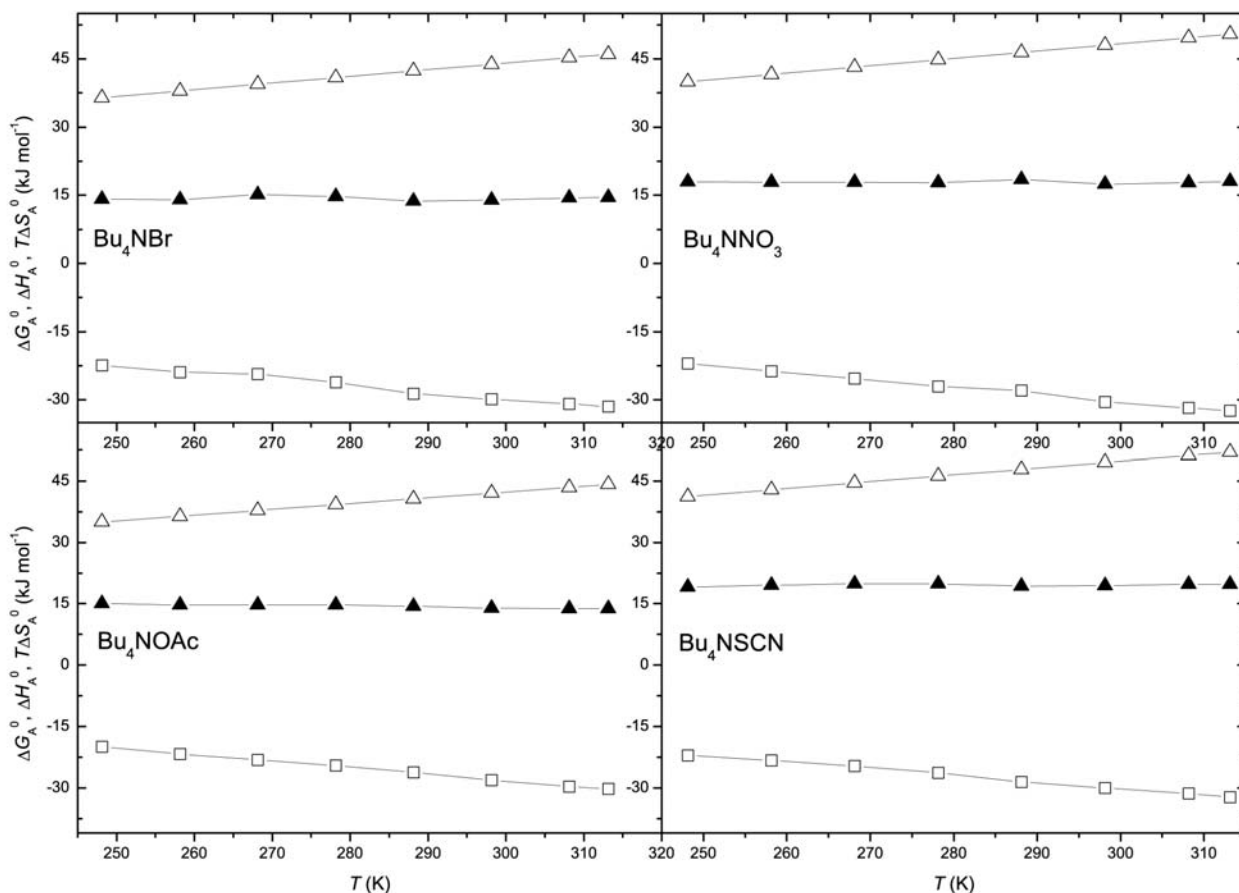

Figure 3. Temperature dependence of thermodynamic functions of association. (□) ΔG_A^0, (△) TΔS_A^0, (▲) ΔH_A^0.

Table 6. Coefficients of equation $\Delta G_A^0(T) = A_0 + A_1(298.15 - T)$ and ΔH_A^0 (298.15 K) for the systems under investigation.

	$A_0 = \Delta G_A^0(298.15K)$ kJ mol^{-1}	$A_1 = \Delta S_A^0 (298.15K)$ kJ mol^{-1} K^{-1}	$\Delta H_A^0 (298.15K)$ kJ mol^{-1} K^{-1}
Bu$_4$NBr	−29.5	+0.147	+14.3
Bu$_4$NNO3	−30.1	+0.161	+17.9
Bu$_4$NOAc	−27.9	+0.161	+14.1
Bu$_4$NSCN	−29.8	+0.161	+19.6

small for all salts. There is no pronounced change of enthalpy and entropy with temperature. As ΔG_A^* constitutes only a minor part of ΔG_A^0, we suggest a preference of electrostatic interactions contributing to the association process.

5. Conclusions

There has been so far no report on the conductivity study of tetrabutylammonium salts in 1-propoxy-2-propanol. In a first experimental attempt comprising Bu_4NBr, Bu_4NNO_3, Bu_4NSCN and Bu_4NOAc, results provide information on the effect of the physical properties of the solvent medium on the association and the transport properties of the electrolyte. The investigation has been performed through the determination of the limiting molar conductivity Λ^∞, the association constant K_A, and the thermodynamic quantities of the ion association process as well as the Eyring's activation enthalpy of the ionic movement $\Delta H^\ddagger$. Conductivity studies were accompanied with precise measurements of pure solvents properties like relative permittivity ε, density d, and dynamic viscosity η, covering the range of temperatures between 248.15 and 313.15 K. On the basis of the results discussed the following conclusions can be drawn.

The K_A and ΔG_A^0 values of the ion-association process indicate that the association of the investigated electrolytes increase with the rise of temperature followed by the decrease of the dielectric constant of the solvent medium. All salts indicate a high degree of association. The Walden product ($W = \eta \Lambda^\infty$) does not show a dependence on temperature confirming that the ions are only weakly solvated. The constancy of the ΔS_A^0 values in the whole temperature range supports the last conclusion.

6. Acknowledgements

7. References

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Povzetek

Določili smo molske prevodnosti Λ n-tetrabutilamonijevega bromida, n-tetrabutilamonijevega nitrata, n-tetrabutilamonijevega tiocianata in n-tetrabutilamonijevega acetata v razredčenih raztopinah ($0.18 \times 10^{-3} \leq$ c/mol L$^{-1} \leq 6.4 \times 10^{-3}$) v 1-propoksi-2-propanolu (PnP) v temperaturnem območju med 248.15 in 313.15 K. V tem temperaturnem območju smo izmerili tudi lastnosti čistega topila (viskoznost, gostoto, dielektrično konstanto). Ti podatki so potrebni za analizo vrednosti molskih prevodnosti s pomočjo kemijskega modela za razredčene raztopine, katere rezultat so vrednosti molskih prevodnosti pri neskončnem razredčenju, Λ^{∞}, ter konstant asociacije, K_A. Temperaturna odvisnost K_A omogoča termodinamsko analizo procesa asociacije ionov, ki je posledica coulombskih in necoulombskih interakcij.