Association of hydrophobic ions in aqueous solution: A conductometric study of symmetrical tetraalkylammonium cyclohexylsulfamates ☆

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ABSTRACT

Tetraalkylammonium salts of cyclohexylsulfamic acid were used as model systems to study the ion-pairing process of hydrophobic ions.

The electric conductivities of aqueous solutions of tetramethyl-, tetraethyl-, tetrapropyl-, tetrabutyl- and tetrapentylammonium salts of cyclohexylsulfamic acid were measured from 278.15 K to 303.15 K (in steps of 5 K) in the concentration range $\sim 0.2 \cdot 10^{-3} < c$ (mol dm^{-3}) $< \sim 6 \cdot 10^{-3}$. Evaluation of the limiting molar conductivity Λ^∞ and the association constant K_A was based on the low concentration chemical model of electrolyte solutions, that includes short-range forces. From the temperature dependence of the limiting molar conductivities Eyring's enthalpy of activation of charge transport was estimated. The standard Gibbs free energy, enthalpy and entropy of the ion-pairing process were calculated from the temperature dependence of the ion-association constants. It was found that in the investigated systems the ion association can be interpreted as strongly enthalpy driven process that does not include any important release of water molecules from the hydration shells of ions. The non-Coulombic contribution to the Gibbs free energy was evident and favours the association process.

1. Introduction

It is well known that tetraalkylammonium (TAA) salts dissolved in water undergo hydrophobic hydration [1], therefore they have been still extensively used as model systems for the investigation of hydrophobic phenomena and various types of interaction. The symmetrical TAA ions (R_4N^+) have long been used as good examples of spherical ions having a large variation in size [2] and ability to form hydrophobic ion pairs with organic and inorganic ions in water.

Evans and Kay [3] studied the conductance behaviour of symmetrical tetraalkylammonium halides in aqueous solutions and found out that the ion association is more expressed for iodides than for other investigated salts. The investigation of hydration and association in solutions of TAA iodides, carried out by Kuba and Hawlicka [4] applying electrical conductivity measurements also, indicates a weak but perceivable association of opposite ions in aqueous solutions. The values reported for the association constant, K_A, range from 5.6 for tetramethylammonium iodide (Me$_4$NI) to 15.3 for tetrabutylammonium iodide (Bu$_4$NI) showing that the size of cation influences the ion-pairing process essentially. K_A is considerably higher than those

obtained by Buchner et al. [5] for bromide analogues by dielectric spectroscopy (K_A (Me$_4$NBr) = 3.0, K_A (Bu$_4$NBr) = 5.6). Despite the fact that the difference could be ascribed to different experimental techniques and models used in these works, it leads to the assumptions that for TAA salts ion association is affected by the size and nature of cation and anion as well.

Recently, the experimental and theoretical studies of the association between TAA salts of increasing chain length with an anionic surfactant, sodium dodecyl sulfate (SDS), in water have been carried out by Pradines et al. [6,7]. The obtained values of K_A are between 24 for Me$_4$NDS and $1.6 \cdot 10^4$ for Bu$_4$NDS. Such an increase of the associability with chain length shows a predominance of the hydrophobic interactions between the alkyl chain of the R_4N^+ cations and the long chain of DS$^-$ over the electrostatic effect.

Thus, in these studies two types of anions were taking into account: relatively small halide anions on one and a large dodecyl sulfate on the other side and therefore the difference in the size between anions and cations was quite big.

The present work deals with the TAA cyclohexylsulfamates, i.e. with salts where both of the ions, cation and anion, undergo hydrophobic hydration and possess quite comparable radii [8].

The electric conductivities of aqueous solutions of tetramethyl-, tetraethyl-, tetrapropyl-, tetrabutyl- and tetrapentylammonium salts of cyclohexylsulfamic acid were measured from 278.15 K to 308.15 K (in steps of 5 K) in the concentration range $\sim 0.2 \cdot 10^{-3} < c$

(mol dm^{-3}) < ~6·10^{-3}. The experimental data were treated in the framework of the low concentration chemical model (lcCM) [9] yielding the limiting molar conductivity Λ^∞ and the association constant K_A. Using the known data of the limiting conductivities of cyclohexylsulfamate anion [10] the limiting conductivities of the tetraalkylammonium ions were evaluated at all temperatures. From the temperature dependence of the limiting molar conductivities Eyring's enthalpy of activation of charge transport was estimated. The standard Gibbs energy, enthalpy and entropy of the ion-pairing process were calculated from the temperature dependence of the ion-association constants. Finally, the non-Coulombic contributions to the Gibbs free energy were estimated.

2. Experimental

2.1. Materials

All tetraalkylammonium salts investigated, i.e. tetramethyl- (Me$_4$NCy), tetraethyl- (Et$_4$NCy), tetrapropyl- (Pr$_4$NCy), tetrabutyl- (Bu$_4$NCy), and tetrapentylammonium cyclohexylsulfamates (Pe$_4$NCy) were obtained by careful neutralization of cyclohexylsulfamic acid (purchased from Sigma) with the corresponding base (Fluka). The purity of the salts was checked after recrystallization from various organic solvents (Me$_4$NCy from 2-propanol, Et$_4$NCy from ethyl methyl ketone, n-Pr$_4$NCy from ethyl acetate, n-Bu$_4$NCy and n-Pe$_4$NCy from cyclohexane) by analysis of the elements C, H and N (Perkin Elmer, 2400 Series II CHNS/O Analyzer) and also by ion exchange of the cation of the salt by the hydrogen ion (DOWEX, Type 50 WX8); a purity of 99.7% at least (Et$_4$NCy) or better, e.g. 99.9% for Bu$_4$NCy was determined. The salts were kept in a vacuum desiccator over P$_2$O$_5$.

The stock solutions for the electric conductivity measurements were prepared on a molal concentration scale by precise weighing, using a digital balance (Sartorius A-200S) accurate to within 3·10^{-4} g.

2.2. Conductivity measurement

The conductivities of the solutions were determined with the help of a three-electrode measuring cell, described elsewhere [11]. The cell was calibrated with dilute potassium chloride solutions [12] and immersed in the high precision thermostat described previously [13]. The temperature dependence of the cell constant was taken into account [12]. The water bath can be set to each temperature using a temperature program with a reproducibility of 0.005 K. The temperature in the precision thermostat bath was additionally checked with calibrated Pt100 resistance thermometer (MPMI 1004/300 Merz) in connection with a Multimeter HP 3458A. The resistance measurements of the solutions in the cell were performed using a precision LCR Meter Agilent 4284A.

At the beginning of every measuring cycle, the cell was filled with a known mass of water (~660 g). After measurement of water conductivity at all temperatures of the temperature program, the stepwise concentration was carried out by successive additions of known masses of stock solution with a gas-tight syringe. After every addition, the temperature program was run by the computer and all measured data (frequency dependent resistance, temperature) were stored and partially shown on display to track the measuring process. A home-developed software package was used for temperature control and acquisition of conductivity data. The measuring procedure, including corrections and extrapolation of the sample conductivity, κ, to infinite frequency, has been previously described [13].

Molar conductivities, $\Lambda = \kappa/c$, of all investigated systems are given in Table 2 as a function of electrolyte molality, m. The latter relates to the corresponding (temperature-dependent) molar concentration, c, via $c = m \cdot d / (1 + M_2 \cdot m)$, where M_2 is the molar mass of the solute and d is the density of the solution. A linear change of d with increasing salt content for diluted solutions was assumed, $d = d_0 + b \cdot m$, where

Table 1

Densities, viscosities and relative permittivities of pure water and limiting conductivities of cyclohexylsulfamate anion in water.

T/K	d_0 [a]	$10^3\,\eta$ [b]	ε [c]	λ^∞ (Cy$^-$) [d]
278.15	0.99997	1.5192	85.897	16.25
283.15	0.99970	1.3069	83.945	19.08
288.15	0.99910	1.1382	82.039	22.05
293.15	0.99821	1.0020	80.176	25.21
298.15	0.99704	0.8903	78.384	28.47
303.15	0.99565	0.7975	76.581	31.86
308.15	0.99404	0.7195	74.846	35.37

Units: T, K; d_0, kg dm^{-3}; η, Pa s; λ^∞, S cm^2 mol^{-1}.
[a] Ref. [14].
[b] Ref. [16].
[c] Ref. [17].
[d] Ref. [10].

d_0 is the density of water, taken from the literature [14] and given in Table 1. The density gradients, b, was determined by measuring the density of stock solutions and the final solution in the conductivity cell, which were determined by the method of Kratky et al. [15] using a Paar densimeter (DMA 5000) at 298.15 K combined with a precision thermostat. As usual, the density gradients b for all examined electrolytes are considered to be independent of temperature and are quoted in Table 2. Considering the sources of error (calibration, measurements, impurities), the specific conductivities are estimated to be accurate within 0.2%.

3. Data analysis

The analysis of conductivity data in the framework of the low concentration chemical model (lcCM) given in Ref. [9] and the literature quoted there, uses the set of equations

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

$$K_A = \frac{1-\alpha}{c\alpha^2 y'_\pm{}^2}; \quad y'_\pm = \exp\left(-\frac{\kappa q}{1 + \kappa R}\right);$$

$$\kappa^2 = 16\pi N_A q\alpha c; \quad q = \frac{e^2}{8\pi\varepsilon\varepsilon_0 kT} \tag{2a-d}$$

$$K_A = 4\pi N_A \int_a^R r^2 \exp\left[\frac{2q}{r} - \frac{W^*}{kT}\right] dr \tag{3}$$

where Λ and Λ^∞ are the molar conductivities at molarity c and infinite dilution, $(1-\alpha)$ is the fraction of oppositely charged ions acting as ion pairs, and K_A is the equilibrium constant of the lcCM with upper association limit R; $y'_\pm$ is the corresponding activity coefficient of the free ions, $(y'_\pm)^2 = y'_+ y'_-$, κ is the Debye parameter, e is the proton charge, ε is the relative permittivity of the solvent, ε_0 is the permittivity of a vacuum and T is the absolute temperature. The other symbols have their usual meaning. W^* is a step function for the potential of mean force between cation and anion due to non-Coulombic interactions.

The coefficients of Eq. (1) are given in Ref. [9]. The limiting slope S and the parameter E are completely calculable when the solvent data are available [14,16,17] (Table 1). The coefficients J_1 and J_2 are functions of the distance parameter R, representing the distance to which oppositely charged ions can approach as freely moving particles in solution.

Analysis of the conductivity data of associated electrolytes are carried out by setting the coefficients S, E and J_1 of Eq. (1) to their calculated values and then usually using three-parameter fits to obtain the limiting values of molar conductivity Λ^∞, the association K_A and the coefficient J_2 by non-linear least squares iterations. A three-parameter evaluation is reduced to a two-parameter procedure for nonassociating electrolytes [11], where usually the coefficient J_2 is