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Conductivity and Dissociation Constants of Quaternary Ammonium Perchlorates and Picrates in 4-Methyl-pentan-2-one†

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The dissociation of 14 ionophores, namely, seven symmetrical (C_1 to C_7) and five asymmetrical quaternary ammonium perchlorates and two tetraalkylammonium picrates (all with linear hydrocarbon chains), in 4-methyl-pentan-2-one was studied at 25 °C ($\varepsilon_r = 12.92$) using the conductance method. The values of the association constants of the quaternary ammonium cation, Ct^+, with ClO_4^- vary from $(7.4 \pm 0.3)\cdot 10^3$ $L\cdot mol^{-1}$ for tetramethylammonium to $(2.4 \pm 0.1)\cdot 10^3$ $L\cdot mol^{-1}$ for tetrahexyl- and tetraheptylammonium; a distinct dependence on the size of the Ct^+, especially for symmetrical cations, is evident. The values of the limiting molar conductivities $\Lambda_0/S\cdot mol^{-1}\cdot cm^2$ vary from 122.8 to 90.0 (± 0.7). The plot of Λ_0 versus the reciprocal cube root of the total van der Waals volume of the cations, $V_{Ct}^{-1/3}$, is close to linear up to tetrapentylammonium and hexadecyltrimethylammonium, while for larger cations (with 21 to 28 carbon atoms) the Λ_0 values stay practically constant. At the same time, symmetrical and asymmetrical cations with the same V_{Ct} values possess equal mobility.

Introduction

The data on equilibrium constants and conductivities of ionophores are of principal importance both for solution chemistry and chemical engineering.[1–7]

The study and interpretation of ionic equilibria and conductivity of electrolytic solutions containing tetraalkylammonium ions (TAA^+) is of special significance for solution chemistry, solvent extraction, phase-transfer catalysis, polarography, colloid chemistry, and so forth. Therefore, the number of papers devoted to the behavior of tetraalkylammonium salts (TAAX) in solutions of various natures is huge.

Meanwhile, despite the numerous data on the equilibrium constants of cation−anionic ($Ct^+ + X^-$) association, K_A, and limiting molar conductivities, Λ_0, of TAAX salts, less attention was paid to the comparison of these parameters for symmetrical and asymmetrical TAA^+ ions.

Indeed, it is natural to expect (and is repeatedly proved experimentally[8–32]) that the Λ_0 values of $N(n\text{-}C_nH_{2n+1})_4X$ salts with fixed X^- ion or of the individual cationic mobilities, Λ_+, decrease along with the increase in n. However, the data for $n > 5$ are few in number.[21,22,24,29,31,32] On the other hand, the asymmetrical cations, for example, $N(n\text{-}C_{18}H_{37})(CH_3)_3^+$ or $N(n\text{-}C_{18}H_{37})(n\text{-}C_4H_9)_3^+$, exhibit a smaller mobility as compared respectively with $N(CH_3)_4^+$ and $N(n\text{-}C_4H_9)_4^+$.[12,14–16] However, there is a lack of data for making firm conclusions about such properties of symmetrical and asymmetrical cations of equal total van der Waals size. Probably, the sole exception is the report of Hughes and Price[24] on the mobilities both of symmetrical TAA^+ ions (C_1 to C_8) and asymmetrical ones, such as $N(n\text{-}C_4H_9)_3(CH_3)^+$ and $N(n\text{-}C_7H_{15})_3(CH_3)^+$ in methyl ethyl ketone. Interestingly, some authors state that in media of low relative permittivity the conductivity of tetraalkylammonium salts is not greatly affected by the length of the hydrocarbon chain of the cation.[33]

The values of molar conductivities of a set of TAA^+ ions with n from 1 (or 2) to 7 (or 8) are available in several solvent systems,[24,29,31,32] but in the case that the viscosity is high, the Λ_0 values are rather small and relatively close to each other. The same concerns the data in nitrobenzene,[9] 1,2-dichlorobenzene,[14] sulfolane,[25] ethylene glycol,[26] and propylene carbonate.[30] In these solvents, except for 1,2-dichlorobenzene, the dissociation degree of salts is high, and thus the comparison of the K_A values is problematic. In some works, the tetraalkylammonium salts studied contained different anions, X^-,[19,22,23,31] and even if the Λ_+ values were estimated, their exact comparison should be hindered by some ambiguities of the dividing procedure.

Some popular solvents such as acetonitrile and acetone are appropriate for the comparison of Λ_0 values, owing to their low viscosity (around 0.3 mPa·s),[11,19,23] but the association ($TAA^+ + X^-$) is less expressed, and thus the corresponding K_A values are low. French and Muggleton[18] report that the disymmetry in the cation markedly reduces the dissociation constant of corresponding picrates in acetonitrile, but actually it deals with a cation with a NH group, able to hydrogen bond.

The set of data for TAAPic in 1,2-dichloroethane reported by Sawada and Chigira[29] is rather complete, but it must be noted that their K_A values are 1.6 times lower than those reported earlier by Tucker and Kraus,[8] while the Λ_0 values agree better.

Therefore, we decided to systematically study the conductance and ion association of a set of 12 ionophores of quaternary ammonium perchlorate type, symmetrical and asymmetrical (including two *N*-alkylpyridinium salts), and two picrates, in 4-methyl-pentan-2-one (methyl isobutyl ketone, MIBK), a solvent with $\varepsilon_r = 12.92$ and $\eta = 0.542$ mPa·s at 25 °C. Here, both $K_A$and Λ_0 values are high enough. The work was aimed to determine and analyze these quantities from the viewpoint of the influence of the size and structure of the cations, Ct^+ (all with linear hydrocarbon chains), also keeping in mind the limited number of data for MIBK as compared with most popular solvents.

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Experimental Section

MIBK (Merck, for synthesis or for extraction analysis) was twice-distilled, and the fraction with $t = (114.2 \text{ to } 114.8)$ °C (99.7/kPa) was used for further work.

All of the below salts were prepared from analytical grade reagents, if not otherwise specified. Tetramethylammonium perchlorate was prepared from tetramethylammonium hydroxide and perchloric acid, four times recrystallized from water, and dried under vacuum to a constant mass at (60 to 70) °C. Tetraethylammonium perchlorate was prepared from tetraethylammonium iodide and sodium perchlorate, three times recrystallized from acetone, and dried under vacuum to a constant mass at (60 to 70) °C. Tetrapropylammonium perchlorate was prepared from tetrapropylammonium bromide and sodium perchlorate, three times recrystallized from acetone, and dried under vacuum to a constant mass at (60 to 70) °C. Tetrabutylammonium perchlorate was prepared from tetrabutylammonium iodide and sodium perchlorate, three times recrystallized from acetone, and dried under vacuum to a constant mass at (60 to 70) °C. Tetrapentylammonium perchlorate was prepared from tetrapentylammonium bromide (Aldrich, ≥ 99 %) and sodium perchlorate, three times recrystallized from aqueous ethanol with mass fraction $\omega = 0.956$, and dried under vacuum to a constant mass at (60 to 70) °C. Tetrahexylammonium perchlorate was prepared from tetrahexylammonium bromide (Aldrich, 99 %) and sodium perchlorate, three times recrystallized from acetone, and dried under vacuum to a constant mass at (60 to 70) °C. Tetraheptylammonium perchlorate was prepared from tetraheptylammonium bromide (Aldrich, ≥ 99 %) and sodium perchlorate, three times recrystallized from acetonitrile, and dried under vacuum to a constant mass at (60 to 70) °C. Hexadecyltrimethylammonium perchlorate was prepared from hexadecyltrimethylammonium bromide (Merck, pharm.) and perchloric acid, three times recrystallized from acetone, and dried under vacuum to a constant mass at a temperature not higher than 60 °C. *N*-Hexadecylpyridinium perchlorate was prepared from *N*-hexadecylpyridinium chloride or bromide and perchloric acid, four times recrystallized from acetone, and dried under vacuum to a constant mass at a temperature not higher than 60 °C. Hexyltriethylammonium perchlorate was prepared from hexyltriethylammonium hydrosulfate and sodium perchlorate, three times recrystallized from water, and dried under vacuum to a constant mass at (60 to 70) °C. Octadecyltrimethylammonium perchlorate was prepared from octadecyltrimethylammonium bromide and sodium perchlorate, three times recrystallized from water, and dried under vacuum to a constant mass at (60 to 70) °C. *N*-Butylpyridinium perchlorate was prepared from *N*-butylpyridinium bromide and silver perchlorate, three times recrystallized from acetone, and dried under vacuum to a constant mass at 30 °C. The preparation and characterization of tetraethylammonium and tetrabutylammonium picrates was described in the previous paper,[34] and the same samples were used in the present study.

Conductance measurements were carried out using platinized platin electrodes in molybdenum-glass cells with the Precison LCR Meter GW Instek LCR-817 apparatus operating at a frequency of 1 kHz. The cells were calibrated using 12 standard aqueous solutions of potassium chloride, within concentration range $(1 \cdot 10^{-4} \text{ to } 0.01)\ \text{mol} \cdot \text{L}^{-1}$. All of the measurements were done at (25.00 ± 0.05) °C. The solutions were prepared by precise weighing of the solid sample, dissolving in the proper amount of the solvent with further dilutions. The analytical balances VLA-200 and GR-202, A&D (Japan) with the uncertainty of weighting respectively (± 0.0002 and ± 0.00001) g were used. The density was calculated using the additive scheme; for the pure solvent, it was taken as $0.7961\ \text{g} \cdot \text{cm}^{-3}$, and for the salts, they were determined experimentally. The correction for pure solvent conductance was used in the calculations of molar conductance values, Λ; the last-named were obtained with an uncertainty of (0.05 to 0.1) %. The conductivity of the pure solvent did not exceed (0.2 to 0.3) % of that of the most diluted salt solution. The experimental data are presented in Table 1. Some typical phoreograms are exemplified in Figure 1.

Results

Data Processing. General Principles. Conductance data were processed using the nonlinear least-squares method to obtain the limiting molar conductance Λ_0 and association constant K_A values. The algorithm and main details of the calculation procedure are described previously.[34,35] The Lee–Wheaton equation[4,36–39] for molar conductivity (see also the Supporting Information) and second approach of the Debye–Hückel theory for activity coefficients were used.

Choice of Distance Parameter R. The parameter R of closest approach distance can be either calculated together with Λ_0 and K_A as a fitted parameter or assigned to a constant value, which should be defined using some external approach. According to the most popular approaches,[2,40] the value of the parameter R can be equated to the following: (i) the Bjerrum distance $R = q = e^2/(8\pi\varepsilon_0\varepsilon_r kT)$, (ii) the sum of ionic radii $R = r_+ + r_-$, and (iii) the sum of ionic radii and solvent molecule diameter $R = r_+ + r_- + d_{\text{solv}}$. We have performed various testing calculations for $N(n\text{-}C_4H_9)_4ClO_4$ in MIBK using the above-mentioned approaches for R. It should be noted that the estimation of ionic radii of quaternary ammonium ions is a separate problem. Taking into account that in Lee–Wheaton model, the parameter R has the meaning of Gurney cosphere,[36] we estimated these values by the quantum-chemical semiempirical AM1 method as a recommended radius for SCRF solvation model calculations in Gaussian 03 package.[41] The results of calculations are summarized in Table 2.

The comparison of data in Table 2 shows that varying the R parameter does not influence the fitted Λ_0 and K_A values within the confidence limit. The fitted value of R is close to that calculated by the ($R = r_+ + r_-$) relationship, but in this case the estimation error is rather large. Thus all conductance data were processed with fixed $R = r_+ + r_-$ values of the distance parameter.

Chemical Equilibrium Scheme. The simple equilibrium of ion association into ionic pairs, $Ct^+ + X^- \rightleftarrows Ct^+X^-$, was always taken into account, whereas ionic triplet formation is questionable. Usually it is accepted that ionic triplet formation becomes noticeable in solvents with very low relative permittivity, $\varepsilon_r < (9 \text{ to } 10)$. For MIBK $\varepsilon_r = 12.92$, and according to Fuoss,[42] the critical concentration of triplet formation is $C_{\text{ctr}} = 1.19 \cdot 10^{-14}(\varepsilon_r T)^3 = 6.8 \cdot 10^{-4}\ \text{mol} \cdot \text{L}^{-1}$. We have performed two testing calculations for the system $N(n\text{-}C_4H_9)_4ClO_4$ + MIBK taking into account the possibility of ionic triplet formation. We assumed that equilibrium constants of formation of cationic and anionic triplets are equal to $K_{T^+} = K_{T^-} = K_T$, and thus four parameters, Λ_0, Λ_{0T}, K_A, and K_T, were to be calculated ($\Lambda_{0T} = \Lambda_{0T^+} + \Lambda_{0T^-}$). In the second calculation we reduced the number of fitted parameters to three by an additional relation $\Lambda_{0T} = 0.693\Lambda_0$.[43] The results are also placed in Table 2. As follows from these results, the Λ_0 and K_A values almost do not depend on chemical equilibrium scheme and can be reliably calculated

Table 1. Molar Conductances of Quaternary Ammonium Perchlorates and Picrates in MIBK at 25 °C

$c\cdot 10^3$	Λ	$c\cdot 10^3$	Λ	$c\cdot 10^3$	Λ
$\mathrm{mol\cdot L^{-1}}$	$\mathrm{S\cdot mol^{-1}\cdot cm^2}$	$\mathrm{mol\cdot L^{-1}}$	$\mathrm{S\cdot mol^{-1}\cdot cm^2}$	$\mathrm{mol\cdot L^{-1}}$	$\mathrm{S\cdot mol^{-1}\cdot cm^2}$
Tetramethylammonium Perchlorate		Tetraethylammonium Perchlorate		Tetrapropylammonium Perchlorate	
0.0093380	112.96	0.016220	91.71	0.063291	85.50
0.0111958	112.31	0.027054	89.78	0.088925	81.65
0.015300	110.65	0.034990	88.84	0.12145	77.78
0.019798	107.69	0.045257	87.37	0.15196	74.41
0.025819	104.77	0.058234	85.25	0.20897	69.85
0.032755	101.39	0.074686	82.97	0.27510	65.70
0.042922	97.55	0.097608	81.18	0.36995	61.20
0.055284	93.36			0.49125	56.94
0.070081	89.42			0.65910	52.59
0.092310	84.68			0.88385	48.38
				1.1831	44.40
				1.5815	40.64
				2.1242	37.08
				2.8434	33.79
				3.7943	30.81
Tetrabutylammonium Perchlorate		Tetrapentylammonium Perchlorate		Tetrahexylammonium Perchlorate	
0.097470	77.25	0.096604	74.26	0.098760	72.68
0.13412	73.72	0.12071	71.86	0.12950	70.52
0.19022	69.30	0.16851	67.98	0.17623	67.22
0.23665	66.17	0.21462	64.69	0.22072	64.46
0.31860	62.16	0.29218	60.57	0.27977	61.33
0.43250	57.65	0.40035	56.23	0.36868	57.77
0.57811	53.48	0.52957	52.45	0.47880	54.33
0.76833	49.50	0.70167	48.74	0.62088	50.90
1.0163	45.74	0.90208	46.84	0.80882	47.50
1.3800	41.80	1.2617	41.33	1.0555	44.10
1.8394	38.33	1.6738	37.99	1.3803	40.90
2.4567	35.08	2.2572	34.72	1.7818	37.95
3.3088	31.98	3.0137	31.77	2.3212	35.08
4.4184	29.20	4.0356	29.01	3.0061	32.44
5.8932	26.71	5.4004	26.50	3.9170	29.95
Tetraheptylammonium Perchlorate		Hexadecyltrimethylammonium Perchlorate		*N*-Hexadecylpyridinium Perchlorate	
0.071785	76.50	0.11718	63.69	0.092384	68.75
0.10356	72.94	0.15128	59.97	0.13292	64.02
0.13175	70.40	0.20964	55.29	0.16909	60.77
0.15937	68.29	0.26363	51.86	0.22611	56.48
0.22438	63.90	0.35837	47.59	0.29544	52.66
0.29737	60.32	0.50710	42.73	0.41379	48.00
0.40503	56.32	0.65885	39.36	0.53882	44.44
0.54379	52.50	0.87057	35.92	0.72135	40.59
0.72664	48.68	1.1681	32.56	0.96707	36.98
0.97751	44.98	1.5473	29.53	1.3033	33.55
1.3065	41.43	2.1055	26.51	1.7191	30.58
1.7510	38.05	2.7972	23.96	2.3176	27.65
2.3546	34.83	3.7599	21.56	3.1196	24.98
3.1488	31.89	5.0115	19.44	4.1698	22.59
4.2077	29.17	6.6834	17.50	5.5689	20.46
Hexyltriethylammonium Perchlorate		Octadecyltrimethylammonium Perchlorate		*N*-Butylpyridinium Perchlorate	
0.094374	80.83	0.10489	63.44	0.10141	75.31
0.13619	76.63	0.13712	60.11	0.13841	70.94
0.17394	73.21	0.17413	56.75	0.17908	66.90
0.21948	69.49	0.22633	53.11	0.23318	62.72
0.28624	65.53	0.28917	49.70	0.31264	57.95
0.37458	61.36	0.38093	45.85	0.42240	53.27
0.48564	57.43	0.48923	42.50	0.55852	48.97
0.63452	53.44	0.63110	39.24	0.75438	44.64
0.81696	49.79	0.81478	36.14	1.0035	40.76
1.0563	46.19	1.0619	33.03	1.3455	36.91
1.3854	42.60	1.3863	30.21	1.7981	33.53
1.8099	39.23	1.8022	27.55	2.4194	30.30
2.3340	36.24	2.3372	25.14	3.2404	27.41
3.0488	33.31	3.0321	22.90	4.3482	24.77
3.9749	30.66			5.7868	22.48

without assuming triplet formation. Therefore, all data were processed using the simple scheme of ion-pair formation.

The resulting Λ_0 and K_A values are summarized in Table 3.

The solubilities of the first two perchlorates in MIBK were limited. Moreover, in the case of tetraethylammonium perchlorate, the measurements in extremely diluted solutions were uncertain, probably due to adsorption on the platinum interface. Therefore, in this case the Λ_0 value was estimated using Kohlrausch's law and the Λ_0 values for $N(n\text{-}C_4H_9)_4ClO_4$, $N(C_2H_5)_4Pic$, and $N(n\text{-}C_4H_9)_4Pic$ determined in the present study. Our results for tetrabutylammonium picrate (Table 3) somewhat differ from those reported by Juillard

Table 1. Continued

$c\cdot10^3$ / $\text{mol}\cdot\text{L}^{-1}$	Λ / $\text{S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$	$c\cdot10^3$ / $\text{mol}\cdot\text{L}^{-1}$	Λ / $\text{S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$
Tetraethylammonium Picrate		Tetrabutylammonium Picrate	
0.090841	85.00	0.10090	74.47
0.13139	82.41	0.13104	72.71
0.16800	79.93	0.17830	70.12
0.21378	77.42	0.22803	67.86
0.28982	74.05	0.30782	64.86
0.39559	70.44	0.41501	61.72
0.51759	67.01	0.56430	58.36
0.69569	63.20	0.75778	55.03
0.93050	59.59	0.99625	51.99
1.2491	55.80	1.3485	48.57
1.6735	52.19	1.8195	45.37
2.2461	48.72	2.4358	42.28
3.0046	45.36	3.2487	39.37
4.0207	42.26	4.3553	36.60
5.3688	39.39	5.8089	34.10

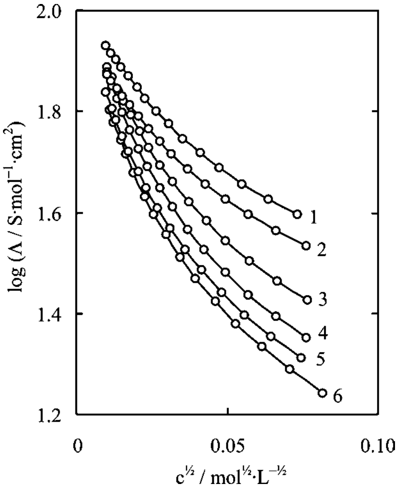

Figure 1. Phoreograms in MIBK: tetraethylammonium picrate (1), tetrabutylammonium picrate (2), tetrabutylammonium perchlorate (3), *N*-butylpyridinium perchlorate (4), *N*-hexadecylpyridinium perchlorate (5), and hexadecyltrimethylammonium perchlorate (6).

and Kolthoff[44] but better agree with the data of Naganawa and Sekine.[45]

Discussion

Though the K_A values of quaternary ammonium perchlorates vary within a relatively narrow range, from $(7.4 \pm 0.3)\cdot10^3$ $\text{L}\cdot\text{mol}^{-1}$ for tetramethylammonium to $(2.4 \pm 0.1)\cdot10^3$ $\text{L}\cdot\text{mol}^{-1}$ for tetrahexyl- and tetraheptylammonium, a distinct dependence on the size of the Ct^+, especially for symmetrical cations, is evident. Indeed, the log K_A values gradually decrease from tetramethyl- to tetrapentylammonium; for tetrahexyl- and tetraheptylammonium, they are equal within the confidence limits (3.38 and 3.40). But in the case of long-tailed cations with three ethyl or methyl groups the K_A values increase: the log K_A values for hexadecyltrimethylammonium and octadecyltrimethylammonium are equal (3.76 and 3.75) and approach that of teteramethylammonium (3.87). The same is the case with *N*-butyl- and *N*-hexadecylpyridinium: log $K_A = 3.69$ and 3.68; the difference of the latter and that for hexadecyltrimethylammonium is too small to warrant a discussion.

Interestingly, the K_A values of the two picrates in MIBK coincide (Table 3), while the regularities observed for TAAPic in 1,2-dichloroethane[8,29] resemble those for TAAClO_4 in MIBK described above. For tetraethylammonium the log K_A value is 0.15 units higher than for tetrabutylammonium.[8,29] For quaternary ammonium picrates in 1,2-dichlorobenzene,[14] the log K_A values decrease from 4.94 to 4.74 on going from tetraethyl- to tetrapentylammonium, while for octadecyltrimethylammonium the value of 5.72 was reported.[14] In nitrobenzene,[9] the log K_A value for teteraethylammonium equals 0.85, while those for tetramethyl-, ethyltrimethyl-, and phenyltrimethylammonium picrates are around 1.4.[9] In pyridine,[12] the corresponding values from tetraethyl- to tetrapentylammonium coincide (log K_A from 2.98 to 2.95), while for picrates in acetonitrile[18] K_A even increase from tetraethyl- to tetrapentylammonium.

In acetone, the difference in log K_A values of tetraethyl- and tetrabutylammonium picrates is 0.11,[11] but processing these experimental data by Lee−Wheaton equation, we obtained for tetrabutylammonium picrate the value log $K_A = 1.94 \pm 0.17$[34] instead of 1.65 reported by the authors,[11] though the Λ_0 value was the same (152.4 $\text{S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$).

Hughes and Price[24] observed the decrease in K_A values of symmetrical tetraalkylammonium iodides and bromides in methyl ethyl ketone along with the lengthening of the hydrocarbon chains (C_1 to C_8), but for methyltripropyl-, methyltributyl-, and methyltriheptylammonium iodides the K_A values exceed those of teteraethyl- and tetrapropylammonium iodides and approach that of tetramethylammonium iodide.

We processed the experimental data of Hughes and Price[24] for tetraheptylammonium and tetraoctylammonium iodides by using our algorithm, equating R to 1.2 nm. The Λ_0 values of (130.8 ± 0.1 and 128.4 ± 0.1) $\text{S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$ coincide with those reported by Hughes and Price (respectively, (130.5 and 128.2) $\text{S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$), while the log K_A values of 2.601 ± 0.002 and 2.594 ± 0.001, obtained by us, are somewhat higher as compared with the earlier data (respectively, 2.490 and 2.488).[24]

Though the conductance data processing shows that the formation of ionic triplets cannot be excluded, this equilibrium is expressed to a very low extent (Table 2). In any case, such complication of the model does not practically influence the K_A and Λ_0 values.

The last-named quantities decrease along with the increase in molar volume. However, inspection of Table 3 reveals two significant points. First, the plot of Λ_0 versus the reciprocal cube root of the total van der Waals volume of the cations, $V_{\text{Ct}}{}^{-1/3}$ (or reciprocal ionic radius, $r_+{}^{-1}$), is close to linearity up to tetrapentylammonium and hexadecyltrimethylammonium, while for larger cations (with 21 to 28 carbon atoms) the Λ_0 values stay practically constant (Figure 2).

Secondly, symmetrical and asymmetrical cations with one and the same V_{Ct} values possess equal mobility, in contrast to

Table 2. Comparative Results of Conductance Data Processing for $N(n\text{-}C_4H_9)_4ClO_4$ in MIBK at 25 °C

optimized parameters	additional relations	R / nm	Λ_0 / $S\cdot cm^2\cdot mol^{-1}$	$\log K_A$	Λ_{0T} / $S\cdot cm^2\cdot mol^{-1}$	$\log K_T$
		Simple Equilibrium Scheme				
Λ_0, K_A, R		0.95 ± 0.10	96.1 ± 2.1	3.44 ± 0.02		
Λ_0, K_A	$R = q$	2.169	94.9 ± 1.3	3.43 ± 0.02		
Λ_0, K_A	$R = r_+ + r_-$[a]	0.89	96.1 ± 0.7	3.44 ± 0.01		
Λ_0, K_A	$R = r_+ + r_- + d_{solv}$[b]	1.31	96.0 ± 0.8	3.45 ± 0.02		
		Equilibrium Scheme with Ionic Triplets				
Λ_0, K_A, Λ_{0T}, K_T	$R = r_+ + r_-$	0.89	95.9 ± 0.8	3.43 ± 0.02	63.7 ± 2.5	1.5 ± 0.5
Λ_0, K_A, K_T	$R = r_+ + r_-$ $\Lambda_{0T} = 0.693\Lambda_0$	0.89	95.4 ± 1.8	3.41 ± 0.07	66.13	1.8 ± 0.8

[a] The used ionic radii (see the text) are 0.56 nm ($N(n\text{-}C_4H_9)_4^+$) and 0.33 nm (ClO_4^-). [b] The used radius for the MIBK molecule equals 0.42 nm.

Table 3. Logarithms of (Cation + Anion) Association Constants and Limiting Molar Conductances of the Salts in MIBK at 25 °C and Total van der Waals Volumes of the Cations[a]

ionophore[b]	Λ_0 / $S\cdot mol^{-1}\cdot cm^2$	$\log K_A$	$R = r_+ + r_-$ / nm	$10^3\cdot V_{Ct}$ / nm^3
$N(CH_3)_4ClO_4$	122.8 ± 0.9	3.87 ± 0.02	0.72	176.38
$N(C_2H_5)_4ClO_4$	107.4[c]	3.75 ± 0.11[d]	0.78	312.46
$N(C_3H_7)_4ClO_4$	102.2 ± 0.7	3.52 ± 0.01	0.85	448.55
$N(C_4H_9)_4ClO_4$	96.1 ± 0.8	3.45 ± 0.01	0.89	584.63
$N(C_5H_{11})_4ClO_4$	92.0 ± 1.0	3.43 ± 0.02	0.93	720.72
$N(C_6H_{13})_4ClO_4$	89.6 ± 0.6	3.38 ± 0.01	0.97	856.80
$N(C_7H_{15})_4ClO_4$	90.3 ± 0.6	3.40 ± 0.01	1.00	992.89
$N(C_6H_{13})(C_2H_5)_3ClO_4$	101.9 ± 0.8	3.50 ± 0.01	0.85	448.55
$N(C_{16}H_{33})(CH_3)_3ClO_4$	92.0 ± 1.0	3.76 ± 0.02	0.91	686.70
$N(C_{18}H_{37})(CH_3)_3ClO_4$	90.0 ± 0.5	3.75 ± 0.01	0.93	754.74
$C_4H_9NC_5H_5ClO_4$	102.7 ± 0.9	3.69 ± 0.01	0.78	294.18
$C_{16}H_{33}NC_5H_5ClO_4$	91.8 ± 0.9	3.68 ± 0.02	0.91	702.43
$N(C_2H_5)_4Pic$	96.3 ± 0.8	3.05 ± 0.02	0.91	312.46
$N(C_4H_9)_4Pic$	85.0 ± 0.7[e]	3.03 ± 0.02[f]	1.01	584.63

[a] The V_{Ct} values were calculated as a sum of van der Waals atomic volumes; the latter were calculated using the van der Waals radii: 0.171 nm (C), 0.116 nm (H), and 0.150 nm (N).[46] [b] All of the hydrocarbon chains are linear. [c] This value was estimated using Kohlrausch's law and the Λ_0 values for $N(C_4H_9)_4ClO_4$, $N(C_2H_5)_4Pic$, and $N(C_4H_9)_4Pic$ determined in this work. [d] Calculated using the Λ_0 value estimated using Kohlrausch's law. [e] In ref 44, the value 93 was reported. [f] In ref 44, the value 3.27 was reported ($K_A^{-1} = 5.4\cdot 10^{-4}$) as determined by the conductance method, while in ref 45 the value of 2.98 ± 0.12 was obtained by solvent extraction method.

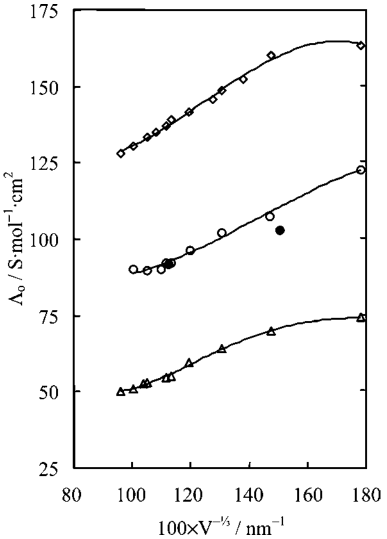

Figure 2. Dependence of the limiting molar conductivities of the quaternary ammonium salts on the reciprocal cube root of the total van der Waals volume of the cations: ◇, tetraalkylammonium iodides in methyl ethyl ketone,[24] ○, TAA$^+$ perchlorates in MIBK; ●, pyridinium perchlorates in MIBK; △, TAA$^+$ picrates in 1,2-dichloroethane (Λ_0 values from ref 29). These data[29] refer both to symmetrical TAA$^+$ ions (up to $n = 8$) and to trioctylmethylammonium and hexadecyltrimethylammonium ions.

their K_A values, which are influenced by localization of the positive charge as well as by steric hindrance.

A variety of r_+ scales is available, but in any case the treatment of our experimental data support the above conclusions. The following sets of values were used: (i) $r_+ = (3V_{Ct}/4\pi)^{1/3}$, where V_{Ct} is a sum of van der Waals atomic volumes, (ii) r_+ as the recommended radius for the SCRF solvation model calculations in the Gaussian 03 package (see above), (iii) r_+ estimated by Lepori and Gianni from group contribution, as reported by Katsuta et al.,[47] (iv) r_+ values recommended by Kuznetsova,[48] and (v) van der Waals r_+ values utilized by Sawada and Chigira.[29] In any case, our first conclusion on the Λ_0 regularities stays valid.

Interestingly, in 1,2-dichloroethane[29] and methyl ethyl ketone[24] the mobilities of symmetric tetraalkylammonium ions continue to decrease up to $n = 8$ (e.g., see Figure 2). However, these data are in line with our observation concerning the mobilities of symmetrical and asymmetrical TAA$^+$ ions of approximately equal size.

Supporting Information Available:

The Lee−Wheaton equation for molar conductivity and related expressions are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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