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CONDUCTIVITY OF SALTS WITH SYMMETRIC AND ASYMMETRIC QUATERNARY AMMONIUM IONS IN SOLUTION

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In this communication, we present new data on the electrical conductivity of symmetric and asymmetric quaternary ammonium salts. The cation-anion association constants and limiting molar conductivities, Λ_0, of a series of tetraalkylammonium and pyridinium perchlorates were determined in acetone. The values of the logarithm of the cation-anion association constants vary within the range of 2.17 to 2.47, with uncertainty of $\pm(0.03-0.11)$. The Λ_0 values decrease monotonously from 230 to 185 $S \cdot mol^{-1} \cdot cm^2$ with an increase in the number of carbon atoms in the cation from 4 to 21. Experimental results were compared with the previously obtained Λ_0 values in methyl *iso*-butyl ketone and other solvents. In all the considered cases, the Λ_0 values coincide within the experimental error for salts with cations having the same number of carbon atoms or van der Waals volume, irrespective of the symmetry of the cations.

Keywords: quaternary ammonium perchlorates, symmetric and asymmetric cations, acetone, electrolytic dissociation, association constants, limiting molar conductivity.

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Introduction

The problem of electrical conductance of ionophores and ion mobility in solution belongs to the most explored in solution chemistry. Among electrolytes used in such studies, the salts containing tetralkylammonium ions, so-called Walden salts, were often used. The decrease in limiting molar conductivity, Λ_0, along with increase in the size of symmetric alkylammonium cations, $N(C_nH_{2n})_4^+$, is numerously proved [1–7]. Surprisingly, corresponding data for asymmetric cations are few in number [5,6]. Previously, we have revealed that the Λ_0 values in methyl *iso*-butyl ketone (MIK) of the tetraalkylammonium perchlorates, irrespective of the symmetry of the cations, exhibit the same dependence on the total van der Waals volume of the cation [6]. In other words, the mobility value of a symmetric and asymmetric tetraalkylammonium ion of the same total van der Waals volume is the same or close. The viscosity, η, of MIK at 25^0C is 0.542 mPa·s, and the difference between the limiting molar conductance of perchlorates of tetramethylammonium and *n*-hexadecyltrimethylammonium is 30.8 $S \cdot mol^{-1} \cdot cm^2$ [6]. In 1,2-dichloroethane, this difference for the corresponding picrates is only 19.6 [5]. This work was aimed to further the investigation to acetone, a solvent of the same chemical nature but with much lower viscosity. This allows obtaining much higher Λ_0 values and their differences, thus additionally verify the above pattern.

Experimental

The synthesis of the salts was described in our previous paper [6]. Acetone of reagent grade was purified as follows. The solvent was treated with potassium

permanganate for several days, adding the oxidizing agent was added as the solution became discolored until a slight coloring remained constant. Acetone was distilled, the middle fraction was collected and left over freshly calcined magnesium sulfate for two weeks. Finally, the solvent was twice distilled, collecting the middle fraction. The water content was 0.02 wt.% as determined by the coulometric Fisher method. The potassium chloride was seven times recrystallized from bi-distilled water, deposited by acetone, and dried under vacuum at 55–75°C to a constant weight.

Electrical conductivity of symmetric and asymmetric tetraalkylammonium perchlorates in acetone were determined at 25.0±0.1°C; the viscosity at this temperature is η=0.303 mPa·s [7]. Electrical resistance measurements were carried out using platinized platinum 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 15 standard aqueous solutions of KCl, within concentration range ($1\cdot10^{-4}$ to 0.01) M. The solutions were prepared by precise weighing of the solid sample, dissolving in the proper amount of the solvent with further dilutions. For every electrolyte, 15 working solutions were used for measurements. The phoreograms are shown in Fig. 1. The results of the measurements were processed using the Lee–Wheaton equation [8].

Results and discussion

The results are presented in Table 1. The van der Waals volumes of the quaternary ammonium cations, V_{cat}, are taken from our previous article [6]. For the tetra-*n*-butylammonium perchlorate, Reinolds and Kraus reported values Λ_0=182.4 S·mol^{-1}·cm^2 and log K_{ass}=2.02 as early as 1948 [10]. The difference can be explained by the difference in the calculation method. The average value of the ratios of Λ_0 in acetone and MIK is 2.02±0.06, while the ratio of the viscosity values is 1.79. The deviation from the «ideal» Walden rule is 13%.

The results confirm the pattern mentioned in the Introduction. Not only the Λ_0 values of the perchlorates of *n*-hexadecyl trimethylammonium and *N*-hexylpyridinium coincide with that of the perchlorate of tetra-*n*-pentylammonium, but those of *n*-hexyl triethylammonium and tetra-*n*-

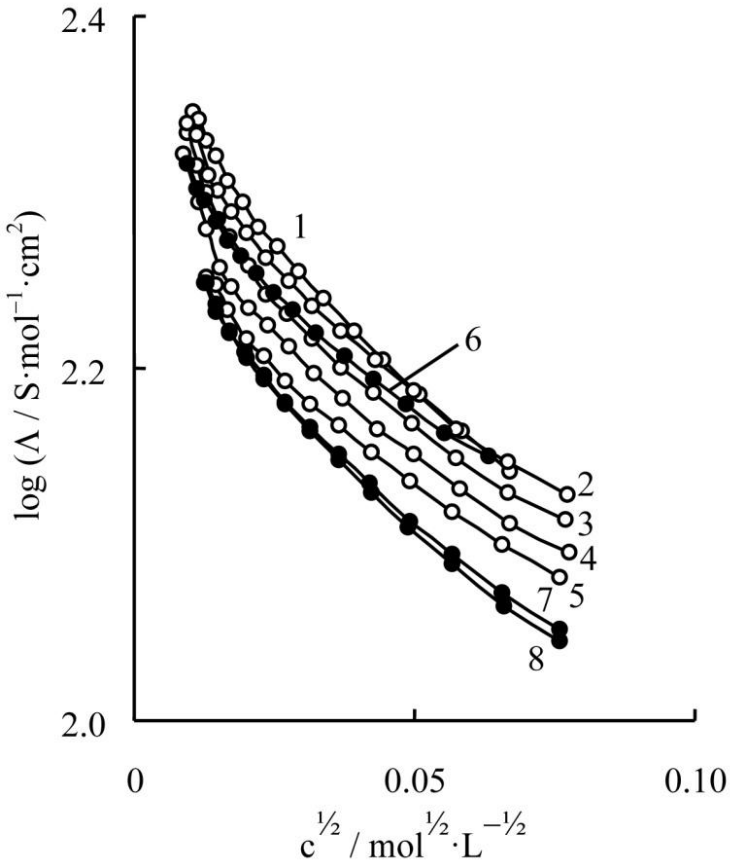

Fig. 1. Phoreograms of quaternary ammonium perchlorate in acetone at 25.0°C: perchlorates of tetramethylammonium (1); tetraethylammonium (2); tetra-*n*-propylammonium (3); tetra-*n*-butylammonium (4); tetra-*n*-pentylammonium (5); *n*-hexyl triethylammonium (6); *n*-hexadecyl trimethylammonium (6); and *N*-hexadecylpyridinium (7)

propylammonium in acetone are close.

The data in 2-propanol [11] for the perchlorates of *n*-hexadecyl trimethylammonium, *N*-hexylpyridinium, and tetra-*n*-pentylammonium are qualitatively similar to the data in Table 1: 27.78±0.15, 24.30±0.20, and 25.48±0.15 S·mol^{-1}cm^2, respectively. However, the high viscosity, 2.073 mPa·s, results in relatively low Λ_0 values.

Now let us discuss some literature data on long-chained alkylammonium ions. Hughes and Price [3] performed a systematic conductometric study of electrolytic dissociation of 23 quaternary ammonium iodides, bromides, and tetraphenylborate in methyl ethyl ketone (η=0.3774 mPa·s at 25^{0}C). Most of them were symmetrical, from tetramethyl to tetra-*n*-octylammonium salts, although some cations contained alkyl chains of different length. These results demonstrated that the number of carbon atoms is of key role for the Λ_0 values. For example, the value for methyltri-*n*-heptyl iodide, 134.93 S·mol^{-1}cm^2, is between those of tetra-*n*-pentyl and tetra-*n*-hexyl iodides, 136.93 and 133.28 S·mol^{-1}·cm^2, respectively; the numbers of carbon atoms are 22, 20, and 24, respectively. However, the longest polymethylene chain in these studies was *n*-octyl.

In 1,2-dihloroethane, the Λ_0 values of *n*-hexadecyl trimethylammonium and tetra-*n*-pentyl ammonium picrates are 54.88 and 54.74 S·mol^{-1}·cm^2 [5]. For tri-*n*-octyl methylammonium and tetra-*n*-hexylammonium picrates with number of carbon atoms of 25 and 24, respectively, Λ_0=52.77 and 53.19 S·mol^{-1}·cm^2, respectively [5].

Many numerical data can be found in the early publications of Kraus group. In methanol (η=0.544 mPa·s), the Λ_0 values for *n*-octadecyl trimethylammonium chloride and bromide are 86.8 and 90.7 S·mol^{-1}·cm^2 [12]. In this case, the number of carbon cations is 21. At the same time, corresponding values for tetra-*n*-pentyl chloride and bromide, Λ_0=87.6 and 91.7 S·mol^{-1}cm^2, respectively.

Some data for long-tailed quaternary ammonium salts are available. In a relatively viscous solvent nitrobenzene (η=1.796) the Λ_0 for picrates of *n*-octadecyl tri-*n*-butylammonium and di-*n*-octadecyl di-*n*-butylammonium are 26.64 and 23.23 S·mol^{-1}·cm^2, respectively [13]. In acetone the corresponding values for the iodides of these cations are 163.6 and 157.2 S·mol^{-1}cm^2, respectively [14]. The number of carbon atoms are 30 and 44, and the V_{cat} values for these two cations are 1.0807 and 1.5369 nm^3, respectively. Moreover, as the ionic mobilities of the I^- and ClO_4^- ions in acetone are close (116.2 and 115.8 S·mol^{-1}cm^2, respectively) [7], the above values for iodide can be considered jointly with the data in Table 1 with a small correction of −0.4.

The dependence of the limiting molar absorptivity on the reciprocal cube root of the V_{cat} value is shown in Fig. 2.

As early as 1929, Walden and Birr [15] analyzed conductivity data of numerous ionophores in acetonitrile and calculated the ionic mobilities in this solvent. Among other results, they estimated the values Λ_+ for $N(n\text{-}C_{16}H_{33})H_3^+$ and $N(C_5H_{11})_3H^+$ as 39.9 and 39.0 S·mol^{-1}·cm^2. Thus, the values are very similar for cations with 16 and 15 carbon atoms, respectively.

The examples discussed, including our data for MIK and acetone, confirm the decisive role of cation size, both symmetric and significantly asymmetric, in determining mobility. Most of the examples relate to ketone solvents. To test the universality of this pattern and its theoretical justification, the next study will focus on ionophores of this group in acetonitrile.

Conclusions

The limiting molar conductivity values of quaternary ammonium perchlorates in acetone decrease monotonically with increasing number of carbon atoms and van der Waals volume of the cations, regardless

Table 1

The logarithm of the association constants and limiting molar conductivity

Electrolyte	10^3V_{cat}, nm^3	log K_{ass}	Λ_0, S·mol^{-1}·cm^2	
		in acetone	in acetone	in MIK[a]
$N(CH_3)_4ClO_4$	176.38	2.47±0.03	230±2	123
$N(C_2H_5)_4ClO_4$	312.46	2.34±0.05	220±2	107
$N(n\text{-}C_3H_7)_4ClO_4$	448.55	2.40±0.07	214±3	102
$N(C_2H_5)_3n\text{-}C_6H_{13}ClO_4$	448.55	2.33±0.07	205±3	102
$N(n\text{-}C_4H_9)_4ClO_4$	584.63	2.36±0.07	203±3	96
$N(CH_3)_3n\text{-}C_{16}H_{33}ClO_4$[b]	686.70	2.34±0.09	185±6	92
$NC_5H_5n\text{-}C_{16}H_{33}ClO_4$[b]	702.43	2.30±0.11	185±7	92
$N(n\text{-}C_5H_{11})_4ClO_4$[b]	720.72	2.17±0.08	187±6	92

Notes: [a] − data for MIK from ref. [6]; [b] − data from ref. [9].

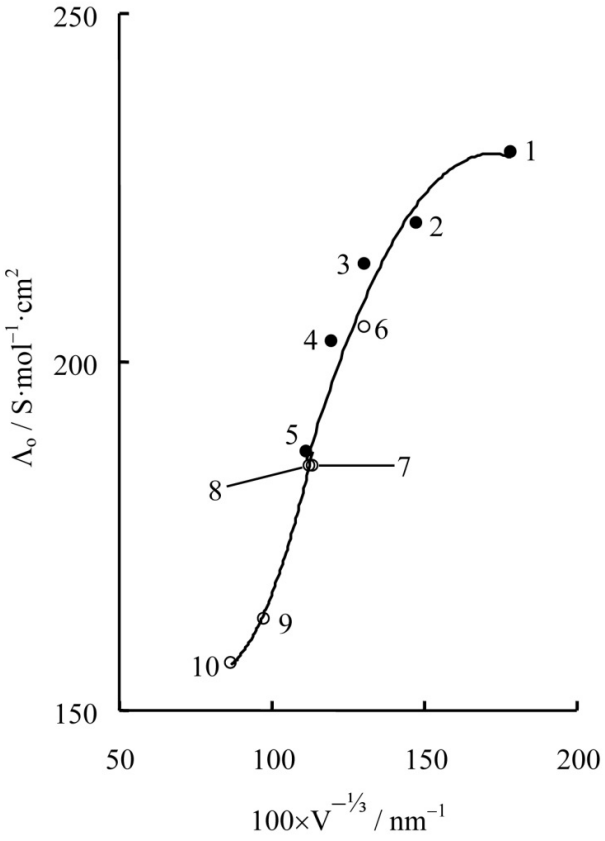

Fig. 2. The dependence of limiting molar conductivity of alkylammonium perchlorates on the reciprocal cubic root of the van der Waals volume of the cation. The points 1–8 correspond to the compounds' numbering in Fig. 1. Points 9 and 10 correspond to *n*-octadecyl tri-*n*-butylammonium and di-*n*-octadecyl di-*n*-butylammonium perchlorates, recalculated from the data of Pickering and Kraus [13]

of their structural symmetry. Several experimental data available in the literature confirm this observation.

Conflict of interest

N.O. Mchedlov-Petrossyan is an Editorial Board Member of the journal but was not involved in the peer-review process or the decision-making regarding this manuscript. All other authors declare no conflict of interest.

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ЕЛЕКТРИЧНА ПРОВІДНІСТЬ СОЛЕЙ З СИМЕТРИЧНИМИ І АСИМЕТРИЧНИМИ ЧЕТВЕРТИННИМИ АМОНІЄВИМИ ІОНАМИ У РОЗЧИНІ

С.Т. Гога, О.В. Лебідь, М.О. Мчедлов-Петросян

У цьому повідомленні ми наводимо нові дані про електропровідність симетричних та асиметричних четвертинних амонієвих солей. Константи катіон-аніонної асоціації та граничні молярні провідності, Λ_0, серії перхлоратів тетраалкіламонію та піридинію були визначені в ацетоні. Значення логарифма констант катіон-аніонної асоціації змінюються в діапазоні від 2,17 до 2,47 з похибкою ±(0,03–0,11). Значення L_0 монотонно зменшуються від 230 до 185 См·моль$^{-1}$·см^2 зі збільшенням кількості атомів вуглецю в катіоні від 4 до 21. Експериментальні результати порівнювали з раніше отриманими значеннями Λ_0 у метилізобутилкетоні та інших розчинниках. У всіх розглянутих випадках значення Λ_0 збігаються в межах експериментальної похибки для солей з катіонами з однаковою кількістю атомів вуглецю або об'ємом Ван-дер-Ваальса, незалежно від симетрії катіонів.

Ключові слова: перхлорати четвертинного амонію, симетричні та асиметричні катіони, ацетон, електролітична дисоціація, константи асоціації, гранична молярна провідність.

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