

Electrostatic Gibbs Free Energy and Solvation Number of Tetraalkylammonium Ions in Pyridine at 25 °C Obtained Using Conductance of Corresponding Ion

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The equivalent conductances for tetraethylammonium perchlorate (TEAP), tetrabutylammonium perchlorate (TBAP), tetrahexylammonium perchlorate (THAP), and tetradodecylammonium perchlorate (TDdAP) were measured in pyridine (Py) at 25 °C. The measured data have been analyzed by Onsager conductance theory. From Kohlrausch's law of independent migration of ion, the limiting ionic conductances of tetraalkylammonium ions were determined using the limiting ionic conductance of perchlorate cited from reference. Using those and viscosity of pyridine, the Stokes and hydrodynamic radii of tetraethylammonium, tetrabutylammonium, tetrahexylammonium, and tetradodecylammonium ions were calculated. And, the solvation numbers of corresponding ions were also calculated using the hydrodynamic and crystallographic radii and the volume of one pyridine molecule. From those results, the model of solvation for those ions was extracted by comparison with the model for ion solvation. And the electrostatic Gibbs free energy (ΔG_{el}) fitted for our solvation model was calculated. Those of corresponding ions in pyridine at 25 °C also increased with increasing radii of tetraalkylammonium ions. This trend of ΔG_{el} was explained by the different ion-solvent interaction between tetraalkylammonium ion and pyridine.

Introduction

Electrochemical conductivity measurements in non-aqueous solvents provide several important parameters. The basic quality of interest is the equivalent or molar conductance of electrolytes at infinite dilution, Λ_{∞} . A second area which has received considerable attention is the study of ion association using electrical conductance Λ as a probe. Determination of the equivalent conductance as a function of concentration of the electrolytes, followed by analysis using an appropriate equation gives rise to a value for K_a , the association constant. Therefore, there have been many publications¹⁻¹² which treated the conductance and association constant of electrolytes in non-aqueous solvent. But to our knowledge, there is no study for the limiting equivalent conductance of tetraethylammonium perchlorate (TEAP), tetrahexylammonium perchlorate (THAP), and tetradodecylammonium perchlorate (TDdAP) in pyridine. Especially, the fact that the nature and size of cation of those supporting electrolytes and solvents play important roles in electrochemical redox potential of C_{60} and the chemical reactivity of redox species of C_{60} has been known.^{13,14} But the conductance study of those electrolytes in pyridine have not been done so much as important. Actually, the conductances of those electrolytes and tetraalkylammonium ions in pyridine should be of interest not only to fullerence researchers, but also to electrochemists in working in a number of different areas involving inorganic and organic molecules.

So, in this study, we have measured the conductances of those electrolytes in pyridine. From Kohlrausch's law of independent migration of ion, the limiting ionic conductance of tetraalkylammonium ions were determined using the limiting ionic conductance of perchlorate cited from reference. From those and viscosity of pyridine,¹⁵ the Stokes and hydrodynamic radii¹ of tetraethylammonium, tetrabutylammonium, tetrahexylammonium, and tetradodecylammonium ions

were calculated. And, the solvation number of corresponding ions were also calculated using the hydrodynamic¹ and crystallographic radii¹⁶ of corresponding ions and the volume of one pyridine molecule. From those results, the model of solvation for those ions were extracted by the comparison with the model¹⁷ for ion solvation. And the electrostatic Gibbs free energy for our solvation model was calculated.

Experimental

Chemicals. Anhydrous nitrogen-packed pyridine was purchased from Aldrich and Fluka Co. and used as received. TEAP, TBAP, THAP, and TDdAP were also purchased from Aldrich, Fluka, and Kodak Co. TEAP and TBAP were recrystallized twice from absolute ethanol and dried in vacuum at 40 °C prior to use. But THAP and TDdAP were used as received.^{13,18}

Instrumentation and Procedure. The conductance measurements were carried out using with a Model CM60V conductivity meter (TOA Instrument Co., Inc.) with 1 kHz frequency. A dip type conductivity cell was used with lightly platinized Pt plates and also purchased from TOA Instrument Co.. The cell constant was determined by cell calibration with a standard conductivity solution obtained from Fisher Co.. The measured value of cell constant is $0.093 \pm 0.002 \text{ cm}^{-1}$ at 25 °C. The temperature control was provided by a thermostat bath (B. Braun Co., Melsungen AG in W. Germany) maintained to ± 0.01 °C.

0.1 M stock solution in pyridine was prepared from weighting portion of the corresponding electrolytes. The working solutions, of concentration varying 10^{-4} M to 10^{-1} M, were prepared by diluted just before experimental. Conductances readings were recorded when they became invariant with time. In our experimental, this took about 40 min. for each measurement. Solvent conductance corrections were not applied to all data, because the specific conduct-

ance of solvent (1×10^{-7}) was negligibly smaller than those of solutions.

Calculations and Theory

The Stokes-law radii r_s of ions and hydrodynamic radii r_h , calculated using the value 4 instead of 6 in the denominator in eq. 1, of ions based on classical hydrodynamics^{1b} were calculated from the limiting equivalent conductance of corresponding ions and viscosity of pyridine obtained from ref. 15.

$$r = |z| F^2 / (6\pi N \eta^0 \lambda_i^0) \quad (1)$$

Here F is Faraday constant, N is Avogadro number. From the hydrodynamic radii r_h calculated from eq. 1 and crystallographic radii r_c cited from ref. 16 and listed in Table 2, the volume of solvation shell^{1c} surrounding ions has been calculated from eq. 2.

$$V_{sh} = (4/3)\pi(r_h^3 - r_c^3) \quad (2)$$

The solvation number S_n^{1c} of ions have been calculated from eq. 3.

$$S_n = V_{sh} / V_{py} \quad (3)$$

where V_{py} is the volume of one pyridine molecule.¹⁵

The Born model of ion solvation approximates the Gibbs free energy of ion solvation, ΔG , through the difference of the electrostatic energy of an ion of charge Ze in vacuum and in a solvent with permittivity ϵ . The empirical Born radius r_B depends on the ion species and on solvent. To calculate Gibbs free energy of ion solvation, the model of ion solvation must be considered. There are two kinds of the models for ion solvation.¹⁷ One is one-layer model, the other is two-layer one. In our model, the ion seems to interact with its environment as follows. Firstly, a cavity of radius r_h is formed in pyridine, and then the ion with its solvation shell is inserted into the cavity interacting with the pyridine by means of dispersion and dipole-induced dipole interactions as if it were uncharged.

Next process is charging process of ion solvation, but there is controversy for charging process. One is that the charging process makes the charge effectively large as much as to produce the electric field which causes the dielectric saturation in the solvation shell. The permittivity (or dielectric constant) of the pyridine in the solvation shell is considered to have the effective-local dielectric constant ϵ . Since this local effect is different from ion to ion, as is q (charge)/ r (radius) ratio, it is reasonable to use the different effective dielectric constants proposed by Noyes.¹⁹

Then, the Gibbs free energy²⁰ in the electrostatic interactive region, *i.e.*, in the n -layers solvation shell becomes

$$\Delta G_{el} = (N_A e^2 / 8\pi \epsilon_0) z^2 \sum_{i=1}^n (1 - 1/\epsilon_i) [(1/r_{i-1}) - 1/r_i] \quad (4)$$

Where, ϵ_0 , ϵ_i , r_{i-1} , and r_i are the dielectric constant of vacuum, the dielectric constant of solvent in the i th solvation shell and the radius to the $(i-1)$ th and i th layer of solvent surrounding ion. If we applied eq. 4 to our model, *i.e.*, $n=1$, ΔG_{el} becomes

$$\Delta G_{el1} = (N_A e^2 / 8\pi \epsilon_0) z^2 (1 - 1/\epsilon_1) [(1/r_c) - 1/r_h] \quad (5)$$

Where, ϵ_1 and r_h are the dielectric constant of pyridine in the first solvation shell and the radius to the first layer of pyridine surrounding ion, respectively. r_h is hydrodynamic radii obtained from eq. 1. r_c is the radius of ion obtained from a crystallographic study.¹⁶ In the right-hand side of eq. 5, the term represents the free energy of electrostatic interaction between corresponding ion and pyridine in the solvation shell. In the mean time, the Gibbs free energy beyond the solvation shell becomes,

$$\Delta G_{el2} = (N_A e^2 / \pi \epsilon_0) z^2 (1 - 1/\epsilon) / r_h \quad (6)$$

Where, ϵ is the dielectric constant of pyridine. If the interaction beyond the solvation region is included, the Gibbs free energy, ΔG_{el} from the electrostatic interactions becomes

$$\begin{aligned} \Delta G_{el} &= \Delta G_{el1} + \Delta G_{el2} \\ &= (N_A e^2 / 8\pi \epsilon_0) z^2 (1 - 1/\epsilon_1) [(1/r_c) - 1/r_h] \\ &\quad + (N_A e^2 / 8\pi \epsilon_0) z^2 (1 - 1/\epsilon) / r_h \end{aligned} \quad (7)$$

The other is that, in later the charging process, the local relative permittivity in the immediate neighborhood of ions is assumed to be equal to the bulk relative permittivity of the solvent. Schellman²¹ suggested that dielectric saturation may not be as important as is usually assumed, in part because electrostriction tends to increase the dielectric constant (or permittivity) of solvent in the vicinity of the ion, opposing the effect due to dielectric saturation. And, Honig²² also found that for charges up to approximately +1, dielectric saturation is less of a problem than is generally believed.

So, we have used the latter because the charge density of tetraalkylammonium ions is not enough to develop the dielectric saturation of solvent in the solvation shell.^{17c}

Then the Gibbs free energy, ΔG_{el} from the electrostatic interactions becomes

$$\Delta G_{el} = (N_A e^2 / 8\pi \epsilon_0) z^2 (1 - 1/\epsilon) / r_c \quad (8)$$

Results and Discussion

Conductance measurements can provide at least three parameters; the limiting equivalent conductance which depend on the size and charge distribution of the ions and on viscosity, dielectric constant, polarizability, and on dielectric relaxation time²³⁻²⁴ of solvent, the association constant K_a , and inter-ionic distance parameter that gives the best fit to the conductance equation. So in obtaining reliable values of Λ_0 and K_a , it is important not only to select in a reasoned manner for a theoretical equation but also a mathematical approach for its solution. But the problem of which theory (or equation) to use for the analysis of conductance data is questionable in non-aqueous solution and all of theories (or equations) yield a approximately the same value of Λ_0 . Therefore, we have chosen Onsager conductance theory for analyzing conductance data. Because Onsager conductance theory only yields the slope at infinite dilution and is normally interested in analyzing data over a finite conductance range.^{1b}

The values of equivalent conductances determined for

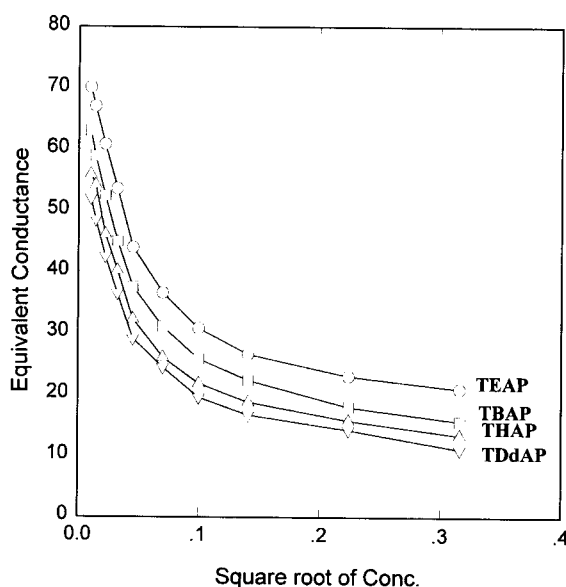
Table 1. Equivalent conductance, Λ , (Scm^2/mol) of tetraalkylammonium perchlorates in pyridine at 25 °C

Conc.	Supporting Electrolyte			
	(TEA)ClO ₄	(TBA)ClO ₄	(THA)ClO ₄	(TDdA)ClO ₄
1×10^{-1}	21.01(21.0) ^a	15.75(16.35) ^a	13.48	11.18
5×10^{-2}	23.04(22.32) ^a	18.02(18.04) ^a	15.78	14.29
2×10^{-2}	26.57	22.34	18.78	16.67
1×10^{-2}	30.79	25.82(26.0) ^a	21.80	19.54
5×10^{-3}	36.54	31.04	26.07	24.41
2×10^{-3}	43.96	37.48	32.25	29.05
1×10^{-3}	53.90	44.99	40.21	36.42
5×10^{-4}	60.78	52.43	46.10	42.49
2×10^{-4}	67.05	58.90	54.21	48.52
1×10^{-4}	70.12	63.01	55.88	52.00
∞	77.69	70.29(70.26) ^b	63.14	59.20

^aKadish, K. M.; Ding, J. Q.; Malinski, T. *Anal. Chem.* **1984**, *56*, 1741. data to be at 22 °C. ^bGill, D. S. *J. Soln. Chem.* **1979**, *8*, 691. Luder, N. F.; Krause, C. A. *J. Am. Chem. Soc.* **1947**, *69*, 2481.

TEAP, TBAP, THAP, and TDdAP in pyridine are given in Table 1 and are plotted vs. square root of concentration in Figure 1.

As shown in Table 1, the equivalent conductances of TEAP, TBAP, THAP, and TDdAP in pyridine decreased with increasing the number of carbon in tetraalkylammonium ions. This trend could be understood by knowing the fact that the mobilities of tetraalkylammonium ions with the same perchlorate counter ion decreased with increasing the number of carbon in tetraalkylammonium ions. The equivalent conductances of TBAP (70.29 Scm^2/mol) is coincident with those of Gill (70.26 Scm^2/mol)²⁵ listed in Table 1, so we used our experimental results of tetraalkylammonium perchlorates for determining the limiting ionic conductance of tetraalkylammonium ions. And shown in Figure 1, the equivalent conductances of TEAP, TBAP, THAP, and TDdAP in pyridine increased but didn't do linearly with

**Figure 1.** Plot of equivalent conductance of tetraalkylammonium perchlorates vs. square root of concentration in pyridine at 298 K.**Table 2.** Limiting ionic equivalent conductance, λ_{∞} , ($\text{S cm}^2/\text{mol}$), Stokes' radius (\AA), r_s , and Hydrodynamic radius, r_h , of tetraalkylammonium ions in pyridine at 25 °C

	ions			
	(TEA) ⁺	(TBA) ⁺	(THA) ⁺	(TDdA) ⁺
λ_{∞}	31.40	24.0(24.0) ^a	16.85	12.91
r_s	3.87	4.96	5.52	7.20
r_h	4.44	5.81	8.27	10.80
r_e^b	4.00	4.94	5.62	7.83

^aLuder, N. F.; Krause, C. A. *J. Am. Chem. Soc.* **1947**, *69*, 2481. ^bCrytallographic radii: *Electrolyte Solution*, **1959**, Ch. 14

decreasing the square root of concentration but between 2×10^{-3} M and 1×10^{-4} M, the conductance data vs. square root of concentration show the linear relationship.

Using Kohlrausch's law of independent migration of ion, the limiting ionic conductance of tetraalkylammonium ions were determined with the limiting ionic conductance of perchlorate (46.29 Scm^2/mol) obtained using Kohlrausch's law and cited from ref. 26. The limiting ionic conductances of tetraalkylammonium ions and the Stokes' law radii r_s and hydrodynamic radii r_h of corresponding ions based on classical hydrodynamics calculated using eq. 1 in pyridine at 25 °C are listed in Table 2.

As shown in Table 2, The limiting ionic conductances decreased with increasing the number of carbon in tetraalkylammonium ions, but the Stokes' law radii r_s and hydrodynamic radii r_h of tetraalkylammonium ions increased with increasing the number of carbon in tetraalkylammonium ions as like the crystallographic radii of tetraalkylammonium ions.

The solvation shell volume, $V_{sh}(\text{\AA}^3)$ of tetraalkylammonium ions calculated using eq. 2, solvation number, S_n of tetraalkylammonium ions calculated using eq. 3 and the electrostatic Gibbs free energy, ΔG_{el} (kJ/mol) of corresponding ions in pyridine at 25 °C calculated using eq. 8 are listed in Table 3 and ΔG_{el} (kJ/mol) of corresponding ions vs the hydrodynamic radii are plotted in Figure 2.

As shown in Table 3, The solvation shell volume, $V_{sh}(\text{\AA}^3)$ of tetraalkylammonium ions increased with increasing the radii of tetraalkylammonium ions. The solvation number, S_n of tetraalkylammonium ions also increased with increasing radii of tetraalkylammonium ions. This trend of the solvation shell volume, $V_{sh}(\text{\AA}^3)$ and the solvation number, S_n of tetraalkylammonium ions was explained by the differences of ion-solvent interaction between tetraalkylammonium ion and pyridine.¹ We used eq. 8. in order to calculate the electrostatic Gibbs free energy, ΔG_{el} (kJ/mol) of tetraalkyl-

Table 3. Solvation shell volume, V_{sh} (\AA^3), solvation number, S_n , and electrostatic Gibbs free energy, ΔG_{el} (kJ/mol) of tetraalkylammonium ions in pyridine at 25 °C

	ions			
	(TEA) ⁺	(TBA) ⁺	(THA) ⁺	(TDdA) ⁺
V_{sh}	98.1	317.0	517.1	1109.3
S_n	0.73	2.36	3.85	7.7
ΔG_{el}	-149.00	-119.95	-105.74	-75.68

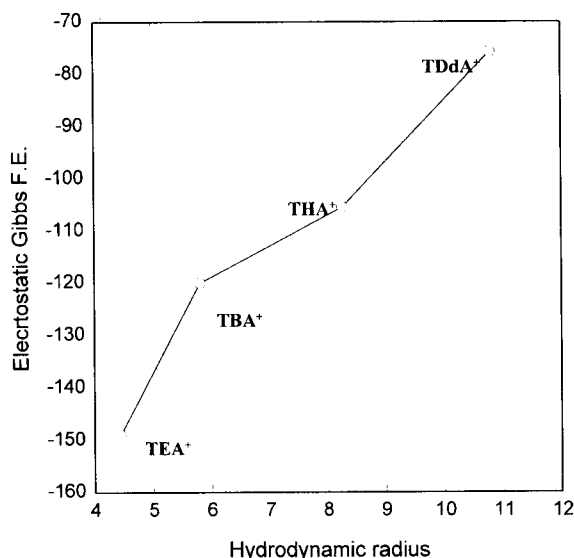


Figure 2. Plot of electrostatic Gibbs free energy vs. hydrodynamic radius of tetraalkylammonium ions in pyridine at 298 K.

ammonium ions in pyridine at 25 °C fitted in our model. Those of corresponding ions in pyridine at 25 °C also increased with increasing radii of tetraalkylammonium ions. This trend of ΔG_{el} was also explained by the different ion-solvent interaction between tetraalkylammonium ion and pyridine. In ref 14, the $E_{1/2}$ of redox processes of C_{60} also increased with increasing radii of tetraalkylammonium ions. This indicates that the redox species of C_{60} with larger cations which were the components of supporting electrolytes used in redox processes of C_{60} have a higher stability. So, the size of tetraalkylammonium ions affect not only the ion-solvent interactions and the Gibbs free energy of solvation but also the $E_{1/2}$ of redox processes of C_{60} . The Gibbs free energy of solvation includes a term for compression of space available to the ion on its transfer from its gaseous states to its solution states. Therefore, the more negative values of the Gibbs free energy of ion solvation mean that the process of ion solvation is spontaneous process in pyridine. Conclusively, the solvation of TEA⁺ ion in pyridine is more spontaneous than that of other ions in same solvent.

It is our hope that the results of this study using conductance of tetraalkylammonium ions give information of Gibbs free energy of ion solvation in pyridine to the subject related the similar study.

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