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Solubilities and Dissolution States of a Series of Symmetrical Tetraalkylammonium Salts in Water

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The solubilities of a series of symmetrical tetraalkylammonium salts, R_4NX ($R=CH_3$—n-C_8H_{17}, including i-C_4H_9 and i-C_5H_{11}; X=Cl, Br, I, NO_3, and ClO_4), in water have been determined over the temperature range between 5 and 45 °C. The solubilities of these salts were found to be strongly dependent upon both the chain length of R of the R_4N^+ cation and upon the partial molar volume of the X^- anion. It has been concluded that these solubilities are closely related with the stability of a "cage-like" water structure, which is presumably formed around the R_4N^+ cation in the solution. A thermodynamic interpretation of the solubility of the R_4NX salts was made by using some thermodynamic properties obtained by a differential scanning calorimetry, together with the enthalpy of the solution calculated from the temperature dependence of the solubility.

It has been pointed out that one of the most important factors which contributes to the stability of a tetraalkylammonium cation in an aqueous solution is the formation of a "cage-like" or "clathrate-like" water structure around its nonpolarizable moieties.[1] This explanation is closely related to a phenomenon in which many tetrabutylammonium salts (or tetraisopentylammonium salts) form unique hydrates having a large number of moles of water.[2] Single-crystal X-ray examinations[3–5] by Jeffrey and his coworkers on these hydrates showed that the central N atom lies at a common vertex of four large polyhedra, which are either tetrakaidecahedra or pentakaidecahedra; each of the four alkyl chains extends into one of the polyhedral cages. Furthermore, other experimental results[6] suggest that such short alkyl chains as $R=C_2H_5$ and $R=n$-C_3H_7 are stably accommodated within a pentagonal dodecahedron. Thus, a "cage-like" water structure around R_4N^+ cations with $R=C_2H_5$—n-C_4H_9, and i-C_5H_{11}, is expected to be fairly stable and to contribute to the elevation of the solubilities in water.

The effect of an anion X^- on the solubility of a R_4NX salt has not been fully discussed. However, the most important effect of an anion X^- on the dissolution state of the R_4NX salts in water may be considered to be a deformative or destructive effect on the "cage-like" water structure around the R_4N^+ cation, owing to the large molar volume of the anion. This consideration comes from the fact that the melting points of the hydrates formed by a series of salts $(n\text{-}C_4H_9)_4NX$ with X=F, Cl, Br, IO_3, NO_3, and ClO_3 decrease almost linearly with increasing the partial molar volume of the X^- anion.[7]

In this study, in order to determine whether the above-mentioned effects of both R_4N^+ cations and X^- anions on the solubilities of the R_4NX salts are generally adequate, the solubilities of various R_4NX salts in water have been measured, especially for salts whose solubility data are not available in literature. Furthermore, some attempts were made at a thermodynamic interpretation of these solubility data.

Experimental

Materials. Most of the symmetrical tetraalkylammonium salts, R_4NX, used were prepared from the corresponding tetraalkylammonium iodides, R_4NI. The iodides with $R=CH_3$—n-C_3H_7 were purchased from Tokyo Kasei Kogyo Co., Ltd. and purified by repeated recrystallization from pure water. The iodides with $R=n$-C_4H_9—n-C_8H_{17}, i-C_4H_9, and i-C_5H_{11}, were sythesized and purified by the same procedure previously reported.[8] Aqueous solutions of all the chlorides and the bromides having $R=i$-C_5H_{11}, n-C_6H_{13}, and n-C_8H_{17} were prepared by neutralizing each tetraalkylammonium hydroxide solution with either a HCl or HBr solution. The hydroxide solution was obtained by treating the tetraalkylammonium iodide with freshly prepared silver hydroxide in water with vigorous shaking, followed by filtration of silver iodide in a CO_2-free atmosphere.[9] Tetraalkylammonium nitrates were obtained by reacting each R_4NI with silver nitrate either in water (for $R=CH_3$—n-C_4H_9) or in acetone-water mixture (for $R=n$-C_5H_{11}—n-C_8H_{17}), followed by filtration of silver iodide and evaporation of the solvent using a rotary evaporator. These nitrates, except for $(n\text{-}C_8H_{17})_4NNO_3$, were purified by recrystallization from water and $(n\text{-}C_8H_{17})_4NNO_3$ from diethyl ether. Tetraalkylammonium perchlorates, R_4NClO_4, with $R=CH_3$—n-C_3H_7 were purchased from Tokyo Kasei Kogyo Co., Ltd. Since the solubilities of tetraalkylammonium perchlorates with long alkyl chains ($R=n$-C_4H_9—n-C_8H_{17}) were quite low, these solubilities were determined by measuring the radioactivity of ^{36}Cl-labeled perchlorates, $R_4N^*ClO_4$. Two radioactive perchlorates with $R=n$-C_4H_9 and n-C_5H_{11} were obtained in the following manner: nonradioactive perchlorate, which was obtained as a precipitate by mixing an aqueous R_4NCl solution with an aqueous solution of $NaClO_4$ and purified by repeated recrystallization from water, was dissolved in hot water containing a small amount of radioactive K^*ClO_4. The radioactive perchlorate solid was then obtained by cooling the solution. The other two radioactive perchlorates, $(n\text{-}C_6H_{13})_4N^*ClO_4$ and $(n\text{-}C_8H_{17})_4N^*ClO_4$, were obtained by the neutralization of each nonradioactive hydroxide solution, which was prepared by the same procedure as mentioned above, with an aqueous solution of $HClO_4$ containing a small amount of K^*ClO_4.

Procedure. The solubilities were determined in the following manner. In a measuring cell (3-cm diameter and 10-cm high) immersed in a constant-temperature bath, each salt was saturated in 10—20 cm^3 of water by vigorous stirring with a magnetic stirrer for 5—30 h. It took more than 20 h until a saturation equilibrium was attained for a sparingly soluble salt like $(n\text{-}C_8H_{17})_4NClO_4$. Then, a given amount of each saturated solution was withdrawn and analyzed by one of the methods listed below according to the magnitude of the solubility values and the types of cations and anions of the samples: (1) determination of the water content using the Karl Fischer titration method; (2) evaporation of water to dryness; (3) titration of either $(n\text{-}C_4H_9)_4N^+$ cation or $(i\text{-}C_5H_{11})_4N^+$ cation with a sodium tetraphenylborate solution;[7] (4) colorimetric determination of the ClO_4^- ion by Methylene Blue-ClO_4^- complex formation;[10] (5) potentiometry using an electrode responding to I^- ion; and (6) an efficiency tracing technique applied to a radioactive ^{36}Cl atom. The Karl Fischer titration was carried out on a MK-II apparatus manufactured by Kyoto Electronics Manufacturing Co. The radioactivity was measured using the TRI-CARB 460C Automatic Liquid Scintillation System manufactured by Packard Instrument Co., Inc. in the same manner as described in the previous papers.[11,12]

The melting points and transition temperatures as well as enthalpies of melting and of transitions were measured using a differential scanning calorimeter, DSC 10 with SSC 580 thermal controller manufactured by Seiko Instruments and Electronics Ltd.

Results and Discussion

(1) Solubilities of a Series of Tetraalkylammonium Salts in Water at 25 °C. The measured solubilities of a series of tetraalkylammonium salts, R_4NX, in water at 25 °C are summarized in Table 1, together with those available in the literature.[8,13–16] For both chlorides and bromides, the solubilities of those with $R=i\text{-}C_5H_{11}$, $n\text{-}C_6H_{13}$, and $n\text{-}C_8H_{17}$, were newly measured in this study. The solubilities of $(i\text{-}C_5H_{11})_4NCl$ and of $(i\text{-}C_5H_{11})_4NBr$ are considerably low compared, for example, with those of $(n\text{-}C_5H_{11})_4NCl$ and of $(n\text{-}C_5H_{11})_4NBr$ since the solid phase which is in equilibrium with a saturated aqueous solution at 25 °C is a clathrate hydrate, $(i\text{-}C_5H_{11})_4NCl(\text{ca. }39)H_2O$ and $(i\text{-}C_5H_{11})_4NBr(\text{ca. }39)H_2O$,[8] respectively. Three systems, $(n\text{-}C_6H_{13})_4NCl\text{-}H_2O$, $(n\text{-}C_6H_{13})_4NBr\text{-}H_2O$, and $(n\text{-}C_8H_{17})_4NCl\text{-}H_2O$, become a two-liquid phase equilibrium at 25 °C, in which a fairly dilute aqueous solution is in equilibrium with a fairly concentrated solution. The concentrations of both phases are also listed in Table 1. The solubilities of the iodides reported in Table 1 are somewhat different from those reported earlier: 0.0622 mol · kg^{-1} for $(n\text{-}C_4H_9)_4NI$;[17] 2.50×10^{-3} mol · kg^{-1} for $(n\text{-}C_5H_{11})_4NI$.[17]

The solubilities of all the nitrates, R_4NNO_3, were determined for the first time. In all cases, a solid phase was found to be anhydrous through the Karl Fischer titration method. It is interesting to note that the solubilities of nitrates with $R=CH_3$—$n\text{-}C_4H_9$ are quite high, whereas those of nitrates with R longer than C_5 are quite low. As a result, the solubility of $(n\text{-}C_4H_9)_4NNO_3$ is about 700-times that of $(n\text{-}C_5H_{11})_4NNO_3$. The reason for this will be discussed below.

The solubilities of perchlorates with $R=CH_3$—$n\text{-}C_4H_9$ are in good agreement with those reported earlier: 0.0747,[15] 0.075,[18] and 0.0753[19] mol · kg^{-1} for $(CH_3)_4NClO_4$; 0.232[15] and 0.217[18] mol · kg^{-1} for $(C_2H_5)_4NClO_4$; 0.0204[18] and 0.0197[19] mol · kg^{-1} for $(n\text{-}C_3H_7)_4NClO_4$; 0.0100[20] and 0.0103[19] mol · kg^{-1} for $(n\text{-}C_4H_9)_4NClO_4$. However, the values reported by Deno et al.,[18] 6.7×10^{-4} mol · kg^{-1} for $(n\text{-}C_5H_{11})_4NClO_4$ and 4.4×10^{-4} mol · kg^{-1} for $(n\text{-}C_6H_{13})_4NClO_4$, are fairly different from our values listed in Table 1. Our values seem to be more exact since a radio tracer technique is appropriate for a determination of such low solubility. The solid phase, which was in equilibrium with the saturated aqueous solution and analyzed by the Karl Fischer titration method, was shown to be anhydrous in all cases. In Table 1, it should be noted that the solubilities of $(i\text{-}C_4H_9)_4NClO_4$ and of $(i\text{-}C_5H_{11})_4NClO_4$

Table 1. Solubilities of Symmetrical Tetraalkylammonium Salts, R_4NX, in Water at 25 °C (in mol · kg^{-1})

R	X				
	Cl	Br	I	NO_3	ClO_4
CH_3	19.06[13]	6.35[14]	0.272[14]	7.12	0.0748
C_2H_5	9.47[13]	14.74[15]	1.75[16]	17.92	0.225
$n\text{-}C_3H_7$	19.00[8]	10.73[8]	0.626[8]	12.42	0.0198
$n\text{-}C_4H_9$	20.53[8]	21.48[8]	0.0658	29.92	0.0106
$i\text{-}C_4H_9$	—	—	—	—	0.0691
$n\text{-}C_5H_{11}$	40.20[8]	0.232[8]	1.80×10^{-3}	0.0428	4.11×10^{-4}
$i\text{-}C_5H_{11}$	0.201[a]	0.095[a]	8.63×10^{-3}	—	1.46×10^{-3}
$n\text{-}C_6H_{13}$	0.088[b] 6.17	0.019[b] 9.04	4.5×10^{-4}	7.86×10^{-3}	7.64×10^{-5}
$n\text{-}C_8H_{17}$	5.7×10^{-4}[b] 15.45	9.0×10^{-5}	8.0×10^{-5}	5.58×10^{-5}	4.31×10^{-6}

This work, except where indicated

a) Solid phase is a clathrate hydrate. b) Two-liquid phase system.

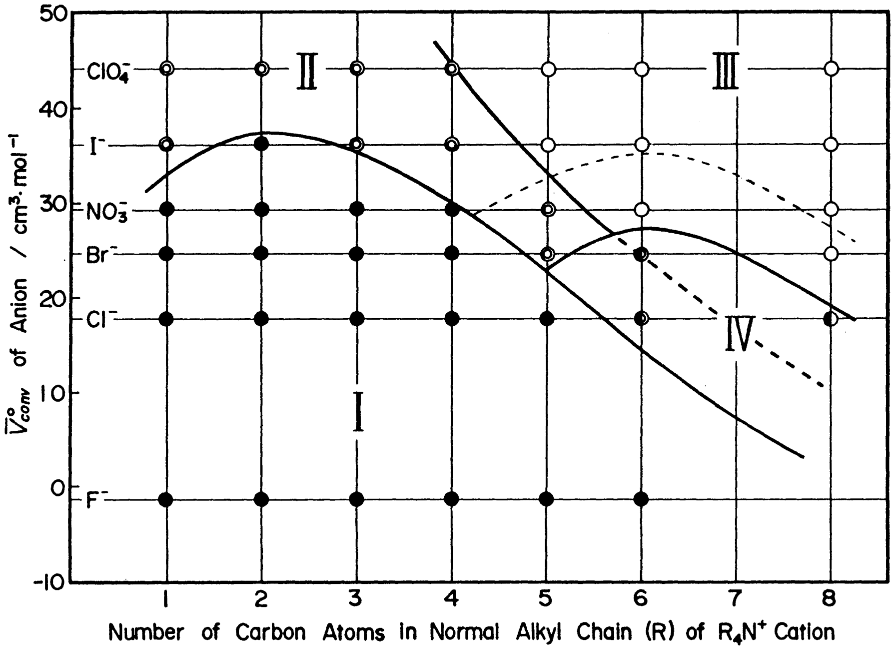

Fig. 1. The relationship between the solubilities of a series of symmetrical tetraalkylammonium salt, R_4NX, in water at 25 °C and the number of carbon atoms in a normal alkyl chain R of the R_4N^+ cation and a conventional partial molar volume of the anion X^- at 25 °C, $\overline{V}^\circ_{conv}$. The solubility of the R_4NX salt is divided into three ranges: ●: higher than 1.0 mol·kg^{-1}; ◎: 0.01—1.0 mol·kg^{-1}; ○: lower than 0.01 mol·kg^{-1}. Three marks ●, ◎, and ○ form the region I, II, and III in this order. The region IV represents a liquid-liquid equilibrium. Precise explanation about the simbols is given in the text.

are about 6.5-times and 3.6-times higher than that of $(n\text{-}C_4H_9)_4NClO_4$ and of $(n\text{-}C_5H_{11})_4NClO_4$, respectively.

The effect of the alkyl chain, R, of the R_4N^+ cation and of the type of the X^- anion on the solubilities of the R_4NX salts in water will be discussed in the following manner. The solubility values are tentatively classified into three concentration ranges: higher than 1.0 mol·kg^{-1}; 0.01—1.0 mol·kg^{-1}; and less than 0.01 mol·kg^{-1}. Using notations ●, ◎, and ○, in this order, all the solubilities of the R_4NX salts, including some fluorides,[8] are represented in Fig. 1. The ordinate of this figure is a conventional partial molar anionic volume at 25 °C, $\overline{V}^\circ_{conv}$, and the abscissa is the number of carbon atoms of a normal alkyl chain R of the R_4N^+ cation. The conventional partial molar anionic volume, i.e., a partial molar anionic volume at infinite dilution based on the assumption that the partial molar volume of a hydrogen ion at infinite dilution is equal to 0, are used as an indication of the effective volume of an anion in a saturated aqueous solution. The values of $\overline{V}^\circ_{conv}$ for the anions discussed in this study are taken from the literature.[21] Symbols ◑ and ◐ in Fig. 1 represent a liquid-liquid phase equilibrium: the mark ◑ indicates a system in which a fairly concentrated solution (in the range of ●, defined above) is in equilibrium with a fairly dilute solution (in the range of ◎); similarly, ◐ indicates a liquid-liquid equilibrium in which the concentration of a dilute solution phase is in the range of ○. It is interesting to note that each symbol (●, ◎, ○, and ◑+◐) gathers within a limited area and forms four domains (I—IV) as shown in Fig. 1. This figure clearly demonstrates the following: (1) that the solubilities of a variety of R_4NX salts in water can be interpreted in terms of two factors, i.e., the chain length of R of the R_4N^+ cation and the molar volume of the X^- anion; (2) as a general trend, the solubility decreases with increasing both the chain length of R and the anionic volume; and (3) the two liquid phase region (IV) appears between region I and III (or II) when the chain length of R becomes fairly long. At 60 °C, for example, domain IV extends to the region shown by a thin dotted line. Tetrahexylammonium salts are most liable to be in a liquid-liquid equilibrium. This would be, at least partly, due to the fact that, for the same kind of anion, the melting points of tetrahexylammonium salts are lower than those both of tetrapentylammonium salts and of tetraoctylammonium salts, as shown below (Table 3).

In Fig. 2, the logarithm of the solubilities (m_{sat}) at 25 °C, given in Table 1, is plotted against the conventional partial molar anionic volumes, $\overline{V}^\circ_{conv}$, for a series of salts having the same R_4N^+ cations. The mark in parenthesis indicates the concentration of a water-rich

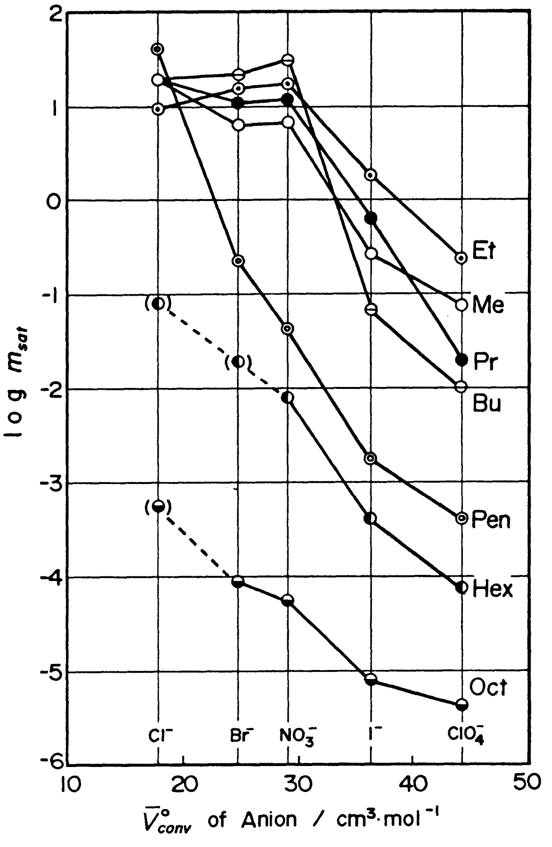

Fig. 2. The relations between the logarithm of the solubilities, m_{sat} (in molality), of a series of R_4NX salts at 25 °C and the conventional partial molar volume of the X^- anion, $\overline{V}^{\circ}_{conv}$. ○: R=$CH_3$; ⊙: R=$C_2H_5$; ●: R=$n$-$C_3H_7$; ○: R=$n$-$C_4H_9$; ◎: R=$n$-$C_5H_{11}$; ◐: R=$n$-$C_6H_{13}$; ⊖: R=$n$-$C_8H_{17}$. The symbol in parenthesis represents the concentration of a water-rich phase in a liquid-liquid equilibrium.

phase in a liquid-liquid equilibrium. Generally, as can be seen for tetrahexylammonium and tetraoctylammonium salts, the solubilities of the R_4NX salts decrease with increasing the $\overline{V}^{\circ}_{conv}$. However, it is noteworthy to point out that (1) the solubilities of tetraethylammonium and tetrapropylammonium salts, except for $(C_2H_5)_4NCl$ and $(n\text{-}C_3H_7)_4NClO_4$, are higher than those of tetramethylammonium salts, in consistent with the observation that the "cage-like" water structure (may be pentagonal dodecahedron) around C_2H_5 and n-C_3H_7 group is more stable than that around a CH_3 group. This is verified by the relationship between the melting points of a series of clathrate-like hydrates of $(n\text{-}C_4H_9)_4NOOCR'$ and the chain length of the R′ group.[6] (2) The solubilities of three tetrabutylammonium salts, $(n\text{-}C_4H_9)_4NCl$, $(n\text{-}C_4H_9)_4NBr$, $(n\text{-}C_4H_9)_4NNO_3$, and of $(n\text{-}C_5H_{11})_4NCl$, are extremely high as compared with the values expected from a monotonous relation between log m_{sat} vs. $\overline{V}^{\circ}_{conv}$, in perfect coincidence with the fact that all of these salts can form a stable clathrate-like hydrate.[7,8] In conclusion, the high solubility of R_4NX salts always corresponds to the ability of a clathrate-like hydrate formation. This suggests that the formation of a stable "cage-like" water structure around the R_4N^+ cation greatly contributes to the high solubility of the R_4NX salt.

In Fig. 3, log m_{sat} is plotted against the number of carbon atoms in a normal alkyl chain R in the R_4N^+ cation for a series of salts with voluminous anions NO_3^-, I^-, and ClO_4^-, respectively. Except for $(n\text{-}C_4H_9)_4NNO_3$, whose solubility is remarkably high, all the other salts cannot form a clathrate-like hydrate;[7]

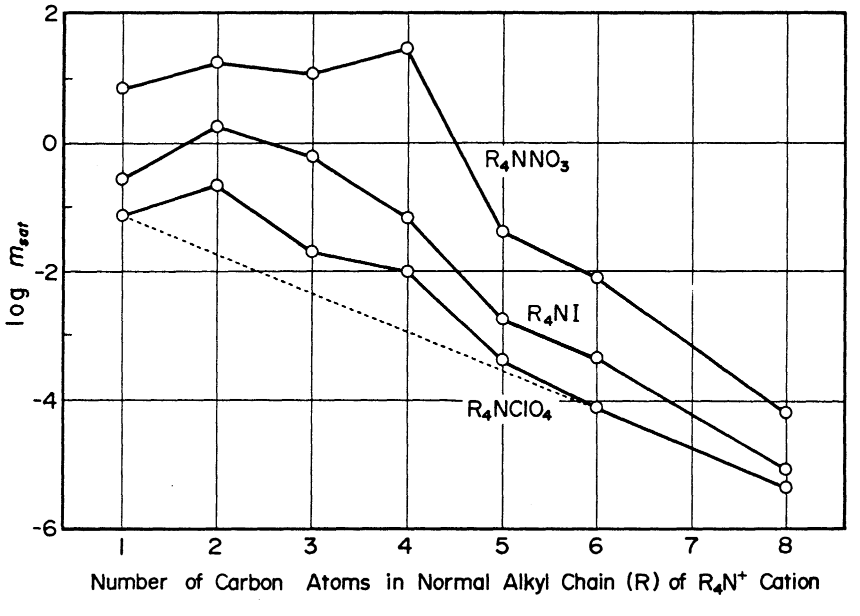

Fig. 3. The relations between the logarithm of the solubilities of a series of R_4NX salts at 25 °C, m_{sat} (in molality), and the number of carbon atoms in a normal alkyl chain R of the R_4N^+ cation. The points corresponding to the salts with the same anions (X=NO_3, I, and ClO_4) are connected by a full line. A dotted line is explained in the text.

Table 2. Solubilities of Symmetrical Tetraalkylammonium Salts, R_4NX, in Water at Various Temperatures

Salt	Solubility m_{sat}/mol·kg^{-1}			
	5 °C	15 °C	35 °C	45 °C
$(i\text{-}C_5H_{11})_4NI$	—	7.60×10^{-3}	1.02×10^{-2}	1.26×10^{-2}
$(n\text{-}C_6H_{13})_4NI$	4.5×10^{-4}	4.1×10^{-4}	6.9×10^{-4}	9.0×10^{-4}
$(CH_3)_4NNO_3$	5.68	6.42	7.92	—
$(C_2H_5)_4NNO_3$	14.71	16.21	19.92	—
$(n\text{-}C_3H_7)_4NNO_3$	8.58	10.42	14.94	—
$(n\text{-}C_4H_9)_4NNO_3$	16.39	22.83	35.75	—
$(n\text{-}C_5H_{11})_4NNO_3$	4.21×10^{-2}	4.11×10^{-2}	4.85×10^{-2}	—
$(n\text{-}C_6H_{13})_4NNO_3$	6.84×10^{-3}	7.34×10^{-3}	—	—
$(n\text{-}C_8H_{17})_4NNO_3$	5.16×10^{-5}	5.46×10^{-5}	6.44×10^{-5}	—
$(CH_3)_4NClO_4$	3.60×10^{-2}	5.17×10^{-2}	0.111	0.148
$(C_2H_5)_4NClO_4$	0.121	0.164	0.318	0.452
$(n\text{-}C_3H_7)_4NClO_4$	1.43×10^{-2}	1.67×10^{-2}	2.59×10^{-2}	3.24×10^{-2}
$(n\text{-}C_4H_9)_4NClO_4$	1.01×10^{-2}	9.95×10^{-3}	1.15×10^{-2}	1.31×10^{-2}
$(i\text{-}C_4H_9)_4NClO_4$	4.51×10^{-2}	5.15×10^{-2}	7.71×10^{-2}	8.74×10^{-2}
$(n\text{-}C_5H_{11})_4NClO_4$	2.59×10^{-4}	3.04×10^{-4}	5.50×10^{-4}	7.66×10^{-4}
$(i\text{-}C_5H_{11})_4NClO_4$	1.37×10^{-3}	1.43×10^{-3}	1.77×10^{-3}	2.25×10^{-3}
$(n\text{-}C_6H_{13})_4NClO_4$	4.85×10^{-5}	5.92×10^{-5}	9.23×10^{-5}	1.40×10^{-4}
$(n\text{-}C_8H_{17})_4NClO_4$	3.27×10^{-6}	3.91×10^{-6}	6.13×10^{-6}	8.01×10^{-6}

i.e., in these solutions a voluminous anion seems to prevent the formation of a stable "cage-like" water structure around the R_4N^+ cation. For the perchlorates, a dotted line is drawn by connecting the point corresponding to $R{=}CH_3$ with the points to $R{=}n\text{-}C_6H_{13}$ and $n\text{-}C_8H_{17}$. Generally, for a sparingly soluble salt solution, log m_{sat} is approximately proportional to $\mu_s-\mu^\circ$ divided by $2.303RT$, where μ_s is the chemical potential of a solid salt and μ° is the standard chemical potential of the salt dissolved in water at a hypothetical concentration of 1 mol·kg^{-1}. If a specific phenomenon such as the formation of a "cage-like" water structure around the R_4N^+ cation does not occur, log m_{sat} will change monotonously upon increasing the number of carbon atoms in R, since both μ_s and μ° are expected to change monotonously with the chain length of R. However, the points corresponding to $R{=}C_2H_5$, $n\text{-}C_3H_7$, and $n\text{-}C_4H_9$, deviate remarkably from the dotted line. This clearly indicates that the formation of a "cage-like" water structure around such cations as $(C_2H_5)_4N^+$, $(n\text{-}C_3H_7)_4N^+$, and $(n\text{-}C_4H_9)_4N^+$ contributes to the elevation of their solubility. A similar discussion can essentially be made for the behavior of the other two lines for R_4NI and R_4NNO_3 in Fig. 3.

(2) Temperature Dependence of the Solubilities of Symmetrical Tetraalkylammonium Salts in Water. The solubilities of a few tetraalkylammonium iodides and of various nitrates and perchlorates over the temperature range 5—45 °C are listed in Table 2. The values at 25 °C are omitted from this table since they are already listed in Table 1. The solid phases of all the salts were found to be anhydrous from Karl Fischer titration. The system $(n\text{-}C_6H_{13})_4NNO_3\text{-}H_2O$ became a liquid-liquid equilibrium at temperatures higher than 28.9 °C. In Fig. 4, the logarithm of the solubilities (expressed in molality, m_{sat}) is plotted against the

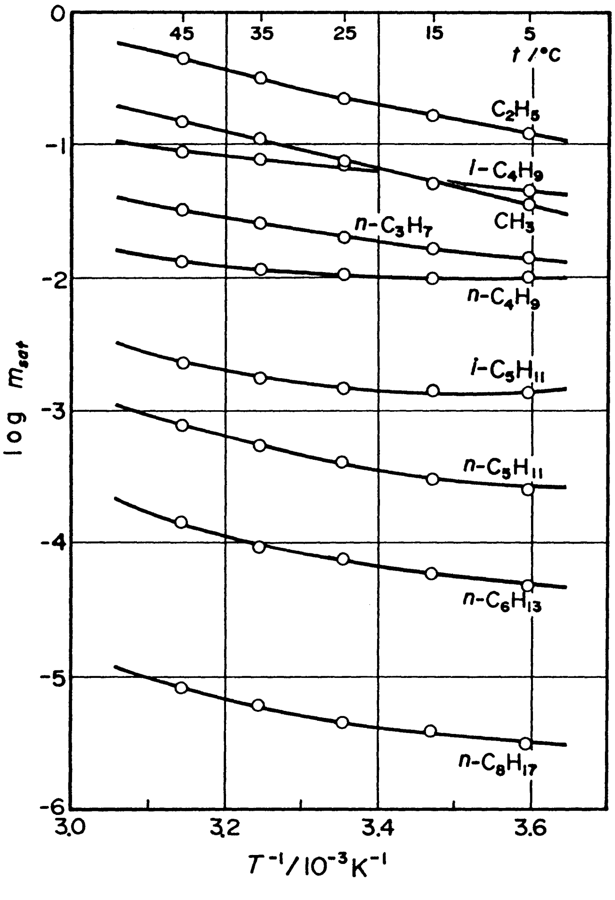

Fig. 4. Temperature dependence of the solubilities of a series of tetraalkylammonium perchlorates, R_4NClO_4, in water. The logarithm of the solubility, m_{sat} (in molality), is plotted against the reciprocal of the absolute temperature. The alkyl group R is shown by each line. The temperature expressed in ordinary Celsius units is shown on the upper side of the figure.

reciprocal of the absolute temperature for a series of tetraalkylammonium perchlorates. A similar plot for the nitrates shows an analogous behavior. This figure clearly indicates that (1) a pronouncely high solubility of tetraethylammonium perchlorate, found at 25 °C as shown in Table 1, is also the case for those at all the temperatures examined; and (2) the slopes $-\partial \log m_{\mathrm{sat}}/\partial(1/T)$ for the perchlorates with R=n-C_3H_7, n-C_4H_9, i-C_4H_9, and i-C_5H_{11} at low temperatures are relatively small as compared with those of the other perchlorates, indicating that the enthalpies of solution of these four perchlorates are somewhat small. This may be due to the evolution of heat owing to the formation of a stable "cage-like" water structure around cations like (n-$C_3H_7)_4N^+$, (i-$C_4H_9)_4N^+$, (n-$C_4H_9)_4N^+$, and (i-$C_5H_{11})_4N^+$ over the temperature range studied. It is interesting to note that this behavior is not eminent for $(C_2H_5)_4NClO_4$ notwithstanding a stable "cage-like" water structure around the $(C_2H_5)_4N^+$ cation is expected as mentioned above. Precise discussion will be impossible since for such a very soluble salt an activity should be used instead of the solubility itself.

(3) Thermodynamic Analysis of the Solubilities of Symmetrical Tetraalkylammonium Salts in Water. If we use a hypothetical liquid supercooled below its melting point as the standard state, the chemical potential of a solid substance at T, μ_2^{s}, is given by

$$\mu_2^{\mathrm{s}}=\mu_2^{\mathrm{l}}+RT\ln a_2, \tag{1}$$

where μ_2^{l} is the chemical potential of the standard state, a_2 is the activity of the solute, and R is the gas constant. The quantity $RT\ln a_2$ can be expressed by[22]

$$RT\ln a_2= -\Delta H_{\mathrm{m}}^{\mathrm{F}}(1-T/T_{\mathrm{m}})+\Delta C_{\mathrm{p}}(T_{\mathrm{m}}-T)+T\Delta C_{\mathrm{p}}\ln(T/T_{\mathrm{m}}), \tag{2}$$

in which ΔC_{p} $(=C_{\mathrm{p}}^{\mathrm{l}}-C_{\mathrm{p}}^{\mathrm{s}})$ is the difference of the molar heat capacities between liquid and solid state, and $\Delta H_{\mathrm{m}}^{\mathrm{F}}$ is the molar enthalpy of melting at the melting point, T_{m}.

Under equilibrium conditions between a solid and a saturated aqueous solution,

$$\mu_2^{\mathrm{s}}=\mu_2=\overline{H}_2-T\bar{S}_2, \tag{3}$$

where $\overline{H}_2$ and $\bar{S}_2$ are partial molar enthalpy and entropy of a solute, respectively, in a saturated solution. Thus, from Eqs. 1 and 3, together with the relation $\mu_2^{\mathrm{l}}=H_2^{\mathrm{l}}-TS_2^{\mathrm{l}}$, we may write

$$(\overline{H}_2-H_2^{\mathrm{l}})-T(\bar{S}_2-S_2^{\mathrm{l}})=RT\ln a_2. \tag{4}$$

The enthalpy term in Eq. 4 can be written as

$$\overline{H}_2-H_2^{\mathrm{l}}=\Delta H_{\mathrm{s}}(\mathrm{sat})-\Delta H_{\mathrm{m}}^{\mathrm{F}}+\Delta C_{\mathrm{p}}(T_{\mathrm{m}}-T) \tag{5}$$

The term $\Delta H_{\mathrm{s}}(\mathrm{sat})$ $(=\overline{H}_2-H_2^{\mathrm{s}})$ represents the molar enthalpy of solution of a solid substance in a saturated solution.

The entropy term in Eq. 4 may be expressed by[23]

$$\bar{S}_2-S_2^{\mathrm{l}}=-R\{\nu_+\ln(X_+^{\mathrm{sat}}/X_+^{\mathrm{l}})+\nu_-\ln(X_-^{\mathrm{sat}}/X_-^{\mathrm{l}})\}+S_2^{\mathrm{E}}, \tag{6}$$

where X_+^{sat} and X_-^{sat} is the mole fraction of the cation and the anion, respectively, in a saturated solution, and similarly, X_+^{l} and X_-^{l} in a hypothetical melt of a solute. The ν_+ and ν_- are the number of moles of cations and anions, respectively, when one mole of a solute dissociates in the solution. S_2^{E} is the excess entropy of the solution and Eq. 6 may be regarded as the definition of S_2^{E}.

By inserting $X_+^{\mathrm{sat}}=(\nu_+\cdot m_{\mathrm{sat}})/(M+\nu\cdot m_{\mathrm{sat}})$, $X_-^{\mathrm{sat}}=(\nu_-\cdot$

Table 3. Melting Point (t_{m}), Transition Temperature (t_{tr}), Enthalpy of Melting ($\Delta H_{\mathrm{m}}^{\mathrm{F}}$), and of Transition($\Delta H_{\mathrm{tr}}$) of Symmetrical Tetraalkylammonium Salts

Salts	t_{m}	$\Delta H_{\mathrm{m}}^{\mathrm{F}}$	t_{tr}	ΔH_{tr}
	°C	kJ·mol^{-1}	°C	kJ·mol^{-1}
(n-$C_3H_7)_4NNO_3$	>250	—	57.6	8.97
(n-$C_3H_7)_4NClO_4$	241.0(237—239[18])	14.2	171.0	11.2
			173.5	4.47
(n-$C_4H_9)_4NI$	146.0(145—147[8])	9.18	116.0	27.1
(n-$C_4H_9)_4NNO_3$	116.1	15.6	89.1	0.21
(n-$C_4H_9)_4NClO_4$	214.5(207—209[18])	12.3	56.0	3.10
(n-$C_5H_{11})_4NI$	134.0(134—135[8])	38.2	121.0	15.2
(n-$C_5H_{11})_4NNO_3$	110.5	29.4	82.5	11.5
(n-$C_5H_{11})_4NClO_4$	116.0(110—116[18])	36.1	88.9	16.3
(i-$C_5H_{11})_4NI$	147.5(146—147[8])	16.0	118.0	23.9
(i-$C_5H_{11})_4NClO_4$	113.0	22.4	98.0	6.60
(n-$C_6H_{13})_4NI$	102.5(103—104[8])	17.7	67.5	28.8
			76.0	5.76
(n-$C_6H_{13})_4NNO_3$	62.0	17.0	44.0	24.8
(n-$C_6H_{13})_4NClO_4$	104.0(105—106[18])	16.8	58.5	23.3
			81.5	5.88
			93.0	2.02
(n-$C_8H_{17})_4NCl$	18—19	22.6	—	—
(n-$C_8H_{17})_4NI$	128.0	48.7	81.5	3.54
(n-$C_8H_{17})_4NNO_3$	110.5	41.0	101.0	2.33
(n-$C_8H_{17})_4NClO_4$	134.0	46.5	70.0	4.68

$m_{sat})/(M+\nu \cdot m_{sat})$, $X^l_+=\nu_+/\nu$, and $X^l_-=\nu_-/\nu$ into Eq. 6, we can get

$$\bar{S}_2-S^l_2=-\nu R\ln\{(\nu \cdot m_{sat})/(M+\nu \cdot m_{sat})\}+S^E_2, \tag{7}$$

where $\nu=\nu_++\nu_-$, M=55.51, and m_{sat} is the solubility expressed in molality. Thus, from Eqs. 2, 4, 5, and 7, the following relation is obtained:

$$-\nu RT\ln\{(\nu \cdot m_{sat})/(M+\nu \cdot m_{sat})\}= \Delta H_s(\text{sat})-\Delta H^F_m(T/T_m)-T\Delta C_p\ln(T/T_m)-TS^E_2. \tag{8}$$

Furthermore, since most of the symmetrical tetraalkylammonium salts discussed here have transition temperatures (as shown later, Table 3) between room temperature and their melting points, the term $-\sum_{tr}\Delta H_{tr}(T/T_{tr})$ should be added to the right side of Eq. 8, where ΔH_{tr} is the molar enthalpy of a transition at a transition temperature, T_{tr}, and summation is carried out with respect to all the transitions when a solid has more than one transition point between T and T_m. Then Eq. 8 becomes,

$$-\nu RT\ln\{(\nu \cdot m_{sat})/(M+\nu \cdot m_{sat})\}= \Delta H_s(\text{sat})-\Delta H^F_m(T/T_m) -\sum_{tr}\Delta H_{tr}(T/T_{tr})-T\Delta C_p\ln(T/T_m)-TS^E_2. \tag{9}$$

In the following discussion, the term containing ΔC_p is omitted for the following reasons: (1) precise information about the values of ΔC_p is not available and (2) the melting points (Table 3) of the salts discussed here are lower than 150 °C, except for $(n\text{-}C_3H_7)_4NClO_4$ and $(n\text{-}C_4H_9)_4NClO_4$, so that the quantity of $\ln(T/T_m)$ is smaller than 0.41 at T=298.15 K. Thus, we use the following equation:

$$-\nu RT\ln\{(\nu \cdot m_{sat})/(M+\nu \cdot m_{sat})\}= \Delta H_s(\text{sat})-\{\Delta H^F_m(T/T_m) +\sum_{tr}\Delta H_{tr}(T/T_{tr})\}-TS^E_2. \tag{10}$$

The melting points, transition temperatures, the enthalpy of melting, and the enthalpy of transition which are determined by differential scanning calorimetry are listed in Table 3, together with some of the melting points reported in the literature. The errors inherent in the determination of the enthalpies of melting and transition are of the order of 5—10 per cent, since calibration of the apparatus was carried out at the melting point of In alone (156.6 °C, and ΔH^F_m=3.3 kJ·mol^{-1}). No transition temperatures and enthalpy data had been reported earlier. For the salts whose ΔH_s(sat) data are available, each term in Eq. 10 at 298.15 K can be calculated from the data given in Tables 1—3; these are listed in Table 4. The ΔH_s(sat) values in Table 4 are either the values obtained by Krishnan et al.[24] or values calculated from the relation $\Delta H_s(\text{sat})=-2R\partial\ln m_{sat}/\partial(1/T)$ using the data shown in Tables 1 and 2. This calculation is reasonable, at least to a first approximation, since this relation was only applied to sparingly soluble salts. The values obtained by Krishnan et al.[24] are based upon the enthalpies of solution in propylene carbonate and the enthalpy of transfer from propylene carbonate to water. Therefore, these values are not exactly equal to the enthalpy of solution of the solid salt at its saturation concentration. However, we use these values as approximate values of ΔH_s(sat) since there are no data available and the other terms listed in Table 4, especially the one containing ΔH^F_m and ΔH_{tr}, are not so accurate.

It is interesting to note that, for the most iodides and perchlorates, the quantity ΔH_s(sat) is almost compensated for by the quantity $\Delta H^F_m(T/T_m)+\sum_{tr}\Delta H_{tr}(T/T_{tr})$, resulting in a large positive value of the $-\nu RT\ln\{(\nu \cdot m_{sat})/(M+\nu \cdot m_{sat})\}$ term corresponds roughly to a large negative value of the excess entropy TS^E_2. In case of the nitrates, not only the values of the ΔH_s(sat) term are generally smaller than the term $\Delta H^F_m(T/T_m)+\sum_{tr}\Delta H_{tr}(T/T_{tr})$, but also the term $-\nu RT\ln\{(\nu \cdot m_{sat})/(M+\nu \cdot m_{sat})\}$ is rather small compared with those of iodides

Table 4. Each Term in Eq. 10 and Calculated Values of Excess Entropy at 298.15 K for Some Symmetrical Tetraalkylammonium Salts

Salt	(A)[a]	ΔH_s(sat)	(B)[b]	S^E_2	S^E_2/n
	kJ·mol^{-1}			J·K^{-1}·mol^{-1}	
$(n\text{-}C_3H_7)_4NClO_4$	35.8	27.2[24]	18.7	−92	−7.7
$(n\text{-}C_4H_9)_4NI$	29.8	17.7[24]	27.3	−132	−8.3
$(n\text{-}C_4H_9)_4NClO_4$	39.0	10.8[24]	10.3	−129	−8.1
$(n\text{-}C_5H_{11})_4NI$	47.8	34.5[24]	39.5	−177	−8.9
$(n\text{-}C_5H_{11})_4NNO_3$	32.1	13.0	32.5	−173	−8.7
$(n\text{-}C_5H_{11})_4NClO_4$	55.4	43.0[24]	41.1	−180	−9.0
$(i\text{-}C_5H_{11})_4NI$	40.3	17.4	29.5	−176	−8.8
$(i\text{-}C_5H_{11})_4NClO_4$	48.8	14.4	22.6	−191	−9.6
$(n\text{-}C_6H_{13})_4NI$	55.2	38.3	44.1	−205	−8.5
$(n\text{-}C_6H_{13})_4NNO_3$	40.5	10.5	38.5	−230	−9.6
$(n\text{-}C_6H_{13})_4NClO_4$	63.5	33.7	40.7	−237	−9.9
$(n\text{-}C_8H_{17})_4NNO_3$	65.0	15.5	33.8	−280	−8.8
$(n\text{-}C_8H_{17})_4NClO_4$	77.8	36.6	38.1	−266	−8.3

a) (A)$=-\nu RT\ln\{(\nu \cdot m_{sat})/(M+\nu \cdot m_{sat})\}$. b) (B)$=\Delta H^F_m(T/T_m)+\sum_{tr}\Delta H_{tr}(T/T_{tr})$.

and perchlorates with the same type of cation because of relatively high solubility of the nitrates (Table 1). Eventually, this situation also results in a large negative excess entropy. The values of S_2^E calculated from Eq. 10 are also listed in Table 4. It is interesting to note that (1) the S_2^E becomes more negative upon increasing the number of carbon atoms of the R_4N^+ cation and (2) for the same kind of cation S_2^E has almost a similar value, irrespective of the kind of anion. This result suggests that the value of S_2^E is mainly determined by the number of carbon atoms of the R_4N^+ cation. Tentatively, if we calculate the excess entropy per mole of carbon atoms, S_2^E/n, n being the total number of carbon atoms of the R_4N^+ cation, this value has almost a similar value ranging from -8 to $-10\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ for all the salts examined here. This value is also listed in the last column of Table 4. The simple average of S_2^E/n is $-8.8\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. Although a quantitative discussion about the behavior of the excess entropy is impossible at present, the behavior of S_2^E (or of S_2^E/n) found in this study will undoubtedly reflect a restricted motion of the carbon chain of the R_4N^+ cation in the solution due to the water networks surrounding the R_4N^+ cation. Unfortunately, it is impossible to discuss the relation between a "cage-like" water structure and the excess entropy defined here, since S_2^E cannot be calculated (for the reasons mentioned below) for many tetraalkylammonium salts to which the existence of a stable "cage-like" water structure in its aqueous solution is expected. The reasons are: (1) a value for ΔH_s(sat) is not available in the literature and its estimation from the temperature dependence of the solubility is inadequate because of the high solubility of the salt concerned, and (2) in general, such a salt has a fairly high melting point and sometimes gradually decomposes at high temperatures, so that accurate values of T_m and ΔH_m^F (and T_{tr} and ΔH_{tr}) cannot be obtained by thermal analyses.

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