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Hydrates of Organic Compounds. VI. Heats of Fusion and of Solution of Quaternary Ammonium Halide Clathrate Hydrates

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The heat of solution in water of four quaternary ammonium halide clathrate hydrates, $R_4NX \cdot nH_2O$ (R= n-C_4H_9, X=F and Cl, n=30; R=i-C_5H_{11}, X=F and Cl, n=39), and the heat of dilution of their aqueous solutions were measured calorimetrically. From these results, the heat of fusion of the clathrate hydrate solid (ΔH_f) and the heat of solution of it in saturated solutions (ΔH_{sat}) were obtained. The ΔH_f was compared with a hypothetical heat of fusion of the same number of moles of ice I as the hydration number of the hydrate. The ΔH_{sat} was about 14 kJ/mol smaller than the ΔH_f in the (n-C_4H_9)$_4$NX hydrates and about 27 kJ/mol smaller in the (i-C_5H_{11})$_4$NX hydrates irrespective of the type of anion. Furthermore, ΔH_{sat} was calculated thermodynamically and it agreed with the calorimetrically obtained value within the experimental error.

Clathrate-like hydrates of quaternary ammonium salts, which were originally found in Kraus' laboratory in 1940[1] and were examined later in detailed structural studies by Jeffrey *et al.*,[2-4] have been known to have some unusual properties in comparison with ordinary gas hydrates. The most striking features are summarized as follows:

(1) They are easily formed by cooling their aqueous solutions at atmospheric pressure and the concentration range from which the hydrate is separated out is very wide, especially for a stable hydrate.[5] (2) Generally these hydrates are very stable, *i.e.*, they have fairly high melting points as compared to ordinary gas hydrates. Melting points at around room temperature are not unusual. (3) The formation of such a hydrate is possible for salts having a variety of anions,[2,5] but a suitable alkyl chain of the cation is almost exclusively limited to the butyl or the isopentyl group.[6]

The thermodynamic properties of aqeous tetraalkylammonium salt solutions have been extensively studied[7] and the results of these studies are often interpreted by structural modifications of water molecules around the cation from analogy with the clathrate hydrates. However little is known about the thermodynamic properties of the clathrate hydrate itself. Such thermodynamic properties as the heat of fusion and of solution of the clathrate hydrate are basic properties not only for the interpretation of the nature of the hydrogen-bonded water networks around the alkyl groups of the cation but also for an application of these hydrates as, for example, a heat reservoir utilizing the heat evolved or absorbed when their states change.

In this paper the author reports the heats of fusion and of solution in water of four clathrate hydrates, (n-C_4H_9)$_4$NF·30H_2O, (n-C_4H_9)$_4$NCl·30H_2O, (i-C_5H_{11})$_4$NF·39H_2O, and (i-C_5H_{11})$_4$NCl·39H_2O, and discusses the effect of the type of the anion and of the alkyl group of the cation on these thermal properties. In addition, the calorimetrically determined heats of solution are compared with those calculated from the data concerning both temperature dependence of the solubilities and concentration dependence of the mean molal activity coefficients.

The hydrates used in this paper are the most convenient ones for calorimetric measurement since they all have relatively high congruent melting points and each hydration number has been well determined in previous phase-diagramatic investigations.[5]

Experimental

Materials. The procedures for preparing and purifying the materials used in this experiment were the same as those in the previous work.[5,8] The concentration of the mother solution was determined by the Karl Fischer titration method for the fluoride solutions and by a standard KNCS titration method (Volhard method) for the chloride solutions.[5]

Calorimetry. A twin-type rotating-microcalorimeter manufactured by Ōyōdenki Kenkyujo (RCM-1N)[9] was used. The mixing cell was a glass cylinder of 45 mm diameter and 30 mm high. Part of it was divided into two compartments by a glass wall and a sample solution and water were loaded into each compartment from a weighed syringe fitted with a stainless steel needle.

The heats of dilution (or solution) at infinite dilution were obtained by measuring heat changes in the following two steps: sample solution (or solid)→0.07 mol kg^{-1} solution→ 0.005 mol kg^{-1} solution. The heat due to a further dilution from 0.005 mol kg^{-1} which was estimated to be smaller than 0.1 kJ/mol, was neglected. The heat evolved in the second stage of dilution was also small compared with that in the first stage of dilution (or solution) and was found to be 0.68 kJ/mol, 0.52 kJ/mol, 1.29 kJ/mol, and 1.14 kJ/mol for (n-C_4H_9)$_4$NF, (n-C_4H_9)$_4$NCl, (i-C_5H_{11})$_4$NF, and (i-C_5H_{11})$_4$NCl, respectively.

In this experiment the following three heats were determined for each salt. These heats and their experimental methods for measuring the heat changes in the first step of dilution (or solution) are summarized as follows:

(i) The Heat of Solution of a Clathrate Hydrate Solid in Water at Infinite Dilution (ΔH_S). A given amount of a sample solution whose concentration was equal to its congruent composition (1.850 mol kg^{-1} for the tetrabutylammonium salts and 1.423 mol kg^{-1} for the tetraisopentylammonium salts) was loaded into one of the compartments of the cell at temperatures a few degrees higher than its congurent melting point (T_C). Then the cell was gradually cooled down, with occasional shaking, until the sample solution solidified after which it was kept standing for about 4 h at a temperature a few degrees lower than the T_C in order to anneal the solid. Next the cell was loaded into the calorimeter, followed by the insertion of water into the other compartment of the cell in amounts which corresponded to a final concentration of 0.07 mol kg^{-1}. After thermal equilibrium was reached, the heat change was

measured when the solid was dissolved in the water.

(ii) The Heat of Dilution in Water of a Metastable Clathrate Hydrate Liquid at Infinite Dilution ($-\phi_{L,C}$). Since the liquid sample whose concentration was equal to its congruent composition could stay in a metastable liquid state for a long time at the measuring temperature (10 °C for the $(n\text{-}C_4H_9)_4NCl$ and 25°C for the other salts) if not cooled down deliberately as in (*i*), its heat of dilution could easily be measured by mixing it with water. A given amount of a sample solution whose concentration was equal to its congruent composition was loaded into one compartment of the cell at a temperature a few degrees higher than its T_C. The cell was then loaded into the calorimeter, followed by the insertion of an adequate amount of water into the other compartment of the cell. After thermal equilibrium was attained, the heat change was measured when both liquids were mixed.

(iii) The Heat of Dilution of a Salt Solution from a Saturated Solution to an Infinitely Dilute Solution ($-\phi_{L,sat}$). The heat of dilution of a given amount of salt solution whose concentration was equal to its solubility at a measuring temperature was measured in a similar way as in (*ii*).

The three heats measured and other heats discussed in later sections are mutually interconnected by the following scheme:

$$\begin{tikzcd}
\text{Clathrate hydrate solid} \arrow[r, "\Delta H_{sat}"'] \arrow[d, "\Delta H_f"] \arrow[rrd, bend left, "\Delta H_s"] & \text{Saturated aqueous solution} \arrow[rd, "-\phi_{L,sat}"] & \\
\text{Clathrate hydrate metastable liquid} \arrow[rr, "-\phi_{L,c}"'] & & \text{Infinitely dilute aqueous solution}
\end{tikzcd}$$

Solubility and Mean Molal Activity Coefficient Measurements. The solubilities of the clathrate hydrate solid in water were measured by the following manner. In a glass cylinder, which was 30 mm diameter and 100 mm high and was immersed in a constant temperature bath, the solid hydrate was saturated in about 10 cm^3 water by vigorous stirring with a magnetic stirrer. Then a given amount of the saturated solution was withdrawn and analyzed. In the case of the fluoride solutions, concentration was determined by measuring the water content by the Karl Fischer titration method for the sample solution which had partially been concentrated by dehydration on P_2O_5 in a desiccator. The standard KNCS titration method (Volhard method[5]) was used for the chloride solutions.

The mean molal activity coefficients ($\gamma_\pm$) for the tetraisopentylammonium salt solutions were obtained from the isopiestic data by the conventional method.[10,11] The apparatus and procedure for the isopiestic measurements were the same as that in the previous work.[12]

Results and Discussion

(1) Fundamental Properties of the Clathrate Hydrates. Prior to the calorimetric experiments we must specify the fundamental properties of each clathrate hydrate such as the hydration number (n), the congruent melting point (T_c), and the solubility in water (m_{sat}). These values are summarized in Table 1. Although somewhat different hydration numbers are found in the literature,[2,5,8,13] we chose 30 for the $(n\text{-}C_4H_9)_4NX$ hydrates and 39 for the $(i\text{-}C_5H_{11})_4NX$ hydrates by reference to our previous phase-diagramatic results.[5] Therefore, the congruent compositions become 1.850 mol kg^{-1} for tetrabutylammonium halide systems and 1.423 mol kg^{-1} for the tetraisopentylammonium halide systems.

Table 1. Fundamental properties of the tetraalkylammonium halide (R_4NX) clathrate hydrates

R_4NX	Hydration number[5]	Mp θ_m[5]	Solubility in water
		°C	mol kg^{-1}
$(n\text{-}C_4H_9)_4NF$	30	28.3	0.920±0.002[a]
$(n\text{-}C_4H_9)_4NCl$	30	15.0	0.561±0.003[b]
$(i\text{-}C_5H_{11})_4NF$	39	31.5	0.293±0.002[a]
$(i\text{-}C_5H_{11})_4NCl$	39	29.6	0.203±0.002[a]

a) At 25 °C. b) At 10 °C.

Calorimetric measurements were carried out at 10 °C for the $(n\text{-}C_4H_9)_4NCl$ system and at 25 °C for the other three systems, taking into account each congruent melting point listed in Table 1.[5]

(2) Calorimetric Measurements. The observed ΔH_s's and ϕ_L's are summarized in Table 2. The physical meaning of these quantities has been explained in the experimental section. Listed values were averages of 4—5 determinations. The error limit attached to each value was estimated by taking into account the dispersion in each measurement as well as the errors inherent in sampling the solution and in determining its concentration.

Narten and Lindenbaum[13] have reported ΔH_s and $\phi_{L,C}$ for $(n\text{-}C_4H_9)_4NF$ hydrate, which are also listed in Table 2. Their values are somewhat higher than the present values. The values of $\phi_{L,C}$ and $\phi_{L,sat}$ for $(n\text{-}C_4H_9)_4NCl$ solutions which are calculated from the heats of dilution data at 25 °C (not at 10 °C) obtained by Lindenbaum[14] are also listed in Table 2. These

Table 2. The heats of solution of the tetraalkylammonium halide (R_4NX) clathrate hydrates and the relative apparent molal heat contents of the aqueous R_4NX solutions

R_4NX	Temperature	ΔH_s	$\phi_{L,c}$	$\phi_{L,sat}$
	°C	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
$(n\text{-}C_4H_9)_4NF$	25	158.6±3.7 (170.6[13])	25.8±0.5 (26.6[13])	12.6±0.2
$(n\text{-}C_4H_9)_4NCl$	10	136.2±4.0	19.5±0.4 (20.5[14])[a]	5.5±0.2 (5.2[14])[a]
$(i\text{-}C_5H_{11})_4NF$	25	223.1±5.0	32.8±1.2	6.2±0.3
$(i\text{-}C_5H_{11})_4NCl$	25	253.0±4.2	29.7±0.3	3.9±0.2

a) At 25 °C.

values are in fairly good agreement with the present data regardless of the slight difference in temperature.

The heat of fusion of clathrate hydrate solid (ΔH_f) and its heat of solution in a saturated aqueous solution (ΔH_{sat}) can be calculated by the following relations:

$$\Delta H_f = \Delta H_s + \phi_{L,c}, \tag{1}$$

$$\Delta H_{sat} = \Delta H_s + \phi_{L,sat}. \tag{2}$$

These heats are tabulated in Table 3 and discussed in the following sections.

TABLE 3. THE HEATS OF FUSION OF THE TETRAALKYLAMMONIUM HALIDE (R_4NX) CLATHRATE HYDRATES AND THE HEATS OF SOLUTION OF THEM IN SATURATED AQUEOUS SOLUTIONS

Hydrate	Temperature	ΔH_f	ΔH_{sat}
	°C	kJ mol^{-1}	kJ mol^{-1}
$(n\text{-}C_4H_9)_4NF \cdot 30H_2O$	25	184 ± 4	171 ± 4
$(n\text{-}C_4H_9)_4NCl \cdot 30H_2O$	10	156 ± 4	142 ± 4
$(i\text{-}C_5H_{11})_4NF \cdot 39H_2O$	25	256 ± 5	229 ± 5
$(i\text{-}C_5H_{11})_4NCl \cdot 39H_2O$	25	283 ± 4	257 ± 4

(3) The Heats of Fusion of Clathrate Hydrate Solids. The heat of fusion of a tetraalkylammonium halide clathrate hydrate may be considered to be made up by the following three terms:

$$\Delta H_f = \Delta H_c + \Delta H_e + \Delta H_h, \tag{3}$$

in which ΔH_c is the change in enthalpy of the hydrogen-bonded water networks (cages) when a clathrate hydrate solid melts, ΔH_e and ΔH_h is the change in electrostatic energy between ions and that in the energy due to additional hydration of ions, respectively. Although it is impossible to discuss each enthalpy change quantitatively, we can reasonably assume that the last two heats, ΔH_e and ΔH_h, are relatively small as compared with the first term, ΔH_c, from the following reasons: (1) The local structure of the melt is expected to be essentially similar to that of the solid state, as exemplified for $(n\text{-}C_4H_9)_4NF$ solution.[13] Thus, interionic distance will not change appreciably when the solid melts. (2) A large extent of additional hydration of the ions cannot be expected from the fact that all the ions are already surrounded by water molecules in the solid state and further that the total amount of water remains constant in the melting process.

Therefore, if we assume that the last two terms of Eq. 3 are negligible as compared with the first term and further that the first term may be approximately expressed as $n \cdot \Delta H_{f,ice}$, Eq. 3 becomes

$$\Delta H_f \simeq \Delta H_c \simeq n \cdot \Delta H_{f,ice}, \tag{4}$$

in which n is the hydration number of a clathrate hydrate, and $\Delta H_{f,ice}$ is a hypothetical molal heat of fusion of ice I at the measuring temperature. This heat of fusion is estimated to be 6.375 kJ/mol at 10 °C and 6.896 kJ/mol at 25 °C taking into account the heat capacity data.[15] Equation 4 has been proved to be fairly adequate for ordinary gas hydrates[16,17] or for some of the liquid hydrates.[18] However, it may not be so appropriate for the tetraalkylammonium salt hydrates since the central N atom of the cation and the fluoride anion (and probably also the chloride anion) replace water molecules within the lattice. This leads to the disappearance of some of the hydrogen bonds and a decrease in the number of stable orientations of the water molecules at sites neighboring the N^+ and F^- (and Cl^-) sites.[3,4,17]

Tentatively, the observed ΔH_f's (Table 3) were compared with the calculated $n \cdot \Delta H_{f,ice}$ in the form of the ratio of the two, $\Delta H_f / n \cdot \Delta H_{f,ice}$. This ratio was 0.89, 0.82, 0.95, and 1.05 for $(n\text{-}C_4H_9)_4NF$, $(n\text{-}C_4H_9)_4NCl$, $(i\text{-}C_5H_{11})_4NF$, and $(i\text{-}C_5H_{11})_4NCl$ hydrate, respectively. This result indicates that the apparent heats of fusion of the tetrabutylammonium halide hydrates are a little smaller (about 85%) than that of a hypothetical heat of fusion of ice I of the same number of moles as the hydration number of the hydrates, whereas those of the tetraisopentylammonium halide hydrates are approximately equal to the corresponding heats of fusion of ice I. The reason for this different behavior in the two series of hydrates can be explained, at least partly, by the following facts; (a) the proportion of the water molecules which are structurally affected by the presence of R_4N^+ cation and F^- anion (or Cl^- anion) is larger in the tetrabutylammonium halide hydrate than in the tetraisopentylammonium halide hydrate since the hydration number of the former is smaller than that of the latter; (b) the hydrogen-bonded water networks in the tetraisopentylammonium halide hydrate seem to be stabler than that in the tetrabutylammonium halide hydrate since the melting points of the tetraisopentylammonium halide hydrates are relatively high and are not so predominantly affected by the kind of anion.[2,5] Furthermore, even $(i\text{-}C_5H_{11})_4NI$ can form a clathrate-like hydrate.[5] Tetrabutylammonium iodide cannot form a clathrate hydrate, presumably because a stabilizing ability of water networks surrounding the butyl chain is not strong enough to overcome the lattice distortion caused by the presence of the bulky iodide anion.

(4) The Heats of Solution of the Clathrate Hydrate Solids in Saturated Aqueous Solutions. From Eqs. 1 and 2, the ΔH_{sat} can be expressed by the following relation:

$$\Delta H_{sat} = \Delta H_f - (\phi_{L,c} - \phi_{L,sat}). \tag{5}$$

The heat in the parenthesis of the right-hand side of the above equation is made up by two heats of dilution which are due to an additional hydration of ions including hydrophobic hydration. It should be noted that, from Table 2 (or 3), this quantity is about 14 kJ/mol for the tetrabutylammonium halide hydrates and about 27 kJ/mol for the tetraisopentylammonium halide hydrates irrespective of the type of the anion and further that these heats correspond roughly to about 10% of the ΔH_{sat} in each hydrate. Therefore, it may be concluded that the heat of solution of a clathrate hydrate has similar values to its heat of fusion and, in turn, the latter heat may approximately be estimated by Eq. 4. The phenomenon that the heat of solution of a solid is close to its heat of fusion is commonly found in the dissolution process of ordinary hydrated electrolytes like $CaCl_2 \cdot 6H_2O$.[19]

On the other hand, the heat of solution of a hydrated electrolyte in saturated solution can be expressed by the following thermodynamic equation:[19]

$$\Delta H_{sat} = -\nu R(1-nm_{sat}/M)^2 \times (1+(\partial \ln \gamma_\pm/\partial \ln m)_{sat}) \times (\partial \ln m'_{sat}/\partial(1/T)), \qquad (6)$$

in which $\nu=\nu_+ + \nu_-$, R=the gas constant, n=the hydration number, m_{sat}=solubility expressed in molality, M=55.51, $\gamma_\pm$=mean molal activity coefficient, $m'_{sat}=m_{sat}/(1-nm_{sat}/M)$, and T=the absolute temperature. Though this equation has been applied to ordinary inorganic hydrated electrolytes and its validity has been verified in several systems,[19] it has not previously been applied to a clathrate hydrate system. Therefore, it is interesting to see to what extent the heat of solution which is calculated by Eq. 6 is compatible with that directly obtained by calorimetry (Table 3).

The values of $(\partial \ln \gamma_\pm/\partial \ln m)_{sat}$ for the two tetrabutylammonium halide solutions were calculated from existing data[20,21] and those for the tetraisopentylammonium halide solutions were newly obtained in this experiment from the isopiestic data. Because of the low solubilities of the two tetraisopentylammonium halide hydrates (Table 1), which are compatible with the concentration limit (about 0.1 mol kg^{-1} [10]) to which an accurate isopiestic measurement can be done, the values of $(\partial \ln \gamma_\pm/\partial \ln m)_{sat}$ for these two halide solutions have errors in the order of 4—5%. The temperature dependence of the solubilities of all the hydrates are shown in Fig. 1. The slopes of $\partial \ln m'_{sat}/\partial(1/T)$, which were obtained by graphical differentiation of Fig. 1, have also some uncertainties since $\ln m'_{sat}$ decreases nonlinearly with increasing $1/T$. The calculated ΔH_{sat} and all the values used for this calculation are summarized in Table 4. These calculated values of ΔH_{sat} agree within experimental error with those obtained by direct calorimetry (Table 3). It is interesting to note that, as is seen from Table 4, the approximate values of the ΔH_{sat} for the two chloride hydrates can be calculated only from the solubility *vs.* temperature data since the values $(\partial \ln \gamma_\pm/\partial \ln m)_{sat}$ are relatively small as compared with unity for these hydrates.

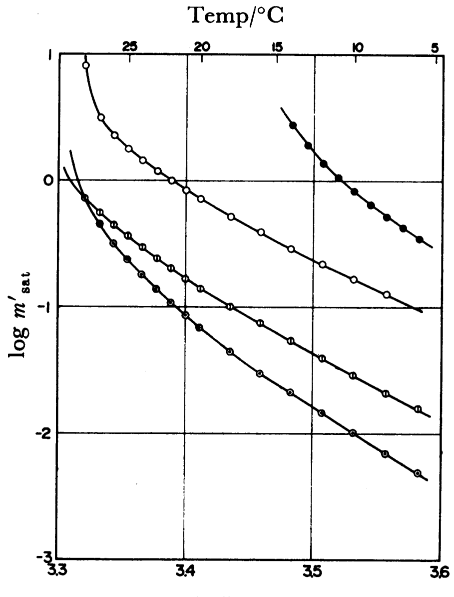

Fig. 1. Temperature dependence of the solubilities (m'_{sat}) of tetraalkylammonium halide clathrate hydrates in water:
$(n\text{-}C_4H_9)_4NF \cdot 30H_2O$ (○); $(n\text{-}C_4H_9)_4NCl \cdot 30H_2O$ (●); $(i\text{-}C_5H_{11})_4NF \cdot 39H_2O$ (⦶); $(i\text{-}C_5H_{11})_4NCl \cdot 39H_2O$ (⊙).

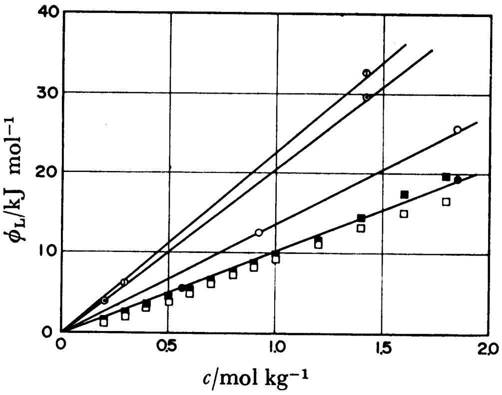

Fig. 2. Concentration dependence of the relative apparent molal heat contents (ϕ_L) of tetraalkylammonium halide solutions:
$(n\text{-}C_4H_9)_4NF$ at 25 °C (○); $(n\text{-}C_4H_9)_4NCl$ at 10 °C (●); $(i\text{-}C_5H_{11})_4NF$ at 25 °C (⦶); $(i\text{-}C_5H_{11})_4NCl$ at 25 °C (⊙); $(n\text{-}C_4H_9)_4NCl$ at 25 °C taken from Ref. 14 (■); $(n\text{-}C_4H_9)_4NBr$ at 25 °C taken from Ref. 14 (□).

(5) The Relative Apparent Molal Heat Contents.

In Table 2, two relative apparent molal heat contents, $\phi_{L,C}$ and $\phi_{L,sat}$, are given for each salt solution. These values are plotted against m in Fig. 2, assuming that ϕ_L is a linear function of m in the concentration range studied rather than a linear function of $\sqrt{m}$ as derived from the limiting law.[11] This assumption seems to be reasonable, at least as a first approximation, as exemplified in Fig. 2 by the data for $(n\text{-}C_4H_9)_4NCl$ and $(n\text{-}C_4H_9)_4NBr$ (at 25 °C) solutions obtained by Lindenbaum.[14] Figure 2 clearly indicates that the increase of ϕ_L with increasing m for the tetraisopentylammonium salt is more marked than that for the tetrabutylammonium salt, irrespective of the type of anion.

Table 4. The tabulation of each term in Eq. 6 and the calculation of ΔH_{sat}

Hydrate	Temp / °C	$(1-nm_{sat}/M)^2$	$1+(\partial \ln \gamma_\pm/\partial \ln m)_{sat}$	$\partial \ln m'_{sat}/\partial(1/T)$ / 10^4 K	ΔH_{sat} / kJ mol^{-1}
$(n\text{-}C_4H_9)_4NF \cdot 30H_2O$	25	0.253±0.001	1.830±0.005	−2.14±0.05	165±4
$(n\text{-}C_4H_9)_4NCl \cdot 30H_2O$	10	0.486±0.003	0.931±0.005	−1.80±0.03	135±3
$(i\text{-}C_5H_{11})_4NF \cdot 39H_2O$	25	0.631±0.003	1.23 ±0.05	−1.84±0.04	237±11
$(i\text{-}C_5H_{11})_4NCl \cdot 39H_2O$	25	0.735±0.002	0.95 ±0.05	−2.27±0.05	263±15

This indicates that the structural modification of the water molecules around the isopentyl group is greater than that around the butyl group. The high stability of the tetraisopentylammonium halide hydrates has already been pointed out in section *(3)*.

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