

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 45, No. 2, 1975

ELECTRICAL CONDUCTIVITIES OF ALKYLAMMONIUM CHLORIDES IN
WATER AT 25°C UP TO 3000 kg/cm²

BY MASAKATSU UENO

The conductivities of dilute aqueous solutions of mono-*n*-propyl-, di-*n*-propyl-, mono-*n*-hexyl-, and mono-*n*-octylammonium chlorides were measured at 25°C as a function of pressure. The limiting equivalent conductivities of the alkylammonium salts were determined by the Fuoss-Onsager equation up to 3000 kg/cm² (1kg/cm²=0.9678 × 10⁵ Pa) and the limiting equivalent conductivities of the alkylammonium ions were obtained up to 2000kg/cm², using the transference numbers by Kay *et al.*¹⁾ and the conductivities by Nakahara *et al.*²⁾ for aqueous KCl solutions. The limiting equivalent conductivity of each salt has a maximum against pressure, while that of the corresponding cation decreases monotonously with increasing pressure like the methyl and the ethyl substituted ammonium ions studied previously^{3,4)}. The Walden products of these alkylammonium ions at infinite dilution decrease with increasing pressure. The negative pressure coefficient of the Walden product of the alkylammonium ion leads us to the conclusion that the water density in the vicinity of the alkyl group is higher than in the bulk.

Introduction

Till now much attention has been paid to the study of organic ions in water from various points of view. Ebert and Lange⁵⁾ measured the osmotic and the activity coefficients of tetraalkylammonium salts in 1928. Everett and Wynne-Jones⁶⁾ determined the entropy and the heat capacity changes accompanying the protonation of mono-, di-, and trimethylamines and found the peculiar nature of the interaction between the alkyl chain and water in 1941. Frank and Evans⁷⁾ studied the solubility of many various compounds in water and again pointed out the anomalous entropy changes for the hydration of non-polar solutes in 1945. They gave a pictorial idea, "iceberg" to the specific hydration. In 1957 Frank and Wen⁸⁾ proposed the "flickering cluster" model for the water structure, on the basis of which the structural aspects of the hydration of organic ions were made clearer. In 1959 Kauzmann⁹⁾

(Received December 4, 1975)

- 1) R.L.Kay, K.S.Pribadi and B. Watson, *J. Phys.Chem.*, **74**, 2724 (1970)
- 2) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **42**, 12 (1972)
- 3) M. Ueno, M. Nakahara and J. Osugi, *ibid.*, **45**, 9 (1975)
- 4) M. Ueno, M. Nakahara and J. Osugi, *ibid.*, **45**, 17 (1975)
- 5) L. Ebert and J. Lange, *Z. Physik. Chem.*, **139A**, 584 (1928)
- 6) D.H. Everett and W.F.K.Wynne-Jones, *Proc. Roy. Soc.*, **A177**, 499 (1941)
- 7) H.S. Frank and M.W. Evans, *J. Chem. Phys.*, **13**, 507 (1945)
- 8) H.S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957)
- 9) W. Kauzmann, *Advan. Protein Chem.*, **14**, 1 (1959)

recognized the tendency for non-polar side chains to adhere to one another in aqueous solutions of proteins or polypeptides and called it hydrophobic bond (the term "bond" was later amended as interaction). In the same year Hertz and Spalthoff¹⁰⁾ studied the chemical shift of H₂O proton resonance in aqueous solutions, which was used by Wicke¹¹⁾ to predict the existence of non-tetrahedral linking of H₂O molecules around non-polar groups. Recent investigations of the hydration of organic ions are more thoroughly reviewed by Wen^{12,13)}.

The interaction between organic ions and water has been studied also at high pressure. Hamann and Strauss^{14,15)}, Lown *et al.*¹⁶⁾, and Høiland¹⁷⁾ obtained the volume changes accompanying the ionization of carboxylic acids. Hamann¹⁸⁾, Tuddenham and Alexander¹⁹⁾, Osugi *et al.*²⁰⁾, and Tanaka *et al.*²¹⁾ determined the volume changes for the formation of micelles in water. Bradley *et al.*²²⁾ measured the solubility of benzene and toluene in water at high pressure, Zipp²³⁾ of *n*-propylbenzene, and Suzuki *et al.*²⁴⁾ of naphthalene. Horne and Young²⁵⁾, Nakahara *et al.*^{26,27)}, and Kay²⁸⁾ reported the conductivities of tetraalkylammonium salts in water at high pressure. The present author *et al.*^{3,4)} studied the pressure effect on the conductivities of Me_nNH_{4-n}Cl and Et_nNH_{4-n}Cl (n=1,2,3) in water in order to examine how much the hydrophobic hydration around lower alkyl chains is important compared with the electrostatic hydration of these alkylammonium ions. In this work longer alkyl chains are introduced to the ammonium ion so that they may increase the contribution of the hydrophobic hydration to the overall hydration of the ions.

Experimental

Mono-*n*-propyl-, di-*n*-propyl-, and mono-*n*-hexylammonium chlorides (PrNH₃Cl, Pr₂NH₂Cl, and

-
- 10) H.G.Hertz and W. Spalthoff, *Z. Electrochem.*, **63**, 1096 (1959)
 - 11) E. Wicke, *Angew. Chem. Int. Ed.*, **5**, 106 (1966)
 - 12) W.-Y. Wen, "Water and Aqueous Solutions", Chap. 15, ed. by R.A. Horne, Wiley-Interscience (1972)
 - 13) W.-Y. Wen, "The Physical Chemistry of Aqueous Systems", p. 155, ed. by R.L.Kay, Plenum Press, New York (1973)
 - 14) S.D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955)
 - 15) S.D. Hamann, "Physico-Chemical Effects of Pressure", Butterworths, London (1957)
 - 16) D.A. Lown, H.R. Thirsk and L. Wynne-Jones, *Trans. Faraday Soc.*, **64**, 2073 (1968)
 - 17) H. Høiland, *J.C.S. Faraday I*, **70**, 1180 (1974)
 - 18) S.D. Hamann, *J. Phys. Chem.*, **66**, 1359 (1962)
 - 19) R.F. Tuddenham and A.E. Alexander, *ibid.*, **66**, 1839 (1962)
 - 20) J. Osugi, M. Sato and N. Ifuku, *This Journal*, **35**, 32 (1965)
 - 21) M. Tanaka, S. Kaneshina, K. Shin-no, T. Okajima and T. Tomida, *J. Colloid and Interface Sci.*, **46**, 132 (1974)
 - 22) R.S. Bradley, M.J. Dew and D.C. Munro, *High Temp.-High press.*, **5**, 169 (1973)
 - 23) A.M. Zipp, Dissertation, Dept. of Chem. Princeton Univ. (1973)
 - 24) K. Suzuki, Y. Taniguchi, T. Ishigami and M. Tsuchiya, *Proc. 4th Int. Conf. High Press., Kyoto*, p. 615 (1974)
 - 25) R.A. Horne and R.P. Young, *J. Phys. Chem.*, **72**, 1763 (1968)
 - 26) M. Nakahara, *This Journal*, **42**, 75 (1972)
 - 27) M. Nakahara and J. Osugi, *ibid.*, **43**, 71 (1973)
 - 28) R.L. Kay, "Water", Vol. 3, Chap. 4, ed. by F. Franks, Plenum Press, New York (1973)

Electrical Conductivities of Alkylammonium Chlorides in Water at 25°C up to 3000 kg/cm² 63

HexNH₃Cl) were from Nakarai Chem. Co., Ltd. and of guaranteed reagent grade. PrNH₃Cl and Pr₂NH₂Cl were recrystallized three times from ethanol-ether mixture and HexNH₃Cl from ethanol-benzene mixture. Mono-*n*-octylammonium chloride (OctNH₃Cl) was prepared by bubbling dried HCl gas into a cold ethanol solution of *n*-octylamine, which had been previously purified by distillation under reduced pressure. The synthesized salt was recrystallized three times from ethanol-benzene mixture. The purity of this salt was gravimetrically checked. All the salts were dried in a vacuum desiccator at room temperature for at least a week prior to use.

All the experimental procedures and apparatuses used are the same as in the previous papers^{3,29)}. The solvent properties (density, viscosity and dielectric constant) at high pressure are shown elsewhere³⁾.

Results and Discussion

Pressure dependence of A° and λ°

The limiting equivalent conductivities of the salts A° , which reflect the ion-solvent interaction, were determined by the Fuoss-Onsager conductivity equation³⁰⁾,

$$A = A^\circ - S\sqrt{C} + E \cdot C \cdot \log C + J \cdot C \quad (1)$$

programed for a rapid electronic computer in the same way as Kay³¹⁾ did. Here, C is the concentration in equivalent per liter and the functions S and E have their usual meaning and J is an adjustable parameter, a function of ion size. The obtained values of A° at high pressure are shown in Tables 1~4 together with the equivalent conductivities of the salts A . The limiting conductivities of the ions λ° were determined up to 2000 kg/cm² with the aid of the two independent measurements for aqueous KCl solutions at high pressure, transference numbers¹⁾ and conductivities²⁾. The high pressure values of λ° are listed in Table 5.

The curve of A° of each salt against pressure has a maximum as can be seen in Tables 1~4, but

Table 1 A° and $A^\circ(p)$ (ohm⁻¹·cm²·equiv⁻¹) of PrNH₃Cl in water at 25°C

$C \times 10^4$ (N)	(concentration at 1 atm)						$A^\circ(p)$
	5.062	10.12	15.19	20.25	30.37	50.62	
1	114.9	113.9	113.5	112.9	111.7	110.6	116.8 ± 0.07
590	116.7	115.9	115.2	114.7	113.5	112.3	118.7 ± 0.07
1100	117.0	116.1	115.4	114.9	113.8	112.5	118.9 ± 0.04
1570	116.4	115.6	114.9	114.3	113.3	112.0	118.3 ± 0.03
2090	115.0	114.2	113.6	113.0	112.0	110.7	116.9 ± 0.02
2590	113.1	112.3	111.7	111.2	110.2	108.9	114.9 ± 0.03
3130	110.5	109.8	109.2	108.7	107.8	106.5	112.3 ± 0.02

29) M. Ueno, K. Shimizu and J. Osugi, *This Journal*, **43**, 33 (1973)

30) R.M. Fuoss and F. Accascina, "Electrolytic Conductance", Interscience Pub., Inc., New York (1959)

31) R.L. Kay, *J. Amer. Chem. Soc.*, **82**, 2099 (1960)

Table 2 $\lambda^{\circ}(P)$ and $\lambda^{\circ}(P)$ ($\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{equiv}^{-1}$) of $\text{Pr}_2\text{NH}_2\text{Cl}$ in water at 25°C

$C \times 10^4(\text{N})$ $P(\text{kg}/\text{cm}^2)$	(concentration at 1 atm)						$\lambda^{\circ}(P)$
	4.988	9.977	14.97	19.95	29.93	49.88	
1	105.0	104.1	103.5	102.7	102.0	100.8	106.8 ± 0.07
590	106.6	105.8	105.2	104.6	103.5	102.3	108.5 ± 0.06
1100	107.1	106.2	105.6	105.0	103.9	102.7	108.9 ± 0.06
1570	106.8	105.8	105.3	104.7	103.6	102.4	108.6 ± 0.06
2090	105.6	104.7	104.2	103.6	102.5	101.4	107.4 ± 0.07
2590	104.0	103.1	102.6	102.1	100.9	99.8	105.7 ± 0.07
3130	101.8	100.9	100.5	99.9	98.8	97.7	103.5 ± 0.06

Table 3 $\lambda^{\circ}(P)$ and $\lambda^{\circ}(P)$ ($\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{equiv}^{-1}$) of HexNH_3Cl in water at 25°C

$C \times 10^4(\text{N})$ $P(\text{kg}/\text{cm}^2)$	(concentration at 1 atm)										$\lambda^{\circ}(P)$
	4.999	5.003	9.997	10.01	15.00	15.01	20.00	20.01	29.99	30.02	
1	107.1	107.3	106.5	106.4	105.8	105.9	105.3	105.3	104.2	104.3	109.3 ± 0.04
590	108.7	108.8	108.0	107.9	107.4	107.4	106.8	106.8	105.9	105.7	110.8 ± 0.03
1100	108.8	108.9	108.0	108.0	107.5	107.4	106.9	106.8	106.1	105.9	110.8 ± 0.03
1570	108.3	108.3	107.4	107.2	106.9	106.7	106.2	106.1	105.4	105.2	110.2 ± 0.05
2090	107.0	106.8	106.1	105.8	105.5	105.3	104.9	104.6	104.1	103.9	108.7 ± 0.07
2590	105.0	104.8	104.2	103.9	103.7	103.3	103.0	102.7	102.3	102.1	106.6 ± 0.08
3130	102.7	102.4	101.7	101.4	101.3	101.0	100.6	100.3	100.0	99.8	104.1 ± 0.09

Table 4 $\lambda^{\circ}(P)$ and $\lambda^{\circ}(P)$ ($\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{equiv}^{-1}$) of OctNH_3Cl in water at 25°C

$C \times 10^4(\text{N})$ $P(\text{kg}/\text{cm}^2)$	(concentration at 1 atm)						$\lambda^{\circ}(P)$
	4.973	9.946	10.13	14.92	19.89	20.26	
1	104.0	103.3	103.6	102.8	102.2	102.0	106.1 ± 0.13
590	105.5	104.8	105.0	104.4	103.9	103.7	107.5 ± 0.08
1100	105.4	104.8	105.0	104.5	103.9	103.8	107.4 ± 0.10
1570	104.8	104.2	104.4	103.8	103.3	103.1	106.7 ± 0.10
2090	103.5	102.9	103.1	102.6	102.0	101.8	105.3 ± 0.10
2590	101.6	101.1	101.3	100.8	100.2	100.1	103.5 ± 0.11
3130	99.3	98.8	99.0	98.5	97.9	97.8	101.1 ± 0.11

Table 5 $\lambda^{\circ}(P)$ ($\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{equiv}^{-1}$) of the ions in water at 25°C

ion $P(\text{kg}/\text{cm}^2)$	PrNH_3^+	Pr_2NH_2^+	HexNH_3^+	OctNH_3^+	Cl^-
	1	40.4	30.4	32.9	29.7
590	39.9	29.7	32.0	28.7	78.8
1100	39.2	29.2	31.1	27.7	79.7
1570	38.6	28.9	30.5	27.0	79.7
2090	37.6	28.1	29.4	26.0	79.3

Table 6 Walden products (ohm⁻¹·cm²·equiv⁻¹·cP) of the ions at 25°C

ion P(kg/cm ²)	PrNH ₃ ⁺	Pr ₂ NH ₂ ⁺	HexNH ₃ ⁺	OctNH ₃ ⁺
1	36.1	27.2	29.4	26.5
590	35.4	26.3	28.4	25.4
1100	35.0	26.0	27.7	24.7
1570	35.0	26.2	27.6	24.5
2090	34.9	26.1	27.3	24.1

the alkylammonium ions do not have a maximum in the plot of λ° vs. pressure. Hence, the present and previous results^{3,4)} lead to the general conclusion that the alkylammonium ions have no maximum in the λ° vs. pressure curve in spite of the existence of a minimum viscosity of water at 25°C³²⁾. The same tendency was found in the case of carboxylate ions³³⁾ with alkyl chains longer than ethyl. This curious phenomenon would be caused by the specific interaction between the alkyl chain and water rather than by the electrostatic interaction as discussed below.

Pressure dependence of the ionic Walden product

The pressure dependence of the ionic Walden product, $W = \lambda^\circ \cdot \eta^\circ$ where η° is the viscosity of water³²⁾, is shown in Fig 1. It is noteworthy that the pressure coefficients of W of all the alkylammonium ions studied are negative at atmospheric pressure as found for the lower homologues^{3,4)}.

Owing to the lack of complete theory for λ° , we used the modified Stokes equation³⁴⁾ to interpret qualitatively the pressure effect on the ionic Walden product. According to the modified Stokes equation, we have

$$W = \lambda^\circ \cdot \eta^\circ = \frac{z e F}{C(r_e) \cdot r_e} \quad (2)$$

and

$$\left(\frac{\partial(W^{(p)}/W^{(l)})}{\partial P} \right)_T = - \left(\frac{W^{(p)}}{W^{(l)}} \right) \left(\frac{\partial r_e}{\partial P} \right)_T \left\{ \frac{1}{r_e} + \frac{1}{C} \left(\frac{\partial C}{\partial r_e} \right)_T \right\} \quad (3)$$

where z , e , F , r_e , and $C(r_e)$ are, respectively, the ionic valence, the protonic charge, the Faraday constant, the effective radius of a hydrated ion and the hydrodynamic parameter being a function of r_e . From Eq. (3), we can get the following qualitative equation.

$$\text{sign of } \left(\frac{\partial(W^{(p)}/W^{(l)})}{\partial P} \right)_T = - \text{sign of } \left(\frac{\partial r_e}{\partial P} \right)_T \quad (4)$$

because the first and third factors in the right-hand side of Eq. (3) are positive³⁴⁾. Since the effective radius is a function of pressure and the hydration number of the ion h at constant temperature, we have

$$\left(\frac{\partial r_e}{\partial P} \right)_T = \left(\frac{\partial r_e}{\partial P} \right)_{h,T} + \left(\frac{\partial r_e}{\partial h} \right)_{P,T} \left(\frac{\partial h}{\partial P} \right)_T \quad (5)$$

32) J.B. Cappi, Ph. D. Thesis, London Univ. (1964)

33) M. Nakahara and J. Osugi, *This Journal*, 45, 1 (1975)

34) M. Nakahara, K. Shimizu and J. Osugi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, 92, 785 (1971)

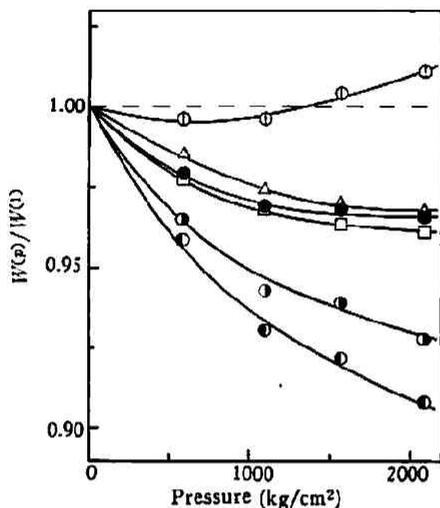


Fig. 1-a Pressure dependence of the ionic Walden products at 25°C

○: NH_4^{++} , Δ : MeNH_3^{++} ,
 □: EtNH_3^{++} , ●: PrNH_3^+ ,
 ●: HexNH_3^+ , ◐: OctNH_3^+
 *from ref. (3) **from ref. (4)

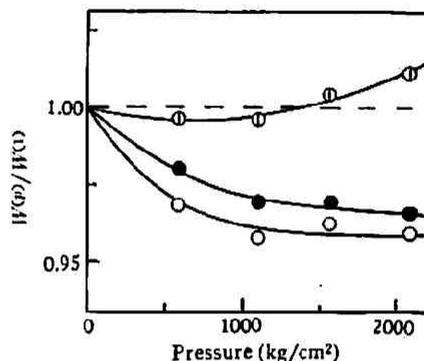


Fig. 1-b Pressure dependence of the ionic Walden products at 25°C

○: NH_4^{++} , ●: PrNH_3^+ ,
 ◐: Pr_2NH_2^+
 *from ref. (3)

where the first term in the right-hand side is negative because the hydrated ion can be compressed by pressure (*i.e.*, compression effect), and the first factor of the second term is positive or zero and not negative at least. Thus in the case of the negative pressure coefficient of W , $(\partial h/\partial P)_T$ in Eq. (5) must be positive from Eqs. (4) and (5). The positive pressure coefficient of the hydration number would suggest that the density of water around the ion is higher than that of the bulk water because pressure shifts the equilibrium toward a denser state³³. The pressure coefficients of W of the alkylammonium ions studied are negative at atmospheric pressure. In view of the above discussion, we can see that the water density around these organic cations is higher than in the bulk. Furthermore, it is supposed that the longer the alkyl chain of the organic ion the stronger the interaction between the alkyl chain and water compared with the electrostatic interaction. Hence, the negative pressure coefficients of W of the alkylammonium ions seem to indicate that the density of water in the vicinity of the alkyl group is higher than that of the bulk water.

The above conclusion seems to be conformed with the following volumetric results. The limiting partial molal volumes of the alkylamines \bar{V}_2° are smaller than the molar volumes of the pure solutes V_2 , and the limiting partial molal excess volumes $\bar{V}_2^{\circ E}(=\bar{V}_2^\circ - V_2)$ is governed by the chain length, being more negative for longer chains³⁵. Furthermore, the partial molal volume per one methylene group decreases with increase in pressure²¹. If the intrinsic compressibility of the methylene group is neglected, the partial molal excess volume per one methylene group decreases with pressure. This tendency could be considered to indicate that the hydration number per one methylene group in-

35) M.V. Kaulgud and K. J. Patil, *J. Phys. Chem.*, **78**, 714 (1974)

creases with pressure because of the higher water-density around the methylene group.

Effect of the alkyl-chain number on W

The pressure coefficient of $W^{(p)}/W^{(1)}$ consists of three factors as shown in Eq. (3). The values of $\{\partial(W^{(p)}/W^{(1)})/\partial P\}_T$ of the ammonium and the n -propyl substituted ammonium ions are negative at normal pressure and the order of their absolute value is



as can be seen in Fig. 1-b. Moreover, the factor $W^{(p)}/W^{(1)}$ around 1 atm is unity for all the ions. Therefore, if it is assumed that the effective radius of the ion enlarges with the increase in the number of the alkyl chain, the magnitude of the third factor of Eq. (3) $\{1/r_e + (1/C)(\partial C/\partial r_e)_T\}$ would be³⁴⁾



Hence, from Eqs. (3), (6), and (7), the following sequence is obtained in regard to the pressure coefficient of the effective radius $(\partial r_e/\partial P)_T$ at normal pressure,



This order is the same as in the cases of $\text{Me}_n\text{NH}_{4-n}^+$ and $\text{Et}_n\text{NH}_{4-n}^+$ ($n=1,2,3$) ions. When the compression effect $(\partial r_e/\partial P)_n, T$ in Eq. (5) is ignored, we are to say that electrostriction can not explain this trend. Then, the sequence of Eq. (8) indicates that if the compression effect is neglected, the interaction between the propyl group and water would produce a denser state around the propyl group as in the cases of methyl and ethyl groups.

On the water structure around alkylammonium ions

The alkylammonium ions RNH_3^+ ($\text{R}=\text{Me, Et, and so on}$) may be classified into breaking ions and making ones from the viewpoint of their influence on the water structure. MeNH_3^+ ion is a structure breaker and RNH_3^+ ions with chains longer than methyl are structure makers, judging from the B-coefficient³⁶⁾ of the Jones-Dole equation of the viscosity. EtNH_3^+ ion lies on the borderline between the breaker and the maker according to the sign of the heat of transfer from H_2O to D_2O ³⁷⁾. Although the methyl group in the alkylammonium ion may instabilize the water structure in co-operation with the electrostatic field produced by the charge, no discontinuity is found in the present volumetric aspect of the interaction between water and such alkyl chains as methyl, ethyl, propyl, and so on.

Several papers have referred to the water structure around the alkyl group, and it has been often said that the interaction between the alkyl chain and water intensifies the hydrogen-bond structure in the vicinity of the alkyl group. In view of the present conclusion that the water molecules around the alkyl group have a denser configuration than the bulk water, there might be a possibility that water around the alkyl chain is structurally similar to that in the crystalline hydrate.

-
- 36) K. Tamaki, Y. Ohara, H. Kurachi, M. Akiyama and H. Odaki, *Bull. Chem. Soc. Japan*, **47**, 384 (1974);
 J.E. Desnoyers and G. Perron, *J. Solution Chem.*, **1**, 199 (1972)
 37) C.V. Krishnan and H.L. Friedman, *J. Phys. Chem.*, **74**, 3900 (1970)
 38) G. Némethy and H.A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962)
 39) W.-Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964)
 40) A.H. Narten and S. Lindenbaum, *J. Chem. Phys.*, **51**, 1108 (1969)

Acknowledgment

The author is grateful to Professor J. Osugi for his helpful suggestions and discussions during the course of this work, and indebted to Professor K. Shimizu for his thoughtful review of the manuscript. He also wishes to thank Dr. M. Nakahara for his careful reading of the manuscript and many valuable comments.

*Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto 606
Japan*