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Sound Velocity in Aqueous Solutions of Ammonium Halides

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The sound velocity in water aqueous solutions increases with increasing temperature and reaches the maximum velocity (V_p) at a peak temperature (T_p). In the present paper, the concentration dependence of T_p and V_p in ammonium halides are reported. It was found empirically that the relationship between the hydration number and the slope ($\Delta T_p/\mu$) of T_p at infinite dilution for many electrolytes is linear, but that for ammonium halides this is not the case.

The sound velocity in water increases with increasing temperatures and reaches a maximum velocity (V_p) at 74 °C, while the adiabatic compressibility of water has a minimum at 64 °C. This temperature for V_p is termed the peak temperature (T_p) of water. This behavior is characteristic of water and aqueous solutions. It is known that water is an associated liquid exhibiting structural equilibrium. The origin of the maximum velocity in water can be explained on the basis of a decrease in the structural compressibility and an increase in the instantaneous compressibility with increase in temperature.

When substances are dissolved in water, the values of T_p and V_p for the solutions shift from those of pure water, since the structural equilibrium of water is also affected by the solutes. Therefore, it is possible to study the effects of solutes on the water structure on the basis of the shifts of T_p and V_p from the values for pure water.

For aqueous solutions of electrolytes, the concentration dependences of T_p have been reported by many investigators.1—6) In the case of solutions of NH_4I,6) a unique behavior of the concentration dependence of T_p was observed, in which the temperature remained nearly constant up to about 4.5 mol %, and then decreased more and more sharply with increase in concentration. While the V_p in aqueous solutions usually increases as compared with that in pure water, it decreases in some cases, such as in solutions of $Pb(NO_3)_2$ and NH_4I.

In the present paper, measurements on NH_4Br and NH_4Cl solutions are extended.

Experimental

Apparatus. A crystal-controlled ultrasonic interferometer operating at a frequency of 5 MHz is used to measure the wavelength of standing waves. The measuring cell containing a solution is immersed in an oil bath controlled to within ±0.1 °C at moderate temperatures and to within ±0.4 °C at higher temperatures. To determine the wavelength one hundred standing waves are used. While the accuracy of the wavelength measurement is ±0.006%, the dominant cause of error in the sound velocity measurements is the temerature fluctuation. So the overall accuracy of the velocity measurements is about ±0.02%.

Materials. NH_4Cl, NH_4Br, and $(NH_4)_2SO_4$ were purified by recrystallization of reagent grade products from water.

Results and Discussion

In Figs. 1 and 2, the sound velocities (V) for NH_4Cl and NH_4Br are respectively plotted against the concentration (μ: mol %) over the temperature (T) range from 20—100 °C at 5 °C intervals. In order to compare

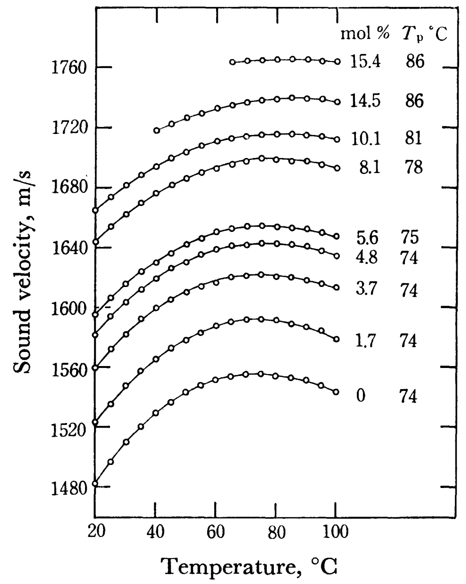

Fig. 1. Sound velocity *vs.* temperature in ammonium chloride aqueous solutions at various concentrations.

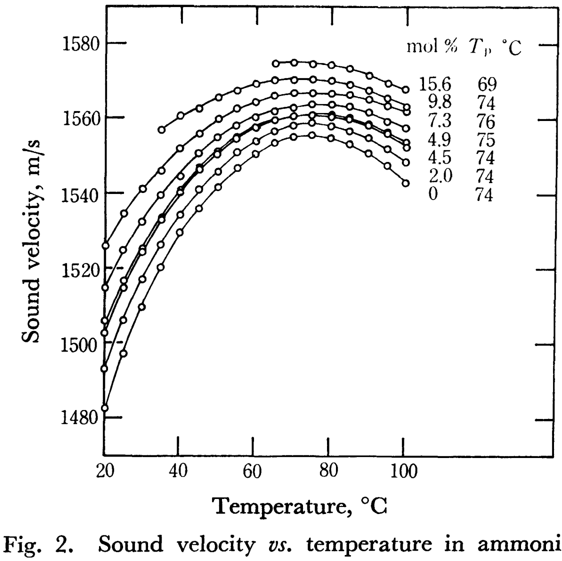

Fig. 2. Sound velocity *vs.* temperature in ammonium bromide aqueous solutions at various concentrations.

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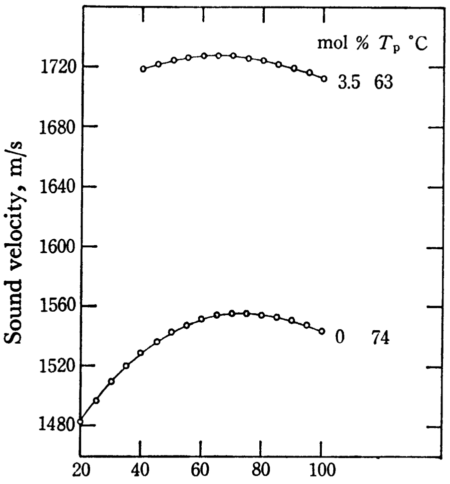

Fig. 3. Sound velocity *vs.* temperature in ammonium sulfate aqueous solutions at various concentrations.

with ammonium halides (NH_4X), the sound velocity in an $(NH_4)_2SO_4$ aqueous solution at 3.5 mol % was measured. These results are shown in Fig. 3.

In all cases of ionic or nonionic aqueous solutions, the $V(T)$-curves are of parabolic type like that of pure water. Except for solutions at high concentrations, the $V(T)$-curves are, within the limits of experimental error, the same as a displaced curve for water. Therefore, the template of curve for water was used to fix the T_p of the solutions, while the V_p in the solutions were also determined at the same time from the smoothed curve of the template. The accuracies of the T_p and V_p values at lower concentrations were within ±1.5 °C and ±1 m/s, respectively. For solutions at high concentrations, the T_p of solutions was successively determined from the smoothed curve for a lower concentration which was previously determined, starting from the template of the curve for water. The accuracies of the T_p and V_p values at high concentrations were within ±2.0 °C and ±1 m/s, respectively. Figures 4 and 5 show, respectively, the V_p and T_p values as functions of concentration for aqueous solutions of NH_4X together with other electrolytes.[6] The values of V_p in electrolytes usually increase with increasing concentration, but there are some exceptions such as NH_4I, $Pb(NO_3)_2$, *etc.*[7] These electrolytes have a heavy ion in the molecule. On the other hand, the values of T_p usually decrease, although there are some rare exceptional cases, with increasing concentration. The results obtained from Figs. 4 and 5 indicate that the slopes ($\Delta V_p/\mu$ and $\Delta T_p/\mu$) at infinite dilution are nearly constant.

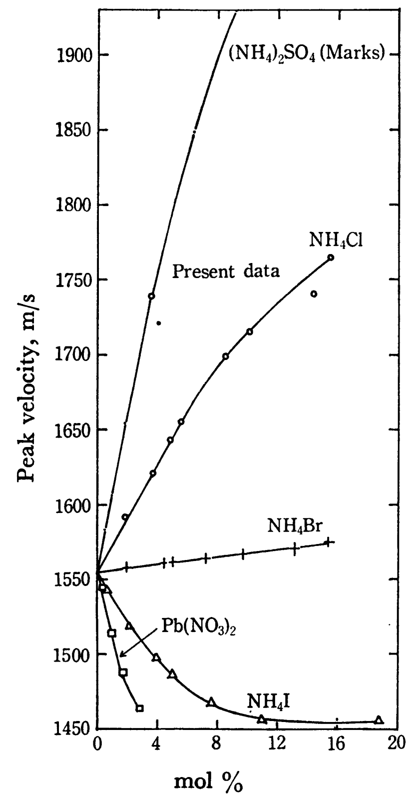

Fig. 4. Peak velocity *vs.* concentration for various solutes.

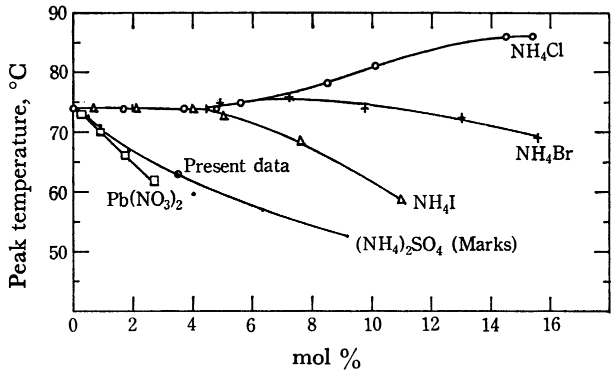

Fig. 5. Peak temperature *vs.* concentration for various solutes.

As can be seen in Fig. 5, the discrepancy between NH_4X and the other electrolytes is evident. First the T_p of NH_4X aqueous solutions are approximately constant to *ca.* 4.5 mol % regardless of the kind of anion,

Table 1. Values of $\Delta V_p/\mu$, $\Delta T_p/\mu$ and hydration number (h) for various electrolytes

	$\Delta V_p/\mu$ m/s/mol%		$\Delta T_p/\mu$ °C/mol%		h[a] at 25 °C
NH_4Cl	+18.0		0		4.2
NH_4Br	+ 1.2		0		3.7
NH_4I	−20.5		0		3.2
$(NH_4)_2SO_4$	+55.0	b)	−3.8	b)	11—12
Li_2SO_4	+66.5		−7.4		14—15
Na_2SO_4	+71.5		−7.8		17—18
K_2SO_4	+62.3		−7.0		15—16
$KHSO_4$	−35.9		−2.6		
$MgSO_4$	+55.0		−5.7		14.8
LiCl	+25.5	c)	+1.2	c)	6.0
NaCl	+27.0		−2.6		7.1
KCl	+26.5		−2.7		6.4
RbCl	+ 6.5		−2.6		
LiBr	+ 5.6		+4.2		5.4
LiI	−13.5		−2.0		4.7
LiOH	+41.0	d)	−4.3	d)	8.7
NaOH	+42.5		−5.0		9.9
KOH	+40.5		−3.8		9.2
$Pb(NO_3)_2$	−45.0		−4.4		10.8[6]

a) Ref. 8. b) Ref. 3. c) Ref. 5. d) Ref. 4.

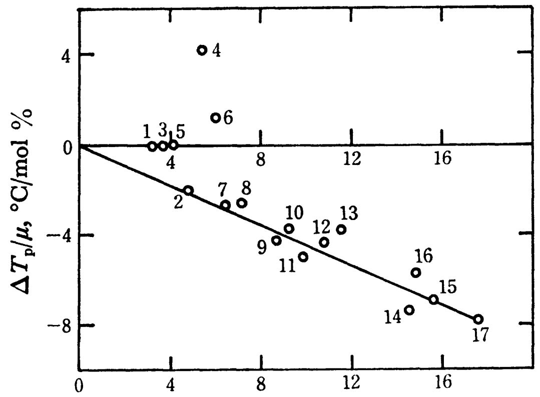

Fig. 6. $\Delta T_p/\mu$ *vs.* *h* for various electrolytes.
1: NH_4I, 2: LiI, 3: NH_4Br, 4: LiBr, 5: NH_4Cl, 6: LiCl, 7: KCl, 8: NaCl, 9: LiOH, 10: KOH, 11: NaOH, 12: $Pb(NO_3)_2$, 13: $(NH_4)_2SO_4$, 14: Li_2SO_4, 15: K_2SO_4, 16: $MgSO_4$, 17: Na_2SO_4.

and secondary, the behaviors of T_p (μ)-curves at higher concentrations beyond *ca.* 4.5 mol % are quite different depending on the anions. On the other hand, the T_p of $(NH_4)_2SO_4$ solutions monotonical decreases with increasing concentration as in many other electrolytes.

The values of $\Delta V_p/\mu$ and $\Delta T_p/\mu$ for various electrolytes[3–6] are summarized in Table 1 together with the hydration number[8] (*h*) of the solutes at 25 °C. Although there are many methods[9] for determining the hydration number, the values of the hydration numbers used here are the results of acoustical measurements obtained on the basis of Passynski's assumption.[10] Since it is necessary to investigate the relationship between *h* and $\Delta T_p/\mu$, in Fig. 6 $\Delta T_p/\mu$ is plotted against *h* for various electrolytes. A large part of them, except for NH_4X, are gathered about the straight line: $\Delta T_p/\mu = -0.44\,h$.

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