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Ultrasonic Absorption in Solutions of Sodium Iodide in Isopropyl Alcohol and Isopropyl Alcohol-Water Mixtures

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Ultrasonic relaxational absorption was observed in solutions of NaI in *i*-PrOH. Assuming the excess ultrasonic absorption to be caused by the relaxation of the dissociation equilibrium of NaI in the solutions, the dissociation and recombination rates of NaI, the Arrhenius activation energy, and the enthalpy and volume changes due to dissociation were calculated; these were compared with the values estimated from other methods. An increase of the dissociation constant of NaI was observed with an increase in the concentration of H_2O in *i*-PrOH–H_2O mixtures.

Strong 1-1 electrolytes such as sodium iodide dissociate completely in aqueous solution. Ultrasonic absorptions due to chemical relaxation are not found in such solution. But in isopropyl alcohol, which has a lower dielectric constant than water, NaI would dissociate incompletely and a dissociation equilibrium would exist between the Na^+ ions, the I^- ions, and the undissociated NaI molecules. Then the excess ultrasonic absorption observed in *i*-PrOH would be caused by the relaxation of the reaction.

Experimental

The ultrasonic absorption spectra of NaI solutions in *i*-PrOH–H_2O mixtures were measured by the ultrasonic pulse method from 10 to 90 MHz at 20 °C. The concentrations of NaI were 0.1—0.3 molality (mol/1000 g solvent) and weight percentages of *i*-PrOH in *i*-PrOH–H_2O mixtures were 50, 60, 70, 80, 90, and 100%. The ultrasonic velocity was measured by the interference of the pulse wave and a continuous wave at 5 MHz.

Results and Discussion

The ultrasonic absorption α/f^2 in solutions of NaI in *i*-PrOH is shown in Fig. 1, where α is the absorption coefficient of amplitude and f the frequency. A single relaxation represented by the next equation fits the curves over the frequency range measured:

$$\frac{\alpha}{f^2}=\frac{A}{1+(f/f_{\max})^2}+B,$$

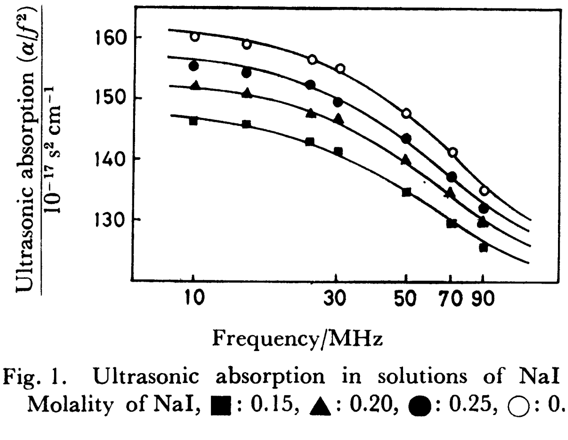

Fig. 1. Ultrasonic absorption in solutions of NaI in Molality of NaI, ■: 0.15, ▲: 0.20, ●: 0.25, ○: 0.30.

where $f_{\max}$ is the relaxational frequency, A the relaxational absorption, and B the non-relaxing absorptions due to viscosity, thermal conduction, *etc.* The relaxation parameters are listed in Table 1.

Table 1. The relaxation parameters in solutions of NaI in *i*-PrOH

Temp °C	Concn of NaI (molality)	A $10^{-17}\,s^2\,cm^{-1}$	B $10^{-17}\,s^2\,cm^{-1}$	$f_{\max}$ MHz
20	0.15	28.6	118	58.0
	0.20	33.3	120	61.3
	0.25	37.0	120	64.0
	0.30	40.0	122	66.8
25	0.15	27.0	110	64.1
	0.20	31.3	110	67.6
	0.25	34.5	110	70.7
	0.30	38.5	112	73.6
30	0.15	26.3	100	69.8
	0.20	30.3	100	73.0
	0.25	33.3	102	76.0
	0.30	37.0	102	78.4
35	0.15	25.6	90	75.8
	0.20	29.4	90	79.3
	0.25	32.3	92	82.1
	0.30	35.7	92	85.8

Here we assume the relaxation to be caused by the following equilibrium:

$$\mathrm{NaI}\ \underset{k_b}{\overset{k_f}{\rightleftharpoons}}\ \mathrm{Na^+ + I^-}.$$

For such an equilibrium the relaxation frequency $f_{\max}$ is given by[1]

$$2\pi f_{\max}=k_f+k_b\sigma\gamma_\pm^2C\left(2+\frac{\partial\ln\gamma_\pm^2}{\partial\ln\sigma}\right),\tag{1}$$

where σ is the degree of dissociation, $\gamma_\pm$ means the ionic activity coefficient, k_f and k_b are the rate constants, and C is concentration. The dissociation constant K can be described by[2]

$$K=\frac{k_f}{k_b}=\frac{\sigma^2C\gamma_\pm^2}{1-\sigma},\tag{2}$$

$$K^{-1}=\frac{4\pi N}{1000}\left(\frac{e^2}{DkT}\right)Q(b),\tag{3}$$

$$b=\frac{e^2}{a_BDkT},$$

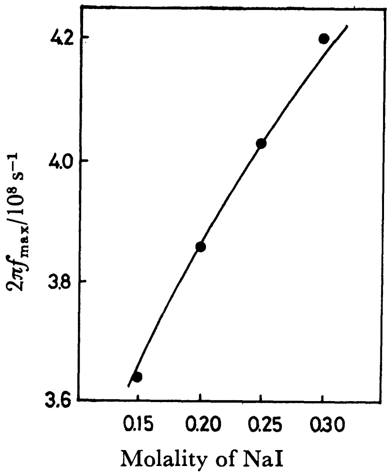

Fig. 2. Relation between f_{max} and concentration of NaI in *i*-PrOH at 20 °C.
●: Experimental value.

Table 2. The kinetic values of NaI in *i*-PrOH

Temp °C	K 10^{-3} M$^{a)}$	k_b 10^{10} M^{-1} s^{-1}	k 10^8 s^{-1}	a_B 10^{-8} cm
20	7.1±1.8	2.4±0.6	1.7±0.1	5.8±1.0
25	6.4±1.8	3.0±0.8	1.9±0.1	5.9±1.0
30	5.9±1.7	3.4±0.9	2.0±0.1	5.9±1.0
35	5.4±1.5	3.9±1.0	2.1±0.1	5.9±1.0

a) 1 M = 1 mol dm^{-3}.

where a_B is the distance between the centers of the two ions forming the ion pair at their closest distance of approach, k is Boltzmann's constant, D dielectric constant, N Avogadro's constant, T absolute temperature, e the electronic charge, and $Q(b)$ is a function of b. By the method of successive approximation,[3] k_f, k_b, K, and a_B were calculated using Eqs. 1, 2, and 3. In Table 2, the kinetic values derived by this process are listed. The experimental and the calculated values of f_{max} are shown in Fig. 2. As may be seen in Table 2, the apparent Bjerrum distance $a_B \simeq 5.9$ Å is larger than the sum of the ion radii 3 Å and is independent of temperature. This result suggest that a solvated ion pair state exists and that the number of solvation would be invariable over the temperature range measured.

The rate constant k_b is given by Arrhenius as follows:

$$k_b = Pe^{-\Delta E/RT},$$

where P is a constant and ΔE is the activation energy.

When $\log k_b$ values are plotted against $1/T$, the activation energy is obtained from the slope. Using k_b values in Table 2, one obtains $\Delta E \simeq 5.4$ kcal mol^{-1}. This value is of the order of magnitude to be expected for a diffusion controlled process.[1] The rate constant k_b, as due to a diffusion controlled process, is given by[4]

$$k_b = \frac{8NkT}{3000\eta}\left(\frac{-b}{e^{-b}-1}\right) \quad (\text{mol}^{-1}\ \text{s}^{-1}),$$

where η is solvent viscosity. By substitution of the numerical values[5] at 25 °C, one gets $k_b \simeq 1.7 \times 10^{10}$ mol^{-1} s^{-1}. The agreement between the calculated and experimental values is fairly good.

The variation of the dissociation constant with temperature is given by

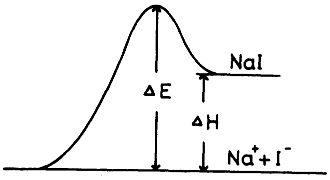

Fig. 3. Energy diagram of NaI in *i*-PrOH. $\Delta E \simeq 5.4$ kcal mol^{-1}, $\Delta H \simeq 3.1$ kcal mol^{-1}.

$$\left(\frac{\partial \ln K}{\partial T}\right) = \frac{\Delta H}{RT^2},$$

where ΔH is the enthalpy change. Taking the K values in Table 2, one gets $\Delta H \simeq -3.1$ kcal mol^{-1}. The energy diagram of NaI in the solution is shown in Fig. 3. The maximum excess ultrasonic absorption per wavelength at the relaxation frequency, μ_{max}, is given by[1,6]

$$\mu_{max} = \frac{\beta}{2\beta RTV}\left(\Delta V - \frac{l}{dC_p}\Delta H\right)^2 \frac{1}{\chi}, \tag{4}$$

$$\chi = \left(\frac{1}{n_{Na^+}} + \frac{1}{n_{I^-}} + \frac{1}{n_{NaI}}\right),$$

where ΔV is the volume change for the reaction, l the coefficient of thermal expansion, C_p the heat capacity at constant pressure, d density, V the volume, β the adiabatic compressibility, and n_{Na^+}, n_{I^-}, and n_{NaI}, are the numbers of the moles of the sodium ion, the iodide ion, and the undissociated sodium iodide. The adiabatic compressibility is obtained from the measured values of ultrasonic velocity. The number of the moles of species n_{Na^+}, n_{I^-}, and n_{NaI} are estimated from the degree of dissociation. Solvent parameters are given in Table 3. By substituting these values in Eq. 4, we find $\Delta V \simeq -15$ cm^3/mol. This value is of the same order as the volume change of NaI in *i*-BuOH:[10]

Table 3. The solvent parameters at 20 °C

d g cm^{-3}	l 10^{-3} deg^{-1}	V m s^{-1}	C_p J g^{-1} deg^{-1}	D (c.g.s.e.s.u.)
0.7854[7]	1.03	1167.6	2.5524[8]	18.6[9]

The ultrasonic absorptions α/f^2 in solutions of NaI in *i*-PrOH–H$_2$O mixtures are shown in Figs. 4, 5, and 6. As may be seen in these figures, the addition of NaI in *i*-PrOH–H$_2$O mixture causes an increase in the magnitude of the relaxational absorption. This increase is attributed to the relaxation of dissociation equilibrium of NaI in the solution, assuming that the relaxational absorption of *i*-PrOH–H$_2$O mixture[11–13] is independent of the concentration of NaI. Therefore we assume the relaxational absorption due to dissociation of NaI to be

$$\left(\frac{\alpha}{f^2}\right)_{\text{solution}} - \left(\frac{\alpha}{f^2}\right)_{\text{solvent}} = \frac{A}{1+(f/f_{max})^2} + B,$$

where $(\alpha/f^2)_{\text{solution}}$ is the absorption of the NaI solution in the *i*-PrOH–H$_2$O mixture and $(\alpha/f^2)_{\text{solvent}}$ is the absorption of the *i*-PrOH–H$_2$O mixture. The relaxation parameters and the kinetic values are listed in Tables 4 and 5. As is seen in Table 5, the dissociation constants

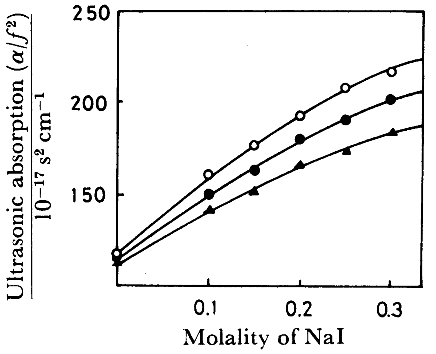

Fig. 4. Ultrasonic absorption in solutions of NaI in 90 wt% *i*-PrOH–10 wt% H_2O mixture at 20 °C. ○: 10 MHz, ●: 30 MHz, ▲: 50 MHz.

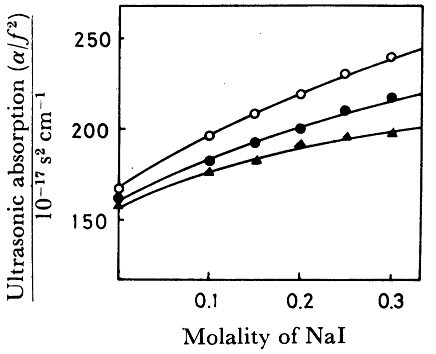

Fig. 5. Ultrasonic absorption in solutions of NaI in 80 wt% *i*-PrOH–20 wt% H_2O mixture at 20°C. ○: 10 MHz, ●: 30 MHz, ▲: 50 MHz.

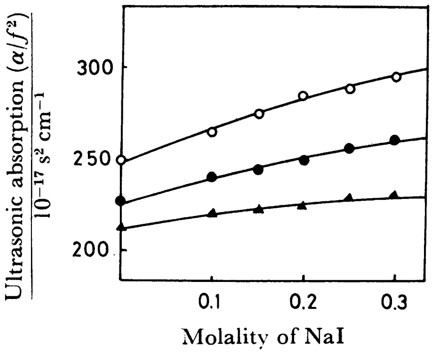

Fig. 6. Ultrasonic absorption in solutions of NaI in 70 wt% *i*-PrOH–30 wt% H_2O mixture at 20 °C. ○: 10 MHz, ●: 30 MHz, ▲: 50 MHz.

TABLE 4. THE RELAXATION PARAMETERS IN SOLUTIONS OF NaI IN *i*-PrOH–H_2O MIXTURE AT 20 °C

Concn of *i*-PrOH (wt%)	Concn of NaI (molality)	A 10^{-17} s^2 cm^{-1}	B 10^{-17} s^2 cm^{-1}	$f_{\max}$ MHz
90	0.1	27.8	16	53.1
	0.15	41.7	18	57.0
	0.2	55.6	20	60.3
	0.25	66.7	22	63.5
	0.3	74.6	24	66.2
80	0.1	22.2	8	47.2
	0.15	32.3	9	50.7
	0.2	41.0	10	53.8
	0.25	48.8	11	55.0
	0.3	55.6	12	57.3

TABLE 5. THE KINETIC VALUES OF NaI IN *i*-PrOH–H_2O MIXTURE AT 20 °C

Concn of *i*-PrOH (wt%)	K 10^{-2} M	k_b 10^{10} M^{-1} s^{-1}	k_f 10^8 s^{-1}	a_B 10^{-8} cm
90	1.0±0.3	1.7±0.5	1.7±0.1	6.0±1.2
80	2.0±1.0	0.8±0.3	1.6±0.1	6.1±2.2

of NaI increase with decreasing the concentration of *i*-PrOH in mixtures. This increase is caused by an increase of dielectric constant in the solution. However, no relaxational absorption due to NaI was observed when the weight percent of *i*-PrOH in *i*-PrOH–H_2O mixtures were lower than 60. Perhaps NaI dissociates completely in such solutions.

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