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Molecular Dynamical Studies on Nitrobenzene in Solutions of Tetraethyl and Tetrabutylammonium Bromides

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The concentration and temperature dependences of the reorientational correlation times of nitrobenzene in solutions of tetraethyl(TEABr) and tetrabutylammonium bromides(TBuABr) have been determined by Raman line shape analysis. Pure liquid nitrobenzene was evaluated for comparison. The reorientational correlation times of nitrobenzene in solutions decreased with increasing concentration of the salts and the apparent activation enthalpy of τ_{or} of nitrobenzene in solutions was larger than in that pure nitrobenzene. From the experimental results, the solution structure of TEABr and TBuABr in nitrobenzene are discussed.

It the studies of ionic association in nonaqueous solvents, nitrobenzene has an important role, because of its high viscosity and high dielectric constant. In these studies, the ionic association constant and the kinetic parameters have been determined by means of various techniques, such as electrical conductance[1-3] and ultrasonic absorption measurements.[4] It has been shown that the association of ions in nitrobenzene type was of the solvent-separated type.

Hyne proposed a model for the specific solvation of the n-$Bu_4N^+Br^-$ ion pair in nitrobenzene.[5] Considering the relative dimensions and the charge distributions of the n-$Bu_4N^+Br^-$ ion-pair and nitrobenzene molecule, it was concluded that it was not improbable that the nitrobenzene acts as a "template for the absorption" of n-$Bu_4N^+Br^-$ ion-pairs and this was comfirmed by NMR studies.

Recently, several molecular dynamical studies of liquid nitrobenzene have been reported using nuclear magnetic resonance[6,7] and depolarized Rayleigh scattering.[7,8] In these studies, the reorientational correlation times of nitrobenzene have been determined and the liquid structure of nitrobenzene discussed. One of the most powerful tools in determining the reorientational correlation times is Raman spectroscopy. It is expected that the reorientational correlation times of the nitrobenzene molecule is a sensitive measure of the solute-solvent interaction, especially the local structure, in solutions.

In this paper, the temperature dependence of the reorientational correlation time of nitrobenzene and the concentration dependence in tetraethyl and tetrabutylammonium bromides–nitrobenzene solutions will be reported. In addition, in order to discuss the effects of viscosity and molecular volume on reorientational motion, the viscosity and partial molar volumes of tetraethyl and tetrabutylammonium bromides in nitrobenzene have been evaluated.

Experimental and Data Analysis

Sample. Nitrobenzene was a commercial product (extra-pure-grade reagent) and was distilled under reduced pressure, after drying by molecular sieves. Tetraethylammonium bromide and tetrabutylammonium bromide, hereafter abbreviated TEABr and TBuABr, respectively, were of extra-pure-grade.

Viscosity and Density Measurements. The density and viscosity were measured, respectively, with an Ostwald type pycnometer and viscometer at 30 °C.

Raman Spectroscopy. The apparatus used consisted of an argon ion laser (800 mW 488 nm) produced by the Coherent Radiation Co., Ltd., and a Laser Raman Spectrometer of JRS-U1 type, JEOL Ltd., Japan.

In order to obtain the reorientational correlation times, the Raman line shape of the ν_{12} (a_1) fundamental mode of ring-stretching,[9] 1004 cm^{-1}, was analyzed. The Raman spectrum was observed at 90° scattering with respect to the linearly polarized incident light. The intensities $I_{isot}(\omega)$ and $I_{anis}(\omega)$ may be determined from the spectra obtained by polarizing the scattered beam parallely, $I_{\parallel}(\omega)$ and perpendicularly, $I_{\perp}(\omega)$ to the electric field vector E of incident light:

$$I_{isot}(\omega) = I_{\parallel}(\omega) - 4/3 I_{\perp}(\omega) \tag{1}$$

$$I_{anis}(\omega) = I_{\perp}(\omega) \tag{2}$$

$I_{isot}(\omega)$ represents the intrinsic vibrational line shape and $I_{anis}(\omega)$ is a convolution of the vibrational line shape and the reorientational spectrum.

The Raman bands measured are broadened by the instrumental slit width and the spectrum obtained is a convolution of the true Lorentzian spectrum and the slit function, $S(\omega)$. The spectral slit function is well approximated by a Gaussian function,[10] and thus:

$$I'(\omega) = N\int_{-\infty}^{\infty} \frac{1}{\beta_L^2 + (\omega-\omega')^2} \exp\left\{-\left(\frac{\omega'}{\beta_G}\right)^2\right\} d\omega', \tag{3}$$

where β_L is the true half-width and $\beta_G = S/2\sqrt{\ln 2}$, where, S is the spectral slit width.

An approximate analytical expression for $I'(\omega)$ in Eq. 3, has been proposed by Kielkopf.[12] It is preferable to estimate the apparent spectral line-width as a function of mechanical slit width by means of the direct calculation of Eq. 3 for each β_L value.

For example, the Raman line shape of the $\nu_{12}(a_1)$ band of nitrobenzene is shown in Fig. 1. The spectral half-width of the Raman line of the $\nu_{12}(a_1)$ band of nitrobenzene was measured as a function of the mechanical slit width S. Figure 2 shows a plot of the apparent spectral line width obatined *vs.* the mechanical slit width of the spectrometer used. In Fig. 2, the solid line shows the relation between the apparent spectral line width calculated by Eq. 3 and the mechanical slit width, $\beta_G = S/2\sqrt{\ln 2}$, assuming the true half-width, β_L, of Lorentzian spectrum. As seen in Fig. 2, the agreement between the values observed and those calculated is extremely good. This indicates that the isotropic and anisotropic line shapes of Raman scattering of the $\nu_{12}(a_1)$ fundamental mode of nitrobenzene is adequately described by the Lorentzian function and the slit function, $S(\omega)$, of the spectrometer used may be well approximated by the Gaussian function. The true half-width, β_L, by fitting the observed spectrum with one calculated from Eq. 3 using the

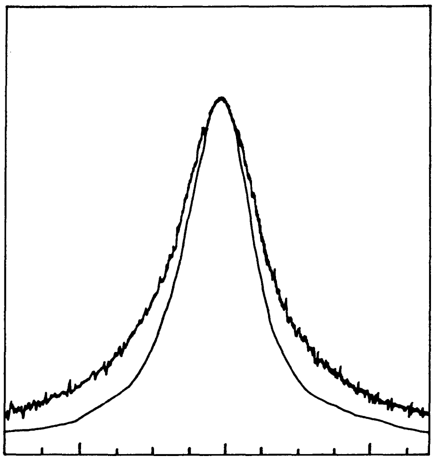

Fig. 1. Raman line shape of isotropic (∥) and anisotropic (⊥) parts of $\nu_{12}(a_1)$ mode (1004 cm^{-1}) of nitrobenzene in tne solution of TBuABr, 0.025 mol/l. (the intensities were normalized each other.)

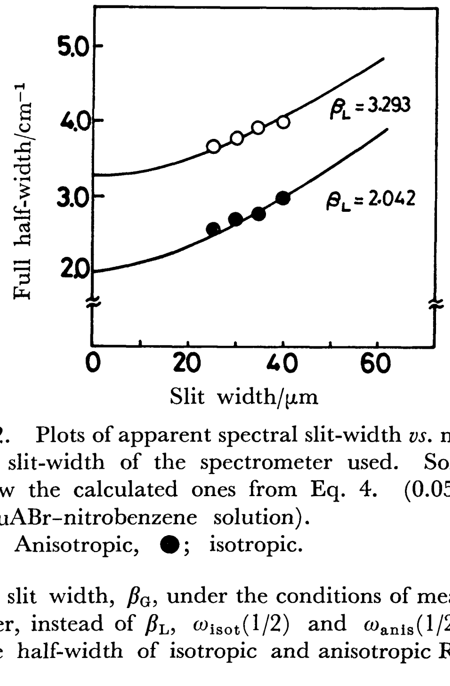

Fig. 2. Plots of apparent spectral slit-width *vs.* mechanical slit-width of the spectrometer used. Solid lines show the calculated ones from Eq. 4. (0.05 mol/l; TBuABr-nitrobenzene solution).
○; Anisotropic, ●; isotropic.

spectral slit width, β_G, under the conditions of measurement. Hereafter, instead of β_L, $\omega_{isot}(1/2)$ and $\omega_{anis}(1/2)$ refer to the true half-width of isotropic and anisotropic Raman line shape.

Thus, the vibrational and reorientational correlation times may be estimated from the half-width of anisotropic and isotropic Raman line shape as follows;

$$\tau_v = (\pi c \omega_{isot}(1/2))^{-1}, \tag{4}$$

$$\tau_{or} = (\pi c \omega_{or}(1/2))^{-1}, \tag{5}$$

where, $\omega_{or}(1/2) = \omega_{anis}(1/2) - \omega_{isot}(1/2)$.

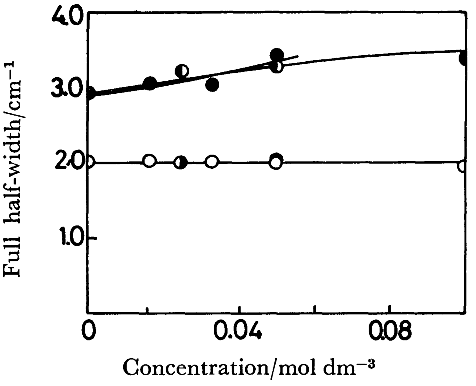

Fig. 3. Concentration dependences of the full half-width of isotropic, $\omega_{isot}(1/2)$, and anisotropic. ω_{anis}-(1/2), parts.
○; $\omega_{isot}(1/2)$, ●: $\omega_{anis}(1/2)$, TEABr-nitrobenzene.
◑; $\omega_{isot}(1/2)$, ◐; $\omega_{anis}(1/2)$, TBuABr-nitrobenzene.

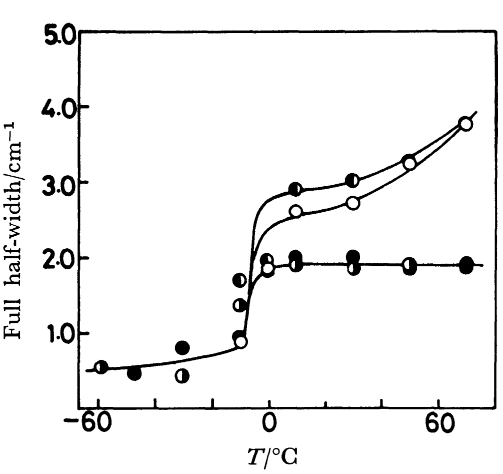

Fig. 4. Temperature dependences of the full half-width.
●; $\omega_{isot}(1/2)$, ○; $\omega_{anis}(1/2)$, neat nitrobenzene,
◑; $\omega_{isot}(1/2)$, ◐; $\omega_{anis}(1/2)$, 0.0333 mol/l, TEABr-nitrobenzene solution.

Results

The polts of $\omega_{isot}(1/2)$ and $\omega_{anis}(1/2)$ against the concentration of TEABr and TBuABr are shown in Fig. 3. The differences in these values of TEABr and TBuABr can not be observed. The values of $\omega_{anis}(1/2)$ increase with increasing concentration, but at higher concentration, the increment increase of $\omega_{anis}(1/2)$ with concentration becomes small. The values of $\omega_{isot}(1/2)$ are however independent of concentration, indicating that the solute molecules, TEABr and TBuABr, do not contribute to the vibrational correlation times of the $\nu_{12}(a_1)$ mode of nitrobenzene in the solutions.

The temperature dependence of $\omega_{anis}(1/2)$ and $\omega_{isot}(1/2)$ of nitrobenzene and nitrobenzene in solutions of TEABr are shown in Fig. 4. As seen, the differences in value of $\omega_{isot}(1/2)$ in pure nitrobenzene and in the solutions could not be observed in the temperature ranges, but at the transition point from solid to liquid phases, the values of $\omega_{isot}(1/2)$ change drastically. This line broadening is thought due to a molecular dephasing process accompanied by molecular collisions in the liquid and/or solution. This mechanism is independent of the solute ions in solutions. The values of $\omega_{anis}(1/2)$ in the liquid phase increase with increasing temperature.

In Table 1, the partial molar volumes and the viscosity *B* coefficients of TEABr and TBuABr in nitrobenzene, obtained from density and viscosity measurements, are summarized together with those in aqueous solutions.

Table 1. Partial molar volumes and B coefficient of TEABr and TBuABr in nitrobenzene

	ϕ°_v/l mol^{-1}		B/l mol^{-1}		$B-2.5\,\phi^\circ_v$/l mol^{-1}	
	Nitrobenzene	Water	Nitrobenzene	Water	Nitrobenzene	Water
TEABr	0.1660	0.1738[a]	0.88_8	0.338[a]	0.473	−0.097
TBuABr	0.3012	0.3004[a]	1.07_7	1.238[a]	0.324	0.487

[a] “Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Processes,” ed by R. A. Horne, Wiley-Interscience, New York (1971).

Discussion

The molecular symmetry of nitrobenzene belongs to the class C_{2v}. In the present work, the $\nu_{12}(a_1)$ mode of nitrobenzene, the ring stretching mode, was used to determine the reorientational correlation time of nitrobenzene by line shape analysis. As clearly indicated by Nafie and Peticolas,[13] the normalized correlation function obtained from the Raman line shape analysis of this mode may be expressed as follows;

$$C(t) = (a^2+b^2+c^2-ac-ab-bc)^{-1} \times \{(b-a)^2\boldsymbol{P}_2[\boldsymbol{u}^y(0)\boldsymbol{u}^y(t)] + (c-a)^2\boldsymbol{P}_2[\boldsymbol{u}^z(0)\boldsymbol{u}^z(t)] + (b-a)(c-a)\boldsymbol{P}_2[\boldsymbol{u}^z(0)\boldsymbol{u}^y(t)] + \boldsymbol{P}_2[\boldsymbol{u}^y(0)\boldsymbol{u}^z(t)]\}, \tag{6}$$

where $\boldsymbol{u}^z(0)$ is unit vector indicating the direction of the molecular z axis at time $t=0$, $\boldsymbol{u}^z(t)$ indicates the direction of the same axis at time t and a, b, and c refer to the Raman tensors of α_{xx}, α_{yy}, and α_{zz}, respectively. Therefore, at this stage, the reorientational correlation time, τ_{or}, obtained from the Raman line shape analysis of the ν_{12} mode of nitrobenzene can not explicitly assigned to a rotational diffusion tensor. Bauer *et al.* concluded by comparison with NMR measurements that the reorientation about the z axis is at least twice as fast as reorientation about the other axis.[7,8] The reorientational motion of nitrobenzene is mainly concerned with motion about the z axis and the τ_{or} obtained, here, is a measure of the local motion of nitrobenznene in the liquid and solutions.

Influence of TEABr and TBuABr on the Molecular Motion of Nitrobenzene. As seen in Fig. 3, the values of $\omega_{isot}(1/2)$, which are related to the vibrational correlation times of nitrobenzene, are independent of the concentration of tetraalkylammonium bromide and its chain length. This indicates that the solute molecules do not affect the molecular vibrational correlation times of nitrobenzene as a solvent.

The plots of reorientational correlation time against the concentration of TEABr and TBuABr are shown in Fig. 5. The reorientational correlation time of nitrobenzene, τ_{or}, as a solvent decreases with increasing concentration of solute, indicating that the interaction between nitrobenzenes is stronger than that between nitrobenzene and TEABr and/or TBuABr. As seen in Table 1, the partial molar volumes of TEABr and TBuABr in nitrobenzene do not greatly differ from in aqueous solutions. This indicates that the molecular diameter and volumes of the tetraalkylammonium ion in nitrobenzene are comparable to those in aqueous solutions. The viscosity B coefficients of both solutions are positive.

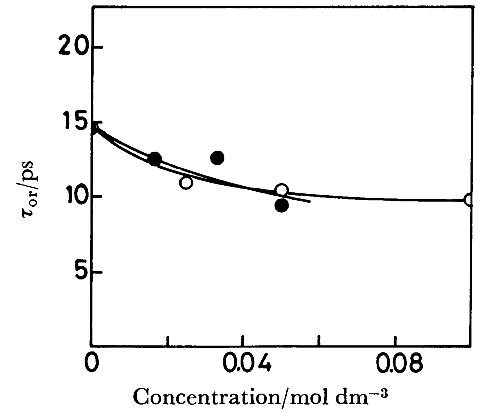

Fig. 5. Plots of τ_{or} *vs.* concentration of salts in solutions.
●; τ_{or} of nitrobenzene in TEABr,
○; τ_{or} of nitrobenzene in TBuABr.

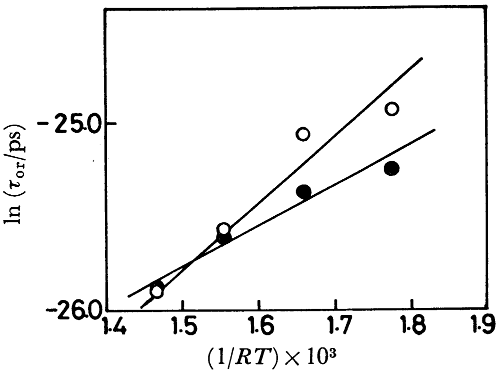

Fig. 6. Plots of $\ln \tau_{or}$ *vs.* $1/RT$.
○; τ_{or} of nitrobenzene in 0.0333 mol/l TEABr solution.
●; τ_{or} of neat nitrobezene.

The values of $(B-\phi^\circ_{ion})$ which are a measure of the ion-solvent interactions do not differ indicating that the ion-solvent interactions remain in TEABr and TBuABr–nitrobenzene solutions. The results mentioned above do not agree with the model proposed by Hyne for specific solvation of n-Bu$_4$N$^+$Br$^-$ ion-pairs and nitrobenzene.

Temperature Dependence of Reorientational Correlation Times of Nitrobenzene in the Pure and Solution States. The relationships between the reorientational correlation times of nitrobenzene in the pure and solution states, τ_{or}, and $1/RT$ are shown in Fig. 6. As seen in Fig. 6, τ_{or} can be expressed by the equation

$$\tau_{or} = \tau^\circ_{or}\exp(U/RT), \tag{7}$$

TABLE 2. REORIENTATIONAL RELAXATION TIMES DETERMINED BY VARIOUS TECHNIQUES

T/°C	τ_{or}(Raman)	τ_{ls}	$\tau_{NMR,p}(C^{13})$	$\tau_{NMR,o,m}(C^{13})$	$\tau_{NMR}(N^{14})$
10	14.8[a]				
20	17.6[e]	40.83[e]			
24		36.0[b]	12.5[b]	8.1[b]	
30	13.1[a]				3.45 (25 °C)[d]
38			9.6[c]	6.6[c]	
50	8.0[a]				
70	5.7[a]				

a) This work. b) Ref. 7. c) G. C. Levy, J. D. Cargioli, and F. A. L. Anet, *J. Am. Chem. Soc.*, **95**, 1527 (1973). d) Ref. 6. e) A. M. Amorim, D. Costa, M. A. Norman, and J. H. Rclarke, *Mol. Phys.*, **29**, 191 (1975).

where U refers to the apparent activation energy. The apparent activation energies, U, estimated from the plots of τ_{or} *vs.* $1/RT$ are 3.5 kcal/mol and 2.2 kcal/mol in the pure and solution states, respectively. The value of U, 3.5 kcal/mol, for pure liquid nitrobenzene is in good agreement with those obtained from the temperature dependence of "quadrupolar" correlation times for the molecular reorientation of liquid nitrobenzene by means of nuclear relaxation experiment of N^{14} [6] and are also comparable to those obtained from the temperature dependence of viscosity of nitrobenzene.

The reorientational correlation times of nitrobenzene in the solution of TEABr (0.0333 mol/l) are shorter than that in the pure liquid state in the temperature ranges and the apparent activation energy of τ_{or} in the solution state is smaller than that in pure liquid state. This indicates that the molecular motion of nitrobenzene is easier in solution than in the pure liquid state.

Bauer *et al.*[8] considered that nitrobenzene forms a "weak" dimer which hinders rotation. The addition of TEABr and/or TBuABr in nitrobenzene breaks the "weak" dimer and consequently nitrobenzene molecule can rotate more freely.

Comparison with Other Relaxation Times. The reorientational relaxation time obtained from the depolarized light scattering spectrum, τ_{LS}, relates to the single particle reorientational relaxation time, τ_s, which can be determined directly by means of Raman line shape analysis:[8]

$$\tau_{LS} = \left(\frac{1+fN}{1+gN}\right)\tau_s, \tag{8}$$

where the parameter, fN and gN, refer to the static and dynamic orientational pair correlation terms, respectively.

The relaxation times determined by several techniques are summarized in Table 2. Alms *et al.*[8] estimated the values of fN and gN as 1.30±0.05 and 0.1±0.0 for neat nitrobenzene. Using the value of τ_{LS}, 36.0 ps, and these values of fN and gN, the single particle relaxation time, τ_s, has been estimated to be 15.8±0.5 ps. This value is in good agreement with those of τ_{or} obtained from the Raman line shape analysis.

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