ations in the oscillator strength are 0% and 0.7%, respectively.

The fact that there are two metastable triplet states, which are not in thermal equilibrium at 300 K, must be interpreted as a consequence of a high potential energy barrier, separating a planar and a twisted form of the triplet-state molecule.

Transient Dielectric Loss Measurements. In order to find out whether or not the triplet with the nonplanar geometry has to be characterized as a twisted intramolecular charge-transfer state,[21] its contribution to the transient dielectric loss of the solution has been investigated. A small laser-induced transient dielectric loss of a solution of 2-naphthaldehyde in cyclohexane is observed at 10.04 GHz. The decay time of the signal is (360 ± 50) ns, which is equal to τ_1^{a}, i.e., the lifetime of the triplet-state Raman scatterer. The transient dielectric loss must therefore arise from the latter type of species. The signal is small compared to that encountered for similar concentrations of transient species, which have similar dipole relaxation times, but transient changes of molecular dipole moments of 10 D.[22] The difference $\Delta\mu$ between the dipole moment μ_{T} in the triplet state and μ_{G} in the ground state is evaluated in the usual manner.[8] A value $\Delta\mu \leq 4$ D is obtained by taking the relaxation time τ equal to 60 ps and the triplet quantum yield $\phi_{\mathrm{T}} = 0.7$.[10] This means that the state does not have charge-transfer character. The lack of charge-transfer character is in agreement with the large difference between the observed transient absorption spectrum and the spectra of the radical cation and radical anion of naphthalene.[23]

Conclusion

Two electronic triplet states of 2-naphthaldehyde get populated at 300 K by optical excitation into the singlet manifold. One of these states resembles the lowest triplet state of naphthalene and it is considered to be a $\pi\pi^*$ state with the excitation localized on the naphthyl group. The resonance Raman spectrum of the molecule in this state does not reveal the C=O stretching vibration, because of non-coplanarity of the aldehyde and the naphthyl group.

A forthcoming paper will discuss the effect of isotopic substitutions in the triplet-state resonance Raman spectra of 2-naphthaldehyde.

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Registry No. 2-Naphthaldehyde, 66-99-9.

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Kinetic Analysis of Association Processes between Oppositely Charged Polymer Latex Particles

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Abstract: The association processes between oppositely charged polymer latex particles could be directly studied by using an ultramicroscope connected to an image-processing system and also spectrophotometric techniques. The relaxation times obtained by the two methods were in good agreement. The forward rate constants (k_{f}) of the association of latex particles obtained from the slope of the plots of the reciprocal relaxation time vs. concentration of latex particles in excess were unexpectedly close to, but slightly smaller than, the theoretical values for the diffusion-controlled association process of neutral species. The k_{f} values were obviously in disagreement with the theoretical values calculated by the theory developed on the point charge approximation. The disagreement persisted even when the counterion association is taken into consideration. The enthalpy and entropy of activation were larger than the theoretical values calculated for diffusion-controlled processes.

The kinetic studies of chemical reactions in general have been performed by measuring the time changes of parameters associated with the reactions. The spectrophotometry is, for example, based on the change of absorbance of reactants and/or products in the course of the reactions. The underlying assumption is that the absorbance is strictly proportional to the concentration of the species in consideration. This assumption would be intrinsically correct in dilute regions. Although we are not questioning the validity of this assumption, it would be quite interesting if we could study various kinetic laws without introducing the assumption. In the present paper, we take the advantage of polymer latex particles being large enough to be seen by an ultramicroscope and carry out a kinetic (naked-eye) study of the association between oppositely charged latex particles as the first of the series of our investigation.

This study also has another significance in colloid science. Polymer latices have been widely used in the diagnosis of various kinds of diseases,[1-3] and even in the therapy of cancers.[4] In the actual diagnosis of diseases, the recognition and estimation of specific compounds in biological samples can be carried out with agglutination methods. Agglutination of latex particles with many electric charges by the increase in ionic strength has been studied extensively.[5,6] However, the basic nature of the association

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Table I. Properties of the Polymer Latices

latex	diameter (Å)	charge no. (per particle)	charge density (μC·cm^{-2})
MATA-2	3000	7.2×10^4	4.0
G-5301	3700	2.7×10^5	10
SS-40	3000	2.0×10^5	11
SS-30	1250	2.3×10^4	7.6
N-300	3000	2.3×10^4	1.3

processes of latex particles (colloidal particles in general), and hence the rate constant of the association at the very initial stage, has not been studied rigorously. The rate of change of the absorbance of colloidal suspension, which is required for the estimation of the so-called stability ratio and hence the rate of coagulation in the framework of the DLVO theory on colloidal stability, was determined at a fairly long time after the onset of coagulation. For example, in one of the previous papers, the absorbance was measured at 1-h intervals.[7] It is of course desirable to determine the association rate at a much earlier stage to examine the precise kinetic equation of coagulation, for example, Smoluchowski's equation, since this equation is derived for "binary" collision. Herein, we report the initial rate of association of polymer latex particles by counting dimer particles.

Experimental Section

Materials. Anionic latex particles, Immutex G-5301 and N-300, were purchased from the Japan Synthetic Rubber Co., Tokyo, and Sekisui Chemicals, Osaka, respectively. The other anionic latices SS-30 and SS-40 were prepared by emulsion polymerization of potassium *p*-styrenesulfonate and styrene with potassium peroxydisulfate as an initiator. A cationic polymer latex MATA-2 was prepared by emulsion polymerization of (3-(methacryloylamino)propyl)trimethylammonium chloride (Fluka, Switzerland) and styrene with a cationic initiator 2-azobis(2-methylpropamidinium) dichloride (Wako Pure Chemicals, Osaka, Japan). The anionic latices G-5301, N-300, SS-30, and SS-40 were converted to the H$^+$ form by using a mixed-bed ion exchange resin, Amberlite MB-3. MATA-2 was purified by repeated washings with pure water with use of an Amicon ultrafiltration apparatus. From electron micrographs using a JEM-100U (Nihon Denshi, Tokyo, Japan) these particles were confirmed to be monodisperse. Table I shows the estimated diameters of these latices. By the conductometric titration, the charge numbers on the surface of the polymer latices were also determined (Table I). Other reagents were commercially available products. To prepare solutions, Milli-Q grade water was used.

Microscopic Observation. The association process was directly observed with a Carl Zeiss microscope (Axiomat) connected with a Carl Zeiss image processing system (IBAS) as described in a previous work,[8] in which the effect of specific gravity on the ordering of latex particles (particularly on the static interparticle spacing) was examined, and the interparticle spacing was compared with the prediction by Sogami's theory. Just after the addition of the anionic latex suspension to the cationic latex suspension in the observation cell, the microscopic observation was started and the progress of the process was recorded in a video tape. By replaying the tape the number of dimeric particles in the visual field was counted at appropriate intervals until it leveled off. By assuming the uniform distribution of the dimeric particles and monomeric ones throughout the suspension, the percents of the dimers were estimated.

Spectrophotometric Measurements. The association processes of polymer latex particles of opposite charges were also studied spectrophotometrically by the absorbance change at 800 nm with a high-sensitivity spectrophotometer (SM-401, Union Engineering, Hirakata, Japan).

Results and Discussion

Since the association in water was too rapid for visual observation, we examined the association in a 30% (w/v) aqueous sucrose solution at 25 °C, in which the association was slowed down because of the enhanced viscosity. The results are as shown in Figure 1, where a 1 M latex suspension denotes 6.02×10^{23} latex particles in 1 L of the suspension. From the semilogarithmic plots of the concentration of dimeric particles in the suspension converted from the dimer percents in the visual field against time, we could obtain the reciprocal of the relaxation time of the association of latex particles of opposite charges as 9.1×10^{-3} s^{-1}. By mixing the anionic latex with an excess amount of cationic latex, clear curves with a single relaxation time could be observed spectrophotometrically as shown in Figure 2. The reciprocal relaxation time measured spectrophotometrically under the same experimental condition as in Figure 1 was 9.4×10^{-3} s^{-1}, which is in good agreement with the value from the microscopy (9.1×10^{-3} s^{-1}). This agreement shows that the relaxation phenomena observed spectrophotometrically corresponds to the binary association of particles of opposite charges provided that the spectrophotometry can be carried out at the very initial stage.

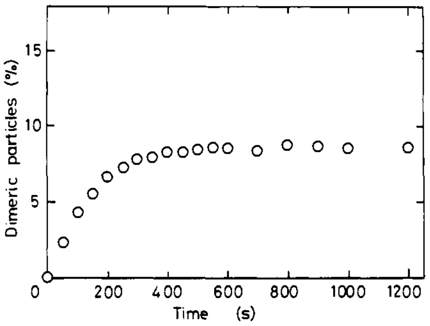

Figure 1. Time dependence of percent of dimeric latex particles in 30% (w/v) sucrose–water at 25 °C. [MATA-2] = 8.1×10^{-11} M, [G-5301] = 8.1×10^{-12} M.

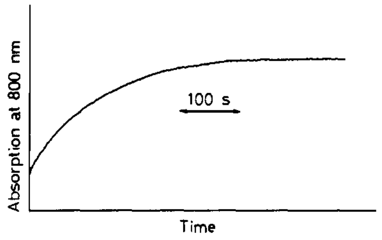

Figure 2. Typical trace of the association process of MATA-2 with G-5301 in 30% (w/v) sucrose–water at 25 °C.

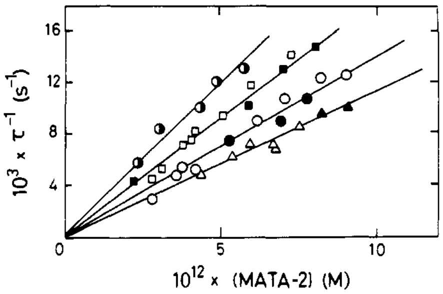

Figure 3. Influence of concentration of MATA-2 on τ^{-1} in H_2O at various temperatures: (△) 15 °C; (○) 20 °C; (□) 25 °C; (◑) 30 °C (with G-5301 of H$^+$ form); (▲) 15 °C; (●) 20 °C; (■) 25 °C (with G-5301 of Na$^+$ form).

Long after the start of the association (≫10 times the relaxation time of the dimerization process), further association processes of dimeric particles with other particles to form trimers, tetramers, and so on were confirmed by the microscopic observation. Correspondingly, the absorbance curve changed in a complicated manner. Thus, the kinetic data obtained long after the onset of the association should not be considered as representing the binary association.

By the pseudo-first-order analysis we could obtain the first-order rate constant k_{obsd} ($=\tau^{-1}$) at various concentrations of the cationic latex as shown in Figure 3.[9] From the slope of Figure 3 we could estimate the second-order rate constant k_f for the association of

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(9) Since the spectrophotometric data at the initial stage were above established as corresponding to the binary association, the subsequent discussion will be conducted on spectrophotometric data in water.

Table II. Rate Constants at Various Temperatures in Water

temp	MATA-2 + SS-40		MATA-2 + G-5301	
(°C)	$10^{-9}k_f$ (M^{-1} s^{-1})	k_b (s^{-1})	$10^{-9}k_f$ (M^{-1} s^{-1})	k_b (s^{-1})
15	1.9^a $(5.8)^b$	0^a $(85)^b$	1.2^a $(5.9)^b$	0^a $(62)^b$
20	2.4^a $(6.5)^b$	0^a $(96)^b$	1.4^a $(6.6)^b$	0^a $(69)^b$
25	3.0^a $(7.7)^b$	0^a $(110)^b$	1.9^a $(7.9)^b$	0^a $(83)^b$
30			2.5^a $(8.6)^b$	0^a $(90)^b$

[a] Spectrophotometric method. [b] Theoretical values for association of neutral species.

the cationic latex with the anionic latex. Table II shows k_f values obtained. In the table are shown the theoretical rate constants for diffusion-controlled association reactions between *neutral* particles of the same sizes as those of the latex particles calculated by the equations[10,11]

$$f = 6\pi\eta R \tag{1}$$

$$D = kT/f \tag{2}$$

$$k_f = 4\pi N_A(D_a + D_b)R_{ab}/1000 \tag{3}$$

$$k_b = 3(D_a + D_b)/R_{ab} \tag{4}$$

where f, η, R, D_a, k, T, N_A, and R_{ab} are the friction coefficient (in g·s^{-1}), the viscosity of the solvent (g·cm^{-1} s^{-1}), the radius of the particle specified by the subscript (cm), the diffusion coefficient of the particle specified (cm^2·s^{-1}), the Boltzmann constant, the absolute temperature, the Avogadro number, and the distance of closest approach between particles "a" and "b" ($=R_a + R_b$ in the case of rigid particles; R_a and R_b are the radii of particles "a" and "b" (cm)), respectively. Note that the theoretical and experimental k_f's are unexpectedly in the same order of magntiude. If we evaluate the influence of the electrostatic interaction between particles by eq 5–7[12-14] theoretical k_f values become much larger than the experimental values (3.3×10^{17} M^{-1} s^{-1} was obtained for the theoretical value of k_f in the case of association of MATA-2 with G-5301)

$$k_f = f_{el}k_{f0} \tag{5}$$

$$f_{el} = Z/[\exp(Z) - 1] \tag{6}$$

$$Z = Z_aZ_be^2/\epsilon R_{ab}kT \tag{7}$$

where f_{el}, k_{f0}, Z, Z_a, Z_b, and ϵ denote the electrostatic factor, the reaction rate constant without electrostatic effects, $Z = U/kT$ (U = potential energy), total analytical charges of particles "a" and "b", and the dielectric constant of the medium, respectively.

Recent transference experiments showed that the so-called counterion association by latex particles was surprisingly much larger than that by linear macroions; in other words, the net charge number is much smaller that the analytical number.[15] Only eight percent of the total analytical number of counterions (H^+) was free for latices having about the same analytical surface charge density as one of our latices, G-5301. Taking this experimental fact into consideration, Z_a and Z_b of the G-5301–MATA-2 system were assumed to be about 2.2×10^4 and 5.7×10^3, respectively, by assuming that the fraction of free counterions is 0.08. Therefore, the theoretical value of k_f was estimated to be 2×10^{15} M^{-1} s^{-1}, which is still much larger than the experimental results. This is probably because the point charge model assumed in the theoretical consideration is far from reality with latex particles. The number of effective charges responsible for the attractive interaction between the latex particles may be even much less than the number of net charges of latex particles. By tentatively assuming the validity of the point charge model, we can roughly estimate the effective charge numbers of latex particles from the observed k_f value, which were 7.2 (Z_a) and 27 (Z_b) for the association of MATA-2 with G-5301, respectively. One of the simplest interpretations is that, in the association processes, only the charges in the relatively narrow surfaces near the collision center play a decisive role; the charges on the surfaces diametrically opposite from the collision center may not be influential because of the relatively large dimension of the latices. A more detailed and quantitative argument could be made by more rigorous calculation without the point charge approximation on the interaction between spheres having surface charges, which is in progress.

Table III. Rate Constants of the Association Process of MATA-2 with Various Anionic Latices at 25 °C[a]

latex	diameter (Å)	charge density (μC·cm^{-2})	$10^{-9}k_f$ (M^{-1} s^{-1})
G-5301	3700	10	1.9
SS-40	3000	11	3.0
SS-30	1250	7.6	1.0
N-300	3000	1.3	0.62

[a] In H_2O.

Table IV. Activation Parameters of Association of MATA-2 with G-5301 in H_2O

$\Delta G^\ddagger$ (kcal·mol^{-1})	5.0 $(4.0)^a$
$\Delta H^\ddagger$ (kcal·mol^{-1})	7.4 $(4.4)^a$
$\Delta S^\ddagger$ (eu)	8.7 $(1.4)^a$

[a] Theoretical values for association of neutral species.

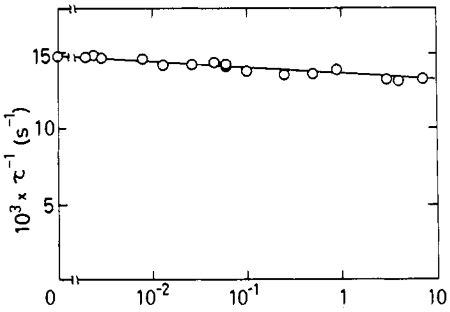

Figure 4. Influence of [NaCl] on τ^{-1} at 25 °C. [MATA-2] = 8.0×10^{-12} M, [G-5301] = 8.0×10^{-13} M. In H_2O.

Table III shows the effects of charge density and the diameter of the anionic particles on the forward rate constants (k_f) of the association with MATA-2. The charge density on the latex surface clearly affects the k_f values, which supports the importance of the electrostatic interaction on the association of oppositely charged latex particles. The claim, that the observed rate constant and the theoretical rate constant calculated for neutral particles (by eq 1–4) agreed with each other, would not be physically sound.

From the Y-intercept of Figure 3 k_b could not be estimated and we can only say that k_b is very small.

Figure 4 shows the influence of sodium chloride on τ^{-1} ($=k_f$[cationic latex] + k_b). From the figure we can claim that the ionic strength does not have a substantial effect on the association of latex particles, because the latex has a large diameter and the number of its effective charges is much smaller than that of its net charges. Harding reported a similar retardation effect of the increase in ionic strength on the agglutination of Al_2O_3 with SiO_2 when the two colloidal particles are oppositely charged.[16]

From the temperature dependence of k_f, we could estimate the activation parameters $\Delta G^\ddagger$, $\Delta S^\ddagger$, and $\Delta H^\ddagger$, which are listed in

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Table IV. Theoretical values calculated for the diffusion-controlled reaction are also shown in the parentheses. In the case of $\Delta G^{\ddagger}$, the experimental results are in good agreement with the theoretical values. As for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, however, the experimental values are larger than the theoretical values. The $\Delta H^{\ddagger}$ value is larger because there is a rate-determining factor that needs a large activation energy in the association reaction. Dehydration of latex particles in the association process as suggested by previous authors[17-19] and conformational changes of charged side chains on the latex surface are possible reasons for the larger experimental values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

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Excimer Laser Photolysis of $V(CO)_6$: Time-Resolved Infrared Studies of Gas-Phase $V(CO)_x$ (x = 5–2)[†]

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Abstract: The photolysis of gas-phase vanadium hexacarbonyl, $V(CO)_6$, has been studied at excimer laser wavelengths (351, 308, 248, and 193 nm) by observing the coordinatively unsaturated transient products, $V(CO)_x$ (x = 5–3 and possibly 2), via time-resolved infrared kinetic absorption spectroscopy. The dependence of the initial fragment distribution on photolysis wavelength is consistent with the model of sequential CO elimination established by similar studies on $Fe(CO)_5$, $Cr(CO)_6$, and $Co(CO)_3NO$. The high reactivity of unsaturated metal carbonyl species with saturated carbonyls to form binuclear complexes is again observed, with rate constants for the reaction of $V(CO)_3$ and $V(CO)_4$ with $V(CO)_6$ found to be of the order 3×10^{-10} cm^3 molecule^{-1} s^{-1}. Infrared assignments for $V(CO)_x$ are supported by kinetic measurements in the presence of added CO. Rate constants for the reaction of CO with $V(CO)_3$, $V(CO)_4$, and $V(CO)_5$ are found as $(0.4 \pm 0.1) \times 10^{-10}$, $(0.5 \pm 0.1) \times 10^{-10}$, and $(0.5 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively, leading to the expectation that ground-state $V(CO)_{3-5}$ share the doublet character of $V(CO)_6$. The infrared assignments are in disagreement with infrared absorption and some ESR studies of $V(CO)_x$ fragments in low-temperature matrices.

The general chemistry of coordinatively unsaturated transition-metal carbonyl species is of major interest due to the demonstrated role of individual species as active catalytic agents.[1-7] Vanadium is one of the limited list of transition metals whose unsaturated binary carbonyls have been reported to have been isolated in low-temperature rare-gas matrices and studied by both infrared absorption and ESR. $V(CO)_5$ was first reported to have been observed by infrared absorption consistent with a D_{3h} geometry following the in situ matrix photolysis of $V(CO)_6$.[8] Ozin and co-workers observed infrared absorptions attributed to $V(CO)_{1-6}$ following vanadium atom/CO co-condensation experiments.[9] Their results are in disagreement with later ESR studies of Morton and Preston on the matrix-isolated species formed following the in situ γ-radiolysis of $V(CO)_6$.[10] These species were assigned as $V(CO)_5$ and $V(CO)_4$, but their reported geometries are at odds with Ozin and co-workers' infrared assignments. Recent ESR measurements by Weltner and co-workers on the lower members of the series, $V(CO)_{1-3}$, formed by co-condensation at 4 K, are also in disagreement with the early matrix infrared absorption work.[11]

Time-resolved infrared absorption techniques have recently been developed which now allow the study of coordinatively unsaturated transient species formed following the ultraviolet photolysis of metal carbonyls in both gas[12-16] and solution phases.[17-20] Weitz and co-workers have reported comprehensive studies, including photolysis wavelength dependence, on the photolysis of $Fe(CO)_5$,[12] $Cr(CO)_6$,[13] and $Mn_2(CO)_{10}$,[14] Fletcher and Rosenfeld have in-

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