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The Effect of pH and Counter Ion of Oxalate Ion on Photoreduction of Methylviologen

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A higher formation of the methylviologen radical cation was observed at higher pH and when the counter ion of an oxalate ion was large in the continuous photolysis of deaerated solutions of methylviologen (MV^{2+})-oxalate ion ($C_2O_4^{2-}$). A dissociation of oxalic acid to the ion depended upon the pH at pH<7 and the dissociation constant of a MV^{2+}-$C_2O_4^{2-}$ complex depended on the pH at pH>10. The calculated absorbance of the MV^{2+}-$C_2O_4^{2-}$ complex at 350 nm, by using the dissociation constants of oxalic acid and the complex, agreed well with the observed absorbance. It was considered that the pH depedence of the $MV^{\dagger}$ formation resulted from the pH dependence of the concentration of the MV^{2+}-$C_2O_4^{2-}$ complex. The effect of a counter ion on the photoinduced electron transfer was explained in terms of the difference in the stability of the complex ion, in which smaller ions (Li^+, Na^+) tended to form more stable complexes than larger ions (NH_4^+, K^+).

Methylviologen (1,1′-dimethyl-4,4′-bipyridinum ion, MV^{2+}) has received considerable attention in recent years as being an efficient electron relay in the photocatalyzed reduction of water to hydrogen.[1] Therefore, reductions of MV^{2+} by various donors were carried out by many researchers.[2] On the other hand, an oxalate ion ($C_2O_4^{2-}$) has been used as a sacrificial electron donor.[3] The oxidation of the oxalate ion leads to the formation of $C_2O_4^{\cdot-}$, which undergoes rapid decomposition to CO_2 and $CO_2^{\cdot-}$. $CO_2^{\cdot-}$ is well-known as a strong donor and gives CO_2 by donating an electron. Such a photoinduced irreversible electron transfer of carboxylic acid is known as the photo-Kolbe reaction.[4] In an electron acceptor–oxalate ion system it is expected that an electron-accepted molecule is stable for a long time because a back electron transfer from the electron-accepted molecule to $C_2O_4^{\cdot-}$ is minimized. Certainly it was reported that the continuous photolysis of a deaerated solution of MV^{2+}-$C_2O_4^{2-}$ generated MV^+ which was stable for a long time.[5]

However, the study was carried out in an aqueous solution at neutral pH; no distinct discussion of the effect of the pH was presented. By elucidating the effect of the pH on the reaction, information on a reaction mechanism and most suitable conditions for a photoinduced electron transfer are given. Furthermore, the effect of a counter ion on a photoinduced electron transfer from an oxalate ion was scarcely mentioned. The photoinduced electron transfer from organic anions have been studied in relation to ion-pair phenomena.[6]

We undertook to investigate photoinduced electron transfer from anions.[7] In this work we carried out a continuous photolysis of the MV^{2+}-$C_2O_4^{2-}$ system and clarified the effects of the pH and counter ions of an oxalate ion on the yield of $MV^{\dagger}$ formation.

Experimental

Materials. Methylviologen dichloride (Nakarai) was used as received. $Li_2C_2O_4$, $Na_2C_2O_4$, $K_2C_2O_4$, and $(NH_4)_2C_2O_4$ were used without further purification. Aqueous solutions were prepared from distilled and deionized water and the pH was adjusted by the addition of KOH or NaOH to a $H_2C_2O_4$ solution.

Method. Aqueous solutions of MV^{2+} including oxalate ion were introduced into a 10 cm-long quarz cell jointed to a 2 mm quarz spectrophotometer cell. The concentrations of MV^{2+} and $C_2O_4^{2-}$ determined the concentration of the MV^{2+}-$C_2O_4^{2-}$ complex. In this study oxalate ions (0.1 M; 1 M=1 mol dm^{-3}) were in large excess to MV^{2+} (0.0025 M), in which about 70% of MV^{2+} formed a complex with the oxalate ions. Solutions for irradiation were thoroughly purged with Ar gas before irradiation, since $MV^{\dagger}$ reactions with O_2 to give MV^{2+} was well-known.[8] Irradiation was performed with a 500 W Xe lamp using an IRA-25S filter in which light longer than 300 nm was passed. Absorbance at 605 nm (extinction coefficient=1.37×10^4 M^{-1} cm^{-1})[9] due to the $MV^{\dagger}$ formed was monitored at determined time intervals.

Results and Discussion

The Effect of pH on the Yield of $MV^{\dagger}$. The pH of MV^{2+}-$H_2C_2O_4$ solutions were adjusted by the addition of KOH (pH; 2.3—12.70); aqueous solutions of MV^{2+}-$H_2C_2O_4$ were irradiated for 5 h. The formation of $MV^{\dagger}$ depended upon the pH, as shown in Fig. 1. The production mechanism of the $MV^{\dagger}$ was complex because two MV^{2+} were reduced by one oxalate ion, despite one MV^{2+} formed complex with one oxalate ion (as described later). To avoid complexity we chose mild reaction conditions in which a small amount of MV^{2+} was reduced. It was expected in such conditions that MV^{2+} would be reduced linearly with the reaction time. However, the production rate of $MV^{\dagger}$ decreased with the reaction time over 2 h (Fig. 1). We must note here that the oxidation of an oxalate ion leads to the formation of two CO_2 which act as acid in an aqueous solution. Since the formation of $MV^{\dagger}$ was slow at low pH, lowering the pH might suppress the formation of $MV^{\dagger}$. The concentration of CO_2 was calculated from the concentration of $MV^{\dagger}$ on the reaction at pH 7.2 for 5 h irradiation. The proton concentration, calculated

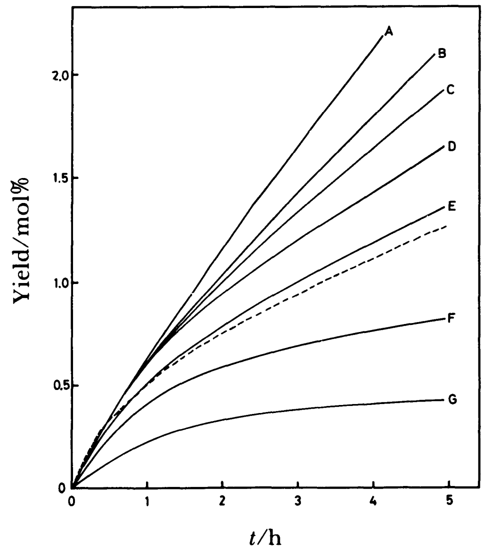


Fig. 1. The effect of pH on the yield of MV^+ in the irradiation of MV^{2+}-$K_2C_2O_4$ solutions. A; pH 12.70, B; 12.18, C; 10.61, D; 7.17, E; 5.60, F; 4.39, G; 3.0. The dotted line is the simulated curve.

from the concentration of CO_2, reached 3×10^{-6} M, which could reduce the pH of the solution from 7.2 to 5.5 if all of the CO_2 was dissolved into the aqueous solution. The Ostwald solubility coefficient of CO_2 was 0.8280 at 25 °C, larger than 0.0341 of Argon gas.[10] However, The quantity of Argon present in the reaction vessel was larger by a factor of 10^4 than that of CO_2. This meant that a large amount of CO_2 was present as gas, indicating that the contribution of CO_2 to pH reduction was small. Certainly, the decrease of the production rate was observed not only at pH ca. 7, but also at low pH ca. 3, in which the proton concentration was an order of 10^{-3} M and CO_2, which evolved from an oxalate ion, could not change the pH of the solution. The decrease in the production rate with the reaction time could be explained in terms of the accumulation of $MV^{\dagger}$. $MV^{\dagger}$ possesses a strong absorption peak around 390 nm (extinction coefficient=4.2×10^4 M^{-1} cm^{-1} (1 M=1 mol dm^{-3}))[9] the extinction coefficient at 350 nm was 6000—7000 M^{-1} cm^{-1}. This value was fairly larger than 8.2 M^{-1} cm^{-1} of the MV^{2+}-$C_2O_4^{2-}$ complex at 350 nm (shown later). If the light intensity was reduced by the absorption of $MV^{\dagger}$ which did not further react, a photoinduced electron transfer should be simply proportional to the absorption ratio of 8.2 [MV^{2+}-$C_2O_4^{2-}$] and 6500 [$MV^{\dagger}$]+8.2 [MV^{2+}-$C_2O_4^{2-}$], in which the extinction coefficient of $MV^{\dagger}$ was assumed to be 6500 M^{-1} cm^{-1} and the absorption by uncomplexed MV^{2+} was ignored. The dotted curve in Fig. 1 represents the calculated relationship between the reaction time and the yield of $MV^{\dagger}$, considering the change of light intensity with the concentration of $MV^{\dagger}$. The decrease in the production rate of $MV^{\dagger}$ with the reaction time was well simulated. It was considered that the accumulation of $MV^{\dagger}$ might suppress the photoinduced reaction, since $MV^{\dagger}$ absorbed the light which was effective for the photoinduced reaction. Namely, $MV^{\dagger}$ acted as a filter to reduce the light.

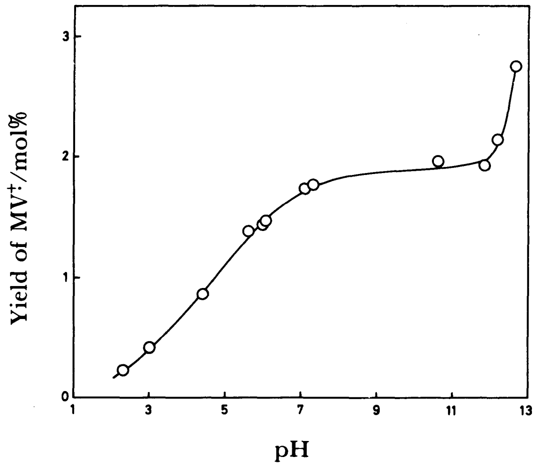


Fig. 2. The effect of pH on the yield of $MV^{\dagger}$ in the irradiation of MV^{2+}-$K_2C_2O_4$ solutions for 5 h.

Higher yields of $MV^{\dagger}$ were observed at higher pH's, as shown in Fig. 2, along with the yield of $MV^{\dagger}$ for 5 h irradiation. An increase of the $MV^{\dagger}$ yield at pH 2—5 and at above pH 11 was steep. It had already been reported that MV^{2+} was reduced to $MV^{\dagger}$ in an alkaline aqueous solution in the absence of air without irradiation,[8b] and that the rate of $MV^{\dagger}$ formation (R_i) obeyed the following rate law: $R_i = k_{obsd}[MV^{2+}]^2[OH^-]^2$: $k_{obsd} = 0.12$ M^{-3} min^{-1} at 25 °C. We applied this rate law to our reaction conditions. The production of $MV^{\dagger}$ was calculated as 0.02 mol% in the conditions at pH 12.7 for 5 h irradiation. The value was fairly small. We could not deny the possibility of the participation of OH^- in the high-pH region on the MV^{2+} reduction; however, the contribution of the reaction to $MV^{\dagger}$ formation must be small.

The Effect of pH on the Absorption of MV^{2+}-Oxalate Solutions. It is well-known that MV^{2+} forms a complex with ionic and neutral species, such as $C_2O_4^{2-}$.[11] The absorption of a MV^{2+}-$C_2O_4^{2-}$ solution at $\lambda > 300$ nm is larger than the absorption of MV^{2+} alone, despite the fact that $C_2O_4^{2-}$ possesses little absorption at wavelengths greater than 300 nm. This is because MV^{2+} forms a complex with $C_2O_4^{2-}$ and absorbs light when $\lambda > 300$ nm.[5] To form the complex with an oxalate ion is one important ability of MV^{2+} on a photochemical reaction, since the complex has been believed to be a photoactive species.[5] The pH dependence of the absorption at 350 nm is shown in Fig. 3. The small change of the spectra in the pH range 7.0—10.0 is the same as which was reported.[5] However, at each oxalate ion concentration (0.02—0.1 M), the increase of the absorbance at pH 2—5 and at above pH 11 was steep. The pH dependence of absorption at

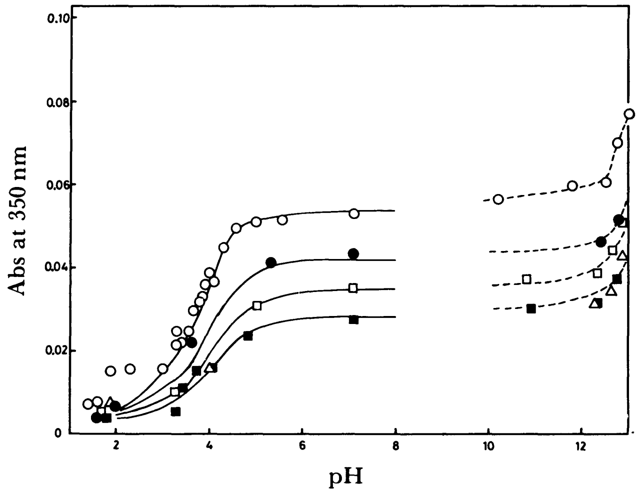


Fig. 3. The absorbance at 350 nm of MV^{2+}-$H_2C_2O_4$ solution whose pH was adjusted by the addition of KOH. Concentration of $H_2C_2O_4$ was 0.1 (○), 0.05 (●), 0.035 (□), 0.025 (■), and 0.02 (△) M and MV^{2+} was 0.01 M. The calculated absorbance by using the concentration of the MV^{2+}-$C_2O_4^{2-}$ complex and its ε_{350} was shown as the solid line.

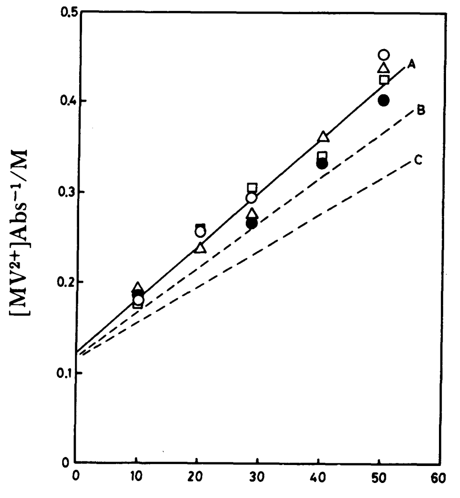


Fig. 4. The Benesi-Hildebrand analysis at 350 nm for the MV^{2+}-Li^+ (○), Na^+ (●), K^+ (△), or NH_4^+ (□) oxalate ion solutions. The pH was 7.1 (A), 12.35 (B), and 12.65 (C).

$$M_2C_2O_4 \longrightarrow 2M^+ + C_2O_4^{2-} \qquad (1)$$

$$C_2O_4^{2-} + H^+ \rightleftharpoons HC_2O_4^- \qquad (2)$$

$$HC_2O_4^- + H^+ \rightleftharpoons H_2C_2O_4 \qquad (3)$$

$$MV^{2+} + C_2O_4^{2-} \rightleftharpoons [MV^{2+}, C_2O_4^{2-}] \qquad (4)$$

$$[MV^{2+}, C_2O_4^{2-}] \xrightarrow{h\nu} [MV^{+\cdot}, C_2O_4^-] \qquad (5)$$

$$[MV^{+\cdot}, C_2O_4^-] \longrightarrow MV^{+\cdot} + C_2O_4^- \qquad (6)$$

$$[MV^{+\cdot}, C_2O_4^-] \longrightarrow [MV^{2+}, C_2O_4^{2-}] \qquad (7)$$

$$C_2O_4^- \longrightarrow CO_2^{-\cdot} + CO_2 \qquad (8)$$

$$MV^{2+} + CO_2^{-\cdot} \longrightarrow MV^{+\cdot} + CO_2 \qquad (9)$$

$$MV^{+\cdot} + C_2O_4^- \longrightarrow MV^{2+} + C_2O_4^{2-} \qquad (10)$$

$$MV^{2+} + Cl^- \longrightarrow MV^{2+}Cl^- \qquad (11)$$

$$MV^{2+}Cl^- + Cl^- \rightleftharpoons MV^{2+}(Cl^-)_2 \qquad (12)$$

Scheme 1.

350 nm was similar with that of the $MV^{+\cdot}$ yield for 5 h irradiation. Since a complex with a 1 : 1 stoichiometry had already been clarified by a Job's plot,[5,12] the Benesi-Hildebrand analysis for a 1 : 1 donor–acceptor complex[13] was carried out for the absorbance of MV^{2+}-$M_2C_2O_4$ ($M=Li^+$, Na^+, K^+, or NH_4^+) solutions at 350 nm. Although Fig. 4 shows some scatter, an almost linear relation was observed and the effect of the counter ion on the spectra was small. Little effect of the counter ion on the spectra indicated that $M_2C_2O_4$ was completely dissociated into $C_2O_4^{2-}$ and 2 M^+ (Eq. 1 in the Scheme 1). A Benesi-Hildebrand analysis yielded $K_3=20.4\ M^{-1}$ and $\varepsilon_{350}=8.2\ M^{-1}\ cm^{-1}$, which were almost identical to the reported values for K^+, 21 M^{-1} and 7.2 $M^{-1}\ cm^{-1}$, respectively.[5] The dissociation equilibrium constants of Eqs. 2 and 3 were reported as being 14500 and 17.5 $M^{-1}\ cm^{-1}$.[14] These values enabled us to calculate the concentration of $C_2O_4^{2-}$ in the reaction solution. The absorbance at 350 nm was calculated from the concentration of $C_2O_4^{2-}$, the values of K_3, ε_{350} of the complex and ε_{350} of uncomplexed MV^{2+} (ca. 0.9 $M^{-1}\ cm^{-1}$). The calculated absorbance (as shown in the solid line in Fig. 3) agreed very well with the observed value. This indicated that MV^{2+} could form the complex with only $C_2O_4^{2-}$ and that K_3 did not change in the pH range 2—8. Above pH 10, oxalate dissociates completely. This means that an increase in the amount of the oxalate ion was not the reason. And another reason was present for the increase in the absorbance at 350 nm and the yield of $MV^{+\cdot}$ with a pH in the high pH range. The Benesi-Hildebrand analysis was further applied for the absorbance at 350 nm in the high pH range as shown in Fig. 4. Here, lines B and C are best fit lines at pHs 12.35 and 12.65, respectively. Higher K_3s 23.3 and 28.5 M^{-1} than that in the lower pH range were obtained. This indicated that the increase of the formation of MV^+ with pH at above pH 10 might have resulted from an increase in the MV^{2+}-$C_2O_4^{2-}$ complex concentration, since the concentration of the MV^{2+}-$C_2O_4^{2-}$ complex increased with K_3.

The Effect of Ionic Strength and a Counter Cation on the Yield of $MV^{+\cdot}$. It was reported that modest concentrations (<0.5 M) of ions had a negligible effect on the yield of $MV^{+\cdot}$.[2c] However, in this study a

Table 1. The Effect of a Counter Ion of Oxalate Ion on the Yield of $MV^{+\cdot}$ after the Irradiation for 5 h

Counter ion of oxalate ion	pH	The yield of $MV^{+\cdot}$	Ion radius
		mol%	Å
Li^+	6.09	1.07	0.60
Na^+	6.00	1.22	0.95
Na^+	6.11	1.22	0.95
K^+	6.00	1.43	1.33
K^+	6.06	1.46	1.33
NH_4^+	6.49	1.71	1.43

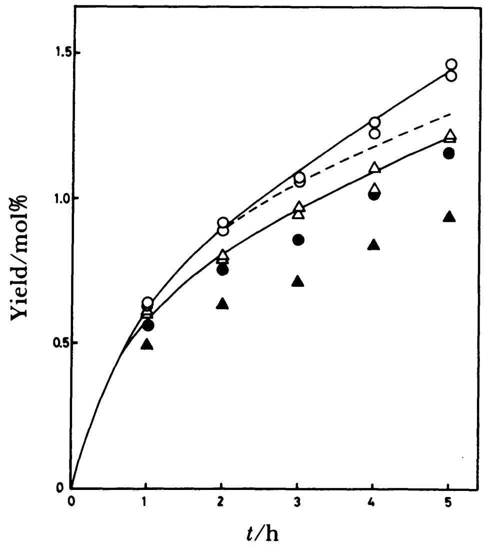


Fig. 5. The yields of $MV^{+\cdot}$ in the irradiation of the MV^{2+}-oxalate solutions. The pH was adjusted by using KOH (○, ●) or NaOH (△, ▲) with KCl (●, ▲) or without KCl (○, △). The dotted line was the results in which pH was adjusted by using the 1:1 mixture of NaOH and KOH solutions.

detrimental effect of an ionic strength on the yield $MV^{+\cdot}$ was observed, even at low ionic strength, upon the addition of KCl. The ion strength increased from 0.1 to 0.3, as shown in Fig. 5. The dissociation equilibrium constant of Eq. 12 in the scheme had been estimated from conductance measurements as being 0.1 M.[2b,15] The dissociation equilibrium constant of Eq. 11 was not reported; however, it was reported that the value was fairly larger than that of Eq. 12. If MV^{2+} existed as $MV^{2+}Cl^-$ initially, 3.4% of $MV^{2+}Cl^-$ could associate with Cl^- since initial concentration of MV^{2+} of our conditions was 0.0025 M. However, addition of KCl (0.2 M) increased the concentration of dichloride complex as large as 66.8%. The detrimental effect of anionic species, such as Cl^- on the yield of $MV^{+\cdot}$ might have resulted from the complex formation of MV^{2+} with Cl^-, which reduced the concentration of the photo active MV^{2+}-$C_2O_4^{2-}$ complex.

The yields of $MV^{+\cdot}$ in the solutions in which pH was adjusted by KOH were larger than that in the solutions in which pH was adjusted by NaOH as shown in Fig. 5. The yield of $MV^{+\cdot}$, in which a mixture of the KOH and NaOH solution was used as a pH moderator, was between them. MV^{2+}-$C_2O_4^{2-}$ solutions with other counter ions, Li^+ and NH_4^+ were also irradiated. The yield of $MV^{+\cdot}$ for 5 h irradiation increased with the ion radius of the counter ion (Table 1).

The effect of cationic species on photoinduced and electroinduced electron transfer from anions had been already discussed from the standpoint of a contact and loose ion pair.[6] For example, the rate constant of electron transfer from free biphenylide radical ions ($B^{-\cdot}$) to pyrene was $4.8\times10^{10}\,M^{-1}\,s^{-1}$; however, the rate constant from sodium biphenylide radical ions ($B^{-\cdot}$, Na^+) was $0.6\times10^{10}\,M^{-1}\,s^{-1}$.[6a] We have already reported that in electron transfer from the 9*H*-thioxanthene-9-one 10,10-dioxide ($TO\text{-}SO_2$) radical anion to diaryl disulfides, the order of the rate constant of electron transfer is as follows.[7a] $(TO\text{-}SO_2)^{-\cdot}$ is free radical anion.

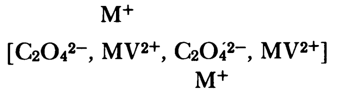
$$(TO\text{-}SO_2)^{-\cdot} > (TO\text{-}SO_2)^{-\cdot}, K^+ > (TO\text{-}SO_2)^{-\cdot}, Na^+.$$

Smaller ions tended to form more stabilized ion pairs (contact ion pairs) since their charge densities were larger than those of larger ions. It was considered that a contact ion pair stabilized ion species and electron transfer from a cation contacted anion became slow compared to that from a solvent-separated ion or free ion. In the contact ion pair system, the ion contact was known to cause a blue shift in the absorption maximum;[16] however, we could not clarify the shift from the absorption of the MV^{2+}-$C_2O_4^{2-}$ complex since the absorption of uncomplexed MV^{2+} overlapped with that of the complex. The effect of a solvent-separated ion pair on a photoinduced electron transfer from a donor to MV^{2+} was reported by Mandell and Hoffman in the photo reduction of MV^{2+} using EDTA as the donor.[2c] They reported that EDTA formed ion pairs not only with MV^{2+} but also with $[Ru(bpy)_3]^{2+}$ and that electron transfer proceeded more easily than under conditions in which SO_4^{2-} was used instead of EDTA because SO_4^{2-} could not form any ion pairs.

$$[Ru(bpy)_3^{2+}\cdots EDTA\cdots MV^{2+}] \rightarrow$$

$$[\mathrm{Ru(bpy)_3}^{3+}\cdots\mathrm{EDTA}\cdots\mathrm{MV}^{\dot{+}}] \rightarrow [\mathrm{Ru(bpy)_3}^{2+}\cdots\mathrm{EDTA_{ox}}\cdots\mathrm{MV}^{\dot{+}}]$$

It was also reported that at high concentrations of MV^{2+} (>1 mM), MV^{2+} existed as an aggregate surrounded by $C_2O_4^{2-}$. In such aggregates, a participation of counter cation (M^+) with a MV^{2+}–$C_2O_4^{2-}$ aggregate was probable, although the spectroscopic effect of M^+ on the absorbance at 350 nm was not observed, as shown in Fig. 4. A possible sketch of the aggregate (dimer) of MV^{2+}–$C_2O_4^{2-}$ and participation of M^+ with the aggregate is as follows.



$$\overset{M^+}{\underset{M^+}{[C_2O_4^{2-},\ MV^{2+},\ C_2O_4^{2-},\ MV^{2+}]}}$$

It was considered that smaller ions (Li^+, Na^+) tended to form more stable complexes with the MV^{2+}–$C_2O_4^{2-}$ aggregate than larger ions (K^+, NH_4^+) if the participation of M^+ with the aggregate occurred. It was also considered that a photoinduced electron transfer from the oxalate ion to MV^{2+} was more likely to occur in less stabilized complexes, such as the NH_4^+ or K^+ oxalate–MV^{2+} complex, than in a stabilized complex by the small ions, such as Li^+ or Na^+.

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