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Cationic Effect on the Polarographic Reduction of Nickel(II) in Acetonitrile

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The polarographie behavior of nickel(II) acetate salts dissolved in acetonitrile solvent containing small quantities of acetic acid has been investigated in various natures and concentrations of supporting electrolytes. A single reduction wave is observed in the solutions of lithium perchlorate or sodium perchlorate. The limiting current has an intermediate nature of both diffusion- and kinetic controlled polarographic current. A double wave, on the other hand, is observed in the solutions of tetraalkylammonium perchlorate supporting electrolyte such as $(CH_3)_4NClO_4$, $(C_2H_5)_4NClO_4$ or $(n\text{-}C_4H_9)_4NClO_4$. The limiting current of the first step exhibits an intermediate nature of both diffusion and kinetic currents, and that of the second step is kinetic in nature. The effect of the nature and concentration of electrolyte on the visible absorption spectra of acetatonickel(II) complexes in acetonitrile containing small quantities of acetic acid are also discussed. On the basis of evidence, a mechanism which involves a substitution reaction of acetatonickel(II) complexes with the supporting electrolytes is proposed. The substitution reaction in tetraalkylammonium perchlorate solutions is thought to be the rate-determining step. The first step of a double wave is also thought to be due to the inhibition of charge transfer process by the weakly absorption of tetraalkylammonium cations of supporting electrolytes on the DME.

The supporting electrolyte effects in a non-aqueous electrochemistry have been reported by several investigators and, especially Murray and Kenneth Hiller[1] have done extensive works on the polarography of metal β-diketone chelate compounds.

The polarographic behaviors of nickel(II) ion in an acetonitrile solvent have been reported by several investigators. Kolthoff and Coetzee[2] observed a single reversible reduction wave with the half-wave potential of -0.33 V *vs.* SCE in an acetonitrile solution containing a 0.1 M sodium perchlorate. Popov and Geske,[3] on the other hand, obtained a double wave with the half-wave potentials of -0.69 V and -1.22 V *vs.* Ag-$AgNO_3$ electrode, in the same solvent containing 0.1 M

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[1] R. W. Murray and L. Kenneth Hiller, Jr., *Anal. Chem.*, **39**, 1221 (1967).

[2] I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852 (1957).

[3] A. I. Popov and D. H. Geske, *ibid.*, **79**, 2074 (1957).

tetra-*n*-butylammonium perchlorate. Two-reduction steps for nickel(II) ion have also investigated in an acetonitrile[4] or a benzonitrile solvent[5] containing 0.1 M tetraethylammonium perchlorate. Iwamoto *et al.*[5] attributed the two-steps to the reduction of two kinds of nickel(II) species, and concluded that the second step involves the reduction of hydrated nickel(II) ions. The more easily reduced species, however, was not understood except the case of the presence of chloride ions. The first step in an acetonitrile solvent containing 0.1 M tetraethylammonium perchlorate and a small amount of chloride ions was involved the reduction of nickel(II)-chloride complex ions and the catalytic nature of the first wave has been established by Nelson and Iwamoto.[4]

The cationic effect of the supporting electrolyte for the polarographic reduction of nickel(II) ions has been carried out in an aqueous solvent[6,7] and an ethanol solvent,[8] respectively.

A distorated polarographic waves of nickel(II) ions in various kinds of natures and in various concentrations of supporting electrolyte solutions were initially reported by Gierst[6] and were later expanded by Dandoy and Gierst.[7] Dandoy and Gierst interpreted the polarographic behavior of nickel(II) ions in non-complexing media in terms of the dehydration kinetic current.

In the course of the studies for the reduction of acetatonickel(II) complexes in an acetonitrile solvent, the present authors observed a pronounced variation of the polarographic behaviors with the supporting electrolytes employed. Acetatonickel(II) complexes containing a small amount of acetic acid gave a single reduction wave in lithium perchlorate or sodium perchlorate supporting electrolytes, the two-reduction steps, on the other hand, were observed in the solutions of various tetraalkylammonium perchlorate supporting electrolytes.

The limiting current exhibited an intermediate nature of both diffusion and kinetically controlled polarographic currents, that of the second step in tetraalkylammonium perchlorate solutions, especially, was kinetic in nature.

The cationic effect is discussed on the basis of the chemical reaction of acetatonickel(II) complexes with cations of supporting electrolytes proceeding to the charge transfer process, and the inhibition of the charge transfer of nickel(II) ion, freeing of acetate ions from acetatonickel(II) complexes, by the weakly adsorption of tetraalkylammonium ions on the dropping mercury electrode.

Experimental

Reagents. Extra pure reagent acetonitrile purchased from Nakarai Chemicals Ltd. (Kyoto) was purified by a modified procedure of Forcier and Olver's method.[9] The purity was checked by the polarographic and spectrophotometric method.[10] The content of water was determined with Karl Fisher titration. Water content was approximately 2 to 5 mM.

Guaranteed reagent acetic acid and acetic anhydride were purified with the procedures given in the literature.[11]

Analytical reagent nickel(II) acetate salt ($Ni(CH_3COO)_2 \cdot (H_2O)_4$) was recrystallized three times from an aqueous solution containing 5 M acetic acid. The analysis of nickel(II) acetate salt gave the following result.

Found: C, 19.53; H, 5.79%. Calcd for $Ni(CH_3COO)_2(H_2O)_4$: C, 19.31; H, 5.67%.

Hexaaquonickel(II) perchlorate was prepared and recrystallized with the procedure given in the literature.[12] $Ni(H_2O)_6(ClO_4)_2$ was dried under a vacuum oven to constant weight at 110°C for 60 hr, and the formula $Ni(H_2O)_2(ClO_4)_2$ was obtained as reported by Hill and Nyholm.[13] The analysis of $Ni(H_2O)_2(ClO_4)_2$ gave the following results.

Found: Ni, 19.0±0.8, ClO_4, 65.8±1.4%. Calcd for $Ni(H_2O)_2(ClO_4)_2$: Ni, 19.99, ClO_4, 67.74%.

Lithium perchlorate was prepared by neutralizing the aqueous solution of lithium hydroxide, to pH about 5 with perchloric acid, evaporating and recrystallizing three times from water.

Anhydrous lithium perchlorate was obtained by drying in a vacuum oven at 150 to 160°C for 60 hr.

Anhydrous sodium perchlorate was obtained by drying sodium perchlorate monohydrate (B. D. H.) in a vacuum oven at 110 to 115°C for 40 hr.

Tetramethylammonium perchlorate was prepared by neutralizing a 10% tetramethylammonium hydroxide solution (Tokyo Kasei Kogyo Co., Ltd.) to pH 6 with 3 M perchloric acid. After evaporating at

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4) I. V. Nelson and R. T. Iwamoto, *J. Electroanal. Chem.*, **6**, 234 (1963).

5) R. C. Larson and R. T. Iwamoto, *J. Am. Chem. Soc.*, **82**, 3239 (1960).

6) L. Gierst, "Transactions of the Symposium on Electrode Processes," ed. by W. Yeager, Wiley, New York (1961), pp. 106—138.

7) J. Dandoy and L. Gierst, *J. Electroanal. Chem.*, **2**, 116 (1961).

8) K. Tanaka and R. Tamamushi, *Rev. Polarog.*, **14**, 259 (1967).

9) G. A. Forcier and J. W. Olver, *Anal. Chem.*, **37**, 1447 (1965).

10) J. F. O'Donnell, J. T. Ayes and C. K. Mann, *ibid.*, **37**, 1161 (1965).

11) J. A. Riddick, E. E. Toops, Jr., "Organic Solvent," Interscience Publishers, New York (1955), p. 394.

12) A. E. Wickenden and R. A. Plane, *Inorg. Chem.*, **4**, 404 (1965).

13) N. S. Hill and R. S. Nyholm, *J. Chem. Soc.*, **1959**, 3997.

room temperature in a desicator containing calcium chloride under lower pressure, the salt was recrystallized three times from a purified acetonitrile solvent, and dried in a vacuum oven at 60 to 65°C for 40 hr. Tetraethylammonium perchlorate was prepared with the procedure in the literature,[4] recrystallized several times from water and subsequently three times from a purified acetonitrile, and dried in a vacuum oven at 60 to 65°C for 40 hr.

Tetra-*n*-butylammonium perchlorate was prepared by neutralizing a 40% tetra-*n*-butylammonium hydroxide solution (B. D. H) to pH 6 with perchloric acid. The salt was recrystallized several times from ethyl alcohol, and dried in a vacuum oven at 80°C for 40 hr.

Tetramethylammonium acetate ($(CH_3)_4NCH_3COO$) was prepared by a similar procedure with the one given in the literature,[14] and recrystallized three times from a purified acetonitrile and dried in a vacuum oven at 50 to 55°C for 30 hr. The analysis of tetramethylammonium acetate gave the following results.

Found: C, 54.01; H, 11.48; N, 10.49%. Calcd for $(CH_3)_4NCH_3COO$: C, 54.11; H, 11.35; N, 10.52%.

Procedures. Current-potential curves and current-time (*i-t*) curves during the life of a mercury drop at the constant potential were obtained with a Underkofler and Shain type potentiostat[15] based on operational amplifier K2-XA and stabilized amplifiers K2-P and K2-PA of Philibrick Researches Inc. (Boston). Polarograms were recorded with a Yokogawa X-Y Recorder, PRO-11A type. Current-time curves were recorded with a Riken Denshi SP-G2 type recorder.

In the following section, the word "current" denoted by means of the maximum current obseved just before the mercury drop. Measurements were made at 25±0.1°C unless otherwise stated. A beaker type cell was used. The test solution was connected to an aqueous saturated calomel electrode (SCE) through a pair of glass frit junctions arranged to prevent water contamination of the test solution. A platinum foil electrode served as the counter electrode was placed in the glass tube with a glass frit, the glass tube was contained with the test solution.

The dissolved oxygen in the solution was removed by bubbling a pure nitrogen gas through the solution. The two-type dropping mercury electrodes were used. The electrode A had an *m* value of 1.48_2 mg/sec and a drop time, t_d, of 5.02 sec in a deaerated 0.1 M sodium perchlorate acetonitrile solution at −0.70 V *vs.* SCE and at 50 cm mercury height. The electrode B and an *m* value of 1.33_4 mg/sec and a drop time, t_d of 4.98 sec in a deaerated 0.1 M lithium perchlorate acetonitrile solution at −0.8 V *vs.* SCE and at 60 cm mercury height.

The measurements of the visible and ultraviolet absorption spectra were carried out with a Hitachi EPS-3T spectrophotometer at a room temperature.

Results

The current-potential curves of acetatonickel(II) complexes were obtained in the acetonitrile solutions of various natures and concentrations of supporting electrolytes. The typical current-potential curves are given in Fig. 1.

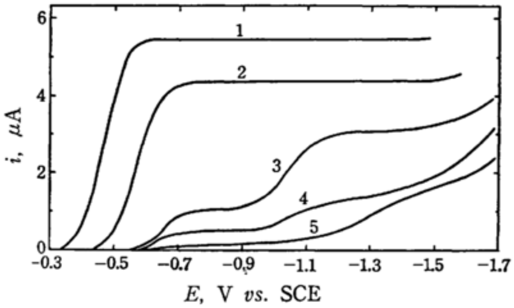

Fig. 1. Current-potential curves of 0.5 mM acetatonickel(II) complexes in various supporting electrolyte solutions containing 0.4% acetic acid and 0.2% acetic anhydride: (1), 0.05 M $LiClO_4$; (2), 0.05 M $NaClO_4$; (3), 0.05 M $(CH_3)_4NClO_4$; (4), 0.05 M $(C_2H_5)_4NClO_4$; (5), 0.05 M $(n\text{-}C_4H_9)_4NClO_4$. (Electrode A)

Figure 1 shows the current-potential curves in the solutions of various univalent electrolytes containing 0.4% acetic acid and 0.2% acetic anhydride in volume. The polarographic data of acetatonickel(II) omplexes in various supporting electrolyte solutions are summarized in Table 1.

TABLE 1. EFFECT OF SUPPORTING ELECTROLYTE ON THE REDUCTION OF ACETATONICKEL(II) CONPLEXES IN 0.05 M PERCHLORATE SOLUTIONS CONTAINING 0.4% ACETIC ACID AND 0.2% ACETIC ANHYDRIDE (Electrode A)

M^+	Concen. of Ni(II) mM	$E_{1/2}$ V *vs.* SCE	Reciprocal slope of log-plot mV	*x* value[a] at $i_l=kt^x$
Li^+	0.5	−0.47	82	0.29
Na^+	0.5	−0.58	80	0.33
$(CH_3)_4N^+$	1.0	−0.63[b]	78	0.54
		−1.05[c]	135	0.62
$(C_2H_5)_4N^+$	1.0	−0.60[b]	68	0.53
		−1.1 [c]	——[d]	0.64
$(n\text{-}C_4H_9)_4N^+$	4.0	−0.56[b]	70	0.63
	2.0	−1.2 [c]	——[d]	0.63

a) The slop of the plot of log *i* *vs* log *t* for the current-time curve during the life of a mercury drop at the potential region giving the limiting current.
b) Ist. reduction step.
c) 2nd. reduction step.
d) Not determined because of maximum.

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[14] W. F. Luder, P. B. Kraus, C. A. Kraus and R. M. Fuoss, *J. Am. Chem. Soc.*, **58**, 255 (1936).

[15] W. L. Underkofler and I. Shain, *Anal. Chem.*, **35**, 1778 (1963).

A single irreversible reduction wave was obtained in the solution of lithium perchlorate or sodium perchlorate. In the tetraalkylammonium perchlorate electrolyte solutions, on the other hand, the wave was found to split into two-steps; the first step was observed at the potential range from −0.5 V to −1.1 V *vs.* SCE, and the second one at more negative potential regions than −1.1 V *vs.* SCE. The limiting current decreased with the increasing radius of cations of supporting electrolytes, and was found not to be purely diffusion controlled from the results of the measurements of current-time curves. In a solution of tetraalkylammonium perchlorate supporting electtrolyte, especially, the limiting current of the second reduction step was found to be kinetic in nature.

Effect of Acetic Acid, Acetic Anhydride and Water. The effects of the concentration of acetic acid, acetic anhydride and water on the current-potential curves were investigated. Table 2 presents the limiting currents, half-wave potentials and slopes of the log-plots which are obtained at 0.5 mM acetatonickel(II) complexes in a 0.1 M lithium perchlorate solution containing the various concentrations of acetic acid.

TABLE 2. EFFECT OF ACETIC ACID ON THE REDUCTION OF 0.5 mM ACETATONICKEL(II) COMPLEXES IN 0.1 M $LiClO_4$ SOLUTIONS (Electrode B)

Concen. CH_3COOH %	i_l μA	$E_{1/2}$ V *vs.* SCE	Reciprocal slope of log-plot mV
0.2	4.83	-0.47_0	82
0.4	4.79	-0.47_3	80
0.8	4.80	-0.47_5	82
2.0	4.74	-0.47_8	87
4.0	4.66	-0.48_2	107
10.9	4.43	-0.49_3	110

No appreciable change was observed in the half-wave potential with the change of the concentration of acetic acid. On the other hand, the decrease of the limiting currents and the increase of the slopes of the log-plots were found with the increasing concentrations of acetic acid.

The polarographic behavior of nickel(II) ions in acetic acid solvent has been investigated by Coulter and Iwamoto,[16] who reported that nickel(II) ions in an acetic acid solvent containing a 1.0 M lithium perchlorate gave a single irreversible reduction wave with the half-wave potential of −0.645 V *vs.* SCE and the slope of the log-plot of 127 mV.

In this experiment, the current-potential curves were drawn out in an acetonitrile solution containing the higher concentration of acetic acid than 10% in volume.

The limiting currents, half-wave potentials and slopes of the log-plots at 0.5 mM acetatonickel(II) complexes in a 0.1 M lithium perchlorate and 0.4% acetic acid solution containing various concentrations of acetic anhydride are represented in Table 3.

TABLE 3. EFFECT OF ACETIC ANHYDRIDE ON THE REDUCTION OF 0.5 mM ACETATONICKEL(II) COMPLEXES IN 0.1 M $LiClO_4$ CONTAINING 0.4% ACETIC ACID (Electrode B)

Concen. of $(CH_3CO)_2O$ %	i_l μA	$E_{1/2}$ V *vs.* SCE	Reciprocal slope of log-plot mV
0	4.85	-0.47_2	82
0.1	4.86	-0.47_0	81
0.2	4.84	-0.47_8	81
0.4	4.80	-0.47_6	81
1.0	4.77	-0.48_1	83
4.0	4.71	-0.48_5	82
10.0	4.61	-0.48_3	83

No appreciable change was observed in the half-wave potentials and slopes of the log-plots, but the limiting currents decreased gradually with the increasing concentration of acetic anhydride.

In the solution of tetraalkylammonium perchlorate electrolytes in the absence of acetic anhydride, on the other hand, a maximum wave appeared at the second reduction step when the measurements were made at a higher concentration of acetatonickel(II) complexes than 1.5 mM, the maximum wave, however, was suppressed by addition of 0.2% acetic anhydride in volume.

In the following sections, acetic anhydride was not added unless otherwise stated, because the measurements were carried out at the concentration of 0.5 mM acetatonickel(II)

TABLE 4. EFFECT OF WATER ON THE REDUCTION OF 0.5 mM ACETATONICKEL(II) IN 0.1 M $LiClO_4$ SOLUTIONS CONTAINING 0.4% ACETIC ACID (Electrode B)

Concen. of water %	i_l μA	$E_{1/2}$ V *vs.* SCE	Reciprocal slop of log-plot mV
0.04	4.78	-0.47_2	79
0.2	4.73	-0.47_8	81
0.4	4.72	-0.48_2	80
0.8	4.70	-0.49_8	83
2.0	4.67	-0.53_5	83
4.0	4.61	-0.60_5	85

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[16] P. D. T. Coulter and R. T. Iwamoto, *J. Electroanal. Chem.*, **13**, 21 (1967).

complexes.

The effect of water content on the reduction wave in a 0.1 M lithium perchlorate solution was also investigated as shown in Table 4.

The half-wave potentials and slopes of the log-plots were not affected up to 0.4% water content. At higher concentrations than 2% water, the half-wave potentials shift to more negative potentials and the limiting currents decrease, with the increasing concentrations of water.

Effect of Concentration of Lithium Perchlorate. Appreciable variations were observed in the current-potential curves for the reduction of acetatonickel(II) complexes by changing the natures and concentrations of supporting electrolytes. The typical current-potential curves for the reduction of 0.5 mM acetatonickel(II) complexes containing 0.4% acetic acid and various concentrations of lithium perchlorate are reproduced in Fig. 2.

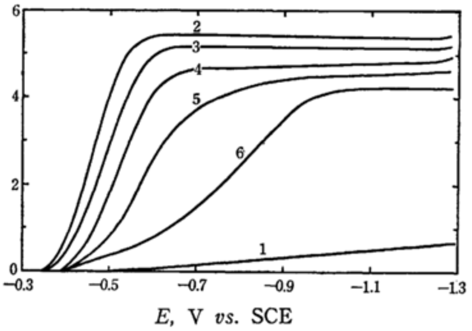

Fig. 2. Effect of concentration of lithium perchlorate on the current-potential curves of 0.5 mM acetatonickel(II) complexes containing 0.4% acetic acid: (1), 0 M; (2), 0.05 M; (3), 0.1 M; (4), 0.2 M; (5), 0.4 M; (6), 1.0 M $LiClO_4$. (Electrode A)

The limiting current decreases and the reduction potentials shifts to more negative potentials, with the increasing concentrations of limthium perchlorate. An ill-defined reduction wave was observed in the absence of supporting electrolyte.

Effect of Mixed Electrolytes. Stepwise addition of lithium perchlorate up to a concentration of about 10 mM to 0.5 mM acetatonickel(II) complexes in tetraalkylammonium perchlorate solution causes an increase in heights of the limiting currents and a shift of the reduction potential to less negative potentials.

A double wave obtained in a tetramethylammonium perchlorate solution changes gradually to a single one by the stepwise addition of lithium perchlorate up to a concentration of about 5 mM as presented in Fig. 3.

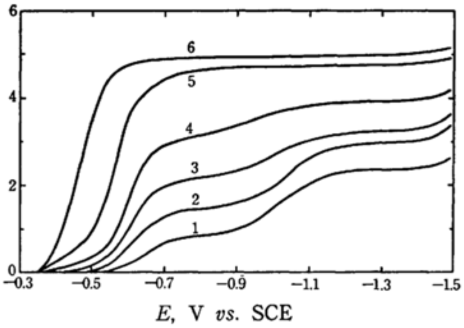

Fig. 3. Current-potential curves of 0.5 mM acetonickel(II) complexes in tetramethylammonium perchlorate solutions containing 0.4% acetic acid and various concentrations of lithium perchlorate at ionic strength 0.05: (1), 0 M; (2), 2×10^{-4} M; (3), 5×10^{-4} M; (4), 1×10^{-3} M; (5), 5×10^{-3} M; (6), 5×10^{-2} M $LiClO_4$. (Electrode B)

TABLE 5. EFFECT OF LITHIUM PERCHLORATE ON THE REDUCTION OF 0.5 mM ACETATONICKEL (II) COMPLEXES IN $(CH_3)_4NClO_4$ SOLUTIONS CONTAINING 0.4% ACETIC ACID AT IONIC STRENGTH 0.05 (Electrode B)

Concen. of $LiClO_4$ mM	1st wave		2nd wave	
	i_l μA	x at $i_l=kt^x$	i_l μA	x at $i_l=kt^x$
0	0.85	0.52	2.35	0.62
0.1	1.20	0.46	2.72	0.56
0.2	1.50	0.43	2.98	0.56
0.5	2.22	0.41	3.20	0.53
1.0	3.20	0.39	3.88	0.46
3.0	4.18	0.38	4.43	0.46
5.0	4.70	0.35	4.75	0.42
50	4.96	0.31	5.02	0.30

At the potentials of −0.82 V and −1.30 V *vs.* SCE corresponding to the potentials to the first and the second reduction step, respectively, in a tetramethylammonium perchlorate solution, the measurements of current-time curves were made at various concentrations of lithium perchlorate. Table 5 shows the limiting currents and slopes of the plots for log *i* *vs.* log *t* which are obtained from the current-time curves of the first drop.[17] The currents increase and the slopes of the plots of log *i* *vs.* log *t* decrease with the increasing concentrations of lithium perchlorate at the constant ionic strength.

At more concentrations than 5 mM lithium perchlorate, no appreciable difference was observed in the currents and slopes of the plots

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[17] J. Kůta and I. Smoler, "Progress in Polarograhy," Vol. 1, ed. by P. Zumann and I. M. Kolthoff, Interscience Publishers, New York (1962), pp. 43—63.

of both the first and second steps.

Similar changes of the current-potential curves and the current-time curves by the stepwise addition of lithium perchlorate were observed in the solutions of tetraethylammonium perchlorate or tetra-*n*-butylammonium perchlorate supporting electrolytes.

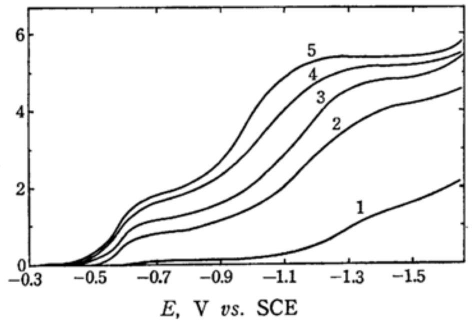

Fig. 4. Current-potential curves of 0.5 mM acetatonickel(II) complexes in tetra-*n*-butylammonium perchlorate solutions containing 0.4% acetic acid and various concentrations of lithium perchlorate at ionic strength 0.05: (1), 0 M; (2), 1×10^{-3} M; (3), 2×10^{-3} M; (4), 5×10^{-3} M; (5), 1×10^{-2} M $LiClO_4$. (Electrode A)

Figure 4 shows the current-potential curves obtained in a tetra-*n*-butylammonium perchlorate solution containing various concentrations of lithium perchlorate.

In this case, the limiting current of the second step increases with the increasing concentrations of lithium perchlorate up to about 10 mM. The limiting current of the second step obtained in a solution containing 40 mM tetra-*n*-butylammonium perchlorate and 10 mM lithium perchlorate becomes nearly equal to the limiting current obtained in a solution of 0.05 M lithium perchlorate alone. On the other hand, no appreciable enhancement of the limiting current of the first step by the stepwise addition of lithium perchlorate is observed as compared with the degree of the increase of that of the second step.

Spectral Studies. The measurement of the visible absorption spectrum of acetatonickel(II) complexes were carried out in the solutions of various kinds of electrolyte. Figure 5 shows the spectra of 50 mM nickel(II) acetate salts in various natures of electrolyte solutions at the constant concentration.

The absorption bands shifted to shorter wavelengths with the decreasing radius of cations of electrolyte. Similar shifts of the absorption bands were also obtained by the increasing concentrations of electrolyte. The typical absorption spectra of acetatonickel(II) complexes in various concentrations of lithium perchlorate are reproduced in Fig. 6.

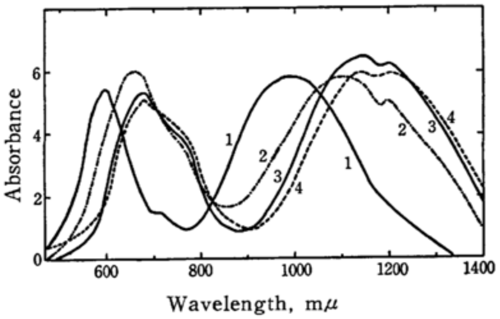

Fig. 5. Visible absorption spectra of 50 mM acetatonickel(II) complexes in various electrolyte solutions containing 1.6% acetic acid: (1), 0.01 M $HClO_4$; (2), 0.25 M $LiClO_4$; (3), 0.25 M $NaClO_4$; (4), 0.25 M $(C_2H_5)_4NClO_4$.

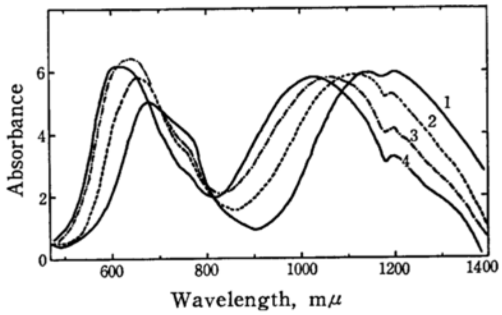

Fig. 6. Visible absorption spectra of 50mM acetatonickel(II) complexes in various concentrations of lithium perchlorate solutions containing 1.6% acetic acid: (1), 0 M; (2), 0.1 M; (3), 0.5 M; (4), 1.0 M $LiClO_4$.

No appreciable change of the absorption bands in the case of tetraalkylammonium perchlorate electrolyte was observed.

Discussion

Spectrophotometric Studies. Nickel(II) acetate salt ($Ni(CH_3COO)_2(H_2O)_4$) does not dissolve in an acetonitrile solvent alone, but dissolves easily in the same solvent in the presence of a small amount of acetic acid or acetate salts such as tetramethylammonium acetate or tetra-*n*-butylammonium acetate which dissolve in an acetonitrile solvent alone.

The visible absorption spectrum of acetatonickel(II) complexes in an acetonitrile containing 1.6% acetic acid shows four bands and, the band positions are nearly equal to those of hexaaquo-nickel(II) ion in an aqueous solvent or the nickel (II) acetate salt dissolved in an aqueous solvent containing 20%

TABLE 6. ABSORPTION MAXIMA OF NICKEL(II) COMPLEXES IN AQUEOUS AND ACETONITRILE SOLVENTS

Compound	Solvent	Band position*				Ref.
$Ni(OAc)\cdot 4H_2O$	CH_3CN, 1.6% Acetic Acid	8.55(0.78)	13.33(0.66)	14.82(0.71)	25.13(1.46)	
$Ni(OAc)_2\cdot 4H_2O$	H_2O, 20% Acetic Acid	8.66(0.45)	13.89(0.41)	15.15(0.38)	25.25(0.79)	
$Ni(H_2O)_6(ClO_4)_2$	H_2O	8.70(0.32)	13.50(0.31)	15.40(0.23)	25.30(0.68)	18
$Ni(OAc)_2\cdot 4H_2O$	CH_3CN, $HClO_4$**	10.21(0.82)	13.92(0.16)	16.93(0.77)	27.23(0.92)	
$Ni(H_2O)_2\cdot 2H_2O$	CH_3CN	10.20(0.82)	13.9 (0.17)	16.95(0.76)	27.20(0.90)	
$Ni(CH_3CN)_6(ClO_4)_2$	CH_3CN	10.40(0.74)	13.90(0.15)	17.20(0.66)	27.20(0.80)	19
$Ni(CH_3CN)_6(BF_4)_2$	CH_3CN	10.53	13.94	17.09	27.56	20

* Band positions in 10^3 cm^{-1}; log ε in parentheses.

** Nickel(II) acetate salt was dissolved in acetonitrile containing 1.6% acetic acid, and then the solution was titrated with anhydrous perchloric acid dissolved in acetic anhydride.

acetic acid, as seen from Table 6.

The absorption spectra of a number of octahedral nickel(II) complexes have been listed in Table 6. The extinction coefficients of acetatonickel(II) complexes in an acetonitrile containing 1.6% acetic acid are larger than those of hexaaquonickel(II) ions in an aqueous solvent or nickel(II) acetate salts dissolved in the same solvent containing 20% acetic acid. In an aqueous solution, the intensity of the absorbance of nickel(II) ions is enhanced by the addition of acetate ions, because of the formation of the species, $Ni(OAc)_2$ or $Ni(OAc)^+$, as have been reported by Watelle-Morion.[21]

These results suggest that appreciable quantities of acetato complexes of nickel(II) are formed in an acetonitrile solvent containing a small amount of acetic acid and, that acetatonickel(II) complexes in the same solution is in an octahedral configuration coordinated with six oxygen atoms.

A potentiometric titration of acetatonickel(II) complexes in an acetonitrile solvent containing a small amount of acetic acid with an anhydrous perchloric acid shows that acetatonickel(II) complexes are quantitatively titrated in the same solvent, at a mole ratio of two of perchloric acid to one of nickel(II) acetate salt.[22] In addition to the potentiometric titrations, the color of the solution changes successively from green to blue with the increasing concentration of perchloric acid, the spectra of the solution at the equivalent point is similar to those of $Ni(H_2O)_2(ClO_4)_2$ salt dissolved in an acetonitrile as shown in Fig. 5 and Table 6.

Consequently, it is found that acetatonickel(II) complexes in an acetonitrile solvent containing a small amount of acetic acid is in an octahedral configuration coordinated with two acetate ions and four neutral acetic acid or water molecules.

Table 6 also indicates that appreciable quantities of $(Ni(CH_3CN)_6)^{2+}$ are present in the solution when acetatonickel(II) complexes were titrated with an anhydrous perchloric acid or, $Ni(H_2O)_2(ClO_4)_2$ salt was dissolved in an acetonitrile.

The fact that nickel(II) ion forms a complex ion with acetonitrile, thus freeing acetate ions for the reaction with the acid titrant, may be explained by the following reaction:

$$\{Ni(OAc)_2(HOAc)_x(H_2O)_{4-x}\} + 2\,HClO_4 + n\,CH_3CN \longrightarrow Ni(CH_3CN)_n^{2+} + 2\,ClO_4^- + (2+x)HOAc + (4-x)H_2O \tag{1}$$

where HOAc refers to acetic acid.

In the case of addition of lithium perchlorate to the acetonitrile solutions containing acetatonickel(II) complexes and a small amount of acetic acid, the spectrophotometric measurements shows that the spectra of acetatonickel(II) complexes shift to lower wavelengths with the stepwise addition of lithium perchlorate as seen from Fig. 6, the spectra, however, is not consisted with those of nickel(II) perchlorate in an acetonitrile solvent, at the mole ratio of twenty times of lithium perchlorate to nickel(II) acetate salt. Similar shifts of spectra of acetatonickel(II) complexes to shorter wavelengths were observed by addition of the other perchlorate salts. The magnitude of the shift to lower wavelengths decreases in the order of $LiClO_4$, $NaClO_4$, $(CH_3)_4NClO_4$, $(C_2H_5)_4NClO_4$ and $(n\text{-}C_4H_9)_4NClO_4$ at the constant concentration of perchlorate salts, and in the case of the addition

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18) W. Manch and W. C. Fernelius, *J. Chem. Educ.*, **38**, 192 (1961).

19) A. E. Wickenden and R. A. Drause, *Inorg. Chem.*, 4, 404 (1965).

20) B. J. Hathaway, D. G. Holan and A. E. Underhill, *J. Chem. Soc.*, **1962**, 2444.

21) G. Watelle-Morion, *Compt. rend.*, **246**, 3610 (1958).

22) S. Ikeda andE. Itabashi, unpublished results.

of tetraalkylammonium perchlorate the shift is very small.

A reasonable explanation of these results is possible by considering the substitution of acetate ions by acetonitrile in acetatonickel(II) complexes which may be written by the following equation.

$$\{\mathrm{Ni(OAc)_2(HOAc)}_x\mathrm{(H_2O)}_{4-x}\} + 2\,\mathrm{MClO_4} + n\,\mathrm{CH_3CN} \rightleftharpoons \mathrm{Ni(CH_3CN)}_n^{2+} + 2\,\mathrm{ClO_4}^- + 2\,\mathrm{MOAc} + x\,\mathrm{HOAc} + (4-x)\mathrm{H_2O} \qquad (2)$$

where M refers to the cation of electrolyte.

The above reaction is considered to proceed quantitatively on employing perchloric acid as an electrolyte, and to be in equibrium in the case of the other electrolytes such as alkali metal perchlorates or tetraalkylammonium perchlorates.

Polarographic Studies. On the polarographic studies, the limiting currents of acetatonickel(II) complexes in various supporting electrolytes at the constant concentration, decrease with the radius of cation of the supporting electrolyte present in the solution.

A single irreversible reduction wave is observed in the solutions of lithium perchlorate or sodium perchlorate, the limiting current shows an intermediate nature of both diffusion- and kinetic-controlled polarographic currents, which were found from the results of the measurement of current-time curves.

The two-reduction steps, on the other hand, are observed in the solution of tetraalkylammonium perchlorate, the limiting current of the second step is kinetic in nature, as seen from Table 1.

The character of the limiting current is also seen from the temperature coefficients of the limiting current. It has been stated that if the temperature coefficient is greater than +2% per degree, the current is probably not a diffusion-controlled.[23] The measurement of the limiting current for the reduction of nickel(II) perchlorate in an acetonitrile solvent containing 0.1 M lithium perchlorate as a supporting electrolyte were made at the temperature over range 0.3 to 35°C, indicating that the temperature coefficient was 1.9% per degree. The result of the measurement of the current-time curve also suggest that the limiting current for the reduction of nickel(II) perchlorate in an acetonitrile containing 0.1 M lithium perchlorate is diffusion-controlled.

In the case of the reduction of acetatonickel(II) complexes in the same solvent containing 0.4% acetic acid, the temperature coefficients in a 0.1 M lithium perchlorate solution are 2.3% per degree at lower temperatures and, 3.5% per degree at higher temperatures than 20°C. The temperature coefficients in a 0.05 M tetramethylammonium perchlorate solution, on the other hand, are 4.4% and 6.1% per degree for the first and the second step, respectively, at the temperature range over 0.3 to 35°C.

Consequently, the limiting currents for the reduction process of acetatonickel(II) complexes in an acetonitrile solvent containing 0.4% acetic acid and various supporting electrolyte are undoubtedly not entirely diffusion-controlled.

The authors assume that the chemical reaction expressed in Eq. (2) is a rate determining step and, $\{\mathrm{Ni(OAc)_2(HOAc)}_x\mathrm{(H_2O)}_{4-x}\}$ in Eq. (2) is an electro inactive and $\mathrm{Ni(CH_3CN)}_n^{2+}$, produced by freeing of acetato ions from nickel(II) acetate, is electroactive polarographically.

This assumption may be suggested from the results of the spectrophotometric studies, the dependence of the limiting current on the nature of cation of the supporting electrolytes present in the solution and the enhancenment of the limiting current in a tetraalkylammonium perchlorate supporting electrolyte solution with the stepwise addition of lithium perchlorate.

The polarographic inactivity of $\{\mathrm{Ni(OAc)_2}$-$\mathrm{(HOAc)}_x\mathrm{(H_2O)}_{4-x}\}$ is ascertained from the following experiments. Nickel(II) acetate salt dissolved containing 0.4% acetic acid gives an ill-defined and little reduction wave in the absence of a supporting electrolyte as seen from Fig. 2. If acetatonickel(II) complexes are electroactive, a well-defined and apparent reduction wave with a migration current would be observed.

Nickel(II) acetate salt dissolved in an acetonitrile solvent in the presence of 1 mM tetramethylammonium acetate and 0.05 M tetramethylammonium perchlorate, on the other hand, undergoes two reduction steps with the half-wave potentials of −1.7 V and −2.25 V *vs.* SCE, respectively, as shown in Fig. 7.

In an acetonitrile solution containing acetic acid, the reduction wave of acetatonickel(II) complexes at more negative potentials than −1.8 V *vs.* SCE is not observed by discharge of hydrogen ion. For that reason, the measurements of current-potential curves of acetatonickel(II) complexes were carried out in the absence of acetic acid.

With a 1 mM tetramethylammonium acetate

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[23] L. Meites, "Polarographic Techniques," Interscience, New York (1955), pp. 78—82.

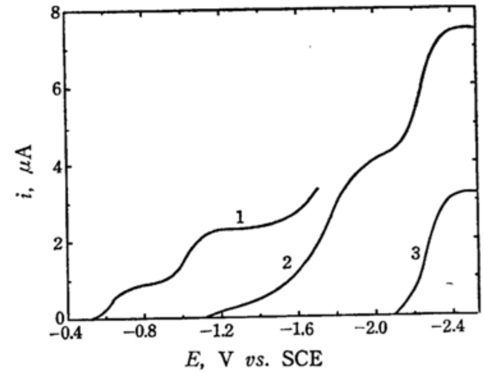

Fig. 7. Current-potential curves of 0.5 mM acetatonickel(II) complexes (curves 1 and 2), and 1 mM tetramethylammonium acetate (curve 3) in 0.05 M $(CH_3)_4NClO_4$ solutions.
(1) 0.5 mM $Ni(OAc)_2$, 0.4% acetic acid
(2) 0.5 mM $Ni(OAc)_2$, 1 mM $(CH_3)_4NOAc$
(3) 1 mM $(CH_3)_4NOAc$. (Electrode B)

and 0.05 M tetramethylammonium perchlorate solution in the absence of nickel(II) acetate salt, a single reduction step with the half-wave potential of −2.23 V *vs.* SCE is observed.

The second reduction step in the presence of nickel(II) acetate salts suggests that it involves the reduction of acetate ions.

The ill-defined first reduction step may be due to the reduction of nickel(II) ions, although it is uncertain whether nickel(II) ions are acetatonickel(II) complexes or nickel(II)-acetonitrile complexes, which are produced by freeing of acetate ions from acetatonickel(II) complexes. The limiting current of the first reduction step is not a pure diffusion-controlled, but shows an intermediate nature of both diffusion and kinetic controlled currents. Under these conditions, consequently, the reduction wave obtained in an acetonitrile solution dissolved nickel(II) acetate salts with a small amount of acetic acid is not thought to involve the polarographic reduction of nickel(II) ions coordinated with acetate ions could not proceed up to the potentials of −1.7 V *vs.* SCE.

The increase of the limiting current with the decreasing radius of the cation of supporting electrolyte present in the solutions, indicates the increase of the equilibrium concentrations of $Ni(CH_3CN)_n^{2+}$.

The addition of lithium perchlorate in the solutions of tetraalkylammonium perchlorate electrolytes causes an enhancement of the limiting current and also a decrease of the slopes of the plots of $\log i$ *vs.* $\log t$ during a life of mercury drop at the constant potential, as presented in Table 5 in the case of the results in tetramethylammonium perchlorate solutions, indicating that the equilibrium concentrations of $Ni(CH_3CH)_n^{2+}$ increase gradually with increasing concentrations of lithium perchlorate, and the rate-determining step change gradually from the chemical reaction (2) to the diffusion process of $Ni(CH_3CN)_n^{2+}$.

A similar enhancement of the limiting current in tetraalkylammonium perchlorate electrolyte solutions is also observed by addition of a small amount of sodium perchlorate instead of lithium perchlorate, lithium perchlorate being more efficient than sodium perchlorate for the enhancement of limiting current at the constant ionic strength.

The two reduction steps in a solution of tetramethylammonium perchlorate electrolyte changes to a single one at a less mole ratio of lithium perchlorate to nickel(II) acetate salts than ten.

On the other hand, a double wave in the solutions of tetraethylammonium perchlorate or tetra-*n*-butylammonium perchlorate electrolyte is also observed under the conditions that the enhanced limiting current of the second step becomes nearly equal to the limiting current obtained in the solution of lithium perchlorate electrolyte alone, as shown in Fig. 3.

These data indicate that the charge transfer reaction of nickel(II) ion is inhibited by the weakly absorption of tetraalkylammonim ions at the dropping mercury electrode.

The conclusion is also supported by the results presented in Fig. 8.

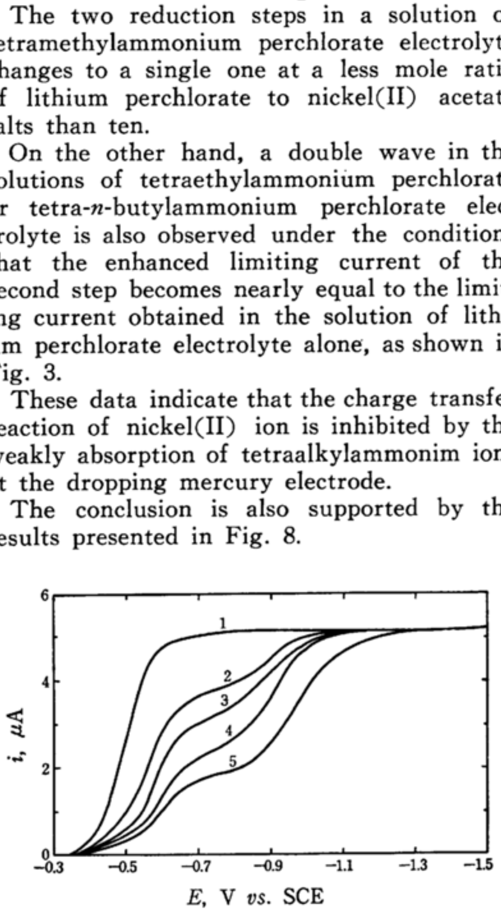

Fig. 8. Effect of tetra-*n*-butylammonium perchlorate on the current-potential curves of 0.5 mM acetatonickel(II) complexes in lithium perchlorate solutions containing 0.4% acetic acid at ionic strength 0.1: (1), 0 M; (2), 5×10^{-3} M; (3), 1×10^{-2} M; (4), 2.5×10^{-2} M; (5), 5×10^{-2} M $(n\text{-}C_4H_9)_4NClO_4$. (Electrode A)

A single wave obtained in the solution of lithium perchlorate supporting electrolyte is found to split into the twosteps by the addition of tetra-*n*-butylammonium perchlorate. The limiting current at the potential over range −0.6 V to −1.0 V *vs.* SCE is not only suppressed but also becomes gradually independent on the heights of a mercury reservoir, with the increasing concentrations of tetra-*n*-butylammonium perchlorate, and reduction potentials shift to more negative potentials.

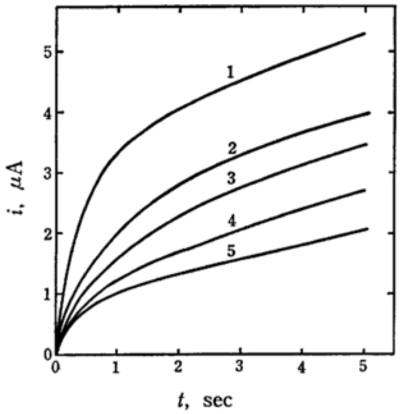

Fig. 9. Current-time curves of 0.5 mM acetatonickel(II) complexes measured at −0.75 V. *vs.* SCE in lithium perchlorate solutions containing 0.4% acetic acid and various concentrations of $(n\text{-}C_4H_9)_4NClO_4$ at ionic strength 0.1: (1), 0 M; (2), 5×10^{-3} M; (3), 1×10^{-2} M; (4), 2.5×10^{-2} M; (5), 5×10^{-2} M $(n\text{-}C_4H_9)_4NClO_4$ present. (Electrode A)

This unusual situation is also evident from the results of the measurements of the current-time curves given in Fig. 9. The stepwise addition of tetra-*n*-butylammonium perchlorate at the ionic strength 0.1 causes to decrease the maximum current observed just before the mercury drop and also to depress the current from the initial stage of the formation of a mercury brop. The current at the first step observed at −0.75 V *vs.* SCE, in the presence of a 50 mM tetra-*n*-butylammonium perchlorate shows the property of the kinetic current. At more negative potentials than −0.8 V *vs.* SCE, the reduction current rises again and reaches to a full height, and becomes almost independent on the presence of tetra-*n*-butylammonium perchlorate.

The profiles of the current-time curves changes successively from the curve 5 to 1 in Fig. 9 in the presence of 50 mM tetra-*n*-butylammonium perchlorate by means of the shift of the potential from −0.75 V to −1.3 V *vs.* SCE. A single wave obtained in the sulotion of lithium perchlorate supporting electrolyte also splits into a double one by the stepwise addition of the other tetraalkylammonium perchlorate instead of tetra-*n*-butylammonium perchlorate. But the suppressing action is found to decrease in the order of $(n\text{-}C_4H_9)_4N^+$, $(C_2H_5)_4N^+$ and $(CH_3)_4N^+$ at the definite concentration.

These phenomena may be explained by taking into consideration the weak absorption of tetraalkylammonium cations on the DME. It is well known theoretically[24] and experimentally[25] that the weakly surface-active substances with considerably higher concentrations make the limiting current decrease and also change successively the drop life dependence of the instantaneous current from a $t^{1/6}$ to a $t^{2/3}$.

Tetraalkylammonium ions in an aqueous solvent has been found to act as a relatively strong surface-active substances on DME.[26] In an acetonitrile solvent, however, they would act as a weakly surface-active substance.

In conclusion, with nickel(II) acetate salts dissolved in an acetonitrile solvent containing a small amount of acetic acid the nickel(II) ion is in an octahedral configuration coordinated with two acetate ions and four neutral acetic acid or water molecules.

The reaction mechanism of the polarographic reduction of acetatonickel(II) complexes can probably be represented by the following sequence:

$$\begin{aligned}&\{Ni(OAc)_2(HOAc)_x(H_2O)_{4-x}\}\\&\quad+2\,MClO_4+n\,CH_3CN\\&\overset{K_{eq}}{\rightleftharpoons} Ni(CH_3CN)_n^{2+}+2\,ClO_4^-+2\,MOAc\\&\quad+x\,HOAc+(4-x)H_2O \qquad (2')\end{aligned}$$

$$\begin{aligned}&Ni(CH_3CN)_n^{2+}+2\,e\longrightarrow\\&\quad Ni(Hg)+n\,CH_3CN \qquad (3)\end{aligned}$$

where HOAc refers to acetic acid, $MClO_4$ represents a supporting electrolyte, K_{eq} the effective equilibrium constant in the bulk solution, substance $\{Ni(OAc)_2(HOAc)_x(H_2O)_{4-x}\}$ is not reduced at the potential at which $Ni(CH_3CN)_n^{2+}$ is reduced under the experimental conditions.

The limiting current obtained in lithium perchlorate or sodium perchlorate supporting electrolyte solutions exhibits an intermediate nature of both diffusion and kinetic controlled currents. In tetraalkylammonium perchlorate supporting electrolyte solutions, the chemical reaction (2′) is a rate-determining step. The first step of a double-wave in a tetraalkyl-

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24) H. Matsuda, *Rev. Polarogr.*, **14**, 87 (1967).

25) R. W. Schmid and C. N. Reilley, *J. Am. Chem. Soc.*, **80**, 2087 (1958).

26) P. Delahay, "Double Layer and Electrode Kinetics," Interscience Publishers, New York (1965), p. 228.

ammonium perchlorate solution is due to the inhibition of charge transfer of nickel(II) ion by the weak adsorption of tetraalkylammonium ions on the DME.

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