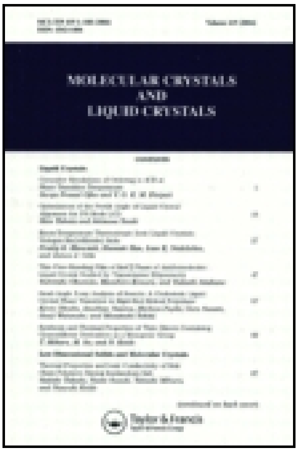

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

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Version of record first published: 04 Oct 2006.

To cite this article: Hai Sun , Gilda Neshvad & Morton Z. Hoffman (1991): Energy Gap Dependence of the Efficiency of Charge Separation upon the Sacrificial Reductive Quenching of the Excited States of Ru(II)-Diimine Photosensitizers in Aqueous Solution, Molecular Crystals and Liquid Crystals, 194:1, 141-150

To link to this article: http://dx.doi.org/10.1080/00268949108041159

Mol. Cryst. Liq. Cryst., 1991, vol. 194, pp. 141–150
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Printed in the United States of America

ENERGY GAP DEPENDENCE OF THE EFFICIENCY OF CHARGE SEPARATION UPON THE SACRIFICIAL REDUCTIVE QUENCHING OF THE EXCITED STATES OF Ru(II)-DIIMINE PHOTOSENSITIZERS IN AQUEOUS SOLUTION

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Abstract The yield of oxidized and reduced products released into the bulk solution upon electron-transfer quenching is the critical parameter governing the efficacy of a redox photosensitizer. The cage escape efficiency (η_{ce}) is a measure of the competition between back electron transfer (k_{bt}) and diffusional separation (k_{ce}) of the geminate redox pair formed within the solvent cage in the quenching act. Values of η_{ce} have been obtained for the sacrificial reductive quenching of the excited states of homo-and heteroleptic Ru(II)-diimine complexes of bpy (2,2-bipyridine), bpz (2,2'-bipyrazine), and bpm (2,2'-bipyrimidine) by TEOA and EDTA. The values of η_{ce} vary with the ground-state reduction potentials of the complexes, describing a strong U-shaped dependence for EDTA, but a much weaker dependence for TEOA. Plots of $\log(k_{bt}/k_{ce})$ vs ΔG_{bt}^{o} exhibit well-defined bell-shaped curves, indicating that k_{bt} traverses the "normal" and "inverted Marcus" regions if k_{ce} has a constant value for all the one-electron reduced photosensitizers.

Keywords: reductive quenching, Ru(II)-diimine complexes, charge separation, EDTA, triethanolamine, Marcus theory

INTRODUCTION

The efficiency by which the redox products from the electron-transfer quenching of the excited state of a photosensitizer are released into bulk solution is the most critical quantity limiting the overall yield of charge separated species from a photochemical system. The interpretation of the efficiency of cage escape (η_{ce}) is based on the mechanistic model (reactions 1-3) in which the diffusional encounter of the excited state by an electron-transfer quencher results in the formation of a geminate redox pair within the solvent cage; escape of the redox species out of the cage competes kinetically with back electron transfer within the cage to reform the original ground-state materials.[1]

$$M^{*} + Q \rightarrow [M^{+/-}...Q^{-/+}] \qquad k_{en} \qquad (1)$$

$$[M^{+/-}...Q^{-/+}] \rightarrow M + Q \qquad k_{bt} \qquad (2)$$

$$[M^{+/-}...Q^{-/+}] \rightarrow M^{+/-} + Q^{-/+} \qquad k_{ce} \qquad (3)$$

The value of η_{ce} is a measure of the competition between back electron transfer (k_{bt}) and diffusional escape (k_{ce}) of the geminate pair (equation A).

$$\eta_{ce} = k_{ce}/(k_{ce} + k_{bt}) \tag{A}$$

From the Eigen equation that describes the diffusion of charged species in solution,[2] k_{ce} is expected to be more-or-less dependent on the charges on the species, ionic strength, solvent dielectric constant, solvent viscosity, temperature, and the extent of ion-pairing among the various species within the cage. Back electron transfer reaction is between very reactive species separated by rather short distances; the theories of intramolecular electron transfer[3] place k_{bt} within the "normal" and "inverted Marcus" region, where an increase in exoergicity results in an increase and a decrease in the rate, respectively. The value of k_{bt} is predicted to be dependent on ΔG_{bt}^{o}, the distance between the species, the solvent reorganization energy, and the degree of adiabaticity of the transfer.[4]

If, in a series of photosensitizer-quencher pairs, k_{ce} and the parameters that affect k_{bt}, except ΔG_{bt}^{o}, can be maintained constant (or nearly so), the variation of η_{ce} would be dependent only on the variation of the exoergicity of the back electron-transfer reaction. Indeed, Ohno and coworkers[5-8] have shown in a number of papers that the reductive quenching of the excited states of Ru(II)-diimine complexes (RuL^{2+}) by aromatic amines and methoxybenzenes yields a bell-shaped dependence of k_{bt} on ΔG_{bt}^{o} with a maximum at ~-1.7 eV.

In these previous studies, the overall processes have been reversible, *i.e.*, the redox species in bulk solution undergo electron transfer, thereby being annihilated; under such conditions, there is no net charge separation. If, on the other hand, the oxidized form of the reductive quencher converts rapidly, irreversibly, and sacrificially into a species that itself cannot be reduced, self-annihilation of the charge carriers cannot occur, resulting in the net separation of charge. For EDTA (pK_a 0.0, 1.5, 2.0, 2.7, 6.1, 10.2)[9] and triethanolamine (TEOA; pK_a 7.8)[10] as reductive quenchers (D), their one-electron oxidized forms ($D_{ox}^{\cdot}$) convert into reducing radicals ($D_{red}^{\cdot}$) that are capable of transforming methylviologen (MV^{2+}) into $MV^{+\cdot}$.[11,12] For Ru(II) complexes containing bpy (2,2'-bipyridine), bpz (2,2'-bipyrazine), and bpm (2,2'-bipyrimidine) as ligands, the reductive quenching of their excited states ($^{*}RuL^{2+}$) results in Ru(II) species that contain a coordinated ligand radical ($RuL^{+\cdot}$) capable of reducing MV^{2+}.[13-15]

Thus, the reductive quenching of $^{*}RuL^{2+}$ by D in the presence of MV^{2+}

will result in the generation of $MV^{+\cdot}$ in bulk solution, the quantum yield (Φ) of which can be measured. From a value of Φ and a knowledge of the overall mechanism (reactions 4-10), the value of η_{ce} can be obtained from equation B.

$$RuL^{2+} + h\upsilon \rightarrow {}^{*}RuL^{2+} \qquad \eta_{*} \qquad (4)$$

$$^{*}RuL^{2+} \rightarrow RuL^{2+} + h\upsilon' \qquad k_{o} \qquad (5)$$

$$^{*}RuL^{2+} + D \rightarrow RuL^{+\cdot} + D_{ox}^{\cdot} \qquad k_{q}, \eta_{ce} \qquad (6)$$

$$RuL^{+\cdot} + D_{ox}^{\cdot} \rightarrow RuL^{2+} + D \qquad k_{et} \qquad (7)$$

$$D_{ox}^{\cdot} \rightarrow D_{red}^{\cdot} \qquad k_{tr} \qquad (8)$$

$$RuL^{+\cdot} + MV^{2+} \rightarrow MV^{+\cdot} + RuL^{2+} \qquad k_{red} \qquad (9)$$

$$D_{red}^{\cdot} + MV^{2+} \rightarrow MV^{+\cdot} + \text{products} \qquad k_{red}' \qquad (10)$$

$$\Phi = 2\eta_{*}\eta_{q}\eta_{ce}\eta_{tr} \qquad (B)$$

Here, η_{*} is the efficiency of generation of $^{*}RuL^{2+}$ in reaction 3, which is taken as unity.[16] η_{q} is the efficiency of quenching; $\eta_{q} = k_{q}[D]/(k_{q}[D] + k_{o})$. η_{tr} is the efficiency of transformation reaction 8 in competition with annihilation reaction 7. For EDTA in alkaline solution, reaction 8 appears to occur unimolecularly by proton elimination from the carbon atom *alpha* to the amine and carboxylate groups;[11] for TEOA, transformation occurs via reaction 8a, for which the rate constant is reported to be 3.3 x 10^{6} $M^{-1}s^{-1}$.[17] The values of k_{red} and k_{red}' are of the order of 10^{8}-10^{9} $M^{-1}s^{-1}$,[11-15] making reactions 9 and 10 rapid and quantitative in the presence of mM concentrations of MV^{2+}. Thus, for EDTA, and TEOA at sufficiently high concentrations, $\eta_{tr} \sim 1$. Under those conditions, and in alkaline solution where $RuL^{+\cdot}$ remains deprotonated, $\Phi = 2\eta_{q}\eta_{ce}$; as $\eta_{q} \rightarrow 1$, $\Phi \rightarrow 2\eta_{ce}$. This treatment predicts that a plot of $1/\Phi$ *vs* $1/[D]$ be linear with an intercept $= 1/2\eta_{ce}$ and a slope $= k_{o}/2\eta_{ce}k_{q}$.

$$TEOA_{ox}^{+\cdot} + TEOA \rightarrow TEOA_{red}^{\cdot} + TEOA + H^{+} \qquad (8a)$$

In this study, Φ was determined in the continuous photolysis of solutions containing RuL^{2+}, MV^{2+}, and EDTA or TEOA in alkaline solution. The complexes chosen were homo- and heteroleptic complexes of bpy, bpz, and bpm, the excited states of which can be reductively quenched by EDTA and TEOA. The six complexes used, $Ru(bpz)_{3}^{2+}$ [zzz], $Ru(bpz)_{2}(bpm)^{2+}$ [zzm], $Ru(bpm)_{2}(bpz)^{2+}$ [mmz], $Ru(bpz)_{2}(bpy)^{2+}$ [zzy], $Ru(bpy)(bpz)(bpm)^{2+}$ [yzm], and

$Ru(bpm)_3^{2+}$ [mmm], have reduction potentials ranging from -0.50 to -0.73 V,[13,14,18] offering the opportunity to probe the dependence of η_{ce} as a function of ΔG_{bt}^{o} across a narrow range for sacrificial reductive quenching, and to compare the results with those obtained previously by other workers for quenching by nonsacrificial electron donors.

EXPERIMENTAL

Methylviologen dichloride (Aldrich) was recrystallized three times from ethanol and dried by suction and vacuum. TEOA (Fluka) was fractionally distilled three times. EDTA (as its disodium dihydrogen salt), and all other materials were Baker or Aldrich reagent grade and were used without further purification. The Ru(II) complexes, as their PF_6^- salts, were prepared by the methods of Rillema et al.[19,20] Distilled water was further purified by passage through a Millipore purification train. The solutions were buffered with 4 mM $NaHCO_3$ or borate, and adjusted to pH 8.5 for EDTA and pH 10.0 for TEOA with HCl or NaOH. The ionic strength was adjusted to 1.0 M with Na_2SO_4.

Luminescence quenching experiments were made by using a Perkin-Elmer MPF-2A spectrofluorimeter. Excited-state lifetime measurements were made with a Nd:YAG pulsed laser system with excitation at 355 nm; details of the apparatus have been described before.[21] Continuous photolysis were performed by using a Bausch & Lomb high-intensity monochromator in conjunction with a 100-W quartz halogen lamp and photon counter. All experiments were conducted at the ambient temperature (~22°C).

RESULTS

Values of k_q were calculated from linear Stern-Volmer plots (I_0/I *vs* [D]) for the luminescence from $^*RuL^{2+}$ and a knowledge of τ_0 (= $1/k_0$). Values of Φ for the RuL^{2+}(50 μM)/MV^{2+}(7 mM)/EDTA system at pH 8.5 and the RuL^{2+} (50 μM)/MV^{2+}(7 mM)/TEOA system at pH 10.0 were obtained from plots of the absorbance of the solution at 605 nm, the absorption maximum of $MV^{+\cdot}$ (ε_{605} = $1.37 \times 10^4\ M^{-1}cm^{-1}$),[22] as a function of irradiation time; in all cases the plots were linear for the formation of ≤20 μM $MV^{+\cdot}$.

An example of the plot of Φ as a function of [EDTA] is shown in Figure 1; the corresponding double reciprocal plot is shown in Figure 2. From the intercept and/or the slope of those plots, values of η_{ce} were evaluated.

Table I shows values of E°(2+/+), k_q, τ_o, and η_{ce} for the systems studied. Also given are values of η_{ce} obtained from pulsed laser flash photolysis experiments that have been already reported.[14,23] The coincidence in those values gives confidence to the efficacy of the evaluation presented here.

Table I. Data for the systems examined in aqueous solution.

RuL^{2+}	t_o μs	k_q (TEOA)[a] $M^{-1}s^{-1}$	k_q (EDTA)[b] $M^{-1}s^{-1}$	E°(2+/+)[c] V	η_{ce} (TEOA)	η_{ce} (EDTA)
zzz	0.95	2.5×10^8	4.5×10^8	-0.50	0.49 0.47 [d]	0.70 0.70 [d]
zzm	0.71	1.0×10^8	1.7×10^8	-0.55	0.52	0.62
mmz	0.58	3.8×10^7	5.4×10^7	-0.61	0.51	0.51
zzy	0.44	4.0×10^7	5.1×10^7	-0.63	0.49	0.55
yzm	0.27	6.3×10^6	6.8×10^6	-0.67	0.58	0.64
mmm	0.081	2.1×10^7	2.7×10^7	-0.73	0.66 0.6 ± 0.2 [d]	0.73

[a] pH 10.0; $\mu = 1.0$ M (Na_2SO_4) [b] pH 8.5; $\mu = 1.0$ M (Na_2SO_4) [c] ref. 18 [d] by laser flash photolysis

DISCUSSION

The data in Table I show that as $^*RuL^{2+}$ becomes more difficult to reduce, as indicated by the increasingly more negative value of the reduction potential of the ground state, E°(*2+/+) being ~2 eV more positive than E°(2+/+), k_q decreases, as expected for "normal Marcus" behavior. The values of η_{ce} for EDTA as the reductive quencher clearly describe a U-shaped dependence on E°(2+/+), while those for TEOA show a plateau for the more easily reduced complexes and increasing values of η_{ce} as the strength of the $RuL^{+\cdot}$ reductant increases. Irrespective of these differences, it is clear that both sacrificial systems exhibit "inverted Marcus" behavior, with the yields of redox products released into bulk solution increasing as the driving force of back electron transfer increases.

Equation A can be rewritten (equation C) so that the experimental values of η_{ce} can be transformed into k_{bt}/k_{ce} ratios.

$$k_{bt}/k_{ce} = \eta_{ce}^{-1} - 1 \tag{C}$$

Because of the logarithmic dependence of rate constants and free energy terms, it is customary to plot log k_{bt}/k_{ce} *vs* ΔG_{bt}^{o}; if k_{ce} is constant, the plot will reflect the dependence of k_{bt} on the driving force of the back electron transfer reaction. Unfortunately, for the systems examined here, the redox potentials for the sacrificial donors are not known. Because of the rapid transformation reactions that the $D_{ox}^{\cdot}$ radicals undergo, reversible CV waves cannot be obtained, making the observed irreversible changes unsuitable for evaluation. It should be noted that Tazuke reported a value of 0.90 V (*vs* SCE) for $E_{1/2}(TEOA_{ox}^{+\cdot}/TEOA)$ in CH_3CN;[24] our attempts to reproduce that value have been frustrated by the irreversibility of the system. Thus, rather than having ΔG_{bt}^{o} as the abscissa of the plot, we are forced to use $E^{o}(2+/+)$ in Figure 3. As a result, an absolute comparison of the driving forces of the systems, and a quantitative application to theory cannot be made.

Nevertheless, a relative comparison of the behavior of the sacrificial systems reported here and the nonsacrificial systems involving analogous Ru(II) complexes reported by others is instructive. In the first place, quenching by EDTA and TEOA results in different apparent dependences of k_{bt} on the thermodynamics of back electron transfer. Secondly, the bell-shaped curve for EDTA occurs over a rather narrow energy range of less than 300 mV. According to the classical electron-transfer theory of Marcus,[25,26] the maximum value of k_{et} occurs when $-\Delta G_{bt}^{o} = \lambda$, the reorganization parameter that is the sum of the intramolecular and solvent dipole orientational barriers to electron transfer; normal and inverted behavior occur when $-\Delta G_{bt}^{o} < \lambda$ and $> \lambda$, respectively.

TEOA is an analogue of the neutral amines used in the previous studies,[5-8] and might be expected to describe a bell-shaped curve with approximately the same curvature for a similar back electron-transfer reaction. The dependence for TEOA shown in Figure 3 may be a portion of such a curve, truncated because of the limitations of $E^{o}(2+/+)$ from the complexes used; no other complex in this bpy/bpz/bpm homologous series has a smaller negative value than does $Ru(bpz)_3^{2+}$, and those with more negative values than Ru-

$(bpm)_3^{2+}$ cannot have their excited states quenched by TEOA (or EDTA).

In the case of EDTA, the bell-shaped curve observed is qualitatively in agreement with theory,[25-28] but the marked narrowness of the curve requires that a further explanation be sought for that system. It should be noted that this quantitative study may be the first in which such a highly charged reductive quencher has been used in a purely aqueous medium. In addition, the experiments here were performed at a high ionic strength (1 M), so that the interactions among the geminate species, ions, and solvent molecules would be expected to contribute significantly to the structure and overall potential energy of the solvent cage.

Furthermore, there is no doubt that the ground and excited states of the photosensitizers are ion-paired in the presence of the relatively high concentrations of $EDTA^{3-}$ needed to effect quenching. In an earlier work,[31] we suggested, in order to explain the dependence of η_{ce} on $[Ru(bpy)_3^{2+}]$ in the quenching of the excited state by MV^{2+} in the presence of EDTA, that photosensitizer cations can establish a labile equilibrium to form aggregates mediated by the EDTA. One can visualize, in the present case, the existence of RuL^{2+} $...EDTA^{3-}...RuL^{2+}$ species in solution that can be photonically excited, causing that structure to be carried into the solvent cage. Because of the possible presence of EDTA in the structure of the solvent cage as well, the back electron-transfer reaction cannot be characterized in a simple way. It is clear that more detailed examinations of the dependences of η_{ce} on solution medium parameters in polar solvents must be undertaken.

Regarding the values of η_{ce} exhibited by EDTA, we noted earlier[23] that they were paradoxically large, considering the opposite charges on the $RuL^{+\cdot}$ and $EDTA^{2-\cdot}$ species that must diffuse apart in the cage escape process; unless k_{bt} were anomolously small, one would expect η_{ce} to be much smaller. We had proposed, in connection with the photoexcitation of MV^{2+}/EDTA ion-pairs, that EDTA undergoes its unimolecular transformation within the solvent cage;[12] if this process occurs in the present case, $\eta_{ce} = k_{tr}/(k_{tr} + k_{bt})$, and the plot in Figure 3 should represent, for EDTA, the dependence of $\log k_{bt}/k_{tr}$ on ΔG_{bt}^{o}. Inasmuch as k_{tr} would have a constant value for the series of photosensitizers, the preceeding arguments concerning the origins of the narrowness of the curve for k_{bt} would still be valid. Nevertheless, it remains an intriguing possibility that, for EDTA as the reductive quencher, the transformation reaction is the step that occurs in kinetic competition with back electron transfer within the solvent cage.

Acknowledgment. This research was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

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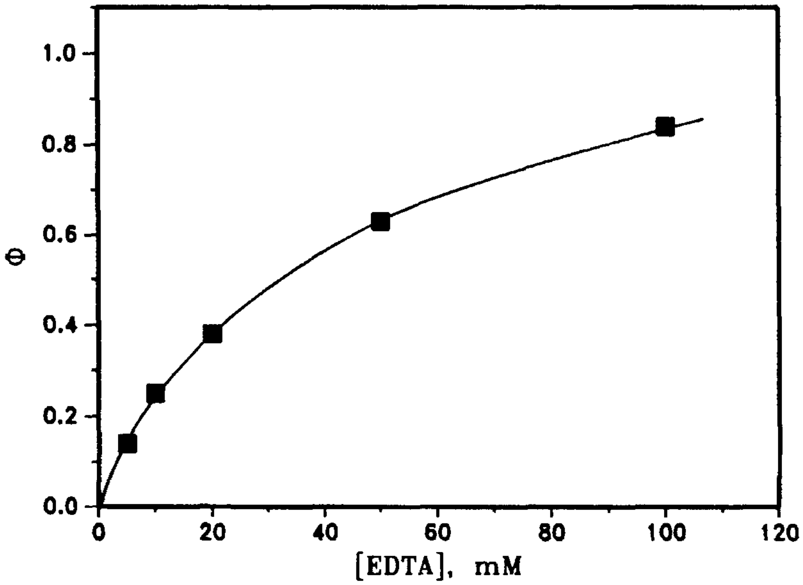

FIGURE 1 Dependence of Φ on [EDTA] for the quenching of $^{*}Ru(bpm)_2(bpz)^{2+}$.

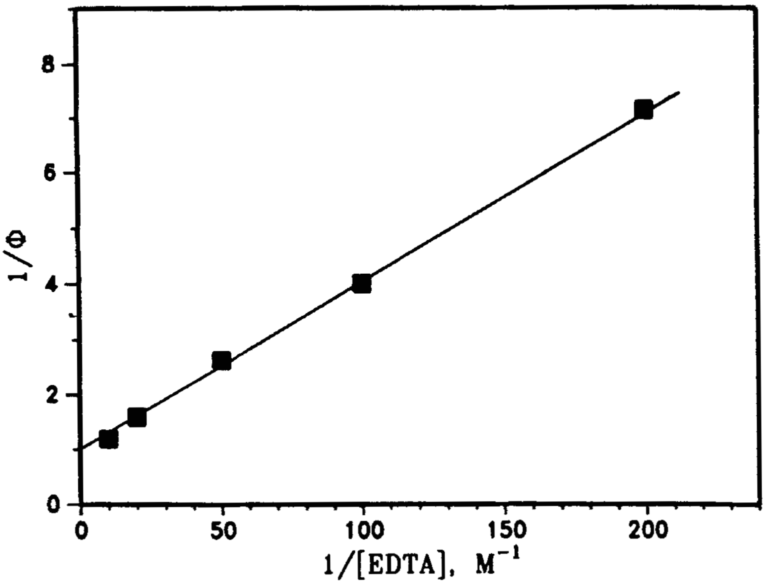

FIGURE 2 Plot of 1/Φ *vs* 1/[EDTA] for the quenching of $^*Ru(bpm)_2(bpz)^{2+}$.

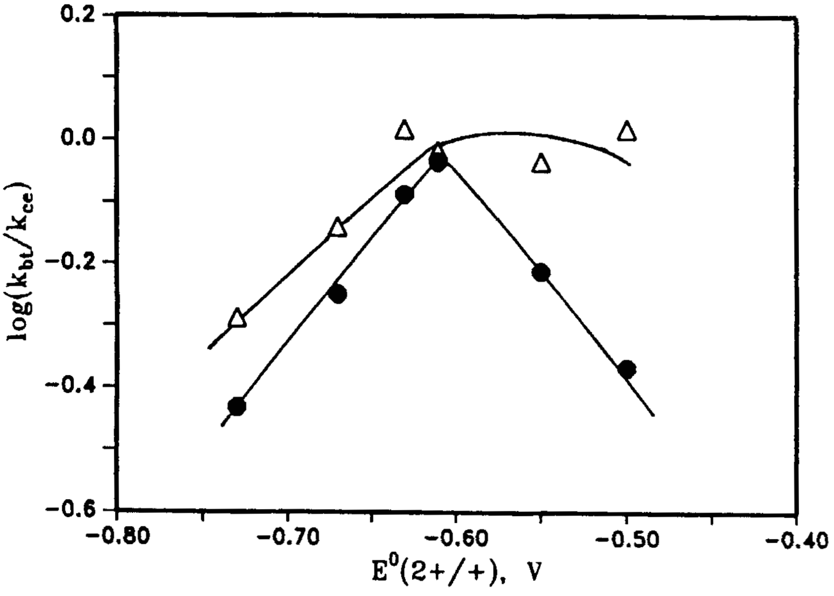

FIGURE 3 Dependence of log k_{bt}/k_{ce} on E°(2+/+); (●) EDTA, (Δ) TEOA.