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Solvent Effects on the Redox Properties of Cu Complexes Used as Mediators in Atom Transfer Radical Polymerization

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Solvent effects on the redox properties of six Cu(I) complexes used as mediators in atom transfer radical polymerization (ATRP) have been studied using cyclic voltammetry. The six ligands used were tris[2-(dimethylamino)ethyl]amine, *N*-(*n*-propyl)-2-pyridylmethanimine, *N*,*N*,*N*′,*N*′,*N*′-pentamethyldiethylenetriamine, 1,1,4,7,10,10-hexamethyl-triethylenetetramine, 2,2′-bipyridine, and 1,4,8,11-tetraaza-1,4,8,11-tetramethyl-cyclotetradecan. The solvents used were DMSO, DMF, MeCN, MeOH, IP, and BuOH. Significant solvent effects were observed and quantitatively analyzed in terms of Kamlet−Taft relationships. The resulting Kamlet−Taft equations were found to successfully describe the solvent effects and could thus be used as tools for the design of ATRP in new solvents. The solvent sensitivity of the different ligands and the nature of the solvent effects are also discussed to some extent.

Introduction

Atom transfer radical polymerization (ATRP) is a successful method for the preparation of macromolecules with narrow polydispersities and predefined molecular weights.[1] The process is initiated by an alkyl halide (R−X) and mediated by a transition-metal complex in a low oxidation state. Copper(I) halides (Cu(I)X) are most frequently used in conjunction with nitrogen-based ligands (L). The metal complex controls the polymerization reaction by mediating a dynamic equilibrium between the propagating radicals and the dormant halide-capped polymer (eq 1). The rate of propagation is governed by the equilibrium concentration of the propagating radicals ($R_p = k_p[R^\bullet][M]$), which in turn is governed by the ATRP equilibrium. As detailed below, the overall equilibrium constant ($K_{eq} = K_1$) can be expressed as the product of the equilibrium constants of a set of elementary processes ($K_1 = K_2K_3K_4$).

$$\text{R−X} + \text{Cu(I)X/L} \rightleftharpoons \text{R}^\bullet + \text{X−Cu(II)X/L} \qquad (1)$$

$$\text{Cu(I)X/L} \rightleftharpoons \text{Cu(II)X/L} + \text{e}^- \qquad (2)$$

$$\text{R−X} + \text{e}^- \rightleftharpoons \text{R}^\bullet + \text{X}^- \qquad (3)$$

$$\text{X}^- + \text{Cu(II)X/L} \rightleftharpoons \text{X−Cu(II)X/L} \qquad (4)$$

Matyjaszewski et al. have shown that the redox properties of the metal complex are one of the parameters controlling the ATRP kinetics.[2] In general, more reducing Cu(I) complexes induce a faster polymerization,[3] that is, give a higher equilibrium concentration of the propagating radicals. The ligands tune the activity of the transition-metal ion, judging from ATRP conducted at high temperature in bulk or in nonaqueous media. Even so, ATRP is effective for the polymerization of hydrophilic monomers in aqueous solution.[4] However, polymerization is much faster than in nonpolar media and a poor “living” character is very often observed. This has been ascribed to polarity effects on the stability of the polymerization intermediates as well as to a competitive complexation of ligand and water molecules to the copper center.[5] In a recent paper, we were able to show that the redox properties of the Cu(I) complexes control the ATRP kinetics also in aqueous solution.[6] Interestingly, we were able to show that the rate of polymerization could be estimated from the thermodynamics of eqs 1−4 with surprisingly good accuracy. Furthermore, by taking solvent effects on the thermodynamic properties and on the rate constant for propagation into account, we were able to reproduce the difference in ATRP kinetics between water and bulk. This study also showed that the redox properties used for the correlation with ATRP kinetics must be determined at the same solvent/monomer ratio as used for the polymerization. No correlation could be found between ATRP kinetics and the redox properties in pure water. Furthermore, the relative trend found for a series of Cu(I) complexes in aqueous media differs from the corresponding trend in organic media. This indicates that the redox properties are sensitive to solvent effects. Hence, to find a predictive tool for ATRP kinetics and design of ATRP systems, quantitative relationships describing solvent effects on the redox properties of Cu(I) complexes are needed.

Properties in solution, for example, solubility, rates of reactions, and free energy and enthalpy of equilibria, can often be described by so-called linear free energy relationships or linear solvation energy relationships.[7] One of the most successful relationships has been found to be the Kamlet−Taft expression [eq 5], where XYZ is the property of interest, XYZ_0, *a*, *b*, *s*, and *h* are solvent independent coefficients characteristic of the process, α is the hydrogen bond donor ability of the solvent, β is the hydrogen bond acceptor or electron pair donor ability to form a coordinative bond, π^* is its dipolarity/polarizability parameter, and δ_H is the Hildebrand solubility parameter, which is a measure of the solvent−solvent interactions that are interrupted in creating a cavity for the solute.[7,8]

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$$\mathrm{XYZ} = \mathrm{XYZ}_0 + a\alpha + b\beta + s\pi^* + h\delta_H \qquad (5)$$

For some processes, any of the coefficients XYZ_0, a, b, s, or h may be negligibly small, so that the corresponding terms do not play a role in the characterization of the solvent effects for these processes. This approach has been criticized for not separating specific and nonspecific effects.[9] Alternative approaches that separate specific and nonspecific effects have also been elaborated, for example, by Fawcett, Reichardt, Koppel, and Palm[9−11] and more recently by Drago and co-workers.[12,13]

The Kamlet−Taft expression has been found to describe solvent effects on one-electron reduction potentials of dications, radical cations, neutral molecules, and radical anions fairly well.[14] The magnitude of the solvent effects has been found to depend roughly on the charge localization reflected by the gas-phase ionization potential or electron affinity.[14] In a recent paper, it was shown that the hydrogen bond donor ability was the solvent property of main importance for the one-electron reduction potential of amine radical cations.[15] In addition, a series of studies by Svaan and Parker have shown that the entropy as well as the enthalpy contribution to the redox potential closely follow the charge localization.[16−22] This indicates that the relatively weak solvation of neutral molecules and radicals can be regarded as solvent independent and that the main contribution to the solvent effect originates from differences in ion solvation. As the observed trend is quite rough, it is plausible that different families of compounds may follow slightly different trends due to differences in solvation of the neutral species. Solvents with more extreme properties (e.g., hexafluoro-2-propanol, which has very high hydrogen bond donor ability) can be expected to deviate from Kamlet−Taft expressions as a result of significantly stronger solvation of the neutral species. Even so, hexafluoro-2-propanol did not show any significant deviation from the Kamlet−Taft expression derived for the amine radical cations.

In this work, we have measured the redox potentials of six different Cu(I) complexes (the ligands are shown in Chart 1) commonly used in ATRP in six different solvents using cyclic voltammetry. The observed solvent effects are analyzed in terms of the Kamlet−Taft relationship.

Experimental Section

CuBr (99%, Aldrich) was used as received. The ligands tris[2-(dimethylamino)ethyl]amine ($\mathrm{Me_6}$-TREN) and *N*-(*n*-propyl)-2-pyridylmethanimine (*N*-pr-PMA) were prepared according to literature procedures described respectively by Ciampolini and Nardi[23] from tris(2-aminoethyl)amine (98%, Aldrich) and Haddleton et al.[24] All other ligands were purchased from Aldrich and used as received, that is, *N*,*N*,*N*′,*N*′,*N*′-pentamethyldiethylenetriamine (PMDETA; 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA; 97%), 2,2′-bipyridine (Bpy; 99%), 1,4,8,11-tetraaza-1,4,8,11-tetramethylcyclotetradecan ($\mathrm{Me_4}$−cyclam; 98%). The Cu/ligand ratio was 1:1 for all complexes except the bipyridine complex for which the ratio was 1:2.

CHART 1: Structures of the Nitrogen-Based Ligands Used

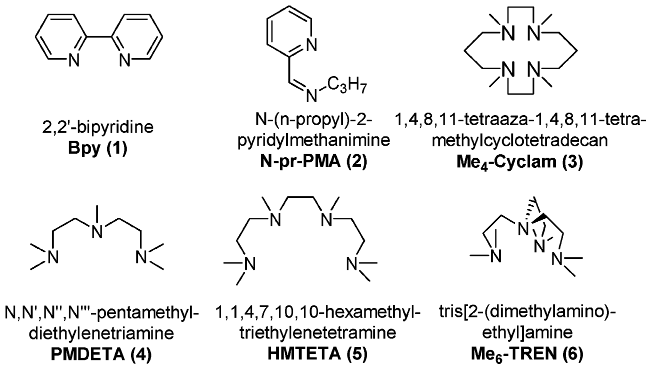

TABLE 1: Half-Wave Potentials for Cu(I) Complexes in Various Solvents (V vs $\mathrm{Fc^+/Fc}$) and Peak Separation (Difference between Anodic and Cathodic Peaks in mV) in Brackets

ligand\solvent	DMSO	DMF	MeCN	IP	BUOH	MeOH
HMTETA	−0.564	−0.491	−0.487	−0.403	−0.379	−0.286
	[274]	[144]	[192]	[216]	[140]	[120]
PMDETA	−0.69	−0.642	−0.489	−0.477	−0.492	−0.527
	[210]	[110]	[148]	[56]	[66]	[170]
Bpy	−0.421	−0.381	−0.421	−0.342	−0.355	−0.291
	[94]	[140]	[152]	[50]	[72]	[66]
N-pr-PMA	−0.341	−0.311	−0.283	−0.245	−0.195	−0.151
	[194]	[160]	[308]	[84]	[116]	[86]
$\mathrm{Me_6}$-TREN	−0.787	−0.764	−0.717	−0.809	−0.794	−0.567
	[80]	[70]	[88]	[60]	[94]	[202]
$\mathrm{Me_4}$−cyclam	−0.431	−0.374	−0.34	−0.364	−0.389	−0.306
	[64]	[66]	[50]	[66]	[76]	[84]

The solvents DMSO, DMF, MeCN, MeOH, IP, and BuOH were purchased (purest grade available) from Aldrich and used as received. The supporting electrolyte used was 0.1 M tetrabutylammonium tetrafluoroborate (Apollo-F).

Cyclic Voltammetry. Cyclic voltammetry was performed with a PAR 263A potentiostat/galvanostat interfaced to a base PC using the EG&G Model 270 software package. The cell was a standard three-electrode setup using a 3 mm diameter glassy carbon working electrode, a platinum coil counter electrode, and a calomel reference electrode. The scan rate was 500 mV/s and full IR compensation was employed in all measurements.

Results and Discussion

Oxidation of the Cu(I) complexes can be described by the following reaction:

$$\mathrm{Cu(I)L}_n \rightleftharpoons \mathrm{Cu(II)L}_n + \mathrm{e}^- \qquad (6)$$

Hence, solvent effects on the redox properties can be attributed to changes in the free energy of solvation for the two oxidation states. The redox process can also be expressed by combining the following three reactions:

$$\mathrm{Cu}^{2+} + \mathrm{e}^- \rightleftharpoons \mathrm{Cu}^+ \qquad (7)$$

$$\mathrm{Cu}^{2+} + n\mathrm{L} \rightleftharpoons \mathrm{Cu(II)L}_n \qquad (8)$$

$$\mathrm{Cu}^{+} + n\mathrm{L} \rightleftharpoons \mathrm{Cu(I)L}_n \qquad (9)$$

Thus, when comparing solvent effects on different Cu(I) complexes, the difference in solvent dependence is simply due to solvent effects on the stability of the Cu(I) and Cu(II) complexes, that is, the ratio between K_8 and K_9.

The measured potentials and the Kamlet−Taft parameters for the solvents used in this study are collected in Tables 1 and 2, respectively.

As can be seen in Table 1, the redox properties of all the Cu(I) complexes investigated here (compared to ferrocene) are significantly affected by the nature of the solvent. In practice, solvent effects on redox properties are usually quantified by one-electron reduction potentials measured against a reference redox couple for which the solvent sensitivity is assumed to be very small. Ferrocene is one possible candidate.

TABLE 2: Kamlet−Taft Parameters[8,25]

solvent	α	β	π^*	δ_H
DMSO	0	0.76	1	12
DMF	0	0.69	0.88	12.1
MeCN	0.19	0.4	0.75	11.9
MeOH	0.98	0.66	0.6	14.5
IP	0.76	0.84	0.48	11.5
BuOH	0.84	0.84	0.47	11.4

In a previous work on solvent effects on redox properties of radical cations, significant solvent effects were only observed for radical cations having a higher reduction potential than the ferrocenium ion.[14,15] The charge of radical cations having lower potential was too delocalized to be significantly affected by changes in the solvent properties. As can be seen in Table 1, all the Cu(I) complexes have potentials significantly lower than that of ferrocene but still display significant solvent dependence.

The solvent dependence can be illustrated in several ways. In Figure 1 we have plotted the half-wave potentials for the Cu(I) complexes in a given solvent against the corresponding potentials determined in DMSO.

From this plot we can see that the relative trend in half-wave potentials is roughly the same in all the organic solvents. A fairly good linear correlation can be obtained when comparing the potentials in DMSO and DMF. This is not completely unexpected because the Kamlet−Taft parameters for these two solvents are very similar. For the same reason, there is also a linear correlation between the potentials determined in 2-propanol and those in 1-butanol. On the basis of previous studies of solvent effects on the redox properties of fairly simple organic radical ions, we would have expected significantly better linear correlations between all the organic solvents used in this work.[14,15]

In Figure 2 we have plotted the half-wave potentials for a given complex in the different solvents included in this study against the corresponding data for the HMTETA complex. This type of plot illustrates the relative solvent sensitivity of the different complexes. A linear correlation indicates a similar solvation mechanism, and a slope <1 indicates lower solvent sensitivity than for that of the HMTETA complex.

As can be seen, the *N*-pr-PMA, Bpy, and Me_4−cyclam complexes roughly follow the same trend as the HMTETA complex, while the PMDETA and Me_6-TREN complexes clearly deviate from the general trend. From the slopes of the linear correlations we can obtain the solvent sensitivity for the *N*-pr-PMA, Bpy, and Me_4−cyclam complexes relative to the HMTETA complex as 0.71, 0.48, and 0.31, respectively. Again, based on previous experience from simple organic radical ions, we would have expected significantly better linear correlations between the potentials of all the different complexes. These expectations are based on the previously mentioned correlations between solvent sensitivity and charge localization and between redox potential (or ionization potential) and charge localization for structurally similar compounds.[14,15] This is clearly not applicable to Cu complexes where the redox center and, thereby, the change in charge is localized on the Cu ion. For these compounds there is no correlation between redox potential and solvent sensitivity. Instead, the redox properties as well as the solvent sensitivity are largely governed by the nature of the ligands. A low reduction potential of the Cu(II) complex reflects a high stability of the Cu(II) complex relative to the corresponding Cu(I) complex, while a more positive reduction potential reflects a lower stability of the Cu(II) complex relative to the corresponding Cu(I) complex. Interestingly, the stability of the Cu(II) complex relative to the corresponding Cu(I) complex appears to depend on the number of free amino end-groups and on the flexibility of the ligand, for example, Me_6-TREN with three free amino end-groups gives the lowest potential in all organic solvents, followed by PMDETA and HMTETA, both having two free amino groups. Me_4−cyclam, containing four amino groups in a rigid ring structure but not as free end-groups, gives a significantly more positive reduction potential. This implies that oxidation of the Cu(I) complex involves ligand rearrangement, which is facilitated by flexible ligands. Structural studies of Cu(I) and Cu(II) complexes also reveal differences between the two oxidation states.[26] In most solvents, Bpy and *N*-pr-PMA give even higher potentials. Hence, the presence of amino groups as opposed to imino groups also appears to be of importance. The rationale for this is most probably the difference in proton (cation) affinity between amines and imines.

The solvent sensitivity (quantified by the difference between the highest and the lowest reduction potential for a given ligand) of the different Cu complexes also seems to be connected to the structure of the ligand. The ligands having higher degrees of freedom (i.e., free rotation) appear to form complexes with higher sensitivity to the nature of the solvent than ligands having lower degrees of freedom (i.e., more rigid structures). Hence, HMTETA, Me_6-TREN, and PMDETA display the strongest solvent sensitivity, while Me_4−cyclam (the most rigid structure) displays the weakest solvent sensitivity. The rationale for this is that the more rigid the structure, the less it will be affected by the solvent.

The solvent-independent coefficients from the analysis of the solvent effects in terms of the Kamlet−Taft relationship (eq 5) are presented in Table 3.

As can be seen, the general quality of the correlations is fairly good for all ligands. In Figure 3 the potentials for all complexes in all solvents estimated using the Kamlet−Taft relationships presented in Table 3 are plotted against the corresponding experimental values.

The Kamlet−Taft relationships obviously describe the solvent effects very well. Judging from the plot in Figure 3 and the previously observed relationships between the redox properties of the Cu(I) complex and the kinetics for ATRP, Kamlet−Taft relationships could indeed be useful tools for the design of ATRP in new solvents.

To extract physicochemical information from the obtained Kamlet−Taft relationships, the relative importance of the different solvent properties must be evaluated. This can be done from so-called beta coefficients derived according to eq 10, where x' (x' denotes a', b', s', or h') is the partial regression coefficient (or "beta coefficient"), $|x|$ is the absolute value of the regression coefficient ($|a|$, $|b|$, $|s|$, or $|h|$), y_i is the Kamlet−Taft parameter (α_i, β_i, π_i^*, or δ_{Hi}) of a given solvent (i), $\bar{y}$ is the average value of this quantity ($\bar{\alpha}$, $\bar{\beta}$, $\bar{\pi}^*$, or $\bar{\delta}_H$) in a given set of solvents, E_i^0 is the potential measured in a given solvent, and $\bar{E}^0$ is the average value of the potentials in a given set of solvents.[27]

$$x' = |x|\sqrt{\frac{\sum_{i=1}^{n}(y_i - \bar{y})^2}{\sum_{i=1}^{n}(E_i^{\,0} - \bar{E}^0)^2}} \qquad (10)$$

The relative importance of a given parameter can be calculated from the beta coefficients using eq 11.

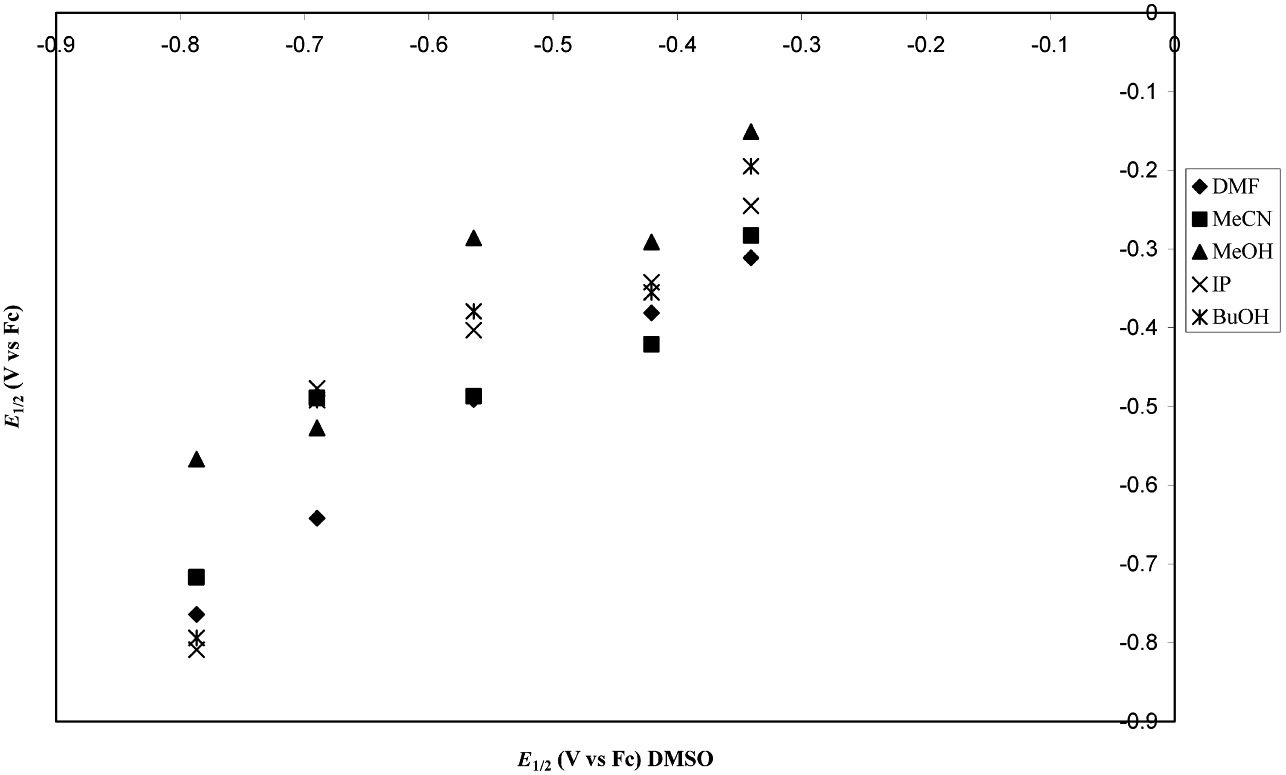

Figure 1. Half-wave potentials for Cu(I) complexes in DMF, MeCN, MeOH, 2-PrOH, and BuOH plotted against the corresponding potentials determined in DMSO.

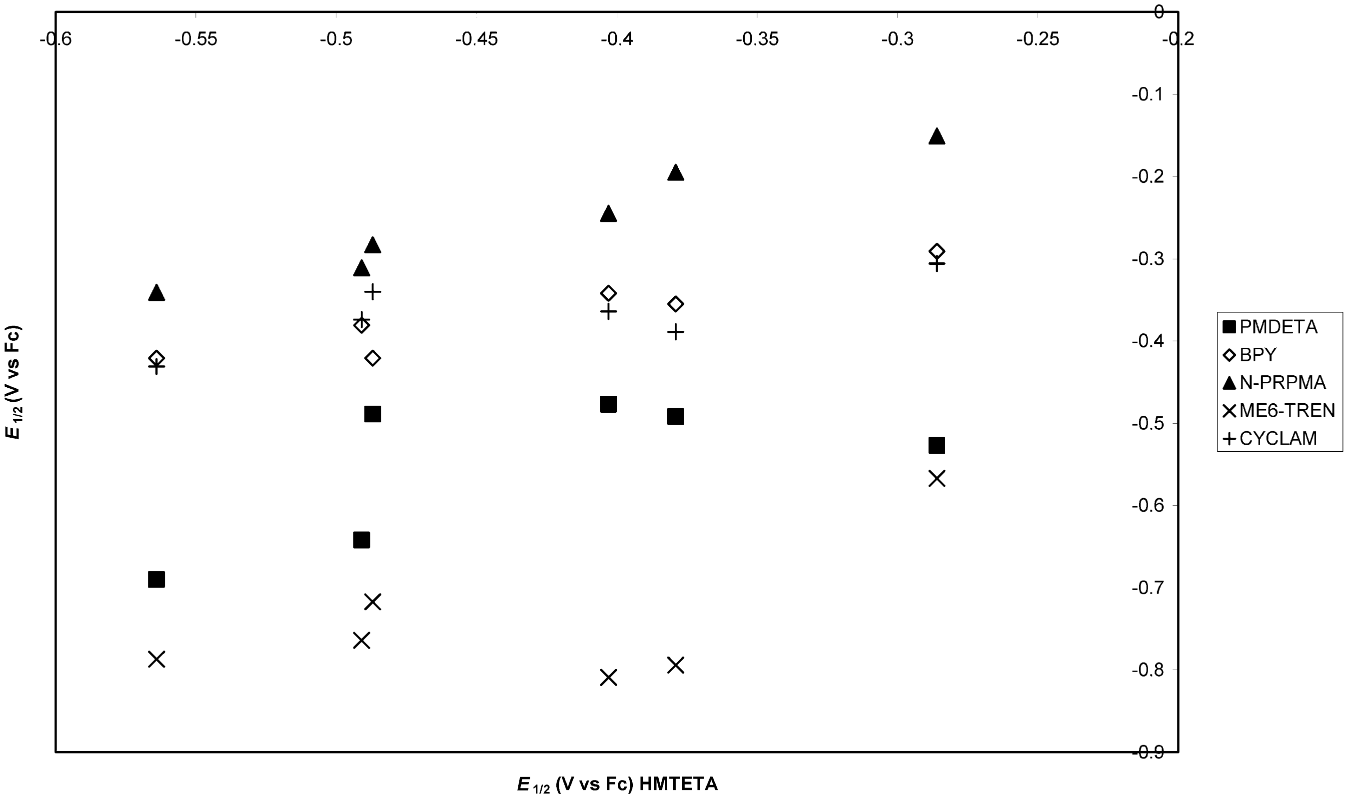

Figure 2. Half-wave potentials for PMDETA, Bpy, N-pr-PMA, Me_6-TREN, and Me_4−cyclam complexes in the different organic solvents included in this study plotted against the corresponding data for the HMTETA complex.

This equation gives the relative importance of α, the hydrogen bond donor ability of the solvent. The relative importance of β, π^*, and δ_H can be calculated in the same way. The relative importance of the Kamlet−Taft solvent parameters for the different Cu(I) complexes are summarized in Table 4.

As can be seen, the solvent dipolarity/polarizability (π^*) is the most important parameter for HMTETA, PMDETA, Bpy, and Me_4−cyclam. For *N*-pr-PMA, the hydrogen bond donor ability (α) dominates, while for Me_6-TREN, the Hildebrand solubility parameter dominates. Admittedly, too few solvents are

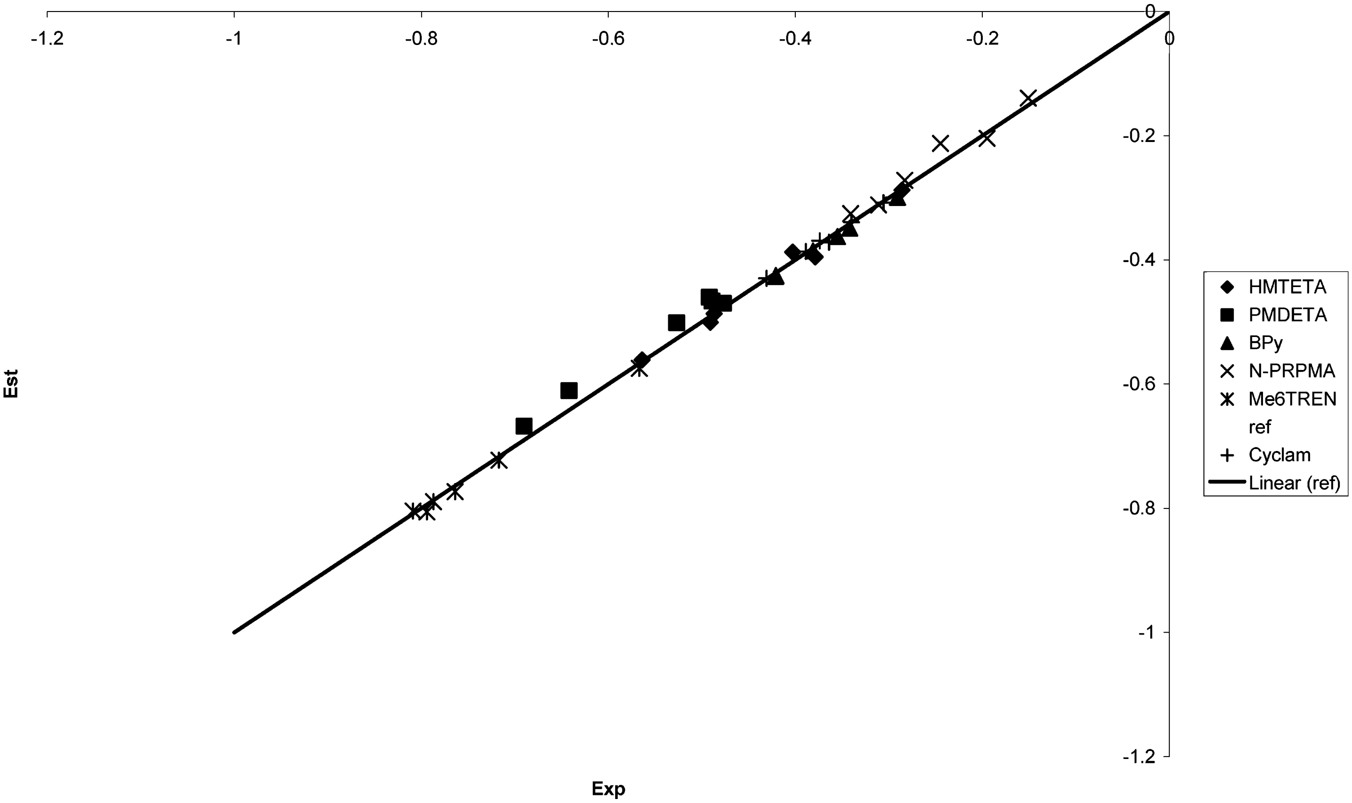

Figure 3. Half-wave potentials for all complexes in all solvents estimated using the Kamlet−Taft relationships presented in Table 3 plotted against the corresponding experimental values.

TABLE 3: Kamlet−Taft Coefficients for Cu(I) Complexes

ligand	XYZ_0	a (α)	b (β)	s (π^*)	h (δ_H)	R^2	F^a
HMTETA	−0.89 ± 0.18	−0.08 ± 0.16	0.08 ± 0.11	−0.50 ±0.29	0.064 ± 0.027	0.988	20.4
PMDETA	0.12 ± 0.14	0.06 ± 0.13	−0.30 ± 0.09	−0.32 ± 0.23	−0.02 ± 0.02	0.991	26.9
Bpy	−0.82 ± 0.002	−0.147 ± 0.001	0.179 ± 0.001	−0.392 ± 0.003	0.054 ± 0.000	1.00	6.6×10^4
N-pr-PMA	−0.42 ± 0.24	0.10 ± 0.21	−0.04 ± 0.14	−0.08 ± 0.38	0.017 ± 0.036	0.960	6.0
Me_6-TREN	−1.39 ± 0.09	0.06 ± 0.08	−0.19 ± 0.06	0.02 ± 0.15	0.06 ± 0.01	0.996	62.6
Me_4−cyclam	−0.53 ± 0.06	−0.18 ± 0.05	−0.06 ± 0.03	−0.43 ± 0.09	0.048 ± 0.009	0.993	35.2

[a] The *F* statistic, or the *F* observed value can be used to determine whether the observed relationship between the dependent and the independent variables occurs by chance.

$$\bar{a} = \frac{a'}{a' + b' + s' + h'} \tag{11}$$

included in this study to allow a quantitative physicochemical comparison. However, the obvious difference between the branched claw-like amine Me_6-TREN and the linear amines HMTETA and PMDETA indicates a difference in solvation mechanism upon oxidation of the corresponding Cu(I) complex. The main difference is that Me_6-TREN, unlike all the other ligands, appears to be completely independent of solvent dipolarity/polarizability for the solvents investigated here. Me_6-TREN is one of the most active ligands used for ATRP and is known to successfully mediate the polymerization of a wide range of monomers at room temperature. PMDETA and HMTETA usually require a higher polymerization temperature than Me_6-TREN.

TABLE 4: Relative Importance of Kamlet−Taft Solvent Parameters

ligand	$\bar{a}$	$\bar{b}$	$\bar{s}$	$\bar{h}$
HMTETA	0.15	0.06	0.47	0.32
PMDETA	0.16	0.29	0.41	0.14
Bpy	0.27	0.12	0.35	0.26
N-pr-PMA	0.51	0.07	0.20	0.22
Me_6-TREN	0.21	0.24	0.03	0.52
Me_4−cyclam	0.34	0.04	0.39	0.23

In general, increasing solvent dipolarity/polarizability stabilizes the Cu(II) complex relative to the Cu(I) complex and thereby lowers the half-wave potential. The observed solvent dipolarity/polarizability insensitivity could serve as an indication for the charge being effectively screened from the solvent by the Me_6-TREN ligand.

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