prepared by hydrolysis of $ReO_2(CH_2CMe_3)_2(O\text{-}t\text{-}Bu)$, a reaction that presumably involves $ReO_2(CH_2CMe_3)_2(OH)$ as an intermediate.[17] All of these preparations must be carried out in the absence of light, because **6**, like its alkoxide congeners, is light-sensitive.

In conclusion, we have synthesized alkoxide and thiolate Re(VII) dioxo complexes of the type $ReO_2(CH_2CMe_3)_2(ER)$. The alkoxides are decomposed by light in a process which may involve homolytic Re–OR bond cleavage. $Re_2O_5(CH_2CMe_3)_4$, a product of alkoxide decomposition, has been structurally characterized and found to have a $[O_2Re\text{–}O\text{–}ReO_2]^{4+}$ core. We know of no other rhenium compounds with a d^0–d^0 $[O_2M\text{–}O\text{–}MO_2]$ core,[18] nor of any other organometallic examples.

Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. D.M.H. thanks Professor D. Coucouvanis for helpful discussions.

Supplementary Material Available: Details of the X-ray structure determinations and tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles for **2** and **6** (21 pages). Ordering information is given on any current masthead page.

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Received May 9, 1989

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Articles

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Electron-Transfer Reactions in Mixed Solvents. An Electrochemical Probe of Unsymmetrical Selective Solvation

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Received March 30, 1989

One of the unique aspects of electron-transfer reactions in mixed solvents is the possibility for unsymmetrical selective solvation of reactants versus products. We have developed a versatile electrochemical method, based on reaction-entropy measurements, to detect its occurrence. The method is illustrated by results for five related redox systems: $Ru(NH_3)_6^{3+/2+}$, $Ru(NH_3)_5(py)^{3+/2+}$, $Ru(NH_3)_4(bpy)^{3+/2+}$, $Ru(NH_3)_2(bpy)_2^{3+/2+}$, and $Ru(bpy)_3^{3+/2+}$ (bpy = 2,2′-bipyridine; py = pyridine), in mixtures of acetonitrile and dimethyl sulfoxide as solvent. The key finding is that a sharp increase (and a more gradual decrease) in reaction entropy occurs over the range of solvent composition where unsymmetrical selective solvation is significant. The dependence of the reaction entropy for $Ru(NH_3)_5(py)^{3+/2+}$ on mixed-solvent composition can be described fairly well by a simple statistical model. There are difficulties, however, in understanding the magnitudes of the observed entropy effects.

Introduction

One of the unique aspects of electron-transfer (ET) reactions in mixed solvents is the possibility for unsymmetrical selective solvation of reactants versus products.[1,2] The occurrence of this effect is important because it may lead to substantial increase in the Franck–Condon barrier to electron transfer and presumably, therefore, to significant rate effects.[1,2] Indeed, in an earlier study of intramolecular ET in the dimer $[(NH_3)_5Ru\text{–}4,4'\text{-bpy–}Ru(NH_3)_5]^{5+}$ (4,4′-bpy = 4,4′-bipyridine) in mixtures of CH_3CN and dimethyl sulfoxide (DMSO) as solvent, we found that differential solvation could increase the barrier to optical electron transfer by as much as 1100 cm^{-1}.[1] The effect was also noted by Curtis and co-workers in their study[2] of a related system, $[(bpy)_2ClRu\text{–pz–}Ru(NH_3)_4(py)]^{4+}$ (bpy = 2,2′-bipyridine; py = pyridine; pz = pyrazine). In addition, there is growing evidence that unsymmetrical selective solvation (ground versus excited state) can play an important role in single-chromophore photophysical and photochemical events.[3,4]

Given the known or suspected significance of unsymmetrical selective solvation in mixed-solvent reactions, the invention of methods to identify its occurrence would clearly be desirable. We have, in fact, developed two such methods.[1,5] The first is based upon a measurement of metal-to-metal charge transfer energies (E_{op}^{MMCT}) in symmetrical mixed-valence systems, as a function of mixed-solvent composition. For example:

$$\begin{aligned}&(1-x)CH_3CN,xDMSO\cdot\\&\qquad[(NH_3)_5Ru^{III}\text{–}4,4'\text{-bpy–}Ru^{II}(NH_3)_5]^{5+}\cdot\\&\quad yDMSO,(1-y)CH_3CN \rightarrow (1-x)CH_3CN,xDMSO\cdot\\&\qquad[(NH_3)_5Ru^{II}\text{–}4,4'\text{-bpy–}Ru^{III}(NH_3)_5]^{5+*}\cdot\\&\qquad\qquad yDMSO,(1-y)CH_3CN \quad (1)\end{aligned}$$

In eq 1, redox-state-dependent secondary coordination ($x \neq y$, where x, y, $1-x$, and $1-y$ signify fractional occupancies of the second sphere) can lead to an extra difference between final and initial state energies, and this difference (ΔE) appears as an additional contribution to E_{op}^{MMCT}. This method is clearly limited to mixed-valence systems. Furthermore, it is only semiquantitative, since additional solvent-dependent factors are known to affect E_{op}^{MMCT}.[1b,6]

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[5] Besides these two methods, a hybrid method has been described in ref 2.

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The second approach is also spectroscopic. It relies upon an analysis of the solvatochromic behavior of charge-transfer transitions associated with individual oxidation states:[1,5,8]

$$\Delta E = E^{\mathrm{MLCT}}(\text{mixed}) + E^{\mathrm{LMCT}}(\text{mixed}) - E^{\mathrm{MLCT}}(\text{pure}) - E^{\mathrm{LMCT}}(\text{pure}) \quad (2)$$

In eq 2, E^{MLCT} is the energy of a metal-to-ligand charge-transfer transition for the lower oxidation state, E^{LMCT} is the energy of a ligand-to-metal charge-transfer transition for the higher oxidation state, and "mixed" and "pure" describe the solvent composition. A rationale for eq 2 has been given in an earlier publication.[1a]

For a variety of reasons the second approach is likely to be more accurate than the first.[1] Furthermore, the second one should be more broadly applicable. For example, one can use eq 2 (but not eq 1) to evaluate differential solvation effects in bimolecular self-exchange reactions like eq 3. In eq 3, ΔE would describe

$$\begin{aligned}&(1-x)\mathrm{CH_3CN},x\mathrm{DMSO}\cdot[(\mathrm{NH_3})_5\mathrm{Ru^{III}L}]^{3+} + \\ &\quad (1-y)\mathrm{CH_3CN},y\mathrm{DMSO}\cdot[(\mathrm{NH_3})_5\mathrm{Ru^{II}L}]^{2+} \rightarrow \\ &\quad (1-x)\mathrm{CH_3CN},x\mathrm{DMSO}\cdot[(\mathrm{NH_3})_5\mathrm{Ru^{II}L}]^{2+} + \\ &\quad (1-y)\mathrm{CH_3CN},y\mathrm{DMSO}\cdot[(\mathrm{NH_3})_5\mathrm{Ru^{III}L}]^{3+} \rightarrow \\ &\quad (1-y)\mathrm{CH_3CN},y\mathrm{DMSO}\cdot[(\mathrm{NH_3})_5\mathrm{Ru^{II}L}]^{2+} + \\ &\quad (1-x)\mathrm{CH_3CN},x\mathrm{DMSO}\cdot[(\mathrm{NH_3})_5\mathrm{Ru^{III}L}]^{3+} \quad (3)\end{aligned}$$

the solvational energy difference between the intermediate pair and either the initial or final set of redox states. Obviously, the analysis of eq 2 would also be applicable (with a correction of 0.5) to the unimolecular (i.e., electrochemical half-reaction) analogue:

$$\begin{aligned}&(1-x)\mathrm{CH_3CN},x\mathrm{DMSO}\cdot[(\mathrm{NH_3})_5\mathrm{Ru^{III}L}]^{3+} + \mathrm{e^-(electrode)} \rightarrow \\ &\quad (1-x)\mathrm{CH_3CN},x\mathrm{DMSO}\cdot[(\mathrm{NH_3})_5\mathrm{Ru^{II}L}]^{2+} \rightarrow \\ &\quad (1-y)\mathrm{CH_3CN},y\mathrm{DMSO}\cdot[(\mathrm{NH_3})_5\mathrm{Ru^{II}L}]^{2+} + \\ &\quad (y-x)\mathrm{CH_3CN} + (x-y)\mathrm{DMSO} \quad (4)\end{aligned}$$

Although the second analysis (eq 2) is anticipated to be more widely applicable than the first, it is still not a particularly general method; many redox couples lack (in one or both oxidation states) the spectral handles required by either approach. (Indeed, in our earlier study[1] of the decaammine dimer (eq 1), spectral interferences prevented access to the necessary LMCT transition, forcing us to use a monomeric surrogate for the analysis in eq 2.) Clearly, it would be valuable to have access to a more general, and preferably nonspectroscopic, approach.

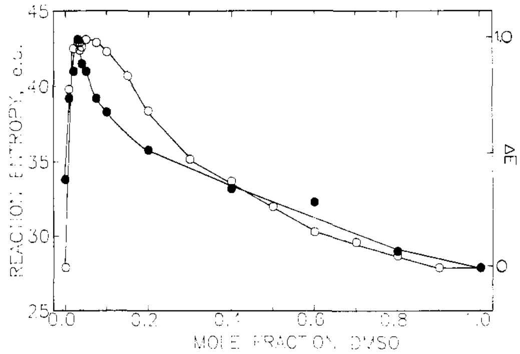

Figure 1. $\Delta S^\circ_{\mathrm{rc}}$ vs solvent composition for reduction of $(\mathrm{NH_3})_5\mathrm{Ru(py)}^{3+}$ in mixtures of $\mathrm{CH_3CN}$ + DMSO (●). Left-hand side: ΔE, from eq 2, versus solvent composition (○). The scale for ΔE is calibrated in units of 1000 cm^{-1}.

In this article we describe the basis for a simple and versatile *electrochemical* probe of unsymmetrical selective solvation. The kernel of the new probe is in the electrochemical assessment of entropy changes ($\Delta S^\circ_{\mathrm{rc}}$) accompanying redox half-reactions.[9b,c,12] (It should be noted that a very similar suggestion was recently made by Curtis and co-workers based on their optical studies of unsymmetrical mixed-valence ions.[2] The corresponding electrochemical experiments are described in the accompanying article.) We reasoned that in reactions like eq 4, where electron transfer is intricately linked to site-to-bulk (or bulk-to-site) solvent translation (i.e., a change in secondary coordination), there should exist an entropy effect beyond that associated with electrostriction or other pure-solvent phenomena. Such an effect should be easy to detect, given that the overall entropy change for a redox half-reaction ($\Delta S^\circ_{\mathrm{rc}} = \bar{S}^\circ_{\mathrm{red}} - \bar{S}^\circ_{\mathrm{ox}}$) can be determined simply from the temperature dependence of the half-reaction formal potential (E_{f}), measured in a nonisothermal cell configuration:[12]

$$\Delta S^\circ_{\mathrm{rc}} \approx F(\mathrm{d}E_{\mathrm{f}}/\mathrm{d}T)_{\mathrm{ni}} \quad (5)$$

Thus, the only chemical requirement for the new method is the availability of a reversible, temperature-stable electrochemical response.

To illustrate the approach, we describe results for five related redox couples: $\mathrm{Ru(NH_3)_6}^{3+/2+}$, $\mathrm{Ru(NH_3)_5(py)}^{3+/2+}$, $\mathrm{Ru(NH_3)_4(bpy)}^{3+/2+}$, $\mathrm{Ru(NH_3)_2(bpy)_2}^{3+/2+}$, and $\mathrm{Ru(bpy)_3}^{3+/2+}$. A compelling reason for selecting these particular couples was the availability of preliminary data suggesting a marked effect of unsymmetrical selective solvation upon the electrochemical exchange kinetics for the spectrally inaccessible $\mathrm{Ru(NH_3)_6}^{3+/2+}$ couple.[9] A second reason was the existence of a large body of background data—both electrochemical[1,2,9] and spectral[1,2,10,11]—relating to ammine-ligand/solvent interactions.

Finally, we describe the adaptation of a simple statistical model for selective solvation.[14] The model is used to calculate entropy changes for the $\mathrm{Ru(NH_3)_5(py)}^{3+/2+}$ couple as a function of solvent composition.

Experimental Section

Materials. Prepurified solvents were obtained from Fischer and Aldrich. Tetraethylammonium perchlorate (TEAP) was obtained from GFS Chemicals. $[\mathrm{Ru(NH_3)_6}](\mathrm{PF_6})_3$ and $[\mathrm{Ru(bpy)_3}](\mathrm{PF_6})_2$ were purchased as chloride salts from Strem and Aldrich, respectively, and metathesized in water with $\mathrm{NH_4PF_6}$. $[\mathrm{Ru(NH_3)_5(py)}](\mathrm{PF_6})_2$,[10a] $[\mathrm{Ru(NH_3)_4(bpy)}](\mathrm{PF_6})_2$,[10a] and $[\mathrm{Ru(NH_3)_2(bpy)_2}](\mathrm{PF_6})_2$[13] were prepared by literature methods.

Measurements. Electrochemical measurements were made in a three-compartment nonisothermal cell[12] (working compartment, nonisothermal bridge, and reference compartment) with the same solvent in all three parts. A gold wire served as a working electrode together with a platinum counter electrode and a saturated (NaCl) calomel reference. Formal potentials were obtained from reversible cyclic voltammograms (typically at 100 mV/s) and by differential-pulse voltammetry using a PAR 174A polarographic analyzer and a Houston Omnigraphic recorder. Differential pulse proved to be particularly useful for discrimination against solvent oxidation with the $\mathrm{Ru(bpy)_3}^{3+/2+}$ couple. The supporting electrolyte in all experiments was 0.1 M TEAP.

For each reaction-entropy determination 7–10 E_{f} measurements were obtained in increments of ca. 4°. For the $\mathrm{Ru(NH_3)_2(bpy)_2}^{3+/2+}$ couple, however, the number of data per determination was somewhat less due to the appearance (particularly in DMSO-rich solvents) of a second, interfering redox couple above 35 °C. The measurement precision was ca. 1.5 eu.

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(7) Blackburn, R. L.; McMannis, G. Unpublished observations.

(8) The assumptions contained in eq 2 have been described in ref 1a. The most important one is that the (ligand)$^+$ or (ligand)$^-$ state created by charge transfer is not significantly preferentially solvated relative to the (ligand)^0 state.

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Table I. Solvent Dependence of Charge-Transfer Spectral Data in Mixtures of Acetonitrile and DMSO

m_{DMSO}	E^{MLCT}, 10^3 cm^{-1} [a]	E^{LMCT}, 10^3 cm^{-1} [b]	$0.5\Delta E$, 10^3 cm^{-1} [c]
0.000	24.63	16.92	-0.02
0.010	24.36	17.98	0.38
0.020	24.16	18.38	0.48
0.030	24.07	18.48	0.485
0.035	24.01	18.54	0.485
0.040	23.98	18.55	0.475
0.050	23.90	18.66	0.49
0.075	23.75	18.80	0.485
0.100	23.64	18.87	0.465
0.150	23.46	18.94	0.41
0.200	23.28	18.98	0.34
0.300	23.04	19.01	0.235
0.400	22.94	19.01	0.185
0.500	22.83	19.01	0.13
0.600	22.73	19.01	0.08
0.700	22.68	19.01	0.055
0.800	22.62	19.01	0.025
0.900	22.57	19.01	0.00
1.000	22.57	19.01	0.00

[a] Absorption maximum for metal-to-ligand charge-transfer in $(NH_3)_5Ru^{II}(py)^{2+}$. Values are ±0.06. [b] Absorption maximum for ligand-to-metal charge-transfer in $(NH_3)_5Ru^{III}(dmapy)^{3+}$.[1b] Values are ±0.06. [c] Defined by eq 2. Values are ±0.04.

UV–vis spectra were obtained with a precision of ca. 1 nm by using a Perkin-Elmer 330 spectrophotometer.

Results

Measurements. Figure 1 shows a plot of $\Delta S°_{rc}$ vs solvent composition (mole fraction m) for the $(NH_3)_5Ru(py)^{3+/2+}$ couple in mixtures of acetonitrile and DMSO. Also shown for the same couple is a plot of ΔE vs solvent composition, where ΔE was calculated by using eq 2. Following earlier studies,[1] the E^{LMCT} data required for eq 2 were obtained by using a surrogate chromophore $[(NH_3)_5Ru^{III}(dmapy)^{3+}]$ (dmapy = (dimethylamino)pyridine), since in the unsubstituted-pyridyl complex the LMCT transition is not cleanly observable. Values for E^{MLCT} and E^{LMCT} for a range of solvent compositions are listed in Table I, along with ΔE values from eq 2. Figure 2a contains plots of $\Delta S°_{rc}$ vs m_{DMSO} for both $Ru(NH_3)_6^{3+/2+}$ and $(NH_3)_4Ru(bpy)^{3+/2+}$. Figure 2b shows similar plots for the $(NH_3)_2Ru(bpy)_2^{3+/2+}$ and $Ru(bpy)_3^{3+/2+}$ couples. Figure 3 shows plots, for all five couples, of E_f (at 23 ± 1 °C) vs solvent composition. In the figure, E_f values are referenced to those for ferrocenium/ferrocene.[16]

Calculations. Frankel, Langford, and Stengle have noted that the entropy of selective solvation (i.e. the extra entropy ΔS_{con} (con = configuration) due to a difference between bulk and secondary coordination layer solvent compositions) can be estimated for regular solutions from relatively simple thermodynamic and statistical considerations.[14] Following Frankel et al., we may write

$$\Delta S_{con} = -S_1 + S_2 + S_3 + S_4 \qquad (6)$$

where S_1 is the configuration entropy of the bulk solvent phase prior to selective solvation, S_2 is its entropy after transfer of $n_{CH_3CN} + n_{DMSO}$ moles to the secondary coordination phase, S_3 is the configuration entropy of the fully assembled secondary coordination phase, and S_4 is the entropy for mixing 1 mol of selectively solvated solute back into $N - n_{CH_3CN} - n_{DMSO}$ moles of bulk solvent. If we make the assumption that the overall secondary coordination number (i.e. $n_{CH_3CN} + n_{DMSO}$) is constant, eq 6 can be rewritten as

$$\Delta S_{con} = R\{[m_{CH_3CN}N \ln m_{CH_3CN} + m_{DMSO}N \ln m_{DMSO}] - (m_{CH_3CN}N - n_{CH_3CN}) \ln [(m_{CH_3CN}N - n_{CH_3CN})/(N - n_{CH_3CN} - n_{DMSO})] + (m_{DMSO}N - n_{DMSO}) \ln [(m_{DMSO}N - n_{DMSO})/(n - n_{CH_3CN} - n_{DMSO})]\} - [n_{CH_3CN} \ln m'_{CH_3CN} + n_{DMSO} \ln m'_{DMSO}] + S_4 \qquad (7)$$

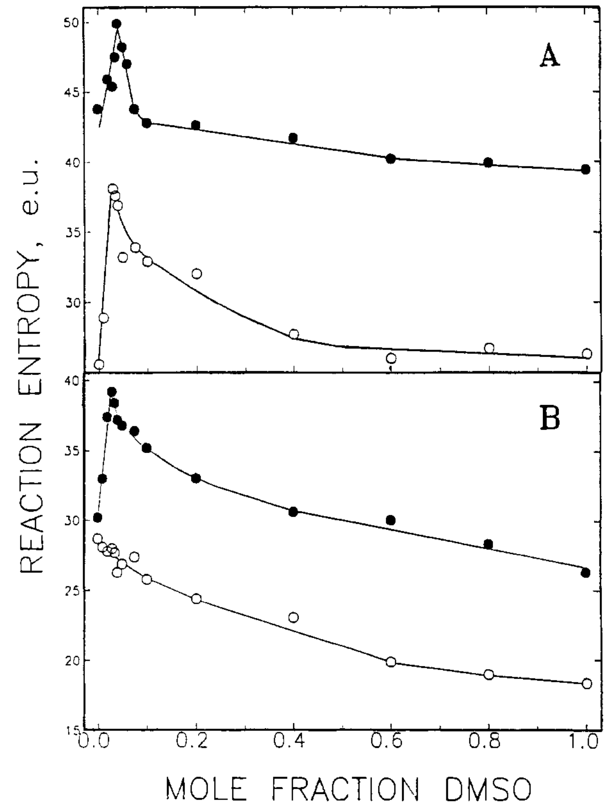

Figure 2. $\Delta S°_{rc}$ vs solvent composition (CH_3CN + DMSO mixtures) for reduction of transition-metal complexes. Panel A: (○) $(NH_3)_4Ru(bpy)^{3+}$; (●) $Ru(NH_3)_6^{3+}$. Panel B: (●) $(NH_3)_2Ru(bpy)_2^{3+}$; (○) $Ru(bpy)_3^{3+}$.

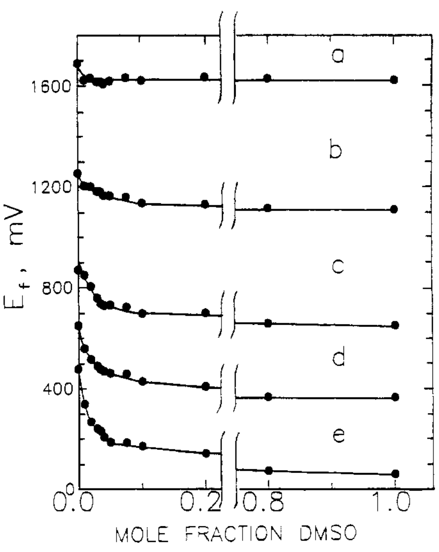

Figure 3. E_f vs solvent composition (CH_3CN + DMSO mixtures) for reduction of (a) $Ru(NH_3)_6^{3+}$, (b) $(NH_3)_5Ru(py)^{3+}$, (c) $(NH_3)_4Ru(bpy)^{3+}$, (d) $(NH_3)_2Ru(bpy)_2^{3+}$, and (e) $Ru(bpy)_3^{3+}$.

In eq 7, n_i represents the number of moles of solvent i in the secondary coordination layer (per mole of solute), m'_i is the mole fraction of solvent i in the secondary coordination layer, m_i is the bulk mole fraction in the initial system (i.e., prior to selective solvation), and N is the total number of moles of solvent. Equation 7 differs slightly from the Frankel expression,[14] because we have formulated our equation for 1 mol of solute (consistent with the definition of $\Delta S°_{rc}$) rather than for 1 mol of secondarily coordinated solvent.

Frankel and co-workers[14] have noted that S_4 will be nearly constant in dilute solutions. In any case, S_4 is unlikely to be redox-state dependent. Further simplification is possible if we realize that the quantity $(m_iN - n_i)/(N - n_i - n_j)$ is very nearly

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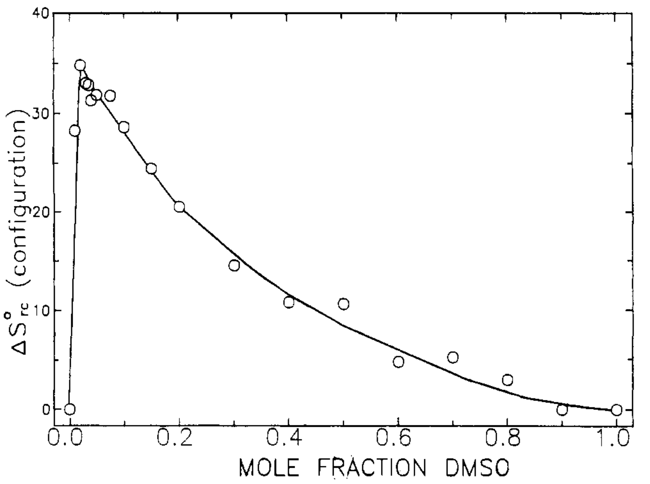

Figure 4. Calculated dependence of ΔS°_{rc}(con) (eq 7–9) on solvent composition (CH_3CN + DMSO mixtures) for $(NH_3)_5Ru(py)^{3+}$ reduction.

equal to m_i for dilute solutions. Substituting into eq 7 and combining terms, we obtain

$$\Delta S_{con} = R(n_{CH_3CN} \ln m_{CH_3CN} + n_{DMSO} \ln m_{DMSO} - n_{CH_3CN} \ln m'_{CH_3CN} - n_{DMSO} \ln m'_{DMSO}) + S_4 \quad (8)$$

Finally, for the redox couple we may write

$$\Delta S^{\circ}_{rc}(\text{con}) = \Delta S^{red}_{con} - \Delta S^{ox}_{con} \quad (9)$$

In eq 9, ΔS°_{rc}(con) is the extra entropy change due to unsymmetrical selective solvation, i.e., the quantity one would anticipate finding in experimental reaction entropy measurements. Note that for *symmetrical* selective solvation $\Delta S^{red}_{con} = \Delta S^{ox}_{con}$ and $\Delta S^{\circ}_{rc}(\text{con}) = 0$.

In order to use eq 6–9, values are required for n_{CH_3CN}, n_{DMSO}, m'_{CH_3CN}, and m'_{DMSO}. All four are difficult to assess with absolute certainty. Nevertheless, estimates of the secondary coordination layer (first solvation layer) composition (m'_{CH_3CN} and m'_{DMSO}) can be obtained from E^{LMCT} and E^{MLCT} by noting that the basis of solvatochromism in these transitions[1] is in specific, short-range ligand–solvent hydrogen-bonding interactions, which necessarily are confined to the second-coordination sphere, and by assuming that the magnitudes of the solvatochromic shifts are linear in the local solvent composition.[17] The corresponding values for n_{CH_3CN} and n_{DMSO} can be obtained if the overall secondary coordination number is known. From NMR studies of $(NH_3)_5Cr(DMSO)^{3+}$ in mixtures of water and DMSO, a limiting value of 10 for n_{DMSO} has been proposed.[18] As a starting point, we propose the same limiting value for the pentaammineruthenium system. Figure 4 shows the resulting plot of ΔS°_{rc}(con) vs solvent composition, calculated for $(NH_3)_5Ru(py)^{3+/2+}$.

Discussion

Redox Potentials. Before considering the variable-temperature redox experiments, it may be useful to examine the E_f data at 23 °C. From Figure 3 it is clear that the ligand composition has a profound influence upon both the formal potential and its response to solvent. For example, in CH_3CN as solvent the potential for reduction of $Ru(NH_3)_6^{3+}$ is much more negative than that for $Ru(bpy)_3^{3+}$ and becomes even more negative in DMSO. For the mixed-ligand complexes there are intermediate effects. From Figure 3, the existence and extent of solvent effects is clearly associated with the presence of ammine ligands.

On the basis of earlier studies,[9a,10b] the solvent-dependent E_f effects (pure solvents) evidently originate from ligand–solvent hydrogen bonding. It has been argued that electron-deficient (acidic) ammine hydrogens can interact in a specific fashion with electron-rich (basic) solvent functional groups and that the interaction is stronger for higher oxidation states. According to this explanation, substitution of a weakly basic solvent like CH_3CN by a stronger base like DMSO should lead to a negative shift in E_f. Also, the shift should increase as the number ammine ligands is increased. Both predictions are confirmed by the present experiments.

A second noteworthy feature of the E_f experiments is the behavior in mixed solvents. For each of the ammine complexes the addition of only small amounts of DMSO is sufficient to shift the formal potential to values nearly as negative as found in pure DMSO. The ability of the minority solvent to provide the dominant influence can be taken as strong evidence for selective solvation.[1a,2,9a] Clearly the E_f experiments provide a useful picture of selective solvation. Nevertheless, it should be noted that they are completely uninformative with respect to *unsymmetrical* effects.

Reaction Entropies. An inspection of Figures 1 and 2 shows that reaction entropies, like E_f values, are significantly influenced by both ligand and solvent composition. For the most part, the results agree well with previous reports, and in those reports[9b,c] the physical–chemical origins of ligand and pure-solvent effects have been discussed. (Nevertheless, it is somewhat surprising that the ΔS°_{rc} value for $Ru(bpy)_3^{3+/2+}$ is so much larger in CH_3CN than in DMSO. From earlier work[9c] that demonstrated an empirical correlation between ΔS°_{rc} and the so-called solvent acceptor number, much closer agreement would have been expected.)

Of more interest is the behavior in mixed solvents. Figure 1 shows that a sharp entropy spike appears at $m_{DMSO} \approx 0.03$ in the ΔS°_{rc} vs m plot for $(NH_3)_5Ru(py)^{3+/2+}$. For comparison, a somewhat broader peak, centered at $m_{DMSO} \approx 0.06$, occurs in the ΔE vs m plot (Figure 1). With the assumption (vide supra) that charge-transfer energies change linearly with the secondary coordination layer composition, ΔE can be taken as a direct measure of the *number* of bound solvent molecules (Δn) that are interchanged (i.e., CH_3CN for DMSO) upon reduction. Scaling is such that a ΔE value equal to E^{MLCT}(pure CH_3CN) – E^{MLCT}(pure DMSO), or E^{LMCT}(pure DMSO) – E^{LMCT}(pure CH_3CN), would correspond to $\Delta n = 10$ (i.e., complete solvation layer interchange). On this basis, the maximum value of Δn in Figure 1 is ca. 4.7.

It is important to note that the maximum entropy change for $(NH_3)_5Ru(py)^{3+}$ reduction does *not* occur at the point of maximum solvation-layer rearrangement. Furthermore, ΔS°_{rc} displays a sharper dependence on solvent composition than does Δn (ΔE, Figure 1). A comparison to calculated configuration entropies (Figure 4) suggests an explanation. From Figure 4, there clearly is excellent agreement between experimental and calculated ΔS°_{rc}(con) vs m_{DMSO} "line shapes". The underlying eq 6–9 show that it is the ln m_i (m'_i) terms that shift and narrow the entropy curves (or line shapes) relative to the Δn or ΔE curves. Thus, for small mole fractions, changes in these terms dominate the calculation. The significance of the ln m_i (m'_i) terms physically is that a given set of solvent molecules becomes labeled entropically in a way that is at least partially defined by the *overall* solvent composition. For example, for $\Delta n = 3$ in the present experiments, there will be an appreciably greater release of entropy (via ln m'_i) if these three molecules are displaced (upon reduction) from a secondary coordination phase that is comprised almost completely of DMSO ($n_{DMSO} \rightarrow 10$) than if they are displaced from a phase that is already well mixed. Similar effects will exist in the bulk phase through terms involving ln m_i (eq 8).

One further point is that the agreement between Figures 1 and 4 suggests that the assumption that charge-transfer energies shift linearly with the secondary coordination layer composition is a valid one. This point is of paramount importance, since the linearity assumption underlies nearly all experimental selective-solvation studies. Furthermore, as Ennix et al. have noted,[2] the assumption is largely an untested one. From the calculation/experiment comparison, the way in which the linearity assumption is at least indirectly validated is, first, in the reliance upon ex-

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(17) See, for example: Langford, C. H.; Tong, J. P. K. *Pure Appl. Chem.* **1977**, *49*, 93.

(18) Reynolds, W. L.; Reichley-Yinger, L.; Yaun, Y. *Inorg. Chem.* **1985**, *24*, 4273. See also ref 2.

(19) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.

(20) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.

perimental E^{MLCT} and E^{LMCT} values to obtain m'_i for the $\Delta S^\circ_{\mathrm{rc}}(\mathrm{con})$ calculations and, second, in the resulting agreement of the calculated entropy curves with experiment.

In contrast to the line-shape part of the problem where there is very good agreement between calculation and experiment, the agreement is poor for the absolute magnitudes of the entropy changes. Thus, from eq 7-9 $\Delta S^\circ_{\mathrm{rc}}(\mathrm{con})$ for $(\mathrm{NH_3})_5\mathrm{Ru(py)}^{3+/2+}$ is expected to reach a peak value of 39 eu. Experimentally (Figure 1) the value is only about 20% of that. (Note that in Figure 1, $\Delta S^\circ_{\mathrm{rc}}(\mathrm{con})$ is given only by the peaked portion of the diagram.)

There are at least three possible explanations for the discrepancy. First, the input parameters for eq 8 could be in error. Of these parameters, m_i is directly measured and m'_i is indirectly measured but appears to be reliable on the basis of the preceding discussion of line-shape phenomena, leaving n_i as the most questionable parameter. The proposed limiting value of 10 for n_i is, in fact, the product of a relatively indirect determination.[17] Nevertheless, given a primary coordination number of 6, a limiting value of 10 for secondary coordination is certainly reasonable. In any case, it is intuitively more appealing than the value of ca. 3 that would be required in order to force agreement between calculation and experiment.[21]

A second possibility is that mixtures of $\mathrm{CH_3CN}$ and DMSO are not regular solutions. This possibility could lead to either positive or negative excess-entropy contributions. The monotonic behavior in Figure 2 of $\mathrm{Ru(bpy)_3}^{3+/2+}$ (for which specific ligand-solvent interactions are largely absent) indicates that, in fact, there are no significant bulk-phase excess-entropy contributions. For the hydrogen-bonded primary solvation phase the answer is less certain. The strongest evidence against a first-layer excess-entropy contribution comes from fits of E^{MLCT} and E^{MMCT} in $\mathrm{CH_3CN}$ + DMSO to a consecutive-equilibrium expression:[2,22]

$$\frac{\delta m}{\delta t} = \sum_{i=1}^{n} \frac{(K^{1/n}Y)^i (i/n) k^{i(i-n)/2} \prod_{j=1}^{i} [(n+1-j)/j]}{1 + \sum_{i=1}^{n} (K^{1/n}Y)^i k^{i(i-n)/2} \prod_{j=1}^{i} [(n+1-j)/j]} \qquad (10)$$

In eq 10, δm is the solvent-induced shift in some measurable quantity (i.e., E^{MLCT} or E^{MMCT}), δt is the total shift, K is a stepwise equilibrium constant, Y describes the bulk solvent composition (for example, Y could be defined as the bulk-solvent mole fraction), n is the number of bound solvent molecules, and k is a parameter that describes how each successive binding step is influenced by the preceding one. Thus, a value of $k = 1$ implies that neither attractive nor repulsive interactions exist between bound solvent molecules.[22] For binding of DMSO to $(\mathrm{py})(\mathrm{NH_3})_4\mathrm{Ru^{III}}$– and $(\mathrm{py})(\mathrm{NH_3})_4\mathrm{Ru^{II}}$– in the binuclear complex $(\mathrm{py})(\mathrm{NH_3})_4\mathrm{Ru}$–pz–$\mathrm{Ru(bpy)_2(Cl)}^{4+/3+}$, the best-fit values for k (based on $n = 8$) are 0.90 and 1.10, respectively.[2] Although any interpretation is necessarily model dependent, the observation that the k values are indeed close to unity suggests that, for both metal oxidation states, the bound-solvent phase does behave as a regular solution.

The third possibility is that eq 2 is insufficiently sophisticated and that the Frankel analysis somehow neglects a key contribution. One point that is *not* considered, for example, is that the overall secondary coordination number might change with solvent composition (or oxidation state). This occurrence would very likely have entropic consequences.

Additional information about unsymmetrical selective solvation can be acquired from a broader comparison of entropy experiments. From Figures 1 and 2, the following are evident: (1) Unsymmetrical selective solvation (or at least its entropic component) is maximized at about the same point (in terms of solvent composition) for each of the four ammine-complex redox reactions. (2) There is no clear relationship between the number of ammine ligands and the magnitude of $\Delta S^\circ_{\mathrm{rc}}(\mathrm{con})$. (3) In the control experiment involving $\mathrm{Ru(bpy)_3}^{3+/2+}$, the spike in the $\Delta S^\circ_{\mathrm{rc}}$ vs m plot is absent, as expected.

From these findings, especially point 2 and earlier discussions, it appears that reaction entropies cannot (yet) be used to quantitate the extent of occurrence of unsymmetrical selective solvation. Nevertheless, from the experiment/calculation comparisons, the measurements do provide a rational and precise probe of differential solvation for a given system. On the basis of the $(\mathrm{NH_3})_5\mathrm{Ru(py)}^{3+/2+}$ couple and on the assumption that $n_{\mathrm{CH_3CN}} + n_{\mathrm{DMSO}} \approx 10$, the limit of detection for changes in secondary coordination is $\Delta n \approx 1$. The results for $\mathrm{Ru(NH_3)_6}^{3+/2+}$ are particularly significant because they show that the entropy probe can be applied with good success to spectrally inaccessible systems.

In summary, reaction entropy measurements represent a simple, sensitive, and potentially widely applicable probe for unsymmetrical selective solvation. We plan to utilize the measurements in ongoing studies of homogeneous and electrochemical electron-transfer kinetics, photoredox processes, and redox conductivity in solvent-swollen polymeric films.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Matching support was provided by the National Science Foundation through the Presidential Young Investigator Program under Grant No. CHE-8552627. Industrial matching funds were generously provided by the Atlantic Richfield Foundation, the James S. Kemper Foundation, Rohm and Haas, Mead Imaging, and the Newport Corp. R.L.B. acknowledges support as a Shell Graduate Fellow.

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(21) On the other hand, an interesting piece of data that supports the notion of a very small secondary coordination number in DMSO/acetonitrile mixtures is the optically estimated free-energy difference of 1.6 kcal/mol of solvent for binding of DMSO to $(\mathrm{py})(\mathrm{NH_3})_4\mathrm{Ru^{III}L}$ vs $(\mathrm{py})(\mathrm{NH_3})_4\mathrm{Ru^{II}L}$, where L is $(\mathrm{pz})\mathrm{Ru^{II}(bpy)_2(Cl)}$.[2] If this value is also applicable to $(\mathrm{NH_3})_5\mathrm{Ru(py)}^{3+/2+}$, then the overall change in redox potential between pure acetonitrile and pure DMSO ($\Delta E_{\mathrm{f}} = -0.284$ V = 6.55 kcal/mol) can be divided by 1.6 kcal/mol of bound DMSO to yield $n_{\mathrm{DMSO}} = 4$.

(22) (a) Covington, A. K.; Newman, K. E. *Adv. Chem. Ser.* **1976**, *No.* **155**, 153. (b) Covington, A. K.; Lilly, T. H.; Newman, K. E.; Porthouse, G. A. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 963, 973.