0.1 *m*, while that for $HReO_4$ drops below $HTcO_4$ at a somewhat larger concentration. The general similarity of the curves in Figure 1 is consistent with Raman line intensity measurements which indicate all three acids to be completely ionized to concentrations as high as 7 M. At higher concentrations, however, there appears to be evidence that condensation and hydration equilibria become increasingly important. The coloration of concentrated $HTcO_4$ and $HReO_4$ solutions suggest such changes or the formation of undissociated acid. With concentrated perrhenic acid the latter possibility appears to be excluded by qualitative Raman studies conducted by Ulbricht et al.[20] In addition to the known band frequencies at 972, 919, 367, and 330 cm^{-1} in $HReO_4$ solutions of 16 and 24 *m*, a new band at 850–854 cm^{-1} appears which may be assigned to a stretching mode of Re–O–Re. Condensation in acid pertechnetate and perrhenate solutions is known to occur, as dark red $Tc_2O_7 \cdot H_2O$ and yellow $Re_2O_7 \cdot 2H_2O$, respectively, are formed from them by evaporation.[21,22]

Registry No. $HClO_4$, 7601-90-3; $HTcO_4$, 14332-45-7; $HReO_4$, 13768-11-1.

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Correlations of Solvent-Exchange Activation Enthalpies

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The kinetics of solvent exchange on an $L_5Ni(solvent)^{2+}$ system, where L_5 is a five-coordinate Schiff base ligand, have been measured in *N,N*-dimethylformamide and acetonitrile, by proton NMR methods. These systems are compared to the corresponding $Ni(solvent)_6^{2+}$ complexes in order to assess the kinetic effect of the coordinated solvent molecules. Contrary to previous proposals it appears that the basicity of the solvent, as measured by Gutmann's donor numbers, does not have a significant influence on the solvent-exchange rates. A correlation of the activation enthalpy for exchange and crystal field and solvation effects is proposed.

Introduction

A correlation of the activation enthalpy for solvent exchange ($\Delta H^{\ddagger}_{ex}$) and solvent basicity has been proposed recently.[1] This correlation was based on the idea[2,3] that, if the mechanism is dissociative, i.e.

$$S_5MS^{2+} \rightarrow \{S_5M\} + S \xrightarrow{*S} S_5M*S \qquad (1)$$
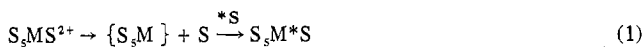
then, $\Delta H^{\ddagger}_{ex} \propto$ (acidity of S_5M) × (basicity of S) and (acidity of S_5M) $\propto$ (acidity of M^{2+}) – (basicity of S). If the solvent basicity is proportional to the Gutmann donor number (D_N), then

$$\Delta H^{\ddagger}_{ex} = aD_N - bD_N{}^2 \qquad (2)$$

where *a* and *b* are empirical fitting constants depending on M^{2+}. This equation was found to satisfactorily correlate 20 out of 23 available experimental values for nickel(II), cobalt(II), iron(II), and manganese(II).

The validity of the assumptions leading to eq 2 has not been tested, however. The present study presents such a test by studying solvent exchange on an (L_5NiS^{2+}) type complex,

where L_5 is a nonexchanging Schiff base ligand.[4] The relationships leading to eq 2 imply that the Lewis acidity of (L_5Ni^{2+}) should be independent of solvent since the acid contains no solvent molecules. Then it is predicted that

$$\Delta H^{\ddagger}_{ex} \propto D_N \qquad (3)$$

Two solvents, acetonitrile and *N,N*-dimethylformamide (DMF), have been studied because they have quite different and well-established D_N values (14.1 and 26.6, respectively). Therefore $\Delta H^{\ddagger}_{ex}$ in DMF is predicted to be almost twice as large as in acetonitrile.

Experimental Section

Materials. The $[Ni(pyDPT)OH_2](BF_4)_2$ and $[Ni(pyDPT)OH_2](PF_6)_2$ salts, where pyDPT represents the pentadendate ligand derived from 2-pyridinecarboxaldehyde and bis(3,3'-aminopropyl)-amine, were prepared by minor modifications of the method described by Spencer and Taylor.[4] Each compound was recrystallized twice from warm water. Anal. Calcd for $[Ni(pyDPT)OH_2](BF_4)_2$: C, 38.62; H, 4.50; N, 12.51. Found: C, 38.71; H, 4.55; N, 12.76. Calcd for $[Ni(pyDPT)OH_2](PF_6)_2$: C, 31.98; H, 3.73; N, 10.36. Found: C, 31.82; H, 3.75; N, 10.28. The compounds were characterized also

by comparison of infrared absorptions (in Nujol mulls) to results reported by Spencer and Taylor.[4]

Solvents were all distilled and stored in vacuo. Acetonitrile (Baker Analyzed) was refluxed for 2 h over P_2O_5 and then distilled onto 3A Linde molecular sieve and finally redistilled and stored over 3A molecular sieve. The N,N-dimethylformamide (Baker Analyzed) was dried first over barium oxide, distilled onto molecular sieve and silver nitrate, and then distilled twice and stored over molecular sieve.

Sample Preparations. Solvent was distilled under vacuum onto a weighed amount of the appropriate salt in a weighed sample tube, and the amount of solvent was determined by weight. When required an internal standard for shift measurements was added to the sample before it was sealed. The internal standards used were 1,4-dimethoxybenzene in acetonitrile and Me_4Si in N,N-dimethylformamide.

In acetonitrile five samples in the concentration range 0.033–0.150 m were studied. In N,N-dimethylformamide four samples in the concentration range 0.105–0.238 m were studied. In all cases the line broadening was found to be a linear function of the nickel(II) concentration.

Two samples in acetonitrile were prepared from material which had been dissolved in acetonitrile, and then the solvent was removed under vacuo and the procedure repeated three times. The infrared spectrum of this material showed that the water had been removed and replaced by CH_3CN (ν_{C-N} at 2300 cm^{-1}). These samples gave the same shifts, T_1's and T_2's, as samples in which the one H_2O had not been removed.

Instrumentation. The ^1H NMR spectra in N,N-dimethylformamide were recorded on Varian Associates A 56/60 and HA-100 spectrometers equipped with standard temperature controllers. Temperatures were determined from the peak separation in methanol and ethylene glycol standards at 60 MHz and with a copper–constantan thermocouple at 100 MHz.

Because of the limited solubility of all salts of Ni(pyDPT)$^{2+}$ in acetonitrile only very small line broadening could be observed in the continuous-wave ^1H NMR spectrum. Therefore relaxation times on this system were measured at 61 MHz by pulsed methods using a Bruker SXP 4-100 pulsed spectrometer and a 14-kG Varian electromagnet and V 3506 flux stabilizer. Transverse relaxation times (T_2) were measured by the standard Carr–Purcell–Meiboom–Gill[5,6] method and longitudinal relaxation times (T_1) were measured by the usual 180–τ–90 pulse sequence. Temperature was controlled by a Bruker B-ST 100/700 and measured with a copper–constantan thermocouple. Chemical shifts in acetonitrile could be measured on the Varian HA-100 spectrometer at 100 MHz.

Results

The solvent proton relaxation rates $T_2^{-1}{}_{\text{obsd}}$ and $T_2^{-1}{}_{\text{solv}}$, in the presence and absence of the paramagnetic species, respectively, were determined from π times the full width at half-height of the NMR signal in DMF and by the CPMG pulse method[5,6] in acetonitrile. The concentration-normalized effect of the paramagnetic ion can be expressed as

$$(T_{2p}P_M)^{-1} = P_M^{-1}(T_2^{-1}{}_{\text{obsd}} - T_2^{-1}{}_{\text{solv}}) \tag{4}$$

where P_M is the mole ratio of solvent bound to the paramagnetic ion to free solvent. An analogous definition is used for $(T_{1p}P_M)^{-1}$.

The temperature dependence of $(T_{2p}P_M)^{-1}$ is given by the equation developed by Swift and Connick,[7] with the addition of the outer-sphere contribution.[1,8] The lifetime of a solvent molecule in the coordination sphere of the metal ion (τ_M) depends on the activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) for exchange; the transverse relaxation rate of the coordinated solvent molecule (T_{2M}^{-1}) depends on C_M' and E_M; the outer-sphere relaxation rate (T_{2O}^{-1}) depends on C_O' and E_O. Explicit equations for these terms are given in recent references.[1,8]

The temperature dependence of the concentration-normalized chemical shift of the solvent resonance ($\Delta\omega_{\text{obsd}}/P_M$) has been given by Swift and Connick[7] in terms of τ_M, T_{2M}, and $\Delta\omega_M$, the chemical shift of the solvent nucleus in the first coordination sphere of the metal ion. A Curie law temperature dependence is assumed for $\Delta\omega_M$, i.e., $\Delta\omega_M = C_\omega/T$.
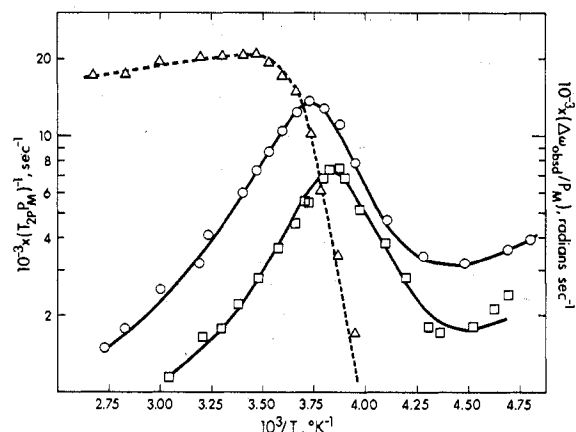

Figure 1. Temperature dependence of $-\log (T_{2p}P_M)$ at 60 MHz ($\square$) and 100 MHz ($\bigcirc$) and $\log (\Delta\omega_{\text{obsd}}/P_M)$ at 100 MHz ($\triangle$) for the solvent CH proton of Ni(pyDPT)$^{2+}$–DMF solutions.

Table I. Least-Squares Best-Fit Parameters for (Ni(pyDPT)DMF)(PF$_6$)$_2$ in N,N-Dimethylformamide

	$T_{2p}P_M^{-1}$		$\Delta\omega_{\text{obsd}}/P_M$	
	100 MHz	60 MHz	100 MHz	60 MHz
$\Delta H^{\ddagger}$, kcal mol^{-1}	11.74	11.76	11.74^a	11.76^a
$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	5.55	5.70	5.50	6.44
$10^{-4}C_M$, deg s^{-1}	6.22	3.21	6.22^a	3.21^a
$E_M = E_O$, kcal mol^{-1}	1.28	1.28^a	1.28^a	1.28^a
C_O/C_M	0.60^a	0.60^a		
$10^{-6}C_\omega$, rad deg	6.34	3.82	6.40	3.77
$10^{-6}A/\hbar$, rad s^{-1}	2.64	2.65	2.67	2.62

^{a} Held fixed at the value indicated during the least-squares fit.

Ni(pyDPT)(PF$_6$)$_2$ in N,N-Dimethylformamide. The results for this system are shown in Figure 1 except that the $(\Delta\omega_{\text{obsd}}/P_M)$ values at 60 MHz have been omitted for clarity. At low temperature $(T_{2p}P_M)^{-1}$ is controlled by T_{2O}^{-1} and then successively by τ_M^{-1}, $\tau_M\Delta\omega_M^2$, and T_{2M}^{-1} as the temperature increases.

The results were analyzed initially by calculating C_ω from the high-temperature limit of $(\Delta\omega_{\text{obsd}}/P_M)$ and the ratio (C_O/C_M) from estimates of interaction distances[10] and expressions for T_{2M}^{-1} given elsewhere.[11] Then with C_ω and (C_O/C_M) fixed, a nonlinear least-squares analysis gave preliminary values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, C_M, and $E_O = E_M$, which then were used to fit the $(\Delta\omega_{\text{obsd}}/P_M)$ results to obtain a best value of C_ω.

It was necessary to fix (C_O/C_M) and hold $E_M = E_O$ because neither the T_{2O}^{-1} nor T_{2M}^{-1} contributions are separately well defined. These strictures are thought to be reasonable because the very short electron spin relaxation time of nickel(II) will control both T_{2M}^{-1} and T_{2O}^{-1}. In addition the effect of these parameters on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is minor. For example varying (C_O/C_M) between 0.32 and 0.85 changes $\Delta H^{\ddagger}$ by less than 0.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ by less than 2 cal mol^{-1} deg^{-1}.

With the limitations noted above the fitting process was repeated to optimize the self-consistency between the four independent data sets. The results are summarized in Table I.

With the usual equations[11,12] and reasonable interaction distances and correlation times it is possible to account for the magnitude and frequency dependence of T_{2M}^{-1} and T_{2O}^{-1}. For example with $r_i = 3.9$ Å, $d_O = 5.75$ Å, $\tau_c = 4.5 \times 10^{-11}$ s, $C_e = 8 \times 10^{22}$ s^{-1}, and $(A/\hbar) = 2.6 \times 10^6$ rad s^{-1}, then at 100 MHz the dipolar and scalar contributions to T_{2M}^{-1} are 1.54 $\times 10^3$ and 257 s^{-1}, respectively, to give a total of 1.80 $\times 10^3$ s^{-1} compared to the experimental value of 1.81 $\times 10^3$ s^{-1}. The calculated outer-sphere contribution is 934 s^{-1} compared to the least-squares value of 1.08 $\times 10^3$ s^{-1}. At 60 MHz the

Table II. Least-Squares Best-Fit Parameters for
$(Ni(pyDPT)CH_3CN)(PF_6)_2$ in Acetonitrile

	$(T_{2p}P_M)^{-1}$ 61 MHz	$(T_{1p}P_M)^{-1}$ 61 MHz	$\Delta\omega_{obsd}/P_M$ 100 MHz
$\Delta H^{\ddagger}$, kcal mol^{-1}	11.67		11.67^a
$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	10.30		10.33
$10^3 C_M$, deg s^{-1}	5.07	3.42	12.5^a
$E_M = E_O$, kcal mol^{-1}	1.68^a	1.68	1.68^a
C_O/C_M	0.688^a	0.688^a	
$10^{-6}C_\omega$, rad deg	-3.64		-6.20
$10^{-6}A/\hbar$, rad s^{-1}	-2.53		-2.59

^{a} Held fixed at the value indicated during the least-squares fit.

Table III. Summary of Solvent Exchange Kinetic Results

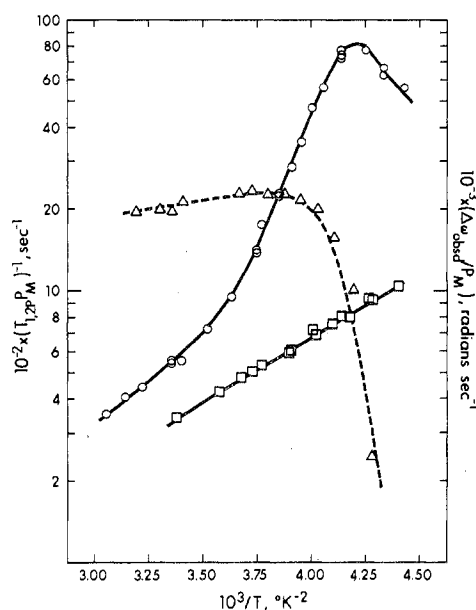| Complex	$k(25\ °C)$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
Ni(pyDPT)DMF$^{2+\ a}$	2.7×10^5	11.7^d	5.6^d
Ni(pyDPT)NCCH$_3$$^{2+\ a}$	3.0×10^6	11.7^d	10.3^d
Ni(DMF)$_6$$^{2+\ b}$	3.8×10^3	15.0	8
Ni(NCCH$_3$)$_6$$^{2+\ c}$	2.7×10^3	15.0	8.5

^{a} This work. ^{b} N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).
^{c} I. D. Campbell, J. P. Carver, R. A. Dwek, A. J. Nummetin, and
R. E. Richards, *Mol. Phys.*, **20**, 913 (1971). ^{d} Uncertainties on
these values are difficult to establish because they result from anal-
ysis of several independent data sets but with some parameters
fixed. In general data sets contained 50–60 points, and 95% con-
fidence limits on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were about ±1 kcal mol^{-1} and ±4
cal mol^{-1} deg^{-1}, respectively.

calculated T_{2M}^{-1} and T_{2O}^{-1} are 936 and 510 s^{-1}, respectively,
compared to the least-squares values of 934 and 560 s^{-1},
respectively.

Ni(pyDPT)(PF$_6$)$_2$ in Acetonitrile. The temperature de-
pendence of $(T_{2p}P_M)^{-1}$ and $(T_{1p}P_M)^{-1}$ at 61 MHz and
$(\Delta\omega_{obsd}/P_M)$ at 100 MHz for this system is shown in Figure
2. The $(T_{1p}P_M)^{-1}$ values provide a well-defined value of E_M
which could not be obtained from the $(T_{2p}P_M)^{-1}$ results because
the $(T_{2M})^{-1}$ contribution to the latter is not well defined. The
difference between $(T_{2M})^{-1}$ and $(T_{1M})^{-1}$ should be due to the
contribution of the scalar relaxation mechanism to the former.
Because of the low solubility of the complex in acetonitrile only
maximum shifts of about 18 Hz at 100 MHz could be ob-
served. Shift measurements at 60 MHz were not attempted.

Analysis of the results by a procedure analogous to that used
for the DMF system gave the results summarized in Table II.
With E_M fixed the value of (C_O/C_M) was varied from 0.36
to 3.1 without significant effect on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The only
effect was to change C_M so that $(C_O + C_M)$ remained nearly
constant.

It should be noted that the T_{2M}^{-1} and T_{1M}^{-1} values are
consistent with values calculated using the usual equations.[12]
With inner- and outer-sphere interaction distances of 5.3 and
10.0 Å, respectively, and a rotational correlation time of 5 ×

Figure 2. Temperature dependence of $-\log (T_{2p}P_M)$ (O) and $-\log (T_{1p}P_M)$ (□) at 61 MHz and log $(\Delta\omega_{obsd}/P_M)$ at 100 MHz (△) for the solvent CH_3 protons of Ni(pyDPT)$^{2+}$–acetonitrile solutions.

10^{-11} s and C_e of 6.5×10^{22} s^{-1}, then the dipolar and scalar
contributions to T_{2M}^{-1} are 172 and 113 s^{-1} and T_{2O}^{-1} is 196
s^{-1}. This total of 480 s^{-1} may be compared to the least-squares
best fit value of 494 s^{-1} at 25 °C. Since the scalar mechanism
does not contibute to T_{1M}^{-1}, the latter is calculated to be 368
s^{-1} compared to the measured value of 330 s^{-1} at 25 °C. It
should be noted that these same parameters predict that T_{2M}^{-1}
should be 2.15 times larger at 100 MHz than at 61 MHz. The
C_M value was adjusted accordingly in fitting the $(\Delta\omega_{obsd}/P_M)$
values. This correction is consistent with the $(T_{2p}P_M)^{-1}$ results
in DMF at 60 and 100 MHz.

Discussion

The results of this study and previous work on nickel(II)
in acetonitrile and DMF are summarized in Table III. To
make a long story short, the present results do not conform
to expectations based on eq 3. The activation enthalpies for
DMF and acetonitrile exchange with Ni(pyDPT)$^{2+}$ are almost
equal, while eq 3 predicts that the value in DMF should be
26.6/14 times larger than that in acetonitrile.

Several factors could be contributing to the failure of eq 3.
First, it might be argued that steric factors in the [Ni-
(pyDPT)(DMF)]$^{2+}$ complex lower the activation energy for
DMF dissociation. However, models indicate that the –N-
(CH$_3$)$_2$ does not interact with the polyamine ligand and the
formyl H atom can easily fit between two cis amine groups.
Secondly, perhaps the donor numbers are not the appropriate
measure of basicity. This has been mentioned by Coetzee and
Karakatsanis,[13] and certainly the donor numbers for water and

Table IV. Crystal Field–Solvation Correlation of Solvent Exchange Activation Enthalpies

	Solvent data		Metal data^a			
	Dq^c	b_S^c	Ni(II) $c_M^b = 4.26$ $a_M^b = 4.26$	Co(II) $c_M = 3.31$ $a_M = 3.16$	Fe(II) $c_M = 2.82$ $a_M = 2.51$	Mn(II) $c_M = 1.80$ $a_M = 1.88$
NH$_3$	3.10	1.63	11.0 (14.8)^e	11.2 (11.9)	(10.4)	8.0 (7.3)
CH$_3$CN	3.03	1.52	15.0 (14.4)	11.4 (11.5)	9.7 (10.1)	7.3 (7.0)
DMF	2.50	4.64	15.0 (15.3)	13.6 (12.9)	11.7 (11.7)	8.9 (9.1)
H$_2$O	2.46	3.58	14.4 (14.1)	11.9 (11.7)	7.7 (10.5)^e	7.9 (8.0)
CH$_3$OH	2.43	5.44	15.8 (15.8)	13.8 (13.5)	12.0 (12.3)	6.2 (9.8)^e
Me$_2$SO	2.25	4.12	13.0 (13.7)	12.2 (11.6)	11.3 (10.5)	7.4 (8.2)

^{a} Values calculated from eq 7 are in parentheses; experimental values are taken from ref 1 where original references are given. ^{b} Units are
(kcal mol^{-1})$^{1/2}$. ^{c} Units are kcal mol^{-1}. ^{d} Based on values given by J. Reedijk et al., *Recl. Trav. Chim. Pays-Bas*, **87**, 129 (1968); **88**, 1095
(1969). ^{e} These values were not used in the final fitting of the data to eq 7.

methanol have been questioned by others.[14,15] However there seems to be little question that DMF is a better donor than acetonitrile and even the preparative and handling properties of the nickel(II) complexes are qualitatively consistent with the greater basicity of DMF.

It must be concluded that the basicity of the nonreacting ligands is only a minor contributor to the magnitude of the activation enthalpy for solvent exchange, rather than a direct factor as implied in eq 2. Even the change to the much more basic amine ligand only lowers $\Delta H^{\ddagger}$ by ~4 kcal mol^{-1}. But the basicity of the exchanging group itself does not explain why acetonitrile and DMF have similar $\Delta H^{\ddagger}$ values. It appears that simple correlations with donor numbers[1,14,15] must be largely fortuitous.

For reasons outlined previously[1] it would still be very useful to have some empirical correlation of $\Delta H^{\ddagger}_{ex}$ values for solvent exchange. Earlier crystal field approaches to this problem[16,17] were abandoned because $\Delta H^{\ddagger}_{ex}$ did not parallel Dq for different solvents. However, the combination of a crystal field and solvation contribution[18] might be satisfactory, i.e.

$$\Delta H^{\ddagger}_{ex}(M-S) = a_M Dq_{M-S} + b_S \qquad (5)$$

where a_M is a constant for the metal ion or for a particular d electronic configuration, and b_S is dependent only on the solvent. Unfortunately Dq_{M-S} depends on both solvent and metal and is known generally only for nickel(II) and cobalt(II). However, the spectrochemical series indicates that to a good approximation

$$Dq_{M-S} = g_M Dq_{Ni-S} \qquad (6)$$

so that

$$\Delta H^{\ddagger}_{ex}(M-S) = c_M Dq_{Ni-S} + b_S \qquad (7)$$

where $c_M = a_M g_M$. A least-squares fit of the available data to eq 7 gave the results summarized in Table IV. Only the values for nickel(II) in ammonia, iron(II) in water, and manganese(II) in methanol are not correlated satisfactorily by eq 7.

It seems reasonable to expect that the a_M values[19] should be similar to those calculated from crystal field theory[16,17] for the different electronic configurations. In fact for nickel(II), cobalt(II), and iron(II) the a_M values are 0.875 ± 0.01 times the theoretical values given by Breitschwerdt[17] for a square-pyramidal intermediate. This ratio would predict that

a_M should be 2.45 for manganese(II) compared to the observed value of 1.88. Although g_{Mn} is somewhat uncertain, it seems unlikely that it is as small as 0.74 as required to obtain a_{Mn} = 2.45 from the best-fit c_M value. Further speculation on this point seems unwarranted at this time.

The values of b_S might be expected to correlate with some bulk solvent property, but we have not found any property for which acetonitrile and ammonia are together at one end of the scale and methanol is at the other end. It has been noted that for ammonia, DMF, water, and dimethyl sulfoxide the enthalpy of evaporation of the solvent equals 2.9 ± 0.4 times b_S. The possible significance of such a correlation has been discussed by Bennetto and Caldin.[20] To fit this correlation the b_S values of acetonitrile and methanol would have to be 2.65 and 3.1, respectively.

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(10) See ref 8, Table II.
(11) See ref 8, eq 4 and 6, for explicit equations and original references.
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