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^{27}Al NMR as a Test of Models of Ionic Solvation

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^{27}Al NMR is used to investigate the preferential solvation of Al^{3+} in a DMF–Me_2SO mixed-solvent system. The results are viewed primarily in terms of the Covington model of ionic solvation. The ^{27}Al spectrum is in the slow-exchange limit at room temperature, which permits the evaluation of several fundamental assumptions for this model. The effect of an inert diluent on preferential solvation is also reported.

Introduction

Because of the solvent dependence of the metal nucleus chemical shift for solvated metal ions, NMR studies of these nuclides have long been used as a direct probe of cationic solvation. These studies are predicated on the assumption that the metal nucleus chemical shift in a binary mixed-solvent system is a direct measure of the preferential solvating ability of the two component solvents. However, these studies have generally been limited to monovalent cations such as ^{7}Li, ^{23}Na, ^{133}Cs, and ^{205}Tl, although a few studies of other cations have been reported.[1,2] The monovalent cation solvates are all in the rapid-exchange limit at room temperature, and only a single averaged resonance is observed in the metal nucleus NMR spectrum for these studies. The chemical shift of this resonance is therefore a weighted average of the chemical shifts of all species present in solution.

A number of approaches have been taken to quantify the competitive solvation in a binary mixed-solvent system. Frankel, Langford, and Stengle[3] introduced the concept of the equisolvation point, which is simply the bulk solvent composition for which the metal ion chemical shift lies midway between the shifts in the pure solvents. Assuming that the chemical shift of the metal nucleus is linearly related to the composition of the primary solvation sphere, the equisolvation point would represent the bulk solvent composition at which both solvents participate equally in the cation solvation sphere. Popov et al.,[4] for example, used the equisolation point model to characterize solvent competition for Na^+ in a series of nonaqueous solvents using ^{23}Na NMR. Shortly afterward, Covington et al.[5-7] proposed a model that describes competitive solvation in terms of n successive equilibria such as shown in eq 1, where n is the ionic solvation number. The Covington model

$$M^+X_{n-i+1}Y_{i-1} + Y \overset{K_i}{\rightleftharpoons} M^+X_{n-i}Y_i + X \qquad (1)$$

has been applied by Dechter and Zink[8] and by Briggs and Hinton[9] to ^{205}Tl solvation studies for nonaqueous solvents as well as by Greenberg and Popov[10] to ^{23}Na studies. In its simplest form, the model treats the successive equilibria in a statistical fashion. In other words, MX_4Y_2 can lose solvent X from four sites while MX_3Y_3 can lose solvent Y from three sites and so $K_3 = {}^4/_3K^{1/n}$, where K is the overall equilibrium constant for complete exchange of X by Y. Implicit in this model are several assumptions: (1) the statistical relation between K_i and K; (2) a solvation number independent of solvent composition; (3) individual K_i values independent of solvent composition; (4) intrinsic shifts for individual solvate species linearly related to the number of solvent Y molecules in the primary solvation sphere. This model has been extended by Covington et al. to circumvent the first two assumptions,[6,7] but the validity of the last two assumptions for these systems is not clear.

The Al^{3+} cation has a higher surface charge density than the monovalent cations, and the solvate complexes can be sufficiently long lived at room temperature to lie in the slow-exchange limit for the ^{27}Al NMR spectrum. This was first demonstrated by Canet et al.[11] for mixtures of H_2O and $(MeO)_3PO$ and later by Delpuech et al.[12] for several organophosphorus solvates. Schneider[13] obtained ^{27}Al spectra for DMF–Me_2SO binary mixtures and with nitromethane as an inert diluent. Resonances arising from seven solvate and mixed-solvate species could be resolved. The chemical shifts were found to be nonliner with substitution, thus violating assumption 4 above, but no attempt was made to quantify the solvent competition process. In a related study, Gudlin and Schneider[14] looked at ligand redistribution when $Al(DMF)_6{}^{3+}$ and $Al(Me_2SO)_6{}^{3+}$ are dissolved in different proportion in nitromethane. A pairwise additivity model was used to characterize the chemical shifts for the mixed solvates, but geometric isomers still could not be resolved, and the system could not be analyzed in terms of a solvent competition process. The equilibrium constants for ligand redistribution, represented by eq 2, were determined and were found not to fit a random model.

$$[MX_{n-i+1}Y_{i-1}]^{3+} + [MX_{n-i-1}Y_{i+1}]^{3+} \rightleftharpoons 2[MX_{n-i}Y_i]^{3+} \qquad (2)$$

We have investigated the ^{27}Al NMR spectra at a higher magnetic field strength for the DMF–Me_2SO solvent system. The results are viewed primarily in terms of the Covington model of preferential solvation and its implicit assumptions outlined above. The ^{27}Al chemical shifts of the solvate complexes are shown to be well represented by a cis pairwise additivity model. Isomer resonances are clearly observable under certain conditions. ^{27}Al relaxation times for the various solvate complexes are well represented by a point charge electrostatic model and serve to unambiguously distinguish the geometric isomers. The stepwise solvent displacement equilibrium constants are evaluated and compared with the results from the Covington model. The effect of an inert diluent on preferential solvation is determined.

Experimental Section

Anhydrous $[Al(DMF)_6](ClO_4)_3$ was prepared by first refluxing 1.5 g of $Al(ClO_4)_3{\cdot}9H_2O$ in 4.5 g of freshly dried and distilled triethyl orthoformate for about 1 h. This solution was allowed to cool and was diluted with acetonitrile. Addition of DMF caused precipitation of the desired complex. The precipitate was washed several times with ether. Solvents were of reagent grade and were dried and distilled with use of standard methods and were stored over 4A molecular sieves.

^{27}Al NMR spectra were obtained at 52.13 MHz with a Nicolet NT-200 NMR spectrometer. Samples were contained in a 12-mm NMR tube with a coaxial 5-mm tube used to contain 0.10 M $Al(ClO_4)_3$ in D_2O as an ^{27}Al chemical shift reference and ^{2}H lock solvent. Relaxation times were measured with use of the inversion-recovery method and were an-

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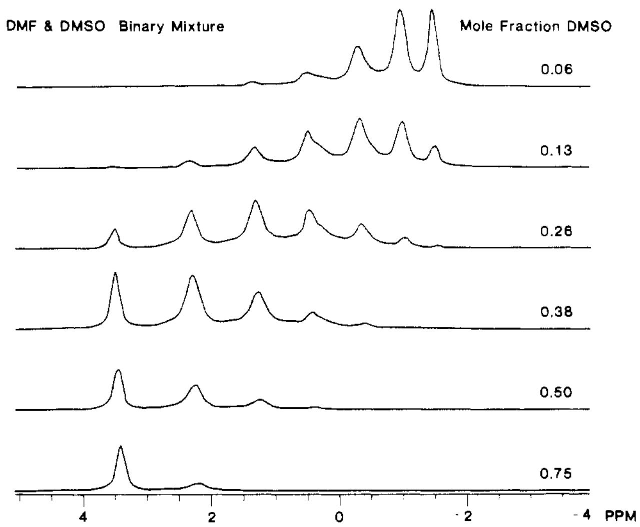

Figure 1. ^{27}Al NMR spectra at 20 °C for several binary mixtures of DMF and Me_2SO. The mole fraction of Me_2SO is indicated.

alyzed with use of a three-parameter nonlinear least-squares fitting routine. Equilibrium constants were determined from relative peak areas. The relative peak areas were obtained by computer integration when the resonances were well resolved and by Lorentizian curve analysis when resonances were incompletely resolved. The ^{27}Al data were fit to the Covington solvation model with use of a generalized three-parameter nonlinear leasts-squares procedure. The three parameters used in the procedure are the ^{27}Al chemical shifts in both pure solvents and the overall $K^{1/n}$.

Results and Discussion

The ^{27}Al NMR spectra for several binary mixtures of DMF and Me_2SO are shown in Figure 1. At room temperature any exchange process such as that represented by eq 1 is clearly in the slow-exchange limit. Seven ^{27}Al resonances are resolvable, representing the species $[Al(DMF)_{n-i}(Me_2SO)_i]^{3+}$ for i = 0–6 from high field to low field. The resonances can be tentatively assigned on the basis of the regular progression in relative peak intensities as the solvent mixtures become Me_2SO rich or Me_2SO poor. Confirming evidence will be described below. All the solvate resonances appear in the octahedral region of the ^{27}Al spectrum;[1] therefore, this system satisfies assumption 2 listed above, that the solvation number for this system is independent of solvent composition. Since the solvates are octahedral species, those for i = 2–4 should exhibit geometric isomerism. Closer inspection of the resonance near 0.3 ppm indicates an asymmetric line shape due to the incompletely resolved overlap of the *fac* and *mer* geometric isomers of $[Al(DMF)_3(Me_2SO)_3]^{3+}$. The cis and trans isomers of the neighboring resonances are not resolvable due to some slight degree of exchange broadening for all resonances, the greater natural line width of the trans resonances (see below), and the low abundances of the trans isomers. A random distribution model for isomeric abundance predicts a cis:trans ratio of 4:1 and a *fac*:*mer* ratio of 3:2.

The chemical shifts of the solvate resonances are only slightly dependent on the bulk solvent compositon. All resonances exhibit a sufficiently small and linear solvent-dependent shift to permit extrapolation of the shifts for each solvate complex to zero mole fraction Me_2SO, and these shifts are listed in Table I. From these extrapolated chemical shifts as well as from the appearance of the spectra in Figure 1, it is clear, as had been pointed out earlier,[14] that the chemical shifts for the individual solvate complexes do not depend in a linear fashion on the composition of the primary solvation sphere. There is a significant increase in the separation of the resonances as the coordination sphere becomes Me_2SO rich, confirming the earlier results[14] and clearly indicating that assumption 4 listed above is not met by this system. A pairwise additivity model was proposed by Vladimiroff and Malinowski[15] to describe nonlinear, substituent-induced chemical shifts for tetrahedral species and was applied successfully to ^{27}Al chemical shifts for four-coordinate mixed tetrahaloaluminates.[16] The justification for the pairwise model arises from a linear correction to the wave function of each substituent group about the central metal ion due to the presence of neighbor groups. When the correction is small, e.g. the changing substituent is remote from the central atom, a linear additivity can be observed as a limit. The pairwise model was first applied to six-coordianate complexes by Kidd and Spinney[17] in their treatment of mixed hexahaloniobates. In their approach, the central metal ion chemical shift for octahedral complexes involving two different ligands X and Y can be described in terms of three empirical parameters (η_{XX}, η_{XY}, and η_{YY}) characterizing the various cis pairwise interactions along an edge of the octahedron. For example, the ^{27}Al shift for *fac*-$[AlX_3Y_3]^{3+}$ is given by $3\eta_{XX} + 6\eta_{XY} + 3\eta_{YY} + C$, where C is the constant of the multiple regression analysis. However, an alternative pairwise model was proposed by Tarasov et al.[18] and characterizes the trans pairwise interactions, again in terms of three empirical parameters. The above complex with the trans model would have a shift given by $3\eta_{XY} + C$. One major difference in the results of the two models is the prediction of upfield positions for the trans isomers relative to those of the cis and for those of the *mer* isomer relative to those of the *fac* when the cis pairwise model is used while the trans pairwise model predicts downfield relative positions for the same isomers. The extrapolated shifts for peaks 3, 4, and 5 are tentatively assigned to *cis*-$[Al(DMF)_4(Me_2SO)_2]^{3+}$, *fac*-$[Al(DMF)_3(Me_2SO)_3]^{3+}$, and *cis*-$[Al(DMF)_2(Me_2SO)_4]^{3+}$ from high field to low field, respectively, on the basis of the anticipated lower abundance and greater natural line width for the other geometric isomer of each pair. Confirming evidence is presented below. The results of fitting the extrapolated chemical shifts to the two models are shown in Table I. The cis pairwise model succeeds in fitting the chemical shifts to within ±0.02 ppm of the observed values. The trans and *mer* isomers are predicted to lie 0.18 ppm to ***high*** field of the cis and *fac* isomers, respectively. The trans pairwise model is less successful in characterizing the chemical shifts with an average deviation of ±0.08 ppm. The trans and *mer* isomers are predicted to lie 0.40 ppm to *low* field of the cis and *fac* isomers. If the trans isomers could be observed and all the isomers confidently assigned, the two pairwise models could be evaluated.

Table I. ^{27}Al Chemical Shifts of Mixed Solvate Complexes in DMF-Me_2SO Binary Mixtures

solvate complexes	shift, ppm: extrapolated[a]	cis model[b]	trans model[c]
$[Al(DMF)_6]^{3+}$	−1.63	−1.61	−1.68
$[Al(DMF)_5(Me_2SO)]^{3+}$	−1.12	−1.14	−1.05
cis-$[Al(DMF)_4(Me_2SO)_2]^{3+}$	−0.46	−0.48	−0.42
fac-$[Al(DMF)_3(Me_2SO)_3]^{3+}$	0.33	0.35	0.21
cis-$[Al(DMF)_2(Me_2SO)_4]^{3+}$	1.17	1.18	1.24
$[Al(DMF)(Me_2SO)_5]^{3+}$	2.17	2.19	2.27
$[Al(Me_2SO)_6]^{3+}$	3.39	3.37	3.30

[a] Linear regression of solvent-dependent shift; ^{27}Al shift reference is 0.10 M $Al(ClO_4)_3$ in D_2O. [b] Parameters from multiple regression analysis: $\eta_{XX} = -3.42$, $\eta_{XY} = -3.30$, $\eta_{YY} = -3.00$, $C = 39.37$. [c] Parameters from multiple regression analysis: $\eta_{XX} = -0.36$, $\eta_{XY} = 0.27$, $\eta_{YY} = 1.300$, $C = -0.60$.

Better resolution in the ^{27}Al spectrum should be obtainable by slowing the rate of exchange or by decreasing the rotational correlation times for the solvate complexes. Both effects can be achieved by using an inert diluent; when the 0.260 mole fraction solution is diluted by an equal or greater volume of nitromethane, the resonances narrow considerably. A comparison of the ^{27}Al spectra for the binary mixture and a 1:3 v/v dilution of this solution

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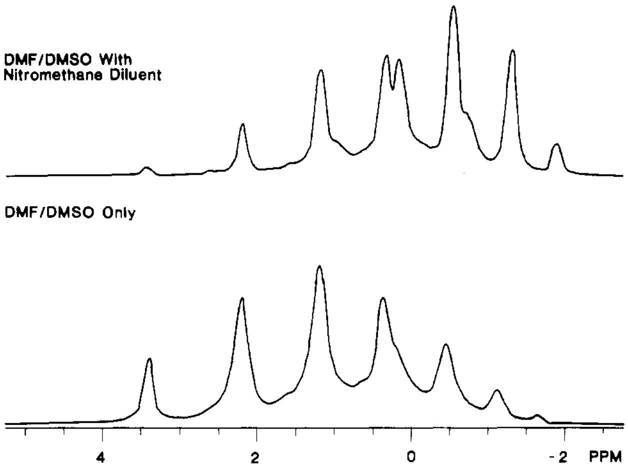

Figure 2. ^{27}Al spectra for a DMF–Me$_2$SO binary solvent mixture with mole fraction Me$_2$SO of 0.260 and for the same solution diluted 1:3 v/v by nitromethane.

Table II. ^{27}Al Relaxation Rates for Mixed-Solvate Complexes in Nitromethane[a]

solvate complex	relative g_ϕ^2 [b]	^{27}Al relaxation rate, s^{-1}
$[\mathrm{Al(DMF)_6}]^{3+}$	0	15
$[\mathrm{Al(DMF)_5(Me_2SO)}]^{3+}$	1.0	18
cis-$[\mathrm{Al(DMF)_4(Me_2SO)_2}]^{3+}$	1.8	18
trans-$[\mathrm{Al(DMF)_4(Me_2SO)_2}]^{3+}$	4.0	29
fac-$[\mathrm{Al(DMF)_3(Me_2SO)_3}]^{3+}$	0	13
mer-$[\mathrm{Al(DMF)_3(Me_2SO)_3}]^{3+}$	3.0	30
cis-$[\mathrm{Al(DMF)_2(Me_2SO)_4}]^{3+}$	1.8	19
trans-$[\mathrm{Al(DMF)_2(Me_2SO)_4}]^{3+}$	4.0	
$[\mathrm{Al(DMF)(Me_2SO)_5}]^{3+}$	1.0	19
$[\mathrm{Al(Me_2SO)_6}]^{3+}$	0	15

[a] Solution of 0.05 M $[\mathrm{Al(DMF)_6}](\mathrm{ClO_4})_3$ in 3:1 v/v DMF:Me$_2$SO (mole fraction Me$_2$SO 0.260) diluted 1:3 with nitromethane.
[b] Electric field gradient tensor invariant relative to the value calculated for $[\mathrm{Al(DMF)_5(Me_2SO)}]^{3+}$.[18]

by nitromethane is given in Figure 2. The isomer resonances are now clearly evident.

The assignment of the isomer resonances can be confirmed by measuring the ^{27}Al spin–lattice relaxation times for the solvate species. The ^{27}Al relaxation should be predominantly quadrupolar at room temperature, which makes it possible to estimate the relative relaxation rates for the solvate complexes from a calculation of the electric field gradients (efg) across the Al^{3+} nucleus. Tarasov et al.[18] used the point-charge model of Valiev and Zaripov[19] to calculate the efg for mixed haloniobate complexes, and Wehrli[20] has applied this approach to chloroaluminate complexes in acetonitrile. Following the approach of Tarasov et al., we show the efg tensor invariant, g_ϕ^2, relative to that for $[\mathrm{Al(DMF)_5(Me_2SO)}]^{3+}$ in Table II. Assuming identical correlation times for the solvate complexes, the relative relaxation rates should exhibit a similar trend. The relative values of g_ϕ^2 clearly distinguish the isomers; the cis isomers should have slower relaxation rates (and narrower lines) than the trans isomers. The *fac* isomer should have quite a slow relaxation rate—comparable to those for the homoleptic solvate complexes. The ^{27}Al quadrupolar relaxation rates are listed in Table II, and the agreement with the relative g_ϕ^2 is reasonably good. The relaxation rates observed for $[\mathrm{Al(Me_2SO)_6}]^{3+}$, $[\mathrm{Al(DMF)_6}]^{3+}$, and *fac*-$[\mathrm{Al(DMF)_3(Me_2SO)_3}]^{3+}$, where g_ϕ^2 is predicted to be zero, probably arise from either contributions of the external solvation sphere to the static efg or collisionally induced asymmetric vibrations in the primary solvation sphere. But the identity of the geometric isomers is clearly established by the relaxation study. The fact that the trans and *mer* isomers lie to high field of the respective cis and *fac* isomers confirms the success of the cis pairwise additivity model over the trans model for these ^{27}Al solvate complexes.

Table III. Solvent Exchange Equilibrium Constants for DMF-Me$_2$SO Binary Mixtures

mole fraction Me$_2$SO	K_1	K_2	K_3	K_4	K_5	K_6	$K^{1/6}$
0.066			3.68	5.58	13.2	19.0	
0.132		2.10	2.90	5.73	15.2	17.3	
0.260	0.81	2.01	3.03	6.17	10.7		
0.387	1.00	1.84	3.64	6.73			
0.510	0.83	2.14					
0.750	1.18						
av K_i	0.96	2.0	3.4	5.6	13	18	4.5
statistical K_i[a]	0.75	1.8	3.4	6.0	11	27	4.5

[a] Calculated by using $K^{1/6}$ and eq 4; see text.

The Covington solvation model[5-7] in its simplest form represents competetive solvation by the series of successive equilibria given in eq 1. The Al^{3+} cation in a DMF and Me$_2$SO mixture would be represented by eq 3. If these equilibria are to form a reliable

$$[\mathrm{Al(DMF)}_{n-i+1}(\mathrm{Me_2SO})_{i-1}]^{3+} + \mathrm{Me_2SO} \overset{K_i}{\rightleftharpoons} [\mathrm{Al(DMF)}_{n-i}(\mathrm{Me_2SO})_i]^{3+} + \mathrm{DMF} \quad (3)$$

basis for a model of solvation, then the individual equilibrium constants K_i must be relatively independent of the bulk solvent composition. ^{27}Al NMR provides a unique way to test this assumption. The equilibrium constants K_1–K_6 for eq 3 were determined for the binary solvent mixtures shown in Figure 1 and are contained in Table III. The equilibria represented by K_2–K_5 involve species existing as geometric isomers; however, no differentiation among isomers is included in the current analysis of these equilibria. The intensities for each isomer pair are summed into a combined peak area and treated as a unit. The overall $K^{1/n}$ for solvent exchange is calculated as the sixth root of the product of the individual experimentally determined K_i's.[5] Given this overall equilibrium constant, a set of K_i's can be calculated on the basis of the statistical treatment[5] in eq 4. The individual

$$K_i = [i/(n - i + 1)]K^{1/n} = [i/(7 - i)]K^{1/6} \qquad (4)$$

experimental K_i values listed in Table III are essentially independent of bulk solvent composition. There is no regular trend with solvent composition; there is merely random scatter. The overall average deviation within all sets of K_i values is about 12%. This consistency is actually quite good, given the wide change in the area ratios of the various pairs of resonances as can be seen in Figure 1. Therefore, it is possible to talk about meaningful stoichiometric equilibrium constants for the individual solvent-exchange steps and assumption 3 in Covington's approach seems valid.

When the average observed K_i's are compared to the K_i's calculated statistically, reasonable agreement is found except at the extremes (i.e. K_1 and K_6), where the deviation exceeds the overall experimental average deviation of about 12%. The overall equilibrium constant, $K^{1/6} = 4.5$, indicates preferential solvation by Me$_2$SO over DMF, which agrees with Schneider's[13] qualitative evaluation on the basis of solvation number. The preferential solvation of Al^{3+} by Me$_2$SO over DMF is consistent with the higher donor number for Me$_2$SO (29.8) vs. that of DMF (26.6).[21] Dechter and Zink[8] had reported preferential solvation of Tl$^+$ by Me$_2$SO over DMF, and a $K^{1/n}$ value of 3.6 can be calculated from their data. However, the effect of cation radius or cation charge density on the degree of preferential solvation is not clear.

The ^{27}Al NMR results provide another means of evaluating the Covington model. If the chemical shifts for the solvate res-

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Table IV. Effect of Inert Diluent on Solvation Equilibria

soln[a]	K_1	K_2	K_3	K_4	K_5	K_6	$K^{1/6}$
binary mixtures (av)	0.96	2.0	3.4	5.6	13	18	4.5
acetonitrile							
1:1	0.84	1.6	3.0	3.8	6.1		(3.5)[b]
1:3	0.62	1.3	2.2	3.1	5.2	16	2.8
nitromethane							
1:1	0.46	1.1	1.8	3.4	5.3	14	2.5
1:3	0.52	0.90	2.0	2.7	5.7	12	2.4
1:9	0.29	0.82	1.4	2.4	4.9	10	1.9

[a] Dilution indicated is v/v of the binary mixture with mole fraction Me_2SO of 0.260. [b] Calculated by assuming a K_6 value of 16–18.

onances are weighted by the peak areas, the weighted average chemical shifts can be fitted with the mole fraction data to eq 5,

$$K^{1/m} = \frac{\delta}{\delta_p - \delta} \frac{1 - \chi_p}{\chi_p} \tag{5}$$

given by Covington et al.[5] for labile systems. For the specific system being evaluated here, δ is the weighted average observed ^{27}Al chemical shift relative to the shift of $[Al(DMF)_6]^{3+}$ for one of the solutions in Figure 1; χ_p is the mole fraction of Me_2SO for that solution, and δ_p is the chemical shift separation between $[Al(DMF)_6]^{3+}$ and $[Al(Me_2SO)_6]^{3+}$. Such a fit of the ^{27}Al data gives $K^{1/6} = 3.1$. The standard deviation in the shift for the fit is 0.05 ppm, which is about 1% of the overall chemical shift range. The poor agreement between the values of $K^{1/6}$ determined by direct means and by the Covington model probably reflects the significance of assumption 4 inherent in eq 5 that the chemical shifts of the solvate complexes are linearly related to the number of Me_2SO molecules in the Al^{3+} solvation sphere. As discussed above, the other assumptions of the Covington model all seem to be reasonably well met by this system.

In addition to the effect on the line widths, dilution of the binary mixtures by an inert solvent such as nitromethane or acetonitrile has a profound effect on the solvation equilibrium. As seen in Figure 2, there is a clear change in the distribution of peak intensities upon dilution. Such an effect had been noted qualitatively by Schneider,[13] who indicated that when the binary mixture was diluted by nitromethane or propylene carbonate, no preferential solvation was observed. The individual and overall *K*'s have been determined for a number of acetonitrile and nitromethane dilutions of the 0.260 mole fraction Me_2SO binary mixture and are collected in Table IV. These solutions represent simple v/v dilutions of the binary mixture by the solvent and by the amount indicated. A general decrease is found for the $K^{1/6}$ values for the ternary diluent systems. Such a decrease indicates a corresponding decrease in the preferential solvating ability of Me_2SO relative to that of DMF. However, preferential solvation by Me_2SO is still indicated since the $K^{1/6}$ values are all greater than unity. Nitromethane appears to have a greater effect on $K^{1/6}$ for a given dilution than does acetonitrile. The origin of the reduction in the preferential solvating ability of Me_2SO by the presence of the inert diluent is not clear. One possibility is that the reduction may be related to the effect of the diluent on solvent structure. From Table IV, it is clear that the reduced $K^{1/6}$ values from fairly uniform reductions in all K_i values. There is no apparent trend with solvation sphere composition. Popov et al.[10] had found in their $^{23}Na^+$ studies that nitromethane and acetonitrile had a "leveling effect" for certain strong donor solvents. Such an effect may be present in the ternary systems above. Interestingly, the diluent also seems to perturb the intensity ratio of the geometric isomers. The *fac*:*mer* isomer ratio is reduced from the 3:2 ratio expected for a random distribution model and found in the binary mixtures to 1:1 in the diluent systems.

Conclusion

The DMF–Me_2SO solvent system seems to seriously violate the assumptions implicit in the Covington model for labile systems only in regard to the assumption of a linear metal ion shift dependence on the solvation sphere composition. In terms of the other assumptions, we have shown that it is meaningful to talk about true stoichiometric equilibrium constants in the analysis of the solvent competition process. The solvation number for this solvent system, with use of Al^{3+}, where the solvation sphere is well defined, is seen to be invariant with bulk solvent composition. Deviation is found in this solvent system between some experimentally determined K_i values and the ones expected from the statistical analysis used in the simplest form of the Covington model. The significance of the deviation is not clear at this point. We are currently extending the ^{27}Al NMR studies to other solvent systems in order to test whether Covington's extensions to the basic model to include nonstatistical distributions of solvated species[6] and changes in solvation numbers[7] are valid and to ascertain the origin of the effect of diluent on solvent competition.

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Registry No. DMF, 68-12-2; Me_2SO, 67-68-5; Al, 7429-90-5; $[Al(DMF)_6]^{3+}$, 27204-42-8; $[Al(DMF)_5(Me_2SO)]^{3+}$, 94781-24-5; *cis*-$[Al(DMF)_4(Me_2SO)_2]^{3+}$, 94781-25-6; *fac*-$[Al(DMF)_3(Me_2SO)_3]^{3+}$, 94781-26-7; *cis*-$[Al(DMF)_2(Me_2SO)_4]^{3+}$, 94781-27-8; $[Al(DMF)(Me_2SO)_5]^{3+}$, 94781-28-9; $[Al(Me_2SO)_6]^{3+}$, 23640-57-5; *trans*-$[Al(DMF)_4(Me_2SO)_2]^{3+}$, 94841-64-2; *mer*-$[Al(DMF)_3(Me_2SO)_3]^{3+}$, 94841-65-3; *trans*-$[Al(DMF)_2(Me_2SO)_4]^{3+}$, 94841-66-4.