

NMR and Sedimentation Studies of a Polymeric Steric Stabilizer for Alumina

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SYNOPSIS

The sedimentation behavior of alumina powder has been studied in the presence of polyvinylpyrrolidone (PVP) and poly(vinylpyrrolidone-co-vinyl acetate) (PVP/VA) in both thermodynamically "good" and "poor" solvents for the PVP homopolymer. PVP/VA provides higher sediment densities than does its PVP homopolymer counterpart. Solution-state ¹³C-T₁ spin-lattice relaxation measurements were made on analogous mixtures both with and without alumina powder. The NMR results suggest that the PVP/VA copolymer is anchored to the alumina powder surface by means of VA moieties, whereas the PVP moieties extend into the continuous phase of the slurry medium. Thus, the higher settling densities that are observed in the presence of PVP/VA can be attributed to a steric stabilization mechanism. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The settling behavior of micron-sized ceramic powders has often been used to provide some indication of dispersion stability.¹ This behavior can be influenced by particle density, shape, and size distribution² and by the presence of either monomeric or polymeric dispersants.³ Since micron-scale ceramic powders like alumina (Al₂O₃) are typically denser than the surrounding solvent medium (3.98 g/cm³ vs. 0.95 g/cm³), the force of gravity will ultimately lead to time-dependent sediment formation. Even with the introduction of steric, electrostatic, and electrosteric barriers to flocculation, the mass and density of micron-scale alumina powder will eventually lead to sedimentation. Moreover, poorly stabilized or flocculated slurries will lead to loosely packed sediments having lower densities than have their well-dispersed counterparts.¹

Flocculation can be controlled by the use of non-ionic polymeric additives that are theorized to form entropic or "steric" barriers that counteract the attractive van der Waal forces between particles.⁴ The

most efficient "protective colloids" are typically block or graft copolymers, where one of the blocks is solvated by the dispersion medium and the other block is "anchored" to the particle surface. The anchor segment can be chemically bonded or adsorbed onto a particle surface.⁵ However, steric stabilization is most efficient when the anchor segment is characterized by low solubility in the solvent medium.⁶

The adsorption of several types of polymers onto various particle surfaces has been studied by numerous techniques including ESR,^{6,7} FTIR,^{6,8} and NMR.^{6,9,10} The resulting trends are often explained with the acid/base concept, where electron donor-acceptor properties are considered to control the relative surface adsorption of competitive species.¹¹ ESR studies of the motional dynamics of poly(vinyl acetate) (PVAC) adsorbed onto Al₂O₃ have shown that little motional narrowing occurs even in the presence of thermodynamically good solvents, which indicates that PVAC has a strong affinity for the alumina surface.⁷

Although Al₂O₃ can be considered to be amphoteric (having both basic and acidic surface sites), the strong affinity between "acidic" PVAC¹² and Al₂O₃ suggests that the Lewis base character of the alumina surface is primarily responsible for adsorption. Polyvinylpyrrolidone (PVP), on the other

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hand, is considered to be more basic in the Lewis sense than is PVAC.¹² Thus, we would expect these two moieties, either in the form of homopolymers or copolymers, to exhibit different adsorption behaviors in the presence of alumina. Since ¹³C-NMR can be used to distinguish between the PVP and PVAC carbonyl groups in a poly(vinylpyrrolidone-co-vinyl acetate) (PVP/VA) copolymer, we have attempted to probe the motional dynamics of the two moieties both in the presence and absence of alumina powder. The PVAC and PVP carbonyls are ideal for such a study since these groups are the likely structural candidates for Al₂O₃ surface interactions with PVP/VA copolymers.

EXPERIMENTAL

Settling density experiments were performed in 25 mL graduated cylinders using Alcoa alumina with an average particle-size diameter of approximately 5 μm and with a total surface area of approximately 0.8 m²/g. Slurries for all settling experiments were prepared by mixing 15 g of Al₂O₃ with 20 g of either pure solvent or with a premixed polymer/solvent vehicle. The final slurries contained 43% inorganic solids by weight and 3.3% polymer by weight alumina where applicable. After 24 h of agitation in a shaker bath at 25°C, aliquots of slurries were weighed into the graduated cylinders. Final equilibrated sediment volumes were converted to a percent of theoretical density by taking the measured density (g/mL) divided by the density of alumina (3.98 g/cm³). Equilibrium densities were typically reached within 24 h.

Solvents from Fisher Scientific included isopropylalcohol (IPA) and a mixture of toluene and IPA at a weight ratio of 2/1. The polymers included K-30 PVP, which was in powdered form, and I-735 PVP/VA (70 mol % PVP) in a 50% by weight IPA vehicle from GAF Chemicals, both of which were synthesized by free radical polymerization.¹³

Solution ¹³C-NMR experiments were performed on the PVP and PVP/VA polymers in deuterated solvents from Cambridge isotopes using a Bruker MSL-400 spectrometer (100.627 MHz resonance frequency for carbon) at 310 K. The solvents included *d*8-IPA and a 2/1 mixture of *d*8-toluene/*d*8-IPA, both of which were used for field-locking and chemical-shift referencing. The polymer was dissolved in the solvents at a concentration of 25% by weight in sealed 10 mm outside-diameter glass tubes. The higher polymer concentration relative to the settling experiments was used to achieve ade-

quate signal to noise for analyses of the PVP and VA carbonyl carbons at 176 and at 170 ppm, respectively. Standard inversion recovery spin-lattice *T*₁ experiments (180°-τ-90°-acquire-recycle)¹⁴ were performed with scalar proton decoupling and with a 10 s recycle time between delays (five times *T*₁), where 15 delay times were used ranging from 1 ms to 10 s. The spectral data from each delay were signal-averaged with 64 transients. *T*₁ values and standard errors from linear regression were taken from the inverse of the slopes of base-line corrected ln(integrated intensity) vs. delay time, τ.¹⁴ All the data were best-fit by a single exponential decay with linear regression correlation coefficients of .99.

After performing the *T*₁ experiments on the vehicle solutions, Al₂O₃ powder was added directly to the NMR tube to yield a slurry containing 2.5% inorganic solids by weight. The sealed tubes were then equilibrated in an ultrasonic water bath for 10 h prior to NMR experiments. The lower concentration of alumina relative to the settling experiments was necessary to prevent excessive settling within the NMR tube during the 13 h duration of a typical experiment. All experiments (with and without alumina) were performed without sample tube spinning in order to prevent centrifugal separation of the inorganic powder that would have otherwise occurred during the course of the experiment. A reproducibility experiment showed that this condition had no effect on resolution or on resulting *T*₁ values.

RESULTS AND DISCUSSION

Sedimentation Behavior: Solvent Effects

The settling densities as a percentage of theoretical for Al₂O₃ in the presence of PVP and PVP/VA are given in Table I as a function of the solvent. Settling densities are also given for the neat slurries con-

Table I Percent Theoretical Settling Density (Standard Error of 2%) for Al₂O₃ Slurries as a Function of Solvent with and without PVP and PVP/VA Polymers

Polymer	IPA	Toluene/IPA (2/1)
—	33	31
PVP	45	—
PVP/VA	54	39

Slurries contain 43% inorganic solids by weight and 3.3% polymer by weight alumina.

taining only Al_2O_3 and solvent. The settling behavior of inorganic powders in a neat solvent system are indicative of the relative solvent affinity for the particle surface,¹⁵ where the best-wetting solvents will generally produce sediments with higher densities. The value of 33% observed in pure IPA is less than the 38% value that we have previously observed in pure ethanol.¹⁶ However, the higher polarity of IPA gives it a much higher affinity for Al_2O_3 than that of pure toluene, which previously has been shown to provide a settling density of only 16%.¹⁶ The settling density in the 2/1 toluene/IPA blend does not differ from the settling behavior of pure IPA, which indicates that the 2/1 mixture contains IPA at a concentration beyond its critical plateau adsorption level, which is consistent with previous studies of toluene/ethanol solvent blends.¹⁶

Sedimentation Behavior: Polymer Effects

Settling densities are higher after the addition of the PVP and PVP/VA polymers to the slurries. The settling density in the presence of PVP is higher than is the density achieved in pure IPA, but the improvement is not as pronounced as the density achieved with the PVP/VA copolymer. Apparently, the incorporation of VA as a comonomer improves the stabilizing characteristics of the system. This result seems reasonable in light of the fact that IPA is a good solvent for PVP, but a poor solvent for PVAC. This would imply that a copolymer of PVP/VA may act as a more efficient steric stabilizer than is PVP homopolymer and that VA moieties may favor surface adsorption over solvation in IPA.

Unlike PVAC homopolymer, PVP is insoluble in toluene. Even when a 2/1 ratio of toluene/IPA is used, PVP homopolymer could not be dissolved at the concentration required for these relative comparisons. Hence, no settling results for PVP could be obtained in the 2/1 toluene/IPA blend. On the other hand, the incorporation of 30 mol % VA comonomer gives the PVP/VA copolymer greater solubility in the 2/1 toluene/IPA blend. However, the introduction of toluene as a cosolvent reduces the observed settling density. This indicates that the stabilizing efficiency of the copolymer is reduced when a poor solvent for PVP, but a good solvent for PVAC, is added to the slurry. This shows that the copolymer is still acting as a stabilizer, but its efficiency is reduced either because the steric barrier of the adsorbed PVP/VA is diminished due to chain contraction of the PVP moieties upon addition of a poor solvent (toluene) or because VA moieties desorb upon addition of a good solvent (toluene).

The molecular weight distribution, the random vs. block character of these copolymers, and the PVP/VA ratio are also variables¹⁷ that could affect the efficiency of VA adsorption. However, the purpose of this study is to further test the idea that VA adsorption is indeed the phenomenon that improves the stabilizing efficiency of these slurries. To accomplish this, we have used ^{13}C -NMR to study the motional dynamics of these moieties both in the presence and in the absence of alumina.

Motional Dynamics— ^{13}C -NMR

The solution ^{13}C -NMR spectra of the carbonyl region for the PVP and PVP/VA copolymers are shown in Figure 1. The carbonyl carbons for the two monomeric units are readily distinguishable, thus making it possible to study the motional dynamics of each moiety. T_1 spin-lattice relaxation times are given in Table II for the polymers in the presence and absence of alumina.

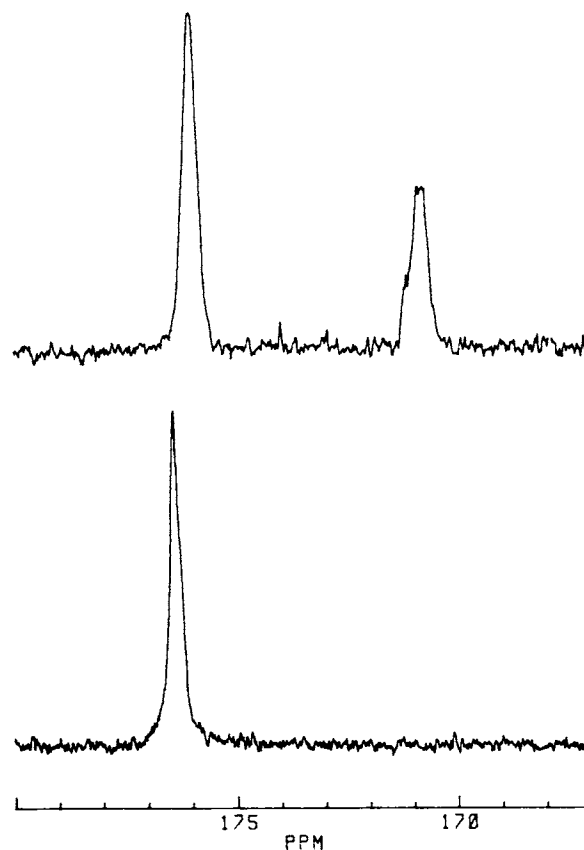


Figure 1 Carbon-13-NMR spectra of the carbonyl region for both the PVP homopolymer (bottom) and the PVP/VA 70/30 copolymer (top) in *d*8-IPA at a 20% by weight concentration. Spectra represent accumulated averages of 64 transients.

Table II Carbon-13 T_1 Spin-lattice Relaxation Times (in s) for Vinylpyrrolidone (VP) and Vinyl Acetate (VA) Carbonyls as a Function of Solvent with and without Alumina (Standard Error ± 0.03 s)

Solvent	Polymer	VP	VA
IPA	PVP/VA	1.70	1.66
IPA/Al ₂ O ₃	PVP/VA	1.68	1.44
Toluene/IPA (2/1)	PVP/VA	1.49	1.52
Toluene/IPA (2/1)/Al ₂ O ₃	PVP/VA	1.53	1.43
IPA	PVP	1.84	—
IPA/Al ₂ O ₃	PVP	2.10	—

Spin-lattice relaxation times for polymers in solution are affected by the MHz components of molecular motion that modulate carbon-proton dipolar interactions.¹⁴ Given that these polymer solutions have relatively low viscosities, the T_1 values will reside on the “fast” motional sides of the T_1 minima, where larger T_1 values would be indicative of an increase in the density of MHz range molecular motions.^{14,18}

Table II shows that the T_1 value for the PVP homopolymer carbonyl in IPA is slightly greater than the T_1 value for the analogous PVP carbonyl in the PVP/VA copolymer. This shows that the motional dynamics of the VP moiety in IPA are slightly hindered by the presence of a VA comonomer. When comparing the carbonyls within the PVP/VA copolymer, it appears that the VA carbonyl has a smaller T_1 than that of the VP carbonyl, which indicates that the VA moieties are experiencing more restricted MHz range mobility. These results are in accord with the expected solubility behavior of the two moieties in IPA, and they are consistent with solvent effects that have been observed in other copolymers.¹⁹

The introduction of toluene, a poor solvent for the VP moiety, causes the T_1 of the VP carbonyl to decrease significantly. In fact, contrary to the PVP/VA copolymer's behavior in IPA, the VP T_1 becomes shorter than the VA carbonyl T_1 . Again, this is consistent with the expected solubility behavior of these two moieties in the presence of “good” and “poor” solvents.¹⁹

Upon addition of alumina to these solutions, the T_1 values for the VA carbonyls decrease to a common value of about 1.4 s independent of the solvent type. The VA carbonyl T_1 values are also consistently shorter than those of the VP carbonyls. The lower molecular mobility of the VA moieties is consistent

with the chain contraction¹⁹ that would be expected for segments that are “anchored” to the alumina surface. The motion of the VA moieties is the same independent of the presence of a poor solvent like IPA or the presence of a good solvent like toluene. This result is consistent with previous studies of PVAC motional dynamics at the alumina interface by ESR.⁷

Although the adsorbed VA group is unaffected by the introduction of toluene, the VP carbonyl T_1 values are decreased, as shown in Table II. This result corroborates with the settling study results and indicates that the VP moieties actually provide a steric barrier for stabilization of these slurries. The steric barrier tends to contract upon the addition of a poor solvent like toluene, as indicated by a decrease in T_1 .¹⁹ This increases the likelihood of flocculation, which leads to the lower settling densities that are observed upon introduction of toluene to the slurry.

The PVP homopolymer carbonyl T_1 actually increases in the presence of alumina. This implies that chain expansion may predominate with increased carbonyl side-group mobility. However, these NMR results cannot be used to directly differentiate between moieties that are portions of solution-extended tails, loops, or surface-bound species. Instead, it must be remembered that these T_1 values represent *dynamic* time averages of carbonyl carbon nuclei that are in equilibrium with adsorbed, partially desorbed, and completely desorbed species. More research will be needed to separate these effects.

CONCLUSIONS

Settling density results indicate that the steric stabilizing efficiency of polyvinylpyrrolidone in alumina slurries is increased by the incorporation of the vinyl acetate comonomer. NMR results show that the vinyl acetate carbonyl moiety exhibits decreased molecular mobility in the presence of alumina, independent of the solvent. However, the vinylpyrrolidone carbonyl exhibits decreased mobility upon addition of a thermodynamically poor solvent for this moiety. Taken together with sedimentation data, these results indicate that the vinylpyrrolidone segment provides a steric barrier to flocculation, whereas the vinyl acetate segment serves as an adsorbed anchor on the Al₂O₃ particle surface.

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Received February 24, 1992

Accepted May 8, 1992