Aqueous and non aqueous chemistry studies of high purity aluminum nitride powders

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The surface chemistry and suspension behavior of aluminum nitride was analyzed using sedimentation and electrophoretic techniques. Aluminum nitride shows an isoelectric point near pH 8.5, very similar to that observed for aluminum oxide powders in the literature. This is attributed to the instability of the nitride in water which results in the formation of the oxide at the surface and is accompanied by the release of ammonia. Nonaqueous electrophoretic measurements indicate that the surface of A1N is heterogeneously composed of both acidic and basic sites. Large positive potentials are achieved in chloroform, an acidic medium and large negative potentials result in dimethyl formamide (DMF), a basic medium. The basic sites appear to predominate on the A1N particles since in the amphoteric liquid,acetonitrile, they exhibit negative potentials as well. Calcining the aluminum nitride powders results in a reduction of the zeta potential in acidic solvents with no observed potential changes in the basic media. This indicates a loss on calcining of surface aluminum hydroxyl groups which make the surfaces more basic. Despite the high zeta potentials for A1N dispersions in the acidic chloroform and in the basic dimethyl formamide, these media have significantly different settling behaviors in 5 volume % solids suspensions. The acidic chloroform causes formation of loose powder flocs and voluminous sediments, while the basic DMF provides excellent dispersibility and dense sediment. This is attributed to the lower dielectric constant of chloroform which results in lower electric fields and therefore smaller repulsion forces between particles. In addition, A1N dispersions in the low dielectric constant pyridine solvent have low zeta potentials in dilute suspensions. However, in more concentrated suspensions, pyridine yields sediments as dense as those in dimethyl formamide.

Key words: Aluminum Nitride, Surface Chemistry, Sedimentation, Dispersion.

Introduction

The covalent nature of aluminum nitride ceramics can pose limitations to the attainment of full density during sintering [1-5]. Better sinterability can be achieved with finer particle sizes [6]. In addition, finer particles also enhance the packing efficiency, reducing pore sizes to allow more uniform shrinkage. Much of this control of particle size and particle packing can be achieved thorough colloidal processing techniques [7-10]. However, this requires knowledge of the surface properties of the ceramic and the proper choice of dispersion media. It is the purpose of this paper to investigate some of the important parameters governing suspension stability of aluminum nitride powders in various (organic) media.

Background

The stabilization of a colloid results from the interfacial chemistry between the liquid medium and the solid. The most widely accepted theory is that proposed

by Derjaguin, Landau, Verwey, and Overbeek known as the DLVO theory [11, 12]. In its simplest interpretation, the interaction of particles in suspension becomes a competition between Van der Waals attractions and electrostatic repulsion due to solid-liquid interfacial charge buildup. Charges result from a variety of mechanisms including dissociation of surface groups [13], adsorption of ion or surfactants [14] or isomorphic substitutions [15]. A highly polar medium like water can allow the dissociation of salts which can affect the distribution of the charge at the surface. Less polar media do not as effectively support this dissociation and rely on other charging mechanisms such as proton or electron transfer between the liquid and the particles.

The charges on the surface are balanced by equal but opposite charges in the bulk of the solution which are attracted to the surface by Coulombic forces. The distribution of this charge in the double layer varies with the concentration of ionic charges in the medium as evidenced in the conductivity and the dielectric constant of the media. As a result, a steady decline of potential exists with distance from the surface of the particle in suspension. The distribution of this diffuse charge has been treated in the literature [16-20].

For nonaqueous dispersions, the charge is generated by acid - base reactions of the media with the solid surface. Basic solvents donate electrons to (or accept

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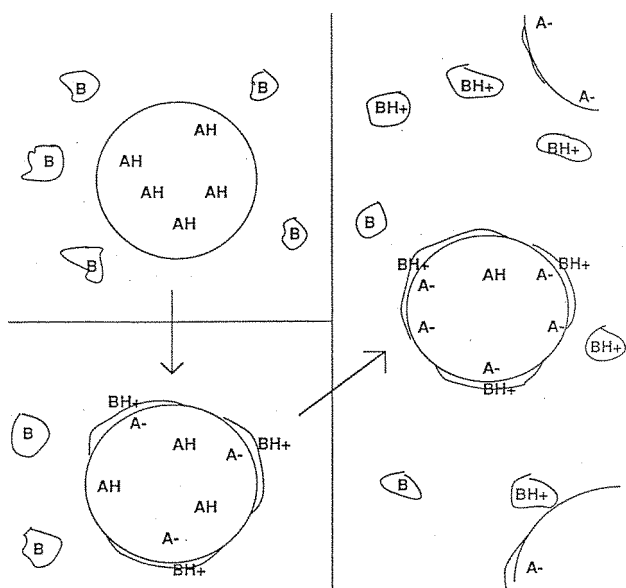 Fax: +1-610-758-3526
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Fig. 1. Acid-base charging mechanism (reference 21).

protons from) acidic sites on particles and basic sites on solids donate electrons to (or accept protons from) acidic sites in the media (Fig. 1). The process involves an adsorption of the basic media molecules onto the surface of the particle, an exchange of electrons (to empty available orbitals on the acidic sites), and the desorption of the basic media with a net charge resulting from the acid-base reaction [21]. The desorbed molecules then become the counterions for the charged particles in suspension and give rise to the counterion layer.

The repulsion between particles occurs when the diffuse layers overlap. Upon overlap, the free energy of the double layer rises to provide a barrier to further approach. However, beyond a very close critical distance of approach, van der Waals attractions dominate to cause flocculation of the particles.

The repulsion energy between particles is represented by the Derjaquin equation [11]:

$$Ue = 2\pi \in_r \in_0 a(\psi_0^2) \ln(1+e^{-KH})$$

Where $\in_r$ is the dielectric constant of the medium, $\in_0$ is the permittivity of free space, H is the interparticle separation, and K is the reciprocal of the Debye length (taken by definition to be the distance from the particle surface at which the surface potential drops to 1/e of its initial (surface) value). The Debye length $1/K = (\in_r \in_0 KT/2n_0 Z^2 e^2)^{1/2}$, where k is the Boltzman constant, T is the absolute temperature, Z is the number of electronic charges per counterion, and n_0 is the number of counterions per unit volume.

The counterion concentration is very strongly dependent on the dielectric constant of the medium. Since organic media of low dielectric constant tend to have very low ionic concentrations (n_0), the Debye lengths become very large in these media. The high values observed for

the ratio of $\in_r/n_0$ results in surface potentials which decay slowly with the distance from the surfaces. Therefore, in organic media, the zeta potential defined as the potential at the shear plane (i.e. the portion of the diffuse layer which remains fixed with the solid and travels with the solid) is essentially equal to the surface potential so the latter can be approximated by the zeta potential [22]. The attractive forces dominate upon close approach of two particles and result from the dispersion forces generated by fluctuating dipoles on the A1N particles [23]. The magnitude of these forces is presented in attraction potential equation:

$$V_R = -aA_{s/l/s}/12H$$

where A is the Hamaker constant for the particular solid/liquid system under investigation, a is the particle radius, and H is the interparticle separation. The combination of the attractive and repulsive forces determines colloid stability. A plot of the summation of these attractive and repulsive forces as a function of interparticle separation result in critical distances of approach over which high potential energy barriers will contribute to colloid stabilization and low energy wells (primary and sometimes secondary minima) occur over which attraction forces dominate to cause flocculation. Good stability then depends on the energy barrier to flocculation such that suspended particles can remain apart to settle slowly and individually. In this way, the most efficient packing arrangements can be obtained.

Experimental

Tokuyama Soda *Grade F aluminum nitride powders were used in this work. These contained approximately one weight percent oxygen, 200-400 ppm carbon, and trace levels of calcium, magnesium, silicon, and iron. (Table 1). The as-received powders were subjected to an x-ray photelectron spectroscopic analysis using magnesium K alpha x-rays as the radiation source. Survey and window scans were performed to determine the peaks present overall and the contributions to each from more than one binding state of the element in question.

Sedimentation studies were performed using approximately 4.5 volume percent solids suspensions. The dispersion procedure involved sonication of the powder in the organic liquid with an ultrasonic probe for

Table 1. Vendor* Quoted Chemical Analysis of A1N Powder

Component	Content
Ca	83 ppm
Fe	< 10 ppm
Si	36 ppm
C	220 ppm
N	33.5 wt%

*Tokuyama Soda, Incorporated; Yamaguchi, Japan

approximately one minute followed by hand stirring. The organic media employed were of varied acid/base character and varied dielectric constant. These were dried using 3 Å 4-8 mesh molecular sieves (Aldrich Chemical Company, Incorporated.). The sieves were pre-washed with hexane and vacuum dried 24 hours prior to being thermally activated at 200-250°C under vacuum for several hours. All solvents and powders were stored in a nitrogen-filled moisture controlled dry box (Braun MB 150**) equipped with a moisture analyzer.

Zeta potentials were measured on dilute milliliter suspensions containing approximately 3-5 milligrams of powder. The electrophoresis unit (Pennkem 3000) was equipped with a high voltage cell (capable of 500 V/cm) with computer-controlled intake and mobility measurement. Suspensions were consistently prepared eight to twelve hours in advance of performing the study. Prior to use, the instrument was focused regularly by taking readings on a standard colloid (latex spheres) at the front wall, back wall, and center of the chamber. Values were compared and adjustments of the computer-controlled laser focus were performed as needed. Cell bores were calculated for each solvent, based on their viscosities. Multiple readings of mobility were taken for each sample and the average value reported. Mobility values were calculated from the Henry equation [24, 25] which relates the particle mobility(μ) to the zeta potential ξ by the equation: $\xi = 1.5\ \mu v/\epsilon_r \epsilon_0 (1/f(Ka))$. In this equation, v and ϵ_r are the velocity and relative dielectric constant respectively, of the liquid and ϵ_0 is the permittivity of free space. The value f(Ka) represents a correction factor for particle conductance, field distortion, etc. and is a function of the particle size, a, and the Debye length 1/K.

Values used for the present work in the various organic media, assuming a particle size (radius) of 0.25 µm were based on the quoted specific surface area of the powder, are listed in Table 2.

Conductivities of the particles in suspension were obtained using a teflon cell attached to a twelve volt battery and measuring the current with an ammeter. Some flocculation studies of suspended particles were performed on a Coulter N4 photon correlation spectrometer. Suspensions were ultrasonically dispersed prior to placement in the counter.

Results and Discussion

X-Ray Photelectron Spectroscopy Results

Figure 2 shows the XPS survey scan obtained for the as-received powders.

The plot of peak intensity versus binding energy shows peaks corresponding to the oxygen 1s peak (531 ev), the nitrogen 1s peak (397 ev) the aluminum 2s and 2p states, and carbon. Window regions were set around each peak to determine possible contributions to each
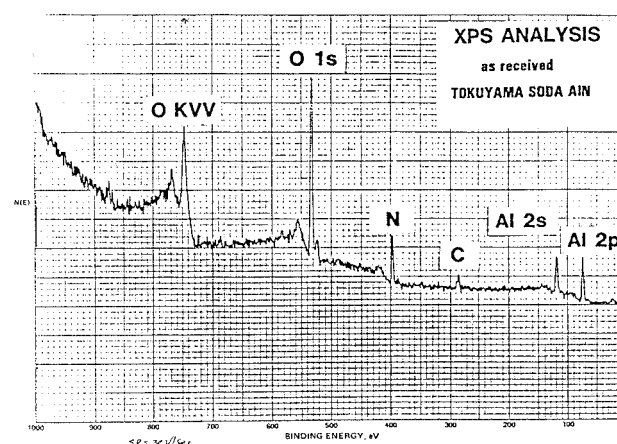

Fig. 2. X-Ray photoelectron spectroscopy analysis of as received AlN powder.

Table 2. Conductivities, mobilities, correction factors and zeta potentials used for surface analysis of dilute aluminum nitride suspensions

Organic	Conductivity (1/OHM-M)	Mobility (M²/V.S)	Correction Factor	Zeta Potential (mV)	
				with correction	as measured
acetic	3.00E-7	-2.22E-9	1.159	-16.2	(-14.0)
anhydride acetonitrile	3.85E-5	-4.07E-8	1.084	-63.5	(-58.5)
chloroform	5.20E-6	-6.31E-9	1.116	+114.3	(102.4)
dimethyl formamide	3.40E-5	-2.10E-8	1.121	-77.9	(-69.4)
ethyl acetate	7.20E-7	-5.24E-9	1.075	-62.6	(-5.81)
methyl alcohol	–	+5.54E-9	–	+16.3	–
methyl ethyl ketone	3.20E-6	-1.23E-8	1.282	-45.2	(-23.4)
methylene chloride	7.20E	+4.44E-9	1.089	+34.1	(+31.3)
nitrobenzene	1.84E-5	-6.00E-9	1.158	-59.3	(-51.2)
nitromethane	2.40E-5	-1.67E-8	1.091	-48.0	(-44.0)
pyridine	2.20E-6	-6.76E-10	1.084	-9.07	(-8.37)
triethyl amine	2.20E-9	-9.25E-11	–	–	–
toluene	4.00E-10	-1.40E-10	–	-5.25	–

from more than one binding state of the atoms. The binding energies observed were compared to those found in the literature for various compounds in order to assess the atomic environment of the surface atoms in the aluminum nitride powders. The oxygen 1s peak corresponds to the binding energy of oxygen to aluminum in the compound Al_2O_3 [26] The nitrogen peak at 397 ev corresponds to aluminum nitrogen bonding as in AlN [27]. No peaks were observed in the 401 ev region, which would indicate oxygen-nitrogen bonding [28]. Thus the surface of AlN appears to be heterogeneously composed of alumina and aluminum nitride with no evidence of any oxynitride formation.

Electrophoretic Determinations of the Zeta Potential: – Aqueous Studies

Figure 3 shows the zeta potential results for aqueous suspensions of aluminum nitride in deionized water
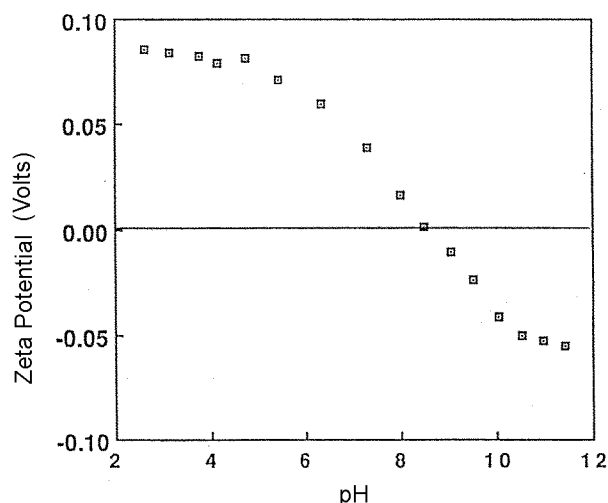
Fig. 3. Zeta Potential of AlN as a function of pH for 0.001 M concentration of KNO_3 supporting electrolyte.
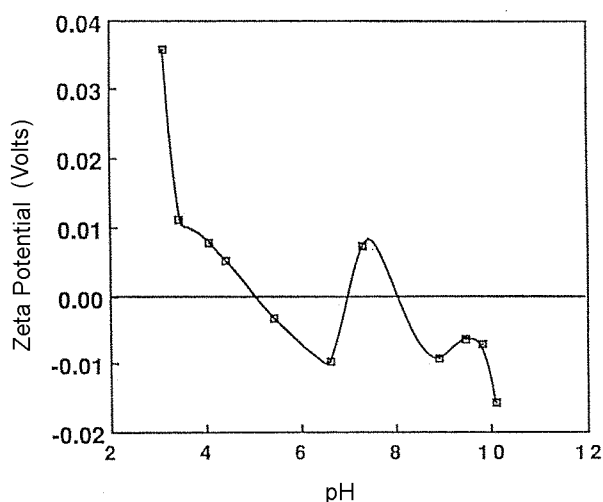
using a 0.001 M KNO_3 supporting electrolyte. The pH was altered with additions of nitric acid or potassium hydroxide. The isoelectric point occurs at a pH of approximately 8.5 to 9, similar to what is quoted for various aluminum oxides [29]. Increasing the concentration of the supporting electrolyte to 0.1 molar resulted in erratic behavior for the zeta potential as shown in Fig. 4. The potential declines from positive values of 36 mv at low pH (3.14) and reaches zero at pH 5. It becomes more negative until pH 7 is reached where it becomes positive again. For pH values greater than 8, the potential declines again toward very negative values.

A light scattering analysis was performed on the Coulter N4 on the same suspension over the same pH range (Fig. 5). The unimodal particle size exhibits a maxima at the same pH values at which the zeta potential changes sign. This would be expected based on the fact that the zero potential yields a poor electrostatic repulsion and therefore contributes to flocculation. The erratic behavior may well be a result of specific adsorption of the supporting electrolyte due to its rather high concentration.

Electrophoretic Determination of the Zeta Potential – Nonaqueous Studies

In non-aqueous media, the electric charges on the particles result from acid-base interactions of the surface sites with the medium. Acidic particles in one basic media become negatively charged while basic particles in the acidic media become positively charged. The magnitude and sign of the charge can be obtained from electrophoresis experiments and this can provide information on the predominance of sites on the powder particles.

Figure 6 shows the zeta potentials measured from the various solvents using dilute suspensions. Prior to the
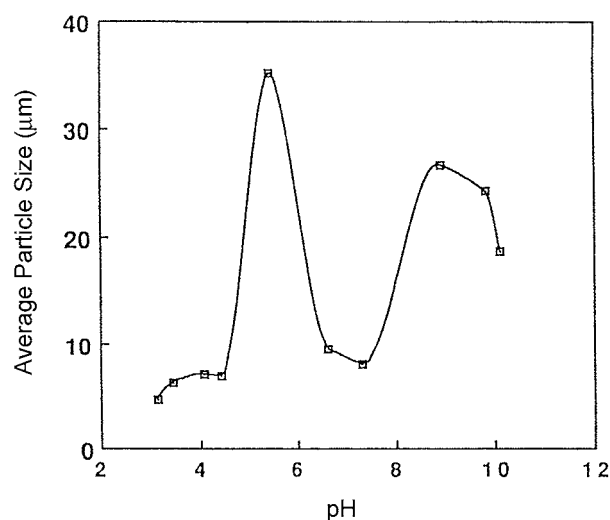
Fig. 4. Zeta potential of AlN as a function of pH for 0.1 M concentration of KNO_3 supporting electrolyte.

Fig. 5. Particle size of flocs for AlN as a function of pH for the concentrated salt (0.1 M KNO_3) suspension.
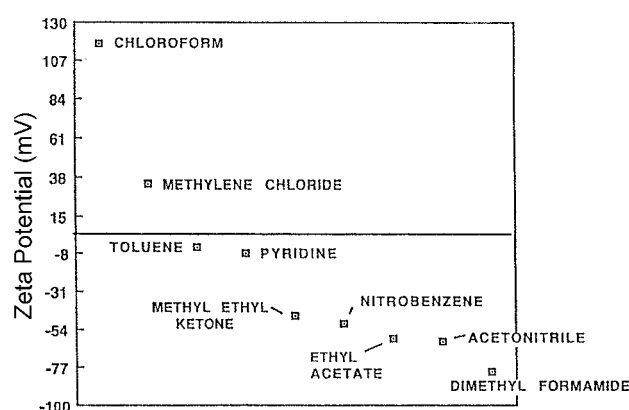
Fig. 6. Zeta potential of AlN in various organic media.

electrophoretic measurements the conductivities of the same suspensions were determined and the values of the conductivities are listed in Table 2 along with the mobilities and zeta potentials. The values in parentheses under the zeta potential column represent the as-measured potentials. These exclude the correction factor listed in the previous column for each particular system.

Toluene and pyridine, both bases, yield extremely small (negative) potentials of -5 to -9 mV respectively, while the oxygen bases ethyl acetate and (MEK) methyl ethyl ketone show larger negative potentials of -63 and -45, respectively. Acetonitrile and nitrobenzene are acid-base complexes and are interesting cases since they can act equally strong as an acid or a base depending upon the nature of the dispersed species. If the powder is predominately basic, these solvents act acidic and yield positive potentials. If the surface is predominately acidic, negative potentials will result. The present results indicate that the surface of aluminum nitride is predominately acidic. The low dielectric constant of toluene and the low zeta potential it produces, two of the key variables involved in the repulsion potential equation, are consistent with the large sedimentation volumes observed for the organic liquid. Positive potentials are obtained in the acids methylene chloride, methyl alcohol, and chloroform, indicating that basic sites exist on the particles to donate electrons to (or accept protons from) the solvent. A rather high potential develops in the

Table 3. Zeta potential comparison for heat treated* and untreated aln and comparsions with untreated alumina

Organic Medium	Zeta Potential (mV)		
	Heat Treated	Untreated	Untreated
	AlN	AlN	Al_2O_3**
Dimethyl formamide (DMF) (base)	−73.4	−77.9	−44.0
acetonitrile (acid/base)	−64.5	−63.5	−43.1
Chloroform (acid)	+52.2	+114.3	+21.2
methyl alcohol		+16.3	+20.4

*1000°C, 16 hours in N_2-5%H_2 atmosphere
**SUMITOMO AKP (as-received)

acidic chloroform (+114 mV).

Table 3 shows zeta potential results for heat-treated and as-received AlN in various organic liquids. Heat treating the AlN powders at 1000 degrees C does not appear to affect the acidity of the powders as the basic media (acetonitrile and dimethyl formamide) yield the same zeta potentials as the untreated powders. However, the acidic solvent chloroform shows a much lower positive potential than the untreated case. This could result from the elimination of basic sites on the surfaces of the powders during the heat treatment.

Lyklema [22] claims that trace amounts of water in solvents or on solids can affect the measurement of the zeta potential. For very polar media, water can absorb at the interface where it is believed to obscure the electrokinetic effect. In a polar (low dielectric constant) media, adsorbed water is believed to enhance the basicity of the solid. However, in most cases, trace water often refers to the alteration of powder surfaces to OH groups or rather, an hydroxylated surface which really is not water at all. Therefore the observed reduction of the potential with heat treatment is consistent with the conversion of the OH surfaces to oxide surfaces.

Also shown in Table 3 are the values for untreated as-received alumina dispersed into the same three organics. It exhibits similar behavior as the AlN powders, with negative potentials occurring in the basic media aceto-nitrile and DMF (indicating a predominance of acidic sites) and positive potentials in the acidic chloroform. Included in this table are the results for AlN and Al_2O_3 dispersions in alcohol. In this case, the oxide behaves in a very acidic manner, even toward the acidic methyl alcohol. Apparently these oxide powders are extremely dry since water contamination has been shown to change the sign of the potential from negative to positive for aluminum oxide particles dispersed in lower alcohols [30]. Freshly calcined alumina is quite acidic with Al^{3+} sites acting as the acidic sites [31]. However, when hydrated to AlOH groups, the surface is basic.

Sedimentation

Sedimentation experiments were performed to provide practical information on the preparation of dense ceramic microstructures from the organic media studied. Dispersions were prepared in a consistent manner and were qualitatively compared after settling for a designated period of time (3 weeks). Figure 7 shows the results of these organics.

Chloroform and methylene chloride are acidic (hydrogen donors or electron acceptors) and exhibit large settling heights (>60cc). The oxygen base methyl ethyl ketone (MEK) exhibits a much lower sediment volume (23cc). Acetonitrile and monoethanolamine are amphoteric. The nitrile carbon in acetonitrile and the alcohol group in the ethanolamine provides the electron acceptor sites while the nitrogen constituents on each yield the
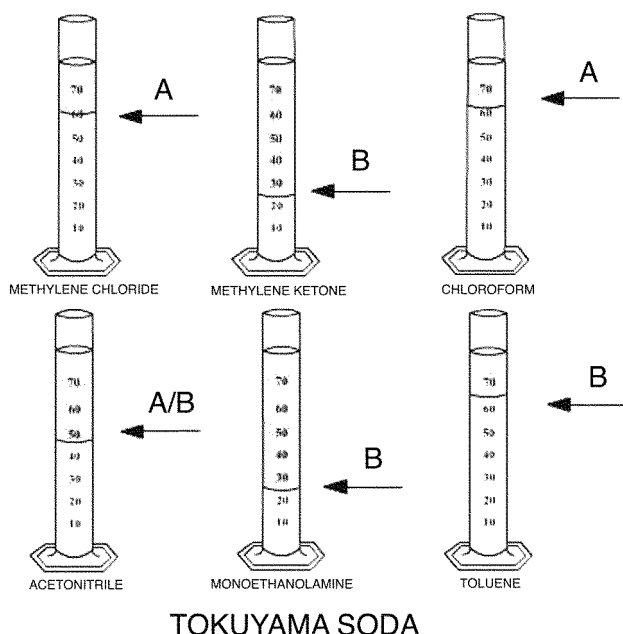
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Fig. 7. Sedimentation volumes of AlN in six organic media.

electron donor sites and lend to their basicity. The sediment volumes of these two different solvents differ. Acetonitrile yields a sediment volume of 47cc, lower than those of the strong acids and larger than that of the basic MEK. Ethanolamine however yields a settling volume nearer to that of the basic MEK (21cc). The weakly basic toluene, whose basicity is derived from the electron donation from the pi bonds constituting the ring structure for this compound, yields settling heights equal to those of the strong acids chloroform and methylene chloride.

According to theory, minimum settling heights for a solid in suspension occur when predominately acidic particles are placed into basic media or visa versa. Acids in acid and bases in bases do not form stable suspensions since there exists no mechanism of electrostatic stabilization in these situations to cause interparticle repulsion and thus decrease flocculation. When flocs build, the particles cannot pack themselves efficiently as strong van der Waals attractions between them does not allow them to slide past each other to arrange themselves into the most efficient packing arrangement.

In addition to the van der Waals attractions, flocs can form via a mechanism involving contacts between hydrophilic particles in an organic medium. If water is present on the particles, then upon contact, the water can bridge the particles into a floc. Liquid media which have a greater affinity for the solid will displace the water and yield a separation of the particles, thus providing a stabilizing mechanism. This requires that the particles are easily wetted by the acid or the base in which they are dispersed to make the particles hydrophobic, so they can act to repel particles upon close contact.

The large sedimentation volumes observed for the

strongly acidic media appear to indicate that the surface of the aluminum nitride powders is predominately acidic. The smaller settling heights acetonitrile and monoethanolamine, which possess more basic character, and the strong base MEK are consistent with this finding. However, the weekly basic toluene provides settling heights as large as the strong acids requiring investigations of other factors entering into the stabilization process.

Analysis of the Derjaguin equation for particle stability shows that in addition to the zeta potential (which is determined by the acid/base reaction), the dielectric constant plays an important role. In the previous sedimentation experiments, the dielectric constants of chloroform, methylene chloride, and toluene were low (4.08, 9.81, and 2.38 respectively). All yielded large sedimentation volumes of greater than 60cc. The methyl ethyl ketone and acetonitrile (18 and 37 respectively) exhibited lower sedimentation volumes. In order to test the effect of the dielectric constant on the colloid stability, a variety of organics of different acid/base character and dielectric properties were obtained.

Figure 8 shows the sediment volumes for low dielectric constant organics ($\epsilon_r < 12$). The number in parentheses represents the dielectric constant and the number in the bar graph indicates the zeta potential measured from dilute suspensions for the organic in question. Again, it is observed that the weak base toluene yields a large sedimentation volume. This would be consistent with its low dielectric constant and zeta potential. The acids chloroform and methylene chloride result in volumes as large as the toluene even though the large positive zeta potentials develop in this solvent (114 mV). The stronger bases triethylamine (TEA) and ethyl acetate lower the sedimentation volume to approximately 50cc even though the triethylamine has a dielectric constant similar to that of the toluene (2.42). Finally, pyridine, a strong nitrogen base with a
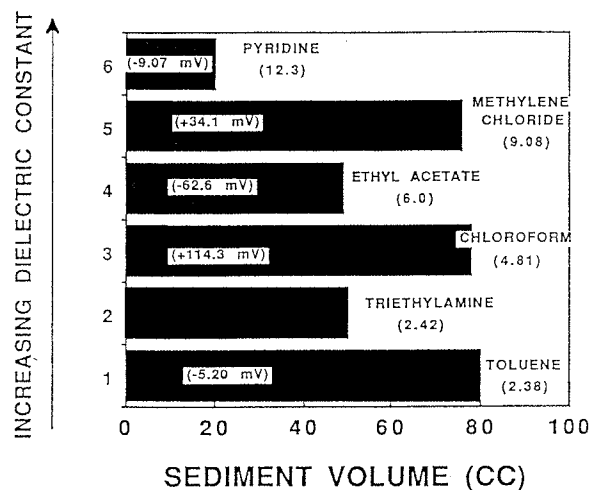

Fig. 8. Sediment volume versus dielectric constant for low dielectric constant media.
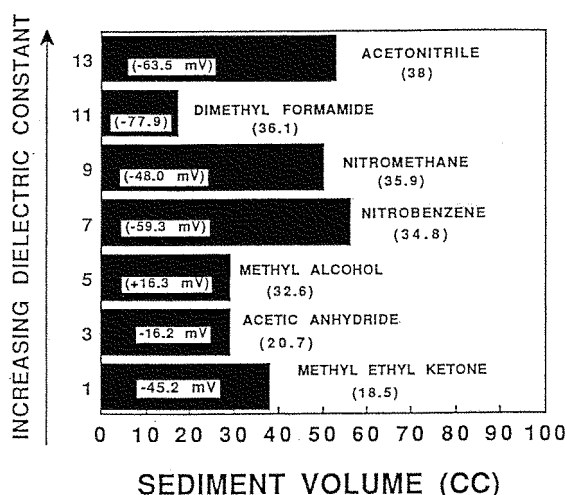
Fig. 9. Sediment volume versus dielectric constant for high dielectric constant media.

Fig. 10. Sediment volume as a function of volume percent DMF in methanol.

low zeta potential value of -9 mV yields the smallest sedimentation volume for the low dielectric constant organics studied (20cc).

Figure 9 exhibits a similar series of sedimentations with the dielectric and zeta potential information. All these sedimentation heights are less than the low dielectric constant series. The bases methyl ethyl ketone (MEK), dimethyl formamide (DMF) and acidic anhydride yield smaller sedimentation volumes. Furthermore, the acidic methanol (CH_3OH) yields a similar settling height as the basic acetic anhydride (ϵ_r=20) and slightly better than the MEK (ϵ_r=18.5). Acetonitrile and nitrobenzene, which have both acidic and basic character, yield similar sediment volumes as does the nitromethane and greater than the high dielectric constant bases. Dimethyl formamide, with a dielectric constant of 36.7 and a significant potential of -78 mV (the largest of the bases measured) produces the smallest volume. In addition, DMF (ϵ_r=36.7) and pyridine (ϵ_r= 12.3) exhibit exactly the same settling behavior: both yield approximately the same volume and maintain an extremely cloudy supernatant. Methanol (acid) provides a cloudy supernatant as well, but not as cloudy as pyridine and dimethyl formamide.

The pyridine and DMF cases pose an anomaly. DMF possesses a higher dielectric constant and yields a larger (negative) potential than pyridine. However, both are excellent dispersants. This may suggest different stabilization mechanisms in operation for these two systems. Perhaps the pyridine is strongly adsorbed to the AlN so as to make the surface hydrophobic, separating particles which would otherwise be bridged by water present on the surfaces of the solid. This is likely since the potential developed in pyridine is so low (5 mV). Further analysis of the stabilizing factors are required.

The sedimentation results of Fig. 10 show that the effect of the dielectric constant alone is not sufficient to
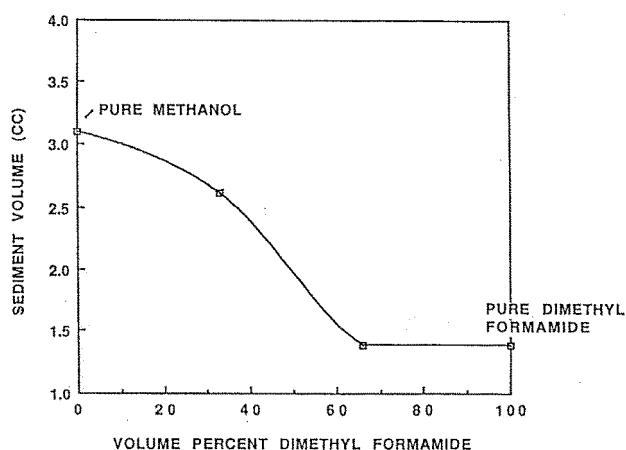
predict suspension behavior. In this, case, an acid and a base of similar dielectric constant (32 for the acidic methanol, and 36 for the basic DMF) were used. Sedimentation heights fall approximately 60% as the concentration of the basic DMF is added to the methanol. No obvious trend is observed with increased dielectric constant.

Calculations of the debye length (1/K)

The Debye length defines the decay of the potential energy curve as a function of the distance from the surface to the particle. It is defined as follows:

$$1/K = dx/d\ln(\Psi) = [(\epsilon_0 \epsilon_r \, kT/2n_0Z^2e^2)]^{1/2}$$

where ϵ_r is the dielectric constant of the medium n_0 is the number of counterions and is dependent upon the dielectric constant as well. Thus for colloid stability, there exists a complex relationship among the dielectric constant, the zeta potential, and the Debye length all of which enter into the equation defining interparticle repulsion.

The Debye length can be estimated from the knowledge of the diffusion constant of counterions in the media (D), the dielectric constant of the media (ϵ_r) and the colloid conductivity (σ). These are related by the Klinkenburg-van der Minne[32] equation:

$$1/K = (\epsilon_r \epsilon_0 \, D/2\sigma)^{1/2}$$

This is the equation used for the calculations of Debye lengths in this work. The diffusion coefficient can be estimated from the Stokes-Einstein equation ($D=kT/6\pi r \eta$) where r is the radius of the particle (or diffusing species) and η is the medium viscosity.

Values used for this calculation are given in Table 4 where the radius of the molecular species is calculated from its molecular weight and density assuming spherical geometries.

The value of the Debye length determines how rapidly the diffuse layer drops off with distance from the particle surface. The higher this value, the smaller

Table 4. Parameters in klinkenberg-van der minne equation for calculation of the debye length

| Organic	Molecular	Density	R	Viscosity	D	1/k
	Weight (g/mol)	(g/cc)	(cm)	(poise)	(m²/sec)	(1/m)
acetic anhydride ((CH$_3$CO)$_2$)	102.09	1.082	3.34E-3	8.32E-3	7.85E-10	-5.1E-8
acetonitrile	41.05	0.786	2.75E-8	3.45E-3	2.30E-9	1.0E-7
chloroform	119.38	1.492	3.17E-8	5.42E-3	1.27E-9	7.2E-8
dimethyl formamide	73.10	0.944	3.13E-8	8.02E-3	8.69E-10	6.4E-8
ethyl acetate	88.11	0.902	3.38E-8	4.41E-8	1.46E-9	2.1E-7
methyl alcohol	32.04	0.791	2.52E-8	5.47E-3	–	–
methyl ethyl ketone	72.11	0.805	3.29E-8	4.00E-3	1.66E--9	6.5E-8
methylene chloride	84.93	1.325	2.94E-8	4.12E-3	1.80E-9	1.0E-7
nitrobenzene	123.11	1.196	3.44E-8	2.03E--2	3.07E-10	5.1E-8
nitromethane	61.04	1.127	2.78E-8	6.20E-3	1.27E-9	9.2E-8
pyridine	79.10	0.978	3.18E-8	9.74E-3	6.93E-10	1.0E-7
toluene	92.14	0.867	3.48E-8	5.58E-3	1.12E-9	5.4E-6

the change of potential with distance and therefore the smaller the force of repulsion. The values of the calculated Debye lengths were used along with known dielectric constants and measured zeta potentials to calculate repulsion energy values as a function of the interparticle separation (H). The particle radius of 0.25 μm was assumed for the value of the particle radius (a) appearing in the equation. This was calculated from the quoted specific surface area of approximately 4.0 m²/g assuming spherical particles.

Also, in order to estimate the van der Waals attractions between the particles, the following equation was employed:

Attraction Potential $V_A = -A_{s/1/s}$ (a/12H)

where H is the interparticle separation, a is the particle radius, and A is the Hamaker constant for the solid-liquid system of interest. The Hamaker constant depends on the dispersion force attractions between the particles and the media. However, as such data is not always easily available, an approximation for the Hamaker constants is used as determined by Gregory [33]. In this analysis, the Hamaker constant is estimated from the dielectric constant of the solid and the liquid. (this is a reasonable assumption since the Hamaker constant is a material-specific value related to the polarizabilities of the molecules in the material.)

For the solid, A_{solid} (in kT units)=113.7[ϵ_r-1)²/ (ϵ_r+1)$^{1.5}$ (ϵ_r+2)$^{0.5}$]. An analogous expression is derived for the liquid. Thus, repulsion and attraction potential values were located for each of the organic media and summed to give the total potential. The summation of these potentials are given in Fig. 11 for the 0.25 μm particle assumption. The rise in the maximum in the potential provides an energy barrier to further approach of the particles such that the particles repel each other. The smaller this maximum is, the easier it is for the particles to approach close enough for van der Waals attractions to take over and cause flocculation. The
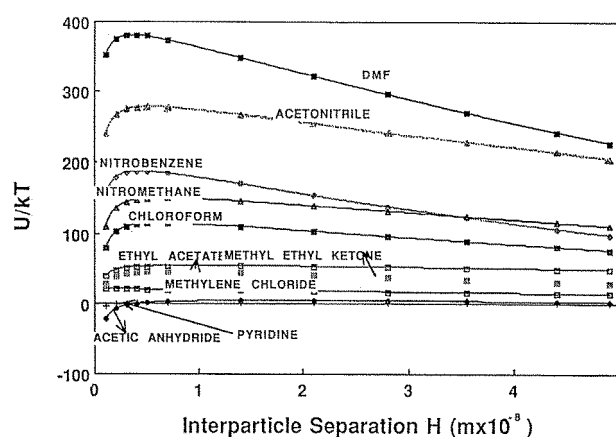
Fig. 11. Total particle interaction energy as a function of interparticle separation for the various organic systems.

dimethyl formamide yields a large maximum as expected from the sedimentation results. However, the pyridine curve appears the same as the toluene plot, giving essentially flat curves. However, unlike toluene, the pyridine provides as stable suspensions as the DMF solvent.

Conclusions

The following observations have been made:

1) High purity aluminum nitride powders exhibit isoelectric points at pH 8.5, similar to that of aluminum oxide powders in water.

2) Nonaqueous electrophoretic measurements of AlN powders indicate that the surfaces are heterogeneously composed of acidic and basic sites. Acidic sites predominate.

3) Calcining AlN at 1000°C for 16 hours results in a reduction in the basicity with no change in the acidic behavior.

4) Energy versus interparticle separation calculations based on measurements of dilute suspensions of AlN in

various dried organic media support the observation that dimethyl formamide is an excellent dispersant for AlN. However, similar calculations for pyridine do not support the excellent dispersion capabilities it possesses for AlN. Therefore, comparisons of sedimentation volumes for concentrated suspensions of powder to models of stability behavior based on dilute suspensions can lead to erroneous assumptions about suspension behavior. This is most likely due to the fact that conductivity and therefore the Debye length differ with solids concentrations. That is, the higher surface area to volume ratios in concentrated suspensions provide much higher concentrations of counterions.

The differences observed for the DMF and the pyridine may be attributed to two different mechanisms of stabilization. The pyridine may be stabilizing the AlN by strongly adsorbing on the solid surface, displacing the water molecules at the solid-liquid interface, making the surface hydrophobic, and thus preventing water bridging mechanisms from inducing flocculation. The strong adsorption of the pyridine may account for the low zeta potential observed for this superior dispersant.

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