Dispersant-Binder Interactions in Aqueous Silicon Nitride Suspensions

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Abstract

In aqueous slurry processing of silicon nitride, the interaction of dispersant and binder on the surface of particles was studied to identify the effect of these additives on ceramic powder processing. Polymethacrylic acid (PMAA) and polyvinyl alcohol (PVA) were used as dispersant and binder, respectively. The adsorption isotherms of PMAA and PVA for the silicon nitride suspension were determined, while the adsorption of PMAA was differentiated in the mixed additive system by ultraviolet spectroscopy. These experiments were done in order to investigate the effect of these organic additives on the physicochemical properties of silicon nitride suspensions. The electrokinetic behavior of silicon nitride was subsequently measured by electrokinetic sonic amplitude (ESA). As PMAA adsorbed onto silicon nitride, the isoelectic point (pH_{icp}) shifted from pH=6.7 to acidic pH, depending on the surface coverage of PMAA. However, adsorption of PVA did not change the pH_{icp} of suspensions, but did decrease the surface potential of silicon nitride moderately. The rheological behavior of silicon nitride suspensions was measured to assess the stability of particles in aqueous media, and was correlated with the electrokinetic behavior and adsorption isotherm data for silicon nitride.

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OBJECTIVES AND IMPACTS ON CERAMIC PROCESSING

- To indentify two way interaction between dispersant and binder
- To have a stabilized aqueous silicon nitride suspension

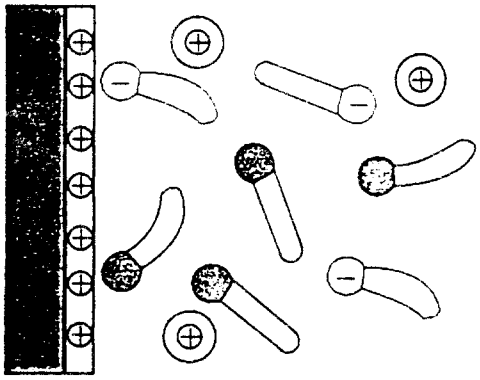
- A tool to control interparticle forces between particles for Ceramic Shape Forming Process:
  - Dispersion
  - Controlled Flocculation
  - Flocculation
- Homogeneous Ceramic Green Body

CHARACTERIZATION METHODS

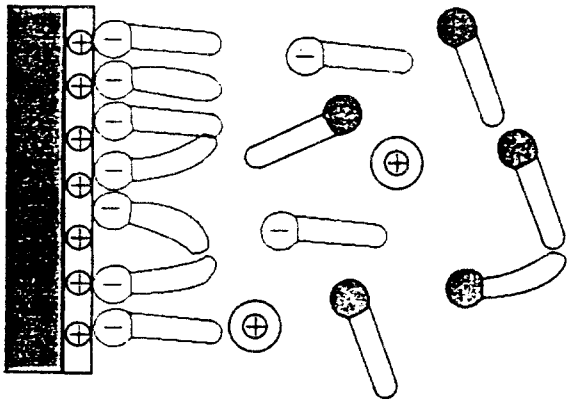
- **Surface Potential Measurement:** ***Analysis of Surface Chemistry***
- **Adsorption Isotherms:** ***Polymer Adsorption on Ceramic Surfaces***
- **Rheology:** ***Stablility of Silicon Nitride Suspensions***

Materials

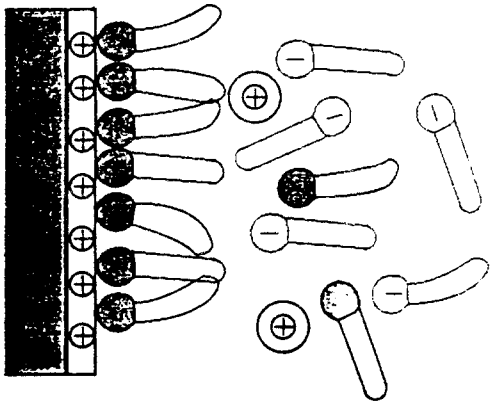
- **Powder:** Silicon Nitride (Ube E-10, Japan)
  median particle size = 0.4 mm
- **Dispersant:** Poly(methacrylic acid) (PMAA)
  $\{-CH_2-C(CH_3)(COOH)-\}_n$
- **Binder:** Poly(vinyl alcohol) (PVA)
  $\{-CH_2-CH(OH)-\}_n$
- **Deionized H_2O**



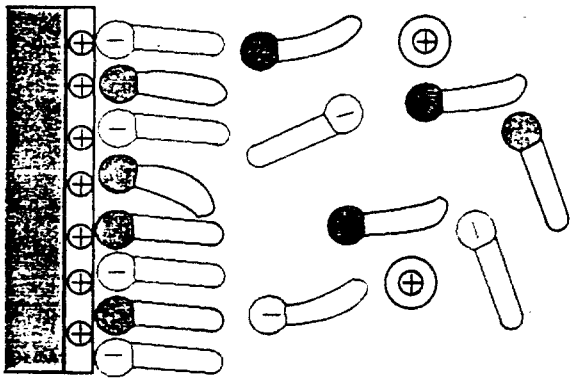
Non-Adsorption



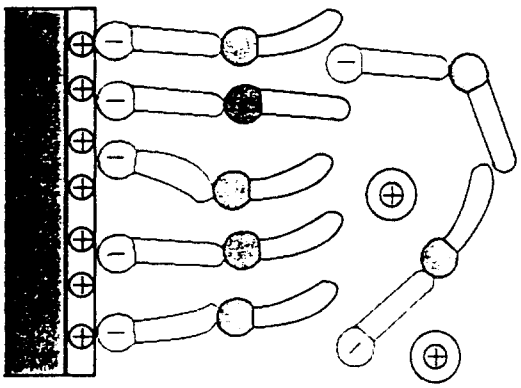
Individual Adsorption



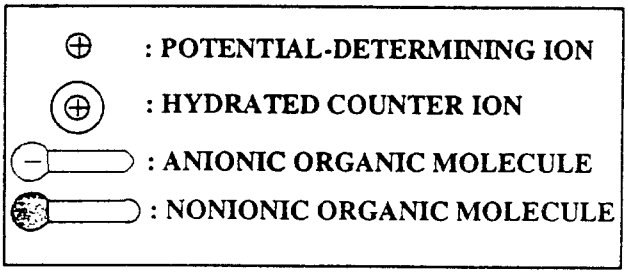
Individual Adsorption



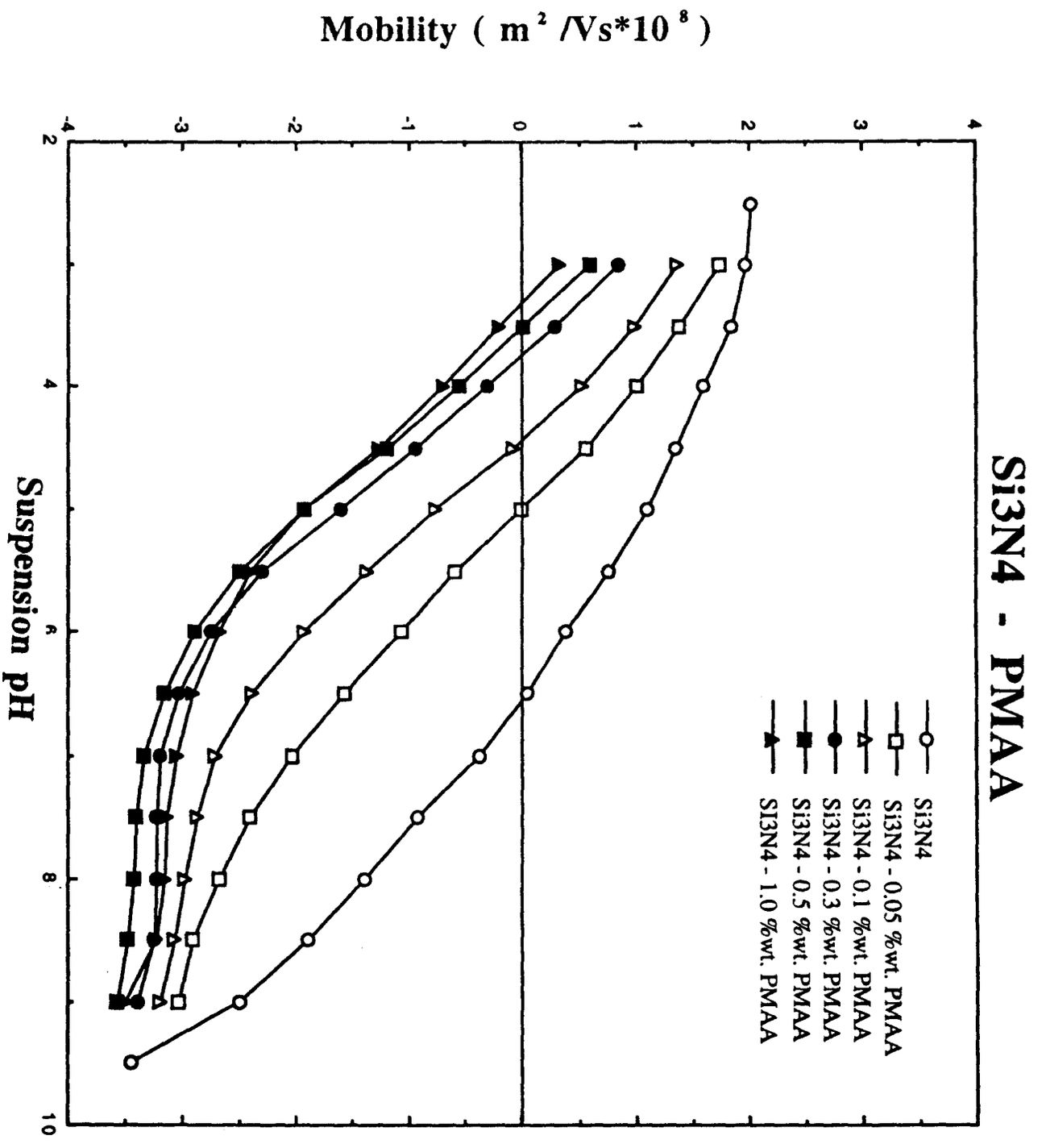
Competitive, Displacement, & Coadsorption

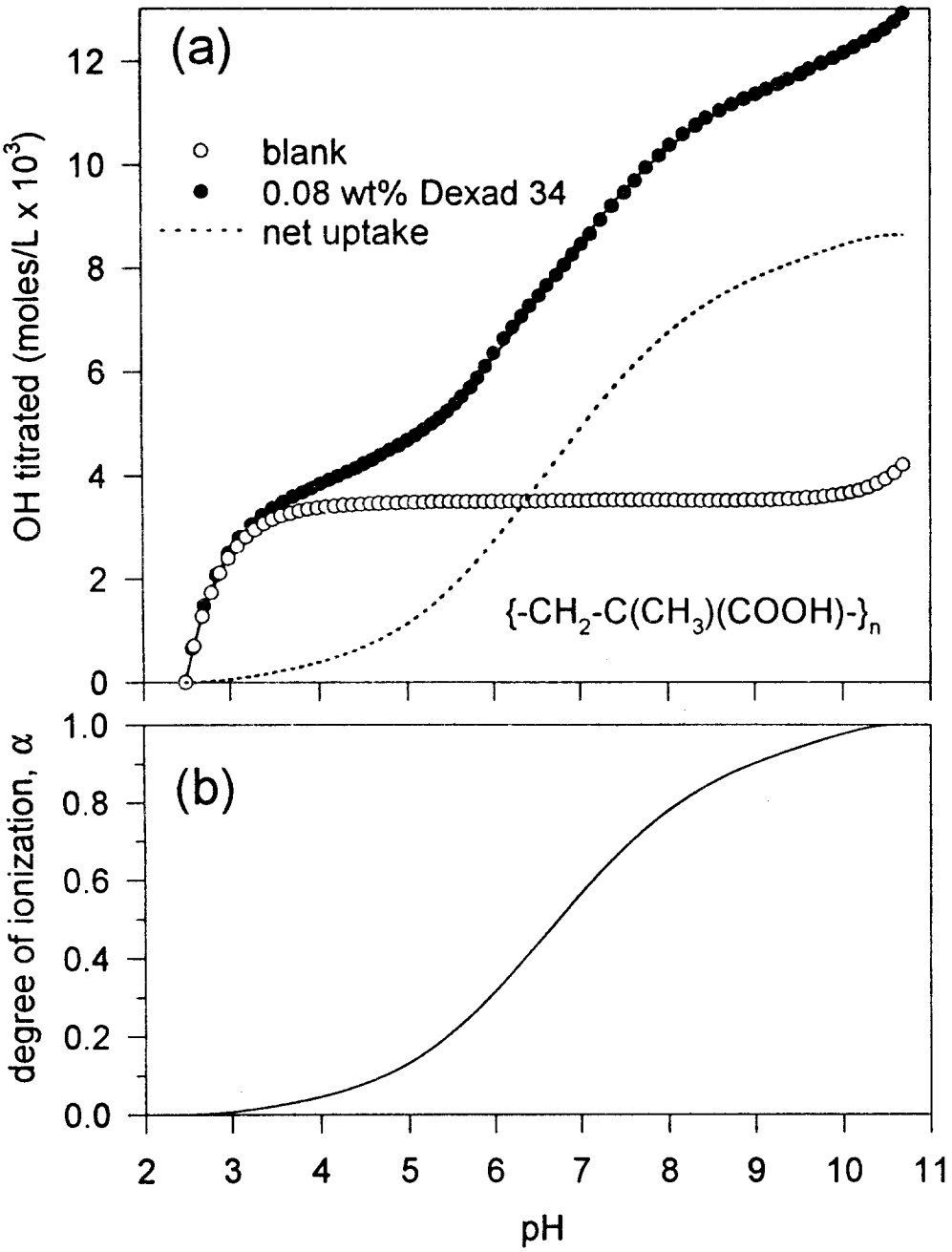


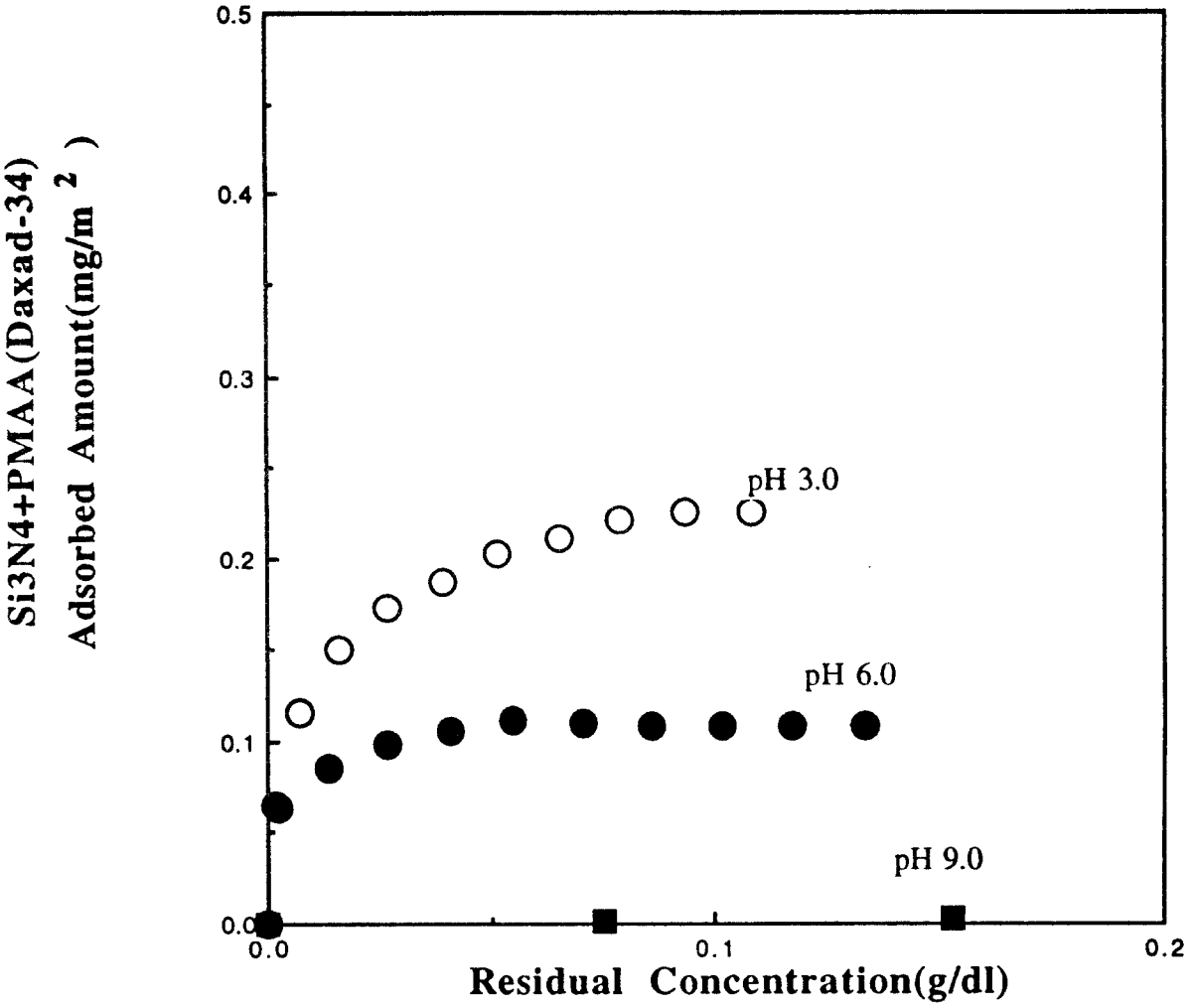
Complexation

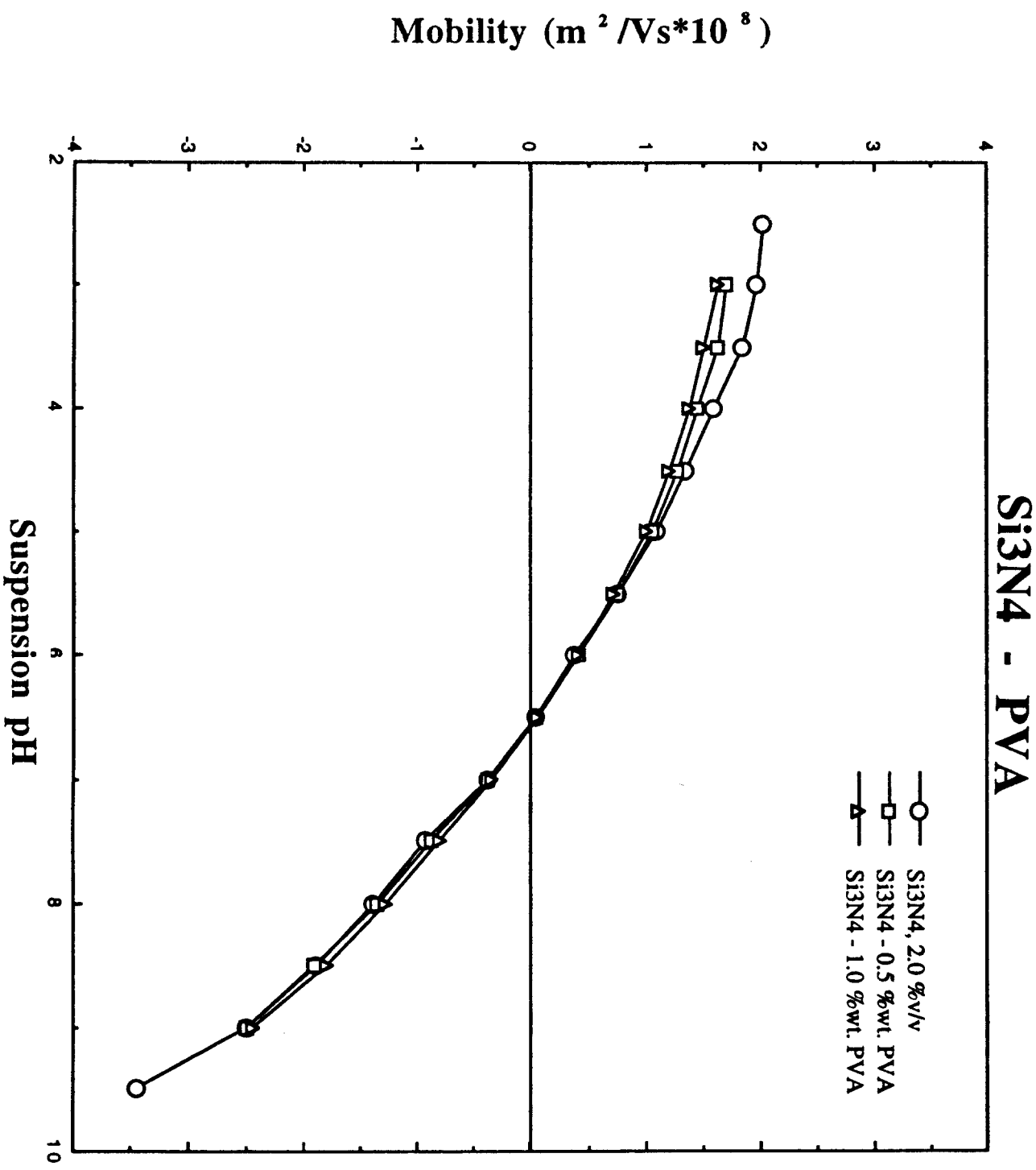


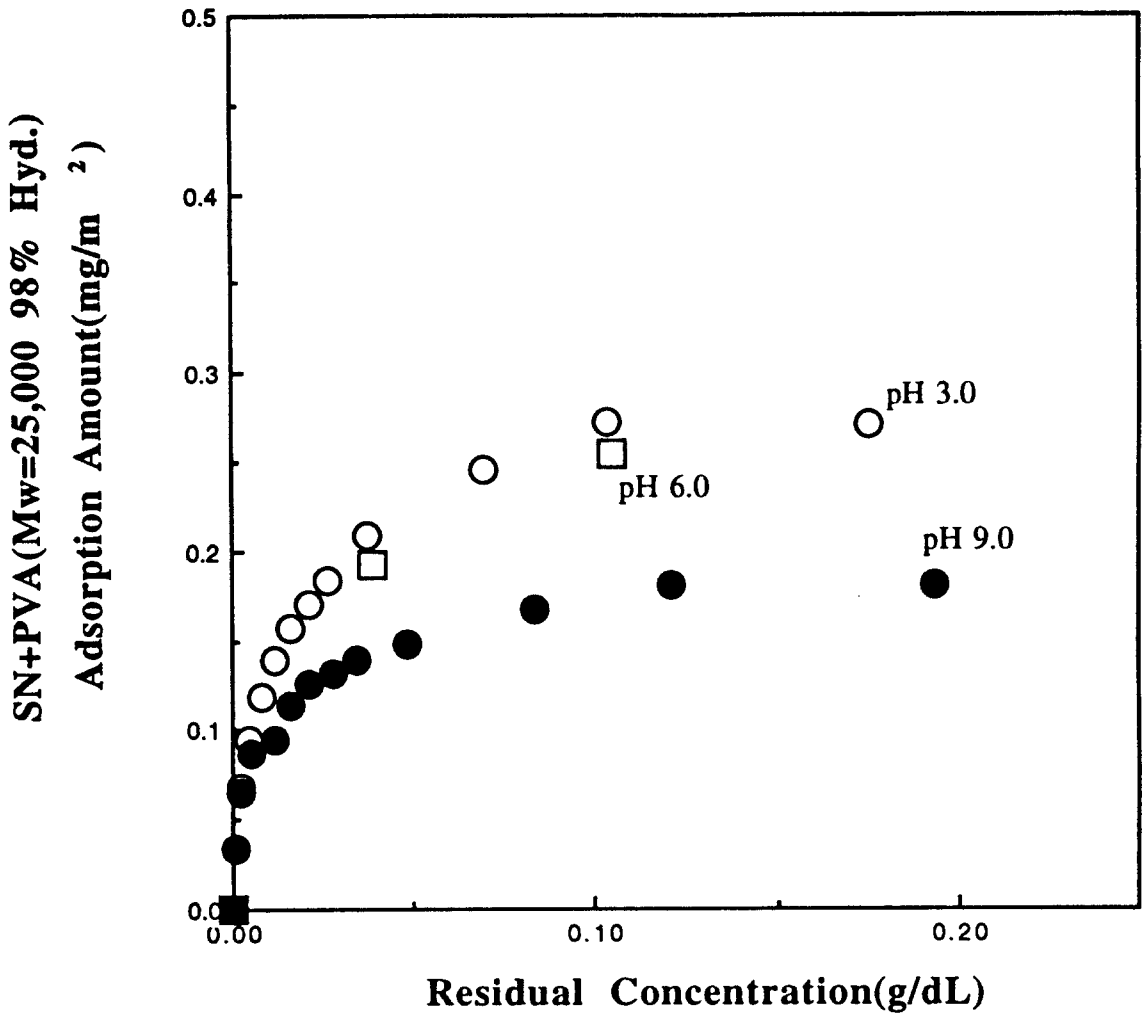
Schematic representatives of the electrical double layer in the presence of surface active organic molecules

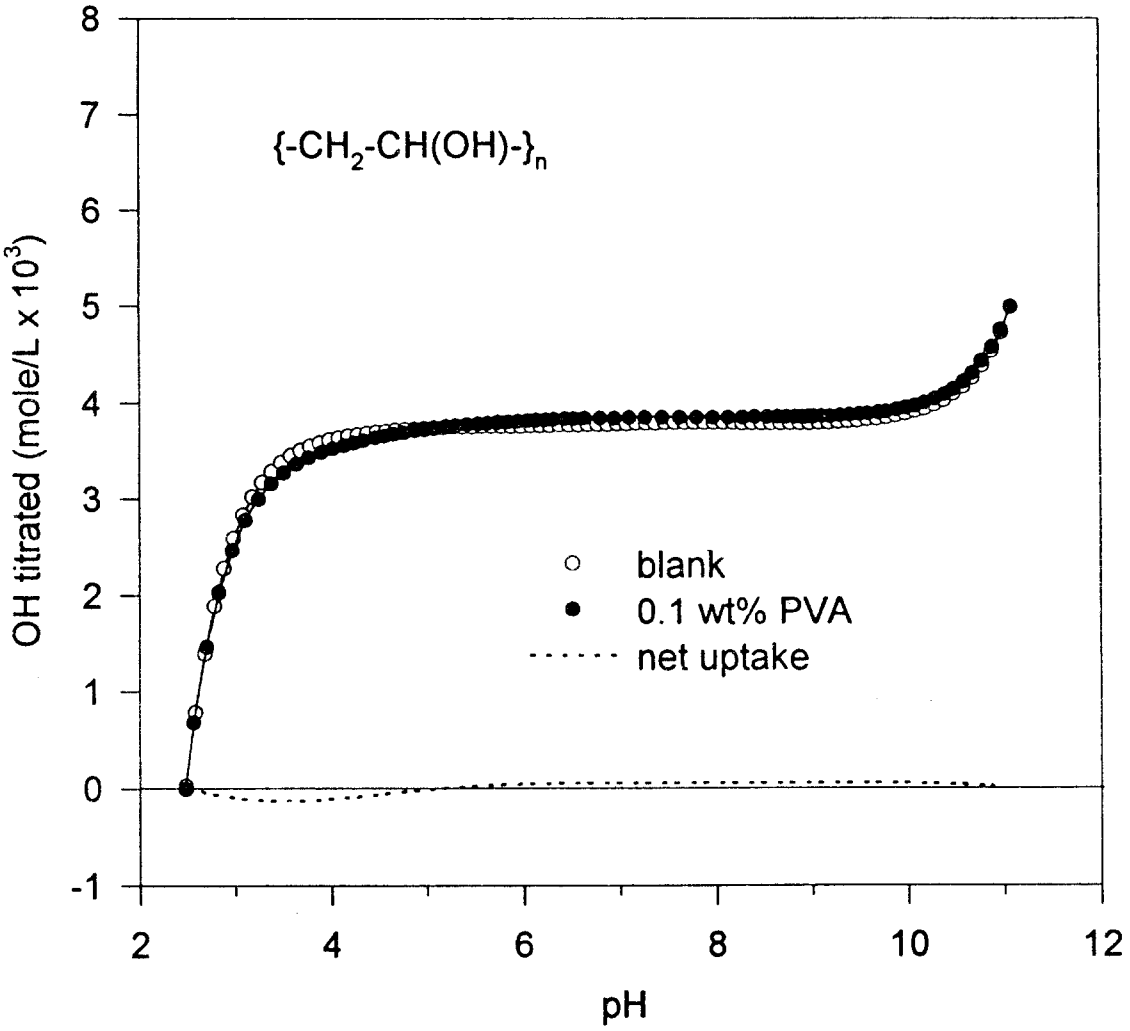

Mobility (m² /Vs*10⁸)
Si3N4 - PMAA
Suspension pH
Si3N4
Si3N4 - 0.05 %wt. PMAA
Si3N4 - 0.1 %wt. PMAA
Si3N4 - 0.3 %wt. PMAA
Si3N4 - 0.5 %wt. PMAA
SI3N4 - 1.0 %wt. PMAA

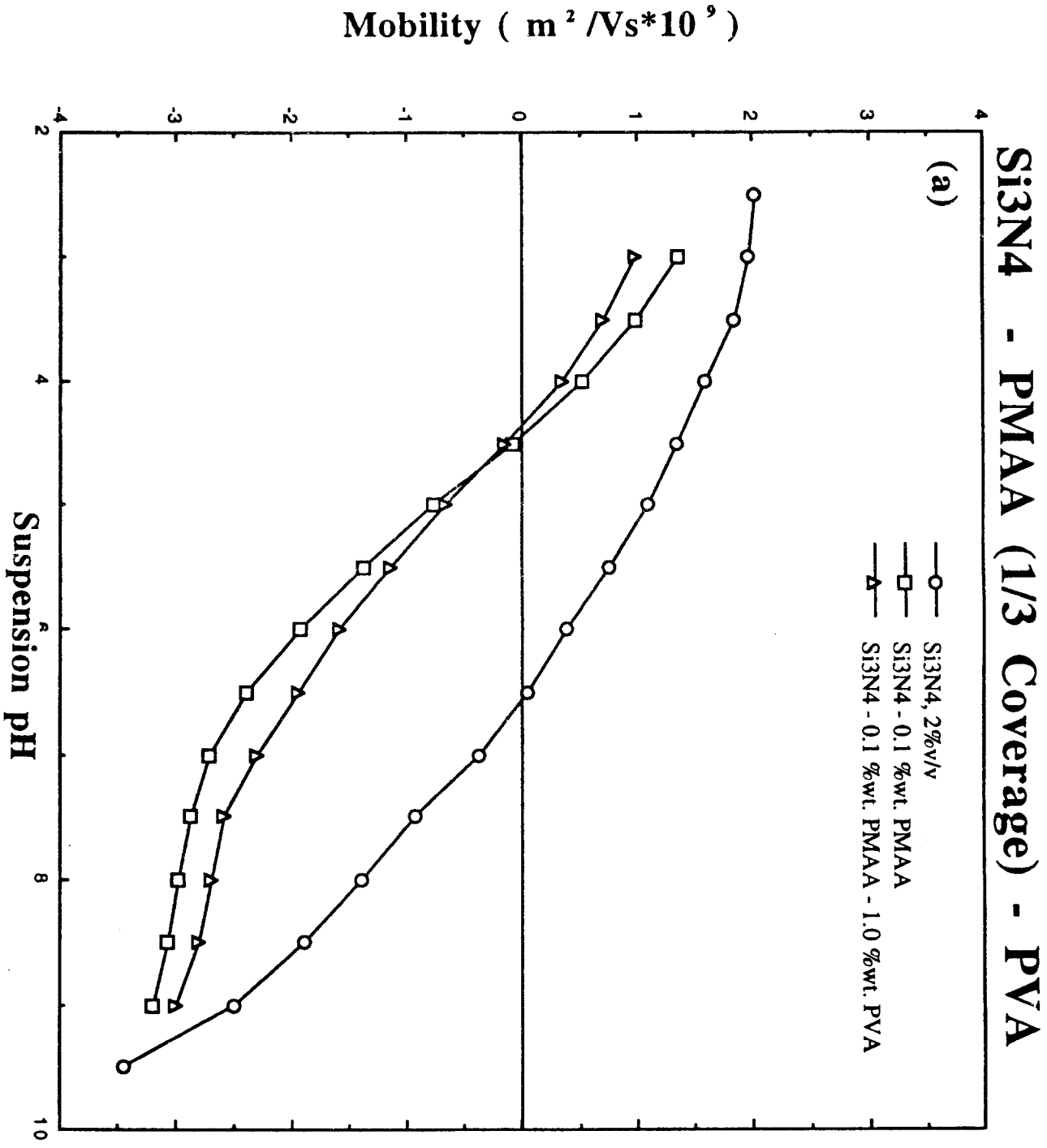

(a)
blank
0.08 wt% Dexad 34
net uptake
{-CH2-C(CH3)(COOH)-}n
OH titrated (moles/L x 10^3)
0
2
4
6
8
10
12
(b)
degree of ionization, α
0.0
0.2
0.4
0.6
0.8
1.0
2
3
4
5
6
7
8
9
10
11
pH

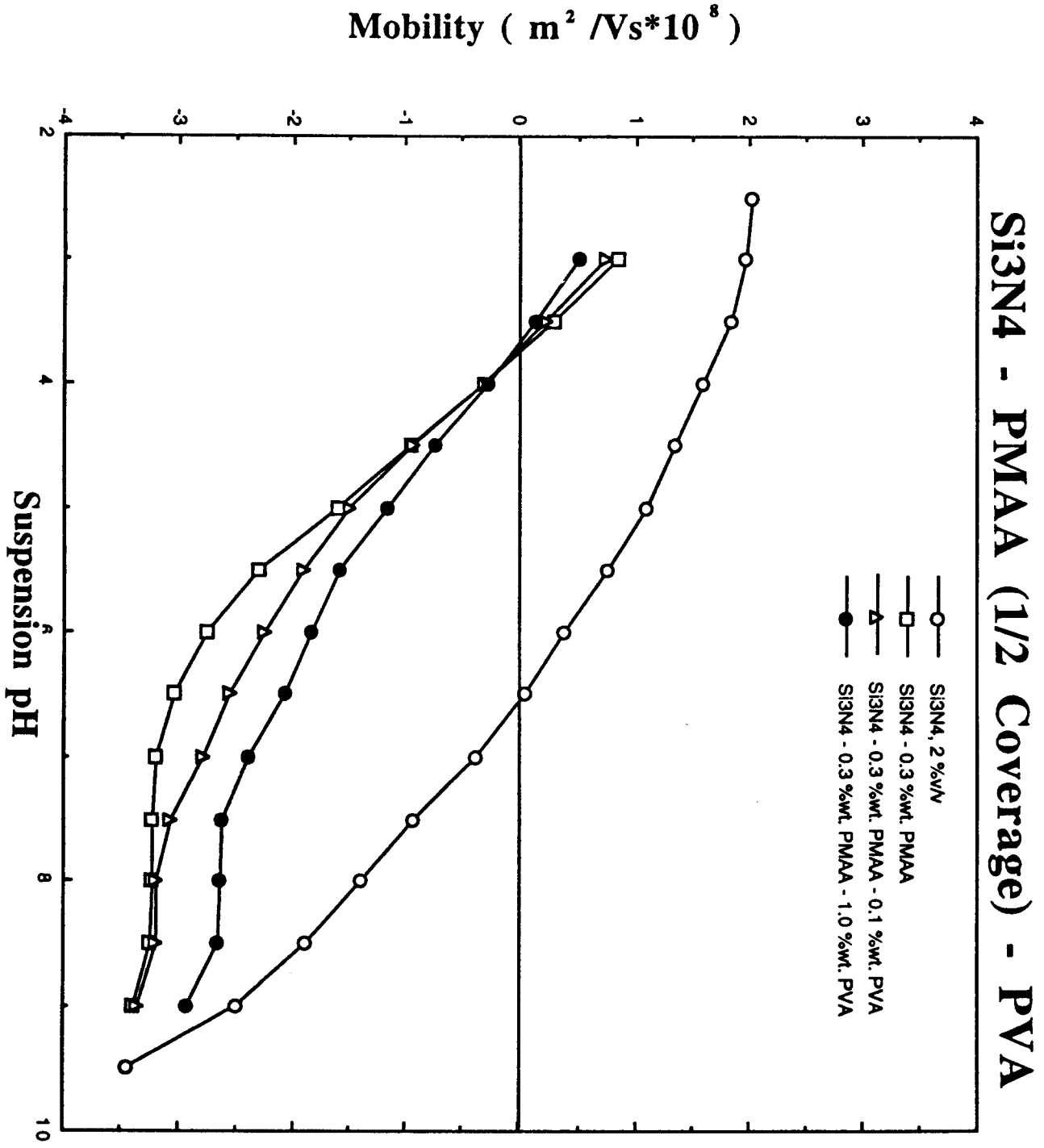

Si3N4+PMAA(Daxad-34)
Adsorbed Amount(mg/m 2)
0.5
0.4
0.3
0.2
0.1
0.0
pH 3.0
pH 6.0
pH 9.0
0.0
0.1
0.2
Residual Concentration(g/dl)

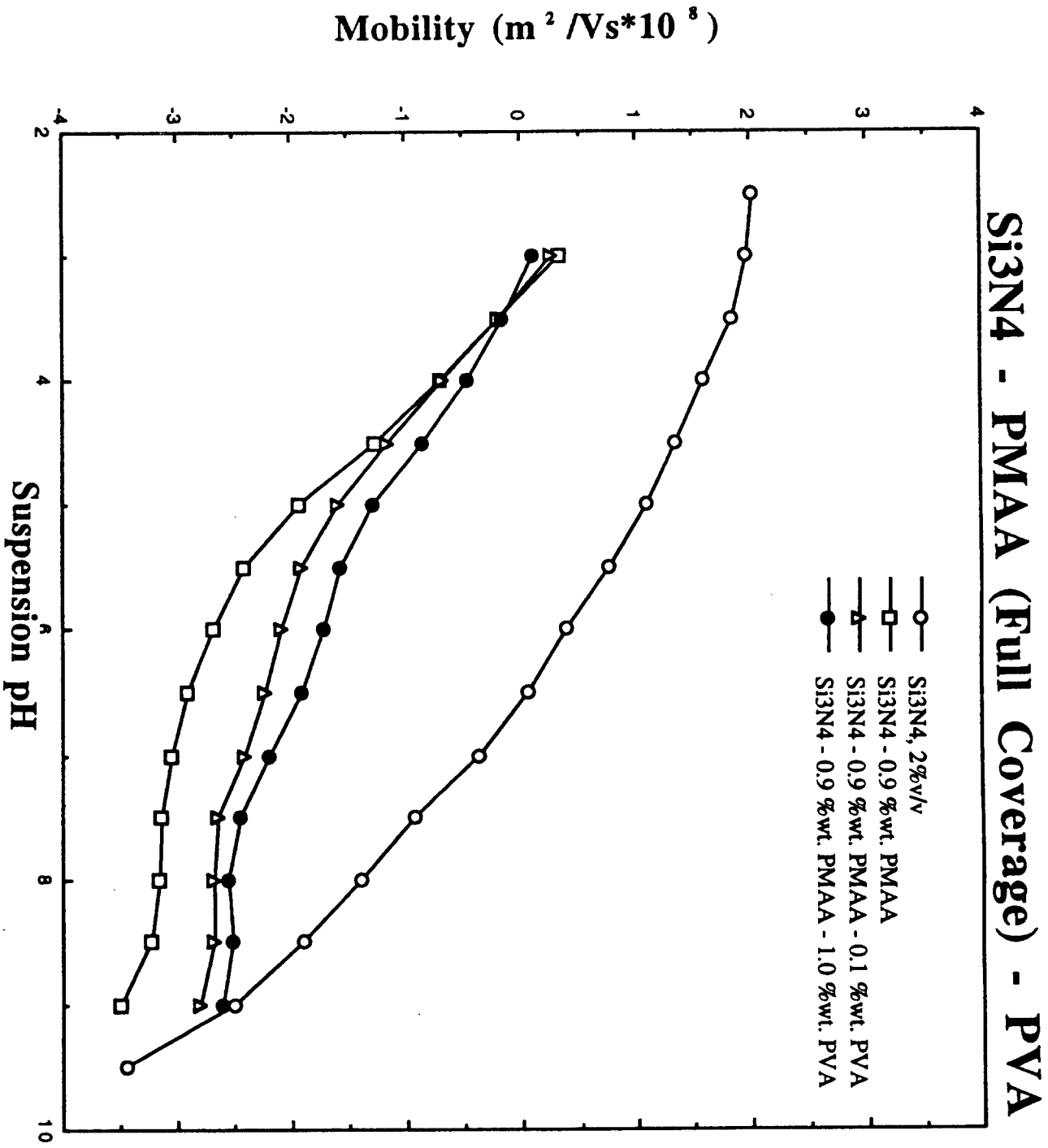

Mobility (m ² /Vs*10 ⁸)
Si3N4 - PVA
Suspension pH
Si3N4, 2.0 %v/v
Si3N4 - 0.5 %wt. PVA
Si3N4 - 1.0 %wt. PVA

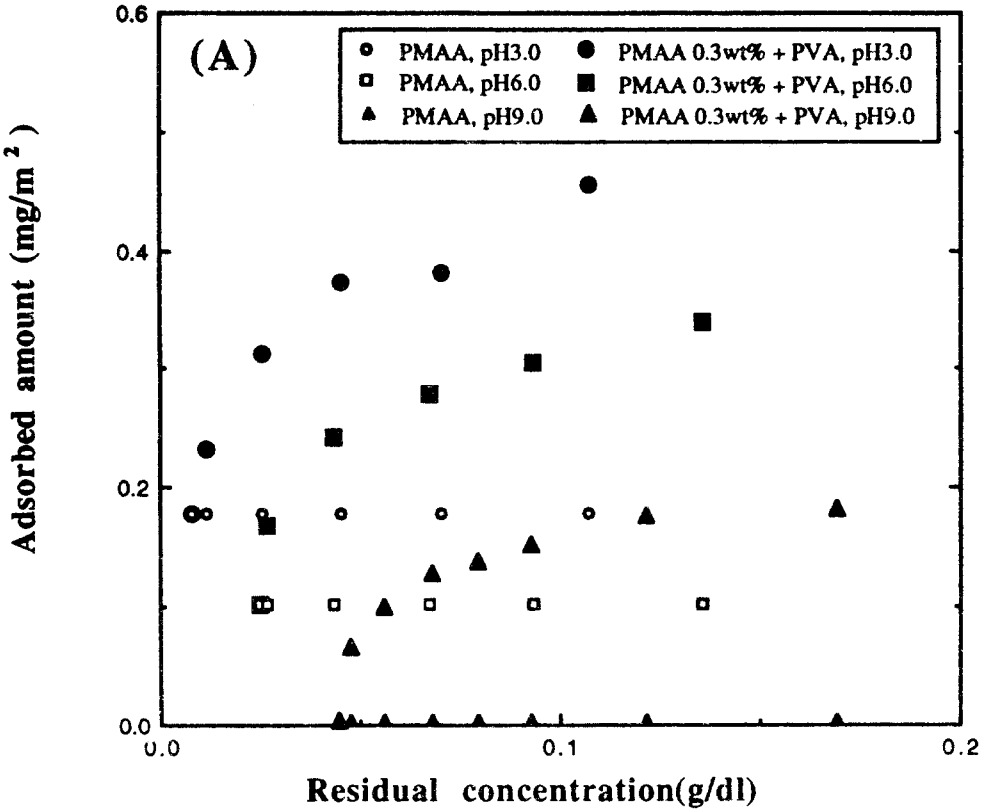

SN+PVA(Mw=25,000 98% Hyd.)
Adsorption Amount(mg/m ²)
0.5
0.4
0.3
0.2
0.1
0.0
0.00
0.10
0.20
pH 3.0
pH 6.0
pH 9.0
Residual Concentration(g/dL)

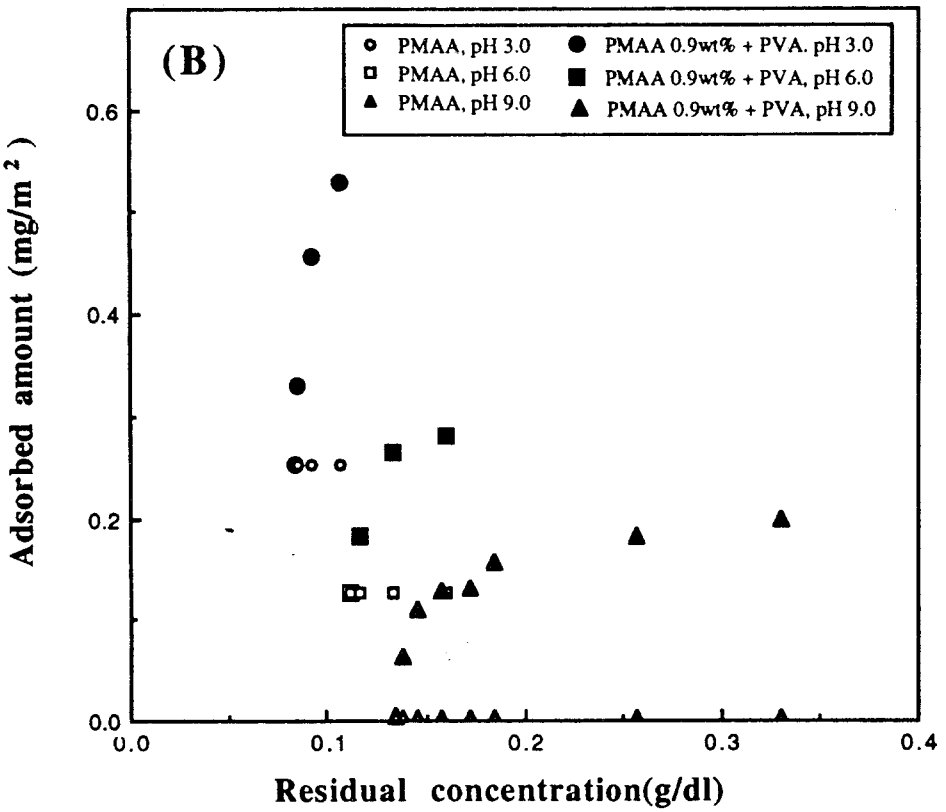

{-CH2-CH(OH)-}n
OH titrated (mole/L x 10^3)
pH
blank
0.1 wt% PVA
net uptake
8
7
6
5
4
3
2
1
0
-1
2
4
6
8
10
12

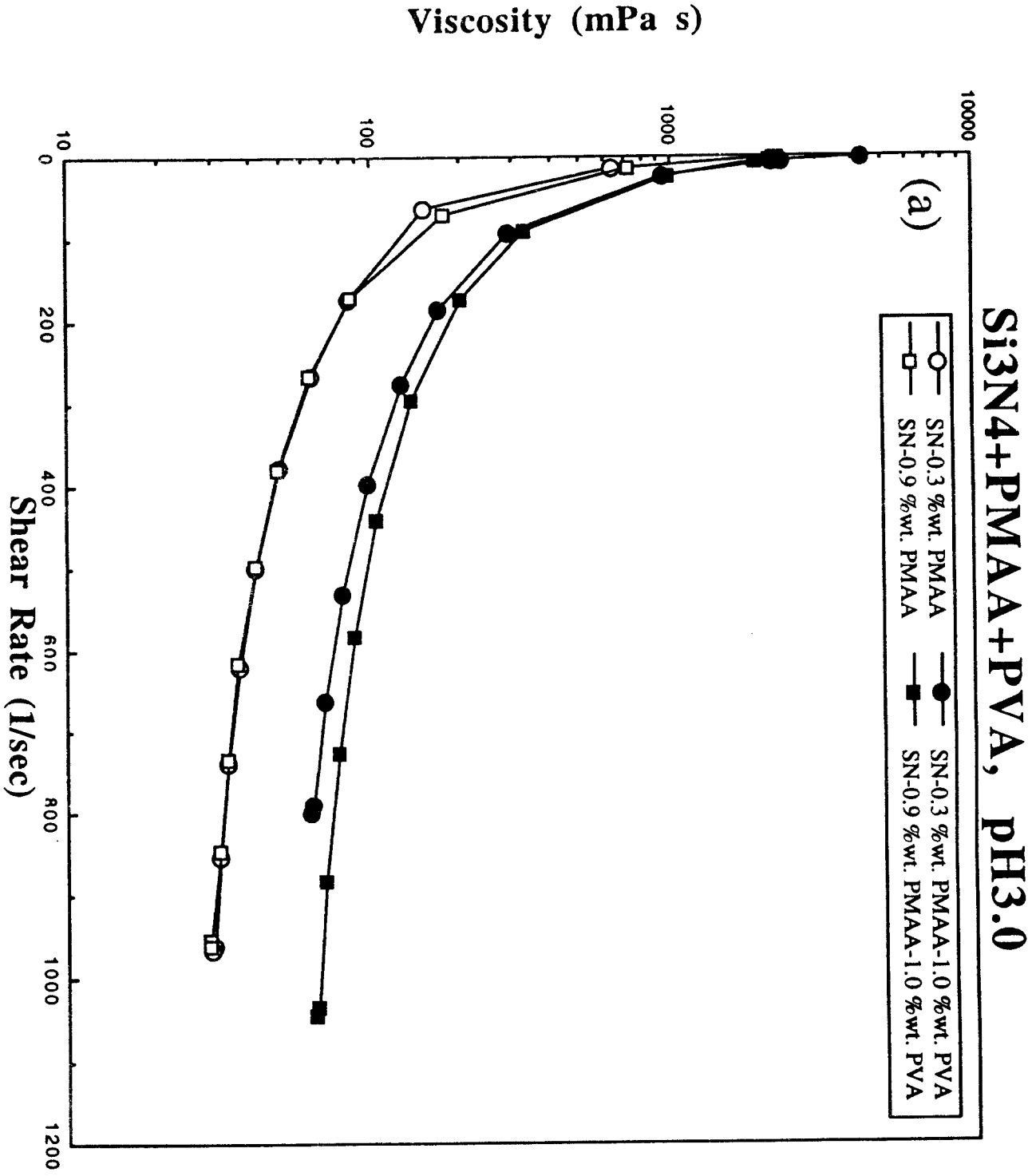

Si3N4 - PMAA (1/3 Coverage) - PVA
Mobility (m²/Vs*10⁹)
Suspension pH
(a)
Si3N4, 2%v/v
Si3N4 - 0.1 %wt. PMAA
Si3N4 - 0.1 %wt. PMAA - 1.0 %wt. PVA
-4
-3
-2
-1
0
1
2
3
4
2
4
6
8
10

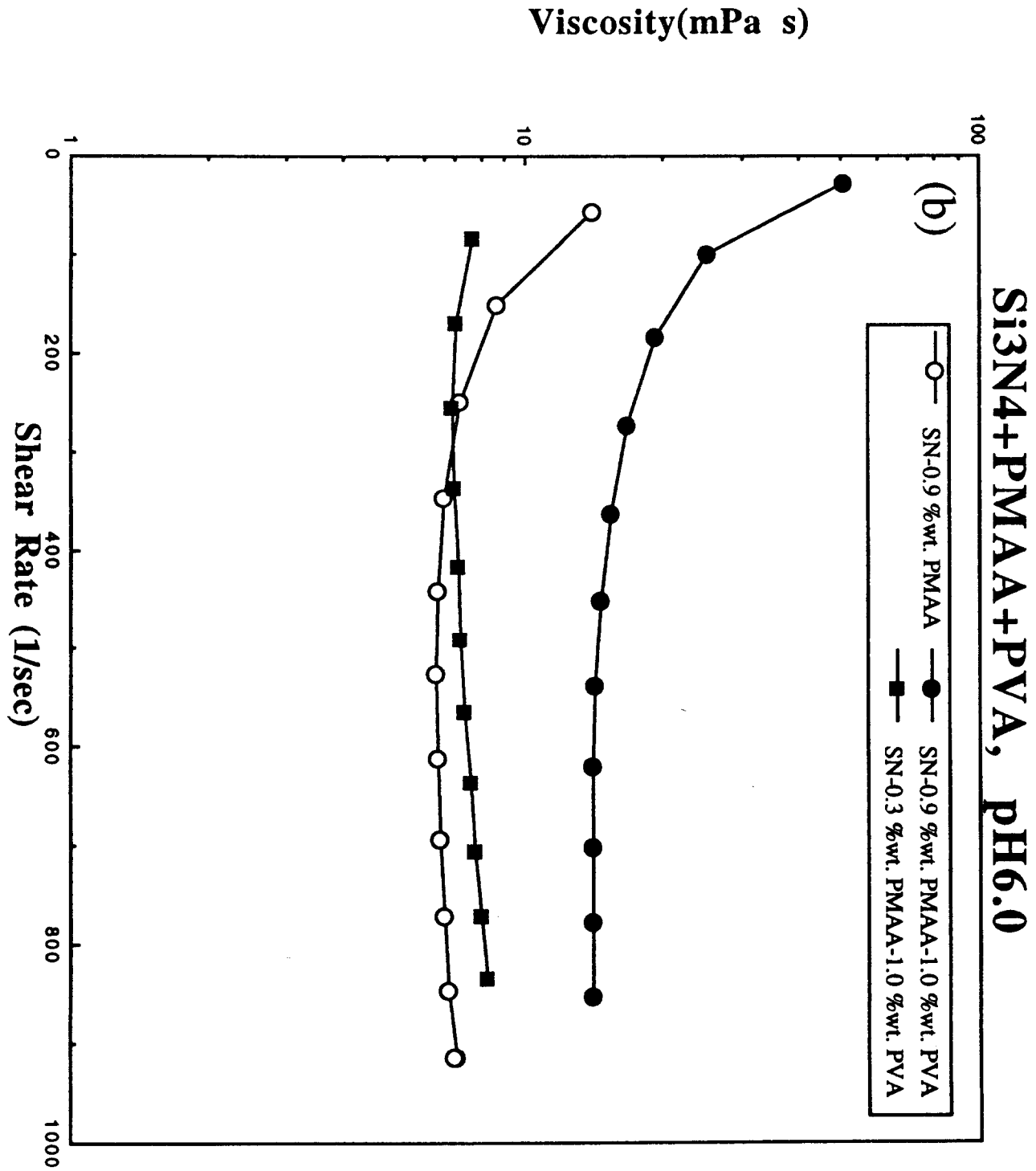

Si3N4 - PMAA (1/2 Coverage) - PVA
Mobility (m² /Vs*10⁸)
Suspension pH
Si3N4, 2 %w/v
Si3N4 - 0.3 %wt. PMAA
Si3N4 - 0.3 %wt. PMAA - 0.1 %wt. PVA
Si3N4 - 0.3 %wt. PMAA - 1.0 %wt. PVA

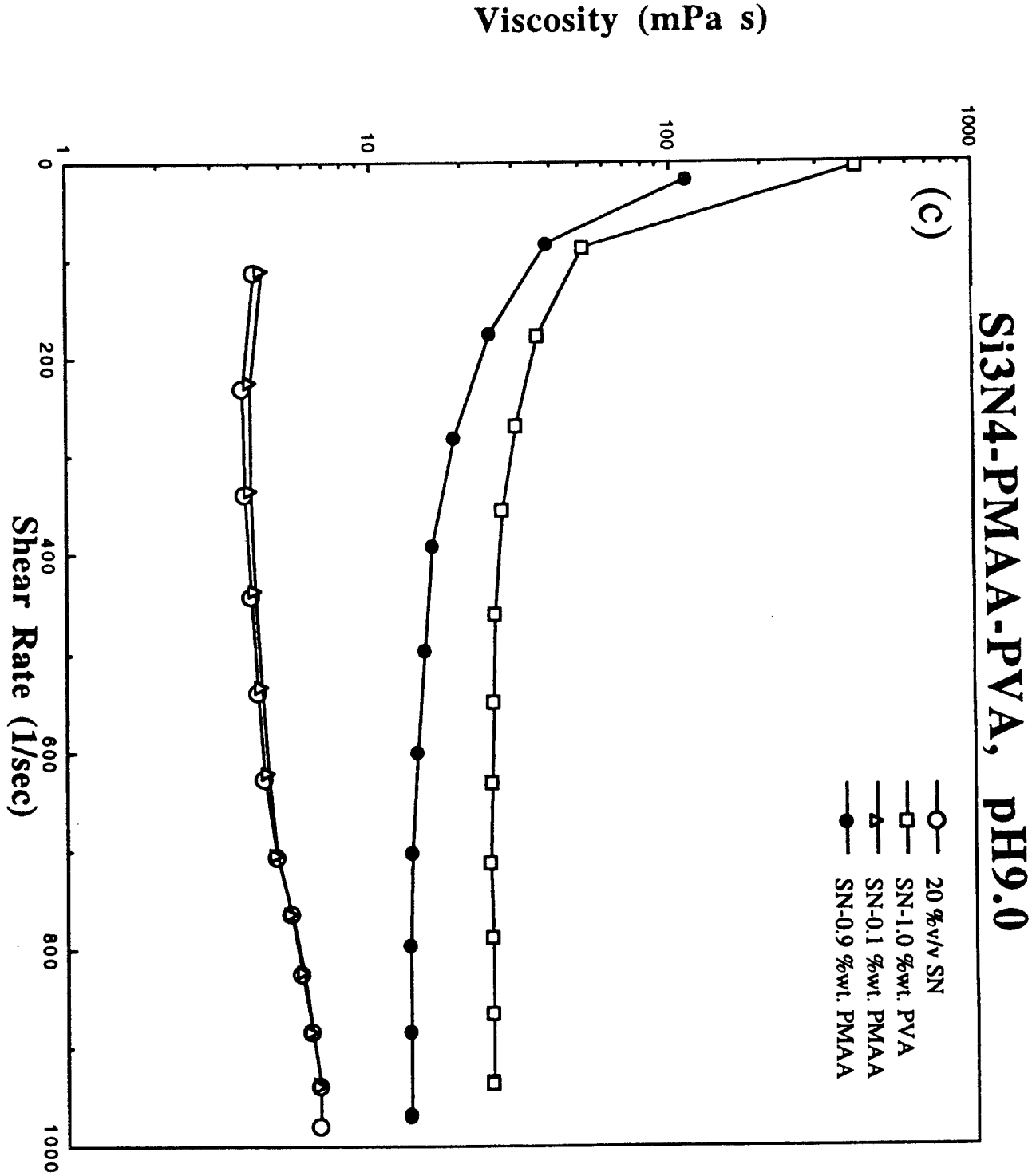

Si3N4 - PMAA (Full Coverage) - PVA
Mobility (m ² /Vs*10 ⁸)
Suspension pH
Si3N4, 2%v/v
Si3N4 - 0.9 %wt. PMAA
Si3N4 - 0.9 %wt. PMAA - 0.1 %wt. PVA
Si3N4 - 0.9 %wt. PMAA - 1.0 %wt. PVA

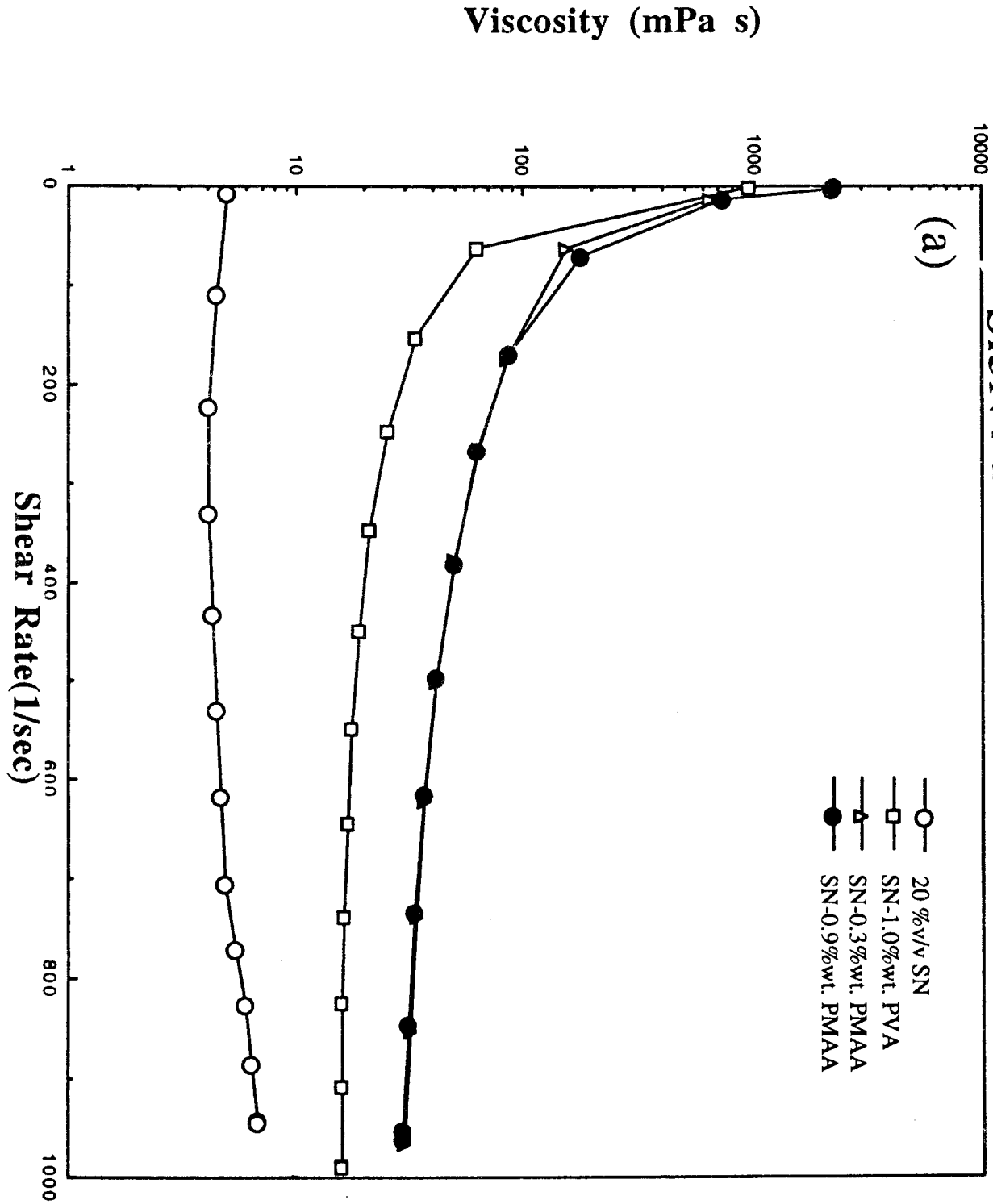

(A)
PMAA, pH3.0
PMAA, pH6.0
PMAA, pH9.0
PMAA 0.3wt% + PVA, pH3.0
PMAA 0.3wt% + PVA, pH6.0
PMAA 0.3wt% + PVA, pH9.0
Adsorbed amount (mg/m²)
Residual concentration(g/dl)
0.0
0.2
0.4
0.6
0.1

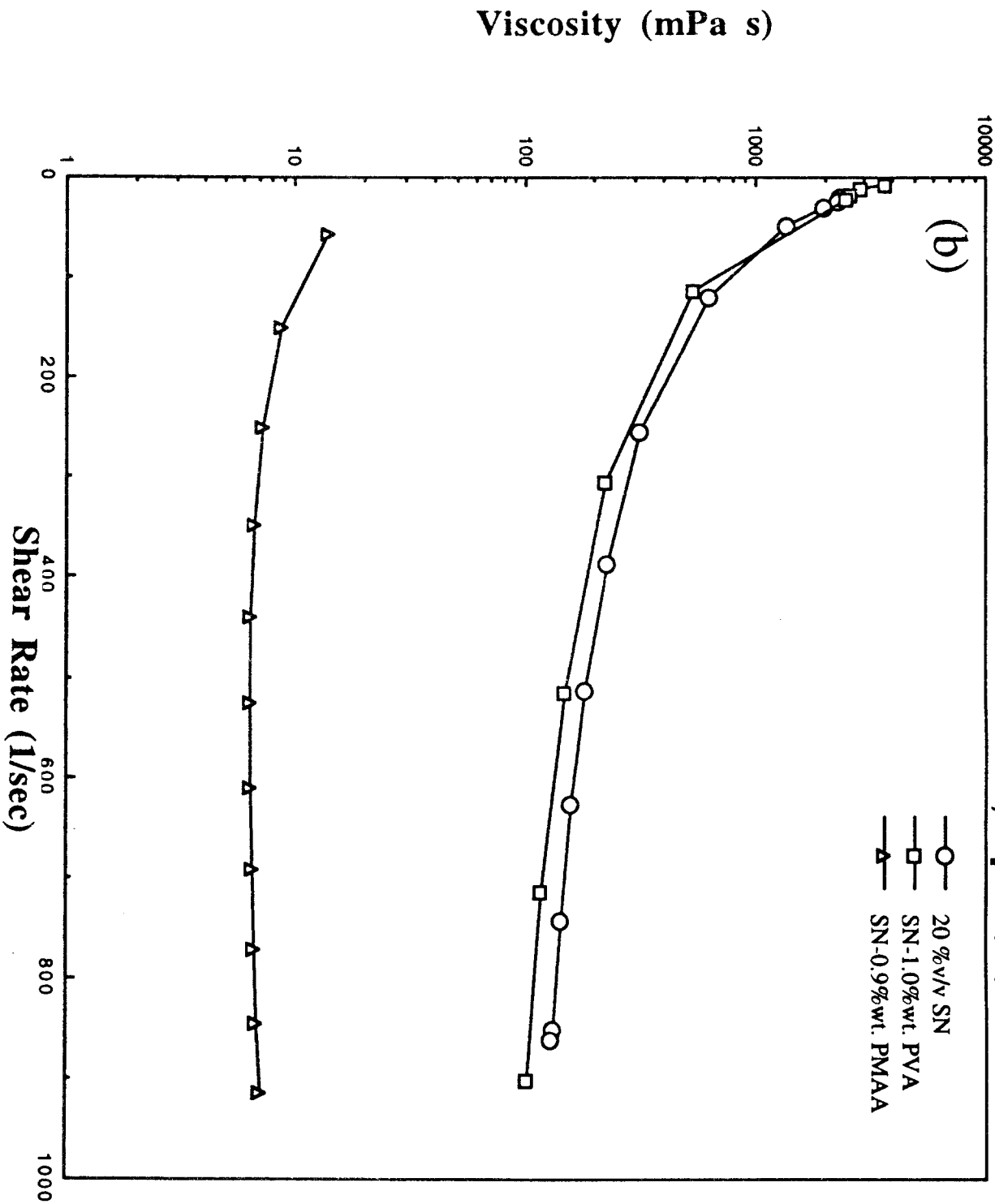

(B)
PMAA, pH 3.0
PMAA, pH 6.0
PMAA, pH 9.0
PMAA 0.9wt% + PVA. pH 3.0
PMAA 0.9wt% + PVA, pH 6.0
PMAA 0.9wt% + PVA, pH 9.0
Adsorbed amount (mg/m²)
Residual concentration(g/dl)
0.0
0.2
0.4
0.6
0.1
0.3

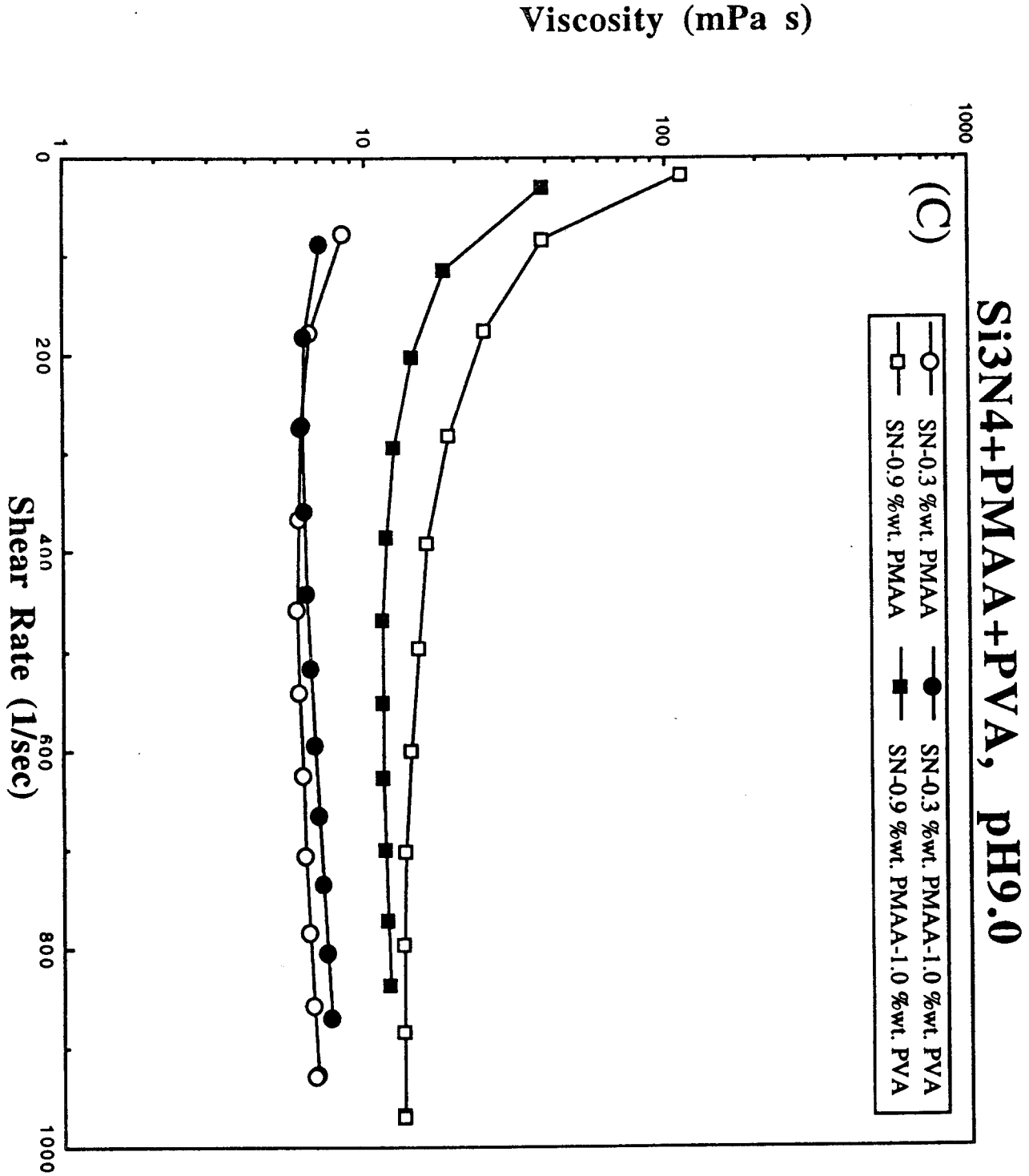

Viscosity (mPa s)
Si3N4+PMAA+PVA, pH3.0
(a)
SN-0.3 %wt. PMAA
SN-0.9 %wt. PMAA
SN-0.3 %wt. PMAA-1.0 %wt. PVA
SN-0.9 %wt. PMAA-1.0 %wt. PVA
Shear Rate (1/sec)
10
100
1000
10000
0
200
400
600
800
1000
1200


Viscosity(mPa s)
Si3N4+PMAA+PVA, pH6.0
(b)
SN-0.9 %wt. PMAA
SN-0.9 %wt. PMAA-1.0 %wt. PVA
SN-0.3 %wt. PMAA-1.0 %wt. PVA
Shear Rate (1/sec)
1
10
100
0
200
400
600
800
1000


Viscosity (mPa s)
Si3N4-PMAA-PVA, pH9.0
(c)
20 %v/v SN
SN-1.0 %wt. PVA
SN-0.1 %wt. PMAA
SN-0.9 %wt. PMAA
Shear Rate (1/sec)
1
10
100
1000
0
200
400
600
800
1000


Viscosity (mPa s)
Si3N4-PMAA-PVA, pH3.0
(a)
20 %v/v SN
SN-1.0%wt. PVA
SN-0.3%wt. PMAA
SN-0.9%wt. PMAA
Shear Rate(1/sec)
1
10
100
1000
10000
0
200
400
600
800
1000


Viscosity (mPa s)
10000
1000
100
10
1
0
200
400
600
800
1000
Shear Rate (1/sec)
(b)
Si3N4-PMAA-PVA, pH6.0
20 %v/v SN
SN-1.0%wt. PVA
SN-0.9%wt. PMAA


Viscosity (mPa s)
Si3N4+PMAA+PVA, pH9.0
(C)
SN-0.3 %wt. PMAA
SN-0.9 %wt. PMAA
SN-0.3 %wt. PMAA-1.0 %wt. PVA
SN-0.9 %wt. PMAA-1.0 %wt. PVA
Shear Rate (1/sec)
1
10
100
1000
0
200
400
600
800
1000

Conclusions

- **Electrokinetic Sonic Amplitute Analysis:**

  Simple, Fast and relatively Accurate

- **PMAA And PVA Adsorptions :**

  Highly dependent on silicon nitride suspension pH

- **Interactions Between PMAA and PVA:**

  - PMAA adsorption dominate and does not change with PVA addition
  - PVA coadsorbed on silicon nitride surface after PMAA adsorption