



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

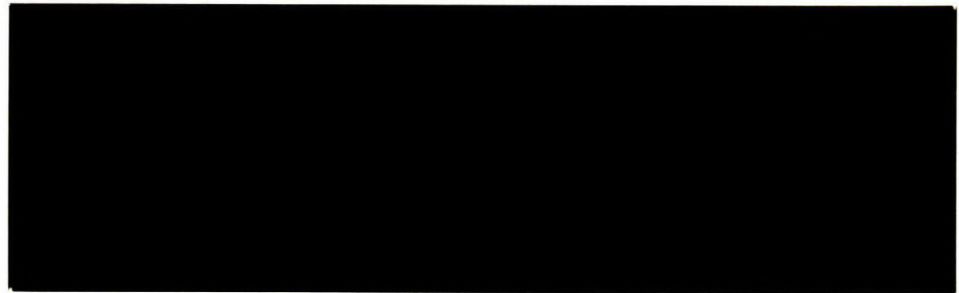
CANMET

Canada Centre for
Mineral and Energy
Technology

Centre canadien de la
technologie des
minéraux et de l'énergie

**Coal
Research
Laboratories**

**Laboratoires de
recherche sur
le charbon**



WRC 92-075(J)

01-0004636

Canada 



**DYNAMIC AND EQUILIBRIUM SURFACE TENSION
OF AQUEOUS POLYACRYLAMIDE SOLUTIONS**

Yuming Xu, Chandra W. Angle, Hassan A. Hamza

Division Report WRC 92 - 75 (J)

December 1992

43 RP

Dynamic and Equilibrium Surface Tension of Aqueous Polyacrylamide Solutions

by

Yuming Xu* , Chandra Angle**, Hassan A. Hamza***

ABSTRACT

Surface tension of eight different polyacrylamide samples was measured using du Nouy ring, Wilhelmy plate, and maximum bubble pressure methods over a wide concentration range. Experimental results were found to agree with available literature data for diluted solutions of similar polymers.

The aqueous polyacrylamide solutions were found to be surface active. The surface tension of the polymer solutions showed a similar behavior to solutions of surfactant. It was noted that the surface tension of polymer solutions decreased linearly with increasing logarithm of concentration; at high concentrations, surface tension remained constant or nearly constant. A possible "CMC-type" behaviour was observed for these polymer solutions and the suggested "CMC" values were calculated based on surface tension and electroconductivity measurements. The experimental results showed that the carboxylic or cationic substituted polyacrylamides are more surface active than the unsubstituted polyacrylamides.

* Research Scientist, ** Colloid Scientist, *** Manager, Western Research Center, CANMET, Energy Mines and Resources Canada, Devon, Alberta.

RESUME



CONTENTS

| | <u>Page</u> |
|---|-------------|
| ABSTRACT | i |
| RESUME | ii |
| INTRODUCTION | 1 |
| EXPERIMENTAL | 4 |
| Material | 4 |
| Measurement Methods | 5 |
| RESULTS AND DISCUSSION | 8 |
| Dynamic and Equilibrium Surface tension | 8 |
| Comparison to available literature values | 10 |
| Effect of substituted functional groups | 11 |
| Dependence of concentration and CMC | 13 |
| CONCLUSIONS | 15 |
| ACKNOWLEDGEMENTS | 16 |
| REFERENCES | 17 |

TABLES

No.

| | |
|--|----|
| 1. Suggested CMC for aqueous PAM solutions | 20 |
|--|----|

FIGURES

| | |
|--|----|
| 1. Surface tension for PAM solutions (PAM-2) | 21 |
| 2. Surface tension for PAM solutions (PAM-3) | 22 |

| <u>No.</u> | <u>Page</u> |
|--|-------------|
| 3. Surface tension for PAM solutions (PAM-1) | 23 |
| 4. Surface tension for Percol745. | 24 |
| 5. Surface tension for Percol 724 | 25 |
| 6. Surface tension for Percol 722 | 26 |
| 7. Surface tension for Percol 763 | 27 |
| 8. Surface tension for Percol 757 | 28 |
| 9. Dependence of dynamic surface tension on bubble frequency | 29 |
| 10. Conductivities of PAM solutions (PAM-2) | 30 |
| 11. Conductivities of PAM solutions (PAM-3) | 31 |
| 12. Conductivities of PAM solutions (PAM-1) | 32 |
| 13. Conductivities of Percol 745 | 33 |
| 14. Conductivities of Percol 724 | 34 |
| 15. Conductivities of Percol 722 | 35 |
| 16. Conductivities of Percol 763 | 36 |
| 17. Conductivities of Percol 757 | 37 |
| 18. CMC values for Percols as a function of cationicity | 38 |

INTRODUCTION

Polyacrylamide (PAM) is one of the most widely used water-soluble polymers. In addition to its well-known applications in flocculation for enhancing solid-liquid separation and in soil conditioning for improving infiltration, polyacrylamide plays an important role in enhanced oil recovery techniques such as polymer and polymer/surfactant flooding. In these techniques, aqueous polymer solutions are used as mobility control agents to sweep the oil reservoir. As a result of these applications the rheological and flow properties of the polymer solutions have been investigated extensively. However, the surface or interfacial tension of the polymer solutions has not been given much attention, although these properties are very important in enhanced oil recovery and other industrial processes. For example, the operation of a flotation process requires the knowledge of surface tension because the bubbling behaviour is directly influenced by the surface tension. Experimental data on the surface tension of aqueous polyacrylamide solutions are sparse, and most are for dilute solutions. Data on the surface tension for concentrated solutions are very rare.

Miaw measured the surface tension of very dilute polyacrylamide (Separan AP-30, Dow Chemical Company) solutions in the concentration range of 0-500 ppm using capillary rise and du Nouy ring methods (1). He observed that the surface tension of PAM solutions was about the same as that of pure water in the concentration range he studied. Paul also measured the surface tension of very dilute Separan AP-30 (Dow Chemical Company) solutions over a concentration range of 0-200 ppm using capillary rise method (2). For these very dilute solutions Paul found that the surface tension was almost independent of the concentration and was about the same as for water. Shima et al.

measured the surface tension of PAM (Aronfloc A-20P, Toagosei Chemical Inc., Japan) solutions over a concentration range of 0-10 000 ppm (3-5). They obtained the similar results for dilute solutions. However, for higher concentrations (>2000 ppm) they found that the surface tension of the solutions was lower than that for water. Hu et al. also measured the surface tension of PAM (Separan AP-30) solutions in the concentration range of 0-1000 ppm using the maximum bubble pressure method (6). They found that the surface tension of Separan AP-30 solutions was about the same as or slightly higher than found for water. Their results show that the surface tension of Separan AP-30 solution at 1000 ppm was approximately 5% higher than that for pure water. Prud'mamm and Long reported several experimental data for concentrated PAM solutions (0-2.3 wt%) measured with pendent drop method (7). They studied two polyacrylamide samples, one from Aldrich with low carboxyl content and the other from Dow Chemical Co. with 30% carboxyl content. They found that both PAMs decreased the surface tension of water significantly. For example, the surface tension of a PAM solution was 42 dyne/cm at a concentration of 2.3 wt% compared to 72.8 dyne/cm for pure water. Recently Ishiguro and Itarnett reported the surface tension values of Separan AP-30 (Dow Chemical) in the concentration range of 0-2000 ppm, showing that the values were about the same as those for water (8). Huang et al. studied the effects of biopolymer (xanthan) and partly hydrated polyacrylamide on the interfacial tension between acidic crude oil and alkaline solutions (9). They reported that the interfacial tension can be reduced by one to two orders of magnitude with the addition of polymers.

In addition to the polyacrylamide solutions, other water-soluble polymer solutions were also studied. For example, Sandescu and Simionescu

investigated the interfacial phenomena on ternary acrylic copolymer solutions, acrylonitrile/vinyl acetate/alpha-methyl styrene (91/6/3) in 85 wt% ethylene carbonate aqueous solution (10). They found that the surface tension decreases with the increase of polymer concentration, molecular weight, polar group content in the copolymer, and the temperature.

The surface tension for some non-aqueous polymer solutions and molten polymers have also been reported in the literature (11-18). Ueberreiter et al. measured the surface tension of various molecular weight polystyrene-benzene solution using du Nouy ring method (11). They studied the time dependence of the surface tension of the polymer solutions and used the well-known Avrami equation to describe the kinetic behaviour of the surface tension. Their results showed that the equilibrium surface tension of polystyrene solutions decreases with the increase in concentration of the polymer. In their subsequent series of publications (12-15) these authors have also studied the surface tension of polystyrene, polymethylmethacrylate, and polyisobutylene in different organic solvents using either du Nouy ring or Wilhelmy plate method. Shinozaki et al. measured interfacial tension of polystyrene-methylcyclohexane, polystyrene-heptamethylnonane and poly(dimethyl siloxane)-phenylethyl ether solutions to study the temperature dependence of the interfacial tension (16). Their surface tension data were obtained by using the sessile drop method. Ober et al. used the du Nouy ring method to measure the surface tension of Polystyrene and PDMS (poly dimethylsiloxane) in toluene (17). These two polymer solution systems were representative for repulsive interface and attractive interface, respectively. They found that for repulsive interface the surface tension of polymer solutions can be represented by $\gamma - \gamma_0 = \beta \Phi_b^\alpha$ where γ_0 is the surface tension of the solvent and Φ_b is the volume fraction of the polymer solute. For

attractive interface these authors observed a progressive decrease of the surface tension with an increasing concentration of polymer. Sauer et al. used modified Wilhelmy plate method to measure the surface tension of many molten polymers (18). They studied the effect of molecular weight, viscosity, and temperature on the surface tension. Their results show that the surface tension of molten polymers was very slightly dependent on molecular weight and viscosity.

The previous investigations, as briefly summarized above, have shown that the surface tension of polyacrylamide solutions and other polymer solutions can be reduced by an increase in the polymer concentration. In addition to the fact that the data for surface tension of PAM solutions at high concentration is sparse, none of the above studies have been carried out systematically over a wide range of solution concentrations. As part of our research on the waste water and sludge treatment we have measured the surface tension of different PAM solutions over a broad concentration range.

EXPERIMENTAL

MATERIALS

Eight different PAM samples have been studied in this work. All were supplied by commercial chemical companies. They can be described as follows:

Nonionic

One nonionic PAM sample (PAM-1) with the average molecular weight of 5-6 million was supplied by Aldrich Chemical Company.

Anionic

Two partially carboxylated PAM samples with the same average molecular weight of 2×10^5 but different carboxyl content were also supplied by Aldrich Chemical Company. Sample 1 (PAM-2) has a low carboxyl content (10%) while the carboxyl content for sample 2 (PAM-3) is 70%.

Cationic

Five cationic PAM samples which have the same molecular weight but different cationicities were supplied by Allied Colloids. The molecular weight for these samples is 8-10 million. The cationicities for these samples are as follows: Percol 745, 3.7%; Percol 724, 7.4%; Percol 722, 23.6%; Percol 763, 41.8%; and Percol 757, 62.7%.

The nonionic and anionic polymer solutions were prepared by introducing 100 mL deionized water into a beaker in which a known amount of polymer powder had been placed. The water was gently stirred until all polymer powder was dissolved. The solutions were set to stand overnight before the measurements were conducted. The cationic PAM solutions were prepared by the following method as suggested by the manufacturer. The known amount of Percol sample was slowly added into 100 mL of denioned water as it was stirred at 1300 rpm. The solution was kept stirring for about 1 hour.

MEASUREMENT METHODS

Several different methods have been used by previous investigators for surface tension measurements of polymer solutions. They include du Nouy ring (11-13,17), capillary rise (1-5,8), maximum bubble pressure (6), pendent drop (7), and Wilhelmy plate (15, 18) methods. Three different methods were used in this work for the surface tension measurements: du Nouy ring, Wilhelmy plate, and Maximum bubble pressure. All measurements were conducted at 20°C.

du Nouy Ring Method

The du Nouy ring tensiostat was supplied by Fisher Scientific (model 21). The ring used was a 6-cm platinum-iridium (90-10 wt%) ring. The measurements were performed in a semi-automatic model. The ring was first immersed into the

polymer solution and then slowly raised by a small electrical motor at a fixed speed. When the ring was detached from the surface of the liquid the tension force was recorded directly in the tensiometer. The surface tension was calculated by multiplying the reading in the meter by a correction factor which is a function of the force, ring size, and the densities of two phases. The calculation can be summarized by the following two equations:

$$\gamma = P f \quad \text{Eq 1}$$

$$(f - a)^2 = P / (D - d) \times 4b / (\pi R)^2 + K \quad \text{Eq 2}$$

where P is the reading in the meter, $a=0.725$, $b=0.0009075$, D and d are densities of the lower phase and upper phase, R is the radius of the ring, r is the radius of the wire of the ring, and $K=0.04534-1.679 r/R$.

Wilhelmy Plate Method

In Wilhelmy plate method, a thin rough platinum plate was suspended from one arm of the CAHN-2000 electrobalance. The perimeter of the plate is 1.998 cm measured using a caliper. The plate was cleaned with distilled water and then flamed in a butane flame before it was attached to the balance. The liquid level of the polymer solution was slowly raised until it just immersed the bottom edge of the plate and a capillary rise of the liquid at the plate was observed. The liquid was then very carefully lowered and a maximum weight reading was obtained as measured by the electrobalance. This weight was then used to calculate the surface tension by the following equation:

$$\gamma \cos \theta = \Delta W / p \quad \text{Eq 3}$$

where ΔW is the change in the weight from the balance, p is the perimeter of the plate, and θ is contact angle of the liquid on the plate. Because of the high surface energy of the platinum and the relatively rough surface of the plate, the contact angle is almost zero for most liquids. Therefore Eq 3 can be reduced to

$$\gamma = \Delta W/p \quad \text{Eq 4}$$

Maximum Bubble Pressure Method

The third apparatus used for surface tension measurement in this work was SensaDyne 6000 surface tensiometer. In this method two capillaries of different radii (4.0 mm and 0.5 mm, respectively) were immersed beneath a polymer solution surface. Nitrogen gas was bubbled through these two capillaries. The pressure of the gas bubble in the end of the capillary is expressed by

$$P = \Delta\rho gL + 2\gamma/r \quad \text{Eq 5}$$

where $\Delta\rho$ is the density difference between the liquid and gas and L is the hydrostatic height to the bottom of the bubble. When two capillaries of different diameters having the same hydrostatic height were placed in the liquid, a differential pressure signal was produced. This differential signal was directly related to the surface tension of the liquid by the following equation:

$$\Delta P = 2\gamma(1/r_1 - 1/r_2) \quad \text{Eq 6}$$

where ΔP is the pressure difference across the two tubes, r_1 and r_2 are the end radii of the two capillaries. Equation 6 shows that the maximum bubble pressure difference is directly proportional to the surface tension of the liquid. Therefore, two liquids of known surface tension can be used as standards to establish the calibration curve of ΔP against γ . This calibration curve allows the determination of surface tension of an unknown sample from the measurement of the bubble pressure difference, ΔP . In this work, deionized water (72.8 dyne/cm, 20°C) and pure isopropanol (21.3 dyne/cm, 20°C) were used as high and low surface tension standards, respectively, for calibrating the instrument. The measurements were conducted at a fixed bubble frequency, 1 bubble per second.

Conductivity Measurement

For each solution the electroconductivity was also measured using a conductivity meter (model CDM83) supplied by Radiometer, Copenhagen. A large test tube containing the solution to be measured was maintained in a constant water bath at 20°C. The conductivity cell was then placed into the solution. The glass tube was kept in the water bath until a constant conductivity value was obtained.

RESULTS AND DISCUSSION

DYNAMIC AND EQUILIBRIUM SURFACE TENSION

Figure 1 shows the surface tension for anionic polyacrylamide (low carboxyl content) solution as a function of concentration. The surface tension for this sample was measured by three different methods: du Nouy ring, Wilhelmy plate, and maximum bubble pressure. The results indicate that the surface tension obtained from the ring and the plate methods are in excellent agreement throughout the entire concentration range. Therefore, only the du Nouy ring and bubble pressure methods were used for the subsequent measurements of high-carboxyl-content anionic PAM and nonionic PAM solutions. The results for these two samples are shown in Fig. 2 and 3, respectively.

The surface tension for five cationic PAM samples was measured only by the maximum bubble pressure method. The results for these samples are illustrated in Fig. 4 to 8.

The surface tension values for three nonionic and anionic PAM samples measured by the maximum bubble pressure method show differences from those obtained with the ring or plate method. This may be due to the fact that the former is a dynamic tension while the latter is an equilibrium value. For a pure

liquid the two methods give the same value, but for a solution, the dynamic surface tension is bubble-frequency-dependent (Hua et al.,19-21). At high frequency, gas bubbles through the liquid very quickly and there is not enough time for the surface-active species to diffuse to the bubble interface, which results in a higher surface tension value than the equilibrium value. Hua et al. have shown that for very dilute surfactant solutions the dynamic surface tension should approach those of solvent at high bubble frequency (19). As bubble frequency becomes lower (longer bubbling time), the dynamic surface tension value approaches the equilibrium value. The rate at which the dynamic surface tension approaches the equilibrium surface tension value is determined by the properties of the solution. Hua et al. have discussed the dynamics of surfactant solutions in detail (19). They represented the change in the behaviour of dynamic surface tension with time by four regions: induction, rapid fall, mesoequilibrium (γ_m), and equilibrium (γ_∞). They revealed that for some solutions, mesoequilibrium surface tension may be the same as the equilibrium value while for other solutions the mesoequilibrium value may never reach to the equilibrium surface tension. Our dynamic surface tension data were obtained at the frequency of 1 bubble per second at which the large polymer molecules cannot reach an equilibrium state. This may explain why our results obtained using the du Nouy ring (equilibrium method) disagreed with those obtained using dynamic measurements at the frequency of 1 bubble per second.

Because dynamic surface tension is dependent on bubble frequency or time, therefore, it is recommended that bubble frequencies should be reported along side the corresponding surface tension values unless surface tension data are equilibrium or mesoequilibrium values. In order to investigate how the surface tension of a polymer solution changes with the bubble frequency we measured the surface tension of two polymer solutions (PAM-3, 0.1wt% and

1wt%) at different frequencies as shown in Fig. 9. As can be seen from this graph, at low frequencies the surface tension increases rapidly with the increase in frequency. At higher frequencies, the increase in surface tension with frequency becomes slower. It is noteworthy that at higher frequencies the surface tension for the dilute solution (0.1wt%) is higher than the surface tension of water. For example, at a frequency of 7.8 bubbles per second, the surface tension value reaches to 74.4 dyne/cm.

COMPARISON TO AVAILABLE LITERATURE VALUES

Hu et al. used the maximum bubble pressure method to determine the surface tension for several different aqueous polymer solutions including PAM (6). They reported the surface tension for Separan AP-30 in the concentration range of 0-1000 ppm over the temperature range of 20 to 60°C. Their results were slightly higher than the surface tension of water. For instance, at a concentration of 1000 ppm their surface tension values were about 5% higher than those of water. Bearing in mind that their measurements were conducted by the bubble pressure method, their results were in fact dynamic surface tension values. Although the authors did not mention the bubble frequency at all, it is likely that their results were not obtained at very low frequencies because the dynamic surface tension increases with an increase in frequency. As shown in Fig. 9 at high frequencies our surface tension values for dilute solution (0.1%), which is the same as the maximum concentration that Hu et al. measured (1000 ppm) are also higher than that for water.

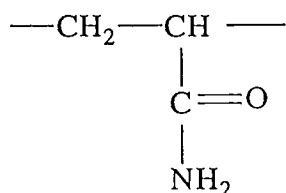
Miaw's (1), Paul's (2), and Ishiguro's (8) equilibrium surface tension data, all obtained by the capillary rise method, are for dilute solutions in the concentration ranges 0 to 200 ppm, 0 to 500 ppm, and 0-2000 ppm, respectively. Their data show that the surface tension values are about the same as those for

water and are independent of the concentration over these low concentration ranges. Although our measurements were not at such low concentrations our data at the lowest concentration (0.01wt%) approach the value of surface tension of water as shown in Fig. 1-3. This is in agreement with the results of these authors.

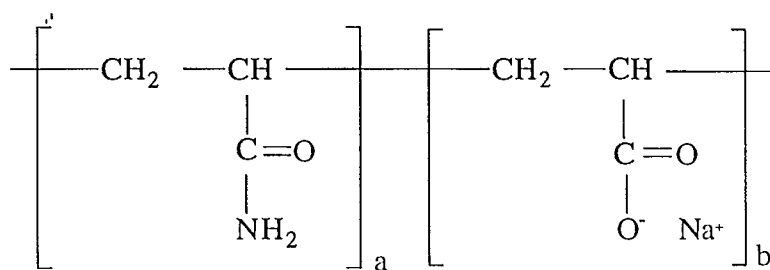
Shima's data show that the surface tension of PAM solution slightly decreases with increasing concentration over the concentration range of 0 to 10000 ppm (3-5). Our results, displayed in Fig. 1 to 3, show the same trend. As concentration increases the equilibrium surface tension decreases. At high concentrations the surface tension of the PAM solution can be reduced to as low as 30 dyne/cm. Similar values have been observed by Prud'momm and Long who reported the surface tension of aqueous PAM solution at 2.3 wt% to be 42 dyne/cm (8).

EFFECT OF SUBSTITUTED FUNCTIONAL GROUPS

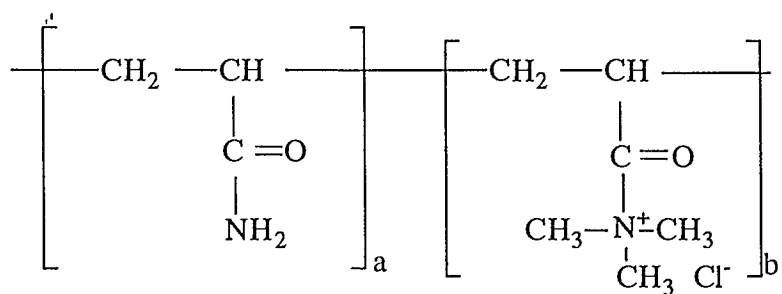
The chemical structure for the backbone of nonionic, anionic, and cationic polyacrylamides can be represented by the following formulas:



Nonionic



Anionic



Cationic

For nonionic PAM the functional groups are amine. In anionic PAM, amine groups are partially hydrolyzed and are substituted by carboxyl groups. In Percol samples (cationic PAM), part of the amine groups are substituted by amino groups.

The fact that the surface tension of PAM solutions can be reduced significantly indicates that the polyacrylamide molecules have some surface activity. Figures 1 to 3 illustrate that the equilibrium surface tension for higher-molecular-weight nonionic PAM solutions is higher than those for carboxylic modified anionic PAM solutions at the same concentration. At very dilute concentrations the surface tension values for the three PAM samples are about the same because the surface tension of the solutions approaches that of water. However, when the concentration increases, the surface tension for the high-carboxyl anionic PAM (70% carboxyl group) solution decreases the most rapidly and that of the nonionic PAM decreases the most slowly. This implies that the carboxylic groups (-COOH) are more surface active than the amine (-NH₂) group. Figures 4 to 8 show that at very dilute concentrations the dynamic surface tension for all five percol samples is about the same. At higher concentrations the surface tension for samples with higher cationicities is lower than that for

those with lower cationicities. As an example, at the concentration of 0.2%, the surface tension for Percol 745 (3.7% cationicity) and 724 (7.4%) are 66 mN/m, while the surface tension for Percol 722 (23.6%) is 60 mN/m, that for Percol 763(41.8%) is 30 mN/m, and that for Percol 757 (62.7%) is 31 mN/m. It should be mentioned that the molecular weights for all Percol samples are the same. The only difference between them is the cationicity. Therefore, the difference in dynamic surface tension among these samples is likely caused by difference in the extent of cationicity. This leads us to conclude that the substituted cationic groups are more surface-active than the unsubstituted amine groups.

DEPENDENCE OF CONCENTRATION AND CMC

It is well known that there are three distinct regions in a graph of surface tension versus logarithm of concentration for ordinary surfactant solutions. The first region is in the low concentration range where the surface tension of the solution stays close to the surface tension of water or decreases slightly as the concentration increases. In the second region, the surface tension decreases rapidly and almost linearly with the logarithm of the concentration. When the concentration reaches a certain value called critical micelle concentration (CMC), the surface tension becomes almost constant (third region). At or above this concentration the molecules form "micelles" and the surface tension becomes constant since the individual molecules in the solution are at equilibrium with the micelles. From Fig. 1 to 3 it is seen that the variation of the equilibrium surface tension with concentration for the three PAM solutions is similar to the behaviour of surfactant solutions. An obvious leveling off of surface tension is observed for each of our three PAM solutions, which suggests that a phenomenon similar to CMC may also exist in the aqueous polymer solutions. Moreover, it is interesting to note that the dynamic surface tension declines dramatically at the same

concentration at which equilibrium surface tension starts to be constant. Beyond this concentration the dynamic surface tension either levels off or decreases slightly. The dynamic surface tension for Percols as shown in Fig. 4 to 8 exhibits a similar trend. This strongly suggests that a phase change or molecular aggregation must occur above this concentration. This concentration could be considered analogous to CMC. However, more work is required to verify this. We use the term "CMC" loosely here only to emphasize the similar surface tension behaviour of polymer and surfactant solutions.

For aqueous polyacrylamide solutions most previous investigations were for dilute concentrations and no information can be found in the literature regarding whether a similar "CMC" exists in an aqueous polymer solution. To support this finding, we may cite the work of Barakat et al. (22). These authors have studied the surface tension and critical micelle concentration of some polymer surfactants such as ethoxylated alkylphenol-formaldehyde. The molecular weights for these polymeric surfactants were from 5300 to 8600. The authors found that the CMC values for the polymeric surfactants are about the same order of magnitude as those obtained for monomers.

This interesting observation prompted us to conduct some electroconductivity measurements. The conductivity results are shown in Fig. 10 to 17. Surprisingly, the conductivity values of the aqueous polymer solutions show a similar behaviour to a surfactant solution. For a surfactant solution a graph of conductivity versus the concentration would show a slope decrease over the CMC concentration. As a matter of fact this is another common method of determining the CMC for surfactant solutions. Figures 10 to 17 demonstrated that the slope of the conductivity versus the concentration of the polymer becomes smaller at approximately the same concentration at which the surface tension starts to become constant. Therefore our conductivity measurements provide

further evidence for the possible existence of CMC in aqueous polyacrylamide solutions.

Table 1 gives suggested CMC for these polyacrylamide solutions determined from equilibrium surface tension, dynamic surface tension, and conductivity measurements. It is seen that the CMC values obtained from equilibrium and dynamic surface tension measurements agree very well for all the three samples. The CMC values obtained from conductivity measurements are in excellent agreement with those obtained from surface tension measurements for the sample PAM-1 and most Percol samples, and in fair agreement for samples PAM-2 and PAM-3.

Figure 18 shows the correlation between the suggested CMC and the cationicity. It shows that the CMC decreases with the increase in cationicity. However, at high cationicity the CMC value increases. Extrapolating the CMC value to 0% cationicity gives the CMC value about 1%. This value is very close to the CMC of sample PAM-1, which has 0% cationicity and has a slightly lower molecular weight than the Percol samples..

CONCLUSIONS

1. The experimental results reported here indicate that an aqueous polyacrylamide solution is surface active. Surface tension can be reduced significantly at high concentrations.
2. Although the equilibrium surface tension measured with the du Nouy ring or Wilhelmy plate does not agree with the dynamic surface tension measured using the maximum bubble pressure method at a bubble frequency of 1 bubble per second, they follow a similar trend.

3. The carboxyl groups and cationic substituted functional groups are more surface active than the nonionic amine groups.
4. The surface tension of a polyacrylamide solution behaves like that of the surfactant solutions in that a similar CMC phenomenon was observed for all polymer samples. In the concentration range below the CMC the surface tension decreases with increasing concentration. At concentrations higher than CMC the surface tension either stays constant or changes slightly.
5. The CMC values obtained using different methods are in good agreement.
6. A good correlation between CMC value and cationicity of the polyacrylamide was obtained.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support provided by PERD. We thank Professor Hai-Ke Yan (visiting professor from P.R. China) for his helpful advices. We also thank Dr. Dilip Sengupta for his assistance in preparing Percol solutions.

REFERENCES

1. Miaw, C.B. "A study of heat transfer to dilute polymer solutions in nucleate pool boiling"; Ph.D. thesis, University. of Michigan, Ann Arbor; 1978.
2. Paul, D.D. "nucleate pool boiling in drag-reducing polymer solutions"; Ph.D.thesis, University of Wisconsin, Madison; 1982.
3. Shima, A., Tsujino, T, and Tanaka, J "Studies of bubble behavior and non-newtonian viscosity of polymer solutions (Report 1)"; Rep Inst High Speed Mech 46: 103-129; Japan, Tohoku university; 1983.
4. Tsujino, T., Shima, A., and Tanaka, J. "Studies of bubble behavior and non-newtonian viscosity of polymer solutions (Report 2)"; Rep Inst High Speed Mech 46: 131-151; Japan, Tohoku university; 1983.
5. Tsujino, T., Shima, A., and Tanaka, J. "Studies of bubble behavior and non-newtonian viscosity of polymer solutions (Report 3)"; Rep Inst High Speed Mech 46: 153-180; Japan, Tohoku university; 1983.
6. Hu, R. Y. Z., Wang, A. T. A., and Hartnett, J. P. "Surface tension measurement of aqueous polymer solutions"; Exp Therm Fluid Sci 4: 723-729; 1991.
7. Prud'Homm, R.K.and Long, R. E., "Surface tension of concentrated xanthan and polyacrylamide solutions with added surfactants."; J Colloid Interface Sci; 93: 274-276; 1983.
8. Ishiguro, S. and Hartnett, J. P., "Surface tension of aqueous polymer solutions"; Int Comm Heat Mass Transfer 19: 285-295; 1992.
9. Huang, Y.-D., Yang, P.H., and Qin, T.L., "A study on the dynamic interfacial tension of acidic crude oil/alkali (alkali-polymer) systems"; In

Situ 13: 259-274; 1989.

- 10 Sandescu, F and Simionescu, G.I., "Interfacial phenomela on concentrated polymer solutions in the spinning process", Rev Roum Chim 32: 21-28; 1987
11. Ueberreiter, K., Morimoto, S., and Steulmann, R. "Surface tension of polymer solutions I. kinetics of formation of the surface"; Colloid & Surface Sci 252: 273-277; 1974.
- 12 Morimoto, S. and Ueberreiter, K."Surface tension of polymer solutions II. Poly- γ -benzyl-L-glutamate in N,N-dimethylformamide, dioxane and dichloroacetic acid solutions"; Colloid Polymer Sci 253:1009-1019; 1975.
13. Okubo, M. and Ueberreiter, K., "Surface tension of polymer solutions, 5. Temperature dependence of surface tension of polystyrene-decalin and cyclohexane, polymermethylmethacrylate-heptanone and polyisobutylene-benzene theta-solutions."; Colloid Polymer Sci 256: 591-593; 1978.
14. Ueberreiter, K and Okubo, M."Surface tension of polymer solutions VI. Kinetic analysis of surface tension of polystyrene and polymethylmethacrylate theta-solutions", Colloid polymer Sci 256: 1030-1031;1978.
15. Okubo, M. and Ueberreiter, K. "Surface tension of polymer solutions, 7. Surface tension and heat of dilution of polystyrene-cyclohexane theta-solution", Colloid polymer Sci 256: 941-943; 1978.
16. Shinozaki, K., Abe, M., and Takuhei, N. "Interfacial tension of demixed polymer solutions over a wide range of reduced temperature"; Polymer 23: 722-727; 1982.
17. Ober, R. Paz, L., Taupin, C., and Pincus, P., "Study of the surface tension of polymer solutions: theory and experiments. 1. good solvents"; Macromolecules 16: 50-55; 1983.
- 18 Sauer, B. and Dipaolo, N. V., "Surface tension and dynamic wetting of

polymers using the wilhelmy method: applications to high molecular weights and elevated temperatures"; J Colloid Interface Sci 144:527-537; 1991.

19. Hua, X. Y. and Rosen, M. J. "Dynamic surface tension of aqueous surfactant solutions 1. Basic parameters"; J Colloid Interface Sci 124: 652-659; 1988
20. Rosen, M.J. and Hua, X. Y. "Dynamic Surface tension of aqueous surfactant solutions, 2. Parameters at 1 s and at mesoequilibrium"; J Colloid Interface Sci 139: 397-407; 1990.
21. Hua, X. Y. and Rosen, M. J. "Dynamic surface tension of aqueous surfactant solutions 3. Some effects of molecular structure and environment"; J Colloid Interface Sci 141: 180-190; 1991.
22. Barakat, Y. Gendy, T.S., and Mohamad, A.I., "Polymeric surfactants for enhanced oil recovery. part I - Critical micelle concentration of some ethoxylated alkylphenol-formaldehyde nonionics", Brit. Polymer J; 21: 383-389; 1989.

Table 1 - Suggested CMC for aqueous PAM solutions

| Sample | CMC (wt%) | | |
|------------|---------------------------|-----------------------|-------------------|
| | From equilibrium γ | From dynamic γ | From conductivity |
| PAM-1 | 0.9 | 1.0 | 1.0 |
| PAM-2 | 4.2 | 4.6 | 3.0 |
| PAM-3 | 1.7 | 2.0 | 3.2 |
| Percol 745 | | 0.59 | 0.56 |
| Percol 724 | | 0.35 | 0.35 |
| Percol 722 | | 0.30 | 0.28 |
| Percol 763 | | 0.21 | 0.15 |
| Percol 757 | | 0.31 | 0.26 |

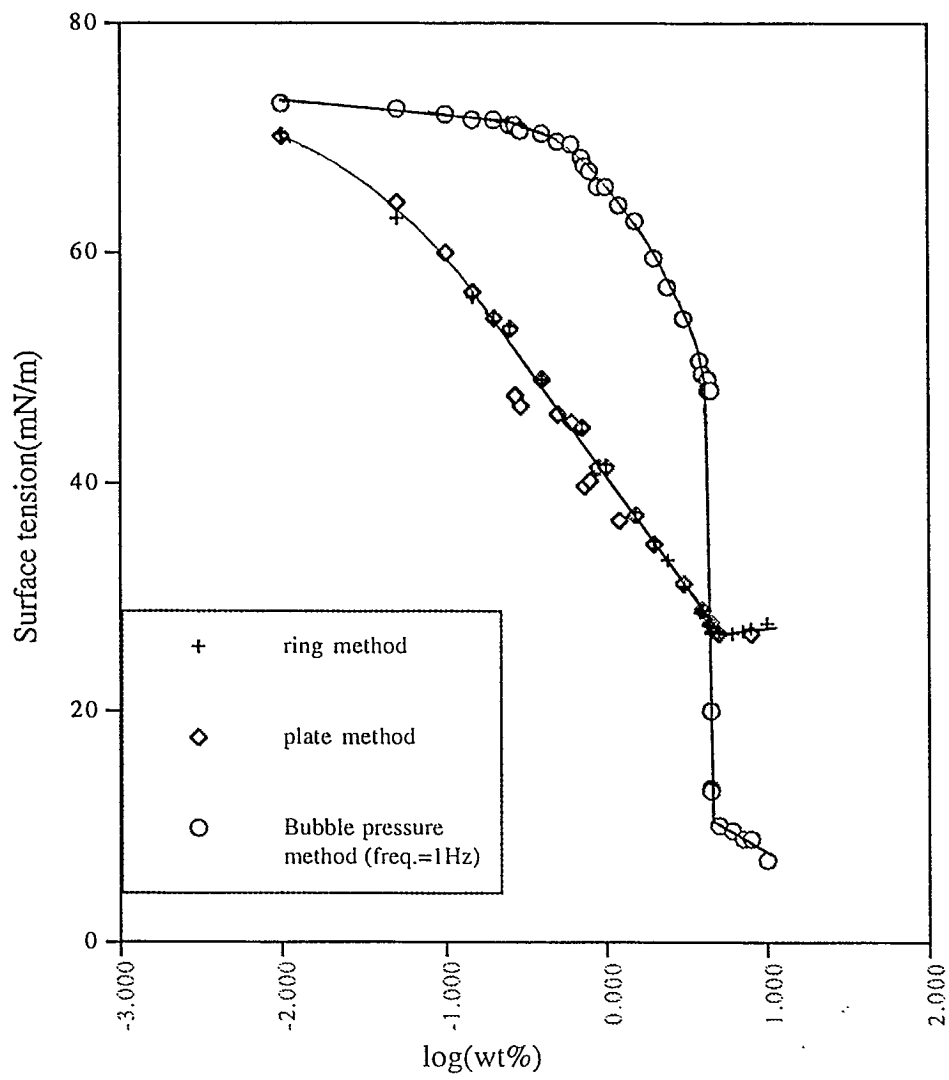


Fig. 1 - Surface tension for PAM solutions (PAM-2)

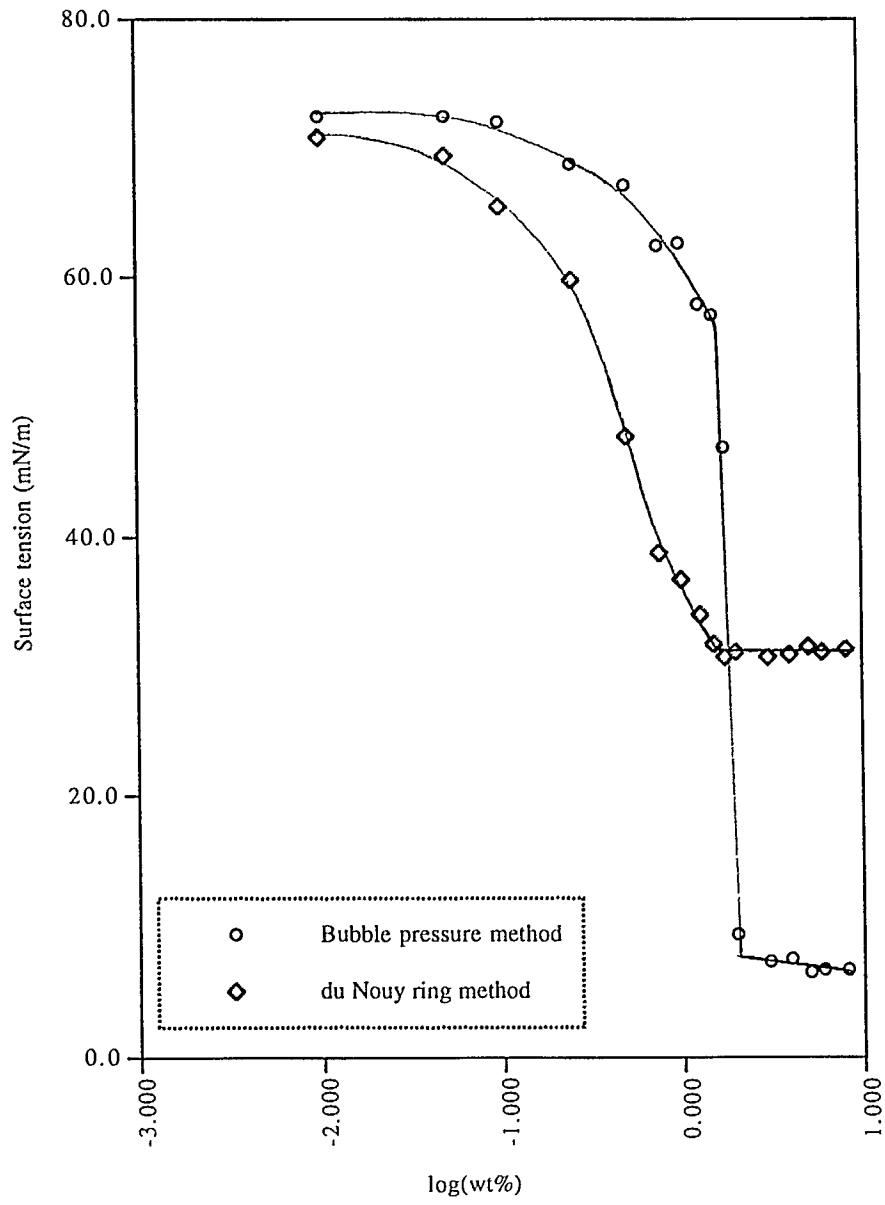


Fig. 2 - Surface tension for PAM solutions (PAM-3)

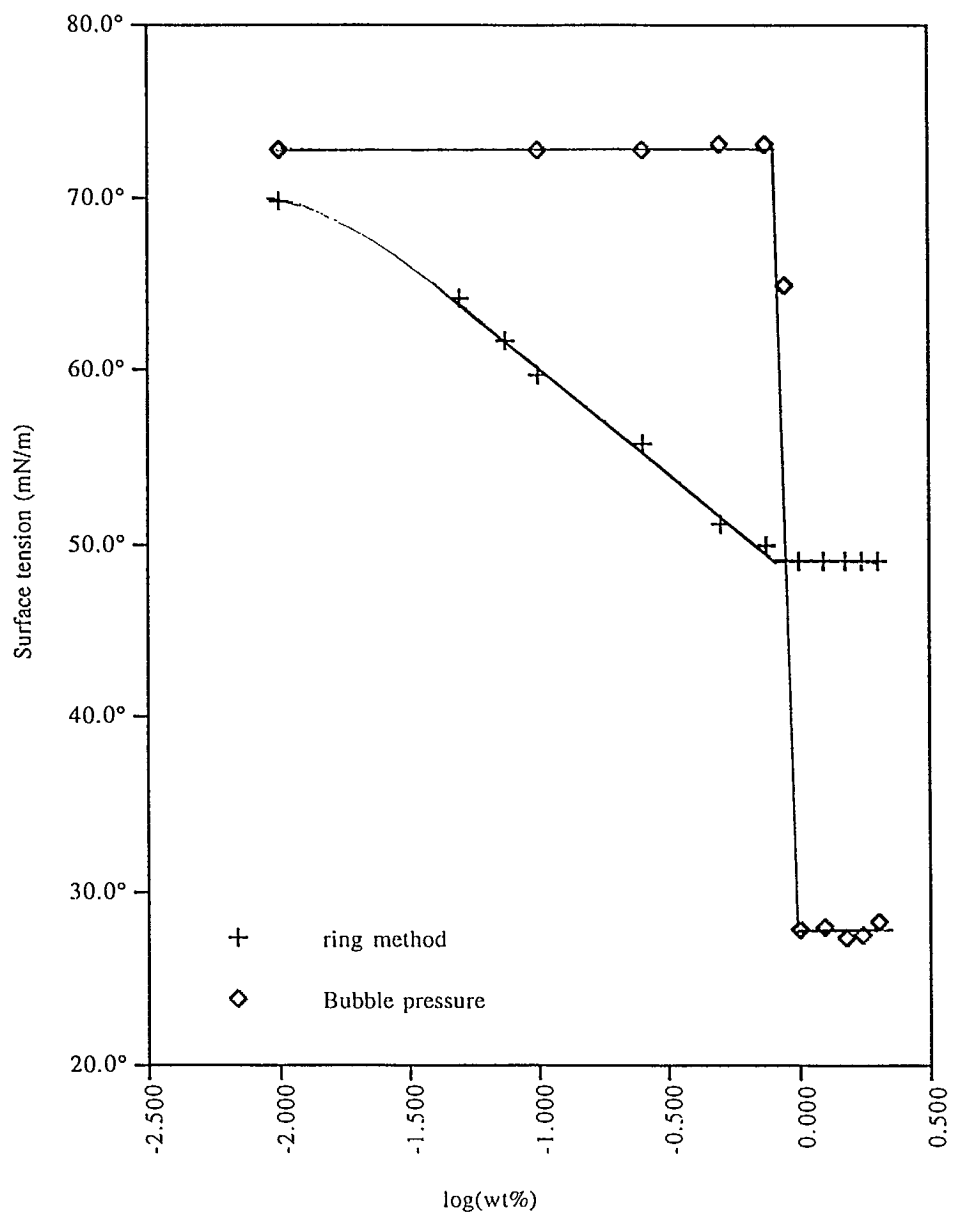


Fig. 3 - Surface tension for PAM solutions (PAM-1)

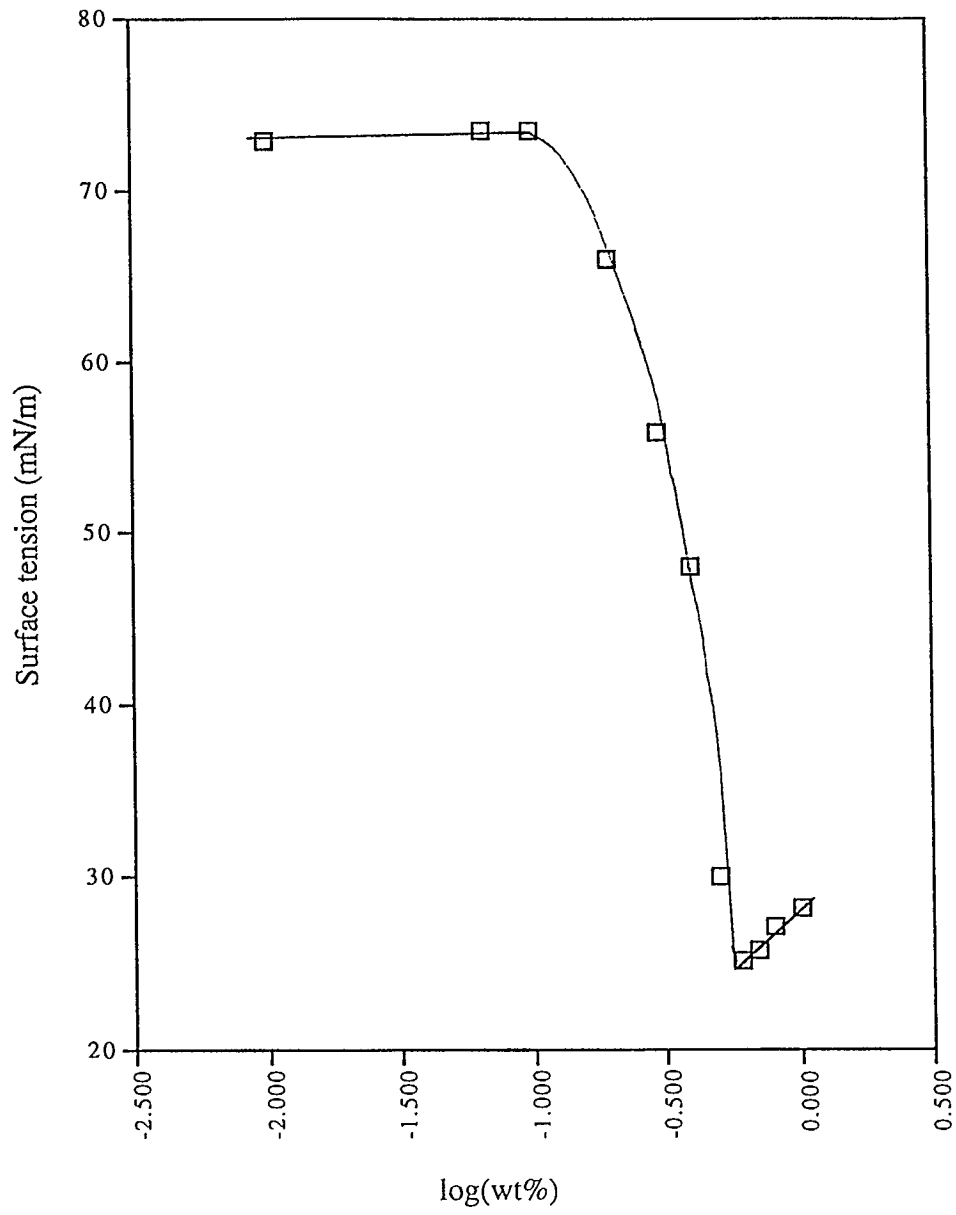


Fig. 4 - Surface tension for Percol 745.

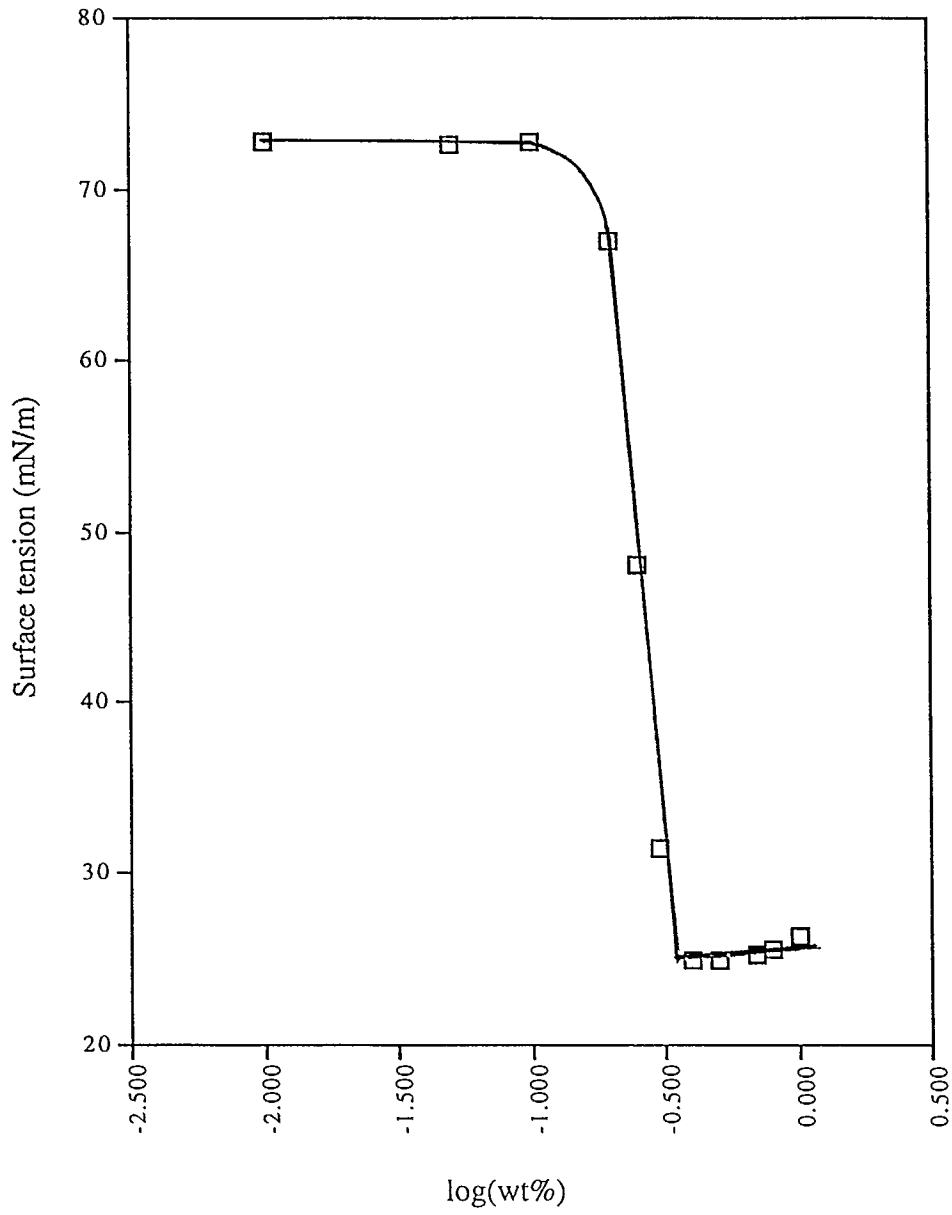


Fig. 5 - Surface tension for Percol 724

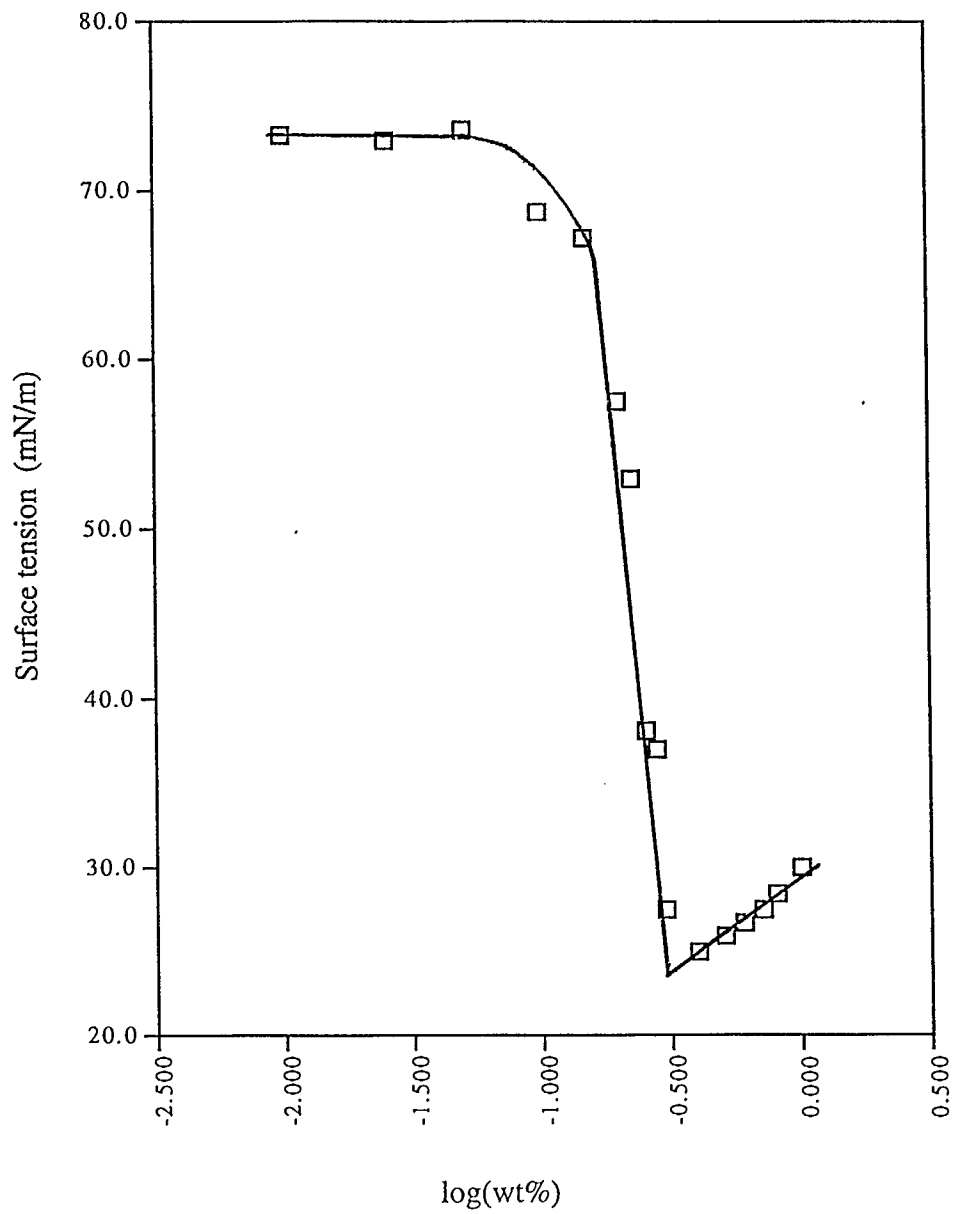


Fig. 6 - Surface tension for Percol 722

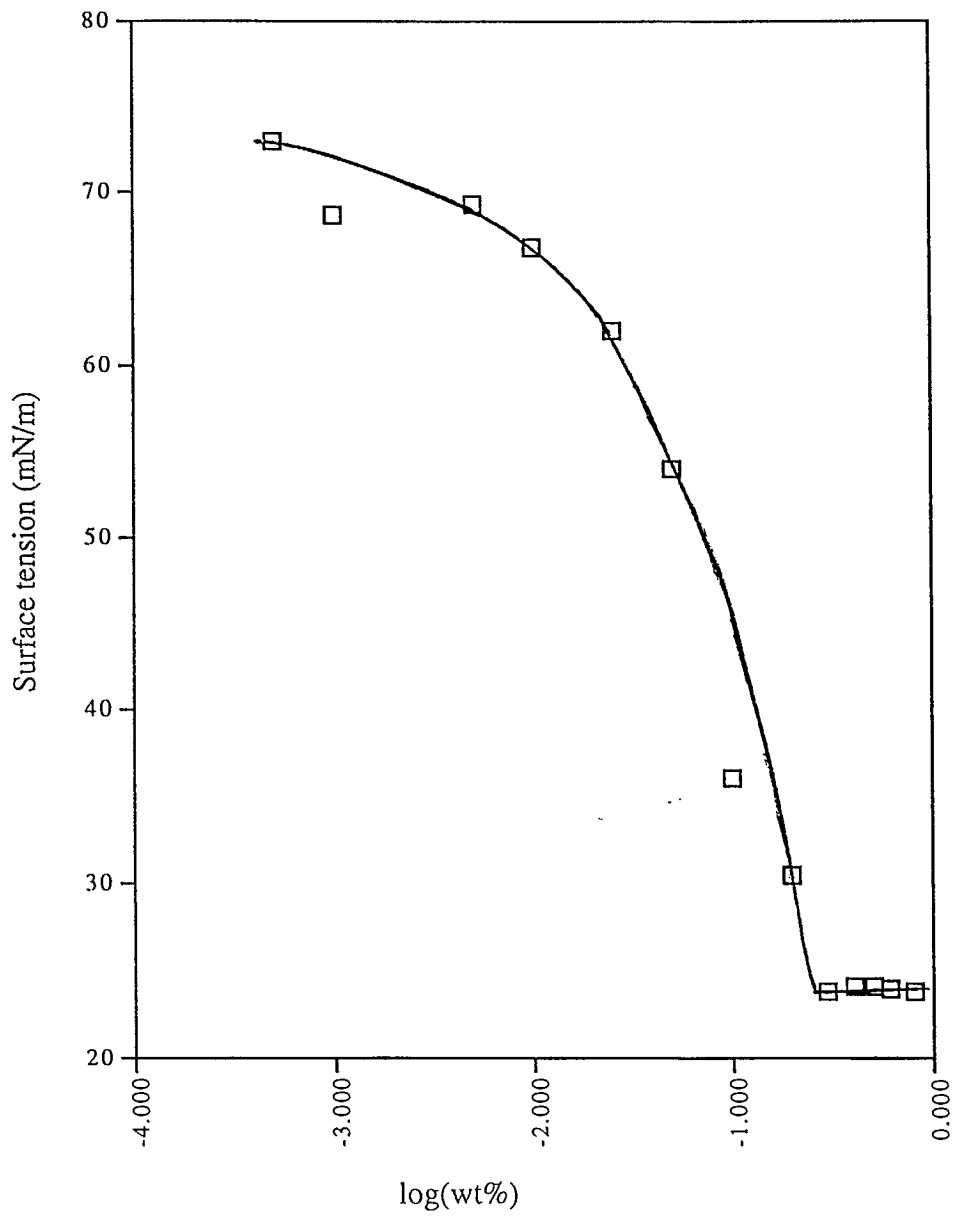


Fig. 7 - Surface tension for Percol 763

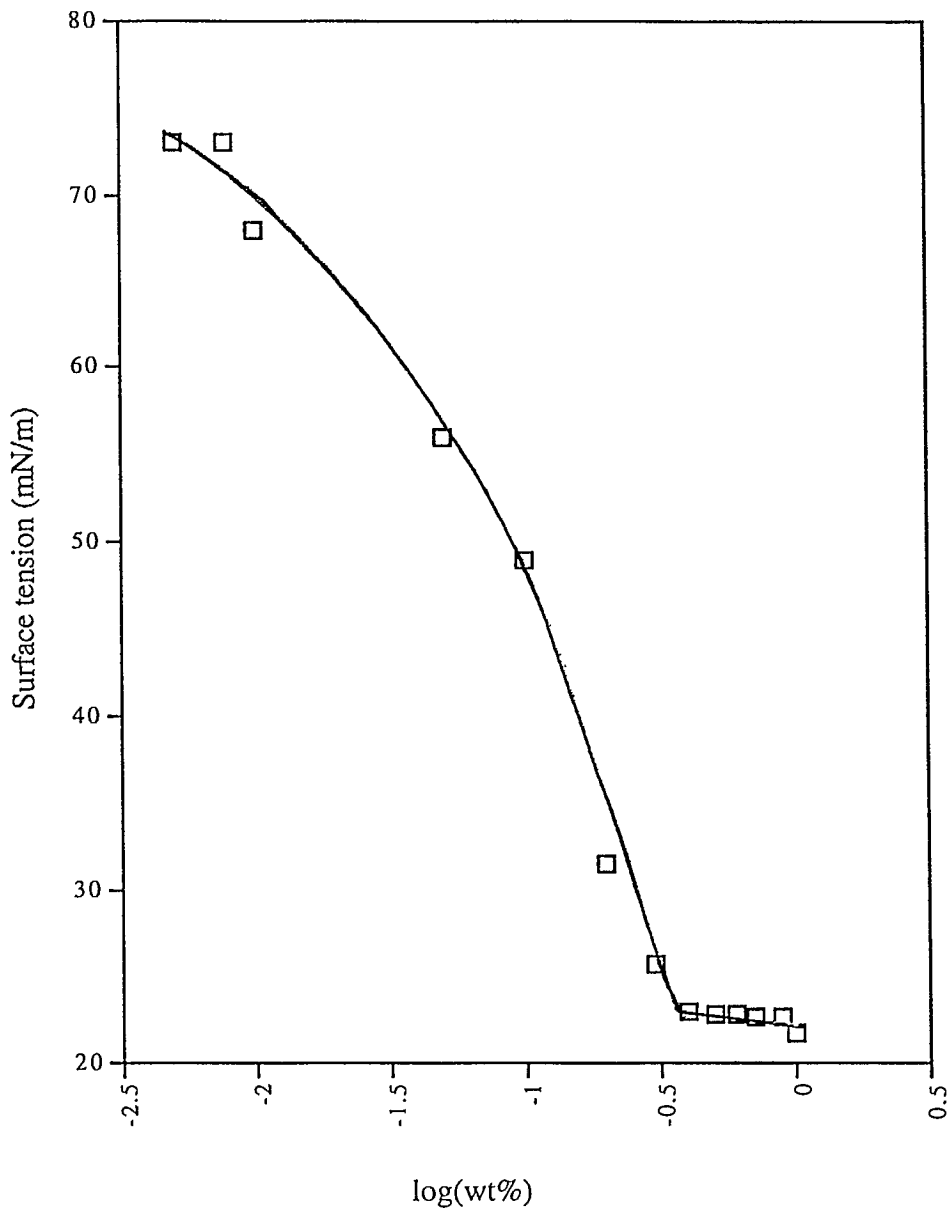


Fig. 8 - Surface tension for Percol 757

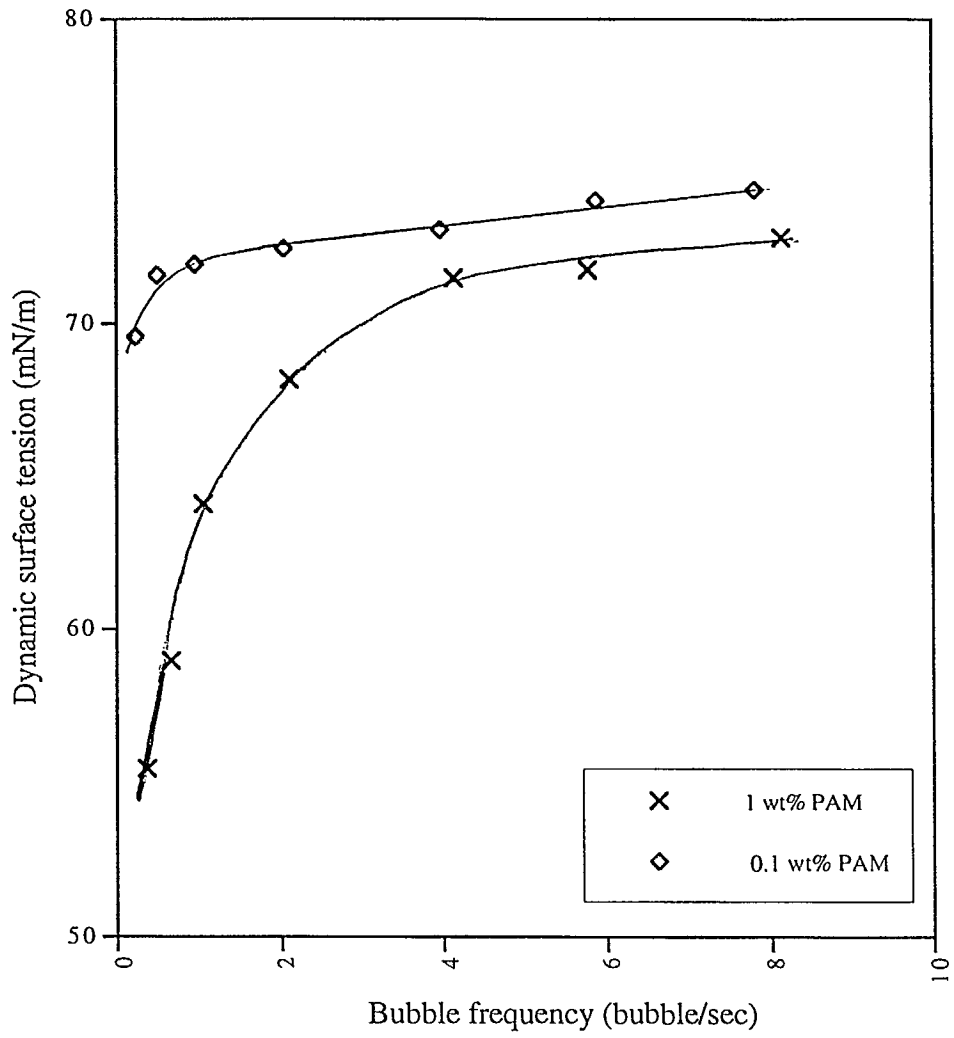


Fig. 9 - Dependence of dynamic surface tension on bubble frequency for PAM solutions

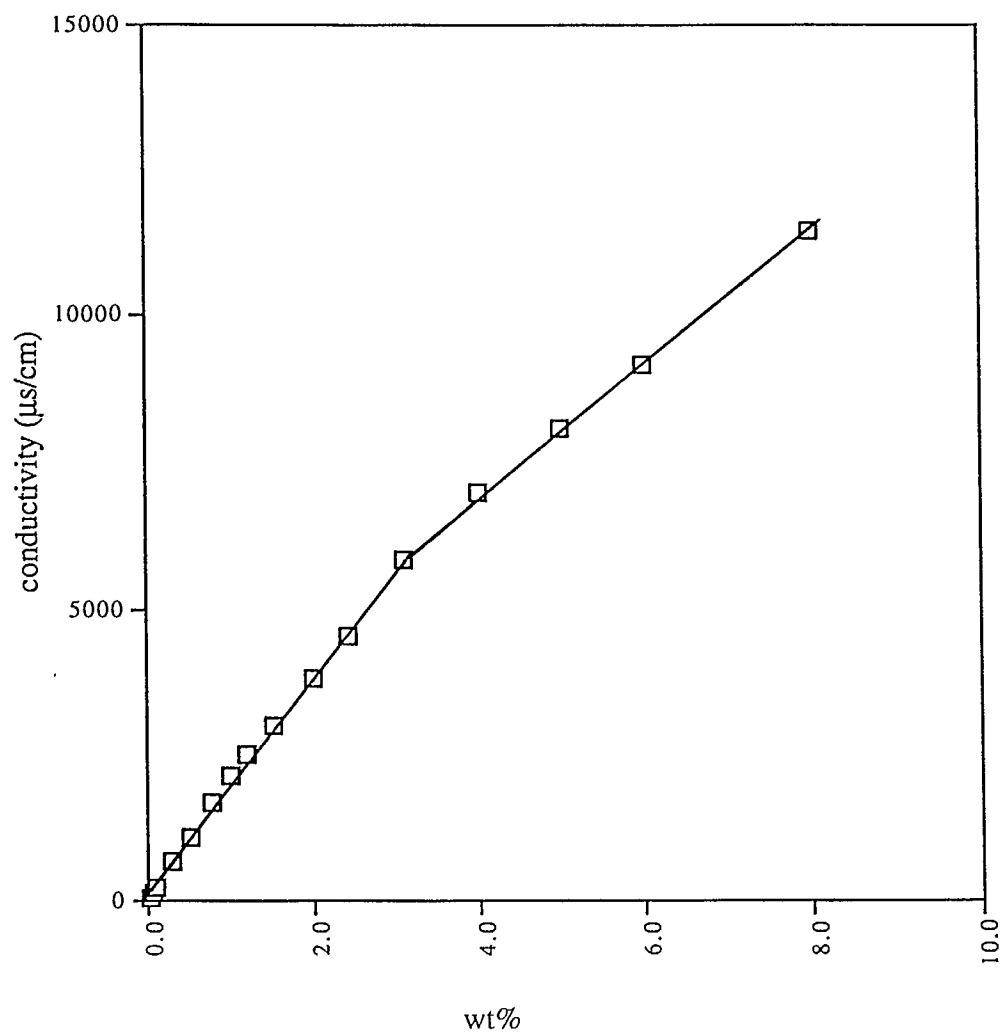


Fig. 10 - Conductivities of PAM solutions (PAM-2)

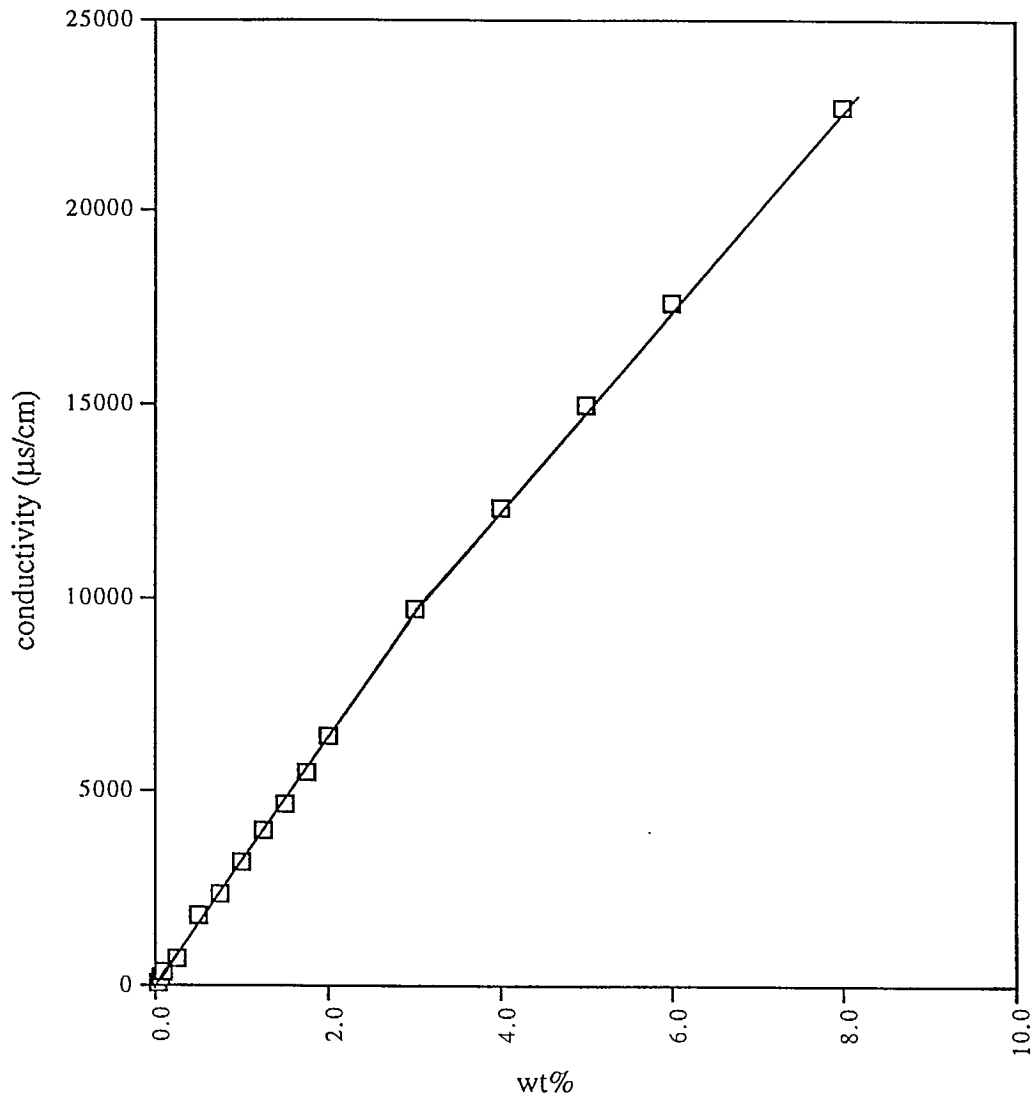


Fig. 11 - Conductivities of PAM solutions (PAM-3)

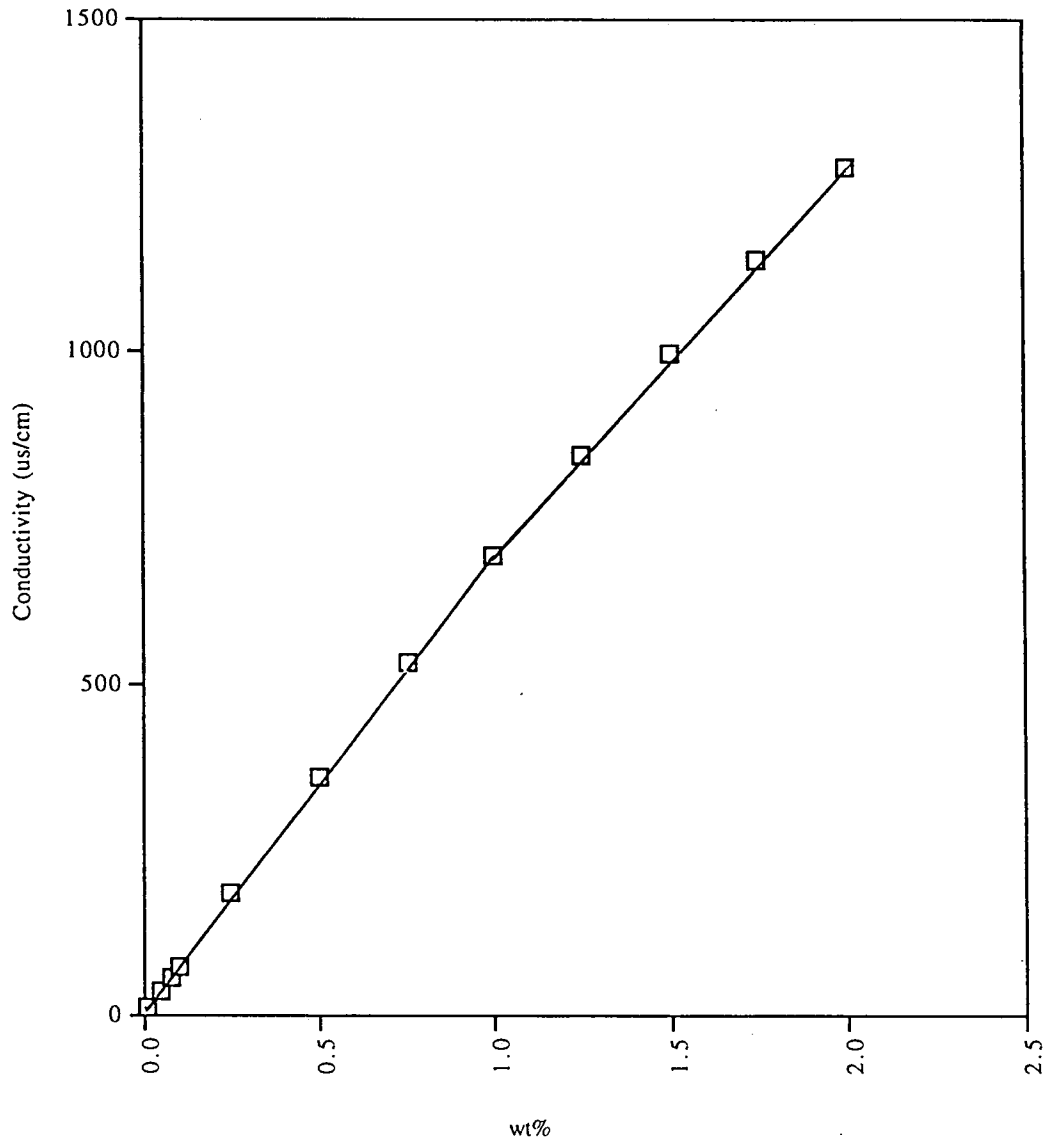
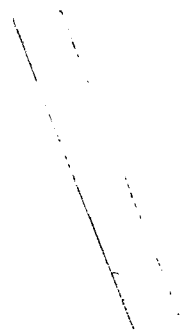


Fig.12 - Conductivities of PAM solutions (PAM-1)



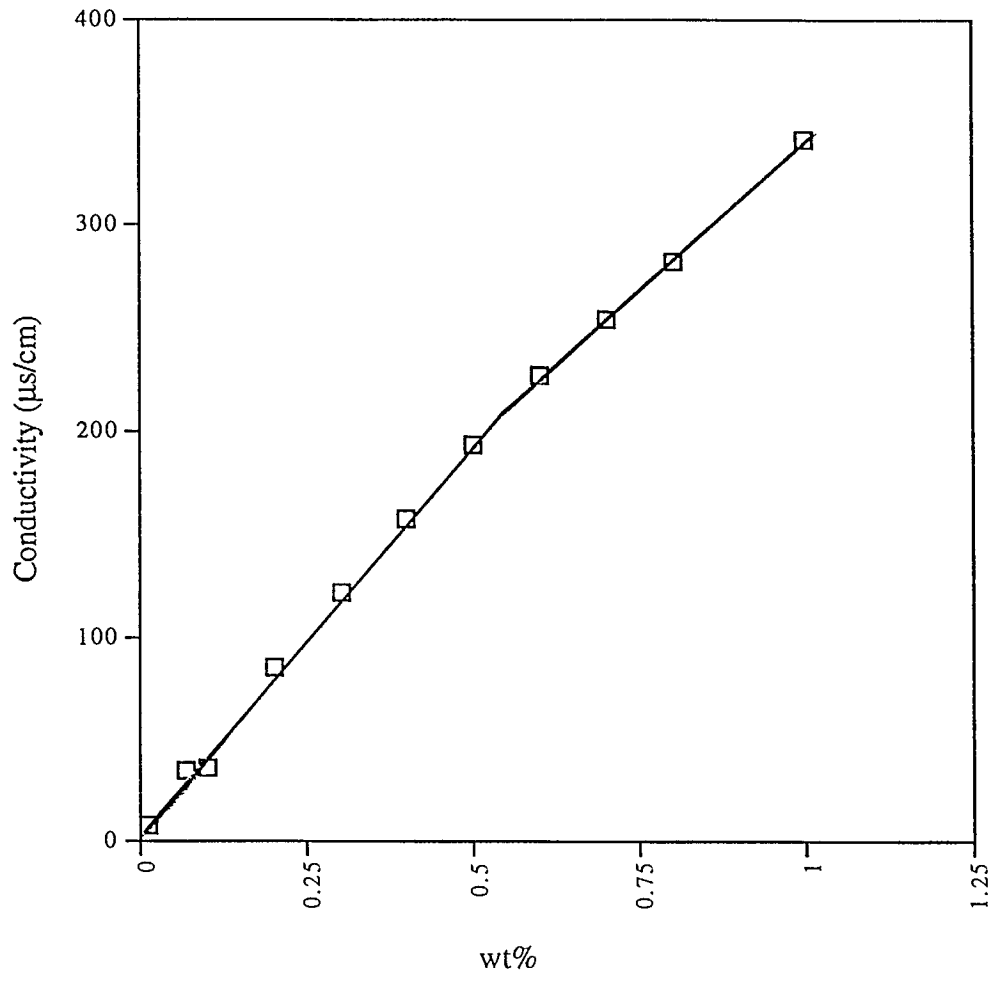


Fig. 13 - Conductivities of Percol 745

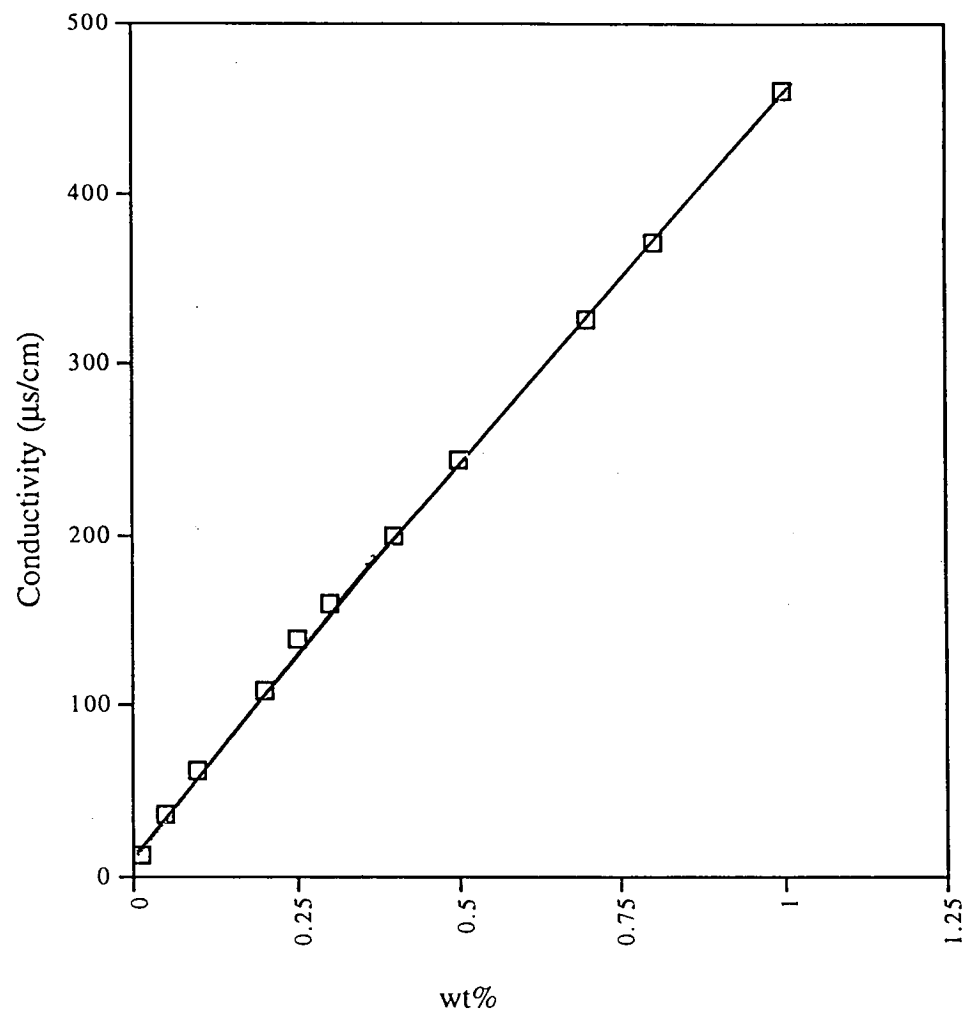


Fig. 14 - Conductivities of Percol 724

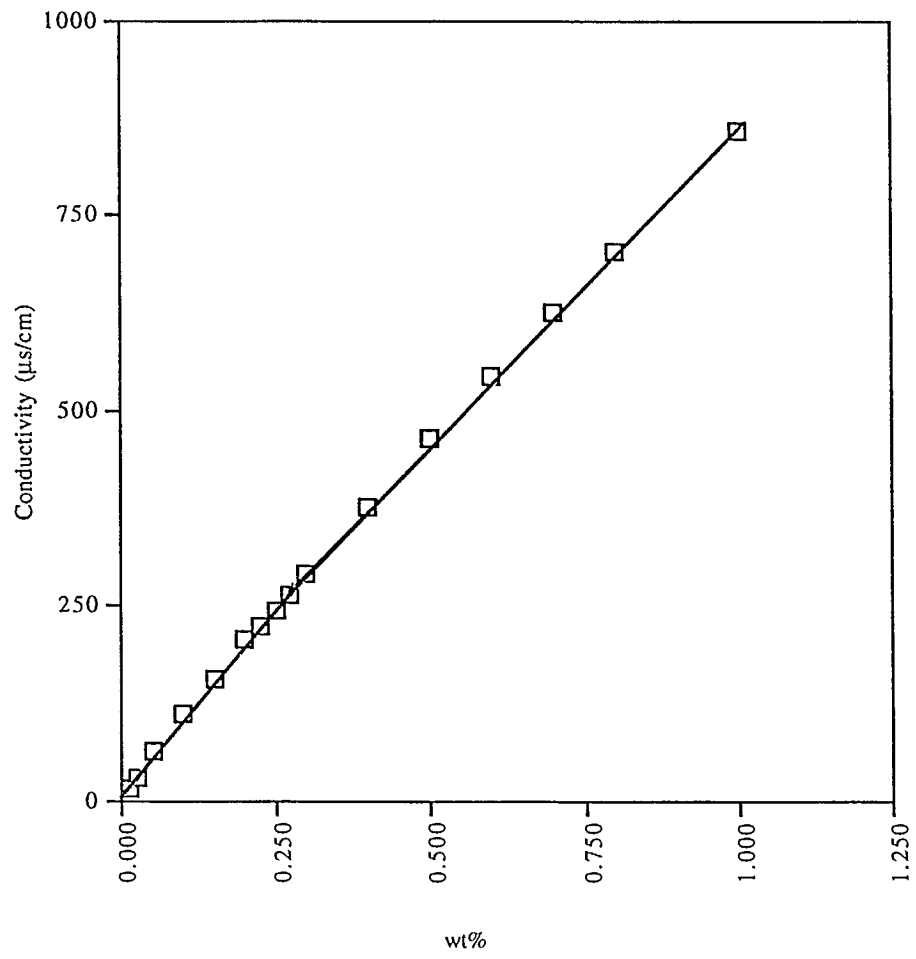


Fig. 15 - Conductivities of Percol 722

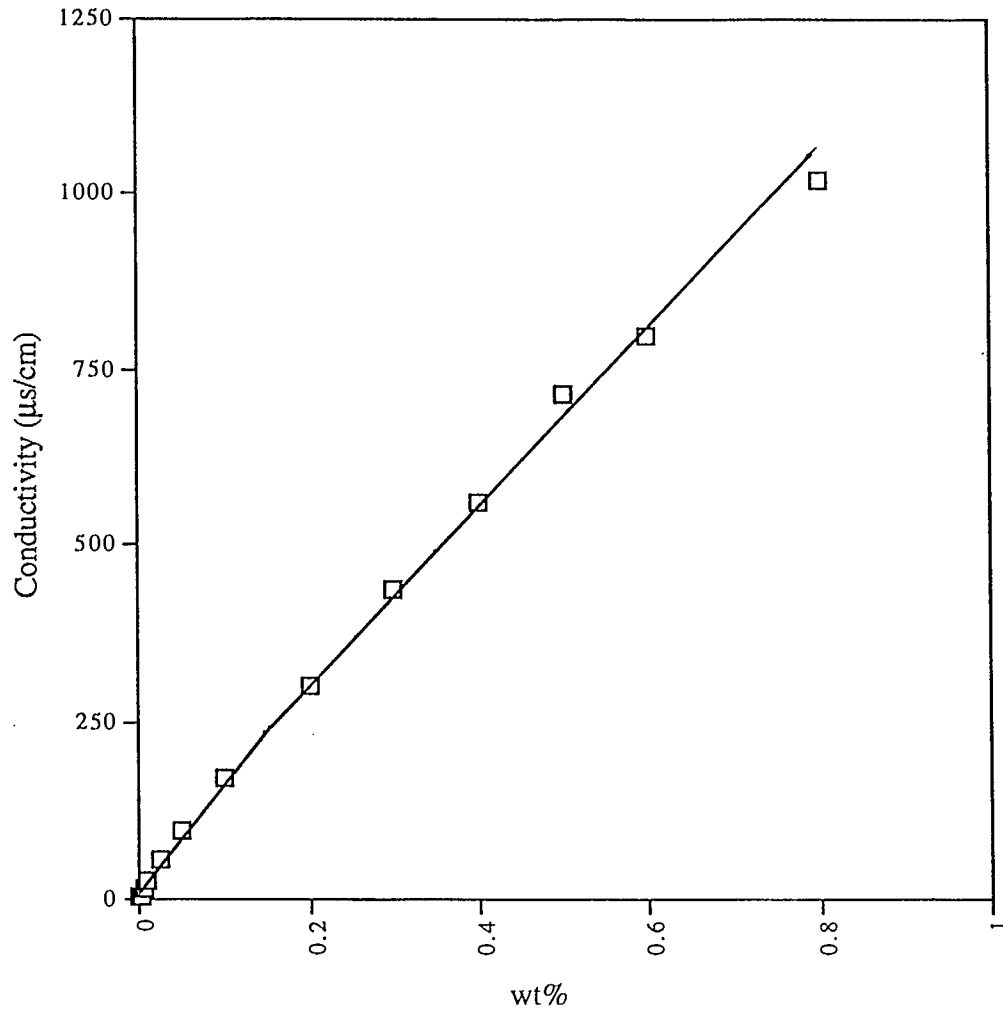


Fig. 16 - Conductivities of Percol 763

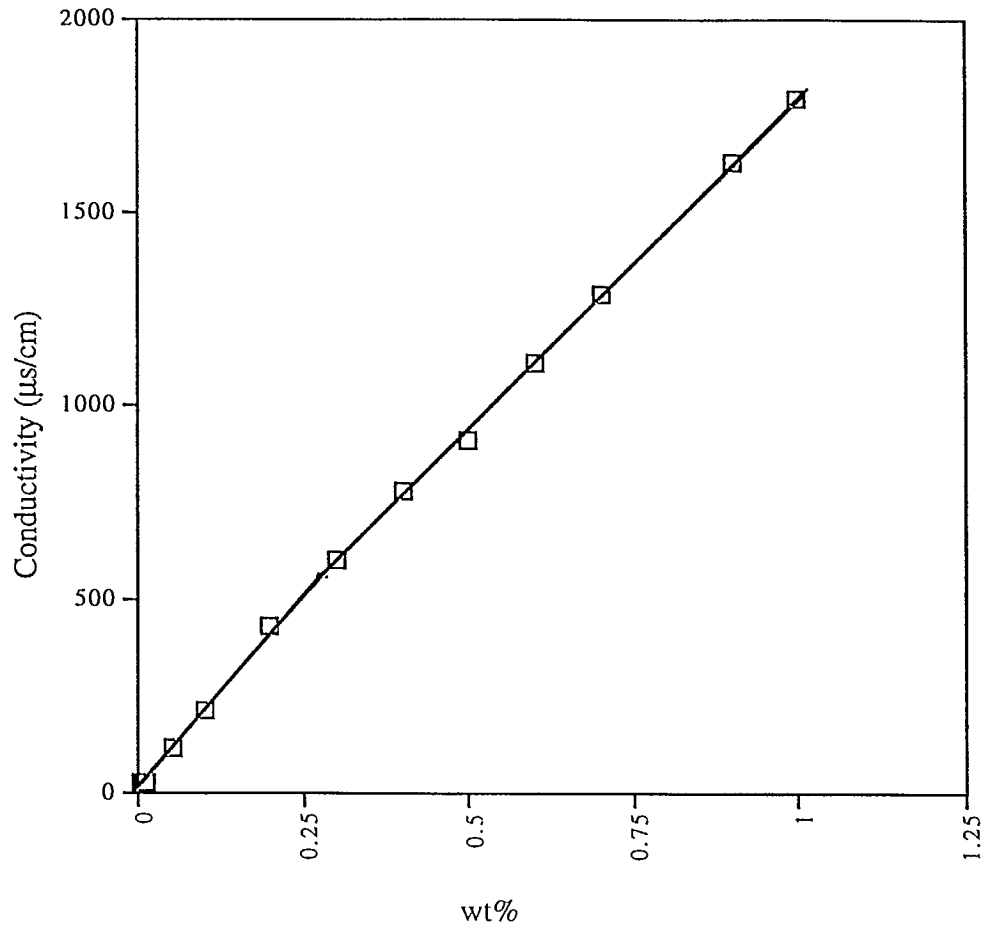


Fig. 17 - Conductivities of Percol 757

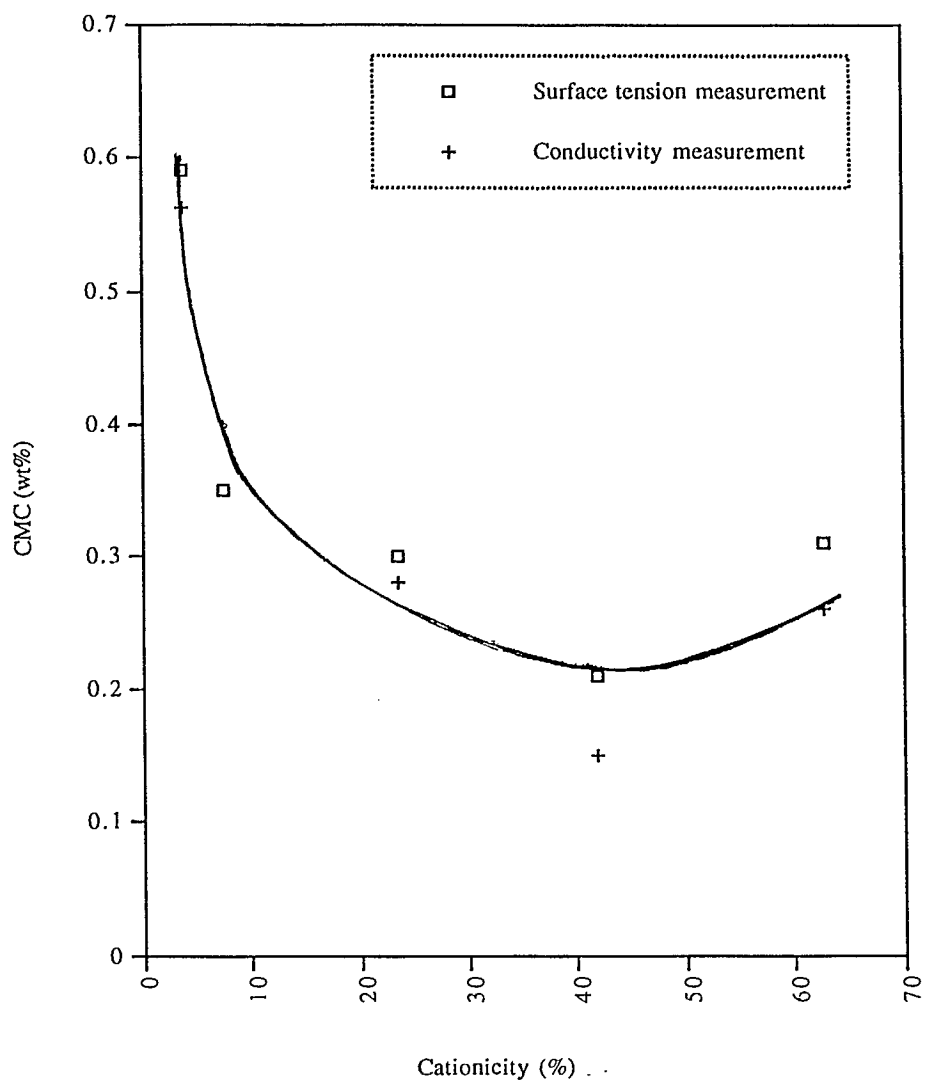


Fig.18 - CMC values for Percols as a function of cationicity

