POLYMER COLLOID GROUP NEWSLETTER

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7 October 1981

The next major event in the Group's calendar will be the second NATO Advanced Study Institute on 'Polymer Colloids' to be held at Bristol 29 June - 9 July 1982: this has now been confirmed. Gary Fochlein is the Institute Director and he will be circulating details in due course.

It is intended to hold a 4th Gordon Research Conference on 'Polymer Colloids' in the summer of 1983: this time John Vanderhoff will be the Chairman.

In the more immediate future there will be a one day Informal Discussion in London on Monday 14th December 1981 under the auspices of the Colloid and Interface Science Group of the Faraday Division of the Royal Society of Chemistry. Details appear on a subsequent page.

The 13th annual Lehigh Short Course on 'Advances in Emulsion Polymerization and Latex Technology' will be held 7 - 11 June 1982. Details will be available from Dr M.S.El-Aasser, Emulsion Polymers Institute, Building No. 5, Lehigh University, Bethlehem, Pennsylvania 18015, USA.

There will be four sessions in the Polymer Colloids Symposium at the American Institute of Chemical Engineers National Meeting at Houston, Texas 27 - 31 March 1983:1. Kinetic Aspects and Reactor Engineering, 2. Interfacial Aspects, 3. Colloidal Aspects, 4. Relation of Properties of the Latex to the Process used. Further details should appear in 1982 Newsletters.

The papers given at the June 1980 Symposium on 'Science and Technology of Emulsion Polymers' at Lehigh are now in course of publication in the 'Journal of Dispersion Science and Technology' (Publishers: Marcel Dekker).

The proceedings of the Las Vegas 1980 'Emulsion Polymers' Symposium were due for publication under the title 'Emulsion Polymers and Emulsion Polymerization' as A.C.S. Symposium Series No. 165 on August 22 nd. (ISBN 0-8412-0642-2).

Applied Science expect to publish 'Emulsion Polymerization of Vinyl Acetate' (papers given at the Lehigh Symposium in April 1980) in October 1981 at £24. Postage £1.30 extra outside the U.K. Publishers address is Ripplesida Commercial Estate, Barking, Essex, IG11 0SA, England.

The book (edited by I. Piirma) on 'Emulsion Polymerization' should also be published by Academic Press on 8th January, 1982.

Details of the Plastics and Rubber Institute's International Conference 'POLYMER LATEX II' are that it will be held at the Institution of Electrical Engineers in London 15-17 June, 1982. Papers on emulsion polymerisation, on the properties and testing of natural and synthetic latices, and on their applications (e.g. to carpet backing, non-woven fabrics, paints, adhesives, paper coating etc.) are invited. Proposals (title + 250 word summary) should reach Mr R.H.Craven, The Plastics and Rubber Institute, 11 Hobart Place, London SW1W 0HL by 16th November 1981.

Contributions to the Spring Newsletter shout be sent to Dr A.S.Dunn, Chemistry Department, UMIST, P.O. Box 88, Manchester M60 1QD, England to arrive by Monday 19th April 1982. Contributions should not normally exceed three pages including any graphs etc., typed single-spaced whenever possible. Try to avoid concluding pages containing only a few lines of text!

A.S.D.

MINUTES of the ANNUAL BUISNESS MEETING of the POLYMER COLLOID GROUP held on Thursday 16th July 1981 at Tilton School, New Hampshire.

Present: P. Bagchi, D. Bassett, J.S.Dodge, A.S.Dunn, R.M.Fitch, J.W.Goodwin, F. Hansen, A. Klein, I. Krieger, M. Nomura, R.H.Ottewill, G.J.Poehlein, I. Piirma, D.G.Rance, A.A.Robertson, R. Rowell, F. Saunders, J.W.Vanderhoff, Th. van der Ven, and R.G.Gilbert (representing D.H.Napper) (20)

Future arrangements. Gary Poehlein said that he expected to have a decision as to whether the proposed second N.A.T.O. Advanced Study Institute on 'Polymer Colloids' to be held a Bristol in 1982 would go ahead before the end of July. A favourable decision was anticipated but some new constraints has been introduced which would require some revisions of the provisional plans. The maximum budget was limited to £ 35 000 compared with the original estimate of £ 49 000: this meant that it was unlikely that it would be possible to pay full expenses to anyone. The number of main speakers had to be limited to 15. Publication of the proceedings was now mandatory: up to 15 additional papers could be included in the publication. Camera ready copy would be required by the publisher 4 weeks after the end of the Institute. Since the Institute would immediately precede the 1982 IUPAC Symposium on Macromolecules at Amherst, Massachusetts in which a number of participants were likely to be involved it was proposed that the dates should be Tuesday 29 June - Friday 9 July to provide more flexibility for travel to Amherst.

IUPAC Document on the preparation of model colloids. Pranab Bagchi would circulate an outline of this document for comments.

Membership: It was felt that it would be desirable for the Utrecht group to be represented and Bob Fitch undertook to approach Vrij. It was noted that there was also now an active group in East Germany at the Institut fur Polymerenchemie at Teltow under Gerhard Reinisch but it was decided to leave any invitation to this group over until next year.

1982 Annual Meeting : It was expected that this could be held in Bristol during the A.S.I.

Polymer Colloid meetings sponsored by other bodies. John Vanderhoff reported that El Aasser had been asked to convene a group to arrange a Symposium to form part of the A.I.Ch.E. Houston meeting 27-31 March 1983.

Ron Ottewill reported that the Royal Society of Chemistry Faraday Division would hold a General Discussion on 'Concentrated Colloidal Dispersions' at Loughborough 16-18 September 1983.

TRANSLATIONS FROM 'POLYMERS BASED ON VINYL ACETATE'

Most of the List of Contents of 'Polimery na Osnove Vinilatseta' (1978) gleaned from Referatnye Zhurnal through Chemical Abstracts appeared in the May 1980 Newsletter but no copy of this book seems to have reached either Britain or America. However Professor Yeliseyeva has sent me photocopies of two of the papers which relate to polyvinyl alcohol.

Rozenberg, Knyazeva, Medvedeva, Nikolaev, & Tyazhlo "Synthesis of partially hydrolysed poly(vinyl acetate)" (12 pages, about 3000 words)

Sorokin, Kuz'etsova, Budtov, Domnicheva, Broitman, Meija, & Rozenberg, "Effect of conditions for the synthesis of poly(vinyl alcohol) on the properties of its solutions" (5 pages, about 1500 words)

Professional translations from Russian are expensive (e.g. £ 6 per 100 words) but could be minimised if shared between interested groups. If members who would be prepared to pay £25 for a copy of a translation of these two papers let me know, I can arrange to have the translation done.

A.S.Dunn, Chemistry Dept., UMIST, P.O. Box 88, Manchester M60 1QD

EMULSION POLYMERISATION

An Informal Discussion arranged by the Colloid and Interface Science Group (Faraday Division - Royal Society of Chemistry) will be held in the Scientific Societies Lecture Theatre, 23 Savile Row, London W1, on Monday, 14th December 1981.

The Discussion will be preceeded by the A.G.M. of the R.S.C. Group at 9.45 a.m.

Programme

Chairman - Dr M. J. Jaycock

10 a.m. Nucleation and Growth of Polymer Latex Particles in Emulsion Polymerisation
Professor D.H.Napper (University of Sydney, Australia)

11.15 a.m. Evaluation of Rate Coefficients for Radical Desorption from Polymer Particles during Emulsion Polymerisation
Dr B.W.Brooks (Loughborough University of Technology)

12 noon Aspects of the Seeded Emulsion Polymerisation of Styrene
Dr D.C.Blackley (National College of Rubber Technology)

Chairman - Professor R.H.Ottewill

2 p.m. Seeded Growth Polymerisation of Styrene
Dr J.W.Goodwin, Dr J.S.Jayasuriya, Professor R.H.Ottewill (Bristol)

2.45 p.m. Renucleation in the Seeded Emulsion Polymerisation of Styrene
Dr A. S. Dunn and Mr S.A.Hassan (UMIST)

3.30 p.m. Polyelectrolyte Stabilised Latices
Dr T. Corner (ICI Corporate Laboratory, Runcorn)

The Registration Fee (inclusive of VAT, lunch, coffee and tea) is £13.50 for members of the R.S.C. Colloid and Interface Science Group and students and £ 16 for others.

Remittances should reach Dr J.W.Goodwin,
School of Chemistry,
Cantock's Close,
University of Bristol,
BRISTOL, BS8 1TS

by Friday, 4th December 1981.

FURTHER DEVELOPMENTS IN THE THEORY OF COMPARTMENTALISED FREE-RADICAL POLYMERISATION REACTIONS

D. C. Blackley, National College of Rubber Technology,
The Polytechnic of North London, Holloway, London N7 8DB.

The background to the theory of compartmentalised free-radical polymerisation reactions is described in some detail in a series of papers on this subject from our group which have appeared in recent years (1-5). Hitherto, the theory as we have developed it has been concerned with predicting the time-dependence of the distribution of locus radical populations for reaction systems which are not in a steady state, and with predicting the time-dependence of such cognate matters as the average number of radicals per reaction locus. We are currently extending the theory to prediction of the evolution of the locus-size distribution as the reaction proceeds. To this end, we have introduced a generalisation of the locus population distribution generating function used in the papers which we have published so far. In this generalisation, the generating function is re-defined in such a way as to take account of the possibility that the reaction loci which are present in the reaction system at any instant may have different sizes as well as containing different numbers of propagating radicals.

We define the function $n_i(t,v)$ to be such that $n_i(t,v)\delta v$ is the number of reaction loci per unit volume of reaction system which at time t contain exactly i propagating radicals and also have a volume which lies between v and $v+\delta v$. Thus $n_i(t,v)$ is a measure of the frequency density of the sub-class of loci containing i radicals at time t which also have volumes in the vicinity of v. In our papers published so far, we have used the symbol $n_i(t)$ to denote the number of loci per unit volume of reaction system which at time t contain i radicals regardless of locus size. The relationship between $n_i(t)$ and $n_i(t,v)$ is clearly

$$n_i(t) = \int_0^\infty n_i(t,v)\,dv \qquad \ldots\ldots\ldots (1)$$

where the limits of integration are intended to indicate that the integration is taken over the entire range of locus volumes within the reaction system. It also follows that the quantity

$$\sum_{i=1}^{\infty} i\, n_i(t,v)\,\delta v \qquad \ldots\ldots\ldots (2)$$

is equal to the total number of radicals which at time t are present in those loci in unit volume of the reaction system which have volumes between v and $v+\delta v$.

The generalised locus population distribution generating function which we introduce is denoted by $\Psi(\xi,t,v)$, where ξ is the auxiliary variable. The formal definition of the function $\Psi(\xi,t,v)$ is

$$\Psi(\xi,t,v) = \sum_{i=0}^{\infty} n_i(t,v)\,\xi^i \qquad \ldots\ldots\ldots (3)$$

The relationship between this locus population generating function and the generating function which we have used previously is easily shown to be

$$\Psi(\xi,t) = \int_0^\infty \Psi(\xi,t,v)\,dv \qquad \ldots\ldots\ldots (4)$$

The following properties of $\Psi(\xi,t,v)$ follow immediately from its definition:

(i) $$\Psi(1,t,v) = \sum_{i=0}^{\infty} n_i(t,v) = N(t,v) \qquad \ldots\ldots\ldots (5)$$

where $N(t, v)$ is such that $N(t, v)\delta v$ is the total number of reaction loci per unit volume of reaction system which at time t have volumes between v and $v + \delta v$.

(ii) $$\int_0^\infty \Psi(1, t, v)\,dv = \Psi(1, t) = N \qquad \ldots\ldots\ldots (6)$$

where N is the total number of reaction loci per unit volume of reaction system.

(iii) $$n_r(t, v) = \frac{1}{r!}\left(\frac{\partial^r \Psi(\xi, t, v)}{\partial \xi^r}\right)_{\xi=0} \quad \text{for } r = 0, 1, 2, \ldots \qquad \ldots\ldots\ldots (7)$$

(iv) $$\sum_{i=1}^{\infty} i n_i(t, v) = \left(\frac{\partial \Psi(\xi, t, v)}{\partial \xi}\right)_{\xi=1} \qquad \ldots\ldots\ldots (8)$$

Thus $(\partial\Psi/\partial\xi)_{\xi=1}$ is equal to the total number of radicals which at time t are present in those loci in unit volume of the reaction system which have volumes between v and $v + \delta v$. The average number of propagating radicals per locus at time t for the class of loci which have volumes between v and $v + \delta v$ is therefore

$$\bar{r}(t, v) = \frac{\{\partial \Psi(\xi, t, v)/\partial \xi\}_{\xi=1}}{\Psi(1, t, v)} \qquad \ldots\ldots\ldots (9)$$

The average number of propagating radicals per locus for the reaction system as a whole can be expressed in terms of $\Psi(\xi, t, v)$ in various ways, e.g.,

$$\bar{r}(t) = \frac{\int_0^\infty (\partial\Psi/\partial\xi)_{\xi=1}\,dv}{\int_0^\infty \Psi(1, t, v)\,dv} \qquad \ldots\ldots\ldots (10)$$

where for convenience Ψ has been written for $\Psi(\xi, t, v)$ in the numerator.

We hope that, by using the generating function $\Psi(\xi, t, v)$, we will be able to obtain further predictions for the behaviour of compartmentalised free-radical polymerisation systems in the non-steady state.

References

1. D. T. Birtwistle and D. C. Blackley, J. Chem. Soc. Faraday Trans. I, 1977, 73, 1998
2. D. T. Birtwistle and D. C. Blackley, J. Chem. Soc. Faraday Trans. I, 1978, 74, 2051
3. D. T. Birtwistle, D. C. Blackley and E. F. Jeffers, J. Chem. Soc. Faraday Trans. I, 1979, 75, 2332
4. D. T. Birtwistle and D. C. Blackley, J. Chem. Soc. Faraday Trans. I, 1981, 77, 413
5. D. T. Birtwistle and D. C. Blackley, J. Chem. Soc. Faraday Trans. I, 1981, 77, 1351

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Preparation of Monodisperse Seed Latices.

Mr S.A.Hassan is engaged on an investigation of the conditions under which new particles are formed in the seeded emulsion polymerisation of styrene. The detection of new particles on electron micrographs is greatly facilitated by the use of a monodisperse seed latex. The most popular method of preparing a monodisperse latex involves the use of a mixture of a non-ionic emulsifier but in recent work from Sydney (Hawkett, Napper, & Gilbert, J.C.S. Faraday Trans I 1980, 76, 1344) a monodisperse seed latex is prepared using a single emulsifier (Aerosol MA). This is convenient when studying seeded systems because the same emulsifier can be used in the seeded system.

The Sydney seed recipe involves the use of a high temperature (90 °C) with persulphate initiator. The question therefore arises whether the narrow particle size distribution is a result of the use of this particular emulsifier or whether it is simply a consequence of having a very high rate of initiation. Initially we thought that the monodispersity was a result of the use of this particular emulsifier which has a very high c.m.c. but it now seems that having a high rate of initiation (as a consequence of the high temperature used) is the more important factor since monodispersed latices can also be produced with other emulsifiers (e.g. potassium octadecanoate) when persulphate initiation is used at 90 °C. Using Aerosol MA (Cyanamid) with ~~.767~~ % w/v (6.17×10^{-3} mol dm^{-3}) persulphate we get a monodisperse latex with particle radius 51.5 nm when the emulsifier concentration is 1.34 % w/v on the water phase on the basis of the active material: Aerosol MA80 is stated to be 80% active. According to H.B.Klevens (J. Am. Oil Chem. Soc. 30 (1953) 74) this is the c.m.c. (0.042 mol dm^{-3}). Hawkett et al. used a rather ~~higher~~ emulsifier concentration (~~2.8~~ 1.34 % active w/v) and got a rather smaller particle size (46.5 nm) as one might expect.

However we have also used a similar emulsifier, Lankropol KMA 60 (Diamond Shamrock) at the same concentration of active material. This gives a much larger particle size (100 ± 5 nm) with good reproducibility. Although Lankropol KMA and Aerosol MA are similar products they are evidently not equivalent. Both are sodium di(methyl amyl) sulphosuccinate. The alkyl groups could nevertheless differ. Lankropol KMA is made with 98% 4-methyl-2-pentanol i.e. the secondary alcohol but the specification of the methyl amyl alcohol used by Cyanamid presumably differs.

Potassium octadecanoate (i.e. stearate) was used at the same temperature and initiator concentration at concentrations between the c.m.c. (as measured at 60 °C) and 10 times the c.m.c. (i.e. $0.4 - 4.0 \times 10^{-3}$ mol dm^{-3}) A monodisperse latex was obtained at 5 x (c.m.c.) i.e. 2.0×10^{-3} mol dm^{-3}, when the particle size was 58.3 nm . Evidently the emulsifier concentration does also influence the particle size distribution.

By preparing a monodisperse latex with the same emulsifier as is to be used in subsequent experiments on seeded polymerisations the difficulty which would be caused by introduction of a different emulsifier or emulsifier mixture with the seed can be avoided without the need for a difficult or tedious procedure (dialysis etc.) to remove the original emulsifier from the seed latex.

Polymer Colloid Group Newsletter

News from The UConn

by R. M. Fitch

Some members may wish to obtain copies of manuscripts or reprints which have become available recently. Drop me a line if you do.

1. Azad, Fitch and Nomura, "The Effect of 'Non-Reactive' Additives on the Kinetics of Emulsion Polymerization", in Emulsion Polymerization, D. Bassett, Ed., A.C.S. Symposium Series (1981).

2. Fitch, "Particle Nucleation and Growth", ibid.

3. Liang and Fitch, "Kinetics of Diffusion of Small Molecules across Polymer Monolayers", J. Colloid Interface Sci., Freundlich Gedenkschrift, to be published.

4. Azad and Fitch, "Adsorption Behavior of Hydroxypropyl Cellulose at the Trichloroethylene/Aqueous Interface", submitted for publication.

5. Fitch and Azad, "The Behavior of Amphiphilic Polymers at Liquid/Liquid Interfaces", to be submitted for publication.

6. Fitch, Mallya, McCarvill and Miller, "Kinetics of Hydrolyses Catalyzed by Acidic Polystyrene Colloids", Abstracts (but really preprints) of Communications, 27th Int'l. Symp. Macromol., Strasbourg, July, 1981, p. 503.

Some of our work in progress is reported on below:

Jane Clarke: Particle/Surface Interactions

A study is underway to investigate particle/surface interactions. Previously other authors (1) have concentrated on systems with imposed hydrodynamic forces. In the present study deposition/adsorption of particles is observed under "static" conditions i.e. with no imposed hydrodynamic force.

Monodisperse polystyrene latex particles made under emulsion polymerization conditions utilizing the BAg initiator, which results in strong acid, non-hydrolyzable sulphonate groups on the surface, are being used. The particles in electrolyte solution are observed adhering to surfaces e.g. glass, polystyrene, mica, utilizing an optical microscope under dark field conditions. Preliminary results indicate an increase in this adsorption with increasing salt concentration, as expected. Measurement of the diffusion coefficient of the particles shows them to be moving with Brownian motion only. So it is hoped that a theoretical analysis of the data will be possible considering sphere/plate interactions. The potential energy of interaction may then be broken down initially into two main contributions: electrostatic repulsion and van der Waals attractive energies. Certainly other factors also influence these interactions, prominent among which is surface roughness. Attempts will b made to incorporate such factors into the analysis.

(1) G.E. Clint, J. H. Clint, J. M. Corkill and T. Walker, J. Colloid Interface Sci. 44, 121 (1973).

Contribution to Polymer Colloid Newsletter
from the
Colloid & Surface Chemistry Group
Department of Physical Chemistry
University of Melbourne.

This is the first contribution to the Newsletter from the Group in Melbourne. The Group (under Prof. Tom Healy) has an established tradition of research into inorganic, mainly oxide, colloids. The arrival of Andy Homola, and his stay of around 4 years (ending in 1978), saw the Group venture into the world of polymer latex colloids. The amount of activity with these colloids has had its ups and downs - The development by Andy Homola and Bob James of an amphoteric latex led to its use in diverse areas such as colloid stability (Homola, James and Healy, Faraday Trans I, 73, 1977, 1436) and as a substrate for adsorption of aqueous silica (Furlong, Freeman & Lau, J. Colloid Interface Science 80, 1981, 21).

The Groups current interests in latex colloids are summarized as follows:

(1) "Adsorption of heavy metals on amphoteric latex colloids"
(Graduate student Ian Harding & Prof. T.W. Healy)

Aim: to determine the role of surface potential, as measured by the isolectric point, on the adsorption of hydrolysable metal ions on amphoteric latex colloids.

(2) "Size control of amphoteric latices"
(Ian Harding Dr Neil Furlong & Prof. Healy)

Aim: to determine the controlling factors on the size of amphoteric latices both between different latex recipes and of a given latex sample.

(3) "Analysis of potentiometric titrations of amphoteric latex colloids"
(Ian Harding & Prof. Healy)

Aim: to develop a theoretical relationship between the capacitance of a latex at the p.z.c. $\left(\frac{d}{dpH}(\sigma_o)_{\sigma o} = 0\right)$ and the total number of surface sites.

(4) "The theoretical relationship between electrophoretic mobility and zeta-potential"
(Graduate student Rob Lamb and Dr Lee White)

Aim: to provide experimental verification for a maximum in the mobility of a carboxyl latex colloid by adsorbing a charged surfactant on that surface.

(5) "The effect of purification procedures on surface charge and potential of an amphoteric (zwitterionic) polystyrene latex"
(Ian Harding and Prof. Healy).
This work has recently been written up for the Journal of Colloid and Interface Science. - a summary is given below.

As can be seen from the titles listed most of the Group work is concerned with the Homola/James amphoteric latex and constitutes the Ph.D. program of Ian Harding. We hope to give more details of projects (1) (2) and (3) in forthcoming newsletters as Ian Harding completes his Ph.D.

Dr Neil Furlong
Melbourne 15/7/81.

"The effect of purification procedures on surface charge and potential of an amphoteric (zwitterionic) polystyrene latex"

Amphoteric polystyrene latices were prepared via the method of Homola and James (1). By varying the acid (carboxyl) and base (amine) content, monodisperse latices with i.e.p. 5.4, 6.1 and 8.0 were prepared along with a polydisperse latex of i.e.p. 6.0. Each of these latices were cleaned by the techniques of dialysis, ultrafiltration, ion exchange, activated charcoal cloth equilibration and centrifugation-decantation. Electron microscopy and surface tension results indicated that only the techniques of ultrafiltration and centrifugation-decantation could remove all detectable impurity from latex dispersions. Conductometric/potentiometric titration data supported this, with considerably higher titration data resulting from dialysed, ion exchanged and charcoal cloth equilibrated latices over centrifuged and ultrafiltered latices. Furthermore, with dialysis, ion exchange and/or charcoal cloth equilibration, the observed capacitances at the p.z.c. were greater than is theoretically possible. For monodisperse samples, microelectrophoresis proved insensitive to differences between the various cleaning techniques although the i.e.p. of a polydispersed sample was found to be dependent on the cleaning procedure.

(1) Homola, A., and James, R.O., J. Colloid Interface Sci., 59, 123 (1977).

COLLOID RESEARCH AT MCMASTER UNIVERSITY - RECENT DEVELOPMENTS

1) Continuous Emulsion Polymerization of Vinyl Acetate

The new reactor configuration discussed in Polymer Colloid Group Newsletter (May 15, 1981) is being operated in a dynamic mode to achieve broader particle size distributions. A sinusoidal variation of the split between reactors 1 and 2 with respect to time gives forced but controllable oscillations of number of polymer particles leaving reactor 1. This technique can be used to broaden the PSD beyond that found for a single stirred tank reactor.

2) Continuous Emulsion Polymerization of Styrene/Butadiene

A dynamic model is being developed for the continuous emulsion polymerization of styrene/butadiene. This model will be used to design a reactor train for SBR production with emphasis on minimizing the control problem associated with oscillations in polymer particle generation. An attempt is being made to achieve higher conversions and productivity through use of advanced techniques for controlling long chain branching and hence processability. This work is being sponsored by Australian Synthetic Rubber Company.

3) Recent Capital Purchases

The Federal Government of Canada has recently decided to increase significantly its support of University Research and particularly to increase funding for equipment purchases. Our group has recently benefitted with a grant for a Waters 150C gel permeation chromatograph. Rumours have it that a very large grant to build a miniplant consisting of six high pressure (5 liter) stirred tank reactors with ancilliary computer-controlled pumps and detector systems will be shortly forthcoming. This miniplant would be used to study SBR production at leas' initially.

The work reported herein was done in collaboration with Dr. J.F. MacGregor McMaster University.

(Contribution to Polymer Colliods Group Newsletter, from Dr. A.E. Hamielec, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada).

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Kinetics of Emulsion Copolymerization
I. Theoretical Part

Mamoru Nomura,* Masayuki Kubo*
and
Kazumi Fujita*

(Received Aug. 31, 1981)

This paper clarifies that the kinetic theories developed so far for emulsion homopolymerization are applicable without any modification to the prediction of the average number of radicals and their kinds in the particles formed in emulsion copolymerizations, if the average rate coefficient for radical desorption from the particles, the average termination rate constants in the particle and water phases, and the average propagation rate constant defined in this paper are employed in place of those for emulsion homopolymerizations.

INTRODUCTION

Although emulsion copolymerization is industrially more common and important than emulsion homopolymerization, the kinetic study of this system has to date received scant attention in the literature compared to bulk or solution polymerizations. This may be due mainly to the complicated mechanism involved in this system. Recently, Lin et al.[1] studied the kinetics of emulsion copolymerization of styrene (ST) and acrylonitril(AN) in an azeotoropic composition using our kinetic model[2] developed for the emulsion copolymerization of methyl methacrylate(MMA) and styrene(ST). Napper et al.[3] also proposed a mathematical model of an emulsion copolymerization system which can predicts the time evolution of the copolymer composition and copolymer sequence distribution. However, their model is inconvenient because of its complexity only for the purpose of predicting the rate of emulsion copolymerization and the average copolymer composition without complicated and time-consuming calculations.

In this study, it is clarified that the kinetic theories so far developed for emulsion homopolymerization are applicable without any

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modification to the prediction of the average number of radicals and their kinds in the polymer particle formed in emulsion copolymerization systems, if the average rate coefficient for radical desorption from the particles, the average termination rate constants in the particle and water phases, and the average propagation rate constant defined in this paper are employed in place of those for emulsion homopolymerization.

KINETIC THEORY FOR EMULSION HOMOPOLYMERIZATION

In emulsion homopolymerization, the number of polymer particles containing n radicals(N_n) satisfies the following steady-state balance equation[4]:

$$\frac{dN_n}{dt} = (\frac{\rho_a}{N_T})N_{n-1} + k_f(n+1)N_{n+1} + k_{tp}[\frac{(n+2)(n+1)}{v_p}]N_{n+2} - (\frac{\rho_a}{N_T})N_n$$

$$- k_f nN_n - k_{tp}[\frac{n(n-1)}{v_p}]N_n = 0 \qquad (1)$$

The overall rate of radical entry into the particles(ρ_a) in Eq.(1) is represented by:

$$\rho_a = k_a[R_w^*]N_T = r_i + \sum_{n=1}^{\infty} k_f nN_n - 2k_{tw}[R_w^*]^2 \qquad (2)$$

where k_f is the rate coefficient for radical desorption from the particles, k_{tp} is the rate constant for radical termination in the particles, N_T is the number of polymer particles in cc-water, k_a is the rate constant for radical absorption by the particles, $[R_w^*]$ is the radical concentration in the water phase and k_{tw} is the rate constant for radical termination in the water phase.

Equations (1) and (2) are converted into nondimensional forms shown by;

$$\alpha N_{n-1} + m(n+1)N_{n+1} + (n+1)(n+2)N_{n+2} = \alpha N_n + mnN_n + n(n-1)N_n \qquad (1')$$

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2 \qquad (2')$$

By solving the simultaneous equations(1') and (2'), one can get the average number of radicals per particle($\bar{n}$) as a function of the parameters, α', m and Y which are predictable from operational variables. The general solution to Eq.(1') for $\bar{n}$ which involved a variable parameter, α was first given by Stockmayer[5], but was later corrected by O'Toole[6] to give a physically more acceptable result for small but finite rates of radical desorption from the polymer particles:

$$\bar{n} = \sum_{n=1}^{\infty} nN_n / N_T = \frac{a}{4}\frac{I_m(a)}{I_{m-1}(a)}, \quad a^2 = 8\alpha \qquad (3)$$

where I_m is the modefied Bessel function of the first kind and

$$\alpha = \frac{\rho_a v_p}{k_{tp} N_T} \quad (4) \qquad \alpha' = \frac{r_i v_p}{k_{tp}} \quad (5)$$

$$m = \frac{k_f v_p}{k_{tp}} \quad (6) \qquad Y = \frac{2 k_{tw} k_{tp}}{k_a^2 N_T v_p} \quad (7)$$

Noting that Eq.(3) involved a variable parameter, α, Ugelstad et al.[7] solved the simultaneous equations(2') and (3) for $\bar{n}$ as a function of the parameters, α', m and Y, and plotted $\log \bar{n}$ against $\log \alpha'$ over a wide range of m values at several fixed values of Y.

APPLICATION TO EMULSION COPOLYMERIZATION SYSTEMS

For simplicity, let us consider an emulsion copolymerization system where two comonomers, A and B are copolymerized and note a single polymer particle which contains n radicals, where the numbers of A-radicals and B-radicals are n_a and n_b, respectively. Then, we have:

$$n = n_a + n_b \quad (8)$$

By establishing balance equations on n_a, n_b and n, and applying steady state assumption, we have:

$$\frac{dn_a}{dt} = \left(\frac{\rho_a \alpha_a}{N_T}\right) - 2k_{tpaa}\left(\frac{n_a^2}{v_p}\right) - k_{tpab}\left(\frac{n_a \cdot n_b}{v_p}\right) - k_{fa} n_a$$
$$- (k_{pab} + k_{mab})[M_{bp}] n_a + (k_{pba} + k_{mba})[M_{ap}] n_b = 0 \quad (9)$$

$$\frac{dn_b}{dt} = \left(\frac{\rho_a \alpha_b}{N_T}\right) - 2k_{tpbb}\left(\frac{n_b^2}{v_p}\right) - k_{tpba}\left(\frac{n_b \cdot n_a}{v_p}\right) - k_{fb} n_b$$
$$- (k_{pba} + k_{mba})[M_{ap}] n_b + (k_{pab} + k_{mab})[M_{bp}] n_a = 0 \quad (10)$$

$$\frac{dn}{dt} = \frac{d(n_a + n_b)}{dt} = \left(\frac{\rho_a}{N_T}\right) - 2k_{tpaa}\left(\frac{n_a^2}{v_p}\right) - 2k_{tpab}\left(\frac{n_a \cdot n_b}{v_p}\right) - 2k_{tpbb}\left(\frac{n_b^2}{v_p}\right)$$
$$- (k_{fa} n_a + k_{fb} n_b) = 0 \quad (11)$$

It is clear that the values of the termination and desorption rate terms in Eq.(11) a e at the highest equal to the value of the term, (ρ_a / N_T). Considering that $\rho_a \simeq r_i \simeq 10^{13}$ molecules/cc-water.sec and $N_T = 10^{14} \sim 10^{15}$ particles/cc-water, the last two terms on the right-hand side of Eqs.(9) and (10) are dominating and hence, Eqs.(9) and (10) can be rewritten with very good accuracy as:

$$(k_{pab} + k_{mab})[M_{pb}]n_a = (k_{pba} + k_{mba})[M_{pa}]n_b \qquad (12)$$

Using Eq.(12), we define that:

$$A = \frac{n_b}{n_a} = \frac{(k_{pab} + k_{mab})[M_{pb}]}{(k_{pba} + k_{mba})[M_{pa}]} = (\frac{k_{paa}}{k_{pbb}})(\frac{\gamma_b}{\gamma_a})(\frac{1 + C_{mab}}{1 + C_{mab}})(\frac{[M_{pb}]}{[M_{pa}]}) \qquad (13)$$

Considering that propagation rate constant(k_p) is far greater than chain transfer constant(k_m), the above equation reduces to:

$$A = (\frac{k_{paa}}{k_{pbb}})(\frac{\gamma_b}{\gamma_a})(\frac{[M_{pb}]}{[M_{pa}]}) \qquad (13')$$

where C_m is the chain transfer constant to monomer and γ is the reactivity ratio.

From Eqs.(8) and (13) we have:

$$n_a = (\frac{1}{1 + A})n \qquad (14) \qquad n_b = (\frac{A}{1 + A})n \qquad (15)$$

Equation (1) can be used for expressing a balance on the number of particles containing n radicals in an emulsion copolymerization system, if the average rate coefficient for radical desorption and the average rate constant for radical termination in the particles defined as follows are employed in place of those for emulsion homopolymerization.

(1) Average rate coefficient for radical desorption, $\bar{k}_f$:

$$\bar{k}_f n N_n = (k_{fa} n_a + k_{fb} n_b) N_n$$

Introducing Eqs.(14) and (15) leads to:

$$\bar{k}_f = (\frac{1}{1 + A})k_{fa} + (\frac{A}{1 + A})k_{fb} \qquad (16)$$

where k_{fa} is the rate coefficient for A-radical desorption and given by:[2)]

$$k_{fa} = K_{oa}[\frac{C_{maa}\gamma_b + C_{mba}[M_{pb}]/[M_{pa}]}{\gamma_a(1 + (K_{oa}\bar{n}_t/k_{paa}[M_{pa}])) + [M_{pb}]/[M_{pa}]}] \qquad (17)$$

$$C_{maa} = \frac{k_{maa}}{k_{paa}}, \quad K_{oa} = \frac{12 D_{wa}\delta_a}{m_{da} d_p^2}, \quad \delta_a = (1 + D_{wa}/m_{da}.D_{pa})^{-1} \text{ and } \gamma_a = \frac{k_{paa}}{k_{pab}}$$

where D_w is the diffusion coefficient for escaping radicals in the water phase and D_p is the diffusion coefficient for escaping radicals in the particle, m_d is the partition coefficient for escaping radicals between the water and particle phases, $[M_p]$ is the monomer concentration in the particle and d_p is the particle diameter.

(2) Average rate constant for radical termination in the particle, $\bar{k}_{tp}$: when n>>1, the following relationship holds with good accuracy.

$$\bar{k}_{tp}[\frac{n(n-1)}{v_p}]N_n \simeq \bar{k}_{tp}[\frac{n^2}{v_p}]N_n = (\frac{k_{tpaa}n_a^2 + k_{tpab}n_a \cdot n_b + k_{tpbb}n_b^2}{v_p})N_n \qquad (18)$$

Thus, we have:

$$\bar{k}_{tp} = (\frac{1}{1+A})^2[k_{tpaa} + Ak_{tpab} + A^2k_{tpbb}] \qquad (18')$$

Even when the value of n is near one, $\bar{k}_{tp}$ defined by Eq.(18') is considered to be a good approximation for the average rate constant for radical termination in the polymer particles from statistical point of view.

In the case of emulsion copolymerizatio, therefore, Eqs.(1) and (2) are rewritten as:

$$\frac{dN_n}{dt} = (\frac{\rho_a}{N_T})N_{n-1} + \bar{k}_f(n+1)N_{n+1} + \bar{k}_{tp}[\frac{(n+2)(n+1)}{v_p}]N_{n+2} - (\frac{\rho_a}{N_T})N_n$$
$$- \bar{k}_f nN_n - \bar{k}_{tp}[\frac{n(n-1)}{v_p}]N_n = 0 \qquad (19)$$

$$\rho_a = \bar{k}_a[R_w^*]N_T = r_i + \sum_{n=1}^{\infty}\bar{k}_f nN_n - 2\bar{k}_{tw}[R_w^*]^2 \qquad (20)$$

It is clear from Eqs.(19) and (20) that one can use Eqs.(1') and (2') without any modification for predicting the average number of total radicals per particle($\bar{n}_t$) in an emulsion copolymerization system, if the average coefficients, $\bar{k}_f$, $\bar{k}_{tp}$ and $\bar{k}_{tw}$ are used in place of k_f, k_{tp}, k_{tw} in Eqs.(1') and (2').

We define here the average number of A-radicals per particle($\bar{n}_a$), the average number of B-radicals per particle($\bar{n}_b$) and the average number of total radicals per particles($\bar{n}_t$), which satisfy the following relationships:

$$\bar{n}_t = \sum_{n=1}^{\infty} nN_n/N_T = \sum_{n=1}^{\infty}(n_a+n_b)N_n/N_T = \sum_{n=1}^{\infty} n_aN_n/N_T + \sum_{n=1}^{\infty} n_bN_n/N_T = \bar{n}_a + \bar{n}_b \qquad (21)$$

where

$$\bar{n}_a = \sum_{n=1}^{\infty} n_aN_n/N_T = \sum_{n=1}^{\infty}(\frac{1}{1+A})nN_n/N_T = (\frac{1}{1+A})\bar{n}_t \qquad (22)$$

$$\bar{n}_b = \sum_{n=1}^{\infty} n_bN_n/N_T = \sum_{n=1}^{\infty}(\frac{A}{1+A})nN_n/N_T = (\frac{A}{1+A})\bar{n}_t \qquad (23)$$

It is apparent from Eqs.(22) and (23) that $\bar{n}_a$ and $\bar{n}_b$ also fulfill Eq.(13), that is;

$$A = \frac{n_b}{n_a} = \frac{\bar{n}_b}{\bar{n}_a} \qquad (13)$$

Under normal conditions, termination reaction in the water phase is usually negligible. This corresponds to the condition that Y= 0. The values of $\bar{n}_t$ calculated at Y= 0 using Eqs.(2') and (3) are plotted against α' value in Figure 1. It is inconvenient to use Eqs. (2') and (3) directly, so that several empirical or approximate equations for $\bar{n}_t$ are derived in the case of Y= 0 as follows:[8)]

1) when m= 0

$$\bar{n}_t = (\frac{1}{4} + \frac{\alpha'}{2})^{1/2} \tag{24}$$

2) when instantaneous termination is dominating in the particles and $\bar{n} < 0.5$,

$$\bar{n}_t = \frac{1}{2}(-C + \sqrt{C^2 + 2C}), \quad C = \frac{\alpha'}{m} = \frac{r_i}{\bar{k}_f N_T} \tag{25}$$

Equation (25) is reduced to:

when $C \to \infty$, $\bar{n}_t = 0.5$ (26)

and when $C < 10^{-2}$ $\bar{n}_t = (C/2)^{1/2}$ (27)

3) when $\bar{n}_t < 0.2$,

$$\bar{n}_t = [\frac{\alpha'}{2}(1 + \frac{1}{m})]^{1/2} \tag{28}$$

4) when $m \to \infty$ or $\bar{n}_t >> 0.5$

$$\bar{n}_t = (\alpha'/2)^{1/2} \tag{29}$$

Equation (24) is an emprical equation developed by Ugelstad et al.[9)]

RATES OF EMULSION COPOLYMERIZATION AND COPOLYMER COMPOSITION

Rates of emulsion copolymerization are expressed by:

for A-monomer,

$$R_{pa} = -\frac{dM_a}{dt} = k_{paa}[M_{pa}]\bar{n}_a N_T + k_{pba}[M_{pa}]\bar{n}_b N_T \tag{30}$$

for B-monomer,

$$R_{pb} = -\frac{dM_b}{dt} = k_{pbb}[M_{pb}]\bar{n}_b N_T + k_{pab}[M_{pb}]\bar{n}_a N_T \tag{31}$$

However, If we use the average propagation rate constants defined by

$$\bar{k}_{pa} = \frac{k_{paa} + A k_{pba}}{1 + A}, \qquad \bar{k}_{pb} = \frac{k_{pab} + A k_{pbb}}{1 + A} \tag{32}$$

equations(30) and (31) are simplified as:

$$R_{pa} = -\frac{dM_a}{dt} = \bar{k}_{pa}[M_{pa}]\bar{n}_t N_T \tag{30'}$$

$$R_{pb} = -\frac{dM_b}{dt} = \bar{k}_{pb}[M_{pb}]\bar{n}_t N_T \tag{31'}$$

The total rate of emulsion copolymerization(R_{pt}) is given by:

$$R_{pt} = R_{pa} + R_{pb} = (\bar{k}_{pa}[M_{pa}] + \bar{k}_{pb}[M_{pb}])\bar{n}_t N_T \qquad (32)$$

The composition of copolymers formed in an emulsion copolymerization system can be calculated by the following equation derived from Eqs.(30) and (31).

$$\frac{dP_a}{dP_b} = \frac{-dM_a}{-dM_b} = \frac{R_{pa}}{R_{pb}} = \frac{[M_{pa}]}{[M_{pb}]}\left(\frac{\gamma_a[M_{pa}] + [M_{pb}]}{\gamma_b[M_{pb}] + [M_{pa}]}\right)$$

$$= \frac{\bar{k}_{pa}[M_{pa}]}{\bar{k}_{pb}[M_{pb}]} \qquad (33)$$

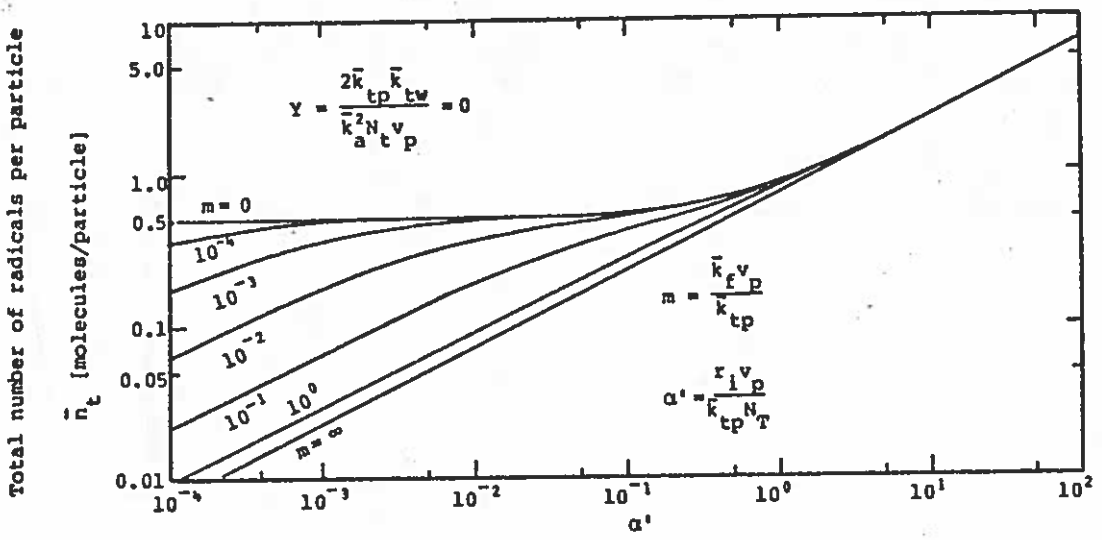

Figure 1. Average number of total radicals per particle, $\bar{n}_t$, as a function of the parameters α' and m

TO CONCLUDE

It has already been shown that radical desorption from the particles plays an important role in kinetic behavior and Eqs.(25) and (17) explain well the rate of emulsion copolymerization of ST and MMA in the range where the number of total radicals per particle $\bar{n}_t$ is less than 0.5.[2] The kinetic behavior of the same emulsion copolymerization system where $\bar{n}_t$ is higher than 0.5 has been analyzed using Eq.(29) and the results will be shown elsewhere.[10]

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Polymer Colloids Group Newsletter
Contribution from University of Akron

Reported by I. Piirma

In a typical emulsion polymerization of styrene using an ionic emulsifier such as sodium dodecyl sulfate, the number of latex particles is usually assumed to become constant at a rather low conversion, ca. 10-20%. We have found that the polymerization using Emulphogene BC-840 (a nonionic surfactant) as the sole emulsifier, the polymerization conversion versus time curve did not follow the conventional course. Instead of a short induction time and a fast but constant rate thereafter, a relatively slow rate was observed up to 20% conversion. After that, at an inflection point, the rate of polymerization increased suddenly. At the time of the inflection point, a large number of small particles were generated causing the rate of polymerization to increase rapidly. Before this inflection point no small particles were observed at all in the system. These observations indicate that perhaps there are two different mechanisms operating in a polymerization stabilized by the non-ionic BC-840 emulsifier. For particle size distribution Woods et al. have reported monodisperse particle size distribution in their studies of styrene polymerization with mixed surfactants. A series of polymerizations were run using constant amounts of BC-840 and adding very small amounts of SDS. We found that the onset of the inflection point varies with the amount of SDS present in the system.

The results are summarized in Tables I, II and III.

TABLE I

Rate of Polymerization Using Constant Amounts of BC-840 and Very Small Amounts of SLS

Surfactant Charged	Rate (%/min) Before Inflection Point	Inflection Point (% Conversion)
BC-840 2.58g	0.09	40
0.0025g SLS/2.58g BC-840	0.13	43
0.0050g SLS/2.58g BC-840	0.19	49
0.0100g SLS/2.58g BC-840	0.22	53
0.0200g SLS/2.58g BC-840	0.35	62
0.0400g SLS/2.58g BC-840	0.46	65
0.0500g SLS/2.58g BC-840	0.58	None

TABLE III

The Ratio of Number of Small Particles to Number of Large Particles in the Systems of Constant Amounts of BC-840 and Added Small Amounts of SDS

Surfactants	Ratio
BC-840 2.58g	3.3
0.0025g SLS/2.58g BC-840	2.5
0.0050g SLS/2.58g BC-840	0.7
0.0100g SLS/2.58g BC-840	0.4
0.0200g SLS/2.58g BC-840	0.3
0.0400g SLS/2.58g BC-840	0.1
0.0500g SLS/2.58g BC-840	0*

*Approximate zero by our measurements

Higher than 0.05g SDS/2.58g BC-840 resulted in a monomodal, monodisperse particle size distribution.

TABLE II

Effect of Trace Amounts of SDS in Fixed BC-840 on Number and Size Distribution of Latex Particles

Surfactant Charged*	Conversion (%)	D_w(Å)	D_n(Å)	D_w/D_n	N_p/ml x 10^{-14}
BC-840 2.58	39.3	1930	1850	1.03_9	0.61
	52.1	770	690	1.11_1	11.25
		1950	1880	1.03_7	
BC-840 2.58 SLS 0.0025	38.4	1530	1460	1.04_5	1.19
	56.4	730	640	1.13_2	14.23
		1550	1500	1.03_2	
BC-840 2.58 SLS 0.005	42.5	1420	1380	1.03_0	1.59
	55.0	630	560	1.11_7	12.49
		1520	1490	1.02_6	
BC-840 2.58 SLS 0.01	50.2	1350	1320	1.02_4	2.18
	64.6	670	600	1.10_6	10.05
		1420	1390	1.02_2	
BC-840 2.58 SLS 0.02	51.4	1380	1360	1.01_3	2.04
	65.7	580	500	1.16_5	12.18
		1410	1400	1.01_2	
BC-840 2.58 SLS 0.04	65.4	1190	1150	1.03_1	4.21
	78.4	650	550	1.17_0	7.57
		1310	1280	1.02_1	

*Unit: g/54g H_2O

Title: Steady-State Analysis of Emulsion Polymerization in a Seed-Fed Continuous Stirred-Tank Reactor (CSTR)

By: Gary W. Poehlein, School of Chemical Engineering
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Ugelstad and coworkers presented a rather general solution to the Smith-Ewart recursion equation for monodisperse latex particles. Their results are presented in the form of plots of $\bar{n}$ vs α' with m as the curve parameter and Y changing between plots. Figures 1 and 2 are typical examples of Ugelstad's results.

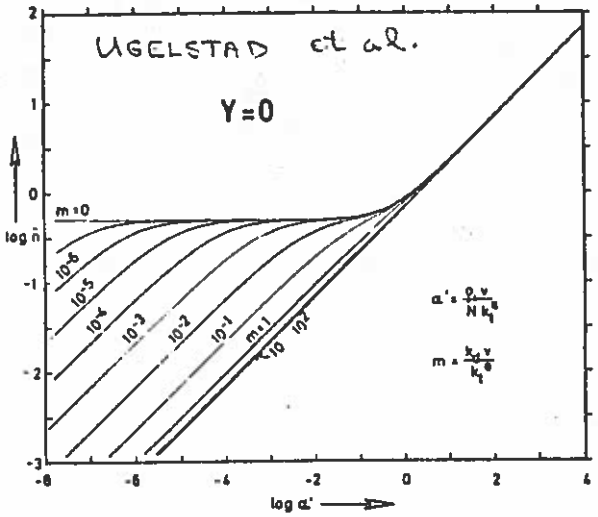


FIG. 1—Average number of radicals per particle, $\bar{n}$, as a function of the parameters α' and m for $Y = 0$ [see Equations (101)–(103)]. Reprinted by permission of J. Polym. Sci.[41]

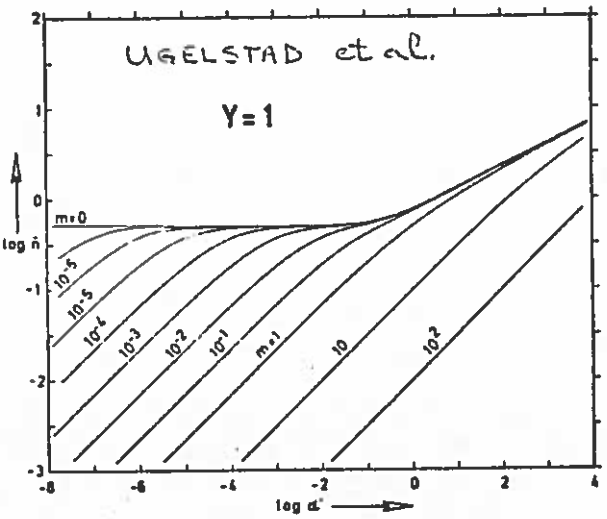


FIG. 2—Average number of radicals per particle, $\bar{n}$, as a function of the parameters α' and m for $Y = 1$. Reprinted by permission of J. Polym. Sci.[41]

The dimensionless parameters used are defined as follows.

$\bar{n}$ = average number of free radicals per latex particle -- averaged over the particle population or averaged over an individual particle in a time sense.

$\alpha' = (\rho_i v/Nk_t)$; where ρ_i is the rate of initiation of free radicals, v is the volume of the monomer-swollen polymer particles, N is the particle concentration and k_t is the termination rate constant in the polymer particles.

$m = (k_d v/k_t)$; where k_d is a radical desorption constant.

$Y = (2Nk_t k_{tw}/k_a^2 v)$; where k_{tw} is a rate constant for termination in the water phase and k_a is a radical absorption constant.

We have developed a steady-state model for a single CSTR which is fed with a monodisperse feed stream. This model takes into account the broad age distribution among the particles in the effluent stream of the CSTR as well as the kinetic mechanisms of radical desorption and aqueous phase termination. The model is based on continuum diffusion theory for radical transport rates. Dimensionless groups, some of which are analogous to those used by Ugelstad, are defined below. The particle size used in the definition of these groups is the volume of the monomer-swollen seed particles, $\langle v_{po} \rangle$.

$\langle \bar{n} \rangle$ = $\bar{n}$ averaged over the latex particle size distribution in the effluent stream.

$\alpha'_c = \rho_i \langle v_{po} \rangle / Nk_t$

$\gamma = m\langle (v/\langle v_{po} \rangle)^{1/3} \rangle$; where the $\langle\rangle$ imply an average of the expression within.

$Y_c = 2Nk_t k_{tw}/[4\pi D_w N(3/4\pi)^{1/3} \langle v_{po} \rangle^{1/3}]^2 \langle v_{po} \rangle$; where D_w is the radical diffusivity in the water phase.

β (a new group) = $\langle v_{po} \rangle / \theta K_1 [M]_p$; where θ is the reactor mean residence time, K_1 is a kinetic constant related to the growth rate of the latex particles and $[M]_p$ is the monomer concentration in the particles.

The appropriate equations were solved with the aid of a digital computer. Typical results are shown in Figures 3, 4 and 5. Figure 3 shows plots of dimensionless particle diameter distributions as a function of β for the case of $\gamma = Y_c = 0.0$ and $\gamma_c' = 5.1 \times 10^{-3}$. Larger values of the reactor mean residence time, θ, (lower β) lead to broader size distributions. Values of $\bar{n}$ for individual particles are marked on the different curves.

Figure 4 shows a very interesting phenomena. Namely, that bimodal particle size distributions can be produced in a steady-state reactor if the radical desorption mechanism is functional. Measurement of these distributions could provide some very valuable information in studying radical desorption.

Figure 5 is a plot of $\langle \bar{n} \rangle$ vs α_c' with γ as the parameter for fixed value of β and Y_c. This plot is analogous to Ugelstad's plots except the added parameter β is present to account for reactor mean residence time. Further studies with the CSTR model will be conducted during the next year.

FIGURE 3: Influence of the Parameter β on the Dimensionless Particle Diameter Distribution for $\alpha_c' = 5.1X10^{-3}$, $\gamma = Y_c = 0.0$

Curve No.	β	$\langle\bar{n}\rangle$	$\langle D \rangle$
1	0.0071	.5625	3.80
2	0.0035	.5932	4.72
3	0.0018	.6471	6.01

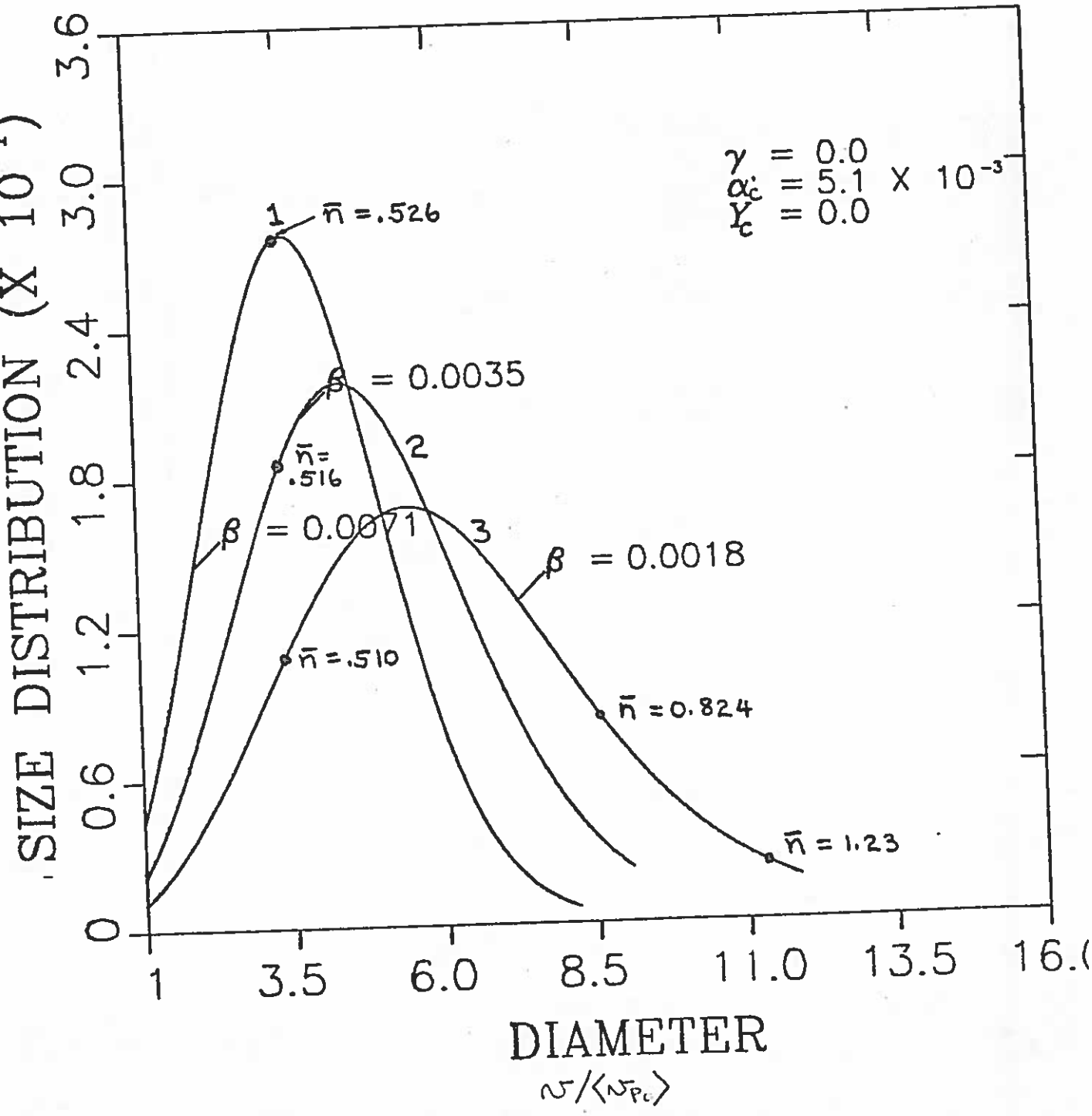


FIGURE 4: Influence of the Parameter β on the Dimensionless Particle Diameter Distribution for $\alpha_c' = 3.2X10^{-6}$, $\gamma = 1.0X10^{-6}$ and $Y_c = 0.0$

Curve No.	β	$\langle\bar{n}\rangle$	<D>
1	0.0071	.2811	2.82
2	0.0035	.3033	3.58
3	0.0018	.3211	4.55

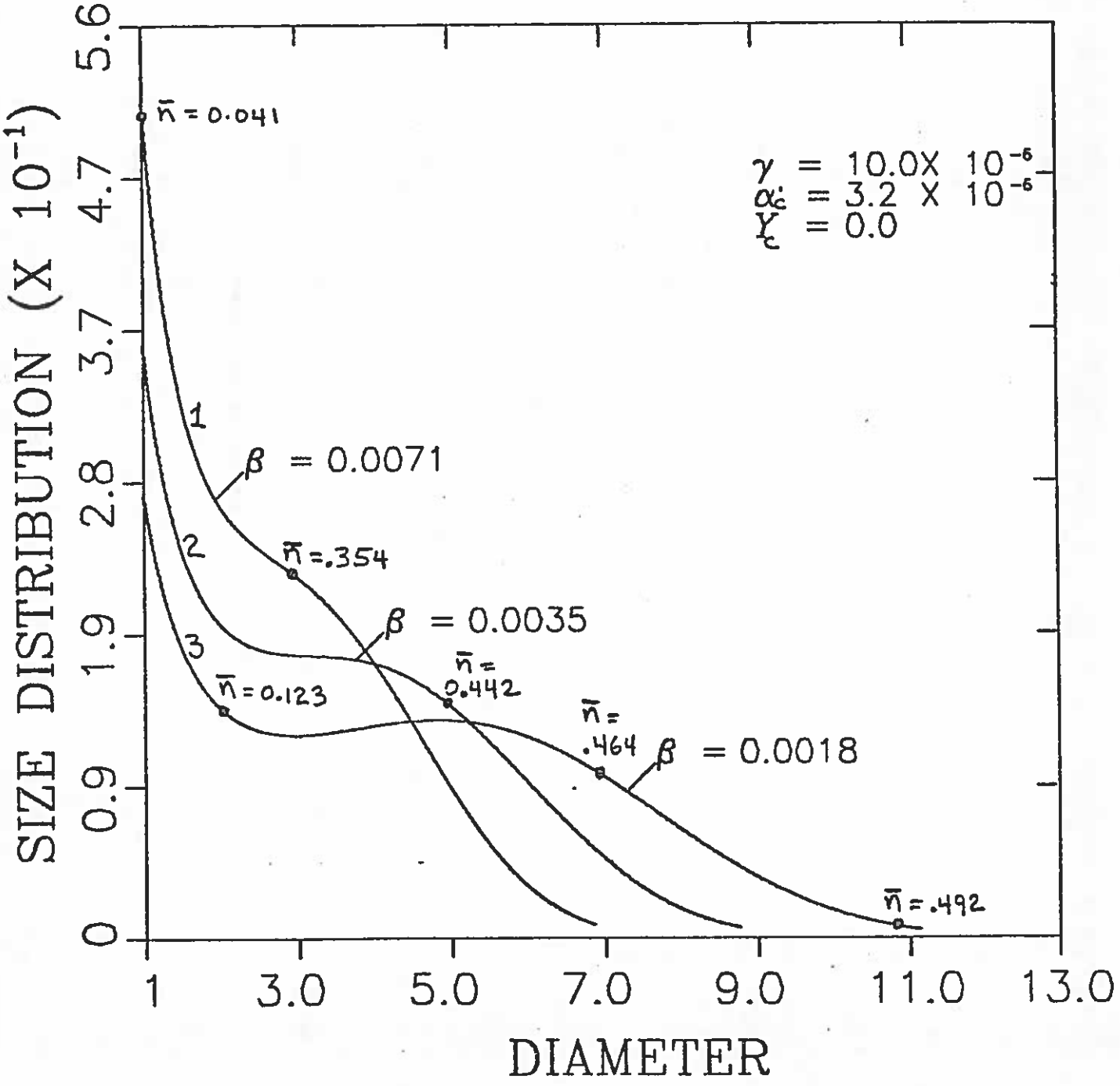
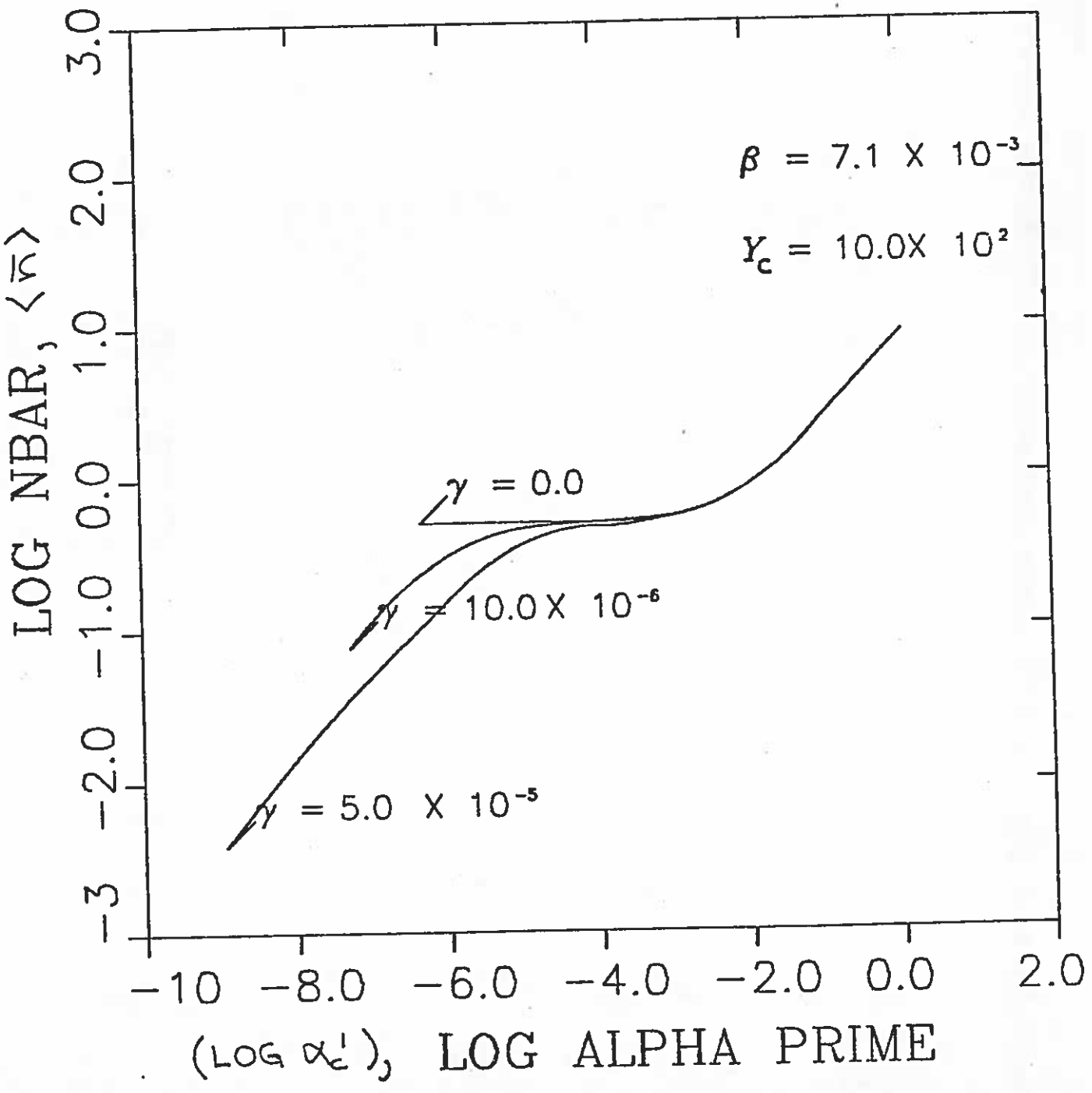


FIGURE 5: Average Number of Radicals Per Particle Over the Size Distribution as a Function of γ for $\beta = 0.0071$ and $Y_c = 1000.0$



CONTRIBUTION TO POLYMER COLLOID GROUP LETTER

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25 SEP Recd

1. Diffusion of Spheroidal Particles in Poiseuille Flow

The translational diffusion of spherical and axisymmetric particles can be characterized by the mean-squared displacement of the particles in a general linear flow. Recently the theory for the translational diffusion of axisymmetric particles in simple shear flow has been worked out. The displacement most amenable to experimental verification is the displacement along the flow direction x_3, which according to the theory equals:

$$\langle \Delta x_3^{*2} \rangle = t^* + \frac{1}{3} t^{*3} + (q - 1 \{g_3(t^*)\ t^* + \frac{1}{3} c_2\ t^{*3}\} \quad . \qquad [1]$$

Here $x_3^* = Pe_t^{1/2}\ x_3/b$, with $Pe_t = Gb^2/2D_\perp$ being the translational Peclet number; $\Delta x_3^* = x_3^* - x_3^*(Pe_t = \infty)$, $x_3^*\ (Pe_t = \infty)$ being the distance traveled by a particle in the absence of diffusion; G is the rate of shear, b a characteristic particle dimension, $D_\perp$ is the translational diffusivity of a particle perpendicular to the axis of revolution, $q = D_\parallel / D_\perp$, $D_\parallel$ being the diffusivity parallel to the axis of revolution, c_2 is a constant depending on the initial orbit constant and the axis ratio of the particle, and $g_3(t^*)$ is an initially damped oscillating function of time $t^* = Gt$ or order unity. At times $t^* >> 1$ the displacement of an axisymmetric particle is identical to that of a sphere with effective diffusion constant $D_{eff}/D_\perp = 1 + (q - 1)\ c_2$.

As can be seen from [1] the first two terms of the r.h.s. are due to pure diffusion and shear-enhanced diffusion respectively. The last term accounts for the effect of the shape and the initial orientation of the particle.

Experiments have been initiated to verify quantitatively this result using the new traveling microtube device. Doublets of latex spheres (1 μm diameter) were tracked along the microtube (30 cm length and 200 μm diameter) for long periods of time (about 30 min). The experiments were carried out under the condition of primary doublet formation and the displacement of touching doublets, for which all the diffusivity expressions are known, has been observed. Fig. 1 shows the results of an ensemble of 16 doublets in flow with relatively strong translational diffusion ($Pe_t = 1$). The solid line corresponds to the case of doublets with orbit constant C = 1 calculated from eq. [1]. The plot shows the transition from pure diffusion (at short time of shearing) to the "convective diffusion", where the plot should be linear with slope 3. Actually the best fit of the linear part of the experimental points gives a slope of 2.8, which is quite good considering the number of particles.

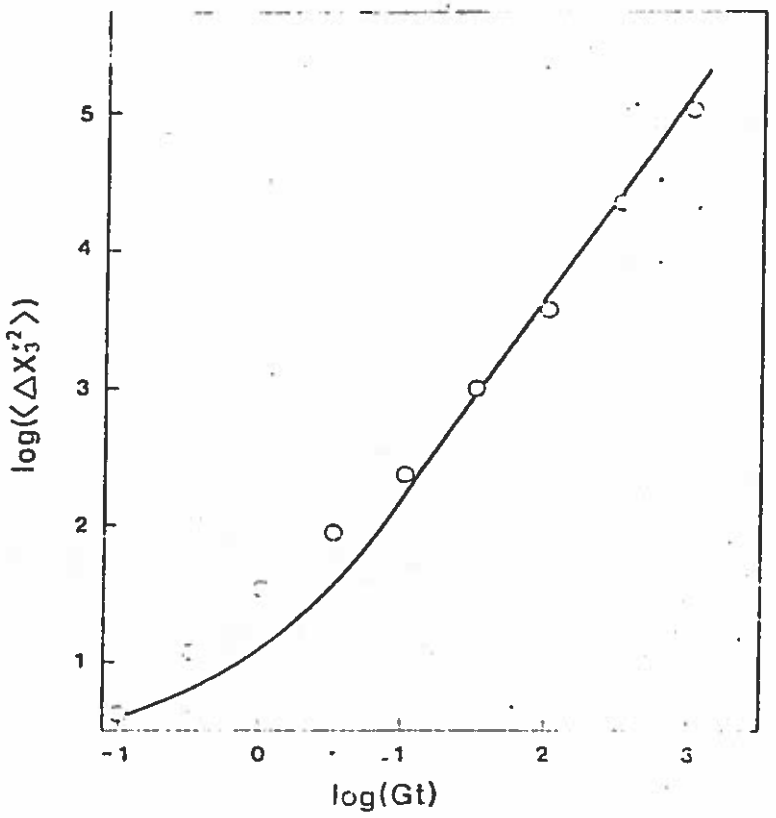

Fig. 1 - Mean-squared displacement in the direction of flow as a function of time. Solid line calculated from eq. [1]; circles are experimental observations.

The observed discrepancies in the early stages of shearing may be due to the precision with which initial velocities can be determined and also to the limited amount of particles. Also, the intercept of the linear part is related to the ratio $D_{eff}/D_{\perp}$, where D_{eff} is the effective diffusion coefficient, which turned out to be equal to 1.01, i.e. greater than 1 in qualitative agreement with the theory for the case of prolate spheroids; for doublets of touching spheres, depending on the orbit constant, $1 \leq D_{eff}/D_{\perp} \leq 1.04$.

2. Kinetics of Coating by Colloidal Particles

The kinetics of coating by colloidal particles is affected by blocking effects and by coagulation of the colloidal system. When the primary energy minimum is shallow, escape of particles by thermal motion is possible. Experimental evidence and theoretical considerations regarding the nature of adhesion forces suggest that due to mechanical and electrical changes in the contact area these forces increase with time. Such aging effects may influence the ability of particles to detach either by thermal motion or by external or hydrodynamic forces.

These effects produce a non-linear dependence of the coating density (expressed in particles per unit area of the collector) on time. A phenomenological model of the coating process proposed by us offers the possibility of a quantitative description of the coating process. Experimental data obtained by direct microscopic observation of the coating process led us to conclude that small particles deposited in a primary energy minimum, are not able to move tangentially although they can escape from the surface even in laminar flow. On the basis of the proposed theory it was estimated that the surface effectively blocked by deposited particles may be 20 to 30 times greater than their geometrical cross-section. This suggests that for the collector surfaces studied the effect of surface heterogeneity plays an important role in the coating process.

3. Deposition of Colloidal Particles in Turbulent Flow

Mass transfer of colloidal or aerosol particles to solid walls has been considered by adopting two models for the flow in the viscous sublayer of the turbulent boundary layer. The influence of finite particle dimensions and external force fields was taken into account. After estimating mean values of flow parameters characterizing the downsweep and the periodically developing boundary layer model for the flow in the viscous sublayer, general and limiting formulae describing the rate of mass transfer have been derived. Some results are shown in Fig. 2.

Comparison with experimental data suggests that the downsweep model describes the mass transfer in disperse systems better than the developing boundary layer model, especially for larger particles. It was found that the former can be successfully used, up to moderate values of the Reynolds number, for particles smaller than 2 μm.

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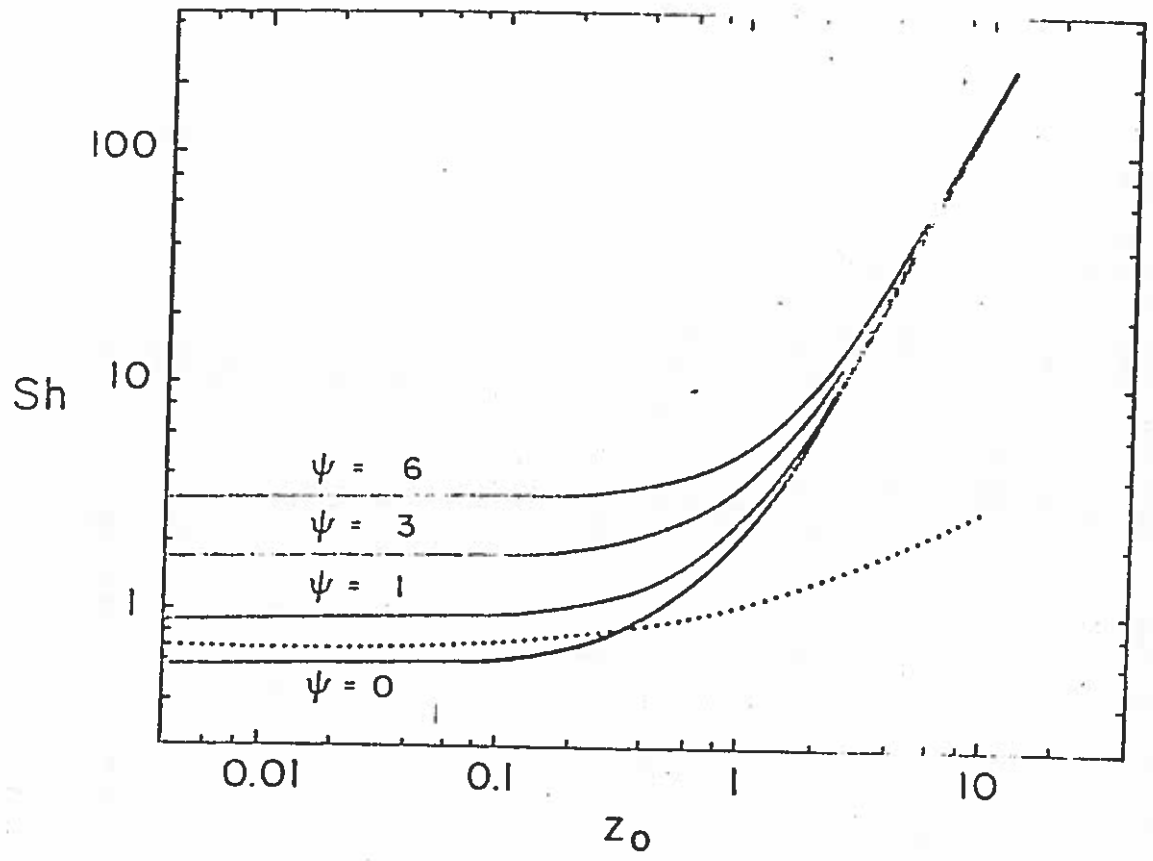

Fig. 2 - Mass transfer under turbulent flow conditions. Computed Sherwood number Sh (dimensionless deposition rate) vs. z_o (dimensionless interception parameter) for various ψ, accounting for the influence of gravity and electric fields. The solid lines denote the results obtained from the downsweep model and dotted line for the developing boundary layer model for the flow in the viscous sublayer of the turbulent boundary layer.

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DEPARTMENT OF CHEMISTRY
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September 15, 1981

The following paper was presented at the Colloid Symposium held at Case Western Reserve University in June, 1981. A generalization of the idea of using chemical desorption as a means of characterizing surface philicity was presented at the Gordon Conference on Polymer Colloids. We hope to be able to extend this work to the characterization of the surfaces of polymer colloids.

SURFACTANT BINDING AND THE ELECTROPHILICITY OF COAL

by

J. J. Kosman and R. L. Rowell

Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01003

ABSTRACT

The cationic surfactant, ATLAS G-271, N-soya N-ethyl morpholinium ethosulfate, 35% aqueous solution, has been shown to be an effective stabilizer for coal-oil mixtures (COM). Analysis of the coal phase separated from a COM by centrifugation showed that the surfactant was quantitatively associated with the coal. Removal of the surfactant from the coal phase was studied by solvent extraction and a correlation was found between surfactant removal and increasing solvent electrophilicity whereas no correlation was found between surfactant removal and solvent nucleophilicity. It was proposed that the surfactant was adsorbed on the coal surface as an ion-paired unit with the polar head group oriented toward electron donating sites on the coal matrix and the hydrocarbon tail extending outwards. The work has been extended to include slurries at 30 wt.% coal and 0.3 wt.% surfactant for coal-mineral oil, coal-no. 6 fuel oil, coal-water and coal-sea water. The coal-water slurries show a correlation of surfactant removal by more electrophilic solvents but differences in detail from the COM suggesting a difference in the strength of the surfactant binding arising from solvation effects.

LATEX COMPOSITIONS CONTAINING BLOCKED ISOCYANATOETHYL METHACRYLATE

F. L. SAUNDERS

CENTRAL RESEARCH-POLYMER RESEARCH
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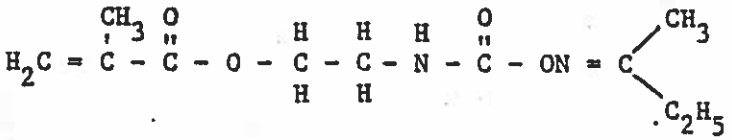
Latex polymer compositions containing isocyanatoethyl methacrylate blocked with methylethyl ketoxime (IEM-MEKO) were prepared and the thermal dissociation to free NCO and resultant polymer crosslinking studied by IR analysis and swell index measurements on film samples. Compositions investigated were 1) styrene (S)/butyl acrylate (BA)/IEM-MEKO; 2) S/BA/IEM-MEKO latex formulated with active hydrogen compounds; and 3) S/BA/IEM-MEKO copolymerized with vinyl acids or hydroxy monomers. The effect of "urethane" catalysts on the deblocking/curing reactions was also investigated.



(IEM-MEKO)

Deblocking temperature for IEM-MEKO is in the range of 150-170°C. Deblocking and crosslinking appears to proceed concurrently at these temperatures. Addition of T-12 catalyst (dibutyltin dilaurate) promotes the crosslinking reaction. Formulation of the latex polymer with a polyether polyol results in an isocyanate-hydroxyl reaction under deblocking conditions. This reaction is also promoted by T-12 catalyst.

Polymer compositions containing IEM-MEKO and acrylic acid (or methacrylic acid) show an increase in the amount of deblocked NCO reacted with increasing acid content. Methacrylic acid appears more effective than acrylic acid. Catalysts did not significantly change the deblocking or curing reaction of these compositions.

Hydroxy-containing monomers such as hydroxyethyl acrylate incorporated into the IEM-MEKO polymer react with the NCO groups formed under deblocking conditions. T-12 catalyst appears to promote this reaction.

Possible applications for these latex compositions are crosslinkable coatings, binders and adhesives.

THE FORMATION OF "INVERTED" CORE-SHELL LATEXES

D. I. Lee And T. Ishikawa*

Designed Latexes & Resins
Dow Chemical U.S.A.
Midland, Michigan 48640

ABSTRACT

It has been found that when hydrophobic monomers were polymerized in the presence of highly hydrophilic polymer seed particles, the second-stage hydrophobic polymers formed cores surrounded by the first-stage hydrophilic polymers, resulting in "inverted" core-shell latexes.

The formation of "inverted" core-shell morphology was studied using two polymer pairs; a soft polymer pair [EA/MAA (90/10)]/[S/B] (60/40)] and a hard polymer pair [EA/S/MAA (50/40/10)]/[S]. It was found that in the case of the soft polymer pair systems, the formation of "inverted" core-shell morphology was equally complete, regardless of the molecular weight of the hydrophilic polymer molecules, whereas in the case of the hard polymer pair systems, the efficiency of inversion was dependent on the molecular weights of both hydrophilic and hydrophobic polymers. The present study suggests that the formation of "inverted" core-shell latexes depends not only on the hydrophilicity, interfacial tension, and molecular weight of the hydrophilic polymer molecules, but also on the extent of phase separation between two polymers.

Per Stenius
The Swedish Institute for Surface Chemistry, Stockholm.

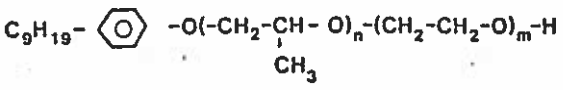
20 SEP Recd

ADSORPTION OF NONIONIC SUFACTANTS ON POLYSTYRENE LATEX

Nonionic surfactants, comprized of a hydrocarbon- and a polyethylene oxide chain, are very effective in stabilizing polymer latexes. When the chain length of the water-soluble polyethylene oxide is increased it is found that on the one hand the salt stability increases but on the other hand the tendency to adsorb on a latex surface decreases. Using solution thermodynamics it can be shown that this observed decrease in adsorbing tendency is due to an increase in water solubility of the surfactant.

It is therefore of interest to decrease the water solubility by either increasing the hydrocarbon- or decreasing the polyethylene oxide chain. Since the latter leads to a decreased salt stability, surfactants with longer hydrophobic chains have been tested.

The surfactants have been made more hydrophobic by incorporating polypropylene oxide into the molecules, i.e. adsorption of surfactants with the following structure has been studied;



At low surfactant concentrations the adsorbed amount increases rapidly with increasing surfactant concentration, as shown in figure 1. This rapid rise is due to the high affinity of the surfactant to the latex surface, At higher concentrations, however, the adsorbed amount is almost independent of surfactant concentration. Here a vertically oriented close packed monolayer is obtained, from which the cross sectional molecular surface area, a_2, can be obtained.

Figure 2 reveals that the cross-sectional molecular surface area is strongly dependent on the number of ethylene oxide units, m, in a molecule. There is, however, no effect of the incorporated propylene oxide groups on the molecular surface areas. This is consistent with a vertically oriented surfactant layer at close packing, where the molecular surface area is dictated by the strongly hydrated polyethylene oxide chain.

The apparent adsorption free energies, as obtained from the adsorption isotherms, are listed for the different surfactants in table 1. This quantity corresponds to the energy required to tear off one square meter of a close packed adsorbed layer. The results reveal that the incorporation of polypropylene oxide groups into the surfactant molecules clearly does not improve the adsorption characteristics. Our conclusion, therefore is that the polypropylene oxide entity does not show any appreciable hydrophobic interaction to enhance the adsorption strength.

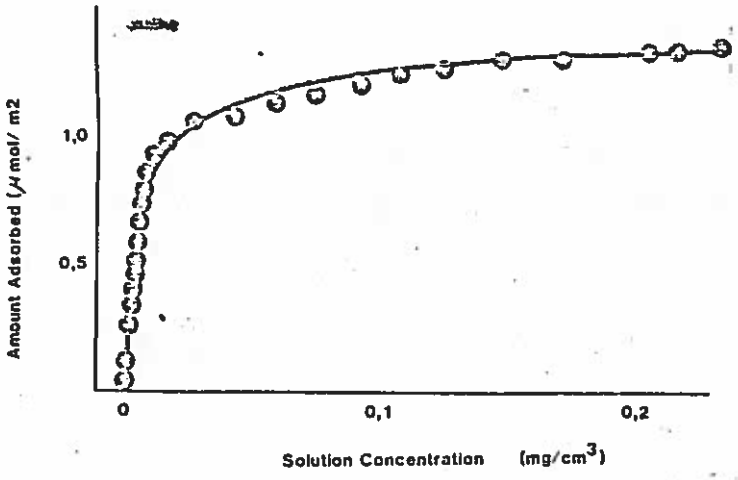


Fig.1

Fig. 1 The amount of adsorbed surfactant as a function of surfactant concentration in solution

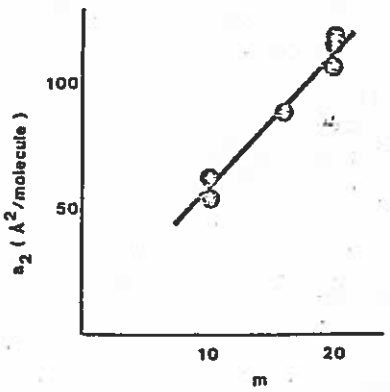


Fig.2

Fig. 2 The cross sectional molecular surface area, obtained at close packing on the surface, as a function of the number of ethylene oxide units in the molecule

Table 1 Apparent adsorption free energies for surfactants with the indicated structure

m	n	$\Delta E/mJ/m^2$
10	5	101
	0	118
16	16	75
20	21	56
	8	56
	0	58
50	0	29

Polymer Colloid Group, contribution from John Ugelstad.

The work in our group has to a large extent been concentrated around preparation of monodisperse particles of various sizes and of different chemical structure.

1. We have improved and simplified the procedures for the preparation so that we now in one cycle can increase the particle size 10 to 20 times in diameter corresponding to volume increase of 1000 to 8000 times. Particles up to 50 μm have been produced.

2. We have introduced different chemical groups on the surface especially OH, NH_2 and COOH groups. This has been done by chemical modification of styren-divinylbenzene particles or it has been carried out by copolymerization with the proper monomer like hydroxyethyl acrylate, acrylic acid, glycidyl metacrylate etc.

3. We have produced magnetic particles of sizes 2 and 10 μm.

4. We have started cooperation with the Radium Hospital in Norway for application of our particles. Abstracts of two papers on application of monodisperse particles are included.

5. Rembaum has applied our magnetic particles for cell separation. This work was presented at the Fourth International Conference on Surface and Colloid Science in Israel July 5-10. 1981. A complete paper is in press.

6. We have also in Trondheim started work on coupling proteins to the surface of the particles by different methods.
   a) Reaction of OH-groups with CDI.
   b) Reaction of OH-groups with tosylchloride.
   The activated particles are treated with radioactive IgG, and the resulting particles analyzed for their capacity of binding corresponding AB2.

7. We have written two chapters to the book of Piirma, one concerning particle Formation (authors F.K.Hansen and J.Ugelstad), and one "Effect of Additives on Emulsion Polymerization" (authors: J.Ugelstad, P.C.Mørk, A.Berge, T.Ellingsen and A.A.Khan).

FOURTH INTERNATIONAL CONFERENCE ON SURFACE AND COLLOIDAL SCIENCE.

New Immuno reagents. Large monodisperse polymeric spheres.

J.Ugelstad, A.Rembaum and R.C.K.Yen, University of Trondheim and the Propulsion Laboratory, California Institute of Technology, USA.

Small Monodisperse Polymeric spheres are made to absorb large amounts of monomer by a two step swelling procedure which yields an emulsion of monodisperse monomer droplets. Subsequent polymerization leads to formation of monodisperse polymeric spheres with a standart deviation of less than 1-0/0. Different compositionsof large size (Greater than 10 microns) monodisperse spheres may be synthesized by this method, which also allows the preparation of porous as well as magnetic particles. Reactive functional groups may be formed on the surface of these polymeric spheres by Co gamma irradiation in the presence of Acrolein. The resulting monodisperse Hybrid spheres react with a variety of antibodies and may provide a source of valuable new immunoreagents.

KININ 1981 · MUNICH
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ABSTRACT REPRODUCTION FORM

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AN IMMUNORADIOMETRIC ASSAY FOR THE DETERMINATION OF GLANDULAR KALLIKREIN IN RAT SERUM. L Johansen, K Nustad *, TB Ørstavik and J Ugelstad **. Dept. Physiol. Biochem. Dental Fac. Univ. Oslo, * Dept. The Norw. Radium Hosp. Oslo, ** Dept. Univ. Trondheim, Norway.

The demonstration and quantification of glandular kallikrein in blood has been impaired by the presence of kallikrein inhibitors in plasma also when quantified by the classical radioimmunoassay.

We have developed an immunoradiometric assay for measurement of glandular kallikrein in blood, in which such inhibitors do not interfere.

Immunoglobulins (IgG) purified for immunspecificity against rat salivary gland kallikrein, was covalently bound to polystyrene microspheres. The complex cuold be stored for at least 1 month without any loss of binding-capacity for kallikrein.

In the first incubation glandular kallikrein in standards or samples was adsorbed to the antikallikrein-polystyrene complex. Quantification of the adsorbed kallikrein was done by a second incubation with radiolabelled antikallikrein (IgG). As standards, pure rat salivary kallikrein was used in the range from 0.125 to 2 ng per ml per 1.5 ug antikallikrein bound to the microspheres. Non-specific binding was less than 1 %.

When this assay was used to quantify glandular kallikrein in rat serum, 10.8 ± 0.3 ng/ml was found. Quantification of the immunoreactive substance in blood in different aliquotes parallelled the standard curve. Recovery of salivary gland kallikrein added to serum samples, was 85-90 %.

This method permits the measurement of glandular kallikrein also in biological fluids where kallikrein inhibitors are present, like blood.

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ABSTRACT REPRODUCTION FORM

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COVALENT COUPLING OF ANTIBODIES TO MONODISPERSE PARTICLES.

K.Nustad, L.Johansen, T.Ellingsen, A.Berger and J.Ugelstad.
Central Lab.,The Norwegian Radium Hospital; Dept. of Physiology, Dental Faculty, University of Oslo; SINTEF and Lab. for Industrial Chemistry, University of Trondheim, Norway.

Monodisperse polymer particles made by a new method (Ugelstad et al. Adv.Coll.Interf.Sci. 13, 101,1980) with hydroxyl or amino groups were used to immobilize antibodies.
Rabbit IgG (primary antibodies) and sheep IgG (secondary antibody) were covalently bound to the particles using cyanogen bromide, carbonyl-di-imidazole or glutaraldehyde as coupling agent. The function of the immobilized antibodies were tested varying the coupling method, antibody concentration and particle size and type.

Insolubilized sheep anti-rabbit IgG was used in several radio-immuno-assays including one for rat glandular kallikrein.

Particle bound rabbit anti-rat-glandular kallikrein was used in an immuno-radiometric assay for the determination of glandular kallikrein in serum (see separate Abstract).

Mechanism of Core-Shell Emulsion Polymerization (II)

(T.I. Min, A. Klein, M.S. El-Aasser, J.W. Vanderhoff).

Objectives:

1. To obtain information about the control of the morphology in core-shell emulsion particles.

2. To investigate Thin-Layer Chromatographic separation of core-shell particle systems according to the difference in chemical composition.

Progress:

A Polybutyl acrylate (PBA) seed latex was prepared in a 2-liter reaction flask under the conditions of Run No. 1 in Table I. The seeded emulsion polymerizations of styrene were carried out in a 300-ml flask under the conditions of Run Nos. 2, 3, and 4 in Table I, respectively.

TABLE I

CONDITIONS OF PBA/PS CORE-SHELL EMULSION POLYMERIZATION

Run No.		1	2	3	3-50	4
Emulsion (No. 1) (prepared according to Run No. 1).	(cc)	-	100	100	100	100
BA	(cc)	300	-	-	-	-
ST	(cc)	-	30.8	30.5	15.4	30.5
$K_2S_2O_8$	(gm)	2.43	0.24	0.24	0.12	0.24
SDBS*	(gm)	3.75	-	-	-	-
Water	(cc)	667.4	30	30	30	30
Temp	(°C)	70	70	70	70	70
Time	(hr)	24	8	8	8	8

Run No. 2: Equilibrium swelling process in seeded emulsion polymerization.
Run No. 3: Semi-batch process in seeded emulsion polymerization.
Run No. 4: Batch process in seeded emulsion polymerization.
*SDBS Sodium Dodecylbenzene sulfonate.

The addition of styrene monomer for the seeded emulsion polymerizations was accomplished using three differing methods as follows: (1) Equilibrium swelling process, in which the total amount of monomer was preliminarily absorbed in the seed emulsion particles at 4°C for 3 days before the seeded emulsion polymerization was begun, (2) Semi-batch process, in which the total amount of monomer was continuously added to the reaction flask from a micro feeder dripping at a constant rate of 8 ml/hr., and (3) Batch process, in which the total amount of monomer was simultaneously added to the reaction flask just before the seeded emulsion polymerization was started.

The final products of each run were steam stripped to remove any residual monomer. Cleaning of the latex samples was conducted using the serum replacement cell as a filtering device in order to remove surfactant and unreacted initiator, etc. For this purpose, a 0.01μ pore size nuclepore membrane was employed, and the filtration time was one week for each sample.

TLC Separation

In the previous report (GRPR No. 15, p. 29), a preliminary Thin-Layer Chromatographic separation was described for homopolystyrene, homopolybutyl acrylate, and styrene-butyl acrylate copolymer. The binary system, CCl_4 + Ethyl acetate was employed as developing solvent.

The conventional TLC separation for core-shell particle systems was performed using the binary CCl_4 + Ethyl acetate (60 : 11.5 by volume). Thus a chromatogram for sample #3 and #3-50 in which the samples were separated into three final spots could be obtained. In Figure 1 is shown the chromatogram obtained using the binary solvent. The two spots, located at 0 and 10 cm, are assigned respectively to PBA and PS by a simultaneous development of their reference samples. The medium tailing spots might, in an intuitive manner, be identified with BA-ST copolymer species. This TLC result indicates that BA-ST core-shell particle system prepared in this emulsion polymerization contains BA-ST grafted copolymer chain molecules.

Quantitative Analysis of the Chromatograms

For quantitative analysis of the chromatogram obtained by the foregoing TLC procedures, we employed the other technique, which may be called "thin layer-FID" chromatography. The core-shell emulsion polymer samples prepared by the different methods of monomer addition during the seeded emulsion polymerization, Run Nos. 2, 3, and 4 were employed.

The separation was carried out on a thin quartz rod of 0.9 mm in diameter and 150 mm in length, coated with silica gel of 75 μm thickness (Iatron Thinchrod-SII). After the development

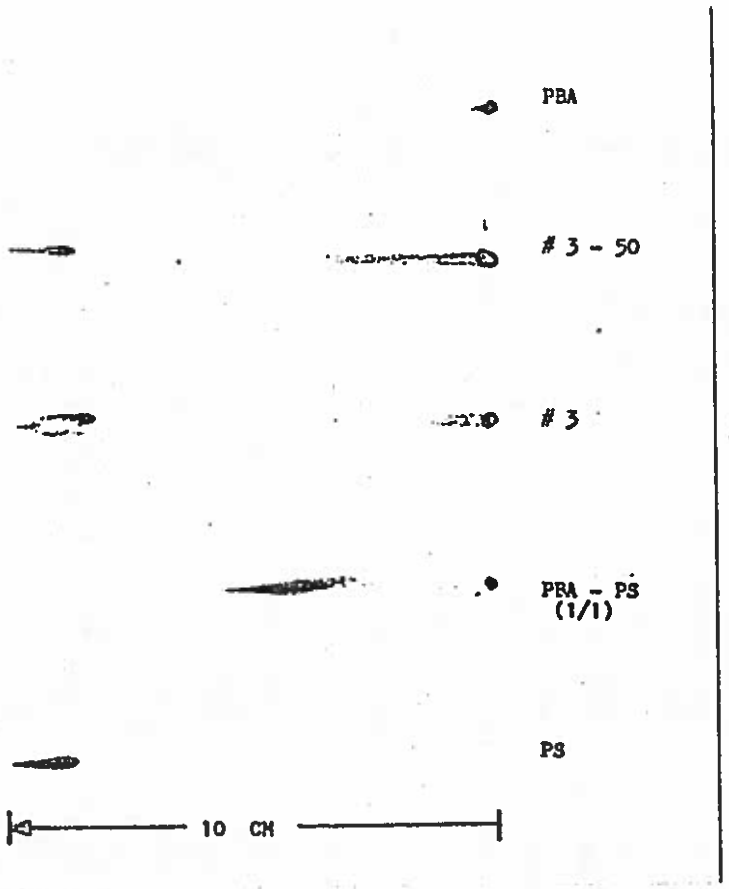

Figure 1: TLC chromatograms obtained for PBA-PS core-shell composite polymers, #3 and #3-50, and reference samples.

the thin quartz rod was dried by vaporizing the developer solvent in the same manner as for the chromatoplate. At the end of the run, the rod was placed for analysis in an apparatus equipped with a flame ionization detector (FID), (Iatroscan TH-10 TLC/FID Analyser, Iatron Co., Ltd., Tokyo, Japan). It was found that the chromatographic behavior for a given polymer sample obtained with this thin quartz rod (e.g., R_f-values) were almost the same as those obtained with the conventional chromatoplate. However, the following "two-stage" development was carried out for the quantitative analysis. The primary development condition has been chosen in such a way that the component shell-polystyrene (s-PS) and PBA-g-PS migrate up to the solvent front whereas the core-polybutyl acrylate (c-PBA) component remains immobile on the starting level. In practice, the solvent front was set at 7 cm above the starting level and a binary of CCl_4 + Ethyl acetate was used as the initial developer. After the primary development had been completed, the thinrods were dried and subjected to the secondary development, which employed chloroform as developer. With this procedure, only s-PS migrated up to a higher solvent front, set at 10 cm.

The results thus obtained for sample Nos. 2, 3, and 4 are shown in Figure 2. The three peaks for each sample appeared on the chromatogram, indicating the separation of sample into three component species, i.e., c-PBA, PBA-g-PS, and s-PS, from right to left in the figure. The area of each peak allows us readily to

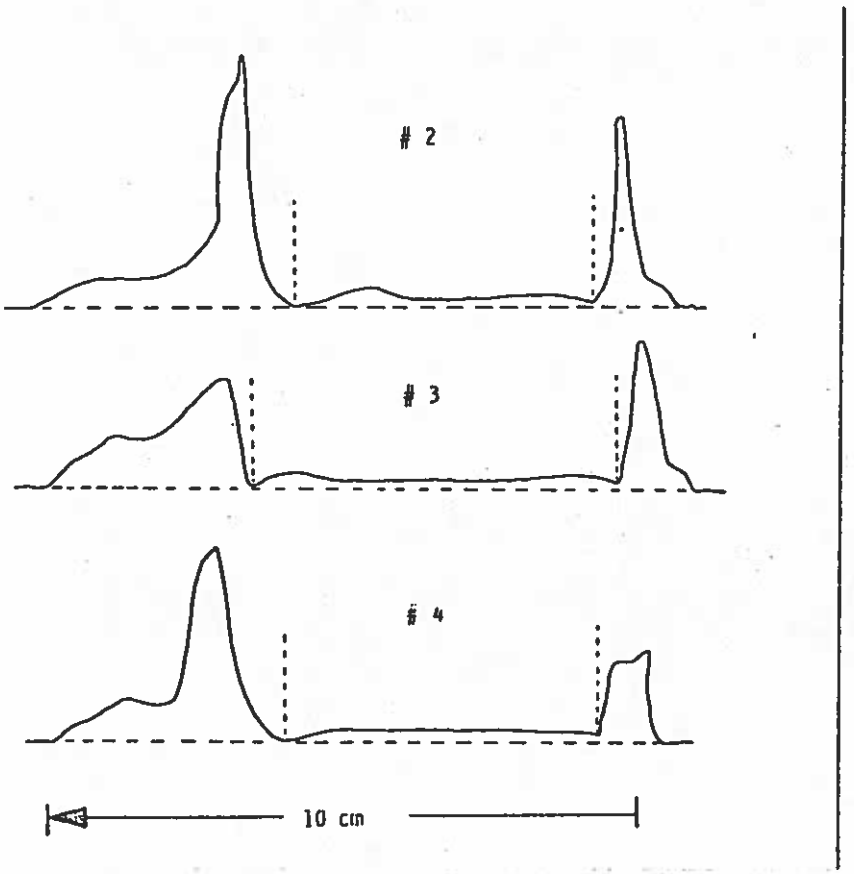

Figure 2: Thin layer-FID chromatographic scanning curves of PBA-PS core-shell composite polymers, #2, #3, and #4.

determine quantitively the amount of each component species; which requires knowledge of factors to convert the FID-response to the specific amount of the component. The conversion factors are generally different for each chemical species, and can be determined experimentally as follows. A series of FID scans were made for known amounts of each chemical species, namely, homopolystyrene and homopolybutyl acrylate, to determine the conversion factors between FID-response and the corresponding polymer amount. The conversion factors deduced were 138.9 and 57.7 units/μg for PS and PBA (which will be denoted α_s and α_b) respectively.

Chemical Constitution of Core-Shell Particle System

The amount of true graft copolymer species, which appears as the intermediate spot, cannot be evaluated directly with the aid of the conversion factors because the composition is not known. Hence, each amount of PBA and PS constituting the true graft copolymer species has been estimated by taking two quantities into account, first is the overall composition of core-shell emulsion polymer products, while the other is the amounts of TLC-separated c-PBA and s-PS, which were determined by FID.

An example of the estimation will be given below for sample 2. It might be deduced that the weight fraction of PS was 0.5 because the conversion was almost 100%. The sample size applied to TLC was 10.0 µg. After the chromatogram was subjected to analysis with FID, the amounts of c-PBA and s-PS were found to be 4.2 and 4.4 µg, respectively. Hence it is pertinent to regard the amount of the grafted polybutyl acrylate (g-PBA) as,

$$(10 \times 0.5 - 4.2)\mu g = 0.8\ \mu g$$

and that of the side-chain (g-PS) as,

$$(10 \times 0.5 - 4.4)\mu g = 0.6\mu g.$$

Since the amounts of g-PBA and g-PS are known the FID-response for the graft copolymer species can be calculated using the conversion factors, and then compared to the observed value. The calculated FID-response is $(0.8\alpha_b + 0.6\alpha_s) = 129.5$, which is in agreement with the observed response from the areas under the second peak in Figure 2. The same agreement was found for samples 3 and 4, as is shown in Table II. From this the conclusion can be drawn that the present separation technique is excellent not only qualitatively but also quantitatively. All of the analysis results are summarized in Table II.

TABLE II
RESULTS OBTAINED BY THIN LAYER-FID CHROMATOGRAPHY FOR PBA-PST CORE-SHELL POLYMERS [1]

Sample Code	FID-response (Arbitrary Unit)			Polymer Wt.[3] calc. (µg)		Wt. fr.	Chem. Constitution and Structu		
	Up.[2]	Med.	Low	Up.	Low.	PST		µg	Wt. fr
#2	703.4	130.5	243.4	4.4	4.2	0.5	s-PS	4.4	0.44
							g-PS	0.6	0.06
							g-PBA	0.8	0.08
							c-PBA	4.2	0.42
#3	577.4	206.8	277.6	3.7	4.8	0.5	s-PS	3.7	0.37
							g-PS	1.3	0.13
							g-PBA	0.2	0.02
							c-PBA	4.8	0.48
#4	686.4	163.2	213.0	4.3	3.8	0.5	s-PS	4.3	0.43
							g-PS	0.7	0.07
							g-PBA	1.2	0.12
							c-PBA	3.8	0.38

1) Sample size applied to TLC was 10.0 µg.
2) Location of component on chromatogram.
3) Conversion factors were 138.9 units/µg and 57.7 units/µg for PST and PBA, respectively.

The Weight Percent of Grafted PBA

From Table II the weight percent of grafted polybutyl acrylate namely, g-PBA (g-PBA + c-PBA)$^{-1}$ x 100, can be estimated. The values are summarized in Table III. The percent grafting-values may be regarded to be dependent on the method of monomer addition during the seeded emulsion polymerization. The percent grafting-value for sample 4, prepared by the batch process, shows a higher value, which is almost the same as that for sample 2, prepared by the equilibrium swelling process. These results indicate that the amount of grafted core-PBA might be due to the mobility of the added styrene monomer absorbed in the seed polymer particles during the seeded emulsion polymerization.

TABLE III

WEIGHT PERCENT OF GRAFTED POLYBUTYL ACRYLATE

Sample code	#2	#3	#4
Addition method	Swelling	Semi-batch	Batch
% grafting	16	4	24

Future Work:

1. Determination of morphology of the core-shell emulsion particles by combined TLC, TEM, SEM techniques.

2. Preparation of core-shell emulsion particles from the polybutyl acrylate seed emulsion and varying amounts of added styrene monomer, and correlation of the morphology with the percentage of glassy material.

Preparation of Polystyrene Latex as a Model Colloid (A. Kamel, M.S. El-Aasser, J.W. Vanderhoff).

Objective:

To prepare a model polystyrene latex with a definite type of functional group, i.e., sulfate, hydroxyl, or carboxyl groups.

Progress:

During this period A. Kamel completed his Ph.D. Dissertation entitled "The Preparation and Surface Characterization of Polystyrene Latexes as Model Colloids". The Thesis has been accepted by the Graduate School at Lehigh. The Thesis abstract is as follows:

> "The purpose of the present investigation was to prepare a model colloid with one type of surface group. Several conventional polystyrene latexes were prepared, cleaned by a mixed bed of anionic and cationic resins, and their surfaces characterized by conductometric titration. All latexes carried a strong-acid group; no weak-acids were detected.
>
> Polystyrene latexes carrying only hydroxyl groups have been prepared by hydrolyzing the sulfate groups on aging the ion-exchanged latexes at room temperature. The hydrolysis step was acid-catalyzed, and occurred only after ion-exchange to the acid form. To inhibit the hydrolysis, the H^+-counterions were ion-exchanged to the Na^+-form. Heating the ion-exchanged latexes appreciably enhanced hydrolysis, also increasing the glass-contact surface area through the introduction of Pyrex glass beads, led to a slight enhancement in hydrolysis.
>
> The latex in the hydroxyl form was oxidized into the carboxyl form by means of potassium persulfate oxidant. A new and alternate procedure included heating the ion-exchanged sulfate form of the latex in the presence of Pyrex glass beads.
>
> Polystyrene latex 520', whose recipe contained water, styrene, potassium persulfate, and sodium bicarbonate, initially carried only sulfate groups; these were first hydrolyzed to the hydroxyl form and

then later oxidized fully to the carboxyl form. The latex was monodisperse stable and exhibited the same size and molecular weight in all three forms. Dissolving the latex in dioxane-water mixture, followed by ion-exchange and titration, showed the presence of buried sulfate groups.

The electrophoretic mobility behavior of latex 520' was studied as a function of pH. All three forms of the latex displayed the same trends, showing no changes at intermediate pH ranges, while at lower pH the mobility decreased, with the hydroxyl and carboxyl forms showing a charge-reversal behavior. In alkaline pH, the mobility first increased slightly before decreasing at higher pH. These trends were explained in terms of ion adsorption and acid-base interactions.

At neutral pH, all three forms of the latex exhibited, approximatley, the same zeta potential, ca. -60 mV; the presence of that potential on the latex in the hydroxyl form suggested that the charge on colloidal dispersions could originate from the preferential adsorption of hydroxyl ions or form contact electrification. Calculations based on the DLVO Theory showed that the stability of the different forms of latex 520' increased in the following order: sulfate > carboxyl >> hydroxyl.

Argon gas adsorption measurements gave surface areas that were in good agreement with those obtained from electron microscopy. The complete reversibility of the inert-gas adsorption indicated that the polymer surface was nonporous. The adsorption of water and 2-propanol vapors showed that the surface was mostly hydrophobic with only few polar sites. The sulfate group displayed the strongest interaction of functional groups with water and 2-propanol molecules on the sulfate group was suggested. The results showed a good correlation between gas adsorption and conductometric titration techniques."

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Critical Micelle Concentration and Adsorption Isotherms Using the Madison-Kipp SensaDyne 5000 Maximum Bubble Pressure Surface Tension Instrument.

(N.J. Earhart, M.S. El-Aasser, F.J. Micale, J.W. Vanderhoff).

Objective:

1. To measure and determine the critical micelle concentration of various surfactants.

2. To determine the adsorption isotherms of sodium lauryl sulfate (SLS) on various concentrations of polystyrene latex particles.

Progress:

Instrumentation

The Madison-Kipp SensaDyne 5000 is a surface tension measuring instrument that is based on the maximum bubble pressure technique. The basic instrument, Figure 1, consists of (a) the electronics package, (b) sensor package, (c) inert gas supply, 2 sensor probes (d,e) of large and small orifices, and (f) thermistor probe.

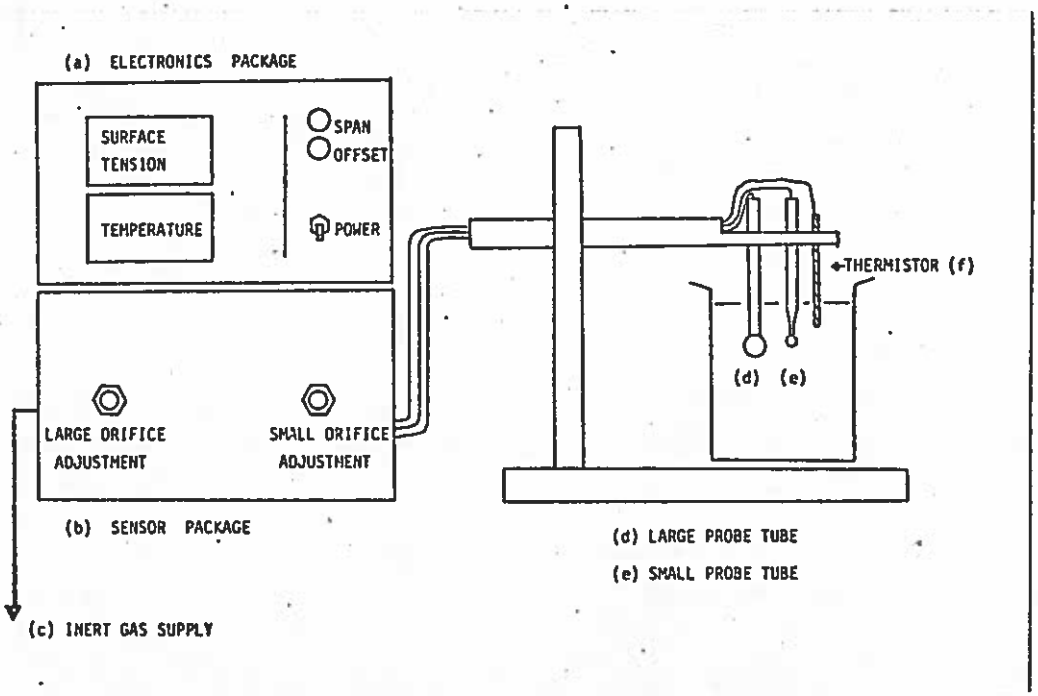

Figure 1: Madison-Kipp Sensadyne 5000

The instrument measures surface tension by the use of an internal differential pressure transducer. The inert gas supply enters the sensor package and the bubble rate in water is established (approx. 1 bubble/second at each orifice). The differential pressure transducer detects the pressure signals from the large and small probe orifices as the bubbles are formed and released. The differential pressure transducer then yields an output signal which is the difference in pressure created from the large and small orifices. The signal is processed and then displayed in digital form on the electronics package display along with the temperature (°C) which is measured by the thermistor probe. The instrument is calibrated using distilled-deionized water and heptane. Calibration involves the use of a simple calculation which involves knowledge of the reference surface tension values for water and heptane (W_r, H_r respectively) at temperature T, and the SensaDyne measured surface tension values for water and heptane (W_m, H_m respectively) at the same temperature.

$$\frac{W_r - H_r}{W_m - H_m} = \text{ratio R} \qquad (1)$$

$$\text{ratio R} \times W_m = W_c$$

The span control on the electronics package is adjusted to the W_c value, the offset control is adjusted to the reference surface tension value of water, W_r. The calibration is now complete, water and heptane are both rechecked to insure correct calibration. The calibration process requires only a few minutes.

When the surface tension measurements are taken the probes are lowered to a constant depth. The surface tension readings come to equilibrium in approximately 1 minute at which time the correct surface tension and temperature values can be obtained from the display.

The laboratory set-up in use involves a constant temperature water bath set at 25°C in connection with a 50ml water jacketed beaker. A magnetic stir-bar is placed into the beaker which in turn is placed on an adjustable lab-jack.

The CMC determinations along with the adsorption isotherm studies were carried out by placing 30ml of fluid into the jacketed beaker with the surfactant solution added via a volumetric pipet. The sample solution is stirred, equilibrated followed by surface tension measurements.

The surfactant used for all of the adsorption studies is sodium lauryl sulfate (SLS). The SLS was cleaned of any impurities such as lauryl alcohol by Soxhlet extraction with diethyl-ether for 3 hours. The SLS was then vacuum dried and stored in a freezer. A standard stock solution was prepared with a con-

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centration of 1.60×10^{-2} moles/liter. The adsorption isotherms were determined for SLS on 1900Å-polystyrene latex particles, that were cleaned by the serum replacement technique. Alcohol-water systems studied used ethanol and isopropanol.

Results

Several surface tension-concentration curves were generated for SLS, as shown in Figure 2. The curve denoted by the circles was made using an SLS stock solution of 1.15×10^{-2} moles/liter which was lower than the concentration of the stock solution used in the other two curves (1.60×10^{-2} moles/liter). The average surface tension for the curves shown at the CMC is 40.1 dynes/cm with a standard deviation of 0.6 dynes/cm. The average CMC is 5.7×10^{-3} moles/liter with a standard deviation of 7.8×10^{-4}. This CMC value differs from a literature value of 8.2×10^{-3} moles/liter by 2.5×10^{-3} moles/liter[Rosen, M.J., "Surfactants and Interfacial Phenomena", John Wiley and Sons, Inc., N.Y., N.Y. (1978)].

The ICI Monoflor 51 surfactant was tested to see its effectiveness in lowering the surface tension of water. As Figure 3 shows, using the fluorinated surfactant the surface tension of water can be lowered considerably with just a small amount added to the water. The value of surface tension at 1.00% surfactant is higher by approximately 3 dynes as compared to the reported ICI value of 25 dynes/cm.

Figure 4 shows the decrease of the surface tension of water upon the addition of an alcohol. In each case, ethanol and isopropanol, the surface tension of water is lowered by a considerable amount with the addition of a small amount of alcohol. Future work might involve adsorption studies of surfactants on polystyrene latex particles in an alcohol system.

Figure 5 is the result of the addition of 2 and 5 percent by weight polystyrene latex particles to water, and then adding the stock SLS solution to generate a graph of surface tension versus concentration of SLS. From the three lines on the graph, the amount of surfactant adsorbed and the area occupied per surfactant can be determined. One problem encountered with the Madison-Kipp instrument is that when measuring water + additives at high surface tensions (greater than 65 dynes/cm) a considerable amount of scatter in the readings is noticed. These fluctuations can reach + 1.0 dynes/cm. This scatter questions the values obtained during the measurements of the surface tensions higher than 65 dynes/cm.

The surface concentration of surfactant and the surface area per the adsorbent polystyrene particles can be calculated by the following equations that are found in Rosen's book:

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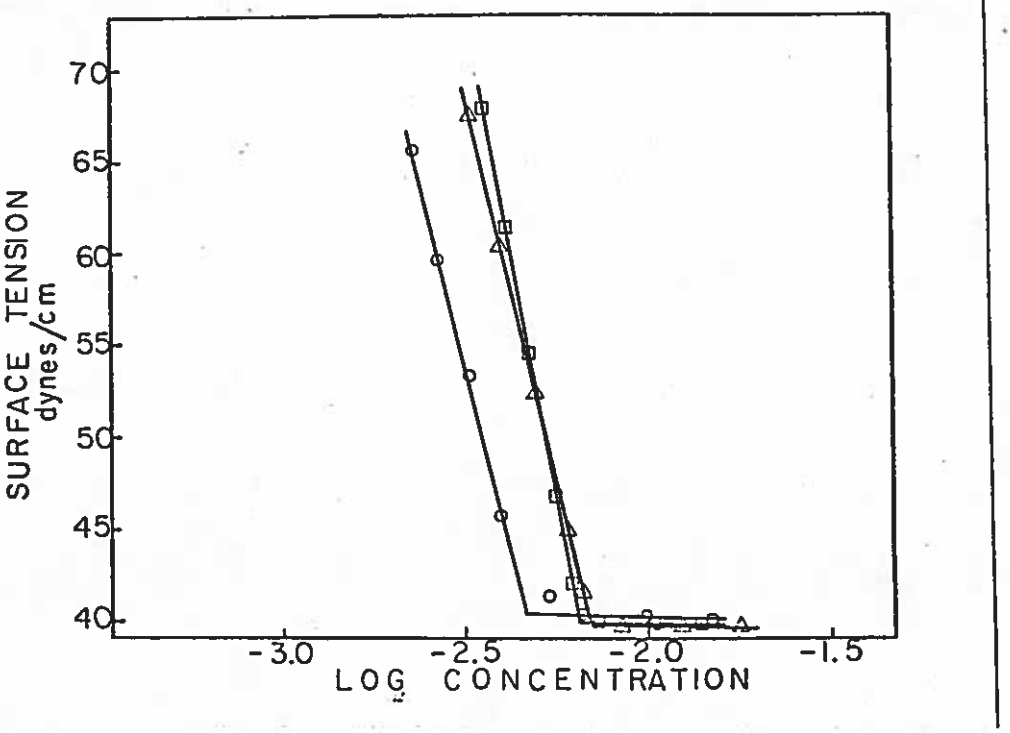

Figure 2: Surface tension vs. log concentration for sodium lauryl sulfate. ○ *CMC = 5.50 x* 10^{-3} *moles/liter,* △ *CMC = 6.60 x* 10^{-3} *moles/liter,* □ *CMC = 5.10 x* 10^{-3} *moles/liter.*

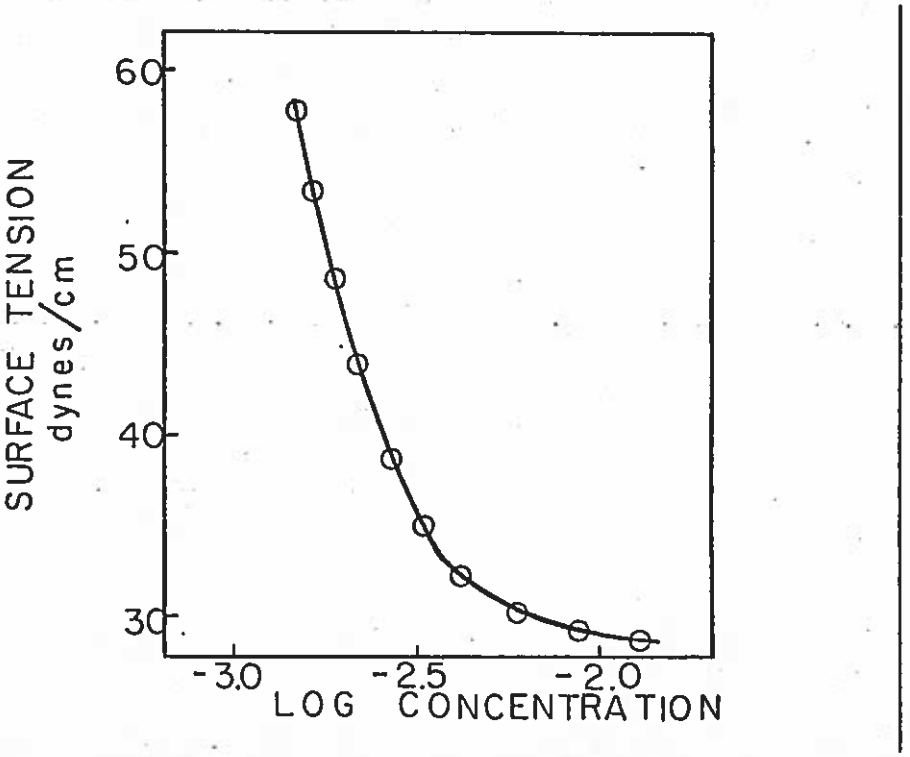

Figure 3: Surface tension vs. log concentration of I.C.I. Monoflor 51, non-ionic surfactant.

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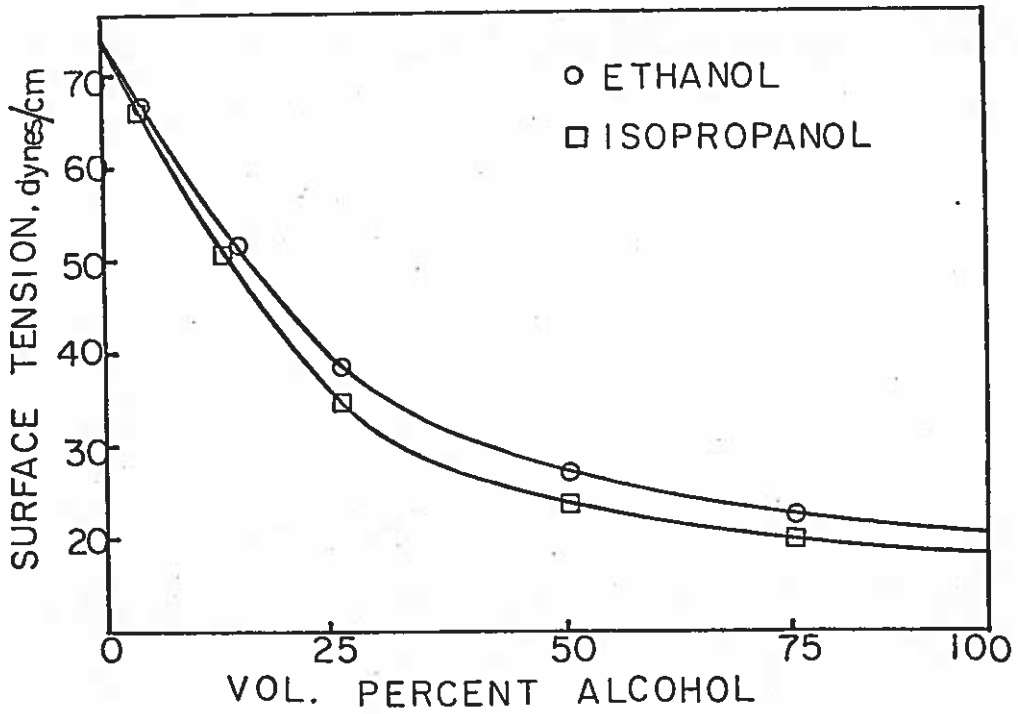

Figure 4: Surface tension versus volume percent alcohol.

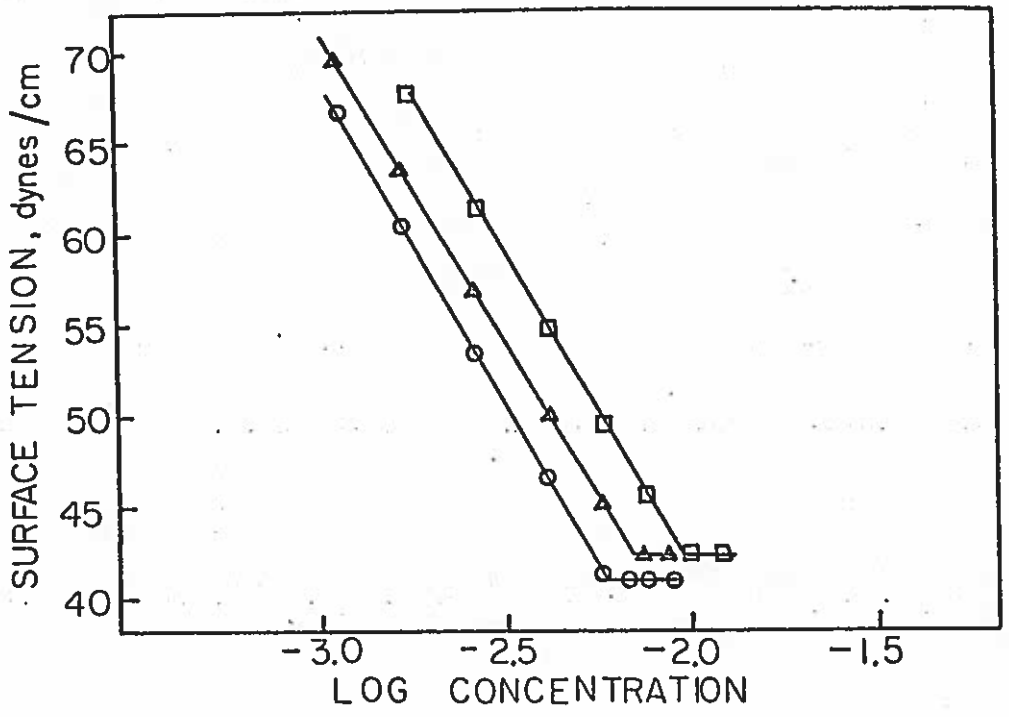

Figure 5: Surface tension vs. log concentration.
○ SLS calibration curve, CMC = 5.60 x 10^{-3} moles/liter;
△ 2% by weight 1900 Å polystyrene in water
□ 5% by weight 1900 Å polystyrene in water

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$$C_2^s = \frac{(C_{2,0} - C_2) \times V}{a_s \times m}$$

Where: $C_{2,0}$ = concentration of surfactant (moles/liter) before adsorption
C_2 = concentration of surfactant at the saturation point
V^2 = volume of liquid in liters
m = mass of adsorbent particles
a_s = surface area per unit mass of the solid adsorbent, in cm^2 per gram

The surface area per adsorbate molecule on the adsorbent a_2 in square angstroms is given by:

$$a_2 = \frac{10^{16}}{N\, C_2^s}$$ Where N is avagadro's number

The values for C_2^s and a_2 are calculated for both the two and five percent by weight polystyrene systems at the saturation point. Three values were calculated and the average value with the standard deviation is reported:

Sample	C_2^s moles/cm^2	std. dev.	a_2 (A^2)	std. dev.
2%	4.04×10^{-10}	3.07×10^{-11}	41.14	1.34
5%	3.47×10^{-10}	2.08×10^{-11}	47.93	2.08

The experimental error encountered is with the addition of each 1ml of stock SLS solution to bulk solution. The 1ml pipet is calibrated to ±0.6% of the correct volume. The maximum number of 1ml additions was 38, the percent error in volume then is 22.8%. When using the 22.8% volume correction the average values of C_2^s and a_2 fall within this range.

The Madison-Kipp SensaDyne 5000 performed very well during the experiments carried out. The only problem was the scatter obtained at surface tensions greater than 65. The instrument gives fast readings that are very reproducible. The CMC curve on something of the same nature can be generated very fast and with relative ease in comparison with some of the other surface tension measuring devices.

Future Work:

1. To compare the performance of the Madison-Kipp SensaDyne 5000 with the other more "classical" surface tension techniques such as the Wilhelmy Plate and the Du Nouy Ring.

2. To measure the surface tension of polystyrene latex particles in aqueous and nonaqueous solution with solids

reaching up to 50 percent.

3. To check the applicability of the SensaDyne 5000 in following the percent conversion during the course of emulsion polymerization process by measuring the change in surface tension with time.

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Electrokinetic Properties of Polystyrene Latexes
(R.V. Mann, F.J. Micale, J.W. Vanderhoff).

Objectives:

1. To compare results obtained from three microelectrophoresis instruments over a range of particle sizes and types, and suspending mediums.

2. To explore and further define the preparative and analytical capabilities of continuous particle electrophoresis.

3. To study particle size analysis through Brownian motion.

Progress:

Effort this period was concentrated on the comparison and evaluation of three commercially available microelectrophoresis instruments. The instruments evaluated in this study were the Rank Mark II, the PenKem System 500, and the PenKem System 3000.

The Rank Brothers Mark II microelectrophoresis instrument has both a circular capillary cell and a flat cell. The capillary cell alone was used for the comparison of results between the three instruments. The entire cell is immersed in a water bath and illumination is provided by a light source outside the bath positioned at a 90° angle from the microscope objective. The electrophoresis cell is filled with the sample and the electrode plugs are inserted. Care must be taken to avoid the presence of air bubbles in the cell and imperfect sealing of the electrode plugs. About 10 ml of sample is required for a measurement.

Measurements are made by direct observation of the movement of individual particles. For these measurements it is important that the microscope objective be focused at the stationary flow level, i.e. the level of zero solvent flow.

In this geometry it is also important that the objective be focused at the center of the capillary and the measurements be taken on particles in that region. With the attached timer the particles are timed as they move across the grid marks. From a knowledge of the applied voltage gradient and the measured particle velocity, the electrophoretic mobility of the particle can be calculated.

In the course of measuring a sample it is necessary to determine the mobility of several particles to get a good average value. To measure a complex mobility distribution the mobility of many particles must be determined. In this way bimodal or more complex

distributions may be measured.

The PenKem System 500 has a flat cell positioned horizontally with a laser light cource illuminating the cell from the side and a microscope objective focused from the top at a 90° angle from the light source.

The cell contains electrode compartments and no seals are necessary. The cell is filled from a syringe and inserted in position under the microscope. Care must be taken, particularly with solutions containing a high concentration of surfactant, to avoid the formation of bubbles in the cell. About 25 ml of sample are needed for measurement. In a flat cell arrangement the zero solvent flow layer is a plane and only the vertical focusing of the objective is important. In this geometry the zero solvent flow level is a horizontal plane, and the point of reference is fixed by focusing on the top of the cell.

Inside the microscope is a rotating cube prism which causes a horizontal movement of the microscope image. When a voltage gradient is applied across the cell the particles will move horizontally and the rate of rotation of the prism is adjusted until the particle image appears stationary. The instrument displays the zeta potential as calculated from Smoluchowski's equation. At the point where the particle image is stationary the displayed zeta potential is the zeta potential of the sample. The zeta potential can be converted to electrophoretic mobility by dividing by an appropriate constant. The instrument can also directly display the conductivity of the sample.

This method allows the measurement of the entire particle cloud simultaneously and an average mobility value can be quickly obtained.

The PenKem System 3000, has a circular capillary cell inside a constant temperature water bath. A laser light source illuminates the cell from the top and the light passing through the cell is rotated 90°. All sample loading and focusing is done automatically and is controlled from a computer terminal. A variety of error messages will appear on the terminal to warn of incorrect loading, bubbles in the cell, leaks from the cell etc. The system requires from 1 to 3.5 ml of sample per measurement.

The light from the cell is passed through a rotating grated disk and impinges on a photomultiplier tube which generates an electric signal which is fed to a frequency tracker. The frequency shift of the light passing through the cell is proportional to the velocity distribution of the particles. The system automatically applies a voltage gradient across the cell, measures the velocity distribution of the particles, and calculates the electrophoretic mobility distribution. In a typical measurement the system will take thirty-two averages of this type, changing the electrode polarity each time. This means that an average

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value generated is based on the velocity distribution of dozens of particles measured thirty-two times. The system will display on the terminal the conductivity of the sample, the pH, the average mobility value, the error in that value, and the relative turbidity of the sample. By use of a spectrum analyzer and a chart recorder the system generated mobility distribution histograms which show mobility versus light scattered by the sample.

The objective of this comparison between the different commercially available electrophoresis instruments is to evaluate their reliability, limitations, and advantages. The PenKem system 500 and system 3000 are new instruments and few results from them have been reported in the literature thus far. The colloidal particles used in this study were 2.02 μm diameter polyvinyl toluene, 1.1 μm, 0.375 μm, 0.091 μm polystyrene, pigment grade TiO_2, and graphitized carbon black. The surface of these particles were not characterized for this study. These systems were chosen to cover a wide range of particle size and surface properties. The electrolyte concentration of the solutions ranged from that of deionized water to 0.1 M NaCl. These solutions were chosen to cover a wide range of ionic strengths because of the Joule heating effects which occur at higher ionic strengths.

Measurements were taken of each dispersion several times by each instrument and the average values reported for comparison. Each instrument showed some deviation around a mean value. This deviation was found to be a small percentage of the total mobility value. Each dispersion was measured ten to twenty times on the system 3000, six to nine times on the system 500 and twice on the Rank Mark II. Care was taken to duplicate the method of preparation of the dispersions for measurement in each instrument. In all cases the solution was prepared and the colloid then added, with the measurement taken immediately afterwards. Only small amounts of a dispersion were prepared at a time and fresh dispersions were prepared for each measurement.

Table I is a summary of the results for dispersions in several concentrations of sodium lauryl sulfate (SLS) solutions and sodium chloride solutions. Results could not be obtained for the 0.091 μm polystyrene particles on the Rank Mark II because of visibility problems. Results shown in previous work suggests that 0.109 μm is the smallest diameter of a polystyrene particle which can be observed in the Mark II. Figure 1 shows electrophoretic mobility as a function of pH for TiO_2 in deionized water for the three instruments; Figure 2 shows mobility versus pH for 2.02 μm polyvinyl toluene; Figure 3 shows mobility versus pH for carbon black, and Figure 4 shows mobility versus pH for 0.091 μm polystyrene.

The excellent agreement between all three instruments, shown in Table I and Figures 1-4, demonstrates the reliability of these instruments for determining the absolute value of the electrophoretic mobility of a dispersion. The reproducibility for any given instrument furthermore, was excellent and always within the

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TABLE I

COMPARISON OF ELECTROPHORETIC MOBILITY VALUES USING THE PENKEM SYSTEM 3000, PENKEM SYSTEM 500, AND THE RANK MICROCAPILLARY

Mobility Units: μm cm/volt second

Results are for Particles Suspended in 10^{-3}M SLS

	2.02 μPVT	1.1 μPS	0.357 μPS	0.091 μPS	Carbon Black	TiO_2
PenKem 3000	-6.46	-5.53	-3.14	-4.40	-2.31	-2.42
PenKem 500	-6.38	-5.53	-3.24	-4.02	-2.35	-2.25
Rank	-6.18	-5.35	-3.26	-----	-2.33	-2.40

Results are for Particles Suspended in 10^{-4}M SLS

	2.02 μPVT	1.1 μPS	0.357 μPS	Carbon Black	TiO_2
PenKem 3000	-3.69	-3.50	-3.32	-2.40	-1.93
PenKem 500	-3.67	-3.57	-3.31	-2.37	-1.86
Rank	-3.82	-3.52	-3.26	-2.39	-2.10

Results are for Particles Suspended in 10^{-1}M NaCl

	2.02 μPVT	1.1 μPS	0.357 μPS	0.091 μPS
PenKem 3000	-1.46	-1.49	-0.97	-0.75
PenKem 500	-1.47	-1.73	-0.94	-1.18
Rank	-1.42	-1.52	-1.03	------

Results are for Particles Suspended in 10^{-2}M NaCl and 10^{-3}M SLS

	2.02 μPVT	1.1 μPS	0.357 μPS	TiO_2
PenKem 3000	-7.61	-6.50	-5.07	-3.02
PenKem 500	-7.81	-6.70	-5.13	-3.07
Rank	-7.48	-6.61	-5.14	-2.88

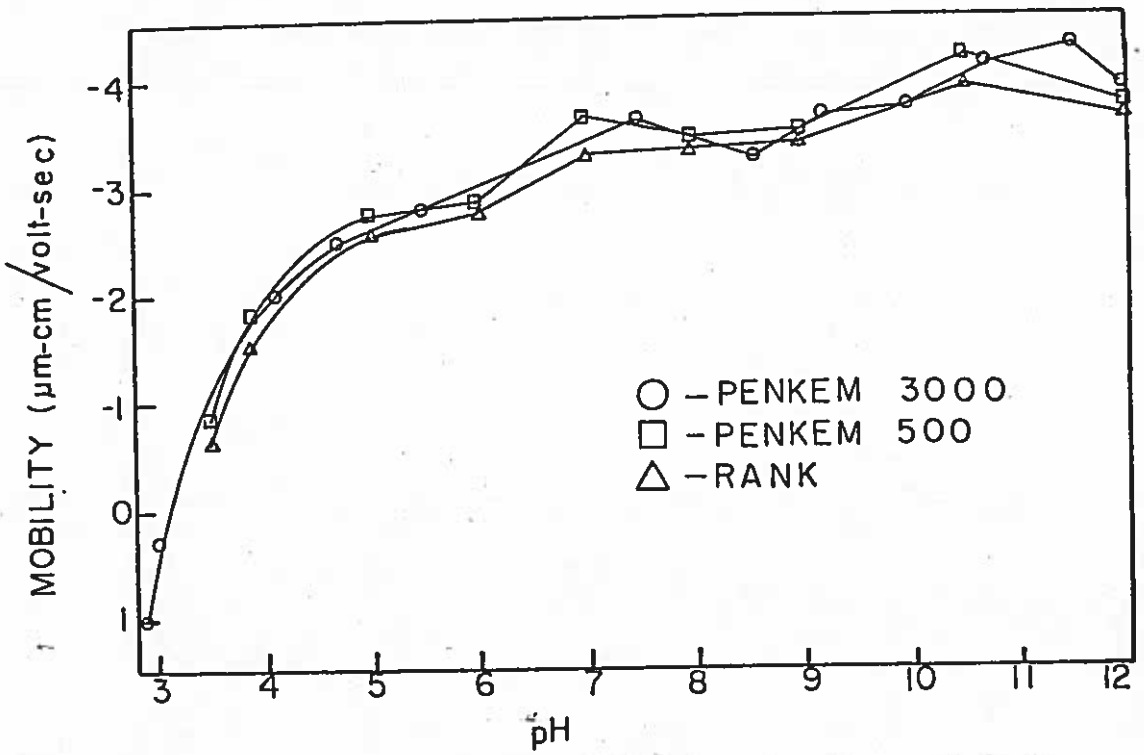

Figure 1: Mobility vs. pH for Pigment Grade TiO_2

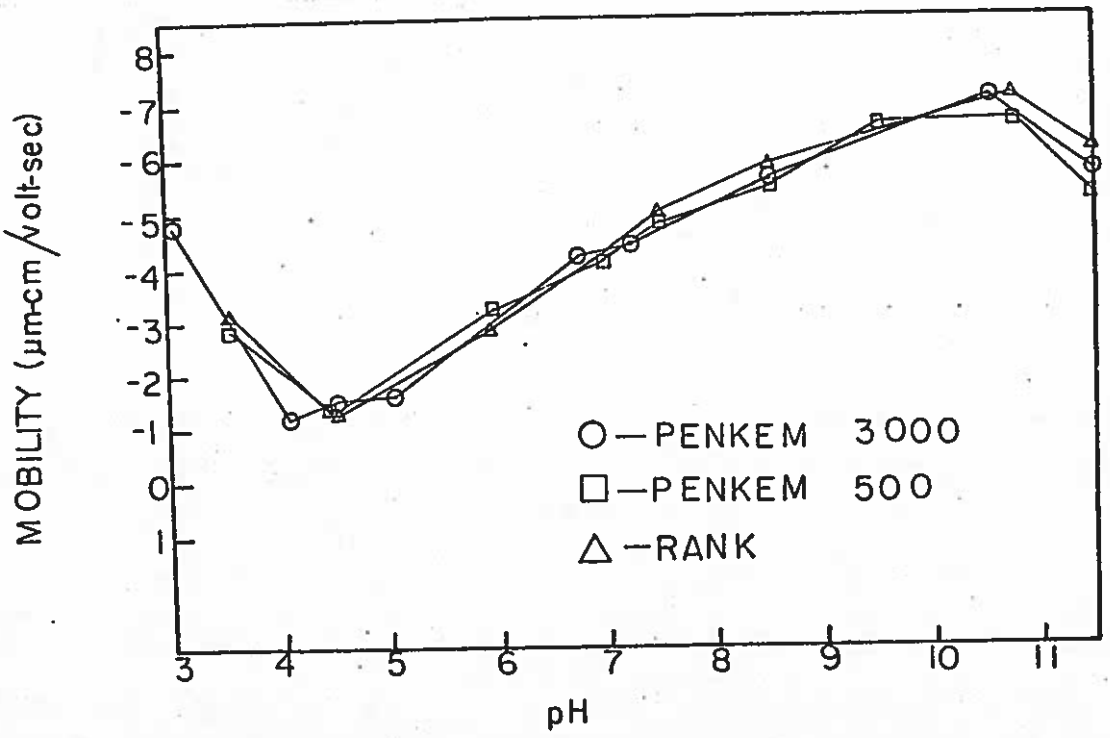

Figure 2: Mobility vs. pH for 2.02 μm Polyvinyl Toluene

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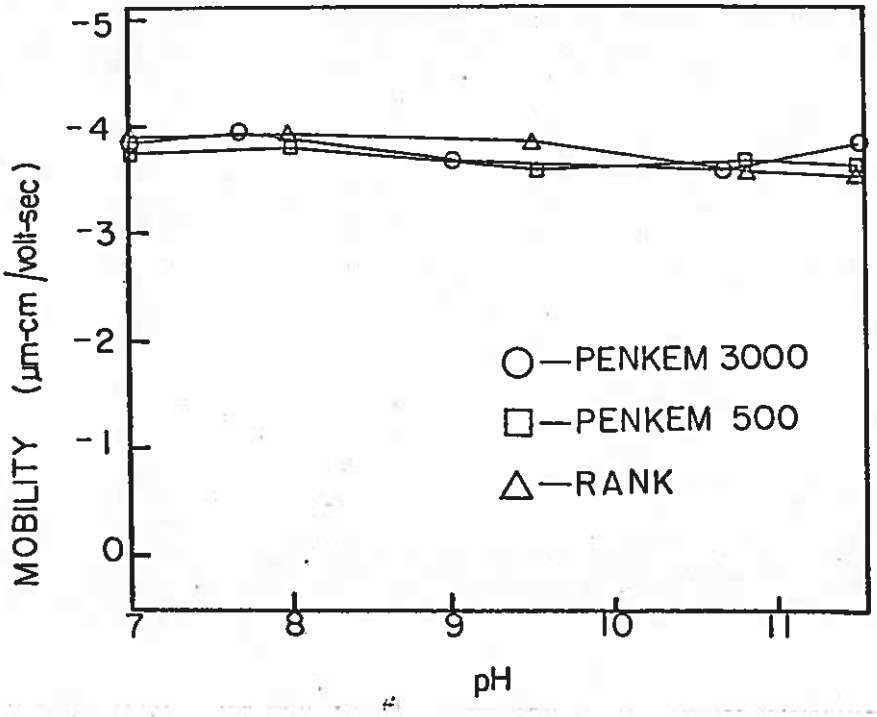

Figure 3: Mobility vs. pH for Carbon Black

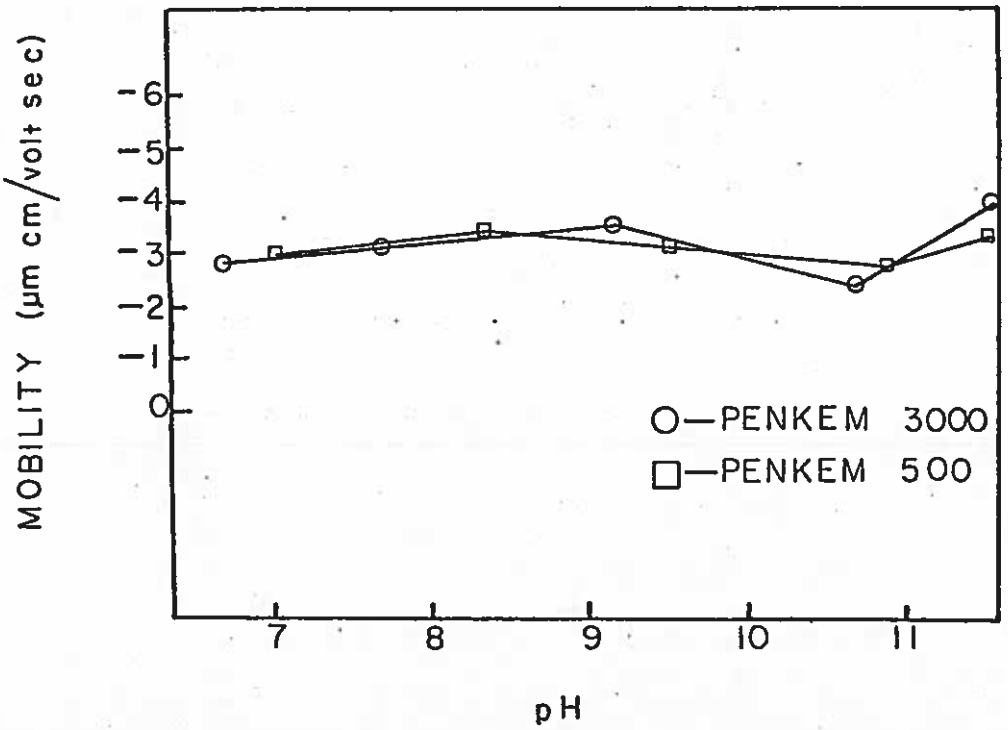

Figure 4: Mobility vs. pH for 0.091 μm polystyrene

scatter observed between instruments. The Rank Mark II was found to be most limited detecting smaller particles. The PenKem 500 was more prone to thermal convection at high electrolyte levels.

An important experimental consideration for the comparison of these instruments is the time needed per measurement and the ease of measurement. Considered for this comparison is a sample easily observable on all three instruments with a fairly uniform mobility distribution.

The time for a single measurement including data generation, sample loading, and cell rinsing on the PenKem system 3000 is from two to four minutes. All of the operation is totally automated. The time of measurement can be determined by the operator through the selection of the number of averages taken per measurement. It was not uncommon for over one hundred measurements to be taken each day. In general the operator is only limited by the time taken for sample preparation.

Since the measurement on the 3000 is totally automated, the results are not "user dependent". The results are not a function of experimental technique and there is no operator eyestrain or fatigue. No special skill or technique is needed for data generation once the instrument has been properly calibrated.

For the PenKem system 500 the time needed per measurement, including sample loadings and cell rinsing is from ten to twenty minutes, depending on the operator's technique. Usually ten to twenty measurements can be taken in a single day. There can be some variance in results with different techniques. The focusing is simplified in that the operator must only be concerned with vertical focusing where the vertical position has been well established. The "user dependent" aspect of the measurement is the uncertainty or variation in judgement of the point where the particle field appears stationary. Some experience and acquired technique is necessary to make quick and repeatable measurements.

The Rank Mark II, while being more versatile than the System 500, is more difficult to operate and somewhat more demanding on the user. A measurement can take from fifteen to forty-five minutes. The greater time is caused by the need to take measurements on a representative number of particles to obtain a good average value. Usually ten measurements can be taken in a day.

The operation of the Mark II is the most experimentally difficult and "user dependent" of the three instruments. The nature of the measurements can cause considerable operator fatigue and eyestrain. The focusing of the microscope objective is critical and it is advised that once proper focusing has been achieved the operator should make several measurements without so focusing the microscope. The "user dependent" part of the measurement is the judgement of which particles should be considered for measurement and uncertainty in the timing of the particles as they move

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across the grid. Since for circular geometry the zero solvent flow level is a line segment, and it is important that measurements be taken on particles as close to the center of the microscope image as possible after the cell capillary has been properly centered microscopically.

Errors in timing the particle movement can cause great variation in mobility results. The operator must adjust the applied voltage to cause the particles to move quickly enough to allow quick measurement and to not lose sight of them but slow enough so that the uncertainty in the timing is not a significant fraction of the total time of measurement. Considerable experience is needed to operate the Rank Mark II quickly and accurately. Of the three instruments the Mark II is the most prone to operator induced error.

A frequent problem with electrophoresis measurements is to determine the electrophoretic mobility distribution of a sample with a complex distribution. Both the Rank Mark II and PenKem 500 can measure complex distributions only with great difficulty. Depending upon the nature of the distribution, between 100 to 200 particles must be measured individually which is both tedious and time consuming. The PenKem 3000, however, automatically measures the electrophoretic mobility distribution in order to print out an average mobility, and only requires a command through the computer to obtain this information on a recorder. Figures 5 and 6 show typical results obtained from the PenKem 3000 for mixed dispersions of fixed red blood cells and polystyrene latexes. This feature is extremely important for evaluating dispersions of unknown properties.

Another application of the PenKem System 3000 is the measurement of the horizontal velocity component of the Brownian movement of a colloidal dispersion. A measurement of this type is made by determining the velocity distribution of a dispersion with no voltage gradient applied.

The Einstein relation,

$$\overline{\triangle}^2 = \frac{R\,T\,t}{3\,N\eta\pi r}$$

where $\overline{\triangle}$ = the average horizontal displacement produced by Brownian movement in time t.

R = molar gas constant

T = absolute temperature

t = time

N = Avogadro's number

η = the viscosity of the suspending medium

r = the radius of the colloidal particle

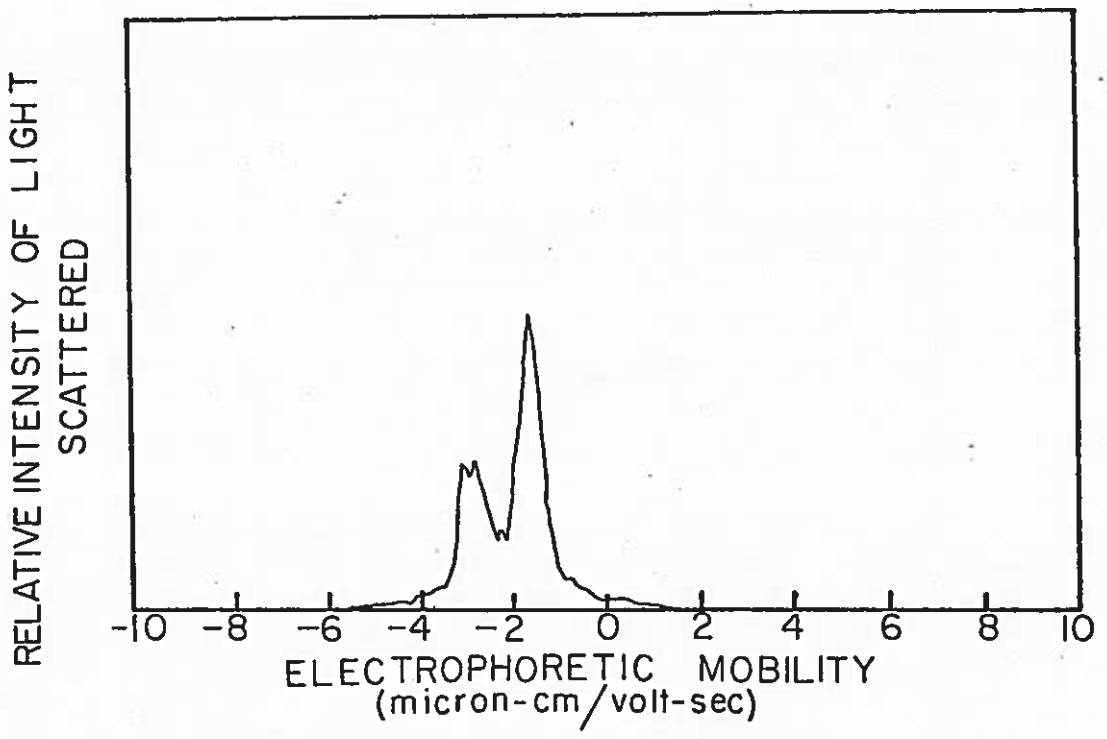

Figure 5: Electrophoretic Mobility Distribution of Turkey and Cow Fixed Blood Cells in D-1 Buffer. Data is from the PenKem System 3000.

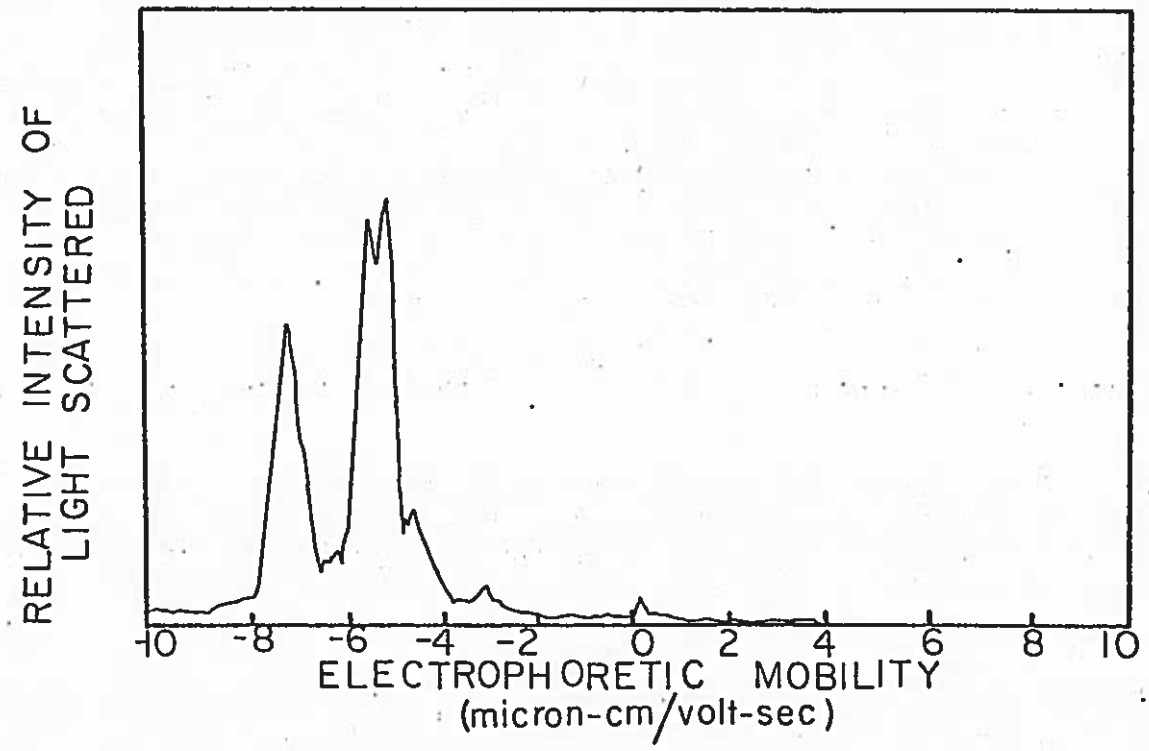

Figure 6: Electrophoretic Mobility Distribution of 1.1 μm Polystyrene and 0.357 μm Polystyrene in 10^{-2}M NaCl and 10^{-3}M SLS. Data is from the PenKem System 3000.

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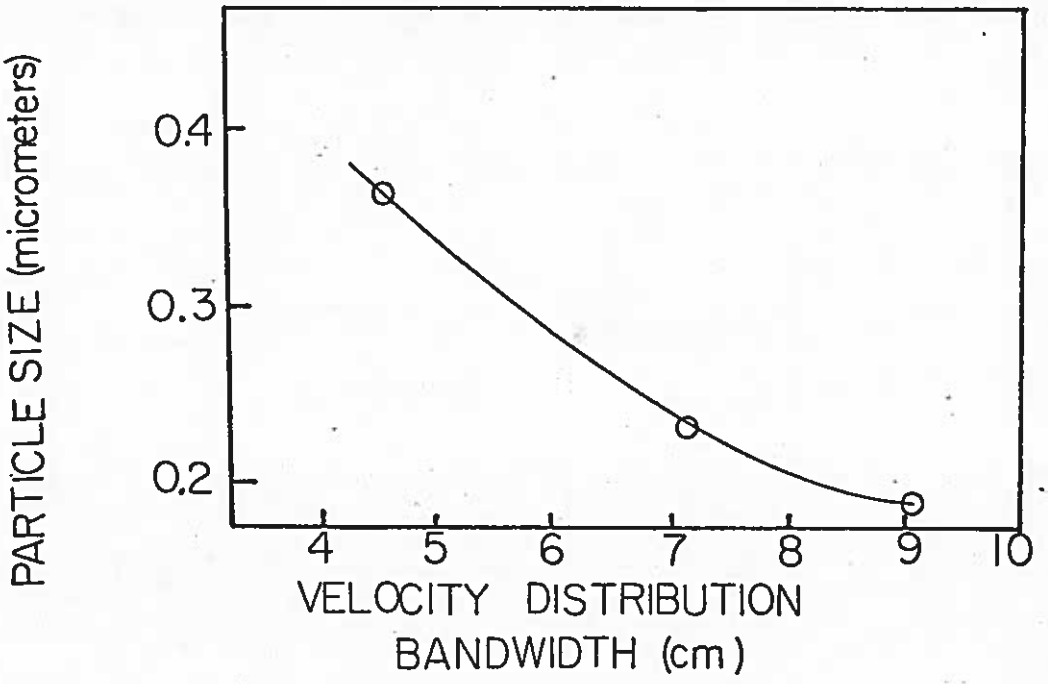

Figure 7: The Velocity Distribution Band width of the Brownian Movement of 0.357 μm Polystyrene.

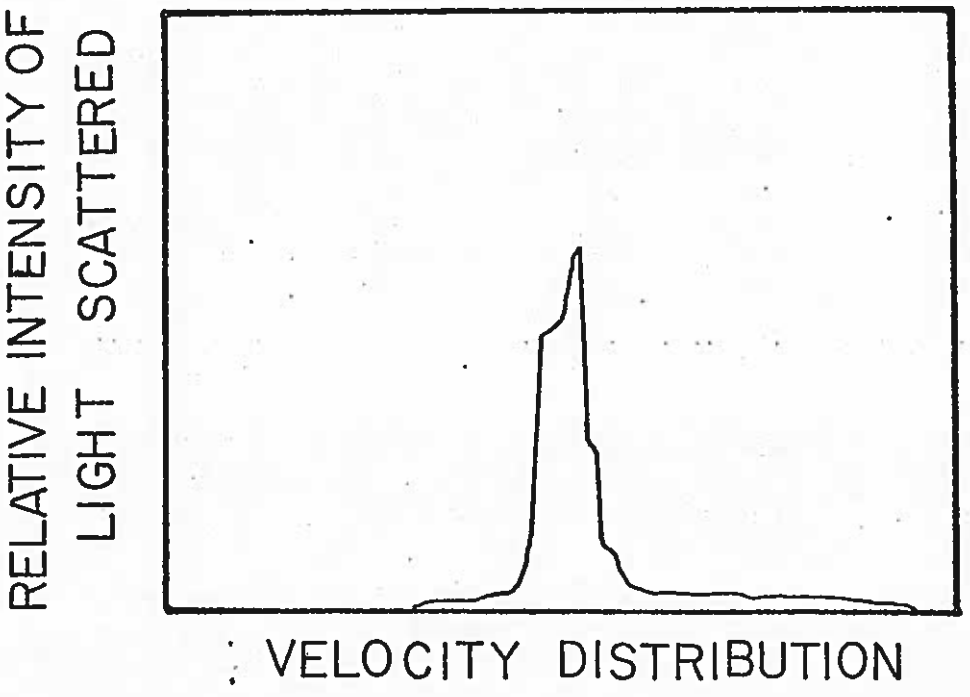

Figure 8: Particle Diameter vs. Velocity Distribution Band width of the Brownian Movement of Monodisperse Polystyrene Latexes.

shows the relationship between the particle velocity and size. The velocity distribution band width produced by the PenKem System 3000 is a relative measure of the minimum particle size present in the dispersion. A typical result is shown in Figure 7 for 0.357 μm polystyrene. Figure 8 shows particle size versus velocity distribution band width for several monodisperse polystyrene latexes.

Future Work:

1. Continue the investigation into the performance of the CPE with an emphasis on comparisons of separations made on the CPE and the PenKem system 3000.

2. Further investigate particle size analysis through Brownian movement using the PenKem System 3000. Areas of interest are the determination of particle size distributions from the shape of the velocity distributions and further definition of the accuracy and limitations of this analytical method.

3. Begin preparatory work for the construction of a prototype model of an electrophoresis cell capable of making physical separations based on differences in electrophoretic mobility. The proposed system will utilize a knowledge of the charge on the cell wall and a externally applied counterflow to produce a flat solvent velocity profile.

APPENDIX

Calculation of Core and Total Phase Volume Fractions

The quoted weight for weight percentage solids values comprise both the polymer core and the stabiliser sheaths of the particles, whilst the measured particle diameters are for the polymer core only.

Based on values of 130 Å (1.3×10^{-8} metre) for the stabiliser barrier thickness (Ref. 12) and densities of 1.18 for the polymer core and of 0.79 for both stabiliser and continuous phase (Ref. 3), the following results were obtained for the phase volume fraction occupied by the particle cores alone (ϕc) and the total phase volume fraction, occupied by the whole particle (core and sheath).

Solids	Phase Volume Fraction	
(% w/w)	ϕc	ϕt
60.0	0.495	0.534
65.0	0.547	0.591
67.5	0.574	0.620