

BULLETIN



BRITISH SOCIETY OF RHEOLOGY

1969, No. 3, Vol. 12

Hon. Editor:

JOHN HARRIS,
Schools of Chemical Engineering
The University,
Bradford,
Yorks. U.K.

NOTICE TO INTENDING CONTRIBUTORS

The B.S.R. Bulletin is now available as a vehicle for several categories of communication by Members.

1. Technical papers (two copies required).
2. Descriptive papers of general interest.
3. Letters which may be either
 - (i) technical or
 - (ii) non-technical.

The technical papers will be refereed and so will technical letters but the latter only by one person. Descriptive and non-technical material will be published if it is of general interest.

In addition, project reports and computer information will be published.

It is hoped that B.S.R. members will find rapid publication sufficiently attractive to warrant submitting work.

BULLETIN VOLUME NUMBERS

The Council has now decided that the *Bulletin* shall have the *same* volume numbering as Rheology Abstracts. Therefore those members of the Society who hold Number 1 and Number 2 of this year's (1969) editions should change the volume number from 1 to 12. The change has already been incorporated in the front cover of this (Number 3) edition.

FOREWORD

One of the main features of the Society's activities for this year is the award of the Gold Medal of the British Society of Rheology to Professors D. M. Dowson and G. R. Higginson for a joint competition entry entitled "The role of lubricant rheology in engineering applications of elastohydrodynamic lubrication." The subject matter is clearly one at the interface between rheology and an area of science more recently classified as tribology. Professor Dowson and Professor Higginson are to be congratulated on establishing a bridge between two areas of science which should be capable of considerable development in the future. Perhaps a joint meeting will be arranged at some time in the future between the Society and the Tribology Group of the Institution of Mechanical Engineers which would be a logical follow up, because the implication in the award is that there is an important practical application of rheology. Certainly the flow properties of lubricants are very important in lubrication although there are of course other factors which affect the efficiency of lubricants in addition to rheological properties, especially under arduous operating conditions.

The rheology of films under extreme pressures has hardly begun at the present time. Here is a new area which must be worthy of some of the available resources of this country. Perhaps a meeting in the nature of a feasibility study is the necessary first step.

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COUNCIL (TO 16.9.69)

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SHEAR RATE DEPENDENCE OF VISCOSITY PARAMETERS

G. P. Pearson, M.Sc., A.R.I.C., F.S.D.C.,
School of Polymer Science,
University of Bradford,
Bradford 7,
England.

Synopsis

The various factors which affect the viscosities of dilute solutions of high polymers are discussed. Attention is then drawn to the fact that under certain circumstances the value for the intrinsic viscosity $[\eta]$ of a polymer in a particular solvent may be in error unless the determination of this parameter has been carried out at, or extrapolated to, zero shear rate conditions.

1. Basic Considerations

The relationship between dilute solution viscosity and polymer concentration c in a given solvent at a given temperature has been described by various functions, all of which have been used to obtain $[\eta]$, the intrinsic viscosity.

The commonest is that due to Huggins¹;

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c$$

where η_{sp} = specific viscosity defined as:—

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o}$$

and

η = viscosity of solution.

η_o = viscosity of pure solvent.

k' = Huggins or slope constant.

The value of k' varies between 0.3–0.5 and is a constant for a particular polymer/solvent system at a given temperature.

The production of a rectilinear plot of η_{sp}/c against c is generally correct for flexible polymers and extrapolation to zero concentration is relatively easy. For precise work the Method of Least Squares is normally employed to give the best value of k' and $[\eta]$ from the experimental data.

If the chains are stiff, for example in the case of cellulose and its derivatives which owe their inherent stiffness to the glucosidic link and inter-molecular H-bonding, the plots may show upward curvature. In such cases an expression due to Martin² is more often employed:—

$$\log (\eta_{sp}/c) = \log [\eta] + k'' [\eta]c$$

where k'' is another constant.

The intrinsic viscosity is readily obtainable from either type of plot by extrapolation to zero concentration.

$[\eta]$ is related to the molecular weight of the chains in solution and more particularly to the hydrodynamic volume of the chains. It should be noted, at the outset, however, that the value of $[\eta]$, besides being some function of the polymer, is also a function of temperature and solvent, the solvent dependence being demonstrated in Table 1.

Table 1.—Solvent dependence of $[\eta]$ for Cellulose Nitrate
(Nitrogen content 12.55%, Molecular Weight 240,000,
Temperature 25°C)³

Solvent	$[\eta]$
Acetone	3.46
N-amyl methyl ketone	5.18
Ethyl acetate	4.67
N-butyl acetate	5.49
Cyclohexanone	4.52
Nitrobenzene	6.04

For a given polymer in a good solvent, polymer-solvent contacts are preferred and the chains will tend to be extended if the polymer is sufficiently flexible, and relatively high values obtained for $[\eta]$. For the same polymer in a thermodynamically bad solvent, polymer-polymer contacts will predominate and the polymer will tend to coil, thus reducing the hydrodynamic volume and hence the value of $[\eta]$. In the case of stiff polymers, i.e. cellulose and its derivatives, the solvent effect on $[\eta]$ is not so marked.

Notwithstanding, however, the above purely thermodynamic and hydrodynamic considerations, there is a correlation between the intrinsic viscosity of a polymer and its molecular weight. The most used relationship is that due to Mark-Houwink⁴:—

$$[\eta] = K \bar{M}^\alpha$$

where K and α are constants for a particular polymer-solvent system at a given temperature. The precise significance of K is debatable but the value of α gives some indication of the stiffness or flexibility of the polymer in the solvent. Values of α between 0.5–0.8 are taken to imply flexibility of the chains, whereas values in the range 0.8–1.0 are usually indicative of stiff chains.

Some K and α values for cellulose nitrate are given in Table 2.

Table 2.—K and α values for Cellulose Nitrate (Nitrogen Content 12.5%, Temperature 25°C)³

Solvent	$10^4 \times K$	$\alpha (\pm 0.02)$
Acetone	1.43	0.81
N-Amyl methyl ketone	1.95	0.82
Ethyl acetate	1.83	0.82
N-Butyl acetate	3.00	0.79
Cyclohexanone	3.96	0.75
Nitrobenzene	3.17	0.79

Intrinsic viscosities are usually determined using capillary viscometers, and with experience the technique is relatively simple and quick. The values of K and α are, of course, previously obtained from a knowledge of the molecular weights of carefully fractionated material, osmotic pressure measurements normally being used to determine the molecular weight of each fraction. The viscosity molecular weight $\bar{M}_v$ is statistically nearer the weight average $\bar{M}_w$ and for extremely accurate work the parameters K and α should be determined from such methods as light-scattering to yield $\bar{M}_w$. However, light scattering equipment is expensive and requires above average expertise in its manipulation. As a consequence of this, osmotic pressure methods, though yielding $\bar{M}_N$ values are normally employed.

2. Non-Newtonian Effects

Irrespective of the method of determination of the molecular weight of the various fractions, the viscometric method for determining the molecular weight of a given sample of polymer involves the measurement of solution viscosity. In dilute solution, however, high molecular weight material will exhibit non-Newtonian behaviour at high rates of shear, this deviation normally being pseudoplastic in character. This means that the viscosities as determined, particularly at high shear rates, will be somewhat lower than the true value at zero rate of shear.

The shear dependence of $[\eta]$ may be attributed to deformation and orientation of the chains in solution and at high rates of shear the molecules, particularly if their molecular weight is high, tend to align themselves in a direction parallel to the capillary axis. As a consequence, the measured viscosity is therefore an apparent viscosity and as shown in Table 3, this may require considerable correction if the results are to be meaningful.

Table 3.—Variation of $[\eta]$ with Shear Rate⁶ (Cellulose Nitrate at 25°C in Acetone)
($\bar{\gamma}$ values range from 200 to 2,000 sec⁻¹)

$\bar{M}_N$	$[\eta]$ uncorrected	$[\eta]$ at zero shear	% Difference in $[\eta]$
700,000	21.0	23.3	11.0
550,000	16.1	17.0	5.6
375,000	12.7	13.1	3.2
300,000	9.8	10.0	2.0
90,000	3.9	3.9	—

Various viscometers have been described⁵ to facilitate the determination of η and hence $[\eta]$ at zero rate of shear, the most popular being the multiple bulb capillary viscometer. This instrument enables the viscosity to be measured at different shear rates and enables the operator to determine the viscosity at zero shear rate by extrapolation.

The mean shear rate in a conventional capillary viscometer is given by:—

$$\bar{\gamma} = \frac{8 V}{3\pi r^3 t}$$

where V = volume of bulb

r = capillary radius

t = time of efflux

$\bar{\gamma}$ = mean shear rate.

In order to obtain $[\eta]$ values of very low or zero shear rate, two extrapolations have to be carried out. First, for each concentration the calculated values of η sp/c are plotted against the $\bar{\gamma}$ values calculated according to the above relationship for each of the bulbs of the viscometer. This plot is then extrapolated to zero $\bar{\gamma}$ and the values of η sp/c at $\dot{\gamma}_0$ obtained.

Now, from Martin's equation, $\log (\eta \text{ sp/c})$ at $\dot{\gamma} = 0$ is plotted against c on semi-logarithmic paper and graphic extrapolation to $c = 0$, yields an intercept which is a measure of $[\eta]$ at zero rate of shear. The method is fully described in a paper by Schurz⁶.

Typical results showing the variation of $[\eta]$ with shear rate for cellulose nitrate in acetone are shown in Table 3. There it can be seen that the percentage difference between the high shear rates and zero shear rate values of $[\eta]$ can be quite large, and that this difference increases, quite markedly, with increasing molecular weight.

With respect to these differences, it can only be concluded that molecular weight determinations, based on the intrinsic viscosity method, may be seriously in error if values of $[\eta]$ at finite shear rates, rather than zero shear rate, are used in the calculations.

3. References

1. Huggins, M. L., J.Amer.Chem.Soc. 64, 2716 (1942)
2. Martin, A. F., A.C.S. meeting, Tennessee (1942)
3. Pearson, G. P., and Moore, W. R., Polymer 1, 144 (1960)
4. Houwink, R. J.Prak.Chem. 157, 15 (1940)
5. Cragg, L. H. and Van Oene, H., Canad.J.Chem. 39, 203 (1961)
6. Schurz, I., and Immergut, E. H., J.Polymer Sci. 9, 279 (1952)

BRITISH SOCIETY OF RHEOLOGY—VICTORIAN BRANCH (AUSTRALIA)

Annual General Meeting

The Ninth Annual General Meeting was held on Friday, August 15th, at 7.30 p.m., in the Private Dining Room of the Monash University Union.

The meeting was followed at about 8 p.m. by a discussion on "Some General Aspects of Blood Flow," presented by Professor R. L. Whitmore, Head of the Department of Mining and Metallurgical Engineering, University of Queensland. Professor Whitmore has recently published a book entitled "Rheology of Circulation."

RHEOLOGY SURVEY 1970

In preparing to compile a completely new edition of the Survey of Rheological Research in Britain in 1970 we are anxious to send out questionnaires to any workers who were either omitted from the 1968 revision of the survey or have recently begun this type of work.

If you know of anyone who comes under either category would you please send his name and address to:

Dr. J. M. Hobbs,
Properties of Fluids Division,
National Engineering Laboratory,
East Kilbride,
Glasgow,

or telephone East Kilbride 20222, Ext. 243.

FILM NOTES FOR RHEOLOGICAL BEHAVIOUR OF FLUIDS

An eight-page illustrated pamphlet, "Film Notes for Rheological Behaviour of Fluids," has been recently published by the Encyclopaedia Britannica Educational Corporation. Copies in bulk may be ordered, as item number 21613, from Encyclopaedia Britannica Educational Corporation, Sales Service Department, 425 N. Michigan Avenue, Chicago, Illinois 60611, for five cents a copy. Single copies may be obtained gratis from Hershel Markovitz, Carnegie-Mellon University, Mellon Institute, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213.

COMPUTER PROGRAM CATALOGUE

In the fourth edition of the *Bulletin* in 1968 several new features were introduced, one of them being the computer program section which is intended as a vehicle for the dissemination of computer program information of use to rheologists.

Two further significant developments of this service have taken place in that the computing laboratory of the University of Bradford will now accept data processing in rheology as a service to members of the British Society of Rheology. Secondly, rheologists need to characterise solid-liquid systems and powders by obtaining size distribution data of the divided solids using instruments such as the Coulter counter. Very recently the catalogue of Coulter Counter Computer Programs, compiled at the University of Bradford, has become available. It is described below.

Data Processing Service (I.C.L. 1909)

As a complementary facility to the publication in the *Bulletin* of program abstracts it has been arranged that data processing for members can be accommodated in the computing laboratory at the University of Bradford. It is realised that many potential program users would wish to use their own facilities which are probably free and convenient, but a few may not be so well endowed, and it is really with these users in mind that the service has been created as an alternative to obtaining a service at the original source of the program. With this facility in existence there should be scarcely anyone who is aware of an available program they would like to use and yet is unable to obtain a service.

Not all language facilities are available for use in the computing laboratory at Bradford; non-availability will be indicated on the published abstract.

Standard charges at present operating rates for data processing are as follows:

1. Data preparation—£2 10s. per hour (it is preferable for users to prepare data themselves).
2. Computing—commercial and industrial users £60 per hour. Educational establishments by individual arrangement.
3. Graph plotting—£12 per hour.

Potential users of this service may contact:

Dr. R. J. Ord-Smith,
Computing Laboratory,
The University,
Bradford 7,
Yorkshire, U.K.
Tel. No. Bradford 29567, Ext. 217.

Coulter Counter Computer Program Library

Many of the essential features of the computer program catalogue for the field of rheology are already evident in the recently published catalogue relating to Coulter counter programs. Copies of the catalogue are available from Dr. R. J. Ord-Smith at the address given above.

The catalogue is a collection of some 21 program abstracts from various sources, all relating to the Coulter counter. Further editions of the catalogue will be published from time to time as the accumulation of abstracts dictates.

BRITISH SOCIETY OF RHEOLOGY

Computer Program Catalogue

Publication Abstract

1. Author
2. Establishment
.....
..... Tel. No.
3. Program Abstract
.....
Input Data
.....
Output Data
.....
4. Program date
5. Language
6. Computer requirements
.....
.....
7. Type of Input/Output
8. References
.....
.....
.....
9. Related programs
.....
.....
10. Available for copy/data processing
.....
.....

Return to: Dr. J. Harris,
Postgraduate School of Chemical
Engineering,
University of Bradford,
Bradford 7, U.K.

Additional blank abstract sheets are available as required from the above address.

BRITISH SOCIETY OF RHEOLOGY

Computer Program Catalogue

Publication Abstracts

Abstract No. 1

1. Author
Peter R. Willett
2. Establishment
The Olympic Tyre and Rubber Co. Pty. Ltd., Cross Street,
West Footscray, Victoria, Australia. 3012
Tel. No. 68.1211
3. Program Abstract
Analysis of Viscoelastic results obtained from the Rheovibron,
model DDV-II Viscoelastometer on elastometers and textiles
Input Data
Temperature, $\tan \gamma$, Dynamic force, dial setting of Amplitude
factor and $\tan \gamma$ range, sample dimension.
Output Data
Temperature, $\tan \gamma$, E^* , E' , E'' , $E''/(E^*)^2$, oscillating force and
Amplitude, Energy loss as $f(E')$ and $f(E'')$.
4. Program date
April, 1969
5. Language
Fortran
6. Computer requirements
Program used on an I.C.L. 1902 computer
7. Type of Input/Output
Card Input/printer output
8. References
None
9. Related programs
None
10. Available for copy/data processing
Program available for copy

Abstract No. 2

1. Author
Dr. M. P. Brocklebank

2. Establishment
Monsanto Chemicals Ltd., Newport, Monmouthshire, U.K.
3. Program Abstract
The program predicts the phase lag and amplitude ratio of a cone and plate oscillatory system. Viscoelastic fluids used are Oldroyd 2 constant and Maxwell models and program is ideally suited for Weissenberg rheogoniometry.
4. Program date
August, 1968
5. Language
Fortran II
6. Computer and store requirements
About 4K core storage
7. Type of Input/Output
Card Input/Line printer output
8. References
 - (1) Walters, K., and Kemp, R. A., Chapter 18 of "Polymer Systems," Proc. Annual Conf. Brit. Soc. Rheol. '66
 - (2) Walters, K., Quart. Journ. Mech. Appl. Math. 13 444, 1960
 - (3) Brocklebank, M. P., Ph.D. Thesis, University of Wales '69
 - (4) Weissenberg Rheogoniometer Manual, Sangamo Controls, Bognor Regis
9. Related programs
None
10. Available for copy/data processing
Card deck, listing and explanatory notes obtainable from author

Abstract No. 3

1. Author
A. K. M. Abdul Quader
2. Establishment
Department of Chemical Engineering, University of Bradford, Bradford 7
3. Program Abstract
Calculates Reynolds number, friction factor, velocity profile based on Bowen formula; and wall shear stress experimental friction factor, generalised Reynolds number. Inputs required: flow rate, pressure drop, tube diameter, Bowen constants, power law constants and fluid density

4. Program date
April 30th, 1969
5. Language
Fortran
6. Computer and store requirements
I.C.L. 1909, 4224
7. Type of Input/Output
Card/Line printer
8. References
None
9. Related programs
None
10. Available for copy/data processing

NOTES ON MEETINGS

The London and South Eastern Branch of the Institution of Chemical Engineers, jointly with the Society of Chemical Industry, is organising a half-day symposium on Non-Newtonian Fluid Technology, to be held at the Cafe Royal, Regent Street, London, W.1, on Thursday, November 20th, under the chairmanship of Professor J. F. Richardson, University College of Swansea. Registration starts at 1.30 p.m. and the symposium begins at 2 p.m.

1. Non-Newtonian Technology in the China Clay Industry
by Dr. K. M. Beazley, English Clays Ltd., St. Austell, Cornwall.
2. Non-Newtonian Technology associated with some Food Products
by Dr. A. E. Hawkins, Unilever Ltd., Colworth House, Sharnbrook, Bedfordshire.
3. Rheological Aspects of Lubrication
by Mr. J. F. Hutton, Shell Petroleum Company Ltd., Thornton Research Centre, P.O. Box 1, Chester.
4. Processes in the Plastics Industry
by Dr. S. J. Skinner, Monsanto Ltd., Corporation Road, Newport, Monmouthshire.
5. The Need for a Unit Operations Approach in Non-Newtonian Technology
by Professor W. L. Wilkinson, Department of Chemical Engineering, University of Bradford.

UNIVERSITY OF BRADFORD

School of Polymer Science

A post-experience course on "The Chemistry, Properties and Applications of Polypropylene" will be held on November 27th and 28th, 1969.

Papers will be presented on the chemistry, manufacture and properties of polypropylene, together with such fabricating processes as injection, extrusion and extrusion blow moulding. Film and fibre applications of this important polymer will also be considered, together with a paper on applications development.

Fee for the course: £12.

Further details and forms of application may be obtained from the Registrar, University of Bradford, Bradford 7.

POLYMER CHAIN FLEXIBILITY

A conference on Polymer Chain Flexibility is being organised by the British Polymer Physics Group at the University of Essex in Colchester from 11.30 a.m. on Wednesday, January 7th, until 12 noon of Friday, January 9th, 1970. The aim is to review the concepts of flexibility and stiffness including such topics as mean-square dimensions and viscosities in solution, glass transitions in bulk polymers, the relevant properties of biopolymers, rheological effects such as non-Newtonian flow, the extent to which solution and bulk properties can be correlated, and the usefulness of models which treat chain flexibility in terms of rotational or bending potentials, etc. Those interested in offering lectures (25 minutes) and/or attending the conference should obtain fuller details from Professor M. Gordon, Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex, England, as soon as possible.

REQUEST FOR PUBLICATIONS

The following request for publications has been received. Any member of the B.S.R. able to satisfy is urged to write direct to the author mentioning the price required.

1. Proceedings of the First International Congress on Rheology, Sheveningen, 1948 (North Holland, Amsterdam, 1949).
2. Proceedings of the Second International Congress on Rheology, Oxford, July, 1953 (Butterworths, London, 1954).

Communications to:

R. J. Wilis,
Chemical Engineering Department,
University of Queensland,
St. Lucia, Brisbane 4067,
Queensland,
Australia.

LIBRARY NEWS

Information has come to hand (via the Victorian Branch, Australia) of a new journal to be published by the D. Reidel Publishing Company, Dordrecht, Holland. The title of the publication is "Journal of Texture Studies" and the editors-in-chief are P. Sherman and A. S. Szczesniak.

The information indicates that the publication is to be an international journal of rheology, psychorheology, physical and sensory testing of foods and pharmaceuticals. It is intended to publish contributions in the following categories:

Review Papers
Letters to the Editor
Research Notes
Abstracts
Book Reviews.

No doubt this journal will be added to the list of publications covered by Rheology Abstracts.

DIARY

Meetings (1969)

- 7 October. Lecture—Scientific Measurement applied to the Arts. Thompson Lecture. London.
- 7 and 9 October. Conference—Ultrasonics for Industry by Ultrasonics for Industry, 32 High Street, Guildford, Surrey.
- 13–15 October. Symposium—Gums and Thickeners. Society of Cosmetic Chemists, Oxford.
- 23 October. Symposium—Heat transfer and fluid flow in electrical machines. London. I.Mech.E.
- 12 November. Symposium—Plastics in motor cars: present and potential applications for thermoplastics and reinforced plastics. Plastics Inst., London.
- 16 to 17th November. Conference—International Rubber Conference, Moscow.
- 20 November. Symposium—Non-Newtonian fluid technology. I.Chem.E., London.
- 5 December. Conference—Fault finding in thermoplastics. Plastics Inst., London.

1970

- 7-9 January. Conference—Polymer chain flexibility. British Polymer Physics Group. Essex University, Colchester.
- 19 and 20 February. Convention—The use of grease as an engineering component. I.Mech.E., London.
- 11 March. Symposium—New fabricating methods for plastics. Plastics Inst., Cardiff.
- 18 March. Conference—Production engineering in reinforced plastics. Plastics Inst., London.
- 23-25 March. Convention—Thermodynamics and fluid mechanics. I.Mech.E., Glasgow Univ.
- 24 March. Conference—Product performance testing. Plastics Inst., Bath.
- 31 March-3 April. Conference—Physical and structural lines of the yield, deformation and fracture of polymers. Joint I.P.S. Brit. Poly. Phys. Group, B.S.R., I.R.I., and Matl. Sci. Club meeting at Cambridge.
- 16 and 17 June. Conference—Polymers in high performance applications. Joint Soc. of Plast. Engineers and Plastics Institute meeting at Institute of Electronic Engineers, London.
- 29 September-1 October. Conference—Advances in polymer science and technology No. 3. Chemistry of liquid and thermoplastic co-polymers. Plastics Inst.

Dates to be arranged:

April. Short course—Non-Newtonian Technology. Schools of Chem. Engrg., Bradford Univ.

July. Symposium—Body Engineering. I.Mech.E., Cranfield, Beds.

SITUATION VACANT

National Institute of Agricultural Engineering

The National Institute of Agricultural Engineering is one of the largest agricultural research institutes financed by government grant through the Agricultural Research Council. It lies mid way between Bedford and Luton in 200 acres of formal gardens and parkland. The Institute has a very wide range of work concerned with the introduction of modern engineering in agriculture and horticulture.

MECHANICAL ENGINEER or PHYSICIST is required in the Materials Engineering Department to take charge of research on the mechanical characteristics of agricultural soils (which are compressible, rate dependent, etc., and may exist in several states). The work is aimed first at identifying the principal mechanical properties and then providing means of measuring them possibly through the solution of simple cases of two-dimensional or axisymmetric flow.

A knowledge of continuum mechanics (e.g. plasticity, visco-elasticity) will be needed. The work will require an extensive programme of experiment involving X and gamma ray techniques. Experimental assistance will be provided. Instrumentation, data logging, computer and statistical services will be available.

Appointment will be in the Senior Scientific Officer/Scientific Officer grades.

Salaries:	Senior Scientific Officer	£2,021-£2,491
	Scientific Officer	£1,071-£1,827

F.S.S.U. Superannuation

Ref: ED/69/16B

Application forms from: The Secretary, N.I.A.E., Wrest Park,
Silsoe, Bedford.