THE
RHEOLOGY
LEAFLET

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SOCIETY OF RHEOLOGY

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ELEVENTH ANNUAL MEETING

The eleventh annual meeting of the Society will be held this Fall, probably in October, and certainly in either New York or Washington. The Executive Committee regrets that a more definite announcement cannot be made at this time. They will report their final decision in the next issue of the Leaflet.

In the meantime, all members are invited to offer papers for presentation at the meeting, either by themselves or by their associates. Professor R. H. Ewell of Purdue University, Lafayette, Indiana, has been appointed Chairman of the Program Committee, and will be glad to receive offers of papers either completed or in preparation.

Papers always take longer to prepare than we anticipate. Better get an early start.

We are discussed in NATURE

The activities of the Society of Rheology were mentioned in the "News and Views" section of the June 10th issue of NATURE. They say in part: "Rheology is one of those fields which include several sciences—physics, chemistry and physical chemistry and, of late years, biology. Its importance and scope are only now beginning to be generally recognized. Given the necessary increase in support, the Society should then fulfill a very useful function. It would be especially valuable if its finances reached the point where it became possible to list (without full abstracting) all papers bearing on the subject. Now the Society is staking its reserves on the drive for increased membership in such manner that they will be exhausted in two years if the drive fails. It is to be hoped that the Society will receive the required support." We appreciate these encouraging words.

"The Science of Rheology and the Plastics Industry" is the title of an interesting article written by Dr. G. W. Scott Blair and published in British Plastics for March, 1939. The principal theme is that the plastics industry may profit by a scientific approach to the phenomena of deformation. On the other hand the author suggests that the scientists adopt more practical and less confused definitions of such commonly used terms as "plasticity." He takes exception to the definition of a plastic solid as given on Page 15 of The Rheology

Leaflet No. 7. It appears that the word "plastic" means an entirely different thing to a physicist than to the so-called "plastics industry".

Dr. Scott-Blair illustrates the manner in which various branches of technology may have problems which have their roots in the same basic physical laws. He points out that: "Failure to realize the "oneness" of the science of Rheology is a very great hindrance to progress in many industries today, not least in the plastics industry. So much time would be saved if the research worker would realize that his problems are not unique, that some other worker in an entirely different field is facing the same difficulties, and that in some cases solutions have already been found." The Society of Rheology is designed as a natural meeting place for workers whose diverse lines of research have such a common fundamental base.

The author has recently been attempting to correlate definite and measureable physical properties with the psychological factors involved in the craftsmanship of a skilled workman. This is an extremely involved problem which industry will eventually solve. The present writer remembers a period of some fifteen years ago when he developed a sense of feel which enabled him to determine the suitability of a plastic for successful moulding. Valuable as such rule of thumb tests may be, the position of a company depending on such control is apt to be an untenable one. Dr. Scott Blair refers to this as the "Bill" method or the psycho-rheological basis of craftsmanship and gives credit to the high skill of the craftsmen and acknowledges our debt to them. He concludes that "to replace such men by machines which do not correctly integrate the physical factors required in the product is inexcusably bad business."

The author, who is a member of the Society of Rheology recently wrote "An Introduction to Industrial Rheology" which was reviewed in The Rheology Leaflet No. 8.

REPORT OF COMMITTEE ON NOMINATIONS

The Constitution of the Society provides that officers be elected biannually by a letter ballot of the membership. The By-Laws provide that candidates be nominated by a nominating committee appointed by the President, and that these nominations be published nine months in advance of the election.

The next election will take place in advance of the annual meeting for 1939 which will probably be held in October. At the last meeting President Mooney appointed a nominating committee consisting of R. H. Ewell, R. L. Peek, Jr., and W. H. Herschel, Chairman. The list of candidates prepared by this committee is given below.

The By-Laws further provide for additional nominations to be received upon the petition of three active members up to six months before the election, and that ballots be mailed to all members three months in advance of the election. As it has been impossible to publish the nominations before this date, the Secretary will receive petitions for additional nominations up to September 1 and will mail ballots to the members sometime between September 1 and October 1.

The committee on nominations submits the following slate for the 1939 election:

For President:
A. S. Hunter; E. I. du Pont de Nemours & Co.
Buffalo, N. Y.

For First Vice-President:
J. H. Dillon; Firestone Tire and Rubber Co.
Akron, Ohio.

For Second Vice-President:
R. H. Ewell; Purdue University,
Lafayette, Ind.

For Secretary-Treasurer:
Howard R. Lillie; Corning Glass Works
Corning, N. Y.

For Editor:
W. P. Davey; Pennsylvania State College
State College, Pa.

For Associate Editor:
H. F. Wakefield; Bakelite Corporation
Bloomfield, N. J.

Committee on Nominations
W. H. Herschel,
Chairman

The nominee for President was the first secretary of the Society, an office which he held until a severe sickness compelled him to lighten his load. He is forty-two years of age and has been engaged in industrial research for about twenty years. He is research physicist and physical chemist in the rayon division of E. I. du Pont de Nemours and Co.

J. H. Dillon, thirty-four years of age, has been a physicist for the Firestone Tire and Rubber Company since receiving his Ph.D. from Wisconsin in 1931. His work has been on the physical properties of rubber, and many articles on the extrusion type rubber plastometer have appeared under his authorship.

R. H. Ewell, thirty-one years old, has been a member of the faculty of Purdue University since 1937 when he received his Ph.D. from Princeton where he worked with Professor Eyring. He is known for his work on the plasticity of ceramic materials and on the viscosity of solutions. Readers of the Journal of Applied Physics will remember his recent article on the reaction rate theory of viscosity.

The nominee for Secretary-Treasurer has served for two consecutive terms as chairman of the program committee. He has done outstanding work on the rheological properties of glasses at the physical resarch division of the Corning Glass Works, Corning, New York.

The nominee for Editor is Research Professor of Physics and Chemistry at The Pennsylvania State College, State College, Pa. He is known for his researches on crystal structure and X-rays.

H. F. Wakefield has been engaged in research and development work on resins and plastics for about fifteen years, all of that time having been spent with the Bakelite Corporation, Bloomfield, N. J.

AN ACKNOWLEDGMENT

One of the interesting papers at the Pittsburgh meeting was that of Dr. E. P. Irany of Shawinigan Chemicals, Ltd., on "Viscosity and Constitution." It is a continuation of Dr. Irany's contribution to the Journal of the American Chemical Society for September, 1938. Editor Arthur B. Lamb has given his permission to repeat this paper and it is a pleasure to acknowledge his kindness. Lack of space prevents the presentation of more than an abstract but it is easily available for those who wish to review it in detail. The summary is given as it appears in the original article.

The Viscosity Function

E. P. Irany. J. Am. Chem. Soc. 60, 2106-2115 (1938).

The problem of obtaining a straight line curve for viscosity-concentration relationships of ideal mixtures is solved by a graphical method. With this scale derived by graphical analysis all such ideal mixtures appear as straight lines. The function of this scale is called "Viscosity Function ϕ". The scale is generally valid if volume concentrations are used. Non-ideal effects such as association, dissociation and compound formation are easily and accurately recognized by deviations of the curve from a straight line. Various examples of ideal mixtures are shown by curves and compared with literature references in which ideal mixtures are selected by other means. By the author's method no exceptions are found in the generally accepted ideal mixtures.

Certain applications can be made on solid substances using volume concentrations. Some resins and electrolytes are included. Additional evidence is given as to the liquid state of solids in solution.

The same scale can be used for the viscosity-temperature function; therefore the general laws underlying the effect of dilution and temperature are identical.

Associated materials will give straight lines if the association remains constant but will give deviations with changing association.

For viscosity-pressure functions a different scale is required. These functions are generally additive but are difficult to express mathematically.

S u m m a r y

Due to our insufficient knowledge of the structure of liquids it is impossible to formulate the basic and generally valid laws which relate liquid viscosity with variables of condition, such as volume (dilution), temperature and pressure. There is no real proof that such laws of broad validity exist, or that they are recognizable.

A method of graphical analysis was used in providing this evidence which may be summarized in three postulates:

. 1. A function of viscosity exists, $\phi(\eta)$ or the "ϕ scale", which is generally additive in terms of volume; i. e., of dilution in ideal mixtures.

2. A function of viscosity exists which is generally additive in terms of temperature. This function or functional scale is identical with the above, ϕ ; temperature and dilution have the same quantitative effects upon viscosity.

3. Another function of viscosity exists, $\pi(\eta)$, or the "π scale", which is generally additive in terms of pressure.

If viscosities are plotted in these functional scales, all normal or "ideal" additivity is represented as a straight line. Deviations from this course are very accurately recognizable and significant.

Thus the diagrams reveal "non-ideal" conditions; i. e., associative or dissociative tendencies which could not be detected by other means. Extrapolation into the critical region suggests important conclusions regarding state discontinuity. The scale shows the correct magnitude of the internal pressures of liquids which, according to this evidence, are characteristic for whole series of related substances.

VISCOSITY and CONSTITUTION

Ernest P. Irany, Shawinigan Chemicals Limited
Presented at the 10th Annual Meeting, Society of Rheology

Many attempts have been made to explain the relationship between the viscosity of liquids and their chemical constitution, and many interesting rules have been proposed; nevertheless, the problem is still very far from any general solution. This is not at all surprising if we try to realize the difficulties.

To begin with, we do not know beyond doubt what, precisely, a liquid is. Within the classical concepts we find no really convincing answer as to what distinguishes the liquid state and liquid structure from that of gases compressed to a comparable density, yet, there are, of course, very real differences. More recently, statistical theory has been introduced into this problem, and physicists ascribe much significance to several purely mathematical solutions already proposed. However, it would be premature to expect too much at once; statistical theory is primarily, a mathematical device, which depends, as any other, on the fundamental premises made; the solutions appear in the form of indeterminate equations which can only be applied with further arbitrary assumptions. In any case, we have no definite concept of liquid structure which allows us to make any practical use of it.

Furthermore, we are also quite uncertain about what to regard as the physical unit in liquids. Is it the chemical molecule as we define it by its structural formula, is it a group of such individual molecules, is it an entity of quite different description?

We know to-day that molecules as such do not exist in crystals; as fully self-contained units they appear only in gases. All we can presume about liquids is that the chemically defined molecules must be in some intermediate condition, neither as fixed and diffused as in solids, nor as mobile and independent as in gases. Beyond this, everything is speculation.

With so much uncertainty about the nature of the liquid state and the meaning of chemical constitution within it, there is at present little hope for valid quantitative comprehension of macroscopical physical properties, including, of course, viscosity. There are numerous formulations of supposedly general additive relationships between chemical constitution and viscosity but no matter whether or not they are fortified by some kind of theoretical considerations, we must regard them all as empirical.

It is not the purpose of this paper to give a survey of these proposed rules, but rather, to take stock of our attitude towards the problem and to make some constructive suggestions.

Most modern authorities agree upon the dependence of liquid

viscosity on constitutional volume, i. e., the molecular or an associated volume; many even postulate a direct additivity in such terms. Furthermore, collisional and diffusional effects are taken into account. There is, however, a singular and quite explicit agreement in disregarding the inter-molecular attractions the existence of which, of course, cannot be questioned.

A few quotations will exemplify this apparent consensus of opinion:

Bingham, in "Fluidity and Plasticity", 1922:

" . . . it is generally agreed that there is a second cause of viscous resistance, which, without any good reason in its favour, has been repeatedly attributed to the attraction between the molecules.   . . . No reasonable hypothesis has been proposed to extricate us from this dilemma, on the basis of cohesion, hence, we are forced to look for some other cause."

McLeod, Trans. Faraday Soc., 21, (1925), 151:

"Viscosity in liquids is, in fact, as in gases, due to a transference of momentum, and does not depend on any property of the molecule except its weight. It is true the 'free space' and the degree of association may be governed largely by the 'chemical affinity' between the molecules, but 'internal friction' in liquids is not itself a function of the surface of molecules, and is not therefore analogous to the friction between solid bodies."

Hatschek, in "The Viscosity of Liquids", 1928,

"McLeod is no doubt right in considering attempts to represent the mechanism of viscosity as friction between molecular surfaces to be merely false analogies."

Staudinger and Heuer, B. 63, (1930), 222.

These authors propose a linear relation between the viscosity of polymer-homologous substances in solution, and their molecular weight. This rule, known as "Staudinger's Viscosity Law", is based on a formula by Einstein in which an ideal case without inter-particle attractions is assumed.

Why these authorities commit themselves so definitely against recognition of the effects upon viscosity, of the inter-molecular forces cannot well be understood. On the contrary, it is quite evident that liquid viscosity cannot be explained without them.

The main argument rejects the idea of quasi-mechanical friction between "molecular surfaces". Of course, there are no "surfaces" on

the bodies of the molecules, and the concept of macroscopical friction cannot be applied to a sub-molecular medium; to think of liquid structure as of a miniature ball mill would be crude indeed. Nevertheless the analogy between liqiud viscosity and mechanical friction is not entirely absurd; in fact, it may yet assume great interest in view of the most up-to-date theories on the structure of liquids. The common trend of these theories is towards the conviction that liquids are not mere assemblies of molecules in random motion and distribution, but that there is some kind of local concentration and orientation, neither fixed nor permanent, but containing the element of organized structure. But then, if we are justified in conceiving of a multi-molecular structure, we may also think of friction in the ordinary sense— mechanical friction which depends on inter-molecular attractions.

Inter-molecular forces are at a possible minimum in certain substances, particularly in the paraffin hydrocarbons. This can be easily deduced from all their physical and chemical properties. It so happens that they are available in an extremely long and unbroken series, and it is a matter of course that they are always chosen as the first objects of study in the verification of a new rule of consitutional additivity. Very often indeed, the new rule is sustained quite well among them, for the increments are so regular that almost any approximation or assumption will fit beautifully, and there are no inter-molecular forces which, through their irrationality, may cause discord. The great number of facts reproducible within this series is impressive, and this is very likely to suggest that a rule or a law of fundamental validity has been found. However, as soon as the new formula is applied to substances outside the protected field of the paraffin hydro-carbons, exceptions begin to appear.

As long as the discrepancies can be considered exceptions, supplementary explanations are in order; if we have limited ourselves to view viscosity entirely in volume terms, the most logical way out is to assume molecular association. Hence, we find appended to most rules of additivity, elaborate tables of "association factors", which disagree widely, depending on their source. Actually, these association factors represent the inadequacy of the original premises.

There are two very weighty arguments against these factors. First, they are all fractional numbers, which would indicate the presence of several species of different association; since all these derive from one mother substance and are convertible into one another, they could exist only in a very sensitive equilibrium, subject to conditions. However, it is possible to show (*) that there is no variable

(*) Irany, J. Am. Chem. Soc., 60, 2106, (1938).
        Nearly all pure substances, with the exeception, e.g., of the lowest alcohols and fatty acids, give straight lines in the functional viscosity diagrams, over the whole recorded ranges of temperature and pressure.

association in pure liquids, except only a few. If nevertheless, we assume association of great permanence, we meet the other objection: all mixtures would have to be ideal, and all would have to obey the same law. This is in conflict with all known facts. Between truly ideal mixtures in which mutual interference among the molecules can be disregarded, and those in which definite molecular association occurs, there is a continuous graduation which can only be ascribed to inter-molecular forces of varied intensity.

So far, it may seem that there is very little indeed that may justify our ability to talk about "Viscosity **and** Constitution"; nothing that would lend significance to the little word "and". I must also disappoint those who may still expect me to offer a panacea of my own. I can only indicate what in my opinion would be an approach to the problem.

We may define a hypothetical equation of the liquid state— a function of the variables p, v, and T,—pressure, volume, and temperature. Of course, we do not know the exact mathematical form of this equation but, presumably, it contains various material constants, a, b, c, . . . , and some general constants, R, S, ... We are then—again hypothetically—capable of deriving from this equation of state every physical property of the liquid under given conditions. Thus,

$$\text{Equation of State: } F\ (p,\ v,\ T;\ a,\ b,\ c,\ ...;\ R,\ S,\ ...) = 0 \quad (1)$$

$$\text{Viscosity } \eta \ = \ \phi\ (p,\ v,\ T;\ a,\ b,\ c,\ ...;\ R,\ S,\ ...) \quad\quad (2)$$

By means of the equation of state we can substitute one of the three variables into the general expression of the viscosity; thus, we derive three part functions of viscosity,

$$\eta = f_1\ (T;\ a\ ,\ b\ ,\ c\ ,\ ...;\ R\ ,\ S\ ,\ ...)\ \text{ p=const.} \quad (3a)$$

$$\eta = f_2\ (p;\ a\ ,\ b\ ,\ c\ ,\ ...;\ R\ ,\ S\ ,\ ...)\ \text{ T=const.} \quad (3b)$$

$$\eta = f_3\ (v;\ a\ ,\ b\ ,\ c\ ,\ ...;\ R\ ,\ S\ ,\ ...)\ \text{ T=const.} \quad (3c)$$

The first of these represents the viscosity-temperature function, say, under atmospheric pressure; the second, the viscosity-pressure function at a constant temperature; the third, the viscosity-concentration function where an ideal diluent may be assumed. These are the relations in which viscosity measurements are available. The three sets of material constants in these equations,

$$a_1,\ b_1,\ c_1,\ ...\ ,\ a_2,\ b_2,\ c_2,\ ...\ ,\ a_3,\ b_3,\ c_3,\ ...\ ,$$

are parameters in which the nature of the substance, in other words, its constitutive elements, are expressed; among them we must try to detect fundamental regularities. Unfortunately, however, we neither know the mathematical equations in which they occur, nor their actual values.

Where mathematical analysis of the problem fails, there still remains the possibility of employing the empirical method of graphical comparison. In this case we do not need the knowledge of the explicit functions, but instead, rely entirely upon measurement. Fortunately, the fundamental regularities of viscosities are of a kind that can be recognized and, to a certain extent, evaluated by this simple method.

For details I must refer to the original paper on this subject (*); I shall repeat here only very briefly what will be necessary for further understanding.

The diagramatical representation of the three viscosity functions (3a), (3b), (3c), yield in each case sharply ascending curves if absolute viscosity units are used as ordinates. It is possible, however, to construct a scale of viscosities for each diagram which make all curves drawn in it appear as perfectly straight lines, provided that abnormal affects are absent. (Fig. 1). This transformation merely means that the functional curvature has been transferred into a functional viscosity scale; in this form we are much better able to recognize the inherent regularities. Among these three viscosity scales or functions, two have been found identical—those of the temperature and the concentration diagrams; that of the pressure function is different. I called the first one $\phi(\eta)$, and the latter $\pi(\eta)$.

Accordingly, we can say that the complete behaviour of a pure substance—its equation of state—is determined by two general scales which are common for all substances, and by the number of elements which determine three straight lines. The two general scales must be represented by the general constants R, S, ... in the above equations; the elements of the individual lines, i.e., intercepts, gradients, etc., by the material contsants a, b, c, ... The question now arises, as to the necessary and sufficient number of these constitutive elements.

One given viscosity measurement determines one point in each diagram; to this we have to add another one, respectively, which brings the total to four. However, we have to take into account the identity of two of the scales—actually, the temperature function can be considered a special case of dilution, i.e., with a substance of no viscosity, or a void. In other words, their revelence for constitution is the same. This reduces the number of independent material factors to three.

(*) Irany, loc.cit. C. A. 32,8867; 1938 (Copy attached)

However, we can still simplify this absolute requirement. Viscosity under high pressures is seldom under survey; the usual pressures of one, even of several, atmospheres have no appreciable effect upon viscosity, so that we are justified in saying that, ordinarily, we compare viscosities in strictly "corresponding" states with regard to pressure — at the external pressure nil. This eliminates another material constant, leaving only two. These are indispensable; no rule of constitutive viscosity can be generally valid unless it postulates two independent parameters of different computation.

However, there are special cases, series of structurally related substance, of which it can be safely said that the inter-molecular forces are either negligible or constant for all members. For example,

(a). homologous series of non-polar substances; e.g., the paraffin hydrocarbons;

(b). polymer-homologous series, each member of which is composed of a large but different number of identical polar groupings, e.g., polyvinyl derivatives.

In these two cases one of the two constitutive parameters becomes a serial constant; the other is then fully descriptive for the individual member, and is additive in any structural terms convenient to use, such as molecular volume, molecular weight, number of constituent groupings, degree of polymerisation. Of course, this simplification is applicable only within a given series of the above description. Failure to observe this very important limitation is the common error which invalidates the numerous single-parameter rules of additive viscosity and the supplementary tables of association factors.

Among the paraffin hydrocarbons the increments are so regular that the constitutional problem of viscosity is reduced to its greatest simplicity. If the viscosities are plotted in the functional ϕ scale against reduced absolute temperatures, T/Θ , the lines coincide almost completely. Hence, $\phi = K\ T/\Theta$, where K is a serial constant, and

Θ , the critical temperature, appears as the constitutive parameter. The problem resolves to that of the additivity of the critical temperature, reversely, the critical temperature of a hydrocarbon can be computed from a single viscosity measurement.

What can be done with graphical analysis in the case of the polymer-homologues may be shown on the series of polyvinyl acetates. Since these are colloids of enormous and unknown molecular weight, the distinction by critical temperatures is meaningless; the

constitutive parameter must be defined through the viscosity-concentration relationship of solutions.

If the viscosities of polyvinyl acetate solutions are plotted in scale against concentration, no straight lines appear, but curves whose trend indicates strong associative or solvating effects between solute and solvents of various description. (Fig. 2.). In order to recognize quantitative relationships in these deviations from the straight course, the same method can be applied as in the construction of the ϕ scale itself; except for the difference that in the present instance not the ideal viscosity function, but some specific effects of polarity are to be "linearized".

Let us first consider several polyvinyl acetates of different average chain length, dissolved in the same solvent, e.g., benzene. We choose any one of them as a standard, and arbitrarily represent its viscosity-concentration curve as a straight line; using the measured viscosities as fixed points, we can construct a viscosity scale Γ, which embodies the characteristic viscosity function of that particular polyvinyl acetate in benzene solution. (Fig. 3), But if now the benzene solutions of other polyvinyl acetates of smaller or greater molecular complexity are plotted in the same diagram, all appear as straight lines. (Fig. 3a).

This is very striking proof of the fact that all polyvinyl acetates, no matter of what chain length, are constituted in exactly identical form.

Analogous scales can be determined for other solvents, e.g., ethyl acetate (Fig. 3b), butyl acetate, pyridine, dioxan, tetrachlorethane (Fig. 3c), etc. For each one of these solvents a scale function of viscosity is obtained which straightens the concentration curves of all polyvinyl acetates into perfectly straight lines.

Upon comparing these specific Γ scales of the various solvents, it is found that a majority of them are actually one and the same. This again, is very significant: it must be concluded that the solvents of this group all behave in a normal manner towards the solute; that the solvation effects which make the solutions non-ideal, are typical of polyvinyl acetate.

In these Γ scale diagrams, different polyvinyl acetates give lines of various gradients; the greater the complexity, the steeper the line. Suppose now that the line of one particular specimen is drawn at the same angle in every one of the solvent charts, and that the respective scales are adjusted accordingly; we then discover that the lines of the other polyvinyl acetates appear under the same angle in

each chart, that the complete diagrams can be super-imposed upon each other with the greatest accuracy. (Fig. 4).

Here we find revealed a regularity which is independent of the solvent, and which, therefore, must be a constitutive property of polyvinyl acetate as such. What we have achieved by manipulating the functional scales is to cancel out the effects of the inter-molecular forces, and to isolate, in graphical terms, the purely serial relationship.

That this method is generally applicable to true polymer homologues, can be shown in another series—the polyvinyl alcohols. These are insoluble in organic solvents, but soluble in water. Fig. 5. shows that aqueous solutions of different polyvinyl alcohols · can also be "linearized" in a common functional scale.

We may now refer to one of those rules of constitutional additivity which, except for their neglect of the inter-molecular forces, rest on reasonable premises—the much debated "viscosity law" of Staudinger (*).

Einstein (**) derived a formula for the viscous resistance in an ideal case—that of spherical, rigid, and non-polar particles dispersed in a viscous liquid, without assumption of mutual attractions:

$$\eta = \eta_0 \, (1 - K C_v)$$

where η is the viscosity of the whole fluid system, η_0 that of the medium; C_v is the volume concentration of the dispersed phase, and K a constant. Because of the disregard of the inter-particle attractions, this model system is not applicable to real solutions, but under the limitation of maximum dilution, Staudinger transformed it into

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = K_m \cdot M \cdot C \cdot \ldots \cdot \frac{\eta - \eta_0}{c} = (K_m \, \eta_0) \, M$$

where η_{sp} is termed "specific viscosity", K_m is a constant valid for a given polymer-homologous series in a given solvent, M the molecular weight, and c the concentration. In a diagram where absolute viscosity is plotted against concentration, the term $(\eta - \eta_0)$ /c appears as the gradient of the curve in the vicinity of the origin. (Fig. 6).

Our functional Γ scales of viscosity represent these same curves as straight lines throughout their course; their gradient is constant, and there is no need now to limit the rule to low concentrations. The reasoning that led from Einstein's ideal formula to Staudinger's approximation is formally acceptable, if only we write Γ for η i.e., if we substitute absolute viscosity by that function Γ of it which,

* Staudinger, Die hochmolekularen Verbindungen, Berlin, 1932
** Einstein Am. Phys. 19 (1906), 289

according to precept, compensates for the effects of the inter-molecular forces:

$$\Gamma_{sp} = \frac{\Gamma - \Gamma_o}{\Gamma_o} = K_m \cdot M \cdot c$$

where Γ_{sp}/c now to be called the "specific viscosity function", is the gradient of the straight line in the Γ diagram. In other words—if we draw a line parallel to the viscosity axis, the intercepts on it must be in proportion of the respective constitutional parameters, in this case equally well expressed in terms of molecular weights, or volumes, or lengths. (Fig. 7).

We have discussed two special cases in which we may have good reason to think that we know and understand the serial relationship. Outside these we must admit our inability of quantitative construction; we must wait for a super-statistical method which is not yet invented.

S u m m a r y

The inter-molecular forces are still neglected in our current concepts of liquid viscosity. The normal paraffins usually provide the testing ground for new empirical rules of constitutionally additive viscosity, but among the members of this series, the inter-molecular forces are negligible, and agreement is deceptively easy. The result is mostly an invalid generalization including substances of pronounced polarity, supplemented by arbitrary "association factors".

According to graphical evidence, the general viscosity function contains at least two independent constitutive parameters. In truly polymer-homologous series one parameter is constant, the other additive; in these cases, constitutional analysis of viscosity is possible by graphical methods, using functional viscosity scales.
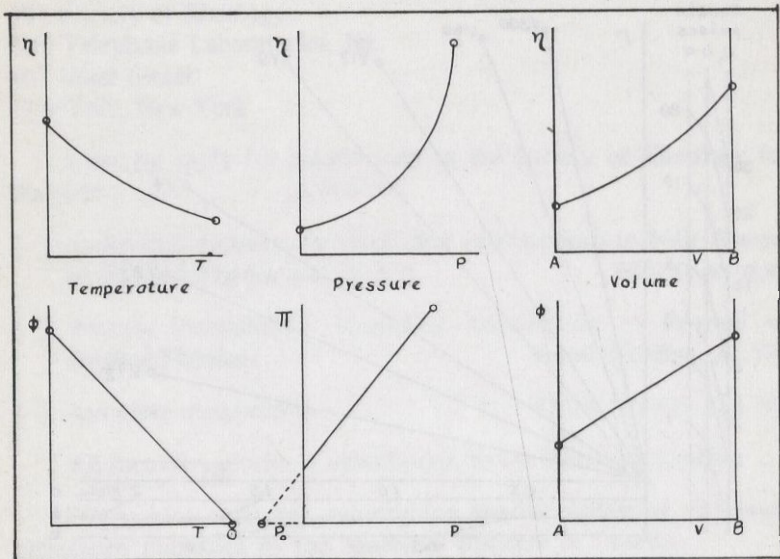
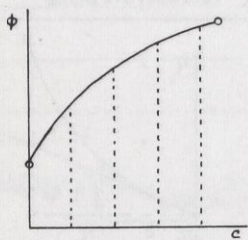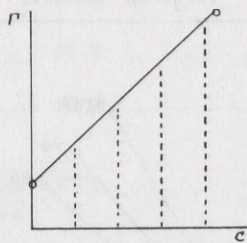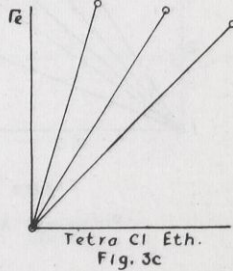Figure 1. The Viscosity Function.

Fig. 2   Concentration, Benzene   Fig. 3

Et. Acetate
Fig. 3a
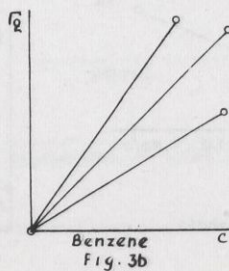
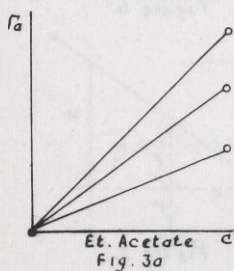Benzene
Fig. 3b
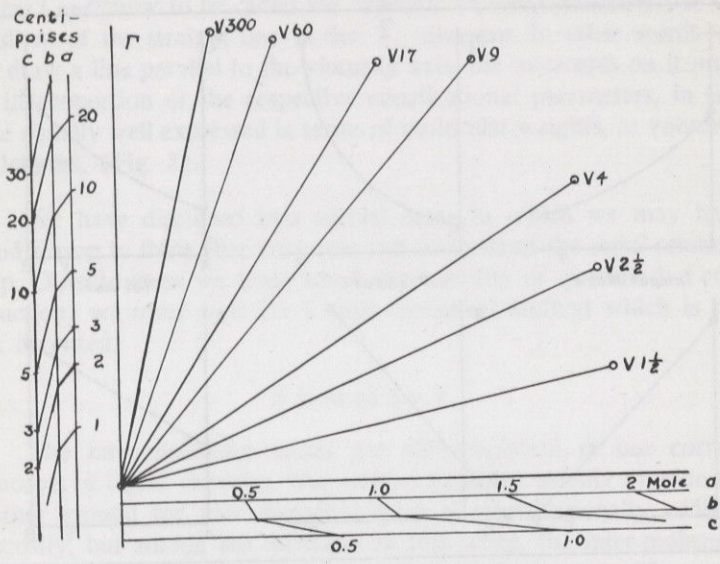
Tetra Cl Eth.
Fig. 3c

Figure 4
Polyvinyl Acetates

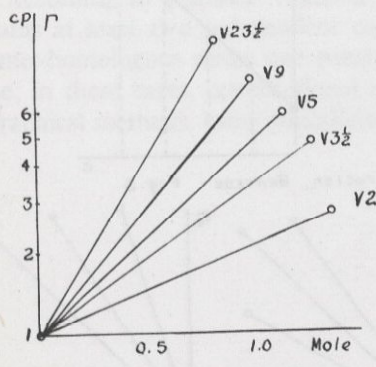a   Ethyl Acetate
b   Benzene
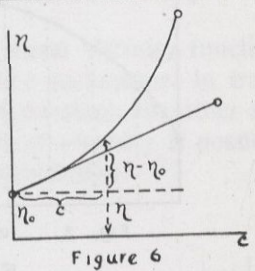c   Tetrachlorethane

Figure 5
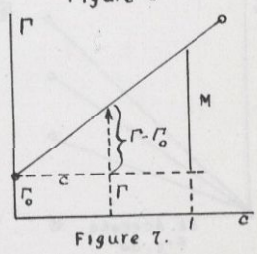Polyvinyl Alcohols

Figure 6

Figure 7.

APPLICATION

Mr. R. L. Peek, Jr., Secretary
The Society of Rheology
Bell Telephone Laboratories, Inc.
463 West Street
New York, New York

I hereby apply for membership in the Society of Rheology for the year .... as follows:

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