formed was filtered off and the filtrate diluted with 50 ml. of water. When this was evaporated on a hot-plate until 25 ml. remained and made acid to Congo red paper with hydrochloric acid, 2-(β-ethoxyethoxy)-4-methylquinoline-7-arsonic acid precipitated.

2-(β-Ethoxyethoxy)-quinoline-5-arsonic acid was obtained from 2-chloroquinoline-5-arsonic acid by the same method used in preparing 2-(β-ethoxyethoxy)-4-methylquinoline-7-arsonic acid.

Summary

1. It was proved that 2-hydroxy-4-methyl-7-aminoquinoline rather than 2-hydroxy-4-methyl-5-aminoquinoline resulted when equimolecular quantities of *m*-phenylenediamine and ethyl acetoacetate condensed in an autoclave at 130°.
2. A number of quinoline amines were produced by the reduction of nitroquinolines.
3. Several 2-hydroxyquinoline and 2-chloroquinolinearsonic acids were obtained from the corresponding quinoline amines by diazotization and coupling with sodium arsenite. The monosodium salt of 2-hydroxy-4-methylquinoline-7-arsonic acid was made.
4. The hydrolysis of 2-chloroquinoline-8-arsonic acid resulted in the formation of 2-hydroxyquinoline-8-arsonic acid.
5. 2-Chloro-4-methylquinoline-7-arsonic acid and 2-chloroquinoline-5-arsonic acid reacted with the monosodium salt of ethylcellosolve to give 2-(β-ethoxyethoxy)-4-methylquinoline-7-arsonic acid and 2-(β-ethoxyethoxy)-quinoline-5-arsonic acid, respectively.

LINCOLN, NEBRASKA RECEIVED JUNE 8, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, SHAWINIGAN CHEMICALS, LTD.]

The Viscosity Function

BY E. P. IRANY

Viscosity is well defined as a physical quantity and accurately measurable. Yet, so far, its relations to temperature, pressure, dilution, chemical constitution, and so forth, are somewhat obscure.

Numerous empirical rules have been proposed but none of them can claim general validity or real physical significance. It may even be questioned whether the task of formulating the exact viscosity laws is not far beyond our present knowledge of the liquid state as such.

It is the main purpose of this paper to offer evidence that such laws exist and can be expressed. Of course, without reliable mathematical assumptions, explicit formulas cannot be derived; the method adopted is one of graphical analysis. It will be shown that, if applied to the large number of measurements and data already available in the literature, this method reveals in them fundamental but so far undiscovered regularities.

Viscosity may be considered a form of friction if the latter is explained in terms of internal forces. Few molecules—probably none—are in so perfect equilibrium that no attractions would be active between them. These forces are chemical by nature though not in intensity, and it is obvious that they are the cause of the mutual interference with motions and mobility of the molecules which is observable as viscosity. The effect may vary between actual chemical union, association, and mere transitory attraction.

For considerations of viscosity the usual distinction between associated and non-associated liquids is only secondary. It is conceivable that a substance may be so perfectly associated that in its larger complexes all residual forces are well compensated; reversely, in a non-associated liquid the identity of the molecules as the structural units may be preserved, but not their independent mobility. Hence, the fundamental distinction should rather be drawn between "ideal" and "non-ideal" conditions, depending not only on existence and magnitude of the intermolecular forces but, primarily, on their constancy. What the mobile entities are—molecules or molecular complexes of some kind—is immaterial as long as problems of internal constitution are not dealt with; for the time being, these must be left outside the scope of this investigation.

The supposed general law of viscosity can only appear in substances of constant structure and force disposition. The question now arises as to where to find and how to recognize "ideal" liquids which may serve as objects of study. Experimental proof of "ideality" such as, *e. g.*, derived from other physical properties, is of doubtful value because it seems that viscosity is still very sensitively affected by intermolecular conditions which would not reveal themselves distinctly enough in calorimetric, gravimetric, or cryoscopic effects.

Recourse must therefore be taken to mere assumption that certain substances are ideal and may be accepted as standards. The best choice are the paraffin hydrocarbons because all that is known about them not only suggests that they are as nearly ideal as possible, but also that this condition is maintained through the whole series which covers the entire range of measurable viscosities.

I. The Viscosity Function of Dilution

Ideal Mixtures.—If two liquids are miscible in such a manner that no specific effects appear between them which depend on and vary with the composition of the mixture, the system can be considered ideal.

For example, the components may be a viscous paraffin oil and a light petroleum fraction with widely differing viscosities at the same temperature. The viscosities fall upon a sharply ascending curve (Fig. 1). This curve represents in graphical form a presumably simple case of the law according to which viscosities should be additive or computable. By selecting any other pair of standard hydrocarbons, a whole series of such curves could be drawn across the diagram.

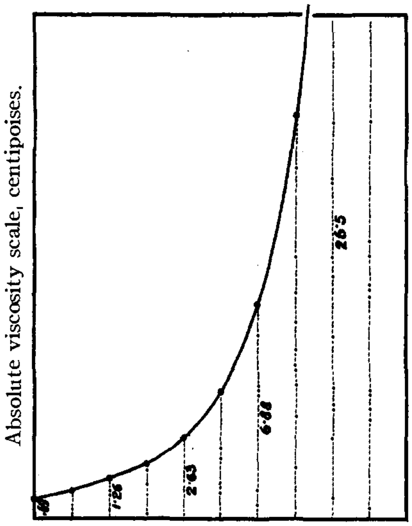

Fig. 1.

If a given system of other components were now to be examined for ideality, one would select two paraffins of the same respective viscosities and construct the ideal curve between them; the mixture under survey would then be recognizable as ideal if its curve coincided with that of the standard.

However, it would be much more convenient to compare in a diagram in which the ideal course would appear as a straight line. For any single standard curve this is easily realized by plotting viscosity not in absolute units, but in a scale which compensates for the curvature in such a manner that a straight line results. This scale would then embody the unknown law according to which viscosities are additive.

There have been numerous attempts to formulate such viscosity functions empirically. For example, the function log (viscosity) has been proposed by Arrhenius.[1] In this case the scale embodying the law of additivity is the logarithm of the natural value of the viscosities, *i. e.*, a semi-log diagram may be used. However, this rule is only a very imperfect approximation, neither accurate nor generally valid. The same applies to other such assumptions, *e. g.*, reciprocal viscosity ("fluidity") by Bingham,[2] or its cube root, by Kendall–Monroe.[3] The true mathematical form of the scale function is unknown, it can only be represented by graphical means.

How the scale function is determined from a number of points fixed by actual viscosity measurements is shown in Fig. 2.

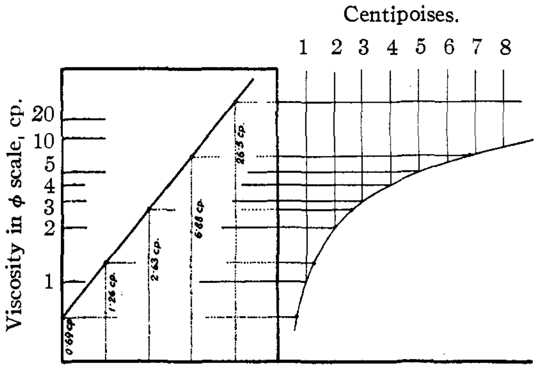

Fig. 2.

A straight line of any convenient position and gradient is assumed to represent the original curve; its intersections at the given mixtures yield the fixed points, and the scale is completed by means of an interpolation curve.

If this is done with other standard curves representing ideal mixtures, a very interesting regularity appears: the resulting scale is always the same, no matter from what particular pair of

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(1) Arrhenius, *Biochem. J.*, **11**, 112 (1917).

(2) Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, 1923.

(3) Kendall and Monroe, THIS JOURNAL, **39**, 1787, 1806 (1917).

components it has been derived. In other words, there is a general function of viscosity according to which it is additive in ideal mixtures. In terms of graphical analysis: *In a diagram in which the scale of viscosity is adjusted so as to make one given ideal mixture appear as a straight line, all other ideal mixtures appear also as straight lines.*

This rule holds with complete accuracy in all ideal mixtures; it is not restricted to those composed of paraffin hydrocarbons, but is independent of the nature of the components. The function expressed in the scale is neither logarithmic, nor otherwise readily representable in mathematical form. It will be referred to as the "Viscosity Function ϕ." This "ϕ-scale," completed over a considerable range of viscosities, appears in Fig. 3.

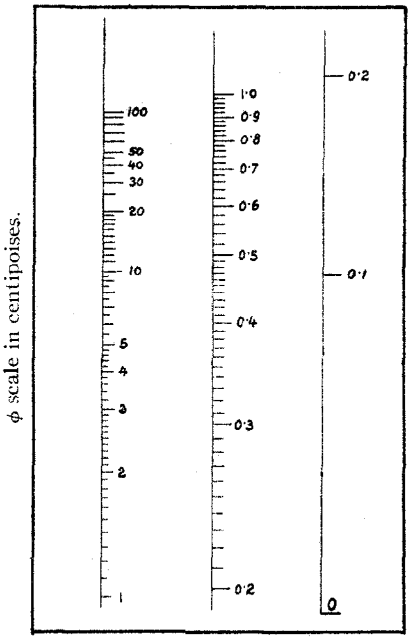

Fig. 3.

The question as to what units should be chosen for the concentrations of the components, *i. e.*, weight, volume, molarity, etc., has been controversial, and each one of the previously proposed empirical rules was based on different terms. It can be shown that the ϕ scale is generally valid if volume concentrations are used, and that all other units of quantity fail to reveal any regularity. Hence, *the unit of quantity with reference to viscosity is volume.*[4]

Various examples of ideal mixtures are shown in Fig. 4. Apart from systems consisting of paraffin hydrocarbons, others of entirely different nature have been described in the literature. Thus, Kendall and Monroe[3] concluded from exact calorimetric, cryoscopic, and density measurements that the following four systems should be ideal:

Benzene–Ethyl benzoate
Benzene–Benzyl benzoate
Toluene–Ethyl benzoate
Toluene–Benzyl benzoate

All these systems appear as straight lines in Fig. 4, including the last-mentioned which failed to satisfy the authors' empirical cube root formula—an exception which they were unable to explain. Actually, there is no exception.

Kendall and Wright[5] investigated other pairs, ethers and esters which should give ideal mixtures. One of these

Phenyl ether–Phenetole

is also shown in Fig. 4.

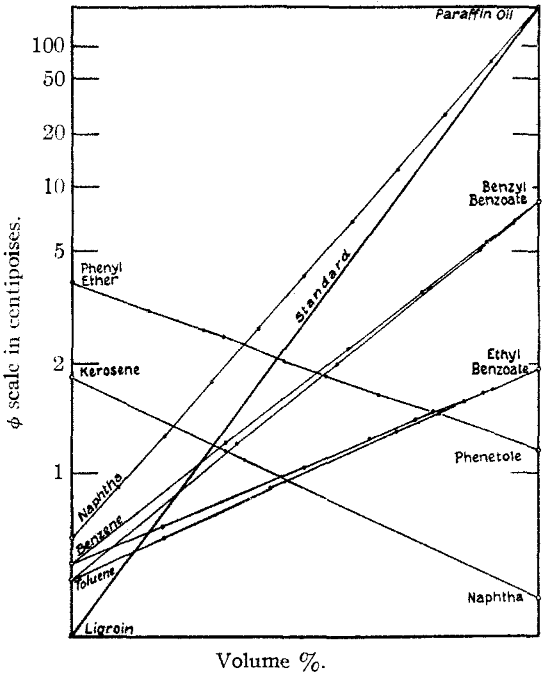

Fig. 4.

Ideal solutions of solid substances can be regarded as ideal mixtures, and they follow the same law. If the viscosities in ϕ scale are plotted against volume concentrations, straight lines result, Fig. 5. Even very complex substances, such as some resins, obey the ϕ function very accurately, also highly concentrated electrolytes, *e. g.*, zinc chloride in water.

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[4] All data used in the diagrams have been recalculated in volume percentages.

[5] Kendall and Wright, THIS JOURNAL, **42**, 1776 (1920).

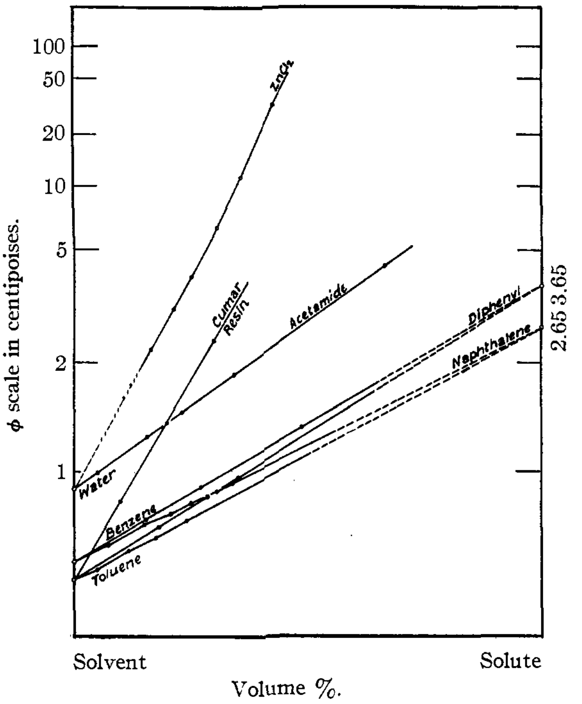

Fig. 5.

Solids in solution are, in fact, components of a liquid system. The straight lines may be extrapolated as far as 100% solute; the viscosity thus intercepted would be that of the solute itself if it could exist in liquid form under the given conditions. It will be seen later that such viscosities, though not readily realizable, have a physical significance; they are the same as those obtained by extrapolating the temperature function below the melting point.

Kendall and Monroe[3] offer evidence for the ideality of

Naphthalene in benzene	Diphenyl in benzene
Naphthalene in toluene	Diphenyl in toluene

In the scale of their assumed cube root formula the extrapolated viscosities of the solutes vary with the solvent: 2.25 and 1.83, respectively, for naphthalene, and 3.44 and 2.82 for diphenyl. In the ϕ scale, however, the lines of each solute converge exactly toward the same point on the 100% axis—2.65 cp. for naphthalene and 3.65 cp. for diphenyl. The temperature function of naphthalene, extrapolated to 25°, gives 2.75 cp., which is in very good agreement with the above value.

Ternary ideal mixtures can be computed in the same manner as binary ones. First, two of the components are combined according to their volume ratios, and the resulting ϕ ordinate is then proportioned against the third component. Examples of this kind are

Benzene–Ethyl ether–Acetone[6]
Allyl phenyl thiourea–Aniline–Toluene[7,8]

The graphical computation of the viscosities of these mixtures agrees perfectly with the measurements.

Some originally binary mixtures may become ternary if a chemical reaction occurs between the components. However, if the reaction is quantitative, and completely consumes one of them, leaving the other in binary mixture with the reaction product, the system may divide itself into two binary parts: A–(AB), and (AB)–B. Many such cases have been plotted and found ideal; *e. g.*

Chloral–(Chloral hydrate)–Water[9]
Stannic chloride–(Mol. compound)–Ethyl benzoate[10]
Allyl thiocyanate–(Subst. thiourea)–Aniline[8]
Allyl thiocyanate–(Subst. thiourea)–Methyl aniline[11]

All these systems give the same kind of diagram; the ascending branches appear as straight lines intersecting at molar ratios of exactly 1:1. Figure 6 shows the last-mentioned system in absolute viscosity and ϕ scale.

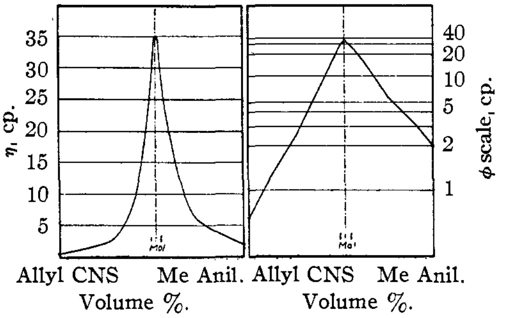

Fig. 6.

Non-ideal Mixtures.—Non-ideal effects occur if either the volume or the force field surrounding the molecules is subject to change. Association generally raises, and dissociation reduces, viscosity from the values it should normally assume. It must be emphasized, however, that these effects need not be real or permanent in order to cause deviations; mere attractions or tendencies in the

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(6) Bingham and Brown, Thesis, Lafayette College, 1921.

(7) Allyl thiocyanate and aniline yield quantitatively allyl phenyl thiourea; the latter forms an ideal binary mixture with excess aniline, and ideal ternary mixtures with toluene.

(8) Kurnakov and Kviat, *Ann. Inst. Polyt. Petrograd,* **20**, 664 (1913).

(9) Dunstan, *J. Chem. Soc.*, **85**, 817 (1904).

(10) Kurnakov, Perelmuter and Kanov, *Ann. Inst. Polyt. Petrograd*, **24**, 399 (1915).

(11) Kurnakov and Zhemchuzhnui, *ibid.*, **18**, 125 (1913).

sense of, *e. g.*, association, would be evident in the viscosity record, without formation of any definite compound.

The difficulty is not in the sensitivity with which viscosity, as a measurable property, responds to these influences; it is mainly in the quantitative evaluation of the results obtained. Empirical formulas are entirely unreliable; they are neither generally valid, nor accurate even within limited ranges. The ϕ scale, however, indicates deviations from the ideal course, no matter how small, or over what range, in the right sense, magnitude and location.

In the following examples the existence of definite association compounds is supported by other evidence, *e. g.*, by maxima in the freezing point curves.

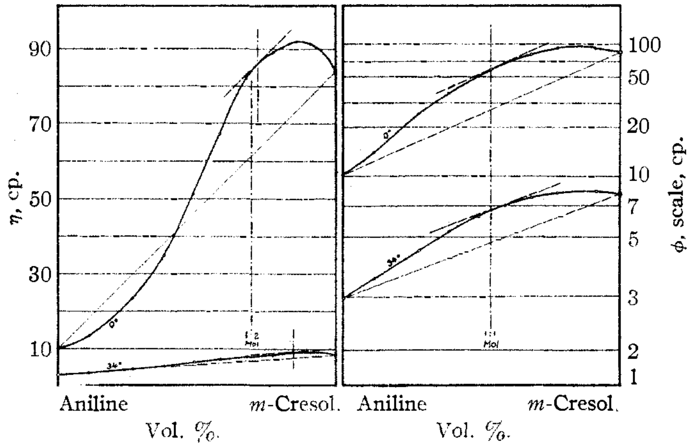

Fig. 7.

Tsakalatos[12] concluded from the absolute viscosities of the systems

m-Cresol–Aniline
m-Cresol–*o*-Toluidine

that compound formation occurred at a ratio of 2:1 moles in both cases. However, Kremann[13] found only 1:1 molar compounds in the freezing point curves. As shown in the diagrams of the first-mentioned system, Fig. 7, the absolute viscosity curves are distorted, and their maxima[14] appear displaced; the ϕ curves deviate steadily toward maxima at exactly equimolar ratios which are not shifted with varying temperature. The second case and many similar systems give analogous figures; among these are, using the data by Bramley[15]

Phenol–Aniline	1:1 mole
Phenol–Dimethylaniline	0.548:0.452 mole
Phenol–Diphenylaniline	No compound

In some cases different compounds seem to occur in the solid and liquid phase. Thus

Phenol–Quinoline[15]

indicate a definite association effect for sharply 1:1 mole. Freezing points show maxima at 2:3 and 2:1 moles, but no singularity at 1:1 mole. The ϕ curve of the system

o-Chlorophenol–Pyridine[15]

has a maximum at 1:1 mole coinciding with the freezing point record; between this mixture and the phenol the ϕ curve, but not the freezing points, shows another sharp maximum.

Where the ϕ curves sag below linearity, dissociation (des-association) either of one or both components must be assumed. Such cases are surprisingly rare; examples are

Phenol–Nitrobenzene[15]
Ethyl alcohol–Benzene[9]

This is interesting, for such "negative" curvatures appear very frequently, not only in absolute viscosity diagrams but also in all empirically assumed scales, particularly where the range of viscosities between the components is considerable. Actually, it seems that associated substances, as a rule, have quite stable constitutional units which do not vary or break down as readily as commonly assumed. This is also evident in their mostly normal response toward temperature changes, as explained in the following.

II. The Viscosity Function of Temperature

Here, again, ideal and non-ideal conditions must be anticipated, depending on the absence or presence of variable individual factors. As in the case of ideal mixtures, the paraffin hydrocarbons may be considered suitable standards.

If the absolute viscosities at different temperatures, *e. g.*, of *n*-octane, are plotted and the resulting curve is straightened into a line by the same method that was used in obtaining the viscosity function ϕ, a scale is obtained which, again, is generally valid. The viscosity–temperature functions of all substances, except those

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[12] Tsakalatos, *Bull. soc. chim.*, **3**, 234 (1908).

[13] Kremann, *Wien. Ber.*, **113**, 878 (1904).

[14] These maxima or minima must be reckoned from the straight line connecting the two terminals and indicating the ideal course. In the points of greatest deviation from this line the tangent to the curve is parallel to it.

[15] Bramley, *J. Chem. Soc.*, **109**, 10, 434 (1916).

of variable nature, appear as straight lines.

There is, moreover, a very significant relation between these two functional scales—the one derived from ideal mixtures, and the other from temperature effects—they are actually identical over their whole extent. *The general law of viscosity relative to temperature is identical with that of viscosity relative to dilution.*

The validity of this postulate has stood the test of all data represented or mentioned in this paper. The complete ϕ scale used in the diagrams and shown in Fig. 3 was assembled from numerous over-lapping sections in which mixture and temperature standards were used indiscriminately. The continuity of the function was found real and precise in all ranges.

Figure 8 shows a selection of liquids, representing various chemical types. The following partial list contains substances which give absolutely straight lines between 0° and their boiling points, using the measurements by Thorpe and Rodger[16] which are recognized as the most accurate on record. Lack of space prevents the reproduction of the diagrams.

Hydrocarbons.—Isoprene, *n*-pentane, isopentane, *n*-hexane, isohexane, diallyl, *n*-heptane, isoheptane, *n*-octane, benzene (0–70°), toluene, *o*-, *m*-, *p*-xylene, ethyl benzene.

Ethers.—Diethyl, methyl propyl, ethyl propyl, dipropyl.

Esters.—Methyl formate, methyl, ethyl and propyl acetates, propionates, *n*- and isobutyrates, valerates.

Ketones.—Acetone, methyl ethyl, diethyl, methyl propyl, methyl butyl.

Halogen Compounds.—Propyl chloride, propyl bromide, propyl iodide, isopropyl chloride, methylene dichloride, chloroform, carbon tetrachloride, ethylene chloride, ethylidene chloride, perchloroethylene, bromine.

Sulfur Compounds.—Methyl sulfide, ethyl sulfide, carbon disulfide, thiophene.

Only very few liquids—the lowest alcohols and fatty acids, for example—show distinct and significant deviations from the straight course, due without doubt to variable association. Even water follows an absolutely straight line with the exception of the well-known anomalous region above its melting point. These examples show very clearly that association in itself does not interfere with normal behavior as long as it remains constant; associated substances may very well conform with ideality.

The almost universal prevalence of ideal conditions in pure substances is important in view of the fact that ideal mixtures are far less common. This suggests that pure substances are in most cases homogeneous, and contain molecular entities of uniform structure. Consequently, the various fractional association factors ascribed to nearly all of them by Ramsay and Shields,[17] Traube,[18] and McLeod,[19] do not seem to have a purely constitutional meaning, *i. e.*, do not correctly represent association.

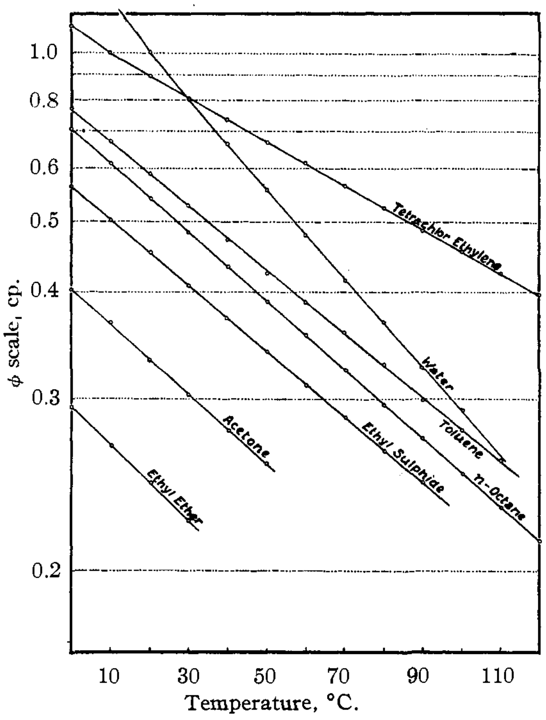

Fig. 8.

The Critical Region.—The present analysis deals with the viscosity of liquids; that of gases is an entirely different phenomenon, and of a negligible order, if expressed in the same measure. The viscosity typical for the liquid state must disappear at the critical temperature; the viscosity of gases is no functional extension of it. One may, therefore, speak of a "zero level of liquid viscosity" at the discontinuity between the gaseous and the liquid states. Since the linearity of the ϕ functions is perfect within the recorded ranges, an extrapolation as far as the critical point may be considered significant.[20]

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(16) Thorpe and Rodger, *Phil. Trans.*, **185**, 397 (1894); *Proc. Roy. Soc.* (London), **60**, 152 (1896).

(17) Ramsay and Shields, *Trans. Chem. Soc.*, **63**, 1089 (1893).

(18) Traube, *Ber.*, **30**, 283 (1897).

(19) McLeod, *Trans. Faraday Soc.*, **19**, 17 (1923).

(20) Data on viscosities above the boiling points of, *e. g.*, benzene, toluene, ether, ethyl and isobutyl acetate, ethyl bromide, carbon tetrachloride, etc., by Heydweiller [*Wied. Ann.*, **59**, 193 (1896)], show that the general straight course continues. Phillips [*Proc. Roy. Soc.* (London), **87**, 48 (1912)] measured viscosities of liquid carbon dioxide within the critical region; these are on a curve which does not merge into that of the gas viscosities, but intersects it.

The linearity of the ϕ function is not affected if, instead of centigrade, reduced absolute temperatures $(1-T/\Theta)$ are used as abscissas. In such a diagram all lines should converge toward one point, because at the critical temperature Θ, or for $T_r = 0$, all liquid viscosities become equal, *i. e.*, nil. As shown in Fig. 9, many lines are crowded together, and reach the critical temperature at a reasonably well defined level which, therefore, can be taken as that of zero liquid viscosity. However, there are also several whose intercepts indicate viscosities of considerable magnitude at their known critical temperatures.

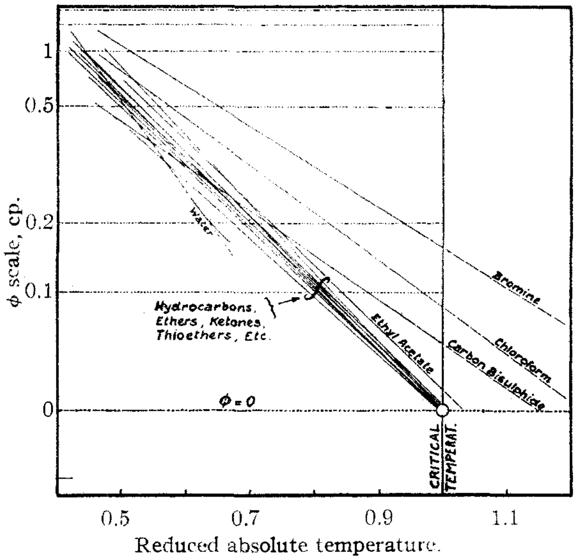

Fig. 9.

This probably means that in these cases the critical temperatures, as of record, are too low, that the observable disappearance of the surface does not mark the end of all liquid structure. That this survival should be most appreciable in substances with strong internal forces, is to be expected and is borne out in Fig. 9.

If then it be justifiable to consider the critical discontinuity expanded over an appreciable temperature interval, this would reach from the conventionally observed critical temperature upward as far as another "limiting" critical temperature which would be defined by the actual and complete disappearance of liquid viscosity.

This critical range can be estimated in Fig. 9; it is represented by the distance from $T_r = 0$ to the intersection of the ϕ line with the zero level.

TABLE I

ABSOLUTE CRITICAL TEMPERATURE

	Observed	"Limiting"	Range
n-Pentane	470	464	...
n-Hexane	507	500	...
n-Heptane	540	541	...
n-Octane	569	572	...
Benzene	565	566	...
Toluene	594	597	...
Ethyl ether	466	474	8
Acetone	508	514	6
Ethyl acetate	525	541	16
Thiophene	590	615	25
Carbon disulfide	550	633	83
Methylene chloride	518	594	76
Chloroform	533	649	116
Carbon tetrachloride	557	676	119
Propyl chloride	494	520	26
Ethyl bromide	499	576	77
Ethyl iodide	554	680	126
Bromine	575	810	235

A peculiar exception is that of water. Its line in Fig. 9 is unusually steep and passes through the zero level at much lower than the critical temperature—the only case of this kind. This is obviously impossible, and it must be assumed that a structural rearrangement occurs at some higher temperature which would cause the curve to reach the critical point. Three viscosity measurements between 100 and 153° seem to indicate this course which is probably due to increasing association.

The expansion of the critical discontinuity into a range which, according to the above estimates, may assume the extent of hundreds of centigrade degrees, is of great fundamental importance. Of course, the correctness of the extrapolation of the ϕ lines depends on the absence of discontinuities in the large temperature ranges within which no viscosity data are available. Viscosity measurements over the entire course and up into the critical region, particularly on such substances as, *e. g.*, bromine, would yield very valuable information.

III. The Viscosity Function of Pressure

Moderate variations of pressure hardly affect the viscosity of liquids. It is necessary to employ thousands of atmospheres in order to study the quantitative relation between viscosity and pressure. Such measurements have been carried out by Bridgman[21] in a specially constructed viscometer.

Absolute viscosity, plotted against pressure in atmospheres, yields curves which, after a very

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(21) Bridgman, *Proc. Nat. Acad. Am.*, **11**, 603 (1925).

gradual ascent, bend sharply upward. In ϕ scale, these curves are not represented as straight lines, but strongly concave toward the pressure axis, Fig. 10.[22]

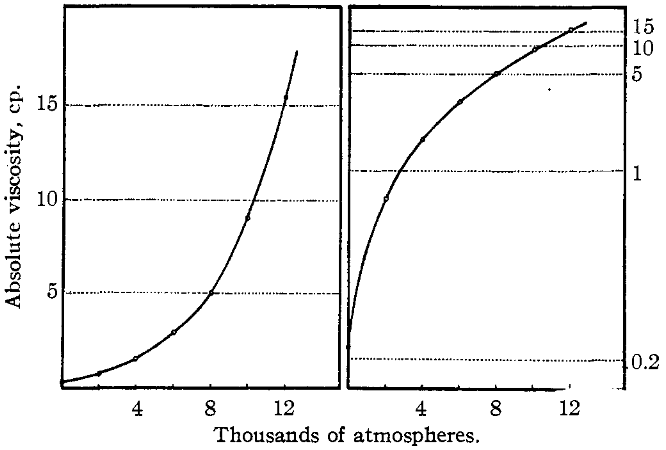

Fig. 10.—Viscosity of *n*-pentane at 30° under high pressures.

The effect of pressure on viscosity, therefore, is not additive in the same function as that of dilution and temperature, but follows a different law.

However, it is possible to rationalize this relation by the same method as was used in the construction of the ϕ scale in Fig. 2. Choosing, *e. g.*, the isotherm of *n*-pentane at 30° as a standard, a functional scale Π can be obtained. This Π scale, shown and applied in Fig. 11, represents the pressure functions of all hydrocarbons, at various temperatures, as well as those of all ideal substances, as straight lines. *All viscosity-pressure functions follow a general law. This law is different from that relating viscosity with dilution and temperature.*

Figure 11 shows Bridgman's data on paraffin hydrocarbons at two different temperatures, and it reveals a very interesting fact: all lines meet in one point.

In this point, viscosity assumes the same value at all temperatures, and for all paraffins. This is conceivable only if the intermolecular forces which control viscosity are counterbalanced by external pressure, so that their effect disappears. Hence, the negative abscissa of the intersection point is the "internal" or cohesional pressure of the liquid, and its level must be that of zero viscosity. That all paraffin hydrocarbons should have the same internal pressure is well in keeping with their known nature and relationship.

The intersections of different isotherms of the same liquid always fall on the zero level of the Π function, except in those cases where association is known to be variable, *e. g.*, water, alcohols, glycerol, etc. The negative pressure intercepts which indicate the internal pressures, are characteristic constants of the normally behaving substances. The values obtained from Π scale diagrams of Bridgman's data agree very well with those deduced by other methods, *e. g.*, from van der Waals' equation or the latent heat of vaporization. It is impossible to reproduce all the diagrams but the resulting internal pressures appear in Table II.

The Π functions of substances of variable association are not linear but they approach the straight course at high pressures, and the negative pressure intercept assumes a definite value.

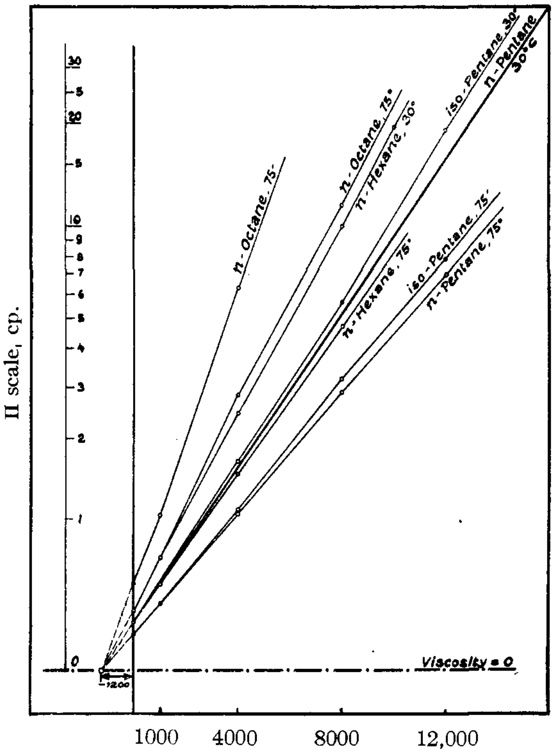

Fig. 11.

In the series of monohydric paraffin alcohols, an interesting regularity is found: the asymptotical intercepts, *i. e.*, the maximum internal pressures

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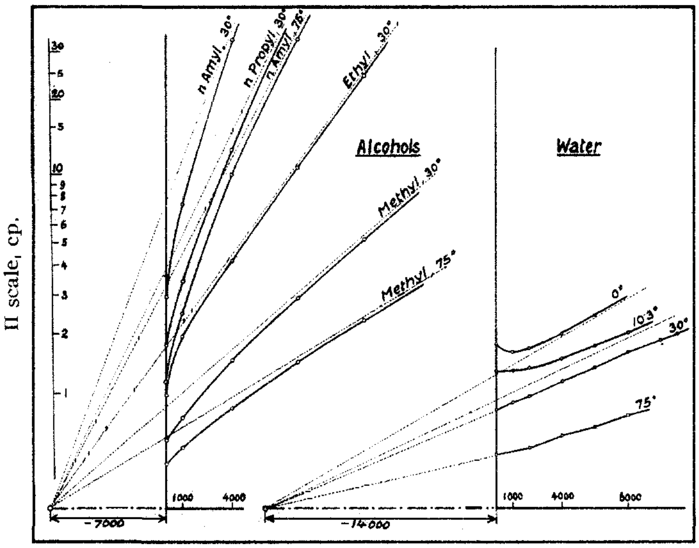
(22) On the convexity of the curves which Bridgman obtained in absolute viscosity scale, he remarked: "This is unusual; most pressure effects become relatively less high at high pressures by a sort of law of diminishing return." The ϕ scale represents this "diminishing return" without inconsistencies and apparently in its true evaluation.

are identical for all members of the series (Fig. 12). It would seem, therefore, that the internal pressure is characteristic, not only for each liquid, but for whole homologous series.



Pressure, atm.

Fig. 12.

The isotherms of water, Fig. 12, run differently; they are convex, but their asymptotes also meet in one point on the pressure axis, with an intercept twice as large as that of the alcohols. Above 30°, the isotherms are straight lines.

TABLE II

		Internal pressures, atm.
All paraffin hydrocarbons		1200
Benzene		1200
Ethyl ether		1400
Chlorobenzene		1400
Alkyl benzenes		1500
Bromobenzene		2000
Chloroform		2300
Aniline		2400
Acetone		2500
Carbon disulfide		2700
Alcohols	(Limit)	7000
Water	(Limit)	14000
Glycerol	(Limit)	14000

IV. The General Viscosity Function; Constitution

The relations of viscosity to volume (dilution), temperature, and pressure must be considered special cases of the equation of state for liquids. The combination of these partial functions into the unknown general law is, of course, beyond the means of the graphical method. Nevertheless, the two functional scales, ϕ and Π, can be used for the computation of all viscosities of normal liquids if three elements are known. These are material factors characteristic for any given substance.

A complete rationalization would have to include that of constitutional additivity of these constants.

Whether the additivity of ϕ in terms of volume, or that of Π in terms of intermolecular attractions, also applies to the constituent parts of the chemical molecule; in other words, whether additive atomic values of ϕ or Π exist, cannot be definitely answered. This depends on precisely what may be understood under comparable conditions, and what kind of unit the "molecule" of a liquid really is.

For the time being, it must be realized that "constitution" to which viscosity phenomena may be related, is not necessarily that accepted in a purely chemical sense. The independently mobile entities whose movements or mobility viscosity records may, but again, may not be the individual chemical molecules.

All available facts point toward the necessity of a finer graduation of intermolecular relationships, apart from, and between complete independence and permanent association. If all these intermediate forms could be included into, and rationalized within a broader concept of constitution, the additive features of viscosity would reveal themselves more clearly.

Summary

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 ϕ 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 Π scale shows the correct magnitude of the internal pressures of liquids which, according to this evidence, are characteristic for whole series of related substances.

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The Dielectric Properties of Acetylenic Compounds. X. Equipment for Measuring Dielectric Constants of Gases. The Polarity of Gaseous Monoalkyl Acetylenes

BY F. J. KRIEGER AND H. H. WENZKE

In order to determine accurately the low moments of the monoalkyl acetylenes it is necessary to abandon the method of solutions used in the previous papers of this series and employ the temperature variation method on the vapors of the materials to be investigated. This paper describes an apparatus for measuring the dielectric constants of gases and a method for determining their polarizations and gives data obtained for five homologs.

Description of Apparatus

The present apparatus for measuring the dielectric constants of gases was designed with a view to ruggedness and stability in operation. It is essentially a beat-frequency oscillator designed for measuring extremely small capacities with great accuracy. It offers as points of superiority over those described by Groves and Sugden[1] and by Zahn,[2] first, alternating current operation for convenience and maintained foolproof operation; second, excellent stability, combined with the comparison capacity method of eliminating residual drift, as mentioned by Zahn, but not used by Groves and Sugden; and, third, a direct-meter reading of zero beat which, because of precautions taken to eliminate entirely any tendency of the two oscillators in the circuit to "lock in," gives a much higher precision of setting than does either the resonance method of Groves and Sugden or the audible-beat method of Zahn.

Inspection of the circuit diagram, Fig. 1, indicates that the disposition of the circuit capacities, together with the capacity to be measured is similar to that used by Groves and Sugden. However, where they use the amplitude of the voltage developed at a particular point on a steep resonance curve as an indication of resonance, we use the heterodyne note between two oscillators. Frequency drift is eliminated by stabilizing one oscillator with a quartz crystal and furnishing the other oscillator with a suitable reference standard for correcting against the effect of drift should any occur.

Vacuum tube V_1, together with the inductance L_1, the capacity C_1, and the crystal X, form an oscillating circuit at a frequency of 500 kc. per second. The crystal is of the low temperature coefficient type and the oscillator is such that constancy may be assured to a precision of six cycles per degree C.

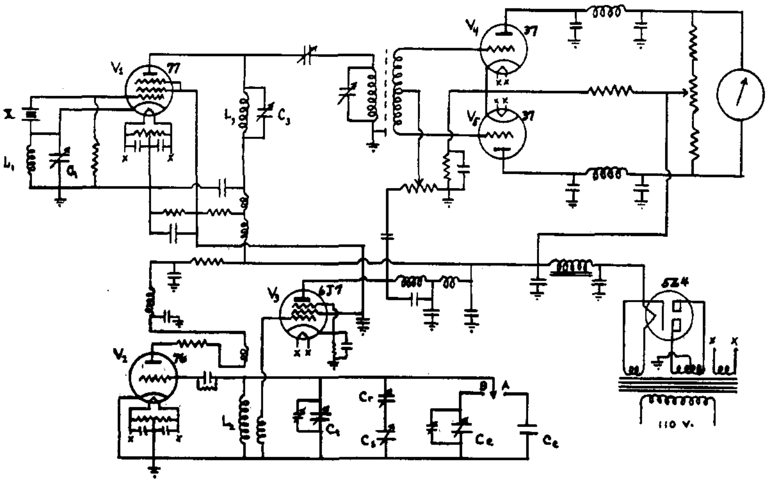

Fig. 1.—Circuit diagram of beat-frequency oscillator used in measuring dielectric constants of gases.

Vacuum tube V_2, the inductance L_2, and the capacities C_t, C_r, C_e and C_s, form the variable oscillator whose frequency is that of the second harmonic of the crystal oscil-

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[1] Groves and Sugden, *J. Chem. Soc.*, 1094 (1934).

[2] Zahn, *Phys. Rev.*, **24**, 400 (1924).