*The Structon Theory of Glasses and Solutions**

By Maurice L. HUGGINS**

(Received August 29, 1955)

Introduction

Many properties of liquids and solids can usefully be considered as dependent on the kinds and numbers of "structon" present. This word, "structon," has been invented by the writer[1,2]. It may be defined as "an atom (or molecule or group of atoms of a given kind) in a given environment." The structon concept is especially valuable when considering properties which are approximately additive—that is, which can be made up of contributions of the different types of structon present. Volume and molar refraction are examples of such properties. Certain thermodynamic functions, such as energy and heat content, would also be expected to be approximately structon-additive. As would be expected, structon additivity is usually somewhat better than atomic or molecular additivity.

The "environment" referred to here is that of closest neighbors only. More distant atoms or molecules are considered to be of negligible influence on the properties dealt with.

This paper deals primarily with solutions—both solid solutions (such as ordinary glasses) and liquid solutions. The usefulness of the structon concept is most evident in dealing with solutions in which different structon types differ so much in stability that, over a composition range, only those few types exist, in significant relative amounts, which are the most stable.

Glasses

Well-annealed sodium silicate glasses conform to this requirement, as will be shown. These glasses have a structural arrangement which was stable at a high temperature and which has been frozen in as the glass cooled. A graph of the volume as a function of the composition (Fig. 1[3-6]) shows straight-line segments, with sharp breaks between them. It has generally been assumed that behavior of this sort indicates compound formation, but x-ray studies[7] give no evidence of compounds.

The writer has proposed[1,2] the alternative explanation that in each composition range there are only a few types of structons, the breaks occurring at compositions at which one type of structon disappears and another appears.

Consider first the structure of pure silica, SiO_2. Many years ago the writer[8] showed that in crystalline silica (quartz) each silicon atom is surrounded by four close oxygen neighbors and each oxygen atom is adjacent to two silicons. The structure may be described as being composed of structons of the two types represented by the formulas Si(4.0) and O(2Si).

It does not matter, for present purposes, whether one considers the forces between adjacent silicon and oxygen atoms to be essentially covalent or ionic. Actually, there is good reason to believe that they are intermediate in character, involving electronpair bonds with a considerable degree of polarity.

In *vitreous* silica, x-ray and other evidence shows that the same two structon types exist, practically exclusively, as in crystalline silica.

If a little sodium oxide is added to silica and a glass is produced, there must of course be some new types of structons. The types to be considered may be limited to a few, either on the basis of simple theoretical considerations or, reasoning by analogy, making use of the large body of information which has been accumulated regarding the structures of *crystalline* silicates. All of the sodium atoms (or ions) would be expected to be surrounded by oxygens, with no sodium-silicon contacts. The number of oxygens around each sodium, for greatest stability, cannot be assumed *a priori*, but a good guess would be six. There would then be structons

* Communication No. 1746 from the Research Laboratories of the Eastman Kodak Company, Rochester 4, New York, U.S.A.

** Fulbright Exchange Professor, Osaka University, and Lecturer, Kyoto University, 1955-56.

1) M.L. Huggins, *J. Phys. Chem.*, 58, 1141 (1954).
2) M. L. Huggins, *J. Am. Ceramic Soc.*, 38, 172 (1955).
3) M.L. Huggins and K.H. Sun, *Glass Industry*, 24, 472 (1943).
4) F.W. Glaze, J.C. Young and A.N. Finn, *Bur. Stand. J. Res.*, 9, 799 (1932).
5) G.W. Morey and H.E. Merwin, *J. Opt. Soc. Am.*, 22, 632 (1932).
6) S.R. Scholes, "Handbook of the Glass Industry", Ogden-Watney Publishers, Inc., New York, N.Y. (1941), p. 61.
7) See, for example, B.E. Warren, *J. Appl. Phys.*, 8, 645 (1937), or *J. Am. Ceramic Soc.*, 24, 256 (1941).
8) M.L. Huggins, *Phys. Rev.*, 19, 363 (1922).

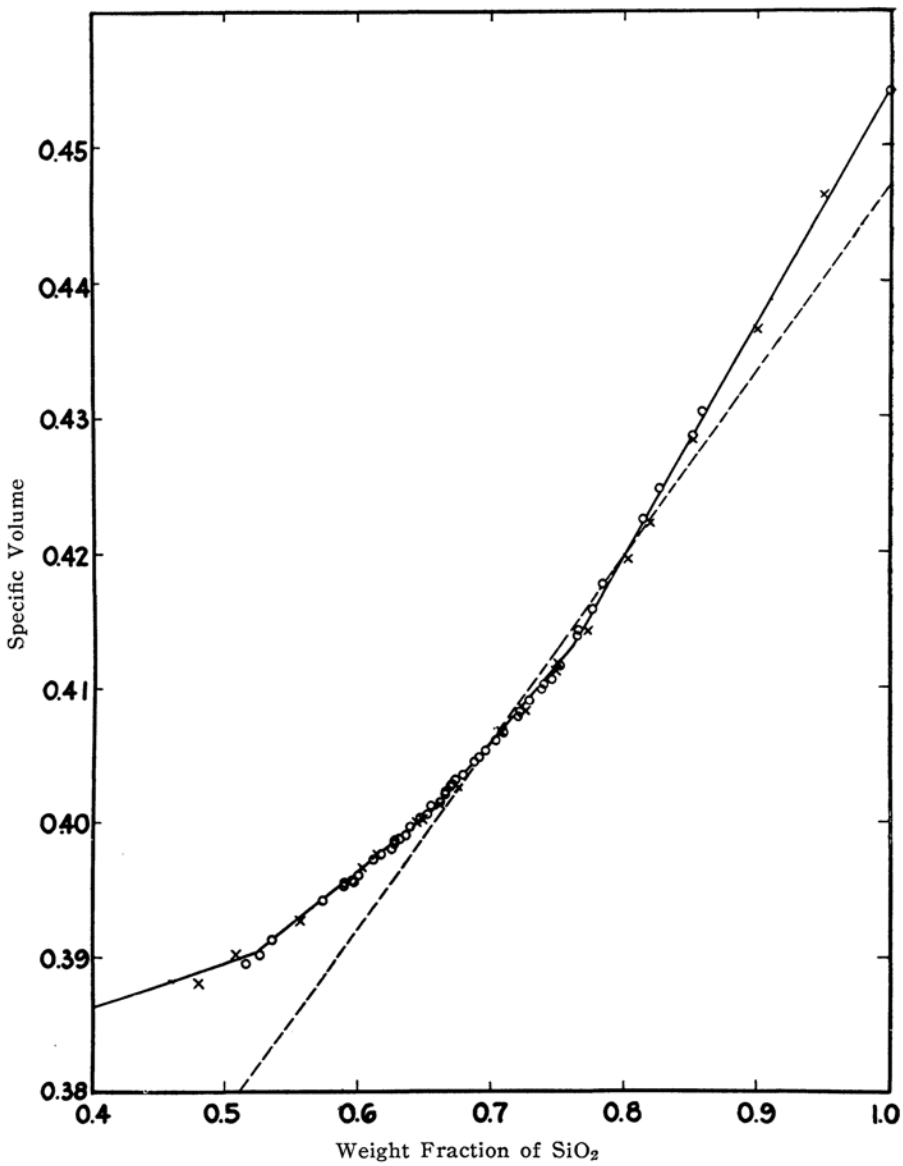


Fig. 1. Specific volumes of sodium silicate glasses[3]. Circles represent data by Glaze, Young, and Finn[4]; crosses denote data by Morey and Merwin[5]. The dashed line represents a relationship given by Scholes[5].

of formula Na(6.0). One would expect some oxygens to be surrounded by two silicons (as in pure silica), plus one sodium. An environment of two silicons and *two* sodiums would require a greater departure from short-range neutrality, and so would be less reasonable. As a rough measure of this departure, one can calculate a hypothetical "structon charge," by considering the structure as composed of sodium, silicon, and oxide *ions* and adding algebraically the charge on an oxygen (-2) and the appropriate shares of the charges on each of the ions surrounding that oxygen: +4/4 for each silicon neighbor and +1/(coordination number of the sodium) for each sodium neighbor.

There must also be oxygen-centered structons in which the central oxygen has less than two silicon neighbors. Oxygen-centered structons with only sodium neighbors (essentially oxide ions) have never been found in silicate crystals and would be unreasonable theoretically. Oxygen-centered structons with only one silicon neighbor would be expected to have some sodium neighbors, enough to give a close approach to regional

neutrality. The number is *a priori* unknown.

The minimum number of structon types capable of giving the over-all composition is five (See the section on "The Structon Number Rule"). For any given set of five types which one chooses to assume, it is easy to compute the limits of existence of the set and, within those limits, the relative numbers of structons of each type. The procedure may be illustrated for the following assumed set:

Si(4.0) Na(6.0) O(2Si) O(2Si, Na) O(Si, 3Na).

For convenience, an amount of glass which contains, on the average, one oxygen atom is considered. The number of structons of each type in this amount of glass is designated as N, with the appropriate structon formula as subscript. The numbers of silicon and sodium atoms in this amount of glass are represented as N_{Si} and N_{Na}, respectively.

With these definitions, the sum of the numbers of oxygen-centered structons equals unity:

$$N_{O(2Si)}+N_{O(2Si,\ Na)}+N_{O(Si,\ 3Na)}=1 \quad (2)$$

The number of oxygen-to-silicon contacts equals the number of silicon-to-oxygen contacts. Hence,

$$2N_{O(2Si)}+2N_{O(2Si,\ Na)}+N_{O(Si,\ 3Na)} =4N_{Si(4.0)}=4N_{Si} \quad (2)$$

Likewise, the number of oxygen-to-sodium contact equals the number of sodium-to-oxygen contacts:

$$N_{O(2Si,\ Na)}+3N_{O(Si,\ 3Na)}=6N_{Na(6.0)}=6N_{Na} \quad (3)$$

The valences must be balanced, to satisfy the requirement that the glass as a whole be electrically neutral. Hence,

$$4N_{Si}+N_{Na}=2 \quad (4)$$

By solving the foregoing equations simultaneously, the numbers of the different types of structon are obtained as functions of the composition. If the composition is expressed as N_{Si}, the equations are as follows:

$$N_{Si(4.0)}=N_{Si} \quad (5)$$
$$N_{Na(6.0)}=2-4N_{Si} \quad (6)$$
$$N_{O(2Si)}=-7+16N_{Si} \quad (7)$$
$$N_{O(2Si,\ Na)}=6-12N_{Si} \quad (8)$$
$$N_{O(Si,\ 3Na)}=2-4N_{Si} \quad (9)$$

The limits of the composition range, within which this assumed set of structons is capable of existence, are the compositions at which the numbers of one or more of the structon types become zero. The maximum value of N_{Si} is 1/2, the value in pure silica. Then, according to Eqs. 6, 8, and 9, the number of structons of each of the types, Na(6.0), O(2Si, Na) and O(Si, 3Na), becomes equal to zero. The minimum value of N_{Si} is 7/16, the composition at which the O(2Si) structons disappear. *This is at precisely the location of the first break in the curve representing the experimental volume data* (See Fig. 2[9,10,11]).

Similar calculations have been made for all other sets of structons which seem at all reasonable. All sets give a lower limit for N_{Si} which is in disagreement with experiment, except those which are like the set just considered, except for replacement of Na(6.0) and O(Si, 3Na) by Na [$(w+3)$O] and O(Si, wNa), with w equal to an integer. The choice of $w=3$, giving the structons tentatively assumed, seems to be the most reasonable. Moreover, other choices lead to disagreement with experiment in the next composition range. It seems necessary to conclude that the chosen set of structons is the one actually existing in these glasses in this composition range.

A similar analysis leads to the conclusion that in Range II, with N_{Si} between 0.40 and 0.4375, the only structons present in significant amounts are the following:

Si(4.0) Na(6.0) O(2Si, Na)
O(2Si,2Na) O(Si, 3Na)

For N_{Si} less than 0.40, there are several possibilities, between which the data now being considered do not enable one to distinguish. A reasonable set for the range $0.375<N_{Si}<0.40$ would be the following:

Si(4.0) Na(6.0) Na(5.0) O(2Si, 2Na) O(Si, 3Na)

This might be followed, for $0.333<N_{Si}<0.375$, by the set:

Si(4.0) Na(5.0) O(2Si, 2Na)
O(Si, 3Na) O(Si, 4Na)

At the sodium metasilicate composition, $N_{Si}=0.333$, the O(Si, 3Na) structons would necessarily disappear. The four remaining types are those occurring in the crystalline compound of this composition[12].

From these assumptions, or any of several others which also appear reasonable, one would expect a break in the property-composition curve at $N_{Si}=0.375$. The contributions of the different structon types might be such, however, as to make the break a very minor one. Experimentally (Fig. 2), the volume data are insufficient to tell whether or not a small break actually occurs at this composition.

From the slopes and intercepts of the straight-line segments of the experimental

9) F. Winks and W.E.S. Turner, *J. Soc. Glass Technol.*, 15, 185T (1931).
10) M.L. Huggins, *J. Opt. Soc. Am.*, 30, 420 (1940).
11) M.L. Huggins, *Ind. Eng. Chem.*, 32, 1433 (1940).
12) P.A. Grund and M.M. Pizy, *Acta Cryst.*, 5, 837 (1952).

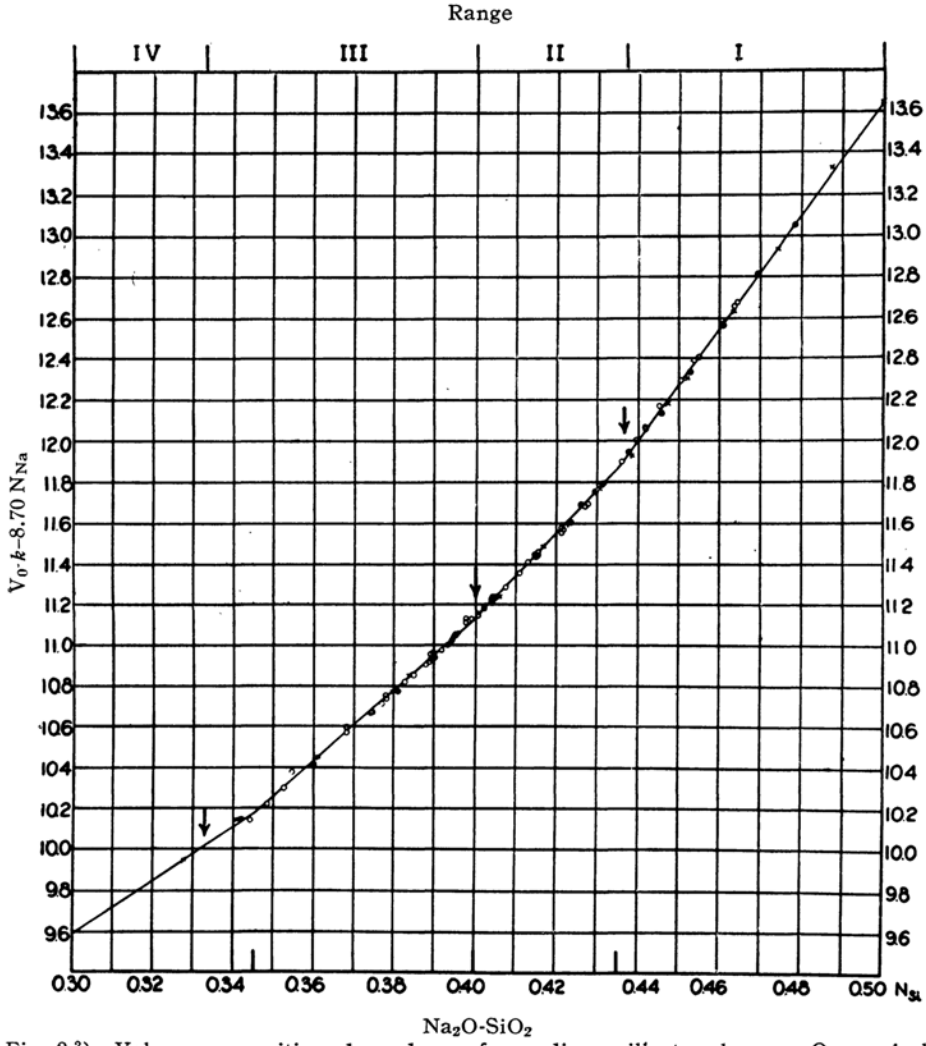


Fig. 2.[2] Volume-composition dependence for sodium silicate glasses. Open circles represent data of Glaze, Young, and Finn[4]; crosses denote data by Morey and Merwin[6]. Solid circles denote data by Winks and Turner[9] The small constant, k, is included to allow for difference in annealing techniques. The straight lines conform to relationships deduced empirically,[10,11] which differ very slightly from those recently obtained theoretically[1,2].

volume-composition curves, it is possible to deduce some relationships between the volume contributions of the different structon types. Their individual contributions, however, cannot be deduced from the data for this system alone. When suitable measurements are made for other systems containing some of the same types of structons, it should be possible to compute the individual structon contributions to the total volume. Similar remarks apply with respect to other additive properties.

Liquid Solutions

The structon types existing in most liquid solutions include not only those in the set giving the lowest free energy, but also others, only slightly less stable, in dynamic equilibrium with them. It is possible, using well-known methods, to develop a quantitative theory of such solutions, relating the numbers of the different types of structons to their relative energies and to the over-all composition. These numbers can then be used as a basis for the theoretical calculation of various additive properties.

The present discussion, however, will be limited to consideration of a few molecular solutions which can be dealt with in much the same manner as the sodium silicate glasses. The essential requirement for this is that there are strong intermolecular inter-

actions of only one type or of only a few types, differing sufficiently in stability from one another. Many solutions in which their is strong intermolecular hydrogen-bonding conform to this requirement. Evidence for this is the observed broken-line dependence of certain properties on composition.

In these solutions it is the *molecular*, rather than the *atomic*, environment which is important for the present purpose, hence "molecular-structon" types will be discussed. Since the hydrogen-bond forces between molecules are much stronger than those of other types, only hydrogen-bonded neighbors need be specified in characterizing the structons.

As a first example, consider dilute solutions of dimethyl formamide and phenol in carbon tetrachloride. As is shown by Fig. 3[13], taken from a recent paper by Arshid et al.,[13] a

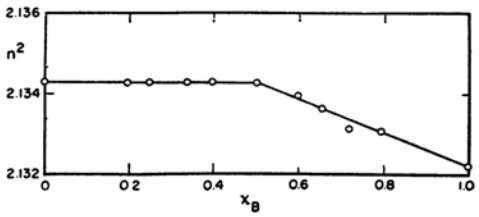


Fig. 3.[13] Variation of refractive index (n) with composition, for solutions of dimethyl formamide (A) and phenol (B) in carbon tetrachloride.

plot of the square of the refractive index against the relative proportions of dimethyl formamide and phenol shows two portions which are essentially straight, meeting at the equimolar composition.

This behavior is consistent with the assumption that the forces between like molecules are much weaker than those between unlike molecules, and that the latter produce a 1:1 complex, presumably by hydrogen-bonding:

$$\underset{\text{A}\cdots\cdots\cdots\cdots\text{B}}{R_2N-CH=O\cdots\cdots HO-C_6H_5}$$

The sets of structons can be represented as follows:

Range I:	A(O)	A(B)	B(A)	
Range II:		A(B)	B(A)	B(O)

Here, A(O) designates an A molecule which has no strong interaction with any of its neighbors, A(B) denotes an A molecule strongly attached to a single B neighbor, etc. (Note that "O" in these molecular-structon formulas represents "zero," not "oxygen").

The experimental curves might also be interpreted in terms of a complex of formula A_2B_2 or A_3B_3 or A_iB_i, with i any integer, but in this case the simplest formula seems as reasonable as any.

The relative numbers of the different types of structons (in Range I, for example) are readily computed from the following relationships between the mole fractions:

$$x_{A(O)}+x_{A(B)}+x_{B(A)}=1 \qquad (10)$$

$$x_{A(B)}=x_{B(A)} \qquad (11)$$

The first of these is a normalizing equation, expressing the requirement that the sum of the mole fractions equals unity. The second shows that the sum of the A-B contacts equals the sum of the B-A contacts. The limits of this range, at mole fractions of phenol equal to zero and 1/2, are the concentrations at which, according to these equations, the mole fraction of at least one of the structon types equals zero.

In the equimolar solution, the only structons present are of the A(B) and B(A) types. From the properties of this solution, one can deduce the contributions of the A·····B complex, but not (without supplementary assumptions) those of the individual structons.

It may be noted that the refractive index squared, which is plotted in Fig. 3, is not itself an additive property, but is related[14,15] by the simple equation

$$n^2=1+\frac{R}{V} \qquad (12)$$

to the (Newton) refraction and the volume, both of which would be expected to be approximately structon-additive. Breaks in the plot of n^2 *versus* composition would be expected, at the same compositions as breaks in the R and V curves, i.e., at the points where changes of structon type occur.

Because of the proportionality between the dielectric constant and the square of the refractive index (for long wavelengths), one would expect dielectric constant *versus* composition curves to exhibit the same sort of

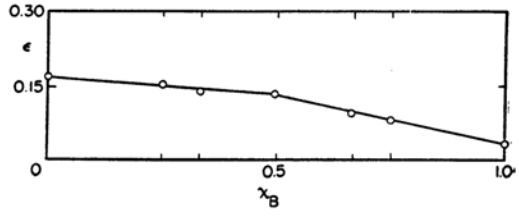


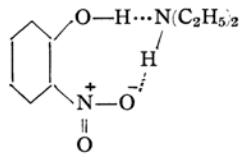
Fig. 4.[16] Variation of dielectric constant (ε) with composition, for solutions of o-nitrophenol (A) and diethylamine (B) in benzene.

13) F.M. Arshid, C.H. Giles, E.C. McLure, A. Ogilvie and T.J. Rose, *J. Chem. Soc.* (London), 1955, 67.

14) M.L. Huggins, *J. Opt. Soc. Am.*, 30, 495 (1940).

15) M.L. Huggins, *J. Am. Chem. Soc.*, 63, 116 (1941).

peculiarities as the corresponding squared refractive index curves. This is illustrated by Fig. 4[16], representing data for solutions of *o*-nitrophenol and diethylamine in benzene[16]. A 1:1 complex is again indicated. A reasonable structure would be that indicated by the formula.



With new definitions of A and B, the discussion given above for the (dimethylformamide)-phenol system is applicable.

The dielectric constant curve[16] (Fig. 5) for

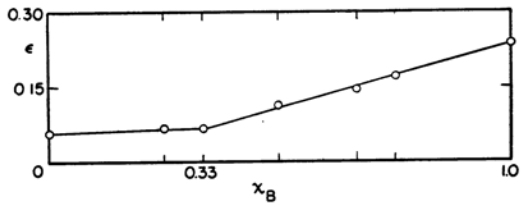


Fig. 5.[16] Variation of dielectric constant with composition, for solutions of azobenzene (A) and aniline (B) in benzene.

benzene solutions of azobenzene (A) and aniline (B) shows a sharp break at the 2:1 composition, indicating the formation of a complex of formula $A_{2i}B_i$, with i indeterminate without further information. The structon sets in the two composition ranges are presumably the following:

Range I: A(O) A(iB) B(2iA)
Range II: A(iB) B(2iA) B(O)

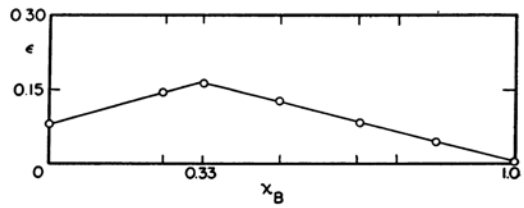


Fig. 6.[16] Variation of dielectric constant with composition, for solutions of phenol (A) and quinol (B) in diethyl ether.

The dielectric constant curve[16] (Fig. 6) for mutual solutions of phenol (A) and quinol (B) in diethyl ether also show a break at $x_B=1/3$. In this case, the most reasonable interpretation is that each phenol molecule is hydrogen-bonded to *two* quinol molecules and each quinol molecule to *four* phenol molecules. To account for the break in the curve, it seems necessary to assume that the hydrogen bonds to the ether molecules are considerably weaker and may be neglected.

An alternative way of looking at this system is to consider the hydroxyl hydrogen atoms (H), the phenol residues (P), and the quinol residues (Q) as the components of the structons, and to assume that every hydroxyl hydrogen is hydrogen-bonded to an oxygen of another hydroxyl. The observed break is then accounted for by the following sets of structon types and hydrogen-bond types:

Range I: P(2H) Q(4H) H(2P) H(P, Q)
H··· bonds: PHP PHQ
Range II: P(2H) Q(4H) H(P, Q) H(2Q)
H··· bonds: PHQ QHQ

The dielectric constant curve[16] for solutions of phenol (A) and azobenzene (B) in water shows two breaks, at $x_B=1/3$ and 1/2 (Fig. 7). This is most simply accounted for

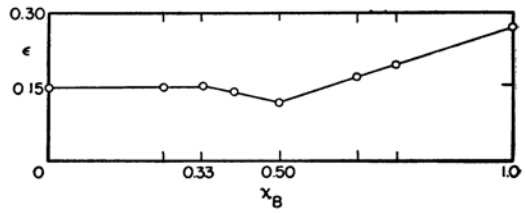


Fig. 7.[16] Variation of dielectric constant with composition, for solutions of phenol (A) and azobenzene (B) in water.

by the following sets of structons and aggregates:

Range I: A(O) A(B) B(2A)
Aggregates: A_2B
Range II: A(B) B(2A) B(A)
Aggregates: A_2B AB
Range III: A(B) B(A) B(O)
Aggregates: AB

An especially interesting system is that of phenyl isothiocyanate (A) and diethylamine (B). The viscosity curve at 25°C, published by Kurnakov and Zemchuzny[17] in 1913, shows a very high, sharp maximum at the equimolar point, suggesting the presence of long-chain polymers (Fig. 8). As the temperature is raised, the height of the peak decreases, presumably because of decreasing average chain length. This indicates that the forces holding the units together in the molecular chain are either hydrogen-bond forces or others of similar magnitude.

The loss factor, ε'', of the microwave dielectric constant likewise shows a peculiar

16) C.H. Giles, T.J. Rose and D.G.M. Vallance, *J. Chem. Soc.* (Londor), 1952, 3799.

17) N. Kurnakov and S. Zemchuzny, *Z. Physik. Chem.*, 83, 481 (1913).

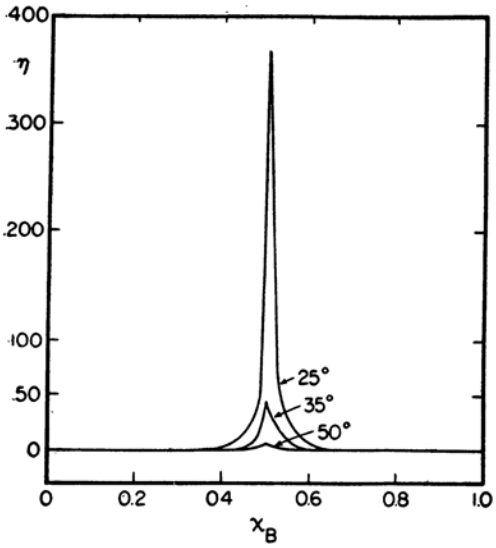


Fig. 8.[17] Variation of viscosity (η) with composition, for binary solutions of phenyl isothiocyanate (A) and diethylamine (B).

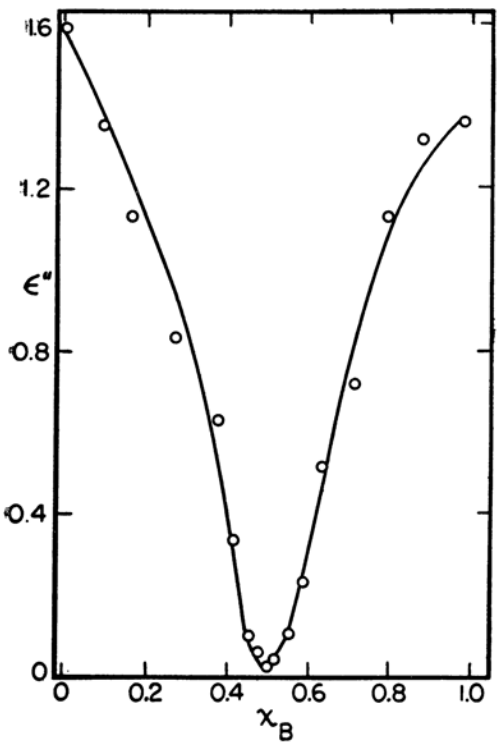


Fig. 9.[18] Variation of microwave dielectric loss (ε'') with composition, for binary solutions of phenyl isothiocyanate (A) and diethylamine (B).

behavior for this system[18]. A low, sharp minimum occurs at the equimolar point (Fig. 9).

18) P.K. Kadaba, *J. Chem. Phys.*, 22, 1465 (1954).

The following sets of structon and aggregate types are tentatively suggested, pending further experimental work, as reasonable ones to account for this behavior:

Range I: A(O) A(B) B(2A)
Aggregates: A_2B
Range II: A(B) B(2A) A(2B)
Aggregates: $(AB)_t$ $(AB)_tA$
Range III: B(2A) A(2B) B(A)
Aggregates: $(AB)_t$ $B(AB)_t$
Range IV: A(2B) B(A) B(O)
Aggregates: AB_2

On this basis, there are only small aggregates in Ranges I and IV, but Ranges II and III contain chain molecules (and perhaps ring molecules also). Assuming strict adherence to this scheme, but neglecting ring formation, the average molecular weight depends on composition as shown in Fig. 10.

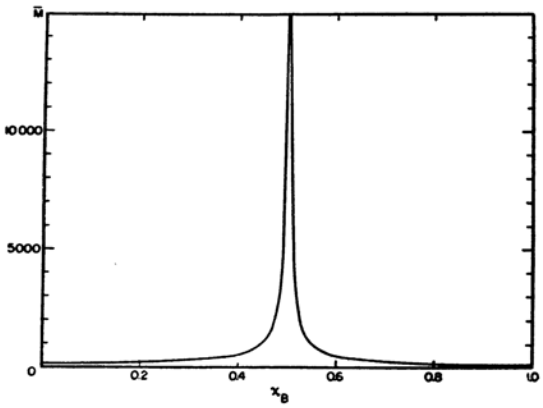


Fig. 10. Variation of calculated average molecular weight ($\bar{M}$) with composition, for binary solutions of phenyl isothiocyanate (A) and diethylamine (B).

The calculated molecular weight curve closely follows that of the 25°C viscosity curve, except that the former goes to infinity at the equimolar composition. This correspondence would be expected theoretically for solutions containing linear polymers[19].

Discussion of the nature of the association between the molecules in these polymer chains will be postponed until later.

In the literature, there are many other examples[13,16,20,21] of property-composition curves, for solution systems, which exhibit sharp breaks. In all cases of which the author is aware, it would be reasonable to assume association, usually involving hydro-

19) M.L. Huggins, *J. Phys. Chem.*, 42, 911 (1938); 43, 439 (1939).
20) V.S. Griffiths, *J. Chem. Soc.* (London), 1952, 1326.
21) G.N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, N.Y. (1923), p. 40.

gen bonds. Structon theory should be applicable, in most instances at least.

Although, in many cases, the breaks in the experimental curves can equally well be interpreted in terms of the formation of compounds or strong complexes of suitable compositions, the structon concept is more general and is more appropriate in cases in which linear or net work polymeric complexes are formed: for example, in the phenol-quinol, (phenyl isothiocyanate)-diethylamine, and sodium silicate systems. Another advantage of this point of view is that it makes possible the calculation of various properties of structon types, these properties presumably being transferable from system to system.

The Structon Number Rule

The minimum number of structon types in a given system at a given concentration or over a given concentration range is given by a rule which can be called "the structon number rule," by analogy with the phase rule[22].

The minimum number (S) of structon types is equal to the number of equations required to fix the numbers of structons of each type. There is one equation for each of C types of contact between structon centers, representing the fact that there are as many B contacts to A centers as A contacts to B centers. There is a normalizing equation, expressing the requirement that the total amount of matter in the structons equals that in the quantity of matter being considered, or the requirement that the sum of the mole fractions equals unity. In many cases (e.g., in the glasses discussed above, other than pure silica), the relative numbers of structons of different types are also limited by a neutrality or valence-balancing equation. There is an additional equation for each degree of composition freedom (F).

The structon number rule can thus be expressed as

$$S=C+F+2 \qquad (11)$$

if the neutrality limitation is required, and

$$S=C+F+1 \qquad (12)$$

otherwise.

Further Development

This theory can obviously be developed and extended in several ways. For example, the contributions of the individual structon types to specific properties of interest can be deduced and interpreted in terms of structon structure. It should be possible to relate the existence of structon types and of particular sets of them to energies of interaction between the atoms, ions, and molecules concerned. A quantitative treatment of these relationships should enable one to deal with systems showing departures from strict linearity of (structon-additive) property-composition curves, rounding at the breaks between ranges, etc., relating these phenomena quantitatively to the presence of structons other than those of lowest energy.

Another line of future extension of the theory is to polymer systems, in which the chief intermolecular interactions are strong attractions between atomic groups of specific kinds.

Summary

In sodium silicate glasses and in many liquid solutions, curves representing the dependence of various properties on composition show distinct breaks. This behavior can be reasonably interpreted in terms of the types of environment around each atom or molecule or atomic group responsible for strong intermolecular interactions, together with the assumption that in these systems only the most stable environments are present in significant amounts. Only closest neighbors need be considered, hence the types of environment can conveniently be described in terms of "structons," each structon type being defined as a given kind of atom (or molecule or atomic group) surrounded by close neighbors in a given way.

The compositions at the breaks in the property curves limit, and in some cases determine uniquely, the types of structon present in and between the different composition ranges.

The structon theory has been applied to sodium silicate glasses and certain liquid solutions, in which there are strong hydrogen-bond interactions between molecules.

The Research Laboratories of the Eastman Kodak Company, Rochester 4, New York, U. S. A.

22) M. L. Huggins, *J. Am. Chem. Soc.*, 77, 3928 (1955).