ViscosityCompositionTemperature Relations in the System Na2O–SiO2

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A CAREFUL examination of viscosity data for the soda-silica system from Heidtkamp and Endell[1] and from Lillie[2] shows that it is very well represented for high temperatures by an equation of the form

$$\log\eta = A + BS_0 + [(C + DS_0)/2.303RT], \qquad (1)$$

wherein a different set of constants is required for each of the following ranges in the value of the silicon-oxygen ratio, S_0,

> above 0.435
> from 0.435 to 0.400
> from 0.400 to 0.345
> below 0.345.

These are the critical values for S_0 used by Huggins and Sun[3] in their density calculations.

A very helpful picture of the log viscosity-reciprocal T curve was derived from a study of the analogous relation for log resistivity. Babcock[4] has given us the relation,

$$\log\eta = \beta \log\rho, \qquad (2)$$

where β is constant for a given composition. This relation is interpreted to mean that that viscosity depends on the mobility of the sodium ion in this system.

It was found that log resistivity[4,5] could be well represented by an equation of the form

$$\log\rho = [\log A - c + (E/2.303RT)]f(T) + c, \qquad (3)$$

where A and E are the characteristic values for $f(T) = 1$ at high temperatures and c is a small constant not affected by $f(T)$. It appears that $f(T)$ must describe a transformation from ionic binding above about 1600°K to ionic-covalent binding which is essentially complete below 700°K. The increase in E is about fifty-five percent of its value below 700°K. This agrees well with an estimate of percent covalent binding from Pauling.[6]

Derivation of a relation for log viscosity from the Maxwell-Boltzmann energy-distribution law, with appropriate considerations for the nature of the transformation, led to an exactly similar equation,

$$\log\eta = [\log A + \log N_0 + (E/2.303RT)]f(T) - \log N_0. \qquad (4)$$

From the derivation

$$A = C(1/N_0),$$

where N_0 is a probability at infinite temperature and C is an effect factor relating N_0 to viscosity. It appears that $f(T)$ must apply to $\log C$ as well as to E. Obviously any change in E, the bond strength, must change the effect of each bond. It is clear too that, in the absence of associations or dissociations, N_0 must not be affected by $f(T)$.

Inasmuch as a suitable relation was derived considering N_0 constant, it appears that the effect of the transformation described by $f(T)$ is not a change in aggregation but simply a tightening of the structure with decreasing temperature.

It appears that $\log N_0$ is simply related to composition. Reasoning from this, and from the nature of C, we are led to the form of Eq. (1) for a composition relation, wherein the critical values of S_0 approximate the compositions where the ratios of silicon atoms to sodium atoms are small integers. This ratio is thought of as the number of sites each sodium atom must visit to permit flow through one interatomic distance.

A detailed presentation is planned for publication as soon as these relations can be further verified and the form of $f(T)$ can be studied more at length.

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The Hydrogen Fluoride Dipole Moment and the Structure of the Dimer*

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QUANTUM mechanics leads to the equation[1]

$$\mu = [9kTP_m/4\pi N(1 - (h^2)/(24\pi^2 IkT))]^{\frac{1}{2}},$$

for the relation between the molar orientation polarization P_m, and the intrinsic dipole moment μ of a diatomic molecule. In this equation k is the Boltzmann constant, h, the Planck constant, N, the Avogadro number, T, the absolute temperature, and I, the moment of inertia. The divergence from classical mechanics is given by the second term within the parentheses in the denominator and becomes appreciable only for molecules of very small moment of inertia. Monomeric hydrogen fluoride, with a moment of inertia of 1.32×10^{-40} c.g.s. unit,[2] is a molecule whose dipole moment should be computed by means of the above equation rather than by the classical expression. When this is done, using the data of Hannay and Smyth[3] and of Oriani and Smyth,[4] one obtains 1.98×10^{-18} as the dipole moment of the HF molecule instead of the previously published value of 1.91×10^{-18} given by the classical equation.

In a recent article Evans and Glockler[5] carried out calculations based on electrostatics for the configuration and potential energy of the hydrogen fluoride dimer. They were led to the conclusions, also reached by Briegleb,[6,7] that an antiparallel arrangement of dipoles represented the structure of minimum potential energy, and that the energy of each of the two hydrogen bonds in the dimer was 11.9 kcal./mole. This configuration, however, fails to explain the large increase in dielectric polarization of hydrogen fluoride vapor observed by the writers[4] as the temperature is decreased and pressure increased, for such an antiparallel arrangement of HF units would have zero dipole moment. These polarization data, together with the electron diffraction studies of Bauer, Beach, and Simons[8] and the vapor density work of Long, Hildebrand, and Morrell,[9] indicate structures for the polymers consisting of chains, some of

which link up to form rings. Furthermore, Tanford[10] has computed a hydrogen bond energy of 6.3 kcal./mole for the one hydrogen bond in the dimer structure based on the zig-zag model given by electron diffraction, from which the entropy of the dimer is calculated. He uses Briegleb's equilibrium constant k for $2HF \rightleftharpoons (HF)_2$, the large error in which introduces but a small error into the bond energy calculation because $\log K$ is used. Thus, the zig-zag model, deduced from electron diffraction experiments and having the polarity necessary to explain the polarization measurements, also leads to a reasonable value for the energy of the hydrogen bond.

The semi-empirical quantum-mechanical treatment also accorded by Evans and Glockler[5] to the hydrogen fluoride dimer indicates a linear configuration, and hence is in qualitative agreement with polarization data. However, the crudeness of the approximations necessary in evaluating the London equation leads to an admittedly unreliable result.

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The Ultimate Liquid Transmission Limit?

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IN a recent paper,[1] the far ultraviolet transmission limits of n-heptane and of two perfluorocarbons were determined as shown in rows 1–3 of Table I. The markedly poorer transmission of the fluorocarbons was surprising, for the extremely low refractive indices of perfluoro compounds had indicated that their transmission limits might lie at shorter wave-lengths than those of the corresponding hydrocarbons. Moreover, the M→V transition in perfluorotoluene is at 1780A,[2] compared with its location in toluene at 1885A.[3] Recently, a carefully fractionated n-perfluorooctane was made available.[4] It transmits to 1592A in an 0.5-mm cell, to 1565A in an 0.03-cm cell, and to 1780–1830A in a 1-cm cell. The cut-offs are very sharp, as indicated by the change of only 30A with a 20-fold change in cell thickness.

The energy at the extreme transmission limit of the perfluorooctane is about 64,000 cm⁻¹. This extends the region of the ultraviolet available for solution studies some 5000 cm⁻¹ from the previous hydrocarbon limit of 58,500 cm⁻¹, which is itself some 10,000 cm⁻¹ above the usual quartz spectrograph ultraviolet limit. This extension from the quartz region is one and one-half times the total frequency spread in the visible between 4000–7000A, and

TABLE I. Transmission limits.

Compound	Source	Purification	Cell thickness	Limit
1. n-C_7H_{16}	Westvaco	sulf. acid and/or silica gel	0.13 mm	1700A*
2. n-C_7F_{16}	du Pont	no treatment	0.5	1800*
3. n-C_9F_{20}	du Pont	no treatment	0.5	1830*
4. n-C_8F_{18}	see reference 4	repeated fractionation b.p. 104.5°C; $n_D^{20}=1.268$	0.03 0.5	1565 1592
5. CF_3-cycloC_6F_{11}	du Pont	no treatment sulf. acid	0.5 0.5	1860 1850
6. $(CF_3)_2$-cycloC_6F_{11}	du Pont	no treatment	0.5	1960

* See reference 1.

offers correspondingly large opportunities for characterization of complex molecules and studies of their electronic behavior.

We may consider whether this limit of 1565A will be the ultimate transmission limit for practical solvents in absorption spectrophotometry. Fluorides transmit better than corresponding hydrides or other compounds because of the high ionization potential of fluorine, higher than that of any other combining element. Similarly, molecules made from second-row elements will transmit better than their heavier analogs. Price[5] and others have pointed out these relations between ionization potentials and spectra. Now second-row fluorides with one central atom, BeF_2, BF_3, CF_4, etc., are either solids or gases. They can be used as solvents only at low temperatures (with decreased solubility) and/or high pressures, or at high temperatures, with possible decomposition of complex solute molecules. Evidently, for a solvent, we need a larger fluoride molecule, with a skeleton of several other atoms such as $-C-C-C-$, $-B-B-B-$, $-B-N-B-$, forming a long enough chain to be liquid at room temperatures. Chains containing O, Si, or S would not be feasible because of their known absorption about 2000A.

The transmission properties of the liquid 8-carbon fluoride chain we have seen here. As for boron chains, BF_3 is formed instead of B_2F_6, and pure fluoroboron chains are probably not possible. If they could exist, or if mixed hydride-fluoride-boron chains existed, they would probably not be transparent below 1700A because of their unsaturation characteristics (conjugated?) as shown by the recently reported maximum of about 1350A for the bridge-like diborane,[6] and as indicated by the absorption of B_5H_9 near 2000A.[7]

As for $-B-N-B-$ chains, we may reason from the unsaturated rings of this type to the little-studied saturated chains. The N→V transition of benzene is at 1835A, of borazole at 1720A, and of perfluorobenzene at 1740A (estimated from perfluorotoluene[2]). For perfluoroborazole, this transition might lie as low as 1625A. Then a saturated $-B-N-B-$ hydride chain might transmit to about 1600A and the fluoride analog to about 1475A. A polymer of BH_2NH_2 is known which is a solid.[8] Its ultraviolet transmission is not known. A similar polymer $(BF_2NF_2)_x$, with $x=3$ or 4, might be a suitable solvent to extend the transmission limit if such a compound could be prepared.

It seems, therefore, that the liquids promising to be more transparent than fluorocarbons are at present largely hypo-