[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, INORGANIC CHEMICALS DIVISION]

Structure and Properties of the Condensed Phosphates. IX. Viscosity of Molten Sodium Phosphates

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The viscosities of $Na_2O-P_2O_5$ melts were measured over a range in composition from an Na_2O/P_2O_5 mole ratio of 1.0 up to 2.14 at temperatures from a few degrees above the liquidus to above 1000, using a special platinum spindle with a rotational viscometer. These melts exhibit Newtonian flow, and both the viscosity and the temperature dependence decrease with increasing Na_2O/P_2O_5 mole ratio. Treatment of the data according to Eyring's absolute rate theory shows that the viscous-flow behavior of these melts is similar to that of long-chain hydrocarbons, and that the flow-unit never exceeds about eight phosphorus atoms, even though the chain length in the quenched glass may run as high as 170 phosphorus atoms or more.

The viscosity of the melt made by heating sodium trimetaphosphate at several temperatures was reported by Arndt.[1] In the present work, these measurements have been extended from the metaphosphate to beyond the pyrophosphate composition in the $Na_2O-P_2O_5$ system. The density and surface tension of these same melts were reported in an earlier paper.[2] These data have been critically examined to arrive at a better understanding of the nature of these materials in the molten state.

Experimental

The materials used in this study, and the general procedure followed in heating the samples are the same as described in an earlier paper.[2] The viscosity measurements were made by using a special platinum spindle with a Brookfield rotational viscometer.[3] The spindle was constructed by welding a thin platinum disc, 2.80 cm. in diameter, to a platinum rod, 0.52 cm. in diameter and 3.0 cm. long, with a constricted section near the top for controlling the liquid level to a fixed height on the spindle. The spindle was calibrated with glycerol and several standard viscosity oils[4] to determine the instrument constant, *K*, in the relation

$$\text{Scale reading} = K\eta(RPM) \qquad (1)$$

where η is the viscosity in poises and *RPM* is the speed of the spindle in revolutions per minute. The average value of *K* was found to be 0.553 with an average deviation of 0.6% over the range in viscosity of 0.5 to 14 poises.

The spindle constant was corrected for the change in the size of the spindle with temperature, by multiplying the value at room temperature by the ratio of the calculated torque at the chosen temperature to the calculated torque at room temperature. A linear plot of *K versus* temperature was constructed for use in this work. The value of *K* ranged from 0.553 at 30° to 0.570 at 1030°.

The calculated torques were obtained by applying the mathematical approximations given by Merrington[5] relating the torque exerted on the spindle by a viscous liquid to the shape and size of the spindle. The total torque on the spindle at full-scale was computed to be 597.5 dyne-cm., as compared to the true mechanically measured spring constant of 685 dyne-cm.; therefore the use of these mathematical approximations, with this particular spindle, for an absolute determination of viscosity would give values that would be high by about 12–13%. This discrepancy in the calculated value is probably due in great part to neglect of the drag between the rotating desk and the bottom of the platinum bucket, as well as to lack of correction for end and edge effects. However, the use of these calculated values for correcting the spindle constant is valid since the correction itself is small, and only the ratio of the calculated torques is involved.

The error in adjusting the liquid level to a certain spot on the constricted portion is, according to the mathematical approximations given by Merrington,[5] *ca.* 0.3% for every 0.2 cm. In practice, it is believed that 0.2 cm. was the maximum deviation in the liquid level.

Results

Measurements made on several melts at rotational velocities ranging from 6 to 30 r.p.m. indicated that they all exhibit Newtonian flow. The viscosity data for the several $Na_2O-P_2O_5$ melts are summarized in Table I. Linear plots of log

TABLE I

VISCOSITY OF MOLTEN SODIUM PHOSPHATES

Viscometer: Brookfield rotational

Na_2O/P_2O_5 mole ratio in melt	Temp., °C.	Viscosity, poises	Data fitted to relation $\eta = al^{b/RT}$ *b*	*a*
1,0	741	5.09		
	751	4.58		
	849	2.28		
	935	1.38		
	1013	0.901	16480–16420	0.00143–0,001427
1.08	707	4,55		
	769	2.84		
	823	1.98		
	914	1.16		
	1001	0.779	14710–14650	,002355–0.002365
1.29	657	2.76		
	732	1.60		
	834	0.910		
	927	.599		
	1017	.440	11350–11230	.00543–0.00549
1.50	822	.706		
	900	.499		
	957	.422		
	1002	.381	8700–8520	.0127–0.0129
1.75	942	.388		
	985	.358		
	1022	.328		
	1064	.304	6760–6620	.0240–0.0244
2.0	1030	.310		
	1048	.292		
	1052	.304		
	1070	.280		
	1077	.286	5290–4840	.0365–0.0399
2.14	995	.334		
	1019	.319		
	1044	.310		
	1070	.283	4780–4380	.0374–0.0409

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(1) K. Arndt, *Z. Chem. Apparatenkunde*, **3**, 549 (1908).

(2) C. F. Callis, J. R. Van Wazer and J. S. Metcalf, THIS JOURNAL, **77**, 1468 (1955).

(3) Multi-Speed Model LVF, Brookfield Engineering Laboratories, Stoughton, Mass.

(4) National Bureau of Standards Oil No. N-20, Central Scientific Company viscosity reference standard numbers 27225-A, 27225-B and 27225-C.

(5) A. C. Merrington, "Viscometry," Longmans, Green and Company, New York, N. Y., 1949.

viscosity coefficient *versus* the reciprocal of the absolute temperature were constructed for each liquid as shown in Fig. 1. From the straight lines in Fig. 1, the data were fitted to the relation $\eta = ae^{b/RT}$, where η is the viscosity in poises, T is the absolute temperature, R is the gas constant in cal./deg./mole and a and b are constants. The values of a and b so obtained are included in Table I. A range in values is given, in agreement with the estimated probable error in the viscosity values. This probable error is large for the liquids with high Na_2O/P_2O_5 ratios, because of the low scale readings.

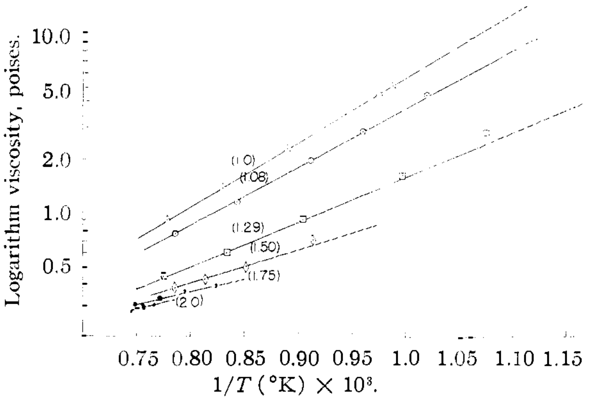

Fig. 1.—Temperature variation of viscosity for various Na_2O/P_2O_5 melts; plot of logarithm viscosity coefficient *versus* reciprocal absolute temperature. The Na_2O/P_2O_5 mole ratios of the melts are given in parentheses.

For convenience in subsequent calculations, the values of a and b were fitted to the following two empirical equations

$$\log b = -0.515\ (Na_2O/P_2O_5) + 4.722 \qquad (2)$$

and

$$a = 0.0298\ (Na_2O/P_2O_5)^2 - 0.0522\ (Na_2O/P_2O_5) + 0.0240 \qquad (3)$$

in terms of the Na_2O/P_2O_5 mole ratio in the melt. The individual deviations from these empirical equations ranged from −3 to +6% in b, excluding the value for Na_2O/P_2O_5 equal to 2.14, and from +10 to −7% in a, again excluding the data for the 2.14 ratio. Tests of the validity of these relations for the melts with high Na_2O/P_2O_5 ratios will have to be made with a different spindle covering a lower range.

Discussion of Results

Viscosity has been treated as a regular kinetic process by the absolute theory[6] of reaction rates to obtain a relation of the form

$$\eta = ae^{b/RT} \qquad (4)$$

where η is the viscosity in poises, T is the absolute temperature, R is the gas constant, b is the activation energy for flow or the difference in enthalpy of the activated and initial states and a is a function of the molar volume and the difference in entropy of the activated and initial states. As previously pointed out,[7] the data reported by Arndt,[1] for sodium metaphosphate can be fitted to equation 4, and are in agreement with the data reported here within ±6%. It has been shown in Fig. 1 that the data obtained in the present work follow equation 4, with only minor deviations over wide temperature ranges. As is well known,[8] Newtonian liquids exhibiting considerable secondary bonding, such as is the case for water, do not follow equation 4 since a plot of log η *versus* $1/T$ has a slight curvature away from the $1/T$ axis. This effect is barely noticeable in Fig. 1.

An approximation of the size of the flow-unit can be obtained by treating the data as was done by Kauzmann and Eyring[9] for long-chain hydrocarbons. The activation energy for flow, b, is plotted as a function of the chain-length of the quenched glass, determined from end-group titrations. Then, for any value of the activation energy, it is assumed that the extrapolated asymptote to such a curve gives the average number of phosphorus atoms in the flow-unit. These flow-units are plotted *versus* the chain length of the quenched glass in Fig. 2, and compared with a similar treatment of the viscosity data of long-chain hydrocarbons. It can be seen from Fig. 2 that the flow-unit never exceeds about eight phosphorus atoms, and that the result is in agreement with that for the hydrocarbons. Thus, during viscous flow, the longer molecule-ions move as sections rather than as whole units. The flow-unit becomes a decreasing proportion of the entire chain with increasing chain length of the quenched glass. For the melt of a random reorganization polymer,[10] such as molten sodium phosphates, it is impossible to state whether the size of the flow unit is determined by (1) the average size of the reorganizing molecular units in the melt or (2) simply by the fact that long, stable chains tend to move as segments. If the rate of jumping of the flow units is slower than the rate of making and breaking the molecule-ions in the reorganization process, item 1 above will hold, whereas, if the opposite is true, item 2 will be the mechanism of the observed flow. Since the some-

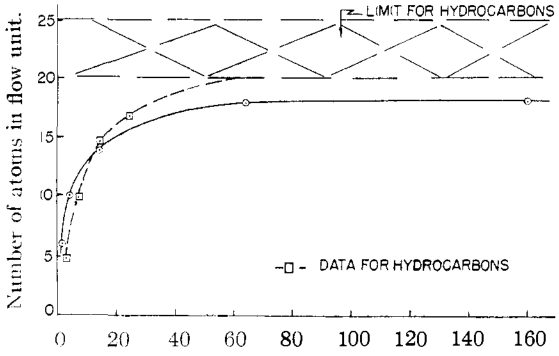

Fig. 2.—Estimated flow units in molten sodium phosphates at various chain lengths in the quenched glasses.

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[6] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

[7] J. R. Van Wazer, *Ind. Eng. Chem.*, **41**, 190 (1949).

[8] J. R. Van Wazer, "Rheology" in "Encyclopedia of Chemical Technology" (Editors: Kirk and Othmer), Volume XI, Interscience Encyclopedia Incorporated, New York, N. Y., p. 734.

[9] W. Kauzmann and H. Eyring, This Journal, **62**, 3113 (1940).

[10] J. R. Van Wazer, *ibid.*, **72**, 644 (1950).

what unreliable evidence of the Eötvös equation as applied to surface tension of the sodium phosphate melts indicates an average size of *ca.* 9 phosphorus atoms per reorganization unit,[2] the flow unit of 8 phosphorus atoms could well be identical to the average-sized fragment in the reorganization process.

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Chain Branching in Glassy Polyphosphates: Dependence on the Na/P Ratio and Rate of Degradation at 25°[1]

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The previously observed occurrence of an initial decrease of both viscosity and *p*H in freshly prepared aqueous solutions of glassy sodium polyphosphate was investigated with samples whose Na/P ratios ranged from 0.968 to 1.055. The phenomenon was observed at Na/P ratios up to 1.01. That the effect was due to the hydrolysis of weak bonds in the polymer molecules was confirmed by showing that the first-order rate constants of both the reduced viscosity decrease and the increase in the number of titratable hydrogen ions were equal. This rate constant was found to be $8(\pm 4) \times 10^{-3}$ min.$^{-1}$ at 25° and was apparently unaffected by the Na/P ratio and the molecular weight of the samples as well as by the *p*H and the NaBr concentration of the solutions. Evidence that these weak bonds occur at branch points in the polymer chains is presented, and by extrapolation of the data obtained in the rate studies the number of branches originally present in the samples is estimated. For glasses with Na/P ratios greater than unity this number is of the order of one branch for every 1000 P atoms.

In a recent paper[2] it was shown that both the viscosity and the *p*H of freshly prepared aqueous solutions of Graham's salts decreased for several hours before attaining constancy. These effects were ascribed to the hydrolytic degradation of the weak P–O bonds at branch points in the polymer chains. However, since Van Wazer's first-order approximation theory did not predict the existence of such branch points in polyphosphate glasses with Na/P ratios equal to or greater than unity,[3] an experimental study was undertaken aimed at correlating the presence and if possible the degree of chain branching of the glasses with their Na/P ratios. Na/P ratios investigated extended from 0.96 to 1.06 with by far the greatest number of samples covering the range from 0.990 to 1.010.

The presence of chain branching in a given sample was detected by the initial viscosity and *p*H changes. In order to confirm the soundness of this procedure, experiments aimed at obtaining further evidence that these changes reflect the degradation of branch points were performed with several of the samples. These experiments included measurement of the increase in titratable hydrogen ion content accompanying the viscosity decrease to prove the chemical nature of the process. The rates of these changes were compared to determine whether the same process was measured by both titration and viscosity methods. From these rate studies an estimate of the order of magnitude of the number of weak bonds (branches) initially present in a glass was obtained. The possibility of impurities being the cause of the weak bonds was also explored.

Since the dependence of the molecular weight of the polymers on their Na/P ratio has apparently not previously been determined for the range of Na/P ratios here under study, and since most samples of Graham's salt described in the literature fall within this range, this dependence is included in this paper as a possibly useful by-product of this research.

Experimental Materials and Methods

Preparation of Polymers.—Monomer samples with known Na/P ratios[4] were prepared as follows. A nearly saturated aqueous stock solution of $NaH_2PO_4 \cdot H_2O$ (Baker, reagent grade) was filtered, and an aliquot of this solution titrated to the first equivalence point of phosphoric acid with either 0.1 *N* NaOH or 0.1 *N* HCl depending on which side of the equivalence point the original sample was.[5] The same aliquot was then titrated to the second equivalence point in order to determine the total amount of phosphate present. From these data the Na/P ratio in the original stock solution was calculated. Varying amounts of NaOH or H_3PO_4 were added to different portions of the stock solution in order to bring each of these portions close to a desired Na/P ratio. The solutions were then evaporated to dryness, and the exact Na/P ratios of the anhydrous monomer samples were determined by titrating weighed aliquots with NaOH or HCl to the first equivalence point.

The polymers were then prepared by fusing the monomer samples in a platinum dish at a constant temperature between 920 and 960° for 12 hours[6] followed by rapid chilling of the melt between cold steel plates.[7]

Characterization of Polymers.—Although there is no reason to believe that the Na/P ratio changes under our mild fusion conditions, the Na/P ratios of most of the polymers were determined nonetheless. This determination depends on the assumption (whose validity is quite well established[2]) that 24 hours after dissolution all the polymer molecules are linear. If this is the case, a Na/P ratio of unity corresponds to the state where there is one hydrogen ion for each chain

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(1) This investigation was supported by a grant from the United States Atomic Energy Commission under contract AT(30-1)1018. These results will be contained in a thesis to be submitted by T. L. Treitler to the Graduate School of Rutgers University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) U. P. Strauss, E. H. Smith and P. L. Wineman, THIS JOURNAL, **75**, 3935 (1953).

(3) J. R. Van Wazer, *ibid.*, **72**, 644 (1950).

(4) Strictly speaking, if the samples contain other metallic cations as impurities, what we call the Na/P ratio is really the ratio of total equivalents of metallic cation to total equivalents of phosphorus.

(5) If the Na/P ratio of the $NaH_2PO_4 \cdot H_2O$ was exactly unity, *i.e.*, if the $NaH_2PO_4 \cdot H_2O$ was perfectly pure, the solution would be at the equivalence point without the addition of acid or base. By the analytical method described in the text it was found that the Na/P ratios of our commercially obtained reagent grade $NaH_2PO_4 \cdot H_2O$ samples varied from 0.995 to 1.007.

(6) A few tests showed that prolonging the fusion time to 24 hours did not affect the properties of the product.

(7) L. F. Audrieth and R. N. Bell, in "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1950, p. 105.