

where L_2 is the partial heat of solution. Specifically L_2 is gotten from the integrated form of Equation 4 and is part of the slope of a straight line obtained from the plot of $\log \gamma_2'$ vs. $1/T$.

The magnitude of the activity coefficient of a given solute depends upon the solvent structure. Realizing that the activity coefficient values indicate the general trend that as the degree of nonideality of the hydrocarbon-solvent pair increases so does the magnitude of the activity coefficient, the following generalizations can be observed.

The nonideality of a binary pair involving a hydrocarbon and an N -monosubstituted amide of a given member of a homologous series is greater than the nonideality of a binary pair involving a hydrocarbon and an N,N -disubstituted amide of the same member.

The nonideality of a binary pair involving a given solute with successive members of the homologous series increases as the carbon number of the homologous series decreases.

The nonideality of a binary pair involving a given solute with a series of compounds varying only with the size

of the N -substituted alkyl group increases as the carbon number of the N -substituted alkyl group decreases.

A greater degree of nonideality exists between a solute and a sulfonyl group than between the same solute and a carbonyl group.

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Physical Properties of Controlled-Solubility Phosphate Glasses

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Viscosities, coefficients of expansion, and birefringence constants of several controlled-solubility phosphate glasses (sodium polyphosphates containing CaO, MgO, or Al₂O₃) were determined. For one of these glasses refractive index, intrinsic density, and crushing strength also were determined.

THE PROPERTIES of silicate glasses have been carefully determined and are readily available in the literature (3). The same is not true for the phosphate glasses. The usual commercial product is a rapidly dissolving linear sodium polyphosphate with an average of from six to 20 phosphorus atoms per chain. By substituting multivalent cation oxides—e.g., CaO, MgO, or Al₂O₃—for part of the Na₂O, series of useful controlled-solubility phosphate (CSP) glasses are obtained (1). Some physical properties of this type of glass were determined and are reported here.

EXPERIMENTAL RESULTS

Thermal properties were determined by the Emhart Glass Testing Laboratories, Hartford, Conn. The method used for coefficient of linear expansion (0° to 100° C) was ASTM C337-57; accuracy was estimated to be $\pm 3.0 \times 10^{-7}$ per °C, and was affected by glass solubility. Test errors that could result from glass solubility were minimized by making

the tips blunt at the bearing ends of the 6-inch test piece. The sequence of "soaking" was from hot to cold to hot in each test. Any difference between the two hot-length readings was assumed to be a result of slow dissolving of glass at the tips. The difference was of the order of -0.00020 inch, a negligible error in the length of the 6-inch rod, but significant if the difference represented a ΔL change. A 0.00020-inch change in the ΔL produces an error of approximately 3.0×10^{-7} expansion unit. The second hot-bath reading was used in each case to determine the ΔL value. The other properties are defined in terms of log viscosity (in poises) and temperature (3). Annealing and strain points (ASTM C336-54T) and softening points (ASTM C338-57) were determined experimentally; the estimated accuracy for each temperature shown in Table I is $\pm 2^\circ$ C. Flow point, working point, gob temperature, and melting temperature were obtained from the three experimentally determined viscosity points by an Emhart proprietary technique; these extrapolated temperatures are

Table I. Properties of Controlled-Solubility Phosphate Glasses

Property	Glass Number								
	1	2	3	4	5	6	7	8	9
Composition, wt. % ^a									
Al ₂ O ₃	1.75	2.25	4.0	5.0
CaO	3.5	4.5	8.0	10.0	9.0	15.0	18.0	22.5	9.5
Na ₂ O	27.75	26.25	21.0	18.0	24.0	16.0	13.0	9.0	11.5
P ₂ O ₅	67.0	67.0	67.0	67.0	67.0	69.0	69.0	68.5	67.5
Temperature, °C ^b									
Strain pt. (14.5)	278	289	320	360	292	336	353	399	401
Annealing pt. (13.0)	294	304	338	381	311	357	375	422	424
Softness temp. (7.65)	353	372	412	460	376	434	...	510	...
Flow pt. (5.0)	412	440	486	539					
Working pt. (4.0)	452	486	536	593					
Gob temp. (3.0)	508	551	607	668					
Melting temp. (2.0)	594	649	714	782					
Coefficient of thermal expansion ^c (× 10 ⁷ per °C)	153	185	165	135	158				
Birefringence constant, m _μ /cm per kg/cm ²	1.50	...	1.70	1.65			1.61		1.71

^aGlass 9 also contained 11.5% MgO. ^bTemperatures correspond to log viscosity (poises), in parentheses, for property as defined in (3), ASTM C336-54T, and C388-57. ^cTemperature range 0° to 100° C.

estimated to be accurate $\pm 10^\circ$ C. The method used works very well for soda-lime silicate glasses and is believed to be applicable to the CSP glasses.

The Na₂O content appears to have the greatest influence on physical properties of the glasses (Table I). A plot of softness temperature *vs.* Na₂O content is linear, with softness temperature decreasing as Na₂O content is increased. The relationship between viscosity and Na₂O content is similar to that for soda-lime-silicate glasses.

A term commonly used in the glass trade is working range index (WRI), defined as the difference in °C between the softness temperature and annealing point. It defines the slope of the viscosity *vs.* temperature curve and is useful in determining if a glass is "quick setting" or "slow setting." Quick setting glasses have lower WRI values than slow setting.

The WRI is increased in soda-lime-silica glasses if SiO₂ is substituted for Na₂O. However, if the SiO₂ remains constant and CaO is substituted for Na₂O, the WRI is decreased. The decrease in Na₂O content appears to produce a similar effect on the phosphate glasses, but they do not respond to the CaO increase at the expense of Na₂O. From this one would assume the structural arrangement, ionic forces, etc., of the two glass families are different.

Data are too limited to draw conclusions regarding the influence of composition on coefficient of thermal expansion and birefringence constant. The coefficients of expansion of the CSP's are about twice those reported (3) for soda-lime silicate glasses. The temperatures (°C) required for specific viscosity properties are about one half those required for soda-lime silicate glasses (3).

Plane-polarized light passing through stressed glass is resolved into two sets of rays, vibrating at right angles to each other, which travel through the glass with different velocities. This "retardation" of one set of rays with respect to the other is dependent on the thickness and composition of the glass and the stress in the glass. The retardation, path-difference, or birefringence can be precisely measured using a Friedel-type compensator (2). If for a given glass the retardation (per unit thickness) caused by a known stress is determined, a birefringence constant (or stress-optical coefficient) can be obtained. Units frequently used are m_μ/cm per kg/cm² (3). Once this constant is known, stress present in the glass can be readily determined by measuring the glass thickness and the retardation of polarized light using a polarimeter (2).

Birefringence-constant measurements were made by Errol B. Shand (3), Corning, N. Y. Bars (6 × 10 × 75 mm) of CSP's were cast, annealed until stress-free, cooled, ground to provide a rectangular cross section, and annealed further if necessary. A small Dillon gage was used to apply a known stress to the bar (effective beam length was 68 mm) while it was in the Friedel-type polarimeter. Wave length (2) of the light used was 600 m_μ and the plot (minimum of four points) of load *vs.* compensator angle (2) was linear.

Using the polarimeter to measure the retardation (m_μ) for a given thickness (cm) caused by an induced stress (kg per cm²), birefringence constants were determined. As a check on the method, constants were measured on two pieces of soda-lime silicate plate glass. Results of 2.51 and 2.45 compared very well with the literature values of 2.4 to 2.6 m_μ/cm per kg/cm² (3). The birefringence constants of some CSP's are given in Table I; values are believed accurate to ± 0.02 unit. Birefringence constants for most silicate glasses range from about 2.5 to 4.0 units (3).

MISCELLANEOUS PROPERTIES

Four additional properties of glass 3 (Table I) were determined. By using immersion oils the refractive index (25° C) was found to be 1.515. By weighing and measuring diameters of 12 essentially perfect spheres, an intrinsic density (25° C) of (2.26 \pm 0.02) grams per cm³ was calculated.

Two properties of glass 3 were compared with those of soda-lime silicate glasses. The phosphate glass was softer than (could be scratched by) soda-lime silicate glass, which has a Mohs hardness of about 5 (3). The force required to crush spheres (12.5-mm diameter) of the two glasses was determined using a Soiltest hydraulic compression tester. For the silicate glass spheres about 2000 pounds was required and for the glass 3 spheres about 1000 pounds.

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