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Density of multicomponent silica-based potential bioglasses: Quantitative structure-property relationships (QSPR) analysis

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Abstract

The results of a quantitative structure-property relationships (QSPR) analysis of multicomponent silica-based potential bioglasses (containing Na_2O, CaO, P_2O_5 and/or ZnO) are here presented. A quantitative model explaining the variation of the density data measured for series of glasses with different compositions has been obtained by means of a structural descriptor derived from molecular dynamics (MD) simulations. A descriptor able to rationalize the variation in density caused by the overall packing degree of the structural units in the glasses examined has been defined. It is worth noting that the descriptor used allows the fitting of glasses with different composition (presence–absence of P_2O_5, ZnO, Na_2O and CaO) in the same correlation. The validity of the QSPR approach, which has recently been introduced for the rationalization and prediction of the technology-related properties of a series of complex multicomponent glasses, is confirmed by this work on a larger series of glasses of various compositions.

Keywords: Glass; Silicate; Computational study; ZnO

1. Introduction

Bioglasses are employed to repair and rebuild damaged tissues, particularly hard tissues, and their final shape must be easily mould with conventional techniques.[1,2] This property is very important, and requires that a series of physical parameters are resticted in defined range of values. One of them is the density, which is one of the simplest physical properties that can be measured, but has a complicated dependence upon the composition.[3]

The density value can be tuned by modifying the glass composition and the introduction of heavier or lighter metals with respect to the base composition gives the most significant variations. However, this is a time-consuming procedure, usually requiring a large number of attempts to obtain the desired value. Alternatively, a number of mathematical expressions are available in literature to predict several composition-dependent properties. Most of them are linear expressions, empirically derived by assuming the additivity of the properties, and, therefore, these models are valid within a narrow concentration range.[4] In particular, several semiempirical methods were developed for glasses containing one network former cation (for example Si); when the glass contains two or more network formers (or intermediate ions) these methods fail[4] and they must be corrected by more complex functions determined by a very large number of experimental density determinations.

In general, a useful tool for the optimization of the final properties of a set of chemical objects is the theoretical quantitative structure-property relationship (QSPR) analysis.[5,6] This technique, which has a corollary in drug design, relates properties to numerical representations of structures through mathematical models, thus, taking an immense practical role in the development of predictive and interpretative models. In this paper we present the results of a QSPR analysis of Zn-doped glasses based on the Bioglass 45S5 composition (Na_2O, 24.4; CaO, 26.9; SiO_2, 46.2; P_2O_5, 2.6 mol%). Theoretical structural descriptors derived from molecular dynamics (MD) simulations have been used to rationalize, in a quantitative way, the variation of experimental data measured for density. This is one of the first time in which a theoretical QSPR approach is applied to the field of inorganic glasses.

The experimental-computational approach to study and rationalize a complex glassy system with quantitative structure-property relationships (QSPR) analysis has been developed

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recently in our laboratory.[7] In the present work, we focalize our attention on a family of bioglasses whose mechanical and chemical properties have been modified by means of addition of ZnO.[7,8] The prediction of these properties can be helpful for the design of new families of potential bioglasses; for this reason we started by applying the QSPR method to a large number of glasses with different composition in order to challenge the prediction ability of the models obtained.

2. Experimental

2.1. Glass preparation

Four different series of glasses were synthesized. The first series has the following composition: $2SiO_2{\cdot}1Na_2O{\cdot}1CaO{\cdot}xZnO$ (KZ series where $x=0$, (K), $x=0.17$ (KZ5), $x=0.34$ (KZ10) and $x=0.68$ (KZ17)).

Three more series are based on the composition $(2-y)SiO_2{\cdot}1Na_2O{\cdot}1.1CaO{\cdot}yP_2O_5{\cdot}xZnO$, with $y=0.10$, 0.20, 0.26. The addition of 3.8, 7.8 and 15.9 mol% ZnO to 45S5 (hereafter H, $y=0.10$ and $x=0$) glass gives rise to HZ5 ($y=0.10$ and $x=0.16$), HZ10 ($y=0.10$ and $x=0.35$) and HZ20 ($y=0.10$ and $x=0.78$), respectively. The substitution of P_2O_5 for SiO_2 gives rise phosphorus rich glasses HP5 ($y=0.20$, 5 mol% P_2O_5) and HP6.5 ($y=0.26$, 6.5 mol% P_2O_5) The zinc-containing glasses are HP5Z5 ($y=0.20$ and $x=0.16$, 3.9 mol% ZnO), HP5Z10 ($y=0.20$ and $x=0.36$, 8.0 mol% ZnO), HP5Z22.5 ($y=0.20$ and $x=0.96$, 18.5 mol% ZnO), HP6.5Z5 ($y=0.26$ and $x=0.17$, 4.0 mol% ZnO), HP6.5Z10 ($y=0.26$ and $x=0.36$, 8.1 mol% ZnO), HP6.5Z15 ($y=0.26$ and $x=0.58$, 12.3 mol% ZnO).

The reagents and experimental conditions for the batch preparations were reported in previous works.[7,8]

The melts were poured into a graphite mould and afterwards ball-milled in agate mill jars and sieved to produce a particle size range of 108–125 μm for the density measurements. The samples were obtained as transparent homogeneous glasses. The molar compositions of the examined glasses are listed in Table 1.

2.2. Glass characterization

Experimental density was determined with a picnometer (Micromeritics, Accupyc 1330) at room temperature with an accuracy of 0.002 g/cm^3. Each value is an average of three independent measurements. We calculated the density values using the mathematical prediction methods[9] of Priven[10] and Demkina.[11] For these type of glasses the use of the two most famous methods, Huggins and Sun[12] and Appen[4] is not possible because they do not consider the cases of glasses containing Zn and P. The calculations were performed using the Sciglass program.[9]

2.3. Computational procedure

The computational procedure for obtaining the structural models of experimental glasses is reported in previous work.[7,8] MD simulations were performed with the DL_POLY® program,[13] using Cerius2®[14] as a graphical interface. We had also simulated two independent glasses (TG1 and TG2), whose experimental density is reported in the literature,[5] instrumental for the validation of the statistical model obtained by QSPR approach. The composition of TG1 and TG2 is reported in Table 1.

Table 1
Batch compositions (mol%) for the general glass formula $2SiO_2{\cdot}1Na_2O{\cdot}1CaO{\cdot}xZnO$ for the KZ series and $(2-y)SiO_2{\cdot}1Na_2O{\cdot}1.1CaO{\cdot}yP_2O_5{\cdot}xZnO$ for HZ, HP5Z and HP6.5Z series and for the testing probe TG1 and TG2 glasses

Glass	x	y	Mol%				
			SiO_2	Na_2O	CaO	P_2O_5	ZnO
K	0	–	50.0	25.0	25.0	–	–
KZ5	0.17	–	47.0	24.2	24.6	–	4.2
KZ10	0.34	–	45.4	23.4	23.2	–	8.0
KZ17	0.68	–	42.6	21.4	21.5	–	14.5
H	0	0.10	46.2	24.3	26.9	2.6	–
HZ5	0.16	0.10	44.4	23.4	25.9	2.5	3.8
HZ10	0.32	0.10	42.5	22.5	24.8	2.4	7.8
HZ20	0.78	0.10	38.8	20.5	22.6	2.2	15.9
HP5	0	0.20	43.7	24.4	26.9	5.0	–
HP5Z5	0.16	0.20	42.1	23.4	25.9	4.7	3.9
HP5Z10	0.36	0.20	40.2	22.4	24.8	4.6	8.0
HP5Z22.5	0.96	0.20	35.7	19.9	21.9	4.1	18.5
HP6.5	0	0.26	42.2	24.3	26.9	6.5	–
HP6.5Z5	0.17	0.26	40.5	23.4	25.8	6.2	4.0
HP6.5Z10	0.36	0.26	38.8	22.4	24.7	6.0	8.1
HP6.5Z15	0.58	0.26	37.0	21.3	23.6	5.7	12.3
TG1	–	–	50.6	–	42.5	–	6.9
TG2	–	–	48.6	–	31.7	–	19.7

3. Results and discussion

3.1. Density

The experimental density values are reported in Table 2, together with density values calculated by the semiempirical Priven[10] and Demkina[11] methods and the structural descriptors derived from the MD simulations. The density data values increase linearly with Zn concentration (Fig. 1a–d) and the coefficients of the linear regression obtained are reported in Table 3. This behaviour suggests an unique structural role for the Zn ion in the glass network in the range of concentrations allowed. The semiempirical Priven[10] and Demkina[11] methods, based on the additivity of the contributions due to each oxide in the glass give rise to straight lines respect to the molar ZnO%. The most significant difference between experimental and calculated values are observed, in all the four series of glasses studied, for the Priven method. Moreover, the density values calculated by both methods diverge markedly with respect to the experimental ones at high ZnO content (ZnO% greater than 4.0% ($x=0.17$)) and in particular the angular coefficients of the linear regression for the experimental plots are systematically higher with respect to calculated ones (see Table 3).The discrepancy in the slope of the experimental linear regression with respect to those obtained by the semiempirical methods high-

Table 2
Experimental and calculated density and the structural descriptors derived from MD simulations

	Exp. dens. ± 0.002 (g/cm^3)	Priven dens. (g/cm^3)	Demkina dens. (g/cm^3)	O_{tot}	$N^0_{bridges}$						N^0_{X-O-X}	$N^0_{X-O-X/O_{tot}}$	Predicted dens. (g/cm^3)	Δ = |Predicted-exp|
					Si–O–Si	Si–O–P	Si–O–Zn	P–O–Zn	Zn–O–Zn					
K	2.718	2.750	2.723	648	206	0	0	0	0		206	0.318	2.725	0.007
KZ5	2.810	2.809	2.809	675	193	0	76	0	1		270	0.400	2.806	0.004
KZ10	2.894	2.856	2.876	695	181	0	155	0	4		340	0.489	2.894	0.000
KZ17	3.028	2.940	2.999	720	157	0	266	0	40		463	0.643	3.046	0.018
H	2.719	2.720	2.733	732	197	10	0	0	0		207	0.283	2.690	0.029
HZ5	2.815	2.767	2.800	751	204	10	71	5	3		293	0.390	2.796	0.019
HZ10	2.900	2.817	2.872	772	178	12	148	17	6		361	0.468	2.873	0.027
HZ20	3.075	2.923	3.051	813	155	8	283	34	58		538	0.662	3.064	0.011
HP5	2.721	2.696	2.749	767	206	31	0	0	0		237	0.309	2.716	0.005
HP5Z5	2.808	2.750	2.793	784	201	21	59	20	2		303	0.386	2.793	0.015
HP5Z10	2.865	2.792	2.864	808	173	31	134	32	7		377	0.467	2.872	0.007
HP5Z22.5	3.116	2.925	3.083	822	144	24	281	65	69		583	0.709	3.111	0.005
HP6.5	2.687	2.683	2.721	788	205	45	0	0	0		250	0.317	2.724	0.037
HP6.5Z5	2.762	2.728	2.788	807	181	52	54	21	3		311	0.385	2.791	0.029
HP6.5Z10	2.857	2.780	2.858	820	175	34	125	42	7		383	0.467	2.872	0.015
HP6.5Z15	2.961	2.833	2.955	830	166	23	191	53	30		463	0.558	2.962	0.001
TG1	2.972			642	231	–	105	–	7		343	0.534	2.938	0.034
TG2	3.116			661	151	–	293	–	19		463	0.700	3.102	0.014

lights the weakness of the additivity approximation for these series of glasses and can be ascribed to the change in the molar volume term of the oxides, in particular in the glass with high ZnO%.

3.2. Molecular dynamics simulations

The force field used for the these glassy system has been validated in previous works,[7,8,15] where it has been confirmed that a simple force field, including only the two-bonded interaction terms and formal charges, is sufficiently adequate to derive structural descriptors to be related to the variation of physico-chemical properties as a function of glass composition. As previously observed,[7,8,15] the introduction of Zn in the network causes an increase in the polymerization since this ion shows a clear preference to bond to bridging oxygen (BO) atoms in a regular tetrahedral geometry in all the glasses studied. The increase of the reticulation degree is detected by the global increment of the number of X–O–X bridges (where X = Si, P, and Zn). In the P-bearing glasses (HZ, HP5Z, HP6.5Z series) the P atom is preferentially found in isolated tetrahedral units surrounded by Na and Ca ions and it is progressively included in the glass network by Zn addition as detected by the increment of the number of P–O–X bridges (P–O–X = P–O–Si + P–O–Zn, see Table 2 and Fig. 2). The increase in the number of bridges is proportional to the higher degree of interconnection of the glass network. Therefore, we can take into account the structural packing caused by the introduction of Zn ions in order to explain the experimental density trend.

Thus, in the present study the results of MD simulations constitute the basis for a QSPR analysis that allows for interpretation and, hopefully, prediction of experimental data. In agreement with our previous work,[7] the descriptor, derived from MD simulations, which better correlates with the experimental density values of the glass series is $N^0_{X-O-X/O_{tot}}$, which is the total number of Si–O–Si, Si–O–Zn, Si–O–P, P–O–P, P–O–Zn and Zn–O–Zn bridges found in the simulated glasses normalized for the total number of oxygen atoms (O_{tot}). This quantity represents an overall descriptor of the degree of polymerization of the glass network. The data values of this descriptor and its components are reported in Table 3, whereas the linear correlation plot of $N^0_{X-O-X/O_{tot}}$ versus the experimental density values is given in Fig. 3.

The positive slope indicates that density increases with the overall packing degree of the atoms in the glasses that have been obtained by adding Zn or substituting P for Si. This is a not obvious result, since the increase in the density values is the effect of the balance between the variation of the weight of the components and the change of the molar volume as a function of the different glass compositions. It is worth noting that this descriptor allows the four series of glasses to be fitted in the same correlation plot. The soundness of this correlation is confirmed by its ability to predict the density values of the two glasses we have chosen for the model validation (Fig. 3 and Table 2). In fact the deviation values Δ for the test glasses TG1 and TG2 are comparable with those determined for the other glasses. The choice of test glasses with a composition

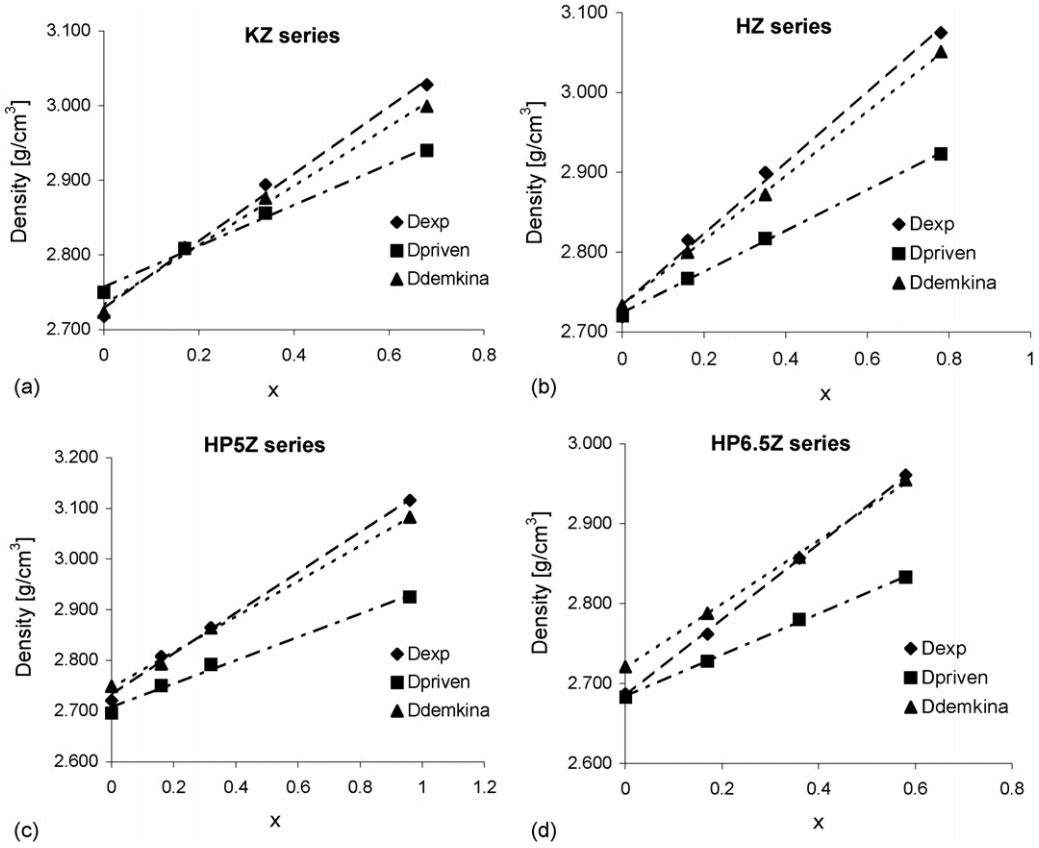

Fig. 1. Experimental, Priven and Demkina density plot as a function of ZnO content for KZ (a), HZ (b), HP5Z (c) and HP6.5Z (d) series.

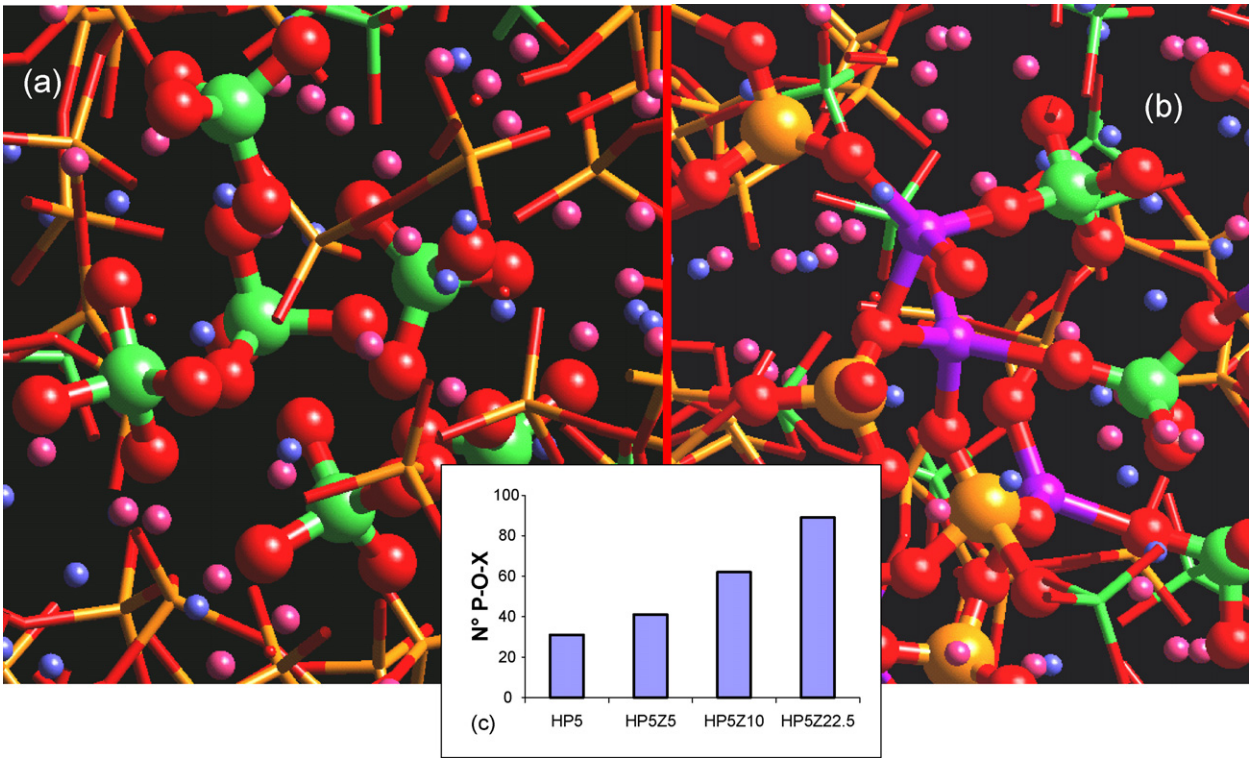

Fig. 2. Snapshot of the simulated HP5 (a) and HP5Z10 (b) glasses showing the zone rich in isolated P tetrahedra characteristics of HP5 and the –Si–O–Zn–O–P–O–Zn– strings formed in HP5Z10 (Si is represented in yellow, Zn in violet, P in green, O in red, Na in pink, and Ca in blue refered to color figure). In (c) is reported the trend of P–O–X bridges at different ZnO content.

Table 3
Linear regression coefficients of experimental, Priven and Demkina density trend plots for the studied glass series

Series	Experimental density			Priven density			Demkina density		
	a	*b*	r^2	*a*	*b*	r^2	*a*	*b*	r^2
KZ	0.452	2.728	0.9936	0.276	2.757	0.9936	0.400	2.733	0.9939
HZ	0.447	2.733	0.9933	0.2582	2.724	0.9987	0.407	2.733	0.9997
HP5Z	0.403	2.733	0.9968	0.2311	2.708	0.9898	0.352	2.746	0.9981
HP6.5Z	0.475	2.685	0.9995	0.260	2.684	0.9992	0.401	2.719	0.9988

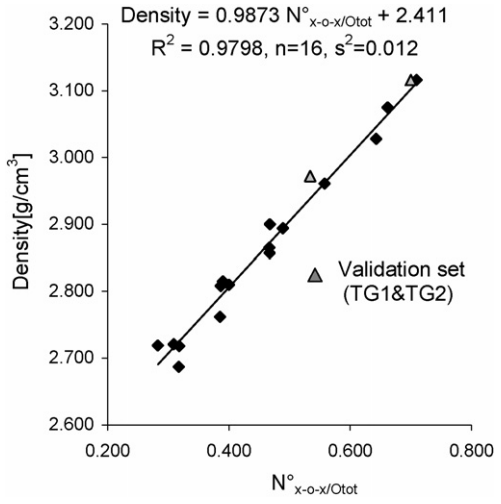

Fig. 3. Correlations between structural descriptor $N^0_{X–O–X/O_{tot}}$ and experimental density measured for the glasses studied.

quite different from the rest of the glass series (glasses without Na and with high Ca content), demonstrates that this correlation function can be used for different types of silicate and phosphosilicate glasses.

Moreover, the correlation we found performs better with respect to that determined with the Priven and Demkina methods (Fig. 4). In particular, the predictions obtained by means of the $N^0_{X–O–X/O_{tot}}$ descriptor at high values of density are closest to the experimental ones with respect to those obtained by the Priven and Demkina methods, confirming that these methods can be applicable to glass with a small ZnO content only.

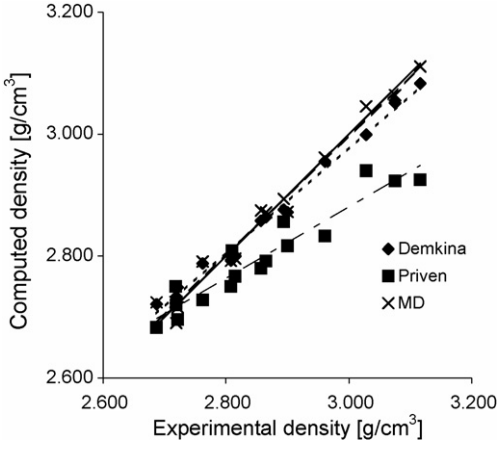

Fig. 4. Correlations between the eperimetal density and computed density by MD, Priven and Demkina methods.

4. Conclusion

In this work a quantitative structure properties relationships approach has been utilized for the rationalization and prediction of complex multicomponent glass density. The results obtained extend the validity of this approach on a large number of glasses (16 glasses are used for the correlation). Moreover, the statistical robustness of the model obtained has been challenged by means of new and not congeneric glasses (TG1 and TG2) furnishing encouraging results.

The statistical model obtained by making use of structural descriptors with high information content can be considered an useful tool for exploiting and rationalizing the large amount of data derived by molecular simulations of the glasses and gaining further insight into the physical processes determining the properties of interest.

We think that this type of approach, tested on density, will be particularly helpful when the correlated properties are complex and difficult to be measured and interpreted.

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