

Data classification with the Vogel–Fulcher–Tammann–Hesse viscosity equation using correspondence analysis

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Abstract

The well-known Vogel–Fulcher–Tammann–Hesse equation (VFTH, $\log_{10}\eta = A + B/(T - T_0)$, η in Pa s and T in K) has been extensively used in the description & characterization of cooperative molecular motion by means of the temperature dependence with viscosity, η , e.g., using Angell's classification. Experimental evidence has been pointed out for the statistical correlation between its three adjustable parameters A , B and T_0 , which may bring questions on the reliability of fitted VFTH parameters. In this work VFTH equation was applied over a wide temperature range (between glass transition temperature, T_g and the melting point, T_m) for 38 oxide glasses, considering simple, binary and ternary compositions of silicates and borates systems. These systems include strong, moderate and fragile glass-forming liquids. For this task was used the Levenberg–Marquart non-linear fitting procedure to find viscosity parameters B and T_0 , maintaining $A = -5$ fixed, intending to reduce the number of adjustable parameters. Despite this restriction, the VFTH equation has shown to adjust very well to experimental data in wide temperature range.

Simple criteria were developed in the past to characterize glass-forming liquids, one of them (due to Angell) is the *strong–fragile* classification. In this work we apply correspondence analysis (CA) to verify the correlation between B and T_0 parameters as well as between T_g and T_m . CA is a descriptive and exploratory technique designed to analyze simple multi-way tables containing some measure of correspondence between rows and columns. From these results is possible to map either borate (and almost fragile) or silicate (usually strong up to near fragile) systems. As a statistical tool, CA corroborates correlation mainly between B and T_0 and justifies the use of B , T_0 and T_g as the main parameters for the fragility indexes $m = BT_g/(T_g - T_0)^2$ and $D = B/T_0$.

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1. Introduction

The dynamics of supercooled liquids is a complex problem that continues to be the focus of many investigations [1]. Glass-forming materials are able to maintain a disordered liquid-like structure below their melting temperature (T_m), if crystallization is prevented. The viscosity of supercooled liquids increases strongly with decreasing temperature. The glass transition temperature (T_g) is

commonly defined as the temperature at which viscosity reaches $\approx 10^{12}$ Pa s.

The most accurate three-parameter equation for viscosity (η) is the Vogel–Fulcher–Tammann–Hesse (VFTH, [2–4]):

$$\log_{10}\eta = A + \frac{B}{T - T_0}, \quad (1)$$

where A , B and T_0 are constants, and T is the absolute temperature. Most literature refers to this as the VFT equation [5–7], excluding one of authors, a preceding fault that only in recent years is being recognized (see Appendix).

The three-parameter VFTH equation serves as basis for treatment of viscous systems, being able to model η in a

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wide temperature range for many different glass-forming liquids. The applicability of the VFTH equation was tested, verified and compared with other models in the following years, such as Avramov–Milchev [8], Macedo–Litovitz [9] and Cohen–Grest [10], among others. The VFTH equation is also widely used for the study of cooperative thermal relaxation processes [8]. More recently the present authors analyzed statistically the VFTH equation by means of principal component analysis (PCA) [11], also showing correlations between the three VFTH parameters.

This work is an attempt to clarify relevant issues related to the use of the VFTH equation, when is pretended to extract the corresponding parameters and possible correlations from fitting of reliable, experimental viscosity data of 21 silicate and 17 borate glass systems measured near T_g to T_m , covering circa 12 (or more) decades on $\eta(T)$. As far as the authors know this is the first study that presents such viscosity data in such systematic way by means of correspondence analysis (CA). The fragile/strong characters obtained from VFTH fit in these systems were also assessed using the CA, which provided a new data set organization.

2. Brief description of correspondence analysis

The role of statistics is to summarize, to simplify and eventually to explain. CA is basically a fairly simple technique from mathematical and computational points of view, and it is primarily a geometric technique rather than a statistical one [12]. It is a useful tool in so different branches of science as biology and public health [13], chemistry [14], nuclear physics [15] and materials science [16].

CA provides tools for analyzing the associations between rows and columns of contingency tables. The main idea of correspondence analysis is to develop simple indices that will show the relations between the row and the columns categories. These indices could give simultaneously which column categories have more “weight” in a row category and *vice versa* [12].

In CA the rows and columns of a data matrix \mathbf{F} are depicted as points in a low-dimensional space. A CA solution is obtained by simultaneously approximating the row and column profiles through minimization of the so-called chi-squared (χ^2) distance. It is well known that the CA solution for both rows and columns can be obtained immediately from the singular value decomposition of the scaled data matrix.

Let us introduce briefly the notation needed for CA. Let \mathbf{F} denote an $n_r \times n_c$ matrix of on which CA is performed. The only restriction on \mathbf{F} is that its elements are non-negative. Let \mathbf{r} be the vector of row sums of \mathbf{F} , that is $\mathbf{r} = \mathbf{F}\mathbf{1}$, and \mathbf{c} the vector of column sums, $\mathbf{c} = \mathbf{F}'\mathbf{1}$, where $\mathbf{1}$ denotes a vector of ones of appropriated length. Furthermore, define n as a sum of all elements of \mathbf{F} , that is, $n = \mathbf{1}'\mathbf{F}\mathbf{1}$.

Defining the scaled data matrix $\tilde{\mathbf{F}}$ as $\tilde{\mathbf{F}} = \mathbf{D}_r^{-1/2}\mathbf{F}\mathbf{D}_c^{-1/2}$, where \mathbf{D}_r and \mathbf{D}_c are diagonal scaling matrices with,

respectively, the elements of r and c on their diagonal. The task of CA is to find k -dimensional coordinate matrices \mathbf{R}_k and \mathbf{C}_k for row and column such that the loss function:

$$\chi^2(\mathbf{R}_k, \mathbf{C}_k) = \|\tilde{\mathbf{F}} - \mathbf{D}_r^{1/2}\mathbf{R}_k\mathbf{C}_k'\mathbf{D}_c^{1/2}\|^2 \quad (2)$$

is minimized. The notation $\|\mathbf{M}\|^2$ denotes the sum of squared elements of \mathbf{M} .

Consider the (complete) singular value decomposition:

$$\tilde{\mathbf{F}} = \mathbf{U}\mathbf{\Lambda}\mathbf{V}' \quad \text{where} \quad \mathbf{U}'\mathbf{U} = \mathbf{I}_{n_r} \quad \text{and} \quad \mathbf{V}'\mathbf{V} = \mathbf{I}_{n_c}, \quad (3)$$

where \mathbf{I}_i denotes the $i \times i$ identity matrix. Then, it is possible to minimize $\chi^2(\mathbf{R}_k, \mathbf{C}_k)$ considering [17]:

$$\mathbf{R}_k = \mathbf{D}_r^{-1/2}\mathbf{U}_k\mathbf{\Lambda}_k^\alpha \quad \text{and} \quad \mathbf{C}_k = \mathbf{D}_c^{-1/2}\mathbf{V}_k\mathbf{\Lambda}_k^{1-\alpha}, \quad (4)$$

where \mathbf{U}_k and \mathbf{V}_k are, respectively, the $n_r \times k$ and $n_c \times k$ matrices of singular vectors corresponding to the k largest singular values gathered, in decreasing order, in the $k \times k$ diagonal matrix $\mathbf{\Lambda}_k$, and α is a non-negative scalar.

From the above equations is possible to show that:

$$\mathbf{R}_k'\mathbf{D}_r\mathbf{R}_k = \mathbf{\Lambda}_k^{2\alpha} \quad \text{and} \quad \mathbf{C}_k'\mathbf{D}_c\mathbf{C}_k = \mathbf{\Lambda}_k^{2(1-\alpha)}. \quad (5)$$

For $\alpha = 1$ we obtained *row principal* coordinates and for $\alpha = 0$ *column principal* coordinates. The approach for CA followed here (Eqs. (2)–(5)) is due to Groenen and van de Velden [17]. An introductory book for CA is that of Greenacre [12].

3. Objectives and realization

The main task of this manuscript was to study in systematic way the statistical correlations between B and T_0 VFTH parameters using CA (maintaining A fixed). A second one is to verify the applicability of VFTH in the same systems, considering a wide temperature range, from T_g to T_m .

The results of VFTH fittings (i.e., the determination of the values of B and T_0) in 21 silicates and 17 borates are shown in Table 1. T_g and T_m are experimental data, mainly measured by differential scanning calorimetry (DSC) using 10 K/min heating rates—see details in Ref. [18]. Viscosity measurements included the use of different methods, as beam-bending, falling ball, torsion, rotating viscometer and fiber elongation [18].

About viscosity data used, an extensive analysis was carried out in all systems presented in Table 1, including experimental procedure and impurity content. Some systems required a careful attention, as for example silica: SiO_2 is largely affected by impurities. Thus, for this case we select the highest viscosity data, which represented the purest systems. A recent review on this particular problem can be found elsewhere [19]. Otherwise, systems as $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ (diopside) presents a so de-polymerized chain structure that any impurity added could not influence viscous flow behavior in wide T [20]. This fact could explain the great agreement in twelve orders of magnitude from different data sources.

Table 1

VFTH viscosity parameters B and T_0 (A was fixed as -5 , η in Pa · s units), plus T_g and T_m values, the measured viscosity temperature range and the corresponding parameters m and D

Glass	B (K)	T_0 (K)	T_g (K)	T_m (K)	ΔT range (K)	m	D
SiO ₂	21254	139	1450	2000	1377–2000	17.9	152.91
Li ₂ O · SiO ₂	5744	276	593	1573	593–1823	33.9	20.81
Li ₂ O · 2SiO ₂	5752	380	727	1306	718–1720	34.7	15.14
Li ₂ O · 3SiO ₂	8218	255	734	1306	747–1873	26.3	32.23
Na ₂ O · SiO ₂	4999	395	687	1362	687–1623	40.3	12.66
Na ₂ O · 2SiO ₂	5538	393	728	1146	684–1173	35.9	14.09
Na ₂ O · 3SiO ₂	7484	287	743	1084	689–1773	26.7	26.08
Na ₂ O · 4SiO ₂	7618	323	765	1423	691–1811	29.8	23.59
K ₂ O · SiO ₂	4395	416	675	1248	675–1301	44.2	10.56
K ₂ O · 2SiO ₂	7461	333	768	1313	748–1679	30.3	22.41
K ₂ O · 3SiO ₂	8334	253	760	1353	773–1673	24.6	32.94
K ₂ O · 4SiO ₂	8471	255	766	1408	764–1673	24.8	33.22
Na ₂ O · Al ₂ O ₃ · 6SiO ₂ (albite)	12281	347	1087	1393	1062–2660	24.4	35.39
CaO · MgO · 2SiO ₂ (diopside)	4826	710	995	1664	960–2066	59.1	6.80
CaO · Al ₂ O ₃ · 2SiO ₂ (anorthite)	5802	785	1113	1825	1082–1973	60.0	7.39
2MgO · 2Al ₂ O ₃ · 5SiO ₂ (cordierite)	8244	583	1088	1740	1073–1798	35.2	14.14
15.45Na ₂ O · 12.81CaO · 71.74SiO ₂ (soda lime silica)	6785	421	819	1283	773–1761	35.1	16.12
2BaO · TiO ₂ · 2SiO ₂ (fresnoite)	3896	750	983	1714	1000–1792	70.5	5.19
PbO · SiO ₂	3694	454	673	1037	685–1616	51.8	8.14
PbO · 2SiO ₂	6001	390	749	1190	646–1073	34.9	15.39
2PbO · SiO ₂	2496	473	613	1016	611–1477	78.1	5.28
B ₂ O ₃	4695	252	540	723	545–1077	30.6	18.63
Li ₂ O · B ₂ O ₃	2557	542	693	1116	690–1333	77.7	4.72
Li ₂ O · 2B ₂ O ₃	2497	616	763	1190	758–1292	88.2	4.05
Li ₂ O · 3B ₂ O ₃	2850	599	768	1155	764–1481	76.6	4.76
Li ₂ O · 4B ₂ O ₃	2908	579	751	1108	748–1173	73.8	5.02
Na ₂ O · 2B ₂ O ₃	2405	600	748	1015	727–1351	82.1	4.01
Na ₂ O · 3B ₂ O ₃	3121	557	746	1039	718–1323	65.2	5.60
Na ₂ O · 4B ₂ O ₃	3172	539	727	1087	708–1333	65.2	5.88
K ₂ O · 2B ₂ O ₃	2888	520	705	1063	654–1317	59.5	5.55
K ₂ O · 3B ₂ O ₃	3403	512	709	1140	709–1369	62.2	6.65
K ₂ O · 4B ₂ O ₃	3588	463	691	1130	644–1393	47.7	7.75
Cs ₂ O · 3B ₂ O ₃	3363	491	693	1110	684–1141	57.1	6.85
BaO · 2B ₂ O ₃	3262	619	810	1183	807–1184	72.4	5.27
SrO · 2B ₂ O ₃	2592	755	911	1270	906–1362	97.0	3.43
PbO · B ₂ O ₃	2171	525	658	983	643–1473	80.8	4.14
PbO · 2B ₂ O ₃	3020	545	738	1048	722–1473	59.8	5.54
PbO · 3B ₂ O ₃	2656	569	728	1023	712–1053	76.5	4.67

Figs. 1a and b present the viscous flow measurements between T_g and T_m for selected silicate and borate glass systems, respectively, and the lines correspond to VFTH fittings for each system. Recently was published that statistical correlation exists between VFTH parameters, mainly B and T_0 , considering just dielectric relaxation in poly(vinyl acetate) [21]. This paper presents results considering 38 oxide glass systems, which viscosity was analyzed in wide temperature range.

4. Results

Table 1 presents thus data used for CA procedure. It is important to note that higher variance corresponds to B values, which range from near 2100 K up to 21,000 K. From these data, 99.99% could be represented by the first two axes (related to B and T_0 , respectively), as presented in

Table 2. Table 3 presents the scores between B , T_0 , T_g and T_m with the corresponding axes.

Figs. 2–4 show results using CA considering different axes. For each figure, the distance between the corresponding row points is a measure of similarity between the row-frequency profiles. The first source of information opposes silicates and borates. For example, from Fig. 2 such oxide glass forming systems are far from each other because their profiles are different, whereas SiO₂ is near B₂O₃ because their profiles are similar. Almost all borates are contained in a region at Fig. 2 (excepting B₂O₃ and K₂O · 4B₂O₃), as indicated. It appears that the whole information is spread onto only two orthogonal eigenvectors, representing 97.63% and 2.36% of the total variance. As expected, one can see that the main information source (related to B) is conveyed to axis 1, and the second source of information (related to T_0) is mostly conveyed to axis 2.

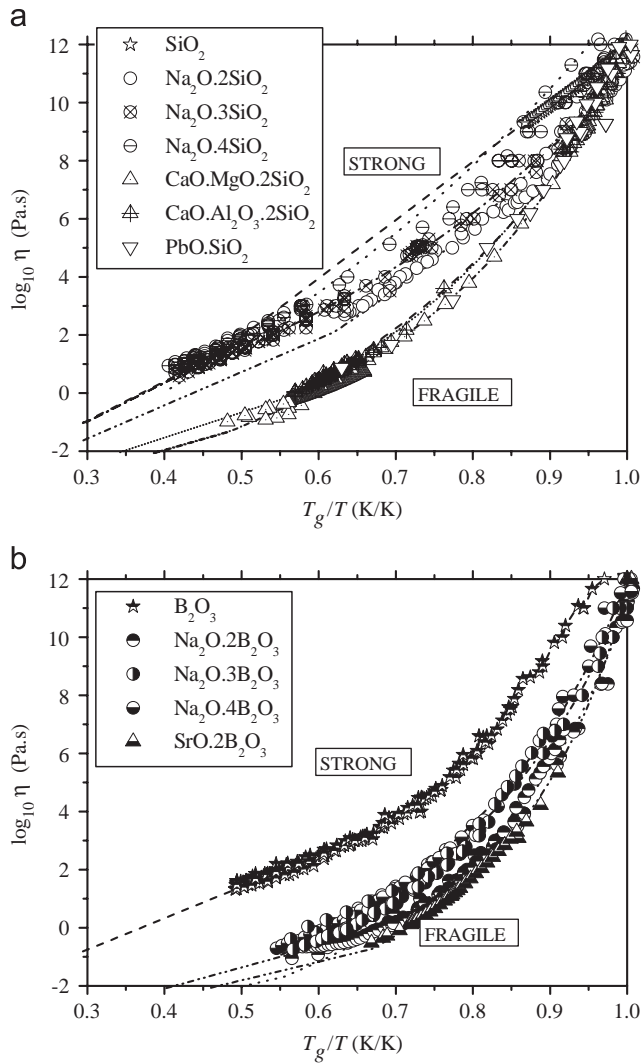


Fig. 1. Scaled experimental viscosity data for silicate (a) and borate (b) systems, showing range from “strong”, characteristic of open tetrahedral network liquids, to “fragile”, typical of ionic and molecular liquids.

Table 2
Eigenvalues, total and cumulative percent of CA analysis done using data from Table 1

CA axis	Eigenvalue	Total percent	Cumulative percent
1	0.062	97.63	97.63
2	0.001	2.36	99.99
3	9.31×10^{-6}	0.01	100.01
4	0	2.01×10^{-10}	100.01

Table 3
Species scores of the parameters B , T_0 , T_g and T_m and its corresponding axes

Parameter	CA 1	CA 2	CA 3	CA 4
B	-68	-13	-70	-70
T_0	253	-176	173	173
T_g	123	-125	157	157
T_m	113	199	133	133

From Fig. 3 there is no relative dispersion but a linear relation between these two new axes. This figure clearly shows opposition between silicates and borates: silica ($-40, -39$) and $\text{SrO} \cdot 2\text{B}_2\text{O}_3$ ($49, 47$), with the moderate ones localized closer to coordinate (0, 0). The main reason for this mapping could be related to the weight of components: from first CA the highest weights come from higher B and T_g values of SiO_2 and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (albite). Borates are distinguishable because of their lower B and (relative) lower T_g values.

Fig. 4 presents statistical correlation between T_0 and T_g . It is possible to distinguish a borate region (that also includes $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ glass) from other silicates, even considering the small variance from such values presented in Table 1.

5. Discussion

As well known, the VFTH needs three parameters to fit, but it is possible to use only two of them if one considers $A = -5$ fixed (in Pa s). For this specific point is possible to give four reasons to proceed in this way: (i) The main physical reason for this choice is that at higher temperatures there is a decrease in structural complexity of the glassy melts [22]. (ii) Considering only VFTH fittings of A , B and T_0 from different sources [18], there is a distribution near $A = -5$, as also verified by Barrer [22] and Angell [23,24]. (iii) From a theoretical point of view, two reasonable approximations to estimate A could be given at least. First, from Maxwell’s definition of shear viscosity, experimental η data from some sources do apply well if one considers A between -1 and -3 with reasonable accuracy (see Ref. [25] and references cited therein). Another way to find the average A value is to consider the theoretical value estimated via Eq. (6), as recently explained [25]:

$$\eta_0 = 10^A = \frac{k_B T}{\lambda^3} \tau_0, \quad (6)$$

where $\tau_0 = h/k_B T$ is a characteristic time of the period of atomic vibrations, h is Planck’s constant, k_B the Boltzmann constant and λ has a value of the order of O^{2-} radius. Using $\lambda = 2.7 \text{ \AA}$ one could obtain $A = -4.5$, a value closer to the assessment proposed. And finally, (iv) recent theories demonstrated that $\log_{10}(\eta(T_g)) - A \approx 17$, thus $A = -5$ [26].

This last point would be clearer considering the fragility index m . A useful way to understand the structural arrangement flowing at near 10^{12} Pa s comes from the fragility parameter, due to Angell [23,24], defined by the steepness index m :

$$m = \left. \frac{d(\log_{10}\eta)}{d(T_g/T)} \right|_{T=T_g}. \quad (7)$$

Thus, Eq. (7) indicates such sensitivity of the liquid structure. The results are plotted in Fig. 1 for silicates (a) and borates (b), wherein m (the derivative of $\eta(T)$ at T_g) seems to increase more pronounced with T_g/T in some glass forming liquids. Such systems are characterized as

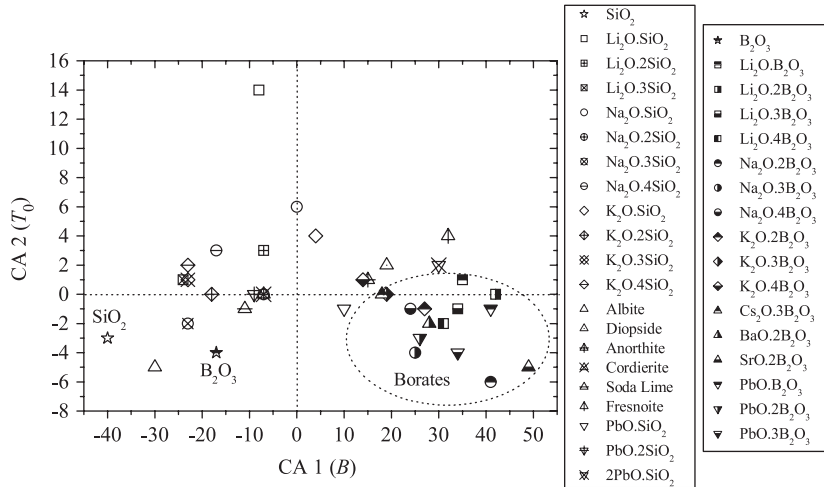


Fig. 2. Correspondence analysis results for axis 1 (related to *B* parameter) versus axis 2 (*T*₀).

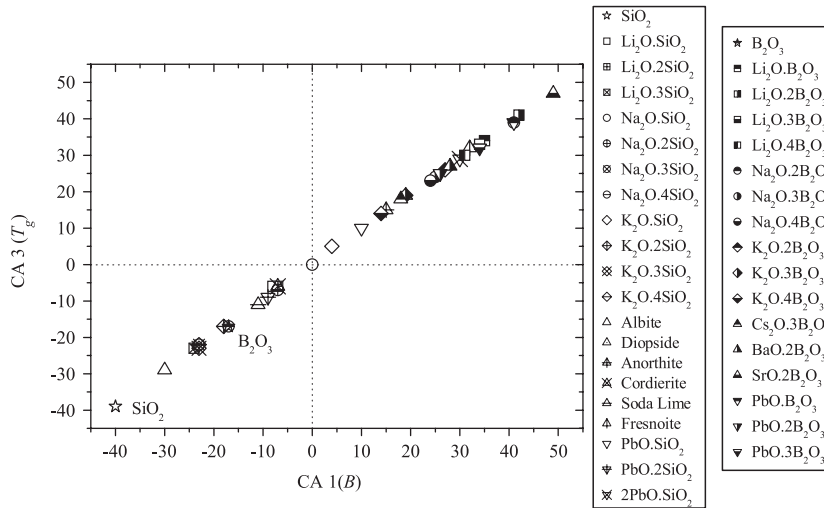


Fig. 3. Correspondence analysis results for axis 1 (related to *B* parameter) versus axis 3 (*T*_g).

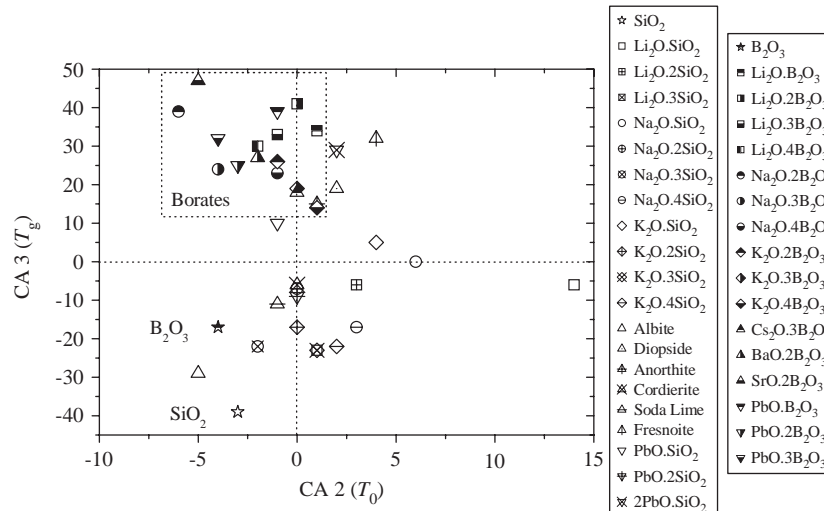


Fig. 4. Correspondence analysis results for axis 2 (related to *T*₀ parameter) versus axis 3 (*T*_g).

strong, moderate or fragile depending on m index. Important to note from Table 1 that almost all binary borate glasses are fragile in a higher or lower level. The fragility index nearly corresponds to the de-polymerization degree, or the increasing of alkali content, according to Avramov's recent finding [27]. One interpretation is that open network liquids like SiO_2 show an Arrhenius variation of the viscosity between T_g and the high-temperature limit and provide the 'strong' liquid edge. Other systems, characterized by simple non-directional coulomb attractions, provide the further limit, 'fragile'.

From the Angell classification, $D = B/T_0$ is the strength parameter, which can be related with fragility [23,24]: a D value higher than 30 represents a *strong* behavior, and a low D (below 30) characterizes a *fragile* system. Relevant information may be obtained from these parameters associated to a given system; this includes insights about glassy structure itself. Moreover, the VFTH parameters may be used to predict system dynamics at temperatures beyond limited experimental procedures. Values of m and D parameters are also presented in Table 1.

As expected, from VFTH results in Table 1 stronger glasses present higher B parameters and lower T_0 , in opposition to the fragile ones. The B parameter also diminishes with alkali content in the lithia, soda and potassium silicate/borate systems, showing the influence of de-polymerization degree.

Finally, there is a relation between the characteristics temperatures T_g and T_0 with m , established by Böhmer and Angell [28]:

$$\frac{m}{m-17} = \frac{T_g}{T_0}, \quad (8)$$

where $\log_{10} \eta(T_g) - A \approx 17$ is the *lower fragility limit* [28]. The resulting plot is in Fig. 5. Please note that SiO_2 near corresponds to this limit, and the opposite can be expectedly observed for all borate glasses. Thus, from

Fig. 5, the agreement of fragility index m with T_g and T_0 parameters of 38 oxide glasses confirmed the validity of $A = -5$ in the present calculations. In other words, the choice of $A = -5$ is essential considering fragility classification.

As presented above, CA allows displaying a low-dimensional data projection. Each value of a variable is represented by a point in the Euclidean space in such a way that the linear distance between any two points may be interpreted in terms of similarity. In addition, the angular distance between two points of different variables corresponds to the strength of the association between the corresponding categories.

It is possible to relate CA results and Angell's classification from the results presented above. For example, from Figs. 2–4 the first source of information opposes the stronger (and moderate) from the fragile systems, i.e., mainly silicates from borates. From Fig. 2 the CA axis 1 (related to B parameter) separates strong from fragile systems. The moderate glasses are near CA 1 origin.

Fig. 3 shows that T_g and B also presents correlation, and is possible to distinguish fragile and strong regions. From Fig. 4 is possible to note that the first and second quadrants include moderate and fragile, and third and fourth the stronger systems.

It is important to note that CA analysis is a strictly statistical tool. Such two-dimensional maps presented in Figs. 2–4 also shows correlation with Angell's classification, in the exact sense of the *spatial distribution* of the glassy systems. It partially justifies the use of B , T_0 and T_g as main parameters to fragility definitions $m = BT_g / (T_g - T_0)^2$ and $D = B/T_0$ by means of the variance in the analyzed data. Also, data analysis proved that VFTH could be considered a useful tool for describing the temperature dependence of viscosity of strong, moderate and fragile glass-forming liquids in wide temperature range (between T_g and T_m).

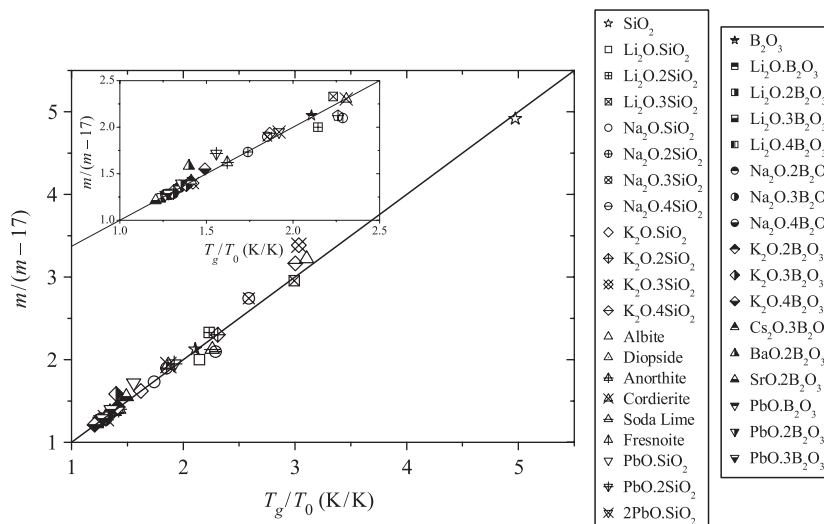


Fig. 5. Observation of the characteristic ratio T_g/T_0 for 38 oxide glasses. Data were determined from experimental T_g , T_0 values and also m from Table 1 considering the VFTH equation for viscosity.

6. Conclusions

The fragility concept is usual to classify glass-forming liquids, but CA showed to be a complementary tool to interpret liquid properties. There are strong correlations between the VFTH B and T_0 parameters and thermodynamic properties, as T_g and T_m in the 38 oxide glass systems analyzed. Correspondence analysis could give another way to interpret VFTH parameters, distinguishing strong from fragile systems, and also differentiating borates from silicates in a *two-dimensional map*. The information obtained from CA illustrates how a low-dimensional graphical representation of what is basically a deterministic trend supports a rich description of the data, also including the fragility classification. The fragility parameter m ranges from 17.9 (SiO_2) to 97.0 ($\text{SrO} \cdot 2\text{B}_2\text{O}_3$). The main merit of CA is to allow an easy graphical criterion to classify glass-forming liquids. The combined use of Angell classification of glass-forming liquids and CA may then provide a better understanding about viscous flow phenomena.

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Appendix

From a historical viewpoint, in resume, Hans Vogel stated succinctly in a German journal of physics [2] that Eq. (1) was useful for describing the viscosity of water, mercury and oil, but presented no data at all (in 1921). Vogel anticipated by 4 years the more complete work of Gordon Fulcher [3], which compared viscosity data of many oxide glasses from the literature with a variety of empirical formulas, and selected Eq. (1) as the most suitable. Although Vogel's paper was unnoticed by Tammann and Hesse [4] (at that time working at Göttingen Physical-Chemistry Institute, Germany), both presented the same equation in 1926 in a study of viscosity of organic liquids (as some alcohols and glycerins with different water percentages), and cited Fulcher's work. Nevertheless, Tammann and Hesse claimed to have discovered Eq. (1) independently, by interpolation of analyzed data.

According to Scherer [5], the paper of Fulcher is the second one most cited at *Journal of the American Ceramic Society*. The VFTH equation is so accurate as an interpolation formula that the NIST American Bureau uses it to represent $\eta(T)$ of standard glasses over ten orders of magnitude (or more). Such equation can be also

explained theoretically by different models, as the free volume [6] or the Adam–Gibbs' [7].

Still about the VFTH equation, some criticisms occurred about its accurate description in wide temperature range [29,30]. According to those authors, the VFTH presents high divergence near T_0 . Although viscosity is certainly finite, this is a minor problem because at temperatures below T_g viscosity is very high and out of practical interest. The important point is that the VFTH could be applied in wide temperature range, and the agreement with experimental data is excellent, covering twelve orders of magnitude with high accuracy.

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