# Concentration dependences of the molar absorption coefficients of the two type of dissolved water (OH⁻ и H₂O) in silicate and magmatic melts (glasses) in the series acidic-basic

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The structural chemical model has been developed to calculate and predict the concentration dependences of the molar absorption coefficients for the two type of dissolved water (OH⁻ и H₂O) in silicate and magmatic melts (glasses) in a wide range of the melt composition from obsidian to basalt. This model was suggested to correct determination of water content in the glasses (melts) and along the diffusion profiles for various types of dissolved water (OH⁻ groups, $4500 \text{ cm}^{-1}$ band) and molecular H₂O, $5200 \text{ cm}^{-1}$ band) by quantitative IR micro spectroscopy.

*Key words: IR-spectroscopy, molar absorption, dissolved water, concentration, silicate glasses, structure, model*

FTIR spectroscopy in the infrared and near-infrared spectral region is the one of the effective methods to quantitative determination the concentrations of water which is dissolved in silicate melts (glasses) at high pressures. Moreover it is really a single method for quantitative determination of water content along the diffusion profiles. Water content in silicate glasses and along the diffusion profiles for various types of dissolved water (OH⁻ groups and molecular H₂O) have been determined by FTIR spectroscopy using of the Beer-Lambert equation:

$$C = 100 \cdot 18.015 \bullet A / \rho \bullet \delta \bullet \varepsilon \tag{1},$$

where $C$ is the concentration (in wt %) of various H₂O species (OH⁻ or H₂O) in the melt (glass), $A$ is the height of the absorption peak (relative %), $\rho$ is the density of the glass (g/l), $\delta$ is the thickness of the platelet (cm), $\varepsilon$ is the molar absorption coefficient of the corresponding water type (l/mol· cm), and 18.015 is the molecular mass of water (g/mol).

The IR spectra of the hydration and diffusion samples were recorded on a Nicolet Magna_IT 860 IR spectrometer equipped with a Nicolet Continum IR microscope (Caltech, USA). Total water contents (C(H₂O) = the sum of water dissolved as OH⁻ groups and H₂O molecules) along the diffusion profiles in the quenched experiments were determined for the samples by FTIR spectroscopy.

Molar absorption coefficients for OH⁻ and H₂O bands in the infrared and near-infrared regions are known to vary with glass composition. Experimental study of the molar absorption coefficients for OH⁻ and H₂O bands even for a single composition of silicate glass is not so easy. *Dixon et al.* [1995] and Mandeville et al. (2002) showed that the molar absorption coefficients for the $5200 \text{ cm}^{-1}$ and $4500 \text{ cm}^{-1}$ bands can be approximated as linear functions of the cation fraction of tetrahedral cations ($T = (Si^{4+} + Al^{3+})/(\text{total cations})$) over a significant compositional range. [*Ohlhorst et al., 2001*] were used of the content of $SiO_2$ in silicate glasses to predict the concentration dependence of molar absorption coefficients for OH⁻ and H₂O bands in the near-infrared regions. In order to enhance the accuracy and reliability of the measured (by IR spectroscopy) concentrations of various water species (OH⁻ and H₂O), a structural–chemical model was developed that makes it possible to calculate and predict the concentration dependence of the molar absorption coefficients of various water species ($\varepsilon$) dissolved in silicate melts (glasses) within the andesite–basalt compositional range [*Persikov et al., 2010*]. In order to characterize the chemical composition, this model employs a structural–chemical parameter (***100NBO/T***): the degree of depolymerization or the coefficient of the relative basicity of

silicate melt, which can be readily calculated from the chemical composition of the melt [*Persikov, 1991; 1998*]. It has been established that this parameter is optimal for expressing distinctive features of the chemical composition and structure of silicate and magmatic melts [*Persikov, 1991; 1998*].

In this study mentioned model has been used for a wide range of the composition of silicate glasses (melts) from obsidian to basalt. The results obtained using of this model are shown at the Fig. 1.
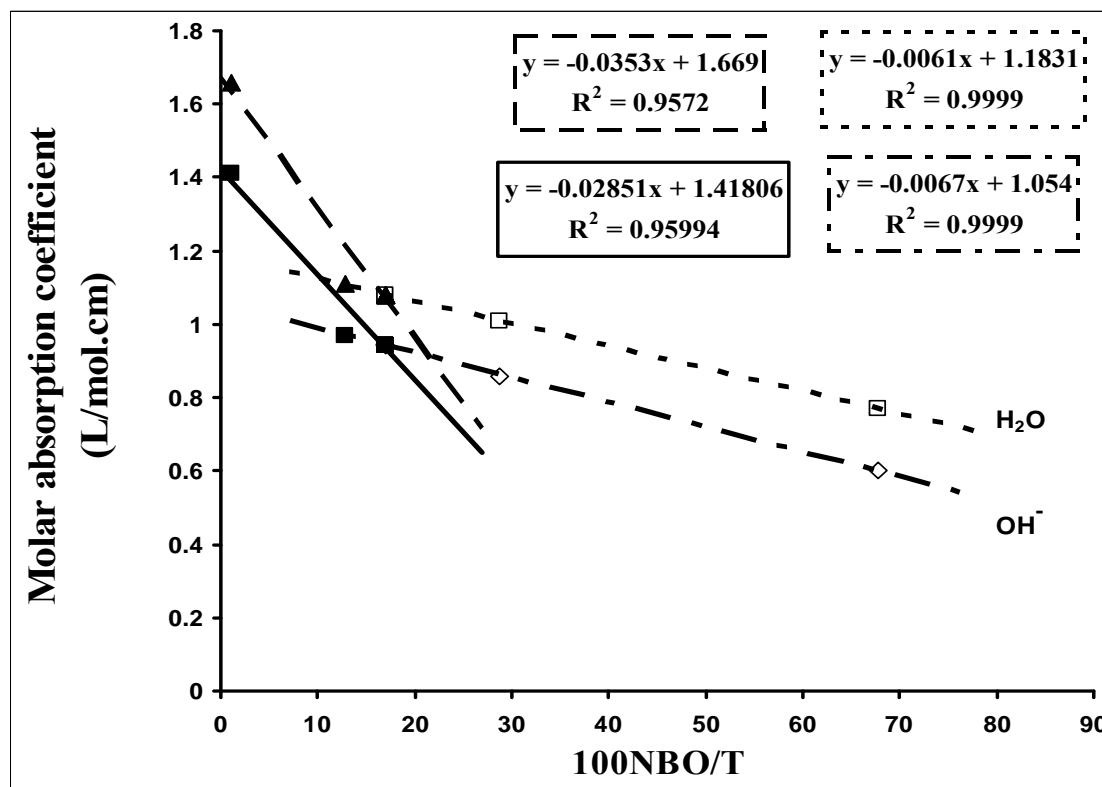


**Fig. 1.** Compositional dependence of molar absorption coefficients in silicate glasses for hydroxyl groups (4500 cm−1 band) and molecular water (5200 cm−1 band) within the obsidian – basalt compositional range (open symbols are the andesite–basalt compositional range [*Persikov et al., 2010*]; closed symbols are the rhyolite–dacite compositional range [*Ohlhorst et al., 2001*])

Simple linear equations proposed for calculating the molar absorption coefficients of the two water species in silicate and magmatic melts (glasses) within the obsidian–basalt compositional range based on the established correlation (Fig. 1) are as follows:

1) for hydroxyl groups ($OH^-$)

within the obsidian–dacite compositional range $\qquad \varepsilon_{4500\ cm-1} = \mathit{1.67 - 0.035 \cdot K}$, (2)

within the andesite–basalt compositional range $\qquad \varepsilon_{4500\ cm-1} = \mathit{1.06 - 0.007 \cdot K}$, (3)

2) for water molecules ($H_2O$)

within the obsidian–dacite compositional range $\qquad \varepsilon_{5200\ cm-1} = \mathit{1.42 - 0.028 \cdot K}$, (4)

within the andesite–basalt compositional range $\qquad \varepsilon_{5200\ cm-1} = \mathit{1.183 - 0.006 \cdot K}$, (5),

where $\mathbf{\mathit{K = 100 \cdot NBO/T}}$ – is mentioned above structural–chemical parameter.

In accordance with the structural model of silicate and magmatic melts [*Persikov, 1991; Persikov, 1998*] the calibration lines used here (Fig. 1) have the two inflection points at the $K \approx 17$ which corresponds to the anhydrous andesite average composition. At this value of **100NBO/T** the dramatic change of melt structure has been done that is the full polymerized framework structure of acidic silicate melts is break down at these points.

The calculated errors of this approximation are $\pm$ 0.10 and $\pm$ 0.09 l/mol·cm for the molar absorption coefficients for the 4500 cm$^{-1}$ and 5200 cm$^{-1}$ bands, respectively. These errors of the molar absorption coefficients are less than the errors which may obtained using the [*Dixon et al. 1995, Ohlhorst et al., 2001 and Mandeville et al., 2002*] correlation. The values of the molar absorption coefficients (extinction coefficients) obtained by Eqs. (3–5) for the two water species dissolved in silicate melts (glasses) studied are as follows:

1) obsidian                              $\varepsilon_{4500\ cm\text{-}1} = 1.36 \pm 0.10$                      $\varepsilon_{5200\ cm\text{-}1} = 1.6 \pm 0.09$

2) haplodacite (Ab90Di8Wo2)              $\varepsilon_{4500\ cm\text{-}1} = 1.11 \pm 0.10$                     $\varepsilon_{5200\ cm\text{-}1} = 1.29 \pm 0.09$

3) haploandesite (Ab77Di19.5Wo3.5)       $\varepsilon_{4500\ cm\text{-}1} = 0.86 \pm 0.10$                     $\varepsilon_{5200\ cm\text{-}1} = 1.01 \pm 0.09$

4) haplobasalt (Ab45Di37Wo18)            $\varepsilon_{4500\ cm\text{-}1} = 0.6 \pm 0.10$                      $\varepsilon_{5200\ cm\text{-}1} = 0.77 \pm 0.09$

In conclusion it should be note that the structural chemical model suggested is allowed to improve the accuracy of the predicted compositional dependence of molar absorption coefficients in silicate glasses for hydroxyl groups (4500 cm$^{-1}$ band) and molecular water (5200 cm$^{-1}$ band) within of acidic-basic range of composition.

**References**

Dixon, J. E., E. M. Stolper, J. R. Holloway (1995). An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids, Part I: Calibration and solubility model, *J. Petrol.,* v. 36, p. 1607–1631.

Mandeville, C. W., J. D. Webster, M. J. Rutherford, B. E. Taylor, A. Timban, K. Faure (2002). Determination of molar absorptivities for infrared absorption bands of $H_2O$ in andesitic glasses, *Am. Mineral.,* v. 87, p. 813–821.

Ohlhorst, S., H. Behrens, F. Holtz. (2001). Compositional dependence of molar absorptivities of near-infrared OH⁻ and $H_2O$ bands in rhyolitic to basaltic glasses, *Chem. Geol.,* v. 174, p. 5–20.

Persikov, E. S. (1991). The viscosity of magmatic liquids: experiment, generalized patterns. A model for calculation and prediction. Applications, *In: Physical chemistry of magmas. Advances in Physical Geochemistry.* L. L. Perchuk & I. Kushiro, Eods., Springer-Verlag. New York, v, 9, p. 1–40.

Persikov, E. S. (1998). The viscosity of model and magmatic melts under P–T-parameters of the Earth's crust and upper mantle, *Russian Geology and Geophysics,* v. 39, No 12, Allerton Press, Inc, New York, p. 1780–1792.

Persikov, E. S., S. Newman, P. G. Bukhtiyarov, A. N. Nekrasov, E. M. Stolper (2010). Experimental study of water diffusion in haplobasaltic and haploandesitic melts, *Chemical Geology,* v. 276, p. 241–256.