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# NUCLEAR MAGNETIC SPECTROSCOPY STUDY OF THE STRUCTURE OF LIQUID GLASSES FOR WELDING ELECTRODES

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Nuclear magnetic spectroscopy was used to study the structure of silicon-oxygen anions (SOA) in the composition of monobasic (Li, Na, K) and binary (LiNa, LiK, and NaK) liquid glasses. It is found that combinations of different forms of connection reflect the structure of silicon-oxygen anions present in the solution, which determines the change of liquid glass viscosity, depending on their chemical composition. Structure of SOA of monobasic liquid glasses is determined by the kind of modifier ion. The larger its size, the weaker is its destructive action on SOA, with preservation of a larger number of bridge bonds, ensuring a higher level of liquid glass viscosity. Binary mixtures of liquid glasses at certain ratios of alkali oxide fractions, demonstrate synergism of viscosity. The fraction of bridge bonds is higher in such glasses. Synergic increase of viscosity is more pronounced in LiK glasses than in LiNa and NaK analogs, although viscosity of monobasic glasses, from which the mixtures were prepared, was the same. 11 Ref., 3 Tables, 3 Figures.

**Keywords:** *arc welding, welding electrodes, manufacturing technology, liquid glass, liquid glass structure, application of NMR spectroscopy technique*

Modern production of welded structures makes increasing requirements to metallurgical, technological, sanitary-hygienic, and service characteristics and quality of coated electrode manufacturing. Many of them are directly connected to the kind and chemical composition of liquid glasses, used as electrode coating binder. Solution of such a multivector problem usually is a compromise. For this reason, binary, for instance, NaK liquid glasses, began to be applied in electrode production. These glasses favourably combine useful characteristics of their components. However, other properties of the combined binder, important for the characteristics of coatings and welding electrodes, often deteriorate. For instance, lowering of water-holding capacity of the binder, electrode coating hygroscopicity and hydrogen content in the deposited metal, is accompanied by lowering of coating strength, and deterioration of sanitary-hygienic characteristics of electrodes. Although combined liquid glasses have been used in local and foreign electrode production for a long time, the cause of the above peculiarities has not been established. Electrode developers are acutely aware of the lack of information about liquid glass structure and properties that would help them solve these problems.

In many silicate technologies the structure of glasses in general and of liquid glasses, in particular, is studied, using a combination of such spectroscopy methods, as infrared (IR), combined light scattering (CLS), X-ray diffraction (XRD), X-ray emission (XES), Laser Raman, extended X-ray-absorption fine structure (EXAFS), and X-ray photoelectron spectroscopy (XPS) [1].

Over the last decades these have been effectively complemented by nuclear magnetic spectroscopy (NMRS) [2-6], which considers liquid glass structure in terms of the ratio of the fractions of bridge and nonbridge oxygen in the composition of silicon-oxigen anions (SOA).

The cited published sources do not provide replies to the questions we are interested in. Many of the investigation techniques used in them are not available to us.

We applied NMR$^{29}$Si technique to study the structure of monobasic (Li, Na, K) and binary (LiNa, LiK, and NaK) liquid glasses, used in welding electrode production.

This technique is based on the phenomenon of resonance absorption of electromagnetic waves by atomic nuclei of the tested substance placed into an external magnetic field [7]. In the case of hydrogen atom nucleus the principle of NMRS looks as follows. The proton has its own spin and magnetic moment. Spatial orientation of proton magnetic vector spin can either coincide with the direction of intensity vector of constant magnetic filed, around which μ will precess, or it can be opposite to it.

**Table 1.** Kinds of connection combined in liquid glass SOA structure

| $Q^4$ | $Q^3$ | $Q^2$ | $Q^1$ | $Q^0$ |
|---|---|---|---|---|
| (O) Si<br>│<br>Si(O)–Si–(O)Si<br>│<br>(O)Si | (O) Si<br>│<br>Si(O)–Si–$O^–$<br>│<br>(O)Si | $O^–$<br>│<br>Si(O)–Si–$O^–$<br>│<br>(O)Si | $O^–$<br>│<br>Si(O)–Si–$O^–$<br>│<br>$O^–$ | $O^–$<br>│<br>O–Si–$O^–$<br>│<br>$O^–$ |

Proton field energy $E$ is greater in the first of the mentioned states than in the second one. If energy is added to the proton, which happened to be in these states by its irradiation by variable electromagnetic field quanta of corresponding frequency, the proton will go into a state with greater energy during pulse action time of 2 μs, while its spin will be directed normal to constant field vector.

In a sample with a large number of mobile protons, an averaged pattern is observed, reflecting the behaviour of an ensemble of resonating nuclei.

In practice, fixed magnetic field intensity is usually used, and the range of frequencies of irradiating pack is varied. Then, the resonance occurs at their certain ratio, which is registered in NMR time scale at detection of the features of energy absorption and subsequent relaxation at interaction with the environment.

When recording the information, extracted by NMR technique, it should be taken into account that:

- signals of atoms, included into the composition of certain functional groups, are observed in strictly defined spectral regions;
- integral intensities of peaks are proportional to the quantity of resonating atoms of different nature;
- nuclei spaced at 1–4 bonds from each other, are capable of causing multiplicity of analytical signals as a result of superfine interactions.

Signal position in NMRS spectra is characterized by the value of their chemical shift relative to the reference signal, coupled with NMR electronic shielding. The unit of chemical shift is part per million (ppm) of instrument frequency. If the substance spectrum is too complicated, it is interpreted using quantum-chemical modeling of electron density distribution between characteristic fragments of the selected coherent structure.

Oxygen atoms in tetrahedrons, differing by atomic ratios $Si:(O)_{4-x}):(OSi)_x$, are the main structural motif of silicon-oxygen anions (SOA) in liquid glasses and are fragments with bridge Si–O–Si ($O_b$) or non-bridge Si–O ($O_t$) bonds. In the latter of the mentioned forms of the bond, oxygen modifications are terminal ones and are coordinated by modifier cations (Li, Na, K, Ca). Depending on $O_t/O_b$ ratio, 5 types of $SiO_4$ tetrahedrons are distinguished, which are designated by $Q^n$ symbol, where $n$ is the degree of connection, i.e. number of bridge atoms of oxygen per one atom of silicon in SOA. Depending on cation type (Li, Na, K or their binary combinations), modulus and concentration of dissolved silicate, $n$ index can vary from 0 up to 4. The higher the value of this index, the greater is the number of bridge (bound) atoms of oxygen $O_b$ in SOA structure (Table 1).

**Investigation procedures, substance compositions and properties of liquid glasses.** Values of chemical shift are determined at room temperature in NMR-spectrometer of AVANSE 400 model, BRUKER, Germany. Intensity of signals of structural groups $Q^n$ in NMR$^{29}$Si of primary analytical spectra was the source of information about the structure of liquid glasses SOA. Absorption due to material, surrounding the measurement zone, was taken into account in idle measurements. Interpretation of NMR-$^{29}$Si spectra by the degree of connection $Q^n$, recorded from liquid glass samples, was conducted after preliminary isolation of the above background from the spectrum.

Chemical composition, data on density and viscosity of monobasic liquid glasses are given in Table 2. Table 3 gives a comparison of connection indices, found at testing monobasic liquid glasses and binary mixture samples made from them. In Figure 1 such a

**Table 2.** Chemical composition, density and viscosity of monobasic liquid glasses

| Glass kind | Modulus | Weight fraction, % | | | | Glass properties | |
|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $Li_2O$ | $Na_2O$ | $K_2O$ | ρ, kg·m$^{-3}$ | η, mPa·s |
| Li | 2.77 | 25.52 | 4.60 | – | – | 1313 | 325 |
| Na | 3.09 | 28.54 | – | 8.40 | 1.70 | 1433 | 325 |
| K | 3.67 | 26.37 | – | 1.66 | 8.93 | 1422 | 360 |

**Table 3.** Chemical composition, density and viscosity of combined liquid glasses

| Number | Second component fraction, wt.% | Fraction of connections, % | | | Viscosity, η, mPa·s |
|---|---|---|---|---|---|
| | | $Q^3$ | $Q^4$ | $\Sigma Q^3 + Q^4$ | |
| LiNa liquid glasses | | | | | |
| 1 | 0 | 38.3 | 26.5 | 64.8 | 325 |
| 2 | 16.3 | 43.5 | 23.4 | 66.9 | 770 |
| 3 | 33.3 | 43.4 | 22.7 | 66.1 | 795 |
| 4 | 50.0 | 36.9 | 30.8 | 67.7 | 815 |
| 5 | 66.7 | 41.1 | 21.0 | 62.1 | 620 |
| 6 | 83.7 | 37.8 | 18.4 | 56.2 | 435 |
| 7 | 100 | 38.1 | 16.0 | 54.1 | 325 |
| LiK liquid glasses | | | | | |
| 1 | 0 | 38.5 | 26.5 | 65.0 | 325 |
| 2 | 16.3 | 37.8 | 25.0 | 62.8 | 1750 |
| 3 | 33.3 | 33.0 | 36.9 | 69.9 | 2115 |
| 4 | 50.0 | 38.4 | 26.9 | 65.3 | 6140 |
| 5 | 66.7 | 40.0 | 26.4 | 66.4 | 20800 |
| 6 | 83.7 | 40.5 | 27.4 | 67.9 | 1300 |
| 7 | 100 | 41.3 | 14.0 | 55.3 | 360 |
| NaK liquid glasses | | | | | |
| 1 | 0 | 38.6 | 15.4 | 54.0 | 325 |
| 2 | 16.3 | 43.5 | 10.3 | 53.8 | 395 |
| 3 | 33.3 | 44.5 | 11.4 | 55.9 | 595 |
| 4 | 50.0 | 45.3 | 12.6 | 57.9 | 545 |
| 5 | 66.7 | 47.0 | 8.0 | 55.0 | 445 |
| 6 | 83.7 | 47.3 | 8.8 | 56.1 | 440 |
| 7 | 100 | 42.0 | 12.8 | 54.8 | 360 |

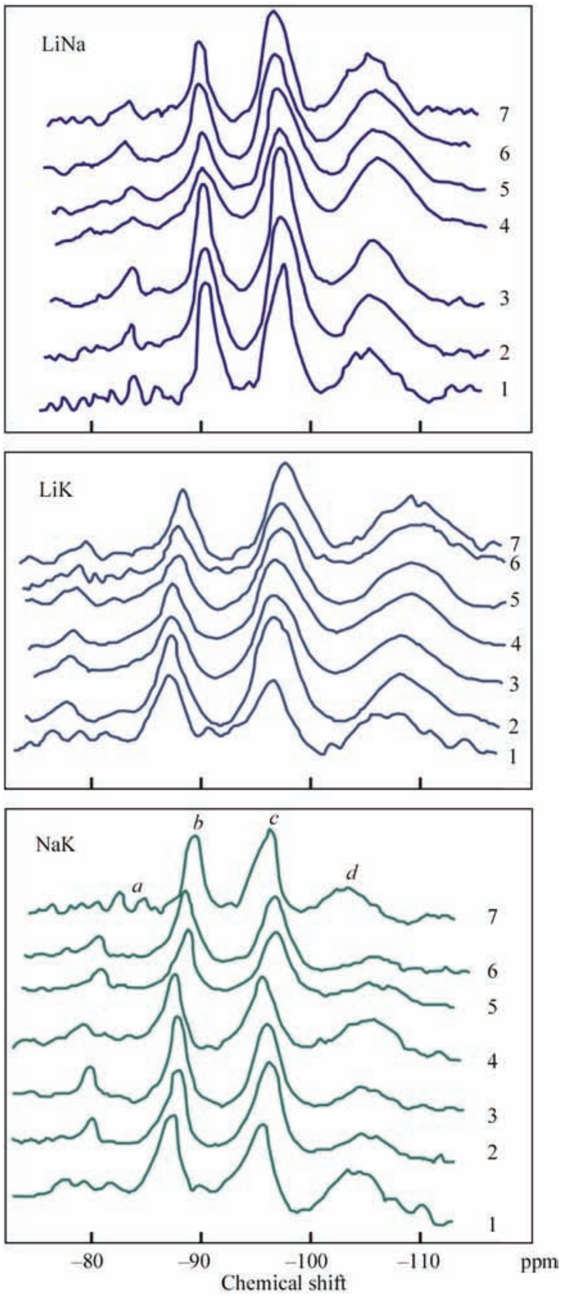

**Figure 1.** Evolution of NMR$^{29}$Si parameters of combined NaK, LiK and LiNa liquid glasses, depending on the ratio of monobasic components in their composition; *a*, *b*, *c*, *d* are the values of integral intensities of signals with values of chemical shift, characteristic for $Q^1$, $Q^2$, $Q^3$, $Q^4$

comparison is given in the graphic form (glass numbers are the same as in Table 3).

As follows from the above data, viscosity of a number of initial monobasic liquid glasses was approximately the same (320–360 MPa·s). Binary mixtures of these glasses demonstrate synergism of viscosity: after mixing, mixture viscosity rises, compared to anticipated additive value. The greater the difference of dimensions of modifier ions in initial glasses, the more clearly is the synergism of their viscosity manifested.

The given data allow making the following generalizations.

SOA structure of monobasic liquid glasses is determined by the kind of modifier ion. The greater its size, the smaller its destructive action on SOA structure: a greater number of bridge bonds is preserved $Q^4$.

In liquid glass mixtures, where the greatest synergic increase of viscosity was manifested, the fraction of bridge bonds rises, compared to the fraction of the respective forms of connection in monobasic glasses. An exception are NaK liquid glasses, where potassium component causes lowering of $Q^4$ yield, starting from small additions, also in the synergic composition.

Change of connections strictly follows the stoichiometry of equations of exchange reaction for LiNa-4 mixture, and less strictly — for LiK-5:

$$2Q^4 \leftrightarrow Q^2 + Q^3. \quad (1)$$

The above glasses demonstrate the highest degree of viscosity synergism.

For NaK glasses the synergic effect is manifested to the lowest degree, and form stoichiometry does not obey equation (1). Signals from forms with different connections differ not only in intensity, but also in width, particularly, $Q^4$. It is possible that they combine not one, but 2 to 3 kinds of connections. Correct separation of superpositions into individual components requires application of special techniques.

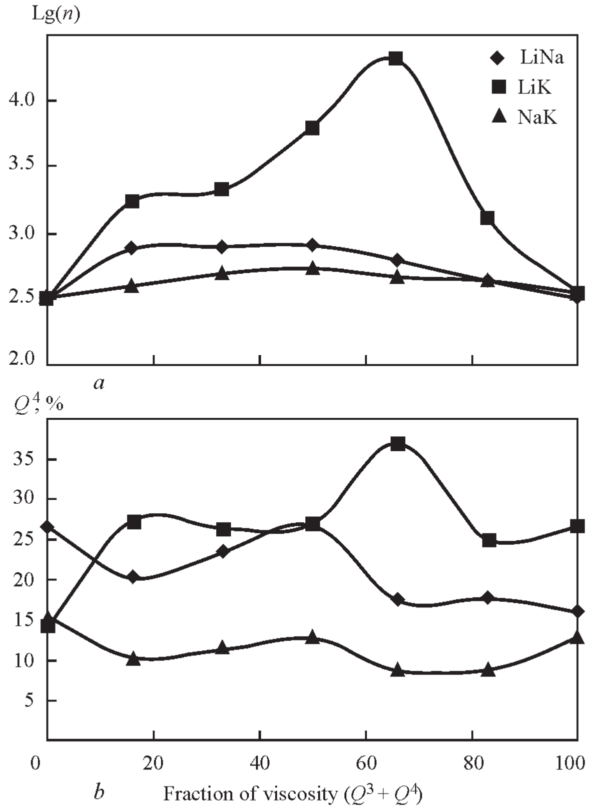

**Figure 2.** Influence of 2nd component concentration on viscosity of LiNa, LiK and NaK liquid glass mixture (*a*), as well as on fraction of $Q^4$ connections (*b*) in SOA structure

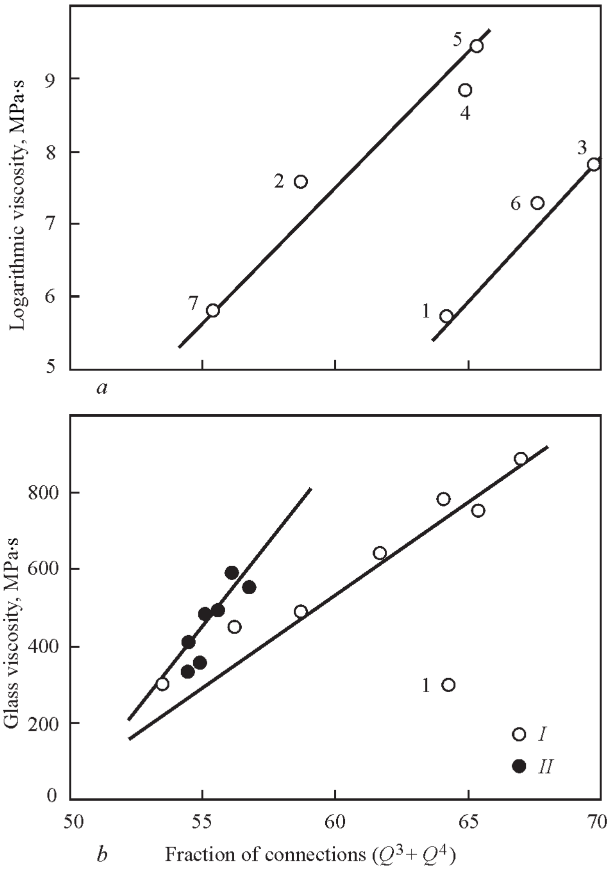

**Figure 3.** Dependence of binary LiK (*a*), as well as LiNa (*b*, I) and NaK (*b*, II) liquid glasses on summary fraction of forms of connection ($Q^3$ + $Q^4$). Figures near the points designate numbers of liquid glass samples

Qualitative connection between viscosity and fraction of $Q^4$ forms in the structure of glasses, responsible for the degree of SOA polymerization, is illustrated in Figure 2. A finer correlation between SOA viscosity and structure can be established, if we use not $Q^4$ yield, but ($Q^3 + Q^4$) sum as the structural index. In Figure 3 such a relationship is demonstrated in the graphic form. Natural coordinates were used for LiNa and NaK liquid glasses with a small synergic effect. For LiK liquid glasses, in which the range of viscosities, associated with synergic effect, was expanded by more than 20 times, because of the large difference in the dimensions of cations (and, therefore, SOA), the logarithmic scale of viscosities was applied.

Directly proportional dependence between viscosity of LiNa, NaK glasses and summary fraction of connection forms ($Q^3 + Q^4$) indicates that both the SOA forms contribute to formation of viscosity effect, competing in structure formation. The difference in the ratio of dimensions of K and NA ions, greater than that of Na and Li ions, can account for larger slope inclination in the graph of the first straight line, than in that of the second. For binary LiK glasses with cations, much more different from each other in their dimensions, synergic increase of viscosity is manifested to the greatest extent.

Established regularities allow a more detailed consideration of the mechanism of synergic effect in the case of melts ($K_2O–Li_2O–SiO_2$) [8]. Energy stability of $LiO_2$ is higher than that of $K_2O$. Owing to a greater fraction of connection forms $Q^4$, the system with lithium oxide is characterized by lower basicity that the system with $K_2O$. As a weak base cation ($((LiOH)_y(H_2O)_x)Li^+$ tetrameters dominate in concentrated water solutions of LiOH), $Li^+$ tends to coordinate in its environment the silicon-oxygen structural units with $Q^2$ and $Q^1$ connections, the yield of which in single-component lithium glasses is insignificant. Lithium cation realizes this ability to a greater extent in liquid glasses with two cations, where it dominates in the competition with K ions.

In its turn, $K^+$ environment will be made up by silicon-oxygen groups $Q^3$ and $Q^4$. Exchange reaction, allowing for competitive coordination and mutual transformation of $Q^n$ forms, is as follows:

$$K_2SiO_3 + Li_2Si_2O_5 \leftrightarrow Li_2SiO_3 + K_2Si_2O_5. \qquad (2)$$

As a result of exchange of silicon-oxygen groups, the lithium component of the mixture will increase, and the potassium component will lower its modulus. Presence of several SOA modifications, each being in cation affected area, hinders their redistribution at shear, and this leads to the respective increase of viscosity.

A weaker manifestation of synergism of viscosity in experiments with LiNa and NaK liquid glasses, is attributable to smaller difference in the dimensions and acid-base characteristics of the compared alkali cations. At higher initial viscosity of monobasic liquid glasses, the synergism of viscosity of their mixtures is manifested to a greater degree [9, 10].

Position of points 1, 3 and 6, which is particularly noticeable in the given logarithmic interpretation of variation of LiK mixture viscosity (Figure 3), is also attributable to the influence of SOA dimensions and acid-base characteristics. For this purpose it is necessary, based on NMR data, to precisely identify not only the forms with different coordination environment, but also their possible isomerization. The fact that viscosity of liquid glass mixture can have not only positive, but often also negative deviation from additive values, particularly, if it was prepared using solutions with initial components with different moduli, was confirmed experimentally [9, 10].

Investigation results allow interpreting the causes for the revealed features of liquid glass influence on water-holding capacity of coatings, hydrogen content in the metal, deposited with low-hydrogen electrodes, and sanitary-hygienic characteristics of electrodes for welding high-alloyed chromium-nickel steels, proceeding from the concepts of structural changes in liquid glasses based on connections in SOA [11].

## Conclusions

1. Complex investigation of monobasic (Li, Na, K) and binary (LiNa, LiK and NaK) liquid glasses, using methods to obtain multilevel information about structural-functional transformations in silicates, allowed revealing discrete structure of alkali liquid glasses. SOA dimensions are determined by dimensions of cations, encapsulated by them. There is a close relationship between the structure-forming ability of various forms of connection, present in SOA structure and viscosity of water solutions formed by them.

2. Structure of SOA of monobasic liquid glasses is determined by the kind of modifier ion. The larger its size, the weaker is its destructuring influence on SOA, with preservation of greater number of bridge bonds $Q^4$, providing a higher level of liquid glass viscosity.

3. In binary mixtures of liquid glasses, manifesting synergism of viscosity at certain ratios of alkali oxides, the proportion of bridge bonds is greater, than in monobasic glasses. Synergic increase in viscosity is manifested to the greatest degree in LiK glasses. There exists a directly proportional relationship between the viscosity of binary liquid glasses and summary fraction of connection forms ($Q^3 + Q^4$): in the regular coordinate grid for LiNa and NaK glasses, showing slight synergism of viscosity, and in the logarithmic coordinate grid for LiK, characterized by stronger effect of synergism.

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