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The Mixed Hydrogen Bonds Network in a Liquid System Ethylene Glycol-Monoethanolamine

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Abstract: The mixed network of hydrogen bonds in the ethylene glycol (EG) - monoethanolamine (MEA) system is described by molecular dynamics (MD) methods, graph theory, and Delaunay simplexes at 300 K in the entire concentration range. It is shown that at low MEA concentrations, all molecules in the system are linked into a spatial network of H-bonds; at high MEA concentrations, this number is 96%. Detailed characteristics of the networks are given. The resulting picture is expanded by studying the system using the Delaunay simplex method. The calculations are compared for different charges on the atoms of the MEA molecule.

Keywords: hydrogen bonds, spatial networks, ethylene glycol, monoethanolamine, molecular dynamics, Delaunay simplexes

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1. INTRODUCTION

Ethylene glycol (EG) and monoethanolamine (MEA) are solvents with wide supercooling of the

liquid phase and are widely used as cryoprotectants in cryobiology. Their water systems are used for long-term preservation of living organs and cells [1,2]. Therefore, the study of mixtures of these solvents is an urgent problem.

Large supercooling of liquid EG and MEA is associated with the stability of the spatial network of hydrogen bonds in these solvents [3-5]. It is of interest to study the mixed network of H-bonds in the EG-MEA liquid system over the entire concentration range.

Table 1.
Physical-chemical properties of EG, MEA and H₂O [6,7]

	EG	MEA	H ₂ O
M	62	61	18
μ, D	2.88	2.27	1.83
DN _{SbCl5}	18.5	41	18
T _{nn} , °C	-12.9	10.3	0
T _{km} , °C	197	170	100
ΔT _{nepeox.}	21	38	40
ρ (25°C), kg/m ³	1.113	1.012	0.99707
η (25°C), MPa·s	16.16	18.95	0.8903
D·10 ⁵ , sm ² /s	0.083	0.055	2.25
β _v , Pa ⁻¹ ·10 ⁻¹¹	37.4	39.6	45.28
Δ _{vap} H, kJ/mol	50	49.83	40.66
ΔH _{evap} /T _b , cal·mol ⁻¹ ·K ⁻¹	25.5	26.9	28.2

In **Table 1**, we present the physicochemical properties of these solvents. The right-hand column shows data for water for comparison.

Noteworthy is the high density of EG and high viscosity of MEA, almost the same compressibility of liquid EG and MEA; a slightly higher dipole moment in the EG molecule and a much higher electron-donating ability of the MEA molecule. Note that EG is mixed with MEA in all ratios. In [8], the densities and viscosities of the EG-MEA system were measured for all concentrations at 293K and compared with other ethylene glycol systems in which the second component did not have a spatial network of H-bonds and differed greatly in chemical properties from EG. From the experimental data, the excess volumes of the mixture and the deviations of viscosities were calculated, which were correlated with the Redlich-Kister ratio [9],

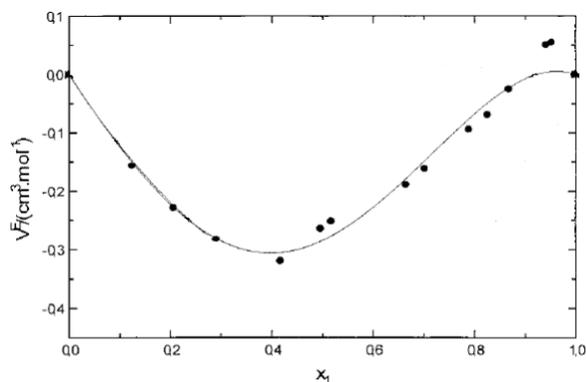


Fig. 1. Excess molar volumes of the EG-MEA system depending on the molar fraction x₁ of EG [8].

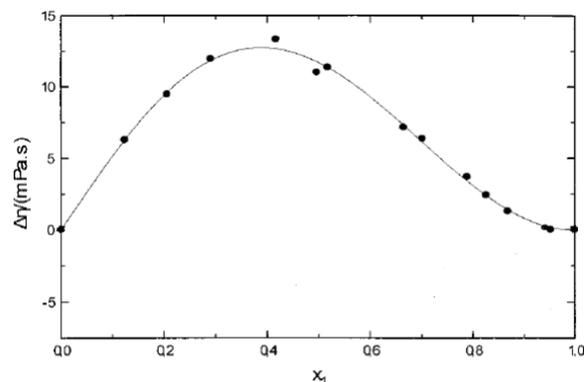


Fig. 2. Deviations of the viscosity of the EG-MEA system depending on the molar fraction x₁ of EG [8].

and negative concentration dependences of the excess volume were obtained with a minimum value at 40 mol% EG and a maximum positive deviation of viscosity also at 40 mol% EG. The results are shown in **Figs. 1** and **2**.

Unfortunately, this is the only information that we found on the physicochemical properties of the EG-MEA system. This work is devoted to the description of mixed networks of hydrogen bonds in the EG-MEA system. Recall that we are dealing with a liquid system - a condensed but mobile phase. When describing a structure, a time coordinate is required. To describe the spatial network of H-bonds, we have chosen the molecular dynamics method, topological methods, and Delaunay simplices. First of all, models of MEA and EG molecules were needed. Two MEA models, differing in partial charges on atoms, and one EG model were considered. **Table 2** shows the partial charges on the MEA and EG atoms for these models.

For the M1 model, the partial charges on the atoms were taken from [10]. For the M2 model, the partial charges on atoms for the OH-CH₂ group were taken the same as for the EG and were obtained from the table “#bond_increments” of

Table 2.
Partial charges on atoms MEA (models M1 and M2) and EG.

Model	O	H(O)	C	H(C)	C	H(C)	N	H(N)
Model M1	-0.683	0.418	0.145	0.060	-0.060	0.060	-0.900	0.360
Model M2	-0.567	0.424	0.027	0.053	-0.175	0.135	-0.528	0.216
Model EG	-0.557	0.424	0.027	0.053				

the force field PCFF [11]. The partial charges on atoms for the $-CH_2-NH_2$ group were taken from quantum-chemical calculations for ethylenediamine (data provided by Yu.V. Novakovskaya).

The relaxations of the densities of the MEA and EG mixtures were calculated for two MEA models. The average values were taken, which were determined in the sections from 3 to 5 ns in the first model M1 and in the sections from 1 to 3 ns in the second model M2. The dependences of the obtained densities on the molar concentration of MEA for two MEA models at a temperature of 300K are shown in Fig. 3 together with the experimental data of [12] for a temperature of 303K — triangles, and from [8] for 293K — inverted triangles. Data M1 – diamonds, M2 – circles.

It can be seen from the figure that the results of calculating the densities of the MEA and EG mixtures strongly differ from the experimental ones for the M1 model and are close to the experimental curves for the M2 model. Therefore, we present our data on the study of a mixed network of H-bonds in the EG-MEA system, based on the M2 model. When discussing the

results, we will refer to the results of calculations using the M1 model (for comparison) in order to show the dependence of the calculation results on the charges on atoms.

The charges on the EG atoms are given in Table 1. They are taken the same as in [6].

It should be noted that for an EG molecule in a liquid, the most common conformer is the gauche conformer tGg' , which is characterized by a weak $C-H...O$ hydrogen bond and the absence of an intramolecular $O-H...OH$ bond [13]. The most widespread in liquid MEA is the $g'Gg$ gauche conformer, with an $O-H...N$ intramolecular bond [14]. This will explain a lot in our results of the study of the EG-MEA system.

Note that the choice of charges is a rather difficult task. The charges depend on the conformation of the molecule, on what role – donor or acceptor – the functional group plays and with which group it forms a hydrogen bond, i.e. from an H-bond partner. Therefore, the selection criterion was the coincidence of the calculation with the experimental data of some property. We chose densities. The calculation by the M2 model coincided with the experiment. Therefore, we will work with the M2 model, sometimes making comparisons with the results of the M1 model.

2. EXPERIMENTAL PART

To study the mixed networks of hydrogen bonds of the liquid EG-MEA system, we used the trajectories of vibration-averaged (V) structures calculated by the molecular dynamics method at a temperature of 300K. At all concentrations, the system contained a total of 1000 EG and MEA molecules in a rectangular computational cell with periodic boundary conditions. The calculated trajectories were preceded by the relaxation of the systems to equilibrium states. The relaxation time was no less than 200 ps. During this time, the densities and various energy contributions to the total energies of the systems reached their stationary values. Then the calculated sections of trajectories with a duration of at least 3 ns followed. The calculations were carried out with a step of 1 fs under the conditions of an NPT ensemble at

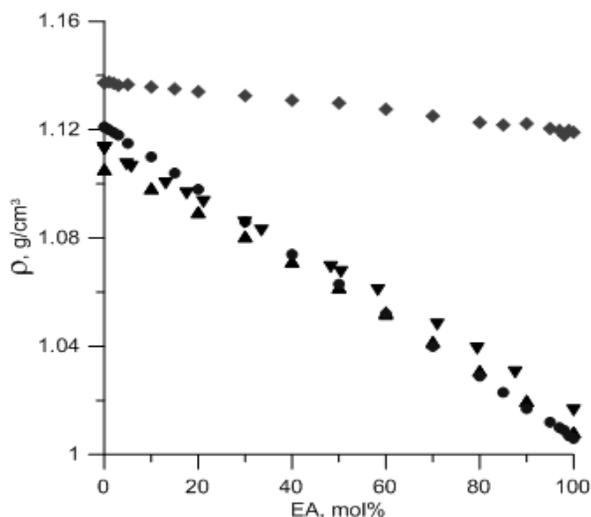


Fig. 3. Dependence of the density of a mixture of MEA and EG on the molar concentration of MEA for two MEA models and their comparison with experiment. ▲ – experimental data at a temperature of 303K [12], ▼ – experimental data at a temperature of 293K [8], ◆ – model MEA M1, ● – model MEA M2.

a temperature of 300 K and a pressure of 1 atm. The atomic coordinates were averaged to obtain V -structures in 0.1 ps. The trajectories contained V -structures recorded with a step of 10 ps.

We analyzed mixtures of EG and MEA containing from 0 to 100 mol% MEA. Specifically: 0, 1, 2, 3, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 85, 90, 95, 97, 98, 99, 100 mol% MEA.

All calculations presented in the work were carried out with V -structures spaced 60 ps apart along the trajectory. A total of 50 structures were considered for each concentration.

The study of networks of hydrogen bonds in solutions is based on the criterion of hydrogen bonds (both intermolecular and intramolecular). It was determined from the radial distribution functions obtained by the molecular dynamics method. The presence of a hydrogen bond was detected if the distance between oxygen or nitrogen of one molecule and oxygen or nitrogen of another did not exceed 3.5 Å, and the distance between oxygen or nitrogen of one molecule and hydrogen of another did not exceed 2.5 Å.

The properties of the network obtained on the basis of the hydrogen bond criterion were investigated in this work by the method of graph theory. Let us recall some concepts of graph theory that are needed in what follows [15]. We will consider molecules of substances as vertices of graphs, and hydrogen bonds between molecules as undirected edges of the graph. A sequence of edges in which the end of one edge is the beginning of another is called a chain. A graph is called connected if for each pair of vertices there is a chain that connects them. The connected component of a graph is a subgraph in which, for any pair of vertices, there is a chain connecting them. The main parameter evaluating the network of hydrogen bonds within the structure is the size of the maximum connected component of the graph containing the largest number of its vertices. It is described by an adjacency matrix. The most complete information on the network of hydrogen bonds is contained in the adjacency matrix for V -structures, constructed using the

hydrogen bond criterion. It is a square matrix with the number of rows and columns equal to the number of graph vertices (the number of molecules in the system). The element of the adjacency matrix with the index (i, j) contains 1 if the i molecule is hydrogen bonded to the j molecule, and 0 if the molecules are not bonded. The units in the matrix can be replaced by some positive coefficient, which expresses one or another property of this edge in the graph.

3. THE DISCUSSION OF THE RESULTS

The first task that we faced in this study was to test the hypothesis that all the molecules of the studied substances for all concentrations form a single network of hydrogen bonds. To find the components of the graph connectivity of the systems under consideration, Tarjan's algorithm was used [16]. The result of its work is the number of connectivity components in the graph, their size, as well as a list of vertices with an indication of their belonging to this or that connectivity component.

Fig. 4 shows a graph of the average (as well as the maximum and minimum) amount of bound components in one structure depending on the number of monoethanolamine molecules in solution. The black triangles at the top and bottom of the graph mark the maximum and

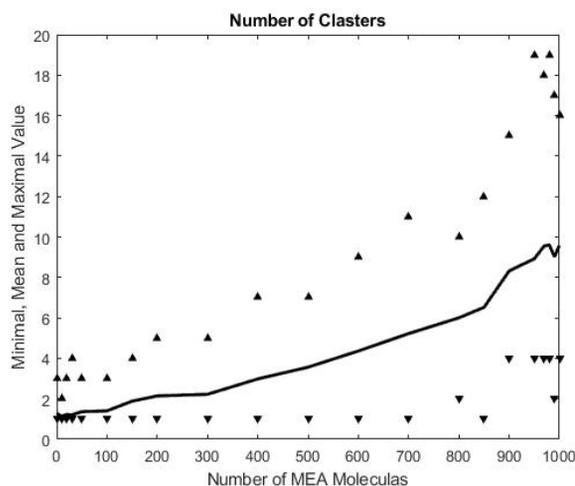


Fig. 4. Average (as well as maximum and minimum) number of bound components in one structure depending on the number of MEA molecules in solution.

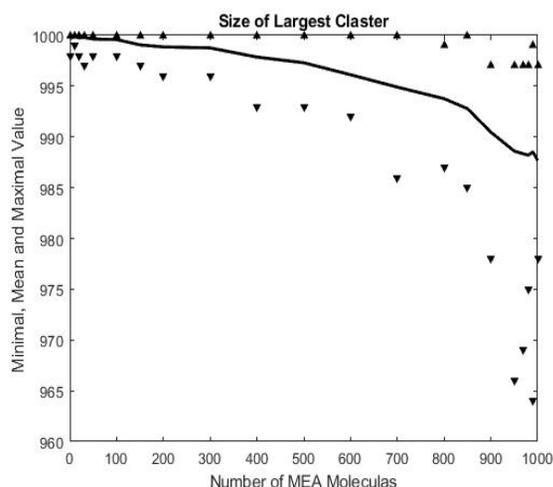


Fig. 5. Average (as well as maximum and minimum) number of molecules in the maximum connected component.

minimum values of this parameter, which makes it possible to estimate the range of its variation.

Fig. 5 shows the average (as well as the maximum and minimum) number of molecules in the maximum bound component.

An analysis of these figures shows that in pure EG and in the case of a small number of MEA molecules, almost all molecules are linked into a three-dimensional network of hydrogen bonds. With an increase in the concentration of MEA molecules, the number of bound components increases and, accordingly, the size of the maximum bound component decreases. This tendency is especially enhanced when the number of MEA molecules in solution becomes more than 900. However, it should

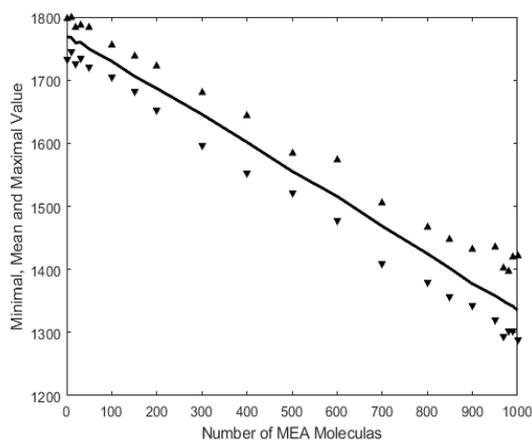


Fig. 6. Average value and range of changes in the number of pairs of molecules in 1 structure that have at least one H-bond, depending on the concentration of MEA in solution.

be noted that even the minimum size of the maximum binding component in solution contains 964 molecules. Thus, more than 96% of molecules in all considered structures for all concentrations are linked by a network of hydrogen bonds. The rest of the connected components in their mass contain only one or two molecules.

Fig. 6 shows the average value and the range of changes in the number of pairs of molecules in 1 structure which have at least one hydrogen bond, depending on the concentration of MEA in solution.

Fig. 7 shows the average number of hydrogen bonds in the structure connecting different pairs of molecules: the number of pairs of EG molecules is shown by the dashed line, the number of pairs of MEA molecules – by a line consisting of dots, the solid line is the number of hydrogen bonds between the EG molecule and the MEA molecule.

It can be seen from the graph that the maximum of hydrogen bonds between different molecules falls on approximately 50% of the MEA concentration. This figure also makes it possible to assert that approximately in the range of 40-70% of the MEA concentration, mixed

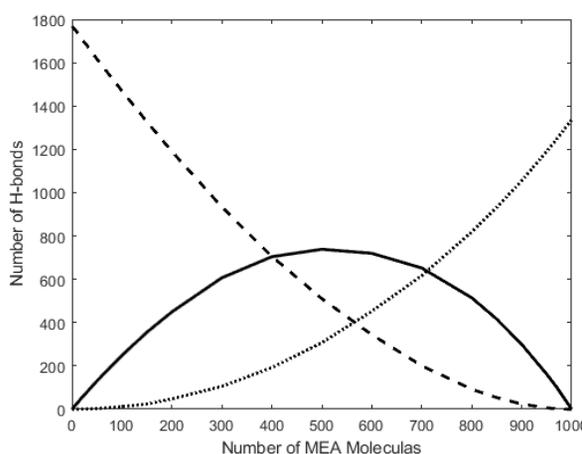


Fig. 7. Average number of hydrogen bonds in the structure connecting different pairs of molecules: the number of pairs of EG molecules is shown by the dashed line, the number of pairs of MEA molecules – by a line consisting of dots, the solid line is the number of hydrogen bonds between the EG molecule and MEA.

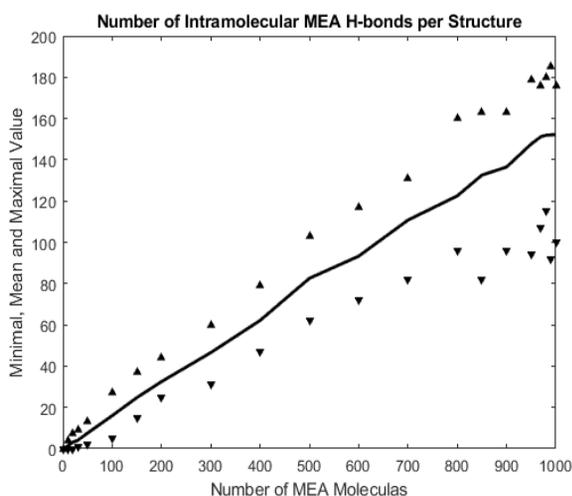


Fig. 8. Average value and range of changes in the number of MEA molecules having an intramolecular H-bond with increasing MEA concentration.

hydrogen bonds between the MEA molecule and EG prevail.

The hydrogen bond criterion allows counting the number of molecules that have an intramolecular hydrogen bond. The total number of such molecules with an increase in the MEA concentration in the solution is shown on average in **Fig. 8**. Just as in Fig. 4, triangles represent the maximum and minimum number of molecules with an intramolecular hydrogen bond for each concentration.

Fig. 9 shows a graph of the number of EG molecules with an intramolecular H-bond

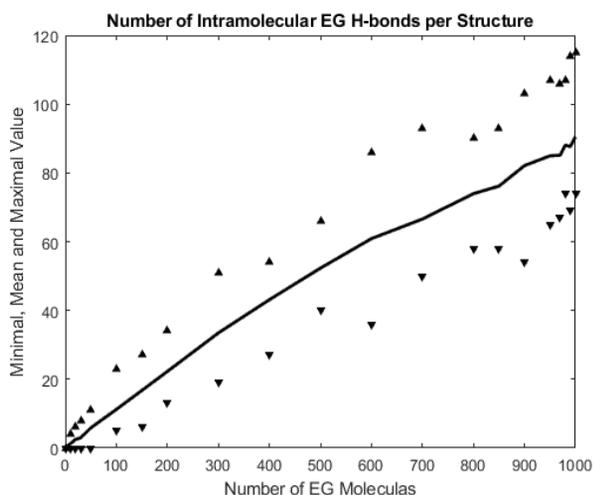


Fig. 9. Average value and range of changes in the number of MEA molecules having an intramolecular H-bond with increasing MEA concentration

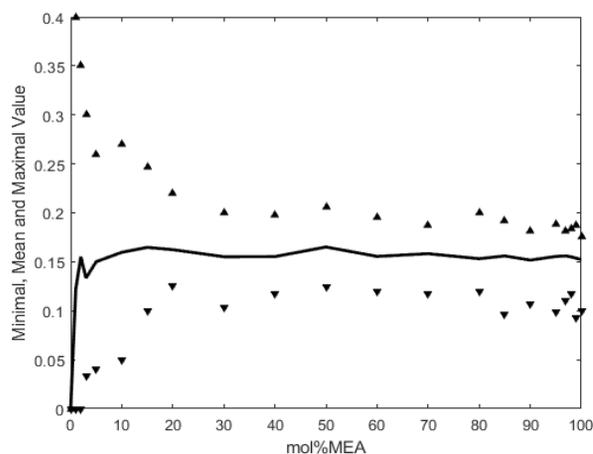


Fig. 10. Average value and range of changes in the relative frequency of appearance of MEA molecules with an intramolecular H-bond.

with an increase in the concentration of EG in solution.

Fig. 10 shows a graph of the relative frequency of appearance of MEA molecules with an intramolecular hydrogen bond. It practically does not change with an increase in the number of MEA molecules. This was to be expected, since the dependence of the average number of intramolecular bonds on concentration, shown in Fig. 8, increases almost linearly.

Fig. 11 shows a graph for the relative frequency of occurrence of EG molecules with an intramolecular H-bond. With an increase in the number of EG molecules, the frequency slightly decreases.

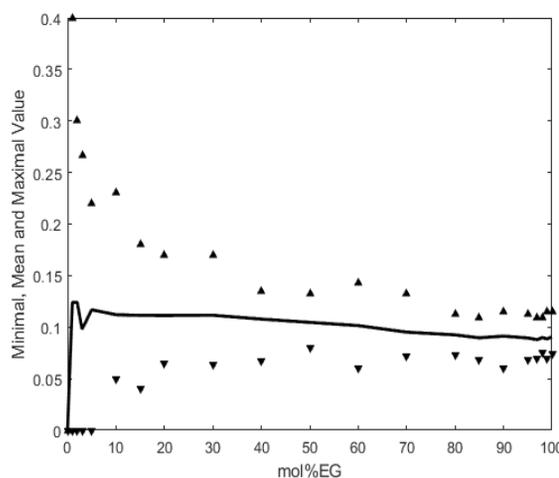


Fig. 11. Average value and range of changes in the relative frequency of appearance of ethylene glycol molecules with intramolecular hydrogen bonds.

Let's proceed the considering the nearest environment of each molecule in solution. The most accurate method for determining which molecules at a given time are in close proximity to the selected molecule is the construction of a Delaunay network, at the nodes of which the molecules of the considered liquids are located.

In this paper, we consider points in space corresponding to the coordinates of the center of mass of molecules. For this three-dimensional system of points, the Delaunay triangulation and the corresponding partition of space into Voronoi polyhedra are constructed taking into account the periodic boundary conditions specified in the calculations by the molecular dynamics method.

Voronoi polyhedra divide all space into regions, in each of which the distance from any point to the molecule located in its center is less than to any other. This makes it possible to split the entire volume of the liquid under consideration into local volumes related to each molecule. Delaunay simplexes (in the three-dimensional space of the tetrahedron), on the contrary, characterize the intermolecular space, since the spheres drawn through the vertices of these tetrahedra do not contain molecules [17], and these spheres can intersect.

Consider an arbitrary molecule in the structure. The construction of the Delaunay triangulation at a specific moment in time makes it possible to select all the molecules in its immediate environment and makes it possible to construct an adjacency matrix for such a network. Comparison of the properties of a network built on the basis of the hydrogen bond criterion and a network built on the basis of Delaunay triangulation is the subject of research.

Fig. 12 shows the average value (solid line) and the range of changes in the number of neighbors for an arbitrary molecule on the Delaunay network. In this case, almost always, the molecule that turned out to be bound to the selected molecule by a hydrogen bond was also its neighbor on the Delaunay network. In each structure, this property was not fulfilled

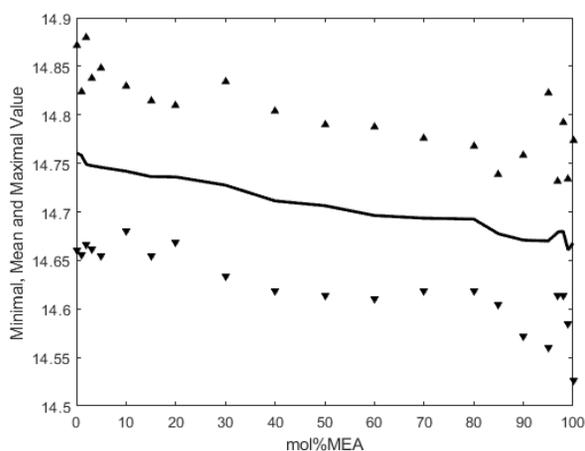


Fig. 12. Average value and range of change in the number of neighbors for one molecule on the Delaunay network.

at most once. This corresponds to a very rare arrangement of molecules, when their centers are far enough from each other, while the hydrogen atom of one of the molecules and the oxygen or nitrogen atom of the other are located so that the hydrogen bond criterion is fulfilled.

Fig. 12 shows that the number of neighbors in the pure EG is about 14.75. With an increase in the MEA concentration, this indicator slightly decreases and becomes equal to about 14.66.

If we look at the average value of the number of H-bonds in one molecule (**Fig. 13**), this indicator decreases from 3.54 in pure EG to 2.68 in pure MEA.

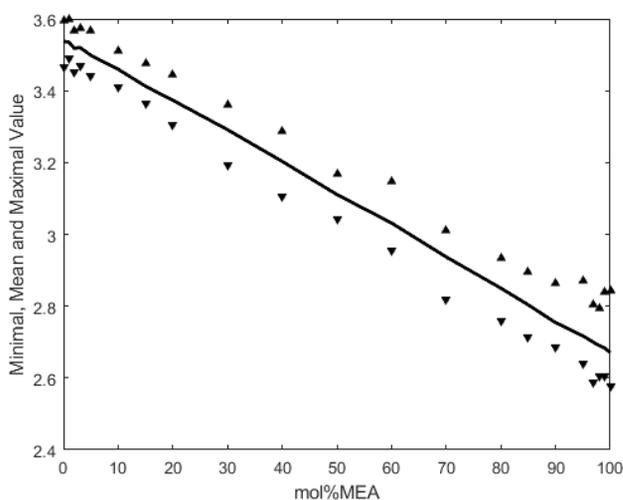


Fig. 13. Average value and range of changes in the number of hydrogen bonds in one molecule.

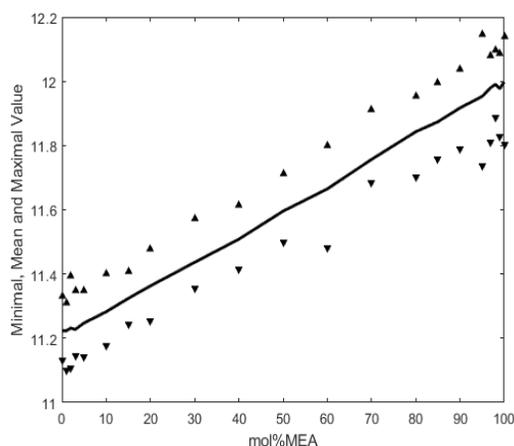


Fig. 14. Average value and range of changes in the number of neighbors of one molecule that are not hydrogen bonded.

We also present a graph of the average value and the range of changes in the number of neighbors of one molecule on the Delaunay network, which does not have H-bonds with it (**Fig. 14**). It can be seen from these figures that with an increase in the amount of MEA, neighboring molecules are less often bound by hydrogen bonds. This affects the number of non-hydrogen-bonded neighbors.

After considering the neighbors of one molecule in the structure, without specifying which molecule it is: EG or MEA, it is interesting to look at these characteristics separately for each type of molecule. **Fig. 15** shows graphs of the average number of neighbors of an EG molecule

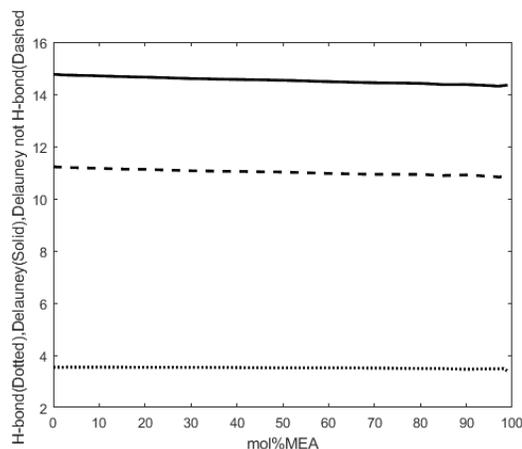


Fig. 15. The average number of neighbors of an EG molecule on the Delaunay network is indicated by a solid line; neighbors having a hydrogen bond with it is indicated by a line consisting of dots; the dotted line shows neighbors that do not have a hydrogen bond with the selected molecule.

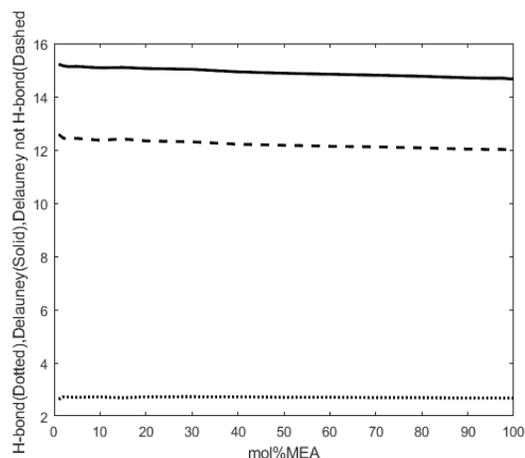


Fig. 16. The average number of neighbors of an MEA molecule on the Delaunay network is indicated by a solid line; neighbors that have a hydrogen bond with it are displayed by a line consisting of dots; the dotted line shows neighbors that do not have an H-bond with the selected molecule.

on the Delaunay network (solid line) that have a hydrogen bond with it – (a line of dots), the dashed line shows neighbors on the Delaunay network that do not have a hydrogen bond with the selected EG molecule. **Fig. 16** shows the same graphs for the MEA molecule. Attention is drawn to the fact that for molecules and EG and MEA all these characteristics practically do not change.

50 structures, which were used to calculate all the characteristics of the environment of the molecules, were selected from the trajectory with an interval of 60 ps. Thus, the total time considered was 3 ns. The total number of different molecules that at least once in the specified time range were neighbors of a given molecule indicates the mobility of molecules in solution. **Fig. 17** shows graphs of the average number of different molecules that were neighbors of a given molecule on the Delaunay network (solid line), had a hydrogen bond with it – (line of dots), the dotted line shows neighbors on the Delaunay network that did not have a hydrogen bond with the selected molecule.

It can be concluded from the graphs that the number of neighbors on the Delaunay network and the number of neighbors that did not have a hydrogen bond with the isolated molecule grows almost linearly with an increase in the MEA concentration in the solution. At the same time,

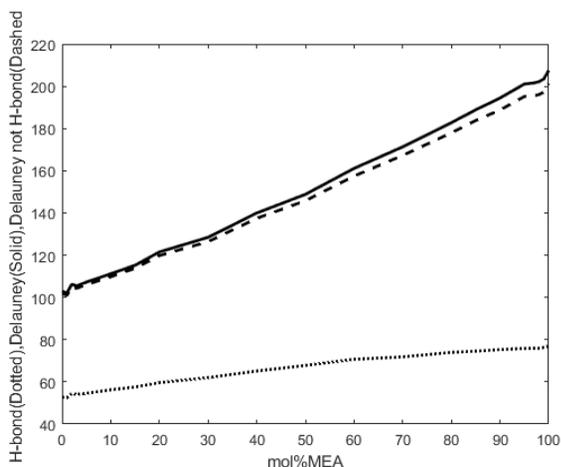


Fig. 17. Average number of different molecules that at least once were neighbors of a given molecule on the Delaunay network (solid line); had a hydrogen bond with it – (a line of dots); the dotted line represents the neighbors on the Delaunay network that have never had a hydrogen bond with the selected molecule.

In numerical terms, this indicator almost doubles. The number of neighbors that at least once had an H-bond with the isolated molecule also increases, but by about 1.5 times.

Let us consider similar indicators for the EG molecule, **Fig. 18**.

The same behavior of the indicator as in the previous figure is also observed in this figure. The total number of different molecules that were

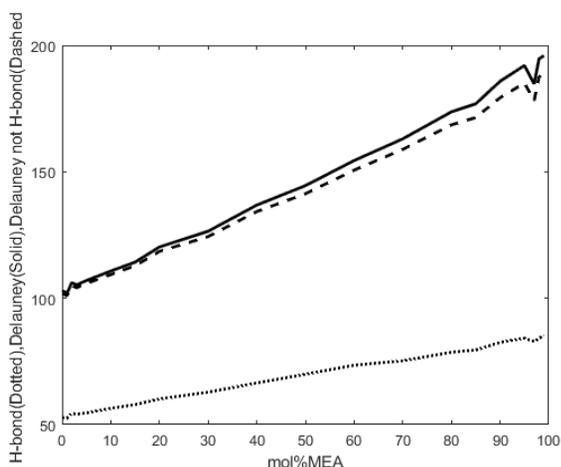


Fig. 18. Average number of different molecules that were neighbors of a given EG molecule on the Delaunay grid (solid line); had a hydrogen bond with it – (a line of dots); the dotted line shows the neighbors on the Delaunay network that did not have a hydrogen bond with the isolated ethylene glycol molecule.

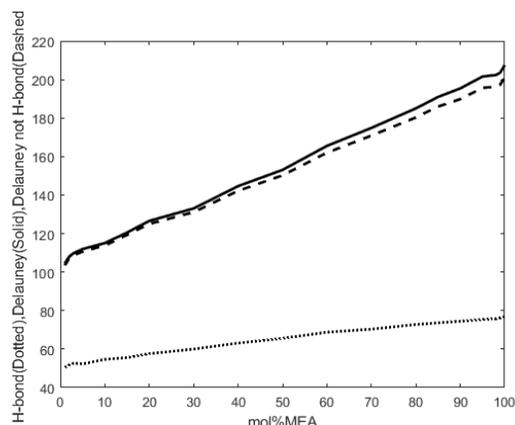


Fig. 19. Average number of different molecules that were neighbors of a given MEA molecule on the Delaunay network (solid line); had a hydrogen bond with it – (a line of dots); the dotted line shows the neighbors on the Delaunay network that did not have a hydrogen bond with the selected monoethanolamine molecule.

neighbors of the EG molecule increased slightly less than 2 times.

Let us consider similar indicators calculated for the MEA molecule, **Fig. 19**. The same behavior of the indicator as in Fig. 17 is also observed here. The total number of different molecules which were neighbors of the MEA molecule also increased by about 2 times.

For each hydrogen bond that we managed to determine using the hydrogen bond criterion, an interesting indicator is the frequency of the appearance of this bond among the 50 structures we considered along the trajectory. **Fig. 20** shows

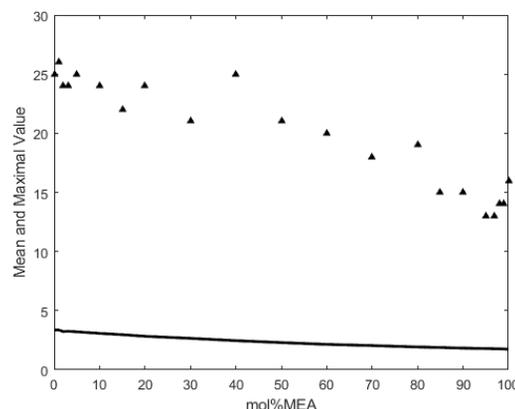


Fig. 20. The average value of the frequency of occurrence of the H-bond among the 50 structures considered is shown by the solid line. Black triangles show the maximum values of the indicator.

the average of this indicator as a solid line. Small triangles, as before, represent the maximum value of the frequency of occurrence of a hydrogen bond.

It can be seen that, in pure EG, the isolated hydrogen bond occurs at a maximum in half of the structures considered. Moreover, this situation is quite rare, since on average this indicator is less than 5 structures. With an increase in the MEA concentration, the maximum number of repetitions of the isolated hydrogen bond decreases to about 30%. A similar indicator is considered for molecules neighboring on the Delaunay network (Fig. 21).

If we consider the maximum value of the neighborhood frequency in this figure, we can see that up to about 20% of the MEA concentration there are pairs of molecules that turned out to be adjacent in almost all the structures considered. However, there are very few such cases, since the average value of this indicator is less than 10. With a further increase in the concentration of monoethanolamine, the maximum value drops to about 30 structures.

In [18], we have already estimated the lifetimes of the hydrogen bond of pure substances EG and MEA using the example of V-structures calculated by the molecular dynamics method at a close temperature of 293K. However, these trajectories were much shorter in time than those

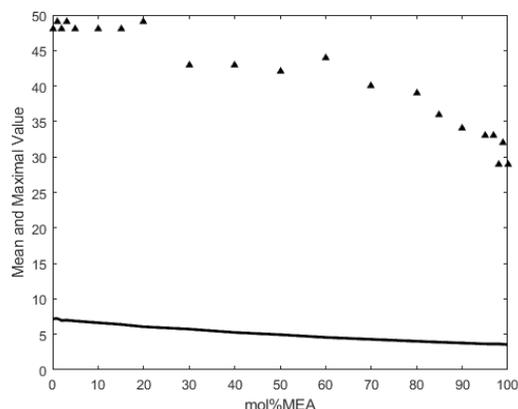


Fig. 21. The average value of the frequency of the neighborhood of two molecules on the Delaunay network among the 50 structures considered is shown by the solid line. Black triangles represent the maximum values of the indicator.

we are considering in this article. Namely, the trajectories for the EG were less than 1.2 ns in duration, and for the MEA, less than 1 ns. The corresponding maximum lifetime for EG was 1168 ps, but for MEA this parameter could not be established, since hydrogen bonds were found that did not break along the entire trajectory. It should be noted that the published MEA results were obtained based on the M1 model for the MEA molecule.

Let us compare the results obtained with the results obtained by us with the M1 model, having considered in detail the conclusions of this work (M2 model).

1. For the M2 model in pure EG and in the case of a small number of MEA molecules, practically all molecules are connected with a three-dimensional network of hydrogen bonds. With an increase in the concentration of MEA molecules, the number of bound components increases and, accordingly, the size of the maximum bound component decreases. This tendency is especially enhanced when the number of MEA molecules in solution becomes more than 900. However, it should be noted that in the worst case, the minimum size of the maximum bonded component in solution turns out to be equal to 964, which indicates that more than 96% of molecules in all considered structures for of all concentrations are linked by a network of hydrogen bonds. For the M1 model, in the entire concentration range, all molecules are bound into a three-dimensional network of hydrogen bonds.

2. For the M1 model, in the entire concentration range, the number of mixed pairs of molecules and pairs of MEA molecules bonded by hydrogen bonds is significantly greater than for the M2 model, while the pairs of EG molecules bonded by hydrogen bonds, on the contrary, are smaller for practically all concentrations than for the M2 model. If we talk about the total indicator, then for the M2 model with an increase in the number of MEA molecules in the structure, the average number of hydrogen bonds in the system decreases by about 30% in pure monoethanolamine. Mixtures

for the M1 model show the opposite tendency for the studied indicator to change.

3. Let us now consider the relative frequency of the appearance of the intramolecular H-bond in the MEA molecule. Comparison of the models for this indicator suggests that the relative frequency of the appearance of MEA molecules with an intramolecular hydrogen bond practically does not depend on the concentration of monoethanolamine, but for the M2 model it is 8 times higher than in the M1 model.

4. Comparison of the relative frequency of the appearance of the intramolecular hydrogen bond for EG molecules with an increase in the EG concentration for the M2 model decreases, while for the M1 model it increases by more than 3 times. Thus, a change in the model of the MEA molecule affects the appearance of an intramolecular H-bond in the EG molecule in solution.

5. Let us now consider such an important indicator as the average value of the number of H-bonds in one molecule. Changing the model of the MEA molecule leads to a decrease in this important parameter in the entire concentration range and to an almost twofold decrease for the M2 model in comparison with the M1 model (in pure MEA).

6. If we talk about the number of neighbors of one molecule on the Delaunay network, then changing the model of the MEA molecule does not significantly affect the dynamics of this indicator. Thus, with an increase in the MEA concentration, neighboring molecules are less often hydrogen bonded.

7. The average number of neighbors of an EG molecule on the Delaunay network, neighbors having a hydrogen bond with it, and neighbors on the Delaunay network that do not have a hydrogen bond with the selected EG molecule do not depend on the choice of the MEA molecule model.

8. As for the MEA molecules, the average number of neighbors on the Delaunay grid also does not depend on the choice of the MEA molecule model. While the number of molecules that have a hydrogen bond with it is about 2 molecules more when considering the M1 model

in the entire concentration range. The total number of different molecules that were neighbors of a given molecule indicates the mobility of molecules in solution. 50 structures, by which we calculated all the characteristics of the environment of the molecules, were selected for the M2 model from the trajectory with an interval of 60 ps. Thus, the total time considered was 3 ns. Comparison of this indicator with the calculations carried out earlier is complicated by the fact that the trajectories obtained for the M1 model were more extended in time and amounted to about 5 ns. So, with an interval of 60 ps, not 50, but 80 structures were considered along each trajectory. However, trends in the change in the total number of various molecules which were neighbors of a given molecule can be traced.

9. For the M2 model, the number of neighbors on the Delaunay network and the number of neighbors that did not have a hydrogen bond with the selected molecule grows almost linearly with an increase in the MEA concentration in the solution. At the same time, in numerical terms, this indicator almost doubles and is about 200 in pure MEA. The number of neighbors that had a hydrogen bond with the isolated molecule also increases, but by about 1.5 times to about 70.

Comparison with the M1 model shows that the trend in these indicators is opposite. The number of neighbors of a molecule with an increase in the MEA concentration for the M1 model decreases all the time and stabilizes at about 30. The average number of neighbors that had a hydrogen bond with the isolated molecule also behaves, but the indicator stabilizes at the level of 10. (Exactly the same tendencies are observed, if we consider separately the MEA molecule and the number of its neighbors and the EG molecule and its neighbors). Thus, it can be concluded that a change in the model of the MEA molecule leads to a significant increase in the mobility of the MEA molecule both in solution and in a pure substance.

10. For each hydrogen bond that we managed to determine using the hydrogen bond criterion, an interesting indicator is the frequency of the appearance of this bond among the 50 structures

we have considered along the trajectory. For the M2 model in pure EG, the separated hydrogen bond occurs at a maximum in half of the structures considered. Moreover, this situation is quite rare, since the average indicator is less than 5 structures. With an increase in the MEA concentration, the maximum number of repetitions of the isolated hydrogen bond decreases to about 30%. It should also be remembered here that 80 structures were considered for the M1 model, and only 50 for the M2 model. Comparison of the change in the indicator also demonstrates significant differences. For the M1 model, the frequency of occurrence of the isolated hydrogen bond, on the contrary, increases significantly (more than 3 times) with an increase in the MEA concentration. The same opposite tendencies are demonstrated by the analysis of the neighborhood frequency on the Delaunay grid. These facts also confirm that a change in the model of the MEA molecule leads to a significant increase in the mobility of this molecule.

4. CONCLUSION

We examined in detail and compared the conclusions of calculations for the second (M2) and first (M1) models of the MEA molecule. Explanation of the difference in the results in the complexity and ambiguity of the choice of the model associated with interactions in a liquid - a condensed but mobile phase. Therefore, the only criterion for the correct choice is comparison with experiment. Therefore, we chose the M2 model.

The main conclusion of comparing the results of calculations of the M2 and M1 models is the lower connectivity of the mixed spatial network of H-bonds (96% – M2, 99.9% – M1) and the high mobility of MEA molecules in the system of the M2 model.

The main calculations were carried out on supercomputers at the MSC RAS and the Keldysh Institute of Applied Mathematics of the Russian Academy of Sciences.

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