

## CLUSTERS OF WATER IN THE COMPOSITION OF ANTIFREEZES

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(Received March 26, 2015; Accepted in revised form April 8, 2015)

**Abstract:** Antifreezes based on water eutectics are widely spread in engineering and by cryo-preservation of biological objects as well. Salts of inorganic and organic acids, alcohols, glycols, glycol ethers, glycerin, acids, bases, amino-acids, and other chemical compounds are suitable here as supplementary means. Part of these compounds is capable to take part in the formation of H-bonds with water molecules, the others do not form H-bonds (CaCl<sub>2</sub>), but they are united into crystal-hydrates of CaCl<sub>2</sub> · 6 H<sub>2</sub>O type. In this case H-bond of water molecules can become the bond of intermolecular-cluster type. It is assumed that basic structural components of liquid water are cyclic penta- (H<sub>2</sub>O)<sub>5</sub> and hexamers (H<sub>2</sub>O)<sub>6</sub>, built with the participation of the long hydrogen bond and capable of producing the crown effect. Cyclic water clusters – short-range order of water in terms of cavity size and the number of oxygen atoms correspond to crown ethers: 15-crown-5 and 18-crown-6, sodium and calcium ions being absorbed into them. Energy estimation of water and ice (snow) interaction with the components of antifreezes: ethylene- and diethylene glycols, ethylene glycol ethers, hydrogen chloride and ammonia is made. Possibility of “ideal” solution formation with low freezing temperatures is shown. The analysis of the eutectics and diagrams of water antifreeze fusion based on the salts, alcohols, ethylene glycol, ethylene glycol ethers, hydrogen chloride and ammonia by comparison with an ideal solution of water concerning cryoscopic constant is carried out. It is established that the coefficient K in the equation of linear melting curve  $y = K \cdot x + b$  for effective antifreezes, in terms of freezing temperature, exceeds the cryoscopic constant of water, that testifies to the destruction of long-range order of water. Penta- and hexamers of water responsible for short-range order of water pass into the eutectics as monomers or oligomers with the degree of cross linking equal to 2–4. To create effective antifreeze it is important to avoid the destruction of cyclic water clusters. It is desirable, as in the case with ethylene, to have the second component of water antifreeze in a cyclic form too. There is an analogy with naphthenic (cyclic) hydrocarbons of oil, which provide mobility of the condensed state. Promising are antifreezes based on mixtures of inorganic and organic compounds.

**Keywords:** Water clusters, penta- and hexamers, H-bond, antifreeze, water cryoscopic constant, crown-effect

UDC 547.422

DOI 10.12737/11468

## INTRODUCTION

Solutions with low freezing temperature based on water (antifreezes) are known in nature and are widely used in the technology of food production. The antifreeze composition comprises salts of inorganic and organic acids, alcohols, glycols, glycerin, acids and bases, amino acids and other compounds.

Formation of solutions is a spontaneous diffusion process proceeding from the thermal motion of constituent particles. Interaction force in the solution is evaluated by the osmotic pressure P, which depends on the concentration of the solute [1].

$$P = \frac{RT}{V_1} \times \ln 1 - x, \quad (1)$$

or after simplification

$$P = RTc, \quad (2)$$

where  $V_1$  is the molar volume of the solvent,  $V_1 = M/\rho$ ; M is the molecular weight;  $\rho$  is the density, x and c is the mole fraction of the solute.

This equation describes the ideal, that is, rather

diluted (thin) solutions ( $10^{-6}$  -  $10^{-2}$  mole / dm<sup>3</sup>), in which osmotic pressure does not depend on the nature of the solvent and solute and is determined only by the number of interacting particles. Osmotic pressure is associated with the numerical average molecular weight of the solute:

$$M = RT \frac{m}{P}, \quad (3)$$

where m is the molar concentration.

The osmotic properties of solutions include lowering the freezing point of the solvent (water) caused by the additive.

$$\Delta T_{fr.} = K \times m, \quad (4)$$

where K is the cryoscopic constant of the solvent or the molar lowering of the solidification temperature of the solution. The indicator T characterizes the solvent and is independent of the nature of the solute (solid, liquid, gas). For water  $K = 1.86$  °C/mole.

For concentrated solutions, it is necessary to introduce osmotic correction factors that reflect the relationship of real and theoretical values. The

composition of the resulting associates in the solution remains unknown, primary water clusters have not been established.

In quantum chemistry to assess the process of dissolution and the formation of associates pair interaction potentials in the system and their sign are used. If the sign is negative, the particles do not interact with each other the solution tends to the ideal and is described by the laws of physical chemistry. If the sign is positive, then the system can have colloidal phenomena in all the diversity [2]. Evaluation is performed by temperature. The upper temperature limit is the temperature of the onset of chemical transformations and the lower - the formation of the solid phase. In our work special points will be - 0°C ( $T_{fr.}$  of water), minus 70°C ( $T_{eut.}$ ), and 198°C ( $T_{boil.}$  of ethylene glycol) for the system water-ethylene glycol. At the temperature of 198°C (more precisely from 180°C) there begins non-catalytic reaction of ethylene glycol formation from water and ethylene oxide or ethylene glycol dehydration to dioxan.

Our most studied compounds: water, alcohols, glycols, salts of mono- and dicarboxylic acids are compounds containing oxygen, capable through an oxygen atom to participate in the formation of H-bonds. At the same time other components of antifreezes (eutectic):  $CaCl_2$ , NaCl, HCl,  $NH_3$  do not contain O atoms and formally they do not have H-bond via oxygen, although there are numerous hydrates:

$CaCl_2 \cdot 6H_2O$ ;  $CaCl_2 \cdot 4H_2O$ ;  $CaCl_2 \cdot 2H_2O$  et al.

The aim of this work is to study the composition of water clusters (hydrates) in antifreezes in the temperature range of 100–200°C. One of the challenges of the work is to found the approaches for the creation of antifreeze formulations.

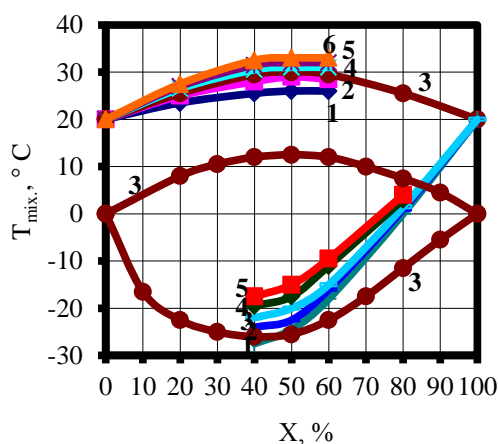
## OBJECTS AND METHODS OF STUDY

The paper accepts:

- the main structural components of liquid water are cyclic penta ( $H_2O$ ) 5 and hexa ( $H_2O$ ) 6 steps, built at the expense of H-bonds [3];
- the concept of H-bond formed due to the shift of the valence electrons in the atom O, H atoms exchange between the water molecules to form cycles or chain structure. The formation of the bond  $[H-O-H \cdots H-O-H]$  through two H atoms (long H-bond) that prevails in the ice is possible [4].

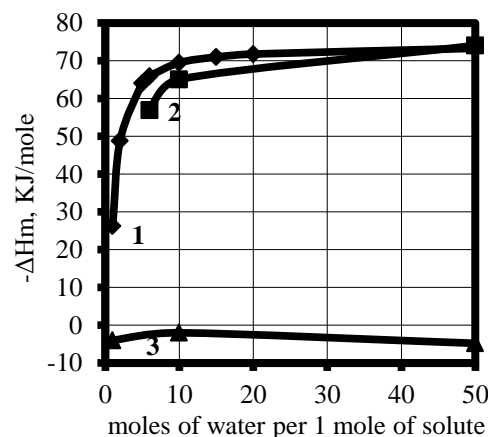
The sign (temperature) of the pair interaction in the ice (water) - antifreeze component and the possibility of solution formation  $T_{fr.} < 0^\circ C$  was determined by mixing ice and water with the second component of antifreeze in Dewar flask. The results are shown in Fig. 1.

Interaction energy of HCl, the salts  $CaCl_2$ , NaCl and water was evaluated by the heat of mixing, taken from [5, 6]. Formation enthalpy of the hydrates  $CaCl_2$  and HCl, containing 5–15 water molecules is virtually identical (Fig. 2).



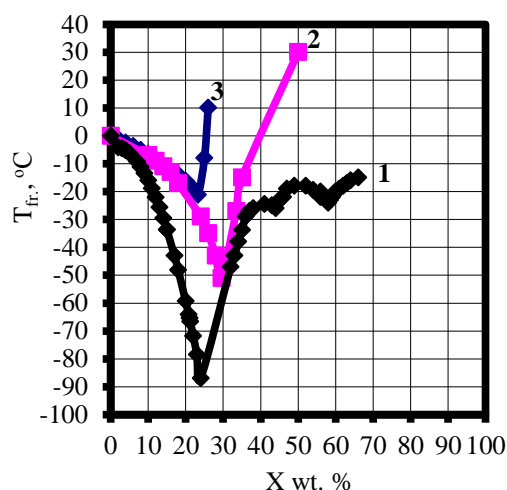
**Fig. 1.** The change of solution temperature depending on the concentration of the component, when mixed with ice and water: (1) ethylene glycol; (2) diethylene glycol; (3) ethyl ether of ethylene glycol; (4) ethyl ether of diethylene glycol; (5) ethyl ether of triethylene glycol; (6) ethyl ether of tetraethylene glycol.

The values for the charting of systems fusibility: HCl- $H_2O$ , NaCl- $H_2O$ ,  $CaCl_2$ - $H_2O$ ,  $NH_3$ - $H_2O$ ,  $H_2O_2$ ,  $H_2O$ , alcohols-water, ethylene glycol-water are drawn from the literature [6]. For ethyl cellosolve, ethylcarbitol, sodium adipate, phase equilibrium of aqueous solutions is studied using visual poly-thermal method of analysis. Sodium adipate was synthesized from adipinic acid and sodium hydroxide of reactive



**Fig. 2.** The heat of dissolution ( $-\Delta N_m$ ) in water: (1) hydrogen chloride; (2) calcium chloride; (3) sodium chloride.

purity. The dependence of  $T_{fr.}$  on the mole and mass fraction of additives is plotted. Fig. 3, 4 show the examples of eutectics with low and high content of the second component. Fig. 5 shows diagrams for tertiary butyl alcohol, ethylene oxide and propylene oxide, the first and third ones were obtained experimentally. For t-butanol the second eutectic is detected on the side of water.

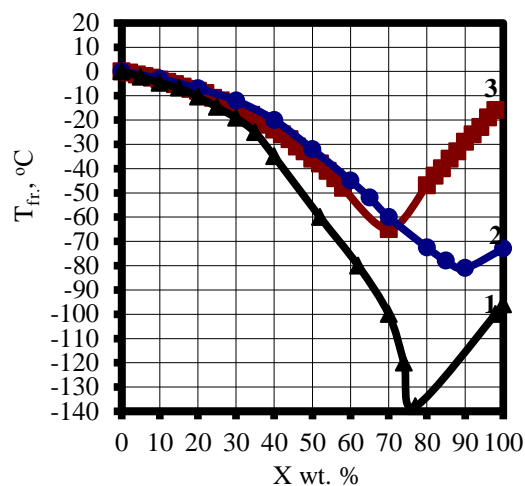


**Fig. 3.** The diagram of systems fusion: (1) HCl-H<sub>2</sub>O; (2) CaCl<sub>2</sub>-H<sub>2</sub>O; (3) NaCl - H<sub>2</sub>O.

The program «Excel» linearizes fusion curves before eutectic in straight lines  $y = K \cdot x + b$ . Points for concentration of less than 10% are excluded. Interpretation of graphs and equations of straight lines is based on the provisions:

- the slope of the line (K) for the ideal aqueous solution of 1.86 corresponds to cryoscopic constant of water;
- the intersection of the line with the y-axis is characterized by the coefficient b and corresponds to the water temperature of a particular cluster structure, these clusters become eutectic.

For the convenience of processing the results binary systems are numbered:



**Fig. 4.** The diagram of systems melting: (1) CH<sub>3</sub>OH-H<sub>2</sub>O; (2) C<sub>2</sub>H<sub>5</sub>(OCH<sub>2</sub>CH<sub>2</sub>)OH-H<sub>2</sub>O; (3) C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>-H<sub>2</sub>O.

- Alcohols: methyl - 1 ethyl - 2, t-butyl - 3;
- Glycols: ethylene glycol - 4;
- Glycol ethers: ethylcellosolve - 5 ethylcarbitol - 6;
- Salts: sodium chloride - 14, calcium chloride - 15 potassium formiate - 7, potassium acetate - 8, sodium adipate - 9, sodium adipate (technological mixture) - 10, 11;
- Hydrogen chloride - 12;
- Ammonia - 13;
- Hydrogen peroxide - 16.

Equations, the coefficients K and b are shown in Table. 1, temperatures and the hydrate number of eutectics are indicated herein.

**Table 1.** Equations, the coefficients K and b, temperatures and the hydrate number of eutectics

№	Component	Equation of the line freezing	(minus)K	b	T <sub>eut.</sub> , °C	Hydration number *	
1	CH <sub>3</sub> OH	Y = - 2.27x + 22.19	2.27	22.19	-138	-	0.5
2	C <sub>2</sub> H <sub>5</sub> OH	Y = - 1.62x + 16.95	1.62	16.95	-130	-	0.2
3	T-C <sub>4</sub> H <sub>9</sub> OH	Y = - 0.80x + 0.17	0.80	0.17	-6	15.0	0.5
4	C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub>	Y = - 1.74x + 3.54	1.74	3.54	-71	-	2.0
5	C <sub>2</sub> H <sub>5</sub> (OCH <sub>2</sub> CH <sub>2</sub> )OH	Y = - 1.58x - 3.04	1.58	-3.04	-80	-	0.5
6	C <sub>2</sub> H <sub>5</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> OH	Y = - 1.98x + 1.85	1.98	1.85	-64	-	0.8
7	KHCOO	Y = - 3.49x + 7.52	3.49	7.52	-55	4.6	-
8	KCH <sub>3</sub> COO	Y = - 4.32x + 5.92	4.32	5.92	-62	5.4	-
9	C <sub>6</sub> H <sub>8</sub> Na <sub>2</sub> O <sub>4</sub> (π)	Y = - 4.00x + 3.61	4.00	3.61	-20	20.0	-
10	C <sub>6</sub> H <sub>8</sub> Na <sub>2</sub> O <sub>4</sub> (II)	Y = - 12.30x + 13.08	12.30	13.08	-46	-	-
12	HCl	Y = - 8.45x + 32.06	8.45	32.06	-85	6.1	-
13	NH <sub>3</sub>	Y = - 4.15x + 46.01	4.15	46.01	-100	2.0	0.25
14	NaCl	Y = - 2.48x + 1.01	2.48	1.01	-21	10.8	-
15	CaCl <sub>2</sub>	Y = - 9.23x + 12.55	9.23	12.55	-55	15.0	-
16	H <sub>2</sub> O <sub>2</sub>	Y = - 1.70x + 6.02	1.70	6.02	-56	2.0	1.3

Note. \* In the leftmost column on the water side, in the right one - from the second component.

## RESULTS AND DISCUSSION

*The analysis of the diagrams of aqueous solutions fusion.*

Several studied systems 1, 2, 4, 5, 6, 14, 16 show: the convergence of the coefficient K and the cryoscopic constant of water ( $K = -1.86$ ) (Fig. 6), but the difference in the eutectic temperature from minus 20 to

minus 138 °C. For the system 14 (NaCl-H<sub>2</sub>O) with  $K = -2.48$  and  $b = 1.01$  eutectic temperature is minus 21.1°C.

Thus, the approach of aqueous solutions to the "ideal" water according to K is a necessary but insufficient condition for the formation of eutectics with low fusion points. Small (hot) ( $b = 6-46$ ) water

clusters should essentially be in the eutectic and the second eutectic component cluster join the structure of water clusters or voids between them. These are the systems  $\text{H}_2\text{O}-\text{HCl}$ ;  $\text{H}_2\text{O}-\text{NH}_3$ ;  $\text{H}_2\text{O}-\text{CaCl}_2$ ; water-alcohols; water- salts of organic acids.

Clusters of liquid water stored in low-temperature eutectic have the water structure of the highest factors  $K$  and  $b$ . If  $K$  is less in absolute value than  $-1.86$  and  $b$  is small, eutectic temperature of the system cannot be low. This example is given by the solution of *t*-butyl alcohol-water ( $K = -0.8$ ;  $b = 0.17$ ), wherein  $T_{\text{eut.}}$  is only  $6^\circ\text{C}$ .

Consider fusion diagrams from water side (Fig. 3). The largest area is occupied by the system water-HCl, NaCl and  $\text{CaCl}_2$  eutectics are absorbed into it. Eutectic temperatures of lithium and sodium hydroxyls are placed directly on the liquidus curve  $\text{H}_2\text{O}-\text{HCl}$ :

–  $\text{LiOH}-\text{H}_2\text{O}$ ,  $T_{\text{eut.}}$  minus  $18^\circ\text{C}$ , composition  $\text{LiOH}\times 9,8\text{H}_2\text{O}$ ;

–  $\text{NaOH}-\text{H}_2\text{O}$ ,  $T_{\text{eut.}}$  minus  $28^\circ\text{C}$ , composition  $\text{NaOH}\times 9,5\text{H}_2\text{O}$ .

Ammonia eutectic from water side (32%  $\text{NH}_3$ ) has  $T_{\text{fr.}}$  minus  $100^\circ\text{C}$ , and hydrate number 2 ( $\text{NH}_3\times 2\text{H}_2\text{O}$ ). Taking into account the association of ammonia molecules in the liquid state at low temperatures, we can only talk about the multiplicity of the number of molecules  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . The confirmation is the eutectic composition from ammonia side, where only 0.25 moles of  $\text{H}_2\text{O}$  falls at 1 mole of  $\text{NH}_3$ . In this case, the composition  $4\text{NN}_3\times \text{H}_2\text{O}$  is more likely.

For aqueous systems there has been previously identified the area of the formation of solid compounds such as clathrates [7], in which the "guest" and "host" are in the weak interaction:  $\text{CH}_4\times 6\text{H}_2\text{O}$ ,  $\text{C}_3\text{H}_8\times 16\text{N}_2\text{O}$ , acetone  $(\text{C}_3\text{H}_6\text{O})_n\times (17\text{N}_2\text{O})_n$ , dioxane  $(\text{C}_4\text{N}_8\text{O}_2)_n\times (18\text{N}_2\text{O})_n$ . Further on mixed clathrate-cluster structures based on the H-bond appear on the liquidus curve before eutectic temperature, which are dominated by the strongest associates of the water molecule, namely  $(\text{H}_2\text{O})_5$  and  $(\text{H}_2\text{O})_6$ , as it has been now established. The formation of mixed structures is the cause of non-stoichiometric ratios in the hydrate, for example  $\text{NaCl}\times 10,8\text{N}_2\text{O}$ .

For the systems  $\text{H}_2\text{O}-\text{NaCl}$ ;  $\text{H}_2\text{O}-\text{CaCl}_2$  and  $\text{H}_2\text{O}-\text{HCl}$  eutectic hydrate numbers make up to:  $\text{NaCl}\times 10,8\text{N}_2\text{O}$  (23.3 wt. %);  $\text{CaCl}_2\times 15\text{N}_2\text{O}$  (29.6 wt. %);  $\text{HCl}\times 6\text{H}_2\text{O}$  (22 wt. %). Eutectic composition  $\text{HCl}\times 6\text{H}_2\text{O}$  corresponds to the azeotrope composition of the second kind for hydrogen chloride and water, which is confirmed by the presence of the chemical (hydrogen) bond of the molecules  $\text{HCl}$  and  $\text{H}_2\text{O}$ .

Heat (enthalpy  $\Delta H_m$ ) of HCl hydration qualifies as the maximum precisely at the ratio of 6 moles of water per 1 mol of HCl, calcium chloride behaves in the same way (Fig. 2), although the complete saturation is achieved with a larger number of molecules of water:  $\text{HCl}\times (10-12)\text{H}_2\text{O}$ ,  $\text{CaCl}_2\times (10-20)\text{H}_2\text{O}$ . Sodium chloride does not virtually interact with water, its  $\Delta N_m$  is less and has a different sign. The molecule of NaCl

apparently absorbs into the structure of liquid water, but solid eutectic includes ice and  $\text{NaCl}\times 2\text{H}_2\text{O}$  [8].

In the case of alcohols, eutectic from water was found only for *t*-butyl alcohol. It has  $T_{\text{fr.}}$   $6^\circ\text{C}$  and contains 22% by weight of alcohol ( $\text{RON}\times 15\text{N}_2\text{O}$ ). From [3] it is known that at the concentration of 22% by weight *t*-butanol is converted from the structuring agent into its water crusher.

Increasing the basicity of the second component of the aqueous solution, for example, alongside with the transition to cyclic glycol ether - ethylene or propylene oxides, is accompanied by the formation of hydrates with positive freezing temperatures. Solid hydrates of ethylene oxide are present in the concentration range 10–70% by weight and have the freezing point plus 6–10.7  $^\circ\text{C}$ . Of particular note is the composition  $\text{C}_2\text{H}_4\text{O}\times 6\text{H}_2\text{O}$  close to 29 % by weight of ethylene oxide [9].

For propylene oxide, crystalline hydrate  $\text{C}_3\text{H}_6\text{O}\times 5\text{H}_2\text{O}$  with the fusion temperature minus 6–7  $^\circ\text{C}$  is typical. In the system of propylene oxide-water, liquidus curve is parallel to the X-axis at this temperature (Fig. 5). While being stored crystalline hydrate  $\text{C}_3\text{H}_6\text{O}\times 5\text{H}_2\text{O}$  loses its monoxide, passing into  $\text{C}_3\text{H}_6\text{O}\times (10-20)\text{H}_2\text{O}$ . In the aqueous solution of propylene oxide there occurs delamination, the lower layer corresponds to  $\text{C}_3\text{H}_6\text{O}\times 5\text{H}_2\text{O}$ . The structures of liquid and that of crystalline hydrate will differ, they can be built according to the type of complex compounds with a different coordination sphere.

From the alcohol side eutectic of tertiary alcohol  $\text{S}_4\text{N}_9\text{ON}$  has  $T_{\text{fr.}}$   $-5^\circ\text{C}$ , and corresponds to the formula  $2\text{ROH}\times \text{H}_2\text{O}$  and its composition is close to the composition of azeotrope. Depression of the eutectic freezing point as compared with the alcohol freezing point is 30  $^\circ\text{C}$ , water substantially destroys the structure of alcohol.

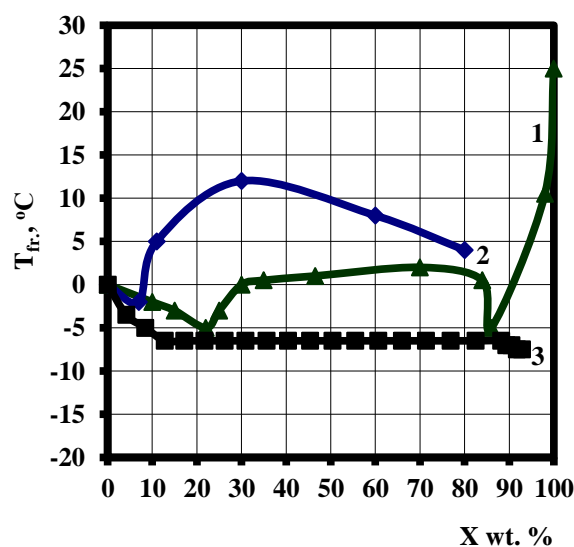
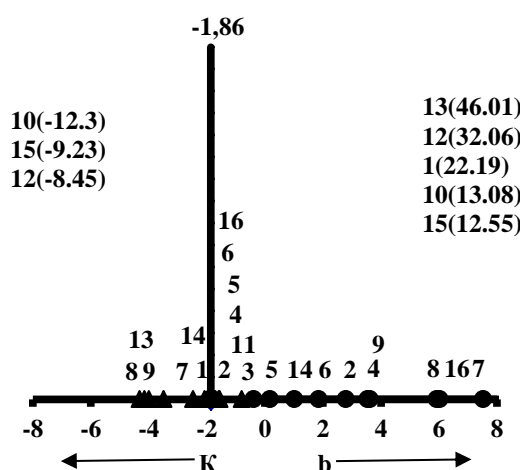


Fig. 5. Diagram of systems fusion: 1 –  $\text{C}_4\text{H}_9\text{OH}-\text{H}_2\text{O}$ ; 2 –  $\text{C}_2\text{H}_4\text{O}-\text{H}_2\text{O}$ ; 3 –  $\text{C}_3\text{H}_8\text{O}-\text{H}_2\text{O}$ .



**Fig. 6.** Dependence of the coefficients  $K$  and  $b$  on the nature of the second component of water eutectics.

It is known [10] that the alcohols in the liquid state are associated as  $\text{ROH} \times n$ , where  $n$  ranges from 3 to 30: methanol 30; ethanol 25; butanol 15; t-butanol 3.

While boiling the trimer of t-butanol is destroyed, an azeotrope of the 1<sup>st</sup> kind is formed with water, in which dimer  $2\text{ROH} \times \text{H}_2\text{O}$  dominates. Methanol has the eutectic  $2\text{ROH} \times \text{H}_2\text{O}$  with the freezing temperature minus 120 °C. Methyl and cellosolves also have eutectics from the alcohol side with low water content  $2\text{ROH} \times \text{H}_2\text{O}$ .

The greatest water influence on alcohols can be seen in the case of cyclohexanol. The eutectic ( $T_{\text{eut}}$ , minus 56 °C, water content of 5 wt. %) is formed by the alcohol-water ratio of 3.4: 1. With water, cyclohexanol forms the azeotrope of the 1<sup>st</sup> kind containing 21 wt. % of alcohol ( $\text{ROH} \times 20.9\text{N}_2\text{O}$ ).

For ethylene glycol (Fig. 4), the range of known eutectics is described by us with the formula  $2\text{C}_2\text{N}_4(\text{OH})_2 \times (2-5) \text{H}_2\text{O}$ . Eutectic composition with the minimum  $T_{\text{fr}}$ , obtained by extrapolating of published results and calculated by the special method of thermodynamic similarity [11, 12] coincided and was 69 wt. % of glycol and 31 wt. % of water. This corresponds to the formula  $2\text{C}_2\text{N}_4(\text{OH})_2 \times 3\text{H}_2\text{O}$  or  $2[2\text{C}_2\text{N}_4(\text{OH})_2] \times 6\text{H}_2\text{O}$ . The formulation allows for dimerization of ethylene in the vapor and the diluted solutions and the cluster cyclization that manifests in the IR- spectrum as the doublet of intramolecular hydrogen bond (3604 and 3614  $\text{cm}^{-1}$ ). Addition of water in the amount of 1–2 moles per mole of glycol does not lead to the destruction of the cyclic bond.

The temperature of this eutectic by extrapolation method is minus 68 °C, by calculation - minus 73,7 °C. The developed eutectic calculation algorithm is used for the aqueous solutions of propylene glycol, diethylene glycol, ethyl cellosolve, and several other esters and gives satisfactory results. The increase in viscosity of eutectic solutions with the temperature lowering requires the introduction of the coefficient of association (polymerization) of homogeneous fragments. Then the formula becomes  $\{2[2\text{C}_2\text{H}_4(\text{OH})_2] \times 6\text{H}_2\text{O}\}_n$ .

Concentrated glycols (ethylene glycol) at room temperature form interaction solids, both with acids and bases (ethylene glycol + boric acid; ethylene glycol + dicyclohexilamine). Dicyclohexilamine also reacts with water, but the solid adduct is melted before its equivalent with ethylene glycol [13]. Glycol alkyl substituents prevent the formation of solid adduct or lower  $T_{\text{fr}}$ . Glycols and glycol ethers may be part of a cluster, but the acting molecular weight herewith is less than that calculated by the rule of proportionality. For mixtures, there is a decrease of viscosity,  $T_{\text{fr}}$ , but the increase in hygroscopicity. There is no volume contraction, and mixes dissolve water well enough. The greatest asymmetry of molecules and clusters based on them, and the minimum freezing temperature are attained in the clusters containing primary OH-group and hydrocarbon radical ( $\text{CH}_3$ -,  $\text{C}_2\text{H}_5$ -) in oxyethylene unit. The ether  $\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-CH}(\text{CH}_3)\text{-CH}_2\text{OH}$  has the  $T_{\text{fr}}$ , minus 80°C. The symmetrical disecundary dipropylenglycol  $\text{CH}_3\text{-CH}(\text{OH})\text{-CH}_2\text{-O-CH}_2\text{-CH}(\text{OH})\text{-CH}_3$  melts at plus 46 °C in the inert atmosphere and cyclizes due to intramolecular H-bonds when being diluted. The addition of water does not destroy the intramolecular loop, the band 3610  $\text{cm}^{-1}$  is preserved, but almost completely suppresses the intermolecular hydrogen bonds (the band 3420 and 3480  $\text{cm}^{-1}$ ) of glycol molecules [14].

The interaction of glycols and their esters with water is exothermic. The thermal effect per unit weight of the compound added to water increases in the series: ethylene glycol < diethylene glycol < ethylene glycol ether < diethylene glycol ether < triethylene glycol ether < tetraethylene glycol ether (Fig. 1).

When ice being added to glycols, temperature decreases and passes through 0 °C in the series: tetraethylene glycol ether < triethylene glycol ether < diethyleneglycol ether < ethylene glycol ether < diethylene glycol < ethylene glycol. Ethylene glycol produces the greatest destruction of ice structure (melting capacity) and transfer to the liquid, the temperature reaching minus 28 °C (Fig. 1). Such behavior is described for  $\text{CaCl}_2 \times 6\text{H}_2\text{O}$ , when calcium hexahydrate is mixed with snow or crushed ice to obtain low temperatures. Anhydrous calcium chloride when mixed with snow or water is heated.

If the drop in temperature leads to the preservation of the "ideal" solutions - antifreezes at water level and the coefficient  $K$  in the equation of linealized liquidus curve is close to the cryoscopic constant of water, then we can talk about saving the water structure in antifreeze.

As it is currently established, in liquid water there dominate cyclic penta- and hexamers based on hydrogen bond. The diameter of the pentamer cavity is 2.8 Å. If we use the model of a long H bond, the structure of cyclic penta- and hexamers corresponds to the crown ethers: 15-crown-5; 18-crown-6 [15]. The diameter of the cavity of these ethers constitutes from 1.7 to 3.2 Å, they absorb into sodium, potassium, calcium ions. If the size of the cavity is not completely consistent, laminate complex is formed, wherein each cation has two or more crown ethers.

## CONCLUSIONS AND RECOMMENDATIONS

Analysis of eutectics and diagrams of aqueous antifreeze fusion, based on salts of inorganic and organic acids, alcohols, ethylene glycol and its ethers, consisted in the comparison with an ideal water solution on cryoscopic constant. It made it possible to reveal cyclic water clusters of  $(\text{H}_2\text{O})_5$  and  $(\text{H}_2\text{O})_6$ , which pass into the eutectics as monomers or oligomers with the degree of cross linking 2–4.

Cyclic water clusters can interact with the

components of antifreezes (salts, acids, bases, neutral molecules) by the type of crown-ethers therefore it is necessary to consider the proportionality of used chemicals.

To create effective antifreezes it is important to avoid the destruction of cyclic water clusters, it is desirable to have, as in the case of ethylene glycol, the second component of water antifreeze and in a cyclic form as well.

Promising are the antifreezes based on mixtures of inorganic and organic compounds.

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