

**NEGATIVE SOLVATION OF IONS IN SOLVENTS
WITH A SPATIAL NETWORK OF H-BONDS**

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This report is devoted to the investigation of near solvation of singly charged ions with different in nature and composition. As a shown in [1], there are the correlation exists between deviation of translational (diffusion) displacement length (\bar{d}) from the Stokes law ($\bar{d} - r_i$) (r_i structural radius of ion) and solvability of these ions according to Samoilov [2]. Parameter ($\bar{d} - r_i$) has been offered as a quantitative measure of ions influence on translational exchange of water molecules of the nearest to ion environment on molecules in bulk water by authors [1]. The inequalities ($\bar{d} - r_i$) < 0 or $\bar{d}/r_i < 1$ has been recommended as a criterion for negative ion solvation, and ($\bar{d} - r_i$) > 0 or $\bar{d}/r_i > 1$ for positive one [1]. By Samoilov [2], the essence of negative solvation is that the bonds I-M are weaker than the bonds between the molecules (M-M), and for positive solvation – on the contrary.

In the present work values \bar{d} for 12 singly charged ions in monoethanolamine (MEA), ethylene glycol (EG) and methanol (MeOH) at 298,15 K based on the literature data on the mobility of these ions have been calculated. We used the author's technique [1] for these calculations.

The sign of the parameter ($\bar{d} - r_i$) for these ions in MEA, EG and in water are given in the table. The sign "+" corresponds to positive solvation, the sign "-" - corresponds to negative one.

Solvent	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Me ₄ N ⁺	Et ₄ N ⁺	Bu ₄ N ⁺	Cl ⁻	Br ⁻	I ⁻	BPh ₄ ⁻
H ₂ O [1]	+	+	-	-	-	-	-	+	-	-	-	+
MEA	+	+	+	-	-	-	-	+	+	+	-	+
EG	+	+	-	-	-	-	-	-	-	-	-	-
MeOH	+	+	+	+	+	-	-	-	+	+	+	-

It shown from the table that the ions Me₄N⁺ and Et₄N⁺ are solvated negatively and the cations Li⁺ and Na⁺ are solvated positively in all these solvents. For others ions sign of parameter ($\bar{d} - r_i$) shows a positive or negative solvation. Therefore the difference ($\bar{d} - r_i$) depended on nature and size of ion and structure of solvent.

As have been established in [1], parameter ($\bar{d} - r_i$) describes a real behavior of an ion in the solution and identically characterizes the short-range solvation in the cases of both positively and negatively solvated ions.

References:

[1] Bulavin V.I., V'yunyk I.M., Lazareva Ya.I. Diffusion and microscopic characteristics of singly charged ion transfer in extremely diluted aqueous solutions // Ukr. J. Phys. – 2017.– Vol. 62, № 9 . – P. 769-778.

[2] O.Ya. Samoilov Struktura vodnyh rastvorov jelektrolitov i gidratacija ionov. – USSR Acad. of Sciences Publ.– Moscow, 1957. – 179 p.