

## EXPERIMENTAL AND THEORETICAL STUDIES ON THE SOLVATION OF POTASSIUM AND CHLORINE IONS IN AQUEOUS DIMETHYLSULFOXIDE SOLUTIONS

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UDC 544.3.032:541.49

Based on experimental (viscosimetric) studies, the physicochemical characteristics of solvated potassium and chlorine ions in dimethylsulfoxide-containing (DMSO) aqueous solutions are determined in the temperature range 25-40 °C. The Hartree–Fock nonempirical method (*ab initio*) with the (6-31+G(*d,p*)) basis set is used to calculate the structural and energy parameters of (K<sup>+</sup>,Cl<sup>-</sup>)/H<sub>2</sub>O and (K<sup>+</sup>,Cl<sup>-</sup>)/(H<sub>2</sub>O+DMSO) complexes in vacuum; the solvent effect is taken into account by the self-consistent reaction field (SCRF) method within the Onsager model. It is found that the solvation of individual ions in water–DMSO mixtures is due to the properties and structural features of the mixed solvent and the nature of the ions.

**DOI:** 10.1134/S0022476615040083

**Keywords:** viscosity, Jones-Dole equation, *B*-coefficient, dimethylsulfoxide, K<sup>+</sup> and Cl<sup>-</sup> ions, *ab initio* calculations, SCRF calculations, ion–molecular complexes.

### INTRODUCTION

The development of the biological and medical fields of modern physical chemistry promotes the studies on the functional actions and interactions of biomolecules, particularly proteins, which depends on the structural stability of these molecules. In electrolyte solutions exposed to various factors, the functional action of proteins can be achieved by different methods: by changing the three-dimensional structure of the solvent or by ion solvation [1, 2]. The state of ions in solutions (positive or negative solvation) depends on many factors such as pH, the temperature of the medium, and the solvent structure [3-5]. The latter often depends on the presence of a cosolvent. The type of the cosolvent determines not only the structure of the mixed solvent but also the state of individual ions. When using aprotic organic solvents (acetonitrile, dimethylsulfoxide (DMSO), or dimethylformamide), the water structure changes owing to the formation of chain and cyclic water–DMSO associates of different sizes. The state and properties of these solutions are studied by both experimental and theoretical methods (quantum chemical calculations) [6, 7].

This paper presents the results of experimental and theoretical studies of solvation processes in the KCl–water–DMSO system.

## EXPERIMENTAL

**Materials and methods.** We used DMSO from Sigma company (Chemical Co, United States) and KCl (chemically pure grade) from AO Reakhim (Russia). Bidistilled water was used to prepare the solutions.

**Viscosimetry.** The relative viscosities ( $\eta_{\text{rel}}$ ) of the potassium chloride solutions were measured in water–DMSO solutions with the modified capillary Ubbelohde viscometer in the temperature range 25–40 °C. The solutions were incubated for 5–7 min. The KCl concentrations were varied in the range 0.0125–0.1 mol/l; the amount of DMSO was 0–2.5 mol/l. The  $\eta_{\text{rel}}$  of the solutions was determined from the equation:

$$\eta_{\text{rel}} = \frac{\eta}{\eta_s} = \frac{t}{t_s}, \quad (1)$$

where  $t$  and  $t_s$  are the flow times of the solution and the solvent. In the calculations the average value for three measurements was used. The viscous-flow activation energy ( $E_\eta$ ) was calculated by the graphical method from the temperature dependence of the relative viscosity by the following equation:

$$\ln \eta = \ln A + \frac{E_\eta}{RT}, \quad (2)$$

where  $\eta$  is the characteristic viscosity of the solution;  $A$  is a pre-exponential factor;  $E_\eta$  is the viscous-flow activation energy; and  $R$  is the universal gas constant.

**The quantum chemical calculations** were performed using the Gaussian 03 software package [8]. The results of preliminary HyperChem 6.0 calculations [9] served as input data for the nonempirical calculations of  $(\text{K}^+, \text{Cl}^-)/\text{H}_2\text{O}$  and  $(\text{K}^+, \text{Cl}^-)/(\text{H}_2\text{O}+\text{DMSO})$  complexes. The results were visualized using the GaussView 3.0 program [10]. The calculations were performed by the Hartree–Fock (HF) nonempirical method with the (6-31+G( $d,p$ )) basis set in vacuum; the solvent effect was taken into account by the self-consistent reaction field (SCRF) method within the Onsager model [11]. The geometry of all the complexes (the structural and energy parameters and theoretical vibrational frequencies of the ion–molecular complexes) was fully optimized by the Gaussian 03 software package. The results also included interaction energies ( $E_{\text{int}}$ ) for the calculated equilibrium configurations of the complexes.

## RESULTS AND DISCUSSION

Being a dynamic property of solutions, viscosity is very sensitive to specific interactions in electrolyte solutions and, therefore, has been successfully used to study the features of ion solvation in solutions. In this respect, it may be of interest to consider the coefficients  $A$  and  $B$  in the Jones–Dole equation [12, 13]:

$$\eta_{\text{rel}} = 1 + A\sqrt{c} + Bc, \quad (3)$$

where  $\eta_{\text{rel}}$  is the relative viscosity of the electrolyte solution;  $c$  is the molecular concentration of the solute;  $A$  is a constant independent of the electrolyte concentration, which characterizes the electrostatic interaction between ions; and  $B$  is a constant determined by the interaction of dissolved ions with the solvent (this constant can be both negative and positive). The constants  $A$  and  $B$  are determined from the linear dependence of  $(\eta_{\text{rel}} - 1)/\sqrt{c}$  on  $\sqrt{c}$ . The slope is  $B$  and the intersection point with the ordinate axis determines the value of  $A$ .

In an aqueous KCl solution in the temperature range 25–40 °C, the coefficients  $A$  and  $B$  increase with increasing temperature, which is well consistent with the data in [12, 14–16]. In water–DMSO solvents in the same temperature range, we see the following pattern: with an increase in the DMSO concentration from 0 mol/l to 2.5 mol/l, the  $B$  value (0.043 l/mol) increases to 0.545 l/mol and  $A$  (0.031 l<sup>1/2</sup>/mol<sup>1/2</sup>) decreases to –0.144 l<sup>1/2</sup>/mol<sup>1/2</sup>. The positive  $A$  value in the aqueous solution indicates a strong ion–ion interaction. In the presence of DMSO, the  $A$  value becomes negative, which indicates the presence of a weak ion–ion interaction in water–DMSO solutions. A negative sign of the  $A$  coefficient indicates weak interactions rather than the ion repulsion [14].

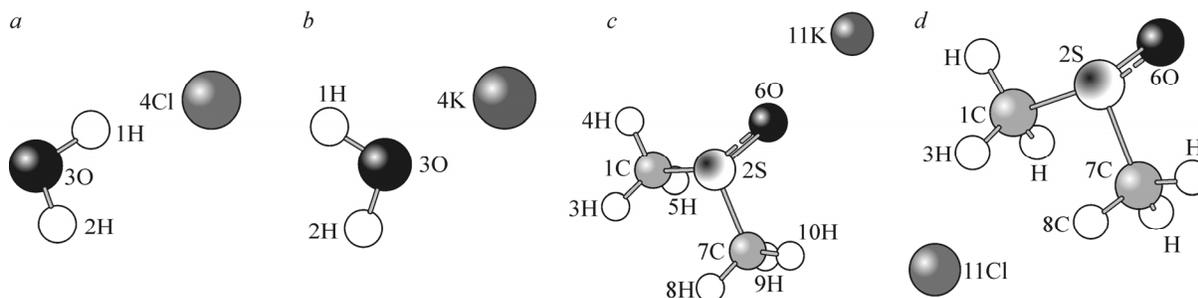
**TABLE 1.** Geometrical (Å, deg) and Energy (Hartree and D) Parameters of the Optimized H<sub>2</sub>O/Cl<sup>-</sup> and H<sub>2</sub>O/K<sup>+</sup> Complexes in Vacuum and in H<sub>2</sub>O

Parameter	RHF/6-31+G( <i>d,p</i> )		Parameter	RHF/6-31+G( <i>d,p</i> )	
	Vacuum	H <sub>2</sub> O		H <sub>2</sub> O/K <sup>+</sup>	Vacuum
H <sub>2</sub> O/Cl <sup>-</sup>			H <sub>2</sub> O/K <sup>+</sup>		
<i>R</i> (O <sub>3</sub> -H <sub>1</sub> )	0.95643	0.95643	<i>R</i> (O <sub>3</sub> -H <sub>1</sub> )	0.94694	0.94689
<i>R</i> (O <sub>3</sub> -H <sub>2</sub> )	0.94272	0.94272	<i>R</i> (O <sub>3</sub> -H <sub>2</sub> )	0.94694	0.94691
<i>R</i> (H <sub>1</sub> -Cl <sub>4</sub> )	2.40062	2.40103	<i>R</i> (O <sub>3</sub> -K <sub>4</sub> )	2.68244	2.68170
∠H <sub>1</sub> -O <sub>3</sub> -H <sub>2</sub>	102.79182	102.79604	∠H <sub>1</sub> -O <sub>3</sub> -H <sub>2</sub>	105.80468	105.84226
∠O <sub>3</sub> -H <sub>1</sub> -Cl <sub>4</sub>	156.37194	156.32289	∠H <sub>1</sub> -O <sub>3</sub> -K <sub>4</sub>	126.97166	127.08433
<i>E</i> <sub>tot</sub>	-535.5906154	-535.5906154	<i>E</i> <sub>tot</sub>	-675.0321585	-675.0321588
Dipole moment	3.2886	3.2880	Dipole moment	1.7422	1.7415

The temperature coefficient of the ion–solvent interactions ( $dB/dt$ ) in aqueous solutions has a small positive value ( $2.4 \cdot 10^{-3}$  l/mol·K) [15]. In the presence of DMSO under the conditions described above, the value of  $dB/dt$  increases sharply ( $3.81 \cdot 10^{-2}$  l·mol<sup>-1</sup>·K<sup>-1</sup>). This suggests that the ion–solvent interactions strengthen with increasing temperature. As shown in [17-19], the  $B$  coefficient depends not only on the size and shape of the dissolved ion but also on its orientation interaction with the surrounding dipole molecules and a change in the solvent structure. Therefore, an increase in the temperature leads to an increase in  $B$  (strengthening of the ion–solvent interactions), which in turn affects the electrostatic interactions between ions. However, it is worth noting that the ion–solvent interaction is also affected by changes in the microviscosity of the solvent. In the KCl–water–DMSO system, the viscous-flow activation energy shows practically no change with increasing KCl concentration, remaining at about 15.5 kJ/mol, and increases with increasing DMSO concentration to  $E_a = 17.6$  kJ/mol. This is also evidence of the formation of water–DMSO bonds in the presence of DMSO, which in turn affects the solvent structure. As shown in [20], the viscosity of a solution increases with increasing number of hydrogen bonds.

Thus, the experimental results for KCl solutions in the presence of DMSO (up to 2.5 mol/l) in the temperature range 25-40 °C show changes in both ion–ion and ion–solvent interactions, which are attributed to changes in the solvent structure.

In addition to the experimental studies, we performed quantum chemical calculations. Table 1 presents the geometrical and energy parameters of the H<sub>2</sub>O/Cl<sup>-</sup> and H<sub>2</sub>O/K<sup>+</sup> complexes in vacuum and water ( $\epsilon = 78.3$ ). As is evident from Table 1, the  $\angle O_3-H_1-Cl_4$  angle decreases and the  $R(H_1-Cl_4)$  bond length increases in the presence of water as compared to vacuum. As shown by the calculated data given in Table 1, the  $\angle H_1-O_3-K_4$  angle increases in the presence of water as compared to vacuum while the  $R(O_3-K_4)$  bond length and the dipole moment decrease. The optimized structures of the H<sub>2</sub>O/Cl<sup>-</sup> and H<sub>2</sub>O/K<sup>+</sup> complexes in the aqueous medium are panels shown in Fig. 1*a* and *b*. Table 2 shows the geometrical and energy parameters of the optimized DMSO/K<sup>+</sup> and DMSO/Cl<sup>-</sup> complexes in vacuum and in the mixed DMSO–H<sub>2</sub>O solvent ( $\epsilon = 76.4$ ). As is evident from Table 2 data, for the DMSO/K<sup>+</sup> complexes, the  $R(S=O)$  bond length decreases by 0.0107 Å and the  $R(O_6-K_{11})$  bond length increases by 0.12407 Å in the mixed solvent as compared to vacuum. In the H<sub>2</sub>O/K<sup>+</sup> complex, the  $R(O_3-K_4)$  bond length shortens by 0.00074 Å in the presence of the solvent. The presence of the mixed solvent



**Fig. 1.** Optimized structures of the complexes: H<sub>2</sub>O/Cl<sup>-</sup> (*a*) and H<sub>2</sub>O/K<sup>+</sup> (*b*) in the (H<sub>2</sub>O) medium, DMSO/Cl<sup>-</sup> in vacuum (*c*), and DMSO/K<sup>+</sup> in the (DMSO–H<sub>2</sub>O) medium (*d*).

**TABLE 2.** Geometrical (Å, deg) and Energy (Hartree and D) Parameters of the Optimized DMSO/K<sup>+</sup> and DMSO/Cl<sup>-</sup> Complexes in Vacuum and in the (DMSO–H<sub>2</sub>O) Medium

Parameter	RHF/6-31+G(d,p)		Parameter	RHF/6-31+G(d,p)
	DMSO/K <sup>+</sup>			
	Vacuum	DMSO–H <sub>2</sub> O		Vacuum
$R(S_2=O_6)$	1.51847	1.50777	$R(S_2=O_6)$	1.50596
$R(C_1-S_2)$	1.79160	1.79360	$R(C_1-S_2)$	1.79188
$R(C_7-S_2)$	1.79158	1.79360	$R(C_7-S_2)$	1.79188
$R(O_6-K_{11})$	2.48987	2.61394	$R(H_3-Cl_{11})$	2.71047
–	–	–	$R(H_8-Cl_{11})$	2.71191
$\angle C_1-S_2-C_7$	99.63055	99.10503	$\angle C_1-S_2-C_7$	98.31039
$\angle S_2=O_6-K_{11}$	167.00435	170.78750	$\angle H_3-Cl_{11}-H_8$	56.68262
$E_{tot}$	-1150.5812633	-1150.5897175	$E_{tot}$	-1011.1198269
Dipole moment	5.8893	7.5074	Dipole moment	7.0829

**TABLE 3.**  $E_{tot}$  and  $E_{int}$  Values (kcal/mol) of the H<sub>2</sub>O/Cl<sup>-</sup>, H<sub>2</sub>O/K<sup>+</sup>, DMSO/Cl<sup>-</sup>, and DMSO/K<sup>+</sup> Complexes in Vacuum and in the Presence of Solvents: H<sub>2</sub>O ( $\epsilon = 78.3$ ) and DMSO–H<sub>2</sub>O ( $\epsilon = 76.4$ )

Complex	RHF/6-31+G(d,p)					
	Vacuum		H <sub>2</sub> O		DMSO–H <sub>2</sub> O	
	$E_{tot}$ , Hartree	$\Delta E_{int}$ , kcal/mol	$E_{tot}$ , Hartree	$\Delta E_{int}$ , kcal/mol	$E_{tot}$ , Hartree	$\Delta E_{int}$ , kcal/mol
H <sub>2</sub> O/Cl <sup>-</sup>	-535.5906154	-12.37698752	-535.5906154	-10.28004069	–	–
H <sub>2</sub> O/K <sup>+</sup>	-675.0321585	-18.15860444	-675.0321588	-16.06184587	–	–
DMSO/Cl <sup>-</sup>	-1011.1198269	-15.92172311	–	–	–	–
DMSO/K <sup>+</sup>	-1150.5812633	-34.18656482	–	–	-1150.5897175	-35.05579029

also affects the dipole moment of the DMSO/K<sup>+</sup> complex, which increases by 1.6181 D, while that of the H<sub>2</sub>O/K<sup>+</sup> complex in H<sub>2</sub>O decreases by 0.0007 D. The results of the quantum chemical calculations reveal that in the mixed DMSO–H<sub>2</sub>O solvent the coordination solvation (complexation) of the K<sup>+</sup> cation by the DMSO electron donating center occurs.

The optimized structures of the DMSO/K<sup>+</sup> complex in the (DMSO–H<sub>2</sub>O) medium and the DMSO/Cl<sup>-</sup> complex in vacuum are shown in Fig. 1c and d. It follows from the data of Tables 1 and 2 that in the presence of the solvent ( $\epsilon = 78.3$ ) the distance of the K<sup>+</sup> ion from the water molecule is 2.68170 Å, and in the mixed solvent ( $\epsilon = 76.4$ ) the distance of the same ion from the DMSO molecule is 2.61394 Å. Thus, it can be concluded from the data that the DMSO/K<sup>+</sup> complex is more stable than H<sub>2</sub>O/K<sup>+</sup>. This conclusion is also supported by the data on interaction energies (Table 3). The theoretical calculations for the DMSO/Cl<sup>-</sup> complex in vacuum and in the medium supplemented the experimental results: in contrast to the DMSO/K<sup>+</sup> complex, DMSO/Cl<sup>-</sup> was found to be instable in the mixed water–DMSO solvent; i.e., here we have negative solvation of Cl<sup>-</sup>.

## CONCLUSIONS

Experimental studies and theoretical analysis of the ionic solvation of KCl in the mixed DMSO–water solvent were performed. According to our results, the DMSO (aprotic solvent) substitution for water molecules in the hydration shell leads to the compensation of the dehydration effect by that of the coordination solvation (complexation) of the K<sup>+</sup> ion by the electron donating center of the nonaqueous component and to the negative solvation of the Cl<sup>-</sup> ion.

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