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DENSITIES AND ELECTRICAL CONDUCTIVITIES OF COPPER(II) CHLORIDE SOLUTIONS IN DIMETHYL SULFOXIDE AND WATER–DIMETHYL SULFOXIDE EQUIMOLAR MIXTURE AT THE TEMPERATURES 298.15, 308.15 AND 318.15 *K*

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Densities and electrical conductivities for copper(II) chloride solutions in DMSO and water–DMSO equimolar mixture have been measured at different temperatures. Apparent molar volumes, partial molar volumes and transfer molar volumes of the solvated copper(II) cations were derived and interpreted in terms of ion-solvent interactions. The ligand-field and temperature effects on the partial molar volumes and electrical conductivities were discussed as well.

***Keywords*:** density, electrical conductivity, copper(II) chloride, dimetyl sulfoxide; apparent, limiting partial, transfer partial molar volumes.

Introduction. Divalent first-row transition-metal ions form well defined coordination clusters in solution in the strongly coordinating donor solvents [1–8]. It has been established that the solvation number of the metal ion is determined by keeping a balance among the increasing contribution due to higher charge of the metal ion, the decreasing contribution due to bulkiness of the solvent molecule, and the ligand field stabilization on the metal ion [1–4]. In the absence of coordinatively active anions the metal cations exist in dimethyl sulfoxide (DMSO) as the well-defined hexa-solvates of the $M(\text{solvent})_6^{n+}$ type (n=2 or 3) [2, 5]. However, it should be noted that metal ions in DMSO solution without the presence of potential ligands are present as the respective tetra-solvates and octa-solvates [5–7]. Moreover, in some solvents, e.g., *N*,*N*-dimethylacetamide and water, the coordination of solvent molecules to the divalent transition metal cations is controlled by the equilibrium between octahedral hexasolvates and tetrahedral tetrasolvates [8]. This is related to the fact that the factors controlling the solvation processes are the donor properties of the solvents, as well as their space requirements, along with the electronic structure of the central metal cation.

It is also known that the volumetric and transport properties of solutions of electrolytes such as divalent first-row transition metal salts in water and organic solvents are fundamental thermodynamic characteristics, which are the object of increasing practical and theoretical interest. The volumetric quantities such as

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limiting values of the apparent molar volumes of metal salts provide direct information on ion-solvent interactions [5, 7, 9–12]. On the other hand, the measurements of electrical conductivities of solutions of transition-metal salts in water and organic solvents elucidated the influence of complex formation on the mobility of metal ions [13, 14].

In this work the novel data on the densities and specific conductances of copper(II) chloride ($CuCl_2$) in DMSO and water–DMSO equimolar mixture at temperatures from 298.15 to 318.15 K are reported over available concentration range. On the basis of densimetric measurements volumetric properties, i.e. apparent molar volumes (V_ϕ), standard partial molar volumes (V_ϕ^0) and transfer partial molar volumes (V_{tr}^0) of $CuCl_2$ in solutions have been calculated.

Materials and Methods. $CuCl_2$ is light brown powder (“Aldrich Chemical Co”, 99.95%), freely soluble in water and sparingly soluble in DMSO. DMSO (“Aldrich Chemical Co”, 99.9% purity) was used without further purification.

The densities of the solutions were measured on an Anton Paar DMA 4500 vibrating-tube densimeter in the temperature range of 298.15–318.15 K. The accuracy of density and temperature measurements was $\pm\ 5\cdot10^{-5}\ g\cdot cm^{-3}$ and $\pm\ 0.03\ K$, respectively. The densimeter was calibrated with dry air and double-distilled water.

The conductivity measurements were made using Jenway Conductivity & pH Meter 4330 with an accuracy of $\pm 1\cdot10^{-5}\ S\cdot m^{-1}$ at a temperature of 298.15 K. The temperature was regulated using MS LAUDA thermostat accurate to within $\pm\,0.1\ K$.

All solutions were prepared gravimetrically using a Sartorius CPA6235 balance with uncertainty of $\pm 1\cdot10^{-3}\,g$.

Results and Discussions.

Densities and Apparent Molar Volumes. The experimental values of densities of $CuCl_2$ solutions in DMSO and water–DMSO equimolar mixture at the temperatures 298.15, 303.15 and 318.15 K are listed in Tab. 1.

As is evident from experimental data (Fig. 1), the increase in temperature leads to the decrease in the density for all systems. Moreover, the values of the densities of $CuCl_2$–DMSO binary solutions are less than the values of the densities of the ternary solutions of $CuCl_2$ in water–DMSO equimolar mixture.

The apparent molar volumes (V_ϕ) of $CuCl_2$ in binary solutions have been calculated by Eq. (1) and in ternary systems have been calculated by Eq. (2) according to the procedure developed in [15, 16]:

$$V_{\phi,2}=\frac{1000\left(\rho_0-\rho\right)}{m\,\rho\,\rho_0}+\frac{M}{\rho}, \tag{1}$$

where M is the molar weight of $CuCl_2$, $g\cdot mol^{-1}$; ρ_0 and ρ are the densities of pure DMSO and binary solutions, $g\cdot cm^{-3}$, respectively; m_2 is the molal concentration of $CuCl_2$ in DMSO, $mol\cdot kg^{-1}$;

$$V_{\phi,3}=\frac{M_3}{\rho}+\frac{\rho_o-\rho}{\rho\,\rho_o}\left(\frac{M_2m_2+1000}{a\,m_2}\right), \tag{2}$$

where M_3 and M_2 are the molar weights of $CuCl_2$ and DMSO respectively, $g\cdot mol^{-1}$; ρ_0 and ρ are the densities of the mixed solvent (water–DMSO) and ternary solutions, $g\cdot cm^{-3}$; m_2 is the molal concentration of DMSO in water–DMSO mixture, $mol\cdot kg^{-1}$; $a=n_3/n_2$, where n_3 and n_2 are the numbers of moles of $CuCl_2$ and DMSO, respectively.

Table 1

Densities of $CuCl_2$–DMSO and $CuCl_2$–(water+DMSO) solutions at the temperature range 298.15–318.15 K

m, $mol \cdot kg^{-1}$	ρ, $g \cdot cm^{-3}$		
	298.15 K	308.15 K	318.15 K
$CuCl_2$–DMSO			
0.0000	1.09561	1.08543	1.07539
0.0120	1.09691	1.08672	1.07668
0.0184	1.09772	1.08753	1.07749
0.0213	1.09821	1.08802	1.07798
0.0289	1.09918	1.08883	1.07895
0.0390	1.10031	1.09012	1.08008
0.0437	1.10096	1.09077	1.08073
0.0595	1.10289	1.09255	1.08251
0.0632	1.10322	1.09319	1.08299
0.0679	1.10387	1.09368	1.08364
0.0728	1.10451	1.09432	1.08428
$CuCl_2$–(water+DMSO), X_{DMSO}=0.5			
0.0000	1.09843	1.08901	1.07953
0.0098	1.09956	1.09031	1.08094
0.0195	1.10084	1.09167	1.08239
0.0292	1.10216	1.09300	1.08372
0.0452	1.10420	1.09482	1.08563
0.0562	1.10526	1.09614	1.08683
0.0626	1.10617	1.09706	1.08776
0.0745	1.10767	1.09853	1.08926
0.0906	1.10974	1.10044	1.09110

Table 2

Apparent molar volumes of $CuCl_2$–DMSO binary and $CuCl_2$–(water+DMSO) ternary solutions at the temperature range 298.15–318.15 K

m, $mol \cdot kg^{-1}$	V_ϕ, $cm^3 \cdot mol^{-1}$		
	298.15 K	308.15 K	318.15 K
$CuCl_2$–DMSO			
0.0184	27.633	27.450	26.794
0.0213	21.477	21.116	20.342
0.0289	20.243	20.441	18.956
0.0390	22.724	22.207	21.456
0.0437	21.125	20.555	19.773
0.0595	21.148	22.657	21.917
0.0632	22.748	20.014	21.401
0.0679	21.711	21.085	20.316
0.0728	21.200	20.557	19.779
$CuCl_2$–(water+DMSO), X_{DMSO}=0.5			
0.0098	31.342	16.817	6.803
0.0195	25.170	14.248	5.031
0.0292	21.711	13.869	7.425
0.0452	21.762	20.363	14.397
0.0562	26.454	21.564	18.385
0.0626	24.824	20.223	17.145
0.0745	24.416	20.766	17.746
0.0906	23.774	22.064	20.108

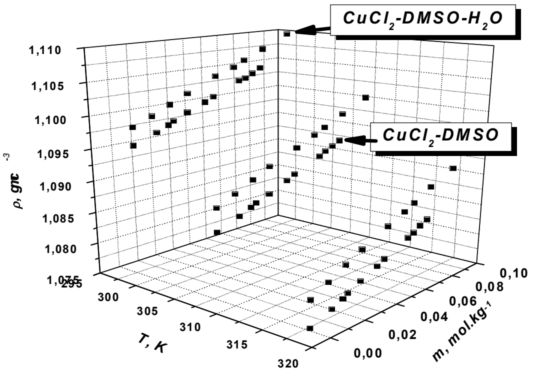

Fig. 1. Densities of $CuCl_2$–DMSO and $CuCl_2$–(water + DMSO) solutions at the temperature range 298.15–318.15 *K*.

The calculated values of V_ϕ for binary and ternary systems are reported in Tab. 2. The influence of water on the volumetric behavior has been taken into account by changing the apparent molar volume compared to the apparent molar volume of the binary solutions of $CuCl_2$. It is interesting that the values of apparent molar volumes for both binary and ternary solutions of copper salt change irregularly with the molality of solutions (Tab. 2). However, with increasing temperature the values of apparent molar volumes evenly decrease.

Standard Partial and Transfer Partial Molar Volumes. The values of V_ϕ^0 were estimated from the plots of V_ϕ versus molality of solutions by extrapolation using the Masson's empirical relation:

$$V_\phi = V_\phi^0 + S_v m^{1/2}, \tag{3}$$

where V_ϕ^0 is the limiting value of the apparent molar volume equal to the standard partial molar volume of the solute at infinite dilution and S_v is an experimentally determined parameter (slope constant).

The transfer partial molar volumes (ΔV_{tr}^0) of $CuCl_2$ from the DMSO to the aqueous DMSO equimolar solution have been calculated by equation

$$\Delta V_{tr}^0 = V_\phi^0\left(\mathrm{CuCl_2} - (\mathrm{water} + \mathrm{DMSO})\right) - V_\phi^0\left(\mathrm{CuCl_2} - \mathrm{DMSO}\right). \tag{4}$$

Table 3

Standard partial and transfer partial molar volumes of $CuCl_2$–DMSO binary and $CuCl_2$–(water+DMSO) ternary solutions at the temperature range 298.15–318.15K

T,K	V_ϕ^0, $cm^3 \cdot mol^{-1}$		ΔV_{tr}^0, $cm^3 \cdot mol^{-1}$
	$CuCl_2$–DMSO	$CuCl_2$–(water+DMSO), X_{DMSO}=0.5	
298.15	24.15	27.02	2.87
308.15	23.46	14.02	–9.44
318.15	23.06	3.59	–19.47

The standard partial and transfer partial molar volumes for $CuCl_2$ binary and ternary solutions at the temperatures 298.15, 308.15 and 318.15 *K* are reported in Tab. 3. It is known that apparent and partial molar volumes of electrolytes solutions have proven to be a very useful tool in elucidating the structural interactions (i.e. ion-ion, ion-solvent and solvent-solvent) occurring in solutions. Partial molar volumes at infinite dilution are considered of particular interest, because of their usefulness in examining ion-solvent interactions, as ion-ion interactions can be assumed to be eliminated at infinite dilution [17].

For an electrolyte solution, the apparent molar volume at infinite dilution refers, by definition, to the fully dissociated salts. The observed apparent molar volumes at finite concentration contain contributions from all the species present in solution, from ion pairs as well as from complexes. However, the high values of the apparent molar volumes in $CuCl_2$–DMSO binary solutions suggest that the copper(II) ions affect fewer solvent molecules. This effect is especially distinct for the $CuCl_2$ in DMSO solution, in which the salt probably exists practically solely as the $CuCl_2(DMSO)_2$ or $CuCl_2(DMSO)_4$ complex according to [1, 7, 18].

The partial molar volume of the solvated ion consists of two major contributions: the intrinsic partial molar volume and the electrostriction partial molar volume [5]:

$$\overline{V}^{0}_{ion} = \overline{V}^{0}_{ion}(\text{intr.}) + \overline{V}^{0}_{ion}(\text{electr.}). \qquad (5)$$

The first of the components is related to the size of the ion and is positive. The second contribution is the direct measure of the ion-solvent interactions. It is mentioned that the first term seems to be negligible for the small $3d^n$ cations, but distinct [5]. Thus, the observed variation of the partial molar volume of the solvated $Cu(ligand)_n^{2+}$ ion is determined by the electrostriction effect due to the metal-ligand bonds. It is also assumed that the partial molar volume of the solvated ion can be represented by the sum of V_ϕ at infinite dilution V_ϕ^0 and the volumes of the first solvation shells of the ions [19], i.e. the molar electrostriction volume of electrolytic solutions will be related from their properties: the compressibility and permittivity of solvents. The molar electrostriction caused by ions at infinite dilution was taken as the differences of their standard partial molar volumes in the solution and their intrinsic volumes [19].

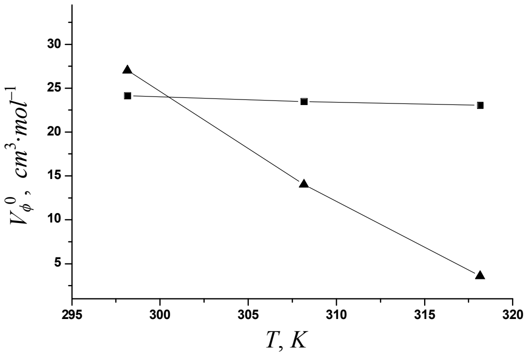

Fig. 2. Standard partial molar volumes of $CuCl_2$–DMSO binary (■) and $CuCl_2$–(water+DMSO) ternary (▲) solutions plotted against temperature.

As it follows from the data (Tab. 3), the values of standard partial molar volumes decrease with an increase in temperature for all solutions of $CuCl_2$. It should be noted that in the presence of water the decrease of standard partial molar volumes with increasing temperatures is most pronounced (Fig. 2). Moreover, the negative values of transfer molar volumes (Tab. 3) indicate greater presence of solute-solvent interactions and electrostrictive solvation of ions in an aqueous medium. We believe that the relation between the partial molar volumes of both systems is most probably a consequence of a stronger electrostriction of water by the Cl^- ions, similar to the case of the $NiCl_2$ and $NiBr_2$ salts [20].

Specific Electrical Conductivity. The specific electrical conductivities (κ) of solutions of copper(II) chloride in DMSO and water–DMSO equimolar mixture at 298.15 *K* are presented in Fig. 3.

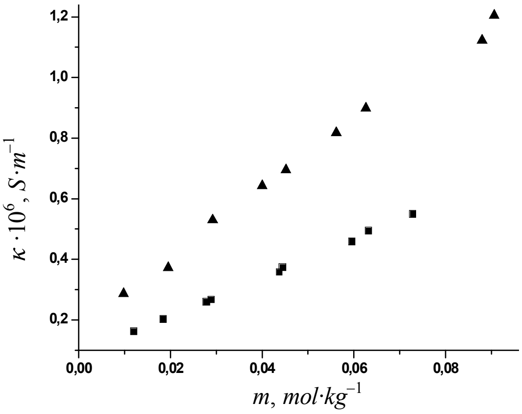

Fig. 3. Specific conductivities of $CuCl_2$–DMSO binary (■) and $CuCl_2$–(water+DMSO) ternary (▲) solutions at 298.15 *K*.

As it follows from Figure, the specific electrical conductivities for both systems increase with the amount of salt in the solutions. However, contrary to binary solutions the increase in the specific electrical conductivities of ternary solutions with increasing concentration is most pronounced. We consider that the dissociation of salt and the amount of free ions in the aquatic environment increase. At the same time the parity of mobility of Cu^{2+} and Cl^- ions in water is reverse according to that observed in DMSO. In water solutions mobility of copper(II) ions is rather higher than in the organic medium. These phenomena are explained by stronger solvation of Cu^{2+} ion in DMSO and the raised viscosity of solutions [21]. On the other hand, in ternary systems the formed strong hydrogen bonds between water and DMSO molecules lead to weakening of the formation of sulfoxide's complexes of copper cation, therefore the motion of free ions increases.

Conclusion. The volumetric results obtained showed that the values of apparent molar volumes for both binary and ternary solutions of copper salt change irregularly with the molality of solutions. In addition, contrary to $CuCl_2$–DMSO binary solutions, the decrease of standard partial molar volumes in the presence of water with increasing temperatures is most pronounced. On the other hand, the specific electrical conductivities for both systems increase as the quantities of salt in solutions are increased. However, contrary to binary solutions the increase of the specific electrical conductivities of ternary solutions with increasing concentration is most pronounced. These phenomena are explained by stronger solvation of copper(II) ions in DMSO and the raised viscosity of solutions. Consequently, the mobility of copper(II) ions in water–DMSO solutions is rather higher than in the pure DMSO medium.

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