

Molar volume and viscosity of solutions of zinc chloride in dimethyl sulfoxide

Z. KODEJŠ and H. ŠPALKOVÁ

*Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences,
CS-160 00 Prague*

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Densities and viscosities of concentrated solutions of zinc chloride in dimethyl sulfoxide have been determined over the temperature range 15–60 °C and the range of salt mole fraction from 0.05 to 0.45. The composition dependences of molar volume and viscosity of the system are compared with those for several aqueous and DMSO solutions, and the influence of complex particle formation in the solutions on their viscosity is discussed.

Определены плотности и вязкости концентрированных растворов хлорида цинка в диметилсульфоксиде в диапазоне температур 15–60 °C и при мольных долях соли в растворе от 0,05 до 0,45. Зависимости величин мольного объема и вязкости системы от состава сравнены для нескольких водных растворов и растворов в ДМСО. Обсуждается влияние образования сложных частиц в растворах на их вязкость.

In our previous studies [1–4] we reported viscosity and conductivity data for highly concentrated solutions of several electrolytes in dimethyl sulfoxide (DMSO). Comparison of the physicochemical properties of electrolyte solutions in DMSO, *i.e.* in an aprotic solvent, with those of aqueous solutions provides important information about specificity of ion–solvent interactions in the two solvents.

Almost all our previous studies were concerned with nitrates as these are highly soluble in both DMSO and water and give us a possibility to study the volumetric and transport properties of solutions over the composition range in which the number of particles of the electrolyte is comparable with that of solvent.

Highly concentrated solutions of $\text{Zn}(\text{NO}_3)_2$, *i.e.* a nitrate of the third transition metal, differ markedly from other nitrates in the behaviour of their molar volume and viscosity [5]. This difference has been attributed to a specific structure of solution involving firmly solvated ions and ion contact pairs. Physicochemical characteristics of the solution at very low DMSO contents, where almost all solvent molecules are involved in the first coordination spheres of ions, are expected to be greatly influenced by the shape and charge of these structural units.

In this connection we found it interesting to study solution properties of the system $\text{ZnCl}_2 + \text{DMSO}$ as complex formation is known to be one of characteristic features of ZnCl_2 in solutions. The effect of complexation was used as a basis for interpreting the experimental data on physical properties of concentrated aqueous ZnCl_2 solutions [6, 7].

Experimental

Zinc chloride (dry, anal. grade, Merck) and dimethyl sulfoxide (dry, anal. grade, Merck) with a maximum water mass fraction of 0.03 % were used as starting materials. The water content of DMSO was analyzed by the K. Fischer method and was found to agree with that stated by the manufacturer within the limits of precision of the analytical method used. Zinc chloride was melted and after spontaneous evaporation of residual water residual oxide species were removed by bubbling dry HCl through the melt.

Stock solutions and all dilutions were made up by weight. The sample compositions were checked by complexometric titration. The uncertainties in the reported values of the salt mole fraction are not more than ± 0.5 %.

The density was measured with a DMA 40 digital vibration densimeter (Paar), with an accuracy of $4 \times 10^{-4} \text{ g cm}^{-3}$ derived from calibration of the densimeter and an allowance of ± 0.05 °C for bath temperature fluctuation.

The viscosity measurements were made with an accuracy of ± 0.5 % by means of a factory calibrated Ubbelohde type viscometer. The flow times ranged between 90 and 500 s. Each viscosity value was calculated from an average of at least three flow times which agreed to within ± 0.1 % and the kinetic energy correction was applied.

Densities and viscosities of samples with salt content within the salt mole fraction range 0.05—0.45 were determined in a thermostatted water bath controlled to ± 0.05 °C at temperatures of 15 °C, 25 °C, 35 °C, 45 °C, and 60 °C.

Results and discussion

The experimentally determined values of density (ρ) and viscosity (η) at 25 °C, 45 °C, and 60 °C are presented in Table 1. The molar volumes were calculated from densities and molecular masses of the components using the mass of the mixture containing 1 mol of the components (salt + solvent). In Fig. 1 the composition dependence of the molar volume is compared with literature data for the systems $\text{ZnCl}_2 + \text{H}_2\text{O}$ [7], $\text{Zn}(\text{NO}_3)_2 + \text{H}_2\text{O}$ [8, 9], $\text{Zn}(\text{NO}_3)_2 + \text{DMSO}$ [5], $\text{NH}_4\text{NO}_3 + \text{DMSO}$ [3], and $\text{AgNO}_3 + \text{DMSO}$ [10]. The plot demonstrates that ZnCl_2 solutions in DMSO, unlike the $\text{Zn}(\text{NO}_3)_2$ solutions, show behaviour similar to that of NH_4NO_3 and AgNO_3 solutions. Comparison with the volumetric properties of aqueous solutions of the two zinc salts cannot be made since the

Table 1

Density and viscosity data of the ZnCl_2 + DMSO solutions

x	$t = 25\text{ }^\circ\text{C}$		$t = 45\text{ }^\circ\text{C}$		$t = 60\text{ }^\circ\text{C}$	
	$\rho/(\text{g cm}^{-3})$	$\eta/(\text{mPa s})$	$\rho/(\text{g cm}^{-3})$	$\eta/(\text{mPa s})$	$\rho/(\text{g cm}^{-3})$	$\eta/(\text{mPa s})$
0.0480	—	—	1.1406	2.147	1.1251	1.632
0.0714	—	—	1.1731	2.730	1.1588	2.034
0.0941	—	—	1.2067	3.589	1.1909	2.642
0.100	1.2361	6.570	1.2152	3.798	1.1997	2.770
0.131	—	—	1.2636	6.027	1.2479	4.171
0.151	1.3109	15.71	1.2892	7.727	1.2734	5.216
0.166	—	—	1.3115	10.50	1.2952	6.645
0.171	—	—	1.3210	11.49	1.3050	—
0.182	1.3570	31.70	1.3350	13.24	1.3190	8.138
0.207	—	—	1.3750	24.65	1.3579	13.53
0.226	1.4290	134.9	1.4066	39.36	1.3902	20.31
0.239	1.4499	217.7	1.4272	56.75	1.4107	27.41
0.241	—	—	1.4265	56.82	1.4098	27.30
0.267	—	—	1.4654	115.9	1.4487	49.61
0.271	1.4953	—	1.4720	136.2	1.4555	56.50
0.286	—	—	1.4909	184.6	1.4733	70.42
0.300	1.5304	1776	1.5115	301.2	1.4968	114.0
0.306	1.5388	2023	1.5183	331.9	1.5026	125.6
0.336	—	—	1.5617	460.4	1.5451	199.0
0.400	—	—	1.6465	1359	1.6334	538.0
0.420	—	—	1.6763	1849	1.6626	697.7
0.448	—	—	1.7103	2904	1.6965	991.4

Equilibrium solubility of ZnCl_2 in DMSO [17]: $t = 25\text{ }^\circ\text{C}$, $x = 0.12$; $t = 45\text{ }^\circ\text{C}$, $x = 0.28$; $t = 60\text{ }^\circ\text{C}$, $x = 0.40$.

available data cover only the water-rich composition range, where the specific ion—solvent interactions do not control the structure.

Fig. 2 provides a comparison of the viscosity of zinc chloride solutions as a function of the salt mole fraction with literature data for several systems [3, 5, 7—10]. Once again, the solutions of ZnCl_2 in DMSO differ from those of $\text{Zn}(\text{NO}_3)_2$ in that their viscosity increases smoothly with composition. The composition dependences of viscosity of ZnCl_2 + DMSO solutions at $45\text{ }^\circ\text{C}$ and $60\text{ }^\circ\text{C}$ were represented by the relations $\log(\eta/(\text{mPa s})) = 0.2826 - 1.262x + 45.35x^2 - 59.69x^3$ and $\log(\eta/(\text{mPa s})) = 0.1759 - 0.9301x + 37.70x^2 - 48.14x^3$, respectively.

The viscosity of $\text{ZnCl}_2 + \text{DMSO}$ solutions was measured as a function of temperature at several salt mole fractions over the temperature range 15–60 °C (besides the values given in Table 1 the viscosity values at 15 °C and 35 °C were measured). The data were fitted to the VTF (Vogel—Tammann—Fulcher) equation.

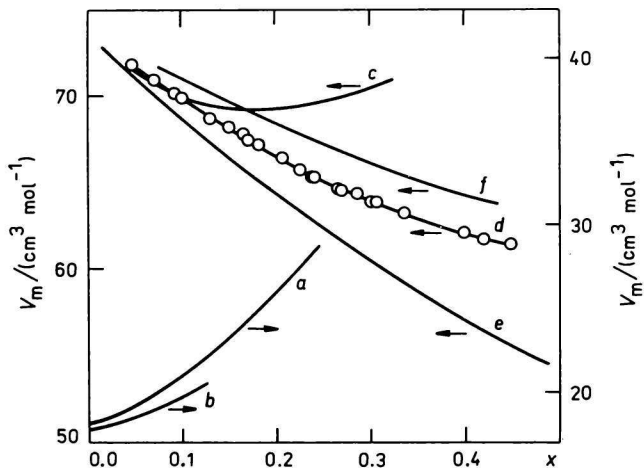


Fig. 1. Molar volume, V_m , as a function of salt mole fraction x .

a) $\text{Zn}(\text{NO}_3)_2 + \text{H}_2\text{O}$, 25 °C; b) $\text{ZnCl}_2 + \text{H}_2\text{O}$, 25 °C; c) $\text{Zn}(\text{NO}_3)_2 + \text{DMSO}$, 60 °C; d) $\text{ZnCl}_2 + \text{DMSO}$, 60 °C; e) $\text{AgNO}_3 + \text{DMSO}$, 60 °C; f) $\text{NH}_4\text{NO}_3 + \text{DMSO}$, 60 °C.

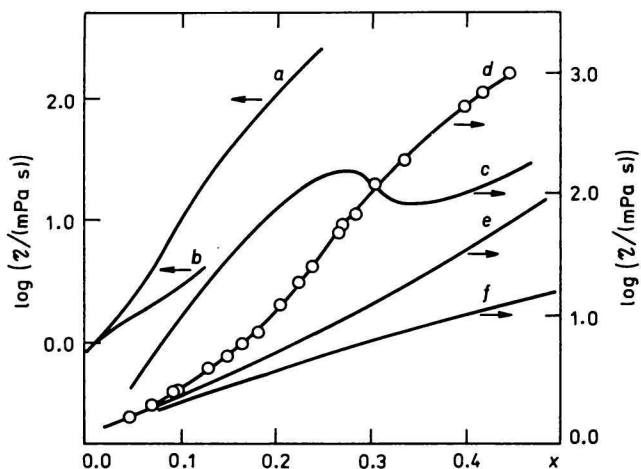


Fig. 2. Viscosity of solutions, η , as a function of salt mole fraction x .

a) $\text{Zn}(\text{NO}_3)_2 + \text{H}_2\text{O}$, 25 °C [8, 9]; b) $\text{ZnCl}_2 + \text{H}_2\text{O}$, 25 °C [7]; c) $\text{Zn}(\text{NO}_3)_2 + \text{DMSO}$, 60 °C [5]; d) $\text{ZnCl}_2 + \text{DMSO}$, 60 °C; e) $\text{AgNO}_3 + \text{DMSO}$, 60 °C [10]; f) $\text{NH}_4\text{NO}_3 + \text{DMSO}$, 60 °C [3].

tion [11], which is commonly used for representation of the non-Arrhenius behaviour of the temperature dependence of viscosity

$$\eta = A \exp (B/(T - T_0)) \quad (1)$$

where A , B , and T_0 are constants characteristic of the solution. The resulting values of the parameters B and T_0 are plotted against the salt mole fraction in Fig. 3. The theoretical models of liquids used to derive the temperature dependence of viscosity, *i.e.* the free volume theory [12] and the cooperative rearrangement theory [13] point to a key role of the parameter T_0 not only in eqn (1) but also in the theory of transport properties. This parameter has been interpreted as the theoretical or ideal glass transition temperature and its thermodynamic nature has been demonstrated. On the basis of the transport theory of liquids and in view of the relation between the rigidity and the T_0 value [14] it has been suggested that the composition dependence of viscosity is governed by the variation of the parameter T_0 with composition. For ideal binary systems T_0 can be calculated as a linear combination of the T_0 values of both components. A linear dependence of T_0 on system composition has been found for several salt + solvent systems [15]. For the system $\text{ZnCl}_2 + \text{DMSO}$ the T_0 parameter was found to be roughly a linear function of the salt mole fraction, a pattern consistent with that found experimentally for the composition dependence of the glass transition temperature, T_g , on salt mole fraction [16] (Fig. 3).

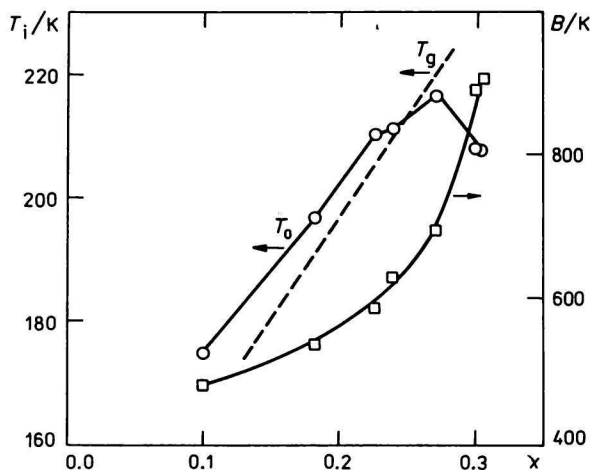


Fig. 3. Variation of the T_0 and B parameters of eqn (1) with composition for the system $\text{ZnCl}_2 + \text{DMSO}$.

x — mole fraction of salt in the system; T_g — glass transition temperature [16].

All the relations discussed above support the conclusion that, in contrast to aqueous solutions [7], the volumetric and transport properties of highly concentrated ZnCl_2 solutions in DMSO can be interpreted without assuming the complex formation. A comparison of the properties of the $\text{Zn}(\text{NO}_3)_2 + \text{DMSO}$ and $\text{ZnCl}_2 + \text{DMSO}$ solutions indicates that the unusual behaviour of viscosity in concentrated $\text{Zn}(\text{NO}_3)_2 + \text{DMSO}$ solutions [5] results not only from a specific behaviour of Zn^{2+} ions in solutions [7] but also from the presence of nitrate ions, which are commonly considered as noncomplexing species.

It is interesting to note that up to $x = 0.3$ the viscosity of a $\text{Zn}(\text{NO}_3)_2$ solution in DMSO is higher than that of a $\text{ZnCl}_2 + \text{DMSO}$ solution of the same salt mole fraction. The opposite situation was found in all the systems studied so far (Li^+ , Ca^{2+}).

A comparison of highly concentrated solutions of ZnCl_2 and $\text{Zn}(\text{NO}_3)_2$ in DMSO and water shows that the two electrolytes have opposite tendencies to complexation and contact ion pair formation in DMSO and H_2O solutions.

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