

Viscosity and molar conductivity of solutions of lithium nitrate in dimethyl sulfoxide

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Density, viscosity, and molar conductivity of the highly concentrated solutions of lithium nitrate in dimethyl sulfoxide were determined in the temperature range 10—60 °C for compositions $x = 9$ —28 mole % LiNO₃. The dependences of investigated quantities on temperature and composition are correlated by means of simple relations. These quantities are compared with the corresponding quantities of the aqueous solutions of lithium nitrate.

Определены плотность, вязкость и мольная электропроводность высококонцентрированных растворов нитрата лития в диметилсульфоксиде в интервале температур 10—60 °C и концентраций $x = 9$ —28 мольных % LiNO₃. Зависимости изучаемых величин от температуры и концентрации представлены в виде простых корреляций. Эти величины сопоставлены с соответствующими величинами для водных растворов нитрата лития.

In our previous studies on transport properties of highly concentrated aqueous solutions [1—4], we directed attention to the relation between the character of the temperature and composition dependences of viscosity and electrical conductivity and the nature of water—solute interactions. In order to gain a deeper insight into this relation, we have undertaken a study of transport properties of salt solutions in dimethyl sulfoxide (DMSO): by comparison with aqueous solutions we attempt to evaluate the influence of the various interactions in solution on the properties of interest [5, 6]. DMSO has been chosen as the alternative solvent because it exists in the liquid state over a wide temperature range, readily dissolves many inorganic salts, and is miscible with water in all proportions. A high solubility of salt allows transport properties to be studied under conditions of interest to us, *i.e.* where ion—solvent and ion—ion interactions predominate in the system.

The aim of this work was to measure viscosity and molar conductivity of LiNO_3 solutions in DMSO over a wide concentration range up to saturated or supersaturated solutions, and to compare the transport properties with those of aqueous solutions.

Experimental

Lithium nitrate (reagent grade, Merck) and dimethyl sulfoxide (anal. grade, Merck) with a maximum water content of 0.03 % were used as starting materials. Lithium nitrate was vacuum-dried at about 120 °C, and then kept over phosphorus pentoxide until it attained constant weight. Samples with required compositions were made up by weight. The sample compositions were not checked during measurements.

The density was measured with a DMA 40 digital vibration densimeter (Paar) with an accuracy of $5 \times 10^{-4} \text{ g cm}^{-3}$.

The viscosity was determined using a BH 2 Höppler viscometer with an accuracy of $\pm 1 \%$.

The electrical conductivity was measured by means of a BM 484 semi-automatic bridge (Metra) with an accuracy $\pm 0.1 \%$. Molar conductivities Λ ($\text{S cm}^2 \text{ mol}^{-1}$) were calculated from experimental electrolytic conductivities κ (S cm^{-1}) and densities d (g cm^{-3}) using the relation

$$\Lambda = \kappa(M_1(1-x)/x + M_2)/d \quad (1)$$

where M_1 and M_2 are the molar masses of DMSO and LiNO_3 , respectively, and x is the mole fraction of nitrate in solution.

Results

Density

Densities of nine samples with LiNO_3 concentrations within the mole fraction range 0.09–0.29 were determined at about seven temperatures from 5 to 60 °C. In order to facilitate calculations of dynamic viscosities and molar conductivities, the densities as a function of temperature and composition were fitted, by analogy with our previous studies, to an empirical relation of the form

$$\{d\} = \sum_{i=1}^3 \{\theta\}^{i-1} \left(\sum_{j=1}^4 a_{ij} x^{j-1} \right) \quad (2)$$

where d denotes the density (g cm^{-3}), θ is the temperature (°C), and x is the mole fraction of salt. The calculated values of the empirical parameters a_{ij} are given in Table 1.

Table 1

Values of the parameters of eqn (2)

	a_{ij}			
	$j=1$	$j=2$	$j=3$	$j=4$
1	1.1162	6.9774×10^{-1}	-2.7230×10^{-1}	1.5926×10^{-1}
2	-6.6965×10^{-4}	-5.8770×10^{-3}	4.0709×10^{-2}	-7.7622×10^{-2}
3	-4.8967×10^{-6}	1.0239×10^{-4}	-6.6973×10^{-4}	1.2929×10^{-3}

Viscosity

Viscosities were determined for the same samples over the same temperature and composition ranges as in the density measurements, with the exception of the most concentrated solution ($x=0.286$) where the temperature range was from 10 to 60 °C.

The viscosity data were fitted to the same equation as used in our previous paper [7]

$$\ln(\eta/(\text{Pa s})) = A_1 + A_2x + (B_1 + B_2x) K/(T - T_1 - T_2x) \quad (3)$$

where x is the mole fraction of salt, T (K) is the temperature, and A_1 , A_2 , B_1 , B_2 , T_1 , and T_2 are empirical parameters. Best-fit parameters obtained by an optimization technique are given in Table 2, along with the mean relative deviation. In view of the accuracy of viscosity

Table 2

Values of the parameters of eqns (3) and (4)

i	A_i	B_i	T_i/K	Mean deviation/%
Viscosity				
1	-9.58	608	115.8	
2	—	1240	219.2	1.9
Conductivity				
1	5.818	-350.4	158.9	
2	-13.22	293.2	161.2	1.4
3	42.14	-8492	-510.8	

measurement, the fit may be considered satisfactory. The value of the parameter A_2 showed no statistically significant difference from zero and therefore, the parameters given in Table 2 were calculated by taking $A_2=0$. The dependence of viscosity on temperature and composition is shown in Fig. 1.

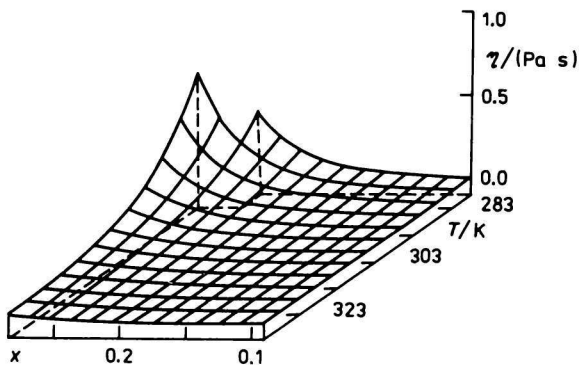


Fig. 1. Dependence of viscosity of the system LiNO_3 —DMSO on temperature and composition.

Molar conductivity

Molar conductivities of the above samples (plus a sample with $x = 0.077$) were calculated from eqns (1) and (2), using electrolytic conductivities determined at about 25 temperatures within the range 10—60 °C.

The molar conductivities as a function of temperature and composition were fitted to an expression of analogous form to eqn (3), with additional parameters included to obtain

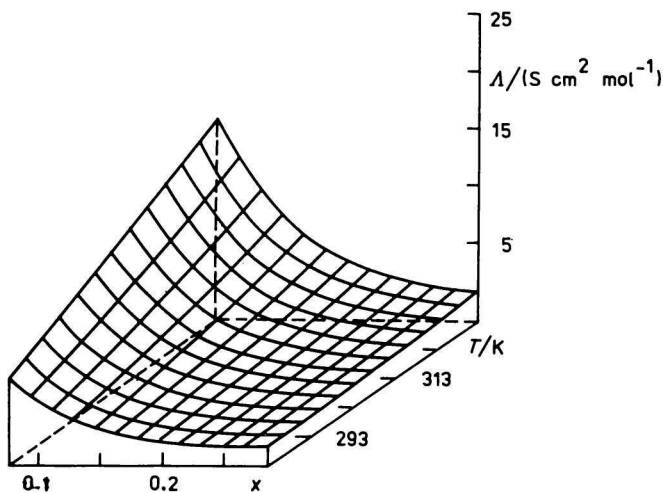


Fig. 2. Dependence of molar conductivity of the system LiNO_3 —DMSO on temperature and composition.

a satisfactory fit to the data

$$\ln (\Lambda / (\text{S cm}^2 \text{ mol}^{-1})) = A_1 + A_2 x + A_3 x^2 + (B_1 + B_2 x + B_3 x^2) K / (T - T_1 - T_2 x - T_3 x^2) \quad (4)$$

The calculated values of the empirical parameters are given in Table 2. The dependence of molar conductivity on temperature and composition is represented in Fig. 2.

Discussion

The temperature dependences of transport properties of LiNO_3 —DMSO solutions show distinct deviations from the Arrhenius behaviour, as evidenced by values of parameters of eqns (3) and (4) listed in Table 2. An increase in the salt concentration brings about a very marked increase of viscosity and a decrease of molar conductivity. These changes become more pronounced with decreasing temperature of the solution.

Eqns (3) and (4) provide a basis for comparing transport properties of given system with other properties characterizing the system, as well as with transport properties of other systems. Suitable rearrangement of eqn (3) yields an expression for temperature as a function of salt concentration at a constant viscosity of the system. Fig. 3 shows isoviscosity lines in the experimentally studied region (shaded area), together with liquidus lines of the phase diagram [8]. The figure also shows

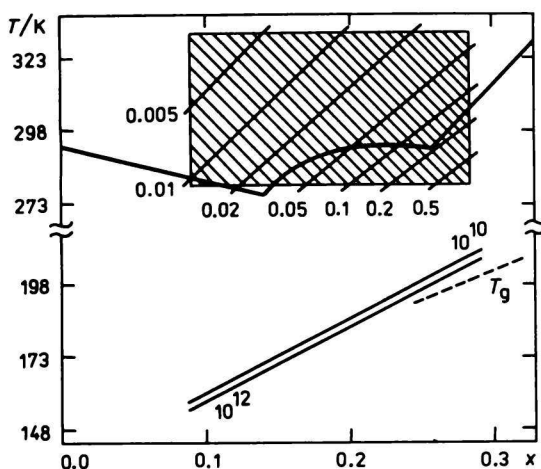


Fig. 3. Phase diagram of the system LiNO_3 —DMSO; isoviscosity lines with indications of viscosity value (Pa s); and temperature of glass transition T_g plotted vs. mole fraction x of salt in the system. The shaded area indicates the experimentally studied region.

experimentally determined [9] variation in glass transition temperature with concentration ($T_g = 142 + 202x$), and calculated isoviscosity lines for viscosities in the vicinity of the viscosity value at the glass transition of the melt as defined by convention (10^{10} – 10^{12} Pa s). Even though the extrapolation involved in the calculation of the isoviscosity lines is very long, only slight differences are found between calculated and experimental T_g values.

The interrelationship between changes in viscosity and molar conductivity is illustrated in Fig. 4, which shows a plot of the product $\eta \Lambda$ against temperature and composition. As with a number of other highly concentrated solutions [5], the plot shows a minimum (at $x = 0.21$ and 25°C). For aqueous solutions of lithium nitrate, this minimum is found at $x = 0.125$ [10].

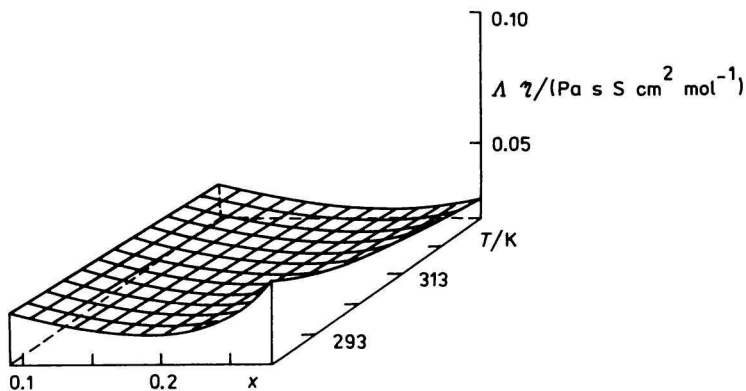


Fig. 4. Dependence of the product $\eta \Lambda$ ($\text{Pa s S cm}^2 \text{ mol}^{-1}$) of the system LiNO_3 —DMSO on temperature and composition.

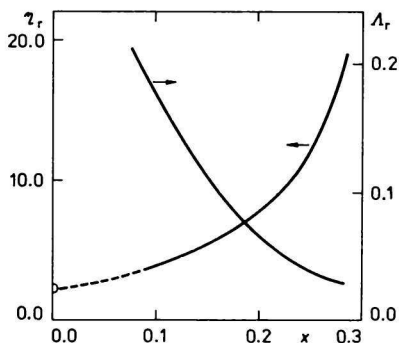
Fig. 5 provides a comparison of the effects of LiNO_3 —DMSO and LiNO_3 — H_2O interactions on transport properties. On the basis of a critical analysis of literature data [10–12], the composition dependences of viscosity and molar conductivity of aqueous solutions at 25°C with x ranging from 0.02 to 0.3 were represented by the relation $\{\eta\} \cdot 10^3 = 0.8496 + 7.2542x + 1224.6x^4$ and $\ln \{\Lambda\} = 4.409 - 9.49x + 2.62x^2$, respectively.

As the salt concentration is increased, viscosity of the system LiNO_3 —DMSO increases and molar conductivity decreases far more markedly than in aqueous solution. Since in the concentration range here investigated the solvent structure is destroyed by the solute, the increase in relative viscosity reflects a more increased ordering in the system LiNO_3 —DMSO compared to the aqueous system. The ratio

Fig. 5. Ratio of transport properties of the systems $\text{LiNO}_3\text{—DMSO}$ and $\text{LiNO}_3\text{—H}_2\text{O}$ plotted vs. mole fraction of salt in the systems at 25 °C.

$$\eta_r = \frac{\text{viscosity LiNO}_3\text{—DMSO}}{\text{viscosity LiNO}_3\text{—H}_2\text{O}};$$

$$\Lambda_r = \frac{\text{molar conductivity LiNO}_3\text{—DMSO}}{\text{molar conductivity LiNO}_3\text{—H}_2\text{O}}.$$



of viscosities of DMSO and water is equal to about two, and hence the increase in relative viscosity indicates that the $\text{Li}^+\text{—DMSO}$ interaction is stronger than the analogous interaction in the aqueous system. Consequently, the structure formed in DMSO is much stronger. This conclusion is in agreement with results of a study of vapour pressures of highly concentrated solutions of LiNO_3 in H_2O and DMSO [13, 14].

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