

Transport properties of the system calcium nitrate— —dimethyl sulfoxide

Z. KODEJŠ, J. NOVÁK, and I. SLÁMA

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

Received 25 August 1980

Density, viscosity, and electrical conductivity of highly concentrated solutions of calcium nitrate in dimethyl sulfoxide were determined in the temperature interval 5—55°C and concentration range 5—20 mole % of salts. The temperature and concentration dependence is approximated by simple relationships. Comparison of the nonaqueous system with aqueous solutions is discussed.

Для высоко концентрированных растворов нитрата кальция в диметилсульфоксиде в диапазоне температур 5—55°C и концентрации 5—20 мол. % определены плотность, вязкость и электрическая проводимость. Температурная и концентрационная зависимость указанных величин была описана при помощи простых соотношений и данные по неводной среде были сравнены с поведением водных растворов.

Highly concentrated aqueous solutions of electrolytes have been studied recently by a number of researchers [1—5]. Besides thermodynamic properties [6], spectral [7] and structural studies [8], attention is paid also to the transport phenomena. Viscosity and electrical conductivity of these systems is investigated not only in the vicinity of liquidus temperature, but also at much lower temperatures, which is possible owing to easy supercooling of some of these very concentrated solutions. These works are motivated by the aim to verify the validity of theories proposed for the description of transport properties and to find reasons for easy supercooling of these systems.

In order to make it possible to generalize knowledge concerning the character of interaction ion—solvent is necessary to investigate also properties of nonaqueous solutions of electrolytes. Preliminary results have shown [9] that also some solutions of inorganic salts in nonaqueous solvents can be supercooled. The aim of this work was the study of viscosity and electrical conductivity of highly concentrated solutions of calcium nitrate in dimethyl sulfoxide (DMSO). DMSO has been chosen as a solvent because of similarity of its properties to water. It dissolves many inorganic salts but because of steric hindrances it solvates mainly cations [10].

Experimental

Components of the system were prepared from calcium nitrate tetrahydrate, anal. grade (Lachema, Brno) and dimethyl sulfoxide anal. grade (Merck). Anhydrous calcium nitrate was prepared by drying the hydrate in vacuum dryer at temperatures below 160°C. The drying procedure was finished by storing the product in a dry-box with phosphorus pentoxide until its constant weight. Analysis of the content of nitrite proved that the nitrate was not decomposed during drying. Samples of desired concentration were prepared by weighing and the concentration of calcium ions was checked in each sample by chelatometric analysis.

The studied physicochemical properties were determined as a function of temperature in the interval 5–55°C (12–60°C in the case of electrical conductivity). The concentration of calcium salt is expressed in mole fraction of salt ranging from 0.05 to 0.2 (respectively from 0.03 to 0.18 in the case of density). In the case of samples having high concentration of salt it was not possible to carry out the measurements in the whole temperature interval because of crystallization. This problem was especially profound in the case of electrical conductivity measurements because the electrodes immersed in solution acted as crystallization centres.

Density was measured by means of digital densimeter DMA 40 (Paar) with precision better than $1 \times 10^{-3} \text{ g cm}^{-3}$. Viscosity was measured by Höppler viscometer BH2 with precision $\pm 1\%$. Electrical conductivity was determined using impedance bridge Tesla BM 484. The electrodes were covered with platinum black and the measurements were carried out at the frequency 1592 Hz with precision $\pm 0.05\%$. The values of viscosity (η) are in units of Pa s and those of molar electrical conductivity (λ) [$0.5 \text{ Ca}(\text{NO}_3)_2$] are in $\text{S cm}^2 \text{ mol}^{-1}$.

Results and discussion

Density

The temperature-concentration dependence of density (d) was approximated by an empirical relationship

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

Table 1

Values of the parameters of eqn (1)

<i>i</i>	<i>a_{ij}</i>			
	1	2	3	4
1	1.1198	1.6275	-1.3735×10^{-1}	-3.5082
2	-8.9655×10^{-4}	-2.0662×10^{-3}	2.7163×10^{-2}	-1.1877×10^{-1}
3	-8.6729×10^{-7}	3.2173×10^{-5}	-3.3070×10^{-4}	1.2442×10^{-3}

where d denotes density (g cm^{-3}), t is the temperature in $^{\circ}\text{C}$, and x is the mole fraction of salt in the system. Mean relative deviation of experimental data from this relationship is 0.07%, the maximum deviation being 0.18%. The calculated values of the coefficients a_{ij} are summarized in Table 1.

Viscosity and electrical conductivity

Temperature dependence of transport properties w (η or λ), was approximated in the studied interval by the following polynomial relationship

$$\ln w = a + b/T + c/T^2 \quad (2)$$

where a , b , c are the empirical constants and T denotes temperature (K). The values of parameters of this equation calculated by fitting sets of experimental data are summarized in Table 2.

For the description of temperature-concentration dependence of viscosity, the relationship (3) was used. This equation was derived assuming that two parameters of Fulcher equation [11] are a linear function of concentration x

$$\ln \eta = A + (E_1 + E_2x)/(T - T_1 - T_2x) \quad (3)$$

Table 2
Values of the parameters of eqns (2)

x	a	$b \cdot 10^{-3}$	$c \cdot 10^{-5}$	Average D	N
Viscosity					
0.0529	- 6.2203	- 1.9373	6.8701	1.2	11
0.0780	- 6.5850	- 1.8538	7.5923	1.3	11
0.0920	- 6.8845	- 1.7227	7.8159	0.6	12
0.112	- 4.4096	- 3.4757	11.489	0.6	11
0.138 ^e	- 8.1713	- 1.2557	9.1003	1.0	7
0.164 ^e	- 6.5842	- 2.5401	12.457	1.7	9
0.193 ^f	48.747	-38.474	71.870	0.2	4
Conductivity					
0.0513	0.61367	2.7559	- 7.3136	0.1	20
0.0675	- 0.20113	3.2127	- 8.3431	0.2	20
0.0776	- 0.94194	3.6672	- 9.3018	0.2	20
0.0925	- 2.2938	4.5037	-11.038	0.1	30
0.110	- 4.0088	5.6331	-13.481	0.2	30
0.124	- 4.9793	6.3272	-15.197	0.2	23

$$D = 100 |(w_{\text{exp}} - w_{\text{calc}})/w_{\text{exp}}|$$

N — number of experimental points used for evaluation of parameters in eqn (2).

Experimental temperature interval: e) 25—60 $^{\circ}\text{C}$; f) 45—60 $^{\circ}\text{C}$.

A , E_1 , E_2 , T_1 , T_2 are the empirical constants, T is temperature (K), and x is the mole fraction of salt in the system. The constants obtained by processing the set of experimental data are summarized in Table 3 together with the values on the system $\text{Ca}(\text{NO}_3)_2\text{—H}_2\text{O}$ taken from [11] and with the evaluation of fitness of the used approximation.

Similar procedure was used also for the description of the temperature-concentration dependence of electrical conductivity. In this case, however, it was assumed that the concentration dependence of all three parameters of the Fulcher equation is quadratic

$$\ln \lambda = A_1 + A_2x + A_3x^2 + (E_1 + E_2x + E_3x^2)/(T - T_1 - T_2x - T_3x^2) \quad (4)$$

Meaning of symbols is the same as in the case of eqn (3). The assumption about the concentration dependence of constants is in agreement with nonlinear character of the isoconductivity lines plotted in the system of coordinates $x\text{—}T$. The values of constants were obtained on the basis of 143 experimental data and they are presented in Table 3. The experimental data on conductivity of the system $\text{Ca}(\text{NO}_3)_2\text{—H}_2\text{O}$ [12] measured over the range of mole fractions of salt from 0.02 to 0.25 were processed in the same way. The calculated values of the parameters of eqn (4) are given in Table 3.

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

i	A_i	E_i	T_i	s
$\text{Ca}(\text{NO}_3)_2\text{—DMSO}$				
Viscosity				
1	-10.01	670.7	115.4	0.032
2	—	3034	315.3	
Conductivity				
1	8.015	- 1093	58.55	0.004
2	- 72.45	15910	2332	
3	346.7	- 98180	- 11090	
$\text{Ca}(\text{NO}_3)_2\text{—H}_2\text{O}$				
Viscosity				
1	- 8.92	290.2	135.2	0.044
2	—	2341	328.8	
Conductivity				
1	7.388	- 517.3	129.4	0.015
2	-24.18	1014	378.2	
3	61.06	- 6696	- 53.56	

s — standard deviation of the dependent variable $\ln w$.

Eqns (3) and (4) enable us to compare the viscosity and conductivity of the studied system with its phase diagram, with temperature of glass transition, and with the interval of the glass-forming ability. After rearranging the equations we obtain the relationships expressing the dependence of temperature on concentration at constant viscosity or conductivity. Constant viscosity straight lines together with liquidus curves of the corresponding phase diagram [13] are shown in Fig. 1.

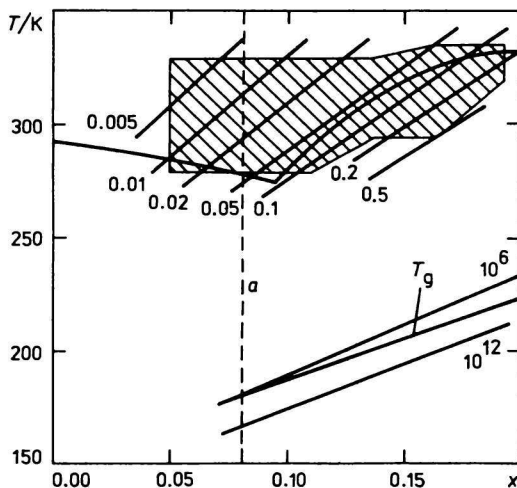


Fig. 1. Phase diagram of the system $\text{Ca}(\text{NO}_3)_2$ —DMSO, isoviscosity lines marked with the value of viscosity (Pa s), and temperature of glass transition T_g plotted vs. mole fraction x of salt in the system.

Shaded area marks the experimentally studied region.

a) Solvent-rich composition limit of the glass-forming ability.

In this figure the experimentally determined glass-forming region and the straight line representing the dependence of glass transition temperature T_g on concentration ($T_g = 149.7 + 362.7x$) [14, 15] are given as well. From this figure it follows that the low concentration limit of the glass-forming region and, therefore, also of supercooling, is given by composition at which viscosity of the system equals approximately 0.04 Pa s at the temperature of liquidus. Very similar value, namely 0.02 Pa s, has been found for some aqueous melts [11]. However, in contradiction to these melts, in the system $\text{Ca}(\text{NO}_3)_2$ —DMSO there is a remarkable difference between calculated course of the constant viscosity straight line at the viscosity value $\eta = 10^{12}$ Pa s, at which the temperature of glass transition is usually defined [16], and the approximation of the concentration dependence T_g . On the basis of contemporary knowledge this discrepancy may be explained by the fact that the studied range of viscosity is too narrow, which makes the extrapolation of viscosity to temperature T_g rather unreliable.

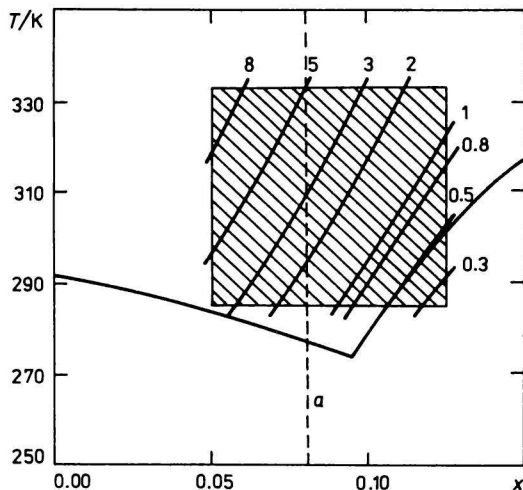


Fig. 2. Phase diagram of the system $\text{Ca}(\text{NO}_3)_2$ —DMSO and isoconductivity curves marked with the value of electrical conductivity ($\text{S cm}^2 \text{mol}^{-1}$) vs. mole fraction x of salt in the system.
a) Solvent-rich composition limit of the glass-forming ability.

The isoconductivity curves are plotted in Fig. 2. The molar conductivity at the low concentration limit of the glass-forming region at the temperature of liquidus reaches the value ca. $1 \text{ S cm}^2 \text{mol}^{-1}$ which further decreases with increasing concentration of salt in solution.

The assessment of the influence of solvent, in our case of DMSO, on transport properties can be made by comparing the concentration dependence of transport properties of both systems, *i.e.* $\text{Ca}(\text{NO}_3)_2$ — H_2O and $\text{Ca}(\text{NO}_3)_2$ —DMSO, at different temperatures. The dependences of relative quantities w_r (which are defined as the ratio of viscosity or conductivity of the nonaqueous solution and aqueous solution) on concentration of salt in solutions are shown in Fig. 3 for several chosen temperatures. Even if one takes into account that the value of viscosity of DMSO is almost twice so high as viscosity of water, it can be observed that the increasing concentration of salt has greater influence on viscosity and conductivity of the nonaqueous solution. In this figure also the value obtained on the basis of experimentally measured conductivity at temperature 55°C and concentration $x = 0.2$ is presented. The shape of the dependences can be explained on the basis of structural changes in solutions. With increasing concentration of salt in solution molecules of solvent cease to be the basic building particles of solution and the transport of charge and of momentum is influenced more by clusters of ions and molecules of solvent. Owing to the size of these particles viscosity of the system increases and its electrical conductivity decreases. Taking into account the

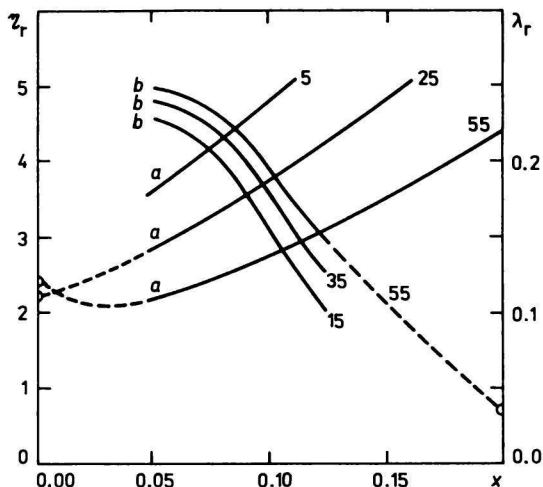


Fig. 3. Dependence of relative transport properties ($w_r = w_{\text{DMSO}}/w_{\text{H}_2\text{O}}$) on composition at a given temperature ($^{\circ}\text{C}$).

x — mole fraction of salt in the system.

a) Viscosity; b) electrical conductivity.

relative size of molecules of DMSO and of water it follows that the ratio of viscosities is an increasing and the ratio of conductivities decreasing function of concentration of salt.

Activation energy of transport properties is defined by the relations $E_\eta = R(\partial \ln \eta / \partial (1/T))$ and $E_\lambda = -R(\partial \ln \lambda / \partial (1/T))$. It was calculated at several temperatures and concentrations by differentiation of eqns (3) and (4). The results are shown in Fig. 4. The decrease in the activation energies with increasing temperature can be explained by thermal expansion of the system and by the weakening of interionic forces, as has been shown in [17]. Similarly as in the case of aqueous analogue of the studied system the activation energy of viscous flow is higher than the activation energy of electrical conductivity. However, this difference is not very remarkable. Similar phenomenon was observed also in other systems [2, 17]. Formation of clusters and associated particles influences both viscosity and conductivity because these parameters are connected with cooperative rearrangement of species. The difference between the two transport parameters is following. While conductivity reflects how easy only electrically charged particles can be rearranged the value of viscosity depends on distribution of particles of different mobility. The difference between the activation energies E_η and E_λ can be explained from this point of view as well. Activation energies for both transport properties in nonaqueous system are greater than the corresponding

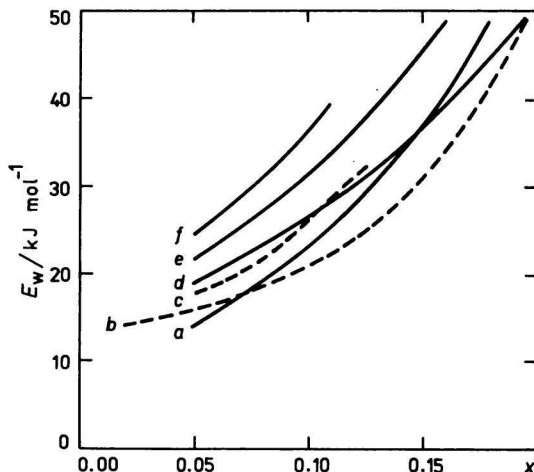


Fig. 4. Dependence of the activation energy of transport properties on concentration of salt in solution.
 x — mole fraction of salt in the system.

a) η (H_2O), 25°C ; b) λ (H_2O), 25°C ; c) λ (DMSO), 25°C ; d) η (DMSO), 55°C ; e) η (DMSO), 25°C ; f) η (DMSO), 5°C .

quantities in aqueous solutions, which can indicate a stronger interaction among species in nonaqueous solution.

Comparison of conductivity and viscosity or comparison of their concentration and temperature dependence can be carried out on the basis of Walden product $\eta\lambda$ which is a function of both the temperature and concentration of salt. The

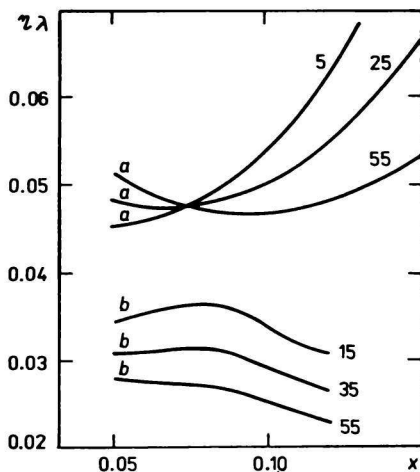


Fig. 5. Dependence of product $\eta\lambda$ ($\text{Pa s cm}^2 \text{mol}^{-1}$) on concentration of salt in solution at a given temperature ($^\circ\text{C}$).
 x — mole fraction of salt in the system.
a) $\text{Ca}(\text{NO}_3)_2\text{—H}_2\text{O}$; b) $\text{Ca}(\text{NO}_3)_2\text{—DMSO}$.

dependence of the value of this product $\eta\lambda$ on concentration at different temperatures is given in Fig. 5. Conductivity of solution is much more influenced by increasing concentration of salt in solution than viscosity. This effect is especially profound at lower temperatures. The relation between values of the Walden product $\eta\lambda$ in aqueous and nonaqueous solutions is influenced by two factors. Viscosity of nonaqueous solution is 2–4 times higher than viscosity of aqueous solution (Fig. 3) but the decrease of conductivity overcompensates this effect. Explanation of these phenomena may be found in complex action of selective cationic solvation in DMSO, in different influence of temperature and salt concentration on the solvation and association equilibria, and in different mechanism of mobility of ions in DMSO and in water.

References

1. Kodejš, Z. and Pacák, P., *Chem. Listy* 75, 337 (1981).
2. Angell, C. A., Williams, E., Rao, K. J., and Tucker, J. C., *J. Phys. Chem.* 81, 238 (1977).
3. Ambrus, J. H., Moynihan, C. T., and Macedo, P. B., *J. Electrochem. Soc.* 119, 192 (1972).
4. Islam, N., Kumar, S., and Singh, K. P., *Bull. Chem. Soc. Jap.* 51, 2712 (1978).
5. Kodejš, Z. and Sláma, I., *Chem. Zvesti* 34, 335 (1980).
6. Leifer, L. and Högfeldt, E., *Acta Chem. Scand.* 27, 4007 (1973).
7. James, D. and Frost, R. L., *Farad. Disc.* (Chem. Soc.) 64, 48 (1977).
8. Baianu, I. C., Boden, N., Lightowers, D., and Mortimer, M., *Chem. Phys. Lett.* 54, 164 (1978).
9. Sare, E. J. and Angell, C. A., *J. Solution Chem.* 2, 53 (1973).
10. Butler, J. N., *J. Electroanal. Chem.* 14, 89 (1967).
11. Sláma I. and Kodejš, Z., *J. Solution Chem.* 8, 801 (1979).
12. Bressel, R. D., *Ph.D. Thesis*. Purdue University, Lafayette, 1972.
13. Pacák, P. and Sláma, I., *Collect. Czech. Chem. Commun.* 46, 1629 (1981).
14. Sare, E. J., *Ph.D. Thesis*. Purdue University, Lafayette, 1971.
15. Malá, J. and Sláma I., *Chem. Zvesti* 35, 207 (1981).
16. Johari, G. P., *J. Chem. Educ.* 51, 23 (1974).
17. Islam, N., Kumar, S., and Singh, K. P., *Z. Phys. Chem. (Leipzig)* 261, 313 (1980).

Translated by P. Fellner