

Molar conductivity of the system calcium nitrate—dimethyl sulfoxide—water

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Temperature and composition dependence of molar conductivity of the system containing calcium nitrate, dimethyl sulfoxide (DMSO), and water was studied. Mole fraction of DMSO in the solvent $y = n_{\text{DMSO}} / (n_{\text{DMSO}} + n_{\text{H}_2\text{O}})$ amounted to 0.2, 0.4, 0.6, 0.8. Mole fraction x of calcium salt in the system changed in the interval $\langle 0.052; 0.20 \rangle$. Temperature dependence of molar conductivity Λ was studied in the interval $\langle 5^\circ\text{C}; 60^\circ\text{C} \rangle$ (x, y being kept constant) and it was fitted to simple Vogel—Fulcher—Tamman equation. The isothermal dependence of conductivity on salt concentration in the mixture and on composition of the solvent ($\text{H}_2\text{O} + \text{DMSO}$) is discussed.

В системе нитрат кальция—диметилсульфоксид—вода изучалась молекулярная электропроводность в зависимости от состава и температуры. Мольная доля ДМСО в растворителе $y = n_{\text{ДМСО}} / (n_{\text{ДМСО}} + n_{\text{H}_2\text{O}})$ составляла 0,2; 0,4; 0,6 и 0,8. Мольная доля x кальциевой соли в системе менялась в интервале $\langle 0,052; 0,20 \rangle$. Температурная зависимость молярной электропроводности Λ в интервале $\langle 5^\circ\text{C}; 60^\circ\text{C} \rangle$ (для $x, y = \text{const}$) была аппроксимирована в виде простого уравнения Фогеля—Фульхера—Тамманна. Обсуждаются изотермическая зависимость электропроводности от концентрации соли в системе и от состава растворителя ($\text{H}_2\text{O} + \text{ДМСО}$).

In a series of papers [1—5] we focused our attention to the investigation of molar conductivity in a model system $\text{Ca}(\text{NO}_3)_2\text{—H}_2\text{O}$ in which a part of NO_3^- ions was replaced by the ions Cl^- , Br^- or I^- . Further we have measured [6] the molar conductivity in highly concentrated system $\text{Ca}(\text{NO}_3)_2\text{—DMSO}$.

The aim of this work was to find how the molar conductivity is changed if water in the system $\text{Ca}(\text{NO}_3)_2\text{—H}_2\text{O}$ is partially replaced by an aprotic dipolar solvent, viz. DMSO.

Experimental

Chemicals

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, anal. grade (Lachema, Brno) and dimethyl sulfoxide, anal. grade (Merck) were used. Anhydrous calcium nitrate was prepared by drying the tetrahydrate in vacuum dryer at 160°C . Samples of the mixture $\text{Ca}(\text{NO}_3)_2$ —DMSO— H_2O having required y and $x=0.2$ were prepared by dissolution of anhydrous calcium nitrate in the mixture DMSO— H_2O of the corresponding composition. Samples having $x=0.167, 0.143$, etc. were prepared by dilution of the basic mixture. Composition of the final systems was checked by the chelatometric titration of Ca^{2+}

Measurement of resistance

The procedure was analogous as in the previous papers [1—6]. Measurement was carried out using a semi-automatic bridge BM 484 (Tesla) and three conductivity cells with the following constants: 183.32 cm^{-1} , 167.32 cm^{-1} , and 160.77 cm^{-1} . Set of 20—25 conductivity measurements was obtained at each composition in the temperature range 5 — 60°C . The molar conductivity Λ ($0.5 \text{ Ca}(\text{NO}_3)_2$) was calculated according to the relation

$$\Lambda = \frac{\kappa}{2h} \cdot \left((M_1 \cdot (1-y) + M_2 \cdot y) \cdot \left(\frac{1-x}{x} \right) + M_3 \right) \quad (1)$$

where κ is the electrolytic conductivity (S cm^{-1}), h is the density (g cm^{-3}), M_1 , M_2 , and M_3 are the relative molar masses of H_2O , DMSO, and $\text{Ca}(\text{NO}_3)_2$, respectively. The unit of the molar conductivity used in this paper is therefore $\text{S cm}^2 \text{ mol}^{-1}$.

Density of the systems, in which y ranged from 0.2 to 0.8 and x from 0.052 to 0.2, was calculated from the twelve-parameter equation

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

where i, j are integers, t is the temperature ($^\circ\text{C}$) and a_{ij} are the constants presented in paper [7].

Pairs of values of molar conductivity and temperature calculated from the experimental data were fitted to the simple form of Vogel—Tamman—Fulcher equation

$$\Lambda = A \exp \left[-B/(T - T_0) \right] \quad (3)$$

where A , B , and T_0 are the constants characterizing the system and T is the thermodynamic temperature. In the studied temperature interval (5°C ; 60°C) the set of 20—25 experimental data is described by the relationship (3) with sufficient precision. The parameters of eqn (3) are presented in Table 1 together with the mean relative error of Λ ($\delta/\%$).

Table 1

The coefficients of eqn (3) for calculation of the molar electrical conductivity ($\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$) of the system $\text{Ca}(\text{NO}_3)_2\text{—DMSO—H}_2\text{O}$
 δ is the mean relative error of molar conductivity

x	0.196	0.169	0.145	$y = 0.2$	0.093	0.079	0.053
T_0/K	199.9	195.8	185.8	175.9	171.7	169.6	162.8
$\ln (\Lambda/S \text{ cm}^2 \text{ mol}^{-1})$	5.892	5.237	5.283	5.429	5.520	5.605	5.343
B/K	862	689	663	634	588	571	556
$\delta/\%$	1.127	0.223	0.277	0.414	0.106	0.144	0.396
x	0.200	0.167	0.143	$y = 0.4$	0.091	0.077	0.052
T_0/K	197.3	193.2	186.4	177.0	170.4	165.9	158.0
$\ln (\Lambda/S \text{ cm}^2 \text{ mol}^{-1})$	6.229	5.371	5.280	5.319	5.514	5.673	6.045
B/K	1022	811	763	707	693	686	682
$\delta/\%$	1.165	0.396	0.180	0.133	0.113	0.103	0.098
x	0.196	0.167	0.143	$y = 0.6$	0.091	0.077	0.052
T_0/K	216.7	187.7	180.1	172.1	166.9	163.3	156.9
$\ln (\Lambda/S \text{ cm}^2 \text{ mol}^{-1})$	4.152	5.112	5.049	5.147	5.309	5.411	5.662
B/K	598	869	814	744	712	680	636
$\delta/\%$	1.027	0.356	0.129	0.125	0.108	0.099	0.096
x	0.196	0.167	0.143	$y = 0.8$	0.091	0.077	0.053
T_0/K	190.9	180.6	176.6	172.8	168.8	165.8	160.3
$\ln (\Lambda/S \text{ cm}^2 \text{ mol}^{-1})$	4.716	4.750	4.751	4.760	4.869	4.953	5.180
B/K	952	903	820	683	616	576	523
$\delta/\%$	0.488	0.150	0.152	0.104	0.085	0.082	0.081

Discussion

In our previous works [6, 7] we investigated transport properties of concentrated solutions of calcium nitrate in dimethyl sulfoxide. We discussed there the differences in viscosity and electrical conductivity between solutions of calcium nitrate in water and in DMSO and the influence of replacement of water with DMSO on viscosity of the ternary system $\text{Ca}(\text{NO}_3)_2\text{—DMSO—H}_2\text{O}$. It has been found that the dependence of viscosity on composition of the solvent is remarkable and that maximum of deviations of relative viscosity from additive behaviour (calculated under the assumption of additive behaviour of both binary systems) is achieved at $y = 0.3$. Therefore it follows that the most important is to investigate the influence of gradual replacement of water by dimethyl sulfoxide on electrical conductivity and to compare it with behaviour of viscosity of the system in question. (For detailed discussion of viscosity reader is referred to the paper [7]).

Using eqn (3) we calculated the values of molar electrical conductivity for mole fractions of calcium nitrate in the interval $\langle 0.05; 0.20 \rangle$ at temperatures 5°C , 20°C , and 50°C . The values of Λ and η for $y = 1$ and 0 are taken from [6—8].

The dependences of molar conductivity Λ at $x = 0.143$ and 0.077 on y is given in Fig. 1. It follows that the dependences of molar electrical conductivity and of

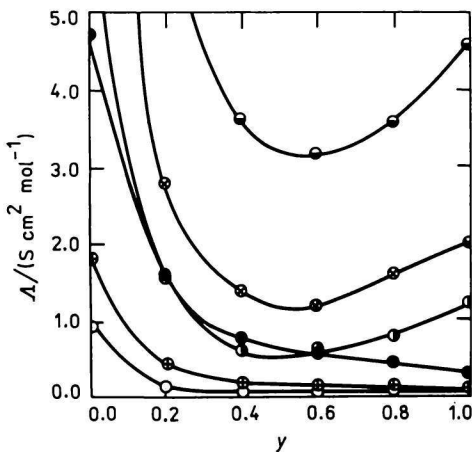


Fig. 1. Dependence of molar conductivity Λ of the system $\text{Ca}(\text{NO}_3)_2\text{—DMSO—H}_2\text{O}$ on mole fraction y of DMSO in solvent plotted for two compositions of calcium nitrate.

$t/^\circ\text{C}$	Mole fraction x of $\text{Ca}(\text{NO}_3)_2$	
	0.143	0.077
5	○	●
20	⊕	⊗
50	●	●

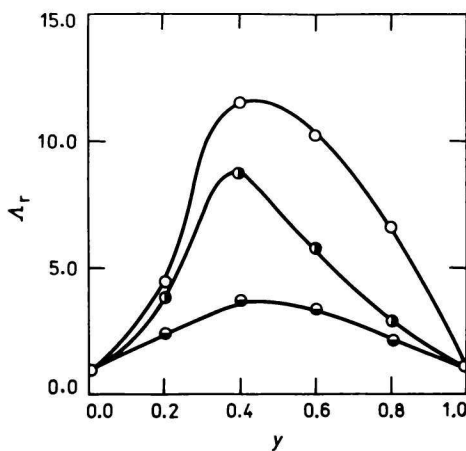


Fig. 2. Dependence of the relative molar conductivity Λ_r on mole fraction y of DMSO in solvent (x denotes the mole fraction of $\text{Ca}(\text{NO}_3)_2$ in mixture).

○ $t = 5^\circ\text{C}$, $x = 0.143$
 ● $t = 5^\circ\text{C}$, $x = 0.077$
 ● $t = 50^\circ\text{C}$, $x = 0.077$

viscosity (see [7]) on a gradual replacement of water by dimethyl sulfoxide differ in character. It should be pointed out that molar conductivity should be compared with fluidity (*i.e.* with reciprocal value of viscosity) because a decrease in molar electrical conductivity corresponds to an increase in viscosity (and on the contrary).

The most striking difference between dependences of viscosity and molar conductivity Λ on gradual replacement of water by DMSO is the absence of remarkable extremum on the function $\Lambda = \Lambda(y)$ at high concentrations of salt. Though the conductivity decreases sharply in the beginning, its value at $y \approx 0.30$ does not differ substantially from electrical conductivity of solutions of calcium nitrate in DMSO. Coincident features in dependence of Λ or η on y (t and x are kept constant) appear when we plot $\Lambda_r = \Lambda_{ad}/\Lambda_{exp}$ vs. y . (Λ_{exp} is the experimental molar electrical conductivity, $\Lambda_{ad} = \Lambda_1 \cdot y + \Lambda_0 \cdot (1 - y)$, Λ_0 and Λ_1 are the molar conductivities of the system at $y = 0$ and 1, respectively.) The dependence $\Lambda_r = f(y)$ has a maximum (Fig. 2) at $y \approx 0.4$, *i.e.* practically in the same region as the analogous quantity for viscosity. This is in accordance also with the results of other papers [9–14].

Apparent activation energy of conductivity $E = -R(d \ln \{\Lambda\})/d(1/T)$ can be used as a measure of interaction force between particles in solution. For appreciation of the influence of composition of mixed solvent on these interactions we plotted in Fig. 3 the dependence of activation energy on composition of the solvent at different temperatures and concentrations. It should be pointed out that the transport properties of concentrated salt solutions do not obey Arrhenius equation and therefore the apparent activation energy is not only the function of composition but also of temperature. From Fig. 3 it follows that at $y = 0.4$ there are maxima on the $E = E(y)$ curves, which indicates a high degree of arrangement of solution having this ratio of water to DMSO. Stability of the arrangement increases again with increasing concentration of calcium nitrate and with decreasing temperature.

Since Λ of the system is closely related to its η , it is suitable to use the Walden's product $k = \Lambda \cdot \eta$ for characterization of the influence of composition of the mixed solvent on Λ and η . In diluted solutions, if the change in molar conductivity is caused only by change in viscosity of the solvent, k is constant. The dependence of Walden's product on y at different mole fractions x of salt and temperatures is presented in Fig. 4. Maximum on the curve for $k = k(y)$ lies at $y \approx 0.2$. It is more remarkable at lower temperatures and higher concentrations of calcium nitrate.

Generally it can be stated that the trends in dependence of Λ and η on gradual replacement of water with DMSO in the system $\text{Ca}(\text{NO}_3)_2$ —DMSO— H_2O are very similar. Some deviations can be explained by different mechanisms of ionic mobility and of viscous flow. *E.g.* the maxima on the curves for $k = k(y)$ (Fig. 4) indicate that the gradual replacement of water with DMSO influences in the beginning more viscosity than electrical conductivity of the system.

The investigation of electrical conductivity confirmed the results obtained in the

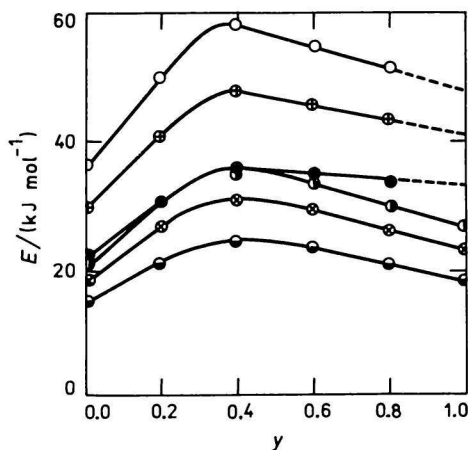


Fig. 3. Dependence of the activation energy $E/(\text{kJ mol}^{-1})$ of molar conductivity on mole fraction y of DMSO in solvent and on the mole fraction x of $\text{Ca}(\text{NO}_3)_2$ in the system.

$t/^\circ\text{C}$	Mole fraction x of $\text{Ca}(\text{NO}_3)_2$	
	0.143	0.077
5	○	●
20	⊕	⊗
50	●	●

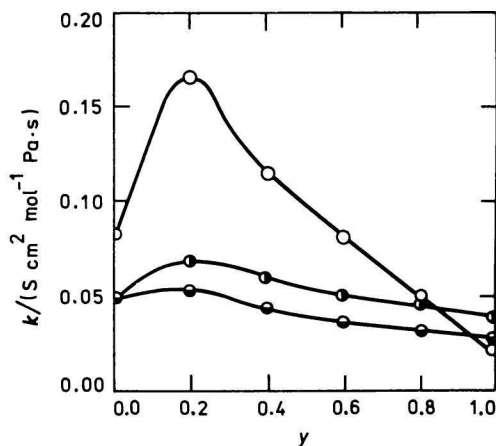


Fig. 4. Dependence of the product of molar conductivity and viscosity $k/(\text{S cm}^2 \text{ mol}^{-1} \text{ Pa}\cdot\text{s})$ in the system $\text{Ca}(\text{NO}_3)_2\text{—DMSO—H}_2\text{O}$ on mole fraction y of DMSO in solvent.

○	$t = 5^\circ\text{C}$, $x = 0.143$
●	$t = 5^\circ\text{C}$, $x = 0.077$
●	$t = 50^\circ\text{C}$, $x = 0.077$

study of viscosity of this system, indicating the increase of strength of the interactions ion—solvent in the mixed solvent [7] in comparison with analogous interactions in water or DMSO. Similarly as in the case of viscosity, a high degree of arrangement of local structures in the system $\text{Ca}(\text{NO}_3)_2\text{—DMSO—H}_2\text{O}$ (when composition of solvent is given by $y = 0.2\text{—}0.4$) was confirmed.

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