

Electrical conductance of the $\text{LiNO}_3\text{—H}_2\text{O—DMSO}$ system

J. NOVÁK

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

Received 21 November 1984

Accepted for publication 26 March 1985

The conductance κ as a function of temperature and composition was investigated in the $\text{LiNO}_3\text{—H}_2\text{O—DMSO}$ system. The mole fraction of dimethyl sulfoxide in the solvent $y = n(\text{DMSO})/(n(\text{DMSO}) + n(\text{H}_2\text{O}))$ was 0.2, 0.4, 0.6, 0.8, and 1.0. The mole fraction of LiNO_3 , x in the system was in the interval $(0.05; 0.30)$. The dependence of conductance on temperature was approximated in the form of the simple Vogel—Tamman—Fulcher equation for the temperature interval $(10^\circ\text{C}; 60^\circ\text{C})$ ($x, y = \text{const}$).

В системе $\text{LiNO}_3\text{—H}_2\text{O—ДМСО}$ изучалась электропроводность κ в зависимости от температуры и состава. Мольная доля диметилсульфоксида (ДМСО) в растворителе $y = n(\text{ДМСО})/(n(\text{ДМСО}) + n(\text{H}_2\text{O}))$ составляла 0,2; 0,4; 0,6; 0,8 и 1,0. Мольная доля LiNO_3 , x в системе лежит в интервале $(0,05; 0,30)$. Температурная зависимость электропроводности в интервале температур $(10^\circ\text{C}; 60^\circ\text{C})$ (при $x, y = \text{const}$) была аппроксимирована в виде простого уравнения Фогеля—Тамманна—Фульхера.

This study is a continuation of the series of papers [1, 2] where the influence of the partial replacement of H_2O by dimethyl sulfoxide in concentrated salt systems was examined. The aim of this work was to find out how the replacement of H_2O by dimethyl sulfoxide manifested itself in magnitude of κ and character of the relationships $\kappa = \kappa(x)$ and $\kappa = \kappa(y)$ within the investigated concentration and temperature interval.

Experimental

Chemicals

LiNO_3 and DMSO were products of Merck. They were anal. grade chemicals. LiNO_3 was purified by crystallization and drying. The control showed that only traces of NO_2^- were present in the final product as well as in the original crude substance. The samples of the $\text{LiNO}_3\text{—H}_2\text{O—DMSO}$ system with required x and y were prepared by dissolving anhydrous LiNO_3 in the $\text{DMSO—H}_2\text{O}$ mixture of corresponding composition.

Measurement of electrical conductance

The procedure was analogous to that one described in our preceding papers [1, 2]. The measurements were performed with a half-automatic bridge BM 484 (Tesla) in three conductance cells the constants of which were: 183.32 cm⁻¹, 167.32 cm⁻¹, and 160.77 cm⁻¹.

The pairs of the values of conductance κ and temperature were approximated in the form of the Vogel—Tammann—Fulcher equation

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

where A , B , and T_0 are constants characterizing the system and T is thermodynamic temperature. The values measured in the investigated temperature interval (10 °C; 60 °C) are in satisfactory agreement with eqn (1).

Results and discussion

The parameters of eqn (1) and mean relative errors δ in % are given in Table 1.

The dependence of conductance κ on salt concentration at 25 °C is represented in Fig. 1. It is obvious that the change in solvent composition has influence on $x (= x_m)$ at which κ reaches its maximum value ($= \kappa_{max}$) on the curve $\kappa = \kappa(x)$ as well as on the value of κ_{max} . This influence shows itself at other temperatures, too.

The character of the relationship between κ and y at 25 °C is to be seen in Fig. 2. We can observe an initial rapid decrease in conductance, but if the content of DMSO in the system increases and exceeds approximately $y=0.4$, it appears that further exchange of water for dimethyl sulfoxide only very little affects the value of κ . That is consistent with the earlier results obtained for the systems: Ca(NO₃)₂—H₂O—DMSO [1]; CaCl₂—H₂O—DMSO; NH₄NO₃—H₂O—DMSO.

Table 1

Coefficients for calculation of κ according to eqn (1) (δ is mean relative error)

	y = 0.20					
x	0.05	0.10	0.15	0.20	0.25	0.30
T_0/K	148.6	148.8	149.5	153.4	159.2	170.8
$\ln(A/(S \text{ cm}^{-1}))$	0.3591	0.6131	0.7549	0.8281	0.8781	0.7512
B/K	597.4	608.3	641.1	657.7	622.7	613.4
$\delta/\%$	0.081	0.092	0.086	0.086	0.089	0.292
	y = 0.40					
x	0.05	0.10	0.15	0.20	0.25	
T_0/K	145.9	149.9	155.0	162.8	168.1	
$\ln(A/(S \text{ cm}^{-1}))$	0.0261	0.4734	0.6586	0.6631	0.7160	
B/K	692.2	741.6	777.6	767.9	774.8	
$\delta/\%$	0.113	0.111	0.126	0.109	0.160	

Table 1 (Continued)

			$y = 0.60$			
x	0.05	0.10	0.15	0.20	0.25	
T_0/K	147.2	154.5	159.2	167.3	170.4	
$\ln(A/(S\text{ cm}^{-1}))$	-0.7147	-0.2469	0.1296	0.2243	0.4590	
B/K	608.2	667.9	754.9	777.6	834.0	
$\delta/\%$	0.092	0.133	0.154	0.142	0.178	
			$y = 0.80$			
x	0.05	0.10	0.15	0.20	0.25	
T_0/K	156.5	161.7	162.6	165.6	159.8	
$\ln(A/(S\text{ cm}^{-1}))$	-1.5103	-1.0648	-0.5831	-0.2656	0.4936	
B/K	455.4	522.2	652.9	751.6	960.4	
$\delta/\%$	0.069	0.085	0.105	0.069	0.211	
			$y = 1.0$			
x	0.02	0.03	0.04	0.05	0.06	0.10
T_0/K	160.1	165.9	164.9	164.7	165.5	168.9
$\ln(A/(S\text{ cm}^{-1}))$	-2.5593	-2.3699	-2.1766	-2.043	-1.9438	-1.7032
B/K	355.9	333.7	343.1	350.5	357.4	391.5
$\delta/\%$	0.126	0.170	0.113	0.079	0.056	0.061

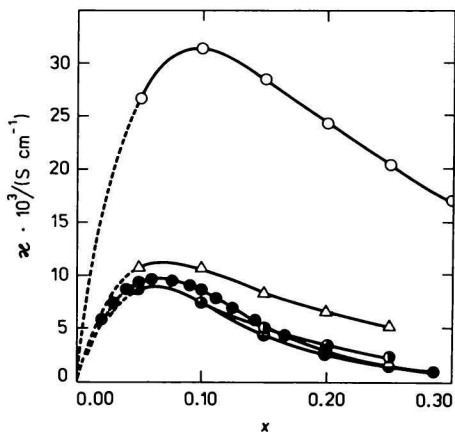


Fig. 1. Conductance κ ($S\text{ cm}^{-1}$) of the $\text{LiNO}_3\text{--H}_2\text{O--DMSO}$ system as a function of mole fraction x of the salt at 25°C for different values of y : \circ 0.20, \triangle 0.4, \bullet 0.6, \blacksquare 0.8, \bullet 1.0. $\kappa_{\max}(y=0.0) = 0.168\text{ S cm}^{-1}$ [6]. A part of the values of κ for $y = 1.0$ is taken from paper [7].

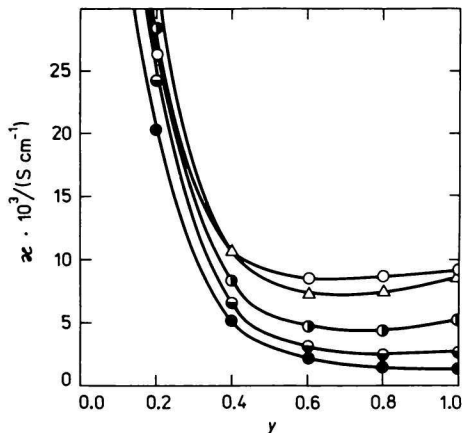


Fig. 2. Conductance κ ($S\text{ cm}^{-1}$) of the $\text{LiNO}_3\text{--H}_2\text{O--DMSO}$ system as a function of mole fraction of DMSO in solvent y at 25°C for different values of x : \circ 0.05, \triangle 0.10, \bullet 0.15, \blacksquare 0.20, \bullet 0.25.

The salt concentration x_m at which κ_{\max} is reached generally depends on temperature as well as on the kind of solvent and dissolved salt. As demonstrated by Fedotov [3], the decrease in number of the molecules of solvent which solvate the ions of dissolved salt shifts the position of x_m towards higher values of x . An increase in number of charges of the ions in which the dissolved salt dissociates results in a shift in x_m towards lower values of x . The shift in x_m as a function of composition of the mixed solvent is interesting (Fig. 3). The position of x_m almost does not change up to $y=0.2$ in a relatively wide temperature interval (10 °C; 60 °C). Then it starts to shift towards lower values. The value of the change in position of x_m varies already little with increasing y from $x > 0.4$. The curve $x_m = f(y)$ exhibits a point of inflection at $y \approx 0.33$, i.e. for the composition of solvent corresponding to $2\text{H}_2\text{O} \cdot \text{DMSO}$.

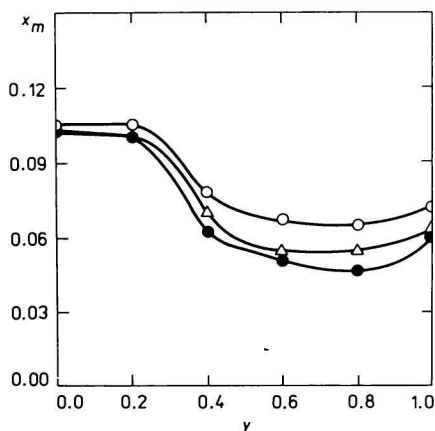


Fig. 3. Variation of x_m with y for the $\text{LiNO}_3\text{—H}_2\text{O—DMSO}$ system at different temperatures: ● 10 °C, △ 20 °C, and ○ 50 °C. The values of x_m at $y=0.0$ are taken from papers [6, 8]

The initial rapid decrease in electrical conductance due to increasing y (Fig. 2) points out a preferential solvation of the Li^+ ions by the molecules of DMSO. It follows from [4] that the hydration or solvation of the NO_3^- ion is negligible. Therefore we are going to pay main attention to Li^+ . Let us assume the affinity of Li^+ with respect to DMSO to be so great that DMSO expels H_2O out of the proximity of Li^+ till H_2O in the first coordination sphere of Li^+ is completely replaced by the molecules of DMSO and, moreover, that the amount of DMSO entering into interaction with H_2O is negligible. If the concentration of salt was $x = 0.05$, the replacement of the H_2O molecules by DMSO was finished at $y > 0.21$ ($n(\text{DMSO}):n(\text{Li}^+) = 4:1$) or at $y > 0.31$ ($n(\text{DMSO}):n(\text{Li}^+) = 6:1$). Up to these concentrations the system should contain $\text{Li}(\text{H}_2\text{O})_4^+$, NO_3^- , $\text{Li}(\text{DMSO})_4^+$, ion pairs consisting of these ions, and H_2O functioning as a solvent. As obvious, the number of particles with larger ionic radius or electroneutral particles present in the system increases. On the other hand, the kind of solvent and overall salt concentration

does not change under these conditions. For this reason, a partial replacement of H_2O by DMSO ought to bring about a decrease in κ of the system. Now let us consider what may take place in the system after all water in the first coordination sphere of Li^+ has been replaced by DMSO. Then DMSO could further interact with H_2O . Provided $2\text{H}_2\text{O} \cdot \text{DMSO}$ [5] arises and practically all water is bound in this compound, the conductance of the system should continue to decrease as far as to

$$y_m = \frac{x(2m-1)+1}{3(1-x)} \quad (2)$$

where y_m is the value of y at which $\kappa = \kappa(y)$ reaches the minimum and m is the number of DMSO molecules in the first coordination sphere of Li^+ . On the basis of the above assumptions, further addition of DMSO into the system ($x, \theta = \text{const}$) should result in a "dilution" of larger particles of solvent, *i.e.* $2\text{H}_2\text{O} \cdot \text{DMSO}$ by smaller particles, *i.e.* DMSO. If the resulting conductance depended solely on the size of solvent particles ($x, \theta = \text{const}$), further increase in y would result in a slight increase in conductance.

The character of the function $\kappa = \kappa(y)$ would not change too much even if the affinities of Li^+ or H_2O with respect to DMSO were smaller. However, the minimum of the curve $\kappa = \kappa(y)$ would not occur at a higher value of y than the above-mentioned values.

The position of y_m of the hitherto investigated systems depends not only on their composition, but also on temperature. It rises with the temperature of y_m . For calculating m from eqn (2), $y_m = y_m(\theta)$ would be bound to converge to some value y_{m0} . Thus the calculation of m necessitates to insert the value of y_{m0} for y_m in eqn (2). The $\text{LiNO}_3\text{—H}_2\text{O—DMSO}$ system is not so stable for $x = 0.05$ and 0.1 at temperatures under 10°C that we could measure its κ . The relationship $y_m = y_m(\theta)$ does not converge in the interval $\langle 10^\circ\text{C}; 60^\circ\text{C} \rangle$. Provided we use the values of y_m found at the lowest temperature for calculating m , $m < 7$ or $m < 4$. The relationship $y_m = y_m(\theta)$ converges in the investigated temperature interval only for $x > 0.10$. Thus we obtain $m \doteq 3.6$ or 2.75 for $x = 0.15$ or 0.20 , respectively. The values ≤ 4 are given in paper [9] for m in the $\text{LiNO}_3\text{—DMSO}$ system. Provided the assumptions used for deriving eqn (2) are valid, it should be $m = \text{const}$ for each value of x . However, this is not the case. Though water is bound to Li^+ less firmly than DMSO, it is the first to be displaced up to $y \rightarrow 1.0$. Thus we may explain a relatively small increase in κ in the interval from $y = 0.7$ to $y = 1.0$. On the other hand, the observed increase in κ at $y \rightarrow 1.0$ for $x < 0.2$ suggests the existence of a compound consisting of H_2O and DMSO in the system. If the compound consisting of H_2O and DMSO did not arise in the system, the character of the relationship $\kappa = \kappa(y)$ should be different (see later).

An increasing concentration of salt in the system finally produces the state where

the number of solvent molecules is just sufficient for filling the first coordination sphere of Li^+ or is eventually less. Then the change in κ due to increasing y is dependent (in the first approximation) on two factors, *i.e.* rise in ionic radii of the charged particles in the system ($\text{Li}(\text{H}_2\text{O})^{\dagger}$ is transformed into $\text{Li}(\text{DMSO})^{\dagger}$) and change in environs where the charged particles occur. Then there is not reason for the conductance of the system to increase at $y \rightarrow 1.0$. We can really see in Fig. 2 that the conductance at $x = 0.25$ continues to decrease as far as to $y = 1.0$. Analogous phenomena were found out by earlier investigations of the $\text{Ca}(\text{NO}_3)_2\text{—H}_2\text{O—DMSO}$ system [1].

References

1. Novák, J., Kodejš, Z., and Sláma, I., *Chem. Zvesti* 38, 387 (1984).
2. Kodejš, Z., Novák, J., and Sláma, I., *Collect. Czechoslov. Chem. Commun.* 48, 1810 (1983).
3. Fedotov, N. V., *Zh. Fiz. Khim.* 53, 2398 (1979).
4. Letellier, P. and Gaboriaud, R., *J. Chim. Phys. Physicochim. Biol.* 78, 829 (1981).
5. Devia, D. H. and Strehlow, H., *Ber. Bunsenges. Phys. Chem.* 83, 627 (1979).
6. Campbell, A. N., Debus, G. H., and Kartzmark, E. M., *Can. J. Chem.* 33, 1508 (1955).
7. Kodejš, Z., Novák, J., and Sláma, I., *Chem. Zvesti* 38, 455 (1984).
8. Valyashko, V. M. and Ivanov, A. A., *Zh. Neorg. Khim.* 24, 2752 (1979).
9. Toth, J. P., Ritzhaupt, G., and Devlin, J. P., *J. Phys. Chem.* 85, 1387 (1981).

Translated by R. Domanský