VISCOSITY, ELECTRICAL CONDUCTIVITY AND DENSITY OF THE SYSTEM AMMONIUM NITRATE–DIMETHYL SULPHOXIDE

Jindřich NOVÁK, Zdeněk KODEJŠ and Ivo SLÁMA

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

Received November 26th, 1982

The density, viscosity, and electrical conductivity of highly concentrated solutions of ammonium nitrate in dimethyl sulphoxide have been determined over the temperature range 10—60°C and the concentration range 7—50 mol% of the salt. The variations in the quantities as a function of temperature and concentration have been correlated by empirical equations. A comparison is made between the transport properties for the present system, aqueous solutions of ammonium nitrate, and calcium nitrate solutions in dimethyl sulphoxide.

In a previous study[1] concerned with the glass-forming ability of some inorganic salts in dimethyl sulphoxide (DMSO), it was found that ammonium nitrate solutions in DMSO form glasses on quenching in liquid nitrogen over a wide concentration range (20—50 mol % of salt). No glass is produced by quenching aqueous solutions of ammonium nitrate. It is well known[2-4] that glass-forming solutions of inorganic salts exhibit the so called non-Arrhenius behaviour around the liquidus temperatures, and that the apparent activation energies of their transport properties increase progressively with decrease in temperature. At the temperature T_0, which is close to the glass transition temperature T_g, the apparent activation energies of transport processes reach values several times those found in the region above the liquidus temperature. Another factor that has a large effect on transport properties of highly concentrated solutions of inorganic salts in water[3,4] and in non-aqueous solvents[5,6] is the salt concentration: the viscosity increases while the molar conductivity decreases progressively with increasing salt concentration.

The aim of the present work was to determine transport properties of ammonium nitrate solutions in DMSO and to compare them with those of aqueous solutions of ammonium nitrate and solutions of other salts in DMSO.

EXPERIMENTAL

Analytical grade ammonium nitrate and DMSO (Merck) were used for sample preparation. The DMSO was a dry product, with a maximum water content of 0·03%. The original NH_4NO_3 was dried in a vacuum oven at a temperature not exceeding 90°C, and the anhydrous salt obtained was stored in a desiccator over phosphorus pentoxide. Samples of required concentration were made up by dissolving weighed amounts of the salt in DMSO. The solution concentrations were not checked analytically, since electrical conductivity determination before and after measurements confirmed that no concentration changes occurred during the measurements.

The density was measured by means of a DMA 40 digital vibration densimeter (Paar, Austria) with an accuracy of $\pm 5 \cdot 10^{-4}$ g cm^{-3}.

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

The electrical conductivity was measured on a BM 484 Tesla semi-automatic bridge. The conductivity cells used had cell constants of 183·32, 167·32, and 160·77 cm^{-1}.

Molar conductivities of samples were calculated from measured conductivities, $\varkappa$ (S cm^{-1}), and densities, d (g cm^{-3}), using the relationship

$$\Lambda = \frac{\varkappa}{d}\left(M_1 \frac{1-x}{x} + M_2\right), \qquad (1)$$

where M_1 and M_2 are the molar masses of solvent and salt, respectively, and x is the mole fraction of salt in solution.

RESULTS AND DISCUSSION

The density of the system NH_4NO_3–DMSO was measured as a function of temperature and concentration over the temperature range $5 \leqq t \leqq 60$°C and the salt concentration range $0{\cdot}07 \leqq x \leqq 0{\cdot}50$. The results were fitted to the empirical equation

$$d = \sum_{i=1}^{3} t^{i-1} \sum_{j=1}^{4} a_{ij} x^{j-1}, \qquad (2)$$

where d is the density (g cm^{-3}), t is the temperature (°C), and x is the mole fraction of salt in the system. The calculated parameters of Eq. (2) are given in Table I.

The viscosity and electrical conductivity were measured over the same concentration range as above, and at temperatures within the ranges $5 \leqq t \leqq 60$°C and $12 \leqq t \leqq 60$°C, respectively.

For highly concentrated NH_4NO_3–DMSO solutions, the dependences of ln Λ and ln φ (fluidity $\varphi = 1/\eta$) on $1/T$ do not follow the Arrhenius equation, as is after all commonly observed for a number of highly concentrated salt solutions[2-6]. It may

TABLE I

Parameters, a_{ij}, of Eq. (2) for density calculation. The mean relative deviation $\delta = 0{\cdot}043\%$

j	$i = 1$	$i = 2$	$i = 3$
1	1·12137	$-1{\cdot}1345 \cdot 10^{-3}$	$1{\cdot}2392 \cdot 10^{-6}$
2	$4{\cdot}0522 \cdot 10^{-1}$	$2{\cdot}5215 \cdot 10^{-3}$	$-9{\cdot}7490 \cdot 10^{-6}$
3	$-1{\cdot}9983 \cdot 10^{-1}$	$-6{\cdot}5024 \cdot 10^{-3}$	$2{\cdot}8680 \cdot 10^{-5}$
4	$3{\cdot}0596 \cdot 10^{-1}$	$6{\cdot}1089 \cdot 10^{-3}$	$-2{\cdot}5261 \cdot 10^{-5}$

however be noted that departures from Arrhenius behaviour for this system are far smaller than those found for $Ca(NO_3)_2$–H_2O and $Ca(NO_3)_2$–DMSO, the systems which have so far been studied most extensively in this respect[5].

Rather surprisingly, the dependence of $\ln \Lambda$ or of $\ln \varphi$ on x for NH_4NO_3–DMSO is represented by a curve convex with respect to the x-axis. With all the systems studied so far the reverse is true[3,7,8].

The data for viscosity and molar conductivity as functions of the salt concentration and the temperature were fitted to the previously proposed equations[9]

$$\ln \eta = A_1 + A_2 x + (B_1 + B_2 x)/(T - T_1 - T_2 x) \qquad (3)$$

$$\ln \Lambda = A_1 + A_2 x + A_3 x^2 + (B_1 + B_2 x + B_3 x^2)/(T - T_1 - T_2 x - T_3 x^2), \qquad (4)$$

where x is the mole fraction of salt, and T(K) is the temperature. The parameters of the above equations were calculated from a set of experimental data by using an optimization technique, and are listed in Table II. The equations provide satisfactory fits as judged from the values of average relative deviations between experimental and calculated viscosity and molar conductivity values. The dependences of fluidity and molar conductivity on salt concentration and temperature are represented in Figs 1 and 2, respectively. The measured range extends somewhat deeper below the liquids curve only at $x = 0{\cdot}50$. The viscosity at this concentration and 50°C, *i.e.* on the liquids curve, has a value of 0·0247 Pa s. As has been shown previously[9], aqueous systems whose viscosities at the liquidus temperatures $\geqq 0{\cdot}02$ Pa s tend to form glass on sufficiently rapid quenching. For the system $Ca(NO_3)_2$–DMSO the

TABLE II

Parameters of Eqs (*3*) and (*4*) for the calculation of viscosity and molar conductivity, respectively

i	A_i	B_i	T_i	δ, %
		viscosity		
1	−8·65	361	144·0	2·6
2	−3·86	2 002	−37·6	
		molar conductivity		
1	5·492	−345·4	155·5	
2	−5·122	−590·4	1·806	0·5
3	9·095	315·2	124·6	

viscosity at the liquidus temperature, corresponding to the low-concentration limit of glass-forming ability, is about 0·04 Pa s, so that the glass formation requires a higher viscosity in this case. For the system NH_4NO_3–DMSO we were able to measure the viscosity at the liquidus temperature ($x = 0{\cdot}50$; $t = 50°C$), where its value is 0·0247 Pa s. Application of the same cooling method as used with $Ca(NO_3)_2$–DMSO allowed the system to be brought into the glassy state. Even though no difficulties were encountered in supercooling NH_4NO_3-DMSO samples with $x = 0{\cdot}50$ by *c.* 30–40°C, rapid crystallization mostly occurred afterwards so that viscosity or conductivity could not be measured over the entire temperature range from *c.* 10 to 60°C. It was apparent that the crystallization was additionally initiated by the presence of platinum black covered electrodes.

Both the molar conductivity and fluidity decrease as the salt concentration is increased and the temperature is decreased. If the decrease in molar conductivity with increasing salt concentration were due only to an increase in viscosity, then the magnitude of the Walden product $w = \Lambda\eta$ should be constant. However, this is not the case with the present system (Fig. 3). At 10°C, the values of w increase starting from the lowest salt concentration, $x = 0{\cdot}077$. Increasing the temperature mitigates the effect: at 40°C no marked increase in w is observed until $x = 0{\cdot}20$. At 60°C the $x-w$ plot shows even a minimum at *c.* $x = 0{\cdot}15$. It may be assumed that at low temperatures association of a part of the NH_4^+ and NO_3^- ions occurs as the salt concentration is increased. This effect is diminished with increase in temperature. As a result, the

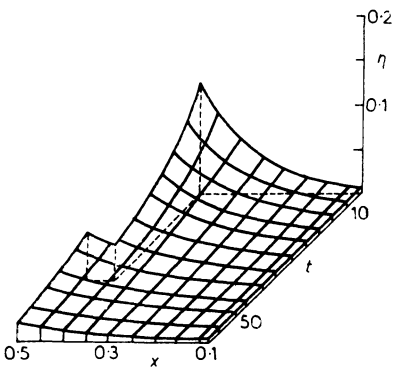

FIG. 1

Viscosity, η (Pa s), as a function of temperature, t (°C), and mole fraction, x, of salt for the system NH_4NO_3–DMSO

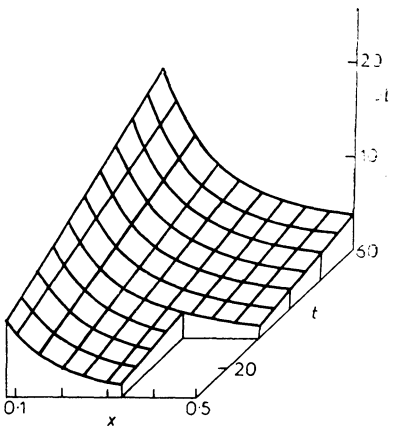

FIG. 2

Molar conductivity, Λ (S cm^2 mol^{-1}), as a function of temperature, t (°C), and mole fraction, x, of salt for the system NH_4NO_3–DMSO

molar conductivity changes more rapidly than does the viscosity as the temperature and the salt concentration are increased. The variation of the Walden product with temperature is practically linear over the whole temperature and concentration ranges investigated.

Comparison of the electrical conductivity behaviour of the systems NH_4NO_3–H_2O and NH_4NO_3–DMSO, based on the values of conductivity, $\varkappa$, will now be made, using published data for the aqueous system[10,11]. Fig. 4 shows the variation in the conductivity of the system NH_4NO_3–DMSO as a function of the salt concentration at several temperatures. At temperatures below 40°C both systems show distinct absolute maxima in the conductivity *versus* concentration plots. At higher temperatures, the maximum is only local for the non-aqueous system, and the conductivity goes on rising as the salt concentration is further increased. Besides, the maximum in the $x-\varkappa$ plot for the aqueous system lies at $x = 0{\cdot}196$ over a wide range of temperatures, while for the system NH_4NO_3–DMSO the position of the maximum is a linear function of temperature within a concentration range $0{\cdot}13 \leqq x \leqq 0{\cdot}22$. The shift in the position of the maximum is considered to be the result of changes in the extent of hydration, or more generally solvation, of ions present in the system[12,13]. The independence of the position of the maximum for the aqueous system on the temperature is the exception rather than the rule. As shown by Fedotov[12], the maxima in $\varkappa = f(x)$ for a series of alkaline metal salts do not change in position in the cases where there is neglible hydration of the ions present, *e.g.*

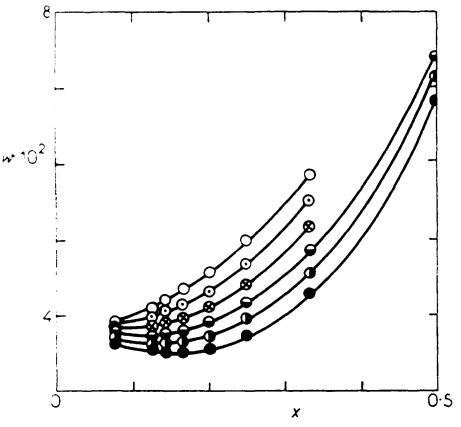

FIG. 3

The Walden product, w, as a function of mole fraction, x, of ammonium nitrate at various temperatures: ○ 10, ⊙ 20, ⊗ 30, ◒ 40, ◑ 50, ● 60°C

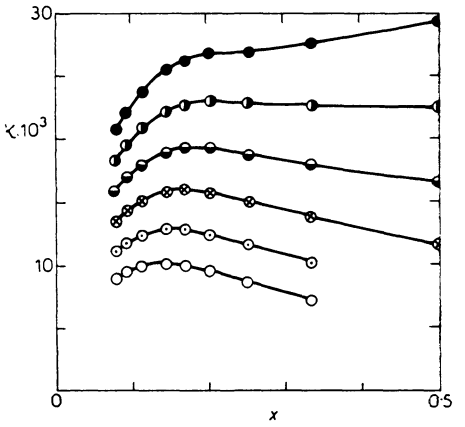

FIG. 4

Variation in conductivity, $\varkappa$ (S cm^{-1}), with mole fraction, x, of ammonium nitrate at various temperatures: ○ 10, ⊙ 20, ⊗ 30, ◒ 40, ◑ 50, ● 60°C

with cesium salts. For hydrated ions the maxima are shifted to higher salt concentrations as the temperature is increased. This is just the behaviour shown by the system NH_4NO_3–DMSO. The fixed position of maxima for the system NH_4NO_3–H_2O may be indicative of a small degree of hydration of the NO_3^- and NH_4^+ ions, whilst the shift of the maximum for NH_4NO_3–DMSO may reflect a certain degree of solvation in thisy system. That the interactions in the system NH_4NO_3–DMSO are stronger compared with those in the analogous aqueous system is also confirmed by the change in the ratios of viscosities and molar conductivities on going from the pure solvents to NH_4NO_3–DMSO and NH_4NO_3–H_2O solutions (Fig. 5): while the viscosity of pure DMSO is only about twice that for H_2O, the relative increase on addition of NH_4NO_3 in an amount corresponding to $x = 0{\cdot}30$ is about tenfold.

As shown by Letellier and Gaboriaud[14], the ionic radii of the nitrate ion in aqueous and DMSO solutions of alkali metal nitrates are not much different (198 and 208 nm, respectively). Hence it may be inferred that the ammonium ion will be solvated preferentially in DMSO. Fig. 6 shows plots of the ratios of molar conductivities and fluidities for the systems NH_4NO_3–DMSO and $Ca(NO_3)_2$–DMSO. Clearly, the effect of increasing the salt concentration on the molar conductivity is greater with $Ca(NO_3)_2$–DMSO than with NH_4NO_3–DMSO. This implies that the NH_4^+ ions is less solvated in DMSO than the Ca^{2+} ions. The analogous ratio of fluidities for the two systems is less affected by changes in the concentration of the salts. This

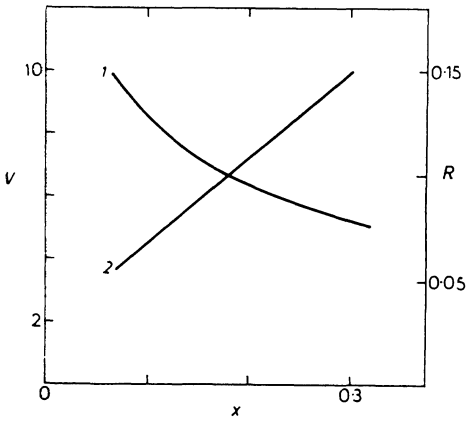

FIG. 5

Ratios of viscosities, V, and of molar conductivities, R, for the systems NH_4NO_3–DMSO and NH_4NO_3–H_2O as functions of mole fraction, x, of ammonium nitrate at 25°C: *1* R, *2* V

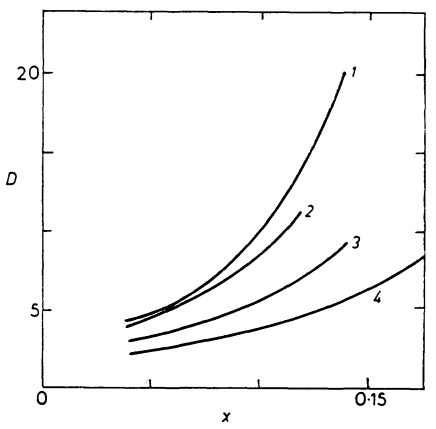

FIG. 6

Ratios, D, of molar conductivities and of fluidities for the systems NH_4NO_3–DMSO and $Ca(NO_3)_2$–DMSO as functions of mole fraction, x, of salt: *1* Λ 15°C, *2* φ 15°C, *3* Λ 60°C, *4* φ 60°C

may most probably be ascribed to the strengthening of ionic interactions in the systems as the number of solvent molecules is reduced, an effect which has a greater impact on conductivity than on fluidity.

REFERENCES

1. Malá J., Sláma I.: Chem. Zvesti *35*, 207 (1981).
2. Angell C. A., Sare E. J.: J. Chem. Phys. *52*, 1058 (1970).
3. Angell C. A., Bressel R. D.: J. Phys. Chem. *76*, 3243 (1972).
4. Ambrus J. H., Moynihan C. T., Macedo P. B.: J. Electrochem. Soc. *119*, 192 (1972).
5. Kodejš Z., Novák J., Sláma I.: Chem. Zvesti *35*, 515 (1981).
6. Novák J., Kodejš Z., Sláma I.: Chem. Zvesti, in press.
7. Angell C. A.: J. Phys. Chem. *70*, 3988 (1966).
8. Bressel R. D.: *Thesis*. Purdue University, Lafayette 1972.
9. Sláma I., Kodejš Z.: J. Solution Chem. *8*, 801 (1979).
10. Dubeau C., Sisi J.-Ch.: J. Chem. Eng. Data *14*, 153 (1969).
11. Gaur H. C., Sharma R. C.: Ind. J. Chem. *15A*, 84 (1977).
12. Fedotov N. V.: Zh. Fiz. Khim. *53*, 2398 (1979).
13. Valyashko V. M., Ivanov A. A.: Zh. Neorg. Khim. *14*, 2752 (1979).
14. Letellier P., Gaboriaud R.: J. Chim. Phys. Physicochim. Biol. *78*, 829 (1981).

Translated by M. Škubalová.