THE DENSITY AND VISCOSITY OF CONCENTRATED SOLUTIONS OF SILVER NITRATE IN DIMETHYL SULPHOXIDE

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Densities and viscosities of silver nitrate–dimethyl sulphoxide solutions have been measured at 5, 25, and 60°C over the range of salt mole fractions from 0·05 to 0·5. The dependence of viscosity on the salt concentration has been expressed by an empirical equation and compared with analogous dependences obtained for aqueous solutions of silver nitrate and solutions of other salts in dimethyl sulphoxide.

In previous studies[1-3] we measured densities and viscosities of solutions of $LiNO_3$, NH_4NO_3, and $Ca(NO_3)_2$ in dimethyl sulphoxide (DMSO) with the aim to elucidate, by comparison with aqueous solutions, the role of DMSO and the influence of its properties and structure on the density and viscosity of highly concentrated solutions. As all the systems involved a common anion, we also studied how the density and viscosity varied with the nature of the cation.

Our interest in solutions of $AgNO_3$ in DMSO has been stimulated by extensive sets of experimental data[4] on the properties of aqueous solutions of $AgNO_3$, which can be used for comparative purposes.

The aim of the present work was to measure densities and viscosities of $AgNO_3$–DMSO solutions at three chosen temperatures over as wide a concentration range as possible, and to compare the results with those published for aqueous solutions of $AgNO_3$ or previously obtained for other nitrates in DMSO.

EXPERIMENTAL

Solutions were made up from DMSO of analytical grade (Merck; dried, a maximum water content of 0·03%) and $AgNO_3$ of the same grade, which had been recrystallized, dried first under vacuum at 60°C and then to constant weight at a temperature not exceeding 80°C. The water content of DMSO was checked by Karl Fischer method. The analytically determined values of the water content agreed with those stated by the manufacturer to within the accuracy of the analytical method used.

Samples of desired compositions were prepared by weight, and the salt concentrations were checked analytically. The maximum relative error in the values of the salt mole fraction given below is $\pm 0·5\%$.

The density was measured by a DMA 40 digital vibration densimeter (Paar). From an analysis of the calibration method and the precision of temperature control, the accuracy of measured densities was estimated to be better than $\pm 4 . 10^{-4}$ g cm^{-3}.

Viscosities were measured to an accuracy of $\pm 0.5\%$ with Ubbelohde viscometers. In calculating each viscosity value from an average flow-time of a minimum of three runs, the viscometer constant stated by the manufacturer was used and the kinetic energy correction was applied.

The determinations of densities and viscosities of solutions over the range of salt mole fractions $0.02-0.5$ were made at temperatures of 5, 25, and 60°C provided the samples were stable at these temperatures and no solid phase separation occurred.

RESULTS AND DISCUSSION

Experimentally determined values of density and kinematic viscosity are listed in Table I. The dependence of the viscosity on the salt concentration at constant temperature was expressed by the empirical equation

$$\eta = b_1 \exp\left(b_2 x + b_3 x^2\right), \qquad (1)$$

TABLE I

Densities and viscosities of AgNO$_3$–DMSO solutions

x	5°C		25°C		60°C	
	d, g cm^{-3}	η, mPa s	d, g cm^{-3}	η, mPa s	d, g cm^{-3}	η, mPa s
0	—	—	1·0956	2·005	1·0607	1·114
0·0201	—	—	1·1367	2·439	1·1017	1·317
0·0272	—	—	1·1510	2·614	1·1161	1·394
0·0496	—	—	1·1986	3·246	1·1632	1·663
0·0701	—	—	1·2405	3·956	1·2050	1·953
0·101	1·3250	—	1·3048	5·376	1·2688	2·512
0·120	—	—	1·3461	6·577	1·3099	2·932
0·140	1·4129	17·08	1·3925	8·271	1·3561	3·526
0·179	1·5045	30·48	1·4839	13·36	1·4471	5·108
0·224	1·6064	60·11	1·5851	22·86	1·5479	7·646
0·242	—	—	1·6286	26·66	1·5912	8·489
0·256	—	—	1·6649	33·50	1·6272	10·02
0·284	1·7600	186·98	1·7381	52·64	1·6998	13·82
0·348	—	—	1·8943	110·6	1·8546	22·28
0·353	—	—	—	—	1·8772	25·68
0·398	—	—	2·0429	290·4	2·0023	41·03
0·489	2·3252	15 188	2·3008	1 116	2·2602	87·43

where b_1, b_2, and b_3 are empirical parameters, and x is the mole fraction of salt in solution. The calculated values of the parameters are given in Table II. Applicability of this equation to the description of the concentration dependence of viscosity of highly concentrated solutions has previously been verified for several systems and its connection with some theoretical models of transport properties has been pointed out[5].

The variation in viscosity with concentration is shown in Fig. 1, along with results for solutions of other salts[1-3] in DMSO and for the aqueous solution of $AgNO_3$ (ref.[4]).

The accumulated data allow us to assess the influence of $AgNO_3$ concentration on the viscosity of $AgNO_3$–DMSO solutions and to compare the silver ion with Li^+, NH_4^+, and Ca^{2+} with respect to their influence on the structure of solution, as in all the cases we are dealing with nitrate solutions.

Comparison of enthalpies of vaporization of water from highly concentrated solutions of silver, ammonium, and lithium nitrates has shown that Ag^+ and NH_4^+

TABLE II

Values of the parameters of Eq. (*1*)

Values	5°C	25°C	60°C
b	3·021	2·028	1·0972
b_2	10·2501	8·8810	8·2511
b_3	14·6920	8·3433	1·6329
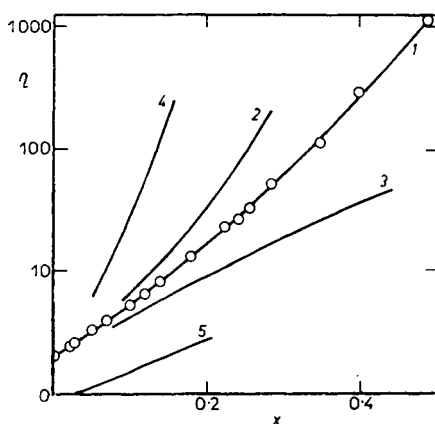
FIG. 1

The viscosity, η(mPa s), as a function of the salt mole fraction, x, at 25°C; *1* $AgNO_3$–DMSO; *2* $LiNO_3$–DMSO; *3* NH_4NO_3–DMSO; *4* $Ca(NO_3)_2$–DMSO; *5* $AgNO_3$–H_2O

ions, unlike Li^+, are practically unhydrated, indicating that they have no pronounced influence on the solution structure[6]. The same conclusion can be drawn from the concentration dependence of vapour pressure or from the related data for the energy of transfer of water from its bulk phase to a concentrated salt solution. For $AgNO_3$ and $Ca(NO_3)_2$ solutions these data have been published by Abraham[7], and for $LiNO_3$ and NH_4NO_3 by Sacchetto[8]. Thus, the strength of ion-solvent interactions in concentrated aqueous solutions follows the order $NH_4^+ < Ag^+ < Li^+ < Ca^{2+}$. This ordering is in accord with conclusions in terms of the structure-breaking and structure-making effects of the ions which have been drawn for dilute solutions of these salts.

The interactions of dissolved salts with DMSO molecules are generally stronger than those with water, as can be judged from results for the vapour pressure of solvent (DMSO or H_2O) above solutions of some salts[9,10], but the order of the ions with respect to the strength of interaction need not, in general, be the same for the two solvents. This conclusion is supported by comparison of viscosities of $AgNO_3$ solutions in water and in DMSO (Fig. 1, curves *1* and *5*).

In DMSO solutions, the two methyl groups sterically shield the positive pole of the solvent molecule dipole, so reducing the probability of anion solvation compared with aqueous solutions. In comparing the interactions of the various salts with a molecule of DMSO, we may therefore assume that the differences observed in the properties of the solutions are virtually identical with differences in cation–DMSO interactions. If we adopt the assumption that the strength of ion–solvent interactions has a profound influence on the viscosity of a solution, we can use viscosity isotherms shown in Fig. 1 for several salts in DMSO to compare the strengths of interactions between the ions involved and the solvent over a wide concentration range. Subject to this assumption, the ordering $NH_4^+ < Ag^+ < Li^+ < Ca^{2+}$ applies to DMSO solutions as well.

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