

## DENSITY AND VISCOSITY OF THE SYSTEM $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O-DIMETHYL SULPHOXIDE}$

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The density and viscosity of the ternary system  $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O-dimethyl sulphoxide}$  were measured over the temperature range  $0 < t < 60^\circ\text{C}$ , with the mole fraction of the salt in the system varied in the range  $0.05 < x < 0.16$ . The temperature and concentration dependences of density and viscosity have been described by empirical equations. The viscosity data show a pronounced dependence on the solvent composition. Maximum deviations of viscosity from the ideal additive behaviour of the two salt-solvent binary systems occur at a mole fraction of DMSO in the mixed solvent of 0.3. The observed dependence is discussed in relation to the structure of the solution.

Previous studies on transport properties and the glass-forming and supercooling abilities of highly concentrated calcium nitrate solutions<sup>1-3</sup> have established that addition of another salt to the binary system  $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ , with the total salt concentration kept constant, generally leads to an increase in viscosity of the system<sup>4</sup>. Also enhanced on addition of a third component is the ability of the system to exist in the supercooled metastable state. All the studies so far reported have used a salt as the third component. It was thus of interest to see what effect the addition of another solvent might have on the behaviour of the binary water-salt system. The aim of the present work was to study the effect of replacing water by dimethyl sulphoxide (DMSO) on the viscosity of the system  $\text{Ca}(\text{NO}_3)_2\text{-solvent}$  at a constant salt concentration. This study is a continuation of our previous work<sup>5</sup> on the viscosity of the binary system  $\text{Ca}(\text{NO}_3)_2\text{-DMSO}$ .

### EXPERIMENTAL

Dimethyl sulphoxide was Merck analytical grade. Anhydrous calcium nitrate was prepared from the salt tetrahydrate (Lachema) by drying in a vacuum oven at a temperature not exceeding  $160^\circ\text{C}$ , and then over phosphorus pentoxide until constant weight. Ternary solutions of desired compositions were made up by weighing all the three components. Calcium ion concentrations of the sample were checked chelatometrically.

The temperature dependences of the density and viscosity of the samples were followed over the temperature range  $5\text{--}60^\circ\text{C}$ . The proportion of the two solvents in the sample was expressed in terms of the mole fraction of DMSO,  $y_{\text{DMSO}} = n_{\text{DMSO}}/(n_{\text{H}_2\text{O}} + n_{\text{DMSO}})$ , where  $n_{\text{H}_2\text{O}}$  and

$n_{\text{DMSO}}$  denote the amounts of H<sub>2</sub>O and DMSO, respectively. The DMSO mole fraction of the samples was varied between 0.1 and 0.8 in steps of 0.1. In most cases six sample with the calcium nitrate mole fraction in the range  $0.05 < x < 0.16$  were prepared for each solvent composition. The temperature range of stability of the most concentrated solutions varied according to the water: DMSO ratio in the system.

The sample density was measured using a Paar DMA 40 digital densimeter accurate to better than  $5 \cdot 10^{-4} \text{ g cm}^{-3}$ . The viscosity was measured by a BH 2 Höppler viscometer with an accuracy of  $\pm 1\%$ . The viscosity values are given in Pa.s units.

## RESULTS

Sets of experimental data on density measured at constant solvent compositions characterized by DMSO mole fractions,  $y_{\text{DMSO}}$ , were fitted to a polynomial approximating the variation in viscosity of the pseudobinary system Ca(NO<sub>3</sub>)<sub>2</sub>-solvent as a function of temperature and salt concentration:

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

where  $t$  denotes the temperature (°C) and  $x$  the mole fraction of calcium nitrate in the system. The values of the coefficients  $a_{ij}$ , calculated on the basis of a set of about 40 data points for each  $y_{\text{DMSO}}$  value, are given in Table I. These values were used to calculate the densities of the solutions in evaluation of experimental data on viscosity. The number of significant figures of the coefficients in Table I has been adjusted to be consistent with their weight in the density calculation. In no case did the relative deviations between calculated and experimental density values exceed 0.2%, in accord with the accuracy of the density determination. Empirical character of Eq (1) and the large number of coefficients involved do not allow conclusions to be made about the dependence of the coefficient value on the solvent composition ( $y_{\text{DMSO}}$ ).

To evaluate the dependence of viscosity ( $\eta$ ) on the solvent composition, it was necessary to approximate the dependence of the viscosity of the pseudobinary solution on the salt concentration and temperature by a suitable function. As in previous papers<sup>5,6</sup> we chose the relationship

$$\ln \eta = A_1 + A_2 x + (B_1 + B_2 x)/(T - T_1 - T_2 x), \quad (2)$$

where  $T$  denotes the temperature (K), and  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$ ,  $T_1$  and  $T_2$  are empirical parameters.

The parameters of Eq. (2) were calculated using sets of experimental data on viscosity measured over the above given temperature and concentration ranges at constant  $y_{\text{DMSO}}$  values. The resulting values of the parameters are given in Table II

TABLE I  
Values of parameters of Eq. (1)

<i>i/j</i>	<i>a<sub>ij</sub></i>			
	1	2	3	4
<i>y<sub>DMSO</sub></i> = 0.0				
1	1.006	6.669	-1.930 · 10 <sup>1</sup>	2.543 · 10 <sup>1</sup>
2	-1.611 · 10 <sup>-4</sup>	-1.119 · 10 <sup>-2</sup>	5.709 · 10 <sup>-2</sup>	-9.474 · 10 <sup>-2</sup>
3	-3.095 · 10 <sup>-6</sup>	4.324 · 10 <sup>-5</sup>	-2.058 · 10 <sup>-4</sup>	3.360 · 10 <sup>-4</sup>
<i>y<sub>DMSO</sub></i> = 0.1				
1	1.051	4.981	-1.280 · 10 <sup>1</sup>	2.078 · 10 <sup>1</sup>
2	-2.623 · 10 <sup>-4</sup>	-1.151 · 10 <sup>-2</sup>	7.671 · 10 <sup>-2</sup>	-1.769 · 10 <sup>-1</sup>
3	-5.559 · 10 <sup>-6</sup>	1.535 · 10 <sup>-4</sup>	-1.358 · 10 <sup>-3</sup>	3.856 · 10 <sup>-3</sup>
<i>y<sub>DMSO</sub></i> = 0.2				
1	1.119	2.715	2.899	-2.109 · 10 <sup>1</sup>
2	-6.824 · 10 <sup>-4</sup>	4.435 · 10 <sup>-4</sup>	-3.041 · 10 <sup>-2</sup>	1.168 · 10 <sup>-1</sup>
3	-2.904 · 10 <sup>-7</sup>	-2.257 · 10 <sup>-5</sup>	4.169 · 10 <sup>-4</sup>	-1.389 · 10 <sup>-3</sup>
<i>y<sub>DMSO</sub></i> = 0.3				
1	1.106	3.100	-6.384	1.808 · 10 <sup>1</sup>
2	-1.171 · 10 <sup>-3</sup>	1.466 · 10 <sup>-2</sup>	-1.769 · 10 <sup>-1</sup>	6.301 · 10 <sup>-1</sup>
3	8.289 · 10 <sup>-6</sup>	-3.206 · 10 <sup>-4</sup>	3.737 · 10 <sup>-3</sup>	-1.336 · 10 <sup>-2</sup>
<i>y<sub>DMSO</sub></i> = 0.4				
1	1.105	2.991	-7.221	1.606 · 10 <sup>1</sup>
2	-6.766 · 10 <sup>-4</sup>	-4.320 · 10 <sup>-3</sup>	4.168 · 10 <sup>-2</sup>	-1.351 · 10 <sup>-1</sup>
3	-3.409 · 10 <sup>-6</sup>	9.757 · 10 <sup>-5</sup>	-9.418 · 10 <sup>-4</sup>	2.838 · 10 <sup>-3</sup>
<i>y<sub>DMSO</sub></i> = 0.5				
1	1.128	2.129	-9.395 · 10 <sup>-1</sup>	-9.258 · 10 <sup>-1</sup>
2	-6.244 · 10 <sup>-4</sup>	-5.737 · 10 <sup>-3</sup>	4.569 · 10 <sup>-2</sup>	-1.306 · 10 <sup>-1</sup>
3	-5.207 · 10 <sup>-6</sup>	1.386 · 10 <sup>-4</sup>	-1.213 · 10 <sup>-3</sup>	3.542 · 10 <sup>-3</sup>
<i>y<sub>DMSO</sub></i> = 0.6				
1	1.124	2.157	-2.698	3.377
2	-8.665 · 10 <sup>-4</sup>	-1.793 · 10 <sup>-4</sup>	2.318 · 10 <sup>-3</sup>	-1.238 · 10 <sup>-2</sup>
3	-4.862 · 10 <sup>-7</sup>	9.416 · 10 <sup>-6</sup>	-8.840 · 10 <sup>-5</sup>	2.717 · 10 <sup>-6</sup>

TABLE I  
(Continued)

<i>ijj</i>	<i>a<sub>ij</sub></i>			
	1	2	3	4
<i>x</i> <sub>DMSO</sub> = 0.7				
1	1.125	2.000	-2.314	2.780
2	-1.011 · 10 <sup>-3</sup>	3.519 · 10 <sup>-3</sup>	-3.401 · 10 <sup>-2</sup>	9.121 · 10 <sup>-2</sup>
3	4.344 · 10 <sup>-8</sup>	-8.671 · 10 <sup>-6</sup>	1.526 · 10 <sup>-4</sup>	-4.894 · 10 <sup>-4</sup>
<i>y</i> <sub>DMSO</sub> = 0.8				
1	1.123	1.855	-1.484	4.115 · 10 <sup>-1</sup>
2	-9.057 · 10 <sup>-4</sup>	-9.167 · 10 <sup>-4</sup>	1.565 · 10 <sup>-2</sup>	-6.384 · 10 <sup>-2</sup>
3	-4.725 · 10 <sup>-8</sup>	9.786 · 10 <sup>-6</sup>	-1.947 · 10 <sup>-4</sup>	8.457 · 10 <sup>-4</sup>
<i>y</i> <sub>DMSO</sub> = 1.0				
1	1.120	1.627	-1.374 · 10 <sup>-1</sup>	-3.508
2	-8.965 · 10 <sup>-4</sup>	-2.066 · 10 <sup>-3</sup>	2.716 · 10 <sup>-2</sup>	-1.188 · 10 <sup>-1</sup>
3	-8.673 · 10 <sup>-7</sup>	3.217 · 10 <sup>-5</sup>	-3.307 · 10 <sup>-4</sup>	1.244 · 10 <sup>-3</sup>

along with previously published<sup>5,6</sup> values of parameters of Eq. (2) for the binary systems Ca(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O and Ca(NO<sub>3</sub>)<sub>2</sub>-DMSO. Because Eq. (2) is of semiempirical character and its parameters are interdependent, one cannot expect the parameters to be smooth and definite functions of *x*<sub>DMSO</sub>.

## DISCUSSION

The effect of change in the solvent composition on the density of the system is illustrated in Fig. 1. Substitution of DMSO for water molecules results in a decrease in the density of the system. The decrease is marked even at low DMSO concentrations, indicating a strong potency of DMSO molecules in disrupting the structure of aqueous solution of calcium nitrate. This effect becomes more pronounced as the salt concentration in the system is increased. The broken line in Fig. 1 is a plot of the relative deviation, *d*<sub>exp</sub>/*d*<sub>ad</sub>, of experimentally found density from the value calculated on the assumption of additivity of the densities of the two binary systems against the solvent composition (H<sub>2</sub>O + DMSO). At constant temperature and Ca(NO<sub>3</sub>)<sub>2</sub> concentration, maximum deviation is found to occur at *y*<sub>DMSO</sub> = 0.4.

TABLE II  
Value of parameters of Eq. (2)

$\gamma$	$A_1$	$A_2$	$B_1$	$B_2$	$T_1$	$T_2$
0.0	- 8.920	—	290.2	2 341	135.2	328.8
0.1	-11.08	8.552	1 035	-702.1	74.46	678.9
0.2	-11.65	4.342	1 418	-999.7	58.26	737.8
0.3	-10.75	4.997	973.6	574.2	105.9	513.8
0.4	- 9.118	-5.034	513.8	3 655	149.6	223.4
0.5	- 9.571	-2.333	620.4	3 167	138.2	277.1
0.6	- 9.121	-8.802	524.8	4 684	139.9	216.8
0.7	- 9.221	-3.243	507.1	3 619	140.5	255.2
0.8	- 8.539	-3.669	303.4	3 828	165.1	157.3
1.0	-10.01	—	670.7	3 034	115.4	315.3

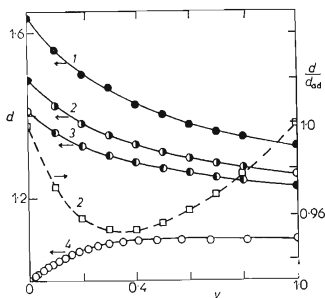


FIG. 1

Density,  $d$  ( $\text{g cm}^{-3}$ ), and relative deviation of density,  $d/d_{ad}$ , from additive behaviour of the ternary system  $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O-DMSO}$  as functions of solvent composition,  $\gamma_{\text{DMSO}}$ , at  $25^\circ\text{C}$ : 1  $x = 0.15$ ; 2  $x = 0.1$ ; 3  $x = 0.08$ ; 4  $x = 0$

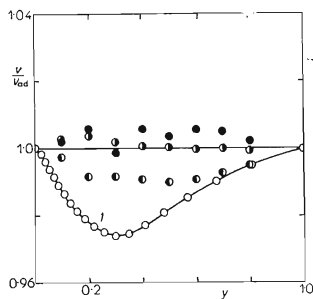


FIG. 2

Relative deviation of the mean molar volume of solution as a function of solvent composition,  $\gamma_{\text{DMSO}}$ , at  $25^\circ\text{C}$ : 1  $\text{H}_2\text{O-DMSO}$ ; ●  $x = 0.15$ ; ○  $x = 0.1$ ; ●  $x = 0.05$

Somewhat different results are obtained when the variation in the mean molar volume of solution is studied as a function of the solvent composition. The mean molar volume is calculated by dividing the mean molecular mass ( $\bar{M} = 164.09x + 18.02(1-x)(1-y) + 78.13(1-x)y$ ) by the density of the solution. The results are shown in Fig. 2. For the mixed solvent alone ( $x = 0$ ) marked deviations from additivity are found, consistent with the existence of positive deviations of the densities<sup>7</sup>. As calcium nitrate is added, the deviations sharply decline, becoming practically zero in the region of concentrated solutions. The negative deviations from additive behaviour of the two solvents have been explained as a result of closer packing due to hydrogen bonding, and possibly also to accommodation of DMSO molecules in the vacancies in the water structure. In the highly concentrated calcium nitrate solutions with which we are concerned here, the original structures of the two solvents are already so disturbed that the formation of ternary system from the binary systems Ca(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O and Ca(NO<sub>3</sub>)<sub>2</sub>-DMSO is not associated with any further structural changes. Thus, from the viewpoint of molar volumes we are dealing with practically ideal mixing. Results obtained at the highest Ca(NO<sub>3</sub>)<sub>2</sub> concentration employed in this study ( $x = 0.15$ ) suggest that positive deviations of molar volumes from additivity may occur at still higher concentrations.

Like in the case of the density, the effect of the solvent composition on the viscosity of the system was evaluated using the quantity  $\eta/\eta_{ad}$ , i.e. the ratio of the actual viscosity of the solution to the viscosity which the solution of a given salt concentration would have at a given temperature if the additivity principle for the properties of the two binary systems Ca(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O and Ca(NO<sub>3</sub>)<sub>2</sub>-DMSO of the same salt concentration was obeyed. In this way one can eliminate the effect of different viscosities of the two binary systems at the same temperature and calcium nitrate concentration, as discussed previously<sup>5</sup>.

The effect of gradual replacement of water molecules by the molecules of DMSO was investigated at several temperatures and salt concentrations. The results (Fig. 3) show that in each of the cases involved there is a marked positive deviation from the additivity principle for the properties of the two binary systems. For all the cases, the maximum deviation occurs within the  $y_{DMSO}$  range 0.3-0.4, and the magnitude of the deviation becomes larger as the salt concentration goes up. The effect of increasing the salt concentration parallels that of decreasing the temperature.

It is of interest to examine how deviations of viscosities from additivity and absolute viscosity values, which in a sense are a measure of the strength of interactions in solution, are interrelated. The plot of  $\eta/\eta_{ad}$  vs  $\ln \eta$  (Fig. 4) clearly demonstrates that the deviations from additivity do not arise solely as a result of stronger interactions between the species, as evidenced by the considerable scatter of experimental points obtained at various temperatures and salt concentrations about the fitted line. The shapes of the curves in Fig. 4 document that the magnitude of the deviation is again directly related to the ratio of water to DMSO molecules in the system.

It is therefore necessary to consider the relation between the structure, and hence the properties, of the solvent and the properties of the pseudobinary system. The mixed solvent  $\text{H}_2\text{O} + \text{DMSO}$  has been dealt with in a number of papers, frequently with conflicting conclusions which have been discussed by Schichman and Amey<sup>8</sup> and Petrella and coworkers<sup>9</sup>. It is assumed that the maximum deviations from additivity found in viscosity and density and  $y_{\text{DMSO}} = 0.3$  are directly connected with the buildup of the aggregates  $\text{DMSO} \cdot 2 \text{H}_2\text{O}$  linked through interactions to the neighbouring molecules. The pattern of dependence of viscosity and of a number of other properties of the mixed solvent upon the solvent composition over the whole concentration range has been interpreted in terms of three models: quasi-clathrate structure of water molecules with inter-lattice position of DMSO molecules; a structure in which the complex  $\text{DMSO} \cdot 2 \text{H}_2\text{O}$  is the predominating species; dipolar structure based on dipole-dipole interactions<sup>10</sup>. However, the evidence advanced in support of these structures is inconclusive<sup>11</sup>, since DTA analysis<sup>12</sup> has only confirmed the existence of the compound  $\text{DMSO} \cdot 3 \text{H}_2\text{O}$ , and thus the position of the maximum deviation appears more likely to correspond to the eutectic point, as suggested previously<sup>13</sup>. The variation in the deviation of viscosity from additivity as a function of the

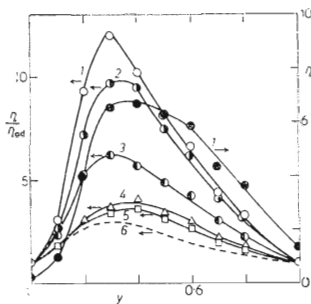


FIG. 3

Viscosity,  $\eta$  (Pa.s), and relative deviation of viscosity from additive behaviour,  $\eta/\eta_{ad}$ , as functions of solvent composition: 1  $x = 0.16$ ,  $5^\circ\text{C}$ ; 2  $x = 0.15$ ,  $5^\circ\text{C}$ ; 3  $x = 0.16$ ,  $25^\circ\text{C}$ ; 4  $x = 0.08$ ,  $25^\circ\text{C}$ ; 5  $x = 0.05$ ,  $25^\circ\text{C}$ ; 6  $\text{H}_2\text{O}$ -DMSO,  $25^\circ\text{C}$

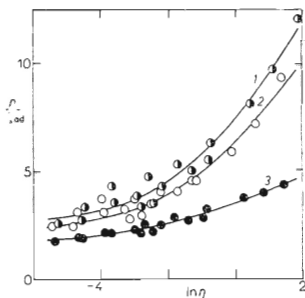


FIG. 4

Relative deviation of viscosity from additive behaviour as a function of viscosity of solution: 1  $y_{\text{DMSO}} = 0.3$ ; 2  $y_{\text{DMSO}} = 0.2$ ; 3  $y_{\text{DMSO}} = 0.7$

mixed solvent composition at 25°C is illustrated in Fig. 3 by the broken line, and the position of the maximum in this plot is seen to coincide with that for the ternary system.

In discussing our observations we must, therefore, start from two established facts. One is the coincidence of the positions of maximum deviations from additivity for several properties of the mixed H<sub>2</sub>O + DMSO solvent, explained in terms of structural aspects, and the other is the fact that at the highest salt concentration employed in this work, *i.e.*  $x = 0.16$ , the ratio of solvent to salt molecules in the solution is equal to 5, indicating that the original structure of the solvent is completely disrupted. This has also been confirmed by the results of the study of molar volumes. At higher salt concentrations, however, the deviations of viscosity from additivity are very pronounced.

The study of the temperatures of liquidus of the ternary system Ca(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O-DMSO provided only semiquantitative results<sup>14</sup>, but demonstrated the existence of a minimum in the variation of the eutonic temperature of the pseudobinary system Ca(NO<sub>3</sub>)<sub>2</sub>-solvent with composition, occurring within  $y_{\text{DMSO}}$  range from 0.2 to 0.4. Calcium nitrate concentrations ( $x$ ) at these eutonic points are assumed to range from 0.077 to 0.094.

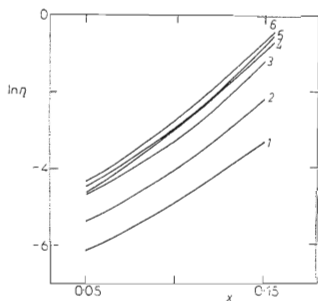


FIG. 5

Viscosity of the system Ca(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O-DMSO as a function of the salt concentration in solution at 25°C: 1  $y_{\text{DMSO}} = 0$ ; 2  $y_{\text{DMSO}} = 0.1$ ; 3  $y_{\text{DMSO}} = 0.2$ ; 4  $y_{\text{DMSO}} = 0.8$ ; 5  $y_{\text{DMSO}} = 0.3$ ; 6  $y_{\text{DMSO}} = 0.5$

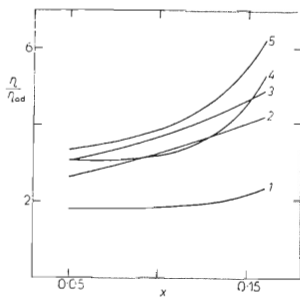


FIG. 6

Relative deviation of viscosity from additive behaviour as a function of salt concentration in solution at 25°C: 1  $y_{\text{DMSO}} = 0.1$ ; 2  $y_{\text{DMSO}} = 0.6$ ; 3  $y_{\text{DMSO}} = 0.5$ ; 4  $y_{\text{DMSO}} = 0.2$ ; 5  $y_{\text{DMSO}} = 0.3$



Considering the above facts we are led to the conclusion that the existence of deviations of viscosities of the ternary system  $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O-DMSO}$  from additivity with a maximum at  $y_{\text{DMSO}} = 0.3$  reflects changes in the properties of the solvent, and is not associated with the position of the eutectic point of the ternary system.

In the concentration range here investigated, the addition of calcium nitrate to the mixed solvent results in an increase in viscosity no matter what the solvent composition, as evident from Fig. 5. The viscosity-concentration curves for the pseudobinary systems are virtually parallel and reflect the shape of the viscosity  $-y_{\text{DMSO}}$  curve for the mixed solvent alone. It is interesting to note that the highest viscosity values do not coincide with maximum deviations from additivity. Specificity of the effect of calcium nitrate consists, however, in that the interactions which give rise to the nonlinearity of the dependence of the solvent viscosity on its composition are not only preserved, but even reinforced on addition of the salt, as documented in Fig. 6.

In view of the salt concentration in the system, we cannot assume the existence of the structure as considered in interpreting the occurrence of the maximum in the variation of the deviation of solvent viscosity from additivity on the solvent composition. Because of the small number of solvent molecules per mole of salt at the concentrations under study, we cannot speak of solvated ions moving freely in the solvent, since even the primary solvation spheres of the ions are not completely saturated. The concepts used for concentrated solutions must be replaced by the picture of a matrix made up of  $\text{H}_2\text{O}$  and DMSO molecules associated by hydrogen bonding, with built-in ions formed by calcium nitrate dissociation. The character of the solution is governed by ion-solvent interactions which reinforce the matrix built up from the solvent molecules.

As a summary it may be stated that the experimental data on viscosity provide evidence of increased degree of ordering of local structures of the mixed solvent on addition of calcium nitrate. These structures are characterized by a certain ratio of water to DMSO molecules. The question of the specificity of calcium nitrate effect remains in need of further study.

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