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Dipraseodymium trisulfate in water-tetrahydrofuran mixtures - New insights into the ionic and solvent structure - Part I

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ABSTRACT

Extensive studies have been made upon the physical and chemical properties of dipraseodymium trisulphate in water and mixtures of water and tetrahydrofurane for a given molar fraction. The purpose of the paper covers two intensions: Firstly we collect new data of the behaviour of the rare earth salt praseodymium sulphate and secondly, the experimental values are suitable to prove a new theoretical model derived by the author[1]. Viscosity and surface tension measurements admit to study the environment near the central ion in relation with the equation of Jones and Dole. Moreover, the molar excess volume could derive by pure density measurements.

KEYWORDS

Praseodymium sulphate;
Viscosity;
Jones Dole Equation;
Molar excess volume;
THF.

INTRODUCTION

Conductivity measurements of electrolyte solutions in binary systems of organic solvents with widely different dielectric constants (DK) give insight into the process of possible ionic association and their dependence upon the solvent composition.

Several quantities of interest were measured to clarify not only the behaviour of the salt in mixtures; moreover, it seems of interest to explain the solution structure near the central ion.

In solvents with a low DK ion-ion interactions favour the formation of ion pairs, ion triplets, and higher ionic clusters. This strongly influences the conductivity of such solutions. Relatively little work was done with mixed solvents and praseodymium sulphate.

The specific conductivity as a system property shall be considered in the second part of this project following soon.

A historically valuable collection of the solution behaviour of chemical compounds in inorganic and/or organic solvents is given in[2].

The use of various compositions of mixtures of water and tetrahydrofurane (THF) allows measurements in media with various DK and conductivities. Generally we are interested in the structure of water near the Pr^{3+}-ion influenced by the organic solvent.

The normal structure of water is undisturbed: It is that of bulk water. Imagine now that the bulk changes and the structure of water near the Pr^{3+}-ion can be divided into three sheets:

In the primary, near the Pr^{3+}-ion, water molecules are immobilized and orientated by the ionic field and the water molecules are completely orientated,

in the secondary, or structure-broken sheet water molecules are partly-orientated,

finally, at sufficient distances from the Pr^{3+}-ion the water structure is unaffected by the ion and displays the tetrahedral bonded networks characteristic of bulk water.

These structural changes in the primary and secondary regions are usually referred to as solvatation. In pure aqueous solutions a three-step reaction of praseodymium sulphate is assumed[3]. Later we shall see that we can assume a cluster ordering of the solvent.

Generally, in pure aqueous solutions the Pr^{3+} state is favoured (assuming a six-fold coordination) and for each step possible above a special equilibrium constant may be formulated:

$$\begin{aligned}&\left[Pr(H_2O)_6\right]^{3+} \leftrightarrow \left[Pr(H_2O)_5OH\right]^{2+} \leftrightarrow \\ &\left[Pr(H_2O)_4(OH)_2\right]^{+} \leftrightarrow \left[Pr(H_2O)_3(OH)_3\right] \;,\end{aligned} \qquad (1)$$

where each ion contributes to the total conductivity. If we assume dissociation completely both the OH^- and $[H_3O]^+$ act upon the Pr^{3+}. Since the Eigen dissociation of H-OH is very low a complete hydrolysis can not be expected (generally the aquo-cation $\left[Ln(OH_2)_n\right]^{3+}$ is more than six-fold coordinated; hence the true hydration number is therefore of great importance).

For the conductivity mechanism however all 'hydrated possibilities' contribute to the total conductivity. Thus for the OH^- -ion the following hypothetical hydrolysis reactions are possible:

$$2\,Pr^{3+} + 2\,OH^- \rightarrow 2\left[Pr\text{-}O\text{-}Pr\right]^{4+} + 4OH^- \;. \qquad (1a)$$

The next step is that THF substitutes water molecules preferred in the secondary sheet. There is no doubt that the structure of the bulk water will be disturbed if one increases the quantity of the organic solvent. This picture of the solvent structure and the ion-solvent interaction will be discussed later. We are also interested into deviations from the simple case of symmetric electrolytes therefore the given asymmetric salt type is a suitable choice.

It is known that electrostatic interchanges are responsible for the increase of the viscosity[6] and a linear dependence of the viscosity difference, say, $\Delta\eta = \eta - \eta_0$ where η_0 means the viscosity of the pure solvent, of the molar concentration is assumed

$$\Delta\eta = k \times \sqrt{c}\;, \qquad (2)$$

where the root term is responsible for the occurrence of the ionic cloud in the electrolytic solution. From eq.(2), the concentration dependence of the relative viscosity $\Delta\eta/\eta$ could derived

$$\eta/\eta_0 = \eta_{rel} = 1 + A\sqrt{c}\;. \qquad (3)$$

For an electrolyte dissociated into two ions the coefficient *A* can be calculated. It depends upon the temperature, the DK of the pure solvent, the valence, and the number of molecules.

The viscosity theory of Falkenhagen was proven by the behaviour of strong electrolytes in the domain of much diluted solutions. Firstly it was shown by Jones and Dole that such solutions can be describe satisfactorily by the empiric equation

$$\eta/\eta_0 = \eta_{rel} = 1 + A\sqrt{c} + B.c\;, \qquad (4)$$

where *A* and *B* are some constant. To determine these constants one has to calculate the quantity

$$\Psi = \frac{\eta_{rel} - 1}{\sqrt{c}}\;. \qquad (4a)$$

Ψ represents a straight line by validity of the eq.(4) and should be satisfied for simple electrolytes. Higher valued asymmetric electrolytes might differ. As shown in[9] the curve must not be a straight line necessarily and electrolytes of higher valence often show an S-like run.

In eq.(4) the coefficient *A* describes the long-range electrostatic interactions and the coefficient *B* is responsible for the solute-solvent interactions.

Note: Eq.(4) is in agreement with experimental data for concentrations up to 0.05M. For higher concentrations one can add a term proportional to the square of the concentration[5] so that we assume a modified form

$$\eta/\eta_0 = \eta_{rel} = 1 + A\sqrt{c} + B.c + D.c^2\;, \qquad (4b)$$

where *D* describes the hydrodynamic interactions.

Studies of the phase equilibrium behaviour and the excess properties of liquid mixtures are of great importance for the design of separation processes and theoretical understanding of the nature of molecular interaction. Thermodynamic analysis and prediction of phase equilibrium as well as thermophysical properties are useful to solve separation problems effectively.

However when dealing with complex mixtures and new processes experimental data are still needed for a reliable process design. Thus we take the opportunity to clarify the behaviour of $\mathbf{Pr^{3+}}$ in different mixtures.

Let x_i, **i = *A*, *B*** be the molar fraction of each component and ρ_i, **I = *A*, *B*** the densities of each component. Further let $\mathbf{M_i}$, **I = A, B** be the molar masses of each component and ρ_m means the density of the mixture. Then the (molar) excess volume is given by

$$\mathbf{V^E = x_A M_A\left(\frac{1}{\rho_m}-\frac{1}{\rho_A}\right)+x_B M_B\left(\frac{1}{\rho_m}-\frac{1}{\rho_B}\right)}. \qquad (5)$$

Surface effects may be expressed in the language of Helmholtz and Gibbs energies.

The link between these quantities and the surface area is the work needed to change the area by a given amount, and the fact that *dA* and *dG* are equal to the work done in changing the energy of a system. The work needed to change the surface area, σ of a sample by an infinitesimal amount dσ is proportional to dσ and one can write

$$\mathbf{dw = \gamma\, d\sigma}\ . \ (6)$$

The minimization of the surface area of a liquid may result in the formation of a curved surface, as in a bubble. Later the surface tension will be important in relation with electrified interfaces.

Note: We refer to the Lippmann Equation[12] where the slope of the electrocapillary curve at any cell potential is equal to the charge density of an electrode. Thus one defines a differential capacity by

$$\mathbf{C=\left(\frac{\partial q_M}{\partial V}\right)=-\left(\frac{\partial^2\gamma}{\partial V^2}\right)}\ , \qquad (6b)$$

where $\mathbf{q_M}$ means the total charge onto the electrode.

EXPERIMENTAL

The TABLE 1 lists the measurement methods which were used to determine the quantities of interest.

The following note introduces a short description of the methods and, exemplified by the density an error estimation is thought.

Note: Densities of the liquids were measured using a pycnometer with water acting as auxiliary liquid. We give an example how one can calculate the error: The entire error is compounded by the weighing error, the error caused by measuring possible small blisters and the error of evaporation. Then, considering Gauß law of error propagation we have

$$\Delta\rho_{tot}=\sqrt{\begin{matrix}\left(\left(\frac{\partial\rho}{\partial \mathbf{m_1}}\right)_{\mathbf{m_2,V}}\Delta\mathbf{m_1}\right)^2+\\ \left(\left(\frac{\partial\rho}{\partial \mathbf{m_2}}\right)_{\mathbf{m_1,V}}\Delta\mathbf{m_2}\right)^2+\\ \left(\left(\frac{\partial\rho}{\partial \mathbf{m_3}}\right)_{\mathbf{m_1,m_2,V}}\Delta\mathbf{m_3}\right)^2+\\ \left(\left(\frac{\partial\rho}{\partial \mathbf{V}}\right)_{\mathbf{m_1,m_2,m_3}}\Delta\mathbf{V}\right)^2\end{matrix}}\approx \mathbf{0{,}001\,g\times cm^{-3}}\ , \qquad (7)$$

where m_1, m_2 and m_3 are masses (empty, plus water, plus water and salt) and V is the volume. Analogues mediations can be performed to calculate the remaining errors of quantities under consideration.

Specific conductance measurements of $Pr_2(SO_4)_3$ (Sigma-Aldrich) in water and its mixtures with THF (Merck) were carried out using a Knick-Digital-Konduktometer assuming a precision of ±0.001mS. The cell constant was 0,91cm^{-1} and the frequency took constantly 8100Hz. To exclude influences of crystal water to the structure of the solvents mixture a water-free sulphate was used. To exclude further any backlashes onto the conductivity of the mixtures conductivity water was used to prepare the samples. The water's conductivity was measured to 0,059mScm-1

The viscosity was determined using a rolling sphere viscosimeter, especially an Anton Paar AMV 200 microviscosimeter based upon the principle of Höppler e.g.[4,5].

Choosing four different angles (per ten steps from 40° to 70°) the dynamical viscosity was determined and the kinematic viscosity could deduced by the help of the density as usually.

The surface tension was measured ten times per sample using the hanging drop method, e.g.[6] by a physics contact angle system OCA15+. The measurement equipment is the standard automated video contact angle metrology for drop shape analysis. Mass measurements were done by a digital electronic analytical balance (Mettler) with a precision of ± 0.01 mg. Adequate precautions were taken to avoid evaporation losses and air bubbles during actual measurements.

Hint : All measurements and preparations were done by a constant temperature that is T=20°C with an estimated deviation of $\Delta T = \pm 0.1°C$.

TABLE 1 : Overview of the measured quantities and their methods including accuracy.

Quantity	Sign	Unit	Measurement method	Accuracy
Density	ρ	$g \times cm^{-3}$	Pycnometer, water as auxiliary liquid	$\Delta\rho=\pm0.001$
Spec. Conductivity	κ	$mS \times cm^{-1}$	Knick-Digital-Konduktometer	$\Delta\kappa=\pm0.001$
Viscosity (dynamical)	η	$mPa \times s$	Rolling sphere viscosimeter	$\Delta\eta=\pm0.010$
Surface tension	γ	$mN \times m^{-1}$	Hanging drop method using a data physics contact angle system OCA15+	$\Delta\gamma= \pm1$
Molar Excess Volume	V^B	$cm^3 \times mol^{-1}$	calculated	$\Delta V^B=\pm0.05$

In TABLE 2 we show exemplified by the series E(n),n=1,…,5, the different amount of water and THF. Further the TABLE 3 lists the varying amount of praseodymium sulphate which can be understood approximately.

TABLE 2 : Water/THF mixtures exemplified by the sample series E1 to E5 whereby x_2 means the molar fraction of THF and x_1 means the molar fraction of water. The star above the sample E5 means that the sample becomes unstable after 72 hours and a white, needle-shaped precipitation could observed.

Sample	c_{H2O}/g	c_{THF}/g	c_{H2O}/mol	C_{THF}/mol	x_2	x_1
E1	49,91	0	2,770	0	0	1,000
E2	44,92	4,45	2,493	0,062	0,024	0,976
E3	39,93	11,24	2,216	0,156	0.066	0,934
E4	34.94	13,35	1,939	0,185	0,087	0,913
E5*	29,25	22,47	1,662	0,312	0,160	0,842

TABLE 3 : Approximate sulphate concentrations in mg and calculated moles of each sample series. Within each series the content of praseodymium sulphate remains constant. The content of the sample series B(N) is of theoretically ones.

Sample series	Approx. sulphate content / mg	Number of moles
A1 – A5*	513	9×10^{-4}
B1 – B5	399	7×10^{-4}
C1 – C5*	285	5×10^{-4}
D1 – D5*	171	3×10^{-4}
E1 – E5	57	1×10^{-4}

Note: Let S_0 be the solubility of THF before addition and let S be the solubility after addition. Further let α_{THF} and α_W be the orientation polarizabilities. One can argue as follows: If the relation $\alpha_W > \alpha_{THF}$ holds then we have the effect of salting out and the effect of secondary solvatation can be assumed by the following dependence:

$$(\mathbf{S}-\mathbf{S_0}) \sim \mathbf{C_1}\left[\frac{\mathbf{C_2}\,(\boldsymbol{\alpha}_{\mathbf{W}}-\boldsymbol{\alpha}_{\mathbf{THF}})}{\boldsymbol{\varepsilon}^2\mathbf{k}\,\mathbf{T}\,\mathbf{r_h}}\right], \qquad (8)$$

where C_1 and C_2 are constants and r_h means the hydratation radius. Base upon the fact that the polarization of water is greater than THF the effect of instability is explained upon a molecular level.

Some notes about the stability are of interest: A star signs unstable solutions. It depends upon time until a white, needle-shaped precipitation could observed. Note that by considering TABLE 3 the salt concentration remains equal within a series. The samples among each other differ by the relation of water/THF. By increasing the content of THF we observe the effect of salting out so that most of the samples A(i), B(i),…. I=5 become unstable in time. However, XRD analysis showed the existence of a special hydrated praseodymium sulphate in non-stoichiometric composition.

The following TABLES contain the dynamical as well as the kinematic viscosity including error estimations. The TABLE 4 lists the values for the dynamical and kinematic viscosity and the TABLE 5 gives the values for the surface tension, the density, and the molar excess volume, respectively.

As mentioned earlier, by known of the dynamical viscosity, it is possible to calculate the quantity Ψ containing the viscosity of the pure solvents, signed by $\boldsymbol{\eta_0}$. These calculated values can be found in the TABLE

6 for each series of interest.

TABLE 4 : Dynamical and kinematic viscosities including error estimations.

Sample	η_d/mPa.s^{-1}	η_k/mm^2.s^{-1}	$\Delta\eta_d/\eta_d$/±%	$\Delta\eta_k/\eta_k$/±%
C1	(1.033±0.002)	(1.038±0.002)	0,194	0,193
C2	(1.631±0.006)	(1.363±0.005)	0,441	0,366
C3	(1.559±0.024)	(1.549±0.024)	1,539	1,549
C4	(1.808±0.013)	(1.800±0.013)	0,719	0,722
D1	(1.09±0.003)	(1.882±0.004)	0,275	0,213
D2	(1.355±0.004)	(1.354±0.004)	0,295	0,295
D3	(1.814±0.006)	(1.807±0.006)	0,331	0,332
D4	(1.988±0.072)	(1.973±0.072)	3,62	3,649
E1	(1.082±0.004)	(1.867±0.007)	0,37	0,375
E2	(1.313±0.003)	(1.313±0.025)	0,228	1,908
E3	(1.799±0.006)	(1.788±0.006)	0,333	0,336
E4	(1.941±0.007)	(1.922±0.007)	0,361	0,364
A1	(1.051±0.003)	(1.922±0.003)	0,285	0,282

TABLE 5 : Surface tension, densities, and the molar excess volume including the errors.

Sample	γ/mN.m^{-1}	$\Delta\gamma/\gamma$/±%	ρ/*g.cm*$^{-3}$	V^E/*cm*^{3}.*mol*$^{-1}$
C1	(69.4±1.07)	1,54	0,9952	--------
C2	(53.86±2.13)	3,95	0,9985	-0,217
C3	(41.51±1.66)	3,99	1,004	-0,705
C4	(46.34±1.28)	2,76	1,0066	-0,954
D1	(41.26±0.70)	1,70	0,5792	--------
D2	(50.11±1.46)	2,91	1,0003	-0,251
D3	(39.70±2.77)	6,97	1,005	-0,726
D4	(37.07±1.07)	2,96	1,008	-0,958
E1	(40.75±0.14)	0,34	0,5796	--------
E2	(50.16±0.55)	1,09	1,0025	-0,285
E3	(41.05±2.86)	6,96	1,0063	-0,754
E4	(38.90±4.63)	11,91	1,0102	-1,034
E5*	--------	------	1,0112	-1,729
A1	(69.56±0.43)	0,62	0,9904	--------

TABLE 6 : Calculated values for the quantity $\Psi = \frac{\eta_{rel} - 1}{\sqrt{c}}$ **per series.**

Series	Ψ	Series	Ψ	Series	Ψ	Series	Ψ
A1	1,49	A2	62,36	C3	105,32	C4	135,6
C1	3,56	C2	83.43	D3	168,21	D4	189,9
D1	4,91	D2	107,23	E3	282,76	E4	312,98
E1	7,55	E2	173,54				

TABLE 7 : The coefficients *A* and *B* of the Jones Dole Equation for each series.

Series	*A*	*B*
Series 1	(10.3±0.5)	(-300±20)
Series 2	(214±26)	(-5452±1236)
Series 3	(428±18)	(-14887±1100)
Series 4	(473±17)	(-16290±1100)

The constants A and B from the Jones Dole Equation can be determined from the intersection and the slope of the $\Psi, \sqrt{c}$ chart. We summarized these values in TABLE 7.

DISCUSSION

First of all we like to clarify the situation near the central ion, say the Pr^{3+}-ion. Observing a decrease in the conductivity (an exact view will be discussed in the second part) one can assume that the Pr^{3+}-ion is surrounded by THF molecules orientated with their oxygen atom in direction to the central ion. The decrease is five times smaller as in pure water. A possible arrangement is assumed in Figure 1.

However this situation may not match the reality as one can see by the effect of salting out occuring. It is also of interest and will be the subject of the second part to estimate the hydration number calculated upon the viscosity by applying Stokes formula. Probably an ordinary hydration by pure water molecules in the first sheet can be preferred and a dynamic view is considered: Water molecules will try to align into a minimum-energy orientation. This means that the water molecule has to reorient (or jump through a small distance) from the position it had in the water structure (this jumping movements will require a finite time. Now it can be considered that this time is used by a THF molecule to move into the position of the former water molecule and will substitute it (a possible formation of THF complex-ions with the Pr^{3+} will not considered).

Let us now discuss the coefficients of the Jones Dole Equation from the TABLE 7. In the following Figures we plotted the square root of the concentration against the quantity Ψ. If the $Pr_2(SO_4)_3$ acts as a strong electrolyte the dependence should be linear (this is also valid for (1,1)-electrolytes or symmetrical ones).

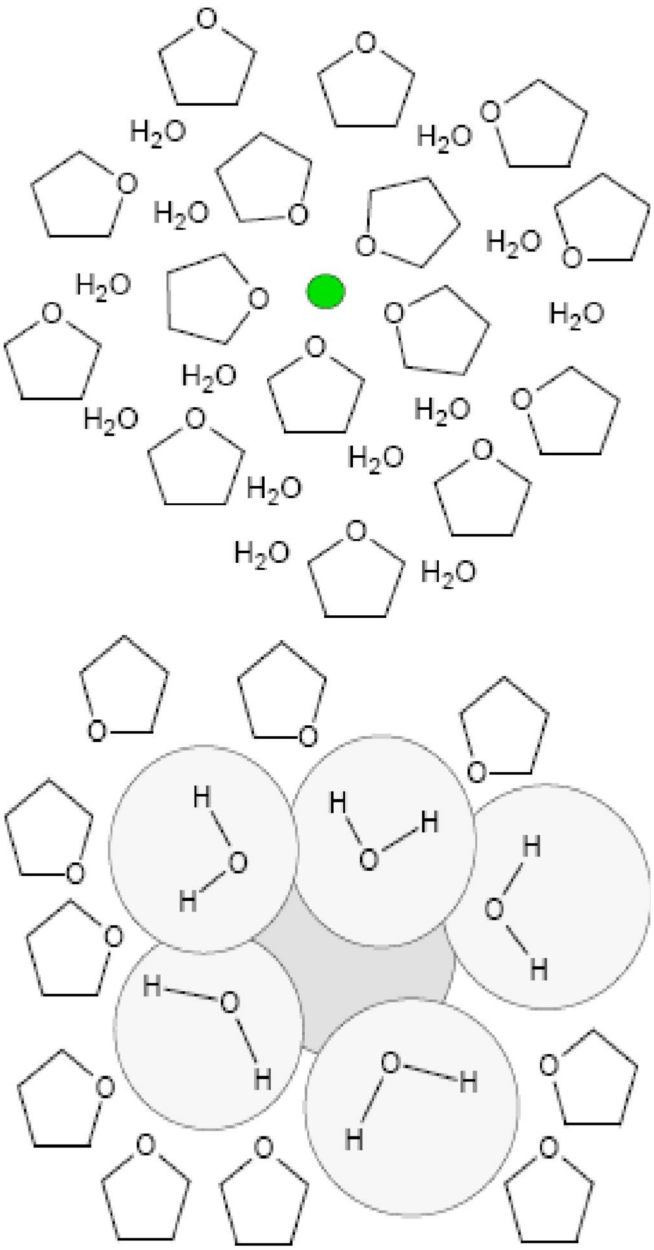

Figure 1 : Two possible states (models) near the environment of the solvated Pr^{3+} -ion which is centred in the middle. Left: The primary sheet consists of orientated THF molecules with interloping water molecules. This picture might be the result of the fact that the conductivity decreases by a factor five since the central ion must carry along the greater THF molecules. Remember that the salt concentration remains approximately constant within each series. Right: Water molecules assuming as spheres surround the central ion (clustering). This covers the situation after solution of the salt in water. Governed by electrostatic forces the THF molecules try to order with the oxygen in direction to the Pr^{3+} -ion building up the second solvatation sheet. Note that the water molecules right are drawn inordinately in relation to THF.

Normally the function $\Psi\left(\sqrt{c}\right)=\frac{\eta_{rel}-1}{\sqrt{c}}$ represents straight lines as one can see in the left sketch of the Figure 2 and the Figure 3, respectively.

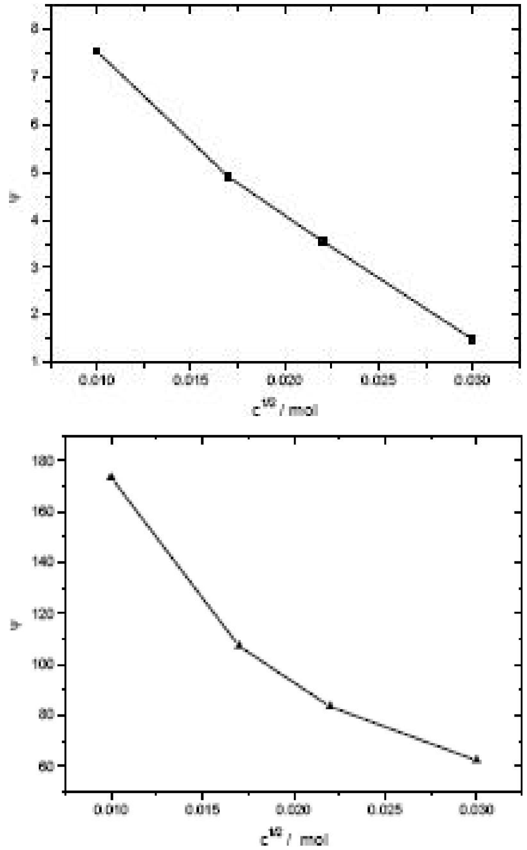

Figure 2 : Dependence of the quantity $\Psi=\frac{\eta_{rel}-1}{\sqrt{c}}$ from the square root of the concentration. Left the Series 1 and right the Series 2. It is seen that the Series 2 does not fulfil a linear dependence showing a clear deviation. A very weak tendency to a nonlinearity in the left sketch is assumed.

It is not easy to analyze the deviation since both the molar fraction of the liquids and the salt concentration changes. But in each case one can prove the fact that the constant B assumes negative values. Preliminary one can say that the constant B contains two parts which can be referred to the ions dissociated in the solution.

It is known that the constant B describes the solute-solvent interactions. Therefore, deviations from the linearity can directly be associated with the solute-solvent interactions.

Further one can see in the right part of the Figure 2 and the Figure 3, respectively, that in the domain of low

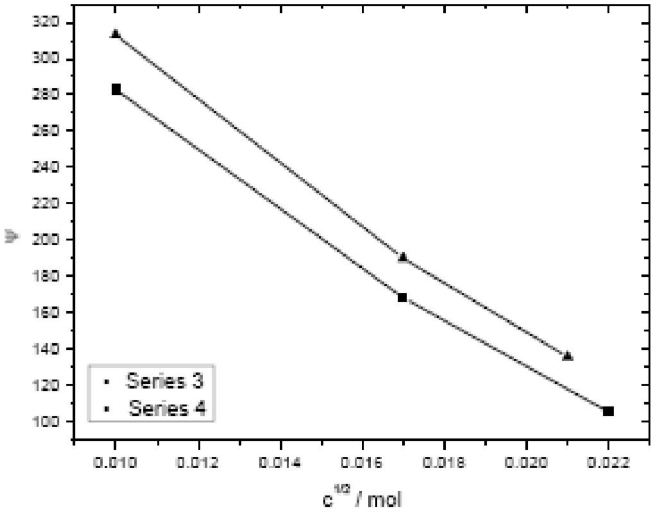

Figure 3 : Dependence of the quantity $\Psi = \frac{\eta_{rel} - 1}{\sqrt{c}}$ from the square root of the concentration for the remaining mixture series. Here the linear law $\Psi(\sqrt{c}) = A + B\sqrt{c}$ is satisfied fulfilled.

concentrations the linear behaviour is valid. Moreover deviations from the linearity referring to higher-valid ions are present. From TABLE 7 it is seen that both the coefficients A and B increase by increasing the salt concentration, otherwise the water content decreases. Therefore it is concluded that both the long-range electrostatic interactions and the solute-solvent interactions increase if the water content diminishes (synonymic with the fact that both the salt concentration and the amount of THF increase).

Note: An example to prove the opposite is the case of B_aC1_2 as a (1, 2) type. Here the value for A is in agreement[13].

Negative values for *B* are found for ions which exert a 'structure-breaking' effect on the solution *(*e.g. they contribute to a considerable increase in the disorder of water when dissolved) such as Rb^+, Cs^+, I^-, $C10^-_3$ and NO^-_3.

Usually, however, the *B* values are fairly large and positive and correspond to ions which are strongly hydrated ('structure makers') such as Na^+, Li^+, Mg^{2+} and La^{3+}[14]. Since we did not found any hints referring to this subject we cannot agree this statement (viscosity studies of La^{3+} in water/THF mixtures for comparing are missed).

Generally, small, highly charged ions influences the water structur near by themselves more than ions of great radius thus the Pr^{3+} should act as a better structure maker than an earth alkaline metal ion.

The surface tension is a further quantity of potential interest relating to a cell potential. Taking into account the Series 1 we performed a plot representing the dependence of the surface tension of the density where a linear connection is observed (Figure 4, left).

Later when we shall deal with our new model the surface tension will be important. We shall further see that we have to stress special assumptions upon the function $q_M(V)$ with V as the potential of the interface and we can write therefore $\int d\gamma = \int q_M dV$.

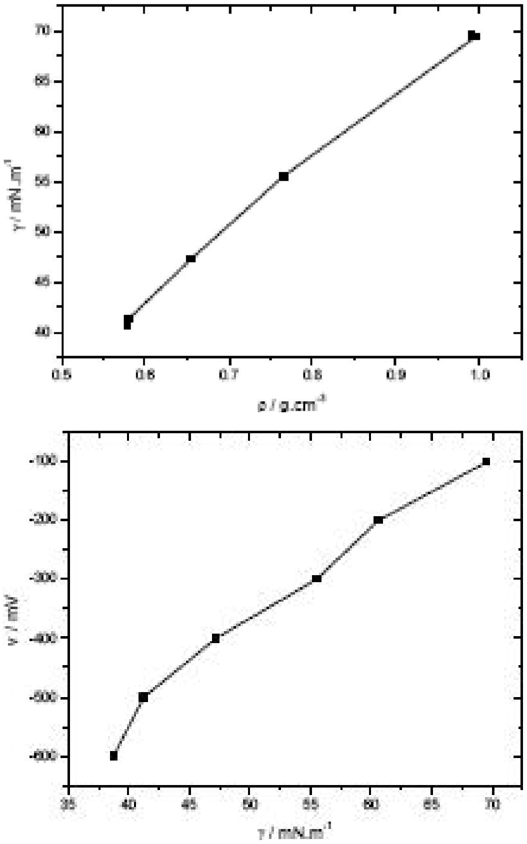

Figure 4 Left : Dependence of the surface tension from the density. A linear connection can be assumed representing by an equation of the general type *y*=kx+d with *k*=(68.3±2.0) and *d*=(1.97±1.54).

Right: The representation of the function qM(*V*) assuming a negative cell potential. Then the(V,*Y*) - curve is described by a linear dependence expressed through *y*=kx+d with k=(-1161±60) and d=(15.51.1).

We show the dependence of $q_M(V)$ graphically leading to a roughly linear connection (Figure 4, right). Otherwise experimentally, it is known that the y versus *V* curve is always a parabola. Why the discrepancy occurs is not known; e.g. a possible explanation might be the model under consideration.

In Figure 5 the dependence of the molar excess volume from the molar fraction of THF is plotted.

It is of interest to stress that a linear dependence only for the Series E could observed. Otherwise the Series C and D show deviations and can be assumed as a special behaviour of (n,m)-electrolytes.

Because there are no other values in the literature for the present system a systematic comparison is not possible. Basically a straight line covers the behaviour of an ideal liquid, therefore, the curves of the Systems C and D match real solutions and the interionic forces become important.

Note that the series differ among each other not only by the salt concentration but also by the molar fraction of water and THF.

Since the Series E contains the fewest amount of the sulphate one can argue that the Series E covers as best the ideal behaviour. By increasing the salt concentration the deviation from the ideal behaviour becomes important.

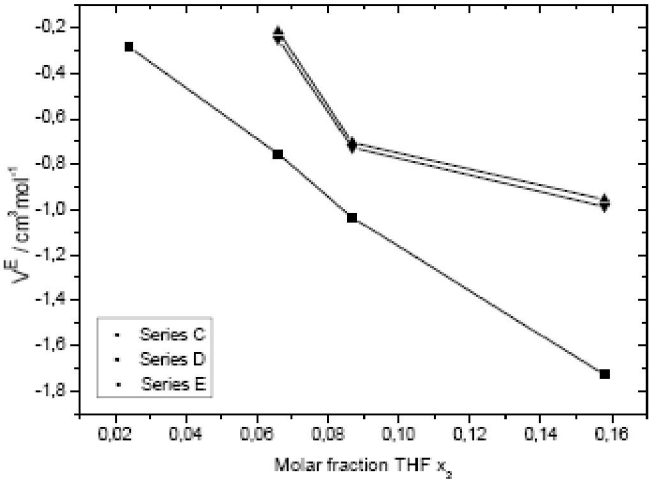

Figure 5 : Dependence of the molar excess volume from the molar fraction of THF. The linear dependence of the Series E reveals to an ideal behaviour of the mixed solution. Deviations from the linearity are observed by the remaining series. The behaviour becomes real more and more and intermolecular forces increase. A possible explanation might be the fact that both the water and THF molecules interchange in the first solvatation sheet.

Note: As shown in TABLE 5 the excess molar volumes for all systems are negative to reach the smallest value for the sample E5 (which has the highest amount of THF). This would indicate that molecular interactions between molecules of water and THF are stronger than interactions between molecules in their pure states (e.g. the sample E2 with very low amount of THF) and attractive forces dominate the behaviour of the solutions.

SUMMARY AND OUTLOOK

In this paper the behaviour of mixtures of praseodymium sulphate in water and THF is studied to the first time. Several physical quantities of interest were measured to explain the structure near the central ion (the Pr^{3+}). Samples of different content of praseodymium sulphate and different amount of water and THF (characterized by the molar fraction) were prepared. Since no reference values in the literature are present comparative studies are not possible.

Also the purpose was to fathom any deviations from symmetric electrolytes so the asymmetric salt type dipraseodymium trisulfate arose as a good option.

It is of interest to stress that some samples became unstable inhibiting an exact analysis. However the instability might be explained by considering the orientation polarizabilities.

As an important feature we applied the Jones Dole Equation to equate the relevant coefficients by known viscosity where some deviations could observe.

The solvatation sheet around the central ion is not yet fully clear; a suitable model is presented.

Also the molar excess volume shows deviations relating to intermolecular forces as well as almost ideal behaviour.

In the second part (in preparation) of the project following soon we shall show how the specific conductivity and related quantities (e.g. the hydration number, ion association) influences each other. It can be expected that the conductivity allow further conclusions. Especially the surrounding of the central ion and possible ion associations shall be described much well.

A further parameter of interest which is not considered in the present study is the refractive index which allows the derivation of the molar polarizability constant together with the DK measured experimentally.

We believe, that, based upon the subject to discuss these quantities in relation with conductivity phenomena in the second part.

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