

Molar refractivity and interactions in solutions

I. Molar refractivity of some monovalent ions in aqueous and dimethyl sulfoxide solutions

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The refractive indices and densities of Li^+ , Na^+ , NH_4^+ , and Ag^+ nitrates, chlorides, and iodides were measured in aqueous and dimethyl sulfoxide solutions in dependence on the salt content. The molar refractivities were calculated and the polarization effects among the ions and on the solvent are discussed.

В зависимости от содержания солей определены показатели преломления и плотности растворов нитратов, хлоридов и иодидов Li^+ , Na^+ , NH_4^+ и Ag^+ в воде и диметилсульфоксиде. Рассчитаны величины молярных показателей преломления, и обсуждаются поляризационные эффекты между ионами и на растворитель.

The molar refractivity reflects arrangements of the electron shells of ions in molecules and yields information about the electronic polarization of ions. The combination of ions to form molecules in a gas or a crystal or complex ions in solution is always accompanied by a change in the properties of the ions themselves. The molar refractivity reflects the changes in the properties due to polarization or to deformation of the electron shells of the ions under the influence of the electric fields of neighbouring ions.

The molar refractivity $[R]$ ($\text{cm}^3 \text{mol}^{-1}$) is defined by the Lorenz—Lorentz expression

$$[R] = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} \quad (1)$$

and its value depends on the wavelength of the light used for measuring the refractive index n , M is the molar mass and ρ is the density. The molar refractivity is related to the electronic polarizability α_e

$$[R] = 4/3\pi N_A \alpha_e \quad (2)$$

(N_A is Avogadro's constant). The molar refractivity is thus a measure of the polarizability of the ion, *i.e.* the ease of displacement of its electron shell with respect to its nucleus.

All further conclusions are based on the assumption that the molar refractivity of the system can be calculated from the individual refractivities of the components. Any deviation from additivity can be regarded as an indication of interactions between ions or between ions and the solvent.

The refractivity values for individual cations and anions in the free gaseous state $[R]_g$, which are a measure of their respective deformabilities, were estimated [1, 2] on the basis of theoretical calculations using the refractivity of the inert elements and the experimental refractivities of the salts.

On the basis of the results of *Fajans* and coworkers [3] it can be concluded that:

a) The refractivity of anions is lowered by neighbouring cations. It is lowered more in the presence of a stronger electric field of the cation (a smaller radius and a greater charge) and more polarizable anion.

b) The refractivity of cations is increased by the neighbouring anions. Anions are thus more consolidated by cations and the electron shell of the cation is less rigid due to the effect of anions.

c) The combination of ions to form molecules or crystals is then accompanied by a net decrease in the refractivity $\Delta[R]$, when consolidating effect of the cation on the anion outweighs the loosening effect of the anion on the cation and *vice versa*.

The refractivity change $\Delta[R]$ is calculated by comparing the refractivity of the molecule or crystal $[R]_c$ with the refractivity of the ions in the free gaseous state

$$[R]_c = [R_{\text{cat}}]_g + [R_{\text{an}}]_g + \Delta[R] \quad (3)$$

Similar to the lowering of the refractivity of a neighbouring anion, cations also lower that of the solvent surrounding it in solution, whereas anions exhibit a loosening effect on the solvent (*i.e.* increase the refractivity). The refractivity values for individual ions in infinitely dilute aqueous solutions (where ions exert no forces on each other) were estimated in the series of works by *Fajans* [3, 4]. Their values are given in Table 1 together with the values for ions in the free gaseous state. The value of $\Delta[R^\circ]_{g-H_2O}$ is the change in the refractivity which accompanies the transition from the free gaseous state to an infinitely dilute solution. This is actually the refractivity change of the solvent but it is usually ascribed to the cation and/or anion as this is useful for any further calculations.

The value of the refractivity of an ion in the free gaseous state $[R]_g$ and the value for an ion in infinitely dilute solution $[R^\circ]$ must be differentiated. The additivity of the ionic refractivities in aqueous solutions at infinite dilution has been confirmed by *Fajans* [4].

Marked deviations from additivity accompany the transition from the state at infinite dilution to that in a crystal. As the solution becomes more concentrated the ions approaching one another more closely, displace the solvent

Table 1

Refractivities of ions in the gaseous state $[R]_g$, in infinitely dilute aqueous solutions $[R^\circ]_{\text{H}_2\text{O}}$, and the change in the refractivity of water due to dissolved ions $\Delta[R^\circ]_{g-\text{H}_2\text{O}}$

Ion	$[R]_g^a$	$[R^\circ]_{\text{H}_2\text{O}}^b$	$\Delta[R^\circ]_{g-\text{H}_2\text{O}}$
	cm ³ mol ⁻¹		
Li ⁺	0.20	-0.32	-0.52
Na ⁺	0.50	0.20	-0.30
NH ₄ ⁺	4.61 ^c	4.31	-0.30
Ag ⁺	—	4.79	—
Cl ⁻	9.06	9.06	0
I ⁻	19.22	19.22	0
NO ₃ ⁻	11.02	11.02	0

a) Value taken from Ref. [2]; b) from Ref. [3]; c) value estimated in this work.

and unite to form complex ions or associates. These processes should cause changes in the refractivity.

Considerable effort has been devoted to determining the refractive indices and understanding polarization phenomena in crystals [5] and ionic melts [6]. Since the time of publishing of the series of works by Fajans and coworkers [4] on the refractivities in aqueous electrolyte solutions, little attention has been paid to this problem. The present paper partially fills this gap and accounts for the dependence of the refractivity on the salt concentration for solutions of Li⁺, Na⁺, NH₄⁺, and Ag⁺ chlorides and nitrates in dimethyl sulfoxide and water. Dimethyl sulfoxide has been chosen as an alternative solvent because of its higher polarizability and greater effective radius compared to water [7]. The interactions with cations are stronger due to the higher donor number of dimethyl sulfoxide and comparison of the changes in the refractivity of the salts in the two solvents can explain some peculiarities of the interactions between the ions and solvents.

This paper attempts to specify the behaviour of ions in solutions of salts using a simple experimental technique.

Experimental

All salts used (anal. grade, Merck) were dehydrated by drying in a vacuum at 110°C for several days to a constant mass. Any decomposition of salts (especially of LiCl) is so small that it cannot be detected analytically (*e.g.* Volhard titration for chloride content). DMSO solutions of the salts showed no evidence of cloudiness.

Dimethyl sulfoxide (DMSO) (anal. grade, Merck) containing less than 0.03 % water,

was used as obtained. Any traces of impurities present in DMSO do not affect the density and refractive index values as was shown in Ref. [7] by comparison of the values measured in our laboratory with those reported by other authors.

The most concentrated samples, used as stock solutions, were prepared according to the equilibrium solubilities of the salts [8—10] by weighing both the salt and the solvent. Samples of lower concentrations were prepared by diluting the stock solution. The compositions of the solutions are expressed in terms of the mole fraction of the salt x .

The density was measured with an accuracy better than $\pm 4 \times 10^{-4} \text{ g cm}^{-3}$ by means of a DMA 40 digital oscillating tube densimeter (Paar, Graz, Austria). The refractive index was determined with a Pulfrich refractometer, type PR-2 (Zeiss, Jena) at a wavelength of 587.6 nm (He, D-line), with an accuracy of $\pm 5 \times 10^{-5}$ units.

The molar refractivity values were calculated from these quantities with an accuracy of ± 0.01 . A similar error could arise from the uncertainty in the solution concentrations which amounted to ± 0.001 mole fraction.

The measurements were performed at 30 and 60 °C and the temperature of water pumped through the measuring cell jackets from a bath was accurate to ± 0.05 °C.

The molar refractivity slightly depends on temperature, $d[R]/dt < 3 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$, which lies within the experimental error for a temperature interval of 30 °C. The refractivity values used in this paper are mostly referred to 60 °C in order to attain higher concentration of the salts, especially in dimethyl sulfoxide. Some measurements in aqueous solutions were carried out at 30 °C.

The numerical values of the density and the refractive index are available as the supplementary material (available from the author upon request). The refractivity values of the crystalline nitrates were calculated from the densities and the geometric mean of the refractive indices published in the *Gmelin Handbook* [11, 12]. The values for crystalline halides were taken from the paper of *Tessmann* [5].

All the refractivity values are referred to a wavelength of 587.6 nm (He, D-line) or 589.3 nm (Na, D-line).

Results and discussion

Upon concentrating aqueous solutions the refractivity of the solution increases because water with a low refractivity value ($[R]_{\text{H}_2\text{O}} = 3.72 \text{ cm}^3 \text{ mol}^{-1}$) is replaced by a salt with a higher value of $[R]_{\text{c}}$. The refractivities of crystalline salts are given in Table 2. On the other hand, as the large DMSO molecule is more easily polarizable, its refractivity value is high ($[R]_{\text{DMSO}} = 20.26 \text{ cm}^3 \text{ mol}^{-1}$) [7] and the refractivity of the solution decreases with increasing concentration. DMSO molecules are replaced by less polarizable cations and anions. The changes in the refractivity of the solutions are almost linear with changing concentration both in water and DMSO (Fig. 1).

In order to estimate the ion—ion and ion—solvent interactions, the refractivity of the salts and/or the individual ions must be considered. The molar

Table 2

Refractivities of salts in infinitely dilute aqueous solutions $[R^0]_{\text{H}_2\text{O}}$, in the crystalline state $[R]_c$, and the refractivity change accompanying dissolution of the crystal $\Delta[R]_{c-\text{H}_2\text{O}}$

Salt	$[R^0]_{\text{H}_2\text{O}}$	$[R]_c^b$	$\Delta[R]_{c-\text{H}_2\text{O}}$
	$\text{cm}^3 \text{mol}^{-1}$		
LiNO ₃	10.71	10.28	0.43
NaNO ₃	11.23	11.03	0.20
NH ₄ NO ₃	15.33	15.15	0.18
AgNO ₃	16.01	15.96	0.05
LiCl	8.74 ^a	7.51	1.23
NaCl	9.26 ^a	8.46	0.80
NH ₄ Cl	13.27 ^a	12.56	0.81

a) Values taken from Ref. [4]; b) from Ref. [5, 11, 12].

refractivity of a salt $[R_x]$ was calculated by subtracting the refractivity of the solvent from that of a solution containing 1 mol of the salt

$$[R_x] = ([R]_{\text{soln}} - (1 - x)[R]_{\text{solv}})/x \quad (4)$$

The refractivities of the solution $[R]_{\text{soln}}$ calculated from eqn (1) for various concentrations were fitted to a polynomial of the type $[R]_{\text{soln}} = a + bx + cx^2$,

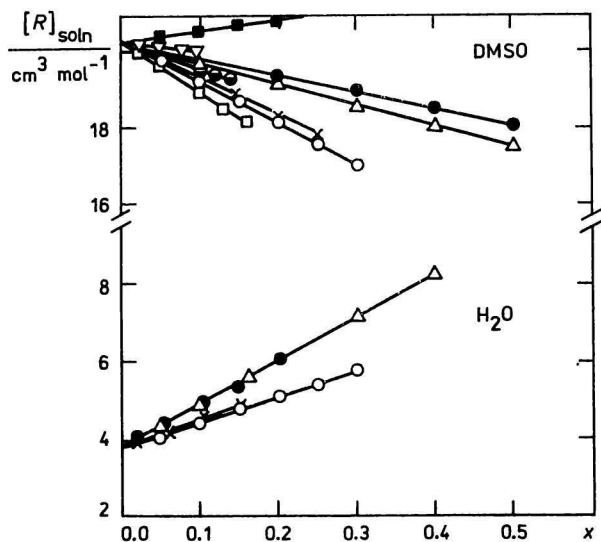


Fig. 1. The molar refractivity of the solution $[R]_{\text{soln}}$ dependent on the mole fraction x of the salt. ■ NH₄I; ▽ LiI; ● AgNO₃; △ NH₄NO₃; ● NH₄Cl; × NaNO₃; ○ LiNO₃; □ LiCl.

where a is the refractivity of the pure solvent taken from the work of Pacák [7]. The refractivities of the solution were recalculated for selected concentrations using the regression constants and these values of $[R]_{\text{soln}}$ were used to evaluate the salt refractivities $[R_x]$ according to eqn (4). The obtained values of $[R_x]$ were plotted as functions of the mole fraction (Fig. 2) and the refractivity of the salt in infinitely dilute solution $[R^\circ]$ was obtained by extrapolation to the value $x = 0$ (Table 2). The refractivity change $\Delta[R^\circ]_{\text{g-solv}}$ can be estimated from comparison with the refractivity values of the free gaseous ions.

$$[R_{\text{salt}}^\circ] = [R_{\text{cat}}]_{\text{g}} + [R_{\text{an}}]_{\text{g}} + \Delta[R^\circ]_{\text{g-solv}} \quad (5)$$

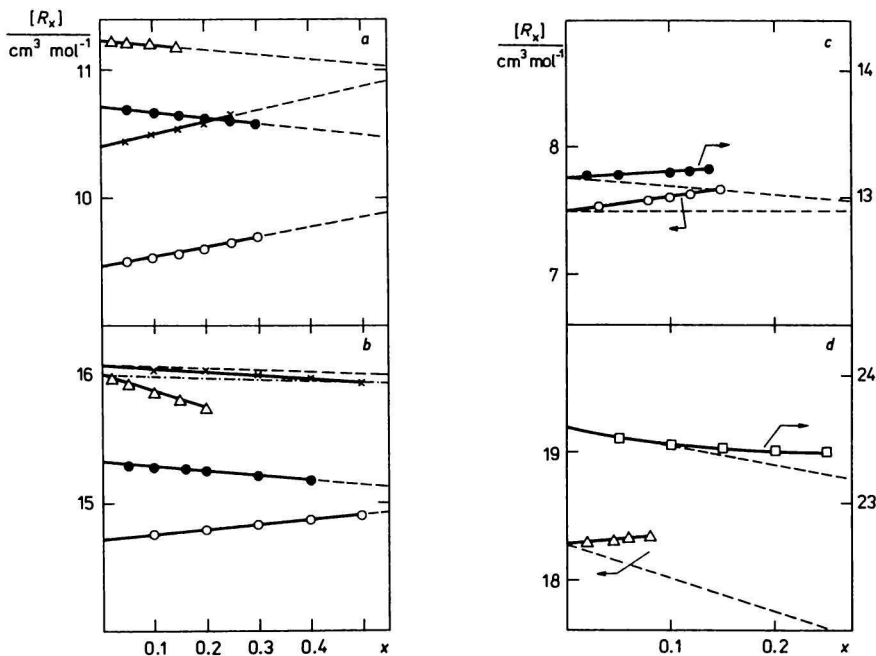


Fig. 2. The molar refractivity of the salt $[R_x]$ dependent on the mole fraction x of the salt. a) Δ $\text{NaNO}_3\text{—H}_2\text{O}$, \bullet $\text{LiNO}_3\text{—H}_2\text{O}$, \times $\text{NaNO}_3\text{—DMSO}$, \circ $\text{LiNO}_3\text{—DMSO}$; b) \times , --- $\text{AgNO}_3\text{—DMSO}$, Δ , $\bullet\text{—}\bullet$ $\text{AgNO}_3\text{—H}_2\text{O}$, \bullet $\text{NH}_4\text{NO}_3\text{—H}_2\text{O}$, \circ $\text{NH}_4\text{NO}_3\text{—DMSO}$; c) \bullet $\text{NH}_4\text{Cl—DMSO}$, \circ LiCl—DMSO ; d) \square $\text{NH}_4\text{I—DMSO}$, Δ LiI—DMSO .

Aqueous solutions

The above calculations can be carried out with ions the refractivity values of which in the free gaseous state $[R]_{\text{g}}$ are known, e.g. Li^+ , Na^+ , Cl^- , and NO_3^- ions [2].

The $[R]_g$ value for the ammonium cation (which is not known) can be estimated from the refractivity change accompanying dissolution of crystalline NH_4Cl in water ($\Delta[R]_{c-\text{H}_2\text{O}} = [R^\circ] - [R]_c$) which is very similar to that for NaCl (Table 2). A similar result is obtained by comparing the dissolution of the nitrate salts. Hence it seems that NH_4^+ cations have a similar polarizing effect on water to sodium cations, *i.e.* $\Delta[R_{\text{NH}_4^+}^\circ] = \Delta[R_{\text{Na}^+}^\circ]$ (Table 2), and thus $[R_{\text{NH}_4^+}]_g = [R_{\text{NH}_4^+}^\circ] + 0.3$. It should be noted that it is difficult to estimate the refractivity value of solid ammonium nitrate which exists in two modifications with different density values. We measured the density of solid ammonium nitrate which was used for preparation of the solutions and the value $\rho = 1.683 \text{ g cm}^{-3}$ (which is the same as that published for powder sample [11, 12]) was used to calculate the refractivity of crystalline ammonium nitrate.

The value of the refractivity of silver(I) nitrate extrapolated to infinitely dilute aqueous solution is higher than the sum of the ionic refractivities taken from the paper of *Fajans* and *Joos* [2] ($\Sigma[R_{\text{ions}}^\circ] = 15.81 \text{ cm}^3 \text{ mol}^{-1}$). This discrepancy could arise from imprecision of the estimation of the value of $[R_{\text{Ag}^+}^\circ]$. In any case, the lower value of the refractivity change accompanying the dissolution of crystalline AgNO_3 $\Delta[R_{\text{AgNO}_3}]_{c-\text{H}_2\text{O}}$ compared with that for NH_4NO_3 reflects a smaller polarizing power of the silver cation on water.

The refractivity of the salt decreased with increasing salt content in aqueous solution (Fig. 2). Net consolidation of easily deformable anions with poorly deformable cations is a result of a stronger effect of the cations on the anions than on the water molecules.

The refractivity of the salt changes linearly with increasing content of the studied nitrates (except Ag^+) and a refractivity value very close to that of the crystal is obtained by extrapolation to the value of $x = 1$ (*i.e.* the pure salt). This behaviour is considered to be additive and it is depicted in Fig. 2 by dashed lines.

The refractivity changes with changing content of the salt were found to be higher for Cl^- than for NO_3^- [4]. The transition from the crystal to an aqueous solution (*i.e.* dissolution) is also accompanied by a greater change in the refractivity $\Delta[R]_{c-\text{H}_2\text{O}}$ for chlorides than for nitrates. It thus follows that nitrate is a less deformable anion than chloride ($r_{\text{Cl}^-} = 0.181 \text{ nm}$), in spite of its greater ionic radius ($r_{\text{NO}_3^-} = 0.232 \text{ nm}$) [13] and higher total refractivity. Only those electron orbitals that are in direct contact with the cation need be considered. The deformability cannot be obtained from the total refractivity but rather from the refractivity per oxygen octet. Thus $[R_{\text{NO}_3^-}]_g = 11.02/3 = 3.67 \text{ cm}^3 \text{ mol}^{-1}$. From this point of view, the refractivities of crystalline nitrates should not differ from those in aqueous solutions, as the refractivity of water has the value $[R_{\text{H}_2\text{O}}] = 3.72 \text{ cm}^3 \text{ mol}^{-1}$. However, water, as a dipole, is attracted less strongly by cations than is the corresponding anion. The electron shell of water is thus

further removed from the cation than the anion electron shell and a cation will have a greater effect on an anion than on a water molecule, resulting in the decrease in the refractivity of nitrate salts with increasing content of the salt in aqueous solutions.

The magnitude of the refractivity changes with changing salt content is for the lithium cation higher than for the sodium cation, which is larger. As pointed out, the effect of the ammonium ion on water and an anion is similar to that of the sodium cation, although the refractivity values for the two cations and their sizes differ greatly ($r_{\text{Na}^+} = 0.095 \text{ nm}$, $r_{\text{NH}_4^+} = 0.148 \text{ nm}$). We assume that only the hydrogen electron orbitals lie in the immediate neighbourhood of the anion or water molecule. When comparing the complex NH_4^+ cation with other cations in question, the respective refractivity per outer electron must be employed as a comparative criterion of the deforming ability, thus obtaining the actual refractivity value $[R_{\text{NH}_4^+}]_{\text{g}} = 4.61/4 = 1.15 \text{ cm}^3 \text{ mol}^{-1}$.

A greater decrease in the refractivity of silver nitrate with changing salt content than corresponds to additive behaviour was observed. It is generally known that the inert gas electron configuration is most effective in shielding the nuclear charge of a cation from its surface. Cations without this configuration have high positive fields at their surfaces and consequently exhibit a high polarizing power. This holds for the silver cation. As the interaction between ions strongly depends upon the interionic distance, it follows from the relatively great decrease in the salt refractivity with increasing concentration of the solution that Ag^+ and NO_3^- form contact ion pairs to a greater extent than corresponds to simple replacement of water molecules by the nitrate anions.

Dimethyl sulfoxide solutions

The extrapolated values of the refractivities of salts in infinitely dilute DMSO solutions are lower than those for aqueous solutions (Table 3). The DMSO molecule is larger and more polarizable than the water molecule [7] and thus a greater decrease in the ionic refractivities accompanying the transition from the free gaseous state to infinitely dilute DMSO solution, $\Delta[R^\circ]_{\text{g-DMSO}}$, can be expected.

In order to evaluate the ionic refractivities in the infinitely dilute DMSO solution, the iodide ion was taken as reference. It is generally known that the larger the ion, the lower the ion—solvent interaction that can be expected. It is assumed that the largest I^- anion has a very small polarization effect on the DMSO molecule and thus, to the first approximation, the observed effect of the salt can be considered to be due to the effect of the cation on the DMSO molecule. This assumption was confirmed in another work on the refractivity of

Table 3

Refractivities of the salts in infinitely dilute DMSO solutions $[R^\circ]_{\text{DMSO}}$, the refractivity changes accompanying the transition from the free gaseous state to an infinitely dilute solution $\Delta[R^\circ]_{\text{g-DMSO}}$, and dissolution of the crystal in DMSO $\Delta[R]_{\text{c-DMSO}}$

Salt	$[R^\circ]_{\text{DMSO}}$	$\Delta[R^\circ]_{\text{g-DMSO}}$	$\Delta[R]_{\text{c-DMSO}}$
	$\text{cm}^3 \text{mol}^{-1}$		
LiNO ₃	9.45	-1.77	-0.83
NaNO ₃	10.40	-1.12	-0.63
NH ₄ NO ₃	14.72	-0.91	-0.43
AgNO ₃	16.09	—	+0.13
LiCl	7.50	-1.76	-0.01
NH ₄ Cl	13.16	-0.49	+0.60
LiI	18.28	-1.14	+2.53
NH ₄ I	23.60	-0.23	+1.43

tetraalkylammonium salts in DMSO solutions which will be published [14]. For this reason, the refractivities of lithium and ammonium iodides were measured in DMSO solutions in dependence on the salt content. (NaI and NaCl were not measured because of their low solubilities in DMSO, less than $x = 0.005$ at 60°C.)

The refractivity of Li⁺ and NH₄⁺ cations in infinitely dilute DMSO solutions was evaluated ($[R^\circ_{\text{LiI}}]_{\text{DMSO}} - [R_{\text{I}^-}]_{\text{g}} = [R^\circ_{\text{Li}^+}]_{\text{DMSO}}$, etc.) from the estimated refractivity values of iodide salts. The refractivity values $[R^\circ]_{\text{DMSO}}$ of the other ions in question (Table 4) can be calculated from the obtained values. The calculated values are mutually consistent and it can be concluded that the ionic refractivities are also additive in infinitely dilute DMSO solutions.

Table 4

Refractivities of ions in infinitely dilute DMSO solutions $[R^\circ]_{\text{DMSO}}$ and the change of the DMSO refractivity due to dissolved ions $\Delta[R^\circ]_{\text{g-DMSO}}$

Ion	$[R^\circ]_{\text{DMSO}}$	$\Delta[R^\circ]_{\text{g-DMSO}}$
	$\text{cm}^3 \text{mol}^{-1}$	
Li ⁺	-0.94	-1.14
Na ⁺	0.02	-0.48
NH ₄ ⁺	4.38	-0.23
Ag ⁺	5.71	—
NO ₃ ⁻	10.38	-0.64
Cl ⁻	8.61	-0.45
I ⁻	19.22	0

The effect of an ion on DMSO expressed in terms of the refractivity change accompanying the transition from the gaseous state to an infinitely dilute solution $\Delta[R^\circ]_{g-DMSO}$ was evaluated by comparing the $[R^\circ]_{DMSO}$ values of ions with their refractivities in the gaseous state $[R]_g$ (Table 4). The magnitude of the refractivity change decreases for various salts in the order Li^+ , Na^+ , NH_4^+ and NO_3^- , Cl^- , I^- . In contrast to aqueous solutions, where the studied anions do not influence water molecules, DMSO is polarized by both nitrate and chloride anions, nitrate exhibiting a stronger effect on the solvent. Conclusions of the work of *Sacchetto* and *Kodejš* [15] also support the idea of interactions between NO_3^- anion and DMSO. The values of the refractivity change $\Delta[R^\circ_{an}]_{g-DMSO}$ are not positive as could generally be expected. Both anions show a polarization effect on DMSO which is equivalent to tightening of the electron shell of the DMSO molecule. This behaviour contrasts with the general rules according to which anions should exert a loosening effect on the solvent and thus should increase its refractivity, and merits further study.

Dissolution of crystalline nitrate salts to form infinitely dilute DMSO solutions is accompanied by a greater decrease in the refractivity $\Delta[R]_{c-DMSO}$ than that for Cl^- and I^- salts (Table 3). Nitrate is thus less polarizable by a cation than the Cl^- and I^- anions, which is in agreement with the lower actual refractivity value of the NO_3^- anion, mentioned above.

With increasing content of a salt in the solution, the cations and anions approaching one another displace the more polarizable DMSO molecules, causing a lower effect of both the ions on the solvent. A positive component is introduced into the change in the salt refractivity and an increase in the salt refractivity can be observed with increasing content of the salt (Fig. 2).

The concentration dependence of the salt refractivity in DMSO solutions of nitrate salts exhibits additive behaviour (Fig. 2a, 2b), whereas positive deviations have been observed for iodide and chloride solutions (Fig. 2c, 2d). The positive deviations from additivity can be explained by solvation of the cations by DMSO. The cations are thus surrounded by DMSO molecules and anion approach is hindered; consequently, interactions between the ions are limited. The positive component introduced into the refractivity change then increases with increasing concentration of the solution. It is assumed that if a higher content of the salt in the solution can be attained, a break on the $[R_x]-x$ dependence would appear for Cl^- and I^- salts at a certain concentration. The refractivity would then decrease towards the value for the crystal.

The silver cation has a high refractivity value $[R^\circ]_{DMSO}$ (Table 4) and thus exhibits a low polarizing effect on DMSO, so that a lower positive contribution to the refractivity change can be expected with changing concentration. Interaction of Ag^+ with the nitrate anion has been found to be stronger than that of other cations and thus formation of ion pairs with the nitrate anion is more

probable, causing negative deviations from additivity. These are not as marked as in aqueous solutions because of the interaction of NO_3^- with the DMSO molecule, introducing a positive component into the refractivity change.

Conclusion

1. Neither chloride nor nitrate anions exert a polarizing effect on water molecules.

2. Dissolution of chloride salts in water is accompanied by a greater decrease in the refractivity than that of nitrate salts.

3. The polarization effect of the ammonium cation on water is similar to that of the sodium cation.

4. No deviation from the additivity in the concentration dependence of the salt refractivity was observed for Li^+ , Na^+ , and NH_4^+ chlorides and nitrates in aqueous solutions.

5. The silver cation, which does not have the inert gas electron configuration, exhibits a stronger polarizing effect on anions than the other studied cations, but a lower effect on the solvent.

6. Additivity of the ionic refractions in infinitely dilute solutions of the salts was found in DMSO solutions.

7. Dissolution of salts in DMSO is accompanied by a decrease in the refractivity for nitrates and by an increase for chlorides and iodides. The latter anions are more polarizable by a cation than is the DMSO molecule.

8. The nitrate and chloride anions exert a polarization effect on DMSO which causes a decrease in the solvent refractivity; the effect of the nitrate anion is stronger.

9. The chloride and iodide anions are influenced by a cation more than nitrates. The refractivity of nitrate salts is additive in DMSO solutions with increasing concentration of the salt.

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