Molar refractivity and interactions in solutions
II. Molar refractivity of tetraalkylammonium salts in aqueous and dimethyl sulfoxide solutions

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The density and refractive index were determined in aqueous and dimethyl sulfoxide solutions of some tetraalkylammonium chlorides, bromides, iodides, and nitrates. The molar refractivities of the individual ions were estimated and the polarization effect of the anions on the solvent is discussed.

Определены величины плотности и показателя преломления растворов хлоридов, бромидов, иодидов и нитратов нескольких тетраалкиламмониевых катионов в воде и диметилсульфоксиде. Определены значения молярных показателей преломления отдельных ионов и охарактеризован поляризационный эффект анионов на растворитель.

The molar refractivity reflects the changes in the properties of the ions due to polarization or deformation of their electron shells under the influence of the electric field of neighbouring ions. The refractivity values of individual ions in the free gaseous state $[R]_g$ calculated by *Pauling* [1] and *Fajans* [2] serve as a measure of their respective deformabilities.

In the previous paper [3], the molar refractivities of some salts were studied in aqueous and dimethyl sulfoxide solutions and individual ionic refractivities at infinite dilution were estimated. Ions exert no forces upon one another in infinitely dilute solutions and the change in the ionic refractivity accompanying transition from the gaseous state to infinite dilution is a measure of ion—solvent interactions. It was found that chloride and nitrate anions did not influence water molecules [4] whereas both the anions exert a polarization effect on dimethyl sulfoxide, which caused a decrease in the solvent refractivity [3].

The refractivity of aqueous and dimethyl sulfoxide solutions of tetraalkylammonium salts was studied in this contribution in order to confirm the polarization effect of the anions on the solvent. It is believed that the large cations do not influence the solvent molecules, so the refractivity change in the studied salts can be ascribed to the effect of the anion alone.

Experimental

Tetraalkylammonium chlorides, bromides, and iodides (anal. grade, Merck) were used as received. The purity of the salts was controlled by Volhard titration for anion content and it was always more than 99 %. Dimethyl sulfoxide — DMSO (anal. grade, Merck) containing less than 0.03 % water was used without further treatment.

Tetramethyl- and tetraethylammonium nitrates were prepared from a 10 % solution of the respective hydroxides by neutralization with HNO_3 at 10 °C. Water was then removed at 60 °C using a vacuum rotatory evaporator. A concentrated solution of the nitrate salt crystallized at 5 °C and, after filtration, was washed with acetone and dried at 60 °C in a vacuum oven. The amount of nitrate anions in the sample was determined spectrophotometrically [5] as 99.6 %.

The determination of the density and the refractive index was described earlier [3]. The total error in the molar refractivity determination was estimated as ± 0.05 cm^3 mol^{-1} It should be noted that the accuracy of the calculated salt molar refractivity decreases with decreasing content of the salt in the solution. At $x < 0.05$, the error may be higher than ± 0.1 cm^3 mol^{-1} The composition of the solutions is expressed in terms of the mole fraction of the salt x.

The measurements were carried out at 30 and 45 °C in DMSO and aqueous solutions, respectively. As the dependence of the molar refractivity on the temperature is less than 3×10^{-4} cm^3 mol^{-1} K^{-1}, the two values measured at 30 and 45 °C can be compared.

All the refractivity values are referred to a wavelength of 586.7 nm (He, D-line). The numerical values of the density and the refractive index are available from the author upon request.

Results and discussion

The molar refractivity of the solution $[R]_{soln}$ (cm^3 mol^{-1}) was calculated using the Lorenz—Lorentz equation

$$[R]_{soln} = \frac{n^2 - 1}{n^2 + 2} \cdot V_m$$

where n is the refractive index and V_m is the molar volume of the solution. The molar refractivities of the salt $[R_x]$ were calculated for various amounts of salt by the method described in the previous paper [3] using the refractivity values of the pure solvents from Ref. [6]. The dependence of $[R_x]$ on the mole fraction of salt is depicted in Fig. 1 and the refractivity values at infinite dilution $[R°]$ were estimated by extrapolation to the value of $x = 0$. The values of $[R°]$ are listed in Table 1 both for aqueous and DMSO solutions. The concentration dependence of the molar refractivity was measured up to saturated solutions of the salts. The empty spaces in Table 1 indicate that the salt was less soluble in a given solvent than would correspond to $x = 0.025$.

Fig. 1. The molar refractivity of the salt $[R_x]$ in dependence on the mole fraction of the salt.
a) ⊗ $(C_2H_5)_4NBr—DMSO$;
× $(C_2H_5)_4NBr—H_2O$;
△ $(C_2H_5)_4NNO_3—H_2O$;
□ $(C_2H_5)_4NNO_3—DMSO$;
○ $(C_2H_5)_4NCl—H_2O$;
● $(C_2H_5)_4NCl—DMSO$.
b) ● $(CH_3)_4NNO_3—H_2O$;
○ $(C_4H_9)_4NI—DMSO$;
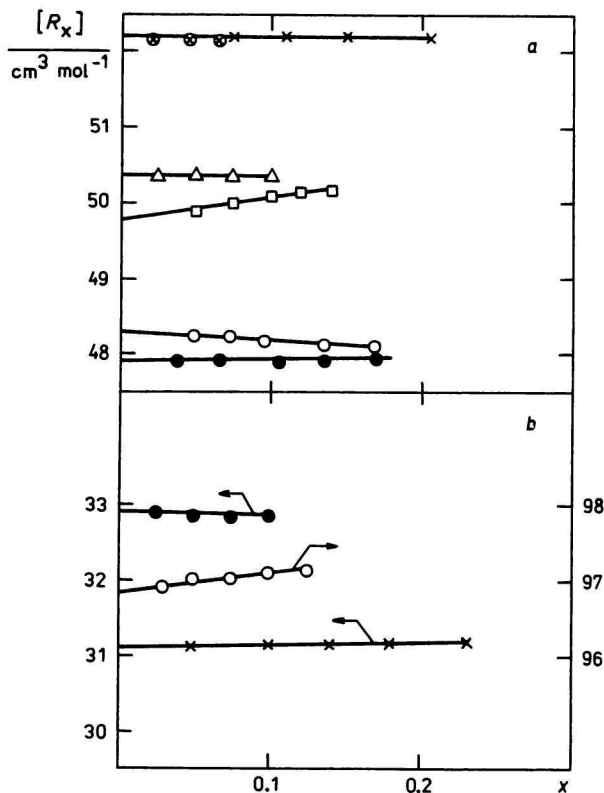× $(CH_3)_4NCl—H_2O$.

Table 1

Refractivities of salts in infinitely dilute aqueous $[R°]_{H_2O}$ and DMSO $[R°]_{DMSO}$ solutions $(cm^3\ mol^{-1})$

Salt	$[R°]_{H_2O}$	$[R°]_{DMSO}$
$(CH_3)_4NCl$	31.1	
$(CH_3)_4NNO_3$	32.9	
$(C_2H_5)_4NCl$	48.26	47.9
$(C_2H_5)_4NBr$	52.2	52.1
$(C_2H_5)_4NNO_3$	50.36	49.78
$(C_4H_9)_4NI$		96.83

The refractivity values of the chloride and nitrate anions in infinitely dilute aqueous and DMSO solutions [3, 4] are listed in Table 2. Using these values, the refractivity of the cations was evaluated assuming the additivity of the ionic refractions in infinitely dilute solutions (Table 3).

Table 2

Refractivities of anions in infinitely dilute solutions in H_2O and DMSO (taken from Ref. [3, 4])

Anion	$[R^\circ]_{H_2O}$	$[R^\circ]_{DMSO}$
Cl^-	9.06	8.61
Br^-	12.67	12.67[a]
I^-	19.22	19.22
NO_3^-	11.02	10.38

a) The result of this work.

Table 3

Refractivities of tetraalkylammonium cations in infinitely dilute solutions in H_2O and DMSO calculated from the equation $[R_{cat}^\circ] = [R_{salt}^\circ] - [R_{anion}^\circ]$. (The refractivity values of anions are given in Table 2.)

Cation	$[R^\circ]_{H_2O}/(cm^3\ mol^{-1})$			$[R^\circ]_{DMSO}/(cm^3\ mol^{-1})$			
	Cl^-	Br^-	NO_3^-	Cl^-	Br^-	NO_3^-	I^-
$(CH_3)_4N^+$	22.04		21.9				
$(C_2H_5)_4N^+$	39.2	39.5	39.34	39.3	39.4	39.4	
$(C_4H_9)_4N^+$							77.6

The molar refractivity reflects the dispersivity of the valence electrons which depends on the mass, charge, and polarizability of the molecule. As an increasing number of electrons take part in the bonding the molecule becomes more readily deformable. Thus, we can expect the refractivity values of the tetraalkylammonium cations to be higher than those of the simple univalent cations [3].
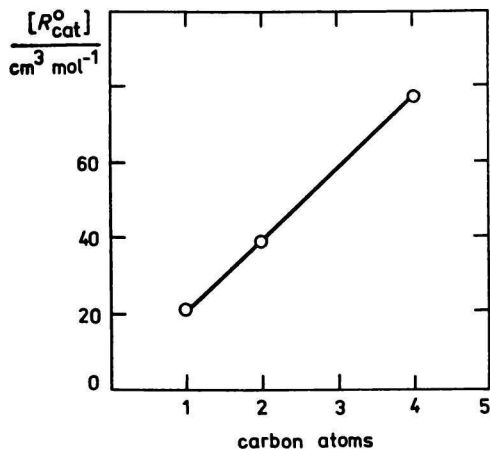

Fig. 2. The molar refractivity of the tetraalkylammonium cations in infinitely dilute solution $[R_{cat}^\circ]$ in dependence on the number of C atoms in the compound.

The refractivities of tetraalkylammonium bromides in infinitely dilute solutions are almost equal both in aqueous and DMSO solutions whereas the refractivity values differ for chloride and nitrate salts (Table 1). None of the studied anions influences the water molecule [4] but chloride and nitrate anions exert a polarizing effect on DMSO [3], which causes a decrease in the salt refractivity. It follows that the bromide anion does not influence the DMSO molecule and it is more than probable that the larger iodide anion will also have no effect on DMSO, as was assumed in the previous paper [3].

The calculated refractivity values of the cations (Table 3) were found to be mutually consistent in both solvents within the measuring error. This confirms the refractivity values of chloride and nitrate anions in infinitely dilute aqueous and DMSO solutions estimated earlier [3].

The dependence of the refractivity of the cations on the number of C atoms is depicted in Fig. 2. The molar refractivity shows constant differences for equal increments of a —CH_2 group, similarly as in homologous series of aliphatic alcohols, acids, and esters [7].

References

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