MOLAR REFRACTIVITIES OF SOLUTIONS OF THE EUTECTIC SILVER NITRATE–THALIUM NITRATE MIXTURE IN WATER AND DIMETHYL SULFOXIDE

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Refractive indices of the $(Ag_{0.516}, Tl_{0.484})NO_3-H_2O$ and $(Ag_{0.516}, Tl_{0.484})NO_3-DMSO$ solutions have been measured at 90 °C over the whole composition range extending from the molecular solvents to the molten electrolyte. The molar refractivities of the melts were calculated from the refractive indices and a set of density values interpolated at the same temperature. Both systems were found to exhibit deviations from the ideal additive behaviour. The molar refractivities of the electrolyte (eutectic mixture $AgNO_3-TlNO_3$) and the solvent were calculated and their composition dependence and the deviations from the additivity are compared and discussed. The molar refractivity was found to be a complex, a less indicative, and a less sensitive indicator of the types and strength of ion–solvent interactions in these melts than the molar volume.

Large number of experimental and theoretical studies have been devoted to the volumetric properties of electrolyte solutions up to now. The investigations performed in dilute solutions range have been rationalized by the concept of the apparent molar volume of the salt, which has helped to understand hydration/solvation phenomena. Partitioning of the apparent molar volume values into individual ionic contributions at infinite dilution brings a possibility to test the independence of ionic contributions.

The refractive index and the derived molar refractivity yield an alternative source of information on the volumetric properties of solutions. The molar refractivity is in fact related to the actual volume of the component in the solution and can be compared with the apparent molar volume calculated from density data[1,2].

Some of our previous studies[3,4] concerned mainly solutions of nitrates and thiocyanates in water and in dimethyl sulfoxide (DMSO). Nitrates are generally highly soluble both in water and in DMSO and experimental results could be used to discuss volumetric behaviour in rather wide range of compositions. Data of medium and highly concentrated electrolyte solutions were frequently treated in terms of deviations from the ideal additive behaviour between molecular solvent and hypothetical supercooled liquid molten electrolyte. In these studies simplifying assumptions were made

concerning the molar refractivity and the molar volume of the hypothetical undercooled liquid electrolyte, as only the molar refractivity of the solid substance and the molar volume of the molten salt at higher temperatures are known in some cases[5].

In the present paper the results of experimental investigation and analysis of volumetric and refractometric properties of the $(Ag_{0.516}, Tl_{0.484})NO_3$–DMSO and $(Ag_{0.516}, Tl_{0.484})NO_3$–$H_2O$ systems at 90 °C, a temperature at which both the molecular solvent and the salt mixture are liquid, are presented.

This rather exceptional opportunity offered by this low-temperature melting salt mixture is used for a discussion of the deviations of both systems from the ideal additive behaviour.

EXPERIMENTAL

Reagent grade $AgNO_3$ and $TlNO_3$ (Lachema, Czechoslovakia) were vacuum desiccated at 120 °C and stored over P_4O_{10}. Reagent grade dimethyl sulfoxide containing no more than 0.03 mass per cent of water (Merck, F.R.G.) was kept in dry atmosphere and weighed in syringes to avoid any exposure to moisture.

In the system $AgNO_3$–$TlNO_3$ the equimolar compound $AgNO_3$. $TlNO_3$ formation with melting point 83 °C and two eutectic points with temperature 82.2 °C and 82.5 °C were described[6]. One of the eutectic mixtures at the Ag/Tl ratio of 1.06 corresponding to 0.515 for the mole fraction of $AgNO_3$ and eutectic temperature 82.5 °C was used in the present study. This choice allows to discuss our results in relation to the extensive investigations carried out by Abraham et al.[7,8] on the corresponding aqueous systems. Aqueous solutions of the selected eutectic mixture are liquid at 90 °C over the entire composition range, while solutions of the salt mixture in DMSO exhibit a solubility gap in the salt mole fraction range from 0.45 to 0.9, where the liquidus temperature of the solutions is in the range between 90 and 120 °C. The temperatures above 90 °C could not be used for the measurement because of the apparatus limitations and high vapour pressure of solvents above the solutions which could significantly modify the composition of the solutions in case of refractivity index measurements.

Solutions were prepared by weighing both the solid eutectic mixture (prepared in advance by melting together the salts) and the solvent (water or DMSO) into small closed glass containers. The vessels were first cooled down in liquid nitrogen, evacuated and slowly heated up to 90 °C thus preventing any loss of the solvent during melting. No additional analytical control of the composition of the samples was made.

The density of the aqueous solutions was measured at 60 and 70 °C with a DMA 40 digital vibration densimeter (Paar, Austria). The analysis of the calibration and the temperature control during measurement gave an estimate of the uncertainty of the measured density as being better than $\pm 1 . 10^{-3}$ g cm^{-3}. The data were combined with the data at 98.5 °C reported by Abraham et al.[7] to get densities at 90 °C by simple linear interpolation.

Density values for solutions of the $AgNO_3$–$TlNO_3$ eutectic mixture in DMSO taken from our previous work[9] were used to calculate the molar volumes, V_m, at 90 °C. The molar volume data reported in Table I were calculated from the smoothed V_m vs x plot to reduce the influence of the scatter of the density values on the refractivity data calculated from refractive indices.

The refractive indices were measured at a wavelength of 587.6 nm (He, D-line) with a PR-2 Pulfrich refractometer (Jena, F.R.G.) with an uncertainty of $\pm 5 . 10^{-5}$ units. The molar refractivity of the solution was calculated from the refractive index and the molar volume with a resulting uncertainty of ± 0.02 cm^3 mol^{-1}.

Errors due to the uncertainty in the composition of the solutions (± 0.0001 units of x) did not exceed the above declared uncertainties.

RESULTS AND DISCUSSION

The experimental values of the refractive index, n, together with the values of molar volume of the corresponding solutions of the $AgNO_3$–$TlNO_3$ eutectic mixture, V_m, both in water and in DMSO are summarized in Table I.

The molar volumes of the solution, V_m, were calculated from the density data, d, by using the relation

$$V_m = \frac{(1-x)M_s + xM}{d}, \tag{1}$$

where x is the salt (eutectic mixture) mole fraction, M and M_s are the molecular masses of the eutectic mixture and of the solvent, respectively, and d is the density of the solution.

Densities of aqueous solutions of the same eutectic $AgNO_3$–$TlNO_3$ mixture were measured at 98.5 °C over the entire composition range from dilute solutions to the molten salt end by Abraham et al.[7]. The system was found to exhibit only a small negative deviation from the ideal additive volumetric behaviour. This fact is surprising if we take into account that the solution can be viewed as a result of mixing of a molecular compound with a molten ionic salt. The nearly ideal behaviour of this system is ascribed to very weak hydration of both cations, a hypothesis which is supported also by the results of previous studies by vapour pressure measurements of the same authors[8].

The replacement of water with DMSO results in a distinct deviation from the ideal additive behaviour of the solution due to much stronger interaction between DMSO (molecular compound) and ionic components of the solution then between water and the same ions[9]. This conclusion was confirmed in our previous studies based on vapor pressure measurement[10], where water and DMSO were compared in sense of their interactions with ionic compounds.

The traditional approach to dilute electrolyte solutions uses the concept of the apparent molar volume of the salt, ϕ, that is defined by the relation

$$\phi = [\,V_m - (1-x)\,V_s^0\,]\,/\,x\,. \tag{2}$$

In this equation V_s^0 is the molar volume of the pure solvent and the other quantities have the above defined meaning.

Detailed discussion of the "apparent molar volume of the salt" concept and its significance for electrolyte solutions data interpretation at low and medium concentrations was presented in our previous paper[11]. Of course, this concept is used mainly for diluted solution of salts, but it can be used over more extended composition range. The use of this concept implies that all the deviations from the volumetric ideality, i.e. the simple additivity of the molar volumes of the pure solvent, V_s^0, and of the molten salt,

V_x^0, are ascribed to the non-ideal volumetric behaviour of the salt and are included in the value of ϕ.

In contrast to this generally used approach, our previous studies on the volumetric behaviour of highly concentrated electrolyte solutions were based on the use of the concept of the apparent molar volume of the solvent[5,12,13].

TABLE I
Experimental values of refractive indices, n, calculated values of molar volumes, V_m (cm^3 mol^{-1}) and molar refractivities, $[R]_{soln}$ (cm^3 mol^{-1}) of solutions of the eutectic mixture AgNO$_3$–TlNO$_3$ (Ag / Tl = 1.06) at 90 °C in H$_2$O and DMSO; x mole fraction of the salt

x	n	V_m	$[R]_{soln}$
(Ag,Tl)NO$_3$–H$_2$O			
0	1.3204	18.66	3.71
0.02	1.3409	19.12	4.02
0.027	1.3474	19.29	4.12
0.05	1.3696	19.83	4.48
0.1	1.4155	21.03	5.27
0.2	1.4828	23.54	6.72
0.3	1.5428	26.18	8.25
0.4	1.5891	28.92	9.75
0.5	1.6218	31.74	11.18
0.6	1.6478	34.62	12.59
0.7	1.6749	37.52	14.10
0.8	1.6938	40.44	15.52
0.9	1.7118	43.34	16.97
1	1.7274	46.20	18.39
(Ag,Tl)NO$_3$–DMSO			
0	1.4473	75.85	20.28
0.1	1.4769	71.38	20.16
0.15	1.4909	69.34	20.80
0.2	1.5047	67.43	19.99
0.25	1.5179	65.62	19..88
0.3	1.5317	63.92	19.80
0.35	1.5444	62.32	19.68
0.4	1.5579	60.80	19.60
0.45	1.5711	59.36	19.51
0.9	1.6939	48.49	18.62
0.95	1.7099	47.36	18.51
1	1.7274	46.22	18.40

A rigorous thermodynamic description of volumetric properties of binary mixtures is based on the use of the partial molar volumes of the components and of their dependence on composition of the mixtures. An analysis of the present work's data in terms of the partial molar volumes is presented in Fig. 1. The values of molar volume of the binary mixtures were fitted to the polynomial of the type $V_m = a + b x + c x^2 + d x^3$ and the partial molar volumes of the solvent and the salt mixture were calculated as a function of the salt content. The limits of the applicability of both above mentioned simplifying concepts are clearly visible in Fig. 1 for both investigated systems. It is evident that the "a.m.v. of the solvent" concept can be used in rather wide composition range, in fact the partial molar volume of the salt mixture in the aqueous system is essentially independent of the composition in the wide range defined by $0.3 < x < 1.0$, while for the DMSO-based systems the partial molar volume of the salt mixture is independent of the composition in the shorter, but still wide, range defined by $0.5 < x < 1.0$. The concept of the "a.m.v. of the salt" on the other hand is strictly applicable only for dilute solutions of the salt mixture, especially in the case of the DMSO-based solutions, as it is visible from the limited composition range where the partial molar volume of DMSO is independent of the composition.

The refractive index and the derived molar refractivity give us an alternative source of information on interactions in solutions as it corresponds to the actual volume of the ions, or molecules, in one mole of the substance.

The molar refractivity of the solution, $[R]_{soln}$, cm^3 mol^{-1}, is defined by the well-known Lorenz–Lorentz relation

$$[R]_{soln} = \frac{n^2 - 1}{n^2 + 2} V_m , \tag{3}$$

where n is the refractive index for the selected wavelength of measurement and V_m is the molar volume of the solution.

It is generally assumed that the refractivity of a system could be calculated as the sum of the refractivities of the individual components if they do not interact between themselves[14]. This assumption is similar to that applied for the molar volumes of the ideal solution.

The molar refractivity data (see Table I) resulting from the present work, which for the first time deals with refractivity of electrolyte solutions covering the whole composition range from a pure solvent to a molten salt, are plotted in Fig. 2 as a function of the molar composition of the melts. Both systems show almost the ideal additive behaviour of the molar refractivity even if a detailed analysis reveals a very small positive deviations of the data points from the straight line. This finding contrasts with the behaviour of the molar volumes, which always exhibit distinct negative deviations from the ideal additivity[5].

The comparison of the results of volumetric and refractivity studies reveals that while the maximum experimental deviations of $[R]_{soln}$ from the additive behaviour are

about 0.1 cm^3 mol^{-1} (i.e. ca 0.8%), deviations of molar volumes are 0.75 and 3.0 cm^3 mol^{-1} for aqueous and DMSO systems, respectively, i.e. 2.3 and 5.1%.

To evaluate changes in polarization or deformation of electron shells with changes of surrounding, i.e. with changes in composition of the system, the approach similar to that adopted for the molar volume data interpretation is used.

If we follow the same line of data interpretation as for the molar volume, we would calculate the values corresponding to the partial molar volume from the molar refractivity data. Unfortunately the deviations of the refractivity of the solutions from the ideal additive behaviour are very small and individual values of the deviations are only by one order higher (see above) than the uncertainty of the data. In such situation any discussion of the resulting partial molar refractivities would be highly speculative.

The molar refractivity of the salt, $[R_x]$, is calculated from the molar refractivity of the solution $[R]_{soln}$ and that of the pure solvent $[R_s^0]$

$$[R_x] = ([R]_{soln} - (1 - x)[R_s^0]) / x . \tag{4}$$

This procedure strictly resembles the calculation of the apparent molar volume of the salt, ϕ (see above).

The eutectic mixture AgNO$_3$–TlNO$_3$ is liquid above 83 °C and the measurement of its refractive index give us not only experimental value of the molar refractivity of the molten salt end of the solutions in water and DMSO, $[R_x^0]$, but also a possibility to
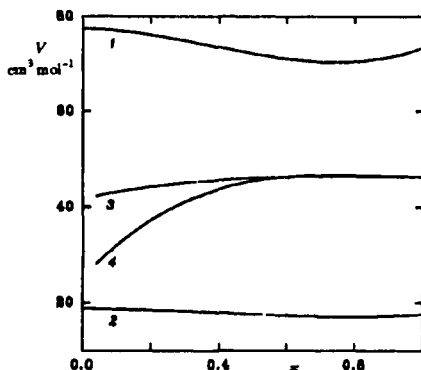

FIG. 1
Partial molar volumes, V of the AgNO$_3$–TlNO$_3$ eutectic mixture and solvents as a function of the mole fraction of the salts in the solution: 1 DMSO, 110 °C; 2 H$_2$O, 98.5 °C; 3 (Ag,Tl)NO$_3$ in H$_2$O; 4 (Ag,Tl)NO$_3$ in DMSO
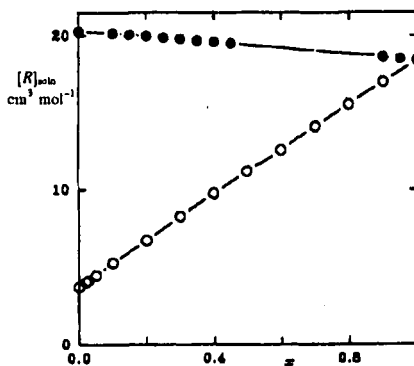
FIG. 2
Variation of the molar refractivity of the solutions of the eutectic mixture AgNO$_3$ + TlNO$_3$ (Ag / Tl = 1.06), $[R]_{soln}$, with composition in aqueous and DMSO solutions at 90 °C (x mole fraction of the salts). The full lines represent the ideal additive behaviour: O salts + H$_2$O, ● salts + DMSO

calculate the apparent refractivity of the solvent (water or DMSO), $[R_s]$ by means of the equation

$$[R_s] = ([R]_{soln} - x\,[R_x^0]) / (1 - x)\,. \tag{5}$$

The composition dependencies of $[R_s]$ and $[R_x]$ are presented in Fig. 3 for both the aqueous and the nonaqueous systems.

For most of the aqueous systems previously investigated it was found that $[R_x]$ is a linear decreasing function of the salt mole fraction, while it increases linearly with the salt content when DMSO is used as the molecular solvent instead of water[1-3]. This finding was ascribed to the formation of "contact ion pairs" in the aqueous solutions, as the possible mutual direct interactions of the cations with the anions provoke a significant decrease of the electronic polarizability and then the refractivity of the ions[3]. In the case of DMSO-based systems the increase of refractivity should be ascribed mainly to a remarkable effect of interactions of the anions on the solvent molecules, which should not work substantially in the case of water as a solvent[1]. The only exception was found for solutions of NH_4I and $AgNO_3$ in DMSO. This was explained by weak interactions between ammonium and silver cations and DMSO molecules.

In the case of the $(Ag,Tl)NO_3$-solutions (Fig. 3) both the aqueous and the non-aqueous systems show a quite similar negative slope for the $[R_x]$ vs x dependence in the dilute solutions range; in both cases, however, no simple straight-line approximation can be used over the whole composition range. Of course, in previous studies[1] on the refractivity of such kind of melts the trend with composition could not be fully understood and discussed due to the rather limited composition ranges accessible for the different binary systems. On the contrary, in the present cases refractivity data are available over the whole composition range, that is up to the molten salt end ($x = 1$). Two important aspects are to be stressed in this line. First, the values of $[R_x]$ at infinite dilution, $[R_x^\infty]_{H_2O}$ and $[R_x^\infty]_{DMSO}$, which are easily obtained by a short extrapolation from the low-concentration data are essentially the same within the limits of their
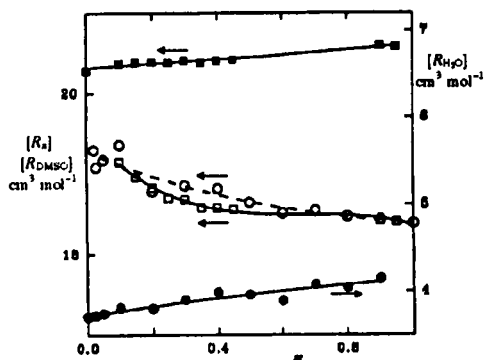

Fig. 3
Molar refractivity of the salts mixture, $[R_x]$, and of the solvents, $[R_s]$, as a function of the mole fraction of the salts mixture, x, at 90 °C: ■ $[R_{DMSO}]$, ● $[R_{H_2O}]$, ○ $[R_x]$ in H_2O, ☐ $[R_x]$ in DMSO. The curves are visual aids only

uncertainties. This behaviour is similar to that previously found for the $AgNO_3$–H_2O and $AgNO_3$–DMSO systems[1], where the values were found to be 16.01 and 16.09 cm^3 mol^{-1}, respectively. Second, the trend of the of the $[R_x]$ dependencies are very similar throughout the whole composition range, and in both cases there is an indication of a tendency of $[R_x]$ to be independent of x in the high-salt-concentration range, that is above $x = 0.4 - 0.5$. Moreover, the total change of $[R_x]$ is quite small, -0.5 cm^3 mol^{-1} over the whole range and about -0.4 from $x = 0$ to $x = 0.5$; these changes can be compared with the changes of $[R_x]$ for $AgNO_3$–DMSO, i.e. about -0.1 cm^3 mol^{-1} from $x = 0$ to $x = 0.5$, and about -0.5 cm^3 mol^{-1} in the same composition range for the $AgNO_3$–H_2O system as it can be argued from Fig. 2 in ref.[1]. From the above considerations it appears that the presence of $TlNO_3$ in the mixed salt with $AgNO_3$ does not greatly modify the main features of the ion–ion and ion–solvent interactions.

The two entitled solutions represent two distinctly different systems from the thermodynamic point of view. While the aqueous solution is one of few systems where positive deviations from the Raoult's law were found[8], the $(Ag,Tl)NO_3$–DMSO system behaves like a typical electrolyte solutions showing negative deviations from Raoult's ideal behaviour[9].

In our previous study on volumetric behaviour[5] we showed that negative deviations from the volumetric ideal additive behaviour should be generally found for solutions of electrolytes and this prediction was confirmed by investigation of both systems[7,9].

The molar refractivity of a solution is a complex function of the refractive index and the molar volume of the system (Eq. (3)). Deviations of these two quantities of electrolyte solutions from additive behaviour are of opposite sign and the slight positive deviations of the molar refractivity from the ideal additive behaviour (see Fig. 2) indicate that these two effects do not balance each other. It is evident, that an almost ideal additive molar refractivity can be found for these systems which are markedly nonideal from a volumetric point of view.

Apart from a complex character of the information about the structure of solutions provided by refractivity, i.e. by $[R]_{soln}$, the sensitivity of this value to the deviation of the system from an ideal behaviour is lower that sensitivity of molar volume.

The character of changes of the "apparent" molar refractivity $[R_s]$ and $[R_x]$ with increasing content of the salt indicates that a straight line approximation used for calculation of refractivity in infinitely dilute solutions $[R_x^\infty]_{H_2O}$ and $[R_x^\infty]_{DMSO}$ can be used only in a restricted interval of composition.

CONCLUSIONS

Molar refractivity is a complex characteristics of ion–ion and ion–solvent interactions in electrolyte solutions that reflects not only polarizability and deformability of the solution components, but also the volumetric parameters of the components.

Both systems with positive and negative deviations from the Raoult's law behaviour exhibit positive deviations from the additivity of refractivities of the components.

The strength of the ion–solvent interactions related with different values of the solvent dipole moment of water and DMSO and easier deformability of the DMSO molecules have no significant effect to the deviations of refractivities from the additivity.

Molar volumes are preferred as the more sensitive characteristics of deviations of the system from an ideal behaviour.

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