Contribution of the concept of simple solutions to calculation of the stoichiometric activity coefficients and density of ternary mixtures of hydroxylammonium or hydrazinium nitrate with nitric acid and water

A.-C. Kappenstein,[a] Ph. Moisy,*[a] G. Cote[b] and P. Blanc[a]

[a] Commissariat à l'Énergie Atomique (CEA), Valrhô, DCC/DRRV/SEMP/LCAA BP 171, 30207 Bagnols-sur-Cèze Cedex, France. E-mail: philippe.moisy@cea.fr
[b] ENSCP, Laboratoire d'Electrochimie et Chimie Analytique (UMR CNRS-ENSCP 7575), 11 rue P. et M. Curie, 75231 Paris Cedex 05, France

Binary data (water activity as a function of the molal concentration) at 25 °C for the principal anti-nitrous compounds used in nitric acid aqueous media—hydrazinium nitrate (HDZN) and hydroxylammonium nitrate (HAN)—are determined by direct water activity measurements. Density variations at 25 °C are also established. Ternary systems involving these nitrate salts and nitric acid are studied from the standpoint of simple solution theory. It is observed that the system HDZN–HNO$_3$–H$_2$O does not exhibit simple behaviour, which is due to the acid–base equilibrium involving HDZN and HNO$_3$ (i.e., N$_2$H$_6^{2+}$ formation). On the other hand, the system HAN–HNO$_3$–H$_2$O which does not undergo major chemical interactions follows satisfactorily the simple solution rule as long as the water activity is higher than 0.84. For ternary simple solutions it is possible to predict activity coefficients for each component by applying the Zdanovskii–Stokes–Robinson rule and the Mikulin relationship.

Introduction

Hydrazinium nitrate (HDZN; N$_2$H$_5^+$,NO$_3^-$) and hydroxyl-ammonium nitrate (HAN; NH$_3$OH$^+$,NO$_3^-$) are routinely used in spent nuclear fuel reprocessing by liquid–liquid extraction in a nitric acid medium. The rapid kinetics of the reactions between these compounds and HNO$_2$[1] limit the quantity of nitrous acid in the medium, and thus control the stability of the oxidation states of the metallic cations in the presence of nitric acid.[2] Hydroxylamine (HA, NH$_2$OH) and hydrazine (HDZ, N$_2$H$_4$) are weak bases (pK_a 6.0 and 7.95, respectively[3]); in the presence of nitric acid, the species considered are thus hydroxylammonium nitrate (HAN) and hydrazinium nitrate (HDZN). In more concentrated acidic media (H$^+$ > 1 M), hydrazine can form HDZN$_2$ (N$_2$H$_6^{2+}$,2NO$_3^-$); the pK_a value of the HDZN$_2$/HDZN couple has been estimated between -1.05[4] and -0.4.[3]

Physicochemical investigations of these systems have addressed three main issues: (1) acquisition of liquid–vapor equilibria at the boiling temperature of binary HDZ–H$_2$O mixtures;[4] (2) cryoscopic measurements of HDZ–H$_2$O,[5] HAN–H$_2$O[6] and HDZ–HDZN–H$_2$O[4] mixtures; (3) determination of thermodynamic quantities for excess mixtures, e.g. of HDZ–H$_2$O.[7] To the best of our knowledge, however, no studies of the activity coefficients at 25 °C of HDZ, HDZN, HA or HAN in water or in ternary mixtures with nitric acid have been published in the literature, although the activity coefficients of nitric acid in aqueous solution have been widely investigated and recently revised.[8]

Two difficulties arise in determining the osmotic coefficient of ternary systems comprising HDZN–HNO$_3$–H$_2$O or HAN–HNO$_3$–H$_2$O, or the activity coefficients of HDZN or HAN in these systems: acquisition of reliable data (nitric acid is a volatile compound), and modeling the activity coefficients of the constituents from a small number of experimental points over a wide range of mixture compositions.

Unlike isopiestic measurements, direct water activity coefficient measurements are compatible with a volatile electrolyte such as nitric acid for calculating the osmotic coefficient Φ.[8] Water activity determinations are found to be very useful for rationalizing and predicting the osmotic coefficient of complex solutions via the simple solution concept initially developed by Zdanovskii,[9] then by Timofeev[10] and Stokes and Robinson.[11] Indeed, many ternary mixtures behave according to the simple solution concept recalled below, which allows the prediction and modeling of the properties of such solutions in a large range of circumstances. However, there are also systems which make more or less an exception to the simple solution rule and it is essential to evaluate the "simplicity" of any given system before attempting to model its properties.

The purpose of this investigation is the study of the simplicity of HDZN–HNO$_3$–H$_2$O or HAN–HNO$_3$–H$_2$O ternary mixtures. This study requires the establishment of binary data in terms of water activity and density of HDZ, HDZN, HA and HAN in water. Since water activity has attracted much attention only recently, the first step was to verify the validity of such measures in comparison with other methods of osmotic coefficient determination. For such a purpose, two particular systems were chosen: urea, a non-volatile anti-nitrous compound whose binary data have been etablished by the isopiestic method,[12] and nitric acid, a volatile solute whose binary data have been recently revised[8] on the basis of cryoscopic measurement and vapor pressure determination.

Theoretical aspects

The simple solution concept initially developed by Zdanovskii[9] (the Zdanovskii–Stokes–Robinson or ZSR rule) to characterize deviations of ternary mixtures from ideality can be stated as follows: a ternary mixture is a simple solution when the isobaric isotherms at constant water activity on a mixture composition diagram (isopiestic curves) are straight

$$\frac{m_1}{m_1^{\text{bi}}} + \frac{m_2}{m_2^{\text{bi}}} = 1 \quad \text{at constant water activity } a_{\text{w}} \quad (1)$$

where m_1 and m_2 are the molal concentrations of solutes 1 and 2 in the ternary mixture, and m_1^{bi} and m_2^{bi} are the molal concentrations of solutes 1 and 2 in a binary mixture of the same water activity. If binary data are available for the solutes constituting the mixture, the ZSR relation can be applied directly to calculate the water activity of the mixture by an iteration. Moreover, for mixtures to which this rule is applicable, Mikulin[14] demonstrated that the activity of a non-electrolytic or salt solute can be expressed as a function of the mixture composition, its water activity and the compositions of binary mixtures of the same water activity:

$$\gamma_{1,\text{st}} = \frac{v_1 m_1^{\text{bi}} \gamma_{1,\text{st}}^{\text{bi}}}{v_1 m_1 + v_2 m_2} \quad (2)$$

where v_1 and v_2 represent the sum of the stoichiometric coefficients of electrolytes 1 and 2; m_1^{bi} and γ_1^{bi} are the molal concentration and activity coefficient of solute 1 in a binary mixture of the same water activity as the ternary mixture; and γ_1 is the activity coefficient of solute 1 in the ternary mixture.

Vdovenko and Ryazanov[15] demonstrated the additive volume property of a ternary solution following the ZSR rule. The density (ρ) of the ternary mixture can thus be expressed as a function of the binary data of the system components:

$$\rho = \frac{M_1 m_1 + M_2 m_2 + 1000}{\dfrac{m_1}{m_1^{\text{bi}}}\dfrac{M_1 m_1^{\text{bi}} + 1000}{\rho_1^{\text{bi}}} + \dfrac{m_2}{m_2^{\text{bi}}}\dfrac{M_2 m_2^{\text{bi}} + 1000}{\rho_2^{\text{bi}}}} \quad (3)$$

where M_1 and M_2 are the molar masses of the ternary mixture components, and ρ_1^{bi} and ρ_2^{bi} are the densities of the binary solutions with the same water activity as the ternary mixture.

This concept allows ternary mixtures to be studied with only a limited number of data points: other than the binary data for each constituent of the mixture, the only experimental data points necessary for the ternary systems are those used to verify that they are indeed simple systems.

Experimental

The reactants used were: hydrazine monohydrate (Aldrich, >99.5% pure), hydroxylamine base (Fluka, approx. 50% solution in water), nitric acid (Prolabo, 68%), lithium nitrate (Prolabo, >98% pure) and urea (Prolabo, >99.5% pure). The hydroxylamine was characterized to within $\pm 0.7\%$ by acid–base titration with hydrochloric acid (Prolabo Normadose 1 M $\pm 0.5\%$). The nitric acid was characterized by density measurement, and the molal concentration was then calculated using nitric acid solution density data established by Gillespie *et al.*;[16] this technique allows the molal concentration to be determined within $\pm 0.05\%$.

The concentrated hydrazinium nitrate and hydroxyl-ammonium nitrate solutions were prepared at low temperature (5–10 °C) by slowly neutralizing concentrated hydrazine and hydroxylamine solutions with concentrated nitric acid to obtain final concentrations of 7.55 mol kg^{-1} for hydrazinium nitrate and 11.33 mol kg^{-1} for hydroxyl-ammonium nitrate. The excess nitric acid (<0.02%) in the HDZN solution and the residual hydroxylamine concentration (<0.3%) in the HAN solution were low enough that their influence on the physicochemical properties of the medium were negligible. All the dilute solutions (binary or ternary mixtures) were prepared gravimetrically from concentrated solutions.

The density values were measured with a vibrating-tube densimeter (Anton Paar DMA 55), calibrated at

25.00 $\pm$ 0.02 °C by solvents with density values certified at 25.0 °C by H. and D. Fitzgerald Ltd. (UK): water, $\rho = 997.04$ kg m^{-3}; dimethyl phthalate, $\rho = 1186.51$ kg m^{-3}; dichloro-propanol, $\rho = 1357.65$ kg m^{-3} and dibromobutane, $\rho = 1819.63$ kg m^{-3}. The density of each solvent was measured three times to plot the calibration curve, which was then used to determine the density within ± 0.05 kg m^{-3}.

The water activity of the mixtures was measured with a variable-impedance hygrometer (Novasina AW Center™) with three independent sensors consisting of a hygroscopic substance sensitive to the relative humidity of the vapor phase with which they are in equilibrium; the sensors also included eVC-100 acid fume prefilters. The device was calibrated in a two-step procedure. First a linear output signal was obtained using six standard solutions of saturated salts with a water activity ranging from 0 to 1;[17] the sensors were then calibrated over a relatively narrow water activity range (0.1 water activity units) in view of measurements within that range. The standard solutions were lithium nitrate solutions with concentrations established by gravimetry to cover the calibration range in steps of 0.01 water activity units. Ten or eleven solutions were used for calibration over a water activity range of 0.1 units. Lithium nitrate was used for several reasons: binary data for this non-volatile salt in aqueous solution have been well established,[18] and the accessible calibration range is relatively broad (≈ 0.4 to 1); moreover, the sensor response to this salt is linear over a water activity calibration range from 0.50 to 0.95.

This calibration procedure ensured an uncertainty tolerance on the water activity measurement (as calculated for a 95% confidence level on the calibration line for an unrepeated water activity measurement) of between ± 0.0015 and ± 0.0035 over the water activity range from 0.50 to 0.80, and between ± 0.0040 and ± 0.0045 for higher water activity values.

Results and discussion

Water activity measurement validity

In order to verify the quality of the water activity measurements obtained with this device, two series of water activity measurements were performed on binary mixtures: one with nitric acid solutions (a volatile electrolyte) and the other with urea solutions (a non-volatile and non-electrolytic solute). The sensors were protected against acid fumes with eVC-100 pre-filters for both series of measurements.

The mean values of three water activity measurements on aqueous nitric acid solutions are indicated in the second column of Table 1, which also indicates in the third column for comparative purposes the values calculated from eqns. (4) and (5) recommended by the NIST,[18] with parameters revised by Charrin *et al.*[8] These parameters were determined by a least square interpolation on the basis of cryoscopic and vapour pressure data of aqueous solution of HNO$_3$.

$$\Phi = 1 - \left\{ \frac{0.5108 \ln 10 |z^+ z^-|}{Ib^3} \left[\begin{array}{l} (1 + b\sqrt{I}) - 4.60517 \times \\ \log(1 + b\sqrt{I}) - \dfrac{1}{1 + b\sqrt{I}} \end{array} \right] \right. \\ \left. - \tfrac{1}{2}cm - \tfrac{2}{3}dm^2 - \tfrac{3}{4}em^3 - \tfrac{4}{5}gm^4 \right\} \quad (4)$$

where $I = m$ and $|z^+ z^-| = 1$ in the case of nitric acid, with the following proposed parameter values: $b = 1.3401$; $c = 0.1793$; $d = -5.990 \times 10^{-3}$; $e = 6.071 \times 10^{-5}$ and $g = 2.934 \times 10^{-7}$, with a correlation coefficient of 0.993.

$$\Phi = -\frac{1000 \ln a_{\text{w}}}{v_i m_i M_{\text{H}_2\text{O}}} \quad (5)$$

Table 1 Experimental water activity values for nitric acid solutions at 25 °C compared with published values[8]

m_{HNO_3}/mol kg^{-1} $\pm 0.4\%$	$a_{w\,meas} \pm 0.003$	$a_{w\,calc}$[8]	Δa_w (%)	$\Delta\Phi$ (%)
1.585	0.944	0.943	0.10	1.84
2.118	0.924	0.922	0.22	3.13
2.584	0.904	0.902	0.22	1.79
3.079	0.882	0.881	0.11	0.62
3.505	0.861	0.863	0.23	1.48
4.008	0.839	0.841	0.24	1.28
4.507	0.818	0.819	0.12	0.52
5.515	0.772	0.774	0.26	1.19
6.005	0.753	0.753	—	0.05
6.516	0.732	0.731	0.14	0.55
7.016	0.709	0.710	0.14	0.15
7.506	0.690	0.689	0.14	0.48
8.006	0.669	0.668	0.15	0.31
8.504	0.648	0.648	—	0.03
9.014	0.627	0.628	0.16	0.35
9.504	0.611	0.609	0.33	0.57
10.000	0.592	0.591	0.17	0.38
10.501	0.574	0.573	0.17	0.39
10.996	0.554	0.556	0.3	0.44
11.502	0.541	0.538	0.55	0.79
11.995	0.523	0.522	0.19	0.21

Table 2 Experimental water activity values for urea solutions at 25 °C compared with published values[12]

m_{urea}/mol kg^{-1} $\pm 0.2\%$	$a_{w\,meas}$	$a_{w\,calc}$[12]	Δa_w (%)	$\Delta\Phi$ (%)
4.588	0.931 ± 0.002	0.930	0.09	1.29
5.637	0.915 ± 0.002	0.916	0.13	1.51
6.550	0.903 ± 0.0025	0.904	0.17	1.66
7.508	0.892 ± 0.0025	0.892	0.01	0.12
8.806	0.877 ± 0.0025	0.876	0.05	0.40
9.713	0.866 ± 0.0025	0.866	0.05	0.32
11.073	0.849 ± 0.003	0.850	0.10	0.62
13.029	0.829 ± 0.0015	0.828	0.10	0.53

where $M_{H_2O} = 18.015$ g mol^{-1}.

The deviation between the calculated water activity ($a_{w\,calc}$) and the measured water activity ($a_{w\,meas}$) remained within 0.25%. The observed deviations between the osmotic coefficient values determined from $a_{w\,calc}$ and $a_{w\,meas}$ were higher, but generally did not exceed 2% for the highest water activities. The higher the water activity for a constant difference Δa_w between $a_{w\,calc}$ and $a_{w\,meas}$, the greater the difference between Φ_{exp} and Φ_{calc}, ranging from 0.21% ($a_w = 0.523$ and $\Delta a_w = 0.002$) to 3% ($a_w = 0.924$ and $\Delta a_w = 0.002$). This evolution is attributable to the change in the variable between a_w and Φ (eqn. (5)).

This device is well suited to measuring the water activity in the case of nitric acid, a volatile solute for which isopiestic measurements are not practicable. The presence of acid fume prefilters did not interfere with the measurement acquisition, although it must be noted that the partial pressure of nitric acid is less than 2% of the total pressure for a nitric acid concentration of 10 mol kg^{-1}. The method allows the water activity to be determined in a much shorter time than transpiration techniques (30 min to 1 h depending on the time required to obtain equilibrium between the sensor and the vapor medium above the solution).

The water activities measured for urea solutions in water were compared with the values obtained by Ellerton and Dunlop by isopiestic measurements.[12] The experimental data reported by these authors were interpolated by eqn. (4) adapted to a non-electrolyte by assuming $I = m$ and $|z^+ z^-| = 1$. The following parameter values were calculated with a correlation coefficient $r = 0.999\,89$: $b = 21.6921$; $c = -0.0768$; $d = 5.1025 \times 10^{-3}$; $e = 2.1069 \times 10^{-4}$ and $g = 3.7527 \times 10^{-6}$.

The measured water activity values $a_{w\,meas}$ (mean of two measurements) for aqueous urea solutions are indicated in Table 2, which also indicates the water activity values $a_{w\,calc}$ calculated by interpolating the osmotic coefficients reported by Ellerton and Dunlop.[12]

Very good agreement was observed over the entire water activity range investigated, generally with less than 0.1% deviation. The acid fume prefilter had no effect on the precision of the water activity measurement, even with a non-volatile solute. Conversely, the differences $\Delta\Phi$ between the osmotic coefficient determined from water activity measurements and the osmotic coefficient calculated from the data provided by Ellerton and Dunlop were significant, but remained at an acceptable level ($\Delta\Phi = 3\%$ in the least favorable case); the evolution of these differences was the same as for nitric acid.

Although this measurement technique is probably less accurate than isopiestic measurement, it provides a means of acquiring water activity data rapidly and, above all, it is suitable for use with some volatile solutes such as nitric acid, for which the isopiestic technique cannot be used. Despite these advantages for obtaining water activity values to investigate mixture deviations from ideality in aqueous media, this system has at least two limitations.

(1) In the case of volatile compounds, the vapor at equilibrium with the aqueous phase no longer consists only of air and water. The compound vapors may strongly interfere with the data acquisition, or even corrode the sensor. In such cases a protective filter adapted to the type of compound studied must be used. Even these filters are not sufficiently effective with highly volatile compounds, however. For example, it was not possible to measure the water activity of mixtures of hydroxylamine (boiling point: 58 °C) in water, as the hydroxylamine fumes resulted in a constant drift in the water activity.

(2) Binary data are generally presented as the variation of the osmotic coefficient *vs.* the solute molal concentration; some methods (including isopiestic methods) are capable of yielding the osmotic coefficient directly. Eqn. (5) is generally used to obtain the osmotic coefficient from the water activity. The uncertainty on the water activity measurement determines the uncertainty on Φ. For relatively low water activity values ($a_w < 0.70$) the error on Φ remains below 2%; for a_w values between 0.700 and 0.800, Φ is known within $\pm 3\%$, and the precision drops to ± 6 or 8% or more at higher a_w values. The uncertainty on Φ is greater than on a_w and tends to increase significantly in dilute media for two reasons: (i) the uncertainty on the water activity measurement increases with the water activity, rising from ± 0.0015 for a_w values between 0.500 and 0.600 to ± 0.0045 for $a_w > 0.900$; and (ii) the logarithmic substitution (eqn. (5)) of the osmotic coefficient for the water activity variable is highly sensitive to the slightest deviation at high water activity values. For water activities above 0.950, the measured values become difficult to interpret, as the precision on a_w is too low to calculate the osmotic coefficients correctly. The time required for the sensor to reach equilibrium also increases considerably, as the vapor pressure approaches that of pure water.

In the absence of reliable experimental data at high water activities (from 0.950 to 1), variations of a_w or of Φ as a function of the solute concentration must be interpreted by extrapolation into the highly dilute range. This method was used to calculate the actinide nitrate activity coefficients by integrating the Gibbs–Duhem relation.[8]

Binary data acquisition (m, a_w, ρ)

The investigation of the ternary systems HAN–HNO$_3$–H$_2$O and HDZN–HNO$_3$–H$_2$O through simple solution theory,

eqns. (1)–(3) requires knowledge of the binary data for each component of the ternary mixture. The variation of Φ for HDZ, HDZN and HAN in aqueous solution was determined by the a_w measurement and then interpolated by eqns. (4) and (5).

The measured water activity and density values are available for binary mixtures of hydrazine (Table S1†) and hydrazinium nitrate (Table S2†). The studied concentrations ranged from 1.02 to 13.03 mol kg⁻¹ for the HDZ–H₂O system and from 0.28 to 7.56 mol kg⁻¹ for the HDZN–H₂O system; the a_w values indicated for the HDZN–H₂O system are the mean of three measurements. Fig. 1 shows the evolution of the osmotic coefficient as a function of the molal concentration determined from the water activity measurements. The osmotic coefficient variations were interpolated over the experimental acquisition range using eqn. (4) recommended by the NIST. The curves in Fig. 1 represent the extrapolation to zero molality.

The following interpolation parameters were used for the hydrazine solutions (HDZ–H₂O system) and for the hydrazinium nitrate solutions (HDZN–H₂O system):

$b_{HDZ} = 5.73873 \times 10^2$ $b_{HDZN} = 2.28634 \times 10^1$

$c_{HDZ} = -4.22986 \times 10^{-1}$ $c_{HDZN} = -3.46134 \times 10^{-1}$

$d_{HDZ} = 6.34567 \times 10^{-2}$ $d_{HDZN} = 3.005117 \times 10^{-2}$

$e_{HDZ} = -4.23211 \times 10^{-3}$ $e_{HDZN} = -4.75944 \times 10^{-4}$

$g_{HDZ} = 1.03759 \times 10^{-4}$ $g_{HDZN} = -7.27229 \times 10^{-5}$

Correlation coefficient   Correlation coefficient
$r_{HDZ} = 0.976$ $r_{HDZN} = 0.984$

The experimental density variation for the binary mixtures of hydrazinium nitrate and water were interpolated by a third-order polynomial; which gives the best correlation coefficient by least square interpolation. Extrapolating to zero molality yields a density of 0.997 54 g cm⁻³, very near the density of pure water at 25 °C (0.997 07 g cm⁻³):

$$\rho = 0.99754 + 0.04177m$$
$$- (2.240132 \times 10^{-3})m^2 + (68.8818 \times 10^{-6})m^3 \quad (6)$$

with a correlation coefficient of $r = 0.999\,77$, where m is expressed in mol kg⁻¹ of water and ρ in g cm⁻³. Recent

data[19] for HDZ–H₂O mixtures show that their density varies only slightly with the molal concentration: ρ varies from 0.997 04 to 1.032 g cm⁻³ over the full hydrazine concentration range (0–100% HDZ). The value of ρ was therefore not measured in this study.

Experimental water activity and density measurements for hydroxylammonium nitrate–water mixtures (HAN–H₂O system) were performed at concentrations ranging from 1.62 to 11.34 mol kg⁻¹ for the water activities, and from 0.42 to 11.34 mol kg⁻¹ for the densities (Table S3†). Water activities are the mean of three measurements. The variation in the HAN osmotic coefficient determined from the a_w measurements is shown in Fig. 2; the following interpolation coefficients were used with eqn. (4) over the experimental acquisition range with a correlation coefficient of $r = 0.992$: $b_{HAN} = 4.689\,05$; $c_{HAN} = -1.979\,060 \times 10^{-1}$; $d_{HAN} = 2.477\,15 \times 10^{-2}$; $e_{HAN} = -1.853\,18 \times 10^{-3}$ and $g_{HAN} = 5.576\,46 \times 10^{-5}$. The osmotic coefficient variations in Fig. 2 represent the extrapolation to zero molality.

The density variation was interpolated using a third-order polynomial expression:

$$\rho = 0.99780 + 0.0440m$$
$$- (2.2683 \times 10^{-3})m^2 + (60.657 \times 10^{-6})m^3 \quad (7)$$

with a correlation coefficient of $r = 0.999\,96$, where m is expressed in mol kg⁻¹ of water and ρ in g cm⁻³. Extrapolating to zero molality yields a density very near that of pure water, despite the lack of data between 0 and 0.42 mol kg⁻¹.

Because of the low boiling point of hydroxylamine (58 °C), no a_w or ρ measurements were performed; microbubbles were observed to form in the vibrating tube densimeter at temperatures as low as 25 °C. The composition of HA aqueous solutions thus appear to be unstable (HA concentration decreases continuously) even at room temperature.

The variations in the mean stoichiometric activity coefficients (γ_{st}) for hydrazine, hydrazinium nitrate and hydroxylammonium nitrate are shown in Fig. 3. The coefficients were calculated from the osmotic coefficient by integrating the Gibbs–Duhem relation:

$$\ln \gamma = -\frac{0.5108 \ln 10 \sqrt{m}}{1 + b\sqrt{m}} + cm + dm^2 + em^3 + gm^4 \quad (8)$$

where the b, c, d, e and g parameters are those of eqn. (4).

Although the osmotic coefficient must be extrapolated to zero molality to determine the γ_{st} activity coefficients, differences were observed in the behavior of the systems studied at low molal concentrations.

The behavior of nitrate salts (notably HAN) appears to be characteristic of a 1 : 1 electrolyte: as the mixture approaches
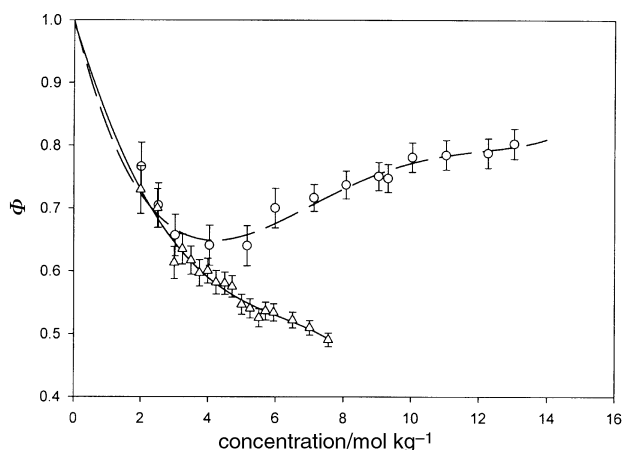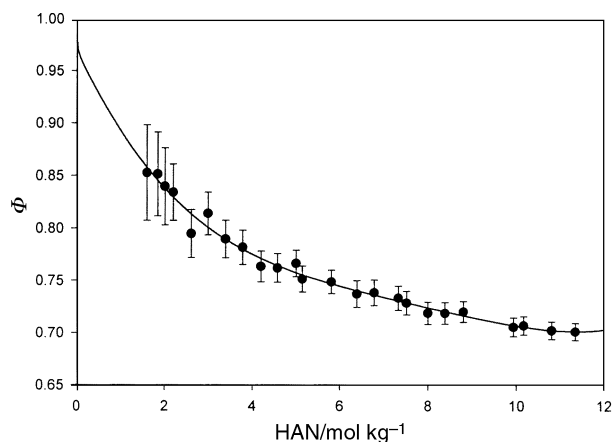

Fig. 1 Osmotic coefficient (Φ) at 25 °C of binary solutions of hydrazine in water (HDZ–H₂O) and hydrazinium nitrate in water (HDZN–H₂O). HDZ–H₂O: (○) experimental data points, – – – interpolation by eqn. (4). HDZN–H₂O: (△) experimental data points, —— interpolation by eqn. (4).

Fig. 2 Osmotic coefficient (Φ) at 25 °C of binary solutions of hydroxylammonium nitrate in water (HAN–H₂O). (●) Experimental data points, —— interpolation by eqn. (4).
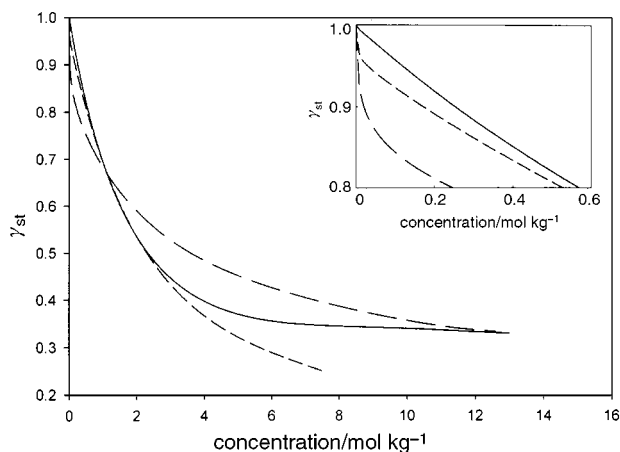
Fig. 3 Activity coefficient (γ_{st}) at 25 °C for hydrazine–water (——), hydrazinium nitrate–water (- - - -) and hydroxylammonium nitrate–water (– – –) systems.

infinite dilution, $\gamma_{st\,HAN}$ tends toward 1 with a slope of $-\infty$.[20] This evolution is attributable to long-range electrostatic interactions, which predominate at weak concentrations, and which involve m^{-n} terms (where $n > 1$).[20] At very high concentrations the rate at which γ_{st} decreases gradually tends to diminish as short-range interactions become increasingly important and eventually predominate. It is more difficult to describe the evolution toward zero molality of the activity coefficient for hydrazinium nitrate, since the y-intercept is insufficiently resolved due to the extrapolation of the osmotic coefficient to zero molality.

For hydrazine, on the other hand, the evolution of $\gamma_{st\,HDZ}$ does indeed appear to be different—notably at low concentrations. At infinite dilution, $\gamma_{st\,HDZ}$ tends toward 1 with a finite slope (Fig. 3). This behavior is characteristic of non-electrolytic solutes for which short-range interactions (*e.g.* van der Waals interaction or dipolar solute–solute interaction) predominate over the entire concentration range.[20] Although the calculations were performed by considering HDZ as a 1 : 1 electrolyte $(N_2H_5^+,\ OH^-)$, the behavior of this compound resembles that of a molecular solute in which electrostatic interactions remain marginal, even in highly dilute media. This observation may be related to physicochemical behavior models of HDZ–H$_2$O mixtures by the theory of associated liquids.[7] Models of this type tend to reveal the presence of hydrated forms of hydrazine, as well as complex HDZ–HDZ dimers (*i.e.* the existence of short-range strong interactions for the HDZ–H$_2$O system).

Ternary systems

The water activity of mixtures of two isopiestic binary solutions was measured to assess the simple behavior of ternary systems. "Simple" behavior implies that water activity of the resulting solutions is identical to that of the two initial binary solutions.

The results of water activity measurements on ternary HDZ–HDZN–H$_2$O and HDZN–HNO$_3$–H$_2$O mixtures are plotted in Fig. 4. The HDZ–HDZN–H$_2$O system was shown to follow the ZSR rule for water activities exceeding at least 0.880 (the behavior of the ternary mixture was not investigated at lower water activities).

In the case of the HDZN–HNO$_3$–H$_2$O system, major differences from simple behavior were observed regardless of the water activity. These differences appear to be attributable to an acid–base reaction between nitric acid and hydrazinium nitrate (the pK_a of the $N_2H_6^{2+}$–$N_2H_5^+$ couple has been estimated between -1.05^4 and -0.4^3). As a result, in a concentrated nitric acid medium (>1 mol kg^{-1}) the chemical
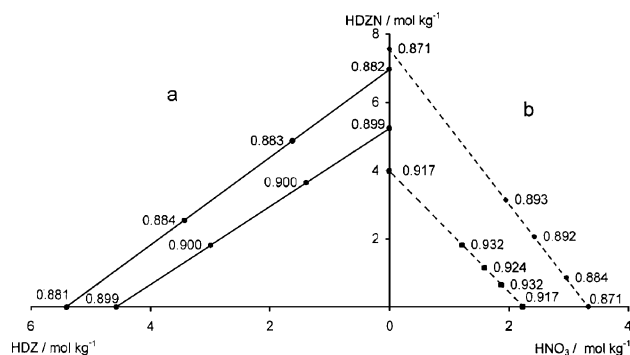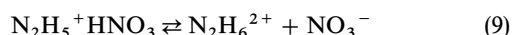

Fig. 4 Water activity measurements at 25 °C for ternary solutions prepared by mixing binary solutions with the same water activity. (a) HDZ–HDZN–H$_2$O, (b) HDZN–HNO$_3$–H$_2$O, (——) isopiestic line, (- - - -) non-isopiestic line.

equilibrium:

$$N_2H_5^+HNO_3 \rightleftarrows N_2H_6^{2+} + NO_3^- \qquad (9)$$

is shifted far enough to the right that $N_2H_6^{2+}$ is present in sufficient quantities in the medium to interfere with the physicochemical properties of the ternary system. Vdovenko and Ryazanov[21] proposed a quantitative interpretation of the deviation from simplicity that allowed the equilibrium constant of formation of new species to be estimated; however, the isopiestic curves for the relevant ternary system must be completely established before this approach can be implemented.

The results of water activity measurements on ternary HA–HAN–H$_2$O and HAN–HNO$_3$–H$_2$O mixtures are plotted in Fig. 5. Because of the presence of hydroxylamine vapors in the HA–HAN–H$_2$O system, only mixtures with low HA concentrations could be studied. HA–HAN–H$_2$O mixtures exhibited simple behavior only for water activity values above 0.870, for which a slight deviation from the ZSR relation is already observed. For water activities above 0.907, however, the ZSR rule was verified.

The HAN–HNO$_3$–H$_2$O system may be considered simple for water activities above 0.840; slight deviations from the ZSR rule are detectable in more concentrated mixtures (Fig. 5). While the observed deviations from simple behavior in HA–HAN–H$_2$O systems can be attributed to their instability (the boiling point of HAN is 58 °C), it is more difficult to explain the behavior of HAN–HNO$_3$–H$_2$O mixtures at $a_w <$ 0.840, as many phenomena are liable to account for such deviations.[21–23]

In the ternary systems for which the ZSR rule is verified, the relations postulated by ZSR in eqn. (1), by Mikulin in eqn. (2)
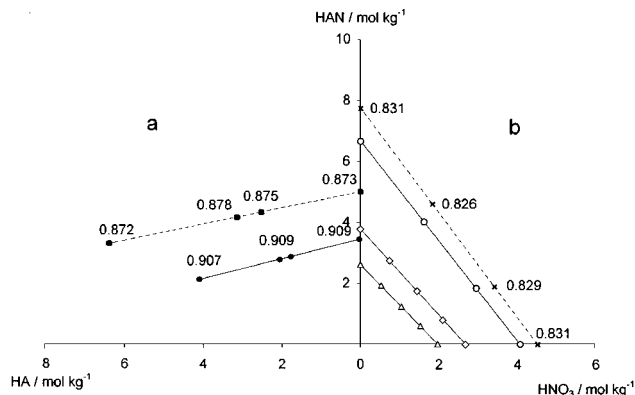

Fig. 5 Water activity measurements at 25 °C for ternary solutions prepared by mixing binary solutions with the same water activity. (a) HA–HAN–H$_2$O, (b) HAN–HNO$_3$–H$_2$O, (——) isopiestic line, (- - - -) non-isopiestic line, (O) $a_w = 0.840$, (◇) $a_w = 0.900$, (△) $a_w = 0.928$.

Table 3 Density (ρ) and activity coefficients of hydroxylammonium nitrate (γ_{st}) and nitric acid (γ_{st}) in the HAN–HNO$_3$–H$_2$O ternary solution at 25 °C

m_{HAN} /mol kg^{-1}	HNO$_3$(0 mol kg^{-1})		HNO$_3$(1 mol kg^{-1})			HNO$_3$ (2 mol kg^{-1})			HNO$_3$(3 mol kg^{-1})		
	$\gamma_{st\,HAN}$	ρ/g cm^{-3}	$\gamma_{st\,HAN}$	$\gamma_{st\,HNO_3}$	ρ/g cm^{-3}	$\gamma_{st\,HAN}$	$\gamma_{st\,HNO_3}$	ρ/g cm^{-3}	$\gamma_{st\,HAN}$	$\gamma_{st\,HNO_3}$	ρ/g cm^{-3}
0.000	—	0.99707	—	0.719	1.02861	—	0.787	1.05822	—	0.880	1.08527
0.250	0.799	1.00867	0.717	0.711	1.03888	0.691	0.781	1.06763	0.671	0.874	1.09379
0.500	0.751	1.01925	0.692	0.704	1.04884	0.669	0.775	1.07677	0.652	0.868	1.10205
1.000	0.683	1.03962	0.646	0.690	1.06787	0.629	0.765	1.09422	0.618	0.860	1.11779
1.500	0.631	1.05894	0.607	0.680	1.08583	0.596	0.759	1.11064	0.589	0.854	1.13256
2.000	0.589	1.07726	0.574	0.673	1.10280	0.568	0.755	1.12611	$a_w < 0.840$	$a_w < 0.840$	—
2.500	0.556	1.09463	0.547	0.669	1.11883	0.544	0.753	1.14069	$a_w < 0.840$	$a_w < 0.840$	—
3.000	0.527	1.11109	0.523	0.667	1.13397	0.523	0.752	1.15444	$a_w < 0.840$	$a_w < 0.840$	—

and by Vdovenko and Ryazanov in eqn. (3) can be used to predict the water activity, the activity coefficients of each ternary system component, and the solution density. The activity coefficients for HAN ($\gamma_{st\,HAN}$) and HNO$_3$ ($\gamma_{st\,HNO_3}$) are indicated in Table 3 together with the densities of ternary HAN–HNO$_3$–H$_2$O mixtures with water activities exceeding 0.840.

In the presence of nitric acid, $\gamma_{st\,HAN}$ diminishes—particularly in the case of low HAN molal concentrations (<1 mol kg^{-1}) for which variations on the order of 7 to 16% are observed for HNO$_3$ concentrations ranging from 1 to 3 mol kg^{-1}. At higher HAN concentrations, the drop in the activity coefficient is less significant: less than 3.5% over the entire HNO$_3$ concentration range for [HAN] > 2 mol kg^{-1}. Similarly, hydroxylammonium nitrate has a smaller effect on the HNO$_3$ activity coefficient: for an HNO$_3$ concentration of 1 mol kg^{-1} and an HAN concentration of 3 mol kg^{-1}, $\gamma_{st\,HNO_3}$ drops by less than 7%. The density values tend to increase slightly in the presence of nitric acid, but to a limited extent: the density increase does not exceed 7–8%.

These observations highlight the importance of the effect of nitric acid on the activity coefficients of hydroxylammonium nitrate, notably at low HAN concentrations in a 1–3 molal nitric acid medium.

Conclusions

This study revealed the importance of water activity measurements for binary or ternary systems involving volatile compounds (such as nitric acid) for which isopiestic measurement techniques are not compatible.

Water activity measurements were used to determine binary data (water activity as a function of the molal concentration) for the principal compounds used to control the nitrous acid concentration: hydrazinium nitrate and hydroxylammonium nitrate. This study was also extended to ternary systems involving these nitrate salts and nitric acid, from the standpoint of simple solution theory. It has been shown that systems with acid–base equilibria cannot exhibit simple behavior (HDZN–HNO$_3$–H$_2$O), whereas systems with no major chemical interactions are characterized by domains within which the ZSR rule is valid. The influence of HNO$_3$ on $\gamma_{st\,HAN}$ could be measured by applying the ZSR rule and the

Mikulin relation to the "simple" HAN–HNO$_3$–H$_2$O system at water activities above 0.840, notably when HAN was present in small quantities in a concentrated nitric acid medium.

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