Supporting Informations

Validity of the simple solution concept for the aqueous quaternary system U(IV) nitrate - U(VI) nitrate - nitric acid - water

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Numerical data for densities

Table S1: Difference between measured and calculated densities (in $g\,cm^{-3}$). The uncertainty on experimental data is $\pm\ 5 \times 10^{-5}\,g\,cm^{-3}$.

a_w		%U(IV) nitrate targeted				
		25%	33%	50%	66%	75%
0.749	$\rho_{exp.}$	1.67385	1.65902	1.62875	1.59857	1.58393
	ρ_{Vdo}	1.72200 ± 0.30084	1.71231 ± 0.27458	1.69210 ± 0,23499	1.67154 ± 0.21844	1.66179 ± 0.22096
	Var.	2.88%	3.21%	3.89%	4.56%	4.92%
	Diff.	0.04815	0.05329	0.06335	0.07297	0.07785
0.784	$\rho_{exp.}$	1.61364	1.60156	1.58998	1.57062	1.56076
	ρ_{Vdo}	1.62226 ± 0.27802	1.61288 ± 0.25344	1.57348 ± 0.21681	1.54905 ± 0.20239	1.53671 ± 0.20460
	Var.	0.53%	0.71%	1.05%	1.39%	1.57%
	Diff.	0.0862	0.01131	0.01649	0.02157	0.02405
0.842	$\rho_{exp.}$	1.50376	1.49206	1.47120	1.44933	1.43860
	ρ_{Vdo}	1.46502 ± 0.24244	1.45432 ± 0.22078	1.43533 ± 0.19012	1.41527 ± 0.17751	1.40558 ± 0.17986
	Var.	-2.58%	-2.53%	-2.44%	-2.35%	-2.30%
	Diff.	-0.03240	-0.03142	-0.02961	-0.02786	-0.02684
0.885	$\rho_{exp.}$	1.39155	1.38306	1.36593	1.34930	1.34102
	ρ_{Vdo}	1.41661 ± 0.22685	1.40974 ± 0.20757	1.39585 ± 0.17852	1.38234 ± 0.16773	1.37566 ± 0.17016
	Var.	1.80%	1.93%	2.19%	2.45%	2.58%
	Diff.	0.02506	0.02668	0.02992	0.03304	0.03463
0.929	$\rho_{exp.}$	1.28045	1.27422	1.26174	1.24833	1.24082
	ρ_{Vdo}	1.29294 ± 0.19896	1.28845 ± 0.18319	1.27957 ± 0.15864	1.26984 ± 0.14924	1.26415 ± 0.15161
	Var.	0.98%	1.12%	1.41%	1.72%	1.88%
	Diff.	0.01249	0.01423	0.01784	0.02152	0.02333

Numerical data for the isopiestic diagram

Table S2: Molalities (in $\mathrm{mol\,kg^{-1}}$) of the different electrolytes in the mixture for a water activity of 0.749

$m_{U(IV)nitrate}$	0.000	0.319 ± 0.068	0.427 ± 0.091	0.642 ± 0.136	0.851 ± 0.180	0.957 ± 0.203	1.265 ± 0.269
$m_{U(VI)nitrate}$	2.691 ± 0.583	2.056 ± 0.428	1.841 ± 0.379	1.417 ± 0.282	1.004 ± 0.188	0.793 ± 0.143	0.189 ± 0.040
m_{HNO_3}	0.543 ± 0.118	0.932 ± 0.145	1.064 ± 0.171	1.326 ± 0.233	1.583 ± 0.301	1.712 ± 0.335	2.089 ± 0.444

Table S3: Molalities (in $\mathrm{mol\,kg^{-1}}$) of the different electrolytes in the mixture for a water activity of 0.784

$m_{U(IV)nitrate}$	0.000	0.293 ± 0.062	0.391 ± 0.083	0.587 ± 0.124	0.779 ± 0.165	0.875 ± 0.185	1.163 ± 0.247
$m_{U(VI)nitrate}$	2.389 ± 0.514	1.826 ± 0.380	1.636 ± 0.336	1.270 ± 0.252	0.901 ± 0.168	0.718 ± 0.128	0.174 ± 0.037
m_{HNO_3}	0.482 ± 0.104	0.843 ± 0.130	0.964 ± 0.155	1.208 ± 0.212	1.445 ± 0.275	1.563 ± 0.307	1.921 ± 0.408

Table S4: Molalities (in $\mathrm{mol\,kg^{-1}}$) of the different electrolytes in the mixture for a water activity of 0.842

$m_{U(IV)nitrate}$	0.000	0.240 ± 0.051	0.322 ± 0.068	0.477 ± 0.101	0.630 ± 0.133	0.722 ± 0.152	0.959 ± 0.203
$m_{U(VI)nitrate}$	1.909 ± 0.407	1.466 ± 0.303	1.317 ± 0.269	1.030 ± 0.203	0.752 ± 0.141	0.577 ± 0.102	0.143 ± 0.030
m_{HNO_3}	0.385 ± 0.082	0.684 ± 0.105	0.787 ± 0.126	0.981 ± 0.172	1.173 ± 0.222	1.288 ± 0.253	1.583 ± 0.335

Table S5: Molalities (in $\mathrm{mol\,kg^{-1}}$) of the different electrolytes in the mixture for a water activity of 0.885

$m_{U(IV)nitrate}$	0.000	0.177 ± 0.037	0.235 ± 0.050	0.354 ± 0.075	0.470 ± 0.099	0.530 ± 0.112	0.705 ± 0.149
$m_{U(VI)nitrate}$	1.437 ± 0.305	1.102 ± 0.227	0.991 ± 0.202	0.767 ± 0.151	0.546 ± 0.101	0.432 ± 0.076	0.105 ± 0.022
m_{HNO_3}	0.290 ± 0.061	0.508 ± 0.077	0.581 ± 0.092	0.728 ± 0.127	0.873 ± 0.165	0.946 ± 0.185	1.165 ± 0.246

Table S6: Molalities (in $\mathrm{mol\,kg^{-1}}$) of the different electrolytes in the mixture for a water activity of 0.929

$m_{U(IV)nitrate}$	0.000	0.123 ± 0.026	0.161 ± 0.034	0.240 ± 0.051	0.323 ± 0.068	0.364 ± 0.077	0.483 ± 0.102
$m_{U(VI)nitrate}$	1.002 ± 0.211	0.764 ± 0.157	0.690 ± 0.140	0.537 ± 0.106	0.379 ± 0.070	0.300 ± 0.053	0.072 ± 0.015
m_{HNO_3}	0.202 ± 0.043	0.354 ± 0.053	0.402 ± 0.063	0.500 ± 0.087	0.602 ± 0.114	0.654 ± 0.128	0.803 ± 0.169

Conversion of molarity into molality

The molar concentration C ($\mathrm{mol\,l^{-1}}$) is related to the molal concentration m ($\mathrm{mol\,kg^{-1}}$) with the following formula:

$$m_i = \frac{1000 C_i}{1000\rho - \sum_j C_j M_j} \tag{1}$$

where ρ is the solution density ($\mathrm{g\,cm^{-3}}$) and M is the molar mass ($\mathrm{g\,mol^{-1}}$). The sum of j components does not include the solvent of the reaction (water here).

Binary data used

The binary data used in this study come from different works. Table S7 shows interpolation from the curves presented in figure S1.

Table S7: Binary data interpolation.

Electrolyte	Interpolation	Reference
HNO_3	$m = -182,8915a_w^5 + 651,5418a_w^4 - 952,4604a_w^3 + 722,3256a_w^2 - 309,3784a_w + 70,8630$	Charrin[1] Gillepsie[2]
U(IV) nitrate	$m = -2306,9145a_w^5 + 9591,2460a_w^4 - 15971,2050a_w^3 + 13309,4196a_w^2 - 5555,0629a_w + 932,5130$	Charrin[1]
U(VI) nitrate	$m = -456,5072a_w^5 + 1708,8740a_w^4 - 2602,5842a_w^3 + 2031,5578a_w^2 - 828,8531a_w + 147,5149$	Ruas[3]

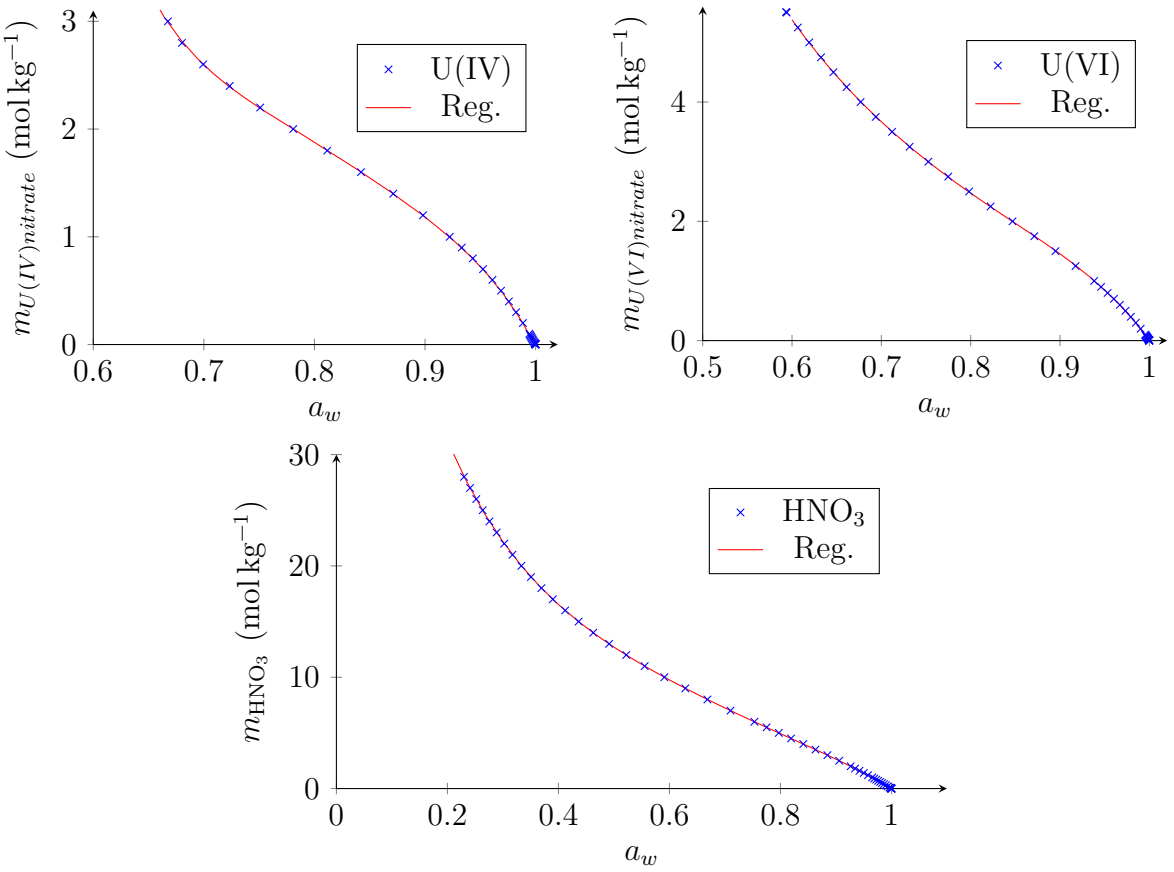

Figure S1: Link between the molality and the water activity of the different electrolytes used.

References

(1) Charrin, N. Contribution à la caractérisation de l'écart à l'idéalité des solutions concentrées d'électrolytes. Ph.D. thesis, CEA Marcoule, 2000.

(2) Gillespie, L. In *International Critical Table of Numerical Data, Physics, Chemistry and Technology*; Washburn, E. W., Ed.; 1928; Vol. 3; p 51.

(3) Ruas, A. Caractérisation de l'écart à l'idéalité de solutions de sels d'actinide et de lanthanide : contribution de la théorie BIMSA. Ph.D. thesis, Université Paris XI, 2006.