PROPOSED SYSTEMS IN VIEW OF APPLICATIONS

	System Id	Salt	Solvent	Solute	Investigated propertiy(ies)	Application
Only fluid Phase Eq	1a	NRS		HC	VLE (solubilities, vaporization of neutral cpds)	Gas storage, Distillation, active ingredient manufacturing
	1b	NRS	Protic	HC	LLE (Solute partitioning)	Extraction, purification
	1c	NRS	Aprotic	HC	LLE (Solute partitioning)	Extraction, purification
Fluid Phase + reaction	2a	NRS		AG	VLE (solubilities)	Gas storage /
	2b	RSB		AG	VLE (solutes partitioning)	gas scrubbing / absorption/ geothermal
	2c	RSA		BG	VLE (solutes partitioning)	gas scrubbing / absorption
	2d	OrgS	Protic		VLE (all volatiles partitioning)	Separation / stripping
	2e	OrgS	Aprotic		VLE (all volatiles partitioning)	separation
	2f	RSB	Protic		VLE (vaporization of neutral cpds)	Evaporation (distillation)
Solid Phase no reaction in the liquid phase	3a	NRS			ELS (solid appearance condition and amount)	salt purification; water treatment
	3b	NRS		HC	ELS (solid appearance condition)	scaling - flow assurance
	3c	NRS	Protic		ELS (solid appearance condition)	scaling - flow assurance
	3d	NRS		HC	ELS (solid appearance condition and amount)	crystallisation of active compounds ; flow assurance
Solid phase + reaction	4a	OrgS			Activities, speciation	Batteries
	4b	MOx			ELS, speciation (pH)	Corrosion, catalyst manufacturing

GAS STORAGE

NEW ENERGIES

New energy technologies require the capacity to store large amount of gases. This may be natural gas or increasingly hydrogen. It may also be a mixture of hydrogen and methane (hythane).

A very efficient large scale solution is to store these gases in salt caverns that contain an aquifer. This aquifer is a brine, most often containing NaCl.

The solubility of the gas to be stored must be determined, as well as the water content of the gas.

Challenge: Pressure conditions are generally high, and very few data exist with high ionic strength water.

salt	co-solvent	solute	Property	Temperature range	Pressure range
NaCl; CaCl$_2$	none	H$_2$; CH$_4$	Ki (VLE) (gas; water)	up to 200 °C	200 bar

GEOTHERMAL

In geothermal applications, water is recovered in temperature conditions that may be supercritical. In these conditions, salts are soluble in molecular form. When temperature is lowered, new types of vapour-liquid equilibrium can appear, where ions appear in both liquid and vapour phases

Challenge: (1) **Data**: measuring VLE and SLE in high temperature conditions may be a real challenge; (2) most of today's **models** consider that the ionic species remain in the liquid phase. This is no longer true in conditions where water has a very low dielectric constant.

salt	co-solvent	solute	Property	Temperature range	Pressure range
NaCl; CaCl2; CaCO3			Ki (VLE) (gas solubility; solvent vaporization)	550 °C	up to 500bar

GAS SCRUBBING

In gas treatment technologies, a solvent is used for removing reactive gases. Chemical solvents are much more efficient as they allow a higher solubility of the gas in the solvent, but regeneration issues may then become important (heat needed to recover the gas from the solvent).

Challenge: Many different types of reacting salts can be used, including organic salts, for which very few data exist.

The enthalpy of reaction and vaporization of the gas is a key piece of information in these processes, since it determines the global energy efficiency.

The loss of solvent through vaporization is often badly studied. This vaporization strongly depends on the speciation in the aqueous phase.

salt	co-solvent	solute	Property	Temperature range	Pressure range
amine salts; NaOH; KOH	Amine	CO_2; H_2S; SO_x; NO_x	Ki (VLE) (gas solubility; solvent vaporization); enthalpies	140 °C	up to 100 bar

EXTRACTION

1b	NRS	Protic	HC	LLE (Solute partitioning)	Extraction, purification
1c	NRS	Aprotic	HC	LLE (Solute partitioning)	Extraction, purification

The objective of extraction processes is to ensure that a solute passes from one liquid phase to another. One of the liquid phases is often aqueous.

Example:

Liquid-liquid extraction is used in the fuel cycle to separate fission products from Uranium and Plutonium.

Challenges: Most of the operations take place at 20-40 °C but for specific safety studies, extrapolation of data are needed from 40 to 100-120 °C leading to major uncertainties.

salt	co-solvent	solute	Property	Temperature range	Pressure range
U, Pu	HNO_3, Tributyl Phosphate; C12 alkane		Ki(VLLE)	20-120 °C	around 1 atm

2d	OrgS	Protic		VLE (all volatiles partitioning)	Separation / stripping
2e	OrgS	Aprotic		VLE (all volatiles partitioning)	separation

NEW ENERGIES

Stripping occurs when a inert gas is used to remove unwanted components from an aqueous phase.

Example:

Alcohols and acids are removed from a fermentor that contains alcohol, water, organic acids and a pH buffer (typically NaOH, KOH or NH_3OH). The volatility of the compounds strongly depends on the pH as a consequence of the speciation of the acid.

Challenge: data exist for some acids; often determined at low concentrations (pKa). No data exist for higher molecular weight acids. In addition, when the concentration is large, non-idealities need to be considered in the liquid phase which means that a model needs to be used. No data exists for these high molecular weight material.

salt	co-solvent	solute	Property	Temperature range	Pressure range
NaOH; KOH; NH_3OH	alcohols (ethanol, propanol)	organic acids	Ki (VLE) (solute; water)	50 °C	1-2 bar

ACTIVE INGREDIENT MANUFACTURING

1a	NRS	HC	VLE (solubilities, vaporization of neutral cpds)	Gas storage, distillation

Alkali hydroxides are commonly used during batch reaction steps for the production of active ingredients. NaCl as well as complex polyatomic salts, like phenolates, can be formed as intermediates. The reaction mixture is further processed, requiring e.g. a distillation (batch or continuous) for a solvent exchange or the distillative separation of residual water. For this purpose, in particular knowledge on the VLE of the solvents as well as the solubility of the salts in different solvent mixtures is of interest.

Challenge: The large variety of possible compounds will necessitate some predictive approach (group contribution method or other kind of property – structure relationships) to extrapolate the data

salt	co-solvent	solute	Property	Temperature range	Pressure range
e.g. Phenolates, NaCl, NaOH, KOH	Various organic solvents (alcohols, ethers, acetonitrile, DMAC, etc.)	phenolates	VLE, SLE		10 - 1013 mbar

ACTIVE INGREDIENT DEVELOPMENT

3d	NRS	HC	ELS (solid appearance condition and amount)	crystallisation of active compounds ; flow assurance

Apart from the process design, in the development phase of new active ingredients, the solubility of complex polyatomic molecules in different buffer and salt solutions is required. These information are of interest in particular in an early development phase, requiring highly predictive models. Depending on the pH, the API might exist in different ionized forms.

Challenge: The large variety of possible compounds will necessitate some predictive approach (group contribution method or other kind of property – structure relationships) to extrapolate the data

salt	co-solvent	solute	Property	Temperature range	Pressure range
NaCl,buffer solutions		API	Solubility of API (SLE)		1 bar

FLOW ASSURANCE

3d	NRS	HC	ELS (solid appearance condition and amount)	crystallisation of active compounds ; flow assurance

EleTher

Formation water typically contains a wealth of ions, which could lead to precipitation of salts at suitable conditions and/or upon mixing with aqueous streams of different compositions. It is important to be able to use limited available data for simple systems and conditions away from those of interest, to develop models that can predict the behaviour of more complex systems and their blending. Common ion effects, effect of ratio of anion/cation, differences with respect to ion valence, are thought to be crucial for the behaviour of these systems.

Challenge: How would $BaSO_4$ or $SrSO_4$ behave at different ratios of the ions, different conditions, and at the presence of $CaCO_3$? How does Total Dissolved Solids affect the model? Can we increase confidence on how we transfer knowledge from simple systems to more complex ones?

salt	co-solvent	solute	Property	Temperature range	Pressure range
Ba, Sr, Ca /SO_4; CO_3	Possibly with alcohols		SLE	40-150 °C	up to 400 bar, with a few applications reaching up to 1000 bar

ifp Energies nouvelles

BATTERIES

4a	OrgS			Activities, speciation		Batteries

Batteries require a high energy intensity, meaning a high content of ionic species. Yet, in aqueous media, the voltage is limited by the decomposition voltage of water. As a consequence, there is an active search for electrolytic media based on organic species, that still dissolve as ions in water. The redox potentials of these products are needed, hence the formation properties and the ionic activity coefficients. Examples are quinones in water. How can we increase confidence on the prediction of dielectric constant for such systems?

Challenge: Very few data exist for (1) solubility; (2) speciation; (3) activity coefficients and (4) formation properties of these organic salts. Everything needs to be done.

salt	co-solvent	solute	Property	Temperature range	Pressure range
Organic salts (benzoquinones)			ionic activity; solubility (SLE) ; speciation		

| 4b | MOx | | ELS, speciation (pH) | Corrosion, catalyst manufacturing |

Corrosion is essentially a redox chemical reaction between a solid and a liquid. This means that the species activity as well as their crystallization tendency must be modeled simultaneously.

Challenge: Few data exist in extreme conditions (e.g. high CO_2 or H_2S pressures, or in the presence of impurities that may affect the reaction -dissolved oxygen).

salt	co-solvent	solute	Property	Temperature range	Pressure range
FeO; FeO_2; …			ionic activity; solubility (SLE) ; speciation	20 – 150 °C	Up to 200 bar

| 4b | MOx | | | ELS, speciation (pH) | | Corrosion, catalyst manufacturing |

Catalyst manufacturing is based on the deposition of well-controlled metallic oxides on a support. In order to make sure that the correct oxide is being deposited, it is essential to control precisely the speciation in liquid phase as a function of pH and temperature condition.

Challenge: Considering the high concentrations, an adequate model must be available to describe non-idealities, in addition to reactive equilibrium. Several solid phases may co-exist, and making sure that the correct one is deposited is a challenge.

salt	co-solvent	solute	Property	Temperature range	Pressure range
MnO; $Ni(OH)$; $NaClO_4$; $NiCO_3$; $Ni(NO_3)_2$; $Ni(HCO_3)$; $HP(Mo_xO_y)$			ionic activity; solubility (SLE) ; speciation	20 – 80 °C	Atm.

NUCLEAR WASTE TREATMENT

The High Liquid Level Waste Concentration collects and concentrates the high liquid wastes which contain most of the activity of the fuel. Due to the number of elements in the liquid solution, speciation is a big challenge that could help to achieve a better management of the corrosion of the boiler and to understand the development of fouling which results in reduced thermal capacity. In addition a chemical reaction between HCOH and HNO_3 producing NO_x takes place in the boiler.

Challenge: No tool exists capable to describe the large amount of reactions that occur in high concentrated solution.

salt	co-solvent	solute	Property	Temperature range	Pressure range
Fission Products (Cs, Pu, Ru, Tc, Zr…)	H_2O/HNO_3	NOx, H_2CO	solubility (SLE) ; speciation	100-120°C	1 bar

Pure salt products are often obtained as a solid that precipitates as a result of a chemical reaction. However, many reactants may coexist in the aqueous phase, and it is essential that the correct solid is precipitated.

Industrial example:

- Precipitated Calcium Carbonate (PCC) is a high value product that can be recovered from marble wastes. It is produced by adding CO2 to a CaO rich aqueous solution.

Challenge: Several solid phases can precipitate. In order to model this correctly, there is a need to parameterize both the aqueous phase thermodynamic up to high salt concentration, and the solid phase(s) formation properties. Both have an impact on the results. Only limited data is available.

salt	co-solvent	solute	Property	Temperature range	Pressure range
CaCO3; CaO		CO2	solubility (SLE) ; speciation	??	??