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Data analysis for electrolyte systems : a method illustrated on alkali halides in water

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Abstract

In the recent years, the need to improve the thermodynamic models, particularly making them more precise and predictable for complex systems, has increased^{1,2}. The complexity of electrolyte systems is due to the strong interactions between ions, the hydration forces that take place during salt dissociation, and the physical forces at high concentrations of solute. Consequently, the existing thermodynamic electrolyte models show some limitations and are far from being completely optimized for industrial simulations. Thermodynamics based on electrolyte mixtures and mixed solvents requires further development and research³. The EleTher Joint Industrial Project (JIP) aims at promoting research in this field. A practical workflow is under development where the first stage consists in analyzing the data.

The present work is part of this larger scope and presents a strategy to analyze the internal and external consistency of experimental data for electrolyte mixtures. The focus is on alkali halide salts in water.

Internal consistency allows testing the quality of data by confronting them to each other and using the thermodynamic relationships between these data. For that purpose, the data are confronted with a model that was initially optimized and the deviations are analyzed. For this purpose, the Electrolyte Non-Random Two-Liquid (eNRTL) thermodynamic model was selected. Some deviations are attributed to the model inadequacy (high temperature or high molalities). Others are to be attributed to data inconsistencies.

On the other hand, the objective of external consistency is to evaluate the consistency between different systems of the same family. The Bromley model is used for this purpose, as it contains a single adjustable parameter. Investigating the trend of this parameter with type of compound or with temperature may provide valuable information regarding the underlying physics, in addition to identifying outliers.

1. Introduction

Electrolyte thermodynamics is one of the major challenges in today's thermodynamic applications. This was already pointed out ten years ago by Hendriks et al.¹ and very recently by Kontogeorgis et al.². The reason why this application domain is so challenging may be summarized in four bullet points:

- The data often refer to simple systems and do not include mixtures related to those of interest in industrial applications (this is perhaps true in many other fields)
- Very few models are available in commercial simulators, and these models allow reaching high salinities and/or high temperature conditions only through strong parameterization efforts. In other words, no truly predictive approach exist, despite the many attempts in the academic community⁴⁻⁶.
- Many electrolyte applications feature reactive compounds, meaning that the true species in a solution may be very different from the apparent species. As a consequence, the number of binary interaction parameters to be considered in the -empirical- equations may become very large.
- Last, but not least, the number of phases that may appear in these applications may be numerous (sometimes several liquids, or more often several solid phases) which implies the necessity to have access to robust and stable algorithms that allow both physical and chemical equilibrium to be computed.

Recently, IFPEN has initiated a joint industry project (JIP) called EleTher to increase the visibility of the efforts in this field.

The first goal of the JIP is to promote activity in this field in the thermodynamic community at large. To this end, we have set up a web site (www.elether.fr) where several example applications are provided, with contact persons in the different partner companies. The second goal is to propose best practices for the workflow that is recommended whenever a new thermodynamic model must be developed for an industrial process (Figure 1).

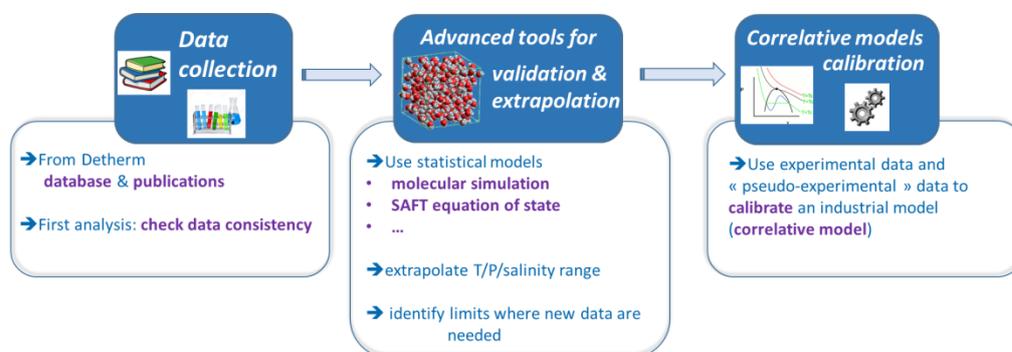


Figure 1. Three steps workflow for EleTher Project

Figure 1 shows the three proposed steps. At first, data needs to be collected: no thermodynamic model can be considered safe unless it has been validated using data. Yet, the data themselves may be scattered or inconsistent. This is why a consistency analysis is recommended, as discussed by various authors⁷. Unfortunately, very often, the data do not lie in the region of interest for the industrial applications. This means that a reliable extrapolation tool must be available. Several methods may exist, from very simple, as graphical extrapolations^{8,9} to very complex as molecular simulations¹⁰, going through advanced equations of state^{5,11}. The resulting values may be called pseudo-experimental, as they are reasonable extrapolations of actual data. At last, the industrial model that is to be used in the process simulator must be parameterized¹², which may be a significant challenge, considering the large number of potential parameters.

This paper is a summary of the work performed during the first year of the JIP. Focusing on a simple example (water + alkali-halides), we have explored some aspects of the first and the second stages of this workflow: data gathering and analysis. For that purpose, the paper has been divided into three main sections. First, the data themselves are presented: both their theoretical definition is explored and their availability. Two sections are next devoted to the consistency analysis: internal consistency and external consistency. A final discussion and conclusion closes this paper.

2. Data investigated

Some property definitions

Mean ionic activity coefficients

The ionic activity coefficient, γ'_i , describes the deviation of the ion activity with respect to a defined 'ideal behaviour'. The ideal behaviour that is usually considered for electrolyte systems is defined as the fugacity being proportional to the molality. The prime refers to the asymmetric definition: its value becomes one at infinite dilution in the solvent. Detailed definitions of this property are given in textbooks, as for example^{5,13} Although some authors publish individual ionic activity coefficients^{14,15} we have in this work only used mean ionic activity coefficients (MIAC) which are defined on a molality basis (indicated by a superscript m) as:

$$\gamma'_{+/-}{}^m = (\gamma_+^r \cdot \gamma_-^n)^{1/\nu} \quad (1)$$

Where the subscripts “+” and “-” point to anion and cation, while r and n are their respective stoichiometric coefficients (here always one), and $\nu = r + n$ is their sum, here 2.

Osmotic coefficients

The osmotic coefficient is a measure of the non-ideal behaviour of the solvent in a mixed solution. The usual definition of the osmotic coefficient (ϕ) is:¹⁶

$$\phi = \frac{-\ln(x_A \cdot \gamma_A)}{\nu x_B} = \frac{-\ln a_A}{Mw_{(A)} \cdot \nu \cdot m_B} \quad (2)$$

It is related to the molality based activity coefficient using the Gibbs-Duhem relationship which can be written as:⁵

$$\phi = 1 + \frac{1}{m_B} \int_0^{m_B} m \frac{\partial \ln(\gamma'^{r+/-m})}{\partial m} dm \quad (3)$$

Where a_A is the activity coefficient of the solvent; $Mw_{(A)}$ is its molecular weight (kg /mol); m_B is the molality of the solute (moles of B/kg solvent). It may be pointed out that the usual definition of an ideal solution ($\gamma_A=1$), yields $\phi =1$ only at low salt content.

Bubble pressures

Another property investigated here is the bubble pressure. In the range of temperature of interest, only the solvents are considered to evaporate, the salts remain in the liquid phase. The equation that must be solved is then (ignoring the Poynting correction and the vapour phase non-ideality is reasonable at low pressure):

$$P = \sum_A^{\text{solvents}} x_A \gamma_A \cdot P_A^\sigma(T) \quad (4)$$

Where $P_A^\sigma(T)$ is the vapor pressure of the solvent A at the concerned temperature (the exponent σ points to saturation). In this work, we consider only water as a solvent.

Relative apparent molar enthalpy of solution

The enthalpy of solution refers to the change of enthalpy when a certain quantity of solute is mixed with the solvent. It is obtained by slowly adding a salt to the solution that is initially pure. Hence, the difference in enthalpy is measured between the mixtures that contain solvent (A) and solute (B) on the one hand, and the compounds taken as pure on the other hand. Yet, the pure solvent is generally a liquid and the pure solute is a solid:

$$h^{Sol} = \frac{(n_A \bar{h}_A + n_B \bar{h}_B') - (n_A h_A^* + n_B h_B^{*,S})}{n_B} \quad (5)$$

Where \bar{h}_A and \bar{h}_B' are the partial molar enthalpies of the solvent (A) and the solute (B), while h_A^* and $h_B^{*,S}$ are the pure component enthalpies; for A in the liquid phase, and for B in the solid phase. The partial molar properties are computed from the reference state properties (pure for A, infinite dilution for B) and the partial molar excess property:

$$\bar{h}_A = h_A^* + \bar{h}_A^E \quad (6)$$

And

$$\bar{h}_B' = h_B^{\infty} + \bar{h}_B^{E'} \quad (7)$$

Where, according to the Gibbs-Helmholtz equation:

$$\bar{h}_A^E = -RT^2 \left. \frac{\partial \ln \gamma_A}{\partial T} \right|_N \quad (8)$$

And

$$\bar{h}_B^{E'} = -RT^2 \left. \frac{\partial \ln \gamma_B'}{\partial T} \right|_N \quad (9)$$

Where the prime indicates that the asymmetric activity coefficient is used (the ideal behaviour -unit activity coefficient- is reached when the solute B is infinitely diluted in the solvent A). Notice that the activity coefficient used here is that based on mole fraction, not molality.

An example of such data is given in figure 2. It shows that the data do not start at zero enthalpy, and it goes through a maximum before showing a decreasing trend.

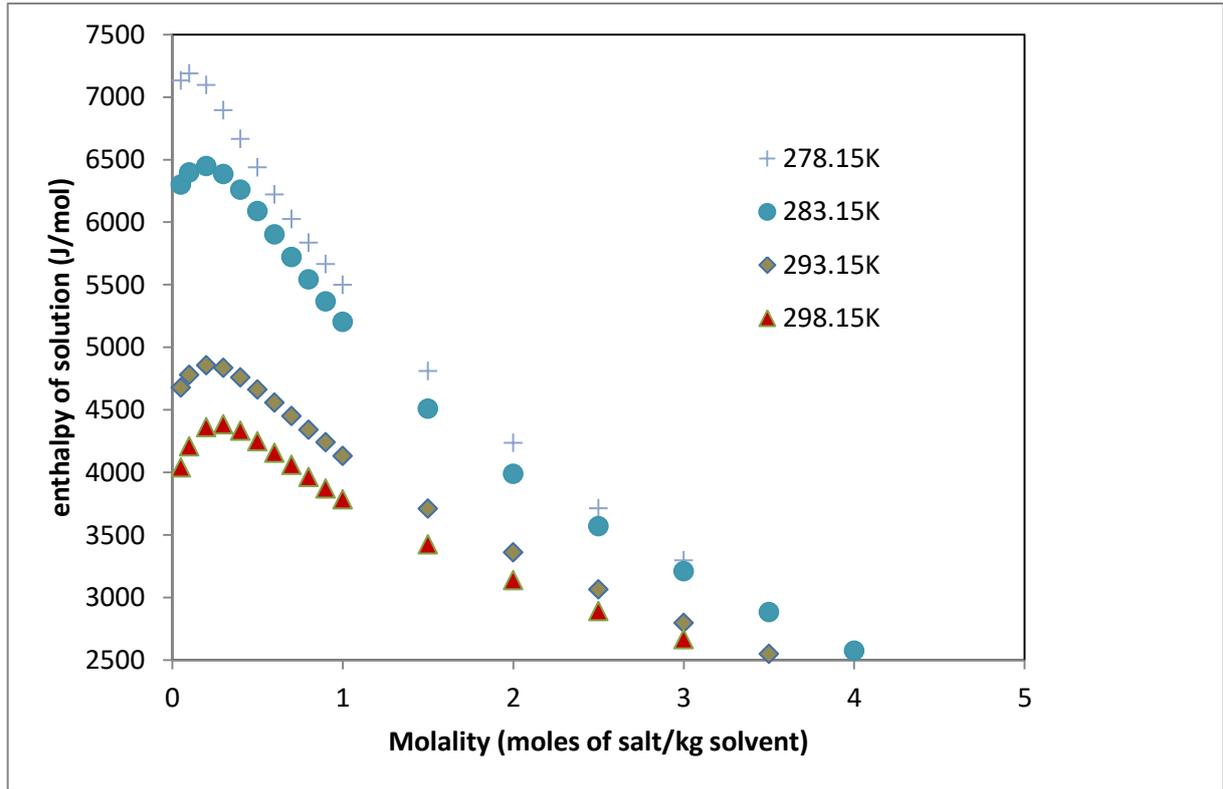


Figure 2: Molar enthalpy of solution of NaCl as given by the DETHERM reference 2008-FEB-20-14:50/15845¹⁷

From equations (5) through (8), the enthalpy of solution can also be written as:

$$h^{Sol} = \frac{h^{M'}}{x_B} + (h_B^\infty - h_B^{*,S}) \quad (10)$$

Where the enthalpy of mixing, $h^{M'}$, is written with a prime because it refers to an asymmetric reference state:

$$h^{M'} = x_A \bar{h}_A^E + x_B \bar{h}_B^E \quad (11)$$

Be careful that the limiting value IS NOT the enthalpy difference between liquid and solid for the solute, $(h_B^\infty - h_B^{*,S})$, because $\lim_{x_B \rightarrow 0} \frac{h^{M'}}{x_B} \neq 0$.

A value of the enthalpy at infinite dilution must therefore be defined before computing the enthalpies of solution from equation (10). Enthalpies at infinite dilution at different temperatures have been determined in order to interpolate to different temperatures. As an example, the enthalpy of solution at infinite dilution for KCl at different temperatures is shown on figure 3.

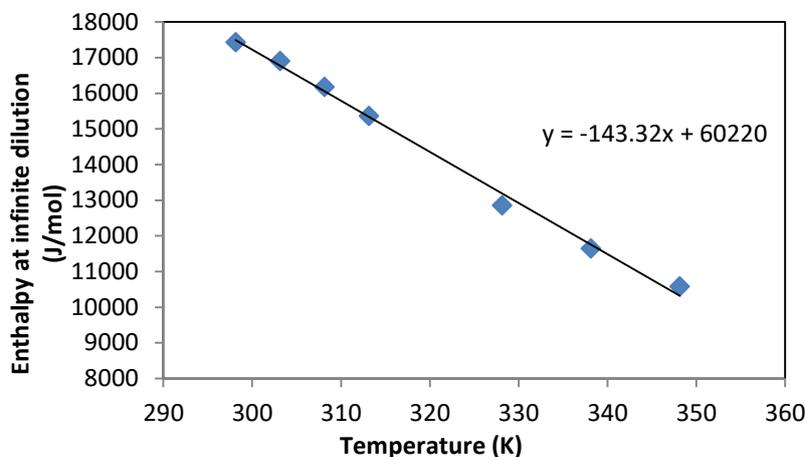


Figure 3. Enthalpy of solution at infinite dilution for KCl at different temperatures

This correlation is used below (internal consistency) for analyzing the data.

Global view of all data.

We focus on monovalent salts in pure water, but will attempt to search a large variety of properties. All data are obtained from the Detherm data base (2018 issue). Supplementary information(pdf in a zip format) provides the list of all available data including the temperature range and the maximum molalities.

The different phase equilibrium properties studied in this work are represented in Table 1.

Table 1. Classification of experimental data properties for different monovalent salts with pure water as solvent. Color codes are provided below the table. An “article” refers to a source of experimental data (one reference).

	Li	Na	K	Rb	Cs
F	7 articles	31 articles	28 articles	7 articles	6 articles
	1 article	2 articles	3 articles	1 article	1 article
	14 articles	11 articles. Data at 3 diff Temperatures	5 articles. Only at 298 K	6 articles. Only at 298 K	6 articles. Only at 298 K
		2 articles		1 article	2 articles
		41 articles	21 articles	11 articles	10 articles

		4 articles	6 articles	4 articles Only at 298 K	4 articles
Cl	117 articles	323 articles	266 articles	42 articles	53 articles
	21 articles.	60 articles.	42 articles.	13 articles. Only at 298 K	17 articles.
	25 articles	43 articles	27 articles	6 articles	5 articles
	15 articles	28 articles	26 articles	4 articles	4 articles
	128 articles	390 articles	374 articles	74 articles	73 articles
	26 articles	47 articles	35 articles	7 articles	18 articles
Br	47 articles	94 articles	112 articles	9 articles	21 articles
	4 articles. Only at 298 K	26 articles.	10 articles. Only at 298 K	4 articles. Only at 298 K	6 articles. Only at 298 K
	11 articles	11 articles	9 articles	1 articles	3 articles
	4 articles	7 articles	6 articles	3 articles	1 article
	44 articles	79 articles	113 articles	20 articles	29 articles
	7 articles	13 articles	11 articles	3 articles	5 articles
I	24 articles	70 articles	74 articles	7 articles	7 articles
	4 articles. Only at 298 K	7 articles. Only at 298 K	7 articles. Only at 298 K	4 articles. Only at 298 K	4 articles. Only at 298 K
	4 articles	7 articles	8 articles	1 article	1 article
		12 articles	9 articles	2 articles	9 articles
	20 articles	52 articles	77 articles	9 articles	9 articles
	4 articles	6 articles	6 articles	3 articles	3 articles

Solid-Liquid equilibrium	Vapor-Liquid equilibrium, isothermal	Activity coefficient	
Density (L)	Liquid-Liquid equilibrium	Enthalpies	Osmotic coefficient

In this representation it can be shown that data for salts and water as solvent is available for a wide range of properties. All properties studied are found for all of the salts. Lithium fluoride (LiF) is the only salt without any data related to activity coefficients: this salt is very insoluble in water. The maximum molality of LiF in water is 0.05 M. It can also be concluded that the majority of the data found was studied at 298.15 K. In addition, the majority of articles concern densities and solid-liquid equilibria.

Analysis of data versus salt solubility in water

The solubility limit of the salts NaCl and LiCl as a function of the temperature are shown in figure 4 and figure 5, respectively. In both graphs the maximum molality found in experimental data analyses for activity coefficients, osmotic coefficients and VLE (bubble pressure) is also represented. With this representation it is possible to identify the regions with gaps in the data that are of interest to be filled by additional measurements. The analysis was limited to 650 K (some data do have been reported up to the critical point of water).

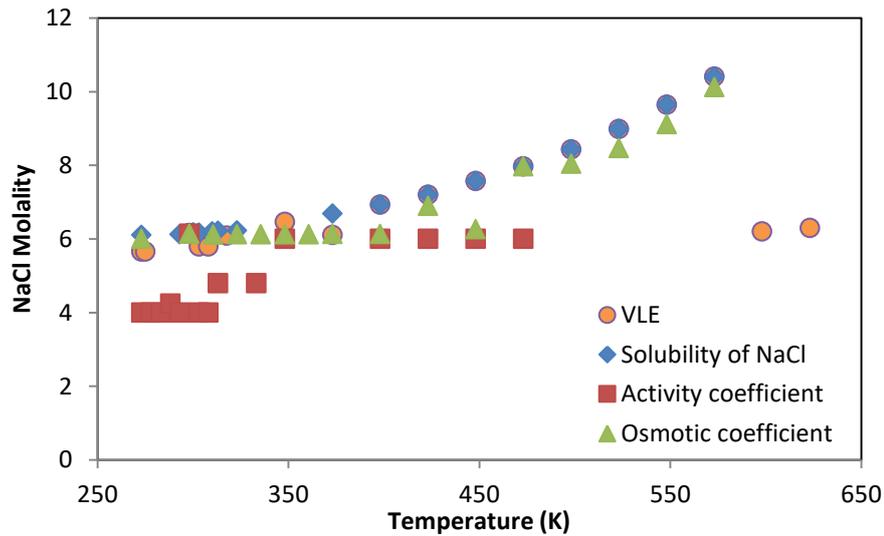


Figure 4. Maximum molality of available data compared to the solubility limit of NaCl.

Figure 4 shows that for NaCl, activity data can be found essentially up to the solubility limit in the full range of temperatures. For the activity coefficients, data are available up to 470 K, while for the osmotic coefficients, the highest reported temperature is 573 K. Bubble pressure data are available in the low temperature region, and again at high temperatures.

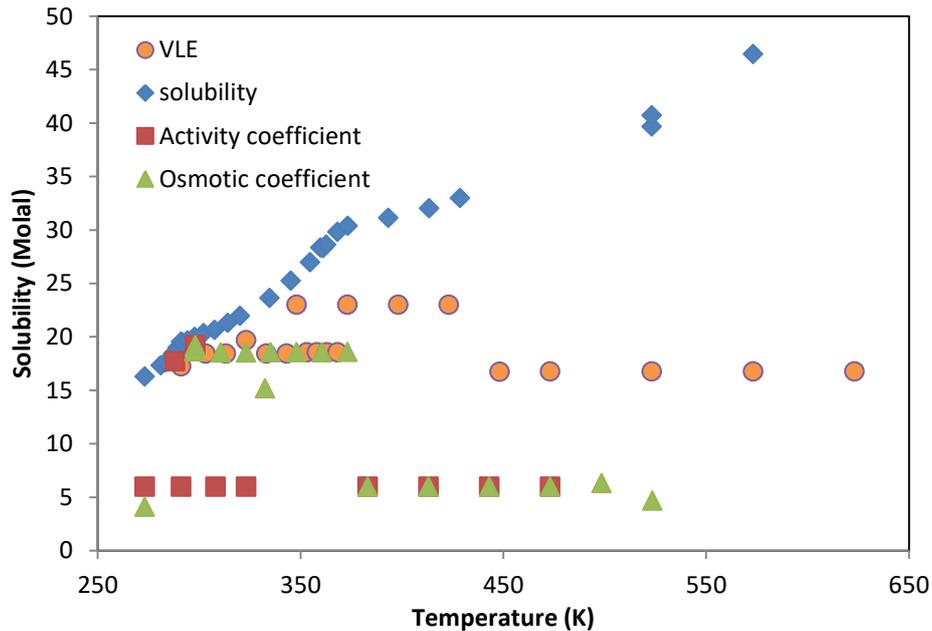


Figure 5. Maximum molality of available data compared to the solubility limit of LiCl.

Figure 5 shows the same representation for LiCl. Here again, activity coefficient data reach 470 K, but the maximum molality is far below the actual solubility limit. Osmotic coefficient data span essentially the same temperature and composition range. Bubble pressure data reaches higher temperatures and molalities, but still do not cover the entire possible region. It is therefore a good example where additional measurements could be of particular benefit.

Figure 6 shows such plots for all monovalent salts. Following observations can be made:

- Solubility data:
 - The amount, quality and temperature range of the solubility data varies largely from one salt to another. Only the highest values, that are compatible with the fluid phase data, are presented.
 - The solubilities sometimes show a kink, indicating a change in crystal structure
 - Low solubilities are observed for the salts (in order) LiF, NaF, KCl, RbBr, and CsI. The largest solubility is found for CsF followed by LiI. The trend indicates follows somehow a relation between cation and anion size, which will be further discussed below.
 - The solubility always increases with temperature, except for LiF and NaF where the solubility shows a maximum. In the case of NaF, bubble pressure measurements have been performed for molalities that seem to be higher than the solubility. It is not possible to state whether solubility data (open diamonds) are wrong or whether the bubble pressure have been measured with an oversaturated solution.
- Activity coefficient data:
 - These data sets are often reported at lower temperatures, and up to a concentration limit that does not reach the solubility.
 - There is always one isotherm available at 298.15 K, but in many cases not more.
 - In almost all instances, no activity data can be found at high temperature/ high molality.
- Osmotic coefficient:
 - These data are slightly more abundant than activity coefficient data, but do often not reach the solubility limit.
- VLE data
 - VLE data sets are the most abundant type of data, especially at high temperature.
- Global:

- It should be stressed that the activity coefficient, osmotic coefficient and VLE data really refer to the same reality: they can be transformed into one another, as was discussed above and will be stressed again in the internal consistency analysis.
- Up to 373.15 K (100°C), data are generally available until the solubility limit. At higher temperatures, data become much scarcer.
- Only NaCl is fully documented.
- RbF and RbI are the least documented.

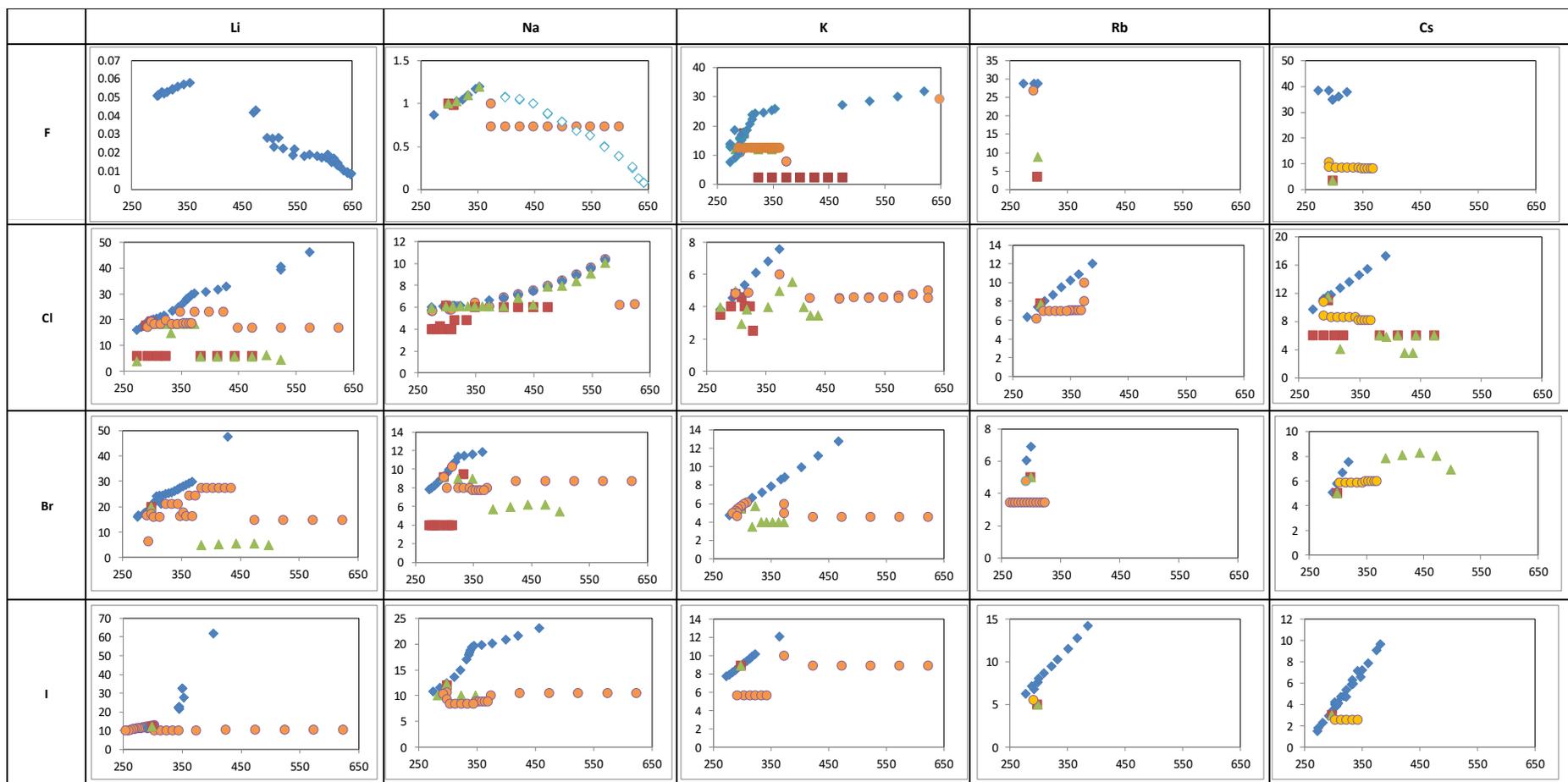


Figure 6. Data availability as a function of temperature for different salts. X-axis shows the temperature (in K), and the Y axis is the molality. The blue diamonds are maximum solubilities of the salts in water, the red squares represents the maximum molality found in activity coefficient data and the green triangles the maximum molality of osmotic coefficient data. The orange circles show the maximum molality for vapor pressure data.

3. Internal consistency analysis

Internal consistency is the analysis of the quality of data for different properties focusing on a specific system using a thermodynamic consistency test. Yet, for using the conventional consistency tests (Point Test, Area test, etc.¹⁸), vapour phase compositions are required, which is not the case for electrolyte systems. This is why only the method based on residuals is used, as proposed by^{19,20}. We use a thermodynamic model that has intrinsically embedded the following thermodynamic relations:

- The Gibbs-Duhem equation relates salt activity coefficients and osmotic coefficients (equation (3))
- The modified Raoult law can be used to test consistency of vapor pressures and solvent activity coefficient (equation (4))
- The Gibbs-Helmholtz equation relates the derivatives of the activity coefficients with the enthalpies of solution (equations (8) and (9))

As an example, we will evaluate a large dataset for a simple system consisting of different types of data. This is performed by comparing the deviations between the selected model and the data. The objective here is to focus on the method rather than on the final results. The deviations are defined as:

$$\text{Relative deviation (\%)} = \frac{X_{\text{calculated}} - X_{\text{experimental}}}{X_{\text{experimental}}} \cdot 100 \quad (12)$$

Where X is the property studied, in this work, it includes the mean ionic activity coefficient (MIAC), the osmotic coefficient and the enthalpy of solution.

The model is expected to behave well and be as accurate as possible. Hence, a correlative model with many parameters is the most suitable. The analysis of the deviations will make it possible to distinguish three types of behaviour:

- The deviations of a majority of datasets will scatter around zero. This scatter is then an indication of the experimental uncertainties.
- Some datasets may feature large deviations. It is then possible that the deviations follow a systematic trend, which can then be attributed to an error in the model correlation
- Some datasets feature large deviations, but lie clearly out of the trend. These will need to be investigated further and perhaps removed due to the fact that they are wrong.

Selection of the model for internal consistency analysis

The model selected for internal consistency analysis is the eNRTL model²¹. The reason for this choice is that for pure water solvent, it is a consistent model (i.e. not a simple correlation, but an expression that is consistently derived from a Gibbs excess energy expression) with a reasonable number of parameters. This is in fact not so for mixed solvents, that are out of the scope of this work. This model is widely used for industrial applications, and specifically in simulations tools such as ASPEN[®]. In this work, the in-house thermo library was used. The model contains three adjustable binary parameters for each pair of species (molecule – ion pair) and for each isotherm: the non-randomness parameter α , and two energy-related parameters that are called $\tau_{\text{water-salt}}$ and $\tau_{\text{salt-water}}$. In this study the non-randomness parameter is fixed to 0.2. The temperature dependence of both τ parameters is taken as follows :

$$\tau = C + D \cdot \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \quad (13)$$

This equation contains only 2 temperature dependent parameters. Hence, equivalent parameters need to be determined, Table 2 shows the parameters used in this work. They have been fitted so as to represent as closely as possible the ASPEN[®] parameters for temperature dependency of τ within the temperature range from 0-100°C.

Table 2.: KCl parameters used in equation (13) to calculate τ (water-salt) ; with $T_{ref} = 298.15K$ (determined so as to fit the Aspen parameters)

	C	D
Water - KCl	8.2007	397.756
KCl - Water	-4.1669	-66.457

Results of internal consistency

In what follows, only one example has been selected to illustrate the procedure: the basic idea is to analyze the deviations of the datasets with respect to a given model. Not all properties are systematically investigated in this paper, as the objective is to propose a procedure. In principle, as many thermodynamic properties as possible should be thus investigated to reach a good thermodynamic consistency. The case study of interest is KCl with the analysis of mean ionic activity coefficient, osmotic coefficient, bubble pressure and enthalpy of solution.

Deviation plots are shown in figure 7 (mean ionic activity coefficients), figure 8 (osmotic coefficients), figure 9 (bubble pressures) and figure 10 (enthalpies of solution). In each of these figures, two subplots are shown, together with a legend that refer to the Detherm UTI²². The corresponding references are available in the supplementary material. The left plot shows the deviations as a function of molality, the right plot as a function of temperature.

If the model and data had been perfect, the deviations would scatter around zero, and the average value of the scatter would provide an indication on the experimental uncertainty. As it is, we in fact see that the points follow some trend. This global trend illustrates the model imperfections. The observed trend-line is an indication of the model inadequacy to describe the physical phenomenon – no model is perfect, the scatter around the trend-line is experimental uncertainty. Two types of imperfections can be identified: either with molality or with temperature. Regarding temperature imperfections, it can be mentioned that at the highest temperatures of interest here, the pressure may reach up to 5 MPa, resulting in the need to correct the bubble pressure calculation equation (4) with the saturated water fugacity coefficient. In fact, the method used here is unable to distinguish between the imperfections related to an oversimplified temperature function for the parameters and this pressure effect. Hence, we only mention temperature imperfection of the model. What we want to identify is whether experimental sets provide deviations that cannot be explained by either of these observations: they do not follow the trend and they show values that lie outside the experimental uncertainty region.

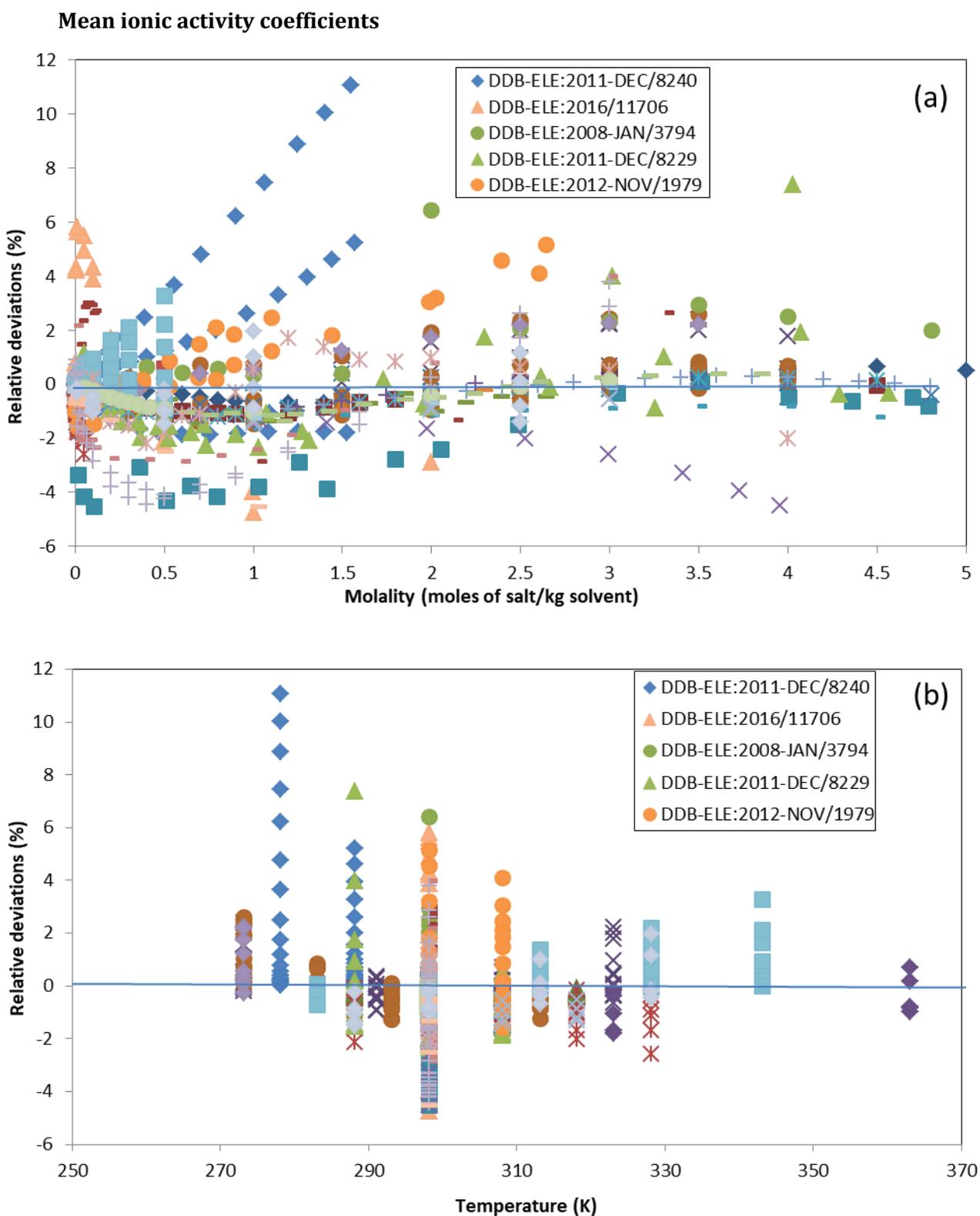


Figure 7. Relative deviations between the data and eNRTL for the activity coefficient of KCl with water as solvent. On the top (a) as a function of molality; on the bottom (b) as a function of temperature. The legend provides the Detherm UTI code²² only for the series that are discussed in the text. All series and corresponding references are available in the supplementary material.

In this analysis, the model appears to perform reasonably well, since the global trend-line essentially follows the zero deviation line. This means that none of the deviations can really be attributed to model imperfections. Yet, following three sets are found to be inconsistent (deviations above 3%): DDB-ELE:2016/11706, DDB-ELE:2011-

DEC/8240 and DDB-ELE:2012-NOV/1979. In the sets DDB-ELE:2011-DEC/8229 and DDB-ELE:2008-JAN/3794, a few outliers can be spotted.

Osmotic coefficient

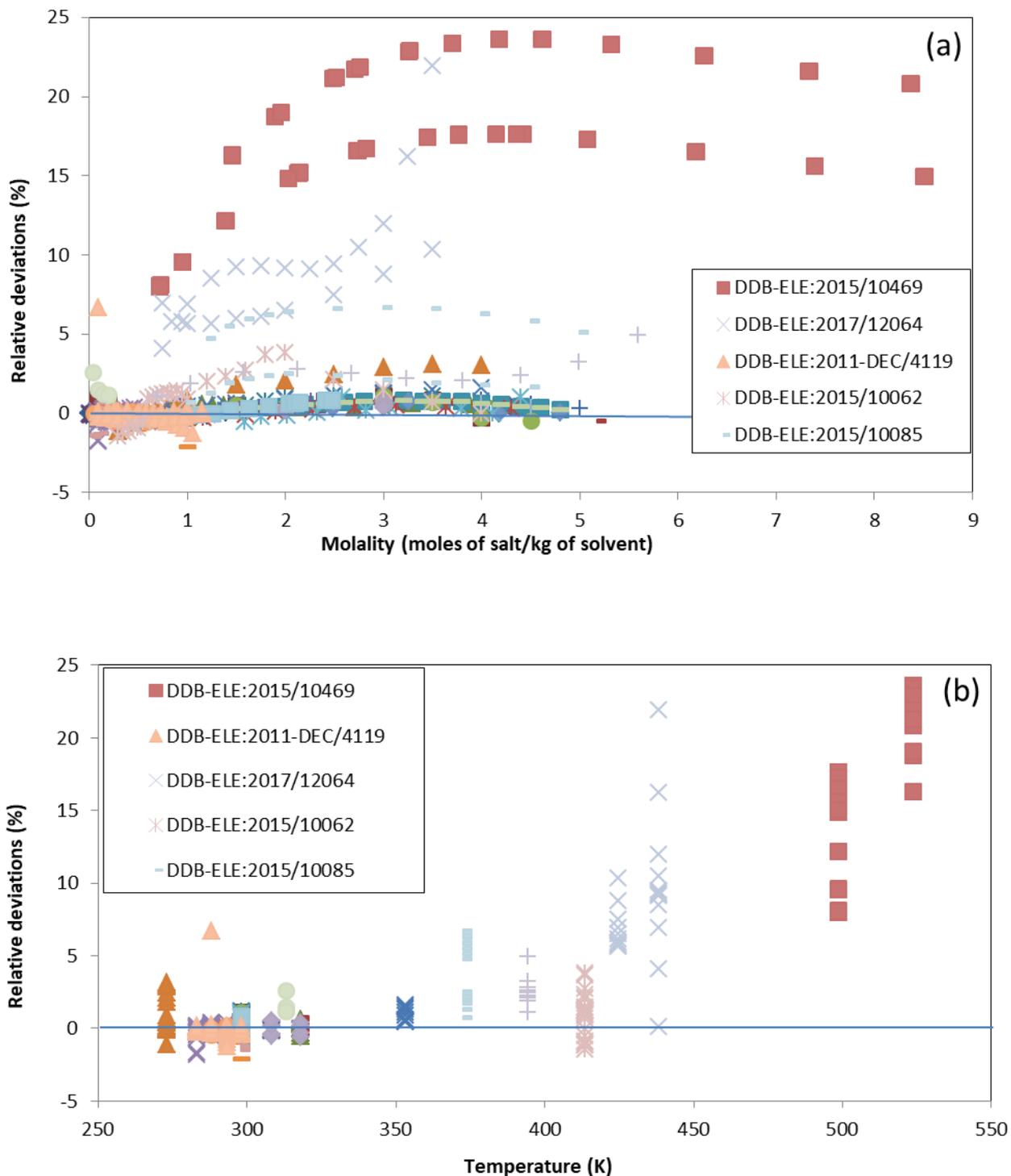


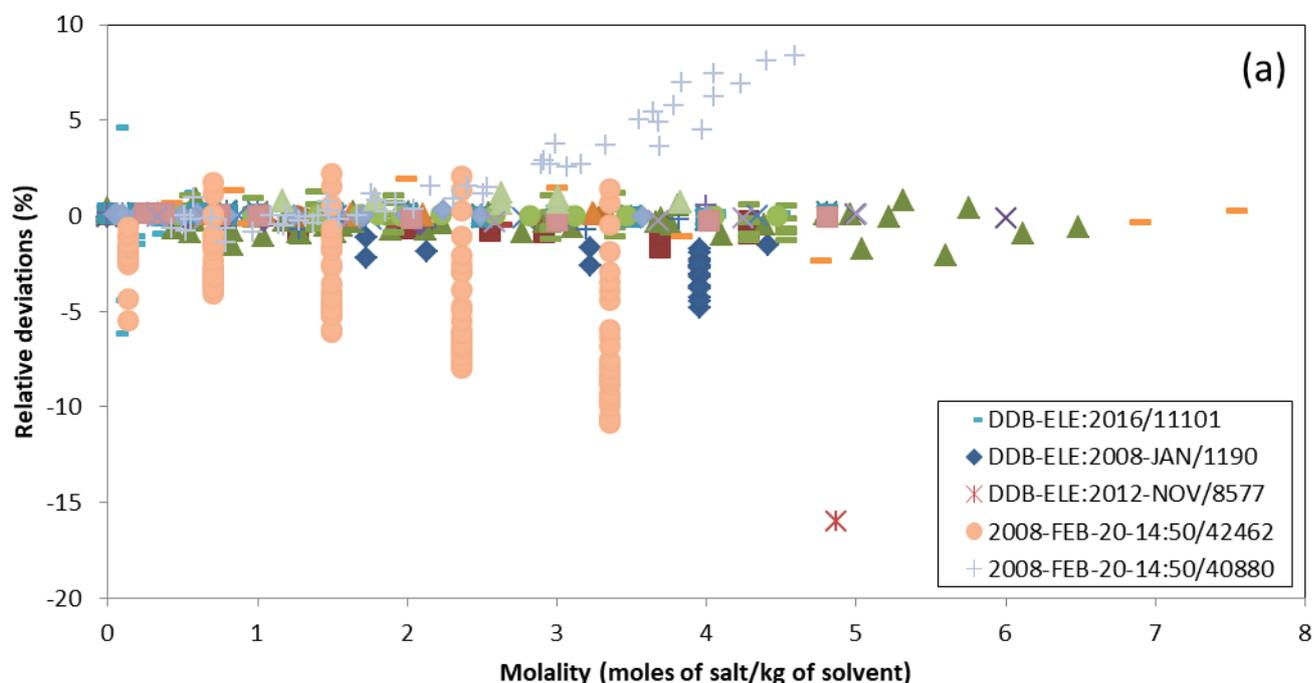
Figure 8: Relative deviations between the data and eNRTL for the osmotic coefficient of KCl with water as solvent. On the top (a) as a function of molality; on the bottom (b) as a function of temperature. The legend provides the Detherm UTI code²² only for the series that are discussed in the text. All series and corresponding references are available in the supplementary material.

In this case, for two sets, DDB-ELE:2015/10469 and DDB-ELE:2017/12064 the deviations are clearly related to a bad temperature extrapolation of the model. However, the trend of the deviations at high temperature is not well established: the data at 372 K (DDB-ELE:2015/10085), 394 K and 413 K (DDB-ELE:2015/10062) show a medium deviation that has the opposite trend as that for 438 and 498 K. It looks reasonable to put in question the data at medium temperature (DDB-ELE:2015/10085).

When looking closer at the data by DDB-ELE:2017/12064, it appears that the points on both plots are very scattered (especially at molalities above 3). Hence, it is safe to consider these data as inconsistent. Considering that one single point of reference DDB-ELE:2011-DEC/4119 has a very large deviation: it is highly probable that this corresponds to a typing mistake, so we shouldn't discard the entire reference for this reason.

Bubble pressure

Data measurements of bubble pressure in the presence of salts are also often available. They can be computed with the same e-NRTL model using equation (4). The water vapour pressure from DIPPR is used. In figure 9 a similar analysis as shown for the previous properties is applied.



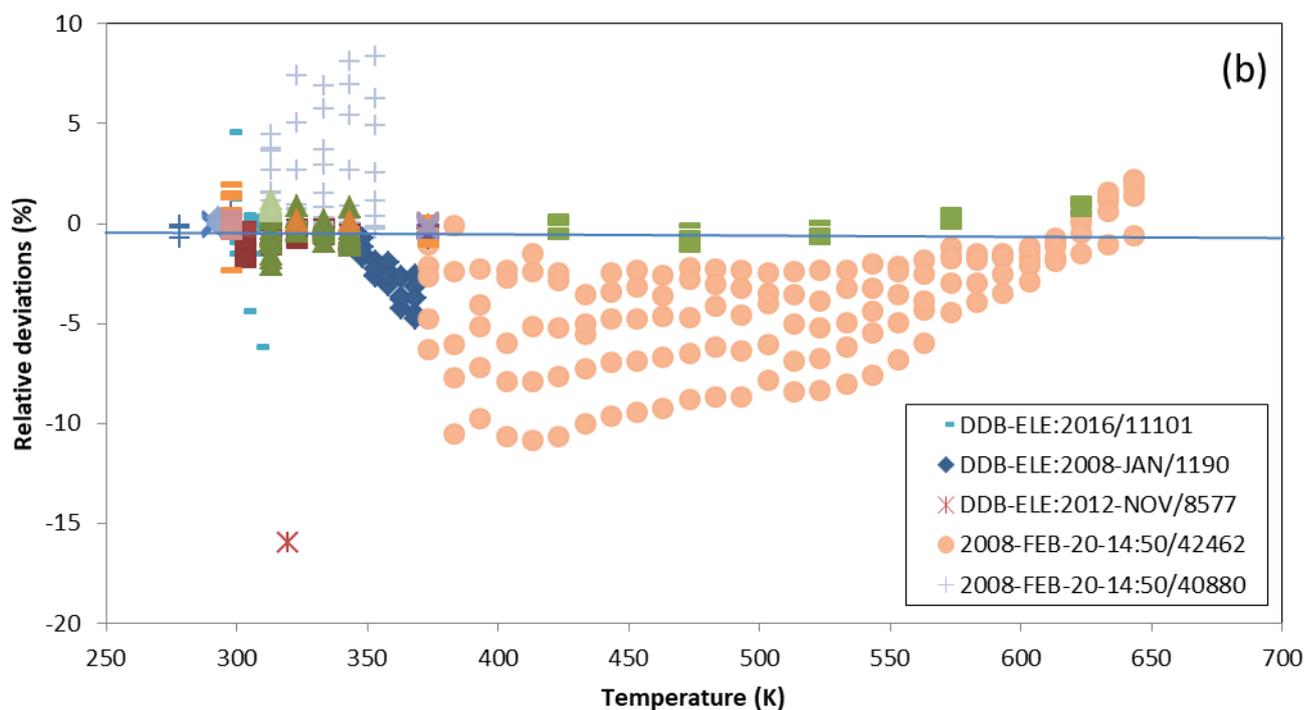


Figure 9: Relative deviations between the data and eNRTL for the bubble pressures of KCl with water as solvent. On the top (a) as a function of molality; on the bottom (b) as a function of temperature. The legend provides the Detherm UTI code²² only for the series that are discussed in the text. All series and corresponding references are available in the supplementary material.

From figure 9, the 5 inconsistent data sets are rather simple to spot. The large majority of the data are very accurate, and the activity coefficient of the solvent (water) deviates very little from unity for molalities up to 5. Hence, this nearly ideal mixing behavior is observed in the investigated region.

It should be mentioned that one dataset is not shown in figure 9 because its deviations were an order of magnitude out of range (2008-FEB-20-14:50/40751). These data should obviously also be discarded.

Enthalpy of solution

The enthalpy of solution is investigated in figure 10.

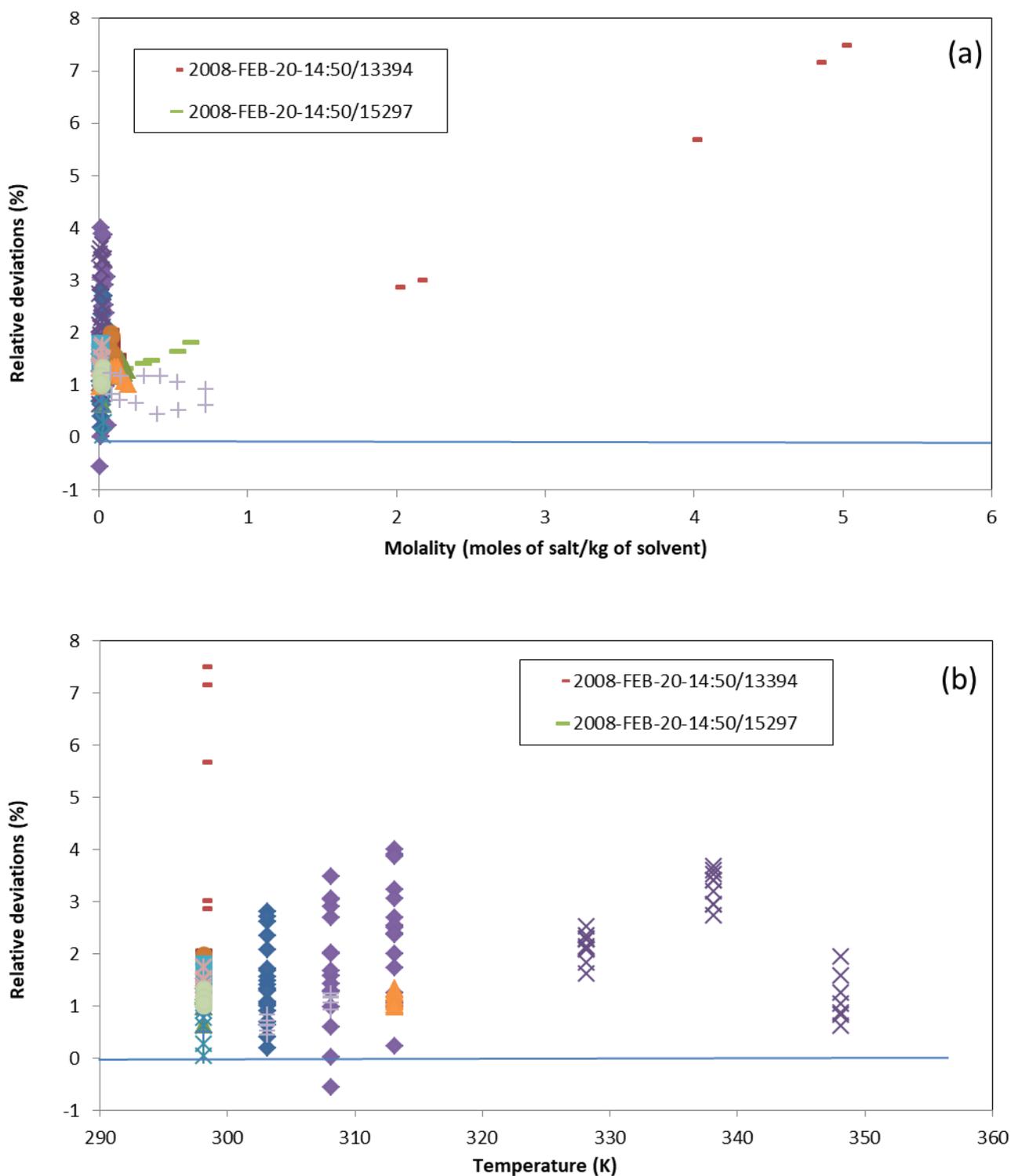


Figure 10 : Relative deviations between the data and eNRTL for the enthalpies of dilution of KCl with water as solvent. On the top (a) as a function of molality; on the bottom (b) as a function of temperature. The legend provides the Detherm UTI code²² only for the series that are discussed in the text. All series and corresponding references are available in the supplementary material.

The plots on figure 10 show a systematic positive deviation. This is probably related to the fact that the parameterization was done without taking this property into account, which is related to the temperature dependence of the activity coefficients.

The largest deviations are observed at high salt concentration (2008-FEB-20-14:50/13394). Yet these are not inconsistencies because other data (2008-FEB-20-14:50/15297) indicate a similar trend. This indicates that the model is not appropriate for extrapolating enthalpies with salt concentration. At low concentration, a large scatter illustrates the difficulty in measuring this property that has a global uncertainty of 3%. No data sets are associated with an obvious inconsistency.

Conclusion of the study for KCl

Table 3 summarizes the observations made for the KCl properties.

Table 3: Deviating sets as observed from the KCl data. The labels correspond to the Detherm UTI code²². The corresponding references are available in the supplementary material.

	Mean Ionic Activity Coefficient	Osmotic Coefficient	Bubble pressure	Enthalpies of Solution
Temperature extrapolation		DDB-ELE:2015/10469		
Concentration extrapolation				2008-FEB-20-14:50/13394 2008-FEB-20-14:50/15297
Inconsistent sets	DDB-ELE:2011-DEC/8240 DDB-ELE:2011-DEC/8229 DDB-ELE:2012-NOV/1979	DDB-ELE:2017/12064 DDB-ELE:2015/10085	2008-FEB-20-14:50/40751 2008-FEB-20-14:50/42462 2008-FEB-20-14:50/40880 DDB-ELE:2016/11101 DDB-ELE:2008-JAN/1190 DDB-ELE:2012-NOV/8577	

Conclusion of internal consistency

The procedure used for the internal consistency analysis leads to three types of deviations:

- Deviations related to model imperfections at high molality
- Deviations related to model imperfections at high temperature
- Deviations related to inconsistent data

The first type of deviations could be reduced by using another model. The second by improving the temperature dependence of the parameters. Only the third type of deviations lead to a possible rejection of the data.

One salt (KCl) is presented in this paper, but three other salts (NaCl, LiCl, CsCl) have been analyzed in a similar way. The results of internal consistency found for NaCl and LiCl are very different. For NaCl more data is available and the deviations are lower than for LiCl. Moreover, the deviations found for NaCl are caused by the model imperfections due to high temperatures or temperatures lower than 25°C. On the other hand, for LiCl some deviations may be explained by measurements at high temperatures or high molality range. The applied model does not properly represent the extreme conditions. Yet, some data are found to be inconsistent. The consistency for each salt must be investigated separately.

4. External consistency analysis

The purpose of the external consistency is to give an overview of the property trend for different chemical systems within the same family of compounds. In what follows, we focus on the molality based mean ionic activity coefficient because this property is well documented and the thermodynamic relationships discussed in section 2 allow to reconstruct many other properties. The activity coefficient has a well-documented shape, showing a minimum with increasing molality. This minimum is a consequence of the balance of forces, the long-range electrostatic forces having the most important impact at low molality, while the opposing trend at high molality is generally attributed to the short range interactions resulting from a competition between ion-solvent and ion-ion electrostatic forces. There is a consensus to describe the low molality solvation forces with a Debye-Hückel or primitive Mean Spherical Approximation (MSA) type equation, while the description of the short range interactions is less evident in the literature. It is our opinion that it is worth investigating the trends provided by the data before deciding on the model to be used.

In the following, we propose a tool that allows investigating the trends. All data used in this analysis have been validated through the internal consistency method.

Method

External consistency methodologies were discussed in the past by other authors: Matthias et al.⁸, Rozmus et al.⁹ and Jaber²³. Their approach consists in a graphical analysis of values that summarize the actual data (typically, they try finding a linear function and analyze slope and intercept).

In this work, the Bromley model²⁴ was selected, essentially because it has been shown that the B parameter has a consistent trend when comparing different salts^{25 26}. It is therefore expected that the Bromley model is more predictive and allows better parameter extrapolation. A drawback of the Bromley model is that the author replaces the mole fraction based activity coefficient (γ_i^*) with the molality based activity coefficient (γ_i^m) without any explanation and without any attempt to perform a correct conversion between the two types of activity coefficients. In other words, the model wrongly assumes that the Debye-Hückel term is molality based²⁷. This error was not

considered in what follows: the model is considered as empirical and the B parameter was systematically fitted to the data.

In order to determine the Bromley parameter B, the standard deviation is minimized for either activity or osmotic coefficients using the same criterion as shown in equation (12).

In order to achieve external consistency, it is important to understand the meaning and influence of the parameters of the model. The Bromley equation is:

$$\ln \gamma' = -A_{\text{DH}} \cdot \frac{|z_c z_A| \sqrt{I}}{1 + \sqrt{I}} + C \cdot I \quad (14)$$

where

$$C/\ln 10 = \frac{(0.06 + 0.6B) \cdot |z_c z_A|}{(1 + \frac{1.5}{|z_c z_A|} I)^2} + B \quad (15)$$

The parameter A_{DH} of the Bromley equation represents the Debye-Hückel interactions at low concentration of salt. This parameter depends on temperature. It is computed from

$$A_{\text{DH}} = \sqrt{2\pi N_A \rho} \left(\frac{e}{\sqrt{4\pi \epsilon_0 \epsilon_r k_B T}} \right)^3 \quad (16)$$

where ρ is the density and ϵ_r is the relative permittivity of the solvent, here water. For the density, DIPPR²⁸ correlation 116 was used:

$$\rho = B_0 + B_1 \tau^{0.35} + B_2 \tau^{2/3} + B_3 \tau + B_4 \tau^{4/3} \quad (17)$$

Where $\tau = 1 - \frac{T}{T_c}$. The dielectric constant is found from²⁹:

$$\epsilon_r(T) = A_0 + A_1 T + A_2 T^2 + \frac{A_4}{T} + A_5 \ln(T) \quad (18)$$

The parameters for equations (17) and (18) are available in Table 4

Table 4 : Water parameters used in equations (17) and (18).

	Dielectric constant, equation (18)		Density (kmol/m ³), equation (17)
A_0	-1664.5	B_0	17.863
A_1	-0.884533	B_1	58.606
A_2	0.000363	B_2	-95.396
A_4	64839.17	B_3	213.89
A_5	308.3394	B_4	-141.26
		T_c	647.096

This yields at 298.15K: $A_{DH} = 1.173816 \text{ (kg/mol)}^{1/2}$. The parameter B represents the increase in the activity coefficient at high molality caused by short range interactions. Consequently, a higher value of the parameter B implies a stronger increase in the activity coefficient. Table 5 shows the parameter B optimized for every system (pure water + monovalent salts) from the activity coefficient data up to 5 M.

Table 5. Values of the parameters B (kg/mol) obtained for Bromley model for different salts at 298.15 K

Ions	Li	Na	K	Rb	Cs
F	No data	0.05029	0.05869	0.07490	0.09895
Cl	0.13450	0.05935	0.02640	0.01745	0.00350
Br	0.15418	0.08077	0.03177	0.01316	-0.00184
I	0.19215	0.10137	0.04572	0.01293	-0.01465

No data was found for the Lithium Fluoride (LiF) activity coefficient due its low solubility in water. For CsBr and CsI salts, B has a negative value. Effect of type of salt

The behaviour of the activity coefficient curves is investigated for different salts in figure 11. In some cases, the activity coefficient increases strongly (e.g. LiCl), whereas, with other salts, the increase is almost insignificant (e.g. CsI).

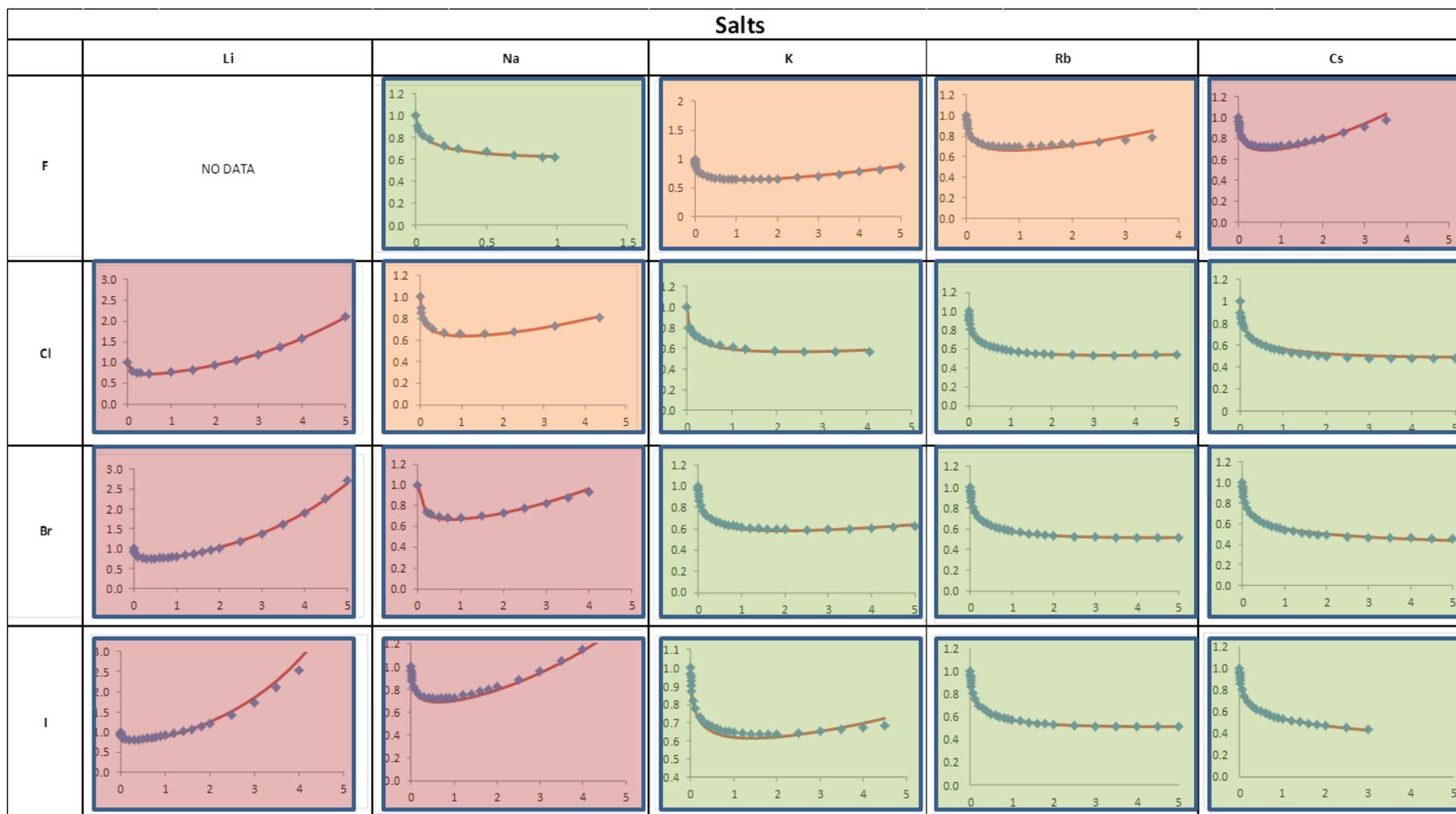


Figure 11: Variation of the activity coefficient with molality for different salts. The x axis refers to the molality and the y axis to the mean ionic activity coefficient. The blue points correspond to the experimental data and the red line is the Bromley model (B as shown in Table 5). The color code refers to figure 14: red means strongly hydrating salts; green means ion-pairing salts; orange is half-way.

Some salts are highly soluble in water (see also figure 6). In fact, the molality scale was sometimes truncated in figure 11 so as to remain within the 5 M scale. The saturation molality of LiBr at 298.15K is 21.68 molal³⁰. Figure 12 shows the representation of the activity coefficient of LiBr.

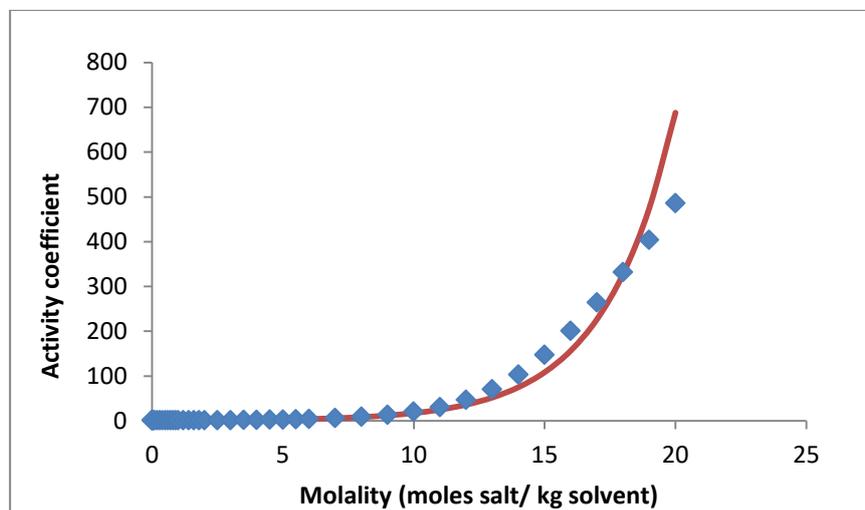


Figure 12. Activity coefficient with Bromley for LiBr with water at 298.15 K, until saturation molality. ($B=0.1627$ kg/mol, different from the value found in Table 5 so as to show the optimal value over this large molality scale). Data from³¹.

In that representation the imperfections of the model due to the high molality are shown. In this and following figure 13, the parameter was fitted over the entire molality scale (i.e. not as shown in Table 5). The Bromley model, fitted until saturation molality, is able to represent the experimental data behavior until 10 molal approximately. Beyond that point, the model does no longer follow the experimental trend. The figure 14 represents the computation of the same data series but for the osmotic coefficient with the Bromley model.

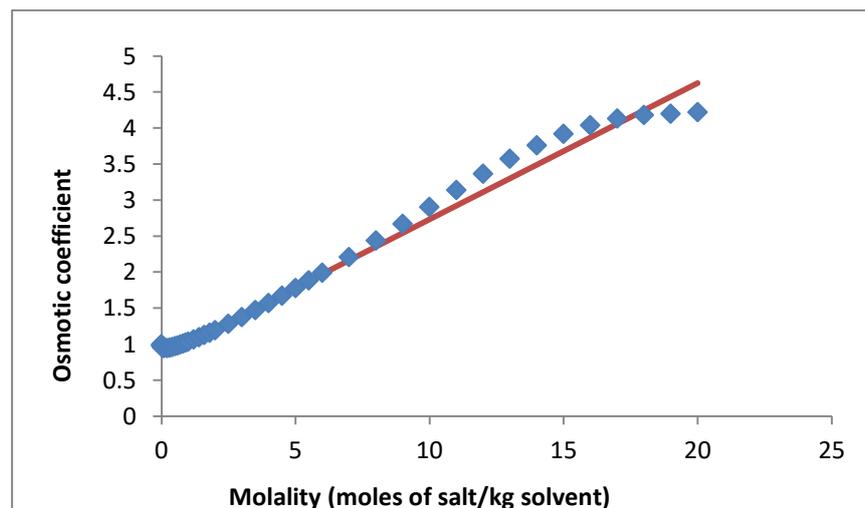


Figure 13. Osmotic coefficient with Bromley for LiBr with water until saturation molality ($B=0.1627$ kg/mol, different from the value found in table 19 so as to show the optimal value over this large molality scale). Data from³¹.

It is interesting to note that at high molality the osmotic coefficient data shows a flattening and stabilizes at $\phi = 4$. That behavior was observed for all the salts at molality higher than 15 M.

Effect of type of salt on the B parameter

The discussion is inspired for a large part by the works of Duignan³² and Collins³³. They introduced the Law of Matching Water Affinities (LMWA), that suggests a relationship between the solvation and the size difference between anion and cation. Using the Pauling diameters (from Ahmed³⁴), the dependence of B on this difference is illustrated in figure 14.

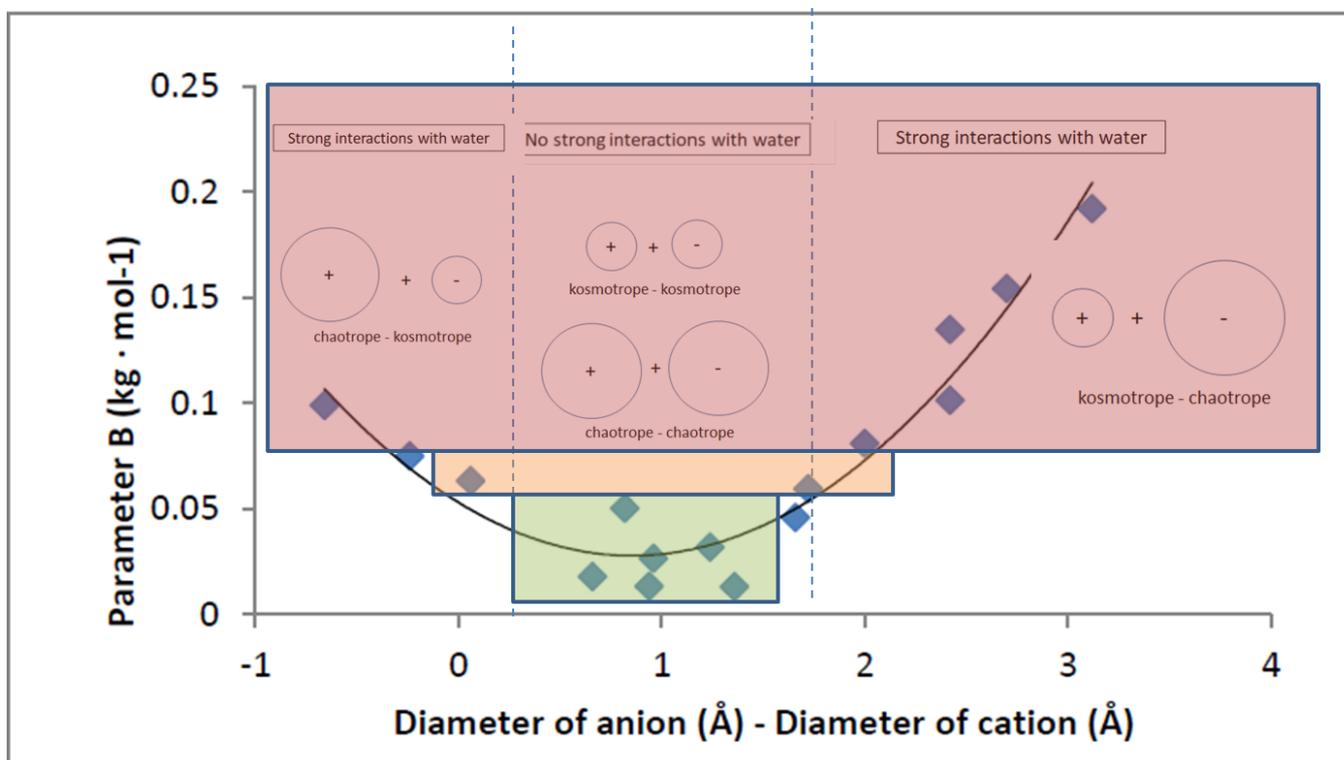


Figure 14. Variation of the parameter B (from Table 5) with the difference of anion and cation diameter. The color code distinguishes between : red, strongly hydrating salts and green, salts with little hydration; orange is intermediate.

The trend shows a minimum when the difference between ionic diameters is equal to 1 Å. The parameter increases more significantly when the diameter of the anion is larger than that of the cation, compared to when the cation is bigger than the anion.

This trend was already brought up and explained by Collins using the Law of Matching Water Affinities³⁵. This law states that there is a different effect on the hydration of ions depending on their charge and their size. According to the author, small ions (with high charge density) are considered kosmotropes, strongly hydrated ions. In opposition, the large monovalent ions (low charge density) are weakly hydrated ions and called chaotropes.

Based on the heat of the solution, the affinity with water according to the ion size can be determined. The combination of two small or two large ions results in an increased trend of ion pairing. On the other hand, the combination of ions with different sizes involves strong interactions with water.

Variation of the parameter B of Bromley with the temperature

It has been observed by some authors³⁶ that the temperature behavior of the activity coefficient is not monotonous: Figure 15 shows that the activity coefficient curves first increase and then decrease with temperature. The experimental data^{37,38} are presented by smoothed lines in order to have a better view and interpretation of the variation.

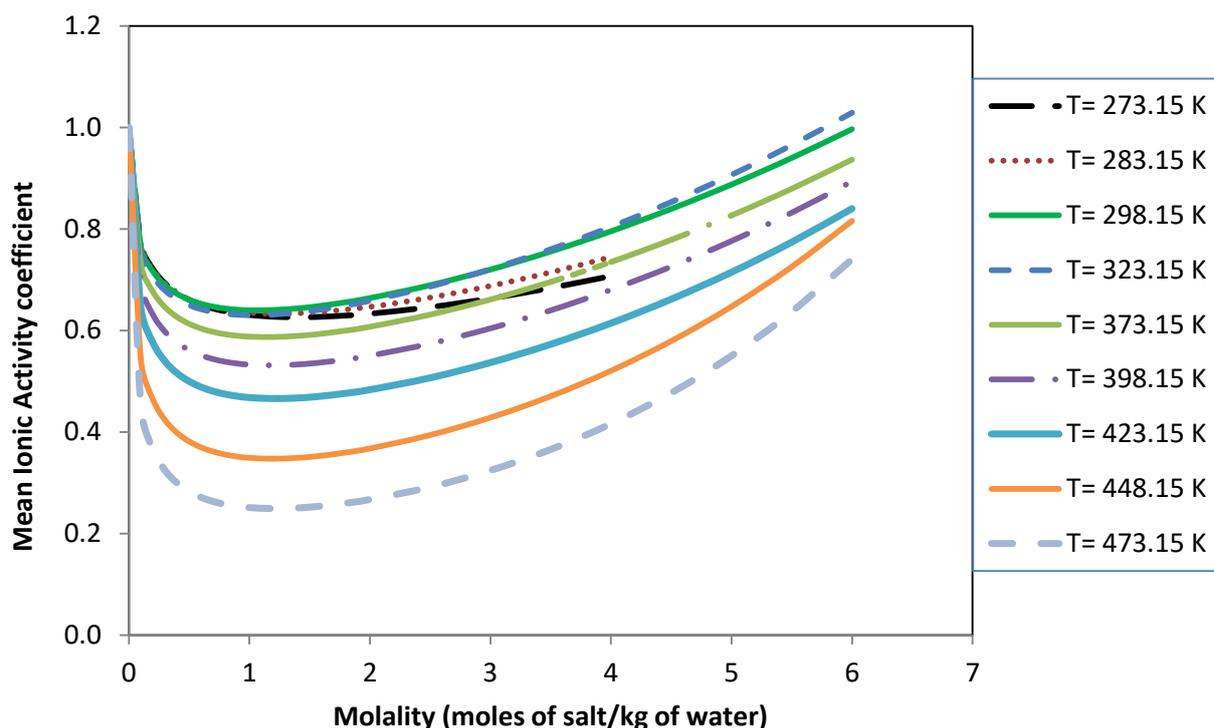


Figure 15. Experimental data for NaCl at different temperatures^{37, 38}.

The observed behavior can be related to the parameter B. The figure 16 indeed shows that the optimized parameter has a maximum around 323.15K.

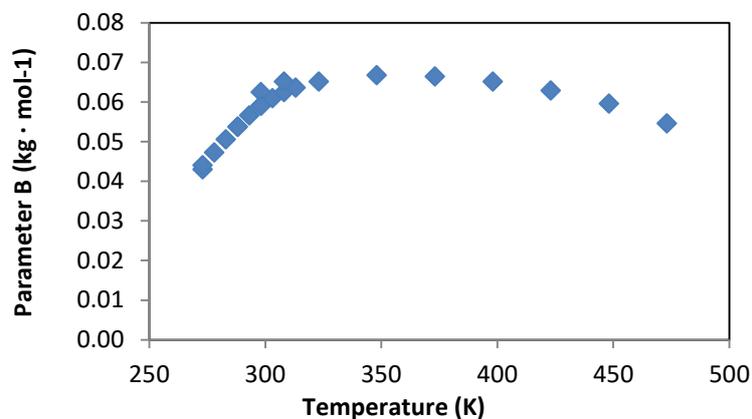


Figure 16. Variation of the parameter B of the Bromley model for NaCl, as determined from the MIAC data of ref^{37, 38} at varying temperature

In a simplified vision where B expresses the balance between water-ion and ion-ion short range interactions, it may be concluded that the relative importance of these two types of interactions changes yielding a maximum close to 323 K. Using this concept, increasing temperature would result in stronger ion pairing as compared to the ion-water ‘solvation’. Obviously, in reality, the phenomena that occur are much more complex, and a more fundamental study would be required to explain this trend.

In order to verify whether that this trend is significant, the same analysis was performed for all monovalent salts. The parameter B was regressed both from osmotic coefficients and activity coefficients in order to be able to extend the temperature range covered.

Figure 17 shows the behavior of the B parameter with temperature for all salts. The blue diamonds are obtained from activity coefficient data, and the red squares from osmotic coefficients.

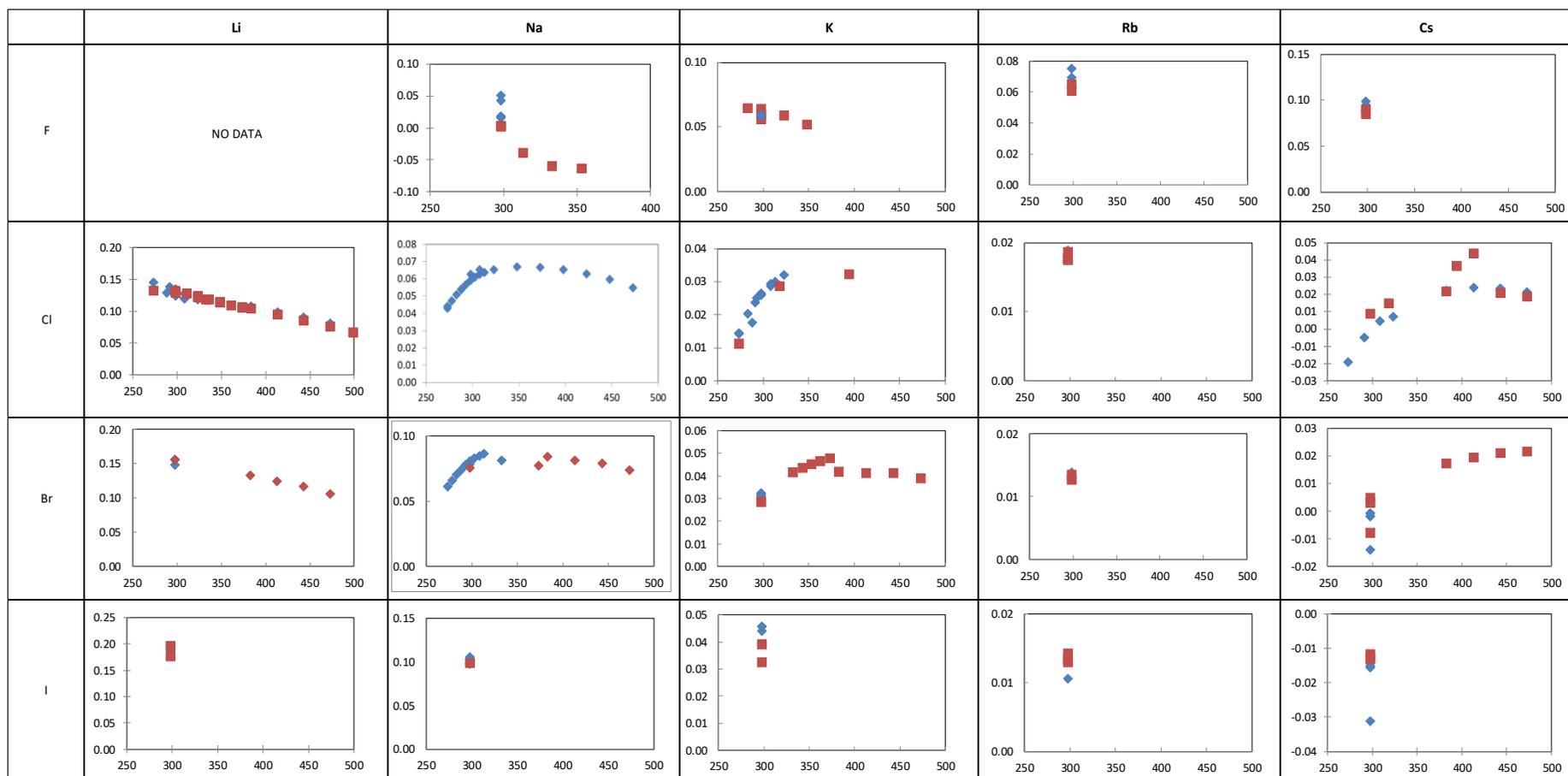


Figure 17. Variation of the parameter B of Bromley adjusted to the activity coefficient and the osmotic coefficient at different temperatures for different salts. The X axis shows the temperature (K) and the Y axis shows the value of B in kg/mol. The blue diamonds are obtained from mean ionic activity coefficients, the red squares from osmotic coefficients.

Several conclusions can be drawn from the figure.

The first conclusion concerns the availability of experimental data at different temperatures for the salts studied: this was already observed from figure 6. For some salts, data are only available at 298.15 K, either for the ionic activity or for osmotic coefficient data. That is the case for all iodide and rubidium salts, as well as for cesium fluoride. For NaF, KCl and NaBr, no activity coefficient data have been found above 300 K. At higher temperatures, only osmotic coefficients data are available for computing the B parameter. It is true that vapour pressure data could also be used, but the uncertainty (and therefore the scatter) on the parameter is then much larger so that they cannot be exploited in this context.

The next conclusion concerns internal data consistency. For example, in the case of CsCl, two points are determined to be inconsistent as they do not follow the same trend as the others. These points are marked with an empty square in the figure. The NaF results show similar type of internal inconsistencies: at 298.15K, it is impossible to reconcile the osmotic coefficient and the activity coefficient results. In fact, no agreement exists even among various sources of activity coefficients as the B parameter varies between 0.016 (DDB-ELE:2008-JAN/4392) and 0.05 kg/mol (DDB-ELE:2008-JAN/2054). We should note that for this particular salt, due to the solubility being small (maximum molality = 1M), the uncertainty on these values are probably rather large.

Finally, we can discuss the external consistency, or the similarity in trend between the observed figures. The maximum of the B parameter with respect to temperature, which was observed for NaCl appears clearly for a number of other salts, (NaBr, KBr and perhaps CsCl). The inflexion temperature is around 340 K for NaCl and 320 K for NaBr. On the other hand, other salts do not present a maximum value of the parameter B. That is the case of LiCl and LiBr. In these cases, the parameter B always decreases with increasing temperature. It may be assumed that the maximum of these salts occurs at very low temperature, but this is pure speculation. It is extremely difficult to reach a conclusion regarding the true temperature trend of the salt activities, and more fundamental experimental work would be more than welcome in this area.

5. Conclusions

This work is performed as a part of the EleTher JIP, whose objective is to define best practices for the development of industrial models. The scope of this work is the analysis of non-reactive, monovalent salts in water and mixed solvents. A large number of data exist for these systems. The data have been collected and analyzed following a thermodynamic method. Several conclusions can be drawn.

Figure 6 shows a summary of the most important available data. Although the data for these types of salts are numerous, they are often limited to specific regions (low temperatures, low molalities, largely investigated salts). Considering the theoretical importance of the alkali halides, it seems that a renewed effort would be welcome to complete the picture.

It is essential to have a more complete view of these ‘simple’ systems in order to better understand the fundamental phenomena occurring in non-reactive electrolytes.

The internal consistency results show that the method of data analysis by calculation of the deviations with the eNRTL is a technique to identify possible inconsistent data. The method finds its limitations due to the fact that the model itself is not capable of reproducing correctly the full range of

available data. This could have been improved through additional parameter regression, but remains limited because of the quality of the eNRTL model itself at very high molalities.

In this work, as an example, four properties have been analyzed: activity coefficient, osmotic coefficient, bubble pressures and dilution enthalpy, for four salts LiCl, NaCl, KCl and CsCl. Several inconsistent datasets have been identified, as summarized in tables 14, through 17.

This work has also brought into light the sensitivity of the data to the model: it is recommended to prefer activity coefficient data since the model is most sensitive to these data. Second are osmotic coefficient data, and last are bubble pressure data.

External consistency was evaluated using the Bromley model. It provides a method to identify relations between the physical properties of the electrolyte systems and the parameter B. Those relations can be used for parameter prediction and properties computations. The parameter B shows a logical trend when it is represented as a function of size difference between anion and cation. For pure water as the solvent, the parameter seems to be a measure of the solvation interactions, according to the Law of Matching Water Affinities.

The variation of the parameter B with the temperature could be analyzed for a large number of salts. It often presents a maximum value with temperature. This was clearly visible with several chlorides and bromide salts (except for Li⁺ as cation, where the trend is systematically decreasing). This observation is worth to further analyze relating it to changes in solvation behavior with temperature.

Supporting Information

Two files are added as supporting information: a zip file that contains pdf documents with the references and details on all data used, and a pdf file providing the references corresponding to the UTI codes used in this paper.

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