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A speciated, conventional Pitzer ion-interaction model for the aqueous Nd^{3+}–H^+–Na^+–K^+–Ca^{2+}–Cl^-–OH^- system at 298 K and 0.1 MPa ☆

Charles S. Oakes [a,*], Anderson L. Ward [b], Nikita Chugunov [c], Jonathan Icenhower [d]

[a] PO Box 201, Trenton, KY 42286, USA
[b] U.S. Department of Energy, Carlsbad Field Office, 4021 National Parks Hwy, Carlsbad, NM 88221, USA
[c] Siena Natural Resources, 301 NW 63rd Street, Oklahoma City, OK 73118, USA
[d] Corning Inc., 21 Lynn Morse Dr, Painted Post, NY 14870, USA

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Abstract

A conventional, speciated Pitzer ion-interaction model at 298 K and 0.1 MPa is presented for the $NdCl_3 + H_2O$ system and mixtures containing HCl, NaCl, KCl, and $CaCl_2$. The model uses Nd^{3+}, $NdOH^{2+}$, $Nd(OH)_2^+$, $Nd(OH)_3^0$, $NdCl^{2+}$, and $NdCl_2^+$ solute species and was fitted to isopiestic, electromotive force (emf), and $NdCl_3{\cdot}6H_2O$ solubility data. The model was then extended to pH values at which $Nd(OH)_3$, $Nd(OH)_2Cl$, and a speculative double salt, $Nd(OH)_3{\cdot}NdCl_3$, are stable. The two hydroxychloride salts enabled the model to join the stability fields of $NdCl_3{\cdot}6H_2O$ and $Nd(OH)_3$ ensuring continuity in the range $2 < pH < 13$. The activity coefficient model developed from the low pH $[NdCl_3 + NaCl](aq)$ system reproduces the solubility of solid $Nd(OH)_3(s)$ in water and NaCl(aq) with only the addition of standard state free energy terms for crystalline (cr) and amorphous (am) $NdOH_3(s)$ and the $Nd(OH)_2^+$ and $Nd(OH)_3^0$ solute species. No Pitzer parameters involving $NdOH^{2+}$, $Nd(OH)_2^+$ and $Nd(OH)_3^0$ were necessary to reproduce the full body of thermodynamic data over an ionic strength range from infinite dilution to the solubility limits of NaCl, KCl, $CaCl_2{\cdot}6H_2O$, $Nd(OH)_3(s)$, the hydroxychloride salts, and for mixtures containing up to 4.5 molal HCl(aq). The model adds only five 'binary' and three 'ternary' Pitzer ion-interaction parameters to the H-Na-K-Ca-Cl-OH parameters in Harvie et al. (1984; hereafter HMW). The model is simpler, compositionally broader, and more accurate than previously published Pitzer ion-interaction models for aqueous neodymium-chloride and -hydroxide solutions containing HCl, NaCl, KCl or $CaCl_2$. The model has ramifications for geochemical modeling and uncertainty quantification of An(III) solubilities used to support certification of evaporite hosted nuclear waste repositories.
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Keywords: Pitzer model; Nuclear waste; Neodymium; Aqueous electrolyte; Thermodynamics

1. INTRODUCTION

Trivalent americium and plutonium account for more than 99% of the total radioactivity slated for disposal at the U.S. Department of Energy's (USDOE) Waste Isolation Pilot Plant (WIPP), and present the greatest risk of environmental radiologic release from the geologic repository (USDOE, 2019a). Due to the inherent difficulties in

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* Corresponding author.
E-mail address: oakescs@gmail.com (C.S. Oakes).

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acquiring high-quality thermodynamic data for aqueous solutions containing trivalent actinides [An(III)], neodymium or other lanthanide [Ln(III)] compounds are used as analogs in thermodynamic measurements and geochemical models of repositories hosted in evaporite deposits (Felmy et al., 1989, 1990; Fanghänel et al., 1999; Neck et al., 2009). Ln(III) hydroxides and mixtures with chloride salts are also of interest to the processing of rare-earth element (REE) ores and intermediate solids produced during refining, e.g., $REE(OH)_3$.

In this study, a conventional, speciated, Pitzer ion-interaction model is developed to predict the behavior of An(III) compounds in geologic environments near 298 K and 0.1 MPa. The resulting thermodynamic model accurately reproduces the properties of $NdCl_3$(aq), and mixtures containing evaporite salts, over a range of pH, including those typical of geologic nuclear waste repositories that use engineered chemical barriers to minimize transport of actinides. The model is compared to a published speciated Pitzer model that is currently used for geochemical modeling in support of recertification of evaporite-hosted nuclear waste repositories.

2. MODEL DESCRIPTION AND PARAMETER DEVELOPMENT STRATEGY

The Pitzer activity coefficient model (Pitzer, 1973) is a virial type, excess Gibbs free-energy function with the form:

$$G^{xs}/w_w RT = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \times \sum_k m_i m_j m_k \mu_{ijk} \quad (1)$$

where $w_w = 1$ kg H_2O, $R = 8.31446$ J·(mol·K)$^{-1}$, T is temperature, m is molality, and I is ionic strength. A detailed description of Equation (1) and further thermodynamic relationships such as individual solute activity and osmotic coefficients are given in Pitzer (1991, pgs 84–93) and Appendix (A3) in Harvie et al. (1984) (hereafter HMW). In brief, the virial coefficients $\lambda_{ij}(I)$ and μ_{ijk} represent two- and three-particle interactions, respectively, involving solutes i, j, and k. The empirical "Pitzer interaction parameters" contained in $\lambda_{ij}(I)$ and μ_{ijk} correct for differences between measured thermodynamic properties and the Debye-Hückel limiting law function, $f(I)$. Consequently, the need for, and the magnitude of interaction parameters should be assessed from data at ionic strengths greater than those addressable by the Debye-Hückel limiting law function. The ionic strength at which solution properties diverge from the Debye-Hückel limiting slope for a given electrolyte charge type varies from salt to salt but is lowered by effects such as ion-association and hydrolysis. For example, the osmotic coefficient limiting law slope for a nominal 3:1 electrolyte such as $NdCl_3$ is more negative than that for a 2:1 electrolyte. Ion-pair formation reduces the weighted average charge ratio at any total neodymium molality ($m_{Nd_{tot}}$) so hydrolysis or ion-pair formation in $NdCl_3$(aq) solutions would cause measured osmotic coefficients to approach infinite dilution with a slope that is intermediate to those for completely dissociated 3:1 and 2:1 electrolyte solutions.

The Pitzer ion-interaction model is designed to reproduce the thermodynamic properties of multicomponent aqueous solutions in geologic or engineering systems through empirical parameters derived from relatively simple systems. Solutions containing a single salt (binary systems) are preferable for the evaluation of parameters ascribed to specific cation-anion interactions, whereas solutions containing two salts (ternary systems) are preferred for evaluation of parameters involving interactions between ions of the same sign. For a generic strong electrolyte, $M_{\nu_M}X_{\nu_X}$, binary interaction parameters, i.e., B^{ϕ}_{MX} and C^{ϕ}_{MX}, are fitted to thermodynamic data for the $MX + H_2O$ system (ν_M and ν_X are the numbers of positive and negative ions of charge z_M and z_X, respectively). B^{ϕ}_{MX} and C^{ϕ}_{MX} are the 2nd and 3rd virial coefficients for single salt systems and, as such, represent the combined effects of short-range interactions between two- and three-particles, respectively. The subscripts MX on B^{ϕ}_{MX} and C^{ϕ}_{MX} are for oppositely charged ions because those interactions are strongest, but two- and three-particle interactions involving the same ion are subsumed into B^{ϕ}_{MX} and C^{ϕ}_{MX}, respectively (cf. Equations 45 and 46 in Pitzer, 1991). These same-ion interactions are different than the 'ternary' 2nd and 3rd virial terms involving different-ions of the same charge type, $\theta_{ii'}$ and $\psi_{ii'j}$, that are fitted to data for systems containing two or more salts (i and i' refer to either two different cations or two different anions, and j refers to an ion of opposite sign). While a nominally 'binary' system such as $Nd(OH)_3 + H_2O$ could form multiple cations so that terms such as $\theta_{Nd,NdOH}$ and $\psi_{NdOH,Nd(OH)_2,OH}$ could conceivably be fitted, doing so would be inappropriate because either the standard state free energy terms (e.g., dimensionless standard state chemical potentials, μ°_i/RT, or equilibrium constants) or the 'binary' activity coefficient terms involving oppositely charged ions would be more significant. Also, for this specific case, the molality of at least one solute in the $\theta_{Nd,NdOH}$ and $\psi_{NdOH,Nd(OH)_2,OH}$ terms is very small and thus the effect of the interactions represented by those parameters would be very small.

B^{ϕ}_{MX} is ionic-strength dependent and contains the parameters $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and $\beta^{(2)}_{MX}$. $\beta^{(2)}_{MX}$ is used for systems in which "ion-association" has a significant effect on the solution properties but explicit recognition of the ion-association is deemed to be unnecessary or undesirable to maintain model linearity. $\beta^{(2)}_{MX}$ is proportional to the association constant for the ion-pair and should always be negative although there are many contrary examples in the literature. Models with positive $\beta^{(2)}_{MX}$ values are invariably malformed, e.g., the osmotic coefficient (ϕ) function diverges from 1 as infinite dilution is approached.

Any of the adjustable terms in B^{ϕ}_{MX} can be zero-valued. However, if the B^{ϕ}_{MX} term is zero, then the C^{ϕ}_{MX} term should also be zero for the seemingly obvious reason that three-particle interactions should be less numerous and consequently less significant than two-particle interactions. The rare Pitzer model with a finite C^{ϕ}_{MX} and zero-valued B^{ϕ}_{MX} for a given interaction is almost certainly a result of the

fitted C^{ϕ}_{MX} counter-acting errant parameters in an underlying model. For example, the aqueous lead-chloride model of Felmy et al. (2000) contains $C^{\phi}_{Na,PbCl_4} = -0.0424$ with the corresponding $\beta^{(0)}_{Na,PbCl_4} = 0.0$ (value in Table 2 of Felmy et al. is errantly listed as –0.424). The Felmy et al. (2000) model is based upon the lead-chloride model of Millero and Byrne (1984; Millero model). The Felmy et al. (2000) combination of a $C^{\phi}_{Na,PbCl_4}$ and null $B^{\phi}_{Na,PbCl_4}$ are almost certainly due to errant parameters in the underlying Millero model. For example, the $C^{\phi}_{Pb,Cl}$ parameter in the Millero model is unwarranted due to the low solubility of $PbCl_2$ and their use of highly soluble $ZnCl_2$ as an analog. The $C^{\phi}_{Pb,Cl}$ tabulated in Millero and Byrne (1984) also contains a sign error that appears to have been used in Felmy et al. (2000).

Because solid solubility in a single salt system at constant temperature and pressure consists of a single datum, the development of isothermal, isobaric interaction parameters from a single salt system requires data that span an ionic strength range, e.g., isopiestic or electromotive force (emf) data. Isothermal, isobaric Pitzer model parameters involving interactions between ions of like sign, i.e., $\theta_{ii'}$ and $\psi_{ii'j}$, can reasonably be evaluated from solubility data for a system containing two or more salts because ionic strength and composition vary in such experiments. However, the model is designed such that ternary parameters should be determined from common-ion systems, e.g., $MX + M'X + H_2O$, rather than mixed-cation and -anion systems such as $MX + M'X' + H_2O$ due to the confounding effects of X–X′, M–M′–X, and M–M′–X′ interactions. Only the minimum set of parameters that are consistent with the physical basis of the parameters and are necessary to reproduce the data within their accuracy should be fitted.

Development of model parameters for the new model followed the structure outlined above. Interaction parameters involving neodymium cationic species [e.g., Nd^{3+}, $NdCl^{2+}$, $NdCl_2^+$] and chloride were fitted to isopiestic data for the $NdCl_3 + H_2O$ system. The mixing terms involving neodymium and other cations were evaluated from emf and solubility data for the respective $NdCl_3 + MX + H_2O$ systems (M = H^+, Na^+, K^+, and Ca^{2+}; X = Cl^- with the stoichiometric ion quantities, v_M and v_X, of the respective ions of charge, z_M and z_X, balanced appropriately).

Aqueous neodymium chloride solutions are subject to hydrolysis and colloid formation during preparation (Spedding et al., 1966). Consequently, stock solutions prepared by Spedding et al. (1976) for their isopiestic measurements were titrated to their equivalence points, e.g., pH ~ 2 for 2.7 mol·kg^{-1} $NdCl_3$(aq), to assure that hydrolysis and colloid formation were minimized. Concerning model development for the $NdCl_3 + H_2O$ system, the $NdOH^{2+}$ species was introduced to produce calculated pH values consistent with those observed by Spedding et al. (1966, 1976). As will be shown, $NdOH^{2+}$ molalities that reproduce $NdCl_3$(aq) solution pH values are less than, or on the order of, 10^{-3} mol·kg^{-1}. For such low molalities, it is inappropriate and unnecessary to fit interaction parameters involving $NdOH^{2+}$. Although the latter point should be evident from first principles, Felmy et al. (1989) demonstrated that the solubility of the nominal solid $Pu(OH)_3$ in chloride brine can be fitted at pH < 9.5 using a Pitzer model for the analog $NdCl_3 + H_2O$ system without any interaction parameters involving ion-pairs.

Because the isopiestic data from Spedding et al. (1976) span a wide ionic strength range and were carefully acquired with meticulous minimization of the effects of hydroxide species, their data are optimal for the evaluation of $\beta^{(0)}_{Nd,Cl}$, $\beta^{(1)}_{Nd,Cl}$, and $C^{\phi}_{Nd,Cl}$. Published models that use only these parameters do not reproduce the properties of the $NdCl_3 + H_2O$ system within the claimed accuracy of Spedding et al. (1976). Differences between the claimed accuracy and a model containing only the $\beta^{(0)}_{Nd,Cl}$, $\beta^{(1)}_{Nd,Cl}$, and $C^{\phi}_{Nd,Cl}$ parameters can be attributed to the formation of significant fractions of Nd-chloride ion-pairs. In this case, $NdCl^{2+}$ and $NdCl_2^+$ are ancillary solutes. However, their inclusion, along with the hydroxide ion-pairs, transforms the model to a nonlinear one with no uniqueness in the parameters nor solute fraction distributions. Inclusion of non-neodymium and non-chloride ions such as Ca^{2+}, Na^+, OH^-, and $B(OH)_4^-$, in the experimental systems used to derive the Pitzer parameters involving neodymium, would further confound the problem. Datasets that include confounding solutes should not be used to evaluate Pitzer model parameters.

If a model for a completely dissociated salt captures most of a fitted property, such as osmotic coefficients, then the difference between the accuracy of the data and the residuals for the model for the completely dissociated salt may be due to ion-pairs. Those differences might be eliminated by the addition of ion-pair dimensionless standard state chemical potentials (μ°_N/RT) or a combination of ion-pair μ°_N/RT terms with $B^{\phi}_{N,Cl}$ parameters (N = $NdCl^{2+}$, $NdCl_2^+$, $NdOH^{2+}$). It is important to recognize that high ionic strengths and high chloride molalities do not by themselves necessitate the inclusion of $C^{\phi}_{N,Cl}$ terms if the ion-pairs have low molalities at all ionic strengths. High anion molality is irrelevant if the molality of a cation in an interaction parameter is always <0.001 mol·kg^{-1}.

The ternary mixing parameters, such as $\theta_{M,Nd}$, can be evaluated from a variety of experimental methods on any common anion system in which both the accessory cations (e.g., M = H^+, Na^+, K^+, Ca^{2+}) and neodymium are highly soluble and complexation reactions are minimized. For example, it would be appropriate to evaluate $\theta_{M,Nd}$ from a non-chloride system, e.g., $MClO_4 + Nd(ClO_4)_3 + H_2O$. The chloride system is obviously convenient for its relevance to ore processing and WIPP applications and is necessary to evaluate whether the $\psi_{M,Nd,Cl}$ term is necessary. While isopiestic data are generally more accurate, we are only aware of solubility data for the 2-salt chloride systems (Shvetsova et al., 1958, 1961, 1968) and consequently, the mixing terms were evaluated against these data.

Like the other Pitzer parameters, the ternary mixing terms are not model requirements – they should only be included, as warranted, to reproduce the data within their accuracy. Given that the mixing terms represent like-ion

interactions these terms are usually not resolvable for ion molalities $<\sim 0.01$ mol·kg^{-1} because electrostatic repulsion and solvent molecules keep such ions well separated. $\theta_{M,Ln}$ or $\theta_{M,An}$ parameters derived from experiments containing only micro-molal (μm) lanthanides or actinides have dubious merit.

3. VALIDATION OF THE HMW MODEL PARAMETERS FOR SUPPORTING ELECTROLYTE SYSTEMS

Model parameters for the underlying systems relevant to this study: $HCl + H_2O$, $NaCl + H_2O$, $KCl + H_2O$, $CaCl_2 + H_2O$ and all related "ternary" interaction parameters, e.g., $\theta_{H,Na}$, $\theta_{H,K}$, $\theta_{H,Ca}$, $\theta_{OH,Cl}$, $\psi_{H,Na,Cl}$, are from Harvie et al. (1984).

To avoid over-fitting, the upper molality bounds of the HMW model for the individual binary subsystems were determined by comparison to osmotic coefficients from high-quality measurements and comprehensive standard models. This was necessary as Harvie and Weare (1980) and Harvie et al. (1984) compared their model almost entirely to solubility data for systems containing two or more salts. Data corresponding to salt molalities above which the respective HMW parameter set does not reproduce the single salt system data within the experimental uncertainties were down-weighted to avoid causing the mixing parameters involving Nd to compensate for errors in the binary system models.

Archer (1992) and Archer and Carter (2000) (hereafter the Archer NaCl(aq) model) produced a polythermal, polybaric Pitzer model for the $NaCl + H_2O$ system that can be used as a calibration standard. Osmotic coefficients, ϕ, calculated from the HMW and Archer NaCl(aq) models (Fig. 1) are well within, or very close to, the accuracy of the Archer NaCl(aq) model ($\Delta\phi < 0.005$, cf. Archer (1992) Fig. 7) over the molality range from infinite dilution to halite saturation at 298 K ($\sim$6.15 mol·kg^{-1}). Consequently, the mixture model for the $NdCl_3 + NaCl + H_2O$ system is not restricted by the HMW model for NaCl(aq) and the halite solubility data for the mixture were equally weighted. The solubility data for $NdCl_3{\cdot}6H_2O$ in $NdCl_3 + NaCl + H_2O$ mixtures were down-weighted by 1000× (effectively no influence) relative to the halite solubility data.

Osmotic coefficients for HCl(aq) at 298 K and 0.1 MPa are compared to the HMW model in Fig. 2. Due to the volatility of HCl, osmotic coefficients for this system are derived from a variety of experiments including emf, freezing point depression, vapor pressure, and heat capacity data rather than direct isopiestic measurements. Osmotic coefficients plotted in Fig. 2A are from the citations in the graphs. Osmotic coefficients from Holmes et al. (1987) are derived from his polythermal, polybaric Pitzer model fitted to a large number of different data types. As shown in Fig. 2B, the HMW model deviates significantly from the data above $m_{HCl} \sim 4.5$ mol·kg^{-1}. Consequently, solubility data used in our evaluation of the $\theta_{H,Nd}$ and $\psi_{H,Nd,Cl}$ parameters were down-weighted by 5 × at $m_{HCl} > 4.5$ mol·kg^{-1} and 10 × at $m_{HCl} > 6.0$ mol·kg^{-1}.

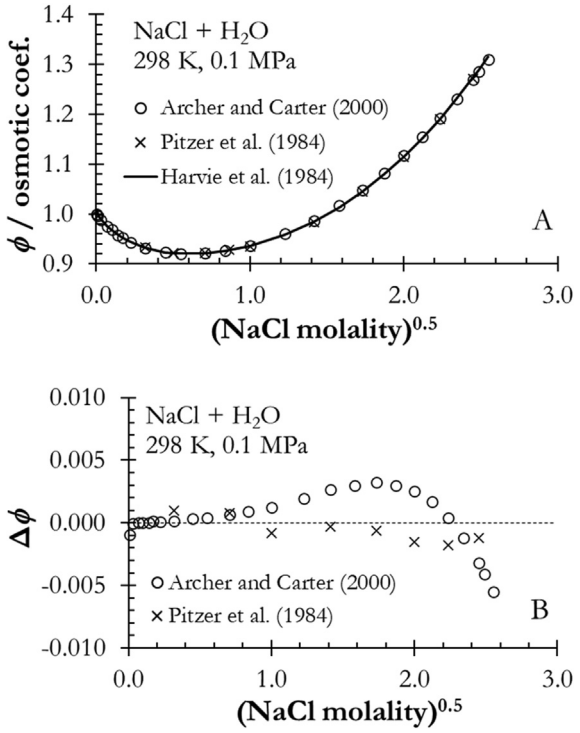

Fig. 1. Comparison of the HMW model for NaCl(aq) osmotic coefficients (ϕ) with values calculated from the temperature (T) and pressure (P) dependent models of Pitzer et al. (1984) and Archer and Carter (2000) (A) and differences in osmotic coefficients ($\Delta\phi$) between the T-P dependent models and the HMW model (B). The Archer NaCl(aq) model was used to recalculate isopiestic data for other salts that used NaCl(aq) as a reference for water activities. Archer (1992) and Archer and Carter (2000) estimated error in ϕ at 298 K as ±0.005. The Pitzer et al. (1984) NaCl(aq) model incorporates the same equations for water properties used by HMW. Halite saturation is $m_{NaCl} = 6.15$ mol·kg^{-1} (HMW halite saturation is $m_{NaCl} = 6.10$ mol·kg^{-1}).

Experimental osmotic coefficients for KCl(aq) at 298 K and 0.1 MPa from several sources are compared to the HMW model in Fig. 3. All of the plotted osmotic coefficients in Fig. 3A are from isopiestic experiments in which NaCl(aq) solutions were used as standards and the KCl (aq) osmotic coefficients were recalculated using the Archer NaCl(aq) model. Differences between the data and the HMW model (Fig. 3B) are within experimental error ($\Delta\phi < 0.005$) over the molality range between infinite dilution and saturation with solid sylvite. Consequently, the mixture model for the $NdCl_3 + KCl + H_2O$ system is not constrained by the HMW model for KCl(aq) and the mixture data were equally weighted.

Experimental osmotic coefficients from several sources for the $CaCl_2 + H_2O$ system at 298 K and 0.1 MPa are compared to the HMW model in Fig. 4. Osmotic coefficients from isopiestic experiments in which NaCl(aq) and KCl(aq) solutions were used as standards were recalculated using the Archer NaCl(aq) and Archer (1999) models, respectively (Fig. 4A). Osmotic coefficients from experiments in which H_2SO_4(aq) standard solutions were used

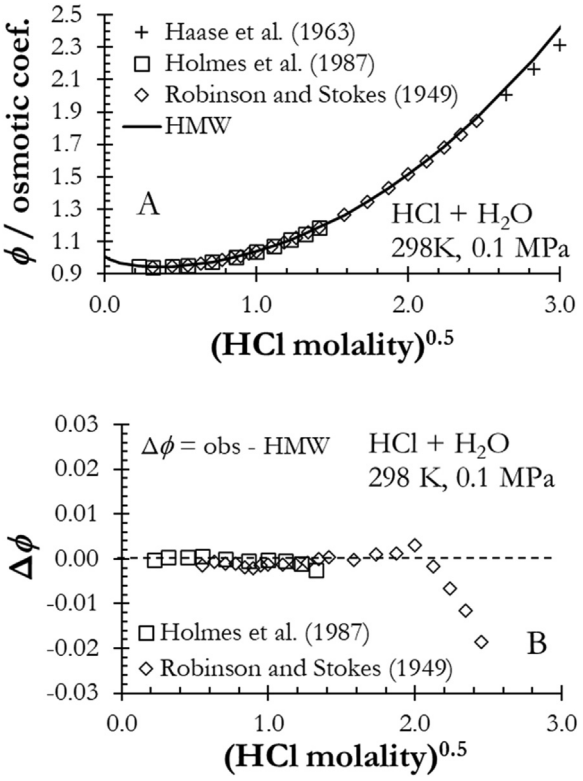

Fig. 2. Comparison of tabulated HCl(aq) osmotic coefficients from the referenced sources to the HMW model for $m_{HCl} < 9$ mol·kg^{-1} (A) and differences ($\Delta\phi$) between the referenced sources and HMW model (B). $\Delta\phi$ exceeds the error of the Holmes et al. (1987) model (~0.3%) at $m_{HCl} > 4.5$ mol·kg^{-1}.

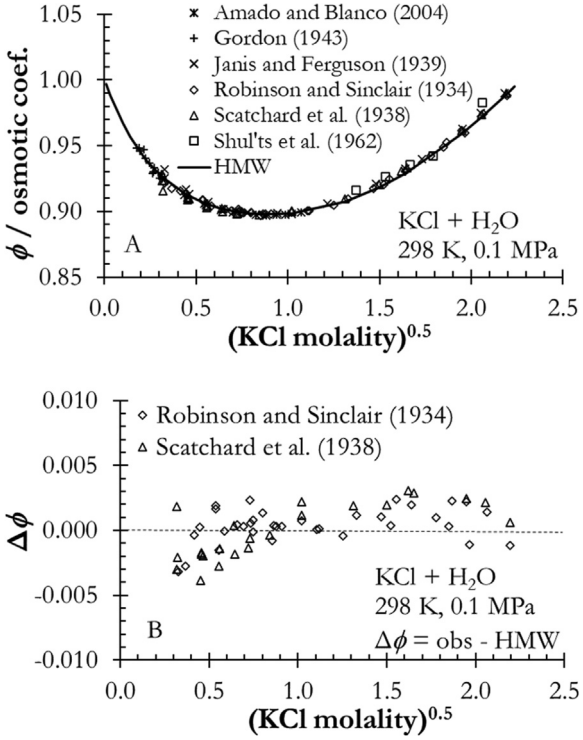

Fig. 3. Comparison of experimental KCl(aq) osmotic coefficients from isopiestic measurements by the referenced sources to the HMW model between infinite dilution and sylvite saturation ($m_{KCl} = 4.79$ mol·kg^{-1}) (A) and $\Delta\phi$ values between the data from Robinson and Sinclair (1934) and Scatchard et al. (1938) and the HMW model (B). The Robinson and Sinclair (1934) and Scatchard et al. (1938) datasets represent the highest quality data of those presented and are reproduced within their accuracy and that of the Archer (1999) model (±0.005).

were recalculated using Rard et al. (1976). Differences between the data and the HMW model (Fig. 4B) are within experimental error ($\Delta\phi < 0.005$) over $0 < m_{CaCl_2} < \sim 3$ mol·kg^{-1}. The HMW model grossly approximates the data to $m_{CaCl_2} \sim 5.5$ mol·kg^{-1}. Our mixture model for the $NdCl_3 + CaCl_2 + H_2O$ system included data for $NdCl_3 \cdot 6H_2O$ solubility in $CaCl_2$(aq) to $m_{CaCl_2} \sim 7$ mol·kg^{-1} but with 2× lower weighting on data at $m_{CaCl_2} > 3.5$ mol·kg^{-1}. The relatively modest down-weighting of the [$NdCl_3 + CaCl_2$](aq) solubility data for $m_{CaCl_2} > 3.5$ mol·kg^{-1} was necessary for the fitted model to converge on $CaCl_2 \cdot 6H_2O$ (antarcticite) solubility. Greater down-weighting of the data for $m_{CaCl_2} > 3.5$ mol·kg^{-1}, similar to that used for [$NdCl_3$ + HCl](aq), causes the $NdCl_3 \cdot 6H_2O$ solubility to be too low at high $CaCl_2$ molalities such that antarcticite formation is unphysically precluded and consequently models with more appropriate weighting did not converge. Consequently, our fitted $\theta_{Ca,Nd}$ value is a compromise between fitting the data within its accuracy and a $\theta_{Ca,Nd}$ value that would result from a more accurate model for the $CaCl_2 + H_2O$ system.

4. PREVIOUS PITZER MODELS FOR AQUEOUS NDCL$_3$

Conventional Pitzer ion-interaction models for the completely dissociated $NdCl_3 + H_2O$ system have been presented by Pitzer and Mayorga (1973), Pitzer et al. (1978), Kodýtek and Dolejš (1986), Kim and Frederick (1988), and May et al. (2011). Because these models do not include liquid phase equilibria, they do not accurately reproduce the pH of $NdCl_3$(aq) solutions and do not reproduce the data within its accuracy over the full molality range. The Kodýtek and Dolejš (1986) model is invalid because it uses a positive $\beta^{(2)}_{Nd,Cl}$.

The Nd^{3+}– Cl^- interaction parameters from the cited studies are reproduced in Table 1 along with the speciated system model parameters from Könnecke et al. (1997) and Neck et al. (2009) (henceforth the Könnecke or Neck models, respectively). The H^+– Cl^- and Ca^{2+}– Cl^- parameters from Roy et al. (2005a) and Könnecke et al. (1997) are also presented because the latter two studies used HCl and $CaCl_2$, respectively, in their experiments. Neck et al. (2009) truncated the Könnecke model by eliminating the $\beta^{(1)}_{M(OH)_2,Cl}$, $C^{\phi}_{M(OH)_2,Cl}$ and $C^{\phi}_{M(OH),Cl}$ terms (in this case, M = Nd^{3+} or An(III)). Parameter differences between the Neck and Könnecke models are insignificant for the $NdCl_3 + H_2O$ system because hydroxide ion-pairs are <0.001 mol·kg^{-1} at all $m_{Nd_{tot}}$. The Könnecke model is of particular interest because it, and models dependent upon it, are used for recertification

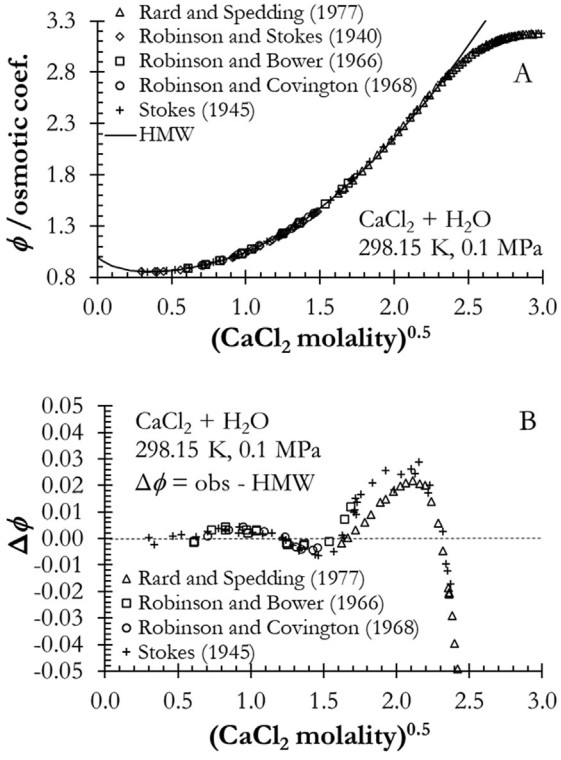

Fig. 4. Comparison of experimental osmotic coefficients from isopiestic measurements by the sources listed in (A) to the HMW model between infinite dilution and supersaturated solutions at $m_{CaCl_2} = 9$ mol·kg^{-1} and differences between the isopiestic data and the HMW model (B) showing that $\Delta\phi$ exceeds experimental error (±0.005) at $m_{CaCl_2} > 3$ mol·kg^{-1}. Saturation with solid $CaCl_2{\cdot}6H_2O$ is at $m_{CaCl_2} = 7.4$ mol·kg^{-1}.

of the US WIPP repository and because the Neck model, used for the German Asse nuclear waste repository, is a derivative of the Könnecke model. Xiong et al. (2017) present the Könnecke parameter set, without acknowledgment, as "the WIPP thermodynamic model".

Oakes et al. (2004) and He and Rard (2015) presented extended Pitzer models with an ionic strength dependent $C^{\phi}_{Nd,Cl}$ term for the completely dissociated, unhydrolyzed system. Although extended, linear Pitzer models can reproduce very high ionic strength solutions more accurately than conventional, linear Pitzer models, the library of parameters is not as extensive as for the conventional form, so their use in calculating the thermodynamic properties of mixed salt systems is restricted.

Experimental osmotic coefficients for $NdCl_3$(aq) solutions are compared to the Pitzer et al. (1978) model in Fig. 5. The Spedding et al. (1976) osmotic coefficients are accurate to better than 0.01 at all $m_{Nd_{tot}}$. The Pitzer et al. (1978) model reproduces most of the data within accuracy of the data to $m_{Nd_{tot}} \sim 2.5$ mol·kg^{-1} (ionic strength ~15 mol·kg^{-1}) but only grossly approximates the experimental data at higher $m_{Nd_{tot}}$. The models of Kim and Frederick (1988), Roy et al., 2005a, and May et al. (2011) also reproduce the osmotic coefficient data within a range of ±0.02 (not shown) which is unsurprising given their similarities to the parameter values of Pitzer et al. (1978).

The Könnecke and Neck models incorporate chloride and hydroxide solute ion-pairs with Pitzer parameters for trivalent Nd, Cm, and Am treated as equivalents. The use of ion-pair species adds model parameters. Consequently, such models should produce smaller residuals between measured and model quantities and enable accurate reproduction of properties such as pH.

Table 1
Pitzer parameters for cation–anion interactions for 298.15 K and 0.1 MPa used in the previously published models for aqueous mixtures of $NdCl_3$ and the other salts examined for this study.

c	a	$\beta^{(0)}_{ca}$ kg·mol^{-1}	$\beta^{(1)}_{ca}$ kg·mol^{-1}	$\beta^{(2)}_{ca}$ kg·mol^{-1}	C^{ϕ}_{ca} kg^2·mol^{-2}	source
Nd^{3+}	Cl^-	0.6117	5.403		−0.02837	Pitzer and Mayorga (1973)
Nd^{3+}	Cl^-	0.5856	5.6		−0.01898	Pitzer et al. (1978)
Nd^{3+}	Cl^-	0.58674	5.6		−0.01882	Kim and Frederick (1988)
Nd^{3+}	Cl^-	0.5877	5.206		−0.01969	May et al. (2011)
Nd^{3+}	Cl^-	0.5268	3.727	5.3	−0.00443	*Kodýtek and Dolejš (1986)
Nd^{3+}	Cl^-	0.5856	5.6		−0.0189755	[1]Roy et al. (2005a)
H^+	Cl^-	0.17557	0.29778		0.000137	[2]Roy et al. (2005a)
Nd^{3+}	Cl^-	0.5856	5.6		−0.016	[3]Könnecke et al. (1997)
MCl^{2+}	Cl^-	0.593	3.15		−0.006	Könnecke et al. (1997)
MCl_2^+	Cl^-	0.516	1.75		0.010	Könnecke et al. (1997)
MOH^{2+}	Cl^-	−0.055	1.60		0.050	[5]Könnecke et al. (1997)
$M(OH)_2^+$	Cl^-	−0.616	−0.45		0.050	Könnecke et al. (1997)
MOH^{2+}	Cl^-	0.055	1.81			[5]Neck et al. (2009)
$M(OH)_2^+$	Cl^-	−0.13				Neck et al. (2009)
Ca^{2+}	Cl^-	0.3261	1.4729		−0.00205	[4]Könnecke et al. (1997)

[1]Parameters originally from Pitzer et al. (1978); [2]parameters originally from Campbell et al. (1993); [3]$\beta^{(0)}_{Nd,Cl}$ and $\beta^{(1)}_{Nd,Cl}$ from Pitzer et al. (1978), $C^{\phi}_{Nd,Cl}$ calculated by methods that are unclear; [4]fit to osmotic coefficient data in Goldberg and Nuttall (1978); [5]difference in sign for $\beta^{(0)}_{M(OH),Cl}$; *$\alpha_1 = 1.6$, $\alpha_2 = 6.0$; all other studies $\alpha_1 = 2$ and $\alpha_2 = 0$. M = Nd^{3+} or An(III).

Table 2
Mixing parameters from Könnecke et al. (1997) compared to similar mixing parameters from other studies.

c	c'	${}^{s}\theta_{cc'}$	a	$\psi_{cc'a}$	Source
Na^+	Cm^{3+}	0.1			Könnecke et al. (1997)
Ca^{2+}	Cm^{3+}	0.2			Könnecke et al. (1997)
Ca^{2+}	$CmCl^{2+}$	−0.014			Könnecke et al. (1997)
Ca^{2+}	$CmCl_2^+$	−0.196			Könnecke et al. (1997)
H^+	La^{3+}	0.278	Cl^-	0.009	Roy et al. (1983)
H^+	Nd^{3+}	0.148	Cl^-	0.003	Roy et al. (2005a)
H^+	Nd^{3+}	0.185	Cl^-	0.013	Felmy et al. (1989)*
Na^+	Al^{3+}	0.335	Cl^-	−0.065	Palmer and Wesolowski (1992)

*Adopted from $\theta_{H,Al}$ and $\psi_{H,Al,Cl}$ (Pitzer, 1975); there is typographical error in Felmy's listed $\psi_{H,Nd,Cl}$ value; Units: $\theta_{cc'}$, kg·mol^{-1}; $\psi_{cc'a}$, kg^2·mol^{-2}.

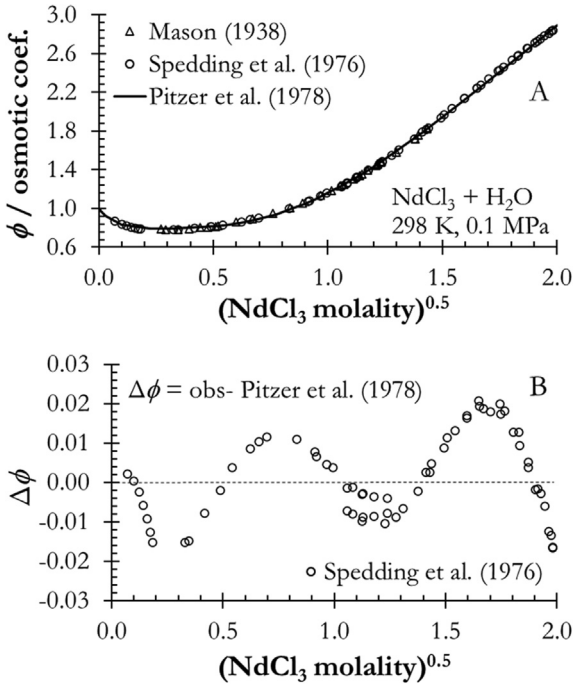

Fig. 5. Comparison of the Pitzer et al. (1978) $NdCl_3$(aq) model to osmotic coefficients from the isopiestic measurements by the cited sources (A) and differences between the Spedding et al. (1976) data and the Pitzer et al. (1978) model (B). The experimental error is ± 0.008.

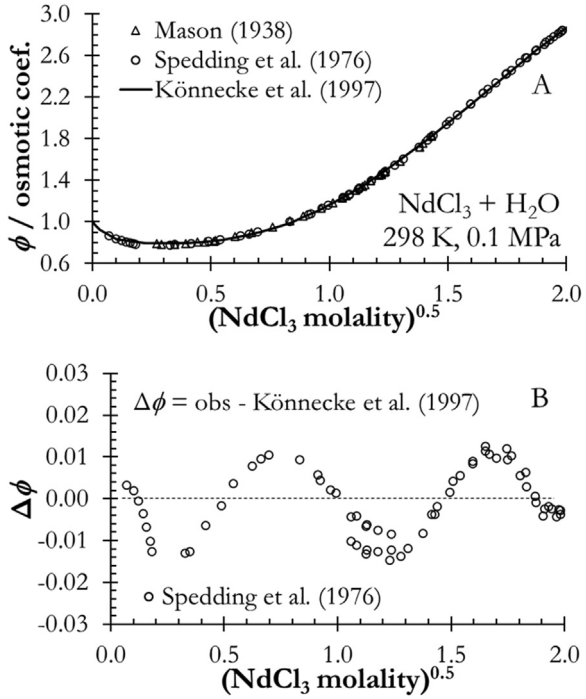

Fig. 6. Comparison of the Könnecke $NdCl_3$(aq) model to osmotic coefficients from the isopiestic measurements by the cited sources (A) and differences between the Spedding et al. (1976) data and the Könnecke model (B). The experimental error is ±0.008.

The Könnecke model is compared to $NdCl_3$(aq) osmotic coefficient data in Fig. 6. The residuals are smaller than for the 3-parameter, fully dissociated salt models; however, the Könnecke model uses 15 binary Pitzer parameters involving five Ln(III)/An(III) species and, consequently, four equilibrium constants. The Könnecke model adopts the Pitzer et al. (1978) $\beta^{(0)}_{Nd,Cl}$ and $\beta^{(1)}_{Nd,Cl}$ values for $\beta^{(0)}_{Cm,Cl}$ and $\beta^{(1)}_{Cm,Cl}$ under the assumption that "the activity properties of $NdCl_3$ and $CmCl_3$ in aqueous solution are identical." Furthermore, it is argued that ion-pair molalities are relatively high at high chloride molalities, and therefore derivation of a $C^{\phi}_{Cm,Cl}$ parameter is warranted even though their m_{Cm} was very low. Their logic is incongruous with the interaction represented by $C^{\phi}_{Cm,Cl}$ and is unjustified because the $\beta^{(0)}_{ca}$, $\beta^{(1)}_{ca}$ and C^{ϕ}_{ca} terms for each specific cation–anion interaction are not independent. However, because their $C^{\phi}_{Cm,Cl}$ term is not vastly different than the $C^{\phi}_{Nd,Cl}$ from Pitzer et al. (1978), the consequence is minor.

The Könnecke model incorporates the ion-pairs $CmCl^{2+}$, $CmCl_2^+$, $CmOH^{2+}$, and $Cm(OH)_2^+$ with non-zero $\beta^{(0)}_{M,Cl}$, $\beta^{(1)}_{M,Cl}$ and $C^{\phi}_{M,Cl}$ parameters for each cation-chloride interaction. Except for the $\beta^{(0)}_{Nd,Cl}$ and $\beta^{(1)}_{Nd,Cl}$terms adopted from Pitzer et al. (1978), their parameterization of interactions

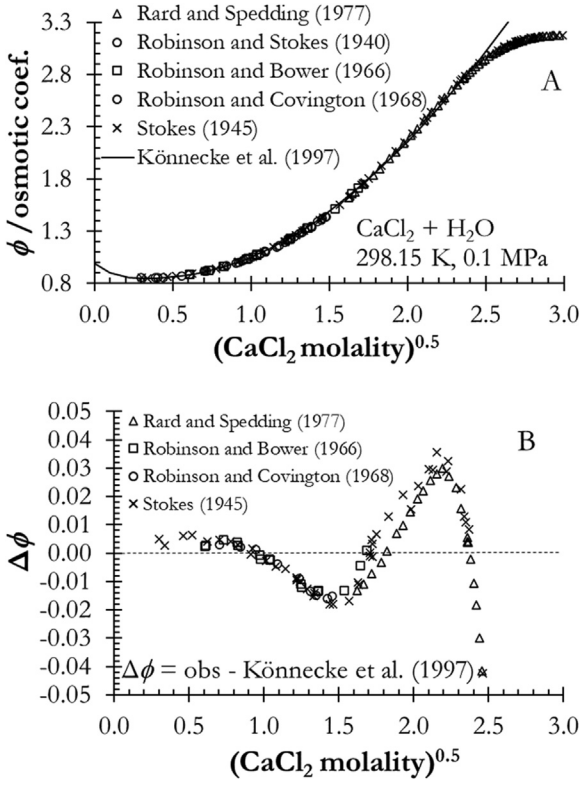

Fig. 7. Comparison of $CaCl_2$(aq) osmotic coefficients from isopiestic measurements by the cited sources to the Könnecke et al. (1997) $CaCl_2$(aq) model (A). The Könnecke et al. (1997) model deviates significantly ($\Delta\phi > 0.005$) from the data at $m_{CaCl_2} = \sim 1.2$ mol·kg^{-1} (B) versus ~ 3 mol·kg^{-1} for the HMW model shown in Fig. 4.

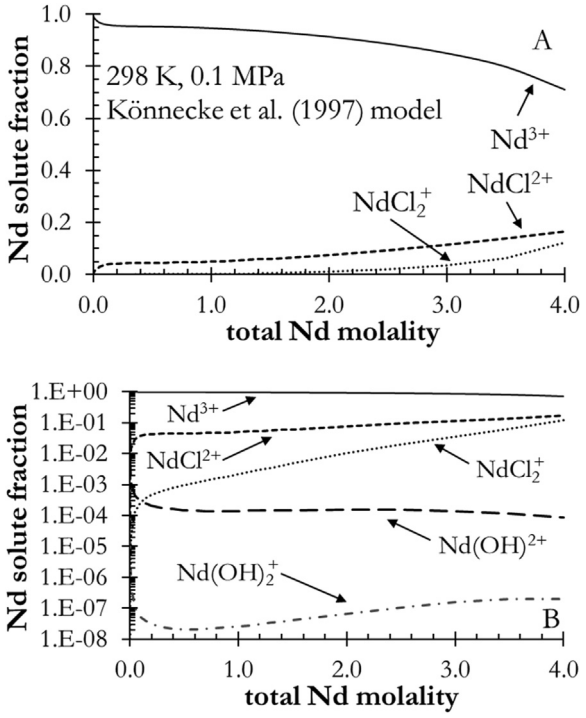

Fig. 8. Mole fraction distributions of major (A) and minor (B) species in $NdCl_3 + H_2O$ system calculated from the Könnecke et al. (1997) model.

involving curium species were based upon spectroscopic measurements of μm_{CmCl_3} in $\sim 2.2 < m_{CaCl_2} < 6.0$ mol·kg^{-1}.

The failure of other $CaCl_2$(aq) Pitzer models at high molalities (e.g., Fig. 4) led Könnecke et al. (1997) to attempt to formulate a new $CaCl_2$(aq) model. Unfortunately, as demonstrated in Figs. 4 and 7, the Könnecke $CaCl_2$(aq) model is inferior to the HMW model. As the Könnecke and Neck $AnCl_3$(aq) models are both dependent on the Könnecke $CaCl_2$(aq) model, and because the latter is not accurate, it would be reasonable to question the accuracy of their $AnCl_3$(aq) models. Conversely, Fig. 6 demonstrates that the Könnecke model comes close to accurately reproducing the $NdCl_3$(aq) isopiestic data. That would appear to negate the argument regarding the impact of the inaccurate $CaCl_2$(aq) model. However, it is more likely that the Cm ion-pair interaction parameters are insignificant or those terms partially cancel. The improvement of their (Cm/Nd)Cl_3(aq) model relative to the unspeciated, conventional $NdCl_3$(aq) Pitzer models is mostly due to the introduction of equilibrium constants for the ion-pairs. Major and minor neodymium solute fractions from the Könnecke model are shown in Fig. 8A and B, respectively. Because Könnecke et al. (1997) used solutions containing only μm_{CmCl_3} and because ion-pairs constitute minor fractions (Fig. 8B), most of the ion-pair interaction parameters in both the Könnecke and Neck models lack justification.

5. REVIEW OF THE KÖNNECKE MODEL FOR $NdCl_3 + MCl_{|z_M|} + H_2O$ MIXTURES (M = NA^+, CA^{2+})

Könnecke et al. (1997) assumed that the mixture parameters, $\theta_{Ca,Cm}$, $\theta_{Ca,CmCl}$, and $\theta_{Ca,CmCl_2}$ were necessary and arbitrarily assigned $\theta_{Ca,Cm} = 0.2$. Values for $\theta_{Ca,CmCl}$ and $\theta_{Ca,CmCl_2}$ were then calculated relative to $\theta_{Ca,Cm}$ (Table 2). They likewise assumed $\theta_{Na,Cm} = 0.1$ but did not calculate values for $\theta_{Na,CmCl}$ and $\theta_{Na,CmCl_2}$. Although binary parameters involving charged species would generally be considered to be more significant than interactions involving neutral species, Könnecke et al. (1997) also assigned values for the neutral solute terms $\lambda_{Na,Cm(OH)_3} = 0.2$ and $\lambda_{Cl,Cm(OH)_3} = 0.2$, apparently to force their model to reproduce their preferred value for the $Am(OH)_3^0$ hydrolysis constant. The parameters involving $Cm(OH)_3^0$ are especially dubious because the $Cm(OH)_3^0$ species (or equivalent $Am(OH)_3^0$ or $Nd(OH)_3^0$) is always $<10^{-5}$ mol·kg^{-1} at 298 K and pH < 13.

Könnecke et al. (1997) validated their mixture model by comparison to the solubility data from Shvetsova et al. (1958). With an estimated error of $\pm$ 0.2 mol·kg^{-1} in Shvetsova's solubilities, the Könnecke model reproduces most of the [NaCl + $NdCl_3$](aq) data. Fig. 9A appears to reproduce their Fig. 4. Conversely, our attempt to reproduce the Könnecke [$CaCl_2$ + $NdCl_3$](aq) model failed to reproduce their Fig. 3 and the Shvetsova et al. (1958) data (our Fig. 9B). In exploring why our implementation of the Könnecke

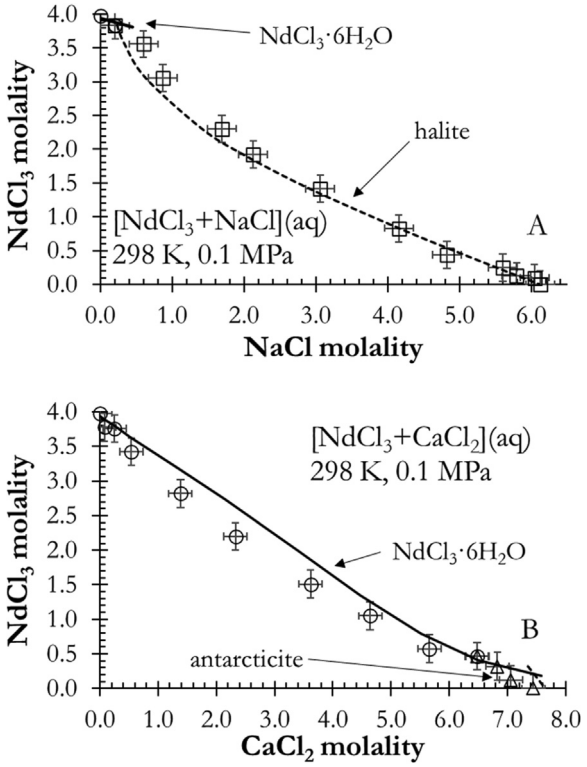

Fig. 9. Comparisons of measured $NdCl_3{\cdot}6H_2O$ and antarcticite solubilities from Shvetsova et al. (1958) to the Könnecke et al. (1997) model that includes their $\theta_{Ca,NdCl}$ and $\theta_{Ca,NdCl_2}$ parameters. This graph should, but does not, replicate Fig. 3 in Könnecke et al. (1997). Könnecke et al. (1997) did not attempt to reproduce antarcticite solubility; that curve is created using the HMW value for $\mu^{\circ}_{CaCl_2{\cdot}6H_2O}/RT$. Short sections of the metastable extensions are shown beyond each 2-solid coexistent point.

$[CaCl_2 + NdCl_3](aq)$ model did not reproduce their graph, we determined that omission of the Könnecke et al. (1997) $\theta_{Ca,CmCl}$, and $\theta_{Ca,CmCl_2}$ terms reproduced their Fig. 3 (our Fig. 10).

Unfortunately, our implementation of the Könnecke model with the $\theta_{Ca,CmCl}$, and $\theta_{Ca,CmCl_2}$ terms reproduced their Fig. 1, whereas the model without the $\theta_{ii'}$ terms did not

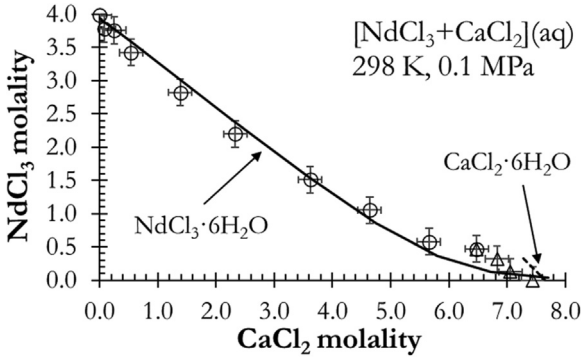

Fig. 10. Reconstruction of Fig. 9B that appears to replicate Fig. 3 in Könnecke et al. (1997) but should not because it omits their $\theta_{Ca,NdCl}$ and $\theta_{Ca,NdCl_2}$ parameters.

(Fig. 11). Könnecke et al. (1997) did not state a precise total curium concentration used to construct their Fig. 1 but mentioned that their experiments contained μm Cm. A range of Cm molalities was explored and 10^{-4} mol·kg^{-1} produced the closest match to their Fig. 1 with slight but discernible differences at lower molalities. It appears that the Könnecke et al. (1997) Figs. 1 and 3 were produced using different parameter sets. Use of the Könnecke model parameters for trivalent actinides and lanthanides, with the HMW parameters for $CaCl_2$, will also produce differences from the relationships shown in Könnecke et al. (1997). This will also be the case with the geochemical parameter set for An(III) used for geochemical modeling to support performance assessment and recertification of the US DOE WIPP nuclear waste repository, i.e., the "WIPP thermodynamic model" cited by Xiong et al. (2017) is internally inconsistent.

6. REVISED PITZER MODEL FOR THE SPECIATED $NdCl_3 + H_2O$ SYSTEM

Our model was derived using the INSIGHT software code developed by Sterner et al. (1997, 1998). INSIGHT contains the NONLIN and GMIN codes (Felmy, 1990, 1995; Felmy et al., 1990) that are "qualified" for WIPP applications. In contrast to NONLIN, INSIGHT includes temperature and pressure functions that allow fitting tem-

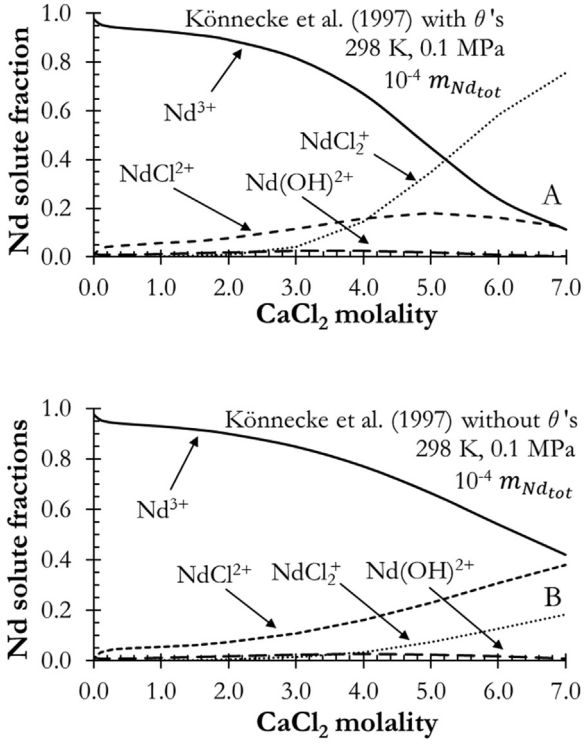

Fig. 11. Neodymium solute fractions in $NdCl_3 + CaCl_2 + H_2O$ system for the Könnecke et al. (1997) model with (A) and without (B) $\theta_{Ca,NdCl}$, and $\theta_{Ca,NdCl_2}$. The $Nd(OH)_2^+$ species does not appear at the depicted scale. (A) reproduces Fig. 1 in Könnecke et al. (1997) but the parameter set is inconsistent with their Fig. 3. (B) is consistent with our Fig. 10 and Fig. 3 in Könnecke et al. (1997).

perature and pressure-dependent G^{xs} properties such as enthalpy, heat capacity, and density. The only difference between the HMW implementation of the Pitzer model and that used for this study is the Hill (1990) and Archer and Wang (1990) models used for water properties in the Debye-Hückel function. The value of the Debye-Hückel slope term, A^{ϕ}, at 298 K and 0.1 MPa from these models is not significantly different from the value used by Harvie and Weare (1980), e.g., 0.39148 versus 0.392 $kg^{0.5}\cdot mol^{-0.5}$, respectively.

The value of $\mu^{\circ}_{Nd^{3+}}/RT$ was taken from the review of Rard (2016) while those for the other neodymium species were fitted. We were unable to satisfactorily reproduce the solubility of solid $NdCl_3\cdot 6H_2O$ using $\mu^{\circ}_{NdCl_3\cdot 6H_2O}/RT$ from Rard (2016), however, our fitted value is different by < 50% of his uncertainty. The inclusion of $NdCl_2^+$ significantly improved the model and $Nd(OH)^{2+}$ was necessary to produce proper pH values. The fitted $\mu^{\circ}_{NdOH^{2+}}/RT$ was relatively uncertain given the low pH values and $NdOH^{2+}$ molalities consistent with the isopiestic data. Dimensionless standard state chemical potentials and a minimal number of Pitzer parameters were fitted simultaneously starting with only the $\beta^{(0)}_{Nd,Cl}$, $\beta^{(1)}_{Nd,Cl}$ and $C_{Nd,Cl}$ parameters ($C_{MX} = C^{\phi}_{MX}/2|z_M z_X|^{0.5}$) followed by iterative trials involving different combinations of $\beta^{(0)}_{NdCl,Cl}$, $\beta^{(1)}_{NdCl,Cl}$, $\beta^{(0)}_{NdCl_2,Cl}$, $\beta^{(1)}_{NdCl_2,Cl}$. The $\beta^{(0)}_{Nd(OH),Cl}$, $\beta^{(1)}_{Nd(OH),Cl}$ and $C_{N,Cl}$ parameters were unwarranted (N referring to generic neodymium ion-pair cations). $\beta^{(0)}_{Nd,Cl}$, $\beta^{(1)}_{Nd,Cl}$, $C_{Nd,Cl}$, $\beta^{(0)}_{NdCl,Cl}$, and $\beta^{(0)}_{NdCl_2,Cl}$ were sufficient to reproduce the binary system osmotic coefficients within their accuracy of 0.3% over the range from infinite dilution to saturation with solid $NdCl_3\cdot 6H_2O$. The final model and residuals are compared to the isopiestic data in Fig. 12.

The corresponding species distributions are shown in Fig. 13. There are some gross similarities to the Könnecke model (Fig. 8) for $m_{Nd_{tot}} > \sim 0.2$ mol·kg^{-1}. For example, the $NdOH^{2+}$ species fraction is relatively constant at $\sim 10^{-4}$, and the $NdCl_2^+$ species fraction increases monotonically with increasing $m_{Nd_{tot}}$ to ~0.1 at solid saturation. However, beyond $m_{Nd_{tot}} \sim 0.2$ mol·kg^{-1}, in our model, $NdCl_2^+$ forms at the expense of the $NdCl^{2+}$ species whereas, in the Könnecke model, the fractions of both chloride ion-pairs increase with increasing total neodymium at the expense of Nd^{3+}.

7. SPECIATED PITZER MODEL FOR $NdCl_3 + MCl_{z_M} + H_2O$ MIXTURES (M = H^+, NA^+, K^+, CA^{2+})

After producing an initial fit to the $NdCl_3 + H_2O$ data the ternary parameter $\theta_{H,Nd}$ was fitted to the $NdCl_3 + HCl + H_2O$ emf and solubility data from Roy et al. (2005b) and Shevtsova et al. (1968). The $\psi_{H,Nd,Cl}$ term was not necessary. Following the recommendation of Mioduski et al. (2009), the 298.15 K Spedding et al. (1976) $NdCl_3\cdot 6H_2O$ solubility of $m_{NdCl_3} = 3.835$ mol·kg^{-1} was favored over the measurements of Shevtsova et al.

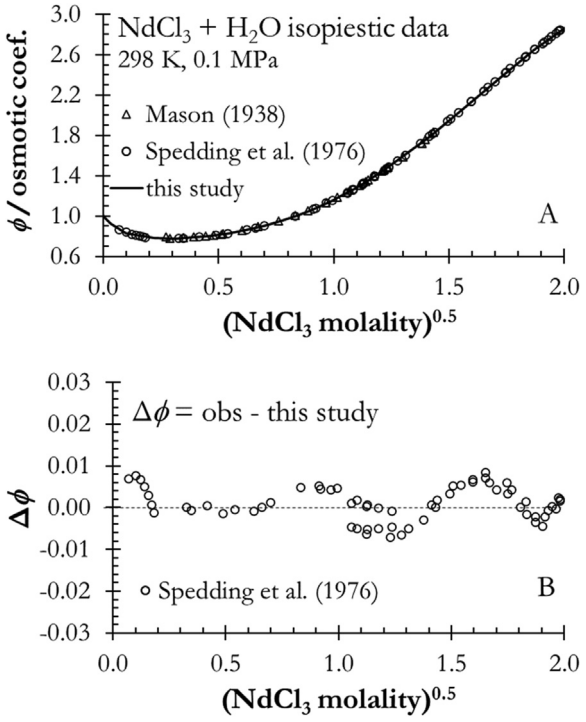

Fig. 12. Comparison of the $NdCl_3$(aq) model derived in this study to measured osmotic coefficients (A). Residuals between the Spedding et al. (1976) and model osmotic coefficients (B) are within experimental error for $0 < m_{NdCl_3} < 3.836$ mol·kg^{-1} ($NdCl_3\cdot 6H_2O$ saturation).

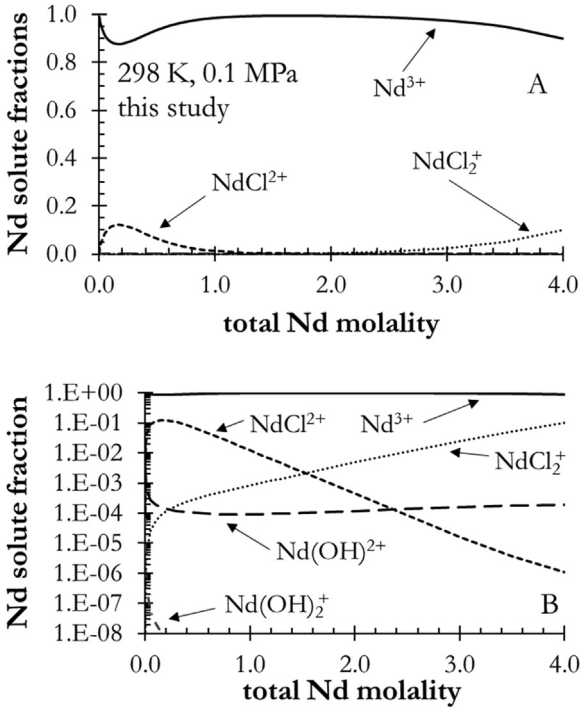

Fig. 13. Major (A) and minor species (B) mole fractions as a function of total neodymium molality in the $NdCl_3 + H_2O$ system calculated from the model developed in this study.

(1968). Our ultimately fitted $NdCl_3{\cdot}6H_2O$ solubility is $m_{NdCl_3} = 3.837\ mol{\cdot}kg^{-1}$.

Except for $\mu^{\circ}_{Nd^{3+}}/RT$, the μ°_i/RT values and binary and ternary Pitzer parameters involving other neodymium species were then refitted to the combined $NdCl_3 + H_2O$ and $NdCl_3 + HCl + H_2O$ datasets using the previously fitted binary and ternary parameter values to initialize the fit. Changes to the previously fitted values were small. Differences between the emf data and our model (Fig. 14) are as much as twice the largest uncertainties cited by Roy et al. (2005b), estimated as 0.06 mV for $I < 1.0$ and 0.11 mV for $I \geq 1.0\ mol{\cdot}kg^{-1}$. Most of the data from Roy et al. (2005b) at $I = 0.01\ mol{\cdot}kg^{-1}$ appear to have much larger uncertainties than claimed and were down-weighted by 10× relative to the other emf data.

The model was then fitted to the solubility data of Shevtsova et al. (1958, 1961) for the $NdCl_3 + NaCl + H_2O$, $NdCl_3 + KCl + H_2O$, and $NdCl_3 + CaCl_2 + H_2O$ systems as tabulated in Mioduski et al. (2009). Except for $CaCl_2{\cdot}6H_2O$, solid and solute μ°_i/RT values for the non-neodymium species were taken from HMW. No additional terms were necessary to reproduce the solid solubilities in the $[NdCl_3 + KCl](aq)$ system. The $\theta_{Na,Nd}$ and $\theta_{Ca,Nd}$ parameters improved the fit to the $[NdCl_3 + NaCl](aq)$ and $[NdCl_3 + CaCl_2](aq)$ systems, respectively. Finally, the new model was evaluated with the EQ3/6 Version 8.0a code (Wolery, 2010), approved by the U.S. Environment Protection Agency for use in WIPP compliance recertification applications since 2011.

Model solubility curves for the four ternary systems are compared to the data in Fig. 15. The aqueous solubility of $CaCl_2{\cdot}6H_2O$ ($7.44\ mol{\cdot}kg^{-1}$) measured by Shvetsova et al. (1958) is closer to the more widely cited value of 7.4 $\pm$ 0.1 $mol{\cdot}kg^{-1}$ (cf. Rard and Clegg, 1997) than the value calculated using $\mu^{\circ}_{CaCl_2{\cdot}6H_2O}/RT$ from HMW ($7.55\ mol{\cdot}kg^{-1}$). A small change in $\mu^{\circ}_{CaCl_2{\cdot}6H_2O}/RT$ to −893.72 produced a solubility of $m_{CaCl_2} = 7.41\ mol{\cdot}kg^{-1}$ which is used herein. Values for μ°_i/RT and the equilibrium constants for the solid and ion-pair dissociation reactions are listed in Table 3. Our fitted Pitzer parameters and those from HMW are listed in Tables 4 and 5.

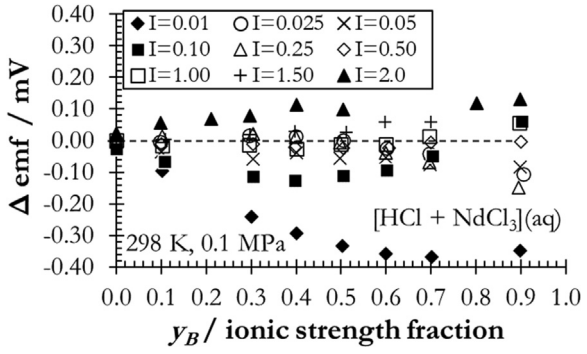

Fig. 14. Residuals between emf data from Roy et al. (2005b) and values calculated from the model developed in this study for [HCl + $NdCl_3$](aq) solutions at varying ionic strengths and ionic strength fractions, $y_B = 6m_{NdCl_3}/(m_{HCl} + 6m_{NdCl_3})$.

The fractional distribution of neodymium solutes from our model for $m_{NdCl_3} = 10^{-4}\ mol{\cdot}kg^{-1}$ in HCl(aq), NaCl (aq), KCl and $CaCl_2$(aq) solutions are shown in Fig. 16.

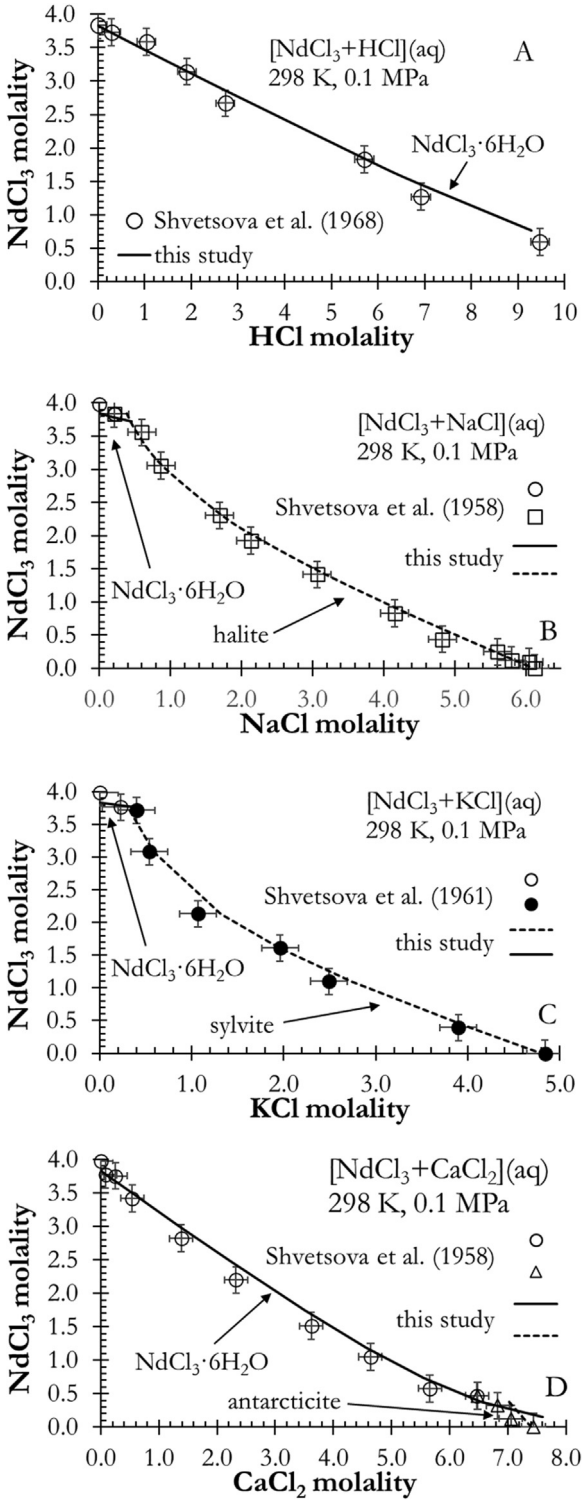

Fig. 15. Comparisons of measured solubilities for: (A) HCl + $NdCl_3 + H_2O$; (B) NaCl + $NdCl_3 + H_2O$; (C) KCl + $NdCl_3 + H_2O$; and (D) $CaCl_2 + NdCl_3 + H_2O$ with values calculated from the model developed in this study.

Table 3
Dimensionless standard state chemical potentials and lg K values at 298.15 K and 0.1 MPa used in our model. Equilibrium constants for hydroxyl-bearing species are for protonation reactions, e.g., $Nd(OH)_x^{3-x} + xH^+ = Nd^{3+} + xH_2O$. Equilibrium constants for the simple chloride species are complete dissociation reactions, e.g., $NdCl_3{\cdot}6H_2O = Nd^{3+} + 3Cl^- + 6H_2O$.

species	μ_i°/RT	lg K	source
$Nd(OH)^{2+}$	−347.249	8.0293	fitted
$Nd(OH)_2^+$	−424.082	16.207	fitted
$Nd(OH)_3^0$	−505.360	22.455	fitted
$NdCl^{2+}$	−324.465	−0.6241	fitted
$NdCl_2^+$	−372.483	1.5202	fitted
$NdCl_3{\cdot}6H_2O$(cr)	−991.990	4.7464	fitted
$Nd(OH)_3$(cr)	−522.649	14.946	fitted
$Nd(OH)_3$(am)	−517.5	17.18	fitted
$Nd(OH)_2Cl$	−496.8	7.624	fitted
$Nd_2(OH)_3Cl_3$	−958.091	12.12	fitted
Nd^{3+}	−270.073		Rard (2016)
Na^+	−105.651		HMW
K^+	−113.957		HMW
Ca^{2+}	−223.300		HMW
OH^-	−63.435		HMW
Cl^-	−52.955		HMW
$CaCl_2{\cdot}6H_2O$(cr)	−893.720	4.1132	fitted
KCl(cr)	−164.840	0.90	HMW
NaCl(cr)	−154.990	1.57	HMW
H_2O(l)	−95.663		HMW

Table 4
Pitzer parameters for cation–anion interactions for 298.15 K and 0.1 MPa used in the model.

c	a	$\beta_{ca}^{(0)}$ kg·mol^{-1}	$\beta_{ca}^{(1)}$ kg·mol^{-1}	$\beta_{ca}^{(2)}$ kg·mol^{-1}	C_{ca}^{ϕ} kg^2·mol^{-2}	source
Nd^{3+}	Cl^-	0.57351	5.3437		−0.014876	fitted
$NdCl^{2+}$	Cl^-	1.1989				fitted
$NdCl_2^+$	Cl^-	0.50869				fitted
H^+	Cl^-	0.17750	0.29450		0.0008	HMW
Na^+	Cl^-	0.07650	0.26640		0.00127	HMW
Na^+	OH^-	0.08640	0.25300		0.00440	HMW
K^+	Cl^-	0.04835	0.21220		−0.00084	HMW
K^+	OH^-	0.12980	0.32000		0.0041	HMW
Ca^{2+}	Cl^-	0.31590	1.6140		−0.00034	HMW
Ca^{2+}	OH^-	−0.17470	−0.23030	−5.7200		HMW

Table 5
Model parameters used in the model for interactions involving ions of like-sign for 298.15 K and 0.1 MPa.

c	c'	${}^s\theta_{cc'}$	a	a'	${}^s\theta_{aa'}$	$\psi_{cc'a}$	$\psi_{aa'c'}$	source
H^+	Nd^{3+}	0.220						fitted
Na^+	Nd^{3+}	0.0379						fitted
Ca^{2+}	Nd^{3+}	0.0282						fitted
H^+	Na^+	0.036	Cl^-	OH^-	−0.050	−0.004	−0.006	HMW
H^+	K^+	0.005	Cl^-	OH^-		−0.011	−0.006	HMW
H^+	Ca^{2+}	0.092	Cl^-	OH^-		−0.015	−0.025	HMW

In contrast to the speciation scheme from the Könnecke model (Fig. 17), there is no pronounced dependency of chloride species distribution upon the identity of the supporting electrolyte. The similarity in the forms and magnitudes of the neodymium solute distribution between Figs. 13 and 16 demonstrates that the relative fraction of

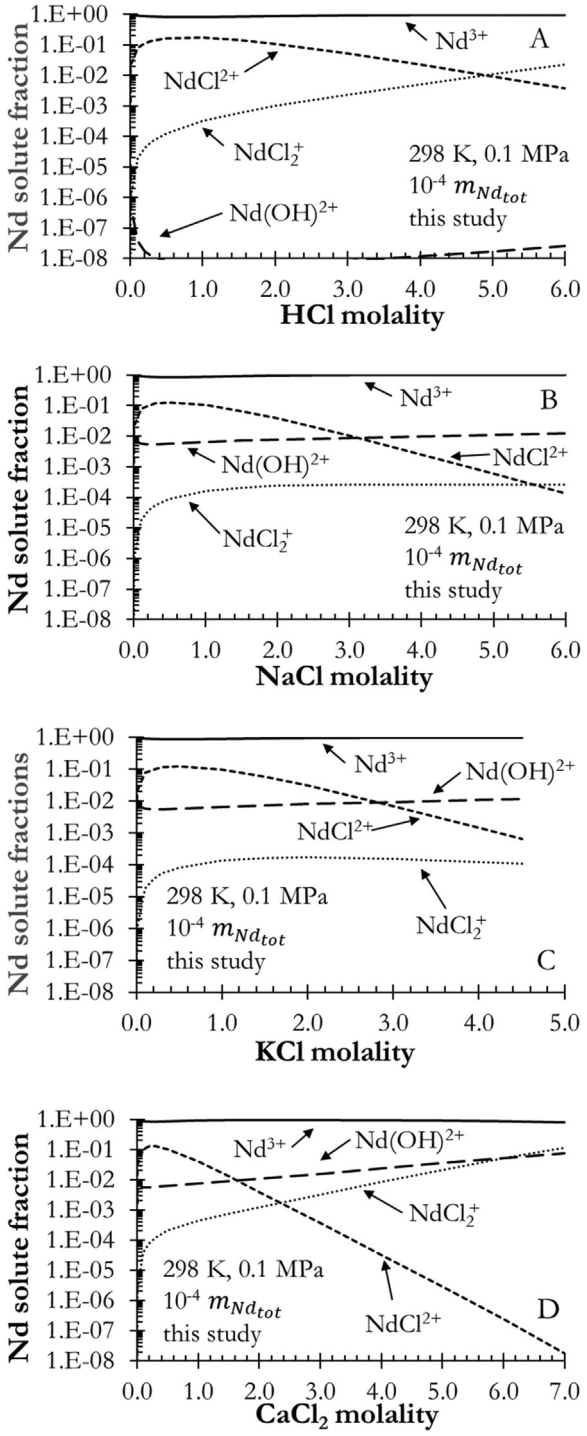

Fig. 16. Neodymium solute mole fractions from our model as a function of (A) HCl(aq), (B) NaCl(aq) (C) KCl(aq) and (D) $CaCl_2$(aq) molality.

each neodymium solute is more a function of ionic strength rather than the identity of the specific electrolytes ($I_{NaCl} = m_{NaCl}$, $I_{CaCl_2} = 3m_{CaCl_2}$ and $I_{NdCl_3} = 6m_{NdCl_3}$).

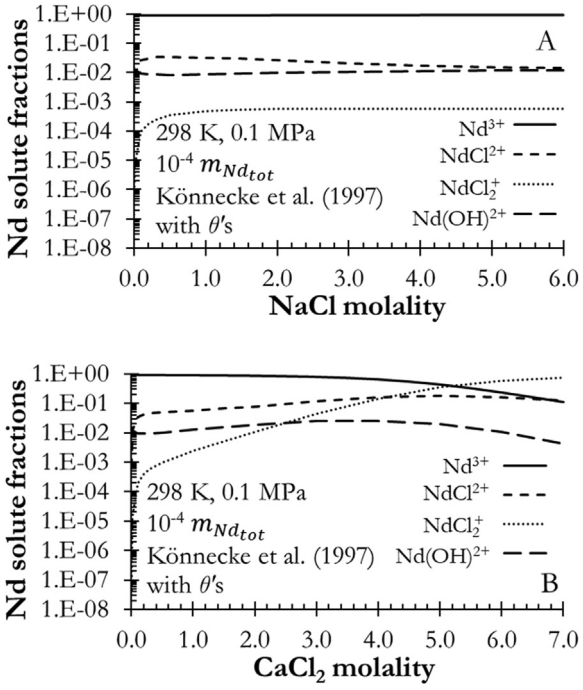

Fig. 17. Neodymium solute mole fractions as a function of (A) NaCl(aq) and (B) $CaCl_2$(aq) molality as calculated from the complete Könnecke model. In contrast to the model produced in this study, neodymium solute speciation from the Könnecke model is more dependent on the identity of other salts in the system. The apparent dominance of Nd ion-pairs at high m_{CaCl_2} is an artifact of the Könnecke $CaCl_2$(aq) model and the use of unwarranted ternary interaction parameters.

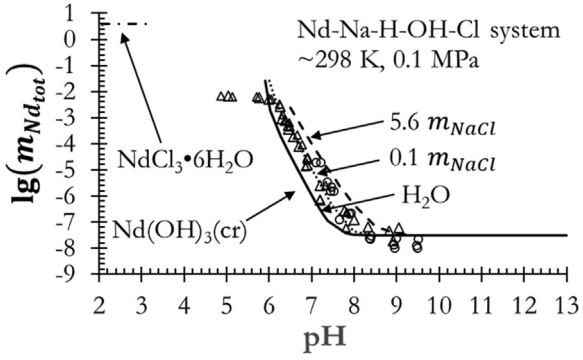

Fig. 18. Solubility curves of $Nd(OH)_3$(cr) in water (solid line) and in 0.1 and 5.6 mol·kg^{-1} NaCl(aq) (dotted and dashed lines, respectively) calculated from the model developed in this study. Solubility data from Silva (1982, circles) and Rao et al. (1996, triangles) are for $Nd(OH)_3$(cr) in 0.1 molal $NaClO_4$(aq) and NaCl (aq), respectively. The Rao et al. (1996) data at pH < 6 are for completely dissolved $Nd(OH)_3$(cr). The model $NdCl_3 \cdot 6H_2O$ solubility, including the metastable extension, is shown as dash-dot line. The calculations used $NdCl_3$ and $Nd(OH)_3$ as the acid and base titrants, respectively.

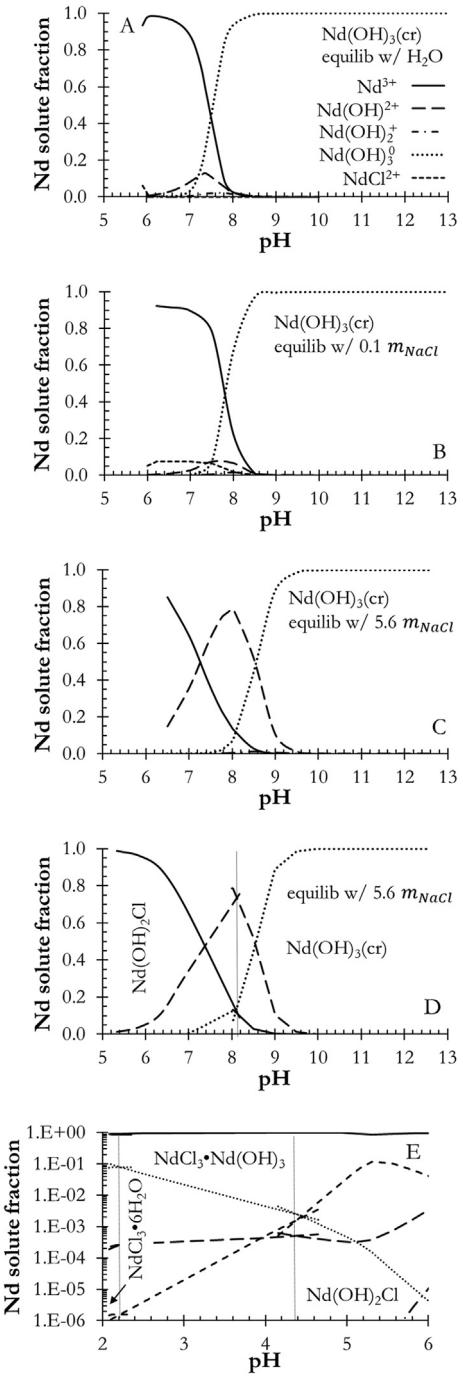

Fig. 19. Neodymium solute mole fractions, calculated from the model developed in this study, for solutions saturated with the Nd $(OH)_3$(cr) (A-C), $Nd(OH)_3$(cr) and $Nd(OH)_2Cl$ (D) and chloride and hydroxychloride salts (E) as a function of pH in water (A and E), 0.1 m NaCl(aq) (B), and 5.6 m NaCl(aq) (C and D). Nd $(OH)_3$(cr) in (C) is metastable with respect to $Nd(OH)_2Cl$ at pH < 8.2. Solid phase transitions in (D and E) are indicated by light vertical lines at intersections of solute curves. The dotted curves in (E) represent $NdCl_2^+$. All other curves correspond to the solute species shown in the legend of (A).

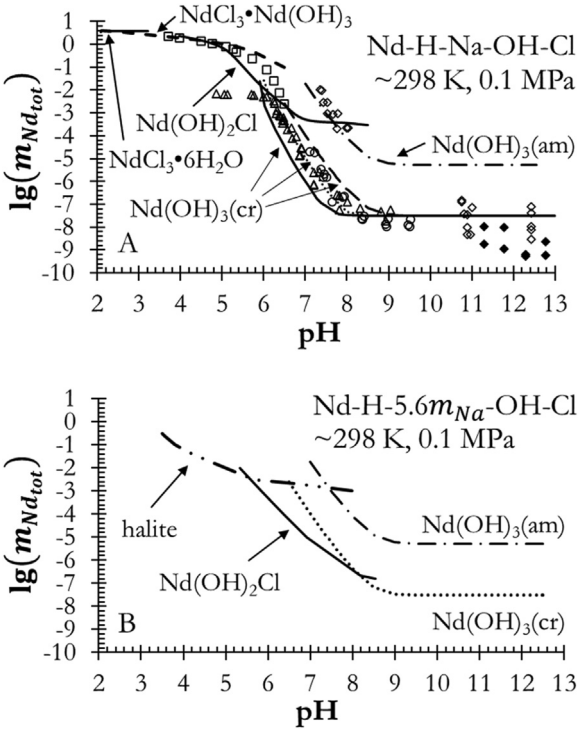

Fig. 20. (A) Comparison of measured and model solubilities for the indicated chloride and hydroxychloride salts in water; Nd $(OH)_3$(cr) in water, 0.1 and 5.6 mol·kg^{-1} NaCl (solid, dotted and dashed lines, respectively); and nominal $Nd(OH)_3$(am) in 5.6 mol·kg^{-1} NaCl (dashed-dot line). Data sources: Spivakovskii and Moisa (1972) (□), Rao et al. (1996) (△), Silva (1982) (○), and Neck et al. (2009) (filled and open ◇, 0.1 and 5.6 m_{NaCl}, respectively). The Neck et al. (2009) data for pH > 10 appear to correspond to $Nd(OH)_3$(cr). (B) Model solid solubilities for indicated solids in 5.6 mol·kg^{-1} NaCl. Metastable extensions are included and those for both hydroxychloride salts (A) and halite (B) intersect the low pH Neck et al. (2009) data.

8. EXTENSION OF THE CHLORIDE MODEL TO TRIVALENT LN- AND AN-SYSTEMS SATURATED WITH SOLID HYDROXIDES AND HYDROXY-CHLORIDES

8.1. Solubility model development for $Nd(OH)_3$ solids

Because $Nd(OH)_3$(s) solubility in water and dilute NaCl (aq) is $m_{Nd_{tot}} < 0.01$ mol·kg^{-1} (Fig. 18) and Nd^{3+} comprises >80 mole% of the neodymium solute species at pH ≤ 7 (Fig. 19), most of the $Nd(OH)_3$(cr) solubility data of Rao et al. (1996) and Silva (1982) can be reproduced through the addition of only the $\mu^{\circ}_{Nd(OH)_3(cr)}/RT$ term. This result is similar to that of Felmy et al. (1989) and our fitted lg $K = 14.95$ for the protonation reaction,

$$Nd(OH)_3(cr) + 3H^+ = Nd^{3+} + 3H_2O \quad (2)$$

is similar to the Rao et al. (1996) value.

The curvature in the $Nd(OH)_3$(cr) solubility curve in the interval $7.5 < pH < 8.5$ was initially produced by manually adjusting the value of $\mu^{\circ}_{Nd(OH)^+_2}/RT$ – again using only the model terms derived from the neodymium-chloride systems and the $\mu^{\circ}_{Nd(OH)_3(cr)}/RT$ previously fitted to the Rao et al. (1996) data atpH < 7.5. Lastly, the value of $\mu^{\circ}_{Nd(OH)^0_3}/RT$ was manually adjusted to produce the invariant $m_{Nd_{tot}}$ solubility curve at pH > 8.5. Once initial values of $\mu^{\circ}_{Nd(OH)^{2+}}/RT$, $\mu^{\circ}_{Nd(OH)^+_2}/RT$, and $\mu^{\circ}_{Nd(OH)^0_3}/RT$ were established, the model was refit with the μ°_i/RT values allowed to adjust. Depending on the $\mu^{\circ}_{Nd(OH)^+_2}/RT$ value, within a 1% uncertainty range, $Nd(OH)^+_2$ can either be the major or a very small fraction of the total Nd solute species near pH ~ 8. The final model that was fit simultaneously to the entire dataset produced the species distribution shown in Fig. 19.

Once the μ°_i/RT values for the solute species and crystalline solid were established, $\mu^{\circ}_{Nd(OH)_3(am)}/RT$ was manually adjusted to match the relatively-high Neck et al. (2009) solubility data for $Nd(OH)_3$(s) (Fig. 20). While the Neck et al. (2009) solid-phase analysis showed their solid to be crystalline, their relatively-high solubilities can be attributed to some fraction of their bulk solid being amorphous or having a higher hydration state. Alternatively, the experiments of Neck et al. (2009) may have suffered from carbonate contamination or formation of metastable hydroxychloride on their initial $Nd(OH)_3$(s) particles. As described below, it is simpler to explain the relatively high solubilities from Neck et al (2009) via these mechanisms than to argue that the Rao et al. (1996) and Silva (1982) data are errant. Again, no additional terms in the activity coefficient model are necessary to reproduce the solubility data for $Nd(OH)_3$(s) regardless of whether the solid is 'amorphous' or crystalline.

Our solubility model for the nominal amorphous/hydrated $Nd(OH)_3$(s) phase is ~2.5 lg units above the body of the Neck et al. (2009) data at pH > 9. Our $Nd(OH)_3$(cr) model roughly bisects the data. The Neck et al. (2009) measurements for different NaCl molalities overlap and are scattered between $10^{-9} < m_{Nd_{tot}} < 10^{-7}$ at pH > 9. It seems reasonable to argue that $Nd(OH)_3$(cr) was the solubility controlling phase at pH > 9 and the lack of any dependence on NaCl molality at pH > 9 is real and consistent with our model. The scatter in their data appears to be an accurate indicator of their measurement uncertainty at pH > 9. The absence of a salt effect on $Nd(OH)_3$(s) solubility at pH > 9 is not surprising as the predominant neodymium solute is $Nd(OH)^0_3$ with $m_{Nd_{tot}} < 10^{-5}$ molal. The effects of any interactions between $Nd(OH)^0_3$ and a supporting electrolyte should be very small due to the weakness of neutral-ion interactions and the very small $m_{Nd_{tot}}$. If the model and solid phase identities are accurate, then at pH < ~8.5 an increase of m_{Na} from 0.1 to 5.6 mol·kg^{-1} produces an ~10 × increase in $Nd(OH)_3$(cr) solubility whereas the apparent difference due to crystalline versus amorphous $Nd(OH)_3$(s) is ~100×.

The discussion above demonstrates that for low-solubility solids with inherent experimental difficulties, such as $Nd(OH)_3$(s), it is neither necessary nor beneficial to derive Pitzer model parameters using only solubility data. The described model-development process and positive results also demonstrate that experiments that attempt to replicate nuclear waste repository chemical systems, and selection criteria designed to include only "repository relevant" data, can impede the development of accurate thermodynamic models. These observations contravene the criteria currently used to formulate the WIPP geochemical model (USDOE, 2019b), e.g. criteria G3 – "include only results of solubility studies", criteria G9 – "exclude studies with dissolved elements or species that are absent in WIPP repository brines", criteria G11 – "include only results from experimental studies carried out under conditions at, or close to those predicted for WIPP disposal rooms. Specifically, … $I \geq 3$ …(2) pcH = 8.0–11.2……" For criteria G9, it's important to note that for data of equivalent accuracy, ternary interaction parameters such as $\theta_{Na,Nd}$, evaluated from a non-chloride common-ion system such as [$NaClO_4 + Nd(ClO_4)_3$](aq), can be as legitimate as a θ_{NaNd} derived from the [$NaCl + NdCl_3$](aq) system. Criteria G1 – exclusion of studies published before 1990 – would have arbitrarily precluded the most important and accurate study used in this paper, i.e Spedding et al. (1976). Criteria G1 would have also excluded Shevtsova et al. (1958, 1961, 1968). Mixture parameters, e.g. $\theta_{c,Nd}$, evaluated from those data are much more reliable than those that might be derived from solubility data for $Nd(OH)_3$(cr) in NaCl(aq), $CaCl_2$(aq), or any combination of multiple salts.

8.2. Solubility model development for solid neodymium-hydroxychlorides

Published solubility curves for Ln(III) or An(III) hydroxides in water and NaCl solutions as a function of pH are frequently shown only for pH > ~6 with no consideration of solubility or phase transformations at lower pH. This is done because geologic nuclear waste repositories are engineered to maintain pH > 7. However, ignoring solubility data at lower pH is a mistake. As demonstrated above, activity coefficient models derived from low pH systems can adequately describe solid solubilities at high pH if the solubilities at pH > 6 are small (e.g. < 0.01 mol·kg^{-1}). Also, the form and position of the solubility curves at pH < 6 can clarify discrepancies between solubility data at pH > 6.

Since our model reproduces the solubilities of both $NdCl_3{\cdot}6H_2O$ and $Nd(OH)_3$(s), it should also reproduce the solubilities of intermediate hydroxychloride salts with only μ°_i/RT terms for the additional solids. Rare-earth element hydroxychlorides with formulas $REE(OH)_2Cl$ and $REE_2(OH)_5Cl{\cdot}xH_2O$ have been observed (Aksel'rud, 1963, Carter and Levinson, 1969, Geng et al., 2008, Zehnder et al., 2010, Lee et al., 2014). Spivakovskii and Moisa (1972) reported solubility data for $Nd(OH)_2Cl$, however, the data may correspond to another hydroxychloride as described below.

Fig. 18 shows that the solubility curve for $NdCl_3{\cdot}6H_2O$ has a very small slope with respect to pH (slightly positive). The increase in $NdCl_3{\cdot}6H_2O$ solubility with increasing pH is counter-intuitive but not inconceivable for a salt that forms aqueous chloride complexes. A solubility curve for

$NdCl_3{\cdot}6H_2O$ with a slope of zero with respect to pH would be consistent with an absence of hydrolysis but as shown by Fig. 20 a near-zero slope is also consistent with the hydroxychloride solubility data from Spivakovskii and Moisa (1972). At pH > 5.5 the Spivakovskii and Moisa (1972) data approach the $Nd(OH)_3$(cr) solubility data of Rao et al. (1996) with a slope <–3. It is conceivable that the Spivakovskii and Moisa (1972) data at pH > 6 correspond to $Nd(OH)_3$(s). However, those data cannot represent stable $Nd(OH)_2Cl$ or $Nd_2(OH)_5Cl{\cdot}xH_2O$ if the solubility measured by Rao et al. (1996) was that for $Nd(OH)_3$(cr).

We first attempted to fit a model containing a single hydroxychloride solid to the Spivakovskii and Moisa (1972) data. However, we were unable to produce a model in which both the $NdCl_3{\cdot}6H_2O$ and $Nd(OH)_3$(cr) solubility curves met the hydroxychloride solubility curve (i.e., fits failed to converge over the full pH range). Attempts to produce a model that assumed the solid to be $Nd_2(OH)_5Cl{\cdot}xH_2O$ failed under all circumstances. Consequently, we defaulted to a model containing two hydroxychloride salts.

A variety of hydroxychloride stoichiometries were tested against the Spivakovskii and Moisa (1972) data with the result that a model that used $Nd(OH)_3{\cdot}NdCl_3$ [or $Nd_2(OH)_3Cl_3$] was consistent with the data at pH < 4.5. Spivakovskii and Moisa (1972) mention that Aksel'rud (1962) formed the 1:1 double salt, but no further information is given. The data may also correspond to other solid stoichiometries, e.g., $Nd_3O(OH)_4Cl_3$. However, our interest is more in demonstrating that the activity coefficient model fitted primarily to data from strictly chloride salt systems at pH < 6 can reproduce the solid solubility data over 2 < pH < 13 through the addition of only μ_i°/RT terms due to low neodymium solute molalities at pH > 6.

The Nd-hydroxychloride solubility curve that joins the solubility curves of $Nd(OH)_3$(cr) and the hypothetical double salt is only constrained by topological requirements and model convergence limits. The Spivakovskii and Moisa (1972) data are concave-down, as is the double-salt's solubility curve. A concave-up curve for the bridging hydroxychloride salt is consistent with the necessary Schreinemakers rules (aka Morey-Schreinemakers rules; cf. Nordstrom and Munoz, 1985; Zen, 1966 for a description of Schreinemakers analysis). A model that contained the $Nd(OH)_2Cl$ salt produced an appropriately shaped curve and was sufficient to complete the sequence of solubility curves starting and ending with $NdCl_3{\cdot}6H_2O$ and $Nd(OH)_3$(cr), respectively. The value of $\mu^\circ_{Nd(OH)_2Cl(xt)}/RT$ was manually adjusted to produce a curve that passed just above the lowest pH $Nd(OH)_3$(cr) solubility data of Rao et al. (1996). This meant that the curve for $Nd(OH)_2Cl$ solubility in 0.1 molal NaCl intersected the highest $Nd(OH)_3$(cr) solubility data of Rao et al. (1996). The choice of this point of intersection was not arbitrary but governed by convergence failures for $Nd(OH)_3$(cr) solubility calculations at pH < 5.9 (e.g., the slope of the metastable extension of the $Nd(OH)_3$(cr) solubility curve with respect to pH becomes almost vertical). The metastable extension of the $Nd(OH)_2Cl$ solubility curve at low pH closely follows the path of the hypothetical double salt so it is conceivable that the Spivakovskii and Moisa (1972) solid was metastable $Nd(OH)_2Cl$ at pH < 4.5; however, that hypothesis is difficult to reconcile with their data at pH > 4.5. Most of the Spivakovskii and Moisa (1972) data can be fitted as $Nd(OH)_2Cl$ (e.g., the curve shown in Fig. 20A can be shifted to higher pH), however, a second hydroxychloride salt is still required at pH < 4.5, and the $Nd(OH)_3$(cr) model fails to intersect with the $Nd(OH)_2Cl$ curve.

Our value of $\mu^\circ_{Nd(OH)_2Cl(xt)}/RT$ is poorly constrained; it can be adjusted with the result that the $Nd(OH)_2Cl$ solubility curve intersects the double salt curve at ~4.2 < pH < 5.3 while still being consistent with the $Nd(OH)_3$(cr) data of Rao et al. (1996) and Silva (1982). The intersection of the double salt and $NdCl_3{\cdot}6H_2O$ solubility curves can shift between 2.1 < pH < 3. We favored a value of $\mu^\circ_{Nd(OH)_2Cl(xt)}/RT$ that produced phase transitions near the low pH extremes of those ranges to reproduce the Rao et al. (1996) data and to minimize the pH range for $NdCl_3{\cdot}6H_2O$ solubility (Figs. 19E and 20A). Our fitted $\mu^\circ_{Nd(OH)_2Cl(xt)}/RT = -496.8$ is more similar to Aksel'rud's (1963) value of –500.91 than the Herm (2015) value of approximately –462. The data underlying the Aksel'rud (1963) value were unavailable, but the Herm (2015) data are discussed below.

Herm (2015) attempted to measure the solubility of Nd $(OH)_2Cl$ in aqueous solutions of NaCl, $MgCl_2$, and $CaCl_2$. Except for Table 5.4 in Herm (2015), none of his figures or table captions state a temperature. Table 5.4 in Herm (2015) shows that all but a $MgCl_2$ experiment were performed at 353 K, yet it is implied in the text that solubility experiments in $m_{NaCl} = 5.6\ mol{\cdot}kg^{-1}$ were also run at ~295 K.

All of the Herm (2015) solubility experiments were conducted at pH > 7.5. Because his $Nd(OH)_2Cl$ solubilities in $m_{NaCl} = 5.6\ mol{\cdot}kg^{-1}$ were similar to the $Nd(OH)_3$(s) solubility data from Neck et al. (2009), Herm assumed that the initial $Nd(OH)_2Cl$ solid converted to $Nd(OH)_3$(s) although his x-ray diffraction (XRD) analyses detected only $Nd(OH)_2Cl$. This assumption creates a quandary. The Herm (2015) model for $m_{NaCl} = 5.6\ mol{\cdot}kg^{-1}$ produces Nd $(OH)_2Cl$ as the stable solid at pH < 8.2, yet Neck et al. (2009) claimed that the solid under those conditions was $Nd(OH)_3$(s). It seems that Herm (2015) would have had to assume that his solid formed a protective rind of Nd $(OH)_3$(s) to explain the similarity of his data with those of Neck et al. (2009). However, because his starting material was $Nd(OH)_2Cl$, there would be no thermodynamic drive to form $Nd(OH)_3$(s) at pH < 8.2.

The shape of our model $Nd(OH)_2Cl$ solubility curve, relative to the $Nd(OH)_3$(s) solubility curve in $m_{NaCl} = 5.6\ mol{\cdot}kg^{-1}$, is similar to that from Herm (2015) but is shifted to lower total Nd molality ($m_{Nd_{tot}}$) by about 3 lg units (Fig. 20B). The shift of the solubility curve for $Nd(OH)_2Cl$ to higher pH and lower $m_{Nd_{tot}}$ with increasing

NaCl molality is consistent with the common-ion, salting-out effect in the reaction:

$$Nd(OH)_3 + Cl^- = Nd(OH)_2Cl + OH^- \quad (3)$$

Our solubility curves for $Nd(OH)_2Cl$ and $Nd(OH)_3$(cr) in $m_{NaCl} = 5.6$ mol·kg^{-1} intersect at about $m_{Nd_{tot}} \sim 10^{-6}$ mol·kg^{-1} and pH ~ 8.2 versus $m_{Nd_{tot}} \sim 10^{-3.5}$ mol·kg^{-1} and pH ~ 8.2 from the Herm (2015) model. Herm (2015) neither considered data sources other than Neck et al. (2009) nor evaluated the consistency of his $Nd(OH)_2Cl$ model with solid solubilities at pH < 7.5. Fig. 15B shows that with halite as the stable solid, $m_{Nd_{tot}} \sim 0.2$ molal at $m_{NaCl} = 5.6$ mol·kg^{-1}. Fig. 20B shows that for the Nd-Na-H-OH-Cl system, halite continues to be the stable solid for $m_{NaCl} = 5.6$ mol·kg^{-1} between 3.5 < pH < 5.5 with $m_{Nd_{tot}} \sim 0.003$ mol·kg^{-1} at pH ~ 5.5: the halite + $Nd(OH)_2$-Cl coexistence point. Projection of our metastable halite solubility curve to pH = 6.5 produces $m_{Nd_{tot}} \sim 0.002$ mol·kg^{-1}, whereas the Herm (2015) model for $Nd(OH)_3Cl$ solubility produces $m_{Nd_{tot}} > 0.1$ mol·kg^{-1} at pH = 6.5. The halite solubility curve from Könnecke et al. (1997), upon which both the Neck et al. (2009) and Herm (2015) models are based, is similar to our model in Fig. 20B, which would place the Neck et al. (2009) and Herm (2015) data at pH < 7.8 in the halite stability field rather than $Nd(OH)_2Cl$ or $Nd(OH)_3$(s) and would imply lower neodymium solubilities than reported. It appears that none of these authors calculated halite solubility at 6 < pH < 8 to assess whether their models and data were consistent.

The coincidence of the Herm (2015) and Neck et al. (2009) solubility data with the metastable extensions of halite in the $m_{NaCl} = 5.6$ mol·kg^{-1} system and $Nd(OH)_2Cl$ and $NdCl_3$·$Nd(OH)_3$ in water indicate that their relatively high $m_{Nd_{tot}}$ measurements may be due to some aspect of their experimental procedure that produced armoring of the neodymium solids with halite or another neodymium solid rather than being due to a difference in $Nd(OH)_3$(s) hydration state or crystallinity. For example, if their solids were treated such that they became coated with the double salt and were subsequently introduced into 5.6 molal NaCl (aq), then recrystallization of the double salt would control neodymium solubility until the transformation was complete. If subsequent solid sampling involved washing with water, then that process could remove any trace of the 'contaminating' solid before XRD analysis or leave a sufficiently low mass fraction as to be undetectable.

Alternatively, solid Nd_2O_3 is known to be rapidly hydrolyzed and carbonated through exposure to humid air (Bernal et al., 1987, 1988a,b, 2004). Consequently, any part of sample preparation that does not remove carbonate introduced through the solid could cause anomalous neodymium solubilities due to unrecognized carbonate contamination and complexation. Even for an experiment run in an 'inert' gas environment, if the solutions were alkaline and sealed, then removal of contaminating CO_2 could be slow. Steps such as sparging or boiling water used to prepare the solutions would not avoid this source of contamination.

9. CONCLUSION

The geologic disposal of nuclear wastes related to nuclear power and weapons production and retirement is a challenging problem for present and future generations. Whether a repository is in salt, crystalline igneous rock, or argillaceous sediment, a common concern to the disposal concepts being considered by the international community is the need to simulate reactions between groundwaters of varying salinity, nuclear waste materials, and the rocks surrounding the repository. This study provides an essential component to that needed capability.

Our thermodynamic model is an analog for trivalent actinides in aqueous chloride solutions that span wide ranges of ionic strength and pH. The model supplements the Pitzer model parameter set of Harvie et al. (1984) that has been widely adopted by the geochemical community. The model reproduces the thermodynamic data more accurately and is much less complex than previously published Pitzer models that have striven to reproduce liquid phase and solid + liquid equilibria involving neodymium-chloride and -hydroxide species in aqueous solutions containing chlorides of sodium, potassium, and calcium. The addition of only eight Pitzer parameters for interactions involving neodymium solutes and the corresponding dimensionless standard state chemical potentials to the HMW model reproduces the isopiestic, emf, and solid solubility data for the Nd^{3+}-Ca^{2+}-Na^+-K^+-H^+-Cl^--OH^- system at 298 K, 0.1 MPa and 2 < pH < 13. No like-sign Pitzer parameters involving neodymium ion-pairs, e.g., $\theta_{Ca,NdCl}$, were necessary to reproduce the data. The sum of neodymium ion-pair mole fractions is less than 0.15 for all neodymium molalities and pH < 6. At pH > 6, $m_{Nd_{tot}} < 0.01$ mol·kg^{-1} and consequently, additional activity coefficient model parameters for the hydroxide ion-pairs are unnecessary. Only the $\beta^{(0)}_{NdCl,Cl}$ and $\beta^{(0)}_{NdCl_2,Cl}$ terms provided additional benefit to the 'bare-ion' interaction parameters.

This study demonstrates that the chemical systems used to evaluate Pitzer ion-interaction parameters should not be too narrowly constrained by the conditions of a researcher's specific application. If the system of interest is a geologic waste repository, in which solid trivalent actinide hydroxides or hydroxy-carbonates might coexist with halite, it is neither necessary nor preferable to evaluate the Pitzer parameters from solubility data for $Am(OH)_3$ or $Nd(OH)_3$ in NaCl(aq) or more complex salt mixtures at near neutral to alkaline pH values. Such systems contain small molalities of the solutes of interest, as well as multiple polynuclear complexes of those solutes, and consequently, it is difficult to deconvolute the relative contributions of the multiple parameter combinations.

Our model may resolve some inter-laboratory discrepancies in $Nd(OH)_3$(s) solubility data and we illustrate conditions for which additional data might improve model validation. Experimentalists examining solid hydroxide and hydroxychloride solubilities in the Nd-H-OH-Cl system should recognize that $NdCl_3$(aq) is acidic and that Nd_2O_3 or $Nd(OH)_3$ are bases and consequently it may be

possible to simplify and "reverse" experiments with respect to pH using only $NdCl_3$(aq), HCl(aq), and Nd_2O_3 or $Nd(OH)_3$. The various solids in Nd-H-Cl-OH mixtures can be synthesized without the use of other salts such as NaOH, $Ca(OH)_2$, or $MgCl_2$ that confound and potentially introduce errors into both experiments and model development.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

Aksel'rud N. V. (1962) *Khimiya Rastvorov Redkozemel'nykh Elementov* (Collected Papers on the Chemistry of Solutions of the Rare Earth Elements).

Aksel'rud N. V. (1963) Hydroxide chlorides and hydroxides of elements of the scandium subgroup and the lanthanides. *Russ. Chem. Rev.* **32**, 353–366.

Amado-González E. and Blanco L. H. (2004) Osmotic and activity coefficients of aqueous solutions of KCl at temperatures of 283.15, 288.15, 293.15 and 298.15 K. A new isopiestic apparatus. *Fluid Phase Eq.* **226**, 261–265.

Archer D. G. (1992) Thermodynamic properties of the NaCl + H_2O system II. Thermodynamic properties of NaCl(aq), NaCl·$2H_2O$(cr), and phase equilibria. *J. Phys. Chem. Ref. Data* **21**, 793–829.

Archer D. G. (1999) Thermodynamic properties of the KCl + H_2O system. *J. Phys. Chem. Ref. Data* **28**, 1–17.

Archer D. G. and Wang P. (1990) The dielectric constant of water and Debye-Hückel limiting law slopes. *J. Phys. Chem. Ref. Data* **19**, 371–409.

Archer D. G. and Carter R. W. (2000) Thermodynamic properties of the NaCl + H_2O system. 4. Heat capacities of H_2O and NaCl (aq) in cold-stable and supercooled states. *J. Phys. Chem. B* **104**, 8563–8584.

Bernal S., Botana F. J., Garcia R. and Rodriguez-Izquierdo J. M. (1987) Behaviour of rare earth sesquioxides exposed to atmospheric carbon dioxide and water. *React. Solids* **4**, 23–40.

Bernal S., Botana F. J., Garcia R. and Rodriguez-Izquierdo J. M. (1988a) Study of the interaction of two hexagonal neodymium oxides with atmospheric CO_2 and H_2O. *J. Mater. Sci.* **23**, 1474–1480.

Bernal S., Botana F. J., Garcia R. and Rodriguez-Izquierdo J. M. (1988b) The chemistry in air of the rare-earth-metal sesquioxides. Comparative study of hexagonal and cubic neodymian samples. *J. Chem. Soc. Dalton Trans.*, 1765–1771.

Bernal S., Blanco G., Gatica J. M., Pérez-Omil J. A., Pintado J. M. and Vidal H. (2004) Chemical reactivity of binary rare earth oxides. In *Binary rare earth oxides* (eds. G. Adachi, N. Imanaka and Z. C. Kang). Springer, Dordrecht, pp. 9–55 (Chapter 2).

Campbell D. M., Millero F. J., Roy R. N., Roy L. N., Lawson M., Vogel K. M. and Moore C. P. (1993) The standard potential for the hydrogen-silver, silver chloride electrode in synthetic seawater. *Mar. Chem.* **44**, 221–233.

Carter F. L. and Levinson S. (1969) The hydrothermal preparation, single-crystal lattice parameters, and decomposition data for some lanthanide dihydroxychlorides and the related hydroxy chloride, $Y_3O(OH)_5Cl_2$. *Inorg. Chem.* **8**, 2788–2791.

Fanghänel Th., Könnecke Th., Weger H., Paviet-Hartmann P., Neck V. and Kim J. I. (1999) Thermodynamics of Cm(III) in concentrated salt solutions: carbonate complexation in NaCl solution at 25°C. *J. Solution Chem.* **28**, 447–546.

Felmy A. R. (1990) *GMIN: A Computerized Chemical Equilibrium Model Using a Constrained Minimization of the Gibbs Free Energy. PNL-7281*. Pacific Northwest Laboratory, Richland, Washington, p. 62.

Felmy A. R. (1995) GMIN, A Computerized Chemical Equilibrium Program Using a Constrained Minimization of the Gibbs Free Energy: Summary Report. In *Chemical Equilibrium and Reaction Models*, vol. 42, pp. 377–407. Chemical Equilibrium and Reaction Models. Soil Science Society of America Special Publication (Chapter 18).

Felmy A. R., Rai D., Schramke J. A. and Ryan J. L. (1989) The solubility of plutonium hydroxide in dilute solution and in high-ionic-strength chloride brines. *Radiochim. Acta* **48**, 29–35.

Felmy A. R., Rai D. and Fulton R. W. (1990) The solubility of $AmOHCO_3$(c) and the aqueous thermodynamics of the system Na^+ - Am^{3+} - HCO_3^- - CO_3^{2-} - OH^- - H_2O. *Radiochim. Acta* **50**, 193–204.

Felmy A. R., Onishi L. M., Foster N. S., Rustad J. R., Rai D. and Mason M. J. (2000) An aqueous thermodynamic model for the Pb^{2+}–Na^+–K^+–Ca^{2+}–Mg^{2+}–H^+–Cl^-–SO_4^{2-}–H_2O system to high concentration: application to WIPP brines. *Geochim. Cosmochim. Acta* **64**, 3615–3628.

Geng F., Matsushita Y., Ma R., Xin H., Tanaka M., Izumi F., Iyi N. and Sasaki T. (2008) General synthesis and structural evolution of a layered family of $Ln_8(OH)_{20}Cl_4{\cdot}nH_2O$ (Ln) Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Y). *J. Am. Chem. Soc.* **130**, 16344–16350.

Goldberg R. N. and Nuttall R. L. (1978) Evaluated activity and osmotic coefficients for aqueous solutions: the alkaline earth metal halides. *J. Phys. Chem. Ref. Data* **7**, 263–310.

Gordon A. R. (1943) Isopiestic measurements in dilute solutions, the system potassium chloride – sodium chloride at 25° at concentrations from 0.03 to 0.10 molal. *J. Am. Chem. Soc.* **65**, 221–224.

Haase R., Naas H. and Thumm H. (1963) Experimentelle Untersuchungen über das thermodynamische Verhalten konzentrierter Halogenwasserstoffsäuren. *Z. Phys. Chem. (N F)* **37**, 210–229.

Harvie C. E. and Weare J. H. (1980) The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO_4-H_2O system from zero to high concentration at 25°C. *Geochim. Cosmochim. Acta* **44**, 981–997.

Harvie C. E., Møller N. and Weare J. H. (1984) The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25°C. *Geochim. Cosmochim. Acta* **48**, 723–751.

He M. and Rard J. A. (2015) Revision of the osmotic coefficients, water activities and mean activity coefficients of the aqueous trivalent rare earth chlorides at T = 298.15 K. *J. Solution Chem.* **44**, 2208–2221.

Herm M. (2015) *Study on the effect of speciation on radionuclide mobilization, C-14 speciation in irradiated Zircaloy-4 cladding and nitrate/ chloride interaction with An(III)/Ln(III)*. Doktors der Naturwissenschaften, Karlsruher Instituts für Technologie (KIT).

Hill P. G. (1990) A unified fundamental equation for the thermodynamic properties of H_2O. *J. Phys. Chem. Ref. Data* **19**, 1233–1274.

Holmes H. F., Busey R. H., Simonson J. M., Mesmer R. E., Archer D. G. and Wood R. H. (1987) The enthalpy of dilution of HCl (aq) to 648 K and 40 MPa. *J. Chem. Thermodyn.* **19**, 863–890.

Janis A. A. and Ferguson J. B. (1939) Sodium chloride solutions as an isopiestic standard. *Can. J. Res.* **17**, 215–230.

Kim H.-T. and Frederick, Jr., W. J. (1988) Evaluation of Pitzer ion interaction parameters of aqueous electrolytes at 25 °C. 1. single salt parameters. *J. Chem. Eng. Data* **33**, 177–184.

Kodýtek V. and Dolejš V. (1986) On the Pitzer equation for the osmotic coefficient of aqueous solutions of 3:1 rare earth electrolytes. *Z. phys. Chem. (Leipzig)* **267**, 743–746.

Könnecke Th., Fanghänel Th. and Kim J. I. (1997) Thermodynamics of trivalent actinides in concentrated electrolyte solutions: modelling the chloride complexation of Cm(III). *Radiochim. Acta* **76**, 131–135.

Lee B.-I., Jeong H. and Byeon S.-H. (2014) Oxychloride–hydroxychloride–trihydroxide phase relationships of rare earths in aqueous solution. *Inorg. Chem.* **53**, 5212–5221.

Mason C. M. (1938) The activity and osmotic coefficients of trivalent metal chlorides in aqueous solution from vapor pressure measurements at 25°. *J. Am. Chem. Soc.* **60**, 1638–1647.

May P. M., Rowland D., Hefter G. and Königsberger E. (2011) A generic and updatable Pitzer characterization of aqueous binary electrolyte solutions at 1 bar and 25 °C. *J. Chem. Eng. Data* **56**, 5066–5077.

Millero F. J. and Byrne R. H. (1984) Use of Pitzer's equations to determine the media effect on the formation of lead chloro complexes. *Geochim. Cosmochim. Acta* **48**, 1145–1150.

Mioduski T., Gumiński C. and Zeng D. (2009) IUPAC-NIST solubility data series. 87. Rare earth metal chlorides in water and aqueous systems. Part 2. Light lanthanides (Ce–Eu). *J. Phys. Chem. Ref. Data* **38**, 441–562.

Neck V., Altmaier M., Rabung T., Lutzenkirchen J. and Fanghänel T. (2009) Thermodynamics of trivalent actinides and neodymium in NaCl, $MgCl_2$, and $CaCl_2$ solutions: solubility, hydrolysis, and ternary Ca–M(III)–OH complexes. *Pure Appl. Chem.* **81**, 1555–1568.

Nordstrom D. K. and Munoz J. L. (1985) *Geochemical Thermodynamics*. The Benjamin/Cummings Publishing Co., Menlo Park, CA, p. 477.

Oakes C. S., Rard J. A. and Archer D. G. (2004) Enthalpies of dilution of $NdCl_3$(aq) at temperatures from 297.89 K to 372.08 K and an extended Pitzer ion-interaction model for the $NdCl_3 + H_2O$ system. *J. Chem. Eng. Data* **49**, 313–325.

Palmer D. A. and Wesolowski D. J. (1992) Aluminum speciation and equilibria in aqueous solution: II. The solubility of gibbsite in acidic sodium chloride solutions from 30 to 70°C. *Geochim. Cosmochim. Acta* **56**, 1093–1111.

Pitzer K. S. (1973) Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **77**, 268–277.

Pitzer K. S. (1975) Thermodynamics of electrolytes. V. Effects of higher-order electrostatic terms. *J. Solution Chem.* **4**, 249–265.

Pitzer K. S. (1991) Ion interaction approach: Theory and data correlation. In *Activity Coefficients in Electrolyte Solutions* (ed. K. S. Pitzer). CRC Press, Boca Raton, FL, pp. 75–153 (Chapter 3).

Pitzer K. S. and Mayorga G. (1973) Thermodynamics of electrolytes. II. Activity and osmotic coefficients of strong electrolytes with one or both ions univalent. *J. Phys. Chem.* **77**, 2300–2308.

Pitzer K. S., Peterson J. R. and Silvester L. F. (1978) Thermodynamics of electrolytes. IX. Rare earth chlorides, nitrates, and perchlorates. *J. Solution Chem.* **7**, 45–56.

Pitzer K. S., Peiper J. C. and Busey R. H. (1984) Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data* **13**, 1–102.

Rao L., Rai D. and Felmy A. R. (1996) Solubility of $Nd(OH)_3$(c) in 0.1 M NaCl aqueous solution at 25°C and 90°C. *Radiochim. Acta* **72**, 151–155.

Rard J. A. (2016) Critical evaluation of the standard molar entropies, enthalpies of formation, gibbs energies of formation and heat capacities of the aqueous trivalent rare earth ions, and the corresponding standard molar entropies, enthalpies of formation and Gibbs energies of formation of the thermodynamically stable $RECl_3 \cdot 7H_2O$(cr) and $RECl_3 \cdot 6H_2O$(cr). *J. Solution Chem.* **45**, 1332–1376.

Rard J. A., Habenschuss A. and Spedding F. H. (1976) A review of the osmotic coefficients of aqueous H_2SO_4 at 25 °C. *J. Chem. Eng. Data* **21**, 374–379.

Rard J. A. and Spedding F. H. (1977) Isopiestic determination of the osmotic coefficients of aqueous $CaCl_2$ solutions at 25 °C. *J. Chem. Eng. Data* **22**, 56–58.

Rard J. A. and Clegg S. L. (1997) Critical evaluation of the thermodynamic properties of aqueous calcium chloride. 1. Osmotic and activity coefficients of 0–10.77 mol•kg^{-1} aqueous calcium chloride solutions at 298.15 K and correlation with extended Pitzer ion-interaction models. *J. Chem. Eng. Data* **42**, 819–849.

Robinson R. A. and Sinclair D. A. (1934) The activity coefficients of the alkali chlorides and of lithium iodide in aqueous solution from vapor pressure measurements. *J. Am. Chem. Soc.* **56**, 1830–1835.

Robinson R. A. and Stokes R. H. (1940) A thermodynamic study of bivalent metal halides in aqueous solution. Part II. The activity coefficients of calcium and barium chloride at 25°. *Trans. Faraday Soc.* **36**, 735–738.

Robinson R. A. and Stokes R. H. (1949) Tables of osmotic and activity coefficients of electrolytes in aqueous solution at 25° C. *Trans. Faraday Soc.* **45**, 612–624.

Robinson R. A. and Bower V. E. (1966) Properties of aqueous mixtures of pure salts. Thermodynamics of the ternary system: water-sodium chloride-calcium chloride at 25 °C. *J. Res. Natl. Bur. Stand. – A Phys. Chem.* **70A**, 313–318.

Robinson R. A. and Covington A. K. (1968) The thermodynamics of the ternary system: water-potassium chloride-calcium chloride at 25 °C. *J. Res. Natl. Bur. Stand. A Phys. Chem.* **72A**, 239–245.

Roy R. N., Gibbons J. J., Peiper J. C. and Pitzer K. S. (1983) Thermodynamics of the unsymmetrical mixed electrolyte HCl-$LaCl_3$. *J. Phys. Chem.* **87**, 2365–2369.

Roy R. N., Roy L. N., Tabor B. J., Himes C. A., Richards S. J., Cummins M. P., Christiansen E. B., Roy C. N., Sharma V. K. and Millero F. J. (2005a) Thermodynamics of electrolyte mixtures: $HCl + NdCl_3 + H_2O$ from 5 to 55°C. *J. Solution Chem.* **34**, 1033–1044.

Roy R. N., Roy L. N., Himes C. A., Richards S. J., LeNoue S. R., Denton C. E., Pesek M. J., Roy C. N., Sangoi N., Gibbs S. N. and Shaffer R. D. (2005b) The system $HCl + NdCl_3 + H_2O$ from 5 to 55 °C: a study of Harned's rule. *J. Solution Chem.* **34**, 1017–1031.

Scatchard G., Hamer W. J. and Wood S. E. (1938) Isotonic solutions. I. The chemical potential of water in aqueous solutions of sodium chloride, potassium chloride, sulfuric acid, sucrose, urea and glycerol. *J. Am. Chem. Soc.* **60**, 3061–3070.

Shevtsova Z. N., Zelova V. S. and Ushakova L. I. (1958) Solubility investigations in the $LaCl_3$-NaCl-H_2O, $NdCl_3$-NaCl-H_2O, $LaCl_3$-$CaCl_2$-H_2O and $NdCl_3$-$CaCl_2$-H_2O systems at 25 °C. Nauk. Dokl. Vyssh. Shkoly Khimiya Khim. Tekhnologiya **3**, 417-421., compiled in Mioduski et al. (2009). *J. Phys. Chem. Ref. Data* **38**, 512 (NaCl, $CaCl_2$).

Shevtsova Z. N., Zhilina L. I. and Eltsberg L. E. (1961) Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. **4**, 176. compiled in Mioduski et al. (2009). *J. Phys. Chem. Ref. Data* **38**, 509 (KCl).

Shevtsova Z. N., Nam L. S., Korshunov B. and Solubility G. (1968) *Russ. J. Inorg. Chem.* Solubility of yttrium and rare-

earth element chlorides in hydrochloride acid solutions at 25 °C, compiled in Mioduski et al. 2009. *J. Phys. Chem. Ref. Data* **38**, 508 (HCl).

Shul'ts M. M., Makarov L. L. and Yu-Jeng S. (1962) Activity coefficients of $NiCl_2$ and NH_4Cl in binary and ternary solutions at 25 °C.. *Zh. Fiz. Khim.* **36**, 2194–2198 (in Russian).

Silva R. J. (1982) *Thermodynamic properties of chemical species in nuclear waste: The solubilities of crystalline neodymium and americium trihydroxides*. Lawrence Berkeley Laboratory Topical Report LBL-15055, p. 63.

Spedding F. H., Pikal M. J. and Ayers B. O. (1966) Apparent molal volumes of some aqueous rare earth chloride and nitrate solutions at 25°. *J. Phys. Chem.* **70**, 2440–2449.

Spedding F. H., Weber H. O., Saeger V. W., Petheram H. H., Rard J. A. and Habenschuss A. (1976) Isopiestic determination of the activity coefficients of some aqueous rare earth electrolyte solutions at 25 °C. 1. The rare earth chlorides. *J. Chem. Eng. Data* **21**, 341–360.

Spivakovskii V. B. and Moisa L. P. (1972) Conditions of precipitation of neodymium hydroxide and hydroxide chlorides. *Russ. J. Inorg. Chem.* **17**, 34–37.

Sterner S. M., Felmy A. R., Rustad J. R. and Pitzer K. S. (1997) *Pacific Northwest National Laboratory report PNWD-SA-4436. Thermodynamic Analysis of Aqueous Solutions using INSIGHT*.

Sterner S. M., Felmy A. R., Oakes C. S. and Pitzer K. S. (1998) Correlation of thermodynamic data for aqueous electrolyte solutions to very high ionic strength using INSIGHT: vapor saturated water activity in the system $CaCl_2$-H_2O to 250 °C and solid saturation. *Int. J. Thermophys.* **19**, 761–770.

Stokes R. H. (1945) A Thermodynamic study of bivalent metal halides in aqueous solution. Part XIII – properties of calcium chloride solutions up to high concentrations at 25°. *Trans. Faraday Soc.* **41**, 637–641.

USDOE. (2019a) Title 40 CFR Part 191 Subparts B and C Compliance Recertification Application 2019. DOE/WIPP-19-3503. SOTERM-III. Appendix SOTERM-2019.

USDOE. (2019b) Title 40 CFR Part 191 Subparts B and C Compliance Recertification Application 2019. DOE/WIPP-19-3503. GEOCHEM. Appendix GEOCHEM-2019.

Wolery T. J. (2010) EQ3/6 A Software Package for Geochemical Modeling. Computer software. https://www.osti.gov//servlets/purl/1231666. Vers. 05. USDOE. 13 Dec. 2010.

Xiong Y. L., Kirkes L. and Marrs C. (2017) Long-term experimental determination of solubilities of micro-crystalline Nd(III) hydroxide in high ionic strength solutions: applications to nuclear waste management. *Aquat. Geochem.* **23**, 359–375.

Zehnder R. A., Clark D. L., Scott B. L., Donohoe R. J., Palmer P. D., Runde W. H. and Hobart D. E. (2010) Investigation of the structural properties of an extended series of lanthanide bishydroxychlorides $Ln(OH)_2Cl$ (Ln = Nd-Lu, except Pm and Sm). *Inorg. Chem.* **49**, 4781–4790.

Zen E.-A (1966) Construction of pressure-temperature diagrams for multicomponent systems after the method of Schreinemakers - a geometric approach. *U.S. Geol. Surv. Bull.* **1225**, 56.

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