

A comparison of Pitzer databases for nuclear waste disposal modelling

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Introduction

Salt rock is one option to host nuclear waste repositories. There, high salinities require the Pitzer formalism to model ion-ion-interactions. Further challenges for the geochemical case of long-term safety assessments are high temperatures and very heterogeneous chemical systems.

Oceanic Salt System

Salt rock is best described by the Oceanic Salt System (Na^+ , K^+ , Ca^{2+} , Mg^{2+} / Cl^- , SO_4^{2-} – H_2O). Differences at 25 °C are caused by missing solubility data, e.g. Thenardite (Fig. 1).

At higher temperatures, sparse temperature-dependent data or the questionable use of solubility data beyond their validity range (e.g. Kieserite and Pentahydrate solubility data for 25 °C) causes strong differences in the results (Fig. 2).

Trivalent Actinides – Nd(III)

Neodymium was used as a chemical analogue for trivalent actinides. Missing anionic hydroxo species (e.g. $\text{Nd}(\text{OH})_4^-$) and differences in solubility data ($\Delta\log K_{\text{sp}} = 3.3$) cause inadequate predictions of the amorphous $\text{Nd}(\text{OH})_3$ solubility in the strongly alkaline medium (Fig. 3).

Tetravalent Actinides – U(IV)

The lack of data for aqueous uranium(IV) carbonate species ($\text{U}(\text{CO}_3)_n^{4-2n}$) produces the inaccurate solubility curve for $\text{U}(\text{OH})_4(\text{am})$ (Fig. 4).

Pentavalent Actinides – Np(V)

Significant differences of the $\log K$ values of aqueous species (NpO_2OH : $\Delta\log K = 5.4$; $\text{NpO}_2(\text{OH})_2^-$: $\Delta\log K = 8.9$) lead to incorrect calculations results of the solubility of amorphous NpO_2OH in strongly alkaline medium (Fig. 5).

Hexavalent Actinides – U(VI)

In contrast to the U(IV) solubility test case, here only minor differences are observed. They are caused by small deviations of the solubility data ($\Delta\log K_{\text{sp}} = 0.9$) and different Pitzer parameter sets (Fig. 6).

Fission product Cs

The virtual absence of solubility data for solid Cs phases (e.g. for CsCl) leads to inaccurate results for the calculated stability fields of solid phases. However, this is not significant for real-world scenarios due to the high solubility of these phases in comparison to other salts (Fig. 7).

This work addresses capabilities and limitations of various Pitzer databases currently in use, by inter-comparison including experimentally determined solubilities. Geochemist's Workbench® [2] was used uniformly as speciation code, all databases being *a priori* transformed to its format.

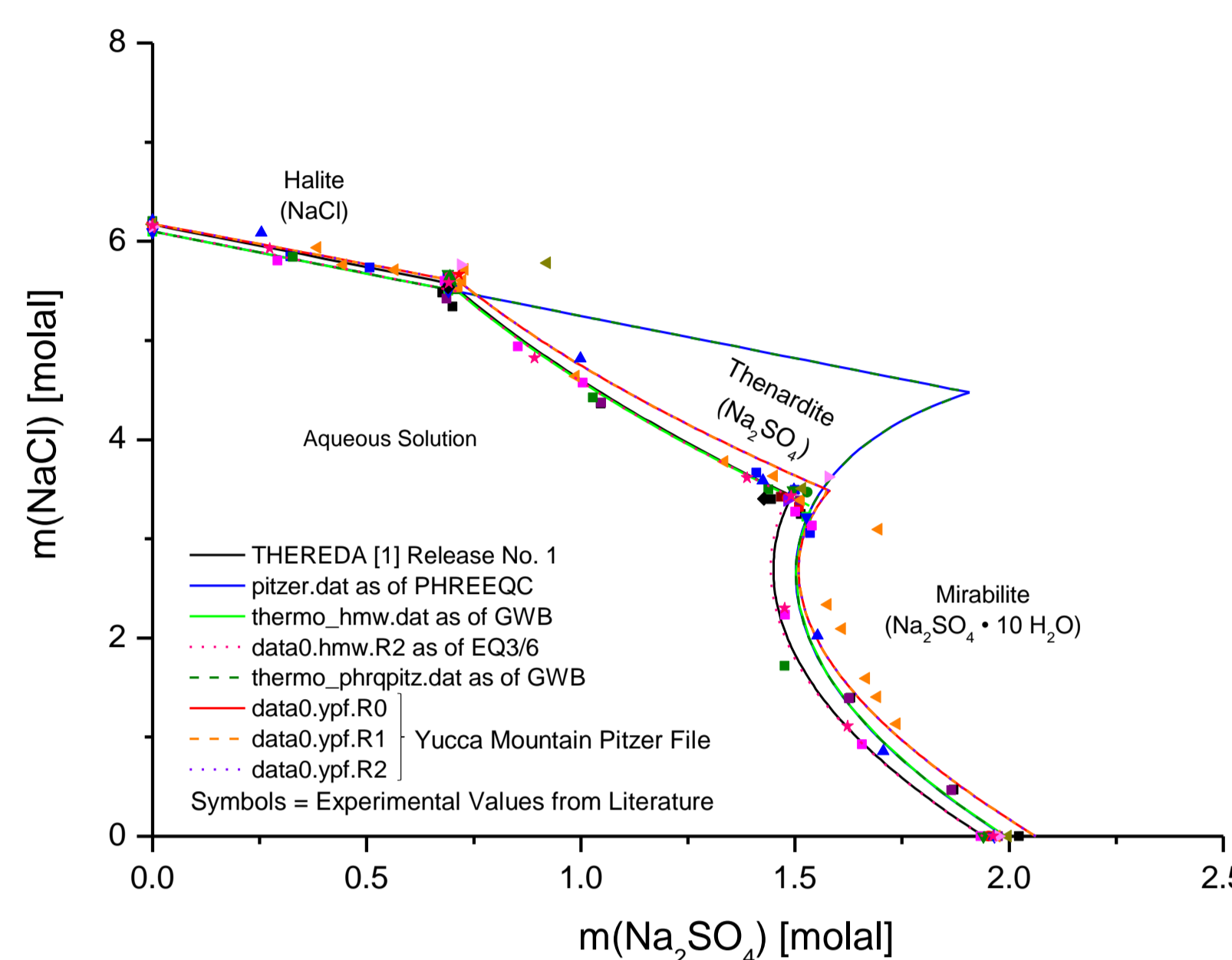


Fig. 1: Stability fields in the system Na^+ , Cl^- , SO_4^{2-} – H_2O , $T = 25$ °C.

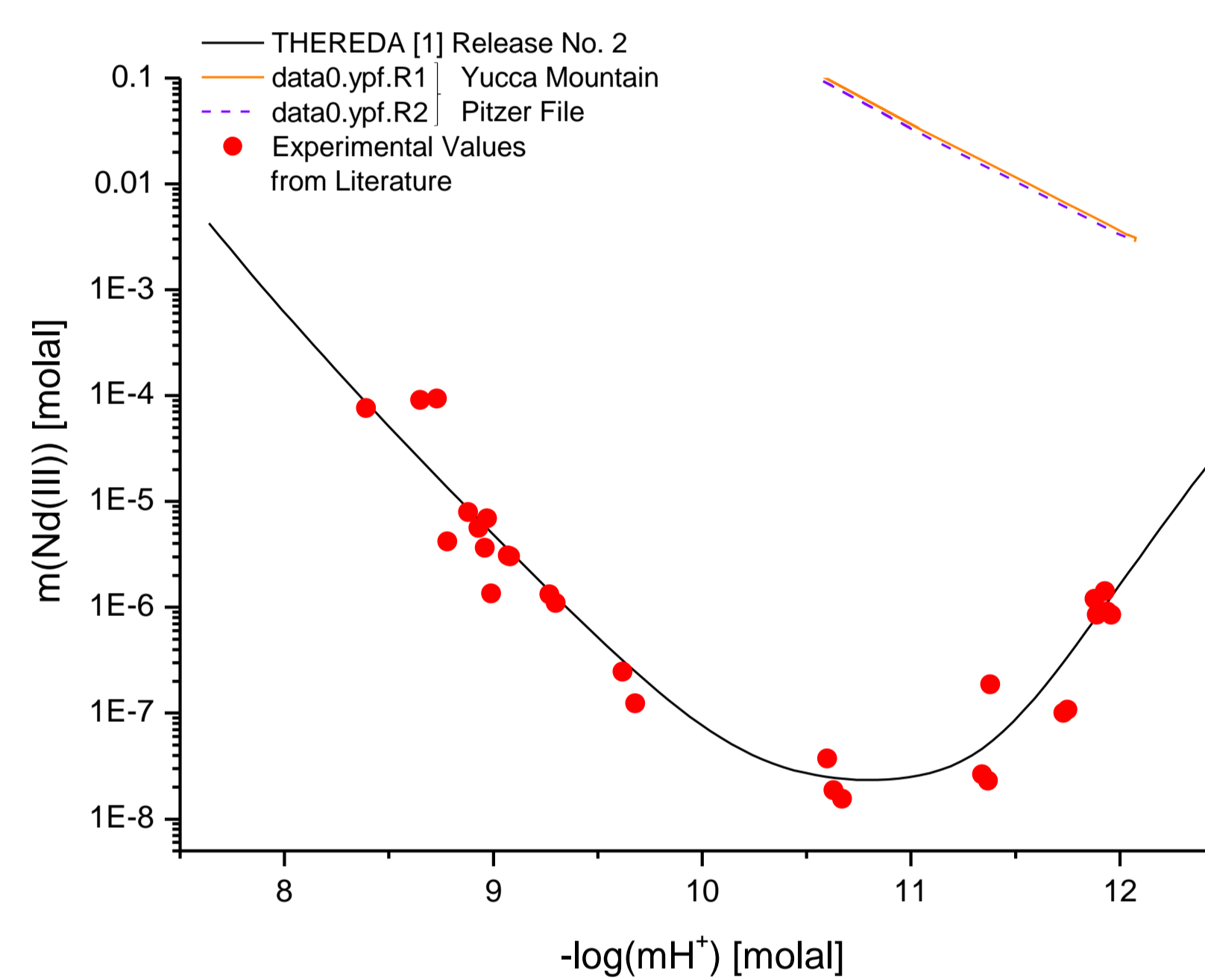


Fig. 3: Solubility of $\text{Nd}(\text{OH})_3(\text{am})$ in 3.86 m CaCl_2 at $T = 25$ °C.

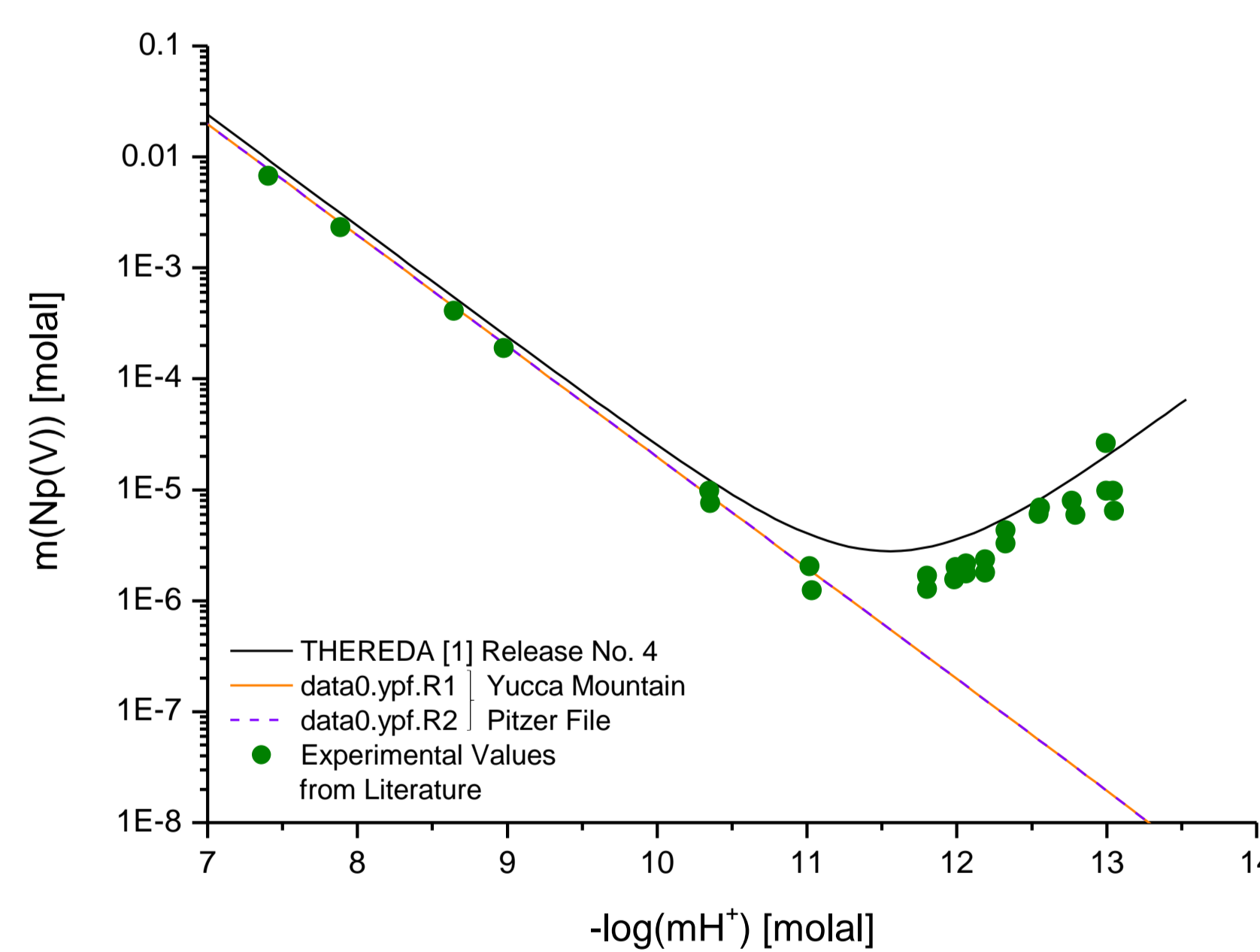


Fig. 5: Solubility of $\text{NpO}_2\text{OH}(\text{am})$ in 1.0 m NaCl at $T = 25$ °C.

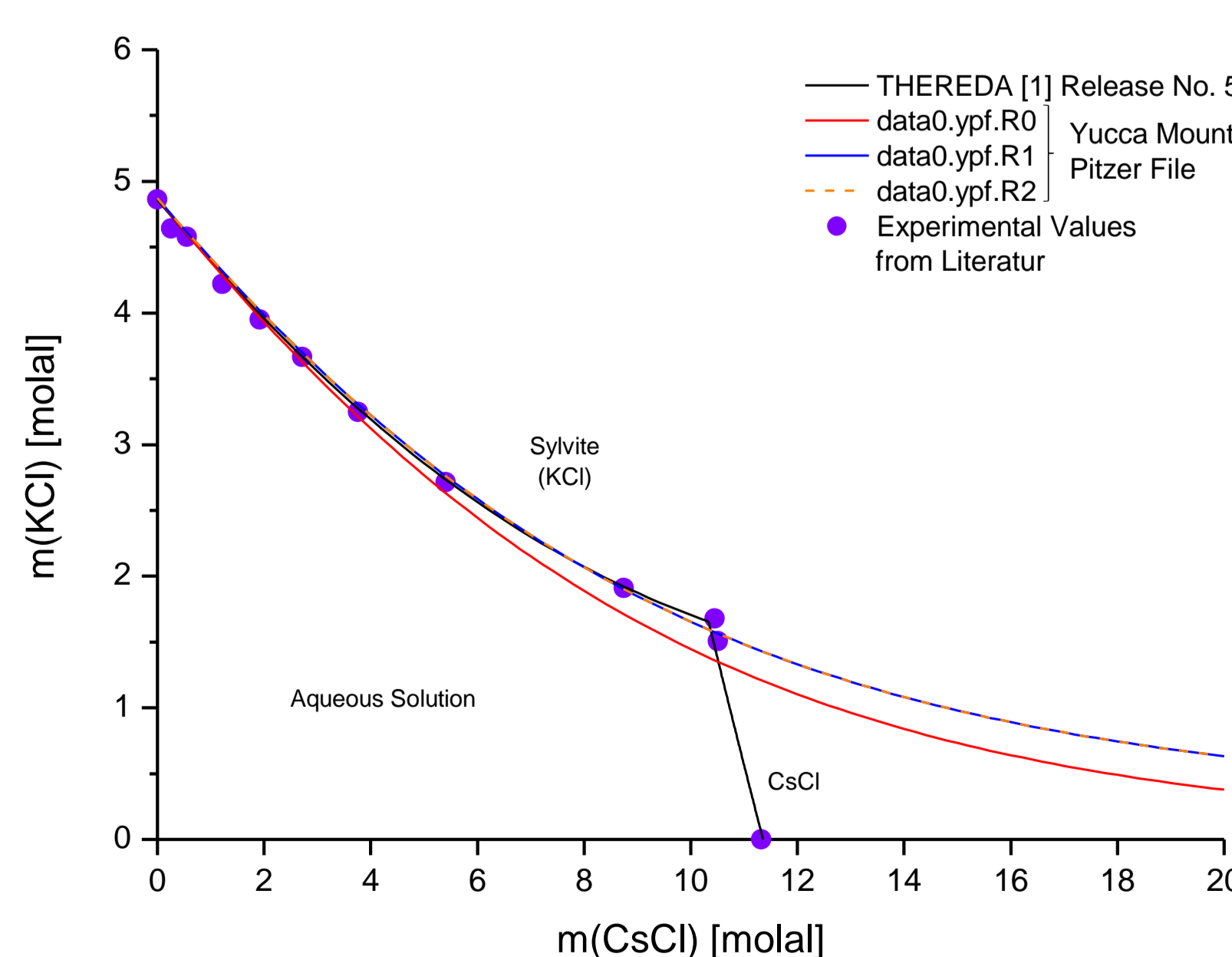


Fig. 7: Stability fields in the system Cs^+ , K^+ , Cl^- – H_2O , $T = 25$ °C.

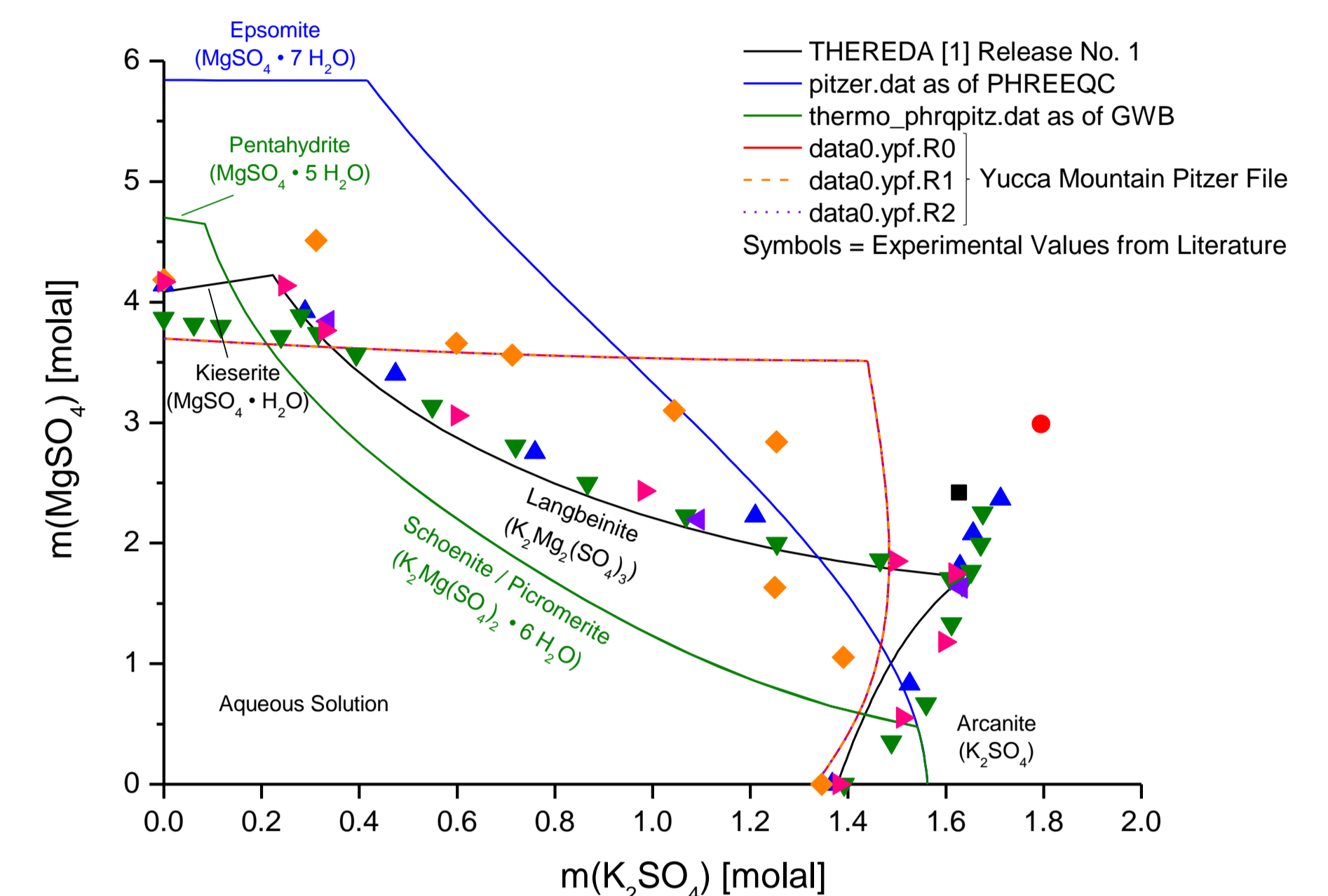


Fig. 2: Stability fields in the system K^+ , Mg^{2+} , SO_4^{2-} – H_2O , $T = 100$ °C.

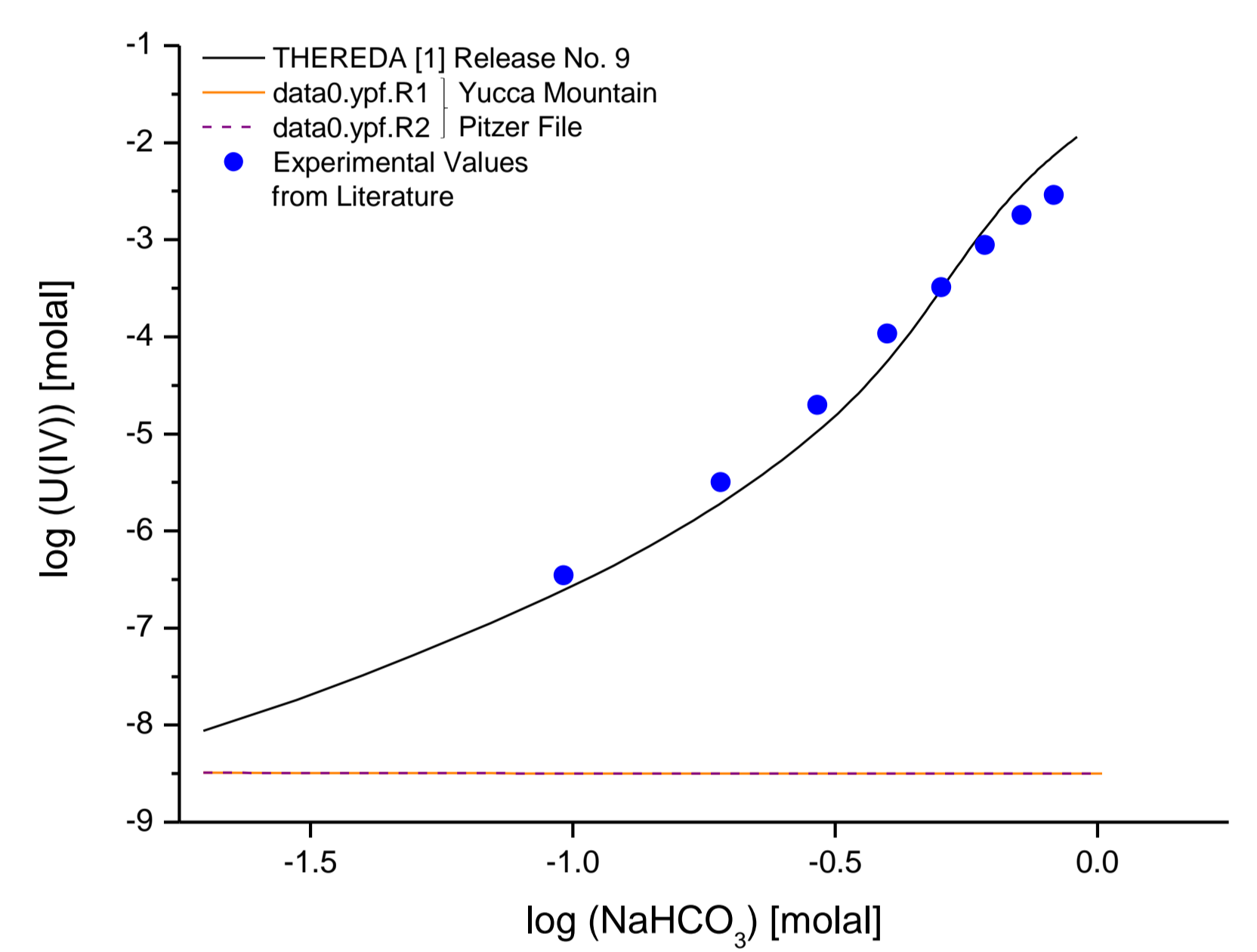


Fig. 4: Solubility of $\text{U}(\text{OH})_4(\text{am})$ in 0.02 up to 1.0 M NaHCO_3 at $T = 25$ °C.

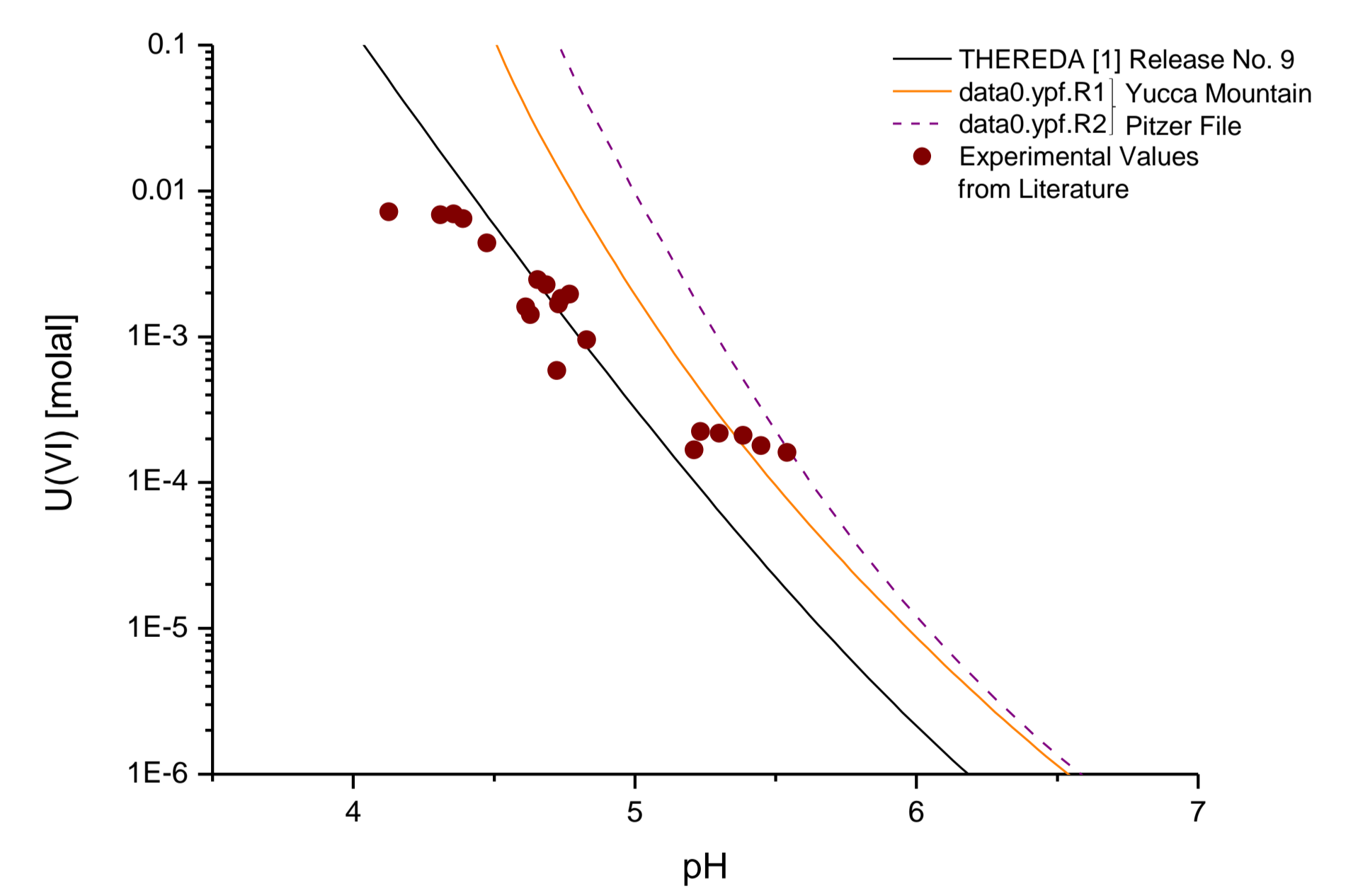


Fig. 6: Solubility of Becquerelite in 1 m CaCl_2 at $T = 25$ °C.

Conclusions

The revealed discrepancies illustrate the need for further database work. Joint benchmark activities could help to identify missing or less reliable data, enhance the quality of all databases and thus eventually increase the confidence in modelling results.

References

- [1] THEREDA <http://www.thereda.de>
- [2] Bethke, C.M. (2008), "Geochemical and Biogeochemical Reaction Modeling" 2nd Ed., Cambridge University Press, 123–134 (see also: <http://www.gwb.com>).

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