

Some highs and lows (and in-betweens) of solubility measurements of solid electrolytes*

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Abstract: Recent solubility measurements of a variety of solid electrolytes in water and aqueous solutions in the author's laboratories are reviewed. The experimental challenge of performing such measurements with high accuracy is demonstrated using the solubility of solid sodium chloride in water at near-ambient temperatures as a paradigm. The special difficulties of measuring low solubilities are demonstrated using Pb(II) sulfate in various aqueous solutions and Pb(II) oxide in sodium hydroxide solutions, and the usefulness of such measurements for obtaining reliable information on homogeneous reactions in solution is briefly discussed. It is also shown, using the alkali metal triflate salts as examples, that determination of the solubilities of even highly soluble salts can be problematic. Lastly, data for the solubilities of a series of sodium carboxylate salts of industrial relevance are discussed and are used to illustrate why the theoretical prediction of solid electrolyte solubilities remains such a challenge.

Keywords: aqueous solutions; carboxylate; electrolytes; lead(II); salts; sodium chloride; solubility; triflate.

INTRODUCTION

The solubilities of substances in solvents are among the oldest of physicochemical measurements [1]. While they would not have been recognized as such at the time, these measurements certainly included the solubilities of solid electrolytes (“salts”) in water. Solubility measurements continue to attract considerable attention although the focus nowadays is mostly on systems relevant to practical applications (chemical processing, hydrometallurgy, hydrocarbon extraction, pharmaceuticals, and so on) rather than systematic investigations based on inherent scientific interest [2]. The undiminished importance of solubility studies is reflected in the continuing success over the last 30 years of the *International Symposium on Solubility Phenomena* and of the IUPAC-sponsored *Solubility Data Series*. The latter, which commenced publication in 1979, currently appears under the aegis of the National Institute of Science and Technology (USA) in the *Journal of Physical and Chemical Reference Data*. The Series will reach its 100th volume within the next year or so, with no end yet in sight.

The measurement of the solubility of a simple, stable (chemically unreactive) salt in a stable solvent like water would nowadays be regarded as rather straightforward by most scientists, although it may be noted that the first book-length monograph devoted to the experimental aspects of solubility determinations appeared as recently as 2003 [3], with one of its stated purposes being to improve the quality of the solubility data being reported in the literature. As anyone who has been directly involved in making accurate solubility measurements can attest, there are as many experimental challenges in

Pure Appl. Chem. **85**, 2077–2144 (2013). A collection of invited papers based on presentations at the 15th International Symposium on Solubility Phenomena and Related Equilibrium Processes (ISSP-15), Xining, China, 22–27 July 2012.

making reliable solubility determinations as there are in other fields of science. A cursory glance at the literature will show there are often major discrepancies, sometimes at order-of-magnitude levels, among independently determined solubilities, even in relatively uncomplicated systems. The question that then naturally arises from this situation is: how accurately can the solubility of a salt in a solvent be measured, given the simplest possible circumstances of a stable, pure, non-solvate-forming, solid salt of “good” solubility, quantifiable by an inherently reliable technique, and an equally amenable solvent?

AN “IN-BETWEEN” SOLUBILITY: NaCl(s) IN H₂O

Measurement of the solubility of crystalline NaCl in liquid water at ambient conditions of temperature and pressure meets all of the above desiderata. It is an ideal example of an “in-between” solubility that is neither too high nor too low to suffer from the problems associated with such situations (see below). In principle, the solubility of NaCl(s) in H₂O(l) should be readily determinable to very high accuracy by evaporative gravimetry, NaCl has a small temperature coefficient of solubility in water, and it does not form hydrates, except at low temperatures [1,4].

More than 100 studies have reported quantitative information on the solubility of NaCl in water at near-ambient conditions [1,4]. A notable result is that determined in the 18th century by Antoine Lavoisier, one of the founders of modern chemistry, which is in respectable agreement with modern values [4]. The reported results have been reviewed on several occasions but the most comprehensive is undoubtedly that of Cohen-Adad and Lorimer [4], published in the IUPAC *Solubility Data Series*. After a critical assessment of all the original publications: with respect to technique, substance purity, equilibration time, etc., these authors accepted as apparently reliable a total of 41 independently determined results for the solubility of NaCl in H₂O at 25 °C. The accepted values showed a spread of 1.4 %, from (26.23 to 26.60) g NaCl/100 g satd. sln. The unweighted average of these values is 26.450 g NaCl/100 g satd. sln., with uncertainties of $1\sigma = 0.073$ ($3\sigma = 0.219$) g NaCl/100 g satd. sln.

Most physical chemists would be surprised to learn that something as straightforward as the solubility of NaCl(s) in water at 25 °C is known only with a relative certainty of 0.26 % (1σ) or 0.78 % (3σ). But perhaps a better estimate is available? As already noted, there have been other reviews of the solubility of NaCl in water. The numerical values given in those reviews are often encapsulated in the form of an appropriate (usually semi-empirical) mathematical model such as a Pitzer equation. De Visscher and Vanderdeelen [5] have compared the results obtained via these models. They showed (see Fig. 1 in ref. [5]) that at 25 °C the solubility recommended by CODATA/NIST [6] is ~0.75 % higher than the IUPAC value [4], while that given by Archer’s well-known model [7] is ~1.2 % lower. Other models, often parameterized on the same data, fared equally badly; only the value of Pitzer et al. [8] agreed within the (1σ) limit of the experimental uncertainty given above. Thus, it must be concluded that there is not at present a more profound source of NaCl solubility data available than the IUPAC review [4].

But perhaps there is something unusual about the NaCl/H₂O system: maybe it is not really a “simple” system after all? To the best of this author’s knowledge, the NaCl/H₂O system behaves as “normally” as would be expected, although it does not appear to be widely known that NaCl(s) is rather difficult to dry completely. This somewhat surprising result has been established unequivocally by Rard et al. [9,10] in a series of commendably precise gravimetric experiments. Most pertinent to the present discussion, it was shown that drying NaCl(s) even at a temperature of ~200 °C in a conventional (open) furnace or oven, which encompasses most reported solubility measurements to date (e.g., see below), leaves ~0.1 mass % residual water [9,10]. The amount is higher at lower temperatures. More surprisingly, the residual water content is *not* decreased even with substantial increases in the drying time. It appears that truly dry NaCl(s) can only be obtained (in an open furnace) by heating to 500 °C. Interestingly, Rard et al. reported ongoing weight losses above 550 °C, which they ascribed to surface hydrolysis:



and thereby concluded that there is only a very small temperature range to obtain truly dry, pure NaCl(s), at least in an open furnace. Note, however, that any residual water in NaCl(s) that has been dried to constant weight at temperatures ≤ 200 °C will only account for a small fraction of the variability observed among independent solubility determinations discussed above. Most of that variability must be ascribed to unknown and unsuspected experimental errors, both random and systematic: a salutary lesson on the difficulties of measuring even simple physicochemical quantities with high accuracy.

In recent years, the solubility of NaCl(s) in water has been determined routinely in the author's laboratories as a quality control measure during the study of the solubilities of various salts in water, some of which are described below. This has produced over 80 separate solubility determinations of NaCl(s) in water at various operating temperatures over the last few years. To support the bona fides of these measurements it is appropriate to briefly describe the solubility apparatus used. The form and operation of this equipment has been described in detail elsewhere [11] so only a short summary is given here. The apparatus consists of a transparent thick-walled polycarbonate bath of ~50 L capacity in which is located a plastic carousel, to which up to 28 stoppered, leak-tight polypropylene syringes containing appropriate amounts of solvent and excess solid can be fitted. The carousel is rotated at ~0.1 rpm, causing the excess solid to gently percolate up and down through the solvent without stirring. The bath temperature is controlled to ± 0.01 K (short term) but maintains an average temperature to within a few mK over many weeks. A key and distinguishing feature of this apparatus is that it allows the saturated solution to be sampled within the bath, exactly at the equilibration temperature. The details of this procedure are given in the original article [11] but it is emphasized that this feature is essential for accurate measurements on very highly soluble salts and/or salts with a large temperature coefficient of solubility. Once the saturated solution has been passed from the "sample" syringe through an appropriate filter (typically 0.45 μm pore size) into a "receiving" syringe, the former can be returned to the carousel for further equilibration while the latter can be removed from the bath for analysis at the experimentalist's convenience.

Saturated solutions of analytical grade sodium chloride (≥ 99.95 mol % purity) were routinely analyzed in quadruplicate (two samples from two separate syringes). Known masses of solution were evaporated to dryness in glass beakers at sub-boiling temperatures (usually ~80 °C) and then dried to constant mass at 150 °C in a laboratory oven at atmospheric pressure. The average solubility obtained at 25 °C from over 50 measurements, after correction assuming 0.15 mass % of residual water in the dried samples [9,10], was 26.45 ± 0.02 g NaCl/100 g sln. This value agrees exactly with the IUPAC-recommended value [4] of 26.450 ± 0.073 g NaCl/100 g sln discussed above. A recent independent study by Pinho and Macedo [12], employing a similar approach to the present work but drying at 120 °C, reported a solubility of 26.483 ± 0.013 g NaCl/100 g sln. After correction for ~0.15 mass % residual water [9,10] in the dried NaCl(s), this result corresponds to 26.44 ± 0.02 g NaCl/100 g sln. The agreement between these recent studies offers hope that the solubilities of simple salts in amenable solvents can, with due care, be determined routinely with a relative accuracy of better than ± 0.1 %, at least at 25 °C. Data with this level of accuracy will provide a very stern test of the reliability of any modeling equation [5].

Data for the solubility of NaCl(s) in water at various temperatures, obtained as described above, are compared in molality (m , mol-solute/kg-solvent) terms with the IUPAC-recommended values [4] in Table 1. Note that no density data are required for the unit conversion. Although rather fewer measurements were performed at temperatures other than 25 °C, the results are again in very satisfactory agreement with the critically assessed IUPAC values. There is some evidence (not presented here) that the slightly high solubility determined at 10 °C may be due to a higher level of occluded water in the NaCl crystals formed at this temperature (NaCl·H₂O crystallizes from saturated solutions at low temperatures [1,4]) but this has not been proven.

Table 1 Comparison of present and IUPAC-recommended [4] solubilities for NaCl(s) in water at various temperatures.^a

$T/^\circ\text{C}$	Present $m/\text{mol kg}^{-1}$	IUPAC(SDS) $m/\text{mol kg}^{-1}$	Difference/%
10	6.123(6) ^b	6.112(16)	-0.18
25	6.153(5)	6.157(16)	-0.07
40	6.223(6)	6.223(16)	0.00

^aNumbers in parentheses are 1σ uncertainties in the last digit of the given molality.

^bLarger amount of occluded water suspected in our dried samples.

SOLUBILITY “LOWS”: MEASUREMENTS ON SPARINGLY SOLUBLE SALTS

There are many difficulties associated with measurement of the solubilities of sparingly soluble salts. First, there are the possible effects of adsorption and contamination: the former producing results that are lower than the “true” value, with the latter typically giving higher-than-true results. With luck, these two effects may cancel each other out! Second, side reactions producing, or interferences from, minor components or impurities in the solutions may produce false results. Third, the most reliable and accurate of the methods of chemical analysis, gravimetry, and titrimetry are usually not applicable to sparingly soluble salts. Finally, there must exist a method of analysis that is appropriate for determining trace amounts of the species of interest in the presence, often in vast excess, of other solution components (i.e., in the medium of interest). All of these problems can be summarized into a single net consequence: increased analytical uncertainty in the measured results. The sort of accuracy that was possible for a well-behaved system like NaCl(s) in water is no longer achievable for the solubilities of sparingly soluble salts. The accuracy attained in practice will vary a great deal from system to system.

Case study 1: $\text{PbSO}_4(\text{s})$ in aqueous solutions

The solubility of Pb(II) sulfate [$\text{PbSO}_4(\text{s})$, anglesite] in aqueous solutions is of great importance in geochemistry and in natural waters, where it may be a significant factor affecting the speciation of the ubiquitous and toxic Pb(II). Despite this importance, a recent comprehensive survey [13] found that there were almost no solubility data available for $\text{PbSO}_4(\text{s})$ in any medium of environmental relevance, apart from water itself. This is surprising because the solubility of $\text{PbSO}_4(\text{s})$ would be expected to show considerable variation with ionic strength due to the divalent charges on the dissolving anions and cations. The solubility of $\text{PbSO}_4(\text{s})$ in high ionic strength media is also of relevance to understanding the behavior of “lead-acid” batteries (Planté cells) as it is a key component of both anodes and cathodes.

Solubility of $\text{PbSO}_4(\text{s})$ in water

$\text{PbSO}_4(\text{s})$ was prepared by metathesis from aqueous solutions of $\text{Pb}(\text{NO}_3)_2$ and Na_2SO_4 . The solid so obtained was filtered off and washed thoroughly with water. The X-ray diffraction (XRD) powder pattern indicated only anglesite was present in detectable amounts. Solubility measurements were performed in water to confirm the validity of the equilibration and analytical procedures, since this quantity is well established in the literature [13]. The water was slightly acidified (to $\text{pH} \approx 5.5$) with perchloric acid to minimize possible hydrolysis effects. Saturated solutions were sampled regularly over extended periods of up to 30 days although equilibrium was normally established within 2 to 3 days. Solubilities were determined by conventional flame atomic absorption spectrophotometry (AAS). Samples were normally analyzed immediately after filtering ($0.4 \mu\text{m}$) into polypropylene vials, to minimize possible adsorption losses.

Repeated determinations at 25 °C gave a value for the total dissolved Pb(II) concentration in solution of $[\text{Pb}^{2+}]_{\text{T}} = (30.7 \pm 1.9) \text{ mg/L} = (1.48 \pm 0.09) \times 10^{-4} \text{ M}$ (mol-solute/L-sln). This uncertainty ($\pm 6\%$ relative), although acceptable, was somewhat larger than expected so further investigations were carried out. XRD patterns indicated that the solid was unchanged anglesite even after extended equilibration periods. Variation of the solution pH by the addition of HClO_4 indicated no significant hydrolysis effects over the range $3.0 \leq \text{pH} \leq 5.5$. Analysis by inductively coupled plasma-optical emission spectroscopy (ICP-OES) gave similar but less precise results. Lastly, multiple ab initio determinations of the solubility did *not* improve the precision. Accordingly, the above result was taken as the present “best estimate” of the solubility of $\text{PbSO}_4(\text{s})$ in water at 25 °C.

For comparison with the literature data and for speciation calculations, it is necessary to convert the observed solubility into K_{s}° , the standard solubility product for the equilibrium:



The *apparent* value of $\text{p}K_{\text{s}} (= -\log[\text{Pb}^{2+}][\text{SO}_4^{2-}] \approx -\log[\text{Pb}^{2+}]_{\text{T}}^2)$ is 7.66. However, this value needs to be corrected for the presence of any $\text{Pb}^{2+}/\text{SO}_4^{2-}$ complexes formed in solution (see eq. 3), for which the association constants are known [13], and also for activity coefficient effects, which, because of the divalent ion charges, are significant even at the low ionic strength corresponding to the solubility. Appropriate allowance for both of these effects gave $\text{p}K_{\text{s}}^{\circ} = 7.80 \pm 0.05$, which is in quantitative agreement with the recent IUPAC-recommended value [13]. It is noteworthy that almost all of the present uncertainty, which is similar to those of the literature values, can be ascribed to the analytical error.

Solubility of $\text{PbSO}_4(\text{s})$ in NaClO_4 media

As noted above, virtually no data exist regarding the solubility of $\text{PbSO}_4(\text{s})$ in solutions with ionic strengths of relevance to natural water systems [13]. Measurements were therefore carried out in NaClO_4 media over the range: $0.01 \leq m(\text{NaClO}_4)/\text{mol kg}^{-1} \leq 5$, using the procedure outlined above. The results obtained at 25 °C are plotted in Fig. 1; analysis was again via flame-AAS. Surprisingly, a precision of about $\pm 2\%$ relative was obtained throughout, despite the presence (in most solutions) of a vast excess of NaClO_4 . In part, this potential problem could be side-stepped because the higher solubility of $\text{PbSO}_4(\text{s})$ at higher ionic strengths (Fig. 1) required large dilutions prior to analysis (the limit of detection for Pb by flame-AAS is quite low). The present results are in excellent agreement with the solitary literature value, obtained in the same medium [14].

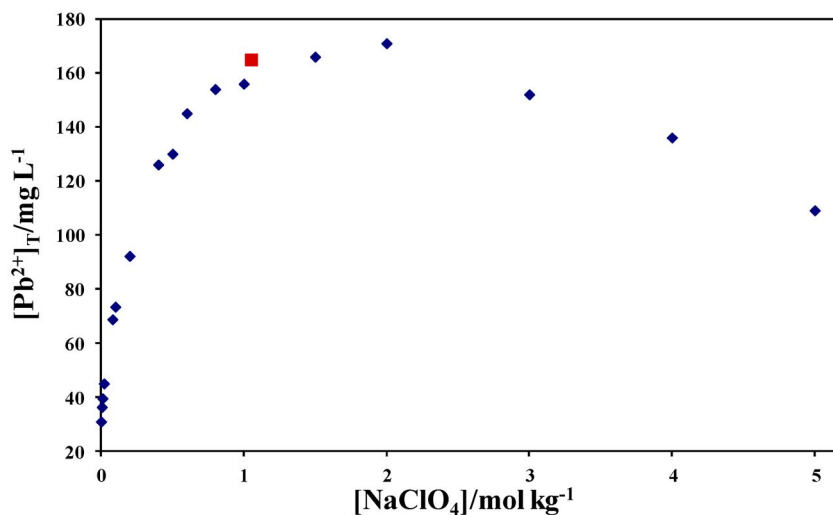
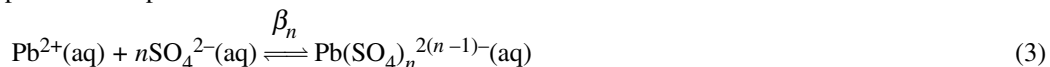


Fig. 1 The solubility of $\text{PbSO}_4(\text{s})$ in $\text{NaClO}_4(\text{aq})$ media at 25 °C: present work (diamonds); literature (square).

Solubility of $\text{PbSO}_4(\text{s})$ in $\text{NaClO}_4 + \text{Na}_2\text{SO}_4$ media

While solubility measurements are relatively little used nowadays in chemical speciation studies, they nevertheless provide a very well-based method for probing homogeneous equilibria in solution. Indeed, solubility measurements can work when all other techniques fail. The $\text{Pb}^{2+}/\text{SO}_4^{2-}$ system is a good example. The complexes formed in solution



are potentially important for the speciation of Pb(II) in marine waters, where the concentration of SO_4^{2-} is modest [13], in lead-acid batteries where it is high [15], and in aqueous aerosols where it may be extreme [16]. While the value of the formation constant of the 1:1 complex, $\beta_1[\text{PbSO}_4^0(\text{aq})]$, is well established, at least in low ionic strength solutions, the existence and strength of higher-order complexes ($n \geq 2$) remains controversial [13]. In part, this is due to the limited applicability of the usual techniques for measuring formation constants (potentiometry, spectroscopy, etc.) as a result of the precipitation of $\text{PbSO}_4(\text{s})$. Solubility measurements turn this problem into an advantage. Figure 2 plots the solubility of $\text{PbSO}_4(\text{s})$ in $\text{NaClO}_4 + \text{Na}_2\text{SO}_4$ mixtures at a constant ionic strength (I) of 1 M. Although the solubility curve looks uninteresting, appropriate numerical analysis yields values of $\log \beta_1 = 1.31 \pm 0.06$ and $\log \beta_2 = 1.51 \pm 0.10$ at $I = 1 \text{ M}(\text{NaClO}_4)$ and 25°C . Both β_n values are broadly consistent with the limited (and not very reliable) values reported in the literature [13]. More importantly, although their uncertainties are fairly large, these β_n values should be well-founded because the only major assumption required for processing the data is the usual one of constant activity coefficients at constant I .

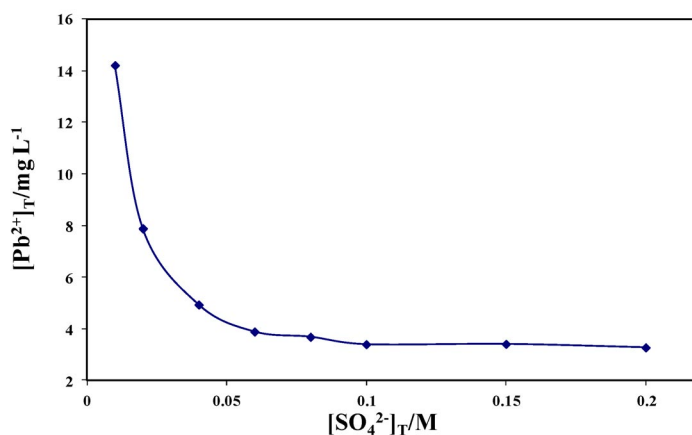


Fig. 2 Solubility of $\text{PbSO}_4(\text{s})$ in $\text{NaClO}_4 + \text{Na}_2\text{SO}_4$ mixtures at $I = 1 \text{ M}(\text{NaClO}_4)$ and 25°C .

Case study 2: PbO (unfinished business)

The formation of the “mononuclear” Pb(II)-hydroxo complexes:



has widespread implications for the chemical behavior of Pb(II) in the environment and in human health and occupational safety [15]. However, despite the numerous investigations reported in the literature these complexes remain inadequately characterized. Controversy still exists even as to the number of complexes formed and in particular whether the highest-order mononuclear species is $\text{Pb}(\text{OH})_3^-$ or $\text{Pb}(\text{OH})_4^{2-}$ [13,17]. Clarification of this issue is important for modeling the behavior of Pb(II) in high pH solutions found in nuclear wastes [18] and industrial Bayer process “liquors” [19].

As for the $\text{Pb}^{2+}/\text{SO}_4^{2-}$ system discussed above, a major reason for this situation is that most of the usual speciation techniques are thwarted by the precipitation of sparingly soluble Pb(II) salts. Other problems in studying the hydrolysis of $\text{Pb}^{2+}(\text{aq})$ have been discussed in detail elsewhere, but it can be reasonably said that the $\text{Pb}^{2+}/\text{OH}^-$ system has some strange characteristics that are not understood at present [17]. Surprisingly little use has been made to date of solubility studies to investigate $\text{Pb}^{2+}(\text{aq})$ hydrolysis, possibly because the thermodynamically stable solid “hydroxide” species is $\text{PbO}(\text{s})$. This compound exists in two forms: massicot (yellow) and litharge (red), with the former being slightly more stable at ambient temperatures [13,20]. Here it should be noted that simple $\text{Pb}(\text{OH})_2(\text{s})$ probably doesn't exist: the white precipitate(s) formed when $\text{OH}^-(\text{aq})$ is added to aqueous solutions of simple Pb(II) salts are “mixed” or “basic” salts, often of variable composition.

As a preliminary investigation of the $\text{Pb}^{2+}/\text{OH}^-$ system, the solubility of massicot has been determined in $\text{NaOH}(\text{aq})$ up to very high concentrations (Fig. 3). While these data have not been obtained at constant I , they show some interesting features. First, the solubilities of massicot at lower concentrations [$m(\text{NaOH}) \leq 5 \text{ mol kg}^{-1}$] are in excellent agreement with those reported by Garrett et al. in 1939 [21], which is probably the most reliable study of this system to date. Second, the slope of the linear portion of the solubility curve is fully consistent with $\text{Pb}(\text{OH})_3^-(\text{aq})$ as the highest-order mononuclear hydroxo complex formed at $m(\text{NaOH}) \leq 2 \text{ mol kg}^{-1}$ [13]. Last, as an indication of the “strangeness” of the $\text{Pb}^{2+}/\text{OH}^-$ system [17], at higher NaOH concentrations where the possible existence of $\text{Pb}(\text{OH})_4^{2-}(\text{aq})$ would be indicated by an upwards trend (increased slope) of the solubility curve, the solubility actually *decreases* slightly (Fig. 3). This unusual feature is possibly indicative of the formation of another stable solid, perhaps a sodium “plumbite” salt, although this has not yet been confirmed. Further measurements on this system, particularly at constant I , are clearly desirable.

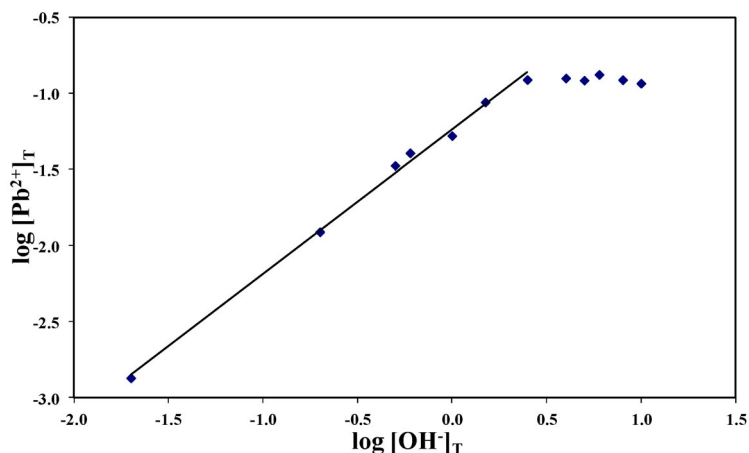


Fig. 3 Solubility of yellow $\text{PbO}(\text{s})$ in $\text{NaOH}(\text{aq})$ at 25 °C.

SOLUBILITY “HIGHS”: MEASUREMENTS ON HIGHLY SOLUBLE SALTS

It is almost counter-intuitive that the determination of the solubilities of readily soluble salts should be problematic (even if their quantitative explanation lies well beyond the existing theories of solution chemistry). Nevertheless, reliable measurements of such systems often present real experimental difficulties. The first is that highly soluble salts frequently form solvates (reflecting their strong affinity for the solvent, which of course contributes to their high solubility in the first place). This problem can be handled by careful characterization of the solid in equilibrium with the saturated solution but because solid-state conversions are often very slow; genuine equilibration may require inordinately long times.

Potentially worse is the situation where only a thin surface layer of the solid, which may be undetectable by conventional XRD analysis, is in equilibrium with the saturated solution. Suffice to say, the literature is replete with incorrect solubility data arising from the failure to achieve true equilibrium between properly defined solid and solution phases [3].

The second problem associated with the measurement of highly soluble salts is also a practical one: such salts often have very large temperature coefficients of solubility. While, as noted above, the present experimental arrangement allows sampling at the equilibration temperature, the subsequent handling required for analysis may be problematic, e.g., as a result of precipitation in the sample-“receiving” syringe [11]. Any such problems are circumvented by placing a known mass of solvent (water) in the “receiving” syringe. A known mass of the saturated solution from the “sample” syringe is then filtered into the receiving syringe, being diluted in the process to well below its solubility limit. Such solutions could then be removed from the bath for analysis without further difficulty (apart from a lot of algebra!).

Case study 3: Alkali metal triflates

Salts of trifluoromethanesulfonic (“triflic”) acid have attracted enormous interest in recent years because the “triflate” anion (F_3CSO_3^-) readily forms stable, redox-inert, room-temperature ionic liquids with many organic cations. The alkali metal triflate salts have also received a lot of attention because their low lattice energies make them soluble in many solvents and their non-complexing character and redox inertness makes them attractive for battery and fuel cell applications. Our particular interest in the alkali metal triflates, however, is to use them to investigate so-called “medium effects” on chemical equilibria at very high ionic strengths, ideally up to industrially relevant levels of, say, 6 M (or even higher if possible). Unfortunately, there is no series of alkali metal salts sharing a common anion that show sufficient solubility for our purpose. The best available at present are the alkali metal chlorides [21] but the solubility of KCl is only 4.2 M at 25 °C (the solubilities of the other alkali metal chlorides are substantially higher) [1]. Equally importantly, Cl^- is far too reactive to provide an “inert” (i.e., non-interacting) medium for many chemical equilibria.

As with all “new” materials, there are significant gaps in our knowledge of the physicochemical properties of the alkali metal triflates. No reliable solubility data in water appear to have been published although various publications reporting measurements of other properties imply that at least the sodium and potassium salts have high solubilities. Accordingly, an investigation of the solubilities of the alkali metal triflates (excluding rubidium) in water was carried out 25 °C using the procedures described above. The salts were synthesized and purified as described elsewhere [22]. During the course of these measurements, another problem concerning quantification of high solubilities became apparent: the lithium triflate was so soluble that the viscosity of its saturated solution became so high that it could barely be filtered, even under substantial applied pressure. Inevitably, this lowered the precision of the solubility measurements for this salt.

The results obtained for the four alkali metal triflate salts are summarized in Fig. 4. Disappointingly for our intended usage, the solubility of cesium triflate turned out to be rather lower than was hoped, although the solubilities of the other three salts are sufficiently high. The solubility of the unstudied rubidium salt will be interesting in terms of the overall pattern. These results are a good example of the difficulties facing theoreticians in predicting the solubilities of “simple” salts. Similar examples abound in the literature [23].

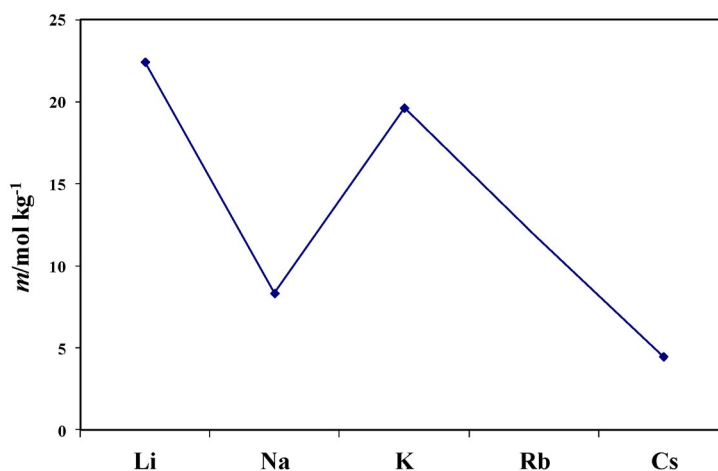
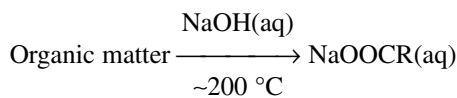


Fig. 4 Solubilities of the alkali metal triflates in water at 25 °C.

SOME “IN-BETWEEN” SOLUBILITIES OF INDUSTRIAL IMPORTANCE

Although scientifically unfashionable, the measurement of solubility data is of great importance in many industrial processes [2]. The absence of such data inevitably means that the “sizing” margins typically built into engineering calculations for plant design and operation must be increased. This is costly and potentially wasteful, especially given that the solubilities of electrolytes cannot in general be predicted with reasonable levels of accuracy by the existing theories of solution chemistry. The solution chemistry group at Murdoch University has a long-standing interest in measuring and understanding the properties of industrial Bayer process “liquors”, the concentrated alkaline aluminate solutions used in the production of purified alumina from bauxitic ores [21,24]. Part of this work has been the development of a comprehensive model of the physicochemical properties of these complex solutions over wide ranges of temperature, pressure, and composition, based on the Pitzer formalism. This model requires knowledge of, for example, the densities and heat capacities of the binary solutions (water + one solute) of each significant component expected in the liquor to be modeled [24].

A key step in the Bayer process is the digestion of the bauxitic ore with hot, concentrated NaOH(aq). Such ores inevitably contain a certain amount of organic matter (humic material, cellulose, etc.), which reacts with the NaOH solution, producing a variety of sodium carboxylate salts [25]:



Some of these carboxylate salts have significant impacts on Bayer process operations, and so their properties are of considerable industrial interest. For modeling purposes [24] these properties need to be measured to very high concentrations (say, up to 6 or 8 M). To avoid potential damage to the measuring equipment, it is essential to know the solubility of these salts. Unfortunately, the existing solubility database for sodium carboxylates is rather limited and of uncertain reliability [1]. Accordingly, a systematic study of the solubility in water of a selected series of these salts has been conducted. The results obtained to date are summarized in Fig. 5.

The solubilities were determined as described above for NaCl(s), i.e., using sub-boiling evaporation of filtered samples of the saturated solutions followed by drying at 120 °C. The approach to equilibrium was followed for extended periods but was usually reached within three days. The reproducibility of the solubilities varied between individual salts but was always better than $\pm 0.2\%$ relative.

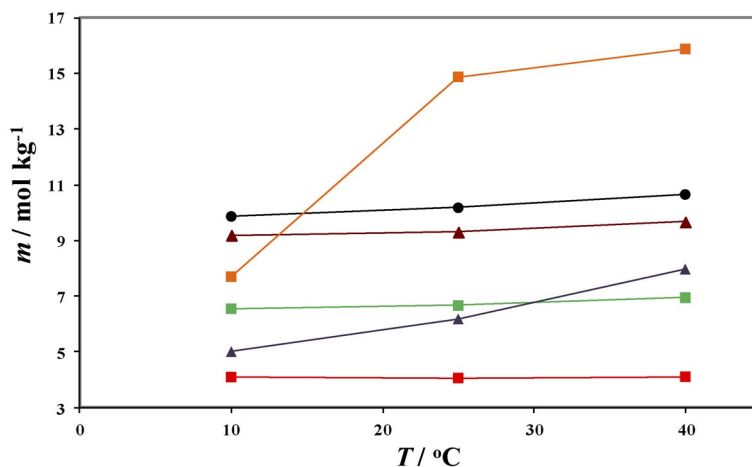


Fig. 5 Solubilities of sodium carboxylate salts in water as a function of temperature; from bottom to top at 10 °C: benzoate, acetate, salicylate, formate, butanoate, propanoate.

There are a number of points of interest arising from the data in Fig. 5. First, with the partial exception of acetate, the solubilities of the aromatic carboxylates, benzoate and salicylate, are lower than the straight-chain salts. Second, their enthalpies of dissolution (reflected in the slopes of the curves) are also smaller. Third, the enthalpies of dissolution of formate (NaOFm) and acetate are of vastly greater magnitude (are much more endothermic) than their longer-chain congeners propanoate (NaOPr) and butanoate (NaOBu). Last, but perhaps most interesting, is that the solubilities of the straight-chain sodium carboxylates in water do not follow a regular pattern going from formate to butanoate, either at 25 °C (Fig. 6) or any of the other temperatures studied (Fig. 5). These experimental results underline very starkly the difficulties facing the development of theories capable of explaining, let alone predicting, the solubilities of even relatively simple salts in solvents.

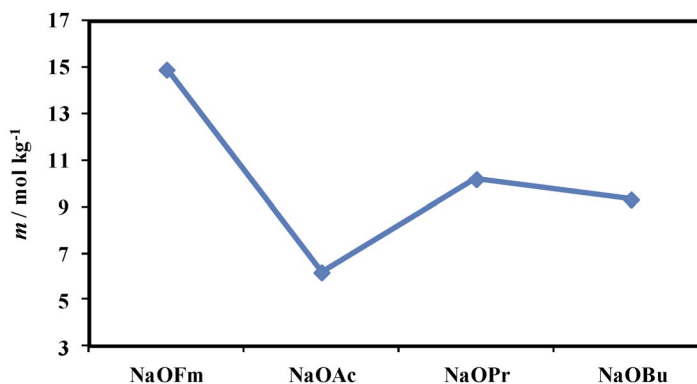


Fig. 6 Solubilities of straight-chain sodium carboxylate salts in water at 25 °C.

ACKNOWLEDGMENTS

The experimental data reported here were obtained by Ms. Sue Farr, whose dedication and enthusiastic contribution is gratefully acknowledged. Thanks are also due to my long-term collaborators Peter May

and Erich Königsberger for numerous stimulating discussions over many years, and to Murdoch University for its ongoing financial support.

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