Solubility of Sodium Oxalate in Concentrated Electrolyte Solutions

Glenn Hefter,[†] Andrew Tromans,[‡] Peter M. May,[§] and Erich Königsberger*,[§]

[†]Chemistry Department, Murdoch University, Murdoch, WA 6150, Australia

[‡]A. J. Parker Cooperative Research Centre for Hydrometallurgy, Murdoch University, Murdoch, WA 6150, Australia

[§]Chemical and Metallurgical Engineering and Chemistry, School of Engineering and Information Technology, Murdoch University, Murdoch, WA 6150, Australia

S *Supporting Information*

ABSTRACT: The solubility of solid sodium oxalate (Na₂Ox) has been measured in a variety of concentrated aqueous electrolyte solutions at $T = 298.15$, 323.15, and 343.15 K by titration of dissolved oxalate with permanganate. The electrolyte solutions studied (not necessarily at all temperatures) were NaCl, NaClO₄, NaOH, LiCl, KCl, Me₄NCl, and KOH at concentrations ranging from approximately 0.5 mol·kg⁻¹ to at least 5 mol·kg⁻¹. Where comparisons were possible, the present results were in excellent agreement with literature data. The solubility of Na₂Ox(s) decreased markedly with increasing concentrations of Na⁺(aq), due to the common ion effect. This decrease was almost independent of the electrolyte anion. A number of ternary mixtures of these electrolytes were also investigated at constant ionic strength. Consistent with the binary mixtures, the solubility of Na₂Ox(s) showed almost no dependence on solution composition at constant Na⁺(aq) concentrations. Solubilities in non-Na⁺ media, with the exception of Me₄NCl, showed small but regular increases with increasing concentration of added electrolyte, probably reflecting activity coefficient variations. The solubility data in certain Na⁺-containing media could be correlated accurately at all temperatures and concentrations using a relatively simple Pitzer model with interaction parameters for Na₂Ox(aq) assumed to be identical to those available in the literature for Na₂SO₄(aq).
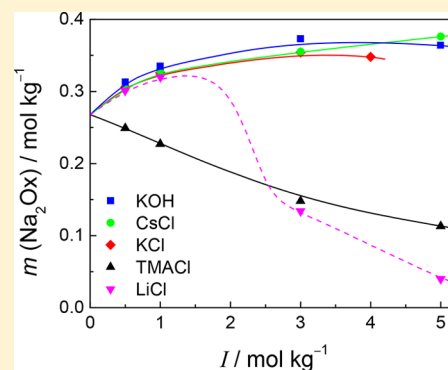
INTRODUCTION

Sodium oxalate (Na₂C₂O₄; hereafter abbreviated as Na₂Ox) has a significant presence in a number of important industrial contexts. For example, in the well-known Bayer process, used to obtain purified alumina from bauxitic ores, Na₂Ox(s) is produced in large quantities as an end-product of the alkaline degradation of organic impurities.[1−3] This creates significant problems in plant operations due to its limited solubility and because it is a crystallization inhibitor for the desired gibbsite product.[1−3] A similar situation prevails in the storage of alkaline nuclear wastes, where Ox²⁻ builds up, and Na₂Ox(s) precipitates, over time, again, due to the degradation of larger organics in such environments.[4,5] Sodium oxalate is also problematic elsewhere in the nuclear industry due to the use of oxalic acid to dissolve certain types of waste (and its subsequent neutralization)[6] and the use of oxalate as a complexing agent or precipitant in the processing of various nuclear fuels.[7] The widespread use of oxalate to remove iron-based scale in pipes and other equipment, because of its ability to bind strongly to both Fe(II) and Fe(III),[8] creates similar management and disposal difficulties.

The solubility of Na₂Ox in aqueous solution can be expressed by the equilibrium:

$$Na_2Ox(s) \rightleftharpoons 2Na^+(aq) + Ox^{2-}(aq) \tag{1}$$
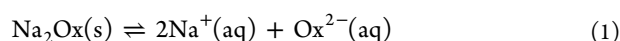
for which the corresponding standard state solubility constant, K_{s0}^o, is strictly written:

$$K_{s0}^o = (a_{Na^+})^2 \times a_{Ox^{2-}} \tag{2}$$

where a_i is the activity of the ion i. Given that activities are related to concentrations c_i by $a_i = c_i\gamma_i$, eq 2 can be written:

$$K_{s0}^o = ([Na^+]\gamma_{Na^+})^2 \times [Ox^{2-}]\gamma_{Ox^{2-}} = [Na^+]^2[Ox^{2-}]$$
$$\times (\gamma_{Na^+}^2\gamma_{Ox^{2-}}) = K_{s0} \times (\gamma_{Na^+}^2\gamma_{Ox^{2-}}) \tag{3}$$

where the square brackets denote concentrations and γ_i is the activity coefficient of the ion i. In addition,

$$K_{s0} = [Na^+]^2[Ox^{2-}] = 4S^3 \tag{4}$$

where K_{s0} is the solubility product (often referred to as the solubility quotient), which is directly calculable from the experimental solubility, S.

Given its commercial importance,[1−8] it is not surprising that the solubility of Na₂Ox(s) in aqueous solutions has received considerable attention, both experimental[9,10] and, more recently, computational.[11−13] The quantitative solubility data available have been compiled and summarized by Linke and

Table 1. Sample Sources and Purities

chemical name [CASRN]	source	initial mass fraction purity	purification method	final massfraction purity	analysis method
aluminum [7429-90-5]	BDH, UK	0.999	none		
cesium chloride [7647-17-8]	BDH, UK	0.999	none		
lithium chloride [7447-41-8]	BDH, UK	0.99	none		
potassium chloride [7447-40-7]	Ajax, Australia	0.998	none		
potassium hydroxide [1310-58-3]	BDH, UK	0.85	see text	0.995	titration with H^+
potassium permanganate [7722-64-7]	Ajax, Australia	≥0.990	see text	0.998	titration with Na_2Ox
sodium aluminate [11138-49-1]	synthesis		see text		
sodium chloride [7647-14-5]	BDH, UK	0.995	none		
sodium hydroxide [1310-73-2]	BDH, UK	0.97	see text	0.999	titration with H^+
sodium oxalate [62-76-0]	Ajax, Australia	0.999	none		
sodium perchlorate [7601-89-0]	BDH, UK	0.99	none		
tetramethylamm-onium chloride [75-57-0]	Aldrich	0.97	see text		

Seidell[9] and more recently by Hummel et al.[10] Most of the data concern the solubility of Na_2Ox(s) in pure water, although some studies reported solubilities in the presence of other electrolytes.[9,14,15] In contrast to the experimental studies, the computational effort has focused on developing models based on the Pitzer formalism[16] that can account for the solubility of Na_2Ox(s) in quite complicated mixtures of concentrated electrolytes.[11−13]

As is well-known, the presence of other electrolytes in solution can profoundly affect the solubility of a given salt in a given solvent at constant temperature and pressure.[17,18] Such effects may be broadly categorized into three types. First is the "common ion effect", which acts directly through the solubility equilibrium to lower the solubility. Second is the complexation of the interacting ions either with each other (self-association/ion pairing) or with any other species present, which enhances the apparent solubility via a competing equilibrium. Third are activity coefficient effects, which include the general effects of ionic strength (I) and the differences between individual electrolytes (usually referred to as "specific ion interactions"). Such effects may lower or raise the solubility depending on the concentration (I) and nature of the other electrolyte(s) present. These types of effects are usually smaller than those due to the first two phenomena.

All of these effects may (or may not) appreciably affect the solubility of Na_2Ox(s) in the complicated matrices that are of most practical interest.[11−13] Given the state of concentrated electrolyte theory,[18] the best way to investigate the relative importance of such effects is by direct experiment. Accordingly, this article reports measurements of the solubility of Na_2Ox(s) in a range of nominally noncomplexing electrolyte solutions, both with and without a common cation, and in selected mixed electrolyte solutions. The measurements extend to industrially relevant high ionic strengths at three temperatures, T = 298.15, 323.15, and 343.15 K.

■ EXPERIMENTAL SECTION

Reagents. The sources, purities, and (where relevant) methods of purification of the reagents used in this work are summarized in Table 1. Briefly, all electrolytes were commercial products of analytical reagent grade and were oven-dried at $T \approx$ 343 K overnight (for cesium chloride, under reduced pressure, $p \approx$ 5 Pa) unless otherwise stated. Solid tetramethylammonium chloride dihydrate (TMACl·$2H_2O$) was recrystallized twice from absolute ethanol[19,20] then dried over silica gel at room temperature and $p \approx$ 5 Pa for 24 h. Solutions of sodium

aluminate ($NaAl(OH)_4$ dissolved in excess NaOH) were prepared from aluminum wire and 20 M NaOH (where M represents the concentration unit mol·(L sln)$^{-1}$). Concentrated NaOH and KOH stock solutions were purified according to the procedure of Sipos et al.[21] Solutions of $KMnO_4$ were prepared from the solid, left to stand for several days, filtered to remove precipitated MnO_2, and standardized (±0.2%) with 0.0500 M Na_2Ox solution immediately before use.[22] The dried Na_2Ox used to standardize the $KMnO_4$ solutions was the same as that used for the solubility measurements. All solutions were prepared from high purity water (Millipore Milli-Q system), decarbonated and deoxygenated by boiling and cooling under nitrogen.

Solubility Determinations. Solubility measurements were made using the apparatus described in detail elsewhere.[23] The advantages of this apparatus are that saturated solutions are sampled exactly at the equilibration temperature, the temperature is controlled precisely (±0.01 K), and up to 28 equilibrations can be performed simultaneously and independently. Temperature was monitored continuously (to ±0.001 K) using a NIST-traceable quartz-crystal thermometer (Hewlett-Packard).[23] Equilibration vessels were 60 mL polypropylene syringes (Terumo) fitted with a purpose-machined polypropylene plunger and a tight-fitting PTFE O-ring. Saturated solutions were separated from undissolved solid by membrane filtration (GHP Acrodisc, 25 mm × 0.45 μm). The sampling protocol was tested by measuring the solubility of sodium chloride in water at T = 298.15 K. Saturated solutions were analyzed by sub-boiling evaporation followed by drying at 343 K to constant weight. After correction for the small amount of occluded water in the dried solid,[24] the solubility of NaCl was found to be 6.159 mol·(kg H_2O)$^{-1}$, which agrees well with the IUPAC-recommended[25] value of 6.160 mol·(kg H_2O)$^{-1}$.

The present solubilities were mostly determined from undersaturation. Randomly selected solutions were also measured from oversaturation by initial equilibration ∼5 K above the desired temperature followed by re-equilibration at the target temperature. Equilibration and sampling were repeated until concordant (≤0.5%) solubilities were obtained. Solubilities obtained by approach from over- and under-saturation agreed, on average, to within 5%, which provides a more realistic estimate of the overall experimental precision. Equilibrium was usually reached within 24 h but many solutions were left for much longer periods as checks.

Oxalic acid is moderately strong with a first protonation constant of log $K_1 \approx$ 3.5 in the ionic strength range investigated

Table 2. Solubility of Na$_2$Ox in Na$^+$-Containing Electrolyte Media at T = 298.15 K and p = 0.1 MPa[a]

medium[b]			solubility[c] S/mol·(kg H$_2$O)$^{-1}$	density[a] ρ/g·cm^{-3}	N[d]	solid phase[e]
c/mol·L^{-1}	ρ/g·cm^{-3}	m/mol·(kg H$_2$O)$^{-1}$				
H$_2$O			0.272(14)[f]	1.0209	6	α
			0.265(14)	1.0209	9	
			0.263(13)	1.0251	9	
NaCl						
0.500	1.0173[g]	0.506[h]	0.132(12)	1.0305	8	α
0.998	1.0370	1.020	0.0703(38)	1.0436	8	α
2.001	1.0753	2.088	0.0280(14)	1.0730	9	α
			0.0318(16)	1.0671	9	
5.001	1.1836	5.611	0.0043(12)	1.1817	9	α
			0.0042(12)	1.1833	9	
NaClO$_4$						
0.507	1.0361[i]	0.521	0.143(11)	1.0460	8	α
0.991	1.0740	1.040	0.078(6)	1.0681	9	α
			0.085(5)	1.0635	9	
3.00	1.225	3.50	0.013(4)	1.2266	6	α
6.99	1.495	10.9	*0.0025(4)*	1.5154	3	α
8.00	1.560	13.8	0.0019(7)	1.5925	6	α
NaOH						
0.507	1.0190[g]	0.508	0.138(10)	1.0320	9	α
1.005	1.0395	1.006	0.077(6)	1.0456	6	α
			0.076(6)	1.0457	10	
3.00	1.115	3.01	0.0177(17)	1.1131	8	α
5.00	1.183	5.09	0.0062(4)	1.1786	10	α
7.00	1.237[i]	7.31	0.0049(4)	1.2109	3	α
8.00	1.265	8.47	0.0037(2)	1.2579	9	α
10.00	1.314	10.9	0.0009(5)	1.3205	7	α
$I \approx 5$ Na(OH, Cl)						
2.00 NaCl + 3.00 NaOH	1.1829[g]	2.11 NaCl + 3.17 NaOH[j]	0.0059(4)	1.1795	10	α
4.00 NaCl + 1.01 NaOH	1.1836	4.40 NaCl + 1.11 NaOH	0.0049(3)	1.1769	5	α
			0.0052(9)	1.1817	8	
4.25 NaCl + 0.75 NaOH	1.1833	4.70 NaCl + 0.83 NaOH	0.0052(4)	1.1815	6	α
4.50 NaCl + 0.50 NaOH	1.1834	5.00 NaCl + 0.56 NaOH	0.0047(3)	1.1821	9	α
			0.0048(4)	1.1832	9	
4.75 NaCl + 0.25 NaOH	1.1835	5.30 NaCl + 0.28 NaOH	0.0048(8)	1.1819	7	α
$I \approx 7$ Na(OH, ClO$_4$)						
2.00 NaClO$_4$ + 5.00 NaOH	1.316[k]	2.30 NaClO$_4$ + 5.74 NaOH	0.0021(2)	1.3164	10	α
5.04 NaClO$_4$ + 2.00 NaOH	1.467	6.55 NaClO$_4$ + 2.60 NaOH	0.0017(6)	1.4669	9	α
			0.0018(2)	1.4679	9	
5.50 NaClO$_4$ + 1.50 NaOH	1.451	7.66 NaClO$_4$ + 2.09 NaOH	0.0024(5)	1.4511	8	α
6.00 NaClO$_4$ + 1.00 NaOH	1.512	8.14 NaClO$_4$ + 1.36 NaOH	0.0018(6)	1.5128	8	α
			0.0019(4)	1.5114	9	
6.50 NaClO$_4$ + 0.50 NaOH	1.492	9.61 NaClO$_4$ + 0.74 NaOH	0.0023(4)	1.4916	6	α
Na(OH, Al(OH)$_4$)						
0.350 NaAl(OH)$_4$ + 0.556 NaOH	1.0461[g]	0.356 NaAl(OH)$_4$ + 0.566 NaOH	0.0735(37)	1.0584	4	α
1.000 NaAl(OH)$_4$ + 2.001 NaOH	1.1457	1.055 NaAl(OH)$_4$ + 2.111 NaOH	0.0089(5)[l]	1.1477	2	α

[a]Standard uncertainties are $u(T)$ = 0.02 K, $u(p)$ = 5 kPa, and $u(\rho)$ = 0.004 g·cm^{-3}. [b]Relative standard uncertainties: $u_r(c)$ = 0.02 and $u_r(m)$ = 0.02. Densities for conversion to molalities are valid at 298.15 K. [c]All solubilities were determined by titration with KMnO$_4$ unless otherwise stated. Numbers in parentheses are combined standard uncertainties in the last significant figure of the solubility. Solubilities in *italics* were obtained from initially oversaturated solutions; others were determined from initially undersaturated solutions unless otherwise specified. [d]Total number of titrations performed on replicate solution samples. [e]Solid phase (XRD): α = Na$_2$Ox. [f]By evaporative gravimetry. [g]Calculated from BAYER.EXE.[11] [h]$m_B = c_B/(\rho - c_B M_B)$, where M_B is the molar mass of solute B in kg mol^{-1}.[10] [i]Taken from the JESS database of physicochemical properties.[26] [j]$m_B + m_C = (c_B + c_C)/(\rho - c_B M_B - c_C M_C)$. [k]Density of solution saturated with Na$_2$Ox. [l]By high performance ion chromatography.

in this study.[26] Thus, the Na$_2$Ox(s) solubility equilibria do not depend on pH in the neutral to alkaline background electrolyte solutions used in this work, none of which undergoes protonation reactions in this pH range. Since the solutions equilibrated with Na$_2$Ox(s) are essentially unbuffered, their pH has little significance and was therefore not recorded.

Saturated solution densities at the target temperatures were determined using a vibrating glass-tube density meter (Anton Paar, Austria, DMA 602) immediately after sampling to avoid precipitation of Na$_2$Ox. Densities of caustic solutions, which had been equilibrated at higher temperatures (323.15 and 343.15 K), were measured using an Anton Paar DMA512P

Table 3. Solubility of Na$_2$Ox in Na$^+$-Containing Electrolyte Media at T = 323.15 K and p = 0.1 MPa[a]

medium[b]			solubility[c] S/mol·(kg H$_2$O)$^{-1}$	density[a] ρ/g·cm^{-3}	N[d]	solid phase[e]
c/mol·L^{-1}	ρ/g·cm^{-3}	m/mol·(kg H$_2$O)$^{-1}$				
H$_2$O			0.317(16)	1.0203	8	α
			0.334(17)	1.0224	5	
NaCl						
1.00	1.037[f]	1.02[g]	0.103(6)	1.0360	5	α
3.00	1.112	3.20	0.0214(11)	1.1001	4	α
5.00	1.184	5.61	0.00705(36)	1.1694	9	α
NaClO$_4$						
1.00	1.075[h]	1.04	0.084(4)	1.078	4	α
3.00	1.225	3.50	0.0136(7)	1.2244	3	α
7.00	1.495	11.0	0.0029(2)	1.5304	9	α
NaOH						
1.00	1.039[f]	1.00	0.118(6)	1.0371	4	α
3.00	1.115	3.01	0.0272(14)	1.1020	4	α
5.00	1.183	5.09	0.013(1)	1.1543	9	α
			0.013(3)	1.1504	4	
7.00	1.237[h]	7.31	0.0046(3)	1.2122	9	α
$I \approx 5$ Na(OH, Cl)						
1.00 NaCl + 4.00 NaOH	1.183[f]	1.04 NaCl + 4.15 NaOH[i]	0.0104(7)	1.1650	9	α
			0.0102(5)	1.1658	4	
3.00 NaCl + 2.00 NaOH	1.183	3.23 NaCl + 2.16 NaOH	0.0082(4)	1.1688	6	α
$I \approx 7$ Na(OH, ClO$_4$)						
2.00 NaClO$_4$ + 5.00 NaOH	1.316[j]	2.30 NaClO$_4$ + 5.74 NaOH	0.00345(17)	1.3009	4	α
5.00 NaClO$_4$ + 2.00 NaOH	1.464	6.48 NaClO$_4$ + 2.59 NaOH	0.0038(4)	1.4040	8	α
			0.0032(3)	1.4219	4	

[a]Standard uncertainties are $u(T)$ = 0.02 K, $u(p)$ = 5 kPa, and $u(\rho)$ = 0.004 g·cm^{-3}. [b]Relative standard uncertainties: $u_r(c)$ = 0.02 and $u_r(m)$ = 0.02. Densities for conversion to molalities are valid at 298.15 K. [c]All solubilities were determined by titration with KMnO$_4$. Numbers in parentheses are combined standard uncertainties in the last significant figure of the solubility. Solubilities in *italics* were obtained from initially oversaturated solutions; other solubilities were determined from initially undersaturated solutions. [d]Total number of titrations performed on replicate solution samples. [e]Solid phase (XRD): α = Na$_2$Ox. [f]Calculated from BAYER.EXE.[11] [g]$m_B = c_B/(\rho - c_B M_B)$, where M_B is the molar mass of solute B in kg mol^{-1}.[10] [h]Taken from the JESS database of physicochemical properties.[26] [i]$m_B + m_C = (c_B + c_C)/(\rho - c_B M_B - c_C M_C)$. [j]Density of solution saturated with Na$_2$Ox at 298.15 K.

Hastelloy vibrating tube density meter.[27] Equilibrated solids were characterized by X-ray diffraction.

Most solubilities were determined by oxidation of dissolved oxalate with standardized KMnO$_4$ solution.[22] The titration protocol was cross-checked in pure water by evaporative gravimetry, which gave essentially identical results (Table 2). Checks for interferences were made throughout by titration of synthetic samples containing known amounts of oxalate in the presence of added electrolyte. Difficulties were encountered only in TMACl. These were overcome by adding a small amount of Mn(II) sulfate to catalyze the oxidation reaction.[22] The solubilities of Na$_2$Ox in NaOH/NaAl(OH)$_4$ solutions were determined using suppressed ion-exchange chromatography with a conductometric detector, an Alltech resin IC column, and a carbonate/bicarbonate mobile phase.

It should be noted that while the solubility of Na$_2$Ox is reported throughout this article on the molality scale (m/mol·(kg H$_2$O)$^{-1}$), many of the electrolyte solutions were prepared, for experimental convenience, using the molarity (c/mol·(L sln)$^{-1}$) scale. The effects of temperature on the latter are negligible in the present context, amounting to less than 2% between 298 and 343 K (assuming the expansivities of the electrolyte solutions to be similar to that of pure water). To reflect the added uncertainty due to the use of molarities, the electrolyte concentrations at the higher temperatures have been rounded to three or fewer significant figures where appropriate. In Tables 2, 3, and 4, molarities were converted to molalities

using densities from various sources (see footnotes). It will also be noted that there are small differences (averaging ca. 0.2%) in the densities of the saturated solutions obtained by approach from under- or oversaturation. These differences reflect minor practical difficulties in determining the densities of saturated solutions (e.g., due to possible precipitation) and are negligible compared with the overall experimental uncertainty in the solubility determinations.

RESULTS AND DISCUSSION

Solubility of Na$_2$Ox in Water. The present results for the solubility of Na$_2$Ox(s) in pure water (Tables 2, 3, and 4) are plotted, along with the extensive literature data,[9,10] as a function of temperature in Figure 1. The agreement between the present and literature values is good (noting that the scale in Figure 1 tends to emphasize small differences). For example, at T = 298.15 K the present average result of 0.267 ± 0.004 mol·kg^{-1}, obtained by three different procedures (Table 2), is in quantitative agreement with the 0.269 mol·kg^{-1} calculated from the value proposed by Linke and Seidell.[9] It is also within the uncertainty limits of the value, 0.28 ± 0.01 mol·kg^{-1}, recommended more recently by Hummel et al.[10] Similar agreement is also apparent at T = 323.15 and 343.15 K (Figure 1, Tables 3 and 4), i.e., solubilities obtained by approach from over- and under-saturation were identical within the limits of overall experimental precision.

Table 4. Solubility of Na₂Ox in Na⁺-Containing Electrolyte Media at T = 343.15 K and p = 0.1 MPa^a

| | medium^b | | | | | |
c/mol·L^{-1}	ρ/g·cm^{-3}	m/mol·(kg H$_2$O)$^{-1}$	solubility^c S/mol·(kg H$_2$O)$^{-1}$	density^a ρ/g·cm^{-3}	N^d	solid phase^e
H₂O			0.385(21)	1.0165	4	α
			0.383(19)		4	
NaCl						
0.50	1.017^f	0.51^g	0.223(12)	1.0195	2	α
1.00	1.037	1.02	0.131(9)	1.0291	3	α
3.00	1.112	3.20	0.0273(16)	1.0945	4	α
5.00	1.184	5.61	0.0099(9)	1.1617	5	α
			0.010(1)		4	
NaOH						
1.00	1.039	1.00	0.140(9)	1.0335	4	α
5.00	1.183	5.09	0.014(1)	1.1604	4	α
			0.017(6)		4	
$I \approx 5$ (Cs, Na)Cl						
1.00 CsCl + 4.00 NaCl	1.268^h	1.15 CsCl + 4.62 NaCl^i	0.0202(12)	1.2425	4	α
2.00 CsCl + 3.00 NaCl	1.359	2.36 CsCl + 3.54 NaCl	0.0175(9)	1.3335	4	α
3.00 CsCl + 2.00 NaCl	1.448	3.63 CsCl + 2.42 NaCl	0.0317(17)	1.4222	4	α
4.00 CsCl + 1.00 NaCl	1.538	4.96 CsCl + 1.24 NaCl	0.083(4)	1.5126	5	α

^{a}Standard uncertainties are $u(T)$ = 0.02 K, $u(p)$ = 5 kPa, and $u(\rho)$ = 0.004 g·cm^{-3}. ^{b}Relative standard uncertainties: $u_r(c)$ = 0.02, and $u_r(m)$ = 0.02. Densities for conversion to molalities are valid at 298.15 K. ^{c}All solubilities were determined by titration with KMnO₄. Numbers in parentheses are combined standard uncertainties in the last significant figure of the solubility. Solubilities in *italics* were obtained from initially oversaturated solutions; other solubilities were determined from initially undersaturated solutions. ^{d}Total number of titrations performed on replicate solution samples. ^{e}Solid phase (XRD): α = Na₂Ox. ^{f}Calculated from BAYER.EXE.[11] $^g m_B = c_B/(\rho - c_B M_B)$, where M_B is the molar mass of solute B in kg mol^{-1}.[10] ^{h}Density of solution saturated with Na₂Ox, corrected to 298.15 K by adding 0.025 g·cm^{-3} as calculated for 5 M NaCl(aq).[11] $^i m_B + m_C = (c_B + c_C)/(\rho - c_B M_B - c_C M_C)$.
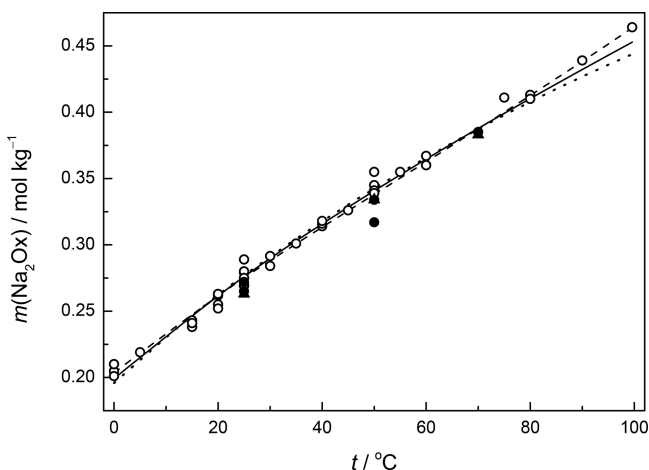

Figure 1. Solubility of Na₂Ox(s) in water as a function of temperature. Present experimental data obtained from: (●) undersaturation; (▲) supersaturation; and (○) literature data.[10] The dotted, solid, and dashed lines correspond to optimizations 1, 2, and 3, respectively, of the present Pitzer model (see text).
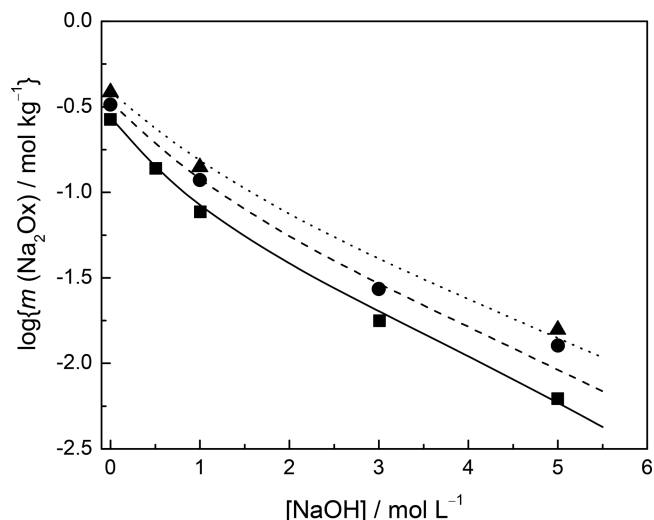

Figure 2. Present experimental solubilities for Na₂Ox(s) in NaOH(aq) at: (■) T = 298.15 K; (●) T = 323.15 K; and (▲) T = 343.15 K. Present Pitzer model: solid line, T = 298.15 K; dashed line, T = 323.15 K; and dotted line, T = 343.15 K.

Solubility of Na₂Ox in Na⁺-Containing Electrolytes.

The experimental solubilities of Na₂Ox(s) in the presence of various Na⁺-containing electrolytes at T = 298.15, 323.15, and 343.15 K are listed in Tables 2, 3, and 4, respectively. Selected data, in NaOH(aq) and NaCl(aq), are plotted as a function of the added electrolyte concentration at the three temperatures in Figures 2 and 3, respectively. Solutions studied at T = 298.15 K (Table 2) included a range of concentrations of NaCl (0.5 ≤ c/M ≤ 5.0), NaClO₄ (1.0 ≤ c/M ≤ 8.0), and NaOH (1.0 ≤ c/M ≤ 10). The same electrolytes were used over slightly more restricted concentration ranges at T = 323.15 K (Table 3), while at T = 343.15 K only NaCl (0.5 ≤ c/M ≤ 5.0) and NaOH

(1.0 and 5.0 M) were investigated (Table 4). Where comparisons are possible, the present results are again in good agreement with the literature data.[9,14] Solubilities obtained from over- and under-saturation generally agreed within the limits of overall experimental precision, although a larger relative disagreement (up to 20%) was occasionally observed for the very low solubilities measured at high Na⁺(aq) concentrations.

Mathematical modeling of the present data in Na⁺-containing media (Figures 1−3) via the Pitzer formalism[16] is described in detail below, but some qualitative comments on the results are
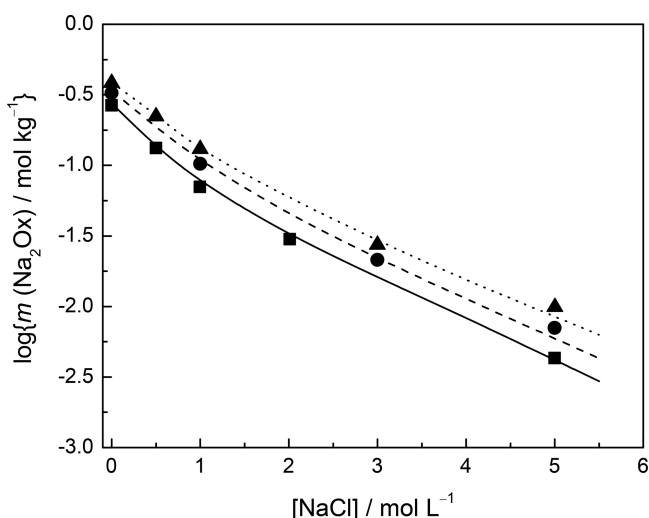
Figure 3. Present experimental solubilities for Na$_2$Ox(s) in NaCl(aq) at: (■) T = 298.15 K; (●) T = 323.15 K; and (▲) T = 343.15 K. Present Pitzer model: solid line, T = 298.15 K; dashed line, T = 323.15 K; and dotted line, T = 343.15 K.

appropriate. As would be anticipated by the application of Le Chatelier's principle to eq 1, there is a pronounced decrease in the solubility of Na$_2$Ox with increasing Na$^+$ concentrations, due to the well-known "common ion effect". What is interesting about this decrease is that it is essentially the same for all four Na$^+$-containing salts, i.e., changing the anion has almost no effect on the solubility of Na$_2$Ox, even at high concentrations of added electrolyte (Figure 4). This uniformity occurs despite the
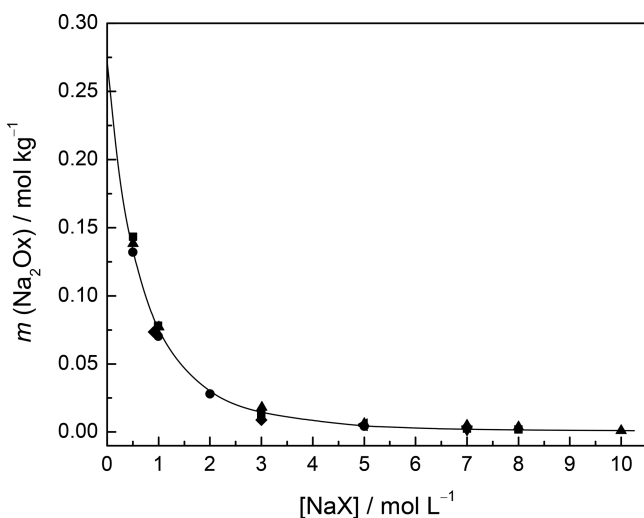
Figure 4. Present experimental solubilities for Na$_2$Ox(s) in Na$^+$-containing media at T = 298.15 K: (●) NaCl(aq); (■) NaClO$_4$(aq); (▲) NaOH(aq); (◆) NaOH(aq)/NaAl(OH)$_4$(aq); (◀) NaOH(aq)/NaCl(aq) at I_c ≈ 5 M; and (▼) NaOH(aq)/NaClO$_4$(aq) at I_c ≈ 7 M. Line is a visual guide only.

fact that the (thermodynamically unmeasurable) activity coefficients of Na$^+$(aq) and Ox^{2-}(aq) might be expected to differ in the presence of these various added electrolytes.[28,29]

Solubility of Na$_2$Ox in Other Electrolytes. The solubilities of Na$_2$Ox(s) in selected non-Na$^+$-containing electrolytes at T = 298.15 K are summarized in Table 5. The electrolytes studied were LiCl, KCl, CsCl, TMACl, and KOH,

all at $0.5 \leq m/\text{mol·kg}^{-1} \leq 5.0$ (4.0 for the less-soluble KCl). The results obtained are compared in Figure 5 as a function of the added electrolyte concentration. The solubilities are almost identical for KCl, CsCl, and KOH, even up to the highest electrolyte concentrations studied. Again, this similarity occurs despite large variations in $\gamma_\pm$ for the added electrolytes (see Figure S1 in the Supporting Information). The same might well be true of LiCl except that Li$_2$Ox(s) starts to precipitate at $m(\text{LiCl}) > 1$ mol·kg^{-1} (Table 5), which accounts for the rapid decrease in the measured [Ox^{2-}] at higher lithium ion concentrations (Figure 5).

The very different behavior of the solubility of Na$_2$Ox(s) in TMACl (Figure 5) is puzzling. No X-ray diffraction evidence was found for the precipitation of (TMA)$_2$Ox(s), and the activity coefficients for TMACl(aq), while not closely similar to the other electrolytes, are not markedly different; indeed they are much closer than those of KOH (Figure S1, Supporting Information). Although the number of water molecules affected by tetraalkylammonium cations is still an open issue,[30] it might be speculated that the somewhat hydrophobic character of TMA$^+$(aq) strengthens the solvent water structure, thereby diminishing the hydration of Na$^+$(aq) and Ox^{2-}(aq) and lowering the solubility of Na$_2$Ox(s).

The solubility of Na$_2$Ox(s) in CsCl ($1.0 \leq m/\text{mol·kg}^{-1} \leq 5.0$) was also determined at T = 323.15 and 343.15 K (Table 6). Time constraints precluded measurements in other electrolyte solutions. The presence of up to 5.0 mol·kg^{-1} of CsCl(aq) has notably little effect on the enthalpy of dissolution of Na$_2$Ox(s), i.e., on the variation of the solubility with temperature (Figure 6).

Solubility of Na$_2$Ox in Ternary Electrolyte Solutions. The solubilities determined for Na$_2$Ox(s) in a limited range of Na$^+$-containing ternary electrolyte solutions (solvent + 2 added electrolytes) are summarized in Tables 2−4. These measurements were made at various fixed ionic strengths, $I_c = 0.5\Sigma c_i z_i^2$, except for the two industrially relevant NaAl(OH)$_4$/NaOH mixtures. Fewer mixtures were studied at T = 323.15 K (Table 3), while at T = 343.15 K (Table 4) only four ternary mixtures of NaCl + CsCl at I_c ≈ 5 M were measured.

The substitution of NaOH(aq) by NaCl(aq) at T = 298.15 K and I_c ≈ 5.0 M resulted, consistent with the data obtained in the binary mixtures (solvent + 1 added electrolyte), in a small but systematic decrease in the Na$_2$Ox(s) solubility from 6.2 mmol·kg^{-1} to 4.3 mmol·kg^{-1} (Table 2, Figure 7). At the very high ionic strength of I_c ≈ 7.0 M, substitution of NaClO$_4$(aq) by NaOH(aq), also at T = 298.15 K, has an essentially random effect on the very small solubilities observed at these Na$^+$ concentrations. These values are again consistent with the observations in the relevant binary solutions (Table 2). Similar effects are apparent at T = 323.15 K (Table 3, Figure 7). Interestingly, the very small Na$_2$Ox(s) solubilities measured vary systematically when NaClO$_4$(aq) is replaced by NaOH-(aq) at I_c ≈ 7.0 M. It is also noteworthy that the solubilities of Na$_2$Ox(s) in the industrially relevant caustic aluminate solutions are consistent with their [Na$^+$], at least at T = 298.15 K (Table 2, Figure 4). In other words, the solubility of Na$_2$Ox(s) in such mixtures is dominated by a simple common ion effect, which is supported by our findings for other thermodynamic properties of NaOH(aq)/NaAl(OH)$_4$(aq) mixtures.[31−33]

As would be expected, substitution of NaCl(aq) by CsCl(aq) at I_c ≈ 5.0 M (Table 4, Figure S2, Supporting Information) results in a significant increase in the solubility of Na$_2$Ox(s).

Table 5. Solubility of Na$_2$Ox in Non-Na$^+$ Electrolyte Solutions at T = 298.15 K and p = 0.1 MPa^a

medium^b m/mol·(kg H$_2$O)$^{-1}$	solubility^c S/mol·(kg H$_2$O)$^{-1}$	density^a ρ/g·cm^{-3}	N^d	solid phase^e
KCl				
0.500	0.306(15)	1.0505	4	α
1.000	0.329(17)	1.0727	4	α
	0.323(16)	1.0723		
3.000	0.354(18)	1.1465	4	α
3.999	0.348(19)	1.1750	4	α
CsCl				
0.500	0.304(15)	1.0896	4	α
1.000	0.329(17)	1.1486	4	α
3.001	0.355(18)	1.3549	4	α
5.000	0.376(19)	1.5259	4	α
KOH				
0.500	0.313(17)	1.0525	4	α
1.000	0.336(17)	1.0773	4	α
	0.333(17)	1.0767	4	
2.999	0.373(19)	1.1603	4	α
4.998	0.364(18)	1.2262	4	α
TMACl				
0.501	0.249(13)	1.0234	4	α
1.000	0.227(13)	1.0186	4	α
3.000	0.149(7)	1.0104	4	α
	0.146(7)	1.0104	4	
5.000	0.113(6)	0.9998	4	α
LiCl				
0.499	0.301(15)	1.0382	4	α
1.001	0.320(16)	1.0496	4	α
	0.321(16)	1.0501	4	
3.000	0.134(7)^f	1.0787	4	α, β
5.000	0.040(3)^f	1.1113	4	β

^{a}Standard uncertainties are $u(T)$ = 0.02 K, $u(p)$ = 5 kPa, and $u(\rho)$ = 0.004 g·cm^{-3}. ^{b}Relative standard uncertainty: $u_r(m)$ = 0.001. ^{c}All solubilities were determined by titration with KMnO$_4$. Numbers in parentheses are combined standard uncertainties in the last significant figure of the solubility. Solubilities in *italics* were obtained from initially oversaturated solutions; other solubilities were determined from initially undersaturated solutions. ^{d}Total number of titrations performed on replicate solution samples. ^{e}Solid phases (XRD): α = Na$_2$Ox; β = Li$_2$Ox. ^{f}Total oxalate concentration in the aqueous phase.
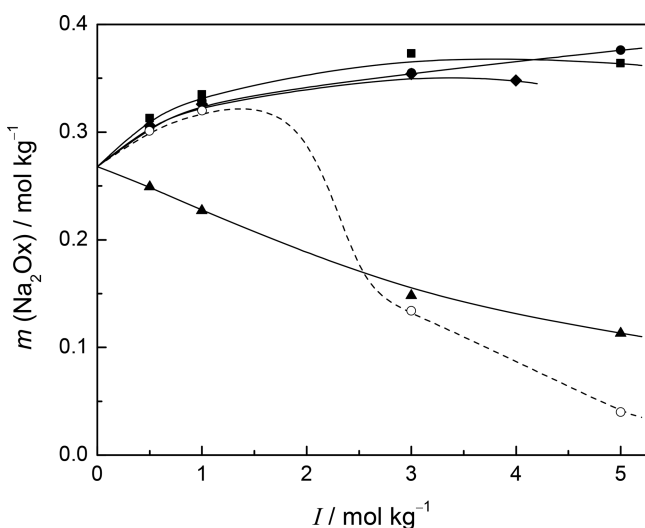

Figure 5. Present experimental solubilities for Na$_2$Ox(s) in electrolyte media not containing Na$^+$ at T = 298.15 K: (●) CsCl(aq); (■) KOH(aq); (◆) KCl(aq); (▲) TMACl(aq); and (○) LiCl(aq). Lines are visual guides only.

Modeling of Na$_2$Ox(s) Solubilities Using Pitzer Equations.

The first Pitzer model to correlate Na$_2$Ox(s) solubilities over wide ranges of solution composition and temperature was that incorporated by Königsberger et al.[11] in their 11-component Bayer liquor (BL) model.[11,31−34] Not long after, Qafoku and Felmy[12] developed a Pitzer model for a more complicated multication system: Na−Ba−Ca−Mn−Sr−Cl−NO$_3$−PO$_4$−SO$_4$−H$_2$O up to high ionic strengths at T = 298.15 K. More recently, Reynolds and Carter[13] derived Pitzer anion−anion and ternary interaction parameters using literature data for the Na$_2$Ox−NaOH−H$_2$O and Na$_2$Ox−NaNO$_3$−H$_2$O systems up to T = 323.15 K.

The Murdoch BL model[11,31−34] includes the major inorganic "impurities" typically found in industrial BLs (sodium carbonate, sulfate, chloride, and fluoride), as well as four carboxylate anions representing organic impurities.[34] For some of the electrolytes relevant to the present study, Pitzer models have been parametrized over wide ranges of conditions. These are (i) NaOH(aq) at 273 < T/K < 523, p ≤ 400 bar, and m ≤ 6 mol·kg^{-1} by Simonson et al.;[35] (ii) NaCl(aq) at 273 < T/K < 573, p ≤ 1000 bar, and m ≤ m_{sat} by Pitzer et al.;[36] and (iii) Na$_2$SO$_4$(aq) at 273 < T/K < 498, p ≤ p_{sat}, and m ≤ 3 mol·kg^{-1} by Holmes and Mesmer.[37] These temperature-dependent Pitzer parametrizations, together with the anion−anion and ternary interaction parameters reported by Pabalan and Pitzer,[38] have been used directly for modeling Na$_2$Ox(s) solubilities in these electrolyte solutions and their mixtures.

Table 6. Solubility of Na_2Ox in CsCl Media at T = 323.15 and 343.15 K and p = 0.1 MPa[a]

$m(CsCl)$[b]/mol·(kg H_2O)$^{-1}$	solubility[c] S/mol·(kg H_2O)$^{-1}$	density[a] ρ/g·cm^{-3}	N[d]	solid phase[e]
T = 323.15 K				
1.026	0.372(19)	1.1585	4	α
4.000	0.469(24)	1.4163	4	α
5.000	0.461(23)	1.4980	4	α
T = 343.15 K				
1.000	0.429(21)	1.1402	4	α
4.000	0.483(24)	1.4166	4	α
5.000	0.522(27)	1.4942	4	α

[a]Standard uncertainties are $u(T)$ = 0.02 K, $u(p)$ = 5 kPa, and $u(\rho)$ = 0.004 g·cm^{-3}. [b]Relative standard uncertainty: $u_r(m)$ = 0.001. [c]All solubilities were determined by titration with $KMnO_4$ from initially undersaturated solutions. Numbers in parentheses are combined standard uncertainties in the last significant figure of the solubility. [d]Total number of titrations performed on replicate solution samples. [e]Solid phase (XRD): α = Na_2Ox.
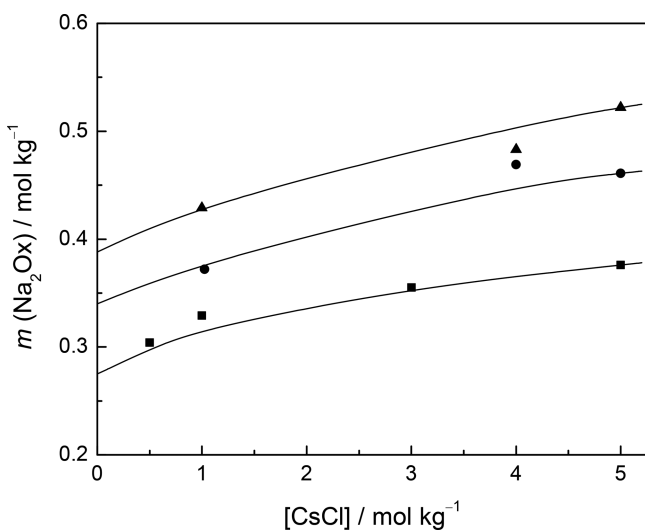
Figure 6. Present experimental solubilities for Na_2Ox(s) in CsCl(aq) media at: (■) T = 298.15 K; (●) T = 323.15 K; and (▲) T = 343.15 K. Lines are visual guides only.
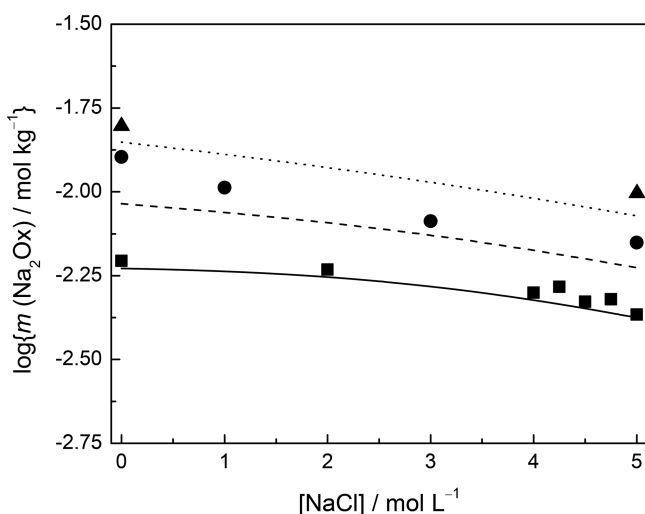

Figure 7. Present experimental solubilities for Na_2Ox(s) in NaOH-(aq)/NaCl(aq) mixtures at $I_c \approx$ 5 M and temperatures: (■) T = 298.15 K; (●) T = 323.15 K; and (▲) T = 343.15 K. Present Pitzer model: solid line, T = 298.15 K; dashed line, T = 323.15 K; and dotted line, T = 343.15 K.

Since the limited solubility of Na_2Ox(s), especially in Na^+-containing media, precludes a direct Pitzer parametrization, the interaction parameters of the well-characterized Na_2SO_4(aq) system reported by Holmes and Mesmer[37] were instead used as proxies for Na_2Ox(aq).[11] Reynolds and Carter[13] have indicated that this choice is consistent with results of their work. For the present study, the Pitzer equations incorporated in the Murdoch BL model were supplemented by the heat capacity and volumetric data for Na_2Ox(aq) reported by Tromans et al.[39]

Using the ChemSage optimizer,[40] the standard Gibbs energy function for Na_2Ox(s) was derived by fitting the aqueous solubility data compiled by Hummel et al.[10] (Figure 1). The results so obtained are broadly consistent with the limited information available in the literature for other thermodynamic properties of the solid. The ChemSage optimizer employs a Bayesian parameters estimation formalism[41] that allows experimental data (solubilities in the present case) and the parameters (the thermodynamic properties of the solid here) to be weighted independently, according to the confidence that can be placed on either set of values. The following series of optimizations investigates the effects of (i) assigning different weights to experimental solubility data, and (ii) allowing the standard molar heat capacity, $C_{p,m}^o$, entropy, S_m^o, and enthalpy of formation, $\Delta_f H_m^o$, for Na_2Ox(s) to vary within certain limits.

Optimization 1. The reported[42] value of $C_{p,m}^o$(Na_2Ox, s, 281 K) = 130 J·K^{-1}·mol^{-1} is inconsistent with the averaged solubility data at both low and high T,[10] where the calculated solubility curve (Figure 1, dotted line) deviates from the experimental data. Assuming the relative apparent molar enthalpy for Na_2Ox(aq) is the same as that of Na_2SO_4(aq),[37] 0.65 kJ·mol^{-1} for $^\phi L$(Na_2SO_4, aq, T = 296.57 K, m = 7.68 mmol·kg^{-1}), the optimized standard enthalpy of formation results in a molar enthalpy of solution, $\Delta_{sol}H_m$ = 17.85 kJ·mol^{-1} for Na_2Ox(s) in water, which falls inside the rather large experimental uncertainty range reported by Menczel et al.,[43] $\Delta_{sol}H_m$(Na_2Ox, s, T = 296.57 K, m = 7.68 mmol·kg^{-1}) = 16.59 ± 1.32 kJ·mol^{-1}. A somewhat higher but more precise value, $\Delta_{sol}H_m$(Na_2Ox, s, T = 298.2 K, 0.1 mol·L^{-1} TMACl) = 18.1 ± 0.1 kJ·mol^{-1}, has been measured in TMACl medium,[44,45] which suggests that dissolution enthalpies in water close to the upper uncertainty limit[43] might be more reasonable. This would support the $\Delta_f H_m^o$ value for Na_2Ox(s) obtained in optimization 1.

Optimization 2. Allowing $C_{p,m}^o$(Na_2Ox, s, T = 298.15 K) to vary over a limited range gives an optimized value of 97.35 J·K^{-1}·mol^{-1} that agrees better with the experimental solubility data (Figure 1, solid line). The deviations at T > 353 K suggest that the two data points at T = 363 and 373 K[14] may be less reliable. The optimized value for $\Delta_{sol}H_m$(Na_2Ox, s, T = 296.57

K, $m = 7.68$ mmol·kg^{-1}) of 17.21 kJ·mol^{-1} is again well within the experimental uncertainty[43] and broadly consistent with the value reported for TMACl medium.[44,45]

Optimization 3. If $C_{p,m}^{\circ}$(Na$_2$Ox, s, $T = 298.15$ K) is allowed to vary completely freely, a value of 54.21 J·K^{-1}·mol^{-1} is obtained, which appears to reproduce the solubility data (Figure 1, dashed line). The optimized value $\Delta_{sol}H_m$(Na$_2$Ox, s, $T = 296.57$ K, $m = 7.68$ mmol·kg^{-1}) of 16.32 kJ·mol^{-1} also agrees with the experimental result.[43] However, close inspection of the calculated solubility curve reveals an implausible inflection point at $T \approx 325$ K, and the optimized value of $C_{p,m}^{\circ}$ is unrealistically small.[42]

These differing evaluations illustrate the dangers inherent in trying to obtain accurate thermodynamic parameters by fitting experimental solubility data alone. The presence of even small errors in the experimental solubilities may produce quite unrealistic values for thermodynamic parameters obtained from such data, particularly parameters involving derivatives.[46] While optimization 2 appears to be a reasonable compromise of all presently available data, no sensible decision on the "best" model can be made until accurate measurements of $C_{p,m}^{\circ}$ for Na$_2$Ox(s) and $^{\phi}L$ for Na$_2$Ox(aq) become available. On the other hand, the solubility predictions resulting from the three optimizations virtually coincide with each other in the temperature range of interest to this study ($293 < T/K < 343$). Outside this temperature range, however, more accurate solubility data are required for establishing a thermodynamically consistent model.

The present Pitzer model enables an independent comparison to be made with the results for the various Na$^+$-containing ternary systems reported in this work along with the values reported by Norris[14] in NaOH(aq) and by Hill et al.[15] in Na$_2$SO$_4$(aq), as none of these data were employed in the parametrization of the model.

Figures 2, 3, 7, and 8 compare the solubilities of Na$_2$Ox(s) predicted from the present Pitzer model and the experimental values from Tables 2−4 in NaOH(aq), NaCl(aq) and some of their mixtures, respectively, and in Na$_2$SO$_4$(aq).[15] The agreement is good for all of these Na$^+$-containing solutions at all temperatures investigated. Unlike the model of Reynolds and Carter,[13] neither anion−anion nor ternary Pitzer
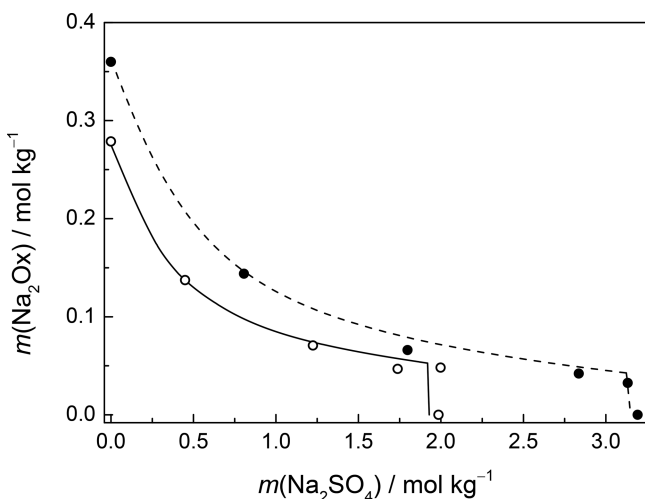
parameters were required for Na$_2$Ox(aq)−NaOH(aq) mixtures (Figure 2). However, for Na$_2$Ox(aq)−NaCl(aq) mixtures (Figure 3) the solubility model was slightly improved by employing just one temperature-independent asymmetric-mixing anion−anion parameter, $^S\theta_{Cl,Ox} = 0.05$. In the (ternary) mixed electrolyte solutions (Figure 7), the predicted solubilities are slightly lower than the experimental values at all three temperatures. However, these differences are either within or close to the experimental uncertainties (Tables 2−4). The present model also agrees well with the Na$_2$Ox(s) solubility data in NaOH(aq) reported by Norris[14] (see Figure 6 of ref 11). It should be emphasized that solubility data for Na$_2$Ox(s) in Na$_2$SO$_4$(aq)[15] were also predicted satisfactorily without using anion−anion and ternary interaction parameters (Figure 8).

The solubility of Na$_2$Ox(s) in Na$^+$-containing salt solutions reflects the activity coefficients, $\gamma_\pm$, of Na$_2$Ox(aq) in these media. Figure 9 compares $\gamma_\pm$ values generated using the present
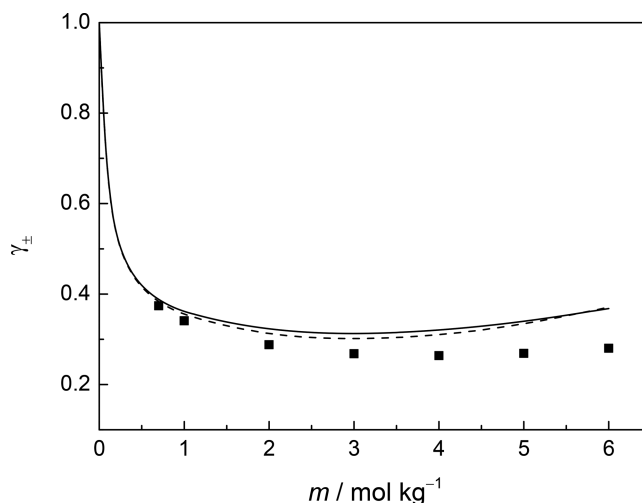

Figure 9. Mean activity coefficients, $\gamma_\pm$, for Na$_2$Ox(aq) and Na$_2$SO$_4$(aq) as a function of added electrolyte concentration at $T = 298.15$ K. Experimental data: (■) Na$_2$SO$_4$(aq) in NaCl(aq).[47−49] Present Pitzer model: solid line, Na$_2$Ox(aq) in NaCl(aq), and dashed line, Na$_2$Ox(aq) in NaOH(aq).

model for Na$_2$Ox(aq) in NaCl(aq) and NaOH(aq) with the experimental activity coefficients reported for Na$_2$SO$_4$(aq) in NaCl(aq).[47−49] The quite good agreement confirms that activity coefficients for Na$_2$Ox(aq) are well-approximated by those for Na$_2$SO$_4$(aq). Of greater consequence, they show that $\gamma_\pm$(Na$_2$Ox(aq)) is essentially constant over the studied concentration ranges of added electrolyte.

■ CONCLUDING REMARKS

The results of this work have significant implications for thermodynamic studies of equilibria in concentrated electrolyte solutions. The observed differences between added background ("swamping") electrolytes, apart from those due to common ions and competitive complexation, are commonly assigned to "specific ion interactions". This terminology implies that the impact of increasing electrolyte concentration is "specific", i.e. due to distinct contributions from interactions among the ions present as expressed, for example, in the SIT,[18] Pitzer,[16] and Scatchard[50] equations.

Figure 8. Experimental solubilities for Na$_2$Ox(s) in Na$_2$SO$_4$(aq) media[15] at: (○) $T = 298.15$ K and (●) $T = 333.15$ K. Present Pitzer model: solid line, $T = 298.15$ K, and dashed line, $T = 333.15$ K.

In the present context, the focus on specific ion interactions seems appropriate for TMACl(aq) where the $Na_2Ox(s)$ solubility is markedly different from every other added electrolyte (Figure 5). However, such a focus obscures some remarkable similarities. Thus, the solubility of $Na_2Ox(s)$ in Na^+-containing salt solutions is evidently only slightly affected by the nature of the anions (Figure 4). Likewise, exchanging K^+ for Cs^+ is of little consequence (Figure 5). This type of "nonspecific" behavior is important (indeed, frequently predominant) and should not be overlooked. Evidently, there are interactions between ions in concentrated electrolyte solutions that are indifferent to the chemical nature of the ion and that vary in ways that track (possibly coincidentally) changes in ionic strength. It is reasonable to think that such effects are caused by ionic charge, even though in concentrated solutions, these are not the long-range Coulombic interactions associated with I in dilute solutions, as is well understood.[16,18] Such effects are, presumably, the explanation for the often-found general dependence of equilibrium constants on I in so-called "indifferent (inert) background" electrolytes even up to high concentrations.[51] However, theoretical (as distinct from computational) progress in this area has, unfortunately, been very limited.[52]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00690.

Graphs showing aqueous activity coefficients of some binary electrolyte solutions and $Na_2Ox(s)$ solubilities in $(Na,Cs)Cl(aq)$ mixtures (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*Tel: +61 8 9360 2301; Fax: +61 8 9360 6498; E-mail: E. Koenigsberger@murdoch.edu.au.

ORCID ⓘ
Peter M. May: 0000-0003-0434-3855
Erich Königsberger: 0000-0002-4606-0741

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Lever, G. Identification of Organics in Bayer Liquors. *Light Metals* **1978**, 71−83.

(2) Guthrie, J. D.; The, P. J.; Imbrogno, W. D. Characterization of Organics in Bayer Liquors. *Light Metals* **1984**, 127−146.

(3) Machold, T.; Macedi, E.; Laird, D. W.; May, P. M.; Hefter, G. T. Decomposition of Bayer Process Organics: Low-Molecular-Weight Carboxylates. *Hydrometallurgy* **2009**, 99, 51−57.

(4) Reynolds, J. G.; Cooke, G. A.; Herting, D. L.; Warrant, R. W. Salt Mineralogy of Hanford High-level Waste Staged for Treatment. *Ind. Eng. Chem. Res.* **2013**, 52, 9741−9751.

(5) Toste, A. P. Degradation of Chelating and Complexing Agents in an Irradiated, Simulated Mixed Waste. *J. Radioanal. Nucl. Chem.* **1992**, 161, 549−559.

(6) Poirier, M. R.; Hay, M. S.; Herman, D. T.; Crapse, K. P.; Thaxton, G. D.; Fink, S. D. Removal of Sludge Heels in Savannah River Site Waste Tanks with Oxalic Acid. *Sep. Sci. Technol.* **2010**, 45, 1858−1875.

(7) Rao, V. K.; Pius, I. C.; Subbarao, M.; Chinnusamy, A.; Natarajan, P. R. Precipitation of Plutonium Oxalate from Homogeneous Solutions. *J. Radioanal. Nucl. Chem.* **1986**, 100, 129−134.

(8) Dellien, I.; Lokke, O. C.; Korvenranta, J.; Nasakkala, E. Thermodynamic Properties of Iron Oxalates and Malonates in Perchlorate Medium. *Acta Chem. Scand.* **1977**, 31a, 473−479.

(9) Linke, W. F.; Seidell, A. *Solubilities of Inorganic and Metal-Organic Compounds*, 4th Ed.; American Chemical Society: Washington DC, 1965.

(10) Hummel, W.; Anderegg, G.; Rao, L.; Puigdomènech, I.; Tochiyama, O. *Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni, and Zr with Selected Organic Ligands; NEA-OECD Chemical Thermodynamics*; Elsevier: Amsterdam, 2005; Vol. 9.

(11) Königsberger, E.; Eriksson, G.; May, P. M.; Hefter, G. Comprehensive Model of Synthetic Bayer Liquors. Part 1. Overview. *Ind. Eng. Chem. Res.* **2005**, 44, 5805−5814.

(12) Qafoku, O.; Felmy, A. R. Development of Accurate Chemical Equilibrium Models for Oxalate Species to High Ionic Strength in the System: Na-Ba-Ca-Mn-Sr-Cl-NO_3-PO_4-SO_4-H_2O at 25 °C. *J. Solution Chem.* **2007**, 36, 81−95.

(13) Reynolds, J. G.; Carter, R. Pitzer Model Anion-Anion and Ternary Interaction Parameters for the $Na_2C_2O_4$-NaOH-H_2O and $Na_2C_2O_4$-$NaNO_3$-H_2O Systems. *J. Solution Chem.* **2015**, 44, 1358−1366.

(14) Norris, W. H. H. The System Oxalic Acid - Sodium Hydroxide - Water. *J. Chem. Soc.* **1951**, 0, 1708−1715.

(15) Hill, L. M.; Goulden, T. P.; Hatton, E. Equilibria in Ternary Systems Containing Oxalates. *J. Chem. Soc.* **1946**, 78−81.

(16) Pitzer, K. S. Ion Interaction Approach: Theory and Data Correlation. In *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, USA, 1991; pp 75−153.

(17) Rossotti, H. *The Study of Ionic Equilibria*; Longman: London, 1978.

(18) *Modelling in Aquatic Chemistry*; Grenthe, I., Puigdomenech, I., Eds.; NEA-OECD: Paris, 1997.

(19) Sipos, P.; Bódi, I.; May, P. M.; Hefter, G. T. The Ionic Product of Water in Concentrated Tetramethylammonium Chloride Solutions. *Talanta* **1997**, 44, 617−620.

(20) Tromans, A.; Hefter, G. T.; May, P. M. Potentiometric Investigation of the Weak Association of Sodium and Oxalate Ions in Aqueous Solution at 25 °C. *Aust. J. Chem.* **2005**, 58, 213−217.

(21) Sipos, P.; May, P. M.; Hefter, G. T. Carbonate Removal from Concentrated Hydroxide Solutions. *Analyst* **2000**, 125, 955−958.

(22) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*; MacMillan: London, 1969.

(23) Capewell, S. G.; Hefter, G. T.; May, P. M. Improved Apparatus and Procedures for the Measurement of Solubility of Rapidly Equilibrating Solid-Liquid Systems to 90 °C. *Rev. Sci. Instrum.* **1999**, 70, 1481−1485.

(24) Hefter, G. T. Some Highs and Lows (and In-betweens) of Solubility Measurements of Solid Electrolytes. *Pure Appl. Chem.* **2013**, 85, 2077−2087.

(25) *Alkali Metal and Ammonium Chlorides in Water and Heavy Water; Solubility Data Series*; Cohen-Adad, R., Lorimer, J. W., Eds.; Pergamon: Oxford, 1991; Vol. 47.

(26) May, P. M. JESS at Thirty: Strengths, Weaknesses and Future Needs in the Modelling of Chemical Speciation. *Appl. Geochem.* **2015**, 55, 3−16.

(27) Sipos, P. M.; Hefter, G.; May, P. M. Viscosities and Densities of Highly Concentrated Aqueous MOH Solutions (M^+ = Li^+, Na^+, K^+, Cs^+ and $(CH_3)_4N^+$) at 25 °C. *J. Chem. Eng. Data* **2000**, 45, 613−617.

(28) Marcus, Y. *Ions in Solution and Their Solvation*; Wiley: Hoboken, USA, 2015.

(29) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; London: Butterworth, 1970.

(30) Marcus, Y. Tetraalkylammonium Ions in Aqueous and Non-aqueous Solutions. *J. Solution Chem.* **2008**, *37*, 1071−1098.

(31) Königsberger, E.; May, P. M.; Hefter, G. Comprehensive Model of Synthetic Bayer Liquors. Part 3. Sodium Aluminate Solutions and the Solubility of Gibbsite and Boehmite. *Monatsh. Chem.* **2006**, *137*, 1139−1149.

(32) Schrödle, S.; Königsberger, E.; May, P. M.; Hefter, G. Heat Capacities of Aqueous Sodium Hydroxide/Aluminate Mixtures and Prediction of the Solubility Constant of Boehmite up to 300 °C. *Geochim. Cosmochim. Acta* **2010**, *74*, 2368−2379.

(33) Hnedkovsky, L.; Königsberger, E.; Königsberger, L.-C.; Cibulka, I.; Schrödle, S.; May, P. M.; Hefter, G. Densities of Concentrated Alkaline Aluminate Solutions at Temperatures from (323 to 573) K and 10 MPa Pressure. *J. Chem. Eng. Data* **2010**, *55*, 1173−1178.

(34) Königsberger, E.; Bochmann, S.; May, P. M.; Hefter, G. Thermodynamics of Impurities in Hydrometallurgical Processes. *Pure Appl. Chem.* **2011**, *83*, 1075−1084.

(35) Simonson, J. M.; Mesmer, R. E.; Rogers, P. S. Z. The Enthalpy of Dilution and Apparent Molar Heat Capacity of Sodium Hydroxide-(aq) to 523 K and 40 MPa. *J. Chem. Thermodyn.* **1989**, *21*, 561−584.

(36) Pitzer, K. S.; Peiper, J. C.; Busey, R. H. Thermodynamic Properties of Aqueous Sodium Chloride Solutions. *J. Phys. Chem. Ref. Data* **1984**, *13*, 1−102.

(37) Holmes, H. F.; Mesmer, R. E. Thermodynamics of Aqueous Solutions of the Alkali Metal Sulfates. *J. Solution Chem.* **1986**, *15*, 495−518.

(38) Pabalan, R. T.; Pitzer, K. S. Thermodynamics of Concentrated Electrolyte Mixtures and the Prediction of Mineral Solubilities to High Temperatures for Mixtures in the System Na-K-Mg-Cl-SO$_4$-OH-H$_2$O. *Geochim. Cosmochim. Acta* **1987**, *51*, 2429−2443.

(39) Tromans, A.; Königsberger, E.; May, P. M.; Hefter, G. Heat Capacities and Volumes of Aqueous Dicarboxylate Salt Solutions of Relevance to the Bayer Process. *J. Chem. Eng. Data* **2005**, *50*, 2019−2025.

(40) Königsberger, E.; Eriksson, G. A New Optimization Routine for ChemSage. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **1995**, *19*, 207−214.

(41) Königsberger, E.; Gamsjäger, H. Analysis of Phase Diagrams Employing Bayesian Excess Parameter Estimation. *Monatsh. Chem.* **1990**, *121*, 119−127.

(42) Cherbov, S. I.; Chernyak, E. L. Measurement of the Specific Heat of Powdered Aluminium Oxide and Sodium Oxalate. *Zh. Prikl. Khim.* **1937**, *10*, 1220−1222.

(43) Menczel, B.; Apelblat, A.; Korin, E. The Molar Enthalpies of Solution and Solubilities of Ammonium, Sodium and Potassium Oxalates in Water. *J. Chem. Thermodyn.* **2004**, *36*, 41−44.

(44) Königsberger, E.; Königsberger, L.-C. Thermodynamic Modeling of Crystal Deposition in Humans. *Pure Appl. Chem.* **2001**, *73*, 785−797.

(45) Sádovská, G.; Wolf, G. Enthalpy of Dissolution and Thermal Dehydration of Calcium Oxalate Hydrates. *J. Therm. Anal. Calorim.* **2015**, *119*, 2063−2068.

(46) Königsberger, E. Prediction of Electrolyte Solubilities from Minimal Thermodynamic Information. *Monatsh. Chem.* **2001**, *132*, 1363−1386.

(47) Platford, R. F. Isopiestic Measurements on the System H$_2$O-NaCl-Na$_2$SO$_4$ at 25 °C. *J. Chem. Eng. Data* **1968**, *13*, 46−48.

(48) Wu, Y. C.; Rush, R. M.; Scatchard, G. Osmotic and Activity Coefficients for Binary Mixtures of Sodium Chloride, Sodium Sulfate, Magnesium Sulfate, and Magnesium Chloride in Water at 25 °C. I. Isopiestic Measurements on the Four Systems with Common Ions. *J. Phys. Chem.* **1968**, *72*, 4048−4053.

(49) Rush, R. M. Parameters for the Calculation of Osmotic and Activity Coefficients and Tables for Twenty-two Aqueous Mixtures of Two Electrolytes at 25 °C. *U.S. At. Energy Comm. Rep., ORNL-4402*; Oak Ridge National Laboratory: Tennessee, U.S.A., 1969.

(50) Scatchard, G. Excess Free Energy and Related Properties of Solutions Containing Electrolytes. *J. Am. Chem. Soc.* **1968**, *90*, 3124−3127.

(51) Hefter, G. T.; May, P. M. Ionic strength lives! *Chem. Br.* **1991**, *27*, 620.

(52) May, P. M.; Rowland, D. Thermodynamic Modeling of Aqueous Electrolyte Systems: Current Status. *J. Chem. Eng. Data* **2017**, *62*, 2481−2495.