Comment on "Volumetric properties of aqueous solution of lithium tetraborate from 283.15 to 363.15 K at 101.325 kPa" [J. Chem. Thermodyn. 120 (2018) 151–156] and its Corrigendum [J. Chem. Thermodyn. 123 (2018) 195–197]

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ABSTRACT

Inconsistencies in the apparent molar volume values for aqueous lithium tetraborate solutions reported by Guo and co-workers are exacerbated in the Corrigendum by Cao and co-workers. At 363 K the discrepancies relative to the corrected values in this work exceed 20 cm^3 mol^{-1} and 100 cm^3 mol^{-1} near 0.01 mol kg^{-1} for Guo et al. and Cao et al., respectively.

TEXT

The purpose of this short communication is to alert readers to an ongoing problem with the published volumetric data for aqueous lithium tetraborate. Recently, Guo et al. [1] reported density values for such solutions in the temperature range from (283.15 to 363.15) K and molality from (0.01 to 0.12) mol kg^{-1}. Apparent molar volumes, for Li$_2$B$_4$O$_7$(aq) were calculated according to Eq. (1)

$$ \tag{1} $$

where is the density of pure water at the same pressure and temperature as the measurement, is the density of the lithium tetraborate solution, is the molality of the solution (moles of Li$_2$B$_4$O$_7$ per kg of water) and (= 169.12 g mol^{-1}) is the molecular mass of Li$_2$B$_4$O$_7$.

While entering these data into our JESS database, we found that the densities and apparent molar volumes reported by Guo et al. [1] were not in accord with Eq. (1). Cao et al. [2] also recognised this issue and published a Corrigendum to Guo et al.'s [1] apparent molar volumes. However, in attempting to address the issue Cao et al. [2] have used values differing from those recommended by IAPWS (International Association for the Properties of Water and Steam) [3] (Fig. 1). This leads to significant discrepancies. Values of consistent with the

IAPWS 95 EOS for pure water [3] have been calculated as part of this work and are given in Table 1.
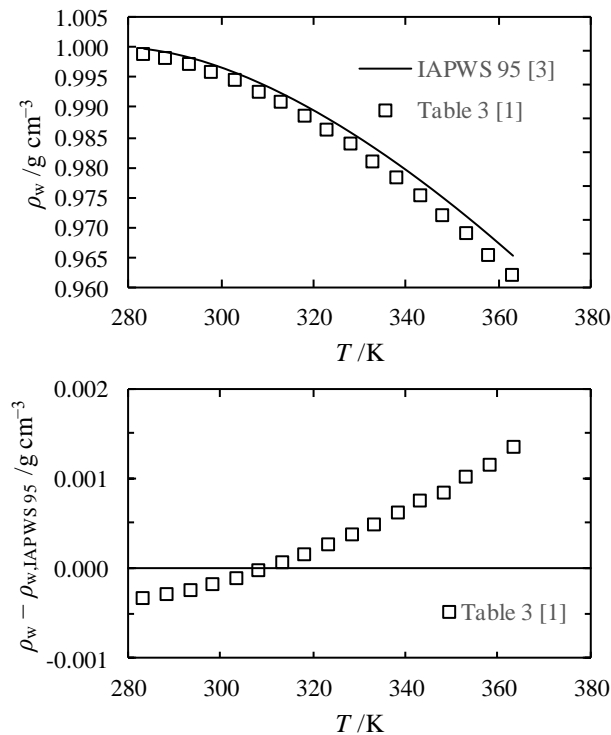

Fig. 1. Density of pure water according to Table 3 of Guo et al. [1] compared to the IAPWS 95 EOS [3].

The errors in Guo et al. [1] and Cao et al. [2] are largest at the highest temperature (Fig. 2) where the deviations from the accepted density of pure water are largest. Guo et al.'s Fig. 4 and Tables 4 and 5 [1], which depend heavily on the values of the apparent molar volumes, are therefore inaccurate and should not be used. Far from confirming that the empirical Pitzer equations optimised by Guo et al. [1] are "reliable" as suggested, this result merely emphasises the underappreciated fact that Pitzer equations with large numbers of basis functions (more than 28 in this case) tend to overfit whatever data are regressed [4] and therefore offer minimal or no predictive capability.

Table 1. Apparent molar volumes of $Li_2B_4O_7(aq)$ calculated using Eq. (1) with   from Guo et al. [1] and   from IAPWS 95 [3].

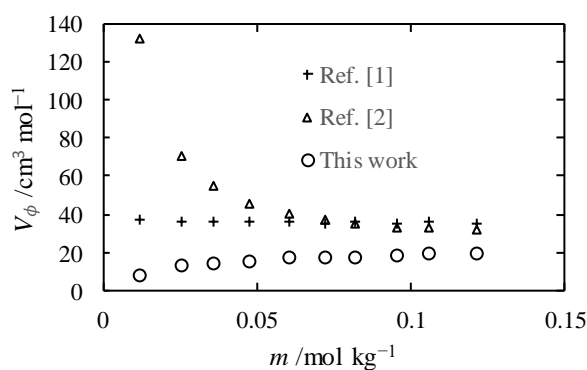| /mol kg^{-1}	/cm^3 mol^{-1}	/cm^3 mol^{-1}	/cm^3 mol^{-1}	/cm^3 mol^{-1}	/cm^3 mol^{-1}
	$T = 283.15$ K	$T = 288.15$ K	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K
0.12151	11.60	13.38	14.83	15.98	16.95
0.10612	12.09	13.87	15.37	16.62	17.57
0.09540	10.45	12.33	13.91	15.11	16.19
0.08169	9.72	11.69	13.19	14.50	15.55
0.07231	8.59	10.55	12.13	13.49	14.56
0.06068	7.70	9.74	11.48	12.80	13.95
0.04792	5.47	7.67	9.49	11.00	12.29
0.03583	3.34	5.47	7.40	9.19	10.43
0.02529	-0.86	1.80	4.21	6.02	7.46
0.01180	-8.67	-6.24	-3.46	-1.08	0.54
	$T = 308.15$ K	$T = 313.15$ K	$T = 318.15$ K	$T = 323.15$ K	$T = 328.15$ K
0.12151	17.75	18.35	18.89	19.20	19.45
0.10612	18.43	19.06	19.62	20.02	20.27
0.09540	16.95	17.68	18.22	18.59	18.89
0.08169	16.47	17.24	17.79	18.15	18.55
0.07231	15.49	16.26	16.91	17.34	17.70
0.06068	14.94	15.73	16.40	16.97	17.28
0.04792	13.19	14.04	14.74	15.32	15.80
0.03583	11.70	12.65	13.39	13.99	14.45
0.02529	8.56	10.00	10.76	11.33	12.11
0.01180	2.31	3.13	5.09	5.79	6.98
	$T = 333.15$ K	$T = 338.15$ K	$T = 343.15$ K	$T = 348.15$ K	$T = 353.15$ K
0.12151	19.65	19.68	19.68	19.52	19.34
0.10612	20.45	20.54	20.50	20.38	20.24
0.09540	19.12	19.14	19.13	19.04	18.92
0.08169	18.75	18.83	18.88	18.84	18.64
0.07231	17.96	17.95	18.05	18.05	17.88
0.06068	17.66	17.72	17.74	17.82	17.69
0.04792	16.15	16.32	16.44	16.63	16.36
0.03583	15.03	15.37	15.37	21.32	15.55
0.02529	12.67	12.89	13.45	13.35	13.63
0.01180	7.69	7.70	8.48	9.64	9.83
	$T = 358.15$ K	$T = 363.15$ K			
0.12151	19.09	19.92			
0.10612	19.92	19.55			
0.09540	18.60	18.23			
0.08169	18.34	17.98			
0.07231	17.59	17.24			
0.06068	17.43	17.10			
0.04792	16.14	15.84			
0.03583	15.41	14.86			
0.02529	13.19	13.03			
0.01180	10.31	8.71			

Fig. 2. Apparent molar volumes for lithium tetraborate at 363.15 K.

Attributes of the apparent molar volumes calculated in this work – in contrast to those of Guo et al. [1] and Cao et al. [2] – are that they follow the correct trend at low concentrations as required by Debye-Hückel theory (Fig. 2) and they are in accord with the relation ——

(Fig. 3), which is appropriate for a 'structure-breaking' electrolyte (Ref. [5] and references within).
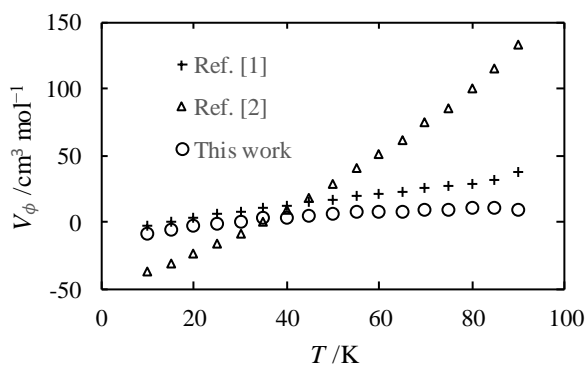

Fig. 3. Apparent molar volumes for lithium tetraborate at 0.018 mol kg^{-1}.

Errors of this kind occur surprisingly frequently [6]. The ongoing cooperative effort between major journals such as The Journal of Chemical Thermodynamics and the NIST TRC Group (the Thermodynamics Research Center of the U.S. National Institute of Standards and Technology) is designed to improve the quality of published experimental thermophysical property data by identifying inconsistencies such as those in Guo et al. [1] prior to publication [6]. However, it appears that in this case the chemical substance in question (Li$_2$B$_4$O$_7$(aq)) was not covered by that program. The onus for ensuring that electrolyte solution properties are correctly published thus lies with authors and reviewers. To detect and eliminate calculation errors of this nature, automated property conversion facilities associated with processable databases for physicochemical properties [7] and solubility [8] of electrolyte solutions are an invaluable tool. Fitting empirical equations with large numbers of adjustable parameters is not recommended.

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