COMPONENTS:	EVALUATOR:
(1) Lithium Bromate; $LiBrO_3$; [13550-28-2]	H. Miyamoto Niigata University Niigata, Japan and M. Salomon US Army ET & DL Fort Monmouth, NJ, USA
(2) Water; H_2O; [7732-18-5]	September, 1984

CRITICAL EVALUATION:

THE BINARY SYSTEM

Data for the solubility of $LiBrO_3$ in water has been reported in four publications (1-4). Mylius and Funk (1) reported the solubility at 291 K, but a typographical error appears to exist: i.e., they reported the solubility as 60.4 mass % or 153.7 g/100g H_2O, the latter being equivalent to 60.58 mass % (evaluators). While it would appear that the original experimental quantity is the 60.4 mass % value, both values are still too low for 291 K, and were therefore rejected (see below).

Simmons and Waldeck (2) reported solubilities over the temperature range of 278-373 K, and Averko-Antonovich (3) reported results over the wide temperature range of 228-416 K. Chemical analyses of the solid phases showed that above 323 K the solid phase is the anhydrous salt, and below 323 K the solid phase is the monohydrate $LiBrO_3.H_2O$ [55698-66-3]. The existence of the monohydrate as the solid phase in the binary system was confirmed by Campbell et al. (4) who studied ternary systems, and using the Schreinemakers' method of wet residues found the monohydrate at 298.2 K.

A summary of the experimental solubilities are given in Table 1. In this table, the evaluators converted the original mass % units to mole fraction units, and the original units and conversions to mol kg^{-1} units can be found in the compilations.

Table 1. Summary of Experimental Solubilities as a Function of Temperature

T/K	χ	Solid Phase	(ref)	T/K	χ	Solid	(ref)
272.1	0.01511	ice	(3)	298.2	0.2016	$LiBrO_3.H_2O$	(2)
268.4	0.03291	"	(3)	298.2	0.2033	"	(4)
263.4	0.05563	"	(3)	308.2	0.2172	"	(2)
253.0	0.08178	"	(3)	309.1	0.2194	"	(3)
233.2	0.1264	"	(3)	318.2	0.2411		(3)
				323.2	0.2510	"	(2)
228.2	0.1399	$LiBrO_3.H_2O$	(3)	323.2	0.2538	"	(3)
233.2	0.1423	"	(3)				
236.5	0.1463	"	(3)	277.2	0.2119	$LiBrO_3$	(3)
241.7	0.1494	"	(3)	290.7	0.2227	"	(3)
246.7	0.1520	"	(3)	318.2	0.2538	"	(3)
252.2	0.1568	"	(3)	318.2	0.2411[a]	"	(3)
256.7	0.1585	"	(3)	326.2	0.2595	"	(2)
262.4	0.1635	"	(3)	328.2	0.2626	"	(3)
266.4	0.1681	"	(3)	329.2	0.2614	"	(2)
273.2	0.1742	"	(3)	338.2	0.2740	"	(3)
278.2	0.1765	"	(2)	343.7	0.2786	"	(2)
288.2	0.1873	"	(2)	353.2	0.2955	"	(3)
291.2	0.1693[a]	"	(1)	358.2	0.2996	"	(2)
291.2	0.1704[a]	"	(1)	373.2	0.3214	"	(2)
293.2	0.1954	"	(3)	373.7	0.3292	"	(3)
298.1	0.2026	"	(3)	384.2	0.3345[a]	"	(3)
				394.2	0.3659	"	(3)
				416.2	0.4233	"	(3)

[a]Rejected data points (see text for discussion).

All data in the above table were fitted to the smoothing equation.

$$Y_\chi = A/(T/K) + B\ell n(T/K) + C + D(T/K) \quad [1]$$

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CRITICAL EVALUATION:

The complex function Y_X in eq. [1] has been defined previously in the PREFACE and in previous critical evaluations (e.g. see the critical evaluation for the binary $LiClO_3$-H_2O system). In applying eq. [1] to the mole fraction solubilities in Table 1, we examined each polytherm individually. For each polytherm, all data were initially fitted to eq. [1] and data points rejected when the difference between the experimental and calculated solubilities exceeded two times the standard error of estimate (i.e. for $X_{exptl} - X_{calcd} > 2\sigma_X$). Based on the final tentative and recommended solubilities, the evaluators plotted small portions of the phase diagram in the regions of phase transitions, and our results for the transition temperatures are given below.

Polytherm for Ice as the Solid Phase. The only data reported for this region of the phase diagram are those of Averko-Antonovich (3). Analyses by fitting these data to eq. [1] showed that all data were acceptable. The smoothing equation for these data is:

$$Y_X = -63264.50/(T/K) - 510.3943\ell n(T/K) + 2812.7729 + 1.032927(T/K) \quad [2]$$

$$\sigma_y = 0.0025 \qquad \sigma_x = 0.0013$$

The smoothed solubilities calculated from eq. [2] are designated as *tentative*, and values at rounded temperatures are given in Table 2.

Polytherm for $LiBrO_3.H_2O$ as the Solid Phase. All data from references (1-4) were fitted to eq. [1], and only the data of Mylius and Funk (1) had to be rejected. The source of the error in this study cannot be ascertained, but the authors did state that the solid phase was the anhydrous salt. The error in identification of the solid phase and in the low values of the solubility at 291 K indicates a systematic error. The smoothed solubilities based on the data from references (2-4) are designated as *recommended* solubilities, and values at rounded temperatures are given in Table 2. The smoothing equation is given in eq. [3].

$$Y_X = -6721.204/(T/K) - 53.5559\ell n(T/K) + 293.2835 + 0.113089(T/K) \quad [3]$$

$$\sigma_y = 0.0071 \qquad \sigma_x = 0.0011$$

The data of Averko-Antonovich (3) indicates a transition from ice as the solid phase to the monohydrate at around 228 K. The evaluators' graphical analysis of the solubility data in this region show this transition to occur at 230.0 K at a mole fraction solubility of $\chi = 0.1408$.

Polytherm for $LiBrO_3$ as the Solid Phase. The only solubility data for which the solid phase is the anhydrous salt was reported in (2 and 3). Two data points at 318.2 K and 384.2 K from (3) had to be rejected, but the remaining 14 data points could be fitted to the smoothing equation with the following results:

$$Y_X = -4827.171/(T/K) - 31.1588\ell n(T/K) + 174.786 + 0.056935(T/K) \quad [4]$$

$$\sigma_y = 0.011 \qquad \sigma_x = 0.0021$$

The smoothed solubilities calculated from eq. [4] are designated as *recommended* values and are given in Table 2.

Both Simmons and Waldeck (2) and Averko-Antonovich (3) found the temperature for the $LiBrO_3.H_2O \longrightarrow LiBrO_3$ transition to be 325 K, and the evaluators find this transition to occur at 325.3 K at a solubility of $\chi = 0.2587$.

Simmons and Waldeck attempted to measure the melting point of anhydrous $LiBrO_3$, and although some decomposition was observed, an "average" value of 521 K was reported. Graphical extrapolation (2) yielded a melting point of 533 K, and eq. [4] predicts a value of 502.8 K.

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CRITICAL EVALUATION:

All tentative and recommended mole fraction solubilities are given in Table 2, and the complete phase diagram based on these data is given in Figure 1.

Table 2. Tentative and Recommended Solubilities Calculated from the Smoothing Equations [2], [3] and [4]

T/K	ice[a]	$LiBrO_3.H_2O$ [b]	$LiBrO_3$[b]
228.2	0.1491[m]	0.1397	
230.0[c]	0.1408	0.1408	
233.2	0.1264	0.1432	
243.2	0.09969	0.1501	
253.2	0.08160	0.1570	
263.2	0.05544	0.1645	
268.2	0.03512	0.1686	
273.2		0.1730	
278.2		0.1777	0.2123[m]
283.2		0.1829	0.2170[m]
293.2		0.1949	0.2264[m]
298.2		0.2019	0.2312[m]
303.2		0.2097	0.2360[m]
313.2		0.2284	0.2460[m]
323.2		0.2527	0.2565[m]
325.3[c]		0.2587	0.2587
333.2			0.2677
343.2			0.2800
353.2			0.2934
363.2			0.3082
373.2			0.3255
383.2			0.3431
393.2			0.3639
403.2			0.3875
413.2			0.4144

[a] Tentative solubilities.

[b] Recommended solubilities

[c] Transition temperatures evaluated graphically by the evaluators.

[m] Metastable solubilities.

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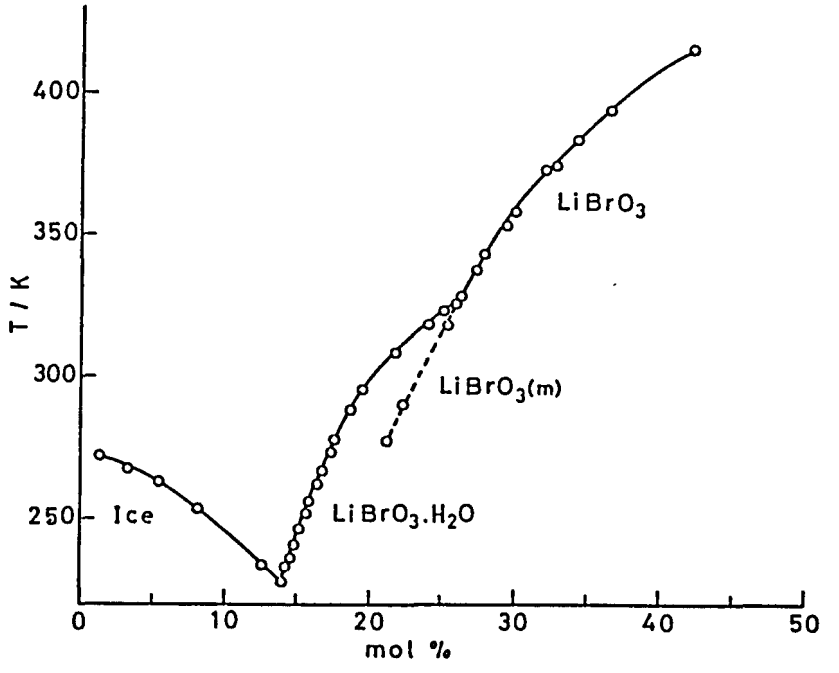
CRITICAL EVALUATION:



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