Density and Refractive Index for Boric Acid + Potassium Chloride + Water and Disodium Tetraborate + Potassium Chloride + Water Systems at (20, 25, and 30) °C

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Densities and refractive indices for two ternary systems, H_3BO_3 (1) + KCl (2) + H_2O (3) and $Na_2B_4O_7$ (1) + KCl (2) + H_2O (3), have been measured at (20, 25, and 30) °C. Experimental study of the first ternary system was carried out for four values of total molality of the mixture ≈(0.25, 0.50, 0.76, and 1.0) mol·kg^{-1}. Values for the dry base mole fraction of boric acid, $y_1 = m_1/(m_1 + m_2)$, for each of the total molalities were approximately 0.25, 0.50, and 0.75. The total molalities of the second ternary system were approximately (0.10, 0.12, 0.14, and 0.17) mol·kg^{-1}. Variations of the dry base mole fraction of disodium tetraborate, y_1, were similar to those of the preceding ternary system. Data are also presented for the density and refractive index of binary systems including boric acid + water and disodium tetraborate + water at the three temperatures cited above. The range of concentrations in the measurements was 0.05−1.0 mol·kg^{-1} for the H_3BO_3 (1) + H_2O (2) system and 0.025−0.17 mol·kg^{-1} for the $Na_2B_4O_7$ (1) + H_2O (2) system. For each ternary system, including the binary systems, the experimental results were fitted to an empirical equation with four non-temperature-dependent parameters.

Introduction

Regions I and II of northern Chile include extensive desert and semidesert areas, which are dominated by saline substrates produced by geologic, geomorphologic, and climatic conditions. In this context, different salts including chlorides and sulfates predominate and are strongly represented in soils, rocks, and waters.[1] About 75 different basins have been observed in this region containing salt deposits, with the Salar de Atacama being one of the most important due to its high content of K^+, Na^+, Mg^{2+}, Ca^{2+}, B^{3+}, Li^+, SO_4^{2-}, and Cl^- ions. The brines of this basin contain boron in the form of borate and free boric acid.[2] The present paper forms part of a broad program to obtain experimental data on the characteristics of multicomponent saline brines in Chile, with particular interest in those containing boron compounds.

Experimental values on the densities of aqueous binary solutions containing boric acid (H_3BO_3) or disodium tetraborate ($Na_2B_4O_7$) are scarce. A few data appear in the International Critical Table,[3] and a few have been reported by Linke and Seidell[4] for saturated conditions. Novotny and Söhnel[5] developed a correlation to estimate densities of binary aqueous solutions for a number of inorganic substances, which include H_3BO_3 and $Na_2B_4O_7$. To our knowledge, there are no experimental data available on the densities of multicomponent aqueous mixtures containing the boron compounds mentioned above. Similarly, there is a lack of experimental data on the refractive index for aqueous multicomponent saline systems. A relatively recent study[6] emphasized the value of using the refractive index for following evaporative processes, as it was a property relatively sensitive to changes in brine concentrations. These authors carried out measurements of refractive index on naturally occurring $Na^+-Cl^--SO_4^{2-}$ brines and proposed a generalized correlation between refractive index and total salt concentration valid between (10 and 60) °C.

The present data form a basic contribution to the knowledge on the chemical nature of the salt brines of northern Chile, which are both interesting in terms of basic geochemistry and also in some cases of potentially high commercial value.

Experimental Section

All reagents used in this research were of analytical grade and used directly without further purification (boric acid, Fluka Co., ≥99%; disodium tetraborate, Merck Co., ≥98%; potassium chloride, Merck Co., ≥99.5%). Boric acid and disodium tetraborate were dried, before use, in an oven for 24 h at 60 °C; after that time, a constant weight was observed. In the same way the KCl was dried but at 100 °C. Water employed was distilled and deionized. The solutions were prepared by mass, using an analytical balance with a precision of $\pm 1 \times 10^{-4}$ g (Denver Instrument Co., model AA-200). The molalities of the solutions were prepared within an accuracy of $\pm 2 \times 10^{-4}$ mol·kg^{-1}. All solutions were filtered before use.

Refractive indices of solutions were measured in triplicate with a Mettler Toledo RE-40 refractometer, with an uncertainty of $\pm 1 \times 10^{-4}$. Densities of solutions were measured in triplicate with a Mettler Toledo DE-50 vibrating tube densimeter; uncertainties of $< \pm 5 \times 10^{-5}$ g·cm^{-3}. For a given temperature and composition, the density and refractive index were measured for three samples of the same solution. Prior to initiation of each run of measurements at a given temperature, the refractometer and densimeter were calibrated using air and distilled deionized water as a reference substance. The values for refractive index[7] and density of water[8] were obtained from the literature. Both the refractometer and densimeter had self-

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Table 1. Densities and Refractive Indices of Binary Systems at Various Temperatures

	20 °C		25 °C		30 °C	
m/mol·kg^{-1}	ρ/g·cm^{-3}	n_D	ρ/g·cm^{-3}	n_D	ρ/g·cm^{-3}	n_D
			$H_3BO_3 + H_2O$			
0.0500	0.99969	1.3333	0.99831	1.3328	0.99774	1.3322
0.1000	1.00079	1.3335	0.99938	1.3330	0.99880	1.3324
0.1998	1.00297	1.3339	1.00153	1.3333	1.00093	1.3329
0.4000	1.00730	1.3347	1.00579	1.3341	1.00514	1.3336
0.6000	1.01153	1.3355	1.00996	1.3348	1.00925	1.3342
0.8000	1.01567	1.3363	1.01406	1.3360	1.01326	1.3351
0.9000			1.01608	1.3362	1.01528	1.3356
1.0000					1.01724	1.3358
			$Na_2B_4O_7 + H_2O$			
0.0250	1.00342	1.3341	1.00198	1.3338	1.00164	1.3329
0.0500	1.00811	1.3353	1.00660	1.3349	1.00595	1.3339
0.0750	1.01274	1.3361	1.01118	1.3358	1.01051	1.3350
0.1000	1.01714	1.3370	1.01554	1.3365	1.01482	1.3359
0.1199	1.02071	1.3375	1.01912	1.3370	1.01859	1.3362
0.1249	1.02156	1.3379	1.01984	1.3371	1.01917	1.3369
0.1399			1.02256	1.3378	1.02177	1.3372
0.1700					1.02689	1.3382
			$KCl + H_2O$			
0.0500	1.00092	1.3335	0.99953	1.3332	0.99895	1.3330
0.1000	1.00330	1.3353	1.00190	1.3342	1.00130	1.3331
0.2500	1.01031	1.3356	1.00878	1.3354	1.00815	1.3347
0.5000	1.02157	1.3381	1.01998	1.3377	1.01929	1.3370
1.0000	1.04320	1.3426	1.04145	1.3419	1.04063	1.3412
2.0000	1.08376	1.3510	1.08152	1.3505	1.08076	1.3496
3.0000	1.12075	1.3583	1.11853	1.3577	1.11742	1.3571
4.0000	1.15470	1.3668	1.15232	1.3644	1.15114	1.3634

contained Peltier systems for temperature control, with a uncertainty of ±0.01 °C. The time to reach the temperature stability was 600 s.

Prior to experimental measurements on systems of interest, some measurements were carried out on KCl + H_2O at 25 °C to obtain comparisons with literature values. For this, eight solutions were prepared in which the concentrations of KCl ranged from (0.05 to 4.0) mol·kg^{-1}. The experimental values obtained were fitted to an equation containing four empirical constants with an average absolute deviation of $\pm 7 \times 10^{-5}$ g·cm^{-3}. Experimental data on density reported by Zhang and Han[9] (21 data) and by Korosi and Fabuss[10] (4 data) were compared with values generated by the fitted equation, obtaining absolute deviations within $\pm 10 \times 10^{-5}$ g·cm^{-3}.

Results and Discussion

Experimental values for density (ρ) and refractive index (n_D) are listed in Table 1 for the boric acid + water and disodium tetraborate + water systems as a function of molality (m) at temperatures of (20, 25, and 30) °C. At constant temperature, it is seen that both density and refractive index increased with increase in molality of the inorganic substance. It was also observed that both properties decreased with temperature at constant molality.

Table 2 lists experimental values for densities and refractive indices for the H_3BO_3 (1) + KCl (2) + H_2O (3) and $Na_2B_4O_7$ (1) + KCl (2) + H_2O (3) systems as a function of molality and temperature. In this table m_T represents the total molality of the mixture and m_1 represents the molality of the boric acid or disodium tetraborate. From Table 2 it can be seen that for a constant total molality, both the density and refractive index of the mixture decreased with increasing temperature and was observed for both ternary systems measured. For each ternary system, including the binary systems, the experimental values of ρ and n_D were fitted to the equation

$$Y = Y_W \exp(A_1 m_1^{A_2} + B_1 m_2^{B_2}) \qquad (1)$$

Table 2. Densities and Refractive Indices of Ternary Systems at Various Temperatures

		20 °C		25 °C		30 °C	
m_T/mol·kg^{-1}	m_1/mol·kg^{-1}	ρ/g·cm^{-3}	n_D	ρ/g·cm^{-3}	n_D	ρ/g·cm^{-3}	n_D
			H_3BO_3 (1) + KCl (2) + H_2O (3)				
0.2517	0.0634	1.00878	1.3352	1.00729	1.3351	1.00668	1.3347
0.2522	0.1262	1.00721	1.3350	1.00575	1.3345	1.00515	1.3339
0.2496	0.1864	1.00564	1.3347	1.00418	1.3342	1.00353	1.3335
0.4970	0.1261	1.01840	1.3372	1.01688	1.3370	1.01614	1.3362
0.5087	0.2547	1.01582	1.3367	1.01430	1.3363	1.01357	1.3355
0.5065	0.3786	1.01271	1.3360	1.01120	1.3356	1.01047	1.3349
0.7652	0.1954	1.02862	1.3396	1.02701	1.3389	1.02622	1.3384
0.7694	0.3855	1.02430	1.3385	1.02269	1.3379	1.02191	1.3372
0.7649	0.5706	1.01973	1.3373	1.01807	1.3367	1.01728	1.3361
1.0266	0.2642					1.03578	1.3402
1.0354	0.5192					1.03017	1.3388
1.0269	0.7647					1.02409	1.3373
			$Na_2B_4O_7$ (1) + KCl (2) + H_2O (3)				
0.1004	0.0251	1.00703	1.3349	1.00556	1.3345	1.00494	1.3339
0.1010	0.0502	1.01051	1.3356	1.00901	1.3352	1.00837	1.3346
0.1005	0.0751	1.01387	1.3363	1.01234	1.3357	1.01166	1.3350
0.1210	0.0302	1.00866	1.3355	1.00719	1.3347	1.00657	1.3340
0.1213	0.0603	1.01281	1.3361	1.01129	1.3356	1.01064	1.3349
0.1210	0.0902	1.01682	1.3368	1.01525	1.3363	1.01455	1.3357
0.1412	0.0353			1.00879	1.3350	1.00815	1.3345
0.1414	0.0704			1.01352	1.3360	1.01284	1.3353
0.1410	0.1053					1.01728	1.3363
0.1723	0.0429					1.01049	1.3349
0.1720	0.0855					1.01609	1.3360
0.1715	0.1279					1.02149	1.3371

Table 3. Parameters of Equation 1 for Density Fits and Refractive Index Fits

property	A_1	A_2	B_1	B_2	AAD[a]
		H_3BO_3 (1) + KCl (2) + H_2O (3)			
ρ/g·cm^{-3}	0.021039	0.979312	0.042555	0.904633	0.00068
n_D	0.002901	0.976784	0.007017	0.893355	0.0002
		$Na_2B_4O_7$ (1) + KCl (2) + H_2O (3)			
ρ/g·cm^{-3}	0.174727	0.978289	0.043363	0.887493	0.00061
n_D	0.026689	0.968713	0.007070	0.887548	0.0002

[a] AAD = $(1/n)\,\Sigma\,[(Y^{\text{exptl}} - Y^{\text{calcd}})/Y^{\text{exptl}}]$.

where m_1 represents the molality of the boric acid or disodium tetraborate and m_2 the molality of the potassium chloride. Y_W may represent either the density (in g·cm^{-3}) or the refractive index of water at the same temperature of the solution[7,8] and Y the density (in g·cm^{-3}) or refractive index of the solution. A_1, A_2, B_1, and B_2 are empirical constants that are independent of temperature; their values are listed in Table 3, which also includes the values for average absolute deviation (AAD) obtained during the fitting process. For the KCl + H_2O system our experimental values at (20, 25, and 30) °C were used.

The variation in density at 20 °C of the H_3BO_3 (1) + KCl (2) + H_2O (3) system with change in its composition is shown in Figure 1. Values for the density of boric acid + water have been included in Figure 1 for comparative purposes, using a dry base mole fraction equal to one. From this figure it can be seen that for a constant total molality the density of the mixture decreases with increase in the dry base mole fraction of the boric acid, showing a tendency of the ρ values to approach those of boric acid + water as y_1 approaches unity. The fact that density of the mixture decreases with increase in the concentration of boric acid can be explained on the basis that values for the density of KCl + H_2O are greater than those for H_3BO_3 + H_2O, as shown by our results obtained at 20 °C. Data obtained for other temperatures showed similar behavior.

Figure 2 shows the variation in density undergone at 30 °C by the $Na_2B_4O_7$ (1) + KCl (2) + H_2O (3) ternary system with change in its composition. This figure also

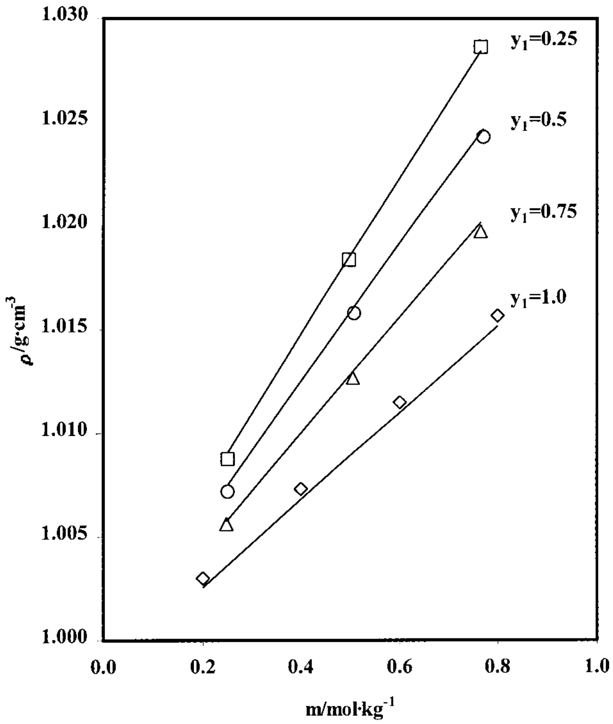

Figure 1. Densities of the H_3BO_3 (1) + KCl (2) + H_2O (3) system at 20 °C. $y_1 = m_1/m_T$: dry base mole fraction of boric acid. Lines were calculated using eq 1.

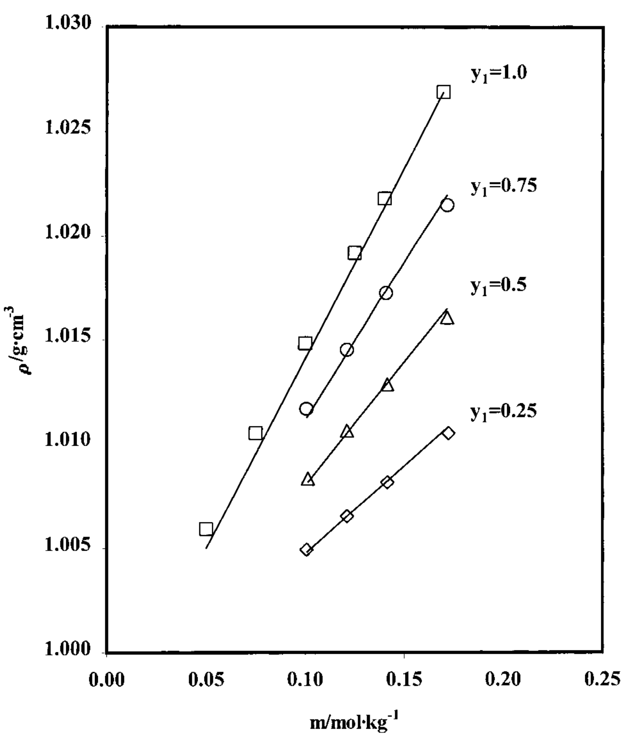

Figure 2. Densities of the $Na_2B_4O_7$ (1) + KCl (2) + H_2O (3) system at 30 °C. $y_1 = m_1/m_T$: dry base mole fraction of disodium tetraborate. Lines were calculated using eq 1.

includes data on disodium tetraborate + water ($y_1 = 1$). In contrast to the prior ternary system, it can be seen that the density of the mixture increases with increase in y_1, nearing values for disodium tetraborate + water as y_1 approaches unity. This observation is explained on the basis of the values for the density of KCl + H_2O now being less than those of $Na_2B_4O_7$ + H_2O, corroborated by comparing the preceding with our measurements made at 30 °C. Behavior similar to that shown in Figure 2 was observed for other temperatures.

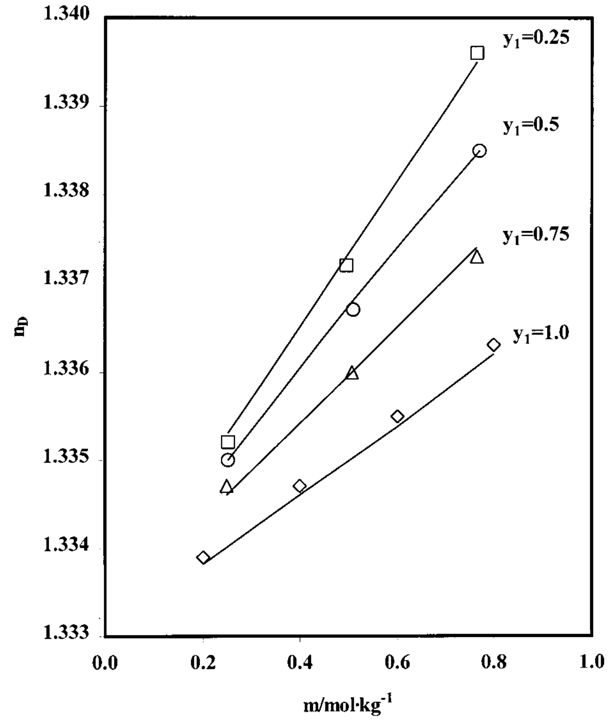

Figure 3. Refractive indices of the H_3BO_3 (1) + KCl (2) + H_2O (3) system at 20 °C. $y_1 = m_1/m_T$: dry base mole fraction of boric acid. Lines were calculated using eq 1.

Refractive indices of ternary systems studied in this research demonstrated behavior similar to that shown for density, as can be observed in Figure 3 for H_3BO_3 (1) + KCl (2) + H_2O (3) at 20 °C.

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