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Density Calculations for (Na, K)BH_4 + (Na, K)BO_2 + (Na, K)OH + H_2O Solutions Used in Hydrogen Power Engineering

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ABSTRACT: Concentrated water−alkaline mixtures of sodium and potassium borohydrides and borates are used as fuel and hydrogen sources in hydrogen power engineering, including low-temperature fuel cells. The performance of such mixtures is determined by their physicochemical properties. An algorithm to calculate the density of mixed solutions of the five-component (Na, K)BH_4 + (Na, K)BO_2 + (Na, K)OH + H_2O system based on density quasi-additivity is proposed. The density−concentration−temperature dependences for aqueous KOH, NaOH, KBO_2, $NaBO_2$, $NaBH_4$, and KBH_4 solutions of any composition in a temperature range of (10 to 50) °C and in the whole concentration range are described mathematically. The technique and algorithm of calculation have been verified by comparison with measured properties.

INTRODUCTION

Now, an essential part of research in hydrogen power engineering and chemical power sources is directed to designing new fuel cells (FC).[1−3] Low-temperature FCs with salt-like borohydrides $NaBH_4$ and KBH_4 as a hydrogen source (fuel) have characteristics comparable with those of the methanol FC and are promising.[4] Such devices contain borohydrides as their concentrated aqueous solutions or suspensions with dissolved hydroxides (NaOH and/or KOH) added. These additives stabilize the solution, preventing hydrolysis of BH_4^-, determining and adjusting its chemical and electrochemical activity. During the FC functioning, its borohydrides gradually oxidize, releasing the contained hydrogen and converting into soluble $NaBO_2$ and/or KBO_2 metaborates.[4]

Therefore, the mixed solution used in the borohydride fuel cell is a five-component water + salt system (Na, K)BH_4 + (Na, K)BO_2 + (Na, K)OH + H_2O of varying composition. As the contained hydrogen is utilized, the concentrations of borohydrides decrease and those of metaborates increase; those of other components do not remain constant as well. These changes in the solution composition are accompanied by essential changes in the physicochemical properties. These properties are extremely important for the proper FC functioning and the maintenance of complex hydrodynamical, thermal, transport, and electrochemical processes inside the FC. The multicomponent nature of the solution strongly complicates the task of detailed determination of these characteristics in the whole concentration−temperature range.

Earlier, we have published a series of papers concerning the phase diagrams of (Na, K)BH_4 + (Na, K)BO_2 + (Na, K)OH + H_2O systems.[5−7] The purpose of the present work is to determine the density of solutions belonging to the (Na, K)BH_4 + (Na, K)BO_2 + (Na, K)OH + H_2O system in the whole concentration range (up to saturated solutions) in a practically important temperature range (10 to 50) °C and to develop an algorithm of density calculations. The results of calculations are compared with literature and our experimental data.

Thus, there are, at least, two different devices with borohydrides, namely, the direct borohydrides fuel cell (DBFC) using electrooxidation of borohydrides and the hydrogen generator (HG) employing hydrolysis of borohydrides. However, our work is not devoted directly to either of these devices; it is devoted to the determination and calculation of the density of borohydride solutions which can be used in both DBFC and HG. BH_4^- hydrolysis occurs in both DBFC and HG, but in the former case, it is an undesirable side process, whereas in the latter case, it is the basis of controllable functioning.

EXPERIMENTAL SECTION

The chemicals used ("reagent grade" quality) were as follows: $NaBO_2 \cdot 4H_2O$ (Vecton Corp, Russia, the analytical reagent content w_{NaBO2} = 0.490 ± 0.003); $KBO_2 \cdot 1.25H_2O$ (Vecton Corp, the reagent content w_{KBO2} = 0.767 ± 0.001); NaOH (Ecros Corp, Russia, the reagent content w_{NaOH} = 0.989 ± 0.002); KOH·xH_2O (Ecros Corp, the reagent content w_{KOH} = 0.898 ± 0.003; water content w_{H2O} = 0.101 ± 0.003); $NaBH_4$ (Aviabor Corp, Russia, the reagent content w_{NaBH4} = 0.974 ± 0.005); KBH_4 (Aviabor Corp, the reagent content w_{KBH4} = 0.971 ± 0.006); distilled water without dissolved carbon dioxide. Each reagent had undergone common chemical analysis to determine the content of the basic substance. No analytically detectable carbonate impurity in the solid reagents was found.

To prepare dry mixtures of the raw reagents, an AGO-2 mill-activator and a CTBRAND ultrasonic crusher were used. Crushing and mixing of reagents were done in a drybox. Weighing with an uncertainty of ± 1 mg was carried out with a GF-600 laboratory electronic balance. All of the subsequent measurements were done in a PolySciens "AlexRedCTD" programmed thermostat at a temperature fixed with an uncertainty of ± 0.01 °C. As the aqueous solutions of borohydrides are quickly self-decomposed, $NaBH_4$ and KBH_4 were dissolved in alkaline solutions.

The solution density was determined by weighing calibrated pycnometers. Each pycnometer was calibrated by triple weighing at a fixed temperature, subsequent triple filling in with distilled

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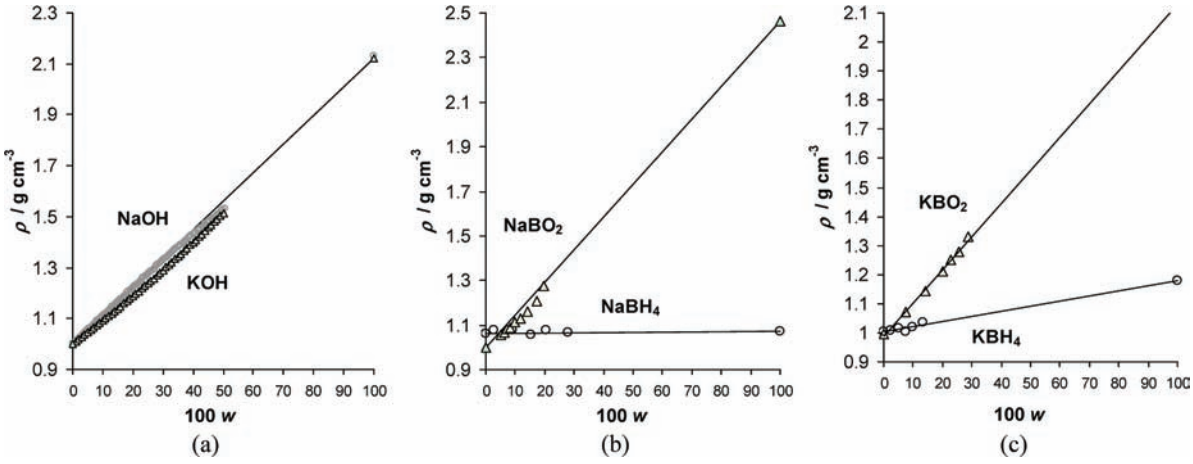

Figure 1. Density ρ of aqueous solutions as a function of the mass fraction w of the dissolved substance. The solid lines correspond to the additive density in the solvent + dissolved substance system. Pure water was used as the solvent for NaOH, KOH, $NaBO_2$, and KBO_2; a 0.14 mol·L^{-1} KOH solution and a 1.546 mol·L^{-1} NaOH solution were used as the solvents for KBH_4 and $NaBH_4$, respectively.

water, thermostatting, and weighing. The average volume value with a relative calibration accuracy was calculated. A typical result of such calibration is as follows: the weight of an empty pycnometer is (5.756, 5.756, and 5.756) g; the weight of the water-filled pycnometer is (10.440, 10.442, and 10.439) g; the average volume of the pycnometer is 4.6975 mL; the relative calibration accuracy is 0.001. Then, each prepared solution was weighed in three calibrated pycnometers; the average density value with a confidence interval was calculated.

RESULTS AND DISCUSSION

The dependences of the water density ρ_{H_2O} and the density of many aqueous solutions on temperature t are known with a high accuracy. The solution density usually decreases with increasing temperature because of the thermal motion amplification of the particles. In the (0 to 4) °C range the density of water rises due to destruction of its ice-like structure; during further heating, the water density naturally decreases. In the temperature range (0 to 60) °C, ρ_{H_2O}/g·cm^{-3} is described by the following high-accuracy polynomial

$$\rho_{H_2O} = 0.999841 + 5.2747\cdot10^{-5}(t/°C) - 7.3060\cdot10^{-6}(t/°C)^2 + 3.0467\cdot10^{-8}(t/°C)^3 \quad (1)$$

It follows from the physicochemical analysis practice for liquid systems that intermolecular interactions are weakly reflected in the density−concentration dependences, these dependences always being close to additive ones. For the majority of systems with noninteracting components the relative deviation of the density from additivity is less than 0.01. For alkaline solutions, their density ρ/g·cm^{-3} strictly linearly depends on the mass fraction w of the dissolved substance up to $w \approx 0.15$:

$$\Delta\rho = \rho - \rho_{H_2O} = aw \quad (2)$$

Concentrated aqueous NaOH and KOH solutions are examples of the systems with strong interactions; the relative deviation of the density from additivity may reach 0.05 for them. For an extension of the concentration range up to saturated solutions ($w \approx 0.5$), it is enough to supplement eq 2 with a square term

$$\Delta\rho = \rho - \rho_{H_2O} = aw + bw^2 \quad (3)$$

where a and b are factors in the equation. References 8 and 9 report appropriate factors for NaOH and KOH solutions. According to ref 8, the density of an aqueous NaOH solution can be described by eq 2 with $a = 1.064$ within the temperature interval (20 to 300) °C, that seems a rough enough approximation. According to ref 9, the density of an aqueous KOH solution can be described by eq 3 with $b = 0.291$ and $a = 0.893$ (10 °C), 0.882 (20 °C), 0.873 (30 °C), 0.863 (40 °C), and 0.857 (50 °C).

Moreover, if we involve the point $\rho(w = 1)$ corresponding to the pure dry solid component ($NaBH_4$: ρ/g·cm^{-3} = 1.07,[10] 1.074,[11] 1.04,[12] 1.08,[13] or 1.035;[14] KBH_4: ρ/g·cm^{-3} = 1.18[10,14] or 1.11;[12] $NaBO_2$: ρ/g·cm^{-3} = 2.46[10] or 2.464;[14] KBO_2: ρ/g·cm^{-3} = 1.178[14]), we will obtain the diagrams represented in Figure 1. It is visible that the experimental points are only slightly deviated from the additive straight line connecting the points of the densities of water and the pure solid component in the systems. In other words, not only homogeneous solutions but also heterogeneous mixtures obey the rule of additivity (eq 2) or quasiadditivity (eq 3 or more complicated equations). Therefore, it could be hypothesized that eqs 2 and 3 can describe the density of all the solutions considered here for FCs with the correct choice of a set of factors a and b.

Measuring the density of aqueous $NaBH_4$ and KBH_4 solutions is only possible under previous alkalinization because of the rapid hydrolysis of BH_4 ions in neutral and, especially, in acidic media.[15] This is especially critical for the more soluble $NaBH_4$. Therefore, as noted in the Experimental Section, the salts $NaBH_4$ and KBH_4 were dissolved in the alkaline solutions. That is why the point $w = 0$ in Figure 1b,c corresponds to the density of a weakly alkaline aqueous solution used as the solvent rather than the density of pure water.

Of course, the density quasiadditivity rule cannot be exact but approximate only. As was noted above, the relative deviation of the density from additivity may reach 0.05 for the systems with strong interactions. These deviations are clearly seen in Figure 1. Hence, the straight lines in Figure 1 connecting the point of the solvent ($w = 0$) and that of the solute ($w = 1$) illustrate this quasiadditivity but are not trend lines (the coefficients of the trend equations are given below).

The quasiadditivity rule enables avoiding rough experimental errors. If the relative deviation of the density from additivity is far

Table 1. Measured and Calculated Densities of Aqueous Binary Solutions of Sodium Metaborate

	t/°C								
	10			25			50		
mass fraction of $NaBO_2$	measured	calculated	$100\lvert(\rho-\rho_{cal})/\rho\rvert$	measured	calculated	$100\lvert(\rho-\rho_{cal})/\rho\rvert$	measured	calculated	$100\lvert(\rho-\rho_{cal})/\rho\rvert$
0.0513[a]				1.0577	1.0531	0.4	1.046	1.0428	0.3
0.0618	1.071 ± 0.004	1.0687	0.22	1.065 ± 0.001	1.0651	0.001	1.055 ± 0.002	1.0544	0.12
0.0703[a]				1.0805	1.0751	0.5	1.0682	1.0640	0.4
0.0822	1.093 ± 0.001	1.0934	0.03	1.089 ± 0.001	1.0892	0.09	1.079 ± 0.002	1.0776	0.003
0.0993[a]				1.1157	1.1100	0.5	1.1024	1.0974	0.5
0.1164	1.137 ± 0.003	1.1367	0.05	1.132 ± 0.002	1.1313	0.03	1.120 ± 0.001	1.1175	0.15
0.142	1.168 ± 0.001	1.1709	0.23	1.159 ± 0.002	1.2059	0.05	1.145 ± 0.001	1.1486	0.32
0.1615[a]							1.19	1.1729	1.4
0.1731	1.216 ± 0.001	1.2142	0.10	1.207 ± 0.001	1.2060	0.08	1.190 ± 0.003	1.1875	0.12
0.1949[a]				1.2735	1.2363	3	1.2419	1.2157	2.1

[a] Data from ref 16.

Table 2. Measured and Calculated Densities of Aqueous Binary Solutions of Potassium Metaborate

	t/°C								
	10			25			50		
mass fraction of KBO_2	measured	calculated	$100\lvert(\rho-\rho_{cal})/\rho\rvert$	measured	calculated	$100\lvert(\rho-\rho_{cal})/\rho\rvert$	measured	calculated	$100\lvert(\rho-\rho_{cal})/\rho\rvert$
0.0764	1.079 ± 0.001	1.0764	0.21	1.072 ± 0.001	1.0716	0.08	1.062 ± 0.001	1.0588	0.3
0.1432	1.152 ± 0.001	1.1506	0.19	1.145 ± 0.002	1.1446	0.05	1.131 ± 0.001	1.1299	0.18
0.2027	1.219 ± 0.001	1.2223	0.3	1.212 ± 0.001	1.2159	0.3	1.198 ± 0.002	1.2005	0.21
0.2294	1.259 ± 0.002	1.2560	0.3	1.248 ± 0.003	1.2496	0.02	1.234 ± 0.001	1.2342	0.04
0.2561	1.290 ± 0.002	1.2908	0.07	1.280 ± 0.002	1.2846	0.4	1.264 ± 0.002	1.2695	0.4
0.2876	1.334 ± 0.001	1.3333	0.13	1.328 ± 0.002	1.3274	0.16	1.313 ± 0.002	1.3128	0.15

above 0.05, an error is quite probable. At construction of Figure 1 we have found an error in the reference data. The value of density of the pure dry potassium metaborate reported in ref 14 (KBO_2; CAS 13709-94-9; density 1.178 g·cm^{-3}) cannot be correct as appears from Figure 1c. We have found no other density data of KBO_2. According to Figure 1c, the density of pure dry solid KBO_2 should be approximately 2.128 g·cm^{-3}.

There are not enough reference data on the densities of alkaline solutions of borohydrides and borates.[3,11,12,16,17] We have summarized the available experimental data (both literature and own ones) in Tables 1, 2, and 3.

Reference 17 reports the gravimetric density of unsaturated aqueous solutions containing (0.06 to 0.14) molar fraction x of KBO_2 in the temperature range (10 to 80) °C. The authors have described the set of their experimental data by the square-law equation

$$\rho = 1.0835 - 0.0038(t/°C) + (3.0044 + 0.047(t/°C))x - (0.476 + 0.1811(t/°C))x^2 \quad (4)$$

However, a comparison of eqs 1 and 4 shows that eq 4 yields a significant error at a small x. Our density data for $NaBO_2$ and KBO_2 solutions (Tables 1 and 2) agree with those given in the primary source.[16]

Reference 3 reports the plot of the density of the aqueous solutions $NaBH_4$ + NaOH at 20 °C without any tabulated data. The concentration dependences of the density satisfy eq 2, and an increase in the content of light $NaBH_4$ in the solution is accompanied by a reduction of its density. However, according to the experimental details of ref 3, the borohydride solutions were prepared by dissolving $NaBH_4$ in alkaline NaOH solutions, and the plot does not consider changing the mass fraction of NaOH at the $NaBH_4$ dissolution. In other words, the measurements of borohydride solutions are executed at varying concentrations of all the components; fixing of the alkalinity is difficultly implemented for such systems. We have tabulated the data of ref 3 using the plot and considering redistribution of the mass fractions. These data together with our experimental data have been included in Table 3.

All of the $\rho(w)$ dependences of NaOH, KOH, $NaBH_4$, KBH_4, $NaBO_2$, and KBO_2 aqueous solutions are described by eqs 2 or 3, and the temperature trend of density is determined by eq 1 and the temperature dependencies of a and b. Table 4 summarizes the calculated factors a and b in eqs 2 and 3 for the considered individual substances in the total range of their solubility. Figures 2, 3, and 4 illustrate how Table 4 has been compiled. The $\rho(w)$ and $\Delta\rho(w)$ dependences for aqueous NaOH, KOH, $NaBH_4$, KBH_4, $NaBO_2$, and KBO_2 solutions were plotted for each temperature, approximated by eq 3, and then the temperature dependencies of a and b were plotted. As the temperature range under analysis is rather narrow, either linear temperature dependences of the factors a and b or no explicit dependence were observed; in the latter case, the averaged coefficient was regarded constant.

Table 3. Measured and Calculated Densities of Aqueous Solutions Relating to the System (Na, K)BH_4 + (Na, K)BO_2 + (Na, K)OH + H_2O

mass fractions							ρ/ g·cm^{-3}			
KOH	NaOH	KBO_2	$NaBO_2$	KBH_4	$NaBH_4$	t/°C	measured	calculated	$100\lvert(\rho - \rho_{cal})/\rho\rvert$	ref
0.0060				0.0254		10	1.011 ± 0.003	1.0113	0.03	our data
						25	1.009 ± 0.009	1.0085	0.05	
						50	1.003 ± 0.004	0.9991	0.34	
0.0064				0.0503		10	1.020 ± 0.001	1.0181	0.21	our data
						25	1.016 ± 0.001	1.0147	0.13	
						50	1.008 ± 0.001	1.0044	0.3	
0.0068				0.0763		10	1.011 ± 0.009	1.0253	1.38	our data
						25	1.006 ± 0.007	1.0210	1.54	
						50	0.995 ± 0.008	1.0092	1.4	
0.0072				0.1002		10	1.032 ± 0.001	1.0321	0.03	our data
						25	1.020 ± 0.016	1.0266	0.64	
						50	1.008 ± 0.013	1.0126	0.5	
0.0076				0.1324		10	1.042 ± 0.002	1.0415	0.02	our data
						25	1.036 ± 0.002	1.0337	0.23	
						50	1.019 ± 0.015	1.0159	0.3	
	0.0298				0.1692	10	1.059 ± 0.002	1.0361	2.2	our data
						25	1.050 ± 0.002	1.0334	1.6	
						50	1.039 ± 0.001	1.0244	1.4	
	0.0276				0.2346	10	1.054 ± 0.002	1.0357	1.8	our data
						25	1.048 ± 0.001	1.0331	1.4	
						50	1.036 ± 0.002	1.0241	1.1	
	0.0724				0.0294	10	1.086 ± 0.001	1.0766	0.9	our data
						25	1.077 ± 0.003	1.0739	0.3	
						50	1.067 ± 0.003	1.0649	0.21	
	0.0659				0.0884	10	1.085 ± 0.001	1.0716	1.2	our data
						25	1.078 ± 0.001	1.0689	0.9	
						50	1.064 ± 0.002	1.0599	0.3	
	0.0614				0.1500	10	1.069 ± 0.003	1.0687	0.04	our data
						25	1.058 ± 0.002	1.0660	0.7	
						50	1.045 ± 0.002	1.0570	1.1	
	0.0581				0.1974	10	1.086 ± 0.004	1.0667	1.8	our data
						25	1.077 ± 0.006	1.0640	1.3	
						50	1.061 ± 0.003	1.0550	0.6	
	0.0917				0.083	20	1.1085	1.0970	1.0	ref 3
	0.0847				0.153	20	1.1017	1.0917	0.9	ref 3
	0.0787				0.213	20	1.0977	1.0872	1.0	ref 3
	0.0734				0.266	20	1.0909	1.0833	0.7	ref 3
	0.1383				0.078	20	1.1492	1.1457	0.3	ref 3
	0.1280				0.147	20	1.1397	1.1369	0.25	ref 3
	0.1192				0.2055	20	1.1316	1.1294	0.19	ref 3
	0.1116				0.256	20	1.1248	1.1230	0.16	ref 3
	0.1849				0.0755	20	1.1967	1.1944	0.19	ref 3
	0.1718				0.141	20	1.1831	1.1826	0.04	ref 3
	0.1604				0.198	20	1.1655	1.1724	0.6	ref 3
	0.1504				0.248	20	1.1519	1.1634	1.0	ref 3
	0.2318				0.073	20	1.255	1.2434	0.9	ref 3
	0.2160				0.136	20	1.2198	1.2288	0.7	ref 3
	0.2018				0.193	20	1.2021	1.2156	1.1	ref 3
	0.2790				0.07	20	1.2957	1.2927	0.23	ref 3
	0.2607				0.131	20	1.2713	1.2754	0.3	ref 3
	0.2445				0.185	20	1.2401	1.2601	1.6	ref 3

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Table 3. Continued

mass fractions							ρ/ g·cm^{-3}			
KOH	NaOH	KBO_2	$NaBO_2$	KBH_4	$NaBH_4$	t/°C	measured	calculated	$100\lvert(\rho - \rho_{cal})/\rho\rvert$	ref
	0.2787				0.0713	20	1.286 ± 0.004	1.2924	0.5	our data
	0.2643				0.1192	20	1.262 ± 0.004	1.2788	1.3	our data
	0.2494				0.1691	20	1.237 ± 0.001	1.2646	2	our data
	0.2361				0.0487	20	1.248 ± 0.004	1.2472	0.06	our data
	0.2260				0.0894	20	1.232 ± 0.002	1.2378	0.4	our data
	0.2150				0.1336	20	1.214 ± 0.001	1.2277	1.1	our data
	0.1880				0.0600	20	1.202 ± 0.001	1.1972	0.4	our data
	0.1758				0.1208	20	1.189 ± 0.001	1.1863	0.2	our data
	0.1657				0.1716	20	1.178 ± 0.001	1.1772	0.0	our data
	0.1411				0.0594	20	1.154 ± 0.001	1.1480	0.5	our data
	0.1307				0.1286	20	1.145 ± 0.002	1.1392	0.5	our data
	0.1194				0.2040	20	1.135 ± 0.002	1.1296	0.5	our data
	0.0922				0.0675	20	1.104 ± 0.001	1.0970	0.6	our data
	0.0852				0.1384	20	1.102 ± 0.002	1.0918	0.9	our data
	0.0777				0.2148	20	1.098 ± 0.002	1.0862	1.1	our data
0.0482				0.1136		10	1.071 ± 0.002	1.0697	0.14	our data
						25	1.063 ± 0.002	1.0628	0.04	
						50	1.053 ± 0.002	1.0467	0.6	
0.0320	0.0228			0.0753	0.0322	10	1.077 ± 0.003	1.0708	0.6	our data
						25	1.069 ± 0.001	1.0654	0.3	
						50	1.059 ± 0.002	1.0517	0.7	
0.0240	0.0342			0.0565	0.0483	10	1.078 ± 0.002	1.0717	0.6	our data
						25	1.069 ± 0.001	1.0669	0.22	
						50	1.057 ± 0.003	1.0544	0.24	
0.0159	0.0453			0.0374	0.0640	10	1.085 ± 0.002	1.0720	1.2	our data
						25	1.076 ± 0.002	1.0680	0.8	
						50	1.066 ± 0.005	1.0567	0.8	
	0.0678				0.0958	10	1.087 ± 0.002	1.0737	1.2	our data
						25	1.078 ± 0.002	1.0711	0.7	
						50	1.066 ± 0.004	1.0621	0.4	
0.0307133	0.01094755	0.08965604	0.03601743			10	1.185 ± 0.002	1.1692	1.3	our data
						25	1.177 ± 0.002	1.1631	1.2	
						50	1.165 ± 0.003	1.1482	1.4	
0.0629303	0.02243106	0.04592535	0.01844955			10	1.157 ± 0.001	1.1455	1.0	our data
						25	1.149 ± 0.002	1.1403	0.8	
						50	1.137 ± 0.003	1.1268	0.9	
0.0154765	0.02206589	0.04517771	0.07259679			10	1.177 ± 0.001	1.1632	1.2	our data
						25	1.168 ± 0.002	1.1576	0.9	
						50	1.156 ± 0.002	1.1435	1.1	
0.031672	0.04515695	0.02311359	0.03714159			10	1.149 ± 0.002	1.1386	0.9	our data
						25	1.142 ± 0.001	1.1342	0.7	
						50	1.130 ± 0.002	1.1222	0.6	
0.0923204		0.06737364				10	1.182 ± 0.002	1.1519	2.5	our data
						25	1.175 ± 0.001	1.1458	2.5	
						50	1.162 ± 0.002	1.1310	3	
0.0466976		0.13631594				10	1.169 ± 0.001	1.1851	1.3	our data
						25	1.162 ± 0.002	1.1784	1.5	
						50	1.152 ± 0.002	1.1626	0.9	
	0.06822882		0.0561182			10	1.140 ± 0.003	1.1338	0.5	our data
						25	1.133 ± 0.003	1.1303	0.3	
						50	1.122 ± 0.002	1.1198	0.23	
	0.03343599		0.1100044			10	1.162 ± 0.001	1.1636	0.08	our data
						25	1.156 ± 0.002	1.1584	0.17	
						50	1.142 ± 0.002	1.1451	0.3	

Table 3. Continued

mass fractions							ρ/ g·cm^{-3}			
KOH	NaOH	KBO_2	$NaBO_2$	KBH_4	$NaBH_4$	t/°C	measured	calculated	$100\lvert(\rho - \rho_{cal})/\rho\rvert$	ref
0.0964	0.0389	0.0022	0.0010	0.0418	0.0166	10	1.149 ± 0.002	1.1427	0.5	our data
0.0859	0.0367	0.0238	0.0115	0.0358	0.0150	10	1.163 ± 0.002	1.1611	0.16	our data
0.0916	0.0334	0.0394	0.0162	0.0345	0.0124	10	1.206 ± 0.003	1.1831	1.9	our data
0.0871	0.0229	0.1001	0.0297	0.0286	0.0074	10	1.279 ± 0.002	1.2451	3	our data
0.0829	0.0219	0.1236	0.0368	0.0242	0.0063	10	1.306 ± 0.004	1.2731	2.5	our data
0.0786	0.0200	0.1436	0.0412	0.0214	0.0053	10	1.359 ± 0.003	1.2943	5	our data
0.0708	0.0171	0.1742	0.0474	0.0182	0.0043	10	1.393 ± 0.005	1.3264	5	our data
0.0697	0.0147	0.1958	0.0464	0.0162	0.0033	10	1.406 ± 0.003	1.3476	4	our data
0.0677	0.0156	0.2093	0.0549	0.0120	0.0026	10	1.437 ± 0.002	1.3725	4	our data
0.0952		0.2283	0.0491			10	1.449 ± 0.003	1.3966	4	our data
0.1180	0.0594	0.0053	0.0030	0.0306	0.0151	10	1.183 ± 0.002	1.1872	0.4	our data
0.1122	0.0524	0.0277	0.0146	0.0260	0.0119	10	1.212 ± 0.002	1.2074	0.4	our data
0.1153	0.0458	0.0510	0.0228	0.0261	0.0102	10	1.245 ± 0.003	1.2357	0.7	our data
0.1209	0.0420	0.0718	0.0281	0.0231	0.0079	10	1.264 ± 0.002	1.2639	0.011	our data
0.1174	0.0374	0.0911	0.0327	0.0221	0.0069	10	1.299 ± 0.002	1.2810	1.4	our data
0.1173	0.0335	0.1172	0.0377	0.0188	0.0053	10	1.334 ± 0.004	1.3106	1.8	our data
0.1161	0.0314	0.1279	0.0389	0.0166	0.0044	10	1.345 ± 0.003	1.3201	1.8	our data
0.1108	0.0276	0.1516	0.0425	0.0154	0.0038	10	1.378 ± 0.003	1.3422	2.6	our data
0.1086	0.0258	0.1611	0.0431	0.0133	0.0031	10	1.384 ± 0.001	1.3496	2.5	our data
0.1064	0.0253	0.1775	0.0475			10	1.430 ± 0.002	1.3685	4	our data
0.1124	0.0273	0.0227	0.0065	0.0683	0.0164	25	1.166 ± 0.002	1.1703	0.4	our data
0.0912	0.0303	0.0336	0.0125	0.0531	0.0173	25	1.179 ± 0.003	1.1673	1.0	our data
0.0919	0.0253	0.0892	0.0278	0.0390	0.0105	25	1.256 ± 0.001	1.2326	1.9	our data
0.0880	0.0223	0.0984	0.0282	0.0423	0.0106	25	1.257 ± 0.004	1.2367	1.6	our data
0.0785	0.0256	0.1102	0.0404	0.0356	0.0114	25	1.284 ± 0.003	1.2563	2.2	our data
0.0748	0.0194	0.1469	0.0429	0.0324	0.0083	25	1.359 ± 0.002	1.2896	5	our data
0.0730	0.0145	0.1976	0.0443	0.0244	0.0048	25	1.382 ± 0.002	1.3431	3	our data
0.0977		0.2082	0.0448	0.0171	0.0032	25	1.416 ± 0.002	1.3630	4	our data
0.0952		0.2283	0.0491			25	1.439 ± 0.003	1.3875	4	our data
0.1189	0.0532	0.0024	0.0012	0.0457	0.0201	25	1.175 ± 0.002	1.1747	0.04	our data
0.1194	0.0490	0.0210	0.0097	0.0403	0.0163	25	1.203 ± 0.003	1.1959	0.6	our data
0.1088	0.0404	0.0455	0.0190	0.0429	0.0157	25	1.220 ± 0.002	1.2108	0.8	our data
0.1140	0.0371	0.0747	0.0274	0.0366	0.0117	25	1.273 ± 0.002	1.2496	1.9	our data
0.1123	0.0337	0.0928	0.0314	0.0341	0.0101	25	1.293 ± 0.003	1.2672	2.0	our data
0.1130	0.0307	0.1148	0.0351	0.0316	0.0084	25	1.336 ± 0.001	1.2921	3	our data
0.1092	0.0279	0.1322	0.0380	0.0290	0.0073	25	1.342 ± 0.004	1.3076	2.6	our data
0.1109	0.0264	0.1440	0.0385	0.0271	0.0063	25	1.353 ± 0.002	1.3212	2.3	our data
0.1086	0.0258	0.1611	0.0431	0.0133	0.0031	25	1.373 ± 0.005	1.3406	2.4	our data
0.1064	0.0253	0.1775	0.0475			25	1.420 ± 0.004	1.3596	4	our data
0.1020	0.0289	0.0049	0.0015	0.0898	0.0250	50	1.132 ± 0.002	1.1281	0.3	our data
0.0928	0.0266	0.0342	0.0110	0.0808	0.0228	50	1.167 ± 0.003	1.1521	1.3	our data
0.0948	0.0243	0.0632	0.0183	0.0732	0.0184	50	1.203 ± 0.003	1.1853	1.5	our data
0.0860	0.0208	0.1079	0.0298	0.0552	0.0130	50	1.260 ± 0.004	1.2285	2.5	our data
0.0774	0.0229	0.1125	0.0374	0.0561	0.0163	50	1.265 ± 0.002	1.2363	2.3	our data
0.0832	0.0181	0.1363	0.0334	0.0536	0.0115	50	1.293 ± 0.003	1.2574	3	our data
0.0727	0.0159	0.1474	0.0364	0.0568	0.0121	50	1.269 ± 0.004	1.2618	0.6	our data
0.1003		0.1870	0.0402	0.0352	0.0066	50	1.356 ± 0.001	1.3169	3	our data
0.0977		0.2082	0.0448	0.0171	0.0032	50	1.400 ± 0.002	1.3426	4	our data
0.0952		0.2283	0.0491			50	1.423 ± 0.002	1.3678	4	our data
0.1262	0.0463	0.0067	0.0028	0.0658	0.0238	50	1.160 ± 0.001	1.1680	0.6	our data
0.1243	0.0445	0.0189	0.0076	0.0573	0.0202	50	1.188 ± 0.004	1.1789	0.8	our data
0.1195	0.0379	0.0462	0.0165	0.0581	0.0181	50	1.222 ± 0.001	1.2018	1.7	our data
0.1210	0.0348	0.0690	0.0223	0.0542	0.0153	50	1.255 ± 0.004	1.2273	2.2	our data

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Table 3. Continued

mass fractions							ρ/ g·cm^{-3}			
KOH	NaOH	KBO_2	$NaBO_2$	KBH_4	$NaBH_4$	t/°C	measured	calculated	$100\lvert(\rho - \rho_{cal})/\rho\rvert$	ref
0.1163	0.0313	0.0873	0.0265	0.0519	0.0137	50	1.261 ± 0.002	1.2418	1.6	our data
0.1159	0.0275	0.1074	0.0288	0.0566	0.0132	50	1.294 ± 0.004	1.2614	2.5	our data
0.1134	0.0269	0.1261	0.0338	0.0415	0.0097	50	1.316 ± 0.001	1.2815	2.6	our data
0.1109	0.0264	0.1440	0.0385	0.0271	0.0063	50	1.339 ± 0.003	1.3013	3	our data
0.1086	0.0258	0.1611	0.0431	0.0133	0.0031	50	1.359 ± 0.003	1.3209	3	our data
0.1064	0.0253	0.1775	0.0475			50	1.404 ± 0.004	1.3403	5	our data

Table 4. Coefficients for Calculation of the Solution Density in the Temperature Range (10 to 50) °C[a]

	dissolved substance					
coefficient	KOH	NaOH	KBO_2	$NaBO_2$	KBH_4	$NaBH_4$
$\rho = \rho_{H_2O} + aw + bw^2$	Density Equation					
a	0.9036 $- 1.039 \times 10^{-3}$ (t/°C)	1.0507	0.9715 $- 2.259 \times 10^{-3}$ (t/°C)	1.0508 $- 4.31 \times 10^{-4}$ (t/°C)	0.25105 $- 2.052 \times 10^{-3}$ (t/°C)	0.03
b	0.295	−0.01	0.695 + 4.42×10^{-3} (t/°C)	1.19 − 9.78×10^{-3} (t/°C)		

[a] w is the mass fraction of the dissolved substance; t is temperature.

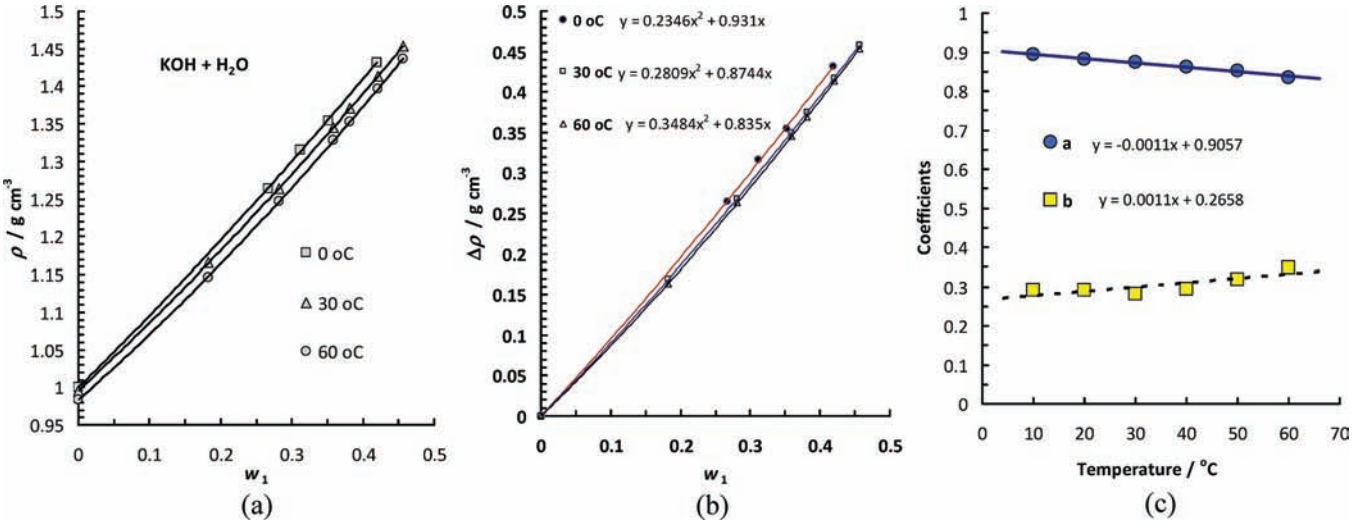

Figure 2. (a) Density ρ as a function of the mass fraction w_1 of the dissolved substance for KOH (1) + H_2O (2) system at different temperatures (data from ref 9), (b) density deviations from pure water $\Delta\rho$, and (c) the temperature dependencies of factors a and b in eq 3 for this system. The trend equations are given in the plots b and c.

Because of the self-decomposition of BH_4^-, the physicochemical properties of only the alkali + borohydride solutions can be studied. An enough concentration of alkali (Figure 1) should be used for maintenance of the solution stability above room temperature. The use of such solutions needs subsequent separation of the contributions of the alkali and borohydride based on the quasiadditivity hypothesis to isolate the role of borohydrides. As the densities of even saturated aqueous solutions of $NaBH_4$ and KBH_4 are close to ρ_{H_2O} and calculated by the above complicated method, this results in a low accuracy. Therefore, for aqueous solutions of $NaBH_4$ and KBH_4 no nonlinearity of the $\Delta\rho(w)$ dependences was reliably detected and eq 2 sufficed. The factor a for aqueous solution of $NaBH_4$ is vanishingly small, and it could be determined only approximately. The contribution of $NaBH_4$ is almost indistinguishable from the contribution of water.

Under hypothesis of the quasiadditivity the densities of water and the individual electrolytes contribute additively to the density of the final solution, including concentrated ones. This property can be used for designing of correlation equations for solution density calculations at any composition and temperature. On the basis of the above principle we have designed an algorithm for density calculations for the (Na, K)BH_4 + (Na, K)BO_2 + (Na, K)OH + H_2O system. The algorithm includes the following steps: (1) input of a temperature t and the content w_i of each electrolyte ($1 \le i \le N$, N

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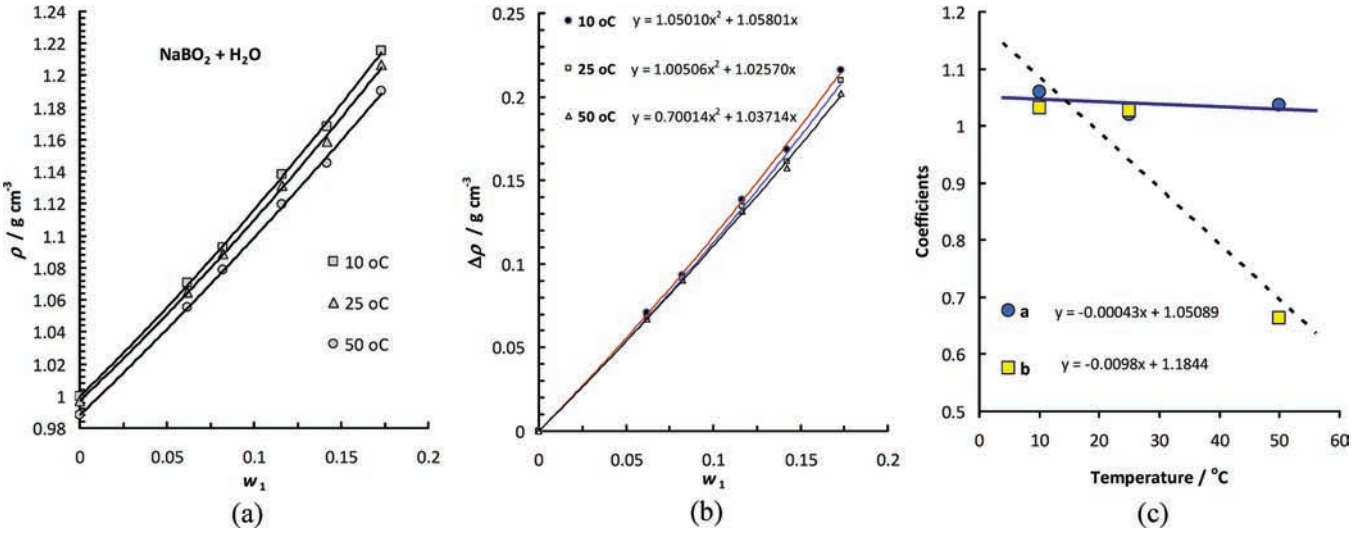

Figure 3. (a) Density ρ and (b) density deviations from pure water $\Delta\rho$ as a function of the mass fraction w_1 of the dissolved substance for $NaBO_2$ (1) + H_2O (2) system at different temperatures and (c) the temperature dependencies of factors a and b in eq 3 for this system. The trend equations are given in the plots b and c.

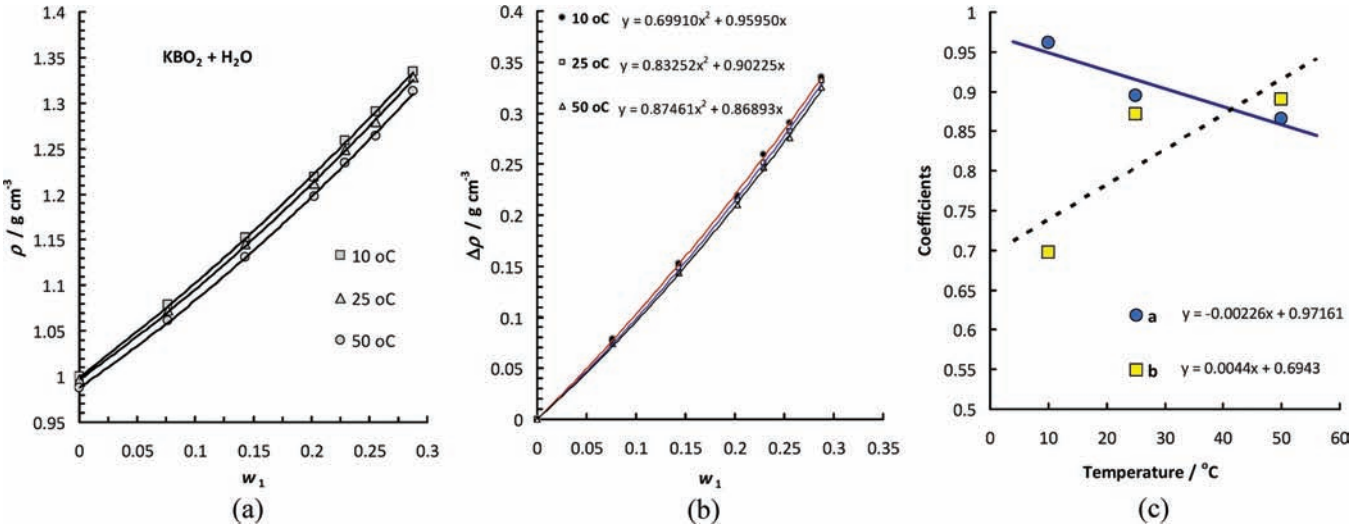

Figure 4. (a) Density ρ and (b) density deviations from pure water $\Delta\rho$ as a function of the mass fraction w_1 of the dissolved substance for KBO_2 (1) + H_2O (2) system at different temperatures and (c) the temperature dependencies of factors a and b in eq 3 for this system. The trend equations are given in the plots b and c.

being the number of the electrolytes) in the solution; (2) calculation of a set of the solution densities for each individual electrolyte ρ_i at the given t and w_i by eqs 2 or 3, using the data from Table 4; (3) calculation of a set of the density deviations from pure water $\Delta\rho_i = \rho_i - \rho_{H_2O}$; (4) algebraic summation of the $\Delta\rho_i$ set for the mixed electrolyte solution; and (5) calculation of the density of this solution $\rho = \rho_{H_2O} + \Delta\rho$. Therefore, the calculation algorithm describes the additive formula

$$\rho = \rho_{H_2O} + \sum_{i=1}^{N} \Delta\rho_i = \rho_{H_2O} + \sum_{i=1}^{N} (\rho_i - \rho_{H_2O})$$

$$= \sum_{i=1}^{N} \rho_i - (N-1)\rho_{H_2O} \quad (5)$$

Hence, one can assert with a practically acceptable accuracy that the density of any fuel solution of the (Na, K)BH_4 + (Na, K)BO_2 + (Na, K)OH + H_2O system at a given temperature can be calculated as a quasiadditive property using the data from Table 4. Tables 1, 2, and 3 present some results of our calculations together with the corresponding experimental densitometric data of some mixtures belonging to the (Na, K)BH_4 + (Na, K)BO_2 + (Na, K)OH + H_2O system at different temperatures. The application of our algorithm provides quite satisfactory results of the calculations, namely, the maximal relative error less than 0.05; for the majority of the mixtures studied the relative error is less than 0.01.

Figure 5 shows a distribution $f(z)$ of the relative errors; the relative errors of calculation $z = (\rho - \rho_{calc})/\rho$ are contained in Tables 1 to 3. This plot is well described by a normal distribution

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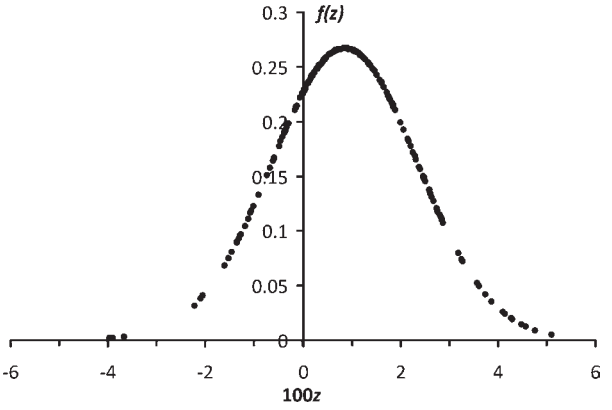

Figure 5. Normal distribution of relative errors z in Tables 1, 2, and 3.

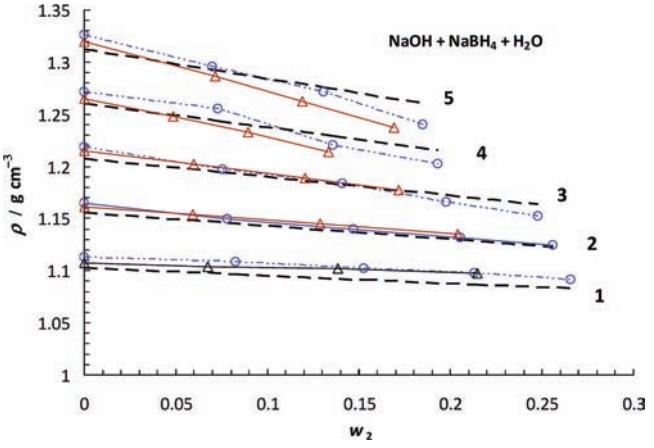

Figure 6. Density ρ of aqueous solutions as a function of the mass fraction w_2 of the dissolved substance for NaOH (1) + $NaBH_4$ (2) + H_2O (3) system at 20 °C. Composition of solvent: (1) $w_1 = 0.1$, $w_3 = 0.9$; (2) $w_1 = 0.15$, $w_3 = 0.85$; (3) $w_1 = 0.2$, $w_3 = 0.8$; (4) $w_1 = 0.25$, $w_3 = 0.75$; (5) $w_1 = 0.3$, $w_3 = 0.7$. Circles, data from ref 3; triangles, our data; dashed lines, calculation by eq 5.

$$f(z) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{(z_i - z_m)^2}{2\sigma^2}\right] \quad (6)$$

where z_m is median of distribution, σ^2 is dispersion. As you can see, the median of relative error distribution is close to zero, but nonzero, $z_m = 0.00865$; that is, the most likely outcome of the algorithm is the value of $\rho_{calc} = 0.99135\rho$ with the relative error of less than 0.01. We believe this result is quite satisfactory. The information contained in Tables 1 to 3 is large but still not representative, so this base is not enough to make adjustments to the algorithm to reach the $z_m \approx 0$.

Figure 6 compares the experimental density of aqueous $NaBH_4$ + NaOH + H_2O solutions at 20 °C (our data and data from ref 3, see above) with those calculated by eq 5 with the usage of the above algorithm. One can see that a satisfactory fit is observed, the calculated lines describe the course of experimental lines in the whole correctly, and the relative deviations are less than 0.02. There are random errors due to experimental inaccuracies and systematic deviations due to the algorithm simplicity (the computed lines are more direct than the experimental lines).

This algorithm is of special value for the discussed five-component system used in hydrogen power engineering. The chemical composition, temperature, and density of the fuel solution are permanently changing in the course of functioning of a DBFC or borohydride HG. Of course, density can be measured. However, no comprehensive study can be performed for such a complex system, while the method proposed allows easy calculating the density of any fuel solution with a practically acceptable accuracy. As is noted in the Introduction, not only water-alkaline borohydride solutions but also an appropriate suspension can serve as fuel for FCs. It is interesting to note that the offered algorithm for density calculations is tolerant to the phase state of the system: the density calculations for a suspension also give a good fit to the experiment.

CONCLUSION

The density of several concentrated water-alkaline solutions of sodium and potassium borohydrides and borates in the temperature range (10 to 50) °C was measured. An algorithm to calculate the density of mixed solutions and suspension of (Na, K)BH_4 + (Na, K)BO_2 + (Na, K)OH + H_2O system was proposed on the basis of this study as well as the literature data available. The algorithm was verified by means of comparison of the measured and calculated density values, a good fit was achieved in most cases.

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