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Volumetric and thermal properties of some aqueous electrolyte solutions Part 5. Potassium bromide and potassium iodide 0.1, 0.5, and 1.0 mol kg^{-1} solutions at temperatures from T=278.15 to 338.15 K

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Abstract

Precise densities of potassium bromide (0.10014, 0.49997, and 0.99962 mol kg^{-1}) and potassium iodide (0.10008, 0.50551, and 0.99993 mol kg^{-1}) aqueous solutions were determined at 1-K temperature intervals from T=278.15 to T=338.15 K, and they are compared with the literature data. Measured densities were expressed as polynomials of temperature, and these polynomials were used in an evaluation of the apparent molar volumes, the cubic expansion coefficients, the apparent molar expansibilities, and the second derivatives of volume with respect to temperature, which are interrelated with the derivatives of isobaric heat capacities with respect to pressure. In the framework of changes in the structure of water, these derivatives are discussed for potassium bromide and potassium iodide solutions.

Keywords: Potassium bromide; Potassium iodide; Electrolytes

1. Introduction

A quantitative description of the volumetric and thermal properties of water and aqueous solutions of electrolytes is of prime importance for various thermodynamic calculations connected with natural and industrial processes and helps in the elucidation of the structure of water and ion–water and ion–ion interactions. Extensive surveys on the subject (see, for example, International Critical Tables [1], Landolt–Börnstein [2], Lobo [3], and Aseyev–Zaytsev [4] tabulations) reveal that these properties are usually known as a function of concentration at one, sometimes at few fixed temperatures but not at constant molality m to permit direct differentiation with respect to temperature T. This situation is changed now, because volumetric properties via density determinations are easily available over a wide temperature range due to the appearance of commercial densimeters (vibrating tubes) equipped with a built-in thermoelectric Peltier-element module for continuous heating or cooling of the sample in a thermostated U-tube.

In a series of our papers [5–8], densities of water and aqueous solutions of electrolytes at fixed molalities 0.1, 0.5, and 1.0 mol kg^{-1} were determined at closely spaced 1-K temperature intervals, usually from T=277.15 to 343.15 K (water, NaCl, and KCl [5], LiCl [6], NaBr [7], disodium and dipotassium tartrates [8], see also Ref. [9] for coefficients of the fitting equations of the type (1) for KBr, KI, and other solutions). From these densities, $\rho(T;m)$, the cubic expansion coefficients, $\alpha(T;m)$, the apparent molar volumes, $V_{2,\phi}(T;m)$, the apparent molar expansibilities, $V_{2,E}(T;m)$, and the second derivatives of volume with respect to temperature, $[(\partial^2 V)/(\partial T^2)]_{P,m}$ were reported. The last quantity is directly related to the change of molar heat

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Table 1
Experimental densities $\rho(T;m)$ of aqueous solutions of potassium bromide and potassium iodide as a function of $\theta=T/K-273.15$

m / θ	KBr			KI		
	0.1[a]	0.5[b]	1.0[c] $\rho(T;m)$/ g cm^{-3}	0.1[d]	0.5[e]	1.0[f]
5	1.00866	1.04254	1.08275	1.01220	1.06071	1.11681
6	1.00864	1.04243	1.08256	1.01217	1.06060	1.11661
7	1.00859	1.04230	1.08236	1.01212	1.06045	1.11638
8	1.00852	1.04214	1.08214	1.01205	1.06030	1.11611
9	1.00844	1.04205	1.08198	1.01201	1.06015	1.11591
10	1.00834	1.04188	1.08173	1.01191	1.05996	1.11563
11	1.00823	1.04170	1.08150	1.01180	1.05978	1.11537
12	1.00812	1.04153	1.08127	1.01168	1.05958	1.11510
13	1.00798	1.04135	1.08102	1.01154	1.05937	1.11482
14	1.00784	1.04115	1.08077	1.01139	1.05917	1.11453
15	1.00767	1.04095	1.08050	1.01125	1.05892	1.11423
16	1.00750	1.04073	1.08023	1.01108	1.05869	1.11392
17	1.00734	1.04052	1.07996	1.01088	1.05846	1.11362
18	1.00715	1.04027	1.07967	1.01069	1.05821	1.11329
19	1.00694	1.04002	1.07937	1.01047	1.05793	1.11296
20	1.00673	1.03977	1.07908	1.01025	1.05766	1.11262
21	1.00649	1.03947	1.07873	1.01002	1.05735	1.11224
22	1.00626	1.03921	1.07842	1.00978	1.05706	1.11190
23	1.00603	1.03892	1.07808	1.00953	1.05676	1.11152
24	1.00580	1.03868	1.07779	1.00928	1.05649	1.11114
25	1.00553	1.03837	1.07744	1.00902	1.05616	1.11078
26	1.00525	1.03804	1.07708	1.00874	1.05584	1.11038
27	1.00499	1.03774	1.07673	1.00847	1.05551	1.10998
28	1.00470	1.03744	1.07638	1.00818	1.05517	1.10952
29	1.00435	1.03708	1.07595	1.00786	1.05477	1.10913
30	1.00405	1.03671	1.07558	1.00756	1.05442	1.10867
31	1.00373	1.03636	1.07519	1.00724	1.05405	1.10824
32	1.00341	1.03601	1.07481	1.00692	1.05367	1.10779
33	1.00309	1.03566	1.07442	1.00659	1.05331	1.10736
34	1.00278	1.03532	1.07402	1.00625	1.05295	1.10693
35	1.00243	1.03494	1.07362	1.00589	1.05255	1.10646
36	1.00204	1.03451	1.07318	1.00553	1.05211	1.10599
37	1.00170	1.03415	1.07277	1.00516	1.05173	1.10547
38	1.00131	1.03373	1.07233	1.00479	1.05130	1.10497
39	1.00092	1.03331	1.07189	1.00441	1.05086	1.10448
40	1.00054	1.03291	1.07144	1.00403	1.05043	1.10398
41	1.00015	1.03249	1.07099	1.00362	1.05000	1.10349
42	0.99977	1.03209	1.07056	1.00321	1.04958	1.10301
43	0.99933	1.03163	1.07006	1.00280	1.04910	1.10247
44	0.99892	1.03119	1.06960	1.00238	1.04864	1.10194
45	0.99849	1.03073	1.06912	1.00197	1.04816	1.10141
46	0.99807	1.03028	1.06865	1.00153	1.04771	1.10089
47	0.99763	1.02983	1.06818	1.00110	1.04723	1.10037
48	0.99720	1.02938	1.06769	1.00065	1.04676	1.09984
49	0.99674	1.02889	1.06717	1.00021	1.04626	1.09926
50	0.99630	1.02843	1.06670	0.99975	1.04579	1.09874
51	0.99584	1.02795	1.06619	0.99929	1.04527	1.09817
52	0.99538	1.02746	1.06569	0.99882	1.04478	1.09762
53	0.99488	1.02695	1.06515	0.99835	1.04425	1.09705
54	0.99442	1.02646	1.06466	0.99786	1.04375	1.09649
55	0.99391	1.02594	1.06409	0.99737	1.04320	1.09590
56	0.99341	1.02542	1.06356	0.99687	1.04268	1.09533
57	0.99293	1.02494	1.06307	0.99637	1.04217	1.09478
58	0.99243	1.02440	1.06250	0.99587	1.04162	1.09419
59	0.99193	1.02388	1.06196	0.99537	1.04109	1.09363
60	0.99142	1.02336	1.06142	0.99483	1.04054	1.09307
61	0.99090	1.02282	1.06086	0.99431	1.03998	1.09248
62	0.99037	1.02227	1.06030	0.99379	1.03942	1.09190
63	0.98982	1.02169	1.05971	0.99323	1.03883	1.09135
64	0.98931	1.02115	1.05916	0.99270	1.03828	1.09076
65	0.98876	1.02057	1.05859	0.99216	1.03771	1.09019

[a] m=0.10014 mol kg^{-1}.
[b] m=0.49997 mol kg^{-1}.
[c] m=0.99962 mol kg^{-1}.
[d] m=0.10008 mol kg^{-1}.
[e] m=0.50551 mol kg^{-1}.
[f] m=0.99993 mol kg^{-1}.

capacity with pressure, $[(\partial C_p)/(\partial P)]_{T,m}$. Hepler [10] was the first to correlate, at least qualitatively, these derivatives at an infinite dilution of solute with the structure of water (the transformation of a strongly hydrogen-bonded structure of water into a "normal" liquid as temperature or pressure increases) and to distinguish between the structure-making and structure-breaking solutes. Similar considerations for aqueous solutions of polar and nonpolar nonelectrolytes were given by Neal and Goring [11] and Sakurai et al. [12,13].

In this work, which continues our previous investigations on the volume–temperature relations in aqueous electrolyte solutions, two more salts, potassium bromide, and potassium iodide are considered. KBr and KI solutions were extensively studied in the literature (for the complete list of references see Refs. [1–4]); however, the quality of reported data is highly uneven. Critical analysis of the apparent molar volumes at T=298.15 K performed by Krumgalz et al. [14] showed that in the calculation of the Pitzer coefficients from 15 available sets of data for potassium bromide, 8 sets should be partially or completely rejected. In the case of potassium iodide, from 11 sets of data, 4 sets were discarded. With regard to the temperature dependence of densities at considered concentrations, the measurements at 5-, 10-, and 20-K temperature intervals were performed with KBr or KI solutions by Prakash et al. [15], Suhrmann and Wiedersich [16], Lengyel et al. [17], Ellis [18], Out and Los [19], Isono [20] and Maksimova et al. [21]. Millero and Drost-Hansen [22] measured densities of m=0.10457 mol kg^{-1} potassium bromide and m=0.10154 mol kg^{-1} potassium iodide solutions at 1-K temperature intervals, but only in the T=293.15 to 313.15 K temperature range. At one temperature, usually at T=298.15 K, densities or $V_{2,\phi}(T;m)$ were reported for the studied concentrations in the investigations of Scott [23], Jones and Talley [24], Jones and Bickford [25], Scott et al. [26], Wirth [27], Halasey [28], McInnes and Dayhoff [29], Dunn [30], Fortier et al. [31], Vorobiev et al. [32], and Millero et al. [33]. Recently, using a pycnometer, Rohman et al. [41] measured densities of KBr solutions (from m=0.0085 to