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Density, Refractive Index, and Specific Refraction of Aqueous Lithium Iodate Solutions

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Densities and refractive indexes of aqueous lithium iodate solutions (0.01–3.0 M) have been determined over the temperature range 18 to 60 °C. From these experimental data, the relative density d/d_{H_2O}, relative refractive index n/n_{H_2O}, specific refraction R, and relative specific refraction R/R_{H_2O} have been calculated. It was found that in the investigated range of concentration the values of R and R/R_{H_2O} are practically independent of temperature but that in the whole range of temperatures both decrease with an increase in solution concentration. The temperature and concentration dependence of all these quantites may be represented by quadratic or linear functions.

Introduction

Solid lithium iodate is an interesting material for scientific investigations. In contrast with a large majority of substances for which data on physical properties of solutions are available in the literature, lithium iodate has a negative temperature coefficient of solubility and its physical properties have been little investigated. In particular, a survey of the existing literature showed that, apart from the data on the density of saturated solutions (*1*), data for undersaturated solutions are either very old (*2*, *3*) or sparse (*4*).

When present in the crystalline form, $LiIO_3$ exhibits nonlinear electrooptic behavior (*5*). For the investigation of the nonlinear properties and for the use of the material in device fabrication, it is grown as single crystals with the lowest possible density of defects. Since 1971 several papers have been devoted to the investigation of its growth in the form of single crystals of good quality under a variety of experimental conditions (*5–8*).

The quality of a crystal grown from solution depends on a number of factors such as temperature, solution concentration, and the presence of impurities. These factors also determine the structure and the macroscopic and microscopic properties of solutions. This means that the quality of a crystal grown from solution depends on the chemical constitution and structure of the solution. In fact, on the basis of a study of the osmotic pressure and density of saturated aqueous solutions, it was concluded that the best lithium iodate crystals are produced from those solutions in which the ions of the solid are least associated (*1*).

As a part of our general research program on the structure of growth media, it was thought worthwhile to study the density and refractive index of aqueous lithium iodate solutions as a function of temperature and solute concentration.

Experimental Section

$LiIO_3$ compound for experimental purposes was synthesized by neutralizing a solution of 1 M HIO_3 to pH 7 by adding analytical grade Li_2CO_3 or LiOH. Solid $LiIO_3$ was obtained by drying this neutral solution to constant weight. By dissolution of a known mass of solid $LiIO_3$ (weighed with an analytical balance up to 1×10^{-5} g accuracy) in double distilled water, 1 L of solution of the desired concentration was prepared at 20 °C.

Density and refractive index measurements were made on 0.6 L of solution contained in a 20 cm long cylindrical glass vessel of 0.75-L capacity. The vessel was placed in a thermostated water jacket whose temperature was regulated by a contact thermometer and measured with a mercury thermometer with an accuracy of 0.05 °C. The temperature variations in the vessel solution were estimated to be less than 0.01 °C.

Density measurements of a solution were carried out by using a hydrostatic balance (accuracy 5×10^{-4} g) and a 10-cm^3 float immersed in the solution. The correct values of density d, considering capillary action and air density, were calculated from the measured density d_m by using the relation: $d = d_m + 0.0002d_m + 0.0012$, verified for water in the temperature range 15–65 °C. Density measurements for solution of a given concentration were made at least twice at a particular temperature. The density values were reproducible to 1×10^4 g/cm^3.

Refractive index data were obtained by using a Carl Zeiss immersion refractometer supplied with three thermoprisms T_1, T_2, and T_3 of refractive index intervals 1.3254–1.3664, 1.3642–1.3999, and 1.3989–1.4360, respectively. T_1 and T_2 were calibrated in the whole temperature interval with water and acetic acid, respectively, while the third was calibrated in such a way that the refractive index values obtained by the second prism corresponded to those by T_3. The correction in the refractive index value was $1 \times 10^6 t$. Reproducibility of the data was within 1×10^{-5}, and the error in the calibration due to temperature was 1×10^{-5}, whence the instrumental error was 2×10^{-5}.

Initially only density measurements were planned and carried out for $LiIO_3$ solutions in the concentration range 0.2–3.0 M. Later, however, refractive index measurements were also planned and the concentration range was extended down to 0.01 M. Consequently, in the 0.2–3.0 M concentration range density measurements were made for one set of solutions, while refractive index data were obtained for another set of solutions prepared again. However, in the 0.01–0.1 M concentration range both density and refractive data were obtained from the same set of solutions.

Results

Experimental density, d (g/cm^3), and refractive index, n, data for aqueous $LiIO_3$ solutions at different temperatures are given in Tables I–III. It may be noted from the tables that density and refractive index values decrease as solution temperature increases but increase as solution concentration increases. Plots of the densities and refractive indenes of the solutions as a function of temperature revealed that the curves for both become increasingly linear as solute concentration increases.

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Table I. Experimental Density Data (g/cm³) for Aqueous $LiIO_3$ Solutions in the Concentration Range 0.01-0.1 M at Various Temperatures

	concentration, M					
t, °C	0.01	0.02	0.04	0.06	0.08	0.10
18	1.0001	1.0015	1.0047	1.0078	1.0109	1.0141
20	0.9997	1.0011	1.0042	1.0074	1.0105	1.0137
22	0.9992	1.0007	1.0038	1.0069	1.0099	1.0132
24	0.9987	1.0002	1.0033	1.0064	1.0094	1.0126
26	0.9982	0.9997	1.0028	1.0059	1.0089	1.0120
28	0.9977	0.9992	1.0023	1.0055	1.0083	1.0114
30	0.9971	0.9987	1.0017	1.0049	1.0078	1.0109
32	0.9965	0.9982	1.0011	1.0043	1.0071	1.0103
34	0.9959	0.9975	1.0004	1.0036	1.0065	1.0097
36	0.9952	0.9967	0.9997	1.0029	1.0058	1.0090
38	0.9944	0.9960	0.9990	1.0022	1.0050	1.0083
40	0.9937	0.9952	0.9982	1.0015	1.0043	1.0074
42	0.9929	0.9944	0.9974	1.0007	1.0035	1.0066
44	0.9921	0.9936	0.9967	0.9999	1.0027	1.0058
46	0.9913	0.9928	0.9959	0.9990	1.0019	1.0050
48	0.9905	0.9920	0.9950	0.9981	1.0011	1.0041
50	0.9896	0.9911	0.9941	0.9972	1.0003	1.0032
52	0.9887	0.9902	0.9932	0.9963	0.9994	1.0023
54	0.9877	0.9893	0.9922	0.9954	0.9984	1.0013
56	0.9867	0.9883	0.9912	0.9944	0.9974	1.0003
58	0.9857	0.9873	0.9903	0.9934	0.9964	0.9993
60	0.9847	0.9863	0.9893	0.9924	0.9954	0.9983

This behavior is presented in Figure 1 for the temperature dependence of the refractive index of solutions.

The experimental data on the densities and refractive indexes of the solutions may be represented by the quadratic equations

$$d = d_0(t) + a_1c + a_2c^2 \quad (1)$$

$$n = n_0(t) + b_1c + b_2c^2 \quad (2)$$

$$d = d_0(c) + a_3t + a_4t^2 \quad (3)$$

$$n = n_0(c) + b_3t + b_4t^2 \quad (4)$$

Here eq 1 and 2 describe the density and refractive index data as a function of concentration, and $d_0(t)$, a_1, a_2, $n_0(t)$, b_1, and b_2 are temperature-dependent constants. Similarly, eq 3 and 4 represent them as a function of solution temperature, and $d_0(c)$, a_3, a_4, $n_0(c)$, b_3, and b_4 are concentration-dependent constants. The experimental data were fitted by the least-squares method, and values of the various coefficient and the standard deviations were determined. These are given in Tables IV–VII.

One notes from Tables IV and V that the values of both $d_0(t)$ and a_1 and of $n_0(t)$ and b_1 decrease with an increase in temperature, but the value of a_2 increases with temperature while that of b_2 remains constant. Tables VI and VII, on the other hand, show that as solution concentration increases, the values of $d_0(c)$, $n_0(c)$, a_4, and b_4 increase, while those of a_3 and b_3 decrease.

Recently, a new equation was proposed to describe the temperature dependence of the density of saturated solutions (*9*). The data on both the temperature dependence of density and refractive index were analyzed according to this new equation, written, respectively, in the form

$$d = d_0' \exp[\beta'(T - T_0')^2] \quad (5)$$

$$n = n_0' \exp[\beta''(T - T_0'')^2] \quad (6)$$

where the coefficients d_0', β', and T_0' of eq 5, and n_0', β'', and

Table II. Experimental Density Data (g/cm³) for Aqueous $LiIO_3$ Solutions in the Concentration Range 0.2-3.0 M at Various Temperatures

t, °C	0.20 M	t, °C	0.40 M	t °C	0.60 M	t °C	0.80 M	t °C	1.00 M
18.0	1.0294	18.0	1.0611	18.0	1.0914	18.0	1.1217	18.0	1.1524
21.1	1.0284	21.3	1.0601	19.7	1.0910	21.5	1.1205	20.8	1.1514
24.4	1.0276	24.5	1.0592	22.1	1.0902	23.0	1.1200	23.8	1.1502
28.3	1.0262	27.8	1.0580	25.5	1.0891	25.9	1.1190	27.2	1.1489
32.2	1.0248	30.7	1.0571	28.9	1.0879	29.1	1.1177	31.4	1.1472
35.6	1.0238	33.2	1.0562	32.2	1.0865	32.2	1.1164	35.2	1.1452
39.2	1.0224	35.8	1.0552	35.9	1.0844	35.4	1.1151	38.8	1.1434
42.5	1.0211	38.3	1.0540	38.4	1.0838	38.4	1.1135	42.4	1.1417
44.6	1.0200	40.4	1.0531	41.2	1.0826	42.3	1.1116	46.5	1.1393
47.2	1.0190	42.8	1.0521	44.3	1.0809	46.5	1.1094	49.2	1.1378
49.8	1.0175	45.6	1.0508	47.6	1.0792	49.4	1.1080	52.4	1.1361
52.8	1.0160	48.7	1.0491	49.7	1.0781	52.9	1.1061	56.0	1.1338
55.4	1.0146	50.6	1.0482	52.1	1.0768	56.4	1.1042	59.2	1.1319
57.8	1.0130	53.4	1.0467	54.5	1.0756	60.0	1.1021	60.6	1.1312
60.2	1.0116	56.0	1.0454	58.6	1.0735				
		59.3	1.0437	61.0	1.0720				

t, °C	1.50 M	t, °C	2.00 M	t, °C	2.50 M	t, °C	3.00 M
17.8	1.2284	18.0	1.3026	17.9	1.3770	17.5	1.4508
19.8	1.2275	20.0	1.3019	20.9	1.3751	20.5	1.4488
21.8	1.2266	22.0	1.3007	24.7	1.3730	22.7	1.4474
23.7	1.2256	23.8	1.3000	29.0	1.3705	26.8	1.4448
26.2	1.2244	25.9	1.2990	33.8	1.3674	29.5	1.4431
28.4	1.2233	27.8	1.2980	38.1	1.3645	32.8	1.4409
30.0	1.2226	29.8	1.2965	41.7	1.3621	36.6	1.4384
32.1	1.2214	32.2	1.2949	45.6	1.3596	40.3	1.4357
34.2	1.2205	34.4	1.2936	49.8	1.3569	44.1	1.4332
35.9	1.2196	36.0	1.2926	53.3	1.3546	48.5	1.4302
37.6	1.2186	37.8	1.2916	55.9	1.3529	52.4	1.4277
40.1	1.2170	40.0	1.2902	58.6	1.3512	56.3	1.4251
42.0	1.2160	42.2	1.2888	60.3	1.3501	59.8	1.4228
44.0	1.2150	44.0	1.2877			61.2	1.4219
46.9	1.2131	46.5	1.2862				
50.2	1.2110	48.1	1.2852				
53.5	1.2092	50.3	1.2836				
56.8	1.2071	52.3	1.2825				
60.0	1.2050	54.1	1.2811				
		56.0	1.2799				
		60.0	1.2773				

Table III. Experimental Refractive Index Data for Aqueous $LiIO_3$ Solutions in the Concentration Range 0.01–3.00 M at Various Temperatures

	concentration, M							
t, °C	0.01	0.02	0.04	0.06	0.08	0.10	0.20	0.40
18	1.333 42	1.333 65	1.334 22	1.334 74	1.335 23	1.335 71	1.338 21	1.343 05
20	1.333 26	1.333 48	1.334 03	1.334 55	1.335 04	1.335 52	1.338 05	1.342 85
22	1.333 07	1.333 27	1.333 83	1.334 34	1.334 83	1.335 30	1.337 84	1.342 64
24	1.332 89	1.333 09	1.333 61	1.334 13	1.334 62	1.335 14	1.337 61	1.342 41
26	1.332 66	1.332 89	1.333 40	1.333 92	1.334 40	1.334 88	1.337 37	1.342 16
28	1.332 44	1.332 66	1.333 18	1.333 70	1.334 18	1.334 64	1.337 11	1.341 90
30	1.332 18	1.332 40	1.332 94	1.333 42	1.333 90	1.334 38	1.336 85	1.341 61
32	1.331 90	1.332 13	1.332 66	1.333 16	1.333 58	1.334 10	1.336 56	1.341 32
34	1.331 64	1.331 86	1.332 38	1.332 87	1.333 36	1.333 82	1.336 27	1.341 00
36	1.331 36	1.331 59	1.332 10	1.332 60	1.333 05	1.333 54	1.335 98	1.340 69
38	1.331 06	1.331 30	1.331 80	1.332 30	1.332 78	1.333 26	1.335 68	1.340 36
40	1.330 78	1.331 02	1.331 52	1.332 00	1.332 48	1.332 95	1.335 39	1.340 00
42	1.330 49	1.330 74	1.331 23	1.331 72	1.332 18	1.332 68	1.335 09	1.339 68
44	1.330 19	1.330 44	1.330 92	1.331 38	1.331 84	1.332 32	1.334 78	1.339 33
46	1.329 86	1.330 12	1.330 56	1.331 05	1.331 52	1.332 00	1.334 44	1.338 99
48	1.329 53	1.329 78	1.330 25	1.330 74	1.331 18	1.331 66	1.334 09	1.338 66
50	1.329 20	1.329 44	1.329 93	1.330 39	1.330 86	1.331 34	1.333 73	1.338 31
52	1.328 87	1.329 12	1.329 59	1.330 06	1.330 54	1.331 00	1.333 39	1.337 96
54	1.328 52	1.328 76	1.329 25	1.329 71	1.330 17	1.330 64	1.333 04	1.337 63
56	1.328 19	1.328 43	1.328 92	1.329 38	1.329 84	1.330 32	1.332 68	1.337 30
58	1.327 80	1.328 05	1.328 55	1.328 99	1.329 47	1.329 95	1.332 33	1.336 95
60	1.327 44	1.327 68	1.328 18	1.328 63	1.329 10	1.329 60	1.331 98	1.336 61

Table IV. Coefficients and Standard Deviations of Eq 1 at Different Temperatures[a]

t, °C	$d_0(t)$, g/cm^3	a_1, (g L)/(cm^3 mol)	$-a_2 \times 10^3$, (g L^2)/(cm^3 mol^2)	SD[b] × 10^5
20	0.998 11	0.155 30	1.666	6.1
30	0.995 62	0.153 48	1.517	5.8
40	0.992 23	0.151 82	1.333	7.6
50	0.988 13	0.150 37	1.135	8.4
60	0.983 26	0.148 94	0.846	10.4

[a] $d = d_0(t) + a_1c + a_2c^2$. [b] SD = standard deviation.

Table V. Coefficients and Standard Deviations of Eq 2 at Different Temperatures[a]

t, °C	$n_0(t)$	b_1, L/mol	$-b_2 \times 10^4$ L/mol^2	SD × 10^5
20	1.333 095	0.024 365	3.236	2.5
30	1.331 990	0.024 042	3.367	1.8
40	1.330 593	0.023 626	2.894	1.5
50	1.329 000	0.023 388	2.920	1.3
60	1.327 266	0.023 250	3.047	2.1

[a] $n = n_0(t) + b_1c + b_2c^2$.

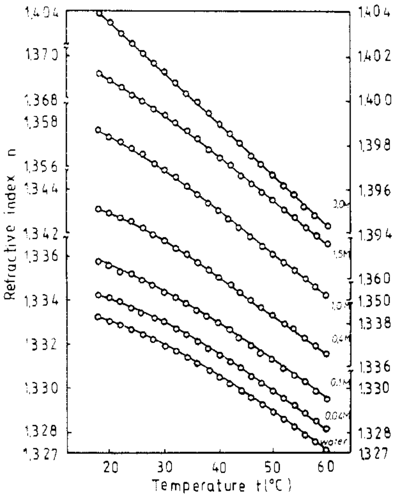

Figure 1. Temperature dependence of refractive index of lithium iodate solutions at selected concentrations. The plot for water is based on the data from *CRC Handbook* (*12*).

T_0'' of eq 6 are functions of concentration. These constants and standard deviations are summarized in Tables VIII and IX.

Table VI. Coefficients and Standard Deviations of Eq 3 at Different Solute Concentrations[a]

concn, M	$d_0(c)$, g/cm^3	$-a_3 \times 10^5$, g/(cm^3 °C)	$-a_4 \times 10^6$, g/(cm^3 °C^2)	SD × 10^5
0.00	1.001 16	7.008	3.835	0.7
0.01	1.002 59	6.874	3.832	0.9
0.02	1.003 86	5.668	3.953	1.7
0.04	1.007 27	7.407	3.778	1.1
0.06	1.010 13	5.633	4.009	1.2
0.08	1.013 79	9.804	3.469	1.0
0.10	1.016 88	8.744	3.716	1.2
0.20	1.031 89	6.979	4.405	3.7
0.40	1.064 85	14.178	3.670	2.3
0.60	1.096 15	19.543	3.314	3.1
0.80	1.126 90	22.835	3.105	2.6
1.00	1.158 03	25.109	3.208	2.9
1.50	1.235 62	36.050	2.508	2.2
2.00	1.312 01	46.719	1.896	4.1
2.50	1.387 64	57.655	0.793	3.4
3.00	1.462 21	64.514	0.243	2.6

[a] $d = d_0(c) + a_3t + a_4t^2$.

Table VII. Coefficients and Standard Deviations Eq 4 at Different Solute Concentrations[a]

concn, M	$n_0(c)$	$-b_3 \times 10^5$, (°C)$^{-1}$	$-b_4 \times 10^6$, (°C)$^{-2}$	SD × 10^6
0.00	1.334 645	5.940	1.088	5.9
0.01	1.334 866	5.697	1.119	5.3
0.02	1.335 032	5.422	1.143	4.4
0.04	1.335 719	6.227	1.062	4.8
0.06	1.336 265	6.345	1.070	4.8
0.08	1.336 818	6.749	1.025	5.4
0.10	1.337 310	6.797	1.020	5.8
0.20	1.339 912	7.288	1.001	5.4
0.40	1.345 126	9.527	0.800	11.4
0.60	1.350 167	10.806	0.717	7.3
0.80	1.354 914	10.544	0.833	8.0
1.00	1.360 208	13.219	0.573	10.3
1.50	1.371 706	13.182	0.643	9.2
2.00	1.383 796	15.381	0.631	9.4
2.50	1.395 802	19.215	0.223	5.3
3.00	1.407 658	20.989	0.203	7.3

[a] $n = n_0(c) + b_3t + b_4t^2$.

These tables show that the values of d_0', n_0', β', and β'' increase whereas those of T_0' and T_0'' decrease with an increase in solute concentration. However, relatively poor values of standard deviation obtained for eq 5 and 6 suggest that eq

concentration, M						
0.60	0.80	1.00	1.50	2.00	2.50	3.00
1.347 93	1.352 66	1.357 56	1.369 04	1.380 75	1.392 29	1.403 83
1.347 68	1.352 44	1.357 29	1.368 78	1.380 43	1.391 88	1.403 40
1.347 44	1.352 20	1.357 00	1.368 50	1.380 10	1.391 44	1.402 92
1.347 18	1.351 94	1.356 74	1.368 18	1.379 76	1.391 04	1.402 48
1.346 92	1.351 66	1.356 48	1.367 88	1.379 40	1.390 64	1.402 04
1.346 62	1.351 38	1.356 10	1.367 57	1.379 07	1.390 24	1.401 62
1.346 33	1.351 05	1.355 80	1.367 23	1.378 68	1.389 86	1.401 20
1.346 00	1.350 71	1.355 44	1.366 89	1.378 29	1.389 41	1.400 71
1.345 70	1.350 37	1.355 06	1.366 52	1.377 83	1.389 00	1.400 28
1.345 36	1.350 01	1.354 69	1.366 14	1.377 46	1.388 67	1.399 88
1.345 00	1.349 68	1.354 32	1.365 76	1.377 02	1.388 20	1.399 40
1.344 68	1.349 34	1.354 00	1.365 38	1.376 63	1.387 74	1.398 96
1.344 35	1.349 00	1.353 66	1.364 99	1.376 20	1.387 32	1.398 51
1.343 99	1.348 64	1.353 25	1.364 60	1.375 78	1.386 94	1.398 03
1.343 66	1.348 28	1.352 89	1.364 23	1.375 36	1.386 48	1.397 52
1.343 30	1.347 90	1.352 50	1.363 86	1.374 88	1.386 06	1.397 12
1.342 93	1.347 54	1.352 12	1.363 50	1.374 49	1.385 61	1.396 59
1.342 59	1.347 15	1.351 74	1.363 09	1.374 06	1.385 18	1.396 20
1.342 25	1.346 80	1.351 37	1.362 70	1.373 66	1.384 78	1.395 82
1.341 85	1.346 42	1.351 02	1.362 31	1.373 25	1.384 36	1.395 22
1.341 51	1.346 03	1.350 66	1.361 92	1.372 76	1.383 91	1.394 80
1.341 16	1.345 60	1.350 28	1.361 54	1.372 35	1.383 48	1.394 34

Table VIII. Coefficients and Standard Deviations of Eq 5 at Different Solute Concentrations[a]

concn, M	d_0, g/cm^3	$-\beta' \times 10^6$, K^{-2}	t_0', K	SD × 10^5
0.00	1.001 32	3.962	265	3.0
0.01	1.002 77	3.938	265	4.0
0.02	1.004 24	3.906	265	8.0
0.04	1.007 53	3.851	264	4.8
0.06	1.010 71	3.845	264	6.4
0.08	1.013 80	3.745	263	5.9
0.10	1.017 30	3.748	262	5.7
0.20	1.033 02	3.976	261	15.9
0.40	1.066 23	3.505	254	8.5
0.60	1.098 82	3.130	245	11.2
0.80	1.130 60	2.897	239	8.5
1.00	1.162 84	2.851	235	9.3
1.50	1.247 31	2.176	207	7.8
2.00	1.337 89	1.589	162	14.3
2.50	1.475 90	0.695	−25	8.9
3.00	1.762 38	0.262	−572	6.5

[a] $d = d_0 \exp[\beta'(T - T_0')^2]$.

Table IX. Coefficients and Standard Deviations of Eq 6 at Different Solute Concentrations[a]

concn, M	n_0	$-\beta'' \times 10^6$, K^{-2}	T_0'', K	SD × 10^5
0.00	1.335 373	0.834	247	2.1
0.01	1.335 567	0.847	248	2.1
0.02	1.335 253	0.971	256	3.4
0.04	1.336 619	0.802	244	1.7
0.06	1.337 169	0.811	244	1.7
0.08	1.337 945	0.769	240	1.8
0.10	1.338 430	0.769	240	2.2
0.20	1.341 221	0.754	237	1.9
0.40	1.347 864	0.607	215	4.0
0.60	1.354 079	0.544	200	2.7
0.80	1.358 255	0.619	210	2.7
1.00	1.367 603	0.433	161	3.4
1.50	1.378 205	0.483	174	3.1
2.00	1.392 664	0.477	157	3.1
2.50	1.431 813	0.183	−100	1.6
3.00	1.457 697	0.159	−196	2.5

[a] $n = n_0 \exp[\beta''(T - T_0'')^2]$.

3 and 4 better describe the temperature dependence of the density and refractive index of aqueous $LiIO_3$ solutions.

A careful inspection of the values for parameters a_3 and a_4 (Table VI), and b_3 and b_4 (Table VII) reveals that at certain concentrations (e.g., 0.02, 0.2, and 1.0 M for density, and 0.02, 0.8, and 1.5 M for refractive index) a sudden increase is observed. These jumps may be associated with the properties of the water (*10*, *11*), used as solvent here, as well as with the measurement errors. In order to eliminate the possible influence of the properties of the solvent water, the data were fitted according to the equations

Table X. Coefficients and Standard Deviations of Eq 7 at Different Temperatures[a]

t, °C	α_0	α_1, L/mol	$-\alpha_2 \times 10^3$, (L/mol)^2	SD × 10^5
20	0.999 91	0.155 58	1.669	6.1
30	0.999 97	0.154 15	1.524	5.8
40	1.000 02	0.153 01	1.343	7.6
50	1.000 09	0.152 19	1.149	8.4
60	1.000 05	0.151 48	0.861	10.4

[a] $d/d_{H_2O} = \alpha_0 + \alpha_1 c + \alpha_2 c^2$.

Table XI. Coefficients and Standard Deviations of Eq 8 at Different Temperatures[a]

t, °C	β_0	$\beta_1 \times 10^2$, L/mol	$-\beta_2 \times 10^4$, (L/mol)^2	SD × 10^5
20	1.000 080	1.8278	2.429	1.8
30	1.000 055	1.8048	2.519	1.4
40	1.000 061	1.7755	2.164	1.1
50	1.000 045	1.7601	2.206	0.9
60	1.000 065	1.7517	2.295	1.6

[a] $n/n_{H_2O} = \beta_0 + \beta_1 c + \beta_2 c^2$.

$$d/d_{H_2O} = \alpha_0 + \alpha_1 c + \alpha_2 c^2 \qquad (7)$$

$$n/n_{H_2O} = \beta_0 + \beta_1 c + \beta_2 c^2 \qquad (8)$$

$$d/d_{H_2O} = \alpha_3 + \alpha_4 t + \alpha_5 t^2 \qquad (9)$$

$$n/n_{H_2O} = \beta_3 + \beta_4 t + \beta_5 t^2 \qquad (10)$$

where the quantity d/d_{H_2O} is relative density, n/n_{H_2O} is relative refractive index, and α_i and β_i are constants. Equations 7 and 8 describe relative density and relative refractive index of the solutions as a function of solute concentration, while eq 9 and 10 express them as a function of temperature. For the calculation of these quantities, the values of d_{H_2O} and n_{H_2O} were taken from the *CRC Handbook* (*12*). The values of the coef-

Table XII. Coefficients and Standard Deviations of Eq 9 at Different Solute Concentrations[a]

concn, M	α_3	$-\alpha_4 \times 10^4$, $(°C)^{-1}$	$\alpha_5 \times 10^6$, $(°C)^{-2}$	SD × 10^5
0.20	1.030 71	–0.033	–0.488	4.1
0.40	1.063 62	0.679	0.412	1.9
0.60	1.094 76	1.095	0.723	2.2
0.80	1.125 64	1.498	1.176	2.2
1.00	1.156 72	1.701	1.178	2.4
1.50	1.234 28	2.786	2.237	2.2
2.00	1.310 31	3.645	2.937	3.8
2.50	1.386 11	4.833	4.515	2.9
3.00	1.460 62	5.461	5.302	2.0

[a] $d/d_{H_2O} = \alpha_3 + \alpha_4 t + \alpha_8 t^2$.

Table XIII. Coefficients and Standard Deviations of Eq 10 at Different Solute Concentrations[a]

concn, M	β_3	$-\beta_4 \times 10^5$ $(°C)^{-1}$	$\beta_5 \times 10^7$, $(°C)^{-2}$	SD × 10^6
0.06	1.001 206	0.245	0.063	2.5
0.08	1.001 635	0.634	0.528	3.0
0.10	1.001 997	0.625	0.509	3.2
0.20	1.003 948	1.014	0.708	3.3
0.40	1.007 860	2.686	2.244	6.1
0.60	1.011 634	3.613	2.876	3.5
0.80	1.015 189	3.392	2.027	2.1
1.00	1.019 159	5.404	4.040	4.6
1.50	1.027 714	5.315	3.542	4.8
2.00	1.036 830	6.926	3.702	4.4
2.50	1.045 827	9.770	6.835	6.7
3.00	1.054 698	10.987	6.954	7.8

[a] $n/n_{H_2O} = \beta_3 + \beta_4 t + \beta_5 t^2$.

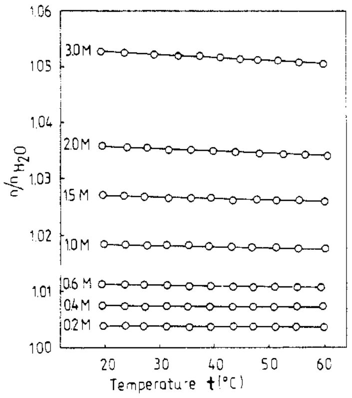

Figure 2. Curves of the temperature dependence of relative refractive index n/n_{H_2O} of aqueous lithium iodate solutions at selected concentrations. For the sake of clarity all data points are not indicated on the curves.

ficients α and β are given in Tables X–XIII.

Tables X and XI show that with an increase in temperature the values of constants α_0 and α_2 increase, those of α_1 and β_1 decrease, while those of β_0 and β_2 are practically invariant. Tables XII and XIII, however, show that with an increase in concentration the values of α_3, α_5, β_3, and β_5 increase while those of α_4 and β_4 decrease regularly. The values of parameters α_3, α_4, α_5, β_3, β_4, and β_5 are not included for solutions having concentrations lower than 0.6 M because of relatively small changes in the values of density and refractive index at these concentrations. It should be noted that the values of parameters α_5 and β_5 are negligible in comparison with the contribution of the linear terms in eq 9 and 10. Therefore, the dependence of n/n_{H_2O} on temperature is practically linear as shown in Figure 2. A similar trend was observed for the dependence of d/d_{H_2O} on temperature.

From the experimental density and refractive index data given in Tables I–III and also using eq 1 to estimate the values of d at temperatures at which only n has been measured experimentally, the specific refraction

$$R = (n^2 - 1)/(n^2 + 2)d \tag{11}$$

and the relative specific refraction

$$R/R_{H_2O} = \frac{(n^2 - 1)}{(n^2 + 2)d} \bigg/ \frac{(n_{H_2O}{}^2 - 1)}{(n_{H_2O}{}^2 + 2)d_{H_2O}} \tag{12}$$

were calculated. In the calculations of R_{H_2O} the data on d_{H_2O} and n_{H_2O} reported in *CRC Handbook* (*12*) were used. These values of R and R_{H_2O} were subsequently fitted to the equations

$$R = A_0 + A_1 t \tag{13}$$

$$R = A_2 + A_3 c + A_4 c^2 \tag{14}$$

$$R/R_{H_2O} = B_0 + B_1 t \tag{15}$$

$$R/R_{H_2O} = B_2 + B_3 c + b_4 c^2 \tag{16}$$

where A_i and B_i are constants.

It was found that in view of small changes in R with temperature, the temperature dependence of R and R/R_{H_2O} cannot be represented satisfactorily by eq 13 and 15. However, the concentration dependence may be represented by eq 14 and 16. The values of the constants for these equations, along with the calculated standard deviations, are listed in Tables XIV and XV. A plot of specific refraction (R) and relative specific

Table XIV. Coefficients and Standard Deviations of Eq 13 at Different Temperatures[a]

t, °C	A_2, cm³/g	$-A_3 \times 10^2$, (cm³ L)/(g mol)	$A_4 \times 10^3$, (cm³ L²)/(g mol²)	SD × 10^5
20	0.206 02	1.729	1.614	3.4
30	0.205 91	1.715	1.576	3.0
40	0.205 84	1.712	1.568	3.8
50	0.205 79	1.700	1.525	3.8
60	0.205 81	1.696	1.503	3.5

[a] $R = A_2 + A_3 c + A_4 c^2$.

Table XV. Coefficients and Standard Deviations of Eq 15 at Different Temperatures[a]

t, °C	B_2	$-B_3 \times 10^2$, L/mol	$B_4 \times 10^3$, (L/mol)²	SD × 10^4
20	0.999 85	8.388	7.823	1.5
30	0.999 66	8.344	7.714	1.4
40	0.999 74	8.324	7.652	1.7
50	0.999 62	8.270	7.448	1.8
60	0.999 73	8.258	7.365	1.6

[a] $R/R_{H_2O} = B_2 + B_3 c + B_4 c^2$.

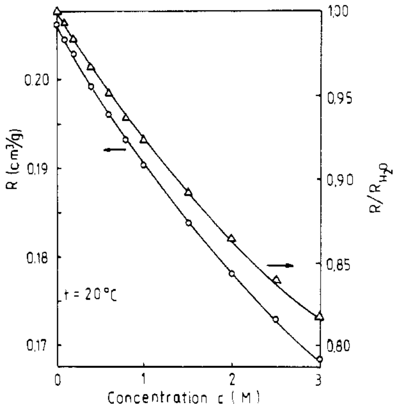

Figure 3. Concentration dependences of specific refraction R and relative specific refraction R/R_{H_2O} of lithium iodate solutions at 20 °C. For the sake of clarity, several actual data points are omitted at lower concentrations.

refraction (R/R_{H_2O}) as a function of solution concentration is shown in Figure 3. Obviously, with an increase in solution concentration both R and R/R_{H_2O} decrease. One also notes from Tables XIV and XV that with an increase in temperature the values of A_2, A_4, B_2, and B_4 decrease while those of A_3 and B_3 increase. One also finds that at a constant temperature t, $A_2 = R_{H_2O}$, $B_2 = A_2/R_{H_2O}$, $B_3 = A_3/R_{H_2O}$, and $B_4 = A_4/R_{H_2O}$ because the molar refraction of solid $LiIO_3$ is practically constant in the investigated range of temperature.

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Glossary

A_0, A_1–A_4	constants in eq 13 and 14
a_0, a_1–a_4	constants in eq 1 and 3
B_0, B_1–B_4	constants in eq 15 and 16
b_0, b_1–b_4	constants in eq 2 and 4
c	solution concentration, M
d	corrected density of solution, g/cm^3
d_m	measured density of solution, g/cm^3
$d_0(c)$, d_0'	concentration-dependent constants in eq 3 and 5, g/cm^3
$d_0(t)$	temperature-dependent constants in eq 1, g/cm^3
d_{H_2O}	density of water, g/cm^3
n	refractive index of solution
$n_0(c)$, n_0'	concentration-dependent constants in eq 4 and 6
$n_0(t)$	temperature-dependent constant in eq 2
n_{H_2O}	refractive index of water
R	specific refraction of solution, cm^3/g
R_{H_2O}	specific refraction of water, cm^3/g
T	temperature, K
T_0', T_0''	constants in eq 5 and 6, K
t	temperature, °C
α_0, α_1–α_5	constants in eq 7 and 9
β_0, β_1–β_5	constants in eq 8 and 10
β', β''	concentration-dependent constants in eq 5 and 6, K^{-2}

Registry No. $LiIO_3$, 13765-03-2.

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Thermodynamics of Binary Mixtures Containing Organic Carbonates. 1. Excess Enthalpies of Dimethyl Carbonate + Hydrocarbons or + Tetrachloromethane†

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Molar excess enthalpy H^E data at 298.15 K are reported for the binary liquid systems dimethyl carbonate + hexane, + heptane, + octane, + decane, + cyclohexane, + methylcyclohexane, + benzene, + toluene, or + tetrachloromethane.

Introduction

Esters of carbonic acid, dialkyl carbonates $CH_3(CH_2)_{n-1}O\text{–}CO\text{–}O(CH_2)_{m-1}CH_3$ and polymethylene carbonates $O\text{–}CO\text{–}O\text{–}(CH_2)_n$, are used in the syntesis of pharmaceuticals, agricultural chemicals, and dyestuffs. They are also used as solvents for many synthetic and natural resins and polymers, and some of them are used in photoengraving as assist agents for silicon circuitry.

In spite of the potential applications of carbonic acid esters there are only a few experimental thermodynamics studies on this class of substances, mainly on cyclic derivatives (*3–5*). In particular, to our knowledge, no data exist on the properties of binary mixtures of dialkyl carbonates $(CH_3(CH_2)_{n-1}O)_2CO$ with normal alkanes. Accordingly, no interaction parameters are yet

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