

Registry No. HCl, 7647-01-0; NaCl, 7647-14-5.

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Supplementary Material Available: The original, unsmoothed experimental data incorporated in Table IA, 3 pages. Ordering information is given on any current masthead page.

Densities and Refractive Indices of Aqueous Zinc Nitrate Solutions

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Densities and refractive indices of aqueous zinc nitrate solutions (0.01–21.6 *m*) have been measured as a function of temperature over the range 20–60 °C. Thermal expansivity (α) for the system shows a maximum near a concentration of 10 *m*, which corresponds to a water:salt mole ratio (*R*) of 6, and tends to attain a limiting value at higher salt concentrations. From the density measurements, apparent molal volumes (ϕ) and partial molal volumes of zinc nitrate (\bar{V}_2) and water (\bar{V}_1) have been calculated. The refractive indices at all compositions vary linearly with temperature and have negative temperature coefficients. An increase in the salt content increases the refractive index of the system, leading to a limiting value beyond ≈ 15 *m*, which corresponds to *R* = 4. The molar refractions have been calculated by using the Lorentz and Lorenz equation and are found to depend upon temperature. The expansivity estimated from the temperature coefficient of the refractive index and the differential forms of the Gladstone–Dale and Lorentz–Lorenz equations agrees well with that estimated from the density data.

Introduction

Continuing our work concerning the measurement of refractive index in molten hydrates and concentrated electrolytic solutions (1–4), we present some results for aqueous zinc nitrate solutions over an extended range of temperature and concentration.

Experimental Section

Zinc nitrate hexahydrate (AR) was used in the present study. The solutions were prepared by weighing the hexahydrate and then making up the solutions with distilled water. Melts with lower water content were prepared by removing calculated amounts of water from weighed quantities of the hydrate melts by continuous evacuation at ≈ 50 °C. All the solutions or melts were transparent.

The densities were measured with a modified manometric densitometer as described earlier (5). The refractive indices were measured on an Abbé-type refractometer. The experimental technique and the precision of measurement were essentially similar to those described earlier (4).

Results and Discussion

The mole fraction (*X*) is not a convenient unit for describing the composition of solutions such as those studied here because of the variation in its magnitude by a factor of about 10^6 over the composition range studied in the present work. Therefore, for the present study the compositions are expressed in terms of molality (*m*) and water-to-salt mole ratio (*R*).

The densities (ρ) for 0.01–21.6 *m* aqueous solutions of zinc nitrate presented in Table I show a quadratic temperature dependence and have been fitted to eq 1. The coefficients *A*,

$$\rho(\text{g cm}^{-3}) = A + Bt + Ct^2 \quad (1)$$

B, and *C* are presented in Table II. The composition dependence of density across the entire concentration range at 60 °C is shown in Figure 1. The data of Jain and Tamamushi (2) for $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ where $2 \leq x \leq 6$ have been included for a facile comparison. The agreement between the two independent studies is better than $\pm 0.5\%$. The expansivity (α) determined from eq 2 passes through a maximum at a concentration of approximately 10 *m* (Figure 1), which corresponds to a water-to-salt mole ratio of six, and tends to acquire a limiting value at higher salt concentrations. The expansivity

$$\alpha_t = -\frac{1}{\rho_t} \left[\left(\frac{d\rho}{dT} \right) \right]_t \quad (2)$$

values are presented in Table II.

The apparent molal volumes of zinc nitrate (ϕ) were calculated (6, 7) from each individual density value using eq 3, where

$$\phi = \frac{1}{d} \left[M_2 - \frac{1000(d - d_1)}{md_1} \right] \quad (3)$$

d is the density of the solution, *M*₂ is the molar mass of zinc

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Table I. Experimental Density and Refractive Index Data for Zinc Nitrate + H₂O Systems^a

<i>m</i> , mol kg ⁻¹	<i>t</i> , °C	ρ , g cm ⁻³	<i>n</i>	<i>m</i> , mol kg ⁻¹	<i>t</i> , °C	ρ , g cm ⁻³	<i>n</i>	<i>m</i> , mol kg ⁻¹	<i>t</i> , °C	ρ , g cm ⁻³	<i>n</i>
0.00746	23.0	0.9983	1.3339	1.02	25.3	1.1422	1.3592	9.48	37.3	1.7863	1.4562
	30.5	0.9963	1.3322		32.7				1.3575	1.4543	
	38.0	0.9938	1.3316		40.2				1.3560	1.4522	
	48.4	0.9889	1.3296		48.3				1.3548	1.4500	
	56.1	0.9844	1.3286		55.7				1.3532	1.4480	
	63.3	0.9794	1.3276		63.5				1.3518	1.4518	
	69.6	0.9726	1.3259		71.4				1.3508	1.4618	
0.0492	23.0	1.0052	1.3351	2.08	22.5	1.2839	1.3830	9.75	47.4	1.8277	1.4599
	30.3	1.0032	1.3342		30.6	1.2788	1.3808		55.3	1.8185	1.4579
	38.5	1.0001	1.3329		38.1	1.2741	1.3790		63.3	1.8088	1.4559
	48.5	0.9957	1.3319		45.9	1.2690	1.3779		71.6	1.7993	1.4538
	56.7	0.9908	1.3299		53.8	1.2635	1.3760		40.5	1.8439	1.4634
	63.3	0.9859	1.3289		62.0	1.2576	1.3742		48.4	1.8349	1.4612
	69.5	0.9816	1.3279		70.5	1.2513	1.3730		57.1	1.8246	1.4589
0.125	23.0	1.0137	1.3372	4.07	23.7	1.4945	1.4159	11.9	65.2	1.8151	1.4566
	30.3	1.0115	1.3361		31.5	1.4880	1.4140		73.0	1.8057	1.4542
	38.7	1.0084	1.3351		39.5	1.4814	1.4134		28.8		1.4758
	47.8	1.0042	1.3341		47.8	1.4745	1.4108		31.2	1.9361	1.4740
	56.1	0.9992	1.3331		55.9	1.4676	1.4092		39.2	1.9267	1.4720
	63.3	0.9946	1.3312		64.1	1.4606	1.4068		47.3	1.9175	1.4700
	69.5	0.9913	1.3302		72.0	1.4533	1.4048		55.1	1.9081	1.4679
0.271	22.6	1.0387	1.3432	5.19	24.5	1.5878	1.4303	15.5	63.0	1.8986	1.4658
	31.9	1.0356	1.3414		31.5	1.5819	1.4289		71.0	1.8887	1.4638
	40.3	1.0323	1.3398		39.0	1.5749	1.4272		33.7	2.0355	1.4848
	48.5	1.0285	1.3375		46.6	1.5681	1.4256		39.8	2.0276	1.4830
	56.3	1.0238	1.3368		54.6	1.5609	1.4237		47.5	2.0183	1.4810
	64.2	1.0188	1.3348		63.0	1.5528	1.4230		55.2	2.0095	1.4790
	71.8	1.0139	1.3331		71.6	1.5444	1.4197		63.5	1.9997	1.4770
0.389	23.4	1.0565	1.3452	6.23	23.3	1.6694	1.4418	21.6	71.3	1.9905	1.4749
	32.0	1.0533	1.3422		31.5	1.6614	1.4400		26.0	2.1336	1.4948
	40.3	1.0498	1.3412		39.7	1.6529	1.4380		29.5	2.1295	1.4940
	48.1	1.0464	1.3402		47.6	1.6452	1.4364		33.2	2.1253	1.4930
	56.5	1.0421	1.3398		55.2	1.6377	1.4346		37.0	2.1207	1.4920
	64.4	1.0373	1.3373		63.2	1.6296	1.4327		40.8	2.1162	1.4910
	71.8	1.0329	1.3361		71.6	1.6210	1.4306		45.0	2.1115	1.4900
0.944	24.3	1.1350	1.3577	7.29	23.9	1.7383	1.4512	21.6	48.8	2.1071	1.4890
	32.0	1.1313	1.3564		31.6	1.7304	1.4498		52.8	2.1023	1.4880
	40.0	1.1270	1.3548		39.3	1.7223	1.4476		56.2	2.0983	1.4870
	48.5	1.1222	1.3532		47.5	1.7136	1.4457		60.6	2.0933	1.4860
	56.6	1.1164	1.3519		55.3	1.7055	1.4439		64.7	2.0886	1.4851
	64.5	1.1111	1.3509		63.4	1.6966	1.4417		68.6	2.0843	1.4841
	72.0	1.1061	1.3499		70.8	1.6886	1.4398		73.0	2.0793	1.4830
				8.38	24.5	1.8014	1.4582		77.0	2.0750	1.4820
					30.7	1.7936	1.4577				

^aUncertainties: densities, ± 0.0005 ; refractive indices, ± 0.0002 .

Table II. Temperature-Density Equations and Calculated Expansivity Values (α) for Aqueous Solutions of Zinc Nitrate

<i>m</i> , mol kg ⁻¹	<i>N</i> ^a	$\rho / (\text{g cm}^{-3}) = A + Bt + Ct^2$				$10^4 \alpha$, deg ⁻¹
		<i>A</i>	$-10^4 B$	$-10^6 C$	10^3SE^b	
0.00746	7	0.9969	-0.2462	0.844	0.46	7.81
0.0492	7	1.0071	-0.0552	0.610	0.18	6.85
0.125	7	1.0184	0.1037	0.419	0.34	6.08
0.271	7	1.0429	0.0808	0.453	0.17	6.38
0.389	7	1.0626	0.1910	0.311	0.10	5.42
0.944	7	1.1450	0.3386	0.284	0.24	6.10
1.02	6	1.1569	0.3849	0.191	0.06	5.45
2.08	7	1.2966	0.5287	0.161	0.06	5.73
4.07	7	1.5128	0.7545	0.097	0.10	5.95
5.19	7	1.6083	0.8068	0.119	0.11	6.10
6.23	7	1.6926	0.9898	0.011	0.13	6.14
7.29	7	1.7626	0.9990	0.066	0.08	6.34
8.38	7	1.8291	1.1493	-0.016	0.25	6.42
9.48	6	1.8821	1.1440	0.017	0.18	6.42
9.75	5	1.8920	1.1877	-0.010	0.15	6.46
11.9	6	1.9709	1.0864	0.100	0.10	6.34
15.5	6	2.0800	1.3871	-0.189	0.20	5.79
21.6	14	2.1639	1.1747	-0.020	0.15	5.49

^aData points. ^bSE = standard error = $[\sum (\rho_{\text{exptl}} - \rho_{\text{calcd}})^2 / (N - 1)]^{1/2}$.

nitrate, *m* is the molality, and d_1 is the density of water at the studied temperature. The ϕ values were plotted against $m^{1/2}$

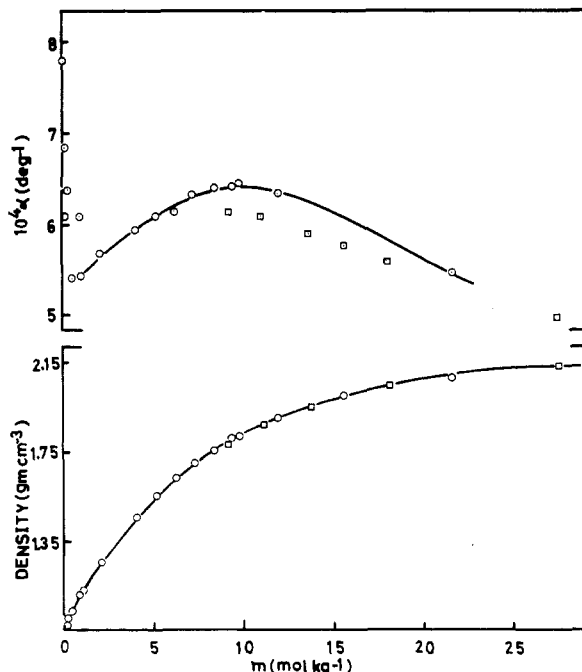


Figure 1. Density (ρ) and expansivity (α) vs. molality (*m*) at 60 °C for Zn(NO₃)₂ + H₂O system: O, present study; □, Jain & Tamamushi (2).

Table III. Apparent Molal Volume-Molality Equations for Zn(NO₃)₂ + H₂O Systems

<i>t</i> , °C	molality range, mol kg ⁻¹	<i>N</i> ^a	$\phi / (\text{cm}^3 \text{mol}^{-1}) = \phi^0 + am^{1/2} + bm + cm^{3/2} - c$				SE ^b
			ϕ^0	<i>a</i>	<i>b</i>	<i>c</i>	
20	0.39–21.6	13	31.22	4.484	1.457	0.198	0.19
30	0.39–21.6	13	34.11	2.830	1.884	0.237	0.18
40	0.39–21.6	13	35.83	2.117	2.043	0.251	0.18
50	0.39–21.6	13	36.99	1.691	2.153	0.262	0.18
60	0.39–21.6	13	37.93	1.252	2.305	0.281	0.18
70	0.39–21.6	13	38.98	0.435	2.627	0.319	0.20

^aData points. ^bSE = standard error = $[\sum(\phi_{\text{exptl}} - \phi_{\text{calcd}})^2 / (N - 1)]^{1/2}$.

(Figure 2). The data (Table III) could be adequately fitted to a third-degree polynomial, viz., eq 4.

$$\phi = \phi^0 + am^{1/2} + bm + cm^{3/2} \quad (4)$$

The partial molal volumes of zinc nitrate (\bar{V}_2) and water (\bar{V}_1) were calculated (6, 7) by using eq 5 and 6. \bar{V}_2 and \bar{V}_1 are

$$\bar{V}_2 = \phi^0 + \frac{3}{2}am^{1/2} + 2bm + \frac{5}{2}cm^{3/2} \quad (5)$$

$$\bar{V}_1 = (18.016/d_1) - 0.018016[\frac{1}{2}am^{3/2} + bm^2 + \frac{3}{2}cm^{5/2}] \quad (6)$$

shown as functions of $m^{1/2}$ in Figure 2. The partial molal volumes vary systematically with composition and tend to reach limiting values at higher salt content. Unlike calcium nitrate solutions (4), no maxima and minima were observed in plots of \bar{V}_1 vs. $m^{1/2}$ for the solutions of zinc nitrate. Values of the apparent molal volume at infinite dilution (ϕ^0) are lower for zinc nitrate than for calcium nitrate, apparently reflecting the difference in the ionic radii of the two cations. The partial molal volume of water (\bar{V}_1) in zinc nitrate solutions at higher salt concentrations is about 8–10% lower than that observed in the calcium nitrate–water system. This indirectly suggests that water molecules in the coordination sphere of Zn²⁺ are more closely packed than they are in the coordination sphere of Ca²⁺, probably due to more covalent character in Zn²⁺–H₂O bonding.

The refractive index (*n*) data presented in Table I show a linear variation with temperature for all the aqueous solutions. The *n*–*t* equations are presented in Table IV. The composition dependence of refractive index at a typical temperature, 60 °C, is shown in Figure 3.

Molar refraction, introduced by Lorentz (8) and Lorenz (9), is one of the best parameters that characterizes the polarization

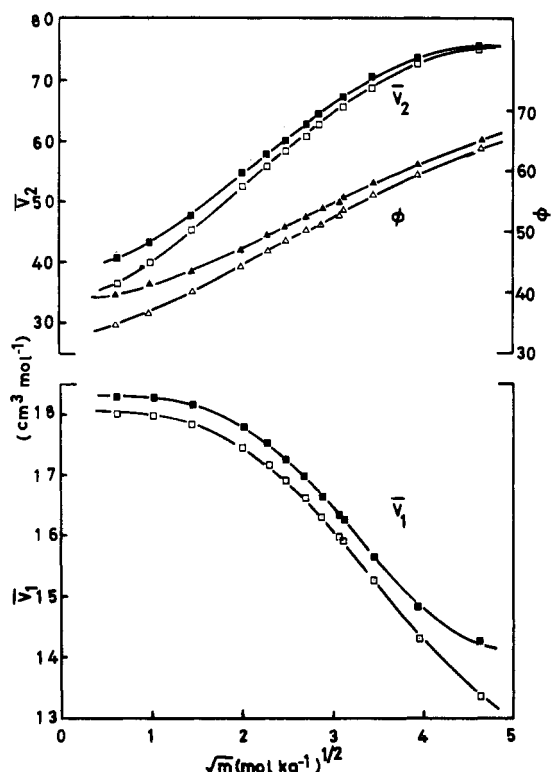


Figure 2. Apparent molal volume (ϕ) and the partial molal volumes of zinc nitrate (\bar{V}_2) and water (\bar{V}_1) shown as a function of molality^{1/2} ($m^{1/2}$ at 60 °C (▲, ■) and 20 °C (△, □)).

phenomenon. The molar refraction of the solute was obtained at 20, 40, and 60 °C (Table IV) from eq 7 in which ϕ is the

$$R_{LL} = \frac{n^2 - 1}{n^2 + 2} \phi \quad (7)$$

apparent molal volume of zinc nitrate. The R_{LL} –molality isotherm at 60 °C is shown in Figure 3. The R_{LL} values show a slight variation ($\approx 3\%$) over the range 20–60 °C. The magnitude of the derivative $(\partial R_{LL} / \partial T)_{p,\lambda}$ for the systems investigated here varies from 2.8×10^{-2} for dilute solutions to 0.42×10^{-2} for the most concentrated solution. When this is compared with the corresponding value of 1×10^{-3} for molten KNO₃–NaNO₃ mixtures (10), one gets the feeling that at such a high salt concentration the zinc nitrate–water system develops a molten salt character. As a first approximation, if the temperature

Table IV. Refractive Index–Temperature Equations and Molar Polarizations for Zn(NO₃)₂ + H₂O Systems

<i>m</i> , mol kg ⁻¹	<i>N</i> ^b	temp range, °C	$n = a - bt$, °C			R_{LL} , cm ³ mol ⁻¹			$10^4 \alpha_{LL}$, deg ⁻¹	$10^4 \alpha_{GD}$, deg ⁻¹	α / α_{GD}	$10^2 (\partial R / \partial T)_{p,\lambda}$
			<i>a</i>	$10^3 b$	10^3SE^a	20 °C	40 °C	60 °C				
0.00746	7	23–70	1.3375	0.162	0.31				4.49	4.93	1.58	
0.0492	7	23–69	1.3389	0.157	0.29				4.33	4.77	1.44	
0.125	7	23–69	1.3407	0.146	0.38				4.01	4.41	1.38	
0.271	7	23–72	1.3478	0.204	0.30				5.50	6.07	1.05	
0.389	7	23–72	1.3485	0.170	0.68	7.35	7.97	8.24	4.56	5.04	1.07	2.22
0.944	7	24–72	1.3616	0.166	0.25				4.26	4.72	1.29	
1.02	7	25–71	1.3636	0.183	0.23	8.16	8.74	8.98	4.67	5.19	1.05	2.05
2.08	7	22–70	1.3873	0.207	0.32	9.33	9.75	9.96	4.94	5.53	1.04	1.57
4.07	7	24–72	1.4217	0.229	0.49	11.19	11.50	11.68	4.96	5.63	1.06	1.22
5.19	7	24–72	1.4356	0.214	0.48	12.17	12.45	12.63	4.44	5.07	1.20	1.15
6.23	7	23–72	1.4472	0.231	0.11	12.82	13.11	13.28	4.64	5.32	1.15	1.15
7.29	7	24–71	1.4573	0.245	0.18	13.52	13.77	13.93	4.82	5.55	1.14	1.02
8.39	7	24–70	1.4647	0.238	0.41	14.08	14.36	14.53	4.57	5.28	1.22	1.12
9.48	5	39–72	1.4717	0.250	0.03	14.68	14.92	15.07	4.72	5.47	1.17	0.97
9.75	5	40–73	1.4749	0.281	0.11	14.92	15.15	15.29	5.30	6.15	1.05	0.92
11.9	7	29–71	1.4829	0.271	0.40	15.88	16.05	16.16	5.00	5.82	1.09	0.70
15.5	6	34–71	1.4934	0.260	0.10	17.04	17.22	17.31	4.66	5.45	1.06	0.67
21.6	14	26–77	1.5013	0.251	0.07	18.63	18.74	18.80	4.40	5.17	1.06	0.42

^aSE = standard error = $[\sum(n_{\text{exptl}} - n_{\text{calcd}})^2 / (N - 1)]^{1/2}$. ^bData points.

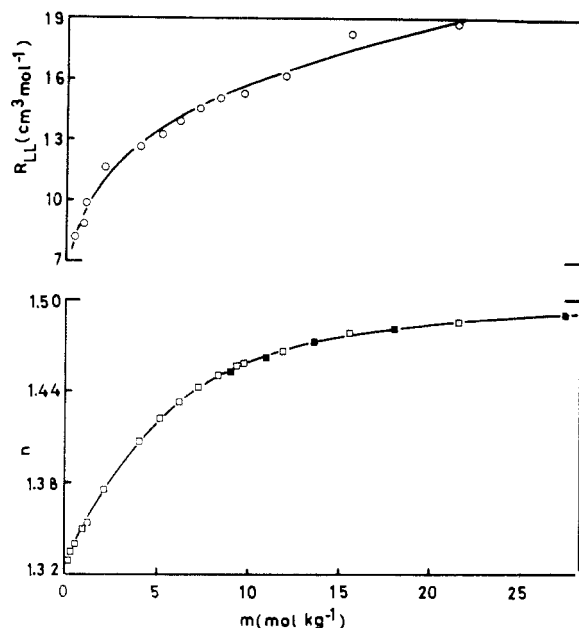


Figure 3. Refractive index (n) and molar refraction (R_{LL}) shown as a function of molality at 80 °C.

dependence of R_{LL} is ignored, the expansivities may be calculated from the temperature coefficient of the refractive index and the differential forms of the Gladstone–Dale and the Lorenz–Lorentz equations (eq 8 and 9). The computed values of

$$\alpha_{GD} = [1/(1-n)] dn/dT \quad (8)$$

$$\alpha_{LL} = [6n/(1-n^2)(2+n^2)] dn/dT \quad (9)$$

α_{GD} and α_{LL} for the zinc nitrate–water system are included in Table IV; note that α_{LL} is always smaller than α_{GD} . The ratio α/α_{GD} decreases with decreasing water content and the value at higher salt content is very similar to that shown by the ionic systems.

Registry No. $Zn(NO_3)_2$, 7779-88-6.

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Electrical Resistivities of Iridium, Palladium, Rhodium, and Tungsten at Temperatures between 295 and 1100 K

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The electrical resistivities of Ir, Pd, Rh, and W are measured at temperatures varying between 295 and 1100 K. A polynomial expression is found to fit our results and other authors' data with deviations smaller than 1% over the whole range of temperatures investigated.

While the electrical resistivities of the platinum group metals and W at low temperatures have been measured several times in the past (1), data in the high temperature range (above 300 K) for Ir, Pd, and Rh are not very abundant and results by different authors are not in good agreement (2, 3). Moreover, much experimental work has been published in the form of small-scale graphs without inclusion of actual figures. The purpose of the present work is to present new resistivity vs. temperature data for the above-mentioned metals and correlate them with algebraic equations.

In order to establish the relationship between resistance and temperature, metal samples in the form of thin wires were inserted into a quartz cell similar to the one described by Rye and Hansen (4) and placed in a temperature-controlled furnace. Resistance measurements were made, after the temperature had stabilized to ± 1 K, using the ohmmeter function of a five-digit digital voltmeter. The temperature within the cell was measured with a chromel–alumel thermocouple located next to the metal sample. A four-wire technique was used to eliminate

Table I. Details of Specimens

quoted purity, %	electrical resistivity at 295 K, $\mu\Omega$ cm	ref
Iridium		
99.9	9.01	present work
99.95	4.65 ^a	5
99.98	5.01	6
Palladium		
99.9	10.56	present work
99.99	10.01 ^a	5
99.99	10.6	6
99.98	10.71 ^a	7
Rhodium		
99.9	4.73	present work
99.93	4.42 ^a	5
99.99	4.78	6
Tungsten		
99.98	5.64	present work
99.98	5.33	6
	5.6	8

^a Adjusted to 295 K from published values.

errors caused by test lead resistances. The accuracy of the voltmeter, which had been calibrated by the manufacturer just before the experiments, was $\pm 0.6\%$ or better in the range of