Table II. Saturated Liquid Densities for R22
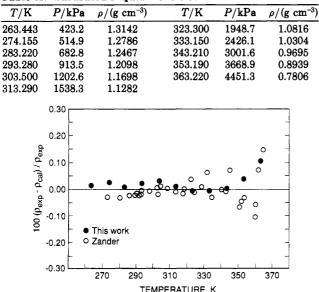
T/K	P/kPa	$\rho/(g\ cm^{-3})$	T/K	P/kPa	$\rho/(g\ cm^{-3})$
263.443	423.2	1.3142	323.300	1948.7	1.0816
274.155	514.9	1.2786	333.150	2426.1	1.0304
283.220	682.8	1.2467	343.210	3001.6	0.9695
293.280	913.5	1.2098	353.190	3668.9	0.8939
303.500	1202.6	1.1698	363.220	4451.3	0.7806
313.290	1538.3	1.1282			

Figure 7. Deviation plot as a function of temperature of saturated liquid densities of (●) this work and (○) Zander (*5*), from eq 3.

work with a limited range of calibration densities. The output of the instrument was correlated with water, which has a density of nearly 1 g/cm³ throughout our temperature range. Our correlation achieved a precision of ±0.02% in density. Our measurements on R22 show that the instrument can measure fluids of considerably different densities with similar accuracy.

In showing this, we also expanded the data on R22, obtaining good agreement with the recent Uematsu data. We also found a regular pattern in departures from the JAR representation.

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(1) R22 obtained from Racon Inc., Wichita, KS, purity data by private communication.
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Refractive Indexes of Aqueous LiBr Solutions

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The refractive indexes of water–lithium bromide solutions were measured in the temperature range from 5.0 to 80.0 °C and in the range of salt concentrations from 0.00 (deionized water) to 58.90 mass %. An electrolyte solution of LiBr in water was chosen for study because of its wide use as an absorption chiller fluid. The concentration of LiBr aqueous solution was determined by argentimetric titration using tetrabromofluorescein (Eosin) as an adsorption indicator and was checked at a few discrete concentrations (10.06, 20.30, and 58.90 mass % LiBr) against the values obtained by gravimetric analysis. The deviation between values obtained using these two techniques was found to be less than 0.27 mass %. The refractive indexes are shown to represent a reliable and convenient way of measuring the concentration of salt (or water) in LiBr solutions with accuracies of ±0.3 mass % salt.

Introduction

Water–lithium bromide solutions are being used in absorption chillers, absorption heat transformers, and absorption refrig-

erating machines (*1–3*). In testing of a prototype absorption machine, it is necessary to obtain the solution concentration at various locations as a function of temperature and time. The technique of withdrawing a sample for refractive index measurement or measuring the refractive index in situ (*4*) is a reliable and convenient method of concentration measurement. Unfortunately, the available data on refractive index of LiBr appears limited to 25 °C (*5, 6*). The scope of this paper deals with measurements of refractive indexes of LiBr solutions as a function of salt concentration and temperature and their reliability as a method for determining solute concentrations.

Experimental Apparatus and Technique

An Abbe-3L refractometer (Milton Roy Co., Type 33-46-10) connected to a constant-temperature circulating bath (VWR, Model 1145, LED set/read circuitry) was used for refractive index measurements. Refractive indexes at discrete salt concentrations and temperatures were determined. The concentration of LiBr in aqueous solutions was determined by argentimetric titration (*7*) using tetrabromofluorescein (Eosin, J. T. Baker Chemical Co., lot no. 546712) as an adsorption indicator. LiBr salt was supplied by EM Science (GR, extra pure; LX0320-6).

Solutions were filtered to remove trace amounts of insoluble impurities. The titrimetric analysis for salt concentration (mass

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Table I. Comparison of LiBr Concentrations Obtained by Gravimetric and Titrimetric Analyses

	mass % LiBr	
gravimetric	titrimetric	deviation
10.08	10.06	+0.02
20.57	20.30	+0.27
59.00	58.90	+0.10

% LiBr) was obtained by weighing about 8–17 g of a LiBr solution (depending on the salt concentration in solution) into a 50-mL beaker. The sample was transferred to a 1000-mL volumetric flask and diluted to 1000 mL with deionized water. Aliquots of 10 and 20 mL (three samples of each) were taken from this diluted LiBr solution with a 10-mL one-mark pipet. The samples were titrated with standardized 0.1081 M silver nitrate solution delivered from a 25-mL buret (readibility ±0.05 mL). The silver nitrate was standardized against 0.05 and 0.10 M potassium bromide solutions. The average of the results from six samples was reported as the concentration of LiBr solution.

In addition, some of these concentrations obtained by titration were checked against the concentrations obtained by gravimetric analysis. Deviations between values obtained by titrimetric and gravimetric analyses were found to be less than 0.27 mass % (Table I). The gravimetric analysis for mass % of the salt was obtained by weighing between 2 and 4 g of the solution sample into weighing bottles and drying them in an oven at 170–180 °C for 13–14 days (dried to constant weight). The rationale for heating up to 180 °C was to ensure that the transition temperature of $LiBr \cdot H_2O \rightarrow LiBr + H_2O$ was exceeded. These samples were then cooled in a desiccator and weighed to obtain the weight of the dry salt. The salt concentration (mass % LiBr) was determined gravimetrically by averaging the results of three samples. The weights of the solution and dried salt (LiBr) were determined with an analytical balance accurate to 0.1 mg. Weighing precision by an operator is approximately 0.3 mg. Hence, we were able to report the mass percent of the salt in the solution obtained by gravimetric analysis correct to four significant figures. In this manner, the mass % of the salt in the solution whose refractive index is measured by the refractometer is known to four significant figures.

Refractive indexes were measured by introducing a thin film of solution between the upper and lower prisms of the refractometer. The temperature of the solution was maintained constant by circulating water from the constant-temperature circulating bath through the refractometer. The flask (125-mL Erlenmeyer flask with stopper) containing about 50 mL of LiBr solution was kept in the constant-temperature bath for approximately 30 min to bring the solution temperature close to the water temperature circulating through the refractometer. The refractive indexes were measured by placing about 1–2 mL of solution on the lower prism of the refractometer. The refractive index was measured directly on the instrument to five significant digits (readability ±0.000 25 refractive index units).

Calibration of Instruments. Checks on the refractometer calibration were carried out by measuring the refractive indexes of deionized water, acetone (EM Science, GR, AX0120-8), 1-octanol (Fisher Scientific Co., lot 863298), and ethylene glycol (Baker, lot C21601) at 20 °C and of deionized water in the range of temperatures from 8.0 to 50.0 °C and comparing the results with reported values (8). The calibration and testing of the refractometer showed that the refractive indexes were accurate to within ±0.0001 refractive index units (Tables II and III). Temperature of the circulating bath could be controlled within ±0.5 °C (average error of ±0.000 09 refractive index units for LiBr solutions). The temperature readings of the circulating bath were monitored by a 0.00–50.00 °C thermometer (for temperatures up to 50.00 °C, readability ±0.05 °C) and by a 0.0–100.0 °C thermometer supplied with the Abbe-3L

Table II. Comparison of Experimental and Literature Refractive Indexes, R, of Deionized (DI) Water, Acetone, 1-Octanol, and Ethylene Glycol (8)

compounds	$t/°C$	$R_{lit.}$	R	deviation
DI water	20.0	1.33299	1.3330	−0.00001
acetone	20.0	1.3588	1.3590	−0.0002
1-octanol	20.0	1.4295	1.4292	+0.0003
ethylene glycol	20.0	1.4318	1.4317	+0.0001

Table III. Comparison of Literature and Experimental Refractive Indexes, R, of Deionized (DI) Water (8)

$t/°C$	$R_{lit.}$	R	deviation
8.0		1.3339	
12.0		1.3336	
16.0	1.333 33	1.3334	−0.000 07
20.0	1.332 99	1.3330	−0.000 01
24.0	1.332 62	1.3326	+0.000 02
30.0	1.331 92	1.3320	−0.000 08
40.0	1.330 51	1.3306	−0.000 09
50.0	1.328 94	1.3291	−0.000 16

refractometer (readability ±0.5 °C).

Error Analysis. Since indeterminate errors are inherent in chemical analyses, it is advantageous to determine the magnitude of these errors, in order to have a more definite knowledge of the reliability of the reported results. The relative error of the result of chemical analysis is equal to the sum of relative errors of all values, which are measured experimentally and used to calculate the analytical result. This does not mean that the relative error always attains this value, but rather that in an extreme case it may attain values up to the sum of relative errors of all measurements. In fact positive as well as negative errors may occur in general and partially compensate for each other (9).

The final result of the titrimetric analyses is influenced by the indeterminate errors in weighing the sample, making up the diluted sample solution to a certain volume, and taking aliquots and by measuring the consumption of a titrant. The overall absolute error values suggested by Eckschlager (9) are ±0.080, ±0.039, and ±0.900 mL for a 25-mL buret, 10-mL one-mark pipet, and 1000-mL volumetric flask, respectively. However, the calibration of a 25-mL buret and 10-mL one-mark pipet with deionized water at 22.00 °C showed that the overall absolute error is ±0.048 and ±0.035 mL, respectively. The relative error of determining the titre is equal to the sum of the relative errors of weighing samples, of diluting, of pipetting, and of the titration (uncertainty of reading the buret and locating the end point). This could be represented by

$$\epsilon\% = \epsilon_1\% + \epsilon_2\% + \epsilon_3\% + \epsilon_4\% \qquad (1)$$

where $\epsilon\%$ = relative error of the titration results, $\epsilon_1\%$ = relative error in weighing samples, $\epsilon_2\%$ = relative error in diluting the sample, $\epsilon_3\%$ = relative error in pipetting the diluted sample, and $\epsilon_4\%$ = relative error in reading the buret. The errors calculated in this manner (Tables IV and V) should be regarded as maximum errors. The actual error may be made virtually negligible by taking the mean of several measurements (9). The maximum error in the determination of the LiBr concentration by titrimetric analyses (Δ (mass %)) ranges from ±0.17 to ±0.78 mass %, depending on size of the aliquots taken (Tables IV and V).

The final result of the gravimetric analyses is influenced by the weight of the sample and the impurities in the chemical used. As mentioned earlier, the weighing precision by an operator is approximately 0.3 mg. The relative error of determining the salt concentration is equal to the sum of weighing the samples and of reweighing the dry sample (dry salt). This could be represented by

$$\epsilon_y\% = \epsilon_{y_1}\% + \epsilon_{y_2}\% \qquad (2)$$

Table IV. Maximum Error in the Titration Results When Aliquots of 10 mL of Diluted Sample Were Taken[a]

mass % LiBr	V_{buret}/mL	M_{sample}/g	ϵ_1%	ϵ_2%	ϵ_3%	ϵ_4%	ϵ%	Δ(mass %)
58.87	5.46	8.7075	0.0069	0.090	0.350	0.879	1.326	0.78
54.58	4.99	8.5834	0.0070	0.090	0.350	0.962	1.409	0.77
49.21	4.61	8.7947	0.0068	0.090	0.350	1.041	1.488	0.73
44.90	4.30	8.9902	0.0067	0.090	0.350	1.116	1.563	0.70
39.93	3.88	9.1216	0.0066	0.090	0.350	1.237	1.684	0.67
29.96	3.05	9.5566	0.0063	0.090	0.350	1.574	2.020	0.61
20.32	2.21	10.2118	0.0059	0.090	0.350	2.172	2.618	0.53
10.07	1.88	17.5217	0.0034	0.090	0.350	2.553	2.997	0.30

[a] Where M_{sample} = mass of sample (g); V_{buret} = buret readings (mL); ϵ_1% = relative error in weighing sample = $(2 \times 0.3 \text{ (mg)})/(1000 \times M_{sample}) \times 100\%$; ϵ_2% = relative error in diluting sample = $(0.900 \text{ (mL)})/(1000 \text{ (mL)}) \times 100\%$; ϵ_3% = relative error in pipetting = $(0.035 \text{ (mL)})/(10 \text{ (mL)}) \times 100\%$; ϵ_4% = relative error in buret readings = $(0.048 \text{ (mL)})/V_{buret} \times 100\%$; ϵ% = relative error of the titrimetric results = $\epsilon_1\% + \epsilon_2\% + \epsilon_3\% + \epsilon_4\%$; Δ(mass %) = maximum error in the mass % LiBr = $\epsilon\% \times$ (mass %)/100.

Table V. Maximum Error in the Titration Results When Aliquots of 20 mL of Diluted Sample Were Taken[a]

mass % LiBr	V_{buret}/mL	M_{sample}/g	ϵ_1%	ϵ_2%	ϵ_3%	ϵ_4%	ϵ%	Δ(mass %)
58.92	10.93	8.7075	0.0069	0.090	0.350	0.439	0.886	0.52
54.41	9.95	8.5834	0.0070	0.090	0.350	0.482	0.929	0.51
49.17	9.21	8.7947	0.0068	0.090	0.350	0.521	0.968	0.48
44.90	8.60	8.9902	0.0067	0.090	0.350	0.558	1.005	0.45
39.88	7.75	9.1216	0.0066	0.090	0.350	0.619	1.066	0.43
29.96	6.10	9.5566	0.0063	0.090	0.350	0.787	1.233	0.37
20.27	4.41	10.2118	0.0059	0.090	0.350	1.088	1.534	0.31
10.05	3.75	17.5217	0.0034	0.090	0.350	1.280	1.723	0.17

[a] Where M_{sample} = mass of sample (g); V_{buret} = buret readings (mL); ϵ_1% = relative error in weighing sample = $(2 \times 0.3 \text{ (mg)})/(1000 \times M_{sample}) \times 100\%$; ϵ_2% = relative error in diluting sample = $(0.900 \text{ (mL)})/(1000 \text{ (mL)}) \times 100\%$; ϵ_3% = relative error in pipetting = $(2 \times 0.035 \text{ (mL)})/(20 \text{ (mL)}) \times 100\%$; ϵ_4% = relative error in buret readings = $(0.048 \text{ (mL)})/V_{buret} \times 100\%$; ϵ% = relative error of the titrimetric results = $\epsilon_1\% + \epsilon_2\% + \epsilon_3\% + \epsilon_4\%$; Δ(mass %) = maximum error in the mass % LiBr = $\epsilon\% \times$ (mass %)/100.

Table VI. Maximum Error in the Gravimetric Results[a]

mass % LiBr	M_{sample}/g	$M_{dried\ sample}$/g	ϵ_{y_1}%	ϵ_{y_2}%	ϵ_y%	Δ(mass %)
58.90	4.8048	2.8346	0.01	0.02	0.03	0.02
20.30	2.8692	0.5903	0.02	0.10	0.12	0.02
10.06	4.5067	0.4543	0.01	0.13	0.14	0.01

[a] Where M_{sample} = mass of sample (g); $M_{dried\ sample}$ = mass of dried sample (g); ϵ_{y_1}% = relative error in weighing sample = $(2 \times 0.3 \text{ (mg)})/(1000 \times M_{sample}) \times 100\%$; ϵ_{y_2}% = relative error in weighing dried salt = $(2 \times 0.3 \text{ (mg)})/(1000 \times M_{dried\ sample}) \times 100\%$; ϵ_y% = relative error of the gravimetric results = $\epsilon_{y_1}\% + \epsilon_{y_2}\%$; Δ(mass %) = maximum error in the mass % LiBr = $\epsilon\% \times$ (mass %)/100.

Table VII. Experimental Refractive Indexes, R, of 58.90 mass % LiBr Solution

t/°C	R	t/°C	R	t/°C	R
20.0	1.4719	40.0	1.4683	70.0	1.4633
25.0	1.4709	50.0	1.4666	80.0	1.4616
30.0	1.4699	60.0	1.4650		

Table VIII. Experimental Refractive Indexes, R, of 54.50 mass % LiBr Solution

t/°C	R	t/°C	R	t/°C	R
15.0	1.4566	30.0	1.4540	60.0	1.4492
20.0	1.4558	40.0	1.4523	70.0	1.4478
25.0	1.4550	50.0	1.4505	80.0	1.4461

Table IX. Experimental Refractive Indexes, R, of 49.19 mass % LiBr Solution

t/°C	R	t/°C	R	t/°C	R
10.0	1.4399	30.0	1.4369	70.0	1.4314
15.0	1.4391	40.0	1.4356	80.0	1.4299
20.0	1.4383	50.0	1.4341		
25.0	1.4376	60.0	1.4326		

where ϵ_y % = relative error of the gravimetric results, ϵ_{y_1}% = relative error in weighing samples, and ϵ_{y_2}% = relative error in weighing dried samples. The maximum weighing error in the determination of the LiBr concentration by gravimetric analyses (Δ (mass %)) is within ±0.02 mass % (Table VI). It should be noted that the weighing errors tabulated in Table VI do not include the error due to the presence of impurities in the salt.

Table X. Experimental Refractive Indexes, R, of 44.90 mass % LiBr Solution

t/°C	R	t/°C	R	t/°C	R
10.0	1.4266	30.0	1.4238	70.0	1.4190
15.0	1.4259	40.0	1.4225	80.0	1.4178
20.0	1.4252	50.0	1.4213		
25.0	1.4246	60.0	1.4201		

Table XI. Experimental Refractive Indexes, R, of 39.91 mass % LiBr Solution

t/°C	R	t/°C	R	t/°C	R
10.0	1.4121	30.0	1.4095	70.0	1.4047
15.0	1.4115	40.0	1.4084	80.0	1.4036
20.0	1.4109	50.0	1.4072		
25.0	1.4102	60.0	1.4061		

Table XII. Experimental Refractive Indexes, R, of 29.96 mass % LiBr Solution

t/°C	R	t/°C	R	t/°C	R
5.0	1.3890	25.0	1.3866	60.0	1.3822
10.0	1.3884	30.0	1.3860	70.0	1.3811
15.0	1.3878	40.0	1.3848	80.0	1.3800
20.0	1.3872	50.0	1.3835		

Table XIII. Experimental Refractive Indexes, R, of 20.30 mass % LiBr Solution

t/°C	R	t/°C	R	t/°C	R
5.0	1.3685	25.0	1.3664	60.0	1.3622
10.0	1.3680	30.0	1.3659	70.0	1.3610
15.0	1.3675	40.0	1.3646	80.0	1.3598
20.0	1.3670	50.0	1.3634		

Table XIV. Experimental Refractive Indexes, R, of 10.06 mass % LiBr Solution

$t/°C$	R	$t/°C$	R	$t/°C$	R
5.0	1.3499	25.0	1.3481	60.0	1.3434
10.0	1.3495	30.0	1.3476	70.0	1.3421
15.0	1.3491	40.0	1.3463	80.0	1.3407
20.0	1.3487	50.0	1.3450		

Table XV. Literature and Experimental Refractive Indexes, R, of Deionized (DI) Water (8)

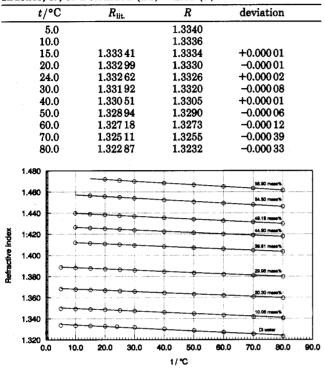| $t/°C$	$R_{lit.}$	R	deviation
5.0		1.3340	
10.0		1.3336	
15.0	1.33341	1.3334	+0.00001
20.0	1.33299	1.3330	−0.00001
24.0	1.33262	1.3326	+0.00002
30.0	1.33192	1.3320	−0.00008
40.0	1.33051	1.3305	+0.00001
50.0	1.32894	1.3290	−0.00006
60.0	1.32718	1.3273	−0.00012
70.0	1.32511	1.3255	−0.00039
80.0	1.32287	1.3232	−0.00033

Figure 1. Refractive index–concentration–temperature (R–X–T) data for aqueous LiBr solutions. –O– represents experimental data.

The total amount of impurities in the LiBr salt was approximately 0.137%. These impurities are chloride (0.1%), iodide (0.02%), sulfate (0.01%), heavy metals (0.001%), barium (0.005%), and iron (0.001%).

Results and Discussion

Results of the refractive index–concentration–temperature (R–X–T) data obtained from the experiments are shown in Figure 1 and are tabulated in Tables VII–XV. The R–X–T data were fitted to a second degree polynomial with R as the dependent variable and concentration (mass %) as the inde-

Table XVI. Coefficients of $R = A_1 + B_1(\text{mass \%}) + C_1(\text{mass \%})^2$ at Fixed Temperature[a]

$t/°C$	A_1	$10^3 B_1$	$10^5 C_1$	N	10^2AAD	10^6RSS
5.0	1.3340	1.4303	1.3446	4	0.5599	0.0288
10.0	1.3340	1.3156	1.6699	7	3.4296	2.2876
15.0	1.3341	1.2450	1.8120	8	4.3310	3.7530
20.0	1.3340	1.1814	1.9353	9	5.6752	6.7016
25.0	1.3363	1.0116	2.1442	8	3.6699	2.4263
30.0	1.3329	1.1890	1.8982	9	5.3126	5.9278
40.0	1.3314	1.2158	1.8495	9	5.1657	5.4378
50.0	1.3299	1.2514	1.7783	9	5.3977	6.3846
60.0	1.3281	1.2772	1.7448	9	4.7327	4.6726
70.0	1.3264	1.3186	1.6785	9	4.7442	4.8453
80.0	1.3242	1.3896	1.5677	9	5.2034	5.8192

[a] Where N = number of data points; AAD = average absolute deviation = $(\sum |d_i|)/N \times 100\%$; $d_i = (R_{obsd} - R_{pred})/R_{obsd}$; RSS = residual sum of squares = $\sum (R_{obsd} - R_{pred})^2$.

pendent variable for each solution temperature, using the least-squares technique. The coefficients of the polynomials are tabulated in Table XVI. The values of mass % obtained by curve fitting are accurate to ±0.3 mass % salt of the analytical concentrations.

Conclusions

We have shown that the refractive index of LiBr in water can be used to determine the solute concentration (mass % LiBr). The refractive indexes are shown to represent a reliable and convenient method of measuring the salt concentration with accuracies of ±0.3 mass %.

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