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Densities and Refractive Indexes of Aqueous (Li, K, Na) NO_3 Mixtures

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This paper describes experimental procedures and techniques for measuring densities and/or refractive indexes of aqueous salt solutions between 25 and 200 °C and with 18.90–90.50 wt % mixed salt ($LiNO_3$, KNO_3, and $NaNO_3$). An electrolyte solution of (Li, K, Na) NO_3 salts in water was chosen for study because of its recent development as a potential high-temperature heat pump fluid, but any other appropriate fluid may be accommodated for study in the apparatus. The densities and refractive indexes are shown to represent a convenient way of measuring the concentration of salt (or water), and accuracies of ±0.8 and ±0.3 wt % total mixed salt were achieved by using the above two methods, respectively. For highly concentrated salt solutions, with their attendant handling problems, this technique of concentration measurement is convincingly more convenient than the traditional methods of titration or gravimetric analysis.

Introduction

The (Li, K, Na) NO_3 aqueous solution was first proposed as a potential high-temperature heat pump fluid by Davidson and Erickson (*1*), who specified the "salt" composition as 53 wt % $LiNO_3$, 28 wt % KNO_3, and 19 wt % $NaNO_3$ or 61, 22, and 18 mol % $LiNO_3$, KNO_3, and $NaNO_3$, respectively. Subsequent computer simulations of heat pump performance by Ally (*2*) indicated that the fluid could possibly offer a 10% advantage in the coefficient of performance (COP) over heat pumps using aqueous lithium bromide. Devan and Wolf (*3*) conducted a series of laboratory screening tests to evaluate the stress corrosion cracking (SCC) properties of type A106B, 2.25 Cr–Mo steel, types 304 and 304L stainless steel, and the nickel-base alloy Monel 400 in the 80 wt % mixed salt ($LiNO_3$, KNO_3, and $NaNO_3$)/20 wt % water environment. These series of 250 °C capsule tests, conducted for times of up to 6 months, indicated that neither SCC nor general corrosion was a problem, with corrosion rates < 2.54 μm/year. These encouraging results served as a forerunner for the present work.

In testing of a prototype heat pump, it is necessary to obtain the solution concentration at various locations as a function of temperature and time. The usual techniques of withdrawing a sample for gravimetric or titrimetric analyses become very difficult if the solution has a strong tendency to crystallize, or when maintaining the system pressure is an important consideration. For these and similar reasons, it is convenient to investigate an in situ method of concentration measurement. The scope of this paper deals with measurements of densities and refractive indexes as a function of total mixed salt concentration and temperature and with use of commercially available densitometers to measure densities in situ and then back-calculate the concentration.

Experimental Apparatus and Technique

The schematic of Figure 1 shows the apparatus used to obtain the density–concentration–temperature (ρ–X–T) data for the (Li, K, Na) NO_3 solutions.

Figure 1 consists of a storage tank through which solution is poured into the boiler during charging and also in which distilled water is contained at a later stage for emergency dilution and cooling. The boiler is fitted with two 300-W–120-V, low-flux heaters from Chromalax, Pittsburgh, PA (Model RINO-30) and a pressure transducer from Omega Engineering Inc. (Model PX931-500GV). A relief valve from Nupro Co. [Model R3A, blue spring 0.345–2.413 MPa (50–350 psi)] is connected and set to vent into a drain if the pressure in either the boiler or the storage tank exceeds 965 kPa (140 psi). A pressure gauge, 0–414 kPa (0–60 psig), also gives a rough estimate of the boiler pressure or vacuum, as the case may be. The solution in the boiler drains into the pump head from a Micropump (Model E5726019) with a pump motor from Cole Parmer Instrument Co. (Model 7144-04, 180–3600 rpm) and a controller from Cole Parmer. The solution when pumped passes through the sensor tube of the vibrating-tube densitometer manufactured by Micro Motion Inc. (Model D-12), sensor DSO12S100, density monitoring system (DMS) (Model DMS1-NA-1-C-SP), and a digital rate totalizer (DRT) (Model DR7115-NA-J-T1). We would like to point out that the internal platinum resistance thermometer mounted on the D-12 sensor tube did not measure the fluid temperature correctly and caused an error in the measurement of densities values during calibration with water. For this reason, it was necessary to insert the two Type K thermocouples near the inlet and outlet sides of the DMS and depend upon their voltage outputs for the correct temperature coefficient of the density. The average of the inlet and outlet temperatures is taken to be the temperature of the solution whose density is being measured. After exiting the D12 sensor, the solution returns to the boiler. The boiler is also connected to a vacuum pump (Duo Seal Model 1402) from Welch Scientific Co.

The absence of leaks in the apparatus of Figure 1 is evidenced by pulling a vacuum (10^{-3} Torr) and observing no perceptible change in pressure over a 72-h period. Leak tightness is important, otherwise minute amounts of undissolved air entrained in the solution will cause an erroneous reading of the liquid density as it flows through the sensor tube.

An Abbe refractometer, Bausch & Lomb (Type 33-45-58), connected to a constant-temperature bath (Lauda thermostat Type K2), by Messgerate-Werk Lauda, is used for refractive index measurements. Densities at discrete concentrations and temperatures were determined with a 25-mL pycnometer calibrated with deionized water at 25 and 80 °C. The pycnometer was kept in the constant-temperature bath until a constant meniscus level was obtained.

Calibration of Instruments. Type K thermocouples were calibrated by using an ice bath at the low-temperature end and a boiling water bath for the high-temperature calibration. The thermocouple temperature agreed with the thermometer readings within ±0.3 °C over the range 0–99.6 °C (boiling point of water at 748.5 mmHg). The readabilities of the thermometers were 0.05 and 0.5 °C for the ice bath and the boiling water

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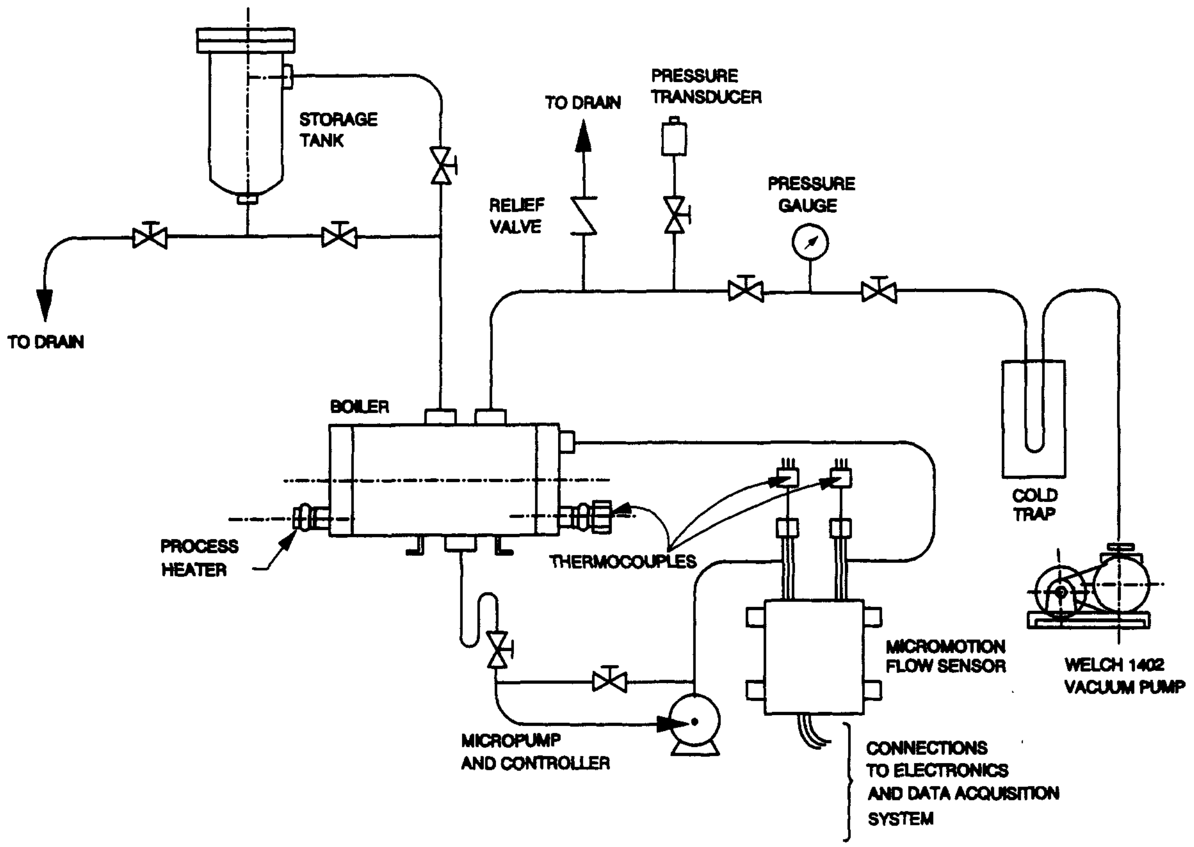

Figure 1. Schematic of apparatus for measuring densities of (Li, K, Na) NO_3 solutions.

bath, respectively. The thermometer accuracy was greater than its readability. The calibration check of the pressure transducer by pressurizing the system with N_2 gas from a cylinder showed that the accuracy was ≈0.06% of full scale or 2.07 kPa (0.3 psig). The calibration of the DMS and associated units were checked by measuring the densities of methanol (American Scientific Products, Lot AP273; water 0.012%, bp 64.7 °C), acetone (J. T. Baker, Inc. Lot B44602; density at 25 °C 0.7849 g/mL), chloroform (E. M. Science, Lot 6073), isopropyl alcohol (Ashland Chemical Co., Lot 071903; density at 25 °C 0.781–0.783 g/mL), and water at 25 °C and comparing the results with reported values (*4*). Comparing the measured density of water between 25 and 170 °C convinced us that the accuracy of the DMS was no better than ±0.006 g/mL, despite the manufacturer's claim of ±0.002 g/mL.

The calibration and testing of the refractometer showed that the refractive index were accurate to within ±0.0001 refractive index units. The calibration of the refractometer was checked by using deionized water, and its refractive index was measured as 1.3325 refractive index units at 25 °C. The temperature of the bath and of the solution in the refractometer could be controlled within 1 °C and was the factor limiting the accuracy of the refractive index measurements.

A fresh solution (usually concentrated) of the (Li, K, Na) NO_3 salts is prepared by dissolving separately weighed amounts of each individual salt in distilled water. $LiNO_3$ salt was supplied by Fisher Scientific, KNO_3 by J. T. Baker, and $NaNO_3$ BY E. M. Science. All salts were ACS Reagent Grade materials. If the salt content exceeds 60 wt %, heating may be required to dissolve it. The solution is filtered under vacuum through 0.45-μm filter paper to remove trace amounts of insoluble impurities. Following dissolution, the final composition is determined gravimetrically by averaging the results of three samples. The samples during the gravimetric analysis are dried in an oven between 110 and 117 °C for approximately 2–3 days, cooled in a desiccator, and weighed. The weights of the solution and dried salt were made by using an electronic balance supplied by Mettler (Model AE 163), accurate to 0.1 mg. The weighing precision by an operator is approximately 0.3 mg. Hence, we were able to report the weight percent of the salt in the solution correct to 4 significant figures. To ensure that the composition of the salts are in the prescribed weight ratio ($LiNO_3$:KNO_3:$NaNO_3$ = 53:28:19), each salt is dried by placing it in a separate crystallizing dish followed by drying in an oven at 117 °C for 3 days. $LiNO_3$ took the longest time to dry and reached constant weight after 72 h of drying. Following this drying period, samples of the salt were put in weighing bottles and placed in a desiccator for about 6 weeks, after which a Karl-Fisher analysis was performed on them to determine water content. These desiccators containing the salt samples were used periodically, but no more than six or seven times over the 6-week period for other related work. The reason for the occasional use was the thought that the water absorbed by these salts over the 6-week period may be representative of the water uptake during the weighing of large quantities of the salt at the time of preparation of a batch solution. The results of the Karl-Fisher analysis, shown in Table I, indicate that the salt samples could be considered essentially dry.

Table I. Karl-Fisher Analysis for Water Content

salt	analysis	result, mg/g	wt % H_2O
$LiNO_3$	H_2O	1.30	0.130
KNO_3	H_2O	1.20	0.112
$NaNO_3$	H_2O	0.25	0.025

After the solution is prepared, it is poured into the boiler via the storage tank. The pump circulates the solution in a closed loop, returning it back to the boiler after passage through the DMS sensor tube. Before the density–temperature data are recorded, a vacuum is pulled on the system to remove noncondensibles (air) by running the vacuum pump for about 1 min. Along with the air, a small quantity of water vapor is also removed, which is barely visible in a condensed form in the cold

Table II. Experimental Densities of 18.90 wt % (Li, K, Na) NO_3 Mixtures

T, °C	density, g/mL	T, °C	density, g/mL
29.6	1.128	93.7	1.070
39.8	1.122	100.1	1.063
49.8	1.112	110.1	1.052
60.3	1.102	120.0	1.043
70.0	1.093	130.0	1.031
79.9	1.084	140.1	1.020
89.9	1.073	149.9	1.009

Table III. Experimental Densities of 35.40 wt % (Li, K, Na) NO_3 Mixtures

T, °C	density, g/mL	T, °C	density, g/mL
30.2	1.258	169.8	1.111
39.8	1.250	179.7	1.101
50.2	1.239	189.0	1.091
59.7	1.230	170.2	1.111
70.6	1.218	160.1	1.122
79.8	1.208	150.0	1.133
89.7	1.197	139.9	1.144
100.0	1.187	130.0	1.155
110.0	1.176	120.1	1.165
120.3	1.164	109.9	1.175
129.9	1.153	100.0	1.185
140.1	1.142	90.0	1.193
150.4	1.131	80.1	1.204
159.9	1.122		

trap. This quantity of water vapor is so small that it leaves the concentration of the solution remaining in the boiler virtually unchanged. Following evacuation, the heaters are adjusted to heat the solution at about 1 °C/min until the solution temperature reaches 200 °C. Thereafter, the heaters are turned off, and the solution is allowed to cool by natural convection to a desired temperature (above crystallization temperature to prevent clogging). During the entire heating and cooling period, the density and temperature of the solution are sampled and recorded in a data file at 20-s intervals. The interfacing of the transducer with a Zenith Model ZW-158-43 computer was achieved by using a data acquisition board from Data Translation Inc. (Model DT-2801-A) and an IEEE-488 interface card which communicates with a Hewlett-Packard (HP) 3497A data acquisition control unit (DACU) and HP 3456A digital voltmeter.

About 125 mL of the prepared solution poured into the boiler is saved for gravimetric, pycnometer, and refractive index measurements. The gravimetric analysis for the weight percent of the salt is obtained by weighing between 2 and 2.5 g of the solution sample in weighing bottles, drying it in an oven at 110 °C for 2–3 days, and reweighing to obtain the weight of the dry "salt". In this manner, we know the weight percent of the salt in the solution whose density is measured by the DMS sensor.

The density of the prepared solution is measured at 25 and 80 °C with a pycnometer. These density measurements serve as a convenient check on the densities measured by the DMS unit. For concentrated solutions that have crystallization temperatures in excess of 80 °C, the pycnometer is maintained at the particular temperature by placing it in an oven. The temperature of the oven could be recorded and controlled to 1 °C. This causes an uncertainty (negligible) of less than 1×10^{-3} g/mL in the density measurement.

The refractive index is measured by placing about 1–2 mL of solution in the refractometer. The temperature of the solution is maintained constant by circulating water from the constant-temperature bath through the refractometer. The refractive index can be measured directly on the instrument to 5 significant digits.

Results and Discussion

Results of the density–concentration–temperature (ρ-X-T) and refractive index–concentration–temperature (R-X-T) data

Table IV. Experimental Densities of 54.54 wt % (Li, K, Na) NO_3 Mixtures

T, °C	density, g/mL	T, °C	density, g/mL
23.7	1.423	110.5	1.343
30.0	1.417	120.3	1.334
40.0	1.408	129.9	1.326
50.0	1.395	140.1	1.317
60.0	1.387	150.0	1.307
70.0	1.380	160.1	1.299
80.4	1.370	170.0	1.290
90.1	1.362	179.8	1.282
100.0	1.353		

Table V. Experimental Densities of 63.91 wt % (Li, K, Na) NO_3 Mixtures

T, °C	density, g/mL	T, °C	density, g/mL
59.7	1.527	140.2	1.443
69.9	1.515	149.9	1.433
79.5	1.504	160.3	1.423
90.0	1.494	169.8	1.413
100.4	1.483	180.1	1.403
109.7	1.474	190.1	1.393
119.9	1.464	199.7	1.383
130.3	1.453		

Table VI. Experimental Densities of 71.37 wt % (Li, K, Na) NO_3 Mixtures

T, °C	density, g/mL	T, °C	density, g/mL
79.7	1.573	140.0	1.514
89.4	1.558	150.3	1.507
99.6	1.549	160.2	1.501
109.4	1.540	170.0	1.493
120.7	1.529	180.3	1.485
129.6	1.521	189.9	1.476

Table VII. Experimental Densities of 75.18 wt % (Li, K, Na) NO_3 Mixtures

T, °C	density, g/mL	T, °C	density, g/mL
74.9	1.631	139.6	1.555
79.9	1.626	150.4	1.547
89.7	1.611	159.8	1.541
100.0	1.600	170.4	1.533
110.2	1.587	180.2	1.525
119.7	1.576	189.9	1.516
130.3	1.563	199.4	1.507

Table VIII. Experimental Densities of 80.28 wt % (Li, K, Na) NO_3 Mixtures

T, °C	density, g/mL	T, °C	density, g/mL
80.7	1.681	150.7	1.610
89.5	1.670	160.3	1.604
101.3	1.658	170.5	1.598
110.5	1.645	180.1	1.592
120.3	1.634	189.8	1.584
130.5	1.625	199.5	1.576
140.0	1.616		

Table IX. Experimental Densities of 82.84 wt % (Li, K, Na) NO_3 Mixtures

T, °C	density, g/mL	T, °C	density, g/mL
95.3	1.740	199.4	1.633
99.8	1.734	180.3	1.647
110.3	1.715	169.9	1.655
119.6	1.704	160.2	1.665
130.3	1.691	149.7	1.677
140.5	1.681	139.8	1.688
149.7	1.672	130.0	1.699
160.3	1.662	120.1	1.708
170.0	1.654	110.1	1.717
180.0	1.646	100.0	1.727
190.2	1.641	94.9	1.734

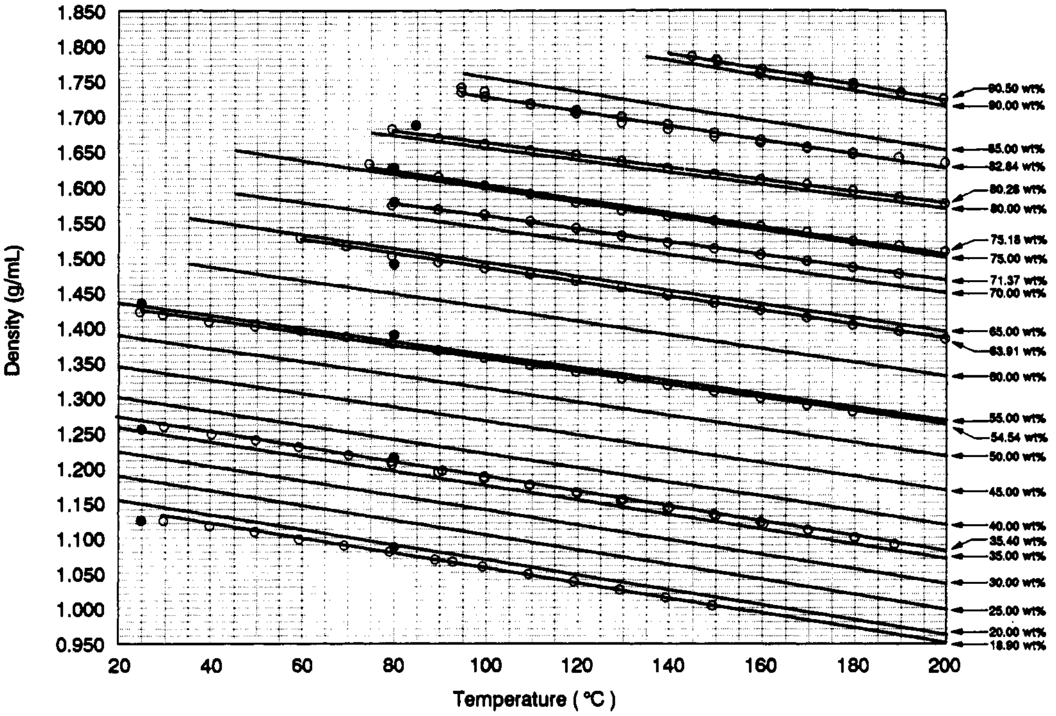

Figure 2. Density-concentration-temperature (ρ-X-T) data for (Li, K, Na) NO_3 solutions: (-O-) experimental data; (—) interpolated values; (●) represents pycnometer measurements.

Table X. Experimental Densities of 90.50 wt % (Li, K, Na) NO_3 Mixtures

T, °C	density, g/mL	*T*, °C	density, g/mL
145.2	1.784	199.6	1.724
150.7	1.778	190.4	1.733
159.8	1.760	180.0	1.745
170.3	1.752	170.4	1.755
180.0	1.743	160.3	1.766
189.8	1.733	150.5	1.780

Table XI. Experimental Refractive Indexes (*R*) of 18.90 wt % (Li, K, Na) NO_3 Mixtures

T, °C	*R*	*T*, °C	*R*
25.0	1.3545	55.0	1.3488
30.0	1.3535	60.0	1.3480
35.0	1.3528	65.0	1.3468
40.0	1.3515	70.0	1.3458
45.0	1.3505	75.0	1.3450
50.0	1.3495	80.0	1.3440

Table XII. Experimental Refractive Indexes (*R*) of 35.40 wt % (Li, K, Na) NO_3 Mixtures

T, °C	*R*	*T*, °C	*R*
25.0	1.3768	55.0	1.3710
30.0	1.3755	60.0	1.3700
35.0	1.3745	65.0	1.3693
40.0	1.3735	70.0	1.3680
45.0	1.3725	75.0	1.3665
50.0	1.3718	80.0	1.3660

Table XIII. Experimental Refractive Indexes (*R*) of 54.54 wt % (Li, K, Na) NO_3 Mixtures

T, °C	*R*	*T*, °C	*R*
30.0	1.4060	60.3	1.4012
41.0	1.4049	70.0	1.3991
45.0	1.4045	80.0	1.3985
50.0	1.4031		

obtained from the experiments are shown in Figures 2 and 3, respectively, and are tabulated in Tables II–XVII. The ρ-X-T and R-X-T data were fitted to a polynomial of degree one with ρ (or R) as the dependent variable and temperature as the independent variable for each total salt concentration, using the least-squares technique. The coefficients of the polynomials are tabulated in Tables XVIII and XIX, respectively. The ρ-X-T data are accurate to ±0.8 wt % salt. The R-X-T data are accurate to ±0.3 wt % salt. Unfortunately, the latter is not an in situ method of concentration measurement; moreover, the limitations of our apparatus confined the R-X-T measurements to temperatures (and concentrations) below those encountered in the operation of a heat pump. Nevertheless, the R-X-T data were extremely useful in confirming gravimetric analyses of solutions during the course of our work. The pycnometer measurements at the respective compositions and tempera-

Table XIV. Experimental Refractive Indexes (*R*) of 63.91 wt % (Li, K, Na) NO_3 Mixtures

T, °C	*R*	*T*, °C	*R*
50.0	1.4145	70.0	1.4105
55.0	1.4135	75.0	1.4098
60.0	1.4125	80.0	1.4088
65.0	1.4115		

Table XV. Experimental Refractive Indexes (*R*) of 71.37 wt % (Li, K, Na) NO_3 Mixtures

T, °C	*R*	*T*, °C	*R*
60.0	1.4295	75.0	1.4265
65.0	1.4285	80.0	1.4258
70.0	1.4275		

Table XVI. Experimental Refractive Indexes (*R*) of 75.18 wt % (Li, K, Na) NO_3 Mixtures

T, °C	*R*	*T*, °C	*R*
75.0	1.4295	90.0	1.4265
80.0	1.4285	95.0	1.4255
85.0	1.4278		

Table XVII. Experimental Refractive Indexes (*R*) of 80.28 wt % (Li, K, Na) NO_3 Mixtures

T, °C	*R*	*T*, °C	*R*
80.0	1.4385	90.0	1.4375
85.0	1.4380	93.0	1.4365

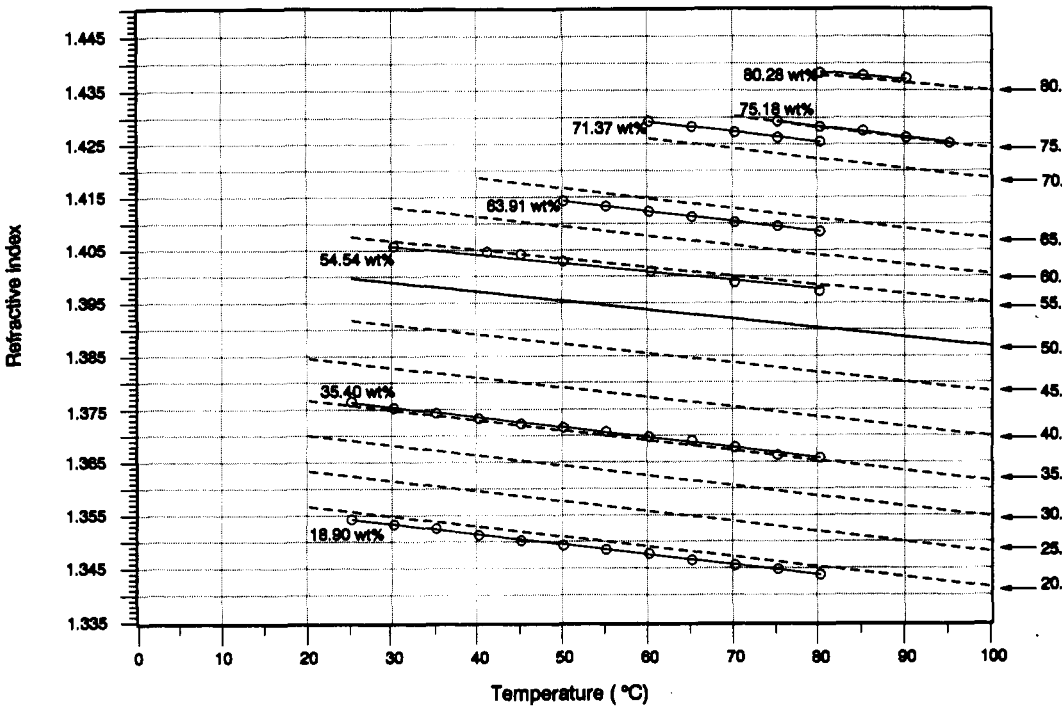

Figure 3. Refractive index–concentration–temperature (R–X–T) data for (Li, K, Na) NO_3 solutions: (–O–) experimental data; (- -) interpolated values.

Table XVIII. Coefficients of $\rho = A + BT$ at Fixed Composition

wt % of (Li, K, Na) NO_3	A, g/mL	$-B \times 10^4$, g/(mL·°C)	N^a	AAD^b	RSS^c
18.90	1.1683	10.6508	524	0.1530	0.0022
35.40	1.2811	10.3408	523	1.5740	1.6719
54.54	1.4473	9.2808	624	0.1238	0.0032
63.91	1.5829	9.9594	491	0.0846	0.0018
71.37	1.6443	8.9103	318	0.1733	0.0039
75.18	1.6993	9.8287	440	0.2002	0.0058
80.28	1.7445	8.5367	331	0.1525	0.0037
82.84	1.8272	10.0243	326	0.1363	0.0030
90.50	1.9404	10.9261	140	0.1116	0.0009

[a] N = number of data points. [b] AAD = average absolute deviation = $(\sum|d_i|)/N \times 100\%$. d_i = (ρ(observed) − ρ(predicted))/ρ(observed). [c] RSS = residual sum of squares = $\sum$(ρ(observed) − ρ(predicted))^2.

Table XIX. Coefficients of $R = A_1 + B_1T$ at Fixed Composition

wt % of (Li, K, Na) NO_3	A_1	$-B_1 \times 10^4$, 1/°C	N^a	AAD^b × 10^2	RSS^c × 10^6
18.90	1.3592	1.9091	12	0.7580	0.1837
35.40	1.3813	1.9178	12	1.2722	0.5659
54.54	1.4114	1.6671	7	2.6102	1.2400
63.91	1.4240	1.9107	7	0.4339	0.0335
71.37	1.4408	1.9000	5	0.4205	0.0250
75.18	1.4446	2.0000	5	0.5604	0.0500
80.28	1.4501	1.4286	4	1.3666	0.1875

[a] N = number of data points. [b] AAD = average absolute deviation = $(\sum|d_i|)/N \times 100\%$. d_i = (R(observed) − R(predicted))/R(observed). [c] RSS = residual sum of squares = $\sum$(R(observed) − R(predicted))^2.

tures are tabulated in Table XX. The properties are measured over a comprehensive range of temperature and total salt concentration.

Conclusions

Table XX. Densities of (Li, K, Na) NO_3 Obtained by Pycnometer

wt %	T, °C	ρ(pycnometer), g/mL	wt %	T, °C	ρ(pycnometer), g/mL
18.90	25.0	1.1248	63.91	80.0	1.4874
18.90	80.0	1.0872	71.37	80.0	1.5787
35.40	25.0	1.2505	75.18	80.0	1.6234
35.40	80.0	1.2140	80.28	85.0	1.6873
54.54	25.0	1.4307	82.84	119.0	1.7075
54.54	80.0	1.3903			

Intensive properties are a convenient and accurate measure of the solute (or solvent) concentration of electrolyte solutions. We have shown that off-the-shelf instruments can be used to measure densities and refractive indexes as a function of concentration and temperature and from them the solute concentration can be determined reliably. The refractive index is a more accurate measure of the concentration (±0.3 wt %) than the density (±0.8 wt %) with the instruments that we used. The latter has the advantage of in situ operation. Some fiberoptic techniques are known to be under development that measure the refractive index of solutions in situ, but their scope is limited to solutions whose refractive indexes are less than 1.46 (*5*).

Acknowledgment

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