UNIFAC with the above interaction parameters.

The experimental tie-line data were also correlated by using the UNIQUAC (*3*) and NRTL (*4*) models. The parameters $(u_{ij} - u_{jj})$ and $(u_{ji} - u_{ii})$ corresponding to the residual excess Gibbs energy contribution of the UNIQUAC equations and the interaction parameters $(g_{ij} - g_{jj})$ and $(g_{ji} - g_{ii})$ for the NRTL equations were estimated by using the method described by Sørensen et al. (*7*). The objective function used to estimate the model parameters was

$$F = \sum_{k} (\min) \sum_{j} \sum_{i} (x_{ijk} - \hat{x}_{ijk})^2 \qquad (2)$$

where the summation indices are $i = 1, 2$ phases, $j = 1, 2, ..., N$ components, and $k = 1, 2, ..., M$ tie lines. Here the x_{ijk} represent the experimental mole fractions and $\hat{x}_{ijk}$ the calculated ones, and min denotes the minimum value of the summation. For the NRTL model, the nonrandomness parameter α_{ij} was set at a value of 0.2.

The UNIQUAC and NRTL parameters, obtained by this procedure, are reported in Table III, together with the average absolute deviations between the experimental and calculated mole fractions.

The experimental measurements on this system showed a small two-phase region at 298 K. According to these results only toluene–isooctane mixtures with less than about 47 mol % of toluene could be separated by the use of diethylene glycol methyl ether. Figure 3 shows the selectivity of this solvent as a function of the solvent-free mole fraction of toluene in the isooctane-rich phase. The solvent selectivity was defined in term of mole fractions as

$$S = \frac{[x(2)^{*}/x(3)^{*}]_{\text{DM-rich phase}}}{[x(2)^{*}/x(3)^{*}]_{\text{isooctane-rich phase}}} \qquad (3)$$

where the indices 2 and 3 represent toluene and isooctane, respectively, and * indicates equilibrium values. The *S* values drop quite rapidly toward a value of 1 at low toluene concentrations. The above results and discussion indicate a low solvent capability of the diethylene glycol methyl ether for the separation of toluene–isooctane mixtures.

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Registry No. DM, 111-77-3; toluene, 108-88-3; isooctane, 540-84-1.

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Density Study of $Mg(NO_3)_2$–H_2O–HNO_3 Solutions at Different Temperatures

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Densities for the $Mg(NO_3)_2$–HNO_3–H_2O system have been measured experimentally; more than 140 measurements were made covering the ranges 30–70 wt % $Mg(NO_3)_2$ and 0–40 wt % HNO_3 at temperatures of 50–145 °C. A mathematical model for the observed density relationships has been developed.

Introduction

This study was undertaken to provide density data for $Mg(NO_3)_2$–HNO_3–H_2O solutions for the conversion of mass to volumetric flow rates for process simulation and design purposes. This activity is part of an effort to develope and demonstrate a simple process for the extractive distillation of nitric acid (*1*, *2*). The specific objectives of the study were to obtain density data for solutions containing 30–70 wt % $Mg(NO_3)_2$ and 0–15 wt % HNO_3 over the temperature range 50–145 °C. A mathematical model of the density data as a function of the weight percent of $Mg(NO_3)_2$ and HNO_3 and temperature was developed and is presented in this publication.

Experimental Section

The experimental procedure is described more completely elsewhere (*3*).

Reagents. Reagent-grade chemicals and demineralized water were used in the preparation of samples and in subsequent analyses. The magnesium nitrate used in these studies was Mallinckrodt $Mg(NO_3)_2 \cdot 6H_2O$ flake. For some tests with high $Mg(NO_3)_2$ concentrations, the original hexahydrate was dehydrated to $Mg(NO_3)_2 \cdot (2.1\text{–}2.2)H_2O$.

Density Measurements. The dilatometers used in this study were designed to contain ~35 mL and were fabricated of Pyrex glass for the study. Calibration was performed by observing and recording the level of the meniscus of water in the graduated regions when equilibrated at 30, 50, 70, and 90 °C.

Density Measurements. Reagents were weighed directly into 500-mL beakers for the preparation of solutions with magnesium nitrate concentrations of ≤55 wt %. Accurate

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Table I. Density of Solutions with 30–35 wt % $Mg(NO_3)_2$

wt %			
$Mg(NO_3)_2$	HNO_3	temp, °C	av density, g/cm^3
30.86	0.0	50	1.252
		70	1.239
		90	1.224
30.89	5.15	50	1.286
		70	1.272
		90	1.257
30.42	10.01	50	1.318
		70	1.303
		90	1.288
30.46	14.94	50	1.353
		70	1.336
		90	1.318
29.58	25.79	50	1.414
		70	1.393
		90	1.377
29.98	34.51	50	[a]
		70	1.451
		90	1.430
33.86	40.02	70	1.522
		90	1.501
35.70	0.0	70	1.284
		90	1.269
		105	1.259
35.43	5.64	70	1.322
		90	1.311
		105	1.297
33.52	11.64	70	1.344
		90	1.326
		105	1.315
34.81	16.86	70	1.396
		90	1.378
		105	1.365

[a] Solution freezes.

Table II. Density of Solutions with 40–45 wt % $Mg(NO_3)_2$

wt %			
$Mg(NO_3)_2$	HNO_3	temp, °C	av density, g/cm^3
40.02	0.0	50	1.351
		70	1.340
		90	1.325
		100	1.318
40.37	0.0	50	1.359
		70	1.346
		90	1.334
		100	1.329
39.92	4.81	50	1.388
		70	1.377
		90	1.360
		100	1.354
40.09	9.79	50	1.422
		70	1.414
		90	1.403
		100	1.393
39.33	15.46	60	1.454
		75	1.438
		90	1.425
		100	1.411
45.63	0.0	75	1.398
		90	1.386
		105	1.376
		120	1.366
45.10	4.66	70	1.431
		90	1.415
		105	1.404
		120	1.392
44.93	10.03	90	1.456
		105	1.443
		120	1.429
43.85	15.47	90	1.481
		105	1.468
		120	1.454
46.21	28.82	90	1.585
		105	1.569
		120	1.555

Table III. Density of Solutions with 50–55 wt % $Mg(NO_3)_2$

wt %			
$Mg(NO_3)_2$	HNO_3	temp, °C	av density, g/cm^3
51.49	0.0	90	1.467
		105	1.458
		120	1.449
50.88	4.25	90	1.483
		105	1.475
		120	1.461
50.85	9.08	90	1.525
		105	1.513
		120	1.499
50.25	13.94	90	1.541
		105	1.527
		120	1.510
		130	1.502
54.17	0.0	90	1.504
		105	1.495
		120	1.482
		130	1.473
53.13	4.04	90	1.514
		105	1.502
		120	1.491
		130	1.479
		135	1.470
54.23	6.02	90	1.541
		105	1.529
		120	1.516
54.86	9.35	90	1.571
		105	1.558
		120	1.546
		130	1.537
52.24	14.57	90	1.566
		105	1.552
		120	1.537
		130	1.526
55.40	21.06	90	1.641
		105	1.626
		120	1.616

weighing and transfer of reagents were not necessary for this preparation since final concentrations could only be targeted for these reasons: (1) when the magnesium nitrate, nitric acid, and water are being heated and stirred during the dissolution, some acid and water are lost by evaporation, and (2) when transferring and heating mixtures containing substoichiometric $Mg(NO_3)_2 \cdot XH_2O$, (MgX), water is adsorbed while the MgX is exposed to the laboratory atmosphere.

The $Mg(NO_3)_2 \cdot 6H_2O$ flake, 70% HNO_3 (sp gr 1.42), and water required to make 190 g of solution were heated and stirred simultaneously. During the same time, three dilatometers were heated to 90 °C in the oven, allowed to cool for 10 min, weighed, and then returned to the oven. When the salt dissolved and the solution was clear (temperature usually 90–100 °C), the dilatometers were removed from the oven, filled while hot to the graduated region, and weighed. The top closure was then sealed in place. The loaded dilatometers were placed in the oven set at the lower temperature of the range of interest (e.g., the 50 wt % $Mg(NO_3)_2$ series, to be heated at 90, 105, 120, and 130 °C, was placed in the oven at 90 °C). After heating at the required temperature for 1.5 h, the liquid level was observed and recorded; then the temperature was raised to the next level, with 1.5 h again allowed for equilibration. At the end of the heating cycle, the dilatometers were removed from the oven and allowed to cool sufficiently so that boiling or gassing would not occur when opened. The hot solutions were immediately transferred to volumetric flasks (200 or 250 mL), allowed to cool to room temperature, and then diluted with water. Aliquots were analyzed for magnesium by a titration with EDTA; nitric acid was determined by a thermometric titration with sodium hydroxide (*4*).

To prepare solutions having $Mg(NO_3)_2$ concentrations of >55 wt %, use of the substoichiometric MgX was required. Con-

Table IV. Density of Solutions with 60-65 wt % $Mg(NO_3)_2$

wt % $Mg(NO_3)_2$	wt % HNO_3	temp, °C	av density, g/cm^3
59.82	0.0	90	1.552
		105	1.540
		120	1.527
		135	1.516
		145	1.506
59.82	0.0	100	1.558
		115	1.546
		130	1.534
57.51	4.38	90	1.571
		105	1.560
		120	1.546
		135	1.534
58.90	8.88	90	1.615
		105	1.603
		120	1.589
		130	1.578
61.00	13.84	90	1.668
		105	1.656
		120	1.641
65.17	0.0	90	1.627
		105	1.617
		120	1.605
		135	1.592
		145	1.583
65.97	5.70	90	1.680
		105	1.668
		120	1.657
		135	1.644
65.60	10.44	90	1.700
		105	1.693
		120	1.676

Table V. Density of Solutions with 70 wt % $Mg(NO_3)_2$

wt % $Mg(NO_3)_2$	wt % HNO_3	temp, °C	av density, g/cm^3
68.47	0.0	90	1.667
		105	1.658
		120	1.646
		135	1.634
		145	1.622
69.41	4.86	90	1.703
		105	1.693
		120	1.681
		135	1.669
68.79	7.97	120	1.702
		130	1.688

tainers with accurately weighed $Mg(NO_3)_2{\cdot}6H_2O$ flake were loaded into the vacuum oven set at 41 °C. The trap for removal of water was immersed in liquid nitrogen, and the system was evacuated. After 5 days of the described treatment, the oven and contents were brought to atmospheric pressure by backfilling with nitrogen. The containers were weighed to determine water loss. From the weight loss determination, the apparent formula of the MgX and the percent $Mg(NO_3)_2$ were calculated. Then the calculated amount of MgX, 70% HNO_3 (sp gr 1.42), and water were mixed to prepare 200 g of solution. The reagents were dissolved while heating to 90–100 °C with stirring; then the reagents were transferred to hot dilatometers, equilibrated, and analyzed as described above.

Results

The experimental data are grouped according to magnesium nitrate content in Tables I–V. The recommended equation for the density of the $Mg(NO_3)_2$–HNO_3–H_2O system is

$$D = 0.9280 + 0.01185M + 0.006215H - 0.0007866T$$

where D = solution density (g/cm^3), M = wt % $Mg(NO_3)_2$, H = wt % HNO_3, and T = temperature (°C). This equation has a standard deviation of 0.006 125 20 g/cm^3 based on 144 experimental points covering the range of 30–70 wt % $Mg(NO_3)_2$ and 0–40 wt % HNO_3 over the temperature range 50–145 °C. Complete information on the model selection and development is presented in ref 3.

Registry No. $Mg(NO_3)_2$, 10377-60-3; HNO_3, 7697-37-2.

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