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Vapor Pressures of Nitric Acid and Water in the Systems HNO_3–H_2O and HNO_3–$Th(NO_3)_4$–H_2O at 50 °C[†]

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The equilibrium compositions of the vapor above nitric acid–water, thorium nitrate–water, and nitric acid–thorium nitrate–water mixtures at 50 °C have been studied as a function of solution concentration by using a transpiration technique. Nitric acid concentrations were varied from 0 to 20 *m* and thorium nitrate concentrations from 0 to 2.5 *m*. Our data for the nitric acid–water system have been combined with literature data to obtain parameters for Scatchard's ion-component model, and these parameters provide a satisfactory description of the system at 50 °C over a wide concentration range. The enhancement, at 50 °C, of the nitric acid vapor pressure by added thorium nitrate was found to be less than that previously determined at 25 °C. The data for the nitric acid–thorium nitrate–water system at 50 °C were fitted to a single multiparameter function.

Introduction

Recently, we reported values for vapor pressures of water (P_W) and nitric acid (P_N) above HNO_3-$Th(NO_3)_4$-H_2O solutions at 25 °C (*1*). It was shown that, although the Scatchard treatment (*2*) was satisfactory for representing the binary system data, an empirical expression provided a better representation of the ternary data obtained for a wide range of thorium nitrate and nitric acid concentrations. Experiments have now been completed for similar mixtures at 50 °C. Since there is marked disagreement between literature data (*3–6*) for the HNO_3–H_2O binary system, vapor pressures for this system have been redetermined. Water vapor pressures for the $Th(NO_3)_4$–H_2O binary system were not available and these have also been measured.

Experimental Section

The details of the transpiration apparatus used to determine the vapor pressures of water and nitric acid have been described previously (*1*). Dried nitrogen was passed through two presaturators and a saturator containing solutions of a particular thorium nitrate and/or nitric acid concentration. The nitric acid and water in the gas stream were then condensed in a collector in a dry ice–acetone bath. The saturators and presaturators were thermostated in a bath at 50.00 ± 0.02 °C, and all portions of the presaturator–saturator system above the surface of the thermostating bath were heated to prevent vapor condensation. Three similar sets of apparatus were attached in series. The third set, used to determine the quantity of dry gas passed through the system, was thermostated at 25.0 °C and contained deionized water in the saturator and presaturators.

The thorium nitrate, nitric acid, and thorium nitrate–nitric acid mixtures were prepared from standardized concentrated stock solutions of thorium nitrate and nitric acid. Details of the preparation and analysis of the stock solutions have been given previously (*1*), as has the procedure for analyzing the material trapped in the collectors during a transpiration run. As discussed in ref 1, the errors in the water vapor pressure measurements were ≤2%, and for runs in which more than 1 mg of nitric acid was transpired, the estimated errors in the nitric acid vapor pressures were ≤5%. For runs in which less than 1 mg of nitric acid was transpired, the errors in the nitric acid vapor pressures increased markedly, being roughly inversely proportional to the quantity of nitric acid collected.

Table I. Solution Concentrations and Experimental (50 °C) Vapor Pressures for the Binary Systems

HNO_3–H_2O			$Th(NO_3)_4$–H_2O	
HNO_3[a]	P_W, kPa	P_N, Pa	$Th(NO_3)_4$[a]	P_W, kPa
0.496	12.04	0.06	0.25	12.22
0.496	12.16	0.06	0.25	12.25
0.745	11.95	0.11	0.50	12.05
0.745	11.92	0.13	0.50	11.98
0.978	11.92	0.22	0.75	11.46
0.978	11.99	0.23	0.75	11.73
1.46	11.74	0.51	0.75	11.50
1.46	11.75	0.53	1.00	11.44
1.96	11.44	0.98	1.00	11.44
1.96	11.52	1.04	1.25	11.15
2.92	10.87	2.36	1.25	11.10
2.92	10.87	2.37	1.52	10.65
3.90	10.46	5.87	1.52	10.88
3.90	10.49	6.07	1.52	10.61
4.86	9.89	10.5	2.07	10.15
4.86	9.92	11.1	2.07	10.14
4.86	9.92	10.8	2.58	9.14
4.86	9.95	11.0	2.58	9.18
6.44	9.10	24.5		
6.44	9.13	25.4		
7.95	8.44	47.3		
7.95	8.45	48.2		
10.0	7.58	84.8		
10.0	7.60	88.2		
12.1	6.75	145		
12.1	6.76	149		
20.1	4.74	581		
20.1	4.69	582		

[a] Concentration, in mol kg^{-1}.

Results and Discussion

Tables I and II give our solution concentrations and experimentally determined vapor pressures for the HNO_3–H_2O,

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Table II. Solution Concentrations and Experimental (50 °C) Vapor Pressures for the Ternary System $Th(NO_3)_4$–HNO_3–H_2O

$Th(NO_3)_4$[a]	HNO_3[a]	P_W, kPa	P_N, Pa
0.50	0.100	11.78	0.08
0.50	0.100	11.86	0.08
0.50	0.247	11.72	0.19
0.50	0.247	11.95	0.18
0.50	0.247	11.80	0.20
0.50	0.491	11.76	0.30
0.50	0.491	11.77	0.27
0.50	0.744	11.44	0.58
0.50	0.744	11.46	0.59
0.50	0.985	11.36	0.84
0.50	0.985	11.32	0.84
0.50	0.989	11.35	0.92
0.50	0.989	11.38	0.99
0.50	0.989	11.19	0.66
0.50	0.989	11.14	1.03
0.50	1.49	11.20	1.59
0.50	1.49	11.24	1.60
0.50	1.98	10.87	2.75
0.50	1.98	10.84	2.77
0.50	1.98	10.81	2.57
0.50	1.98	10.79	2.81
0.50	1.99	10.67	2.05
0.50	1.99	10.73	2.79
0.50	2.99	10.46	6.03
0.50	2.99	10.23	6.02
0.50	2.99	10.26	6.16
0.50	5.97	9.01	27.9
0.50	5.97	8.88	24.8
0.50	5.97	8.68	25.7
0.50	5.97	8.65	26.8
0.51	10.6	6.86	133
0.51	10.6	6.88	135
0.75	7.94	7.61	73.9
0.75	7.94	7.63	73.9
1.00	5.48	8.54	39.2
1.00	5.48	8.57	39.7
1.51	0.498	10.28	2.16
1.51	0.498	10.28	2.26
1.51	2.00	9.48	10.6
1.51	2.00	9.53	10.6
1.51	6.03	7.69	66.6
1.51	6.03	7.78	67.4
2.54	0.501	8.92	5.72
2.54	0.501	8.88	5.65
2.52	2.99	7.74	38.6
2.52	2.99	7.68	38.0
2.53	6.00	6.70	102
2.53	6.00	6.70	100

[a] Concentration, in mol kg^{-1}.

$Th(NO_3)_4$–H_2O, and HNO_3–$Th(NO_3)_4$–H_2O systems at 50 °C. The vapor pressures are relative to a value of 3.1672 kPa for pure water at 25 °C (*7*), as this value was used to calculate the gas volume in each run from the measured quantity of water in the third collector. The vapor pressure of water at 50 °C was also measured, and an average value of 12.43 ± 0.19 kPa was obtained from eight measurements. This is within 0.8% of the literature value of 12.33 kPa (*7*). The water and nitric acid vapors were assumed to obey the ideal gas law for the experimental conditions. Considering the agreement between the experimental and literature values for the water vapor pressures, this approximation is valid for the H_2O/N_2 mixtures, within the limits of the other experimental errors. It is not known how good the approximation is for nitric acid vapor. The work of Yakimov and Mishin (*3*) suggests that nonideality of the HNO_3 vapor should not cause significant errors except, perhaps, for the 20.1 *m* HNO_3 solutions.

HNO_3–H_2O. In Figure 1 our average values for the nitric acid vapor pressure over aqueous nitric acid are plotted for each experimental concentration. Results of Yakimov and Mishin (*3*), Burdick and Freed (*4*), and Küppers (*5*) are shown for comparison. Our experimental values are markedly higher than those of Yakimov and Mishin, especially for nitric acid concentrations below 10 *m*, and are slightly higher than those obtained by Burdick and Freed. The values of Küppers et al. (*5*, *6*) were obtained from isobaric rather than isothermal experiments. Although this makes a direct comparison impossible, isothermal (50 °C) vapor pressure values were calculated by Küppers (*5*) from the isobaric values. These calculated values, shown in Figure 1, are generally higher than our isothermal results, particularly for solutions 5–10 *m* in nitric acid.

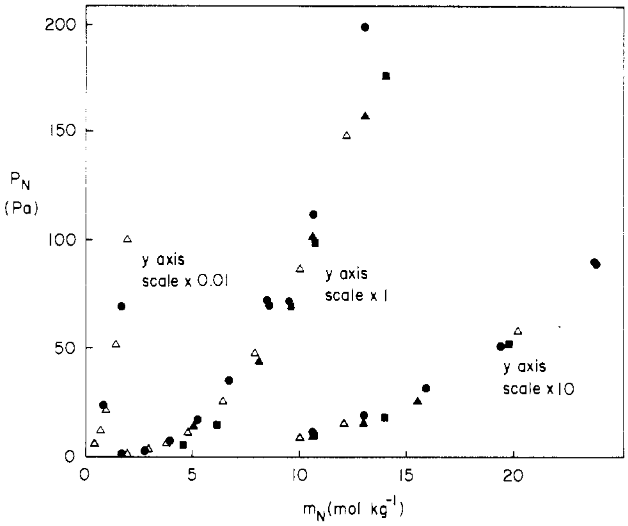

Figure 1. Experimental values for the vapor pressure of HNO_3 above aqueous nitric acid solutions: ●, Küppers (*5*), ■, Yakimov and Mishin (*3*), ▲, Burdick and Freed (4), △, this work.

If the formalism of Scatchard's ion-component model (*2*) is used, the water and nitric acid vapor pressures may be expressed as

$$P_w = P_W^0 \exp[-m_N \lambda \phi] \tag{1}$$

$$\lambda = 2(18.015)/1000$$

$$\phi = 1 + S[(1 + a_{HN} m_N^{1/2}) - 1/(1 + a_{HN} m_N^{1/2}) - 2 \ln (1 + a_{HN} m_N^{1/2})]/a_{HN}^3 m_N + 0.5(B_{HN}^{(1)} m_N + B_{HN}^{(2)} m_N^2 + B_{HN}^{(3)} m_N^3) \tag{2}$$

and

$$P_N = \frac{P_N^0 m_N^2}{(\gamma_N^* m_N^*)^2} \gamma_N^2 \tag{3}$$

$$\ln \gamma_N = \frac{S m_N^{1/2}}{1 + a_{HN} m_N^{1/2}} + B_{HN}^{(1)} m_N + \left(\frac{3}{4}\right) B_{HN}^{(2)} m_N^2 + \left(\frac{2}{3}\right) B_{HN}^{(3)} m_N^3 \tag{4}$$

P_W^0 and P_N^0 are respectively the vapor pressures of pure water and pure nitric acid at 50 °C; m_N is the molal concentration of nitric acid; *S* is the Debye–Hückel constant, which has a value of −1.2305 for water at 50 °C; and $\gamma_N^* m_N^*$ is the mean activity of nitric acid in 100% nitric acid with respect to the standard state in which the molal activity coefficient of nitric acid approaches unity as m_N (in water) approaches zero (*1*). The value of P_N^0 (27.15 kPa) was selected from the analysis of Duisman and Stern (*8*).

The a_{HN} parameter is equivalent to the *Ba* term in the extended Debye–Hückel treatment (*9*). As such, it should be associated with the closest distance of approach of the H^+ and NO_3^- ions in solution and should vary (as *B*) by only a few percent between 25 and 50 °C. Furthermore, the value of a_{HN} would best be defined by fitting activity data for relatively dilute

Table III. Fitted Ion-Component Model Parameters for HNO_3 and $Th(NO_3)_4$ at 50 °C

	HNO_3[a]	HNO_3[b]	$Th(NO_3)_4$[a]
a	1.262[c]	1.262[c]	2.22 ± 0.18
$10B^{(1)}$	1.89 ± 0.19	1.62 ± 0.09	−2.24 ± 0.72
$10^2B^{(2)}$	−1.29 ± 0.29	−0.92 ± 0.11	6.3 ± 2.0
$10^4B^{(3)}$	2.8 ± 1.0	1.6 ± 0.3	−36 ± 13
$\gamma_N^* m_N^*$	243 ± 10	233 ± 6	
χ_ν^2	0.5	4.9	1.2

[a] This work. [b] All data. [c] Fixed, see text.

Table IV. Fitted Parameters for HNO_3–$Th(NO_3)_4$–H_2O Mixtures at 50 °C

	data used		
	P_W	P_N	P_W and P_N
A	4.40 ± 0.95	4.16 ± 0.23	3.79 ± 0.13
B	−0.456 ± 0.085	−0.747 ± 0.070	−0.611 ± 0.036
C	0.014 ± 0.033	0.014 ± 0.028	0.002 ± 0.019
D	0.73 ± 0.34	0.45 ± 0.11	0.408 ± 0.068
χ_ν^2 (for data fitted)	0.2	9.7	5.6
χ_ν^2 (for both HNO_3 and H_2O pressure data)	109	6.6	5.6

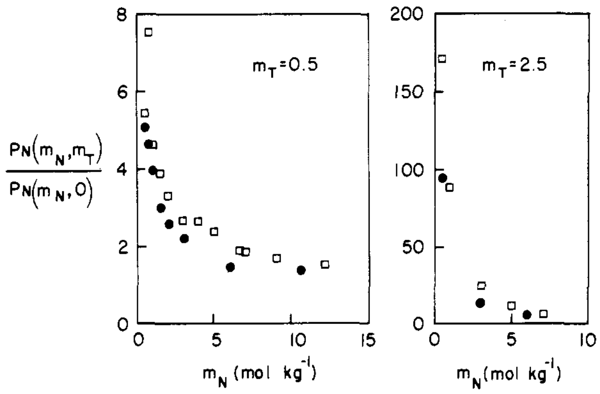

Figure 2. Averaged values of $P_N(m_N,m_T)/P_N(m_N,0)$ for 0.5 and 2.5 m thorium nitrate solutions containing nitric acid: □, 25 °C, ●, 50 °C.

solutions (<0.2 mol kg^{-1}), and such data are sparse for nitric acid solutions at 50 °C. Previously (*1*), we fitted 25 °C literature data for the activity coefficients of nitric acid to the ion-component model. Therefore, for fitting the 50 °C data, the value of a_{HN} was fixed to the value, 1.262, found for 25 °C. The nitric acid and water vapor pressures were fitted simultaneously to eq 1 and 3 to give values for $B_{HN}^{(1)}$, $B_{HN}^{(2)}$, $B_{HN}^{(3)}$, and $\gamma_N^* m_N^*$. Weighting was done by using the uncertainties of the data. The uncertainties were assumed proportional to the measured vapor pressures, and estimated as 2% and 5% of the water and nitric acid vapor pressures, respectively. However, for the nitric acid vapor pressures a minimum error of 1.5 × 10^{-2} Pa was also assumed, thus allowing for the poorer precision of this data at low partial pressures of HNO_3.

Parameters obtained by using our data exclusively and parameters calculated by using our data plus all available literature data (*3*–*6*) are given in Table III. The values of the parameters are all highly correlated. As would be expected, the value of χ_ν^2 is larger for the data from all sources. Error limits for the parameters were established by fitting sets of pseudoexperimental points assumed to be distributed in a Gaussian distribution about each of the actual experimental points. The uncertainties given in Table III represent 90% confidence limits. It can be seen that parameter values calculated from all the nitric acid data and from our data alone are only in fair agreement within the stated uncertainties. Despite the large spread in the literature vapor pressure data, the combined data set gives lower error limits for the ion-component model parameters. Therefore, these parameters for the HNO_3–H_2O system have been used in later calculations with data for the HNO_3–$Th(NO_3)_4$–H_2O system.

Recalculation of the results of Haase et al. (*6*), using 27.15 kPa for the vapor pressure of pure nitric acid (*8*), gives $\gamma_N^* m_N^*$ (=exp(C_2/2)) = 215 ± 19, a somewhat lower value than either result in Table III.

$Th(NO_3)_4$–H_2O. The experimental water vapor pressures at 50 °C for the thorium nitrate solutions were combined with 50 °C osmometric data (*10*) to calculate ion-component model parameters for the $Th(NO_3)_4$–H_2O systems. The data were weighted assuming uncertainties of 2% in the transpiration (water vapor pressure) data and 3% in the osmometric (ΔV) data. Parameter values and uncertainties are given in Table III.

The P_W/P_W^0 ratios derived from our transpiration experiments are slightly greater (by 1–3%) than the ratios at 45 °C calculated from the data of Apelblat et al. (*11*). Extrapolation of their temperature-dependent data (for 25, 35, and 45 °C) would lead to a somewhat smaller increase. However, the difference is within our experimental uncertainties.

HNO_3–$Th(NO_3)_4$–H_2O. On analyzing experimental vapor pressure data obtained at 25 °C (*1*), it was found that neither the Pitzer (*12*, *13*) nor the ion-component (*2*) models provided a satisfactory fit. This is also true for the 50 °C data. In ref 1 an arbitrary function

$$P_N(m_N,m_T) = P_N(m_N,0)\exp[m_T(A + Bm_T)(1 + Cm_N)/(1 + Dm_N)] \quad (5)$$

was proposed for $P(m_N,m_T)$, the nitric acid vapor pressure in the HNO_3–$Th(NO_3)_4$–H_2O system, for nitric acid and thorium nitrate molal concentrations m_N and m_T, respectively. A, B, C, and D are fitting parameters. A corresponding expression was obtained for the water vapor pressures (involving $P_W(m_N,0)$ and $P_W(0,m_T)$), using the Gibbs–Duhem equation. With values of $P_N(m_N,0)$, and $P_W(m_N,0)$, and $P_W(0,m_T)$ calculated by using eq 1 and 3 and the parameters in Table III, the experimental 50 °C vapor pressure data for the three-component system were fitted to these functions. Values of the parameters, separately calculated from the nitric acid vapor pressures, from the water vapor pressures, and from the combined data, are given in Table IV. Weighting of the data was done in the manner described for the data of the HNO_3–H_2O system. Very poor agreement is found if an attempt is made to calculate nitric acid vapor pressures with parameters determined only from the water vapor pressure data, although the converse is not true.

Figure 2 shows how the ratio $P_N(m_N,m_T)/P_N(m_N,0)$ varies with m_N at constant m_T, and compares the results for 50 °C with those for 25 °C. Our experimental ratios from this work and from ref 1 were adjusted slightly by using eq 5 to allow for the fact that the experimental thorium concentrations were not exactly 0.5 and 2.5 m. The values of $P_N(m_N,0)$ were derived by using the parameters in column three of Table III (50 °C) and Table II of ref 1 (25 °C). Where more than one experiment was done at the same concentration and temperature, the average result was plotted. Despite the scatter, it is apparent that thorium nitrate does not enhance the vapor pressure of nitric acid at 50 °C by as much as at 25 °C. The percentage difference is slightly less at high nitric acid concentrations, and is greater for 2.5 m thorium nitrate than for 0.5 m thorium nitrate. The size of the difference (~20–30%) in the enhancement between the two temperatures is somewhat surprising. Nitric acid becomes more highly associated in aqueous solution as the temperature is raised (*14*), but this alone is insufficient to account for the change in the enhancement. Furthermore, hydrolysis of Th^{4+} increases with increasing temperature (*15*). This would be expected to generate extra HNO_3 in the solutions—particularly for solutions with low m_N and high

m_T. The calculated values of the activity coefficient of thorium nitrate in the ternary system are strongly dependent on the fitting function, but, within the error limits of the data, are the same at 50 °C as those found at 25 °C (*1*).

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Isobaric Vapor–Liquid Equilibria of the Ethylbenzene–*p*-Xylene System

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Boiling temperatures were measured for the close boiling ethylbenzene–*p*-xylene binary system at 500, 760, 1250, and 1500 mmHg. The data were correlated by the NRTL equation, and the relative volatility of ethylbenzene to *p*-xylene was calculated.

Introduction

In the recovery of aromatics from oil fractions a mixture of C_8 is obtained which contains ethylbenzene and the isomers of xylene.

The demand for individual pure C_8 has grown very rapidly, recently, since ethylbenzene is the main raw material employed for the manufacture of styrene, and xylene isomers are used to obtain phthalic anhydride and phthalic acids. For example, much of the *p*-xylene is converted to dimethyl terephthalate which is employed to produce polyester fibers.

The purity required for these products in the subsequent processing is usually very high. For example, dehydrogenation of ethylbenzene to styrene requires a product with a purity greater than 99.5%.

The production of individual components of very high purity from C_8 aromatic isomers is difficult because of the low relative volatility. The separation of ethylbenzene (ETB) from *p*-xylene (*p*-X) by conventional rectification requires the use of columns containing more than 200 plates and high reflux ratio since their normal boiling points are very close to each other ($T_{b,ETB}$ = 135.9 °C; $T_{b,p\text{-X}}$ = 138.1 °C).

Several papers have appeared in the literature (*1*–*3*) concerning the effect of adding agents in order to increase the relative volatility. However only few authors (*4*, *5*) report data on the vapor–liquid equilibrium of the ETB–*p*-X binary system.

Because of the closeness of the vapor and liquid compositions, experimental work is difficult, but the effort is justified since relative volatilities must be known with great accuracy in order to design reliable distillation columns.

Values of relative volatility ranging from 1.035 to 1.06 are reported in the literature (*1*, *2*). However, the experimental source of these data is not clear or seems too rough (*1*) for the accurate evaluation of this thermodynamic property.

In any case, the assumption of ideal solution may give unacceptable results because of the criticality of the separation. Furthermore, measurements of excess enthalpies for this system (*6*) show nonzero values which exclude the hypothesis of ideality. The assumption of symmetrical deviation from ideality should be more acceptable.

Therefore, in order to obtain a wider range of information about the thermodynamic behavior of this system, we carried out measurements of boiling temperatures. The deviations from ideality were studied by evaluating the activity coefficients and correlating their values by a suitable model of the liquid phase.

Previous measurements of vapor pressures for pure components were carried out by means of the same apparatus as used for mixtures.

Experimental Section

A pair of Swietoslawski ebulliometers (*7*) was used for the measurements of the boiling points of pure substances or mixtures. The condensers of the ebulliometers were connected together, through a dead volume, to an ejector or to a nitrogen cylinder to ensure the required pressure. An U mercury manometer allowed a rough determination of the pressure.

The pressure is regulated by a valve at the required constant value which is then exactly determined via the boiling point of high-purity water used as reference substance in one of the ebulliometers. The temperature of water and that of the mixture (or pure component) were detected simultaneously by two LAUDA platinum resistance thermometers and a digital display with a ±0.01 °C resolution.

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