tion applies to $\gamma_1^{(P^\circ)}$. The thermodynamic consistency test becomes

$$\left[\left(x_1 \ln \gamma_1^{(P^\circ)} + x_2 \ln \gamma_2^{*(P^\circ)}\right)\Big|_{x_{2,\max}} = - \int_0^{x_{2,\max}} \ln \frac{\gamma_1^{(P)^\circ}}{\gamma_2^{*(P^\circ)}}\, dx_2 \right]_T \qquad (3)$$

where $x_{2,\,\max}$ is the maximum value of x_{O_2} for which data were taken. The left-hand side of Equation 3 is defined as area$_1$ and the right-hand side as area$_2$. Percent inconsistency is then defined as

$$\%\ \text{inconsistency} = 100 \frac{\text{area}_1 - \text{area}_2}{\text{area}_1}$$

These data show an inconsistency of 2.5%. This is considerably better than the data for the −50°C isotherm (*2*) which exhibit an inconsistency of 9.5%.

NOMENCLATURE

f = fugacity, atm
H = Henry's law constant, atm
P = pressure, atm
R = gas constant
T = temp, °C
v = molar volume, cc/g-mol
x = liquid-phase mole fraction
y = vapor-phase mole fraction
γ = activity coefficient
Φ = fugacity coefficient
(P°) = evaluated at P°
$*$ = unsymmetrical convention used
1 = carbon dioxide
2 = oxygen

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Thermodynamic and Physical Properties of Ammonia–Lithium Thiocyanate System

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Vapor pressure data obtained in the concentration range of 40 to about 60 wt % lithium thiocyanate in ammonia and for pressures of 15–200 psia show extremely high negative deviations from Raoult's law. The data were used to compute heats of vaporization from these solutions. Viscosity data were obtained over a temperature range of 75–200°F and concentrations to about 60 wt % salt. The data fit Andrade's equation and produce straight lines amenable to extrapolation to higher temperatures. The densities of the solutions were also measured.

Most of the investigations of thiocyanate salts in the literature involve aqueous or molten solutions. Progress in formulating theoretical descriptions of concentrated nonaqueous electrolytic solutions requires the availability of experimental data presently in meager supply in the literature. Such measurements have been reported earlier by the authors for concentrated monomethylamine solutions of lithium (*4*) and sodium thiocyanate (*5*) and by Blytas (*1*) for ammonia–sodium thiocyanate solutions. The present work reports on such measurements for ammonia–lithium thiocyanate solutions. Experimental data on vapor pressures, solubility, density, and viscosity are given between 75° and 250°F, from 60–40 wt % ammonia, and at pressures from 1–200 psia. These solutions exhibit high negative deviations from Raoult's law. This particular system was chosen because of its possible application to absorption cooling in a gas-fueled air-cooled absorption system.

Most of the literature studies involving ammonia have been carried out at or near its normal boiling point to avoid experimentation at high pressures. Because the present work was carried out in a range of temperatures extending much above room temperature, special equipment was constructed to facilitate measurements at high pressures.

DISCUSSION

Vapor Pressures. Vapor pressure data were obtained utilizing equipment and procedures described by the authors in a recent publication (*4*). The pressure of the mixtures at low- and high-pressure ranges was read with a manometer or a deadweight tester, depending on the pressure range.

The 1000-psi deadweight tester was supplied with a calibration accurate to ±0.1 psia. Measurements, however, were

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only approximately accurate to ±0.5 psia because of the insensitivity of the pressure transducer in the system. For low pressures, a 50-in. mercury manometer was used and was read to ±0.1 mm Hg. Temperatures were measured with copper constantan thermocouples accurate to within ±0.1°F in the temperature range of 75–200°F. The thermocouples were calibrated by comparison to a platinum resistance thermometer from the National Bureau of Standards. The ammonia used was Matheson Co.'s anhydrous ammonia grade with 99.99% ammonia.

The lithium thiocyanate was purchased from a supplier who prepared it by using the method outlined by Lee (3). The wet lithium thiocyanate crystals were further dried at the Institute of Gas Technology (IGT) at 130°C in a rotary kiln in a nitrogen atmosphere until the amount of water in the salt was <1% by weight. Consequently, all solutions of lithium thiocyanate and methylamine prepared for this study contained a small amount of water never exceeding 1% by weight of the total solution.

Table I. Vapor Pressures of Ammonia–Lithium Thiocyanate Solutions

39.3 Wt % salt[a]		45.5 Wt % salt[b]	
Temp, °F	Pressure, psia	Temp, °F	Pressure, psia
82.3	87.9	94.4	72.6
82.5	87.1	107.6	90.5
94.1	105.1	116.3	101.9
94.5	98.6	130.3	125.3
120.1	159.1	130.0	124.5
120.8	161.3	145.7	154.9
133.4	192.7	145.8	154.9
133.7	192.9		
143.2	223.6		
144.3	223.3		

52.6 Wt % salt[c]		59.3 Wt % salt[d]	
Temp, °F	Pressure, psia	Temp, °F	Pressure, psia
99.6	33.4	104.3	15.4
117.1	43.8	124.4	19.6
143.1	64.8	150.1	31.8
167.4	92.9	150.7	29.0
189.5	125.5	163.5	37.1
207.8	159.4	183.5	50.7
		198.9	64.8
		219.5	88.8

[a] 99.67 wt % LiSCN + 0.33 wt % H_2O. [b] 100.00 wt % LiSCN. [c] 99.07 wt % LiSCN + 0.93 wt % H_2O. [d] 99.18 wt % LiSCN + 0.82 wt % H_2O.

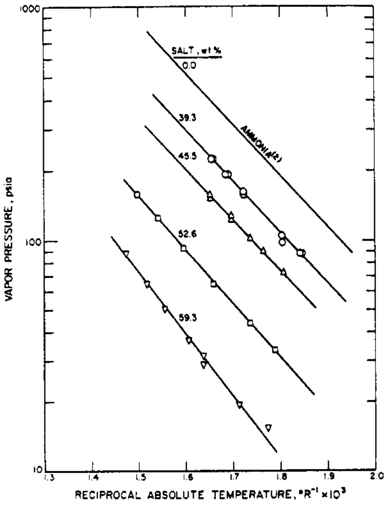

Figure 1. Vapor pressure data of ammonia–lithium thiocyanate solutions

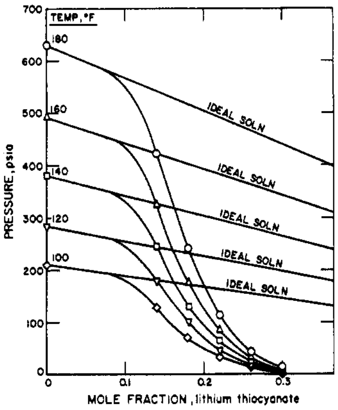

Figure 2. Vapor pressure plot showing extreme negative deviation from Raoult's law

Four different solutions covering the ranges given above were studied. The experimental results are listed in Table I and plotted in the form of log p vs. $1/T$ in Figure 1. Figure 2—a plot of pressure vs. mole fraction lithium thiocyanate—illustrates the high degree of nonideality of the solutions in question.

The experimental data obtained were correlated by means of the generalized equation shown in Table II. The constants in the equation were calculated by regression analysis and are listed in the same table. The objective of this was to provide an analytical expression of vapor pressure as a function of temperature and concentration that would be useful for machine computations. Smoothed values of vapor pressures at regular intervals of temperature and composition were generated from the equation (Figure 3).

Heat of Vaporization. The vapor pressure data (Figure 1) follow well the approximate form of the Clausius-Clapeyron equation, with H_{vap} considered to be a function only of concentration:

$$d\left(\frac{\ln p}{1/T}\right) = -\frac{H_{vap}}{°R} \tag{1}$$

Table II. Parameters for Equation for Vapor Pressures, Psia, for Ammonia–Lithium Thiocyanate System

$$\ln P = \ln x + \sum_{n=0}^{3} a_n(1-x)^n - \frac{1}{T}\sum_{n=0}^{3} b_n(1-x)^n + \frac{1}{T^2}\sum_{n=0}^{1} c_n(1-x)^n$$

System	Ammonia-lithium thiocyanate
Volatile component	Ammonia
Composition range, mole fraction	$0.86 \geq X \geq 0.70$
Temperature range, K	$420 \geq T \geq 290$
Variance	0.7×10^{-2}
Constants	
a_0	13.85
a_1	12.63
a_2	−61.23
a_3	...
b_0	47.59×10^2
b_1	36.39×10^2
b_2	...
b_3	...
c_0	...
c_1	...

Table III. Parameters for Clausius-Clapeyron Equation

Compn salt, Wt %	H_{vap}/R, R^{-1}	Constant	Variance
0	4872	14.05	0.55×10^{-4}
39.3	4922	13.54	0.44×10^{-4}
45.5	5004	13.31	0.49×10^{-4}
52.6	5433	13.20	0.13×10^{-3}
59.3	6422	13.92	0.77×10^{-3}

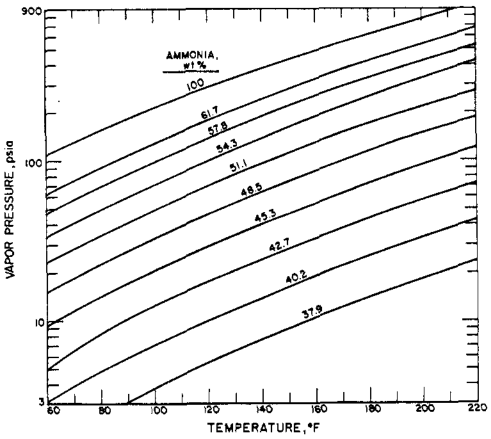

Figure 3. Smoothed vapor pressures for ammonia–lithium thiocyanate system

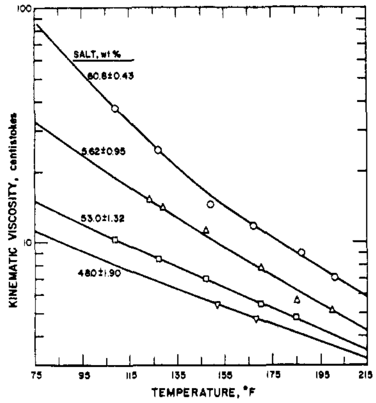

Figure 4. Viscosities of ammonia–lithium thiocyanate solutions

To select the best fit of the Clausius-Clapeyron equation lines, the method of least squares was employed.

The constants of the equations at each concentration and the variances are shown in Table III.

With the right-hand term of Equation 1 shown to be independent of temperature in the region covered by this study, H_{vap} values were computed for the four concentrations shown in Table I as the slope of the straight lines of Figure 1. The values thus obtained were used to derive the relationship shown as Equation 2, which gives the dependence of H_{vap} on concentration, with a variance of 15.64 Btu per mole or a standard deviation of 3.95 Btu per mole:

$$H_{\text{vap}} = 9.67 + 3.97\,X_s + 15.40\,X_s^2 - 23.78\,X_s^3 \qquad (2)$$

It is believed that this equation provides significantly accurate values for engineering calculations. A more rigorous approach that could provide greater confidence in the H_{vap} values would be the differentiation of the vapor pressure equation shown in Table II. In equation 2, H_{vap} is the energy required to vaporize 1 lb-mol ammonia from an infinitely large amount of solution. The units of H_{vap} are 1000 Btu/lb-mol of ammonia, and X_s represents the mole fraction of thiocyanate salt in the solution.

Heats of Solution. When the vaporization is carried out from a finite amount of solution, the solution composition changes. In this case, the required energy, $\Delta H(X_{s_1} \rightarrow X_{s_2})$, to provide 1 lb-mol of ammonia can be obtained from the expression

$$\Delta H(X_{s_1} \rightarrow X_{s_2}) = \frac{X_{s_1} \cdot X_{s_2}}{X_{s_2} - X_{s_1}} \int_{X_{s1}}^{X_{s2}} \frac{H_{\text{vap}}}{X_s^2}\, dX_s \qquad (3)$$

where X_{s_1} and X_{s_2} are initial and final salt mole fractions and H_{vap} is as defined previously.

Viscosity. Viscosity data were obtained utilizing equipment and procedures described earlier (*4*).

Measurements of viscosity were made for four solutions of ammonia and lithium thiocyanate, with the total amount of salt varying between 48.0 and 60.8 wt %, in the region of temperature of approximately 75–200°F (Table IV and Figure 4).

With information obtained on the density of these solutions,

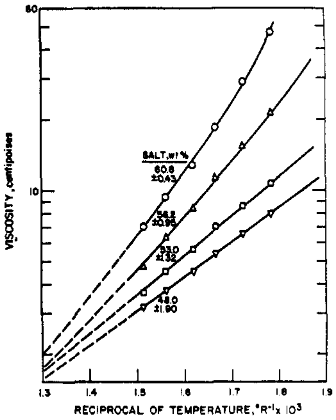

Figure 5. Variation of viscosity with temperature for ammonia–lithium thiocyanate solutions

Table IV. Viscosity Data for Ammonia–Lithium Thiocyanate Solutions

48.0 ± 1.90 Wt % salt[a]		53.0 ± 1.32 Wt % salt[a]	
Temp, °F	Kinematic viscosity, cSt	Temp, °F	Kinematic viscosity, cSt
111.9 ± 0.1	6.71	108.6 ± 0.1	10.31
129.8 ± 0.2	5.47	127.1 ± 0.3	8.50
151.7 ± 0.1	5.48	146.5 ± 0	6.95
168.2 ± 0.1	4.74	169.5 ± 0	5.45
		184.4 ± 0.2	4.80
56.2 ± 0.95 Wt % salt[b]		**60.8 ± 0.43 Wt % salt[b]**	
Temp, °F	Kinematic viscosity, cSt	Temp, °F	Kinematic viscosity, cSt
123.5 ± 0	15.17	75.7 ± 0.3	85.90
128.6 ± 0	14.0	107.0 ± 0	37.60
147.5 ± 0	11.20	127.0 ± 0.3	24.80
170.1 ± 0	7.74	148.7 ± 0.3	14.45
184.6 ± 0	5.65	166.8 ± 0.2	11.75
200.5 ± 0	5.10	187.0 ± 0.3	9.05
		201.2 ± 0	7.09

[a] 98.46 Wt % lithium thiocyanate + 1.54 wt % water. [b] 99.27 Wt % lithium thiocyanate + 0.77 wt % water.

Table V. Density Data For Ammonia–Lithium Thiocyanate Solutions

47.5 Wt % salt[a]		62.6 Wt % salt[b]	
Temp, °F	Density, g/cc	Temp, °F	Density, g/cc
128.1	0.895	98.1	1.010
139.2	0.891	117.9	1.005
149.7	0.887	133.4	1.000
161.1	0.883	150.0	0.992
171.3	0.879	184.9	0.984
189.5	0.873	200.6	0.979
207.8	0.866	226.3	0.971
226.5	0.858	253.0	0.968
234.3	0.856		

[a] 98.46 Wt % lithium thiocyanate + 1.54 wt % water. [b] 99.27 Wt % lithium thiocyanate + 0.77 wt % water.

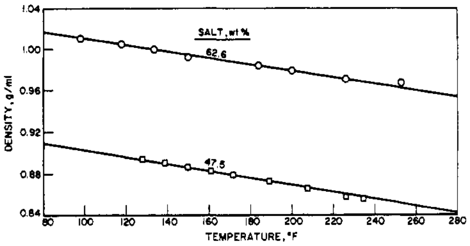

Figure 6. Density data for ammonia–lithium thiocyanate solutions

the kinematic viscosity was converted to absolute viscosity, μ. In this form the data obtained in the range of 75–200°F were extrapolated to 300°F in a log plot of μ vs. $1/T$ (Figure 5).

Density. Density measurements on two solutions were carried out in a specially built glass tube cell, entirely immersed in a temperature-controlled bath. At each temperature the volume occupied by a known quantity of solution was obtained by measuring the level of the solution in the upper capillary by means of a cathetometer. The cell had been previously calibrated by filling to different heights in the capillary with carefully weighed amounts of mercury. The volume of the cell was approximately 4 ml. The cell consisted of a 6-in. long $^1/_4$-in. i.d. lower portion, to which a $^1/_{16}$-in. i.d. and 6-in. long capillary was attached.

The solutions investigated contained 47.5 and 62.6 wt % salt. Densities were obtained in the 80–280°F temperature range, under the solution vapor pressure at each temperature (Table V and Figure 6).

Density data for the two solutions reported were linearly interpolated to obtain densities at four other concentrations: 48.0, 53.0, 56.2, and 60.8 wt % salt.

NOMENCLATURE

H_{vap} = heat of vaporization, 1000 Btu/lb-mol ammonia
p = total pressure, psia
T = absolute temperature, °R
X_s = mole fraction salt
X_{s_1} = initial mole fraction salt
X_{s_2} = final mole fraction salt
μ = absolute, viscosity, cP

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Effect of Aqueous–Ethanol and Aqueous–Dimethylsulfoxide Solvent Systems on Transference Numbers and Mobilities of H^+, K^+, and Cl^-

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The enhancement of the rate of nucleophilic reactions by aprotic solvents has been attributed to decreased solvation and, hence, increased activity of the nucleophile. The verification of this assumption and the evaluation of solvent effects on the anion are complicated by the fact that activity measurements are the average values for the cation and anion. Decreased solvation of the anion may well be accompanied by increased solvation (and decreased activity) of the cation so that the measured activity remains essentially constant. It occurred to us, after trying to evaluate solvent effects on anion activity by emf (*4*) and conductance (*3*) studies, that transference numbers and mobilities were properties which could be determined for individual ions and which would reflect changes in the ion's environment caused by solvent changes. Transference numbers and mobilities were determined for cations and anions of KCl and HCl in aqueous–ethanol and aqueous–dimethylsulfoxide (DMSO) in which the organic portion was varied from 0–60% (v/v). These two organic solvents were chosen as contrasting protic and aprotic solvent types.

EXPERIMENTAL

Apparatus. A modified moving-boundary transference number apparatus was developed which measured the move-

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