Thermodynamic and Physical Properties of Monomethylamine–Lithium Thiocyanate System

ROBERT A. MACRISS, DHARAMVIR PUNWANI, WILLIAM F. RUSH, and WENDELL J. BIERMANN[1]
Institute of Gas Technology, Chicago, Ill. 60616

Vapor pressure data obtained in the concentration range of 0 to about 56 weight % lithium thiocyanate in monomethylamine and for pressures of 1 to 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° to 200° F and concentrations to about 56 weight % salt. The data fit Andrade's equation very well and produce straight lines which are amenable to extrapolation to higher temperatures. The densities of the solution were also measured.

Most of the investigations of thiocyanate salts in the literature involve aqueous solutions. Although dilute aqueous solutions have contributed greatly to the development of physical chemistry, the behavior of very concentrated nonaqueous electrolytic solutions has not been completely understood.

Progress in formulating theoretical descriptions of these concentrated solutions requires the availability of experimentally determined data, which at present are in meager supply in the literature. Such measurements are reported here for solutions of lithium thiocyanate in liquid monomethylamine. Experimental data on vapor pressures, solubility, density, and viscosity are given between 75° and 285° F, from 100 to 55 weight % methylamine, and pressures from 1 to 200 psia. This particular system was chosen for study because of its possible application to absorption cooling in a gas-fueled air-cooled system.

Most of the literature studies involving methylamine 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 was measured by using a 25-mm-bore, 90-cu-cm-capacity glass cell attached to a glass-to-metal pressure connector through an O-ring assembly. The cell was pressure-tested to 34 atm. In operation, a known amount of dry lithium thiocyanate salt is charged to the cell, and, after evacuation and cooling, methylamine is distilled into it until 75 to 90% of the volume of the cell is occupied by the resulting liquid mixture. The contents of the cell (Figure 1) are thoroughly mixed by returning refrigerant vapor (methylamine) from the top of the cell to the bottom of the liquid layer and bubbling the vapor through the liquid. Circulation is accomplished by a magnetically operated plunger pump which is in a closed loop with the equilibrium cell. The equilibrium cell is permanently fixed in a constant-temperature bath. The pres-

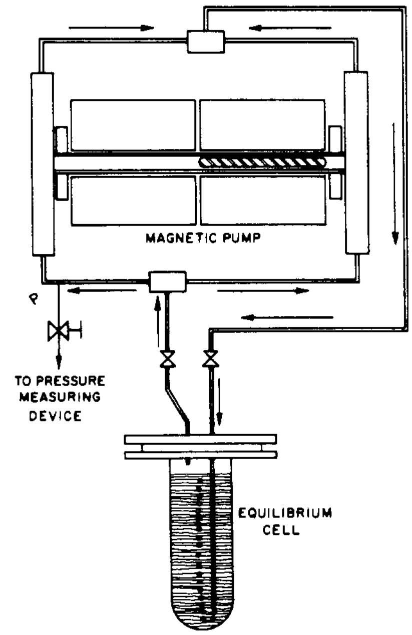

Figure 1. Vapor pressure cell assembly

---

[1] Present address, Research Division, Carrier Corp., Syracuse, N. Y.

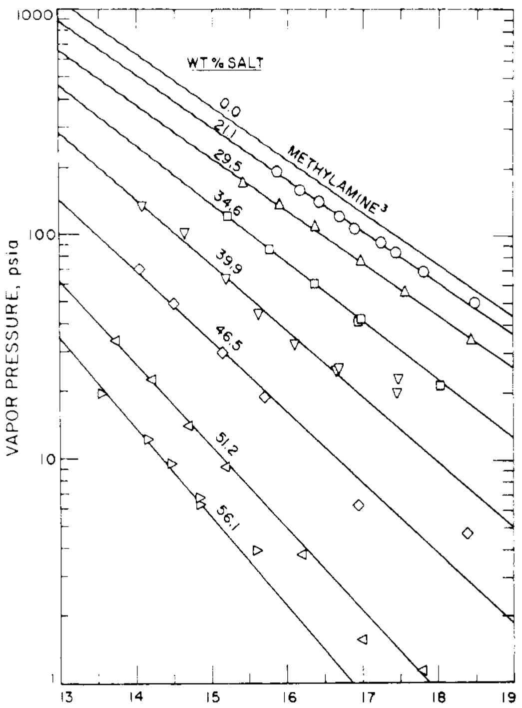

Figure 2. Vapor pressure data of monomethylamine–lithium thiocyanate solutions

Table I. Vapor Pressures of Monomethylamine–Lithium Thiocyanate Solutions

21.1 Wt % Salt[a]		29.5 Wt % Salt[a]		34.6 Wt % Salt[b]	
Temp., °F	Pressure, psia	Temp., °F	Pressure, psia	Temp., °F	Pressure, psia
80.4	50.2	81.4	34.4	93.5	21.43
112.5	81.1	81.6	34.3	93.4	21.63
120.0	94.5	108.7	55.3	93.5	21.53
130.6	107.7	108.9	55.6	129.2	41.4
100.6	68.2	128.5	77.6	128.3	42.3
138.4	121.9	128.7	77.8	150.6	61.5
148.4	139.3	150.4	107.7	173.6	87.5
158.5	159.4	150.4	108.2	197.0	122.0
169.2	191.4	169.0	135.4		
		187.8	168.0		

39.9 Wt % Salt[2]		46.5 Wt % Salt[c]		51.2 Wt % Salt[d]	
Temp., °F	Pressure, psia	Temp., °F	Pressure, psia	Temp., °F	Pressure, psia
83.2	18.50	83.3	4.72	78.4	0.93
102.3	20.30	83.3	4.77	102.4	1.13
102.3	23.10	129.8	6.29	128.2	1.57
138.6	26.17	147.2	7.81	156.9	3.74
138.8	26.37	176.3	18.87	178.7	6.19
160.3	33.3	199.5	29.84	198.4	9.34
177.8	44.7	229.2	48.9	222.3	14.05
198.2	63.9	251.9	70.3	244.9	23.05
223.1	100.8			265.8	34.05
223.0	102.1			285.4	48.35
248.0	135.2				
248.1	138.0				

56.1 Wt % Salt[e]	
Temp., °F	Pressure, psia
180.9	3.87
180.9	3.97
213.1	6.91
213.1	6.13
230.3	9.57
231.1	9.47
247.0	12.27
277.8	19.97

[a] 99.04 wt % lithium thiocyanate + 0.96 wt % water. [b] 99.44 wt % lithium thiocyanate + 0.56 wt % water. [c] 99.75 wt % lithium thiocyanate + 0.25 wt % water. [d] 99.07 wt % lithium thiocyanate + 0.93 wt % water. [e] 98.17 wt % lithium thiocyanate + 1.83 wt % water.

sure of the mixture at low- and high-pressure ranges is read with a manometer or a dead-weight tester, depending on the pressure range.

The 1000-psi dead-weight tester was supplied with a calibration accurate to ±0.1 psia. Measurements, however, were only approximately accurate to ±0.5 psia because of the insensitivity of the pressure transducer in the system. For low pressures, a 50-inch mercury manometer was used and was read to ±0.1 mm of Hg. Temperatures were measured with copper-constantan thermocouples accurate to within ±0.1° F in the temperature range of 70° to 300° F. The thermocouples were calibrated by comparison to a platinum resistance thermometer from the National Bureau of Standards.

The methylamine used had the following impurities:

Trimethylamine	0.11 mole %
Dimethylamine	0.6 mole %
Ammonia	0.37 mole %

The lithium thiocyanate was purchased from a supplier who prepared it by using the method outlined by Lee *(4)*. The wet lithium thiocyanate crystals were further dried at 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 but never exceeding 1% by weight of the total solution.

Seven 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 2. Figure 3, a plot of pressure *vs.* mole fraction methylamine, 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 4).

Heats of Solution and Vaporization. In the literature, heat of vaporization data exist only for methylamine, and are limited to a maximum temperature of approximately 225° F *(5)*.

The vapor pressure data (Figure 2) follow well the approximate form of the Clausius-Clapeyron equation, with H_{vap} considered to be a function only of concentration:

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

This is particularly true for the high-pressure region, which is of primary interest for absorption cooling cycle calculations *(1)*.

To select the best fit of the Clausius-Clapeyron equation lines, the method of least squares was employed. The low-temperature vapor pressure points were excluded from the fit. Inadequate degassing of the solutions caused the data in this region (below 10 psia) to be in error.

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 seven concentrations shown in Table I as the slope of the straight lines of Figure 2. 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 245.4 Btu per mole or a standard deviation of 15.66 Btu per mole.

$$H_{\text{vap}} = 10.7 - 42.36\, X_s + 383.9\, X_s^2 - 944.8\, X_s^3 + 1019\, X_s^4 \quad (2)$$

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

Table II. Parameters for Equation for Vapor Pressures, PSIA, for Monomethylamine–Lithium Thiocyanate System

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

System	Monomethylamine–Lithium Thiocyanate
Volatile component	Monomethylamine
Composition range, mole fraction	$0.88 \geqq x \geqq 0.60$
Temperature range, °K	$300 \geqq T \geqq 400$
Variance	0.8327×10^{-2}
Constants	
a_0	13.96
a_1	36.45
a_2	. . .
a_3	. . .
b_0	53.89×10^2
b_1	40.74×10^3
b_2	29.41×10^3
b_3	. . .
c_0	. . .
c_1	13.37×10^6
T_o, °K	∞

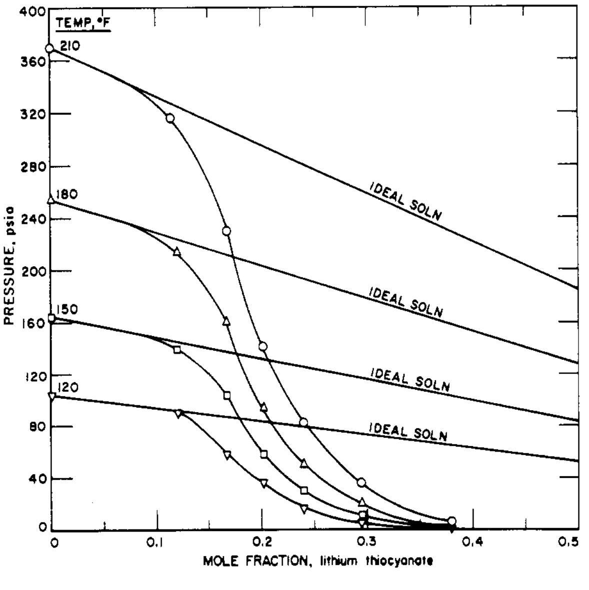

Figure 3. Vapor pressure plot showing extreme negative deviation from Raoult's law

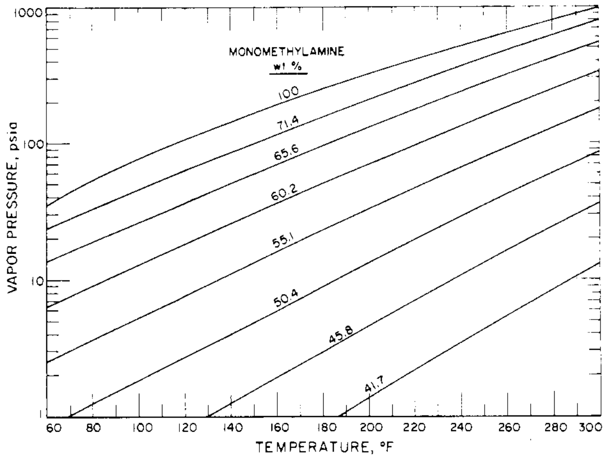

Figure 4. Smoothed vapor pressures for monomethylamine–lithium thiocyanate system

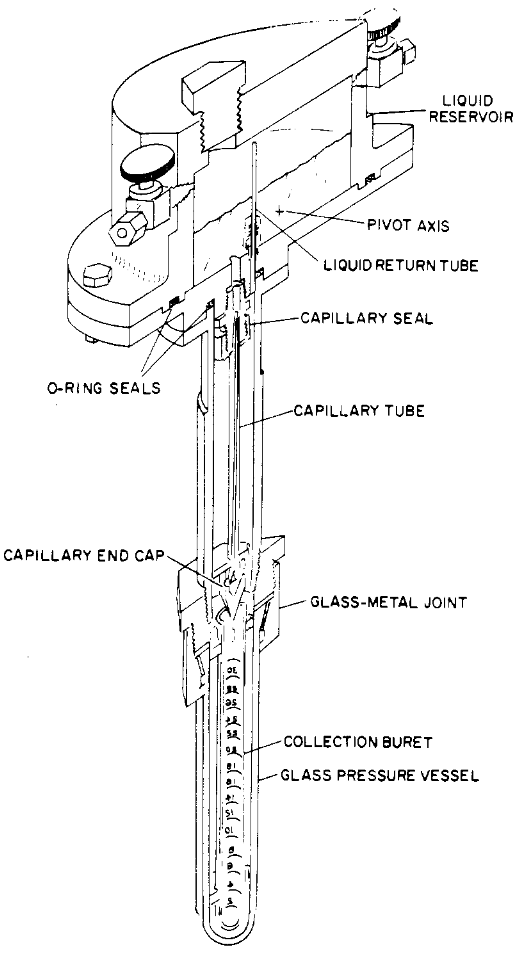

Figure 5. Viscometer assembly

energy required to vaporize 1 lb-mole (31 pounds) of monomethylamine from an infinitely large amount of solution. The units of H_{vap} are Btu/lb-mole of monomethylamine, and X_s represents the mole fraction of thiocyanate salt in the 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 vaporize 1 lb-mole of monomethylamine can be obtained from the expression

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

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

Viscosity. Viscosity was measured in an apparatus suitable for handling methylamine at high temperature and pressure, similar to that reported by Blytas *et al.* (*1*). Viscosity is determined by measuring the time required for a known quantity of solution to flow, under laminar conditions, through a vertical glass capillary of known diameter and length at constant temperature and pressure. The viscosity of the solution is then calculated by use of Poiseuille's formula (2)

$$\mu = \frac{\pi p r^4}{8\, vl} - \frac{m \rho v}{8 \pi\, l} \tag{4}$$

where p is the pressure difference across the capillary, r and l are the capillary radius and length, v is the solution volume rate, solution density, and m is a constant for the viscometer.

The viscometer used in the measurements is shown in Figure 5 and is similar to that used by Blytas *et al.* (*1*), as is the procedure used in carrying out the measurements. All wetted parts of the viscometer were of aluminum or glass. To provide pressure seals, totally confined O-rings of Teflon were utilized. The two glass capillaries used for the measurements have the diameters and lengths shown below.

Capillary I. $r = 1.064 \pm 0.003$ mm $l = 253.5$ mm

Capillary II. $r = 0.661 \pm 0.003$ mm $l = 259.0$ mm

To determine each capillary radius, flow times for two oils of viscosities known to be 5.0 and 9.2 centistokes at 77° F were measured. Several volumes of fluids were used and the capillary radius was calculated employing the known viscosity.

Following the calibration tests, measurements of viscosity were made for five solutions of methylamine and lithium thiocyanate, with the total amount of salt varying between 29.5 and 56.1 weight %, in the region of temperature of approximately 75° to 200° F (Table IV and Figure 6).

With information obtained on the density of these solutions, the kinematic viscosity was converted to absolute viscosity. In this form the data obtained in the range

Table III. Parameters for Clausius-Clapeyron Equation

Composition of Salt, Wt %	H_{vap}/R, °R^{-1}	Constant	Variance
21.1	5143	13.40	0.42×10^{-3}
29.5	5312	13.35	0.52×10^{-3}
34.6	6062	14.03	0.24×10^{-3}
39.9	7227	15.15	0.10×10^{-3}
46.5	7265	14.42	0.12×10^{-2}
51.2	9127	16.09	0.12×10^{-2}

Table IV. Viscosity Data for Monomethylamine–Lithium Thiocyanate Solutions

29.5 Wt % Salt[a]

Temp., ° F	Kinematic viscosity, centistokes
78.5 ± 1.5	3.94
101 ± 0.5	3.42
123.3 ± 0.7	2.90
142.5 ± 0.4	2.51
164.5 ± 0.5	2.31
181.6 ± 0	2.16

34.6 Wt % Salt[b]

Temp., ° F	Kinematic viscosity, centistokes
82.0 ± 1.0	9.9
100.4 ± 0.3	7.4
118.5 ± 0.4	6.3
121.2 ± 0.2	6.5
142.4 ± 0.6	5.05
160.5 ± 0.4	4.65
181.5 ± 0.2	3.80
198.9 ± 0.0	3.45

39.9 Wt % Salt[a]

Temp., ° F	Kinematic viscosity, centistokes
82 . ± 2.5	16.55
109.0 ± 0 .	10.99
129.5 ± 1 .	8.77
152.5 ± 1 .	6.70
169.6 ± 0.1	5.12
186.6 ± 0.1	4.82

46.5 Wt % Salt[c]

Temp., ° F	Kinematic viscosity, centistokes
87.0 ± 1.0	29.4
97.0 ± 1.0	24.5
101.0 ± 1.0	22.0
121.0 ± 1.5	15.9
141.5 ± 1.0	11.7
161.0 ± 0.5	9.1

56.1 Wt % Salt[d]

Temp., ° F	Kinematic viscosity, centistokes
80.5 ± 1.5	138.4
101.0 ± 1.5	88.1
121.2 ± 0.1	62.4
140.0 ± 1.0	44.5

[a] 99.04 wt % lithium thiocyanate + 0.96 wt % water. [b] 99.44 wt % lithium thiocyanate + 0.56 wt % water. [c] 99.75 wt % lithium thiocyanate + 0.25 wt % water. [d] 98.17 wt % lithium thiocyanate + 1.83 wt % water.

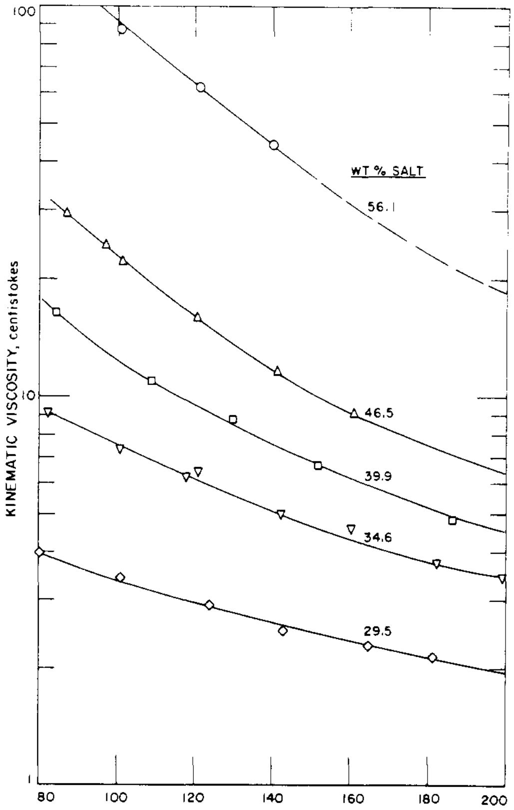

Figure 6. Viscosities of monomethylamine–lithium thiocyanate solutions

of 75° to 200° F were extrapolated to 300° F in a log plot of μ *vs.* $1/T$ (*6*) (Figure 7).

Density. Density measurements on three 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-inch-long, ¼-inch-i.d. lower portion, to which a $\frac{1}{16}$-inch-i.d. and 6-inch-long capillary was attached.

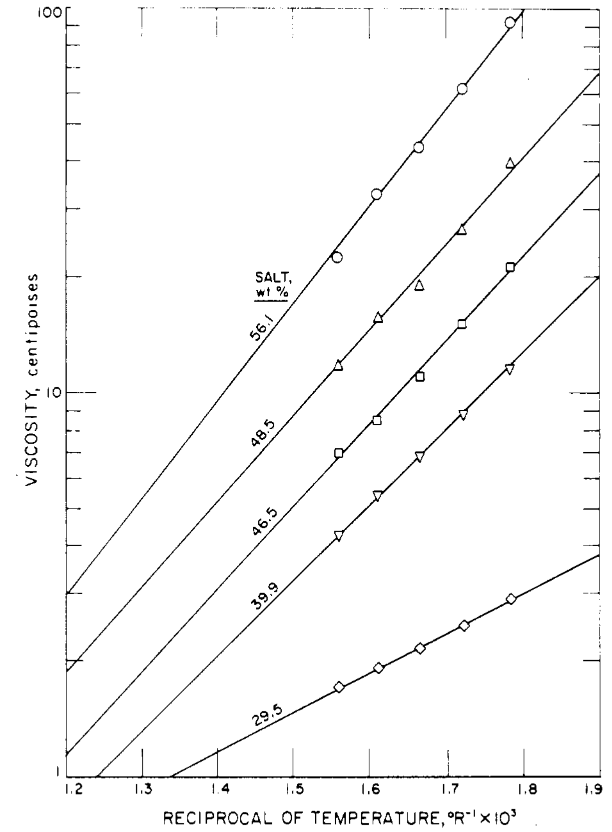

Figure 7. Variation of viscosity with temperature for monomethylamine–lithium thiocyanate solutions

Table V. Density Data for Monomethylamine–Lithium Thiocyanate Solutions

48.5 Wt % Salt[a]		43.6 Wt % Salt[b]		39.9 Wt % Salt[c]	
Temp., °F	Density, g/cc	Temp., °F	Density, g/cc	Temp., °F	Density, g/cc
95.9	0.966	97.1	0.937	86.7	0.928
105.0	0.962	120.4	0.929	115.2	0.921
114.2	0.960	139.0	0.921	138.7	0.905
129.2	0.955	160.4	0.913	155.1	0.903
145.1	0.951	182.7	0.905	174.2	0.896
167.2	0.941	204.3	0.900	189.4	0.891
187.4	0.934	226.3	0.890	214.9	0.881
203.7	0.929	245.1	0.883	...	...
227.0	0.918	...	...	...	...
245.0	0.915	...	...	...	...
268.3	0.906	...	...	...	...

[a] 98.67 wt % lithium thiocyanate + 1.33 wt % water. [b] 98.67 wt % lithium thiocyanate + 1.33 wt % water. [c] 99.04 wt % lithium thiocyanate + 0.96 wt % water.

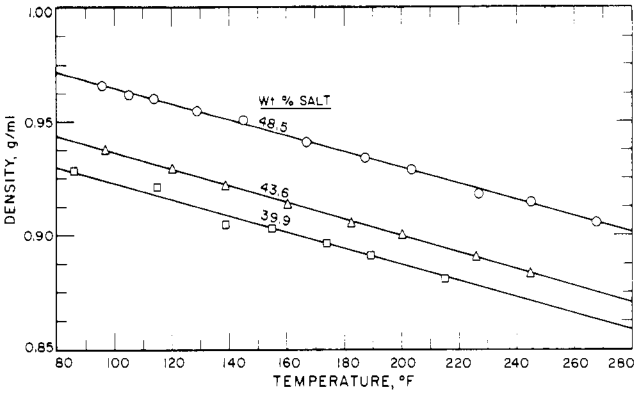

Figure 8. Density data for monomethylamine–lithium thiocyanate solutions

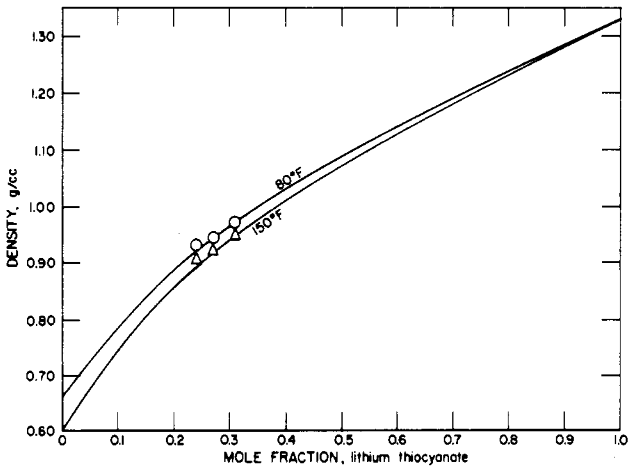

Figure 9. Density-concentration plot for monomethylamine–lithium thiocyanate solutions

The solutions investigated contained 39.9, 43.6, and 48.5 weight % salt. Densities were obtained in the 80° to 280° F temperature range, under the solution vapor pressure at each temperature (Table V and Figure 8).

Density data for the three solutions reported, for pure monomethylamine (*3*), and for pure lithium thiocyanate (1.333 g per cc at 25° C) obtained from the salt supplier were used to obtain densities at two other concentrations—29.5 and 56.1 weight % salt. In the region of about 75° to 185° F, the maximum temperature at which viscosity data were obtained, the density values for these two solutions were obtained by a short interpolation (Figure 9). It does not appear that the error introduced thus could be higher than ±1 to 2% of the density value.

LITERATURE CITED

(1) Blytas, G.C., Ph.D. dissertation, University of Wisconsin, Madison, 1961.
(2) Comings, E.W., "High Pressure Technology," p. 219, McGraw-Hill, New York, 1956.
(3) Felsing, W.A., Thomas, A.R., *Ind. Eng. Chem.* **21**, 1269 (1929).
(4) Lee, D.A., *Inorg. Chem.* **3**, 289–90 (1964).
(5) Macriss, R.A., J. CHEM. ENG. DATA **12**, 28–33 (1967).
(6) Reid, R.C., Sherwood, T.K., "Properties of Gases and Liquids, Their Estimation and Correlation," p. 203, McGraw-Hill, New York, 1958.

RECEIVED for review May 22, 1969. Accepted May 25, 1970. Work done at the Institute of Gas Technology with financial assistance provided by the Alabama Gas Corp., Carrier Corp., Research Division, and Consolidated Natural Gas Service Co., Inc.