

Densities and Viscosities of the Ethanolamines

Ralph M. DiGuillo, Rong-Jwyn Lee, Steven T. Schaeffer, Laura L. Brasher, and Aryn S. Teja*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

This paper reports the densities and viscosities of a series of ethanolamines consisting of monoethanolamine, diethanolamine, triethanolamine, *N,N*-dimethylethanolamine, *N,N*-diethylethanolamine, *N*-methyldiethanolamine, and *N*-ethyldiethanolamine. The densities and viscosities of these ethanolamines were measured up to the normal boiling point of the liquids at atmospheric pressure. The data were correlated using simple expressions and using a modified rough hard sphere model for the viscosity.

1. Introduction

The ethanolamines are an industrially important class of compounds used in the manufacture of cosmetics, pharmaceuticals, surface-active agents, insecticides, and waxes and in the scrubbing of H₂S and CO₂ from refinery streams. Process design using these fluids requires accurate thermophysical properties data. However, few such data have been published in the literature, in spite of the importance of these amines. In this paper, the densities and viscosities of the ethanolamines were measured at temperatures ranging from 298 to 470 K. The results were correlated using simple expressions and were also used to develop a modified rough hard sphere model for the viscosity.

2. Apparatus and Procedure

2.1. Densities. Densities were measured using a high-pressure pycnometer shown schematically in Figure 1. The mass (*M*) of the fluid required to fill a calibrated volume (*V*) in the high-pressure pycnometer was measured and the density obtained from the definition $\rho = M/V$. The pycnometer used in this work is rated up to 580 K and 100 bar and consists of four sample cylinders capped at one end by a high-pressure fitting. The other end of each cylinder was attached through a pipe nipple, an isolation valve, and a quick-connect coupling to a high-pressure hand pump. The pump could be used to pressurize the system in order to suppress boiling, although all measurements were done at atmospheric pressure in the present work. Each stainless steel sampling cylinder had an internal volume of approximately 40 mL. The exact volume of each cell assembly was obtained by calibration with triple-distilled mercury at temperatures up to 423 K. The calibration data were fitted to an appropriate function (either linear or quadratic) for interpolation or extrapolation. Each stainless steel cell was provided with a thermowell into which was inserted a thermocouple (type K) for temperature measurement. Temperature control within ± 0.05 K was achieved by a constant-temperature circulating bath filled with silicone oil.

At the beginning of an experiment, the four density cells were cleaned thoroughly, weighed, and then connected to the system. The density cell assembly was then evacuated, filled with the test liquid, and placed in the oil bath. Usually, 2 h were allowed for temperature equilibrium to be attained. Once equilibrium had been established, the isolation valves were closed and the pycnometers removed from the oil bath and weighed on an electronic balance.

Table I. Comparison of the Density of Water Measured in This Work with the Results of Kell (1)

| <i>T</i> /K | ρ /(kg·m ⁻³) | | |
|-------------|-------------------------------|-------------|--------|
| | this work | Kell (1975) | dev/% |
| 296.04 | 997.31 | 997.564 | -0.025 |
| 309.07 | 993.99 | 993.712 | 0.028 |
| 323.51 | 988.55 | 987.872 | 0.068 |
| 338.30 | 980.79 | 980.473 | 0.032 |
| 353.19 | 972.38 | 971.773 | 0.062 |

The sample temperature was measured using a type K thermocouple which had previously been calibrated against a platinum resistance thermometer (Leeds and Northrup Co., serial no. 709892). The accuracy of the temperature measurement was estimated to be ± 0.1 °C. The system pressure was monitored by a precision pressure gauge (3D Instruments Inc.) rated at 1500 psi with an accuracy of $\pm 0.25\%$ of full scale. The electronic balance (Sartorius Type 1518) used for weight measurement had a precision of ± 0.001 g.

In order to verify the accuracy of the density measurements, the apparatus was used to measure the density of water. The results are listed in Table I along with the values given by Kell (1) for comparison. The results agree within 0.1%.

2.2. Viscosities. Kinematic viscosities (ν) were measured using calibrated Cannon-Ubbelohde capillary viscometers made by International Research Glassware. The equation for the kinematic viscosity is

$$\nu = C_1 t - C_2/t \quad (1)$$

where *t* is the efflux time and *C*₁ and *C*₂ are the viscometer constants. The correction due to kinetic energy, represented by *C*₂/*t* in the above expression, can generally be neglected if an appropriately sized viscometer is used. Thus, measurements of the kinematic viscosity can be obtained directly from the measurements of the efflux times. The viscometers were placed inside thermostated liquid baths in order to keep the temperature constant during the measurement. Two temperature baths, one filled with water and the other with oil, were used in this study. The water bath was used for low-temperature measurements, whereas the oil bath was used at high temperatures (beyond 350 K). The water bath temperature could be held within ± 0.03 K using a Haake recirculation temperature controller (type E3). The oil bath temperature was controlled by a Haake controller (type D3) within ± 0.1 K. Temperature measurement was done by a four-wire platinum resistance thermometer (Yellow Springs Instrument Co.) which had previously been calibrated with a National Bureau of Standards calibrated standard platinum resistance thermometer (Leeds and Northrup Co., serial no. 709892). The accuracy of the temperature measurement was estimated to be ± 0.1 K. An electronic timer accurate to 0.01 s was used to obtain the efflux time. The measured kinematic viscosities were converted to absolute viscosity using the densities measured in this work.

The viscometers used in this work were the same as those in a previously published study by Lee and Teja (2). In the previous work, the accuracy of the kinematic viscosities was estimated to be $\pm 1.5\%$ on the basis of comparisons with reliable data from the literature. As the same experimental apparatus and procedure were used in the present study, the accuracy of the kinematic viscosities measured in the present

Table II. Densities of the Ethanolamines

| substance | T/K | $\rho/(\text{kg}\cdot\text{m}^{-3})$ |
|----------------------------------|-------|--------------------------------------|
| monoethanolamine | 294.4 | 1014.7 |
| | 313.4 | 999.8 |
| | 333.6 | 984.3 |
| | 353.2 | 967.6 |
| | 373.0 | 951.7 |
| | 392.5 | 935.2 |
| | 412.4 | 917.9 |
| diethanolamine | 431.3 | 899.8 |
| | 297.2 | 1094.2 |
| | 313.8 | 1084.4 |
| | 333.7 | 1071.5 |
| | 354.3 | 1057.7 |
| | 374.4 | 1042.5 |
| | 394.7 | 1027.9 |
| triethanolamine | 413.5 | 1013.0 |
| | 432.9 | 998.5 |
| | 295.1 | 1122.2 |
| | 313.1 | 1112.3 |
| | 333.9 | 1100.6 |
| | 354.4 | 1088.7 |
| | 374.4 | 1075.2 |
| <i>N,N</i> -dimethylethanolamine | 395.1 | 1061.1 |
| | 415.4 | 1047.5 |
| | 434.6 | 1035.2 |
| | 299.4 | 883.7 |
| | 308.3 | 874.4 |
| | 323.7 | 861.3 |
| | 337.7 | 848.9 |
| <i>N,N</i> -diethylethanolamine | 352.2 | 835.6 |
| | 367.0 | 821.3 |
| | 382.9 | 806.6 |
| | 397.5 | 791.6 |
| | 296.0 | 880.9 |
| | 313.1 | 866.7 |
| | 332.9 | 848.0 |
| <i>N</i> -methyldiethanolamine | 353.7 | 829.0 |
| | 372.3 | 809.8 |
| | 392.0 | 790.4 |
| | 413.4 | 768.7 |
| | 296.3 | 1037.1 |
| | 327.4 | 1014.3 |
| | 346.3 | 999.6 |
| <i>N</i> -ethyl-diethanolamine | 373.5 | 978.4 |
| | 397.6 | 959.3 |
| | 422.4 | 939.1 |
| | 445.8 | 920.5 |
| | 470.9 | 896.6 |
| | 294.2 | 1013.3 |
| | 322.5 | 992.1 |
| 346.6 | 972.7 | |
| 371.3 | 953.2 | |
| 395.1 | 934.0 | |
| 421.4 | 912.8 | |
| 445.4 | 892.4 | |
| 472.1 | 869.5 | |

work is also estimated to be $\pm 1.5\%$. Taking into account the error in the density, the error in the absolute viscosities is estimated to be $\pm 1.6\%$.

3. Source and Purity of Materials

Monoethanolamine (99+%), diethanolamine (99%), *N*-methyldiethanolamine (99%), *N*-ethyl-diethanolamine (98%), *N,N*-dimethylethanolamine (99%), and *N,N*-diethylethanolamine

Table III. Constants for Equation 2

| substance | a_1 | a_2 | $a_3 \times 10^4$ | AAD/% | MAD/% |
|----------------------------------|--------|-----------|-------------------|-------|-------|
| monoethanolamine | 1181.9 | -0.387 24 | -6.1668 | 0.03 | 0.06 |
| diethanolamine | 1212.0 | -0.178 61 | -7.2922 | 0.03 | 0.05 |
| triethanolamine | 1233.2 | -0.202 36 | -5.8608 | 0.04 | 0.08 |
| <i>N,N</i> -dimethylethanolamine | 1088.1 | -0.502 08 | -6.1169 | 0.04 | 0.09 |
| <i>N,N</i> -diethylethanolamine | 1071.4 | -0.413 88 | -7.7194 | 0.04 | 0.07 |
| <i>N</i> -methyldiethanolamine | 1207.0 | -0.432 65 | -4.7744 | 0.05 | 0.14 |
| <i>N</i> -ethyl-diethanolamine | 1209.4 | -0.578 29 | -2.9971 | 0.02 | 0.04 |

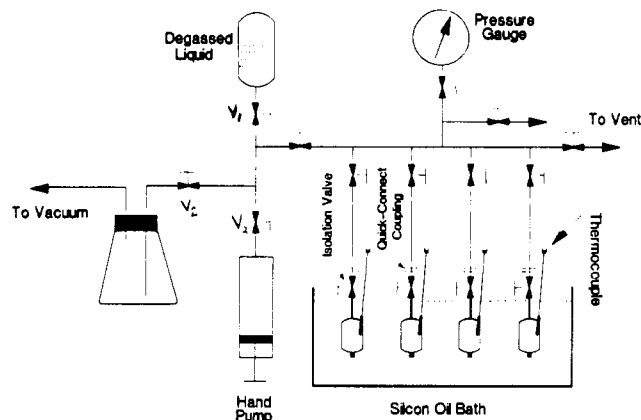


Figure 1. Schematic diagram of the high-pressure pycnometer.

(99%) were obtained from Aldrich Chemical Co. and were used without further purification. Triethanolamine (NF grade) was obtained from Fischer Scientific and was used as received.

4. Results and Discussion

4.1. Density. Table II lists the results of the measurements of the densities (ρ) of the ethanolamines studied in this work. Each set of data was regressed using the polynomial

$$\rho/(\text{kg}\cdot\text{m}^{-3}) = a_1 + a_2(T/\text{K}) + a_3(T/\text{K})^2 \quad (2)$$

The coefficients of eq 2 are given in Table III.

4.2. Viscosity. Table IV lists the results for the absolute viscosities (μ) of the ethanolamines determined from the kinematic viscosities and the densities measured in this work. The data were regressed using the equation

$$\ln [\mu/(\text{mPa}\cdot\text{s})] = b_1 + \frac{b_2}{(T/\text{K}) - b_3} \quad (3)$$

Table V gives the coefficients of eq 3 obtained by regression and also includes the percent deviation between the fitted equations and the experimental data.

The viscosity data were also modeled using a modification of the hard-sphere model of Dymond (3) and Li et al. (4).

In this model, a quantity μ^* is defined by

$$\mu^* = C \frac{(\mu/(\text{mPa}\cdot\text{s})) (V/(\text{m}^3\cdot\text{mol}^{-1}))^{2/3}}{((M/(\text{kg}\cdot\text{mol}^{-1}))R/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}))(T/\text{K})^{1/2}} \quad (4)$$

with

$$C = 6.035 \times 10^5 \text{ mol}^{-1/3}$$

Table IV. Viscosities of the Ethanolamines

| substance | T/K | $\mu/(mPa\cdot s)$ |
|---------------------------------|----------------------------------|--------------------|
| monoethanolamine | 303.6 | 14.86 |
| | 313.4 | 9.89 |
| | 333.4 | 4.99 |
| | 353.4 | 2.90 |
| | 373.4 | 1.85 |
| | 393.5 | 1.268 |
| | 413.6 | 0.918 |
| diethanolamine | 423.7 | 0.796 |
| | 292.9 | 890.5 |
| | 303.8 | 356.0 |
| | 313.2 | 200.9 |
| | 333.1 | 61.22 |
| | 353.1 | 23.40 |
| | 373.2 | 10.53 |
| | 393.1 | 5.67 |
| | 413.2 | 3.38 |
| | 423.2 | 2.70 |
| triethanolamine | 293.5 | 912.4 |
| | 303.5 | 404.2 |
| | 313.5 | 203.4 |
| | 333.5 | 65.50 |
| | 353.6 | 27.28 |
| | 373.5 | 13.61 |
| | 393.5 | 7.70 |
| | 413.7 | 4.80 |
| | 423.7 | 3.89 |
| | <i>N,N</i> -dimethylethanolamine | 294.3 |
| 303.1 | | 2.849 |
| 313.2 | | 2.194 |
| 323.2 | | 1.734 |
| 333.2 | | 1.394 |
| 343.3 | | 1.140 |
| 353.5 | | 0.916 |
| 363.6 | | 0.773 |
| 378.9 | | 0.606 |
| 393.9 | | 0.488 |
| <i>N,N</i> -diethylethanolamine | 295.3 | 4.496 |
| | 303.1 | 3.405 |
| | 313.2 | 2.475 |
| | 323.2 | 1.862 |
| | 338.1 | 1.291 |
| | 353.2 | 0.946 |
| | 374.0 | 0.643 |
| | 394.0 | 0.478 |
| | 414.1 | 0.371 |
| | <i>N</i> -methyldiethanolamine | 293.1 |
| 302.8 | | 57.95 |
| 313.2 | | 34.02 |
| 323.2 | | 21.50 |
| 338.1 | | 11.88 |
| 353.2 | | 7.151 |
| 374.0 | | 3.987 |
| 394.0 | | 2.504 |
| 414.0 | | 1.679 |
| 424.1 | | 1.406 |
| <i>N</i> -ethyldiethanolamine | 292.2 | 92.52 |
| | 303.1 | 47.65 |
| | 313.2 | 28.07 |
| | 323.1 | 17.72 |
| | 338.2 | 9.750 |
| | 353.2 | 5.893 |
| | 374.1 | 3.332 |
| | 394.0 | 2.116 |
| | 414.1 | 1.457 |
| | 424.2 | 1.228 |

where μ is the experimental viscosity, V is the molar volume, M is the molecular weight, and T is the temperature. Dymond (3) showed that for rough hard spheres μ^* is a function of the molar volume and a characteristic volume V_0 :

$$\mu^* = F[V/V_0] \quad (5)$$

In the case of a hard sphere fluid, V_0 is the close-packed volume. In practice, however, V_0 is assumed to be temperature dependent to reflect the fact that real molecules have a

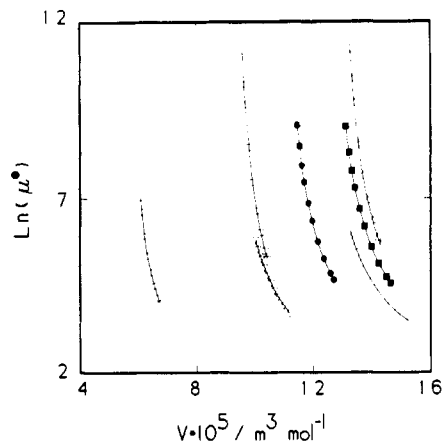


Figure 2. $\ln \mu^*$ vs V for the ethanolamines: O, monoethanolamine; □, diethanolamine; Δ, triethanolamine; ▽, *N,N*-dimethylethanolamine; ◇, *N,N*-diethylethanolamine; ●, *N*-methyldiethanolamine; ■, *N*-ethyldiethanolamine.

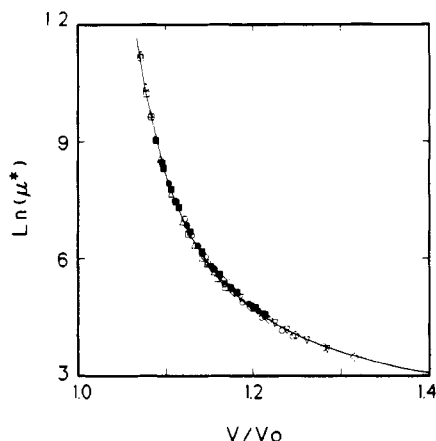


Figure 3. $\ln \mu^*$ vs V/V_0 for the ethanolamines: O, monoethanolamine; □, diethanolamine; Δ, triethanolamine; ▽, *N,N*-dimethylethanolamine; ◇, *N,N*-diethylethanolamine; ●, *N*-methyldiethanolamine; ■, *N*-ethyldiethanolamine. The solid line corresponds to values calculated using eq 6.

soft repulsive potential. A somewhat different approach was adopted in the present work to keep the number of adjustable parameters to a minimum. In our work, V_0 was assumed to be an adjustable constant in the model and advantage was taken of the regularity in the $\ln \mu^*$ vs molar volume relationships shown in Figure 2. When the molar volume of each substance was divided by an appropriate value of V_0 , all the data sets could be reduced to a single curve as shown in Figure 3. It was thus possible to account for the temperature dependence of V_0 indirectly. The curve shown in Figure 3 is given by

$$\ln \mu^* = c_1 + \frac{c_2}{V/V_0 - c_3} \quad (6)$$

where

$$c_1 = 1.48304 \quad c_2 = 0.621357 \quad c_3 = 1.00690$$

Equation 6 may be used to calculate the viscosity of any ethanolamine at a given temperature (and pressure) from knowledge of its molar volume (or density) and a single value of V_0 for the ethanolamine.

The advantage of using this model is the inclusion of the effect of temperature (and possibly pressure) on the viscosity via the molar volume at the given conditions. Figure 4 shows the viscosities of the ethanolamines calculated with the model, and Table VI lists the values of V_0 and gives information about the correlative capabilities of the model. It should be added

Table V. Constants for Viscosity Correlations (Equation 3)

| substance | b_1 | b_2 | b_3 | AAD/% | MAD/% |
|----------------------------------|---------|--------|---------|-------|-------|
| monoethanolamine | -3.9356 | 1010.8 | 151.17 | 0.2 | 0.4 |
| diethanolamine | -5.2380 | 1672.9 | 153.82 | 2.1 | 4.4 |
| triethanolamine | -3.5957 | 1230.3 | 175.35 | 0.2 | 0.5 |
| <i>N,N</i> -dimethylethanolamine | -5.2335 | 1453.6 | 71.773 | 0.5 | 1.3 |
| <i>N,N</i> -diethylethanolamine | -4.2337 | 884.19 | 141.15 | 0.2 | 0.7 |
| <i>N</i> -methyldiethanolamine | -4.3039 | 1266.2 | 151.40 | 0.2 | 0.4 |
| <i>N</i> -ethyl-diethanolamine | -3.9927 | 1090.8 | -164.21 | 0.4 | 0.6 |

Table VI. Constants for Equation 6

| substance | $V_0 \times 10^5 / (\text{m}^3 \cdot \text{mol}^{-1})$ | AAD/% | MAD/% |
|----------------------------------|--|-------|-------|
| monoethanolamine | 5.4059 | 6.5 | 10.5 |
| diethanolamine | 8.9472 | 5.8 | 10.3 |
| triethanolamine | 12.394 | 7.7 | 13.0 |
| <i>N,N</i> -dimethylethanolamine | 8.7229 | 2.3 | 4.3 |
| <i>N,N</i> -diethylethanolamine | 11.606 | 2.5 | 4.8 |
| <i>N</i> -methyldiethanolamine | 10.538 | 5.0 | 6.7 |
| <i>N</i> -ethyl-diethanolamine | 12.054 | 5.9 | 8.2 |

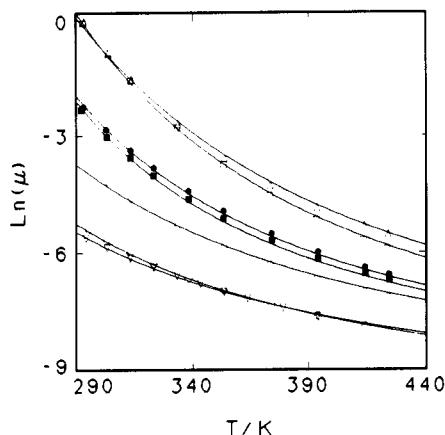


Figure 4. Viscosities of the ethanolamines calculated using the rough hard sphere model: ○, monoethanolamine; □, diethanolamine; △, triethanolamine; ▽, *N,N*-dimethylethanolamine; ◇, *N,N*-diethylethanolamine; ●, *N*-methyldiethanolamine; ■, *N*-ethyl-diethanolamine. The solid lines correspond to the model.

here that the superposition of the viscosity curves means that relative values of V_0 are obtained in our approach. Therefore, V_0 should no longer be considered to be a measure of the close-packed volume. However, it is gratifying to note from

Table VI that the values of V_0 obtained by regression show internal consistency. Thus, the values increase from mono-, to di-, to triethanolamine, and the contributions of the methyl and ethyl groups are about half those of the dimethyl and diethyl groups, respectively.

5. Conclusions

The densities and viscosities of seven ethanolamines were measured at temperatures ranging from 298 to 470 K. A modification of the rough hard sphere model for the viscosity was extended to the ethanolamines by treating the close-packed volume V_0 as an adjustable parameter. The resulting correlation of the data was not as good as the correlation obtained by fitting the data for each of the ethanolamines separately. However, the resulting correlation is simple to use and requires a knowledge only of the molar volume of the ethanolamine and a single value of V_0 for each ethanolamine for the calculation of the viscosity as a function of temperature (and possibly pressure) for that substance.

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Thermal Conductivities of the Ethanolamines

Ralph M. DiGullo, William L. McGregor, and Amyn S. Teja*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

A relative transient hot-wire technique was used to measure the liquid thermal conductivity of seven ethanolamines: monoethanolamine, diethanolamine, triethanolamine, *N,N*-dimethylethanolamine, *N,N*-diethylethanolamine, *N*-methyldiethanolamine, and *N*-ethyl-diethanolamine. Data are reported at temperatures from 298 to 470 K with an estimated accuracy of $\pm 2\%$. The data were correlated with a modified hard sphere model within the accuracy of the measurements.

1. Introduction

The ethanolamines are an industrially important class of compounds. Members of the class are used in the manufacture of cosmetics, surface active agents, pharmaceuticals, plasticizers, corrosion inhibitors, insecticides, herbicides and many other important products. Despite their importance, however, there have been only a few reported studies of properties of the ethanolamines. Our study of these substances included the measurement of the liquid density, liquid viscosity, and liquid thermal conductivity of monoethanolamine, diethanolamine,