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
N,*N*-dimethylethanolamine	-5.2335	1453.6	71.773	0.5	1.3
N,*N*-diethylethanolamine	-4.2337	884.19	141.15	0.2	0.7
N-methyldiethanolamine	-4.3039	1266.2	151.40	0.2	0.4
N-ethyldiethanolamine	-3.9927	1090.8	-164.21	0.4	0.6

Table VI. Constants for Equation 6

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

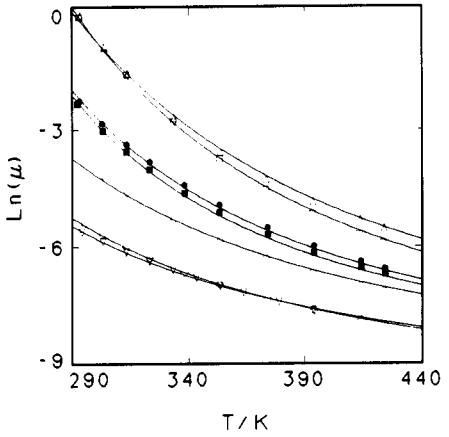

Figure 4. Viscosities of the ethanolamines calculated using the rough hard sphere model: ○, monoethanolamine; □, diethanolamine; △, triethanolamine; ▽, *N*,*N*-dimethylethanolamine; ◇, *N*,*N*-diethylethanolamine; ●, *N*-methyldiethanolamine; ■, *N*-ethyldiethanolamine. The solid lines correspond to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

Literature Cited

(1) Keil, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97-105.
(2) Lee, R. J.; Teja, A. S. *J. Chem. Eng. Data* **1990**, *35*, 385-387.
(3) Dymond, J. H. *Q. Rev. Chem. Soc.* **1985**, *3*, 317-356.
(4) Li, S. F. Y.; Trengove, R. D.; Wakeham, W. A.; Zalef, M. *Int. J. Thermophys.* **1986**, *7*, 273-284.

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Thermal Conductivities of the Ethanolamines

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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*-ethyldiethanolamine. Data are reported at temperatures from 298 to 470 K with an estimated accuracy of ±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,

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triethanolamine, *N*-methyldiethanolamine, *N*-ethyldiethanolamine, *N*,*N*-dimethylethanolamine, and *N*,*N*-diethylethanolamine. In this paper we report results for the thermal conductivity. A companion paper in this issue reports density and viscosity results (*1*).

2. Apparatus and Procedure

The thermal conductivity was measured using a relative transient hot-wire technique. The apparatus and procedure were the same as those reported in a previous study of the thermal conductivity of poly(ethylene glycols) (*2*).

The hot-wire technique consists of a line source of heat immersed in the liquid under study. At the start of the experiment, the line source is made to dissipate heat at a constant rate per unit length for about 2 s. The thermal conductivity of the liquid is determined from the temperature rise obtained. In practice, the line source is approximated by a very fine wire and the thermal conductivity apparatus consists of four parts: a Wheatstone bridge circuit, a data acquisition system, a constant-temperature bath, and a thermal conductivity cell. In the present work, the thermal conductivity cell consisted of a single platinum filament centered in a tubular Pyrex sample container about 0.1 m long. The platinum filament served as a resistor in one arm of the Wheatstone bridge, and the bridge circuit was used to monitor the resistance change of the filament during the measurement. From a previous calibration of the resistance of the wire with temperature, the temperature of the wire could be determined. The thermal conductivity cell was calibrated with dimethyl phthalate to account for heat losses at either end of the filament during a measurement, and corrections were applied to account for the finite physical properties of the wire, the finite extent of the fluid, and any radiation effects. That radiation effects were in fact negligible was confirmed in our previous work (*2*) where our measurements of ethylene, diethylene, and triethylene glycols were compared with the measurements made by Fischer (*3*), who used a concentric cylinder technique and presented results which were corrected for radiation. The present apparatus also avoids problems with polar fluids that others have sometimes encountered. The probable reason is that the platinum wire is centered in a glass cell. Thus, there is no current path from the hot-wire to ground that could interfere with the measurement. The cell does not work with electrolytes however. Complete details of the apparatus are available elsewhere (*2*).

3. Source and Purity of Materials

Ethanolamine (99+%), diethanolamine (99%), *N*-methyldiethanolamine (99%), *N*-ethyldiethanolamine (98%), *N*,*N*-dimethylethanolamine (99%), and *N*,*N*-diethylethanolamine (99%) were purchased from Aldrich Chemical Co. and used without further purification. Triethanolamine (NF grade) was purchased from Fisher Scientific Co. and also used as received.

4. Validation

In order to validate the technique, the thermal conductivity of toluene was measured. Table I lists these results for toluene at ambient pressure as well as the IUPAC (*4*) recommended values. Agreement is within ±1%. On the basis of these comparisons and accounting for the fact that the thermal conductivity of toluene is known only to ±1%, we estimate the accuracy of the present measurements to be ±2%.

5. Results and Discussion

Table II contains the results for the thermal conductivity (λ) of the ethanolamines studied by us. Ambient pressure measurements (see Table II) were done in an air atmosphere. Some measurements (see Table II) were done under pressurized nitrogen to prevent boiling. Each set of data except for the triethanolamine data were fit to a linear function of temperature as follows:

Table I. Thermal Conductivity of Toluene

	$\lambda/(W\cdot m^{-1}\cdot K^{-1})$		
T/K	this work	IUPAC (*3*)	dev/%
298.5	0.1306	0.1310	−0.3
298.9	0.1306	0.1308	−0.2
315.2	0.1259	0.1259	0.0
325.3	0.1232	0.1229	0.2
336.6	0.1192	0.1195	−0.2
353.6	0.1137	0.1144	−0.6
354.7	0.1131	0.1141	−0.9

$$\lambda/(W\cdot m^{-1}\cdot K^{-1}) = a_0 + a_1(T/K) \quad (1)$$

The data for triethanolamine were fit to a quadratic function of temperature because of the curvature exhibited by the data:

$$\lambda/(W\cdot m^{-1}\cdot K^{-1}) = a_0 + a_1(T/K) + a_2(T/K)^2 \quad (2)$$

The curvature is believed to be due to the effect of hydrogen bonding and is typical of highly hydrogen bonded fluids such as water and the poly(ethylene glycols) (*2*). Table III gives all the coefficients for eqs 1 and 2 as well as information regarding the quality of the fit.

The thermal conductivity data were modeled using a variation of the hard sphere model of Li et al. (*5*, *6*). In this model, a characteristic thermal conductivity λ^* is given by

$$\lambda^* = C(\lambda/(W\cdot m^{-1}\cdot K^{-1})) \times (V/(m^3\cdot mol^{-1}))^{2/3}\left(\frac{M/(kg\cdot mol^{-1})}{(R/(J\cdot mol^{-1}\cdot K^{-1}))(T/K)}\right)^{1/2} \quad (3)$$

with

$$C = 1.936 \times 10^7\ K\cdot mol^{2/3}\cdot J^{-1}$$

where λ is the experimental thermal conductivity, V is the molar volume, M is the molecular weight, and T is the temperature. Li et al. (*5*) showed that for rough hard spheres λ^* is a function of the molar volume and a characteristic volume V_0 as follows:

$$\lambda^* = F[V/V_0] \quad (4)$$

In the case of a hard sphere fluid, V_0 is the close-packed volume; in the case of real fluids, it is a function of temperature and reflects the fact that real molecules have soft repulsive interaction potentials. In our work, however, V_0 was treated as an adjustable parameter and advantage was taken of the fact that the λ^* vs V/V_0 relationships for all ethanolamines were similar. Thus, it was possible to eliminate the temperature dependence of V_0 by superimposing the curves of reduced thermal conductivity versus reduced volume for these compounds as described below.

Values of V_0 were determined as follows. λ^* was plotted vs the molar volume for ethanolamine. When the molar volume of each substance was divided by an appropriate value of V_0, all the data sets could be aligned on a single curve as shown in Figure 1. Thus, the thermal conductivities of each substance

Table II. Thermal Conductivities of the Ethanolamines

substance	T/K	λ/ (W·m⁻¹·K⁻¹)	$a_2 \times 10^7$
monoethanolamine	297.8	0.2399	1
	328.1	0.2357	1
	356.3	0.2329	1
	382.0	0.2280	1
	297.9	0.2401	14
	352.8	0.2334	14
	383.3	0.2298	14
	411.3	0.2262	14
	430.4	0.2242	14
	447.1	0.2204	14
N,*N*-dimethylethanolamine	297.6	0.1357	14
	298.2	0.1346	14
	324.5	0.1302	14
	329.5	0.1305	14
	353.6	0.1263	14
	356.1	0.1266	14
	378.9	0.1226	14
	388.9	0.1219	14
	412.1	0.1165	14
	425.1	0.1156	14
	464.5	0.1074	14
N,*N*-diethylethanolamine	297.5	0.1400	14
	325.8	0.1330	14
	354.1	0.1281	14
	383.5	0.1214	14
	412.6	0.1150	14
	443.0	0.1088	14
diethanolamine	295.8	0.2171	1
	325.4	0.2159	1
	354.8	0.2137	1
	383.3	0.2126	1
	412.5	0.2115	1
	442.1	0.2080	1
N-methyldiethanolamine	297.7	0.1685	1
	325.0	0.1676	1
	353.9	0.1663	1
	381.1	0.1653	1
	410.9	0.1636	1
	440.2	0.1613	1
N-ethyldiethanolamine	297.1	0.1666	1
	300.8	0.1655	1
	333.5	0.1628	1
	365.8	0.1597	1
	394.8	0.1570	1
	430.1	0.1536	1
	463.8	0.1489	1
triethanolamine	296.8	0.1884	1
	327.3	0.1941	1
	356.3	0.1956	1
	383.9	0.1983	1
	411.6	0.2000	1
	440.2	0.2005	1
	466.2	0.2003	1

could be represented by a single parameter V_0 and the curve in Figure 1 which is given by

$$\lambda^* = b_0 + b_1(V/V_0) + b_2(V/V_0)^2 \qquad (5)$$

with

$$b_0 = 149.509 \qquad b_1 = -118.165 \qquad b_2 = 27.1010$$

It should be added here that, by superimposing the curves as described above, relative values of V_0 are obtained. Hence, V_0 should not be interpreted as a close-packed volume in eq

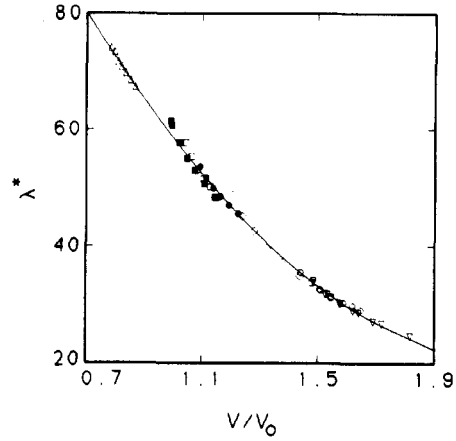

Figure 1. λ^* vs V/V_0 for the ethanolamines: ○, monoethanolamine; □, diethanolamine; △, triethanolamine, ▽, *N*,*N*-dimethylethanolamine; ◇, *N*,*N*-diethylethanolamine; ●, methyldiethanolamine; ■, *N*-ethyldiethanolamine. The solid line corresponds to the fit (eq 5).

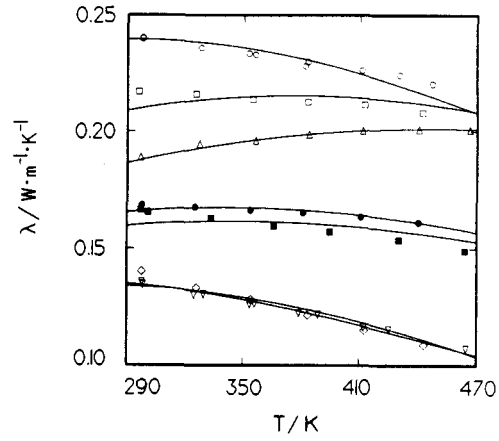

Figure 2. Thermal conductivities of the ethanolamines calculated using the rough hard sphere model: ○, monoethanolamine; □, diethanolamine; △, triethanolamine; ▽, *N*,*N*-dimethylethanolamine; ◇, *N*,*N*-diethylethanolamine; ●, *N*-methyldiethanolamine; ■, *N*-ethyldiethanolamine. The solid lines correspond to the model.

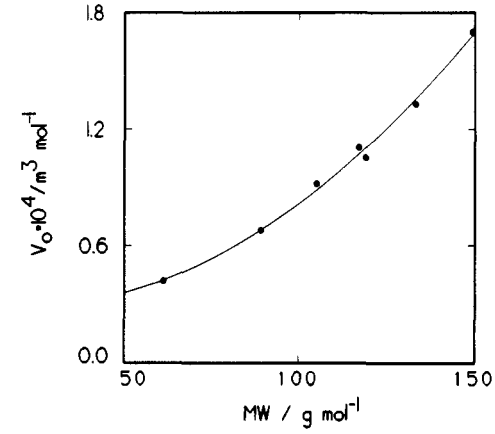

Figure 3. V_0 vs molecular weight for the ethanolamines. The solid line corresponds to the fit (eq 6).

Table III. Constants for Equations 1 and 2

substance	a_0	$a_1 \times 10^4$	$a_2 \times 10^7$	AAD/%	MAD/%
monoethanolamine	0.277 19	−1.250 9		0.2	0.6
diethanolamine	0.234 90	−0.589 52		0.2	0.4
triethanolamine	0.096 596	4.659 6	−5.2255	0.2	0.5
N,*N*-dimethylethanolamine	0.183 47	−1.613 5		0.5	1.0
N,*N*-diethylethanolamine	0.203 07	−2.130 5		0.2	0.5
N-methyldiethanolamine	0.183 68	−0.495 76		0.2	0.4
N-ethyldiethanolamine	0.196 22	−1.003 2		0.2	0.5

Table IV. Constants for Equation 5

substance	$V_0 \times 10^4$/ ($m^3 \cdot mol^{-1}$)	AAD/%	MAD/%
monoethanolamine	0.41851	1.0	2.5
diethanolamine	0.91917	1.6	3.4
triethanolamine	1.6996	0.4	0.8
N,*N*-dimethylethanolamine	0.67864	0.8	1.9
N,*N*-diethylethanolamine	1.1055	2.1	4.5
N-methyldiethanolamine	1.0534	0.6	1.4
N-ethyldiethanolamine	1.3286	2.4	3.8

5. Furthermore, the relative values of V_0 will not necessarily be the same as those obtained in our earlier work on the viscosity of the ethanolamines (*1*).

Figure 2 shows the thermal conductivities of the ethanolamines as calculated from the model. Table IV lists the values of V_0 as well as showing that the model represents the data within the experimental accuracy of ±2%. The original rough hard sphere model has been shown (*5*, *6*) to incorporate the effect of pressure on the thermal conductivity through its effect on the molar volume. This may also be true of the model presented here, but this has not been proven.

An attempt was also made to correlate V_0 for the ethanolamines with other readily available properties. In our case V_0 was found to vary smoothly with the molecular weight of the ethanolamine as shown in Figure 3. Furthermore, the following relationship between V_0 and the molecular weight (MW) was obtained by regression:

$$V_0 = c_0 + c_1(\mathrm{MW}/(\mathrm{kg \cdot mol^{-1}})) + c_2(\mathrm{MW}/(\mathrm{kg \cdot mol^{-1}}))^2 \quad (6)$$

with

$$c_0 = 3.2554 \times 10^{-5} \qquad c_1 = -3.5928 \times 10^{-10}$$

$$c_2 = 8.5999 \times 10^{-15}$$

The average absolute deviation (AAD) for the fit was 2.2%, and the maximum absolute deviation (MAD) was 4.8%. Table V gives the deviation between the calculated thermal conductivities using eq 6 for finding V_0 and the experimental data. Although the predictions are not as good as before, the data are reproduced with an average deviation of 3%. The advantage of using eq 6 is the ability to predict the thermal conductivity of other ethanolamines for which no data have been reported.

Table V. Performance of Equation 6

substance	AAD/%	MAD/%
monoethanolamine	1.9	3.2
diethanolamine	4.2	7.3
triethanolamine	0.9	1.7
N,*N*-dimethylethanolamine	0.9	1.6
N,*N*-diethylethanolamine	4.3	8.5
N-methyldiethanolamine	6.2	7.0
N-ethyldiethanolamine	3.3	5.8

6. Conclusions

The thermal conductivities of seven ethanolamines have been measured at temperatures ranging from 298 to 470 K with an estimated accuracy of ±2%. A modified rough hard sphere model was developed for the ethanolamines by treating the close-packed volume V_0 as an adjustable parameter. The model incorporates the effect of temperature, and possibly the pressure, on the thermal conductivity. The model parameter V_0 was found to vary smoothly with the molecular weight of the ethanolamine, thus making it possible to predict the thermal conductivity from a knowledge of only the molecular weight and the molar volume of the ethanolamine.

Literature Cited

(1) DiGuilio, R. M.; Lee, R. J.; Schaeffer, S. T.; Brasher, L. L.; Teja, A. S. *J. Chem. Eng. Data*, companion paper in this issue.
(2) DiGuilio, R. M.; Teja, A. S. *J. Chem. Eng. Data* **1990**, *35*, 117–121.
(3) Fischer, S. *Warme-und Stoffubertertragung* **1986**, *20*, 183–187.
(4) Marsh, K. N., Ed. *Recommended Reference Materials for the Realization of Physicochemical Properties*; Blackwell Scientific Publications: Boston, 1987.
(5) Li, S. F. Y.; Maitland, G. C.; Wakeham, W. A. *High Temp.—High Pressures* **1985**, *17*, 241–251.
(6) Li, S. F. Y.; Trengove, R. D.; Wakeham, W. A.; Zalaf, M. *Int. J. Thermophys.* **1986**, *7*, 273–284.

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