Viscosity-Temperature Correlation for Liquid Aliphatic Amines

J. K. SHAH, K. J. DE WITT, and C. E. STOOPS
The University of Toledo, Toledo, Ohio 43606

Viscosities of 24 liquid aliphatic amines were experimentally determined in the temperature range from 5° C. to 150° C., wherever it was possible without exceeding the normal boiling point. These amines were divided into five groups, viz., mono-*n*-amines, di-*n*-amines, tri-*n*-amines, iso-amines, and di-iso-amines. Viscosities were correlated by an empirical equation of the type

$$\log_e \eta = B[(1/T) - X] + Y$$

where X and Y are constants for each group and B is related to the number of carbon atoms in the liquid molecule in the following way.

$$B = y_1 + y_2 Z + y_3 Z^2 + y_4 Z^3 + y_5 Z^4$$

In this equation, Z is the square root of the number of carbon atoms in the liquid molecule, and y_1 through y_5 are constants.

THERE presently exist numerous models and theories for the temperature-dependence of liquid viscosity at constant pressure. Because no single theory of liquid transport has yet proven universally applicable, empirically developed relationships still serve as practical aids. The present survey has revealed that viscosity data for most of the liquid aliphatic amines at varying temperatures are lacking and that no general viscosity-temperature correlation for these amines is available.

Andrade (*1*) has developed a simple equation for the viscosity-temperature correlation of nonassociated liquids:

$$\eta = A\,e^{B/T} \tag{1}$$

Many other correlations which have appeared (*3, 4, 5*) are mainly modifications of this basic equation. The present work attempts to develop an empirical model for the viscosity of liquid amines as a function of temperature and the number of carbon atoms in the liquid molecule. This model is also a modification of Andrade's basic equation.

EXPERIMENTAL

The viscosity values of the amines were measured experimentally (*6*), using two types of viscometers. A Contraves (Contraves Co., Zurich, Switzerland) viscometer with a special attachment was used for the measurement of viscosities in the range from 0.5 to 20 centipoise. This is a rotating cylinder type of absolute viscometer with a very narrow gap between two concentric cylinders. It was thoroughly cleaned with acetone and dried before each measurement. The other viscometer, used for viscosities lower than 0.5 centipoise, was of the Cannon-Fenske type. It was calibrated for the two-constant equation (*2*),

$$\eta = D\rho t - E\rho/t \tag{2}$$

using the Cannon Instrument Co.'s calibrating liquid, N-4. The calibration was checked by four amines whose viscosity had already been determined by the Contraves viscometer. The density values which were needed for the Cannon-Fenske viscometer were determined at different temperatures by using a modified pycnometer. A Type T9 Tamson circulation bath was used to control the temperature within 0.25° C. for all viscosity and density measurements. The time of flow of the liquid in the Cannon-Fenske instrument was determined using an electric timer.

At each temperature, a set of five scale readings was taken when using the Contraves viscometer, or a set of five time readings when using the Cannon-Fenske viscometer. The maximum difference in the viscosity values determined from these readings at each temperature was 0.1% in all cases. The viscosity values tabulated in Table I represent an average value of the five determined viscosity values at the temperatures indicated.

MATERIALS

All of the 24 amines studied in this investigation were obtained from the Fischer Scientific Co. and were of commercial grade purity. No attempt was made to further refine these amines.

DISCUSSION

The experimental data presented in Table I were used to ascertain the applicability of Andrade's equation,

$$\eta = Ae^{B/T}$$

to represent the variation of viscosity with temperature. In this equation, η is the viscosity, T is the absolute temperature, and A and B are constants. Plots of $\log_e \eta$ *vs.* $1/T$ were made for all of the amines and yielded linear relationships in all cases except for tri-*n*-hexyl, tri-*n*-heptyl, and tri-*n*-octyl amines, where a slight curvature occurred at the higher viscosity values. These linear relationships emerged from a common point (X, Y) for the following groups of liquids: mono-*n*, di-*n*, tri-*n*, iso, and di-iso-amines.

The straight lines obtained were represented by the function

$$\log_e \eta - Y = B\,[(1/T) - X] \tag{3}$$

where X and Y are the coordinates of the common point for the group and B is the slope of the line for an individual liquid of the group. A range of X, Y, and B values was initially determined from the plots and these values were then optimized by a computer search technique for the minimum standard deviation from the experimental results. The final values of X and Y for each group are tabulated in the first two rows of Table II.

Table I. Viscosity of Liquid Aliphatic Amines, Centipoise

Liquid Amine	Temperature, ° C. 5	10	15	20	25	30	35	40	45	50
n-Propyl		0.464		0.405		0.350		0.311		
n-Butyl	0.769		0.648		0.578		0.511		0.449	
n-Pentyl	0.915		0.823		0.718		0.622		0.535	
n-Hexyl	1.240		1.056		0.905		0.805		0.691	
n-Heptyl			1.583		1.317		1.102		0.929	
n-Octyl	2.313		1.802		1.474		1.232		1.036	
Di-*n*-ethyl		0.386		0.338		0.299		0.268		0.236
Di-*n*-propyl	0.693		0.613		0.525	0.490	0.453	0.435		
Di-*n*-butyl	1.279		1.133		0.946		0.793		0.676	
Di-*n*-pentyl	2.256		1.774		1.438		1.189		1.006	
Di-*n*-heptyl					3.106		2.434		1.995	
Tri-*n*-ethyl		0.419		0.374		0.336		0.304		0.277
Tri-*n*-propyl	0.835		0.718		0.627		0.538		0.471	
Tri-*n*-butyl	2.004		1.600		1.313		1.104		0.941	
Tri-*n*-pentyl	4.231		3.119		2.416		1.941		1.583	
Tri-*n*-hexyl		6.066			3.911			2.775		
Tri-*n*-heptyl	12.486		8.782		6.035		4.569		3.570	
Tri-*n*-octyl	19.610		13.253		9.325		7.067		4.950	
Iso-propyl		0.386		0.344		0.302				
Iso-butyl	0.746	0.690	0.644	0.609	0.569			0.436		0.379
Iso-pentyl	0.908		0.780		0.666		0.572		0.514	
Di-iso-propyl		0.473		0.415				0.333		
Di-iso-butyl	1.009		0.849		0.726		0.630		0.542	
Di-iso-pentyl	1.953		1.572		1.285		1.093		0.933	

	Temperature, ° C. 55	60	65	70	75	80	85	100	125	150
n-Propyl										
n-Butyl		0.360								
n-Pentyl	0.461			0.369		0.333				
n-Hexyl	0.600		0.519		0.456		0.380	0.326		
n-Heptyl	0.803		0.692			0.559		0.437	0.325	
n-Octyl	0.887		0.778		0.673			0.459	0.362	0.292
Di-*n*-ethyl										
Di-*n*-propyl		0.336				0.278				
Di-*n*-butyl	0.583		0.509			0.421		0.354	0.281	0.232
Di-*n*-pentyl	0.855		0.747		0.648			0.487	0.383	0.310
Di-*n*-heptyl	1.650		1.399		1.200			0.883	0.637	0.498
Tri-*n*-ethyl						0.214				
Tri-*n*-propyl	0.421					0.351		0.294	0.239	0.198
Tri-*n*-butyl	0.818		0.705		0.621			0.469	0.369	0.297
Tri-*n*-pentyl	1.330		1.125		0.975			0.709	0.521	0.381
Tri-*n*-hexyl		1.844				1.322		0.994	0.740	0.562
Tri-*n*-heptyl	2.848		2.322		1.934			1.349	0.965	0.729
Tri-*n*-octyl	3.898		3.129		2.569			1.713	1.196	0.887
Iso-propyl										
Iso-butyl		0.387								
Iso-pentyl	0.452			0.398		0.350				
Di-iso-propyl		0.273				0.227				
Di-iso-butyl	0.474					0.365		0.309	0.245	
Di-iso-pentyl	0.789		0.681			0.564		0.450	0.354	0.287

Table II. Values of Constants in the Correlation

Constant	Mono-*n*	Di-*n*	Tri-*n*	Iso[a]	Di-iso[a]
X	0.000095	0.00018	0.00113	0.00007	0.00082
Y	−4.96	−4.75	−3.16	−4.46	−3.62
y_1	−45503.1	10111.7	11292.3	−2379.9	−165.5
y_2	83318.2	−13600.6	−12362.3	3135.2	378.5
y_3	−55376.7	7359.6	5175.5	−679.1	49.3
y_4	16261.3	−1687.2	−895.4	. . .	. . .
y_5	−1772.7	142.7	56.8	. . .	. . .

[a] Second degree fit is given for these substances.

An attempt was made to correlate the values of B with physical properties like the boiling point, molecular weight, number of carbon atoms in a molecule, etc. The square root of the number of carbon atoms in a molecule, Z, gave a reasonably good correlation. The equation

$$B = y_1 + y_2Z + y_3Z^2 + y_4Z^3 + y_5Z^4 \tag{4}$$

is a fourth degree least-squares fit for B in terms of Z. Because of the fewer iso and di-iso substances, a second degree fit was used for these two groups. The constants y_1, y_2, y_3, y_4, and y_5 are tabulated for each group of amines in the third to seventh rows of Table II. Equations 3 and 4 were able to reproduce the 204 experimental viscosity values with a standard deviation of 2.36%.

NOMENCLATURE

A = constant in Equation 1
B = constant in Equation 1; group parameter in Equation 3
D = constant in Equation 2
E = constant in Equation 2
T = absolute temperature, °K.
t = time, sec.
X, Y = group parameters in Equation 3
y_1, y_2, y_3, y_4, y_5 = constants in Equation 4
Z = square root of number of carbon atoms in the liquid molecule

Greek Letters

η = viscosity, cp.
ρ = density, g./cm.^{3}

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Thermodynamic Functions for Halogenated Benzenes

J. B. BUTLER[1] and J. LIELMEZS
Chemical Engineering Department, The University of British Columbia, Vancouver 8, B. C., Canada

Thermodynamic functions (heat capacity, enthalpy, entropy, and free energy) are calculated for 38 halogenated benzenes in the ideal gas state from 298.15° to 1000° K. at 1 atm. of pressure. All the functions were obtained by statistical mechanical means. Agreement with experimental results, where such are available, is satisfactory.

THE RECENT availability of molecular structural and spectroscopic data has enabled the calculation of thermodynamic functions—heat capacity, enthalpy, entropy, and free energy—for 38 halogenated benzenes in the ideal gas state at 1 atm. of pressure. The functions for each given halogenated benzene group, including mono- to hexahalobenzenes and some unsymmetrical dihalobenzenes, were calculated by statistical-mechanical methods, using a digital computer program. The accuracy and scope of this work is bound by its purpose, to present a set of calculated thermodynamic function tables for use in chemical engineering problems.

DISCUSSION

Monohalobenzenes. (Table I, more data deposited with ASIS as Table I.). To calculate the thermodynamic functions for fluorobenzene, the data of Scott and coworkers (*37*), Smith and coworkers (*40*), and the microwave structural data of Bak *et al.* (*2*) were used. The anharmonicity corrections of McCullough *et al.* (*24*) were also employed in this calculation, using the same constants as Scott *et al.* (*37*), with similar results.

The thermodynamic functions for chloro-, bromo-, and iodobenzene were calculated using the data of Whiffen (*48*). The principal moments of inertia were taken from the microwave measurements of Rosenthal and Dailey (*32*),

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[1] Present address: HMCS Yukon, FMO Victoria, B. C., Canada.