Viscosity of Ortho-Substituted Aromatic Amines

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Viscosity measurements were carried out on eight ortho-substituted aromatic amines at 293, 298, 303, 308, 310, 313, 318, 323, and 372 K temperatures. The activation enthalpy of viscous flow was determined. The viscosity in the 293–373 K range can be calculated within an error of 6% from the average activation enthalpy of related compounds (alkylated derivatives).

No viscosity data can be found in the literature relating to ortho-substituted aromatic amines which are liquids at ambient temperature, expect for aniline and *o*-toluidine. The empirical or semiempirical correlations proposed for the calculation of viscosity proved useless for our purposes. This is so partly because there is no nitrogen increment published for Thomas' method (*1*), and the effects of substituents are also unknown. The viscosity of aromatic amines which form associates via hydrogen bonds can be calculated only with large error with Souders' method (*2*).

The ortho 2,6-disubstituted aromatic amines are indispensable intermediates in the pesticide chemistry.

Therefore, the knowledge of their viscosity and the temperature dependence of their viscosity is a must.

Experimental Section

The purity and density data of the aromatic amines tested, aniline (A), *o*-toluidine (OT), 2-ethylaniline (OEA), 2,6-dimethylaniline (DMA), 2-methyl-6-ethylaniline (MEA), 2,6-diethylaniline (DEA), 2-chloroaniline (KA), and 2-chloro-6-methylaniline (KMA), are listed in Table I.

The dynamical viscosity of the above aromatic amines was determined by a Type BH Hoeppler viscosimeter.

The time of fall of the ball between the two extreme works was determined with a digital timer accurate to 0.1 s which gave an error in the measurement of viscosities of ±0.1%. Temperature control using a calibrated thermometer was better than ±0.1 K. Viscosities were determined in the 293–372 K range, at nine temperature settings.

The densities of the aromatic amines were measured by pycnometry taking into account volume changes of the pycnometer at the higher temperatures. Thus the error is about ±0.001 g/cm^3.

Results and Discussion

Measured viscosity values are listed in Table II.

The activation enthalpy of viscous flow reads as

$$H^{\ddagger} = -RT^2(\mathrm{d} \ln \eta/\mathrm{d}T)p \quad (1)$$

After integration and rearrangement

$$\eta = A \exp(\Delta H/RT) \quad (2)$$

After linearization

$$\ln \eta = \ln A + \Delta H/RT \quad (3)$$

It can be seen from eq 3 that a linear relationship exists between the logarithm of dynamical viscosity and the reciprocal absolute temperature. This notion is sustantiated by the measured data (cf. Figure 1). The measured values fit a straight line. The coefficients of this straight line can be obtained by regression analysis (cf. Table III).

Table I. Purity and Density of Aromatic Amines Tested

	purity w/w	density × 10^{-3}, kg m^{-3}
A	99	1.022
OT	>98	1.0053
OEA	>99	0.988
DMA	~97	0.98
MEA	~98	0.968
DEA	~98	0.958
KA	>98	1.22
DMA	97–98	1.526

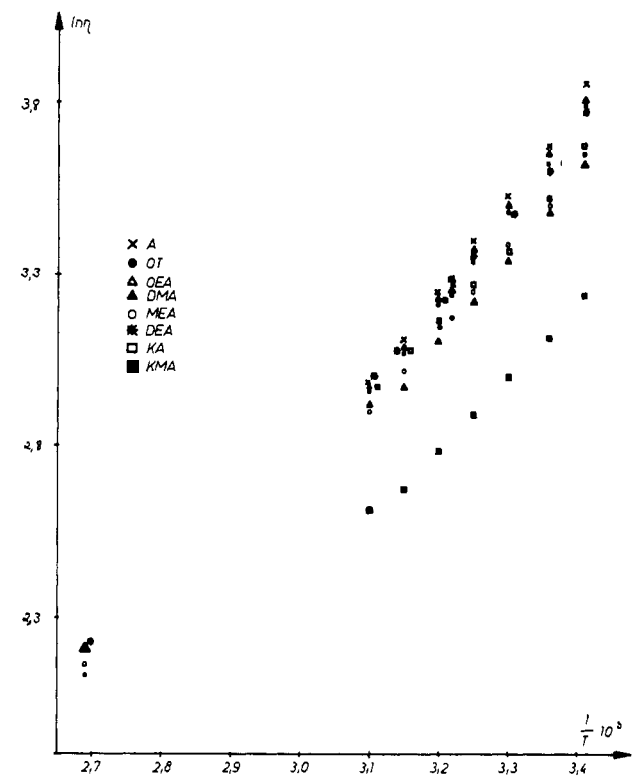

Figure 1. Temperature dependence of the viscosity of aromatic amines.

$$Y = B_0 + B_1X \quad (4)$$

It can be seen in both Figure 1 and Table III that the viscous of aromatic amines at constant temperature—except those of the chloro derivatives—are very similar. Therefore, the viscosities of the alkylated derivatives can be averaged. The coefficients of eq 4 can be also determined from the averaged data. Those values yield the intercept and the activation enthalpy of viscous flow (cf. Figure 2).

$$\ln A = -3.5796$$

$$\Delta H^{\ddagger} = 17.705 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

Thus, the viscosity of ortho-substituted alkylated aromatic amines can be calculated by the equation

$$\eta = 2.789 \times 10^{-2} \exp(17705/RT) \quad (5)$$

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Table II. Viscosity of Aromatic Amines

	dynamical viscosity, mPa·s								
	293 K	298 K	303 K	308 K	311 K	313 K	318 K	323 K	372 K
A	47.08	39.95	34.20	30.00	26.30	25.97	22.55	20.00	9.1
OT	44.50	37.25	32.55	28.20	25.60	24.85	21.50	19.40	8.9
OEA	45.00	38.50	33.25	29.15	25.90	25.24	21.80	19.50	9.1
DMA	37.40	32.60	28.32	25.00		22.26	19.50	18.57	
MEA	38.70	33.50	29.50	26.00	23.90	23.52	20.45	18.20	8.7
DEA	43.70	36.50	32.45	28.50	26.80	25.45	22.00	20.00	9.3
KA	39.44	34.00	29.31	26.26		23.68	21.50	19.56	
KMA	25.60	22.63	20.14	17.99		16.14	14.50	13.65	

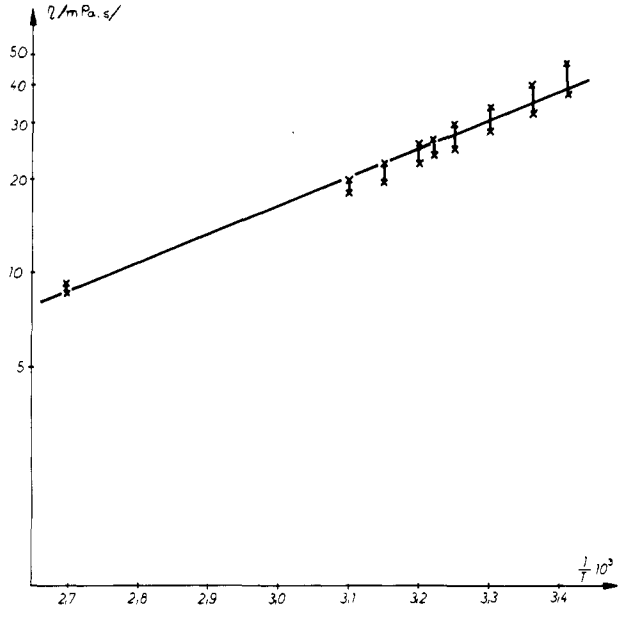

Figure 2. Average viscosity of alkylated aromatic amines.

Table III. Coefficients of the Linear Regression Model and the Activation Enthalpy of Viscous Flow Calculated from Coefficients

	B_0	B_1	H,[a] kJ mol^{-1}	R[b]	N[c]
A	−3.8974	2246.72	18.685	0.994	9
OT	−3.7751	2194.39	18.250	0.944	9
OEA	−3.7683	2198.07	18.281	0.993	9
DMA	−4.1801	2282.23	18.981	0.997	7
MEA	−3.3969	2051.69	17.063	0.997	9
DEA	−3.4827	2107.30	17.526	0.996	9
KA	−3.8292	2192.42	18.225	0.997	7
DMA	−3.6954	2030.27	16.885	0.998	7

[a] H = enthalpy of viscous flow. [b] R = regression factor. [c] N = number of experimental points.

The average relative error of the viscosities of the aromatic amines tested, calculated by eq 5, is 5.96%.

Literature Cited

(1) Thomas, L. H. J. Chem. Soc. 1946, 573.
(2) Souders, M. J. Am. Chem. Soc. 1938, 60, 154.

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Thermodynamic Properties of Solutions Containing an Aliphatic Amine. 1. Excess Volumes of Binary Systems of Triethylamine with Benzene, Toluene, Ethylbenzene, and Isomeric Xylenes at 313.15 K

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Excess volumes, V^E, of binary mixtures of triethylamine with benzene, toluene, ethylbenzene, and three isomeric xylenes at 313.15 K have been computed from the experimental density data. V^E decreases when an alkyl group is added to the benzene ring. For isomeric xylenes, it follows the order *m*-xylene > *o*-xylene > *p*-xylene.

Introduction

As a part of our investigations on the thermodynamics of binary mixtures (*1–3*), we considered it worthwhile to study in detail the dependence of each thermodynamic property of the binary mixture of representative aliphatic amines on the nature

Table I. Physical Properties of Liquids Used

	density at 313.15 K		refractive index (298.15 K)	
solvent	our value	lit. value (*6*)	our value	lit. value (*6*)
triethylamine	0.709 59	0.7092[a]	1.3980	1.398 0[b]
benzene	0.857 63	0.8576	1.4980	1.497 92
toluene	0.847 25	0.8482	1.4940	1.494 13
ethylbenzene	0.849 40	0.8494	1.4932	1.493 20
o-xylene	0.862 83	0.8633	1.5028	1.502 95
m-xylene	0.847 15	0.8471	1.4946	1.494 64
p-xylene	0.843 83	0.8436	1.4932	1.493 25

[a] Calculated from the modified Rackett equation (*8*) with $Z_{RA} = 0.26992$ adjusted to the density value at 298.15 from ref *6*. [b] Reference *7*.

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