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	

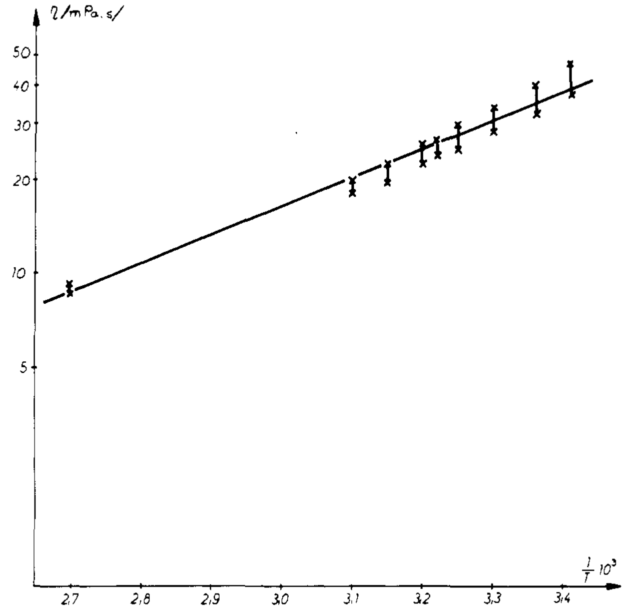

Figure 2. Average viscosity of alkylated aromatic amines.

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*.

Table II. Excess Volumes of Mixing, V^E ($cm^3 \cdot mol^{-1}$), for the Binary Mixtures at 313.15 K

triethylamine (1) + benzene (2)	x_1	0.1381	0.2165	0.2990	0.3922	0.4472	0.5751	0.7156	0.8497
	V^E	0.024	0.027	0.043	0.038	0.024	0.011	−0.001	−0.006
triethylamine (1) + toluene (2)	x_1	0.2225	0.3394	0.4334	0.6427	0.7575	0.8702		
	V^E	−0.245	−0.349	−0.372	−0.395	−0.363	−0.280		
triethylamine (1) + ethylbenzene (2)	x_1	0.1837	0.3725	0.4691	0.5685	0.6728	0.7795	0.8868	
	V^E	−0.264	−0.393	−0.400	−0.388	−0.345	−0.276	−0.195	
triethylamine (1) + *o*-xylene (2)	x_1	0.2217	0.2730	0.3635	0.4073	0.6600	0.7760	0.8402	
	V^E	−0.336	−0.374	−0.427	−0.446	−0.444	−0.360	−0.308	
triethylamine (1) + *m*-xylene (2)	x_1	0.0908	0.1843	0.2772	0.3767	0.4672	0.5717	0.7780	0.8879
	V^E	−0.116	−0.189	−0.257	−0.281	−0.283	−0.281	−0.190	−0.103
triethylamine (1) + *p*-xylene (2)	x_1	0.0903	0.3704	0.5712	0.6756	0.7767	0.8852		
	V^E	−0.220	−0.503	−0.445	−0.403	−0.355	−0.267		

Table III. Parameters of Eq 1 and Standard Deviation $\sigma(V^E)$ of Experimental Values at 313.15 K

	parameter of eq 1				std dev $\sigma(V^E)$, $cm^3 \cdot mol^{-1}$
system 1 + 2	*A*	*B*	*C*	*D*	
triethylamine (1) + benzene (2)	0.0893	−0.2624	−0.0291	0.1970	0.005
triethylamine (1) + toluene (2)	−1.5732	−0.2199	−0.5375	−1.1043	0.009
triethylamine (1) + ethylbenzene (2)	−1.5934	0.3635	−0.3704	−0.8515	0.007
triethylamine (1) + *o*-xylene (2)	−1.8433	−0.1147	−0.6093	−0.1956	0.007
triethylamine (1) + *m*-xylene (2)	−1.1579	0.1084	−0.0745	0.1689	0.007
triethylamine (1) + *p*-xylene (2)	−1.8956	0.7861	−1.2522	−1.2776	0.003

of the other component of the binary mixture. In this paper, we report the volumetric behavior of triethylamine in benzene, toluene, ethylbenzene, and the three isomeric xylenes.

Experimental Section

Benzene, toluene, and ethylbenzene supplied by B.D.H. (Analar reagent grade), *p*-xylene (extra pure) supplied by Reidel, and *o*- and *m*-xylene samples supplied by Pfizer (LR Grade) were purified according to standard procedures (*4*). Triethylamine (Laboratory Reagent Grade supplied by B.D.H.) was purified following the procedure used by Hepler and Fenby (*5*). All of these solvents were fractionally distilled in a column of 15 theoretical plates at a reflux ratio of 1:10, and the middle fraction was collected. The densities and refractive indexes of these liquids have been compared with the literature values (*6*–*8*) in Table I.

The excess volumes of mixing have been calculated from the experimental density data. The solutions for the measurements of densities were prepared by weight, and corrections for buoyancy were applied. The details of the experimental technique for the preparation of solutions and the measurement of density have been described elsewhere (*9*). Each data point reported is an average of at least two different measurements. The duplicate densities agreed within 2×10^{-5} $g \cdot cm^{-3}$. The maximum uncertainty in excess volumes is expected to be ~ 0.007 $cm^3 \cdot mol^{-1}$.

Results and Discussion

The molar excess volumes of mixing, V^E, for the six binary mixtures are recorded in Table II and plotted as a function of composition in Figure 1. The data were fitted to the equation of the form

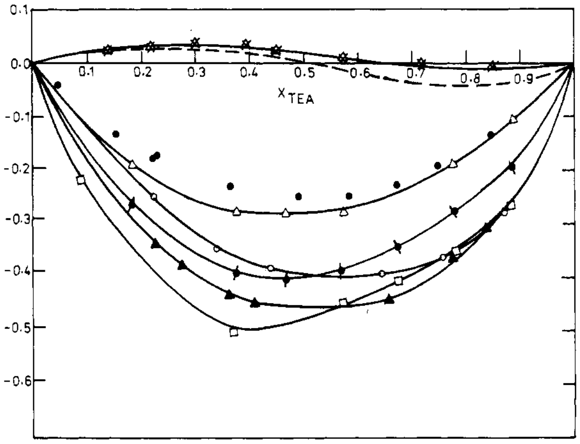

Figure 1. Molar excess volumes of mixing at 313.15 K for the binary mixtures of triethylamine (TEA) + benzene (✡); + toluene (○); + ethylbenzene (⧫); + *o*-xylene (▲); + *m*-xylene (△); + *p*-xylene (□). (---) Calculated from smoothing equation in ref *7* for TEA + benzene at 298.15 K; (●) values of Letcher (*10*) for TEA + toluene at 298.15 K.

$$V^E/(cm^3 \cdot mol^{-1}) = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3] \quad (1)$$

where *A*, *B*, *C*, and *D* are constants and x_1 and x_2 are the mole fractions of triethylamine and aromatic hydrocarbon, respectively. The parameters *A*, *B*, *C*, and *D* evaluated by the least-squares method are recorded in Table III along with the standard deviations $\sigma(V^E)$.

The data for the binary mixtures of triethylamine with benzene and with toluene have been compared with the results of Letcher (*7*, *10*) at 298.15 K in Figure 1. To the best of our knowledge, no V^E data have been reported in the literature for other binary mixtures considered here.

It is observed that V^E decreases when a methyl or ethyl group is added to the benzene ring, which may be due to the increased $n-\pi$ interactions in alkyl-substituted benzene solutions. The substitution of a methyl group in toluene influences V^E and follows the order *m*-xylene > toluene > *o*-xylene > *p*-xylene. It appears that the substitution of the methyl group in toluene at the ortho and para positions favors $n-\pi$ interactions, whereas at the meta position it deactivates the ring for $n-\pi$ interactions.

The results of this paper will be used in the discussion of the following paper.

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Literature Cited

(1) Rao, Y. P.; Suri, S. K. *Thermochim. Acta* **1980**, *36*, 243.
(2) Suri, S. K.; Ramakrishna, V. *J. Chem. Thermodyn.* **1975**, *7*, 573.
(3) Suri, S. K.; Maheswari, R. C.; Yadav, P. L. *Indian J. Chem.* **1974**, *12*, 620.
(4) Riddick, J. A., Bunger, W. B., Eds. "Technique of Organic Chemistry", 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II.
(5) Hepler, L. G.; Fenby, D. V. *J. Chem. Thermodyn.* **1973**, *5*, 471.
(6) American Petroleum Institute Research Project 44, Chemical Thermodynamics Properties Center, Texas A & M University, College Station, TX (Tables dated April 30, 1977, and April 30, 1956).
(7) Letcher, T. M.; Bayles, J. W. *J. Chem. Eng. Data* **1971**, *16*, 266.
(8) Spencer, C. F.; Adler, S. B. *J. Chem. Eng. Data* **1978**, *23*, 82.
(9) Maheswari, R. C.; Suri, S. K.; Tewari, U. S. *J. Chem. Eng. Data* **1979**, *24*, 237.
(10) Letcher, T. M. *J. Chem. Thermodyn.* **1972**, *4*, 159.

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Thermodynamic Properties of Solutions Containing an Aliphatic Amine. 2. Excess Volumes of Binary Mixtures of Triethylamine with 12 Hydrocarbons at 313.15 K

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Molar excess volumes of binary mixtures of triethylamine with *n*-propylbenzenes, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3,4-tetramethylbenzene, diphenylmethane, *n*-hexane, *n*-octane, 2,2,4-trimethylpentane, *n*-dodecane, 2,2,4,6,6-pentamethylheptane, cyclohexane, and methylcyclohexane at 313.15 K have been calculated from the experimental density data. The variation of V^E with the change in size, substitution, and molecular geometry of the hydrocarbon has been discussed.

Introduction

In part 1 (*1*) we reported molar excess volumes for the binary mixtures of triethylamine with benzene, toluene, ethylbenzene, and the three isomeric xylenes. As an extension of that work, we have determined the excess volumes for the mixtures of triethylamine with *n*-propylbenzene, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3,4-tetramethylbenzene, diphenylmethane, *n*-hexane, *n*-octane, 2,2,4-trimethylpentane, *n*-dodecane, 2,2,4,6,6-pentamethylheptane, cyclohexane, and methylcyclohexane. The purpose of these investigations is to provide some information about the thermodynamic properties of amine–hydrocarbon mixtures with a view to understanding the factors determining the unlike interactions between the molecules in such mixtures.

Experimental Section

The sample of triethylamine supplied by Fisher was purified by following the procedure used by Hepler and Fenby (*2*). ACS certified grade *n*-hexane, *n*-octane, and cyclohexane supplied by Fisher, IR and GC analyzed grade *n*-dodecane and methylcyclohexane and puriss grade 1,3,5-trimethylbenzene supplied by Aldrich, reagent grade isopropylbenzene supplied by Eastman, and Baker analyzed reagent grade 2,2,4-trimethylpentane were purified according to standard procedures (*3*). *n*-Propylbenzene and 1,2,3,4-tetramethylbenzene (both IR and GC analyzed grade) and puriss grade 2,2,4,6,6-pentamethylheptane supplied by Aldrich were fractionally distilled at a reflux ratio of 1:10, and the middle fraction was collected. Reagent grade diphenylmethane supplied by Eastman was purified by cycles of fractional crystallization. It was finally distilled under reduced pressure. All of the reagents were stored in brown bottles and fractionally distilled immediately before use. The densities and refractive indexes of the solvents have been compared with the accepted literature values (*4*) in Table I.

Table I. Densities and Refractive Indexes of Liquids Used

	density at 313.15 K		refractive index at 298.15 K	
liquid	our value	lit. value (*6*)	our value	lit. value (*6*)
triethylamine	0.709 32	0.7092[a]	1.3978	1.3980[a]
n-propylbenzene	0.845 08	0.8454	1.4895	1.489 51
isopropylbenzene	0.844 67	0.8447	1.4888	1.488 90
1,3,5-trimethylbenzene	0.848 90	0.8488	1.4969	1.496 84
1,2,3,4-tetramethylbenzene	0.887 84	0.9015[b]	1.5182	1.518 1
diphenylmethane	0.989 92	1.0020[b]		
n-hexane	0.641 09	0.6409	1.3722	1.372 26
n-octane	0.686 56	0.6863	1.3952	1.395 05
2,2,4-trimethylpentane	0.675 29	0.6754	1.3888	1.388 98
n-dodecane	0.734 57	0.7344	1.4194	1.419 52
2,2,4,6,6-pentamethylheptane	0.731 5	0.7417[b]	1.4167	1.416 7
cyclohexane	0.759 67	0.7598	1.4234	1.423 54
methylcyclohexane	0.751 99	0.7520	1.4204	1.420 58

[a] From ref 1. [b] Density at 298.15 K.

The molar excess volumes of mixing have been calculated from the experimental density data. The solutions for the measurement of densities were prepared by weight, and corrections for buoyancy were applied. The details of the experimental technique for the preparation of solutions have been described earlier (*5*).

The densities were measured with a vibrating flow densimeter (Sodev, Inc.). The liquids flowed (at a flow rate of $\sim$0.5 cm^3·min^{-1}) through the densimeter under positive pressure. Water from a thermostat was circulated through the densimeter module at a flow rate of $\sim$2–3 L·min^{-1}. The temperature of the thermostat (313.15 K) was maintained at ±0.001 K by using

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