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Viscosity of Binary Mixtures. IV. Triethylamine with Alkanes and Monoalkylamines at 303.15 and 313.15 K

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Viscosities and densities of seven binary mixtures of *n*-hexane, *n*-octane, isooctane, *n*-propylamine, *n*-butylamine, *n*-hexylamine, and *n*-octylamine with triethylamine have been measured at 303.15 and 313.15 K. Deviations of viscosities from a linear dependence on the mole fraction and values of excess Gibbs energy of activation ΔG^{*E} of viscous flow are attributable to the H-bonding and to the size of the alkylamine and alkane molecules.

KEY WORDS: activation energy; alkanes; alkylamines; *n*-butylamine; density; *n*-hexane; *n*-hexylamine; liquid mixtures; isooctane; *n*-octane; *n*-octylamine; *n*-propylamine; triethylamine; viscosity.

1. INTRODUCTION

As part of a systematic program to investigate molecular interactions in liquid mixtures containing alkylamines, we have reported viscosities η for several binary mixtures of alkylamines with benzene and cyclohexane [1–3]. Furthermore, the viscosities η of binary mixtures of tributylamine with *n*-propylamine, *n*-butylamine, *n*-hexylamine, *n*-octylamine, *n*-hexane, *n*-octane, and isooctane (2,2,4-trimethylpentane) at 303.15 and 313.15 K are reported in the preceding paper [4]. In this paper, we report the viscosities and densities of binary mixtures of triethylamine with the same solvents and at the same temperatures.

2. EXPERIMENTAL

The methods and techniques used to determine the viscosities η and the densities ρ have been described in previous publications [1, 2, 5]. The

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measurements of the kinematic viscosities η/ρ were made with a modified Ubbelohde suspended-level viscometer. Four or five sets of readings for the flow time were taken for each pure liquid or liquid mixture at 303.15 and 313.15 K. The arithmetic mean was taken for the purpose of calculations. The viscometer had been calibrated with doubly distilled water, benzene, and cyclohexane [6]. The densities ρ at 303.15 and 313.15 K of the pure components and the mixtures required for converting kinematic viscosities to absolute viscosities were determined with an Anton-Paar densimeter (Model DMA 60/602). The temperatures were kept constant to within ± 0.02 K. The errors in η and ρ are estimated as 0.002 mPa · s and 0.02 kg · m^{-3}, respectively.

Samples of *n*-propylamine ($C_3H_7NH_2$), *n*-butylamine ($C_4H_9NH_2$), *n*-hexylamine ($C_6H_{13}NH_2$), *n*-octylamine ($C_8H_{17}NH_2$), and triethylamine $(C_2H_5)_3N$ were from Fluka AG, and *n*-hexane (n-C_6H_{14}), *n*-octane (n-C_8H_{18}), and isooctane (2,2,4-trimethylpentane; i-C_8H_{18}) were from Merck, Schuchardt. All the amines were kept over sodium and fractionally distilled twice. The alkanes were dried over a 4-Å molecular sieve (Fluka) and fractionally distilled. Details of the purification procedures have been described previously [2–5].

The purities of the liquid samples were checked by boiling points, gas–liquid chromatography, density, and refractive index and it was found that they were better than 99 mol%.

3. RESULTS AND DISCUSSION

3.1. Viscosities

The experimental results obtained for η and ρ for the seven binary mixtures $(C_2H_5)_3N + n\text{-}C_6H_{14}$, $(C_2H_5)_3N + n\text{-}C_8H_{18}$, $(C_2H_5)_3N + i\text{-}C_8H_{18}$, $(C_2H_5)_3N + C_3H_7NH_2$, $(C_2H_5)_3N + C_4H_9NH_2$, $(C_2H_5)_3N + C_6H_{13}NH_2$, and $(C_2H_5)_3N + C_8H_{17}NH_2$ over the entire range of mole fractions at 303.15 and 313.15 K are presented in Tables I and II. The viscosities in Tables I and II are presented by a polynomial equation,

$$\eta = \sum_{i=0}^{m} A_i x_1^i \qquad (1)$$

The coefficients A_i together with the standard deviations σ are given in Table III. Figures 1 and 2 show the viscosities as a function of the mole fraction x_1 of triethylamine.

Table I. Viscosity and Density of Triethylamine + Alkanes at 303.15 and 313.15 K

	η (mPa·s)		ρ (kg·m^{-3})	
x_1[a]	303.15 K	313.15 K	303.15 K	313.15 K
		$(C_2H_5)_3N + n\text{-}C_6H_{14}$		
0.0000	0.2759	0.2391	650.42	641.31
0.1076	0.2744	0.2432	658.00	648.80
0.2064	0.2760	0.2489	664.86	655.62
0.4089	0.2838	0.2626	678.91	669.56
0.5106	0.2911	0.2710	685.87	676.48
0.6081	0.3002	0.2799	692.51	683.10
0.8040	0.3248	0.3004	705.86	696.36
0.9018	0.3408	0.3125	712.36	702.99
1.0000	0.3592	0.3249	718.96	709.54
		$(C_2H_5)_3N + n\text{-}C_8H_{18}$		
0.0000	0.4830	0.4201	694.61	686.55
0.1983	0.4507	0.3913	698.36	690.13
0.4032	0.4233	0.3701	702.86	692.47
0.5055	0.4110	0.3605	705.26	696.54
0.6044	0.3999	0.3523	707.61	698.88
0.7987	0.3795	0.3379	712.90	703.78
0.9028	0.3694	0.3310	716.02	706.85
1.0000	0.3592	0.3249	718.96	709.54
		$(C_2H_5)_3N + i\text{-}C_8H_{18}$		
0.0000	0.4474	0.4008	684.04	675.80
0.1021	0.4259	0.3815	686.94	678.63
0.2024	0.4088	0.3672	689.93	681.48
0.4012	0.3835	0.3448	696.27	687.62
0.5040	0.3740	0.3369	699.77	690.90
0.5990	0.3676	0.3315	703.14	694.21
0.7989	0.3604	0.3255	710.69	701.55
0.8930	0.3597	0.3244	714.47	705.23
1.0000	0.3592	0.3249	718.96	709.54

[a] x_1 is the mole fraction of triethylamine.

3.1.1. Triethylamine + Alkanes

Figure 1 shows that η increases with the mole fraction x_1 of triethylamine for $(C_2H_5)_3N + n\text{-}C_6H_{14}$, while η decreases for $(C_2H_5)_3N + n\text{-}C_8H_{18}$ and $(C_2H_5)_3N + i\text{-}C_8H_{18}$ at 303.15 and 313.15 K. However, the pattern of viscosity decrease in the two isomers of octane is quite different. Figure 1 also shows that viscosity exhibits negative deviations from a linear dependence on x_1, over the entire range of composition, for all three

Table II. Viscosity and Density of Triethylamine + Alkylamine at 303.15 and 313.15 K

	η (mPa · s)		ρ (kg · m^{-3})	
x_1[a]	303.15 K	313.15 K	303.15 K	313.15 K
		$(C_2H_5)_3N + C_3H_7NH_2$		
0.0000	0.3479		705.55	
0.1027	0.3371		709.54	
0.2061	0.3317		710.95	
0.3991	0.3268		712.83	
0.4950	0.3278		713.76	
0.6009	0.3310		714.91	
0.7911	0.3408		716.77	
0.8925	0.3499		717.68	
1.0000	0.3592		718.96	
		$(C_2H_5)_3N + C_4H_9NH_2$		
0.0000	0.4378	0.3891	728.48	719.18
0.1038	0.4186	0.3692	727.21	717.77
0.2009	0.4019	0.3555	726.02	716.52
0.4065	0.3761	0.3345	723.67	714.21
0.5021	0.3681	0.3290	722.60	713.22
0.5996	0.3611	0.3244	721.86	712.41
0.8010	0.3570	0.3216	720.31	710.84
0.8898	0.3569	0.3228	719.70	710.24
1.0000	0.3592	0.3249	718.96	709.54
		$(C_2H_5)_3N + C_6H_{13}NH_2$		
0.0000	0.7123	0.6134	756.61	748.30
0.1014	0.6552	0.5654	752.91	744.66
0.1952	0.6088	0.5278	749.87	731.45
0.3807	0.5322	0.4639	743.52	734.83
0.4897	0.4934	0.4323	739.24	730.38
0.5912	0.4613	0.4027	735.27	726.32
0.7898	0.4070	0.3627	727.36	718.24
0.8946	0.3827	0.3436	723.25	713.99
1.0000	0.3592	0.3249	718.96	709.54
		$(C_2H_5)_3N + C_8H_{17}NH_2$		
0.0000	1.1646	0.9864	774.14	766.41
0.1056	1.0207	0.8659	770.14	762.29
0.2038	0.9064	0.7719	765.66	757.71
0.4151	0.7044	0.6062	755.76	747.48
0.4978	0.6396	0.5533	751.33	743.22
0.6055	0.5641	0.4916	745.66	736.92
0.8063	0.4488	0.3975	732.65	723.66
0.9007	0.4031	0.3611	726.47	717.28
1.0000	0.3592	0.3249	718.96	709.54

[a] x_1 is the mole fraction of triethylamine.

Table III. Parameters A_i in Eq. (1) and Standard Deviations σ (mPa · s) for the Viscosity of Binary Mixtures at 303.15 and 313.15 K

Mixture	Temp. (K)	A_0	A_1	A_2	A_3	$10^4\sigma$
$(C_2H_5)_3N + n\text{-}C_6H_{14}$	303.15	0.2762	−0.0265	0.1090		5
	313.15	0.2389	0.0384	0.0477		2
$(C_2H_5)_3N + n\text{-}C_8H_{18}$	303.15	0.4822	−0.1601	0.0381		
	313.15	0.4190	−0.1394	0.0461	−0.0364	12
$(C_2H_5)_3N + i\text{-}C_8H_{18}$	303.15	0.4460	−0.2010	0.1157		12
	313.15	0.3993	−0.1755	0.1021		11
$(C_2H_5)_3N + C_3H_7NH_2$	303.15	0.3464	−0.0886	0.1026		11
$(C_2H_5)_3N + C_4H_9NH_2$	303.15	0.4377	−0.2006	0.1229		7
	313.15	0.3887	−0.2016	−0.1875	−0.0499	4
$(C_2H_5)_3N + C_6H_{13}NH_2$	303.15	0.7119	−0.5877	0.3384	−0.1034	7
	313.15	0.6129	−0.4867	0.2711	−0.0720	14
$(C_2H_5)_3N + C_8H_{17}NH_2$	303.15	1.1637	−1.4305	0.8845	−0.2590	10
	313.15	0.9853	−1.1914	0.7614	−0.2380	12

mixtures of triethylamine with alkanes considered here. The negative deviations follow the sequence $n\text{-}C_6H_{14} > n\text{-}C_8H_{18} < i\text{-}C_8H_{18}$. The negative deviations suggest a loss of cohesive energy upon mixing the pure liquids, which may be associated with the disruption of dipole–dipole association of triethylamine molecules.

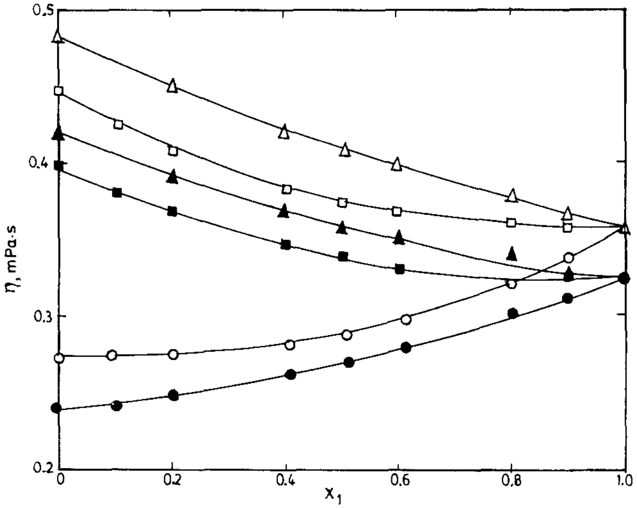

Fig. 1. Composition dependence of the viscosity of triethylamine + alkanes. Alkane: (○) $n\text{-}C_6H_{14}$, (△) $n\text{-}C_8H_{18}$, and (□) $i\text{-}C_8H_{18}$ at 303.15 K and (●) $n\text{-}C_6H_{14}$, (▲) $n\text{-}C_8H_{18}$, and (■) $i\text{-}C_8H_{18}$ at 313.15 K. Solid curves represent Eq. (1).

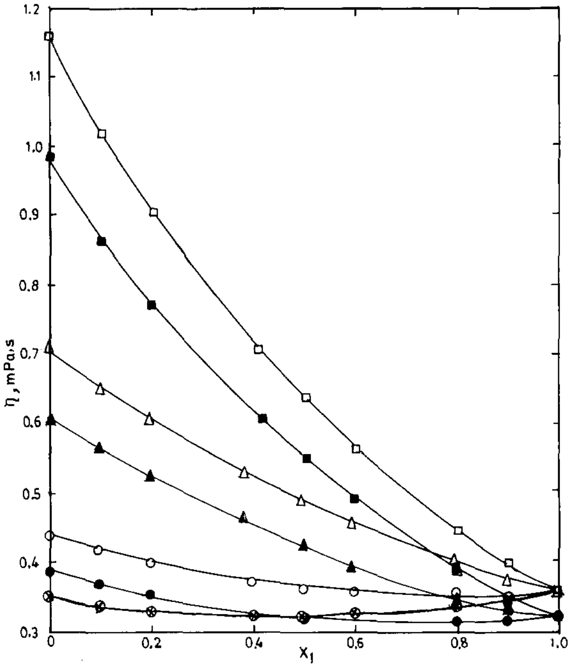

Fig. 2. Composition dependence of the viscosity of triethylamine + n-alkylamine. Alkylamines: (⊗) $C_3H_7NH_2$, (○) $C_4H_9NH_2$, (△) $C_6H_{13}NH_2$, and (□) $C_8H_{17}NH_2$ at 303.15 K and (●) $C_4H_9NH_2$, (▲) $C_6H_{13}NH_2$, and (■) $C_8H_{17}NH_2$ at 313.15 K. Solid curves represent Eq. (1).

3.1.2. Triethylamine + Monoalkylamines

In this series of four mixtures, the two mixtures $(C_2H_5)_3N+C_3H_7NH_2$ and $(C_2H_5)_3N+C_4H_9NH_2$ show minima in the viscosity plots (Fig. 2), whereas the viscosity decreases with the mole fraction x_1 in the mixtures of $(C_2H_5)_3N$ with $C_6H_{13}NH_2$ and $C_8H_{17}NH_2$. The negative deviations from linear dependence on mole fraction x_1 of all the binary mixtures in this series follow the sequence $C_3H_7NH_2 \approx C_4H_9NH_2 < C_6H_{13}NH_2 < C_8H_{17}NH_2$. The negative deviations in this series may be associated partly with a breaking of H bonds in the monoalkylamines.

3.2. Activation Energy of Viscous Flow

On the basis of the theory of absolute reaction rates [7], the excess Gibbs energy of activation ΔG^{*E} of viscous flow may be calculated from

$$\Delta G^{*E} = RT[\ln(\eta V/\eta_2^0 V_2^0) - x_1 \ln(\eta_1^0 V_1^0/\eta_2^0 V_2^0)] \qquad (2)$$

Table IV. Parameters B_i in Eq. (3), Standard Deviations σ, ΔG^{*E}_{max}, and corresponding Mole Fraction x_1

Mixture	Temp. (K)	B_0	B_1	B_2	B_3	σ	ΔG^{**E}_{max} ($J \cdot mol^{-1}$)	x_1
$(C_2H_5)_3N + n\text{-}C_6H_{14}$	303.15	−0.3208	−0.0248	−0.0046		0.0011	−202.4	0.51
	313.15	−0.1216	−0.0031	−0.0112	−0.0638	0.0008	−79.7	0.41
$(C_2H_5)_3N + n\text{-}C_8H_{18}$	303.15	−0.0312	−0.0192	0.0028	0.0357	0.0003	−21.8	0.40
	313.15	−0.0745	−0.0313	−0.0279	0.0237	0.0005	−50.1	0.40
$(C_2H_5)_3N + i\text{-}C_8H_{18}$	303.15	−0.2573	−0.0095	0.0183	−0.0456	0.0003	−162.2	0.50
	313.15	−0.2521	−0.0130	−0.0077	−0.0348	0.0010	−165.5	0.50
$(C_2H_5)_3N + C_3H_7NH_2$	303.15	−0.1618	0.0024	−0.0093	−0.1133	0.0017	−162.8	0.40
$(C_2H_5)_3N + C_4H_9NH_2$	303.15	−0.2431	0.0173	0.0421		0.0013	−152.1	0.60
	313.15	−0.2546	−0.0170	−0.0007	−0.0598	0.0010	−165.6	0.40
$(C_2H_5)_3N + C_6H_{13}NH_2$	303.15	−0.1348	−0.0212	0.0044	−0.0253	0.0005	−84.6	0.49
	313.15	−0.1612	−0.0085	0.0038	−0.0245	0.0009	−104.9	0.49
$(C_2H_5)_3N + C_8H_{17}NH_2$	303.15	−0.0550	−0.0092	0.0082	−0.0662	0.0006	−36.0	0.41
	313.15	−0.1022	0.0063	0.0088	−0.0921	0.0006	−66.2	0.41

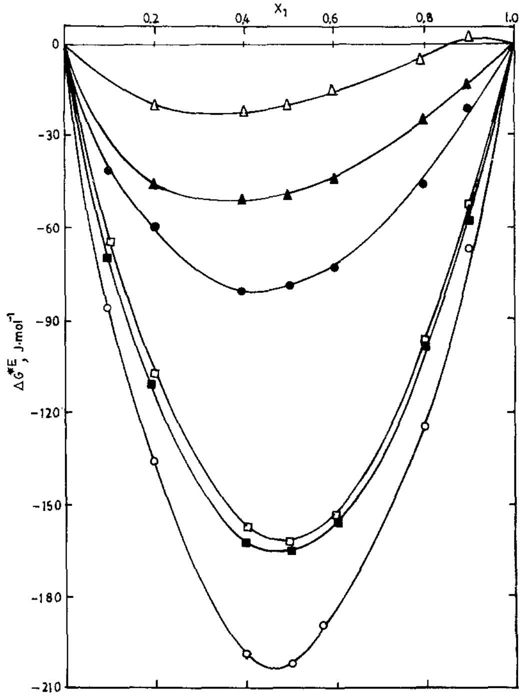

Fig. 3. Variation of ΔG^{*E} with composition for triethylamine + alkanes at 303.15 and 313.15 K. Symbols as in the legend to Fig. 1.

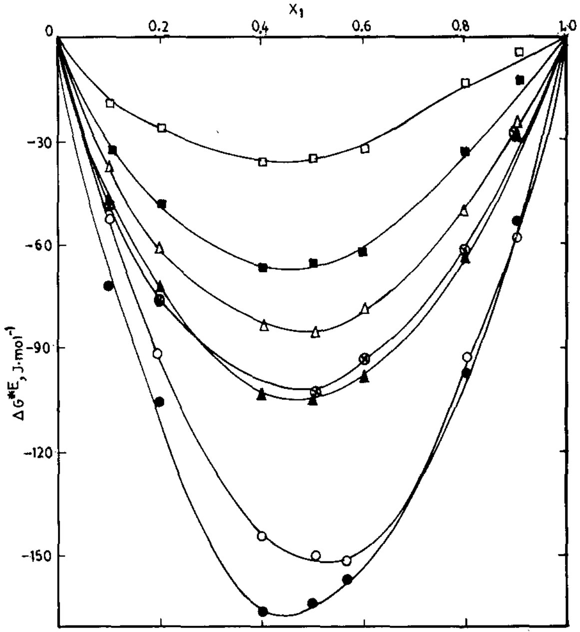

Fig. 4. Variation of ΔG^{*E} with composition for triethylamine + n-alkylamines at 303.15 and 313.15 K. Symbols as in the legend to Fig. 2.

where η and V are the viscosity and molar volume of the mixture and η_i^0 and V_i^0 are the viscosity and molar volume of the pure component i, respectively. The values of $\Delta G^{*E}/RT$ were fitted to the Redlich–Kister equation [8]:

$$\Delta G^{*E}/RT = x_1 x_2 \sum_{i=0}^{m} B_i (1-2x_1)^i \tag{3}$$

The parameters B_i and the standard deviations σ are listed in Table IV. Table IV also includes maximum values of the excess Gibbs energy of activation $\Delta G^{*E}_{\text{max}}$ of flow along with the corresponding mole fractions. The dependence of ΔG^{*E} on the mole fraction x_1 of triethylamine for all the present binary mixtures is shown in Figs. 3 and 4. The values of ΔG^{*E} are estimated to be accurate within $\pm 15\ \text{J}\cdot\text{mol}^{-1}$ for the binary mixtures investigated.

3.2.1. *Triethylamine + Alkane*

Figure 3 shows that the excess Gibbs energies of activation ΔG^{*E} of flow at both temperatures have negative values for all three binary mixtures $(C_2H_5)_3N + n\text{-}C_6H_{14}$, $(C_2H_5)_3N + n\text{-}C_8H_{18}$, and $(C_2H_5)_3N + i\text{-}C_8H_{18}$. Figure 3 also shows the different variation pattern of ΔG^{*E} for the two isomers of octane. The negative values of ΔG^{*E} reduce with the increase in chain length of the alkanes from *n*-hexane to *n*-octane. The values of ΔG^{*E} for $(C_2H_5)_3N + i\text{-}C_8H_{18}$ are more negative than those for $(C_2H_5)_3N + n\text{-}C_8H_{18}$. The negative values of ΔG^{*E} can be attributed to the destruction of the dipole–dipole association in the trialkylamine. The values of ΔG^{*E} follow the sequence $n\text{-}C_6H_{14} < n\text{-}C_8H_{18} > i\text{-}C_8H_{18}$. This study clearly indicates the effect of the size and shape of component molecules on the values of ΔG^{*E}.

3.2.2. Triethylamine + monoalkylamines

Figure 4 shows that the values of ΔG^{*E} are negative for all four binary mixtures of triethylamine with monoalkylamines. The values of ΔG^{*E} at the equimolar composition follow the sequence $C_3H_7NH_2 > C_4H_9NH_2 < C_6H_{13}NH_2 < C_8H_{17}NH_2$. There is no significant effect on the ΔG^{*E} values by altering the temperature from 303.15 to 313.15 K. The negative values of ΔG^{*E} can be explained by considering the breaking of H-bonding in monoalkylamines upon the addition of triethylamine molecules.

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