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### Thermodynamics of organic mixtures containing amines - III: Molar Excess Volumes at 298.15 K for Tripropylamine +n-Alkane Systems - Application of the Flory Theory to N,N,N-Trialkylamine + n-Alkane Mixtures

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# THERMODYNAMICS OF ORGANIC MIXTURES CONTAINING AMINES – III: MOLAR EXCESS VOLUMES AT 298.15 K FOR TRIPROPYLAMINE + *n*-ALKANE SYSTEMS – APPLICATION OF THE FLORY THEORY TO *N,N,N*-TRIALKYLAMINE + *n*-ALKANE MIXTURES

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Molar excess volumes at 298.15 K and atmospheric pressure for tripropylamine + *n*-hexane, + *n*-octane, + *n*-decane, + *n*-dodecane or + *n* hexadecane systems determined from densities measured with an Anton-Paar DMA 602 vibrating-tube densimeter are reported. *N,N,N*-trialkylamine + *n*-alkane systems have been studied using the Flory theory. Better results on excess enthalpies are obtained when the difference in size between the mixture components is large.

The dependence of the excess volume at equimolar composition with the length of the *n*-alkane is correctly described. The simultaneous analysis of the experimental excess volumes and of the excess enthalpies reveal that free volume effects are important in systems formed by triethylamine or tripropylamine and longer alkanes, as well as in those involving tripropylamine or tributylamine and the shorter alkanes.

The Patterson effect is present in the studied mixtures. The more globular amines, triethylamine, tripropylamine or tributylamine are order breakers of the longer alkanes. The amines of very large size, e.g., tridodecylamine, show an ordered structure.

*Keywords:* Tripropylamine; *n*-hexane; Flory theory; *N,N,N*-trialkylamine; *n*-alkane; free volume; interactions; Patterson effect

## 1. INTRODUCTION

Amines are a very interesting class of compounds. Primary and secondary linear amines are weakly self-associated [1,2], as it is revealed by their Trouton's constant (Table I), which is close to that of no self-associated substances, 22 cal mol<sup>-1</sup> K<sup>-1</sup>. For 1-alkanols, this constant is 26.5 cal mol<sup>-1</sup> K<sup>-1</sup> [3]. Tertiary amines show a low dipole moment in gas phase (Table I). Their effective dipole moment, a quantity which gives an indication

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TABLE I Physical constants of some pure amines: molar volume,  $V_m$ , at 298.15 K, critical pressure,  $P_c$ , critical temperature,  $T_c$ , dipole moment in gas phase,  $\mu$ , effective dipole moment,  $\bar{\mu}$ , normal boiling point,  $T_b$ , molar enthalpy of vaporization at  $T_b$ ,  $\Delta H_v$ , and Trouton's constant,  $\Delta H_v/T_b$

<i>Amine</i>	$V_m^a$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$P_c^b$ (bar)	$T_c^b$ (K)	$\mu^b$ (D)	$\bar{\mu}^c$	$T_b^b$ (K)	$\Delta H_v^d$ ( $\text{kJ mol}^{-1}$ )	$\Delta H_v^e/T_b$
Methylamine	44.2	74.3	430	1.3	0.748	266.8	25.60	22.92
Ethylamine	66.6	56.4	456.4	1.3	0.609			
Propylamine	83.0	48.1	497.0	1.3	0.546	321.7	29.55	21.95
Butylamine	99.3	42.0	531.9	1.3	0.499	349.5	31.81	21.75
Dimethylamine	69.4	53.1	437.7	1.0	0.459	280.0	26.40	22.53
Diethylamine	104.2	37.1	496.5	1.1	0.412	328.6	29.06	21.14
Dipropylamine	138.1	29.9	555.8	1.0	0.326	382.5	33.47	20.91
Dibutylamine	170.6	26.4	607.5	1.1	0.322	432.8	38.44	21.22
Trimethylamine (TMA)	94.3	40.9	433.3	0.8 <sup>f</sup>	0.315	276.0	22.94	19.86
Triethylamine (TEA)	140.0	30.3	535	0.9	0.291	362.5	31.01	20.44
Tripropylamine (TPA)	190.3 <sup>g</sup>	23.0 <sup>h</sup>	579.6 <sup>h</sup>	0.74 <sup>f</sup>	0.205			
Tributylamine (TBA)	239.4	18.1	643.0	0.8	0.198	486.6	46.9	23.04
Trioctylamine (TOA)	436.4 <sup>i</sup>	8.05 <sup>h</sup>	932.0 <sup>h</sup>	0.8 <sup>f</sup>	0.146			
Tridecylamine (TDA)	537.2 <sup>j</sup>	5.9 <sup>h</sup>	1110 <sup>h</sup>	0.72 <sup>f</sup>	0.119			

<sup>a</sup>[20]; <sup>b</sup>[43]; <sup>c</sup> $\bar{\mu} = (\mu^2 N_A / 4\pi\epsilon_0 V_m k_B T)^{1/2}$ ;  $N_A$ , Avogadro's number;  $\epsilon_0$ , permittivity of vacuum;  $V_m$ , molar volume at  $T = 298.15$  K;  $k_B$  Boltzmann constant; <sup>d</sup>[44]; <sup>e</sup>units:  $\text{cal mol}^{-1} \text{K}^{-1}$ ; <sup>f</sup>[45]; <sup>g</sup>this work; <sup>h</sup>from Joback's method [43]; <sup>i</sup>[46]; <sup>j</sup>[9].

of the ratio between dipolar and non-polar interactions [4] and which is useful to determine the impact of the polarity of molecules on the bulk properties [5,6] is even lower (Table I). Therefore, mixtures of tertiary amines with aliphatic hydrocarbons, and particularly with homomorphic alkanes, are nearly ideal [7]. So, solid-liquid equilibria of triethylamine (TEA) +  $n$ -alkane systems present an ideal behaviour [8].

The  $H^E$  of symmetrical tertiary amine (hereafter trialkylamine) + alkane mixtures have been extensively investigated in terms of a modification of the Flory theory [9–13], assuming the existence of several contributions to  $H^E$ : chemical, free volume, disordering and steric hindrance. One of the most important conclusions of these studies is that the variation of  $H^E$  with the chain length of the  $n$ -alkane may be regarded as an evidence of the existence of a certain orientational order in long-chain alkanes, destroyed when they are mixed with globular molecules (Patterson effect [14,15]). It leads to an extra endothermic contribution to the  $H^E$ . The short-chain amines, TEA, tripropylamine (TPA), or tributylamine (TBA) are considered as order breakers of the long-chain alkanes [9]. A similar conclusion was stated from the analysis of  $N,N$ -dialkylmethylamine +  $n$ -alkane systems [16] in terms of a different approach, based on the zeroth approximation of DISQUAC [17].

However, there is no a systematic treatment of this type of solutions in terms of the Flory theory [18], probably due to the lack of the needed excess molar volumes,  $V^E$ . Recently, we have determined  $V^E$  for TEA or TBA +  $n$ -alkane systems, as well as presented a short summary of the Flory results for such mixtures [19]. Now,  $V^E$  data at 298.15 K and at atmospheric pressure for TPA +  $n$ -hexane, +  $n$ -octane, +  $n$ -decane, +  $n$ -dodecane, or +  $n$ -hexadecane systems are given. They are useful in order to continue the analysis of the importance of the structural effects on the excess properties of trialkylamine +  $n$ -alkane mixtures. In addition, we extend our study to solutions with amines of very large size (e.g., tridecylamine, TDA, tridodecylamine, TDDA).

## 2. EXPERIMENTAL

### 2.1. Materials

The chemicals, all with stated purities exceeding 98%, were obtained from Fluka and Aldrich. Tripropylamine (puriss p.a. >99.5% GC), *n*-hexane (puriss >99.5%), *n*-octane (purum >99% GC), *n*-decane (purum >98%) and *n*-dodecane (purum >98%) were from Fluka. *n*-Hexadecane (98%) was from Aldrich. Prior to the measurements, the chemicals were carefully dried by adding molecular sieve (Union Carbide type 4A beads, from Fluka). Their densities (in kgm<sup>-3</sup>) at 298.15 and atmospheric pressure, measured in an Anton-Paar densimeter, were: 752.84, 655.27, 698.59, 726.31, 745.56, and 769.98 for TPA, *n*-hexane, *n*-octane, *n*-decane, *n*-dodecane and *n*-hexadecane. They are in good agreement with published values [9,20,21].

### 2.2. Apparatus and Procedure

Binary mixtures were prepared by mass in small vessels of about 10 cm<sup>3</sup>. Caution was taken to prevent evaporation, and the error in the final mole fraction is estimated to be less than ±0.0001. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by I.U.P.A.C [22].

An Anton-Paar DMA 602 vibrating-tube densimeter [23–25], operating under static conditions, was used to determine the densities,  $\rho$ , of the pure liquids and of their binary mixtures. The densimeter was thermostated to ±0.002 K and measurements were carried out at 298.15 K and atmospheric pressure. Details of the experimental technique, auxiliary equipment, calibrations and operational procedure for calculating the  $V^E$  have been described previously [26].

### 2.3. Experimental Results

The results for  $V^E$  as a function of the mole fraction of the amine,  $x_1$ , are collected in Table II. These data were fitted by unweighted least-squares polynomial regression to the equation:

$$V^E(\text{cm}^3\text{mol}^{-1}) = x_1(1 - x_1) \sum_{i=0}^k A_i(2x_1 - 1)^i \quad (1)$$

The number of coefficients  $k$  used in Eq. (1) was determined in every mixture by applying an  $F$  test [27] at 95% confidence level. They are also listed in Table II as footnotes, together with the standard deviations, defined as:

$$\sigma(V^E)(\text{cm}^3\text{mol}^{-1}) = \left[1/N \sum (V_{\text{exp}}^E - V_{\text{calc}}^E)^2\right]^{1/2} \quad (2)$$

Data on  $V^E$  for TPA + *n*-hexane, or + *n*-heptane systems are available in the literature [28]. Our results for TPA + *n*-hexane are lower than those previously published [28]. At  $x_1=0.5$ ; we give  $-0.1737\text{cm}^3\text{mol}^{-1}$  while the value from literature [28] is  $-0.133\text{cm}^3\text{mol}^{-1}$ .

TABLE II Excess molar volumes,  $V^E$ , for tripropylamine(1) +  $n$ -alkane(2) system at 298.15 K and atmospheric pressure

$x_1$	$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$x_1$	$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )
Tripropylamine(1) + $n$ -hexane(2) <sup>a</sup>			
0.0571	-0.0451	0.4472	-0.1764
0.0818	-0.0653	0.4943	-0.1743
0.1512	-0.1084	0.5938	-0.1624
0.2006	-0.1303	0.6403	-0.1523
0.2507	-0.1544	0.7388	-0.1266
0.2985	-0.1657	0.8437	-0.0866
0.3440	-0.1714	0.9473	-0.0319
0.3950	-0.1762		
Tripropylamine(1) + $n$ -octane(2) <sup>b</sup>			
0.1037	0.0064	0.5507	0.0145
0.1042	0.0065	0.5525	0.0143
0.1509	0.0087	0.6998	0.0123
0.2499	0.0119	0.7468	0.0111
0.4517	0.0143	0.8479	0.0079
Tripropylamine(1) + $n$ -decane(2) <sup>c</sup>			
0.0490	0.0109	0.5478	0.0483
0.1065	0.0216	0.5978	0.0465
0.1522	0.0280	0.6335	0.0442
0.2503	0.0402	0.6944	0.0392
0.3010	0.0448	0.7451	0.0342
0.3481	0.0476	0.8421	0.0226
0.3934	0.0489	0.8645	0.0200
0.4493	0.0499	0.9154	0.0130
0.4987	0.0498		
Tripropylamine(1) + $n$ -decane(2) <sup>d</sup>			
0.0576	0.0099	0.4026	0.0407
0.1069	0.0182	0.5089	0.0400
0.1444	0.0231	0.6049	0.0358
0.2049	0.0302	0.6990	0.0307
0.2589	0.0348	0.7981	0.0218
0.3053	0.0374	0.8984	0.0116
Tripropylamine(1) + $n$ -hexadecane(2) <sup>e</sup>			
0.1140	0.0013	0.6456	-0.0086
0.2127	0.0018	0.7004	-0.0111
0.3110	0.0017	0.7998	-0.0151
0.3975	0.0012	0.9435	-0.0077
0.5980	-0.0004		

<sup>a</sup> $A_0 = -0.695$ ,  $A_1 = 0.170$ ,  $A_2 = -0.193$ ,  $A_3 = -0.069$ ,  $A_4 = 0.164$  (see Eq. 1),  $\sigma(V^E) = 0.001$  cm<sup>3</sup> mol<sup>-1</sup> (Eq. 2); <sup>b</sup> $A_0 = 0.0581$ ,  $A_1 = -0.0043$ ,  $A_2 = 0.0128$  (see Eq. 1),  $\sigma(V^E) = 0.0001$  cm<sup>3</sup> mol<sup>-1</sup> (Eq. 2); <sup>c</sup> $A_0 = 0.1990$ ,  $A_1 = -0.0348$ ,  $A_2 = -0.0056$  (see Eq. 1),  $\sigma(V^E) = 0.0003$  cm<sup>3</sup> mol<sup>-1</sup> (Eq. 2); <sup>d</sup> $A_0 = 0.1604$ ,  $A_1 = -0.0405$  (see Eq. 1),  $\sigma(V^E) = 0.0003$  cm<sup>3</sup> mol<sup>-1</sup> (Eq. 2); <sup>e</sup> $A_0 = 0.0171$ ,  $A_1 = -0.1681$ ,  $A_3 = -0.0277$  (see Eq. 1),  $\sigma(V^E) = 0.0005$  cm<sup>3</sup> mol<sup>-1</sup> (Eq. 2).

### 3. FLORY THEORY

#### 3.1. Equations

According to this model [18], the equations for  $H^E$  and  $V^E$  are, respectively:

$$\begin{aligned}
 H^E = & x_1 V_1^* \theta_2 X_{12} / \bar{V} + x_1 V_1^* \varphi_2 ((\bar{V}_1 - \bar{V}_2) / \bar{V}_0) (P_2^* / \bar{V}_2 - P_1^* / \bar{V}_1) \\
 & + (V^E / \bar{V}_0^2) (\varphi_1 P_1^* + \varphi_2 P_2^*)
 \end{aligned}
 \tag{3}$$

TABLE III Physical constants at 298.15 K of pure compounds: isobaric thermal expansivity,  $\alpha$ , isothermal compressibility,  $\kappa_T$ , molar volume,  $V_m$ , and reduction parameters,  $P^*$  and  $V^*$ , needed for Flory calculations

Compound <sup>a</sup>	$\alpha$ ( $10^{-3} \text{ K}^{-1}$ )	$\kappa_T$ ( $10^{-9} \text{ Pa}^{-1}$ )	$V_m$ ( $\text{cm}^3 \text{ mol}^{-1}$ )	$P^*$ ( $\text{J cm}^{-3}$ )	$V^*$ ( $\text{cm}^3 \text{ mol}^{-1}$ )
TEA	1.290 <sup>b</sup> 1.30 <sup>c</sup>	1.424 <sup>b</sup> 1.476 <sup>c</sup>	140.02 <sup>c</sup> 140.78 <sup>c</sup>	459.5 456.9	107.35 107.5
TPA	1.064 <sup>b</sup>	1.230 <sup>b</sup>	190.31 <sup>d</sup>	409.9	150.96
TBA	0.970 <sup>b</sup> 0.983 <sup>e</sup>	1.007 <sup>b</sup> 1.05 <sup>c</sup>	239.71 <sup>c</sup> 240.45 <sup>e</sup>	442.7 441.7	193.08 192.73
TOA	0.832 <sup>f</sup> 0.841 <sup>c</sup>	0.808 <sup>f</sup> 0.838 <sup>e</sup>	436.4 <sup>f</sup> 438.2 <sup>e</sup>	468.5 450.5	359.1 360.0
TDA	0.808 <sup>b</sup>	0.754 <sup>b</sup>	537.2 <sup>b</sup>	475.4	443.9
TDDA	0.787 <sup>b</sup> 0.795 <sup>e</sup>	0.713 <sup>b</sup> 0.738 <sup>e</sup>	635.7 <sup>b</sup> 643.0 <sup>e</sup>	486.2 475.4	527.46 532.71
<i>n</i> -pentane	1.610 <sup>g</sup>	2.180 <sup>g</sup>	116.11 <sup>g</sup>	407.7	85.33
<i>n</i> -hexane	1.387 <sup>h</sup>	1.7039 <sup>h</sup>	131.51 <sup>d</sup>	424.2	99.48
<i>n</i> -heptane	1.256 <sup>h</sup>	1.4606 <sup>h</sup>	147.45 <sup>h</sup>	431.9	113.6
<i>n</i> -octane	1.164 <sup>h</sup>	1.3024 <sup>h</sup>	163.52 <sup>d</sup>	436.8	127.71
<i>n</i> -decane	1.051 <sup>h</sup>	1.1096 <sup>h</sup>	195.9 <sup>d</sup>	447.0	155.71
<i>n</i> -dodecane	0.960 <sup>h</sup>	0.9876 <sup>h</sup>	228.47 <sup>d</sup>	445.2	184.33
<i>n</i> -tetradecane	0.886 <sup>i</sup>	0.872 <sup>i</sup>	261.09 <sup>c</sup>	453.7	213.33
<i>n</i> -hexadecane	0.883 <sup>h</sup>	0.8620 <sup>h</sup>	294.09 <sup>d</sup>	457.0	240.42

<sup>a</sup>For symbols, see Table I; <sup>b</sup>[9]; <sup>c</sup>[19]; <sup>d</sup>this work; <sup>e</sup> $T=303.15 \text{ K}$ ; values calculated using the equations given in [47] for the dependence with  $T$  for  $\alpha$  and  $\kappa_T$ ; <sup>f</sup>[46]; <sup>g</sup>[20]; <sup>h</sup>[48]; <sup>i</sup>[21].

and

$$V^E = (x_1 V_1^* + x_2 V_2^*)(\bar{V} - \varphi_1 \bar{V}_1 - \varphi_2 \bar{V}_2) \quad (4)$$

In Eq. (3),  $X_{12}$  is an adjustable parameter, obtained by fitting the theoretical expression for  $H^E$  to the experimental results and  $\bar{V}_0 = \varphi_1 \bar{V}_1 + \varphi_2 \bar{V}_2$ . The remaining symbols have the usual meaning [29]. The term which depends directly on  $X_{12}$  in Eq. (3) is usually named as the interaction contribution [18] to  $H^E$ . The others terms are the so-called equation of state contribution [18] to  $H^E$ .

### 3.2. Estimation of the Energetic Parameter

In order to apply this model, it is necessary to determine the characteristic parameters of pure compounds ( $V_i^*$ ,  $P_i^*$ ,  $T_i^*$ ,  $i = 1, 2$ ), which are usually calculated from their thermal coefficients. The values used in the present work are listed in Table III.

The energetic parameter  $X_{12}$  was obtained for each system by means of a Marquardt algorithm [27], which minimizes the objective function:

$$X^2(X_{12}) = \sum (H_{\text{exp}}^E - H_{\text{calc}}^E)^2 \quad (5)$$

## 4. DISCUSSION

### 4.1. Experimental Excess Enthalpies

For a given *n*-alkane, at equimolar composition and 298.15 K,  $H^E(\text{TEA}) > H^E(\text{TPA}) > H^E(\text{TDDA})$  (Table IV) as  $\bar{\mu}(\text{TEA}) > \bar{\mu}(\text{TPA}) > \bar{\mu}(\text{TDDA})$  (Table I), and dipole–dipole interactions are stronger in solutions with TEA. It is remarkable that, at 293.15 K,

TABLE IV Molar excess enthalpies at 298.15 K and equimolar composition for trialkylamine + *n*-alkane systems. Comparison of experimental results (exp) with values from the DISQUAC (DQ) UNIFAC (UNIF) or from the Flory's models

System <sup>a</sup>	N <sup>b</sup>	$X_{12}^c$ (J cm <sup>-3</sup> )	$C_{m,2}^{DIS}$	$H^E$ (J mol <sup>-1</sup> )	$\sigma(H^E)^e$ (J mol <sup>-1</sup> )		
					EXP	DQ UNIF	FLORY
TEA + <i>n</i> -C <sub>5</sub>		2.785	67.2	58 <sup>f</sup>			
TEA + <i>n</i> -C <sub>6</sub>	19	3.025	83.7	82 <sup>g</sup>	0.3	7.9/17	4.9
TEA + <i>n</i> -C <sub>7</sub>	12	3.812	109	112 <sup>h</sup>	0.7	1.4/39	1.2
TEA + <i>n</i> -C <sub>8</sub>	19	3.647	94.8	106 <sup>g</sup>	0.3	1.8/12	1.0
TEA + <i>n</i> -C <sub>10</sub>	7	4.573	110.3	136 <sup>g</sup>	3.0	3.2/6.1	2.5
TEA + <i>n</i> -C <sub>12</sub>	9	7.078	160.2	201 <sup>g</sup>	10.0	6.7/18	6.5
TEA + <i>n</i> -C <sub>14</sub>	7	8.408	170.1	258 <sup>g</sup>	11.0	14/56	10.7
TEA + <i>n</i> -C <sub>16</sub>	9	10.334	217.4	322 <sup>g</sup>	20.0	22/82	14.8
TPA + <i>n</i> -C <sub>5</sub>	9	1.266	-9.2	-5 <sup>g</sup>	0.2	40/151	30.2
TPA + <i>n</i> -C <sub>6</sub>		0.838	15.0	9 <sup>i</sup>		0.44/41	2.4
TPA + <i>n</i> -C <sub>7</sub>			35.0	23 <sup>i</sup>			
TPA + <i>n</i> -C <sub>8</sub>	9	1.073	53.7	37 <sup>g</sup>	0.3	2.4/17	2.7
TPA + <i>n</i> -C <sub>10</sub>		1.834	95.0	73 <sup>i</sup>			
TPA + <i>n</i> -C <sub>12</sub>	9	2.922	141.9	118 <sup>g</sup>	1.4	10/38	9.3
TPA + <i>n</i> -C <sub>14</sub>			200.0	178 <sup>i</sup>			
TPA + <i>n</i> -C <sub>16</sub>	9	5.512	250.1	225 <sup>g</sup>	2.5	45/128	40.0
TBA + <i>n</i> -C <sub>5</sub>	4	1.540	-42.2	-18 <sup>j</sup>	0.9	3.4/41	3.0
TBA + <i>n</i> -C <sub>6</sub>	21	0.853	-13.8	-3 <sup>j</sup>	0.2	3.2/30	1.5
TBA + <i>n</i> -C <sub>7</sub>			34.0	15 <sup>i</sup>			
TBA + <i>n</i> -C <sub>8</sub>	19	1.073	74.8	33 <sup>j</sup>	0.3	2.7/5.	3.6
TBA + <i>n</i> -C <sub>10</sub>	5	1.460	125.4	70 <sup>j</sup>	1.6	3.2/15	2.4
TBA + <i>n</i> -C <sub>12</sub>	5	2.451	209.6	119 <sup>j</sup>	1.5	2.5/52	2.0
TBA + <i>n</i> -C <sub>14</sub>	6	3.596	292.8	181 <sup>j</sup>	4.0	8.7/101	8.1
TBA + <i>n</i> -C <sub>16</sub>	7	4.981	398.4	227 <sup>j</sup>	16.0	34/166	32.2
TDA + <i>n</i> -C <sub>8</sub>	8	0.986	167.0	21 <sup>j</sup>	0.3	2.3/9	2.5
TDA + <i>n</i> -C <sub>12</sub>	7	0.202	32.6	4.7 <sup>j</sup>	0.2	0.8/6	0.5
TDA + <i>n</i> -C <sub>16</sub>	7	0.482	238	41 <sup>j</sup>	0.3	1.0/23	2.6
TDDA + <i>n</i> -C <sub>7</sub>	7	2.277	1048	89 <sup>j</sup>	5.9	12.0/69	4.9
TDDA + <i>n</i> -C <sub>8</sub>	8	1.825	906.3	83 <sup>j</sup>	9.6	15.0/65	8.2
	13			64 <sup>k</sup>	1.2		
TDDA + <i>n</i> -C <sub>12</sub>	10	0.372	145.8	17 <sup>j</sup>	2.4	2.5/6	2.2
TDDA + <i>n</i> -C <sub>16</sub>	8	0.112	41.7	5.6 <sup>j</sup>	1.4	1.6/5	1.3

<sup>a</sup>For symbols, see Table I; TDDA, tridodecylamine; <sup>b</sup>number of experimental data points; <sup>c</sup>energetic parameter in Flory theory; <sup>d</sup>second dispersive interchange coefficients for (*a,n*) contacts: Type *a*, CH<sub>3</sub> or CH<sub>2</sub> in *n*-alkanes or trialkylamines; Type *n*, N in trialkylamines; <sup>e</sup> $\sigma(H^E) = 1/N[\sum(H_{exp}^E - H_{calc}^E)^2]^{1/2}$ ; <sup>f</sup>[9]; <sup>g</sup>[11]; <sup>h</sup>[49]; <sup>i</sup>estimated value using DISQUAC; <sup>j</sup>[10]; <sup>k</sup>[32]; T = 303.15 K.

$H^E(\text{TMA} + n\text{-hexane}) = 375 \text{ J mol}^{-1}$  extrapolated [16] from vapor-liquid equilibria data [30] at different temperature) is a much higher value than that for TEA + *n*-hexane (82 J mol<sup>-1</sup> at 298.15 K [11]). It reveals that steric factors play a very important role in these systems.

On the other hand,  $H^E$  increases for a fixed amine (TEA, TPA or TBA), with the length (*n*) of the *n*-alkane (Table IV). The observed increase is larger than expected for the longer alkanes (see below). It has been ascribed to the existence of a certain orientational order in long-chain *n*-alkanes, destroyed when such alkanes are mixed with globular molecules (the so-called Patterson effect [14,15]), which leads to an extra endothermic contribution to  $H^E$ . This behaviour is supported by the variation of  $H^E$  per unit of volume ( $H_v^E$  (J cm<sup>-3</sup>) =  $H^E/(x_1V_1 + x_2V_2)$ ;  $V_i$ , molar volume of component *i*) which is not constant as one might expect [14]. At equimolar composition and 298.15 K,  $H_v^E(\text{TEA} + n\text{-C}_6) \text{ (J cm}^{-3}\text{)} = 0.60$  and  $H_v^E(\text{TEA} + n\text{-C}_{12}) \text{ (J cm}^{-3}\text{)} = 1.09$ . It is

noteworthy that  $H_v^E$  varies more smoothly when, for a given long-chain alkane, we pass from TPA to TBA:  $H_v^E(\text{TPA} + n\text{-C}_{12})$  ( $\text{J cm}^{-3}$ ) = 0.56 and  $H_v^E(\text{TBA} + n\text{-C}_{12})$  ( $\text{J cm}^{-3}$ ) = 0.51. In contrast,  $H_v^E(\text{TDDA} + n\text{-C}_{12})$  ( $\text{J cm}^{-3}$ ) = 0.039. This may be interpreted assuming that TEA is a much better breaker of the orientational order or long  $n$ -alkanes due to its more globular shape [9]. Note that  $H^E(x=0.5; 298.15\text{ K})$  for the tridodecylamine +  $n$ -hexadecane system is  $5.6\text{ J mol}^{-1}$  [10] as both components have a similar ordered structure [9,31].

Moreover, if a liquid is ordered, it might be expected that there would be a displacement of the maximum of  $H_v^E$  towards a low concentration of the disordering component. This situation is observed in, e.g., TEA, TPA or TBA +  $n$ -hexadecane or in TDDA +  $n$ -octane (Fig. 1).

Finally, it is known that when there is a net destruction of order during mixing  $H^E$  decreases and  $V^E$  increases with  $T$  [14,15]. Data on  $H^E$  at different temperatures [10,32] (Table IV) for the TDDA +  $n\text{-C}_8$  system confirm that this amine is an ordered liquid in comparison with the shorter amines.

#### 4.2. Experimental Excess Volumes

As it is known,  $V^E$  is the result of several opposing effects: physical interactions between equal molecules lead to increased volume; interactions between unlike molecules, free volume effects decrease  $V^E$ .

In systems including TEA,  $V^E$  ( $x=0.5$ ) varies in the following sequence: hexane < heptane > octane > decane > dodecane > ... (Table V; Fig. 2). For the shorter alkanes, the interactional contribution to  $V^E$  prevails and  $V^E$  is positive. From octane,

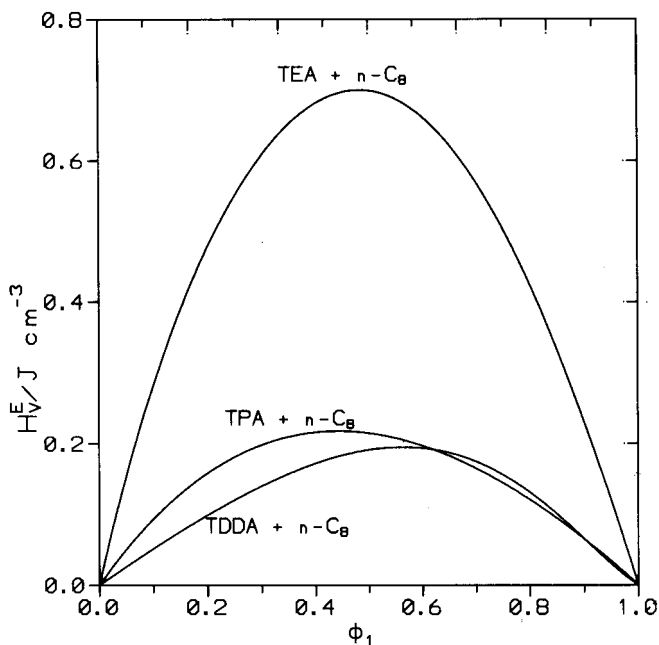


FIGURE 1  $H^E$  per unit of volume,  $H_v^E$ , at 298.15 K vs the volume fraction,  $\phi_1$ , for  $N,N,N$ -trialkylamine(1) +  $n$ -octane(2).



TABLE V Molar excess volumes at 298.15 K and equimolar composition for trialkylamine + *n*-alkane systems. Comparison of experimental results (exp) with values from the Flory's model using the  $X_{12}$  parameters listed in Table IV

System <sup>a</sup>	N <sup>b</sup>	$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )		$\sigma(V^E)^c$ (cm <sup>3</sup> mol <sup>-1</sup> )	
		Exp	Flory	Exp	Flory
TEA + <i>n</i> -C <sub>6</sub>	14	0.0698 <sup>d</sup>	0.0455	0.0006	0.0188
TEA + <i>n</i> -C <sub>7</sub>	9	0.1255 <sup>e</sup>	0.1250	0.0008	0.0022
TEA + <i>n</i> -C <sub>8</sub>	18	0.1184 <sup>d</sup>	0.1198	0.0006	0.0013
TEA + <i>n</i> -C <sub>10</sub>	19	0.0717 <sup>d</sup>	0.0735	0.0005	0.0041
TEA + <i>n</i> -C <sub>14</sub>	10	-0.0544 <sup>d</sup>	-0.0714	0.0006	0.0168
TEA + <i>n</i> -C <sub>16</sub>	10	-0.0979 <sup>d</sup>	-0.0524	0.0010	0.0508
TPA + <i>n</i> -C <sub>6</sub>	15	-0.170 <sup>f</sup>	-0.073	0.0014	0.0803
	10	-0.133 <sup>g</sup>		0.004	0.054
TPA + <i>n</i> -C <sub>8</sub>	10	0.0145 <sup>f</sup>	0.0615	0.0001	0.0347
TPA + <i>n</i> -C <sub>10</sub>	17	0.0497 <sup>f</sup>	0.0557	0.0003	0.0058
TPA + <i>n</i> -C <sub>12</sub>	12	0.0401 <sup>f</sup>	0.0027	0.0003	0.0278
TPA + <i>n</i> -C <sub>16</sub>	9	0.0043 <sup>f</sup>	-0.0887	0.0004	0.0706
TBA + <i>n</i> -C <sub>6</sub>	19	-0.3838 <sup>d</sup>	-0.3853	0.0036	0.0103
TBA + <i>n</i> -C <sub>7</sub>	12	-0.194 <sup>g</sup>			
TBA + <i>n</i> -C <sub>8</sub>	12	-0.0700 <sup>d</sup>	-0.0661	0.0007	0.0029
TBA + <i>n</i> -C <sub>10</sub>	15	0.0411 <sup>d</sup>	0.0443	0.0004	0.0022
TBA + <i>n</i> -C <sub>12</sub>	18	0.0814 <sup>d</sup>	0.093	0.0007	0.0101
TBA + <i>n</i> -C <sub>14</sub>	13	0.1095 <sup>d</sup>	0.0907	0.0008	0.0175
TBA + <i>n</i> -C <sub>16</sub>	13	0.1190 <sup>d</sup>	0.1363	0.0007	0.0219
TDA + <i>n</i> -C <sub>8</sub>			-0.58		
TDA + <i>n</i> -C <sub>12</sub>			-0.19		
TDA + <i>n</i> -C <sub>16</sub>			-0.032		
TDDA + <i>n</i> -C <sub>7</sub>			-0.91		
TDDA + <i>n</i> -C <sub>8</sub>			-0.70		
TDDA + <i>n</i> -C <sub>12</sub>			-0.29		
TDDA + <i>n</i> -C <sub>16</sub>			-0.12		

<sup>a</sup>For symbols, see Table 1; <sup>b</sup>number of experimental data points; <sup>c</sup> $\sigma(V^E) = 1/N[\Sigma(V_{\text{exp}}^E - V_{\text{calc}}^E)^2]^{1/2}$ ; <sup>d</sup>[19]; <sup>e</sup>[49]; <sup>f</sup>this work; <sup>g</sup>[28]; <sup>h</sup>[50].

free volumes effects appear, what is supported by a decreasing of  $V^E$ . For the longer alkanes,  $V^E$  ( $x=0.5$ ) becomes quite negative and the excess curves are skewed to the region of high concentration in the component of smaller molar volume (TEA). This asymmetry of the  $V^E$  curves is characteristic of systems where strong free volume effects are present. In TPA + *n*-alkane mixtures,  $V^E$  ( $x=0.5$ ) varies in a similar sequence: hexane < octane < decane > dodecane > hexadecane (Tables II and V; Fig. 2). However, for the solution with hexane,  $V^E < 0$  and the curve is shifted to the region of low mole fraction in TPA (Fig. 3). Consequently, free volume effects prevail. As in systems with TEA, free volume effects are newly important when longer alkanes are present.

The observed variation of  $V^E$  ( $x=0.5$ ) with *n* is also encountered in many other mixtures: cyclopentane [14], di-*n*-propylether [33], methyl 1,1-dimethylpropylether [34], ethyl 1,1-dimethylethylether [35] or ethyl 1,1-dimethylpropylether [36] with *n*-alkane. It is also encountered in glyme + cycloalkane mixtures [37].

In TBA + *n*-alkane systems,  $V^E$  ( $x=0.5$ ) increases with *n* (Table V; Fig. 2). For the shorter alkanes,  $V^E$  is negative and the corresponding curve is asymmetric. Free volume effects appear, in solutions with shorter alkanes [28].  $H^E$  is even negative for the system with hexane (Table IV). When *n* increases, the negative contribution to  $V^E$  from structural effects are of less importance in comparison to the positive interactional contribution to  $V^E$ , and this magnitude increases.

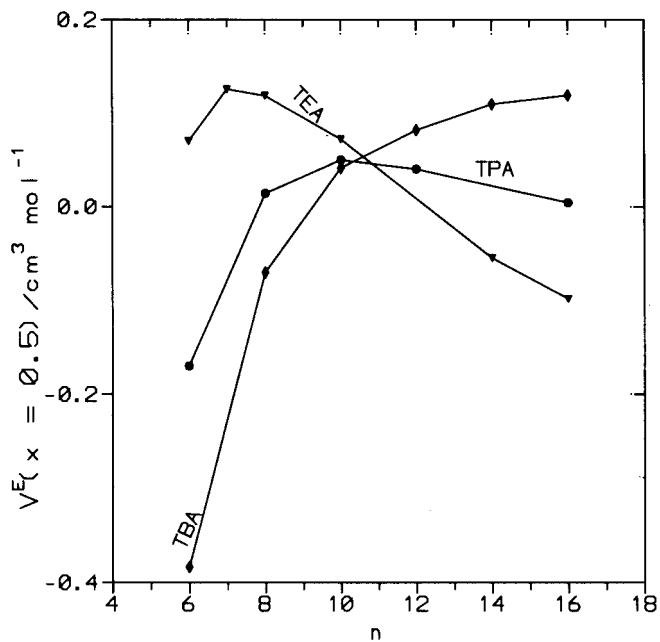


FIGURE 2  $V^E$  at 298.15 K and equimolar composition for  $N,N,N$ -trialkylamine(1) +  $n$ -alkane(2) systems vs  $n$ , the number of C atoms in the  $n$ -alkane (TPA, this work; TEA and TBA [19]).

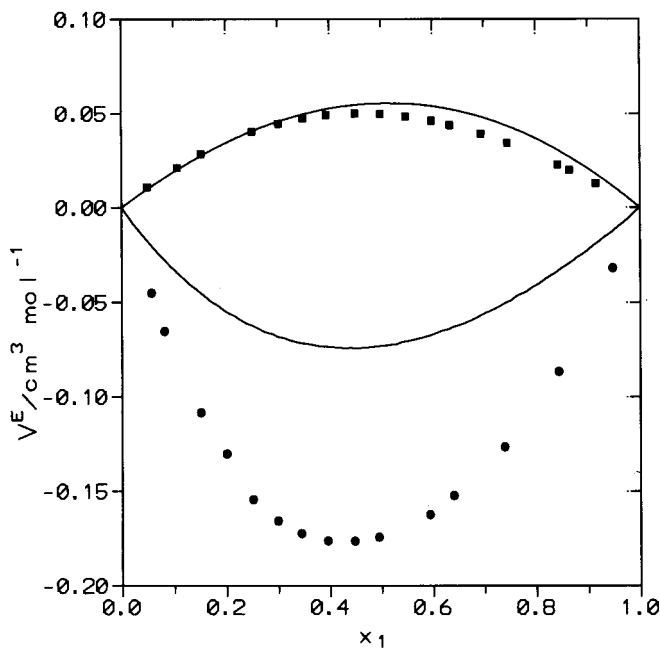


FIGURE 3  $V^E$  at 298.15 K for tripropylamine(1) +  $n$ -alkane(2) mixtures. Solid lines, calculations from the Flory theory. Points, experimental results (this work): ●,  $n$ -hexane; ■,  $n$ -decane.

We note that for  $n \leq 10$ ,  $V^E(\text{TEA}) > V^E(\text{TPA}) > V^E(\text{TBA})$ . In contrast, for  $n \geq 12$ ,  $V^E(\text{TEA}) < V^E(\text{TPA}) < V^E(\text{TBA})$  (Fig. 2). The sign of, e.g.,  $V^E(\text{TEA}) - V^E(\text{TBA})$  depends on the predominant contribution to  $V^E$  (e.g., interactional for  $n \leq 10$  in solution with TEA, and hence  $V^E(\text{TEA}) - V^E(\text{TBA}) > 0$ ). This inversion in  $V^E$  has been also observed in quite different mixtures:  $\text{CH}_3\text{-O}-(\text{CH}_2\text{-CH}_2\text{-O})_m\text{-CH}_3 + n\text{-alkane}$  [37], or 1-alkanol + polyether [38,39].

On the other hand, at 313.15 K and equimolar composition,  $V^E(\text{TEA} + n\text{-dodecane}) = 0.1135 \text{ cm}^3 \text{ mol}^{-1}$  [40]. This value is higher than that at 298.15 K ( $\approx 0.01 \text{ cm}^3 \text{ mol}^{-1}$ , estimated value from those for TEA +  $n$ -alkane systems, Table V). It indicates that there is a net destruction of order upon mixing.

### 4.3. Flory Results on $H^E$

Results on  $H^E$  from the Flory model for the examined mixtures are shown in Table IV (see also Fig. 4 for some selected solutions). We note that the better  $H^E$  results are obtained when the size difference between the mixture components is large (Table IV).

The Flory theory represents  $H^E$  of trialkylamine +  $n$ -alkane systems using  $X_{12}$  parameters which depend on  $n$  (Table IV). This may be regarded as a consequence of the Patterson effect [9,14]. In solutions containing TEA,  $X_{12}$  varies somewhat erratically due to the experimental inaccuracies of the  $H^E$  measurements. In the case of solutions formed by TPA or TBA and a given  $n$ -alkane,  $X_{12}(n)$  shows a minimum (for  $n=8$  in TPA mixtures; for  $n=6$ , in TBA systems; Table IV). In the framework of the Flory theory,  $H^E$  is calculated as the addition of two contributions [18]: the interaction term and the equation of state term. The latter depends on  $V^E$  and on the difference

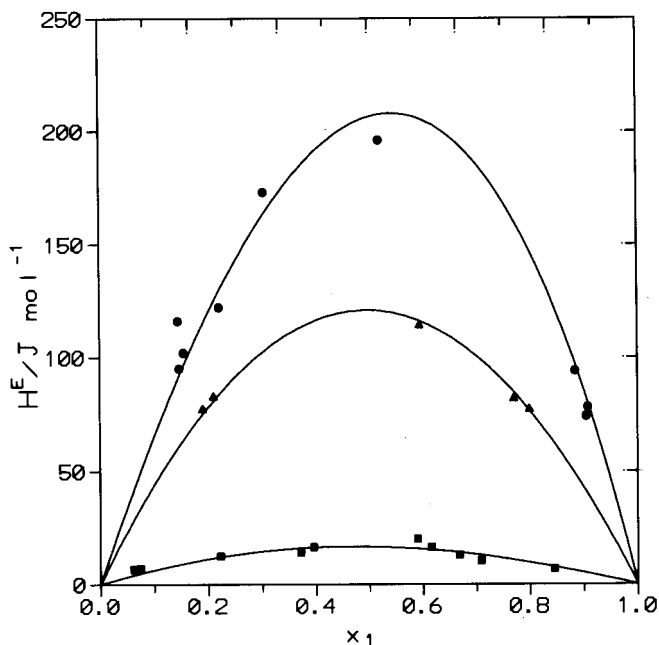


FIGURE 4  $H^E$  at 298.15 K for  $N,N,N$ -trialkylamine(1) +  $n$ -dodecane(2) mixtures. Solid lines, calculations from the Flory theory. Points, experimental results: ●, TEA [11]; ▲, TBA [10]; ■, TDDA [10].

( $\bar{V}_1 - \bar{V}_2$ ). The observed minimum of  $X_{12}(n)$  may be ascribed to equation of state contribution to  $H^E$  is negative and large in absolute value when is compared to the interactional contribution to  $H^E$  (Fig. 5).

We have also correlated the  $H^E$  values using the zeroth approximation of DISQUAC [17]. As it is known, this model is a generalization, in terms of group surface interactions, of the rigid lattice theory developed by Guggenheim [41]. The dispersive enthalpic interchange coefficients,  $C_{an,2}^{DIS}$ , and  $H^E$  vary similarly with  $n$  (Table IV) as in this model  $V^E$  is assumed to be 0. When comparing DISQUAC results for TEA or TBA +  $n$ -alkane systems obtained using interaction parameters dependent on  $n$  with those from the modified UNIFAC model [42] calculated from averaged interaction parameters, we note that UNIFAC fails to represent  $H^E$  for the solutions with the longer alkanes (Table IV). This newly suggests the existence of the Patterson effect in such mixtures. The large decrease of  $C_{an,2}^{DIS}$  in solutions with TDDA when passing from  $n$ -heptane or  $n$ -octane to  $n$ -dodecane may be interpreted in similar way (Table IV).

#### 4.4. Flory Results on $V^E$

Results on  $V^E$  from the Flory model are listed in Table V (Fig. 3). For systems containing TPA, results are somewhat poorer. Nevertheless, the model correctly describes the dependence of  $V^E$  with  $n$ . The decrease of  $V^E$  for large  $n$  values in solutions with TEA or TPA may be due to large differences between reduced volumes of the mixture components.

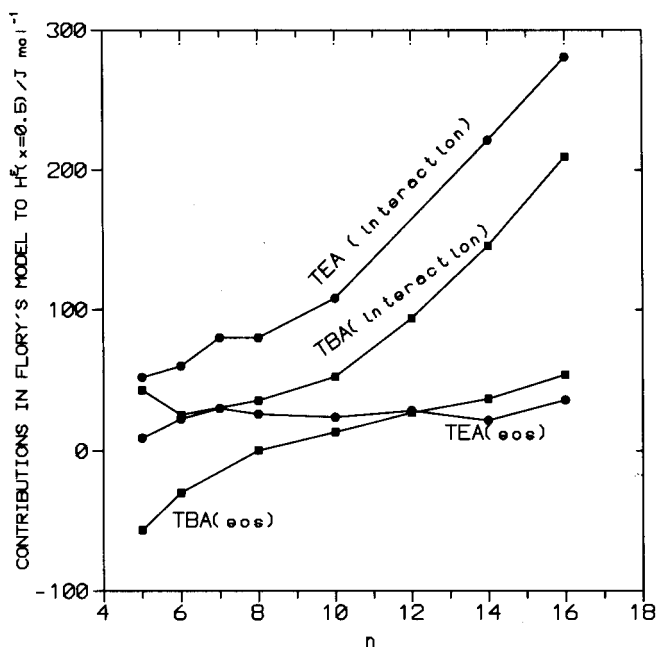


FIGURE 5 Interaction and equation of state contributions to  $H^E$  in the Flory theory [18] (Eq. 3) at 298.15 K and equimolar composition for  $N,N,N$ -trialkylamine(1) +  $n$ -alkane(2) systems vs  $n$ , the number of C atoms in the  $n$ -alkane.

## 5. CONCLUSIONS

Trialkylamine + *n*-alkane systems have been studied using the Flory theory. The model provides better  $H^E$  results for trialkylamine + *n*-alkane systems when the size difference between the mixture components is large. The dependence of  $V^E(x=0.5)$  with the length of the *n*-alkane in systems containing TEA, TPA or TBA is correctly described. The experimental excess volumes reveal that free volume effects are important in systems formed by TEA or TPA and longer alkanes, and in those involving TPA or TBA and the shorter alkanes.

The Patterson effect is present in the analyzed mixtures. The more globular amines, TEA, TPA or TBA are order breakers of the longer alkanes. The amines of very large size, e.g., tridodecylamine, show an ordered structure.

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