

TABLE I
Physical properties of 2,4,6-triarylpyridines (5a-f)

Compound	R ¹	R ²	R ³	Yield %	Recryst. Solvent	m.p. °C	Lit. m.p. °C
5a	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	50	A	135-37	(138) ⁸
b	C ₆ H ₅	3,4-O ₂ CH ₂ C ₆ H ₃	C ₆ H ₅	55	B	150-51	(152-53) ⁹
c	C ₆ H ₅	C ₆ H ₅	3-Phenanthryl	50	C	122-23	(120-21) ¹⁰
d	4-BrC ₆ H ₄	C ₆ H ₅	C ₆ H ₅	58	A	152-53	(150-52) ⁹
e	4-BrC ₆ H ₄	3,4-O ₂ CH ₂ C ₆ H ₃	C ₆ H ₅	60	C	133-35	(136-38) ⁹
f	4-BrC ₆ H ₄	C ₆ H ₅	3-Phenanthryl	65	B	140-41	(140-42) ¹⁰

A = C₅H₅N-EtOH (1:4); B = EtOH; C = CHCl₃-MeOH (1:4)

9. Kendurkar, P. S. and Tewari, R. S., *Z. Naturforsch.*, 1974, **B29**, 552.

10. Tewari, R. S. and Gupta, K. C., *Indian J. Chem.*, 1976, **B14**, 829.

EXCESS GRUNEISEN PARAMETER AND INTERMOLECULAR INTERACTION IN BINARY LIQUID MIXTURES OF TRICHLOROETHYLENE

B. P. SHUKLA, V. N. MISHRA AND S. N. DUBEY
Department of Chemistry, National Degree College, Barhalganj, Gorakhpur 273 402, India.

THE Gruneisen parameter (Γ), which is a dimensionless measure of change in entropy with volume or thermal pressure, has been extended to liquid state for investigating the internal structure, lustering phenomena and remaining quasicrystalline lattice nature¹⁻⁶. By using some thermodynamic relations, Γ can be expressed by the following relation:

$$\Gamma = C^2 \alpha / C_p = \gamma - 1 / T \alpha \quad (1)$$

where C , α , C_p and γ represent sound velocity, thermal expansion coefficient, principal heat capacity at constant pressure and heat capacity ratio respectively. The sum of exponents of Mies' equation has been determined⁷ for liquid mercury, using Gruneisen number, assuming a condensed system of molecules and consisting of harmonic oscillators. Attempts to study Gruneisen parameter in liquid mixtures have been rare⁸. In the present paper the Gruneisen parameter has been extended to binary liquid mixtures and the value of excess Gruneisen parameter has been calculated using the relation

$$\Gamma^E = \Gamma_{mix} - \sum_{i=0}^2 x_i \Gamma_i \quad (2)$$

TABLE I
Excess Gruneisen Parameter for various systems at 30° C

x_1	Γ^E
C ₂ HCl ₃ + benzene system	
0.1112	0.023
0.3679	0.024
0.5456	0.030
0.6064	0.026
0.7435	0.021
0.9459	0.006
C ₂ HCl ₃ + toluene system	
0.1256	-0.005
0.2537	-0.029
0.6721	-0.037
0.7233	-0.028
C ₂ HCl ₃ + <i>p</i> -xylene system	
0.2299	-0.028
0.3390	-0.045
0.5717	-0.080
0.6011	-0.077
0.7598	-0.067
C ₂ HCl ₃ + chloroform system	
0.2299	-0.001
0.3399	-0.002
0.4665	-0.001
0.6863	0.001
0.7221	0.099
0.8367	0.001
C ₂ HCl ₃ + CCl ₄ system	
0.1343	-0.002
0.2258	-0.007
0.3196	-0.002
0.4385	+0.003
0.6352	-0.007
0.7258	-0.008
0.8319	-0.010
0.9439	-0.005

where Γ_{mix} is the pseudo-Gruneisen parameter of the mixture and i denotes the component i . The required data have been taken from earlier measurements⁹.

The Γ^E values for liquid mixtures are given in table 1. The values of excess Gruneisen parameter (Γ^E) have been fitted, by the least square method, to the equation

$$\Gamma^E/x_1x_2 = A + B(x_1 - x_2) + C(x_1 - x_2)^2, \quad (3)$$

where x_1 and x_2 represents the mole fractions of components 1 and respectively and A , B and C are constants which are characteristic of a system. The values of these constants are given in table 2. The Γ^E values plotted against the mole fraction of trichloroethylene given in figure 1 indicates that $\Gamma^E = \Gamma^E(x)$. The excess Gruneisen parameter is positive for $\text{C}_2\text{HCl}_3 + \text{benzene}$, negative for $\text{C}_2\text{HCl}_3 + \text{toluene}$. Still more negative values are obtained for $\text{C}_2\text{HCl}_3 + p\text{-xylene}$. In all these mixtures the maximum Γ^E values are obtained in the vicinity of equimolar concentration. The values of excess Gruneisen parameter for these systems follow the same trend as excess volume (V^E), excess free energy (G^E) and excess adiabatic compressibility (β_s^E) which have been studied earlier⁹⁻¹¹. This trend in the Γ^E value with the trends in the values of V^E , G^E and β_s^E for $\text{C}_2\text{HCl}_3 + \text{aromatics}$ may be explained on the basis of the increasing donor-acceptor interaction of C_2HCl_3 with aromatics having increasing number of CH_3 substituents in the aromatic ring, since the addition of CH_3 substituent to the aromatic ring will increase the π -electron density of the molecule which will act as π -type sacrificial electron donor towards C_2HCl_3 , the C_2HCl_3 molecule acting as π -type sacrificial electron acceptor on account of its reduced electron density due to 3Cl atoms directly attached to the ethylenic linkage.

For the systems trichloroethylene + halomethanes ($\text{C}_2\text{HCl}_3 + \text{chloroform}$ and $\text{C}_2\text{HCl}_3 + \text{CCl}_4$), both negative and positive values of Γ^E are obtained. For the higher concentration range, the Γ^E values have increased for the system $\text{C}_2\text{HCl}_3 + \text{chloroform}$, whereas its values decreased for the system $\text{C}_2\text{HCl}_3 + \text{CCl}_4$. The positive Γ^E for $\text{C}_2\text{HCl}_3 + \text{CHCl}_3$ near higher

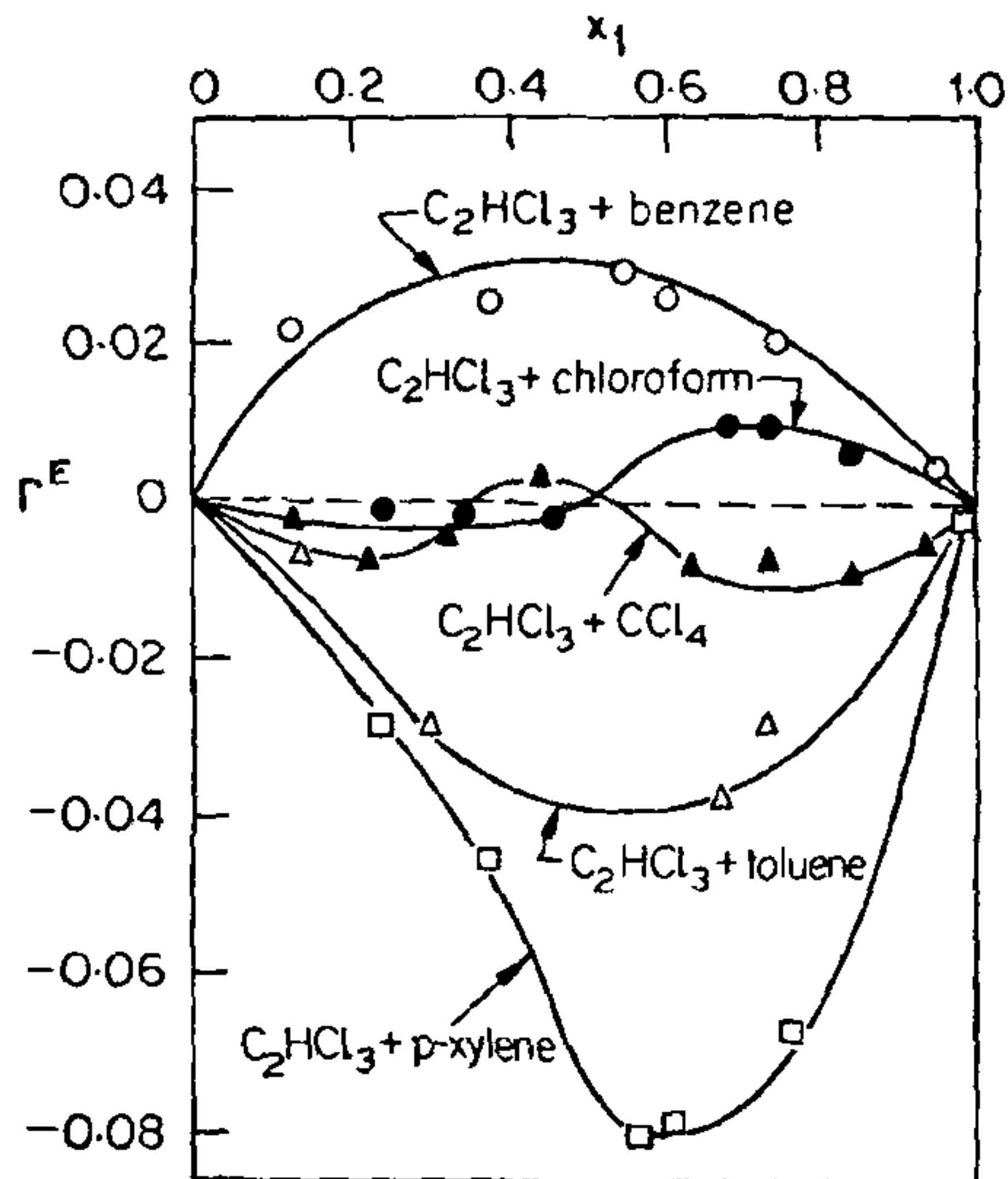


Figure 1. Plot of excess Gruneisen parameter (Γ^E) versus mole fraction of C_2HCl_3 at 303.15 K.

concentration range of C_2HCl_3 may be due to the formation of weak hydrogen-bond, on account of interaction of H atom of CHCl_3 with the π -electrons of ethylenic linkage of C_2HCl_3 . The negative value of Γ^E for $\text{C}_2\text{HCl}_3 + \text{CCl}_4$ may be due to the predominance of dispersion and dipole-induced dipole interaction between the two components, a fact which has been established by the excess viscosity measurements¹².

The authors are grateful to Prof. R. P. Rastogi for encouragement.

18 November 1982; Revised 5 February 1983

1. Knopoff, L. and Shapiro, J. N., *Phys. Rev.* 1970, **B1**, 3893.

TABLE 2

Values of constants A , B and C

System	A	B	C
$\text{C}_2\text{HCl}_3 + \text{benzene}$	0.1119	-0.0683	0.0940
$\text{C}_2\text{HCl}_3 + \text{toluene}$	-0.2229	0.0310	0.3562
$\text{C}_2\text{HCl}_3 + p\text{-xylene}$	-0.2876	-0.2030	0.0886
$\text{C}_2\text{HCl}_3 + \text{chloroform}$	0.0196	0.0424	-0.0479
$\text{C}_2\text{HCl}_3 + \text{CCl}_4$	-0.0109	-0.0321	-0.0754

2. Kor, S. K. and Tandon, U. S., *Solid State Commun.* 1972, **11**, 963.
3. Kor, S. K. Tandon, U. S. and Singh, B. K., *Phys. Lett.* 1972, **A38**, 187.
4. Tandon, U. S. and Pandey, S. K., *Phys. Lett.* 1972, **A41**, 161.
5. Pandey, H. C. and Pandey, L. D., *Phys. Status Solidi*, 1974, **65**, K 149.
6. Jain, R. P. and Pandey, J. D., *Indian J. Pure Appl. Phys.* 1974, **12**, 830.
7. Moelwyn-Huges, E. A., *Physical chemistry*, Pergamon Press, London and New York, p.332 1965
8. Mishra, R. L. and Pandey, J. D., *Chem. Scr.*, 1977, **11**, 65.
9. Nath, J. and Dubey, S. N., *J. Phys. Chem.*, 1980 **84**, 2166.
10. Nath, J. and Dubey, S. N., *J. Chem. Therm.*, 1979, **11**, 1963.
11. Dubey, S. N., Ph.D. Thesis, University of Gorakhpur, 1981.
12. Nath, J. and Dubey, S. N., *Phys. Chem.* 1981, **85**, 886.

ON THE TAXONOMIC POSITION OF *NYCTANTHES ARBOR-TRISTIS* L.

NEETA VAISHAMPAYAN AND Y. N. SHARMA
Botany Department, Government Science College,
Gwalior 474 002, India.

THE systematic position of *Nyctanthes arbor-tristis* is not clear. It was placed in the Oleaceae by Bentham and Hooker¹. A verbenaceous affinity for *Nyctanthes* is suggested by Stant². Airy Shaw³ assigned the genus to the sub-family Nyctanthoideae in the family Verbenaceae. In the present investigation an attempt has been made to compare the amino acid composition of the leaves of the genus *Nyctanthes* with some representative members of both Oleaceae and Verbenaceae for resolving the controversial position of this genus.

Leaves of all the taxa studied were collected locally. Methanolic extracts of leaves were applied directly to chromatographic paper. The solvent system used was *n*-butanol: acetic acid: water (4:1:5 upper layer). Detecting reagent was 3% ninhydrin solution. Different amino acids were identified with simultaneously run standards. A numerical assessment (matching coefficient) was made in the presence of absence of these amino acids.

$$\text{The matching coefficient}^4 = \frac{p+n}{p+n+d}$$

where *p*=positive match, *n*=negative match and *d*=mismatch

In *Nyctanthes arbor-tristis*, five amino acids were encountered on the chromatographic profile. Butyric acid was distributed throughout the families Oleaceae and Verbenaceae excepting *Jasminum grandiflorum*. *Nyctanthes*, all the investigated members of the Verbenaceae except *Jasminum sambac*, all the investigated members of the Verbenaceae except *Callicarpa macrophylla*, *Phyla nodiflora* and *Gmelina asiatica* possess Dihydroxyphenylalanine. Members of the Oleaceae except *J. flexile* and *nyctanthes* resembled each other in lacking glutamic acid which was constantly present in Verbenaceae except *Callicarpa macrophylla*, *Phyla nodiflora* and *Gmelina asiatica*. Histidine, Hydroxyproline and Lysine which are attributed to *Nyctanthes* are variably distributed within Oleaceae and Verbenaceae.

The highest matching coefficient i.e., 94.4% of *Nyctanthes* is with *Jasminum arborescence*. Next to this is an 88.8% association with *J. pubescence*, *J. auriculatum*, *J. humile* and *liqustrum nilgheriense*. With *J. grandiflorum*, *Nyctanthes* has a 77.7% association. *J. flexile* and *J. sambac* have a 72.2% association with *Nyctanthes*. The above results indicate a possible affinity of *Nyctanthes* with Oleaceous taxa as it has a high matching coefficient with them.

Members of Verbenaceae exhibit comparatively low matching coefficients with *Nyctanthes*. *Lantana camara* only has high i.e., 72.2% association with *Nyctanthes*. This is followed by a 50% matching coefficient of *Nyctanthes* with *Caryopteris wallichiana*, *Callicarpa macrophylla* and *Phyla nodiflora*. Both the species of *Gmelina* i.e., *G. arborea* and *G. asiatica* have a 38.8% association with *Nyctanthes*. With *Duranta plumeiri*, *Clerodendron phlomidis* and *Lantana indica*, *Nyctanthes* has 44.4%, 27.7% and 22.2% matching coefficients respectively. *Tectona grandis* exhibits a 33.3% association. The lowest matching coefficient i.e., 16.6% is shown between *Verbena officinale* and *Nyctanthes*.

The majority of studied genera of the family Oleaceae show that they possess high matching coefficients with *Nyctanthes* which indicate a possible relationship of *Nyctanthes* with this family. On the other hand, *Nyctanthes* is far from Verbenaceae as it has comparatively low matching coefficients with verbenaceous members. The present study therefore suggests a better assignment of *Nyctanthes* to the family Oleaceae rather than the Verbenaceae thus supporting the earlier suggestion made by Das and Rao⁵.

The authors are thankful to Prof. S. W. Khandekar for laboratory facilities and one of us (N.V.) to U.G.C. for financial assistance.

23 May 1982; 4 November 1982