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Excess Grüneisen Parameter of Binary Liquid Mixtures

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Abstract. Excess Grüneisen parameter (Γ^E) for five binary liquid mixtures of 1, 1, 2, 2-tetrachloroethane (TCE) with aromatic hydrocarbons at 298.15 K have been evaluated. The variation in the values of Γ for all the binary liquid mixtures clearly indicate the existence of specific interaction between the component liquids.

1. Introduction

In the theory of lattice dynamics[1], Grüneisen parameter has been found to be an important tool to study the thermodynamic and other properties like internal structure, clustering phenomenon and remaining quasi-crystalline lattice nature of the liquid state[2,3]. The study of Grüneisen parameter has been extended for some liquid mixtures[4,5], liquified gases[6], liquid metal alloys[7], liquid higher alkanes[8], castor oil[9] and molten salts[10]. The study of intermolecular interaction in the binary liquid mixtures of 1, 1, 2, 2-tetrachloroethane (TCE) with benzene (I), toluene (II), p-xylene (III), acetone (IV) and cyclohexane (V) at 298.15 K in the light of excess Grüneisen parameter (Γ^E) is a subject of present investigation. The necessary data for the evaluation of Γ^E have been taken from literature[11].

2. Theory

Grüneisen parameter is a dimensionless measure of the change in entropy with volume or thermal pressure and may be expressed as,

$$\Gamma = \left(-\frac{1}{C_v}\right)\left(\frac{\partial S}{\partial \ln V}\right)_T = \left(\frac{V}{C_v}\right)\left(\frac{\partial P}{\partial T}\right)_V$$

$$= \frac{\alpha V}{\beta_T C_v} = \frac{\alpha V}{\beta_s C_p} \quad (1)$$

With the help of some thermodynamic relations, the expression for Γ can be written as,

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(2) $$\Gamma = \frac{U^2 \alpha}{C_p} = \frac{\gamma - 1}{\alpha T}$$

where all the symbols have their usual meanings.

For the i^{th} liquid component in a mixture, it is given by

(3) $$\Gamma_i = \frac{U_i^2 \alpha_i}{(C_p)_i} = \frac{\gamma_i - 1}{\alpha_i T}$$

The value of Γ_{mix} is obtained by the relation,

(4) $$\Gamma_{mix} = \frac{U_{mix}^2 \alpha_{mix}}{(C_p)_{mix}} = \frac{\gamma_{mix} - 1}{\alpha_{mix} T}$$

In a binary liquid mixture, the ideal Grüneisen parameter, Γ_{idl}, is defined as

(5) $$\Gamma_{idl} = \sum_{i=1}^{2} x_i \Gamma_i$$

Thus, the excess Grüneisen parameter, Γ^E, for binary liquid system is given by

(6) $$\Gamma^E = \Gamma_{mix} - \sum_{i=1}^{2} x_i \Gamma_i$$

3. Results and Discussion

The excess Grüneisen parameter, Γ^E, has been evaluated for five binary liquid mixtures namely, TCE + benzene (I), TCE + toluene (II), TCE + p-xylene (III), TCE + acetone (IV) and TCE + cyclohexane (V) at 298.15 K. The values of Γ^E are presented in table 1 for all the systems. Γ^E has been plotted against mole fraction of TCE in fig. 1. An examination of Fig. 1 reveals that the values of Γ^E follow the sequence as under:

benzene > toluene > acetone > p-xylene

The values of Γ^E for the mixture TCE + benzene and TCE + p-xylene can be attributed to the existence of a specific interaction between TCE and the aromatic hydrocarbons which may be due to the formation of weak hydrogen bond through the interaction of the hydrogen of TCE with π-electrons of the aromatic ring. However, there is also a possibility that TCE is involved in the formation of a charge transfer complex with the aromatic hydrocarbons through the interaction of the chlorine atoms with the

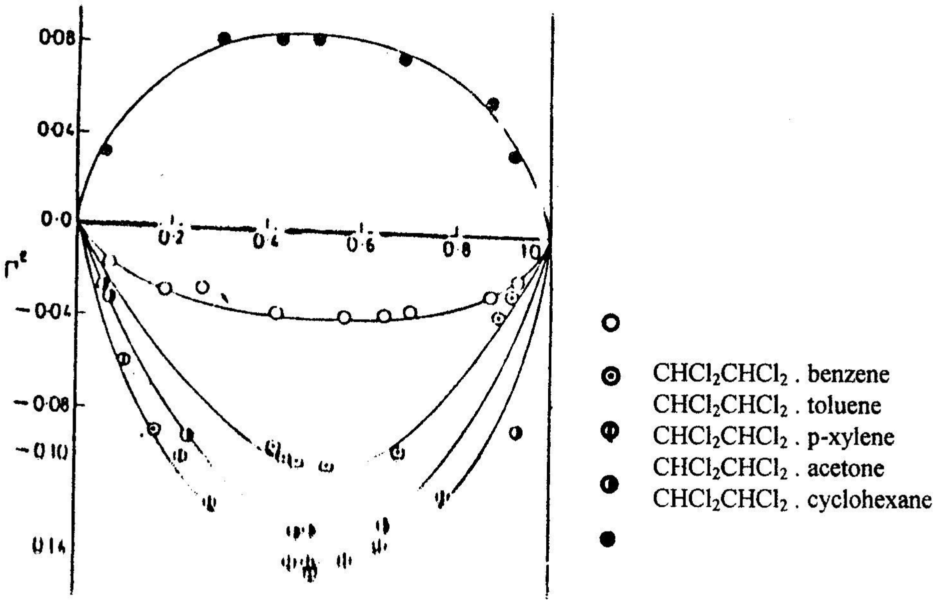

Fig. 1. Plot of Excess Grüneisen parameter (Γ^E) versus mole fraction of $CHCl_2$ $CHCl_2$ at 298.15 K

π-electrons of the aromatic ring. However, there is also a possibility that TCE is involved in the formation of a charge transfer complex with the aromatic hydrocarbons through the interaction of the chlorine atoms with the π- electrons of aromatic ring. The greater negative values of Γ^E in p-xylene than that of benzene can be attributed to the fact that the π-electron density of the aromatic ring is increased in p-xylene due to the presence of two $-CH_3$ groups. For the system TCE + acetone, the negative value of Γ^E shows that there exists a strong specific interaction between acetone and TCE leading to the formation of molecular complex between the two species in the liquid state. The positive value of Γ^E for the system TCE + cyclohexane is an indication of weak molecular interaction between the two components. Therefore, it may be concluded the Γ^E can be used as an important tool to study the intermolecular interaction between the component liquids. The variation of Γ^E with composition clearly indicates the existence of specific interaction between the components. On the basis of greater negative values of Γ^E for the system TCE + p-xylene, existence of strong specific interaction is concluded.

Table 1. Excess Grüneisen parameter for the binary liquid mixture od 1,1,2,2-tetrachloroethane at 298.15 K.

x_1	Γ^E	x_1	Γ^E
(I) TCE (x_1) + benzene (x_2)		(II) TCE (x_2) + toluene (x_2)	
0.0665	-0.0181	0.2623	-0.0894
0.1858	-0.0277	0.4200	-0.0936
0.1860	-0.0280	0.4364	-0.0989
0.2606	-0.0261	0.4586	-0.1008
0.4252	-0.0359	0.5325	-0.1012

0.5705	-0.0366	0.6841	-0.0943
0.6562	-0.0352	0.8942	-0.0340
0.7000	-0.0342	0.9001	-0.0248
0.8679	-0.0268		
0.9337	-0.0196		

(III) TCE (x_1) + p-xylene (x_2)		(IV) TCE (x_1) + acetone (x_2)		(V) TCE (x_1) + cyclohexane (x_2)	
0.0926	-0.0595	0.0604	-0.0295	0.0537	0.0314
0.2279	-0.0991	0.0713	-0.0299	0.3000	0.0839
0.2927	-0.1192	0.2374	-0.0873	0.4164	0.0852
0.4536	-0.1422	0.4579	-0.1309	0.5000	0.0863
0.4964	-0.1411	0.4964	-0.1288	0.6904	0.0820
0.5000	-0.1456	0.6507	-0.1291	0.8832	0.0596
0.5654	-0.1358	0.9267	-0.0831	0.9139	0.0384
0.6447	-0.1342				
0.7785	-0.1144				

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