ISSN 0974 - 9373

Vol. 21 No.1 (2017) **Journal of International Academy of Physical Sciences** pp. 83 - 90

Interaction Studies of Binary Liquid Mixtures through Pseudo-Grüneisen Parameter

Vinay Sanguri and Rupali Sethi

Department of Chemistry
University of Allahabad, Allahabad

Sunil

Department of Physical Sciences
MGCG Vishvavidyalaya, Chitrakoot, Satna (M.P.)

Email: chemsunilshukla@gmail.com

(Received February 12, 2017)

Abstract: Interaction studies of four binary liquid mixtures namely Dipropylene glycoldimethylether (DPGDME)+methanol+1-propanol+1-pentanol+1-heptanol] have been carried out by a dimensionless parameter (pseudo- Grüneisen) Γ. Using the thermal expansivity (α) and heat capacities ratio (ϒ) data for these mixtures, the values of Γ were computed for pure components their binary mixtures and their binary mixtures at 298.15 K and varying compositions. The results are discussed in the light of interactions involving in the mixtures.

1. Introduction

It is well known from the theory of lattice dynamics that the variation of anharmonicity in lattice vibrational frequency,ω, with molar volume, V, is represented by Grüneisen parameter as

$$\Gamma_i = \frac{d \ln \omega_i}{d \ln V} \tag{1}$$

Grüneisen assumed that all Γ are equal then the microscopic Γ_m can be expressed as

$$\Gamma_m = \frac{\alpha V}{C_P B^s} = \frac{\alpha V}{C_v B^T} = \Gamma \tag{2}$$

where B_s and B_T are the adiabatic and isothermal bulk modulus of elasticity, respectively, α, the thermal expansion coefficient, C_p and C_v are the heat capacities at constant pressure and constant volume respectively. The thermodynamic and other properties of solid crystal lattice have been studied using this parameter.

In the year 1970, Knopoff and Shapiro[1] extended this parameter for the structural study of liquids in the form

$$\Gamma = \frac{u^2 \alpha}{C_P} \tag{3}$$

where u is the ultrasonic velocity. By applying the standard thermodynamic relations (4) and (5)

$$\gamma = 1 + \frac{\alpha^2 TV}{C_P} \tag{4}$$

$$\gamma = \frac{C_P}{C_V} = \frac{\beta_T}{\beta_S} = \frac{Pu^2}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{5}$$

(3) takes the form

$$\Gamma\alpha = \frac{1}{T}\left[u^2\left(\frac{\partial V}{\partial P}\right)_T - 1\right] \tag{6}$$

which can also be written as

$$\Gamma = \frac{\gamma - 1}{\alpha T} \tag{7}$$

Here α, ϒ and T stands for thermal expansion coefficient, heat capacity ratio and temperature respectively. Pandey et al[2] employed Grüneisen parameter, for the first time, to study the compression of higher alkanes. After this several workers[3] used this parameter for the structural and physicochemical studies of liquids. The study of Grüneisen parameter, a diagnostic parameter, has been found to be very useful tool for investigating the internal structure, clustering phenomenon and the crystalline lattice nature of liquids. Also, the Grüneisen parameter is a dimensionless measure the change in entropy with volume or the thermal pressure and is usually investigated through the relations.

$$\Gamma = \frac{\alpha V}{\beta_T C_V} = -\frac{1}{C_V}\left(\frac{\partial S}{2\ln V}\right)_P = \frac{V}{C_V}\left(\frac{\partial P}{\partial T}\right)_V \quad . \tag{8}$$

With some thermodynamic transformations the above equation reduces to (7), where α, β_T, β_s, C_v C_p, ϒ and u are respectively thermal expansion coefficient, isothermal compressibility, adiabatic compressibility, heat capacities at constant volume and at constant pressure, the heat capacities ratio and velocity of sound.

Results and Discussion

For the calculation of Grüneisen parameter, Γ, we have employed simple (7), containing only the heat capacities ratio, ϒ= C_p/ C_v, and the thermal expansivity, α. Four binary liquid mixtures were considered for the present calculation. These systems are

(I) Dipropylene glycoldimethylether(DPGDME)+methanol

(II) DPGDME+1-propanol

(III) DPGDME+1-pentanol

(IV) DPGDME+1-heptanol

The results of accurate and precise measurements of densities (ρ) and ultrasonic velocities (u) at 298.15K are reported by Pal and Gaba[4-11]. All the molecular properties of pure component liquids (DPGDME, ethanol, 1-propanol, 1-pentanol and 1-heptanol) are compiled in Table-1. From the calculated values of ϒ and α, Γ_i of pure liquids and mixtures have been obtained using the values of Γ_i and Γ_m, the excess Grüneisen parameter, Γ^E, has been obtained from the relation

$$\Gamma^E = \Gamma_m - \left(x_1\Gamma_1 + x_2\Gamma_2\right),$$

where Γ_1 and Γ_2 are respectively the Γ values of pure liquids 1 and 2, with mole fraction x_1 and x_2. As the size of alkyl group increases the value of Grüneisen parameter increase which indicate larger clustering and more compact lattice structure during interaction. The trend with increasing mole fraction in case of mixture of (DPGDME +alkanols) of lower to higher alkyl chain length follows a continuous increase in Γ_m values showing more of clustering and chain linkage with increasing chain length thereby making the structure more compact and suitable to crystal lattice with defined geometrical shapes.

Amongst the highest mole fraction of each alcohol the value of Γ_m and Γ^E show a trend of constant increasing value with chain length (methanol, propanol, pentanol and heptanol) which proves that ratio of mole fraction and size of group determine the increase in enthalpy with volume or thermal pressure. All the interpretations are supported by data given in Tables 2,3,4, 5 and Fig.1

Table-1 Calculated values of Γ for pure liquids at 298.15K.

Liquids	Γ
DPGDME	1.46
CH_3OH	1.34
C_3H_7OH	1.41
$C_5H_{11}OH$	1.45
$C_7H_{15}OH$	1.49

Table-2 Calculated values of Γm and Γ_E for the binary mixture, PGDME+methanol at 298.15K.

x_1	Γ_m	Γ^E
0.023	0.5895	-0.75077
0.0705	0.6156	-0.73062
0.1312	0.6441	-0.70962
0.1632	0.6574	-0.70032
0.2094	0.6747	-0.68873
0.2514	0.6889	-0.67979
0.3018	0.7041	-0.6708
0.3598	0.7197	-0.66241
0.4036	0.7303	-0.65728
0.4549	0.7415	-0.65237
0.5022	0.7510	-0.64879
0.5449	0.7589	-0.64622
0.6169	0.7709	-0.64314
0.6494	0.7758	-0.64221
0.7083	0.7842	-0.64115
0.756	0.7905	-0.64083

0.8114	0.7972	-0.64099
0.8537	0.8020	-0.64145
0.9047	0.8074	-0.64237
0.9364	0.8106	-0.64313
0.9511	0.8120	-0.64352

Table-3 Calculated values of Γ_m and Γ^E for the binary mixture DPGDME+1-propanol at 298.15K.

x_1	Γ_m	Γ^E
0.0653	0.6308	-0.77947
0.1089	0.6443	-0.76837
0.1451	0.6550	-0.75967
0.2124	0.6737	-0.7447
0.2694	0.6884	-0.73312
0.3041	0.6969	-0.72653
0.3359	0.7044	-0.72077
0.3913	0.7168	-0.71136
0.4561	0.7305	-0.70125
0.5020	0.7396	-0.69464
0.5464	0.7481	-0.68864
0.6139	0.7602	-0.68023
0.6513	0.7666	-0.6759
0.7080	0.7758	-0.66976
0.7572	0.7834	-0.66483
0.8098	0.7912	-0.65993
0.8457	0.7963	-0.65679
0.9067	0.8046	-0.65182
0.9576	0.8113	-0.648
0.9746	0.8134	-0.64678

Table-4 Calculated values of Γ_m and Γ^E for the binary mixture DPGDME+1-pentanol at 298.15K.

x_1	Γ_m	Γ^E
0.0143	0.6185	-0.83509
0.0441	0.6258	-0.82807
0.1045	0.6403	-0.8141
0.1523	0.6514	-0.8033
0.2149	0.6657	-0.7895
0.2431	0.6721	-0.7834
0.2986	0.6843	-0.77162
0.3419	0.6936	-0.76263
0.3740	0.7005	-0.75607
0.4018	0.7063	-0.75047
0.4549	0.7172	-0.73995
0.5038	0.7271	-0.73048
0.5334	0.7330	-0.72485
0.6034	0.7466	-0.71182
0.6553	0.7564	-0.70241
0.6968	0.7641	-0.69504
0.7505	0.7739	-0.68569
0.7962	0.7820	-0.67791
0.8509	0.7916	-0.6688
0.9071	0.8012	-0.65966
0.9476	0.8079	-0.65321
0.9600	0.8100	-0.65126

Table-5 Calculated values of Γ_m and Γ^E for the binary mixture DPGDME+1-heptanol at 298.15K.

x1	Γ_m	Γ^E
0.0609	0.6475	-0.83814
0.1164	0.6573	-0.82688
0.157	0.6645	-0.81862

0.2117	0.6743	-0.80748
0.259	0.6827	-0.79783
0.3132	0.6924	-0.78676
0.3539	0.6997	-0.77842
0.406	0.7090	-0.76774
0.4533	0.7175	-0.75803
0.5056	0.7270	-0.74728
0.552	0.7353	-0.73773
0.5935	0.7428	-0.72918
0.6316	0.7497	-0.72132
0.7137	0.7645	-0.70436
0.7666	0.7741	-0.69342
0.8059	0.7813	-0.68528
0.8495	0.7892	-0.67625
0.9026	0.7988	-0.66524
0.9293	0.8037	-0.6597
0.9527	0.8079	-0.65485

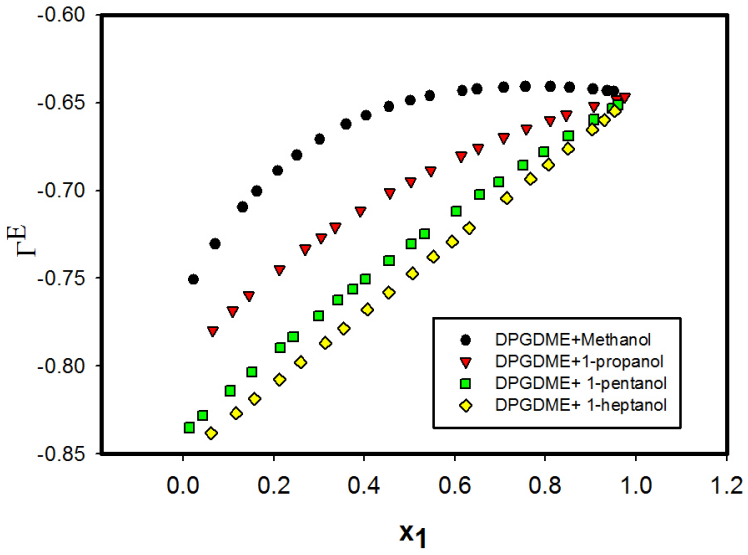

Fig-1. Variation of Excess Grüneisen parameter (Γ^E) with the mole fraction (x1)

References

1. L. Knopoff and J. N. Shaprio,Pseudo- Grüneisen parameters for liquids, *Phys Reo*, **B 1** (1970) 3893-3894.

2. J. D. Pandey and H. C. Pandey, Compressional study of higher alkanes through pseudo- Grüneisen parameters, *Phys Stat Solid*, **65 B** (1974) K149-K151.

3. S. K. Kor and U. S. Tandon, Compressional study of alcohols through pseudo-Grüneisen parameter, Solid State Physics, *Solid State Commun*, **11** (1972) 963-964.

4. S. K. Kor, U. S. Tandon and B. K. Singh, Psudo- Grüneisen parameter for liquid argon, *Phys Letters*, **A 38** (1972) 187-188.

5. J. D. Pandey and H. C. Pandey, Temperature dependence of pseudo- Grüneisen parameter for liquids, *Acustica*, **34** (1975) 115-116.

6. R. L. Mishra and J. D. Pandey, Excess Grüneisen parameter and interaction in binary liquid mixtures, *Acoustica*, **36** (1977) 342-345.

7. R. L. Mishra and J. D. Pandey, Excess Grüneisen parameter and intermolecular interaction in binary liquid mixtures, *Chemica Scripta*, **11** (1977) 65-77.

8. J. D. Pandey and A. D. M. Devid, Pseudo- Grüneisen parameter of molten salts and their mixtures, *J Chem Phys*, **77** (1982) 1064-1066.

9. J. D. Pandey, P. Chandra, R. Sethi and V. Sanguri, Estimation of thermodynamic properties of binary liquid mixtures on the basis of statistical mechanical theories, *Int J Thermodynamics*, **16** (2013) 10-19.

10. P. Mausbach, A. Koster, G. Rutkai, M. Thor and J. Vrabec, Comparative study of the Gruineisen parameter for 28 pure fluids, J. Chem. Phys, **144** (2016)144505-244511.

11. A. Pal and R. Gaba, Volumetric, acoustic and viscometric studies of molecular interactions in binary mixtures of dipropylene glycol dimethylether with 1-alkanols at 298.15K, J. Chem. Thermodynamics, **40** (2008) 818-828.