

## Evaluation of excess free volumes and excess internal pressures of binary solutions of *o*-chlorophenol at different temperatures

G V Rama Rao<sup>a</sup>, A Viswanatha Sarma<sup>b</sup>, D Ramachandran<sup>c</sup> & C Rambabu<sup>c</sup>

<sup>a</sup>Department of Physics, Dharma Appa Rao College, Nuzvid 521 201, Andhra Pradesh

<sup>b</sup>Ultrasonic Research Laboratories, Department of Physics, Andhra University, Visakhapatnam 530 003, Andhra Pradesh

<sup>c</sup>Department of Chemistry, Acharya Nagarjuna University PG Center, Nuzvid 521 201, Andhra Pradesh

*Received 10 December 2004; revised 25 April 2005; accepted 30 May 2005*

Ultrasonic velocity, density and viscosity have been measured experimentally and free volume as well as internal pressure and enthalpy were calculated for the binary mixtures of *o*-chlorophenol with ethyl benzoate, anisic aldehyde and acetonitrile at 303.15, 308.15, 313.15 and 318.15 K over the entire range of composition. Excess values of free volume, internal pressure, enthalpy and Gibb's free energy of activation have been calculated for these systems. The results were discussed in the light of existing theories of molecular interactions involved and chemical constitution of the liquid components.

**Keywords:** Excess free volumes, Excess internal pressure, Ultrasonic velocity, Density, Viscosity, Enthalpy, Binary mixture

**IPC Code:** B01J19/10

### 1 Introduction

During the last two decades, ultrasonic study of liquid mixtures has gained much importance in understanding the nature of molecular interactions and also for investigating the physico-chemical behaviour of such systems. For engineering applications, liquid mixtures, rather than single component liquid systems are used in processing and product formulations. Ultrasonic velocity and related data of liquid mixtures are found to be the most powerful tool in testing the theories of liquid state. In addition, ultrasonic velocity data can be utilized to deduce some useful thermodynamic properties of liquid mixtures, which are not easily accessible by any other means.

Thermodynamic and transport properties<sup>1-5</sup> of liquid mixtures have been extensively used to study the departure of liquid mixtures from ideality. In addition, these properties have been widely used to study the intermolecular interactions between the various species present in the liquid mixtures.

The excess thermodynamic functions<sup>6-10</sup> are sensitively dependent not only on the difference in intermolecular forces, but also on the difference in the size of molecules. Internal pressure and free volume are the fundamental properties of the liquid state which have been studied initially by Hildebrand and Scott<sup>11,12</sup> and subsequently used to investigate

molecular interactions of binary liquid mixtures. Thermodynamic and ultrasonic sound measurements were used to calculate the internal pressure, free volume and enthalpy of liquids and the effects of the change in composition and temperature on the excess free volume, internal pressure and enthalpy of binary mixtures have been evaluated by several researchers<sup>13-18</sup>. The study of excess free volume, excess internal pressure and excess enthalpy provides important information on molecular forces existing in the binary liquid mixtures. The variation of these properties with temperatures and composition for mixtures containing polar molecules and hydrogen bonded components may be complex due to a decrease or an increase in hydrogen bonding interaction due to mixing, depending upon the nature of the liquids whether they are polar or non-polar, the signs and magnitudes of these excess values can throw light on the strength of interactions. The present paper deals with the study of free volume, internal pressure, enthalpy and excess energy of activation of *o*-chlorophenol with ethyl benzoate, anisic aldehyde and acetonitrile at four different temperatures. An attempt has been made to correlate the excess values of these properties with the intermolecular interaction and the effect of temperature on these properties as well as on the intermolecular interaction has also been explained.

## 2 Experimental Details

AnalaR grade *o*-chlorophenol, ethylbenzoate, anisaldehyde and acetonitrile were redistilled and purified by the standard methods described<sup>19,20</sup>. Liquid mixtures of different compositions were prepared by mixing measured amounts of the pure liquids in cleaned and dried flasks. Ultrasonic velocity in three binary systems was measured by a single crystal variable path interferometer (Mittal, model F-81) at a frequency of 1 MHz. The accuracy of the velocity measurements is 0.02%. The densities of liquid mixtures were determined with a bicapillary pycnometer at 303.15, 308.15, 313.15 and 318.15 K over the entire range of composition and weights were taken to an accuracy of 0.05 mg. All the measurements were made at all the temperature with the help of a constant temperature bath (Toshniwal, Model No.GL15.01) with an accuracy of 0.01 K.

## 3 Theory

Hirschfelder *et al.*<sup>21</sup> obtained the relationship between the internal pressure  $P_i$ , the external pressure  $P$  and the free volume  $V_f$  of a liquid as follows:

$$V_f = [KRT/(P_i + P) (\rho + V_f^{1/3}/K)^2]^3 \quad \dots (1)$$

The relationship in Eq. (1) is very important since it shows that free volume of a molecule at a particular temperature and pressure depends only on the internal pressure of the liquid in which it is immersed.

The free volume of the binary mixtures have been computed using its relationship with the ultrasonic velocity and viscosity as follows:

$$V_f = (Mu/K\eta)^{3/2} \quad \dots (2)$$

where  $K$  is a proportionality constant which is independent of temperature having a value of  $4.28 \times 10^9$ . This relationship was established by Suryanarayana and Kuppaswami<sup>22</sup> assuming a cubic lattice structure for the condensed state of matter.

Suryanarayana and Kuppaswami<sup>22,23</sup> used an indirect alternative method for computing the internal pressure of a liquid from its viscosity, density and ultrasonic velocity. On the basis of dimensional analysis, using free volume concept, they derived the following expression for the internal pressure

$$\pi = b RT(K\eta/u)^{1/2} \rho^{2/3}/M^{7/6} \quad \dots (3)$$

where  $b$  is a packing factor and  $\eta$  is the viscosity. The other symbols have their usual meaning.

The enthalpy of a binary mixture is given by

$$H = \pi V_m \quad \dots (4)$$

where  $V_m$  is the molar volume

Excess Gibb's free energy of activation

$$G^E = RT[LN(\eta V) - \{x_1 LN(\eta_1 V_1) + x_2 LN(\eta_2 V_2)\}] \quad \dots (5)$$

where  $R$  is a gas constant,  $T$  the temperature and  $x_1$  and  $x_2$  are mole fractions of pure components of A and B respectively.

The strength of interaction between the component molecules of binary mixture is well reflected in the deviation of the excess functions from ideality. The excess functions are found to be more sensitive towards intermolecular interactions in the binary liquid mixtures.

Excess values for all the parameters are computed using the general formula:

$$Y^E = Y_{\text{exp}} - \{x_1 Y_1 + x_2 Y_2\} \quad \dots (6)$$

where  $Y$  represents any parameter and  $Y^E$  its value,  $Y_1$  and  $Y_2$  denote values of the parameter for the pure liquids and  $Y_{\text{exp}}$  represents corresponding experimental value for the mixture.

Values  $V_f^E$ ,  $\pi^E$ ,  $H^E$  and  $G^E$  were least-squares fitted to the Redlich-Kister type polynomial<sup>24</sup>

$$Y^E = x(1-x) \sum_{i=1}^N A_i (1-2x)^{i-1} \quad \dots (7)$$

The coefficients  $A_i$  of Eq. 7 along with the standard deviation  $\sigma(Y^E)$  are given in Tables 1-3. These coefficients are the adjustable parameters to get best-fit values of  $Y^E$ . The standard deviations  $\sigma(Y^E)$  were calculated by using the relation:

$$\sigma(Y^E) = [\sum (Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2 / m - n]^{1/2} \quad \dots (8)$$

where  $m$  is the number of experimental data points and  $n$  is the number of coefficients considered ( $n=3$  in the present calculation).  $Y_{\text{cal}}^E$  has been obtained from Eq. 7 using the best-fit values of  $A_i$ .

## 4 Results and Discussion

The free volume, internal pressure and enthalpy values are computed from the experimental results of density, viscosity and ultrasonic velocity using standard equations at four temperatures. It is noticed

Table 1—Values of the coefficients of Eq. (7) and standard deviation ( $\sigma$ ) Eq. (8) for the *o*-chlorophenol-ethyl benzoate system

Temp K	$A_0$	$A_1$	$A_2$	$\sigma$
		$V_f^E$		
303.15	-16.6183	12.2062	-2.5289	0.4716
308.15	-11.3443	-6.4138	-7.5465	0.0826
313.15	-20.4035	-3.8838	-11.8901	0.1388
318.15	-33.8700	4.5527	-10.6989	0.1936
		$\pi^E$		
303.15	2340.39	1518.46	2412.23	39.8208
308.15	1706.71	2697.37	1974.31	33.2193
313.15	2070.72	2860.00	2138.11	57.3487
318.15	2016.97	3446.53	1305.32	59.7758
		$H^E$		
303.15	369067	103353	293293	4084
308.15	265258	291087	217522	4121
313.15	315880	283878	222193	6724
318.15	345543	242453	101259	6709
		$G^E$		
303.15	678.17	721.39	-9.31	7.8074
308.15	566.26	573.6	472.26	7.1581
313.15	730.09	556.85	515.71	11.8836
318.15	876.21	463.26	261.55	11.9585

Table 2—Values of the coefficients of Eq. (7) and standard deviation ( $\sigma$ ) Eq. (8) for the *o*-chlorophenol-anisic aldehyde system

Temp K	$A_0$	$A_1$	$A_2$	$\sigma$
		$V_f^E$		
303.15	-11.5571	-1.9338	-2.1651	0.0692
308.15	-15.1181	-2.6819	-2.3895	0.1322
313.15	-17.2082	-5.7218	-8.2042	0.1082
318.15	-18.6415	-2.1961	-4.7353	0.0926
		$\pi^E$		
303.15	7839.26	1391.01	-2818.69	76.21
308.15	7173.84	887.72	-2792.26	118.28
313.15	6164.00	1640.48	-552.27	94.76
318.15	5536.54	854.18	-1296.45	51.75
		$H^E$		
303.15	855061	110642	-315020	7992
308.15	785891	65974	-307030	12253
313.15	679510	142117	-65382	10487
318.15	619763	57892	-142737	5446.3
		$G^E$		
303.15	1387.55	224.35	-314.05	10.2861
308.15	1392.09	287.74	-184.63	11.8073
313.15	1301.71	357.60	22.83	15.6397
318.15	1236.42	138.57	-134.68	10.0560

Table 3—Values of the coefficients of Eq. (7) and standard deviation ( $\sigma$ ) Eq. (8) for the *o*-chlorophenol-acetonitrile system

Temp K	$A_0$	$A_1$	$A_2$	$\sigma$
		$V_f^E$		
303.15	-17.2286	-1.8663	9.4319	0.2319
308.15	-22.8244	-1.9413	22.8590	0.6731
313.15	-23.7530	-0.9471	23.6061	0.5848
318.15	22.3707	1.1799	17.9628	0.4692
		$\pi^E$		
303.15	1533.56	2596.24	-2049.28	40.17
308.15	1946.89	1280.55	-2381.02	62.66
313.15	1920.89	931.60	-2487.97	54.39
318.15	1332.95	935.04	-1218.56	34.46
		$H^E$		
303.15	45393	129410	24178	4709
308.15	98893	90115	-141683	5192
313.15	106550	63793	-148901	930
318.15	93812	75011	-107615	1329
		$G^E$		
303.15	804.6	63.78	85.22	16.5364
308.15	958.87	57.01	-499.68	9.2727
313.15	957.73	-10.73	-480.57	4.1908
318.15	922.16	-6.72	-268.39	5.5159

(Figs 1 and 2) that free volume decreases whereas the internal pressure increases with increase in concentration of *o*-chlorophenol. This suggests the close packing of the molecules inside the shield, which may be brought about by the increasing magnitude of interactions<sup>25,26</sup>.

In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameters such as free volume, internal pressure and enthalpy. The deviation of physical property of the liquid mixtures from the ideal behaviour is a measure of the interaction between the molecules which is attributed to either adhesive or cohesive forces<sup>27</sup>.

In the present study, *o*-chlorophenol is a polar and has self-association character in other polar organic solvents. When ethyl benzoate, anisic aldehyde or acetonitrile is added to *o*-chlorophenol, it results in considerable decrease in intermolecular spaces between the molecules as suggested by Jacobson. This contributes to decrease in free volume and increase in the internal pressure and enthalpy giving rise to the negative  $V_f^E$  and positive  $\pi^E$  and  $H^E$  values as its dilution causes disruption of the aromatic C-H bond stretching. Excess values of  $\pi^E$  and  $H^E$  (Figs 3-5) in the binary mixtures of *o*-chlorophenol with ethyl

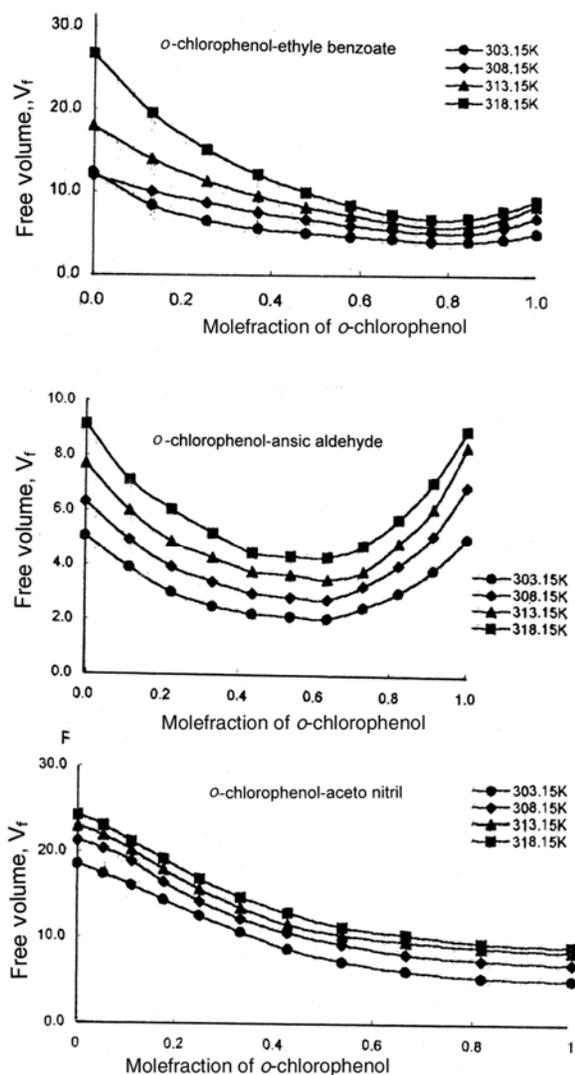


Fig. 1—Variation of free volume with molefraction of *o*-chlorophenol

benzoate and anisic aldehyde show a maximum value at 0.56 mole fraction of *o*-chlorophenol, then decrease with further increase in its concentration. This indicates the weakening of intermolecular interaction between component molecules. The negative values of  $V_f^E$  decrease with increase in the concentration of *o*-chlorophenol, attaining a minimum value at 0.56 mole fraction of *o*-chlorophenol, which indicate the presence of strong molecular interaction. The negative deviation of high magnitude in  $V_f^E$  and positive values of  $\pi^E$  and  $H^E$  indicate the formation of complexes between the hetero molecules of the mixture.

Figures 3-5 indicate clearly that increase in temperature causes variation in the excess thermodynamic properties as the local structure of the liquids are destroyed, thus affecting their

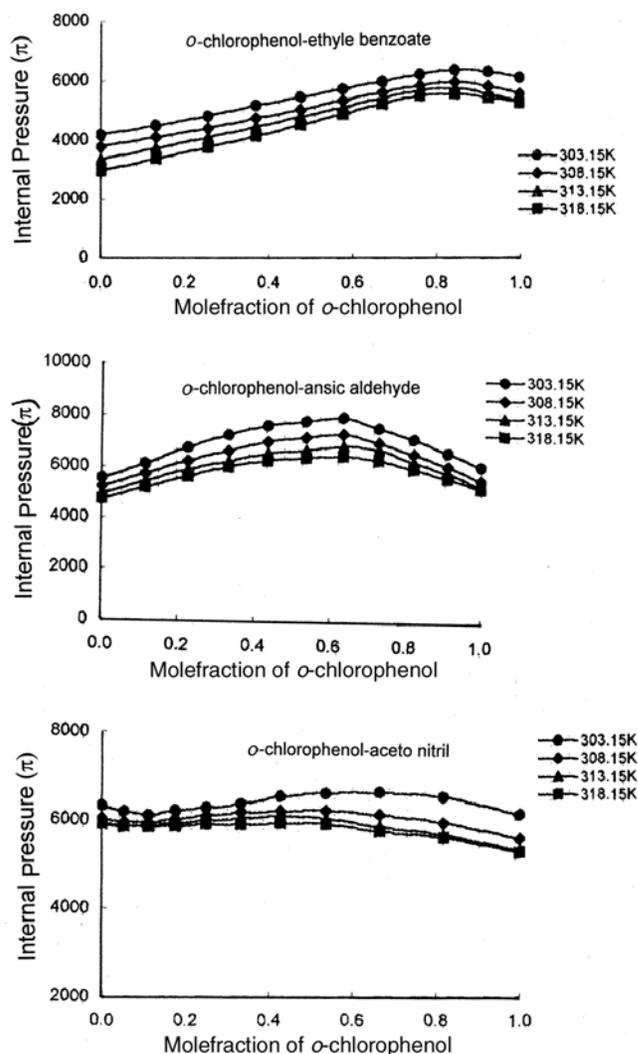


Fig.2—Variation of internal pressure with molefraction of *o*-chlorophenol

intermolecular free length and kinetic energy. Similar results were also reported earlier by several researchers<sup>28,29</sup>. In the present study, values of free volume, internal pressure and enthalpy for the three systems appear to be functions of mole fractions of both liquid components present in the mixtures.

The  $H^E$  values are positive for *o*-chlorophenol-ethyl benzoate and *o*-chlorophenol-anisic aldehyde systems which indicate the existence of strong interactions between the unlike molecules<sup>30</sup>. In the binary mixture of *o*-chlorophenol-acetonitrile, the excess values of  $\pi$  and  $H$  show both negative and positive deviations, thus suggesting weak intermolecular dispersive interaction between the mixing components in lower concentrations of *o*-chlorophenol and strong interactions in higher concentrations<sup>31</sup>.

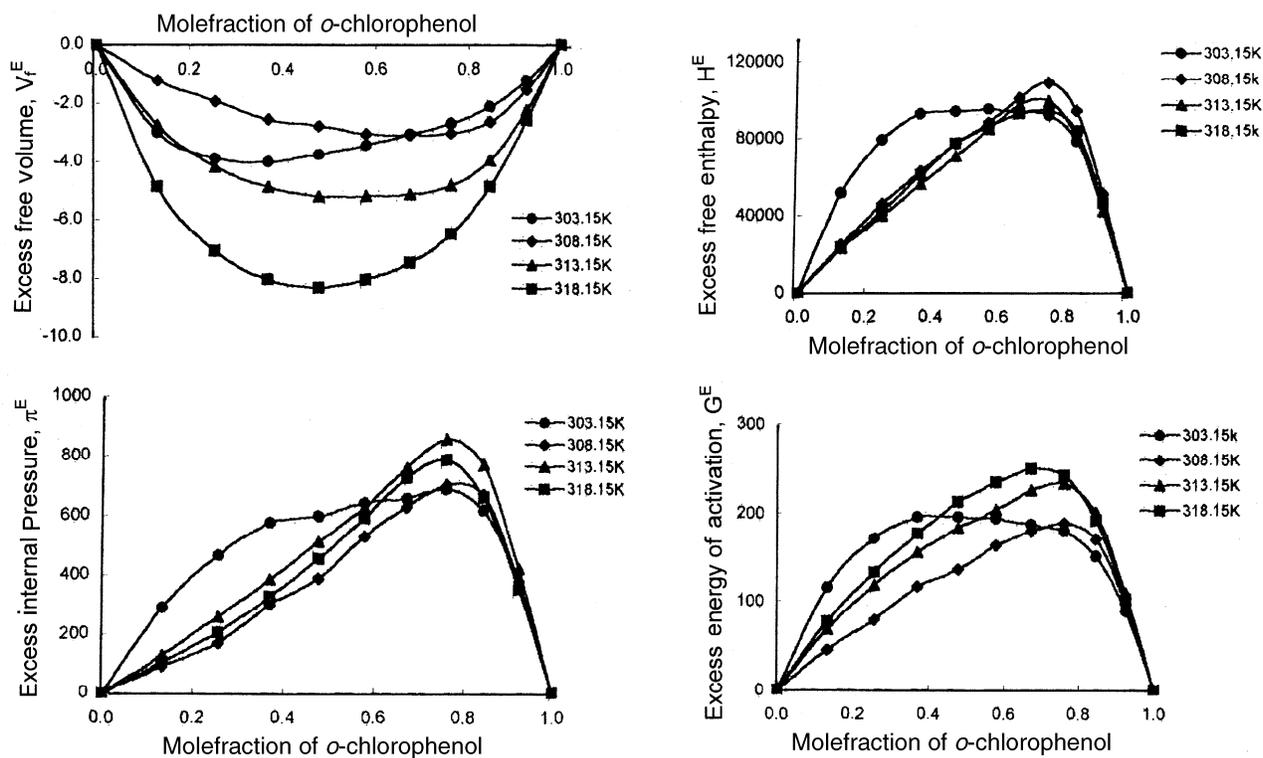


Fig. 3—Variation of excess free volume, internal pressure, enthalpy and energy of activation with molefraction for *o*-chlorophenol-ethyl benzoate system

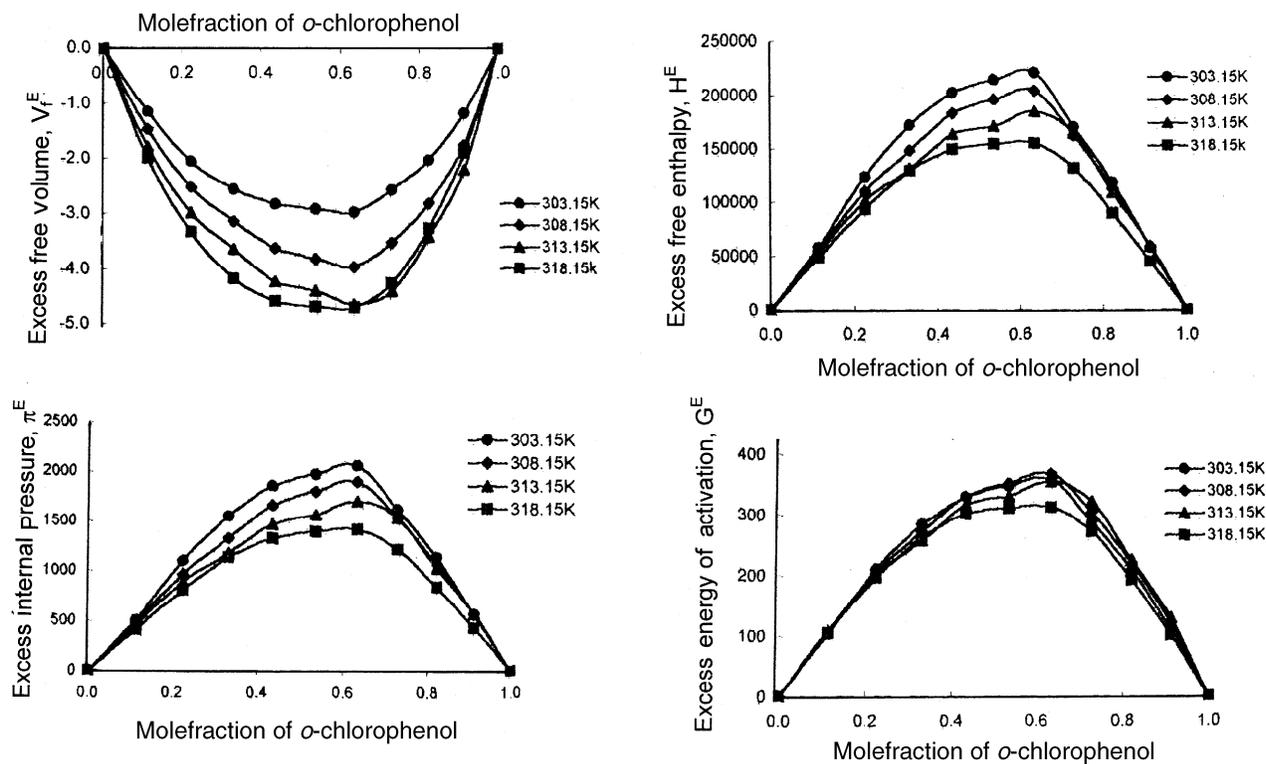


Fig. 4—Variation of excess free volume, internal pressure, enthalpy and energy of activation with molefraction of *o*-chlorophenol for *o*-chlorophenol-anisic aldehyde system

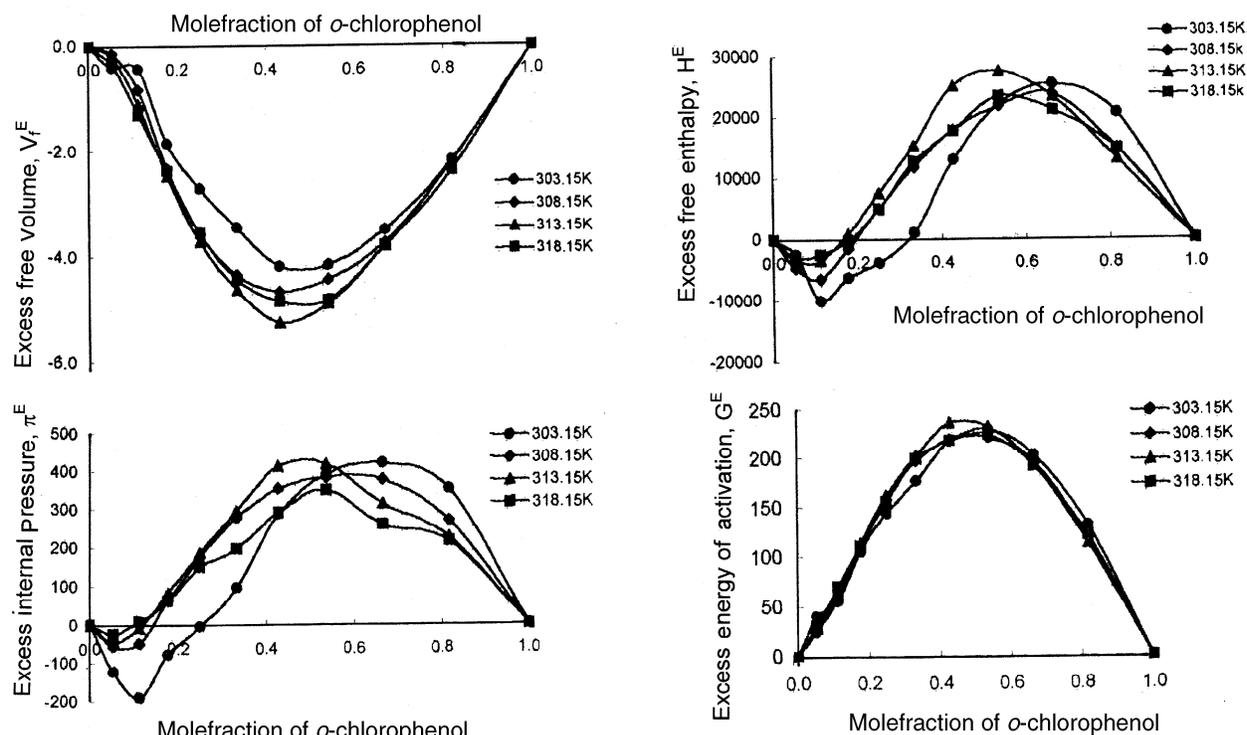


Fig. 5—Variation of excess free volume, internal pressure, enthalpy and energy of activation with molefraction of *o*-chlorophenol for *o*-chlorophenol-acetonitrile system

It is observed that  $G^E$  is positive in all the three systems at all the four temperatures. The positive values of  $G^E$  suggest the complex formation between the components of the mixtures showing strong interaction in the systems, while negative  $G^E$  is indicative of weak molecular interaction. Several attempts have been made by various researchers<sup>32-34</sup> to relate  $G^E$  to chemical interaction. However,  $G^E$  values are affected by different contributions where relative significance appear to vary with the chemical nature and the type of interacting molecules.

## 5 Conclusions

We may conclude that, *o*-chlorophenol which is a self-associating polar organic liquid has a tendency to form complexes with ethyl benzoate, anisic aldehyde and acetonitrile and the increase in its dilution causes disruption of aromatic C-H bond stretching as the self-association of *o*-chlorophenol is disrupted. It is also concluded that Suryanarayana<sup>35</sup> approach for estimating internal pressure and free volume of binary liquid mixtures, based on dimensional analysis using thermodynamic considerations is very well applicable in the present case.

## References

- 1 Rama Rao G V, Sarma A V & Rambabu C, *Indian J Pure & Appl Phys*, 42 (2004) 820.
- 2 Babu P, Chandrasekhar G & Prabhakara Rao N, *Indian J Pure & Appl Phys*, 38 (2000) 88.
- 3 Nikam P S, Mahale T R, *Indian J Pure & Appl Phys*, 39 (2001) 561.
- 4 Glinski J, Chavepeyer G & Jean-Karl Platten, *Chem Phys*, 272 (2001) 119.
- 5 Gonzalez-Salgado D, Tovar, C A, Cerdeirina C A, Carballo E & Romani L, *Fluid Phase Equil*, 199 (2002) 121.9 (2002) 121.
- 6 Nikam P S, Mahale T R & Mehdi Hasan, *Indian J Pure & Appl Phys*, 199 (2002) 121; 37 (1999) 92.
- 7 Ali A, Yasmin A & Nain A K, *Indian J Pure & Appl Phys*, 40 (2002) 315.
- 8 Rajendra V, *Indian J Pure & Appl Phys*, 34 (1996) 52.
- 9 Rama Rao G V, Sarma A V & Rambabu C, *Indian J Chem*, 43A (2004) 2518.
- 10 Suryanarayana C V, *Indian J Pure & Appl Phys*, 27 (1989) 751.
- 11 Hildebrand J H & Scott R L, *Regular solution* (Prentice Hall Englewood Cliff New Jersey, USA) 1962.
- 12 Hildebrand J H & Scott R L, *Solubility of non electrolyte*, 3<sup>rd</sup> Edn, (Reinhold, New York) 1964
- 13 Dhana Lakshmi A, *J Acoust Soc India*, 8(2) (1980) 29.
- 14 Arul G & Palaniappan, *Indian J Pure & Appl Phys*, 39 (2001) 561.
- 15 Pandey J D & Mishra R L, *Acustica*, 39 (1978) 2000.
- 16 Naidu P S, Prabhakara Rao N & Ravindra Prasad K, *Indian J Pure & Appl Ultrason*, 24 (2002) 36.

- 17 Devadoss, Thairiyaraja & Palaniappan, *Indian J Phys*, 77B(6) (2003) 669.
- 18 Prasad N, *Acustica*, 74 (1991) 171.
- 19 Vogel A I, *A text book of practical organic chemistry*, 5<sup>th</sup> Edn (John Willey, NewYork) 1989.
- 20 Riddick, J A, Bunger W B & Sokano T K, *Techniques in chemistry*, Vol 2, *organic solvents*, 4<sup>th</sup> Edn (John Willey, NewYork) 1986.
- 21 Hirschfelder J O, Stevenson D P & Eyring H, *J Chem Phys*, 5 (1937) 901.
- 22 Kuppusami J & Suryanarayana C V, *Indian J Acoust Soc India*, 5 (1977) 102.
- 23 Suryanarayana C V & Kuppusami J, *Indian J Acoust Soc India*, 4 (1976) 75.
- 24 Redlich O & Kister A T, *Ind Eng Chem*, 40 (1948) 345.
- 25 Arul G & Palaniappan L, *Indian J Pure & Appl Phys*, 39 (2001) 561.
- 26 Srinivasulu U & Naidu P R, *Indian J Pure & Appl Ultrason*, 17 (1995) 23.
- 27 Reddy K C, Subrahmanyam S V & Bhimsenachar J, *J Phys Soc Japan*, 19 (1964) 59.
- 28 Rao T S, Veeraiah N & Rambabu C, *Indian J Pure & Appl Phys*, 40 (2002) 850.
- 29 Prasad N, *Indian J Pure & Appl Ultrason*, 25 (2003) 25.
- 30 Naidu P S & Ravindra Prasad K, *Indian J Pure & Appl Phys*, 40 (2002) 264.
- 31 Padma Sree & Ravindra Prasad K, *Indian J Pure & Appl Phys*, 32 (1994) 954.
- 32 Reed T M & Taylor T E, *J Phys Chem Engg Data*, 9 (1964) 442.
- 33 Katti P K & Prakash O M, *J Chem Engg Data*, 11 (1966) 46.
- 34 Singh S N Sudhanshu, Kiran Kumar Barl & Ramesh Kumar Mandal, *Indian J Pure & Appl Ultrason*, 20 (1998) 39.
- 35 Suryanarayana C V, *The liquid state-A new out look*, *J Acoust Soc India*, 5 (1977) 11.