Contents lists available at ScienceDirect



thermochimica acta

Thermochimica Acta

# Topological investigations of thermodynamic properties of binary mixtures containing 2-pyrrolidinone

## J.S. Yadav, Dimple Sharma, V.K. Sharma\*

Department of Chemistry, Maharshi Dayanand University, Rohtak 124001, Haryana, India

## A R T I C L E I N F O

Article history: Received 3 September 2008 Received in revised form 4 February 2009 Accepted 4 February 2009 Available online 13 February 2009

Keywords: Excess molar enthalpies  $H_m^E$ Excess molar volumes  $V_m^E$ Isentropic compressibility changes of mixing  $\kappa_s^E$ Connectivity parameter of third degree  ${}^3\xi$ Interaction parameter  $\chi$ 

## ABSTRACT

Excess molar volumes,  $V_m^E$ , excess molar enthalpies,  $H_m^E$ , and speeds of sound data, u, of 2-pyrrolidinone (i)+ benzene or toluene or o- or p- or m-xylene (j) binary mixtures have been measured as a function of composition at 308.15 K. Isentropic compressibility changes of mixing,  $\kappa_S^E$  have been determined by employing speeds of sound data. The observed data have been estimated by employing Graph theory (which involves topology of the constituents of the mixtures). It has been observed that  $V_m^E$ ,  $H_m^E$  and  $\kappa_S^E$  values predicted by Graph theory compare well with their corresponding experimental values. IR studies lend further credence to the nature and extent of interaction of the proposed structures of molecular species in these mixtures.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

The amide structure is of great interest since it is related to numerous structural problems of molecular biology. Cyclic amides (lactams) are of great interest because nitrogen and carbon of a peptide bond in them are linked by a ring composed of methylene groups, 2-Pyrrolidinone is a cyclic amide (lactam) and on the basis of ab initio studies [1], an enveloped confirmation is assigned to 2-pyrrolidinone. Further 2-pyrrolidinone is known to be associated through intermolecular hydrogen bonding [2–4]. The addition of compound like benzene or toluene or o- or p- or m-xylene may tender either to rupture or enhance the self association of 2pyrrolidinone which in turn would reflect change in topology of the constituents of mixtures. In recent studies [5-8], we have employed topology of the components of the mixtures in terms of Graph theory, (i) to extract information about the state of their existence in pure as well as mixed state, and (ii) to evaluate excess molar volumes, excess molar enthalpies of binary mixtures. Thus it would be of interest to measure thermodynamic properties excess molar volumes,  $V_{\rm m}^{\rm E}$ , excess molar enthalpies,  $H_{\rm m}^{\rm E}$ , and speeds of sound data, u, of 2-pyrrolidinone + aromatic hydrocarbons binary mixtures and to analyze the observed data in terms of Graph theory to gain insight about the state of aggregation of components of mixtures in pure and mixed state.

## 2. Experimental

2-Pyrrolidinone (**2-Py**) [Fluka], benzene, toluene and o-, p-, mxylene (AR Grade) were purified by standard methods [9]. The purities of the samples were checked by measuring their densities (recorded in Table 1) at  $298.15 \pm 0.01$  K and these agreed within  $\pm 0.05$  kg m<sup>-3</sup> with their corresponding literature values [9,10].

Excess molar volumes,  $V_{\rm m}^{\rm E}$  for the binary (i+j) mixtures were determined at 308.15 K as a function of composition in a V-shaped dilatometer that has been described elsewhere [11]. The uncertainties in the measured  $V_{\rm m}^{\rm E}$  values are  $\pm 0.5\%$ .

Excess molar enthalpies,  $H_{\rm m}^{\rm E}$  for binary mixtures were measured at 308.15 K by 2-drop calorimeter (model 4600) supplied by the Calorimetry Sciences Corporation (CSC) USA in a manner as described elsewhere [7] and the uncertainties in the measured  $H_{\rm m}^{\rm E}$  values are  $\pm 1\%$ .

Speeds of sound, *u*, in binary mixtures were measured at  $308.15 \pm 0.01$  K using a variable path interferometer (Model M 84, Mittal Enterprises, India) and a measuring cell. Water from the thermostat was circulated through the cell to maintain the desired temperature. The speeds of sound values for the purified liquids at  $298.15 \pm 0.01$  K (recorded in Table 1) compare well with their corresponding experimental values [12–17]. The uncertainties in the measured speed of sound values are  $\pm 1$  ms<sup>-1</sup>.

Samples for IR studies were prepared by mixing (i) and (j) components in 1:1 (w/w) ratio and their IR spectra were recorded on Perkin Elmer-Spectrum RX-I, FTIR spectrometer.

<sup>\*</sup> Corresponding author. Tel.: +91 1262295012. E-mail address: v\_sharmachem58@rediffmail.com (V.K. Sharma).

<sup>0040-6031/\$ -</sup> see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.tca.2009.02.003

#### Table 1

Comparison of densities,  $\rho$ , and speeds of sound, u, of pure liquids with their literature values at 298.15 K.

Liquid	$\rho (\mathrm{kg}\mathrm{m}^{-3})$		<i>u</i> (m s <sup>-1</sup> )	
	Experimental	Literature	Experimental	Literature
2-Pyrrolidinone	1107.26	1107.22 [11]	1603 <sup>a</sup>	1603.1ª [12]
Benzene	873.62	873.60 [9]	1298	1298.9 [13]
Toluene	862.23	862.19 [9]	1305	1304.0 [14]
o-Xylene	875.91	875.94 [9]	1344	1345.0 [15]
p-Xylene	858.68	856.61 [9]	1310	1309.6 [16]
m-Xylene	860.17	860.02 [9]	1282	1282.2 [17]

<sup>a</sup> Value at 308.15 K.

#### 3. Results

Excess molar volumes,  $V_{\rm m}^{\rm E}$ , excess molar enthalpies,  $H_{\rm m}^{\rm E}$  and speed of sound, *u*, data of **2-Py** (*i*)+ benzene or toluene or o- or por m-xylene (*j*) binary mixtures over the entire range of composition at 308.15 K are recorded in Tables 2 and 3 respectively (plotted in Figs. 1–3). The isentropic compressibility,  $\kappa_{\rm S}$  for (*i*+*j*) mixtures were evaluated from speeds of sound data using Eq. (1)

$$\kappa_{\rm S} = \rho_{ij} u^2 \tag{1}$$

Table 2

Measured molar excess volumes,  $V^{E}$  data for the various (i+j) mixtures as a function of mole fraction,  $x_i$ , of component (i) at 308.15 K.

x <sub>i</sub>	$V^{E}$ (cm <sup>3</sup> mol <sup>-1</sup> )	Xi	$V^{\rm E} ({ m cm}^3{ m mol}^{-1})$
2-Pyrrolidinon	e (i) + benzene (j)		
0.0567	-0.117	0.4556	-0.551
0.1256	-0.236	0.5071	-0.557
0.1867	-0.332	0.5876	-0.539
0.2425	-0.404	0.6573	-0.496
0.2967	-0.463	0.7672	-0.388
0.3560	-0.507	0.8498	-0.278
0.4001	-0.536	0.9121	-0.173
2-Pyrrolidinon	e (i) + toluene (j)		
0.0667	-0.099	0.4873	-0.585
0.1398	-0.208	0.5678	-0.602
0.1927	-0.286	0.6459	-0.577
0.2526	-0.371	0.7332	-0.508
0.3018	-0.431	0.8076	-0.410
0.3467	-0.482	0.8561	-0.325
0.4117	0539	0.9213	-0.196
2-Pyrrolidinon	e (i)+o-xylene (j)		
0.0673	-0.101	0.4964	-0.527
0.1469	-0.215	0.5804	-0.539
0.1973	-0.283	0.6673	-0.503
0.2560	-0.348	0.7569	-0.434
0.3139	-0.410	0.8065	-0.371
0.3742	-0.461	0.8789	-0.257
0.4342	-0.504	0.9314	-0.160
2-Pyrrolidinon	e (i) + p-xylene (j)		
0.0456	-0.065	0.5268	-0.587
0.1096	-0.163	0.6013	-0.573
0.1773	-0.262	0.6973	-0.507
0.2567	-0.381	0.7453	-0.455
0.3327	-0.474	0.8124	-0.364
0.3864	-0.522	0.8581	-0.288
0.4597	-0.568	0.9001	-0.210
2-Pyrrolidinon	e (i) + m-xylene (j)		
0.0894	-0.172	0.5819	-0.455
0.1951	-0.307	0.6491	-0.442
0.2483	-0.352	0.7233	-0.409
0.3265	-0.399	0.7958	-0.353
0.3965	-0.428	0.8359	-0.310
0.4659	-0.447	0.8533	-0.286
0.5140	-0.456	0.9287	-0.166

#### Table 3

Measured molar excess enthalpies,  $H^{E}$  values for the various (i+j) mixtures as a function of mole fraction,  $x_{i}$ , of component (i) at 308.15 K.

x <sub>i</sub>	$H^{\mathrm{E}}$ (J mol <sup>-1</sup> )	x <sub>i</sub>	$H^{\mathrm{E}}$ (J mol <sup>-1</sup> )
2-Pyrrolidino	ne (i) + benzene (j)		
0.0642	-28.0	0.5390	-165.0
0.1193	-56.7	0.5681	-163.9
0.1893	-88.3	0.6369	-148.5
0.2289	-107.9	0.7004	-125.1
0.2721	-126.6	0.7850	-91.0
0.3688	-153.8	0.8539	-59.9
0.4379	-167.7	0.9346	-23.5
2-Pyrrolidino	ne (i) + toluene (j)		
0.0584	-2.2	0.4874	-30.9
0.1056	-5.9	0.5824	-25.0
0.1614	-11.1	0.6258	-21.3
0.2181	-17.4	0.6725	-16.4
0.3086	-25.8	0.7361	-8.3
0.4010	-30.9	0.8134	-0.4
0.4315	-30.7	0.8746	+4.2
2-Pyrrolidino	ne $(i)$ + o-xylene $(i)$		
0.0379	7.4	0.5424	121.0
0.0915	21.9	0.6124	124.4
0.1643	42.3	0.6782	117.7
0.2400	63.7	0.7597	104.9
0.3337	87.2	0.8384	80.8
0.3872	99.6	0.8928	57.1
0.5075	119.9	0.9686	19.9
2-Pvrrolidino	ne(i) + p-xylene(i)		
0.0662	10.8	0.5418	85.5
0.1454	25.1	0.6177	83.7
0.2230	42.2	0.6665	78.8
0.3159	61.4	0.7037	74.5
0.3408	64.1	0.7637	65.9
0.3926	73.4	0.8016	57.0
0.4923	83.1	0.8831	35.7
2-Pvrrolidino	ne $(i)$ + m-xylene $(i)$		
0.0746	51.7	0.5470	164.8
0.1388	84.9	0.6169	162.7
0.2047	112.4	0.6823	152.0
0.2436	125.1	0.7253	142.8
0.3400	146.5	0.8010	121.4
0.3918	155.3	0.8563	96.4
0.4918	166.9	0.9126	67.1

The densities,  $\rho_{ij}$  of binary mixtures were evaluated from their excess molar volumes data using the reaction:

$$V_{\rm m}^{\rm E} = \sum_{i=i}^{j} x_i M_i (\rho_{ij})^{-1} - \sum_{i=i}^{j} x_i M_i (\rho_{ij})^{-1}$$
(2)

where  $x_i$ ,  $M_i$  and  $\rho_{ij}$  are the mole fraction, molar mass and density of component (*i*) of binary mixture. Isentropic compressibility changes of mixing,  $\kappa_S^E$  for binary mixtures were determined using Eq. (3)

$$\kappa_{\rm S}^{\rm E} = \kappa_{\rm S} - \kappa_{\rm S}^{\rm id} \tag{3}$$

 $\kappa_{\rm S}^{\rm id}$  was obtained according to Benson and Kiyohara [18]

$$\kappa_{\rm S}^{\rm id} = \sum_{i} \phi_i \left[ \kappa_{{\rm S},i} + \frac{T V_i \alpha_i^2}{C_{p,i}} \right] - T \left( \sum_{i} x_i V_i \right) \frac{\left(\sum_{i} \phi_i \alpha_i\right)^2}{\left(\sum_{i} x_i C_{p,i}\right)} \tag{4}$$

where  $\phi_i$  is the volume fraction of component (*i*) in the mixture referred to as the unmixed state,  $x_i$  is the corresponding mole fraction, *T* is the absolute temperature, and  $\kappa_{\text{S},i}$ ,  $V_i$ ,  $\alpha_i$  and  $C_{p,i}$  are the isentropic compressibility, molar volume, thermal expansion coefficient, and molar heat capacity of the pure component (*i*), respectively. The values of  $\alpha$  and  $C_{p,i}$  were taken from literature [19].  $\alpha$  value for **2-Py** was evaluated in the same manner as suggested by



**Fig. 1.** Excess molar volumes,  $V_m^E$  at 308.15 K of (I) 2-pyrrolidinone (*i*)+benzene (*j*) ( $\bigcirc$ ); (II) 2-pyrrolidinone (*i*)+toluene (*j*) ( $\bigcirc$ ) mixtures.  $-V_m^E$  (exptl); ---  $V_m^E$  (Graph theory).

Hilderbrand et al. [20]. Such  $\kappa_{S}^{E}$  values for the studied mixtures are recorded in Table 4 and plotted in Fig. 4.

Excess molar volumes,  $V_m^E$ , excess molar enthalpies,  $H_m^E$  and isentropic compressibility changes of mixing,  $\kappa_S^E$  of various binary mixtures were fitted to Eq. (5)

$$X^{E}(X = V_{m} \text{ or } H_{m} \text{ or } \kappa_{S}) = x_{i} x_{j} [X^{(0)} + X^{(1)} (2x_{i} - 1) + X^{(2)} (2x_{i} - 1)^{2}]$$
(5)

where  $X^{(n)}$  (n = 0-2), etc. are the parameters characteristic of (i+j) mixtures and have been determined using the least square method and are recorded along with standard deviation,  $\sigma(X^{E})$  ( $X = V_{m}$  or



**Fig. 2.** Excess molar volumes,  $V_m^E$  at 308.15 K for (III) 2-pyrrolidinone (*i*)+o-xylene (*j*) ( $\Box$ ); (IV) 2-pyrrolidinone (*i*)+p-xylene (*j*) ( $\blacktriangle$ ); (V) 2-pyrrolidinone (*i*)+m-xylene (*j*) ( $\blacksquare$ ).  $-V_m^E$  (expt1); ---  $V_m^E$  (Graph).



**Fig. 3.** Excess molar enthalpies,  $H_m^E$  at 308.15 K for (1) 2-pyrrolidinone (*i*) + benzene (*j*)( $\bullet$ ); (II) 2-pyrrolidinone (*i*) + toluene (*j*)( $\bigcirc$ ); (III) 2-pyrrolidinone (*i*) + o-xylene (*j*)( $\square$ ); (IV) 2-pyrrolidinone (*i*) + p-xylene (*j*)( $\blacktriangle$ ); (V) 2-pyrrolidinone (*i*) + m-xylene (*j*)( $\blacksquare$ ) -  $H_m^E$  (exptl); ---  $H_m^E$  (Graph).

 $H_{\rm m}$  or  $\kappa_{\rm S}$ ) defined by

$$\sigma(X)^{\rm E} = \left[\frac{\sum (X_{\rm expt}^{\rm E} - X_{\rm cal. Eq. (5)}^{\rm E})^2}{m - n}\right]^{0.5}$$
(6)

where m, n are the number of data points and adjustable parameters in Eq. (5) in Table 5.



**Fig. 4.** Isentropie compressibilities changes of mixing,  $\kappa_5^{\text{E}}$  at 308.15 K for (I) 2-pyrrolidinone (*i*)+benzene (*j*) ( $\bigcirc$ ); (II) 2-pyrrolidinone (*i*)+toluene (*j*) ( $\bigcirc$ ); (III) 2-pyrrolidinone (*i*)+o-xylene (*j*) ( $\square$ ); (IV) 2-pyrrolidinone (*i*)+p-xylene (*j*) ( $\blacktriangle$ ); (V) 2-pyrrolidinone (*i*)+m-xylene (*j*) ( $\blacksquare$ ) –  $\kappa_5^{\text{E}}$  (exptl); ---  $\kappa_5^{\text{E}}$  (Graph).

## Table 4

Speeds of sound, u, isentropic compressibilities,  $\kappa_S$ , and isentropic compressibility changes of mixing,  $\kappa_S^E$  for the various (i+j) mixtures as a function of mole fraction,  $x_i$  of component (i) at 308.15 K.

2-Productors () + beneric () 0.064 073 0732 0733 0752 0.078 0733 0753 0753 0753 0.078 0753 0753 0753 0753 0.078 0753 0753 0753 0.079 075 075 075 0.079 075 075 0.079 075 075 075 0.079 077 0.079 077 0.070 070 0.070 0	x <sub>i</sub>	<i>u</i> (m s <sup>-1</sup> )	$\kappa_{\rm S}  ({\rm T}  {\rm Pa}^{-1})$	$\kappa_{\rm S}^{\rm E}$ (T Pa <sup>-1</sup> )
DobisCharPyP32P-81D1440175117531771D1480178107531781D1480178107531781D15251585533383D375215857334411D451516930044421D451516940714181D451516940714181D5521694011393D4791694007387D5574574411384D5571784411384D5571794411384D5571794411384D5571794411384D5571794411384D5161794413384D5171794413384D5181794413384D5191794413384D5191744453384D5191748453384D5191418453383D5291545467131D5291545467134D5391545467134D5391545467134D5391545467134D5391549433324D5391549433324D5391549451452D5391549451452D5391549451451<	2-Pyrrolidinone $(i)$ + benzene $(i)$			
DikisDisDisDisDisDikisDisDisDisDisDissDisDisDisDisDissDisDisDisDisDissDisDisDisDisDissDisDisDisDisDissDisDisDisDisDissDisDisDisDisDissDisDisDisDisDissDisDisDisDisDissDis<	0.0564	1274	703.2	-9.1
0.48819006.96-2.210.2366.23.4-3.830.23713.866.6-3.830.23713.866.6-3.830.43713.860.6-3.830.43713.860.6-3.830.43713.860.6-3.830.43714.7-4.81-4.320.63714.744.71-4.41.80.63714.7744.71-4.830.63714.7744.71-4.830.63714.7644.71-4.830.63714.7744.71-4.830.63714.7564.9-2.720.73213.527.75.3-7.622.790013.2364.3-3.530.73213.964.30-3.530.73413.965.3-3.520.73514.965.43-3.530.74413.965.3-3.520.74514.2443.63-3.530.74443.9-3.53-3.520.74514.943.3-3.530.74514.943.9-3.530.74514.943.3-3.530.74514.943.9-3.540.74514.943.9-3.540.74514.943.9-3.540.74514.943.9-3.540.74514.943.9-3.540.74514.943.9-3.540.74514.943.9-3.540.	0.1149	1291	675.2	-17.7
D281D251D55.4D65.4D72.2D271D36D61.0D38.1D372D36D33.1D38.1D373D36D33.1D38.1D374D48.1D31.1D31.1D558D42.1D49.1D49.1D558D42.1D49.1D49.1D578D42.1D49.1D49.1D611D73.1D73.1D49.1D622D32.1D73.1D49.1D623D33.1D73.1D49.1D424D49.1D49.1D49.1D425D49.1D49.1D49.1D426D49.1D49.1D49.1D427D49.1D49.1D49.1D428D49.1D49.1D49.1D429D49.1D49.1D49.1D429D49.1D49.1D49.1D431D49.1D49.1D49.1D441D49.1D49.1D49.1D441D49.1D49.1D49.1D441D49.1D49.1D49.1D441D49.1D49.1D49.1D441D49.1D49.1D49.1D441D49.1D49.1D49.1D442D49.1D49.1D49.1D443D49.1D49.1D49.1D444D49.1D49.1D49.1D444D49.1D49.1D49.1D444D49.1D49.1D49.1D445D49.1D49.1D49.1D446D49.1D49.1 <t< td=""><td>0.1488</td><td>1300</td><td>659.6</td><td>-22.1</td></t<>	0.1488	1300	659.6	-22.1
D218D060D18D2521364563.3-38.9045731380337.0-42.10045731380337.0-42.1004574904.4-42.1005871497904.4-43.2005871497904.4-35.7005871497467.1-35.700581147.8446.1-354.60718149.9400.7-37.60718149.9400.7-37.60718150.9401.6-27.60718120.9640.0-27.60718120.9640.0-27.60718120.9640.0-35.70718120.9640.0-35.70718120.9640.0-45.50728140.9120.9-463.00739140.9120.9-45.30739140.9120.9-55.20749140.945.3-55.20759141.8154.3-55.20759141.945.3-25.50759141.945.4-55.20759141.945.4-25.20759141.945.4-25.20759141.945.4-35.20759141.945.4-25.20759141.945.4-25.20759141.945.4-25.20759141.945.4-25.2075915.915.9-25.90759141.9 </td <td>0.2261</td> <td>1322</td> <td>625.4</td> <td>-30.2</td>	0.2261	1322	625.4	-30.2
1.75219866.1	0.2718	1336	606.0	-33.8
D42901389137.91.2D43111404489.4-4.2D53821404489.4-4.2D53871407-4.8-4.8D53871407-4.8-4.8D7161469-107.7-4.8D7161469-107.7-4.8D7161469-107.7-2.8D538010.6-2.76-2.6D539157.2-3.5-4.2D736140964.0-3.5D734130364.10-4.35D734130464.0-3.5D734130464.0-3.5D734130464.0-3.5D734130464.0-3.5D735144.4-3.5-5.2D736144.8-3.5-5.2D738144.8-3.5-5.2D738144.8-3.5-5.2D738144.8-3.5-5.2D738144.8-3.5-5.2D738144.8-3.5-7.2D749148-3.5-7.2D749148-3.5-7.2D749148-3.5-7.2D749148-7.4-7.2D749148-7.4-7.2D749148-7.4-7.2D749149-7.4-7.2D749149-7.4-7.4D749149-7.4-7.4D749149-7.4-7.4	0.3752	1368	563.3	-39.9
DABS140520.004.29DS391401495.4-43.2DS391471467.1-4.34DS311473447.1-3.34DS31153441.6-3.34DS32153441.6-3.34DS33141.6-3.34-3.34DS33153441.6-3.34DS3315364.0-3.35DS34130964.0-4.35DS3513467.6-3.37DS44132.364.0-4.35DS34134867.6-3.37DS44143.1-5.22DS50144.814.31-5.22DS50144.814.31-3.52DS59144.845.0-3.56DS59144.945.0-3.56DS59142.145.6-3.36DS59142.145.6-3.36DS59143.145.6-3.36DS59143.145.6-3.36DS59143.145.6-3.36DS59143.145.6-3.36DS59143.145.6-3.36DS59143.145.6-3.36DS59144.145.0-3.66DS59143.145.6-3.36DS59143.145.6-3.36DS59143.145.6-3.36DS59143.145.8-3.46DS59143.145.8-3.46DS59143.1-3.45	0.4379	1389	537.9	-42.1
0.23891.941	0.4851	1405	520.0	-42.9
0.60571477467.1-41.80.7361409448.1-35.40.7361409448.7-36.70.7361400440.7-36.70.737172172.5-16.20.812157172.5-16.20.812129.064.0-27.20.736139.064.0-27.20.737138.064.0-27.20.738139.064.0-35.70.738139.064.0-35.70.739139.056.7-55.70.736149.056.7-55.70.4268139.444.0-50.60.4268149.0-24.2-24.20.737147.445.50-35.60.737147.445.50-35.60.73816238.6-15.60.74914245.6-36.60.723147.445.0-24.20.726139.0610.4-10.90.737138.055.8-15.30.738139.055.9-16.60.737138.055.9-16.20.738149.0451.3-24.30.739138.055.9-16.20.739138.055.9-16.20.739138.055.9-16.20.739138.055.9-15.20.739138.055.9-15.20.739138.055.9-15.20.739139.067.9-24	0.5389	1424	499.4	-43.2
0.6811478448.1	0.6267	1457	467.1	-41.8
0.7161409440.7-36.70.9132156401.6-7.760.913212964.0-7.760.913212964.0-35.90.14213066.0-35.90.1434132364.0-35.90.144132364.0-35.90.14413066.0-35.70.31413066.0-35.50.31413066.0-35.50.31413066.0-35.50.31414053.65-52.20.5190141851.43-56.20.529014445.0-35.50.73314445.0-35.50.73414866.7-31.60.73514445.0-35.60.73214445.0-35.60.73314667.7-10.90.74213667.7-10.90.735137.5-55.9-55.90.73713855.8-55.30.73314057.7-21.00.735139397.7-25.20.73614944.7-24.30.73713855.8-55.30.73814957.9-27.60.73713855.8-55.30.73814944.13-24.30.73713855.8-7.60.738139397.7-15.50.75513037.8-3.80.75513037	0.6811	1478	448.1	-39.4
0.8298157640.16-27.62-3yron8linone ()++oluene ()0.02960.43064.0-32.90.1342130064.0-32.90.1343130264.0-32.90.1344132.364.10-35.90.2358134.8607.6-53.70.2458139.454.19-36.60.2561139.454.19-36.60.2572149.445.10-36.20.2578149.445.10-36.20.2578140.243.56-33.60.2579140.243.56-33.60.257916238.06-11.60.257216238.06-11.60.2572131440.616.00.257213956.7-10.00.257214955.7-10.00.257214955.7-10.00.257214955.7-10.00.257149.556.7-22.20.567145.5496.7-22.00.577149.556.7-22.00.572149.556.9-15.50.572149.556.9-25.10.575145.5496.7-22.10.575145.5496.7-24.30.575149.556.7-25.10.575149.549.7-25.10.75313939.7-15.50.75413945.1-75.20.755149.567.8	0.7316	1499	430.7	-36.7
0.9321572375.3-1622.1yrndianc (1+ tolucn: ()22664.9-22.20.034330066.40-35.90.174132.364.10-45.50.784132.364.10-45.50.3741138055.7.7-58.50.48450.5.7.7-58.50.481149.850.5.7-58.50.481149.850.5.7-58.50.481149.850.5.7-58.50.481149.850.5.7-58.50.481149.845.3.0-38.50.723147.445.3.0-38.50.724142.243.5.6-33.60.724142.243.5.6-33.60.724142.243.5.6-33.60.724138.164.0.7-10.10.824132.444.6.6-12.00.824133.164.0.7-13.10.737138.3558.8-15.30.437138.3558.9-16.60.475148.3-24.3-24.30.475148.3-24.3-24.30.475149.339.7-25.50.565149.545.7-24.30.746149.545.7-24.30.747138.355.8-36.60.758149.545.7-24.30.759149.545.7-24.30.759149.545.7-24.30.759149.545.7-24.30.759	0.8238	1536	401.6	-27.6
2 hynolikinon (i) + toluene (j)	0.9132	1572	375.5	-16.2
0.0026         6449         -272           1342         1309         6640         -3539           0.1784         1323         6430         -485           0.1784         1323         6430         -485           0.3741         1380         563.7         -585           0.3741         1380         563.7         -585           0.480         1494         524         -586           0.480         1494         524         -586           0.5796         1431         465.2         -522           0.5796         1463         464.0         -436           0.5796         1463         464.0         -436           0.5796         1463         464.0         -336           0.5796         1463         464.0         -345           0.5796         133         60.6         1.16           0.584         1524         488         -53.0           0.5976         133         60.7         -12           0.430         1349         50.0         -34.3           0.519         1349         50.0         -24.3           0.519         1349         50.8         -53.3 <td>2-Pyrrolidinone (<i>i</i>) + toluene (<i>j</i>)</td> <td></td> <td></td> <td></td>	2-Pyrrolidinone ( <i>i</i> ) + toluene ( <i>j</i> )			
0.13421309664.0-35.90.73841330643.0-43.50.23551348607.6-53.70.23561349543.9-53.60.42081394544.9-58.60.4208140925.65-53.80.5199141851.43-56.20.51991419445.1-50.20.723140453.0-22.50.7241402453.6-33.60.725156230.6-11.60.726156230.6-11.60.727100-20.20.72813960.61.20.729138358.8-15.30.720138358.9-16.60.721138359.9-16.60.7231405441.3-22.10.7231405441.3-24.10.7231405441.3-24.30.72315037.6-24.30.72314951.4-7.60.72313067.1-7.60.73413967.1-7.60.73512967.1-7.60.735130167.18-3.60.735130167.18-3.60.73613967.1-3.60.73713967.1-3.60.73813967.2-3.60.73914567.3-3.60.73613967.3-3.60.73713967.1	0.0926	1295	684.9	-27.2
0.17841323643.0-43.50.25551348667.6-53.70.37411380950.3-59.50.4680139454.63-59.50.4781148950.63-58.20.59914851.43-59.50.79761474443.0-43.60.77831474453.6-33.60.77841474453.6-33.60.78491492435.6-33.60.78491492435.6-33.60.7849133640.6-11.60.848152.448.8-22.50.9202136677.7-1.00.1433136677.7-1.00.21361346610.4-3.90.403136677.7-1.00.2382136059.8-15.30.40371389550.9-16.60.415414852.70-20.70.4254149.554.4-23.20.4254149.554.4-24.30.755150.9424.7-21.00.733147.9451.8-24.30.73415339.97-75.60.735150.9424.7-21.00.735150.9424.7-21.60.73515339.97-75.60.734132663.7-75.60.73513961.9-44.60.73513961.9-44.60.73513961.9-3	0.1342	1309	664.0	-35.9
2.258134607.6-53.70.274113053.7-59.50.42681304544.9-59.50.4268140952.6-58.20.5796144.845.1-59.50.6769140245.0-59.50.6769140445.0-59.50.67691402450.0-39.50.6769152.4408.3-22.50.6262156.230.6-11.60.2922156.230.6-11.60.2922136.0607.7-10.10.376134.5607.7-10.10.379136.059.8-15.30.474140.959.9-16.60.475140.857.0-20.70.379138.059.9-16.60.475140.950.9-15.60.475140.950.9-16.60.475140.950.9-15.20.675145.546.7-24.30.675149.043.1-24.30.675149.043.1-24.30.786150.943.1-76.10.79713858.9-24.30.793149.043.1-24.30.793149.043.1-24.30.794159.039.1-75.10.795149.069.1-75.60.794159.039.1-75.10.795139.069.1-75.10.795139.069.1 <td< td=""><td>0.1784</td><td>1323</td><td>643.0</td><td>-43.5</td></td<>	0.1784	1323	643.0	-43.5
0.741130503.7-959.50.42861409526.5-558.20.51901418514.3-552.20.5796143.4495.2-52.30.6766143.4495.2-53.60.7123147.4453.0-33.60.7449142.243.5-33.60.848152.4408.3-22.50.9262150.230.6-11.60.848152.4408.3-22.50.9262150.230.6-11.60.237133.1640.61.20.849134.6610.4-3.90.849134.6610.4-3.90.849134.6610.4-3.90.849136.058.8-15.30.849136.058.4-8.40.131640.61.2-7.60.849136.058.4-8.40.737136.058.4-8.40.737136.058.4-8.40.737137.067.4-7.20.744138.059.6-7.40.755145.049.6-7.40.757145.049.6-7.40.756159.042.4-7.50.757149.067.8-7.60.758159.042.4-7.50.757139.167.8-7.60.757139.167.8-7.60.757139.167.8-7.60.757139.151.2-7.8 <td>0.2585</td> <td>1348</td> <td>607.6</td> <td>-53.7</td>	0.2585	1348	607.6	-53.7
0.42681394544.9545.955.960.51991418514.3-55.20.5796143452.0-55.20.57661463464.0-43.60.7123147.443.0-39.50.749152.30.6-10.60.848152.440.63-22.50.926.2152.30.61.10.849133.1640.61.20.4493136.667.7-1.00.1493136.655.8-7.50.4393136.055.8-7.50.4393138.055.8-7.50.4393138.055.8-7.50.4373149.041.3-2.210.567145.549.67-2.42.60.512914954.7-2.42.60.529149.045.18-2.5.10.7864159.045.7-1.00.834159.045.7-2.220.567145.5496.7-2.42.60.785159.045.7-2.220.567145.045.13-2.5.10.785159.045.7-2.220.567145.549.67-2.220.567145.549.67-2.220.567145.549.67-2.220.567145.549.67-2.220.567145.549.67-2.220.567145.549.67-2.220.567145.5-2.57-2.570.557<	0.3741	1380	563.7	-59.5
0.48181409526.5	0.4268	1394	544.9	-59.6
0.5199141854.3-55.20.57961434495.2-52.20.57661463464.0-43.60.71231474453.0-33.60.7491492435.6-33.60.8481524408.3-22.50.826152306.0-11.60.437133640.61.20.4393136627.7-1.00.232130558.8-8.40.439136559.9-16.60.437138558.9-8.40.379138559.9-16.60.437149514.7-22.20.567145496.7-21.00.5129149514.7-22.20.567135396.7-15.50.7331479451.8-24.30.73515037.6-8.32.4ymditome (/) + p-xylene (/)-7.6-7.60.735139673.8-7.60.735139673.8-7.60.735139673.8-7.60.736139673.8-33.60.737139673.8-33.60.738139673.8-33.60.737139673.8-33.60.735139673.8-3.60.737139673.8-3.60.738139673.8-3.60.737139673.8-3.60.737139674.8-3.60.737	0.4818	1409	526.5	-58.2
0.57961434495.252.20.67661463464.043.60.71231474453.039.50.749149.2453.633.60.8481524408.322.50.9262156238.06-11.62-hyroildinone (1)*o-xylene (1)	0.5199	1418	514.3	-56.2
0.67661463464.0-43.60.71231474453.0-33.60.7491492435.6-33.60.848152.4406.3-22.50.3202150.238.6-11.62-Pyrolidinone (i)+o-xylene (i)0.869131640.5120.1493136627.7-1.00.193136636.8-15.30.2136134.6610.4-3.90.23321360568.8-15.30.403713856.9-6.60.475.41408527.0-20.70.512.714044.7-22.20.66714346.7-22.40.475.4140944.7-21.00.56714346.7-2.10.66715943.7-2.10.78515943.7-2.10.785159398.7-7.60.783131653.7-7.60.78313263.9-2.40.785129628.0-2.10.78413951.2-3.10.78413951.2-3.10.78513951.2-3.60.78413951.2-3.60.79713951.2-3.60.79713951.2-3.60.79713951.2-3.60.79713951.2-3.60.797137669.1-3.60.797 <t< td=""><td>0.5796</td><td>1434</td><td>495.2</td><td>-52.2</td></t<>	0.5796	1434	495.2	-52.2
0.712314/445.0-9.950.7649149243.5.6-33.60.848152440.3-22.50.8262156238.0.6-11.62. Pyrolidinone (i) + o-xylene (i)13160.0.513.00.14931354620.7-1.00.1493136620.7-1.00.1493136620.7-1.00.1493136620.7-1.00.1493136620.7-1.00.1493136550.8-1.5.30.4371883550.8-1.5.30.4371893550.9-2.2.20.47541490540.7-2.2.20.56671493496.7-2.2.30.61251450481.3-251.10.70331479451.8-243.30.70331570376.4-8.30.733150688.1-7.60.73313067.3-1.180.73313067.3-1.80.73313167.3-2.100.734132967.3-2.100.73513067.3-2.100.736142553.9-2.160.73713467.3-3.60.73813467.3-3.60.739146.3-3.6-3.70.74015257.9-3.60.75713767.3-3.70.756140752.4-3.70.75715337.9<	0.6766	1463	464.0	-43.6
0.7649         1492         456         -336           0.848         1524         408.3         -225           0.8202         1362         380.6         -11.6           2-Pyrnollinone (i)*o-xylene (j)         121         640.6         12           0.8493         133         627.7         -1.0           0.1493         1346         610.4         -339           0.232         1360         588.4         -8.4           0.179         1383         558.8         -15.3           0.4037         1380         550.9         -66.6           0.4754         440.8         52.0         -20.7           0.4754         140.8         52.0         -23.2           0.4037         1389         51.9         -43.1           0.4754         140.8         52.0         -24.2           0.4754         140.8         52.0         -24.2           0.4754         149.9         44.1         -43.1           0.4754         149.9         44.1         -43.1           0.4754         159.9         45.1         -43.1           0.4754         159.9         45.5         -43.1           0.4854	0.7123	1474	453.0	-39.5
b4481524408.3-22.50.8262156238.06-11.62-yronidimone (i) + o-xylene (j)0.08913164.061.20.04931335627.7-1.00.2136134661.04-3.90.2832136058.94-8.40.3771389558.9-16.50.40371389558.9-16.60.47541408527.0-20.70.51291419514.7-22.20.56671435496.7-24.30.7831479451.8-24.30.78315924.47-21.00.8644153939.97-15.50.9343157037.64-8.32-byrolidinoe (i) + p-xylene (j)-7.6-7.60.785109668.1-7.60.784129668.1-7.60.78513951.3-3.10.785140752.4-3.310.784129668.1-3.60.78513951.2-3.310.785140752.4-3.550.78615.7-3.6-3.60.78715.7-3.6-3.60.78615.7-3.75-3.60.79713951.2-3.750.796140752.4-3.60.79715757.9-1.60.794159461.2-3.760.79515747.7-3.75	0.7649	1492	435.6	-33.6
0.82621562380.6-11.62-Pyrnichinone (1)* o-xylene (1)	0.848	1524	408.3	-22.5
2.4ymidinne (1) + o-xylen (1) 0.089 133 0.1430 1346 60.0 0.2130 1346 60.0 0.2130 1348 60.0 0.2332 1300 589.4 0.2332 1300 589.4 0.2332 1300 589.4 0.2332 1300 580.9 0.4754 1408 527.0 0.2129 1419 514.7 0.2129 1419 514.7 0.2129 1419 451.3 0.2120 1455 46.7 0.2120 1455 49.6.7 0.2120 1450 49.6.7 0.2120 1451 49.6.7 0.2131 1314 67.3.7 0.2131 1314 67.3.7 0.2131 1321 67.3 0.217 1314 51.8 0.2191 49.7 0.2191 4	0.9262	1562	380.6	-11.6
0.0650         131         64.0         1.2           0.1433         1336         627.7         -1.0           0.2136         1346         601.4         -3.9           0.2382         1360         588.4         -8.4           0.379         1383         588.8         -15.3           0.4037         1389         550.9         -20.7           0.5129         1419         514.7         -22.3           0.5667         1455         496.7         -24.3           0.6125         1450         496.7         -24.3           0.6125         1509         441.8         -25.1           0.7033         147.9         451.8         -24.3           0.785         1509         441.7         -21.0           0.8634         153.9         399.7         -15.5           0.785         1509         447.7         -21.0           0.8634         153.9         399.7         -15.5           0.785         1200         67.3         -76.6           0.523         1303         67.3         -31.8           0.2133         1314         683.7         -71.6           0.524         129.7	2-Pyrrolidinone $(i)$ + o-xylene $(j)$			
0.1433136627-1.00.21361360670.4-3.90.23521360589.4-8.40.4751389550.9-16.60.47541408527.0-20.70.5671435496.7-24.30.61251450481.3-25.10.7331479451.8-24.30.7861539399.7-15.50.93431530376.7-7.60.5671333673.8-7.80.7851290698.1-7.80.7851290638.1-7.60.7331314653.7-17.60.7341339611.9-24.60.7351290628.07-23.10.7361393673.8-7.60.737137.9673.9-7.60.738134635.7-7.60.7391358533.9-29.40.49561383551.2-33.10.5871407522.4-35.70.7091463465.2-66.80.790415367.8-5.30.5187133263.7-1.60.795129567.8-5.30.5187133263.7-1.60.795135167.8-5.30.5187135267.8-5.30.5187135167.8-5.30.518135267.8-5.30.518135163.7-1.60	0.0869	1331	640.6	1.2
221361346610.43.90.28121360589.4	0.1493	1336	627.7	-1.0
0.2852         1360         58.84        8.4           0.377         1383         55.8         -15.3           0.4071         1389         550.9         -16.6           0.4754         1408         57.0         -20.7           0.5129         1419         514.7         -22.2           0.5667         1435         496.7         -24.3           0.7033         1479         451.8         -24.3           0.7036         1509         424.7         -21.0           0.8634         1539         399.7         -15.5           0.8634         1539         398.7         -15.3           0.785         1290         678.1         -7.6           0.753         1303         678.8         -13.8           0.7133         1314         653.7         -17.6           0.287         1329         628.0         -22.1           0.334         1314         653.7         -7.6           0.4956         138         57.1         -33.1           0.4956         138         57.1         -33.7           0.4956         138         57.1         -33.7           0.597         157	0.2136	1346	610.4	-3.9
0.3791383558.8-15.30.40371389550.9-16.60.47541408527.0-20.70.51291419514.7-22.20.56671435496.7-24.30.61251450481.3-25.10.70331479451.8-24.30.70331509424.7-21.00.86341539399.7-15.50.83431570376.4-8.32-Pyrolidinor (1) + p-xylen (1)-7.6-7.60.725130367.3-7.60.723130367.3-7.60.7241329688.0-22.10.2878132967.8-3.310.393158583.9-29.40.49361383551.2-3.310.5871407522.4-35.70.7571463465.2-36.80.758157-7.60.757157375.9-7.60.75715741.6-3.370.866153840.17-26.40.937153455.2-36.80.75915747.5-5.30.759157455.2-5.30.75413659.1-5.30.755137455.2-5.30.756137-5.3-5.30.75713766.93-2.10.75713767.7-7.60.75713767.7-7.30.757 <td>0.2832</td> <td>1360</td> <td>589.4</td> <td>-8.4</td>	0.2832	1360	589.4	-8.4
0.40371389550.9-16.60.4754140857.0-20.70.51201419514.7-22.20.56671435496.7-24.30.7031479451.8-24.30.70331479451.8-24.30.86541539399.7-15.50.83431570376.4-7.60.7331479451.8-7.60.86341539376.4-7.60.7331570376.4-7.60.7331570673.8-13.80.15231303673.8-13.80.15331314653.7-17.60.28781329628.0-22.10.3411339611.9-24.60.4935138551.2-33.10.51871391541.8-34.50.61761426502.1-37.10.7091463452.2-36.80.709150141.6-33.70.70791463452.2-36.80.704150141.6-33.70.856153840.7-26.40.93715737.59-15.00.7091431663.7-13.80.704150143.6-33.70.856153840.7-26.40.93715737.59-15.00.704150143.6-33.70.705137663.1-53.30.7241352663.1-53.5	0.379	1383	558.8	-15.3
0.47541408527.0-20.70.5191419547.0-22.30.56671435496.7-22.30.61251450451.8-24.30.70331479451.8-24.30.78651509424.7-21.00.8634153939.7-15.50.3431570376.4-8.32-Pyrolidinor (i) + p-xylene ()-7.6-7.60.7851290698.1-7.60.7231303673.8-13.80.723134653.7-7.60.2878132961.9-24.60.49561381551.2-3310.3741381551.2-3310.51871391541.8-34.50.56851407522.4-35.70.5167142650.1-37.70.5171538401.7-26.60.93571538401.7-26.40.93571538401.7-26.40.93571538401.7-26.40.93571538401.7-26.70.9251295687.8-5.30.1518130569.1-9.50.2871317648.1-13.90.287137648.1-13.90.287137648.1-13.90.284136-9.513.90.5161135069.1-9.50.287137648.1-9.50.287137648.1 <td< td=""><td>0.4037</td><td>1389</td><td>550.9</td><td>-16.6</td></td<>	0.4037	1389	550.9	-16.6
0.1291419514,7-22.20.56671450496,7-243,30.61251450481,3-243,10.70331479451,8-243,30.70361509424,7-21.00.86341539399,7-15.50.93431570376,4-8.32.Pyrolidinor (1) + p-xyler (1)0.7531290698,1-7.60.15231303673,8-13.80.21331314653,7-17.60.23741359611.9-24.60.40931358581.3-24.40.4093138512.2-33.10.51671426502.1-33.10.5171391541.8-34.50.5685140752.4-35.70.6761426502.1-37.10.79041501431.6-33.70.8661538401.7-26.40.935715737.5-15.00.925195669.1-35.70.5161305669.1-9.50.2871317648.1-13.90.284134609.3-9.50.284134609.3-9.50.284134609.3-9.50.285137436-26.30.284134609.3-21.40.28513713762.70.286137-26.5-26.30.28713263.6-9.5 <td>0.4754</td> <td>1408</td> <td>527.0</td> <td>-20.7</td>	0.4754	1408	527.0	-20.7
0.56671435496,7-24.30.61251450481.3-24.30.7031479451.8-24.30.78651509424.7-21.00.86341539399.7-15.50.87431570376.4-8.32-Pyrroldinore (i) + p-xylene (f)-76-760.78531303673.8-13.80.21331303673.8-13.80.21331314653.7-7.60.25741329628.0-22.10.3411339611.9-24.60.4093158551.2-33.10.4093158551.2-35.70.56551407522.4-35.70.57641531431.6-33.70.56551501431.6-33.70.70941501431.6-33.70.70941501431.6-33.70.7571573375.9-15.00.758669.1-9.50.5171391648.1-13.90.7241317648.1-13.90.725657.3-9.50.756137659.6-2.70.463669.1-9.50.75713263.7-18.50.758137659.6-2.60.758137659.6-2.60.759137659.6-2.60.757138559.6-2.60.756140752.4559.6-2.60	0.5129	1419	514.7	-22.2
0.6125     1450     481.3     -25.1       0.7033     1479     451.8     -24.3       0.7085     1509     424.7     -21.0       0.8634     1539     399.7     -15.5       0.9343     1570     376.4     -8.3       2-Pyrolidinone (i) + p-xylene (j)     -7.6     -7.6       0.1523     1303     673.8     -7.6       0.1523     1303     673.8     -7.6       0.1523     1314     653.7     -1.7.6       0.2878     1329     628.0     -22.1       0.3341     1339     611.9     -24.6       0.4093     1358     583.9     -29.4       0.4956     1383     551.2     -33.1       0.5187     1391     541.8     -34.5       0.5685     1407     522.4     -35.7       0.7079     1463     465.2     -36.8       0.7094     1501     431.6     -33.7       0.866     1538     401.7     -25.4       0.9257     1573     375.9     -15.0       0.925     687.8     -5.3       0.518     1305     669.1     -9.5       0.162     137     648.1     -9.5       0.287     1322     623.7	0.5667	1435	496.7	-24.3
0.7033         1479         451.8         -24.3           0.7865         1509         424.7         -21.0           0.6344         1539         399.7         -15.5           0.9343         1570         376.4         -8.3           2-Pyrolidinon (i) + p-xylen (j)         -7.6         -7.6           0.7855         1290         698.1         -7.6           0.1523         1303         673.8         -13.8           0.2133         1314         653.7         -17.6           0.2378         1329         628.0         -22.1           0.3341         1339         611.9         -24.6           0.4093         1358         538.9         -29.4           0.4956         1383         551.2         -33.1           0.5187         1391         541.8         -345.5           0.5685         1407         522.4         -35.7           0.6176         1426         502.1         -37.1           0.7079         1463         465.2         -36.8           0.7904         1501         431.6         -35.7           0.7914         1573         375.9         -15.0           0.792         15	0.6125	1450	481.3	-25.1
0.7865         1509         424.7         -21.0           0.8634         1539         399.7         -15.5           0.9343         1570         376.4         -8.3           2-Pyrolidinone (i)+p-xylene (j)         -         -         -7.6           0.1523         1303         698.1         -7.6           0.1523         1303         673.8         -13.8           0.2133         1314         653.7         -17.6           0.2878         1329         628.0         -22.1           0.341         1339         611.9         -24.6           0.4993         1558         583.9         -29.4           0.4993         1358         581.2         -33.1           0.5187         1391         541.8         -34.5           0.5685         1407         522.4         -35.7           0.5676         1426         502.1         -33.1           0.7090         1463         465.2         -36.8           0.7390         1463         401.7         -26.4           0.9357         153         30.7         -55.7           0.566         1538         401.7         -66.9           0.997	0.7033	1479	451.8	-24.3
0.8634         1539         390,7         -15.5           0.9343         170         376,4         -83           2-Pyrnollinone (i) + p-xylene (j)          -7.6           0.785         1290         698,1         -7.6           0.1523         1303         673,8         -13.8           0.2133         1314         653,7         -7.6           0.2878         1329         628,0         -22.1           0.3341         1329         611.9         -24.6           0.4995         1383         551.2         -33.1           0.5187         1391         541.8         -34.5           0.5685         1407         522.4         -35.7           0.6176         1426         502.1         -37.1           0.7079         1463         465.2         -36.8           0.7904         1501         431.6         -33.7           0.866         1538         401.7         -26.4           0.9357         1573         375.9         -53.5           0.1516         1305         669.1         -9.5           0.287         132         623.7         -18.5           0.287         1341	0.7865	1509	424.7	-21.0
0.9343     1570     376.4     -8.3       2-Pyrrolitinone (i) + p-xylene (j)         0.785     120     673.8     -13.8       0.1523     130     673.8     -13.8       0.2133     1314     653.7     -7.6       0.2376     1329     628.0     -22.1       0.3341     1339     611.9     -24.6       0.4995     1358     583.9     -29.4       0.4995     1383     551.2     -33.1       0.5187     1391     541.8     -34.5       0.5685     1407     522.4     -35.7       0.5685     1407     522.4     -35.7       0.5685     1407     524.4     -34.5       0.5685     1407     524.4     -35.7       0.5685     1407     524.4     -35.7       0.5704     1426     502.1     -37.1       0.7094     1463     465.2     -36.8       0.7904     1501     431.6     -33.7       0.866     1538     401.7     -26.4       0.9357     137     687.8     -53.9       0.1518     136     690.1     -95.5       0.2162     137     648.1     -13.9       0.224     556.6 <t< td=""><td>0.8634</td><td>1539</td><td>399.7</td><td>-15.5</td></t<>	0.8634	1539	399.7	-15.5
2-Pyrnolidinone (i) + p-xylene (j)       -7.6         0.0785       1290       698.1       -7.6         0.1523       1303       673.8       -11.8         0.2133       1314       653.7       -17.6         0.2878       1329       628.0       -22.1         0.3341       1339       611.9       -24.6         0.4093       1358       583.9       -29.4         0.4956       1383       551.2       -33.1         0.5187       1391       541.8       -34.5         0.5685       1407       522.4       -35.7         0.6176       1426       502.1       -37.1         0.7070       1463       455.2       -36.8         0.7070       1463       401.7       -26.4         0.9357       1573       375.9       -15.0         2-Pyrnolidinone (i) + m-xylene (j)       -2       -2         2-Pyrnolidinone (i) + m-xylene (j)       -2       -35.7         0.287       135       669.1       -5.3         0.1518       1305       669.1       -9.5         0.287       132       623.7       -18.5         0.3284       1361       693.1       -24.4 <td>0.9343</td> <td>1570</td> <td>376.4</td> <td>-8.3</td>	0.9343	1570	376.4	-8.3
0.0785       1290       698.1       -7.6         0.1523       1303       673.8       -13.8         0.2133       1314       653.7       -7.6         0.2878       1329       628.0       -22.1         0.3341       1339       611.9       -44.6         0.4993       1358       583.9       -29.4         0.4956       1383       551.2       -33.1         0.5187       1391       541.8       -34.5         0.6176       1407       522.4       -35.7         0.6176       1426       502.1       -37.1         0.7079       1463       465.2       -36.8         0.7904       1501       431.6       -33.7         0.866       1538       401.7       -26.4         0.9357       1573       375.9       -15.0         2-Pyrrolidinone (i) + m-xylene (j)       -9.5       -9.5         0.2925       1397       687.8       -5.3         0.518       1305       669.1       -9.5         0.2162       1317       648.1       -13.9         0.287       1332       623.7       -18.5         0.2164       137       693.1       <	2-Pyrrolidinone ( <i>i</i> ) + p-xylene ( <i>j</i> )			
0.1523     1303     673.8     -13.8       0.2133     1314     653.7     -17.6       0.2878     1329     628.0     -22.1       0.3341     1339     611.9     -24.6       0.4093     1358     583.9     -29.4       0.4956     1383     551.2     -33.1       0.5187     1391     541.8     -34.5       0.5685     1407     522.4     -35.7       0.6176     1426     502.1     -37.1       0.7079     1463     465.2     -36.8       0.7904     1501     431.6     -33.7       0.866     1538     401.7     -26.4       0.9357     1573     375.9     -15.0       2-Pyrrolidinone (i) + m-xylene (j)     -     -     -       2-Pyrrolidinone (i) + m-xylene (j)     -     -     -       0.9357     137     648.1     -13.9       0.2162     1317     648.1     -13.9       0.2184     134     609.3     -21.4       0.331     1350     597.1     -23.7       0.4083     1362     580.1     -26.3       0.4083     1362     580.1     -26.3       0.4083     1362     597.1     -23.7       <	0.0785	1290	698.1	-7.6
0.2133     1314     653.7     -17.6       0.2878     1329     628.0     -22.1       0.3341     1339     611.9     -24.6       0.4093     1358     583.9     -29.4       0.4956     1383     551.2     -33.1       0.5187     1391     541.8     -34.5       0.5685     1407     522.4     -35.7       0.6176     1426     50.1     -37.1       0.7079     163     465.2     -36.8       0.7904     1501     431.6     -33.7       0.866     1538     401.7     -26.4       0.9377     1501     31.6     -33.7       0.866     1538     401.7     -26.3       0.9370     1501     687.8     -5.3       0.9357     1305     669.1     -9.5       0.1518     1305     669.1     -9.5       0.2162     1317     648.1     -13.9       0.287     1321     623.7     -81.5       0.3284     1341     609.3     -21.4       0.3613     1350     597.1     -23.7       0.4083     1362     50.1     -26.3       0.4083     1362     59.6     -29.5       0.5177     1394	0.1523	1303	673.8	-13.8
0.28781329628.0-22.10.33411339611.9-24.60.49031358583.9-29.40.49561383551.2-33.10.51871391541.8-34.50.56851407522.4-35.70.61761426502.1-37.10.70791463465.2-36.80.79041501431.6-33.70.8661538401.7-26.40.93571573375.9-15.02-Pyrrolidinone (i) + m-xylene (j)687.8-5.30.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131350597.1-23.70.46221378559.6-29.50.51771394538.8-31.70.55671428500.3-34.0	0.2133	1314	653.7	-17.6
0.33411339611.9-24.60.40931358583.9-29.40.49961383551.2-33.10.51871391541.8-34.50.56851407522.4-35.70.61761426502.1-37.10.70791463465.2-36.80.79041501431.6-33.70.8661538401.7-26.40.93571573375.9-15.30.9357159667.8-5.30.15181305669.1-9.50.21621317648.1-13.90.2871322623.7-18.50.32841341609.3-21.40.3613135059.6-29.50.46221378559.6-29.50.51771394538.8-31.70.55671407538.8-31.70.5567142850.3-34.0	0.2878	1329	628.0	-22.1
0.40931358583.9-29.40.49561383551.2-33.10.51871391541.8-34.50.56851407522.4-35.70.61761426502.1-37.10.7079163465.2-36.80.79041501431.6-33.70.8661538401.7-26.40.93571573375.9-15.02-Pyrrolidinone (i) + m-xylene (j)-5.3-5.30.15181305669.1-9.50.287132623.7-18.50.32841341609.3-21.40.36131362597.1-23.70.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-34.00.5669128500.3-34.0	0.3341	1339	611.9	-24.6
0.49561383551.2-33.10.51871391541.8-34.50.56851407522.4-35.70.61761426502.1-37.10.70791463465.2-36.80.79041501431.6-33.70.8661538401.7-26.40.93571573375.9-15.02-Pyrrolidinone (i) + m-xylene (j)5.30.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671428500.3-32.80.61691428500.3-32.8	0.4093	1358	583.9	-29.4
0.51871391541.8-34.50.56851407522.4-35.70.61761426502.1-37.10.7079163465.2-36.80.79041501431.6-33.70.8661538401.7-26.40.9357157337.9-15.02-Pyrroldinone (i) + m-xylene (j)867.8-5.30.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131350597.1-23.70.4083162580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-31.70.56691428500.3-34.0	0.4956	1383	551.2	-33.1
0.56851407522.4-35.70.61761426502.1-37.10.70791463465.2-36.80.79041501431.6-33.70.8661538401.7-26.40.93571573375.9-15.02-Pyrrolidinone (i) + m-xylene (j)0.09251295687.8-5.30.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	0.5187	1391	541.8	-34.5
0.61761426502.1-37.10.70791463465.2-36.80.79041501431.6-33.70.8661538401.7-26.40.93571573375.9-15.02-Pyrrolidinone (i) + m-xylene (j)687.8-5.30.09251295687.8-5.30.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131350597.1-23.70.40831362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	0.5685	1407	522.4	-35.7
0.70791463465.2-36.80.79041501431.6-33.70.8661538401.7-26.40.93571573375.9-15.02-Pyrrolidinone (i)+m-xylene (j)2-Pyrrolidinone (i)+m-xylene (j)0.09251295687.8-5.30.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131350597.1-23.70.40831362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-31.70.55671428500.3-34.0	0.6176	1426	502.1	-37.1
0.79041501431.6-33.70.8661538401.7-26.40.93571573375.9-15.02-Pyrrolidinone (i)+m-xylene (j)0.09251295687.8-5.30.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-11.40.32841341609.3-21.40.36131350597.1-23.70.40831362580.1-26.30.40221378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	0.7079	1463	465.2	-36.8
0.8661538401.7-26.40.93571573375.9-15.02-Pyrrolidinone (i) + m-xylene (j)0.09251295687.8-5.30.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131350597.1-23.70.40831362580.1-26.30.40821378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	0.7904	1501	431.6	-33.7
0.93571573375.9-15.02-Pyrolidinone (i) + m-xylene (j)0.09251295687.8-5.30.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131350597.1-23.70.40831362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.56671407523.8-32.80.61691428500.3-34.0	0.866	1538	401.7	-26.4
2-Pyrrolidinone (i) + m-xylene (j)       687.8       -5.3         0.0925       1305       669.1       -9.5         0.1518       1305       669.1       -13.9         0.2162       1317       648.1       -13.9         0.287       1332       623.7       -18.5         0.3284       1341       609.3       -21.4         0.3613       1350       597.1       -23.7         0.4083       1362       580.1       -26.3         0.4622       1378       559.6       -29.5         0.5177       1394       538.8       -31.7         0.5567       1407       523.8       -32.8         0.6169       1428       500.3       -34.0	0.9357	1573	375.9	-15.0
0.09251295687.8-5.30.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131350597.1-23.70.40831362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	2-Pyrrolidinone ( <i>i</i> ) + m-xylene ( <i>j</i> )			
0.15181305669.1-9.50.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131350597.1-23.70.40831362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	0.0925	1295	687.8	-5.3
0.21621317648.1-13.90.2871332623.7-18.50.32841341609.3-21.40.36131350597.1-23.70.40831362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	0.1518	1305	669.1	-9.5
0.2871332623.7-18.50.32841341609.3-21.40.36131350597.1-23.70.40831362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	0.2162	1317	648.1	-13.9
0.3284     1341     609.3     -21.4       0.3613     1350     597.1     -23.7       0.4083     1362     580.1     -26.3       0.4622     1378     559.6     -29.5       0.5177     1394     538.8     -31.7       0.5567     1407     523.8     -32.8       0.6169     1428     500.3     -34.0	0.287	1332	623.7	-18.5
0.36131350597.1-23.70.40831362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	0.3284	1341	609.3	-21.4
0.40831362580.1-26.30.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	0.3613	1350	597.1	-23.7
0.46221378559.6-29.50.51771394538.8-31.70.55671407523.8-32.80.61691428500.3-34.0	0.4083	1362	580.1	-26.3
0.5177 1394 538.8 -31.7 0.5567 1407 523.8 -32.8 0.6169 1428 500.3 -34.0	0.4622	1378	559.6	-29.5
0.5567 1407 523.8 –32.8 0.6169 1428 500.3 –34.0	0.5177	1394	538.8	-31.7
0.6169 1428 500.3 -34.0	0.5567	1407	523.8	-32.8
	0.6169	1428	500.3	-34.0

#### Table 4 (Continued)

Xi	$u ({ m ms^{-1}})$	$\kappa_{\rm S}  ({\rm T}  {\rm Pa}^{-1})$	$\kappa_{\rm S}^{\rm E}$ (T Pa <sup>-1</sup> )
0.7071	1463	465.1	-33.3
0.7898	1498	432.9	-29.2
0.8656	1533	403.9	-22.3

### Table 5

Parameters used in Eqs. (5), (7) and (15) for the investigated binary mixtures at 308.15 K.

```
Parameters
2-Pyrrolidinone (i) + benzene (j)
   V^{(0)} = -2.225, V^{(1)} = 0.011, V^{(2)} = 0.099; \sigma(V^{\rm E}) = 0.003 \,{\rm cm}^3 \,{\rm mol}^{-1}
   H^{(0)} = -675.8, H^{(1)} = 51.1, H^{(2)} = 322.2; \sigma(H^{E}) = 1.7 \text{ J mol}^{-1}
   \kappa_{\rm s}^{(0)} = -173.8, \, \kappa_{\rm s}^{(1)} = -15.8, \, \kappa_{\rm s}^{(2)} = -19.7; \, \sigma(\kappa_{\rm s}^{\rm E}) = 0.3 \, {\rm T} \, {\rm Pa}^{-1}
   ({}^{3}\xi_{i}) = ({}^{3}\xi_{i})_{m} = 1.001; ({}^{3}\xi_{i}) = ({}^{3}\xi_{i})_{m} = 0.666; \alpha_{ij} = 11.139 \text{ cm}^{3} \text{ mol}^{-1}
    \chi'_{ii} = -230.9 \,\mathrm{J}\,\mathrm{mol}^{-1}; \ \chi_{12} = -433.6 \,\mathrm{J}\,\mathrm{mol}^{-1}
    \chi'_{ii} = -61.6 \,\mathrm{T}\,\mathrm{Pa}^{-1}; \chi_{12} = -101.7 \,\mathrm{T}\,\mathrm{Pa}^{-1}
2-Pyrrolidinone (i) + toluene (j)
   V^{(0)} = -2.365, V^{(1)} = -0.648, V^{(2)} = 0.353; \sigma(V^{\rm E}) = 0.003 \,{\rm cm}^3 \,{\rm mol}^{-1}
   H^{(0)} = -121.2, H^{(1)} = 73.6, H^{(2)} = 188.8; \sigma(H^{\rm E}) = 0.3 \text{ J mol}^{-1}
   \kappa_{\rm S}^{(0)} = -229.1, \, \kappa_{\rm S}^{(1)} = 93.5, \, \kappa_{\rm S}^{(2)} = -18.4; \, \sigma(\kappa_{\rm S}^{\rm E}) = 0.3 \, {\rm T} \, {\rm Pa}^{-1}
   ({}^{3}\xi_{i}) = ({}^{3}\xi_{i})_{m} = 1.001; ({}^{3}\xi_{j}) = ({}^{3}\xi_{j})_{m} = 0.840; \alpha_{ij} = 71.242 \text{ cm}^{3} \text{ mol}^{-1}
    \chi'_{ii} = -24.9 \,\mathrm{J}\,\mathrm{mol}^{-1}; \chi_{12} = -127.2 \,\mathrm{J}\,\mathrm{mol}^{-1}
    \chi'_{ij} = -50.5 \, T \, Pa^{-1}; \chi_{12} = -270.2 \, T \, Pa^{-1}
2-Pyrrolidinone (i) + o-xylene (j)
    V^{(0)} = -2.119, V^{(1)} = -0.516, V^{(2)} = 0.113; \sigma(V^{\text{E}}) = 0.003 \text{ cm}^3 \text{ mol}^{-1}
   H^{(0)} = 472.8, H^{(1)} = 219.6, H^{(2)} = -58.2; \sigma(H^{E}) = 1.2 | mol<sup>-1</sup>
   \kappa_{\rm s}^{(0)} = -87.7, \, \kappa_{\rm s}^{(1)} = -88.9, \, \kappa_{\rm s}^{(2)} = 37.3; \, \sigma(\kappa_{\rm s}^{\rm E}) = 0.2 \, {\rm T} \, {\rm Pa}^{-1}
   ({}^{3}\xi_{i}) = ({}^{3}\xi_{i})_{m} = 1.002; ({}^{3}\xi_{i}) = ({}^{3}\xi_{i})_{m} = 1.426; \alpha_{ij} = 20.207 \text{ cm}^{3} \text{ mol}^{-1}
    \chi'_{ii} = 472.1 \,\mathrm{J}\,\mathrm{mol}^{-1}; \ \chi_{12} = -269.3 \,\mathrm{J}\,\mathrm{mol}^{-1}
   \chi'_{ii} = -118.8 \, T \, Pa^{-1}; \chi_{12} = 144.0 \, T \, Pa^{-1}
2-Pyrrolidinone (i) + p-xylene (j)
    V^{(0)} = -2.331, V^{(1)} = -0.439, V^{(2)} = 0.558; \sigma(V^{\text{E}}) = 0.003 \text{ cm}^3 \text{ mol}^{-1}
    H^{(0)} = 332.7, H^{(1)} = 106.3, H^{(2)} = -100.7; \sigma(H^{\rm E}) = 0.8 \, \text{J} \, \text{mol}^{-1}
   \kappa_{c}^{(0)} = -134.0, \kappa_{c}^{(1)} = -84.6, \kappa_{c}^{(2)} = -54.5; \sigma(\kappa_{c}^{E}) = 0.2 \,\mathrm{T} \,\mathrm{Pa}^{-1}
   ({}^{3}\xi_{i}) = ({}^{3}\xi_{i})_{m} = 1.003; ({}^{3}\xi_{j}) = ({}^{3}\xi_{j})_{m} = 1.250; \alpha_{ij} = 52.200 \text{ cm}^{3} \text{ mol}^{-1}
    \chi'_{ij} = 277.6 \,\mathrm{J}\,\mathrm{mol}^{-1}; \ \chi_{12} = -83.9 \,\mathrm{J}\,\mathrm{mol}^{-1}
    \chi'_{ii} = -124.5 \,\mathrm{T}\,\mathrm{Pa}^{-1}; \chi_{12} = 72.1 \,\mathrm{T}\,\mathrm{Pa}^{-1}
2-Pyrrolidinone (i) + m-xylene (j)
   V^{(0)} = -1.810, V^{(1)} = -0.199, V^{(2)} = -0.684; \sigma(V^{E}) = 0.002 \text{ cm}^3 \text{ mol}^{-1}
   H^{(0)} = 662.3, H^{(1)} = 62.8, H^{(2)} = 166.4; \sigma(H^{E}) = 1.6 \text{ J mol}^{-1}
   \kappa_{\rm s}^{(0)} = -123.6, \, \kappa_{\rm s}^{(1)} = -81.3, \, \kappa_{\rm s}^{(2)} = -17.8; \, \sigma(\kappa_{\rm s}^{\rm E}) = 0.2 \, {\rm T} \, {\rm Pa}^{-1}
   ({}^{3}\xi_{i}) = ({}^{3}\xi_{i})_{m} = 1.004; ({}^{3}\xi_{j}) = ({}^{3}\xi_{j})_{m} = 1.174; \alpha_{ij} = 76.376 \text{ cm}^{3} \text{ mol}^{-1}
    \chi'_{ij} = 405.3 \, \text{J} \, \text{mol}^{-1}; \ \chi_{12} = 224.2 \, \text{J} \, \text{mol}^{-1}
    \chi'_{ii} = -115.6 \,\mathrm{T}\,\mathrm{Pa}^{-1}; \chi_{12} = 78.1 \,\mathrm{T}\,\mathrm{Pa}^{-1}
```

## 4. Discussion

We are unaware of any  $V_m^E$ ,  $H_m^E$  and  $\kappa_S^E$  data of the investigated mixtures with which to compare our result.  $V_m^E$  data of **2-Py** (i) + benzene or toluene or o- or p- or m-xylene (j) binary mixtures are negative over entire composition range. H<sup>E</sup><sub>m</sub> data are negative for **2-Py** (i) + benzene (j) and positive for **2-Py** (i) + o- or p- or m-xylene (j) mixtures over whole composition range; however,  $H_m^E$  values change sign from negative to positive for **2-Py** (*i*) + toluene (*j*) mixture at  $x_i > 0.82$ . While  $V_m^E$  data for an equimolar mixture vary in the order: m-xylene > o-xylene > benzene > p-xylene > toluene;  $H_m^E$ data vary as m-xylene > o-xylene > p-xylene > toluene > benzene. Further,  $\kappa_{\rm S}^{\rm E}$  values for **2-Py**+benzene or toluene or p- or mxylene mixtures are negative over the entire composition range. However for **2-Py**+o-xylene mixtures,  $\kappa_{\rm S}^{\rm E}$  values change sign from positive to negative at  $x_i \le 0.14$ .  $\kappa_{\rm S}^{\rm E}$  values for an equimolar mixture vary as: o-xylene > m-xylene > p-xylene > benzene > toluene.

The observed  $H_m^E$  data for these mixtures can be explained if it be assumed that: (i) 2-Py is an associated molecular entity; (ii) there is interaction between  $\pi$ -electrons spilling over nitrogen and oxygen atom of **2-Py** and  $\pi$ -electron cloud of benzene or toluene or o- or p- or m-xylene to form weak p-complex [21]; (iii) interactions between (i) and (j) components of binary mixture then weakens i-i interactions and lead to its depolymerization, (iv) monomers of (i) and (j) then undergo specific interaction to form *i*:*j* molecular entity, (v) there is steric repulsion between 2-Py and toluene or xylene molecules because of the presence of bulky  $-CH_3$  groups.  $H_m^E$  data for **2-Py**+benzene mixture suggest that contribution due to factors (ii) and (iv) far outweigh the contribution due to factor (iii), so that over all  $H_m^E$  values for this mixture are negative. The introduction of one -CH<sub>3</sub> group into benzene (as in toluene) or two -CH<sub>3</sub> groups in benzene (as in xylenes) would increase the  $\pi$ -electron donating capacity of aromatic ring of toluene or xylenes and thus interactions between 2-Py and toluene or xylene must be stronger than that in 2-Py + benzene mixtures. However, at the same time there exists a steric hindrance between **2-Py** and toluene or xylene molecules due to the presence of  $-CH_3$  groups. Higher  $H_m^E$  values for **2-Py**+toluene or xylenes mixtures than those for 2-Py+benzene mixtures suggest that contribution due to hindrance is more than that due to interactions.

Lower values of  $V_{\rm E}^{\rm m}$  and  $\kappa_{\rm S}^{\rm E}$  for **2-Py**+benzene or toluene mixtures than those for **2-Py**+xylene mixtures suggest that benzene or toluene gives relatively more packed structure than xylene in **2-Py**. This may be due to the presence of bulky –CH<sub>3</sub> groups in xylene which restricts the approach of xylene molecule towards **2-Py**.

#### 4.1. Graph theory and results

Excess molar volumes,  $V_{m}^{E}$ , reflect the packing of the constituents in (i+j) mixtures which in turn provides information about the change in topology of *i* or *j* constituents on addition of *i* to *j* in binary (i+j) mixture. Thus analysis of  $V_{m}^{E}$  data of binary mixtures in terms of Graph



Scheme. Connectivity Parameters of various molecular entities

theory that employs the graph—theoretical concept of connectivity parameter of third degree,  ${}^{3}\xi$  of a molecule (which in turn depends on its topology) can provide information about the state of components in pure and mixed state. According to this approach,  $V^{E}$  for a binary mixture is given [22] by

$$V^{\rm E} = \alpha_{ij} \left[ \left( \sum x_i ({}^3\xi_i)_{\rm m} \right)^{-1} - \left( \sum x_i ({}^3\xi_i) \right)^{-1} \right] \tag{7}$$

where  $x_i$  is the mole fraction of component (*i*) and  $\alpha_{ij}$  is a constant characteristic of binary mixture.  $({}^3\xi_i, i=i \text{ or } j)$  and  $({}^3\xi_i)_{\text{m}}$  (*i*=*i* or *j*) are the connectivity parameters of components (*i*) and (*j*) in pure and mixture state and are defined [23] by

$${}^{3}\xi = \sum_{\ell < m < n < o} (\delta^{\nu}_{\ell} \delta^{\nu}_{m} \delta^{\nu}_{n} \delta^{\nu}_{o})^{-0.5}$$

$$\tag{8}$$

where  $\delta_{\ell}^{\nu}$ , etc. reflect degree of *m*, *n*, etc. vertices of the graph of a molecule and are related to maximum valency,  $Z_m$  and number of hydrogen atoms attached to *m*th vertex by relation  $\delta_m^{\nu} = Z_m - h_m$  [24].

The degree of association of (*i*) or (*j*) in pure and mixture state is not known, therefore, we regarded  $({}^{3}\xi_{i})$  (*i*=*i* or *j*) and  $({}^{3}\xi_{i})_{m}$ (*i*=*i* or *j*) as adjustable parameters. These parameters were eval-

uated by fitting  $V_m^E$  data of mixtures to Eq. (7). Only those values of parameters were retained that best reproduced the experimental  $V_{\rm m}^{\rm E}$  data. Such  $({}^{3}\xi_{i})(i=i \text{ or } j)$  and  $({}^{3}\xi_{i})_{\rm m}(i=i \text{ or } j)$  values are recorded in Table 5. Also  $V_m^E$  values {evaluated by employing Eq. (7)} at various mole fractions of (i),  $x_i$ , are plotted in Figs. 1 and 2 and are compared with their corresponding experimental values. A perusal of Figs. 1 and 2 reveals that  $V_m^E$  values compare well with their corresponding experimental values. Thus  $({}^{3}\xi_{i})(i=i \text{ or } j)$  and  $({}^{3}\xi_{i})_{m}(i=i$ or j) values can be relied upon to extract information about the state of aggregation of (i) or (j) in pure and mixed state. Structures were then assumed for **2-Py**, benzene, toluene, o-, p- and m-xylene and their  ${}^{3}\xi'$  values were predicted by employing topology {via Eq. (8)}. These  ${}^3\xi'$  values were then compared with  ${}^3\xi$  values (calculated by Eq. (7)). Any structure or combination of structures that gives  ${}^{3}\xi'$ values which compare well with  ${}^{3}\xi$  values was considered to be a representative structure of that component.

For the investigated (i+j) binary mixtures, we assumed that **2-Py** exists as molecular entities **I**, **II** and **III**.  ${}^{3}\xi'$  values for these molecular entities were then calculated to be 0.903, 1.377, 1.271 respectively.  ${}^{3}\xi_{i}$  values of 1.001, 1.001, 1.002, 1.003 and 1.004, for **2-Py** in (i+j)

mixtures (Table 5) suggest that 2-Py in pure state mainly exists as a mixture of cyclic and open dimer ( ${}^{3}\xi' = 1.321$ ); a small amount of monomer may also be present, or alternatively it may exist as an equilibrium mixture of all these molecular entities ( ${}^{3}\xi' = 1.183$ ). These observations are consistent with observation obtained from ab initio calculations on the different associated structures of 2-Py [25].  ${}^{3}\xi'$  values of 0.666, 0.840, 1.426, 1.250 and 1.174 for benzene, toluene, o-, p- and m-xylene [molecular entities IV-VIII] suggest that they exist as monomers. Connectivity parameters of third degree of components (*i*) and (*j*) in mixed state,  $({}^{3}\xi_{i})_{m}$  (*i*=*i* or *j*) were then calculated and employed to extract information about the state of 2-Py in benzene or toluene or o- or p- or m-xylene. It was assumed that studied (i+j) mixtures contain molecular entity **IX**. In evaluating  ${}^{3}\xi'$  values for molecular entity **IX**, it was assumed that molecular entity IX is characterized by interaction between  $\pi$ -electron cloud spilling over nitrogen and oxygen atom of **2-Py** and  $\pi$ -electron cloud of aromatic ring of aromatic hydrocarbon.  $\delta^{\nu}_{a}$ values for various vertices are shown in molecular entities I-IX and  $\delta^{\nu}(\pi)$  has been assigned [24] value one (where  $\pi$ -electron cloud of molecule is unvalued in interaction with  $\pi$ -electron of another molecule).  $({}^{3}\xi_{i})_{m}$  values of 1.001, 1.001, 1.002, 1.003 and 1.004 for 2-Py in benzene or toluene or o- or p- or m-xylene (Table 5) suggest that investigated mixtures are characterized by the presence of molecular entity IX ( ${}^{3}\xi' = 1.107$ ). The existence of molecular entity IX suggests that addition of 2-Py(i) to benzene or toluene or o- or por m-xylene should have influenced the C=O and N-H stretching of 2-Py and also the ring vibrations of aromatic ring of aromatic hydrocarbon. To substantiate this, we analyzed the IR spectra data of an equimolar mixture of 2-Py(i) + benzene(j) mixture. It was observed while benzene (*i*) in pure state showed ring vibrations at 1582, 1496, 1440 cm<sup>-1</sup> respectively, **2-Py** (*i*) showed vibrations at 1682 (C=0) and 3260 cm<sup>-1</sup> (N-H) [26]. On the other hand, IR spectra of **2-Py** (*i*) + benzene (*j*) mixtures showed characteristic vibrations at 1610, 1512, 1482 cm<sup>-1</sup> (ring vibrations), 1674 (C=O) and 3250 cm<sup>-1</sup> (N-H). The IR spectra of **2-Py** (i) + benzene (j) mixtures thus infer that addition of **2-Py** (*i*) to benzene (*j*) does influence C=O and N-H stretching of **2-Py** (*i*) and also the ring vibrations of aromatic ring of benzene. This lends additional support to the proposed molecular entity IX in these mixtures and also to the assumption made in evaluating its  ${}^{3}\xi'$  values.

 $H_{\rm m}^{\rm E}$  and  $\kappa_{\rm S}^{\rm E}$  data of investigated mixtures were then analyzed in terms of Graph theory. For this purpose we assumed that (i+j)mixtures formation involves following processes: (1) **2-Py** (*i*) is an associated molecular entity, (2) formation of unlike contact between **2-Py** (*i*) and aromatic hydrocarbons (*j*) then influences **2-Py–2-Py** interaction which yield their monomers, (3) monomers of (*i*) and (*j*) then undergo specific interactions to form *i*:*j* molecular entity. Consequently, if  $\chi_{ij}$ ,  $\chi_{ii}$  and  $\chi_{12}$  are molar energy and molar compressibility parameters for *i*–*j*, *i*–*i* and specific interactions respectively. Then change in molar thermodynamic property,  $\Delta X$  ( $X = H_{\rm m}$  or  $\kappa_{\rm S}$ ) due to processes (1–3) would be given [27–29] by

$$\Delta X_1 \left( X = H_{\rm m} \, {\rm or} \, \kappa_{\rm S} \right) = x_i \chi_{ij} S_j \tag{9}$$

where  $S_j$  is the surface fraction of j, defined [27] by

$$S_j = \frac{x_j v_j}{\sum_{i=i}^j x_i v_i}$$

so that

$$\Delta X_1 \left( X = H_{\rm m} \, {\rm or} \, \kappa_{\rm S} \right) = x_i x_j v_j \frac{\chi_{ij}}{\sum x_i v_i} \tag{10}$$

$$\Delta X_2 \left( X = H_{\rm m} \, {\rm or} \, \kappa_{\rm S} \right) = x_i^2 x_j v_j \frac{\chi_{ii}}{\sum x_i v_i} \tag{11}$$

$$\Delta X_3 \left( X = H_{\rm m} \, {\rm or} \, \kappa_{\rm S} \right) = x_i x_j^2 \frac{\chi_{12}}{\sum x_i \nu_i} \tag{12}$$

where  $v_j$  is the molar volume of component (*j*) of (*i*+*j*) mixtures. The overall changes in thermodynamic property,  $X^E (X=H_m \text{ or } \kappa_S)$  due to processes (1–3) then can be expressed by

$$X^{E}(X = H_{m} \text{ or } \kappa_{S}) = \sum_{i=1}^{3} \Delta H_{i} = \left[\frac{x_{i}x_{j}v_{j}}{\sum x_{i}v_{i}}\right] \left[\chi_{ij} + x_{i}\chi_{ii} + x_{j}\chi_{12}\right] \quad (13)$$

For the studied mixtures, if it be assumed that  $\chi_{ii} \cong \chi_{ij} = \chi'_{ij}$  then Eq. (13) reduces to Eq. (14)

$$X^{\rm E}(X = H_{\rm m} \, {\rm or} \, \kappa_{\rm S}) = \left[\frac{x_i x_j v_j}{\sum x_i v_i}\right] \left[(1 + x_i)\chi'_{ij} + x_j \chi_{12}\right] \tag{14}$$

Further  $v_j/v_i = {}^3\xi_i/{}^3\xi_j$  [30]; Eq. (14) can, therefore, be expressed as:

$$X^{\rm E}(X = H_{\rm m} \,{\rm or}\,\kappa_{\rm S}) = \left[\frac{x_i x_j ({}^3\xi_i / {}^3\xi_j)}{x_i + x_j ({}^3\xi_i / {}^3\xi_j)}\right] \left[(1 + x_i)\chi'_{ij} + x_j\chi_{12}\right]$$
(15)

Eq. (15) contains two unknown parameter  $\chi'_{ij}$  and  $\chi_{12}$ . These parameters were evaluated by employing  $X^E$  ( $X = H_m$  or  $\kappa_S$ ) data at two compositions ( $x_i = 0.4$  and 0.5) and were then utilized (recorded in Table 5) to predict  $X^E$  ( $X = H_m$  or  $\kappa_S$ ) data at various values of  $x_i$ . Such  $H^E_m$  and  $\kappa^E_S$  values are plotted in Figs. 3 and 4 and are also compared with their corresponding experimental values.

Examination of Figs. 3 and 4 reveals that  $H_{\rm m}^{\rm E}$  and  $\kappa_{\rm S}^{\rm E}$  values compare well with their corresponding experimental values. This lends additional support to the basic assumptions made in qualitative analysis of thermodynamic data and also to the assumptions made in deriving Eq. (15).

#### Acknowledgements

The authors are grateful to the Head, Chemistry Department and authorities of Maharshi Dayanand University, Rohtak, for providing research facilities.

#### References

- [1] H. Yekeler, A. Guven, R. Ozkan, J. Chem. Eng. Data 13 (1999) 589-596.
- [2] J.A. Walmsley, J. Phys. Chem. 82 (1978) 2031-2035.
- [3] J.A. Walmsley, E.J. Jacob, H.B. Thompson, J. Phys. Chem. 80 (1976) 2745-2753.
- [4] H. Yekeler, J. Comput. Aided Mol. Des. 15 (2001) 287–295.
- [5] V.K. Sharma, R. Romi, Indian J. Chem. 40A (2001) 1277-1281.
- [6] V.K. Sharma, R. Romi, S. Kumar, Thermochim. Acta 417 (2004) 91-97.
- [7] Dimple, J.S. Yadav, K.C. Singh, V.K. Sharma, Thermochim. Acta 468 (2008) 108-115.
- [8] Dimple, J.S. Yadav, K.C. Singh, V.K. Sharma, J. Solut. Chem. 37 (2008) 1099– 1112.
- [9] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents Physical Properties and Methods of Purification, fourth ed., Wiley, New York, 1986.
- [10] P.L. Pirila-Honkanen, P.A. Ruostesuo, J. Chem. Eng. Data 32 (1987) 303– 306;
  - P.A. Ruosteosuo, P.L. Pirila-Honkanen, L. Heikkinen, J. Phys. Org. Chem. 2 (1989) 565–572.
- [11] P.P. Singh, S.P. Sharma, J. Chem. Eng. Data 30 (1985) 477-479.
- [12] J. George, N.V. Sastry, J. Chem. Eng. Data 49 (2004) 235-242.
- [13] K. Tamura, S. Murakami, S. Doi, J. Chem. Thermodyn. 17 (1985) 325–333.
- [14] C.M. Sehgal, B.R. Porter, J.F. Greenleaf, J. Accoust. Soc. Am. 79 (1986) 586– 589.
- [15] S.W. Schaaf, Molecular Acoustics, Havdolt, New Series, Group II, 1967.
  [16] G. Tardajos, M. Diazpena, E. Aircart, J. Chem. Thermodynam. 18 (1986) 683–689.
- [17] N.V. Sastry, J. George, J. Chem. Eng. Data 48 (2003) 977–979.
- [18] G.C. Benson, O. Kiyohara, J. Chem. Thermodynam. 11 (1979) 1061-1064.
- [19] R.C. Weast, Handbook of Chemistry and Physics, CRC, 1987.
- [20] J.H. Hilderbrand, J.M. Prusnitz, R.L. Scott, Regular and Related Solutions, Van-Nonstand Reinheld Compound, New York, 1971.
- [21] K.Ya. Syrkin, K.M. Anisisnova, Dakl, Nauk, SSSR. 59 (1948) 1457-1460.
- [22] P.P. Singh, V.K. Sharma, S.P. Sharma, Thermochim. Acta 106 (1986) 293-307.
- [23] P.P. Singh, Thermochim. Acta 66 (1983) 37–73.

- [24] L.B. Kier, S.H. Yalkowasky, A.A. Sinkula, S.C. Valvani, Physico-chemical Properties of Drugs, Mercel Dekker, New York, 1980.
- [25] H. Yekeler, A. Guven, R. Ozkan, J. Comput. Aided Mol. Des. 13 (1999) 589–596. [26] C.N.R. Rao, Chemical Application of Infrared Spectroscopy, Academic Press, Lon-
- don, 1963.
- [27] M.L. Huggins, J. Phys. Chem. 74 (1970) 371-378.

- [28] M.L. Huggins, Polymer 12 (1971) 387–399.
  [29] P.P. Singh, M. Bhatia, J. Chem. Soc. Faraday Trans. I 85 (1989) 3807–3812.
  [30] P.P. Singh, R.K. Nigam, K.C. Singh, V.K. Sharma, Thermochim. Acta 46 (1981) 175–191.