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Thermodynamic properties of binary mixtures of tetrahydropyran with pyridine and isomeric picolines: Excess molar volumes, excess molar enthalpies and excess isentropic compressibilities

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ABSTRACT

Densities, ρ and speeds of sound, u of tetrahydropyran (i) + pyridine or α-, β- or γ- picoline (j) binary mixtures at 298.15, 303.15 and 308.15 K and excess molar enthalpies, H^E of the same set of mixtures at 308.15 K have been measured as a function of composition using an anton Parr vibrating-tube digital density and sound analyzer (model DSA 5000) and 2-drop micro-calorimeter, respectively. The resulting density and speed of sound data of the investigated mixtures have been utilized to predict excess molar volumes, V^E and excess isentropic compressibilities, κ_S^E. The observed data have been analyzed in terms of (i) Graph theory; (ii) Prigogine–Flory–Patterson theory. It has been observed that V^E, H^E and κ_S^E data predicted by Graph theory compare well with their experimental values.

1. Introduction

Industry demands reliable and accessible reference data on the thermodynamic properties of binary and ternary liquid mixtures. These properties are required for the development of thermodynamic models, engineering applications along with nature and extent of interactions in liquid mixtures. Cyclic ethers are useful solvents due to strong proton accepting ability. Furthers cyclic ether as alone or their mixtures with aromatic hydrocarbons, alkanols or n-alkanes are used in pharmaceutical and cosmetic processes. This has greatly stimulated the need for extensive information about thermodynamic properties of mixtures containing cyclic ether. In our systematic investigations of thermodynamic properties of binary and ternary mixtures containing cyclic ether, excess molar volumes, V^E, excess molar enthalpies, H^E, excess Gibbs free energies, G^E and excess isentropic compressibilities, κ_S^E data of binary [1–3] and ternary [4,5] mixtures have been analyzed in terms of Graph theory (which involves the topology of a molecule). In continuing with our study on thermodynamic properties of cyclic mixtures, we report here the densities, speeds of sound and excess molar enthalpies data of tetrahydropyran (i) + pyridine or α-, β- or γ-picoline(j) mixtures.

2. Experimental

Tetrahydropyran (THP) (Fluka, 98 mol.%), pyridine (Py) (Fluka, 99 mol.%), α-picoline (Fluka, 98 mol.%), β-picoline (Fluka, 98 mol.%), γ-picoline (Fluka, 99 mol.%) were purified by standard methods [6]. The purities of the purified liquids were checked by measuring their densities (recorded in Table 1) using Anton Parr DSA 5000 at 298.15 ± 0.01 K. These values agreed to within $\pm 2 \times 10^{-3}$ kg m^{-3} with their literature values [6,7]. Excess molar enthalpies, H^E for the studied mixtures were measured by a 2-drop calorimeter (model, 4600) supplied by the Calorimeter Sciences Corporation (CSC), USA at 308.15 K in a manner described elsewhere [8]. The uncertainties in the measured H^E values are 1%.

Densities, ρ and speed of sound, u of the pure liquids and their binary mixtures were measured using an anton Parr vibrating-tube digital density and sound analyzer (model DSA 5000) as explained in the literature [9]. The measurements are based on measuring the period of oscillation of a vibrating U-shaped hollow tube filled with the sample. The instrument was calibrated with the double distilled deionized water before each series of measurements. The mole fraction of each mixture was obtained with uncertainty of

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Table 1
Comparison of densities, ρ and speed of sound, u pure liquids with their literature values at a temperature of 298.15 K.

Liquids	ρ/kg m^{-3}		u/m s^{-1}	
	Exptl.	Lit.	Exptl.	Lit.
Tetrahydropyran	879.136	879.16 [7]	1269.88	1270.0 [10]
Pyridine	978.249	978.24 [6]	1417.61	1418.0 [11]
α-Picoline	939.802	939.81 [6]	1380.12	1379.18 [12]
β-Picoline	952.002	951.97 [6]	1424.01	1423.08 [13]
γ-Picoline	950.179	950.20 [6]	1431.50	1431.89 [11]
				1423.97 [14]

1×10^{-4} from the measured apparent masses of the components. All the measurements were performed on an electric balance. The speeds of sound values for the purified liquids at 298.15 ± 0.01 K (recorded in Table 1) compare well with their experimental values [10–13]. However, our speed of sound value for 4-methylpyridine differ by 0.3% from the value reported by Marczak et al. [14]. The uncertainties in the density and speeds of sound measurements are 2×10^{-3} kg m^{-3} and 0.1 m s^{-1}, respectively.

3. Results

Densities, ρ and speeds of sound, u of THP (i) + Py or α-, β- or γ-picoline (j) binary mixtures at 298.15, 303.15 and 308.15 K and excess molar enthalpies, H^E of the same set of mixtures at 308.15 K are listed in Table 2. Densities and speeds of sound values of mixtures were employed to predict excess molar volumes, V^E and isentropic compressibilities, κ_S using

$$V^E = \sum_{i=i}^{j} x_i M_i (\rho)^{-1} - \sum_{i=i}^{j} x_i M_i (\rho_i)^{-1} \qquad (1)$$

$$\kappa_S = (\rho u^2)^{-1} \qquad (2)$$

where ρ is the density of mixture and x_i, M_i and ρ_i are the mole fraction, molar mass and density of component (i), respectively. Excess isentropic compressibilities, κ_S^E values were determined using Eq. (3):

$$\kappa_S^E = \kappa_S - \kappa_S^{\mathrm{id}} \qquad (3)$$

κ_S^{id} values were obtained in the manner suggested by Benson and Kiyohara [15]:

$$\kappa_S^{\mathrm{id}} = \sum_{i=i}^{j} \phi_i \left[\kappa_{S,i} + \frac{T v_i \alpha_i^2}{C_{p,i}}\right] - T\left(\sum_{i=i}^{j} x_i v_i\right) \frac{\left(\sum_{i=i}^{j} \phi_i \alpha_i\right)^2}{\left(\sum_{i=i}^{j} x_i C_{p,i}\right)} \qquad (4)$$

where ϕ_i is the volume fraction of component (i) in the mixed state. $\kappa_{S,i}$, v_i, α_i and $C_{p,i}$ are isentropic compressibility, molar volume, thermal expansion coefficient and molar heat capacity, respectively, of the pure component (i). The α and $C_{p,i}$ values were taken from literature [16]. Such κ_S^E values for the various mixtures are recorded in Table 2. V^E, H^E and κ_S^E data for (i + j) mixtures are plotted in Figs. 1–7.

The observed V^E, H^E and κ_S^E data were fitted to Eq. (5):

$$X^E (X = V \text{ or } H \text{ or } \kappa_S) = x_i x_j [X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}(2x_j - 1)^2] \qquad (5)$$

where $X^{(n)}(n = 0 - 2)$, etc., are the parameters characteristic of (i + j) mixtures. These parameters were determined by fitting X^E ($X = V$ or H or κ_S) data to Eq. (5) using least-squares methods and are recorded along with standard deviations, $((X^E)$ $(X = V$ or H or $\kappa_S)$

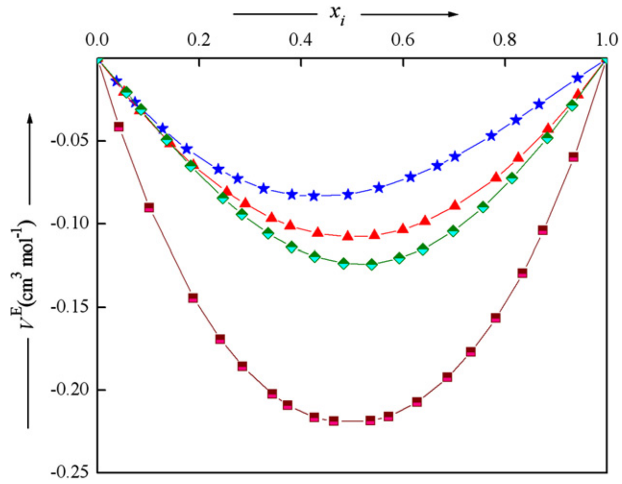


Fig. 1. Excess molar volumes, V^E at 298.15 K: (I) tetrahydropyran (i) + pyridine (j) (■); (II) tetrahydropyran (i) + α-picoline (j) (★); (III) tetrahydropyran (i) + β-picoline (j) (◆); (IV) tetrahydropyran (i) + γ-picoline (j) (▲).

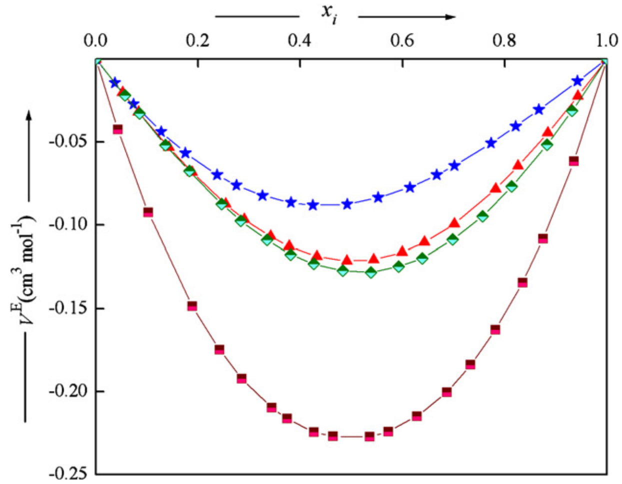


Fig. 2. Excess molar volumes, V^E at 303.15 K: (I) tetrahydropyran (i) + pyridine (j) (■); (II) tetrahydropyran (i) + α-picoline (j) (★); (III) tetrahydropyran (i) + β-picoline (j) (◆); (IV) tetrahydropyran (i) + γ-picoline (j) (▲).

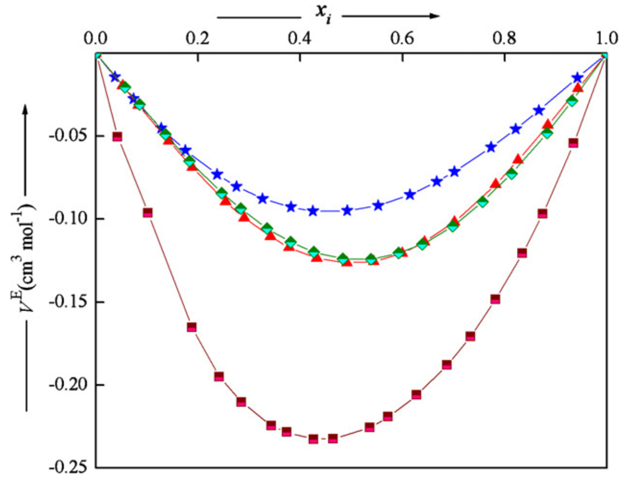


Fig. 3. Excess molar volumes, V^E at 308.15 K: (I) tetrahydropyran (i) + pyridine (j) (■); (II) tetrahydropyran (i) + α-picoline (j) (★); (III) tetrahydropyran (i) + β-picoline (j) (◆); (IV) tetrahydropyran (i) + γ-picoline (j) (▲).

Table 2

Measured densities, ρ; excess molar volumes, V^E, speeds of sound, u; isentropic compressibilities, κ_S and excess isentropic compressibilities, κ_S^E data for the various (i + j) mixtures as a function of mole fraction, x_i, of component (i) at a temperature of 298.15, 303.15 and 308.15 K.

x_i	ρ/kg m^3	V^E/cm^3 mol^{-1}	U/m s^{-1}	κ_S/TPa^{-1}	κ_S^E/TPa^{-1}
Tetrahydropyran (i) + pyridine (j)					
T = 298.15 K[a]					
0.0	978.249	–	1417.61	–	–
0.0427	973.663	−0.0414	1411.86	515.24	−1.83
0.1021	967.309	−0.0903	1403.64	524.71	−4.04
0.1883	958.157	−0.1446	1391.41	539.09	−6.62
0.2415	952.565	−0.1695	1383.71	548.29	−7.88
0.2853	948.002	−0.1859	1377.39	556.02	−8.79
0.3438	941.972	−0.2026	1368.76	566.64	−9.66
0.3742	938.871	−0.2093	1364.19	572.33	−9.95
0.4263	933.597	−0.2168	1356.48	582.12	−10.40
0.4642	929.793	−0.2190	1350.74	589.48	−10.50
0.5364	922.650	−0.2186	1339.81	603.78	−10.40
0.5721	919.167	−0.2162	1334.38	611.01	−10.21
0.6283	913.730	−0.2074	1325.82	622.61	−9.65
0.6872	908.097	−0.1925	1316.86	635.02	−8.82
0.7336	903.711	−0.1771	1309.84	644.96	−8.01
0.7823	899.149	−0.1567	1302.46	655.60	−6.95
0.8351	894.248	−0.1296	1294.44	667.39	−5.55
0.8752	890.543	−0.1041	1288.46	676.41	−4.42
0.9354	885.027	−0.0596	1279.46	690.23	−2.44
1.0	879.136	–	1269.88	–	–
T = 303.15 K[b]					
0.0	973.224	–	1397.37	–	–
0.0427	968.634	−0.0423	1391.42	533.24	−1.93
0.1021	962.276	−0.0925	1382.91	543.42	−4.24
0.1883	953.120	−0.1485	1370.21	558.83	−6.89
0.2415	947.532	−0.1749	1362.22	568.74	−8.14
0.2853	942.969	−0.1922	1355.58	577.12	−8.97
0.3438	936.936	−0.2097	1346.67	588.53	−9.81
0.3742	933.829	−0.2164	1342.11	594.52	−10.22
0.4263	928.553	−0.2244	1334.03	605.15	−10.52
0.4642	924.748	−0.2271	1328.19	613.01	−10.59
0.5364	917.601	−0.2273	1317.07	628.24	−10.51
0.5721	914.108	−0.2242	1311.58	635.93	−10.31
0.6283	908.661	−0.2149	1302.93	648.27	−9.75
0.6872	903.027	−0.2004	1293.91	661.45	−8.93
0.7336	898.628	−0.1839	1286.86	671.98	−8.13
0.7823	894.056	−0.1627	1279.45	683.26	−7.07
0.8351	889.143	−0.1344	1271.47	695.69	−5.72
0.8752	885.431	−0.1081	1265.41	705.31	−4.51
0.9354	879.898	−0.0616	1256.43	719.93	−2.52
1.0	873.992	–	1246.83	–	–
T = 308.15 K[c]					
0.0	968.166	–	1377.11	–	–
0.0427	963.658	−0.0505	1370.94	552.13	−2.04
0.1021	957.232	−0.0964	1362.28	562.92	−4.49
0.1883	948.063	−0.1533	1349.36	579.31	−7.33
0.2415	942.634	−0.1952	1341.09	589.85	−8.65
0.2853	938.037	−0.2104	1334.35	598.74	−9.53
0.3438	931.957	−0.2247	1325.41	610.81	−10.50
0.3742	928.814	−0.2286	1320.64	617.31	−10.81
0.4263	923.491	−0.2328	1312.48	628.62	−11.11
0.4642	919.649	−0.2325	1306.66	636.88	−11.32
0.5364	912.425	−0.2258	1295.36	653.16	−11.11
0.5721	908.895	−0.2193	1289.82	661.34	−10.90
0.6283	903.408	−0.2062	1281.08	674.47	−10.31
0.6872	897.739	−0.1881	1271.93	688.53	−9.37
0.7336	893.335	−0.1709	1264.73	699.83	−8.42
0.7823	888.752	−0.1484	1257.29	711.79	−7.32
0.8351	883.845	−0.1205	1249.19	725.05	−5.83
0.8752	880.16	−0.0968	1243.09	735.25	−4.58
0.9354	874.668	−0.0544	1234.08	750.71	−2.55
1.0	868.831	–	1224.47	–	–
Tetrahydropyran (i) + α-picoline (j)					
T = 298.15 K[d]					
0.0	939.802	–	1380.12	–	–
0.0367	937.731	−0.0138	1376.63	562.71	−1.31
0.0731	935.665	−0.0265	1373.05	566.91	−2.46
0.1274	932.552	−0.0425	1367.74	573.22	−4.11
0.1751	929.795	−0.0547	1362.96	578.96	−5.37
0.2373	926.162	−0.0671	1356.58	586.71	−6.75
0.2752	923.926	−0.0726	1352.58	591.61	−7.41
0.3262	920.901	−0.0786	1347.16	598.34	−8.16

Table 2 (*Continued*)

x_i	ρ/kg m^3	V^E/cm^3 mol^{-1}	U/m s^{-1}	κ_S/TPa^{-1}	κ_S^E/TPa^{-1}
0.3817	917.578	−0.0824	1341.22	605.86	−8.79
0.4248	914.974	−0.0831	1336.46	611.90	−9.07
0.4916	910.915	−0.0823	1328.94	621.61	−9.17
0.5525	907.178	−0.0781	1322.05	630.69	−9.02
0.6147	903.336	−0.0717	1314.88	640.32	−8.54
0.6674	900.064	−0.0649	1308.71	648.71	−7.86
0.7018	897.916	−0.0593	1304.67	654.28	−7.34
0.7736	893.419	−0.0467	1296.28	666.11	−6.04
0.8219	890.381	−0.0372	1290.59	674.29	−4.95
0.8673	887.518	−0.0277	1285.27	682.08	−3.82
0.9428	882.751	−0.0118	1276.47	695.25	−1.73
1.0	879.136	–	1269.88	–	–
T = 303.15 K[e]					
0.0	935.117	–	1361.02	–	–
0.0367	933.031	−0.0143	1357.59	581.52	−1.61
0.0731	930.947	−0.0271	1354.06	585.87	−3.04
0.1274	927.811	−0.0437	1348.55	592.66	−4.86
0.1751	925.036	−0.0567	1343.52	598.91	−6.19
0.2373	921.378	−0.0698	1336.74	607.39	−7.57
0.2752	919.130	−0.0761	1332.51	612.75	−8.23
0.3262	916.081	−0.0822	1326.74	620.15	−8.92
0.3817	912.735	−0.0864	1320.36	628.45	−9.43
0.4248	910.121	−0.0881	1315.36	635.06	−9.66
0.4916	906.032	−0.0875	1307.55	645.57	−9.75
0.5525	902.268	−0.0834	1300.37	655.43	−9.55
0.6147	898.401	−0.0773	1293.03	665.75	−9.11
0.6674	895.101	−0.0698	1286.79	674.71	−8.51
0.7018	892.937	−0.0642	1282.71	680.66	−8.02
0.7736	888.402	−0.0507	1274.15	693.34	−6.73
0.8219	885.337	−0.0404	1268.38	702.09	−5.65
0.8673	882.452	−0.0305	1262.94	710.47	−4.47
0.9428	877.641	−0.0132	1253.81	724.81	−2.12
1.0	873.992	–	1246.83	–	–
T = 308.15 K[f]					
0.0	930.414	–	1339.89	–	–
0.0367	928.307	−0.0142	1336.37	603.19	−1.68
0.0731	926.208	−0.0275	1332.79	607.81	−3.22
0.1274	923.053	−0.0452	1327.20	615.04	−5.16
0.1751	920.257	−0.0585	1322.05	621.72	−6.54
0.2373	916.581	−0.0731	1315.19	630.74	−8.03
0.2752	914.323	−0.0803	1310.93	636.41	−8.76
0.3262	911.259	−0.0876	1305.14	644.23	−9.56
0.3817	907.895	−0.0927	1298.68	653.07	−10.10
0.4248	905.265	−0.0951	1293.68	660.04	−10.41
0.4916	901.153	−0.0949	1285.77	671.23	−10.51
0.5525	897.366	−0.0917	1278.52	681.74	−10.30
0.6147	893.468	−0.0852	1271.12	692.71	−9.84
0.6674	890.140	−0.0773	1264.78	702.28	−9.17
0.7018	887.961	−0.0714	1260.69	708.59	−8.68
0.7736	883.383	−0.0566	1252.02	722.15	−7.25
0.8219	880.292	−0.0456	1246.23	731.44	−6.12
0.8673	877.377	−0.0344	1240.72	740.39	−4.84
0.9428	872.516	−0.0147	1231.51	755.71	−2.29
1.0	868.831	–	1224.47	–	–
Tetrahydropyran (i) + β-picoline (j)					
T = 298.15 K[g]					
0.0	952.002	–	1424.01	–	–
0.0562	948.099	−0.0203	1415.9	526.12	−2.42
0.0848	946.113	−0.0308	1411.81	530.28	−3.62
0.1357	942.576	−0.0491	1404.51	537.81	−5.62
0.1826	939.306	−0.0649	1397.84	544.85	−7.37
0.2461	934.857	−0.0842	1388.75	554.64	−9.48
0.2833	932.236	−0.0941	1383.27	560.61	−10.48
0.3345	928.610	−0.1057	1375.76	568.96	−11.72
0.3813	925.271	−0.1137	1368.64	576.97	−12.48
0.4262	922.049	−0.1195	1361.77	584.84	−13.02
0.4827	917.964	−0.1235	1353.02	595.07	−13.38
0.5378	913.951	−0.1242	1344.31	605.45	−13.32
0.5924	909.933	−0.1204	1335.45	616.22	−12.78
0.6382	906.545	−0.1153	1328.02	625.46	−12.12
0.6982	902.068	−0.1043	1318.12	638.05	−10.78
0.7568	897.664	−0.0899	1308.58	650.56	−9.25
0.8138	893.349	−0.0723	1299.23	663.15	−7.34
0.8825	888.124	−0.0481	1288.18	678.54	−4.82
0.9321	884.334	−0.0284	1280.31	689.85	−2.81
1.0	879.136	–	1269.88	–	–

Table 2 (*Continued*)

x_i	ρ/kg m^3	V^E/cm^3 mol^{-1}	U/m s^{-1}	κ_S/TPa^{-1}	κ_S^E/TPa^{-1}
T = 303.15 K[h]					
0.0	947.449	–	1404.05	–	–
0.0562	943.521	−0.0218	1395.63	544.13	−2.54
0.0848	941.519	−0.0327	1391.38	548.63	−3.78
0.1357	937.954	−0.0517	1383.94	556.65	−5.97
0.1826	934.651	−0.0675	1377.11	564.18	−7.85
0.2461	930.166	−0.0874	1367.79	574.65	−10.12
0.2833	927.522	−0.0974	1362.33	580.91	−11.32
0.3345	923.861	−0.1088	1354.50	589.98	−12.52
0.3813	920.499	−0.1176	1347.26	598.51	−13.38
0.4262	917.247	−0.1231	1340.31	606.88	−14.02
0.4827	913.129	−0.1273	1331.24	617.95	−14.28
0.5378	909.085	−0.1282	1322.36	629.06	−14.22
0.5924	905.038	−0.1247	1313.31	640.62	−13.62
0.6382	901.626	−0.1198	1305.72	650.54	−12.88
0.6982	897.114	−0.1086	1295.59	664.08	−11.38
0.7568	892.682	−0.0946	1285.81	677.56	−9.65
0.8138	888.335	−0.0767	1276.37	690.99	−7.66
0.8825	883.068	−0.0516	1265.13	707.52	−4.91
0.9321	879.246	−0.0311	1257.25	719.53	−2.85
1.0	873.992	–	1246.83	–	–
T = 308.15 K[i]					
0.0	942.831	–	1384.03	–	–
0.0562	938.854	−0.0205	1375.63	562.86	−2.87
0.0848	936.827	−0.0307	1371.38	567.57	−4.27
0.1357	933.219	−0.0487	1363.82	576.11	−6.63
0.1826	929.891	−0.0649	1356.75	584.21	−8.56
0.2461	925.361	−0.0842	1347.21	595.43	−10.93
0.2833	922.691	−0.0937	1341.47	602.26	−12.06
0.3345	919.004	−0.1057	1333.61	611.82	−13.45
0.3813	915.608	−0.1137	1326.24	620.93	−14.35
0.4262	912.336	−0.1199	1319.15	629.88	−15.01
0.4827	908.186	−0.1239	1310.11	641.52	−15.46
0.5378	904.106	−0.1242	1301.21	653.26	−15.51
0.5924	900.027	−0.1204	1292.28	665.32	−15.13
0.6382	896.591	−0.1153	1284.67	675.81	−14.44
0.6982	892.051	−0.1043	1274.69	689.93	−13.16
0.7568	887.584	−0.0895	1264.90	704.17	−11.45
0.8138	883.218	−0.0725	1255.39	718.41	−9.41
0.8825	877.926	−0.0481	1243.91	736.16	−6.36
0.9321	874.092	−0.0286	1235.66	749.28	−3.85
1.0	868.831	–	1224.47	–	–
Tetrahydropyran (i) + γ-picoline (j)					
T = 298.15 K[j]					
0.0	950.179	–	1431.50	–	–
0.0521	946.678	−0.0205	1422.65	521.92	−1.66
0.0832	944.577	−0.0317	1417.47	526.91	−2.63
0.1426	940.548	−0.0515	1407.78	536.47	−4.46
0.1882	937.434	−0.0647	1400.51	543.86	−5.82
0.2536	932.939	−0.0807	1390.11	554.69	−7.53
0.2902	930.406	−0.0879	1384.26	560.91	−8.33
0.3415	926.841	−0.0966	1376.14	569.73	−9.35
0.3782	924.275	−0.1012	1370.29	576.21	−9.92
0.4323	920.471	−0.1056	1361.57	586.01	−10.51
0.4913	916.295	−0.1078	1352.07	596.99	−10.82
0.5437	912.559	−0.1069	1343.57	607.04	−10.80
0.5991	908.587	−0.1034	1334.51	618.01	−10.49
0.6427	905.441	−0.0986	1327.31	626.91	−9.95
0.7015	901.173	−0.0893	1317.68	639.11	−9.02
0.7822	895.277	−0.0723	1304.42	656.46	−7.14
0.8263	892.032	−0.0603	1297.25	666.15	−5.91
0.8846	887.726	−0.0427	1287.92	679.12	−4.12
0.9435	883.352	−0.0221	1278.58	692.49	−2.05
1.0	879.136	–	1269.88	–	–
T = 303.15 K[k]					
0.0	945.413	–	1410.67	–	–
0.0521	941.884	−0.0202	1402.24	539.95	−2.22
0.0832	939.773	−0.0318	1397.22	545.06	−3.47
0.1426	935.733	−0.0533	1387.61	555.03	−5.68
0.1882	932.615	−0.0682	1380.26	562.83	−7.19
0.2536	928.121	−0.0874	1369.66	574.34	−9.06
0.2902	925.591	−0.0965	1363.75	580.92	−9.93
0.3415	922.019	−0.1068	1355.33	590.44	−10.90
0.3782	919.451	−0.1127	1349.31	597.38	−11.51
0.4323	915.637	−0.1187	1340.47	607.80	−12.11
0.4913	911.443	−0.1214	1330.69	619.61	−12.40

Table 2 (*Continued*)

x_i	ρ/kg m^3	V^E/cm^3 mol^{-1}	U/m s^{-1}	κ_S/TPa^{-1}	κ_S^E/TPa^{-1}
0.5437	907.692	−0.1207	1322.01	630.38	−12.30
0.5991	903.687	−0.1162	1312.76	642.11	−11.91
0.6427	900.515	−0.1103	1305.54	651.52	−11.40
0.7015	896.211	−0.0992	1295.65	664.69	−10.31
0.7822	890.253	−0.0784	1282.29	683.15	−8.34
0.8263	886.976	−0.0645	1275.01	693.52	−6.98
0.8846	882.631	−0.0445	1265.48	707.47	−4.91
0.9435	878.225	−0.0223	1255.88	721.94	−2.53
1.0	873.992	–	1246.83	–	–
T = 308.15 K[l]					
0.0	940.821	–	1389.89	–	–
0.0521	936.955	−0.0195	1380.63	559.93	−2.51
0.0832	935.004	−0.0312	1376.22	564.69	−3.96
0.1426	931.541	−0.0530	1368.39	573.29	−6.43
0.1882	928.307	−0.0688	1360.75	581.77	−8.15
0.2536	923.922	−0.0894	1350.54	593.41	−10.30
0.2902	921.331	−0.0992	1344.38	600.54	−11.29
0.3415	917.744	−0.1105	1336.05	610.43	−12.51
0.3782	914.432	−0.1172	1328.04	620.05	−13.11
0.4323	911.254	−0.1236	1320.78	629.07	−13.82
0.4913	907.207	−0.1265	1311.35	641.02	−14.21
0.5437	903.227	−0.1256	1302.07	653.04	−14.10
0.5991	899.247	−0.1206	1292.81	665.35	−13.69
0.6427	895.885	−0.1138	1285.21	675.77	−13.19
0.7015	891.453	−0.1017	1275.03	690.01	−12.01
0.7822	887.030	−0.0791	1264.52	705.04	−9.74
0.8263	882.795	−0.0644	1255.21	718.96	−8.21
0.8846	877.665	−0.0434	1243.94	736.33	−5.78
0.9435	873.901	−0.0212	1235.3	749.88	−3.01
1.0	868.831	–	1224.47	–	–

[a] $V^{(0)} = -0.8802$; $V^{(1)} = 0.0125$; $V^{(2)} = -0.1502$; $\sigma(V^E) = 0.0002$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -41.99$; $\kappa_S^{(1)} = 2.32$; $\kappa_S^{(2)} = -0.04$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}.

[b] $V^{(0)} = -0.9128$; $V^{(1)} = 0.0047$; $V^{(2)} = -0.1449$; $\sigma(V^E) = 0.0002$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -42.48$; $\kappa_S^{(1)} = 2.96$; $\kappa_S^{(2)} = -1.94$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}.

[c] $V^{(0)} = -0.9195$; $V^{(1)} = 0.1850$; $V^{(2)} = -0.1827$; $\sigma(V^E) = 0.0002$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -44.95$; $\kappa_S^{(2)} = 4.17$; $\kappa_S^{(2)} = -0.76$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}; $H^{(0)} = 597.2$; $H^{(1)} = 409.2$; $H^{(2)} = 27.1$; $\alpha\,(H^E) = 1.2$ J mol^{-1}.

[d] $V^{(0)} = -0.3272$; $V^{(1)} = 0.0965$; $V^{(2)} = 0.0279$; $\sigma(V^E) = 0.0001$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -36.72$; $\kappa_S^{(1)} = 2.58$; $\kappa_S^{(2)} = 3.17$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}.

[e] $V^{(0)} = -0.3477$; $V^{(1)} = 0.0888$; $V^{(2)} = 0.0338$; $\sigma(V^E) = 0.0001$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -38.94$; $\kappa_S^{(1)} = 3.29$; $\kappa_S^{(2)} = -4.25$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}.

[f] $V^{(0)} = -0.3787$; $V^{(1)} = 0.0735$; $V^{(2)} = 0.0499$; $\sigma(V^E) = 0.0001$ cm^3 mol^{-1}. $\kappa_S^{(0)} = -41.94$; $\kappa_S^{(1)} = 2.89$; $\kappa_S^{(2)} = -3.79$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}; $H^{(0)} = 711.1$; $H^{(1)} = 355.1$; $H^{(2)} = 67.5$; $\alpha\,(H^E) = 1.4$ J mol^{-1}.

[g] $V^{(0)} = -0.4967$; $V^{(1)} = -0.0342$; $V^{(2)} = 0.1026$; $\sigma(V^E) = 0.0001$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -53.4773$; $\kappa_S^{(1)} = 0.792$; $\kappa_S^{(2)} = 11.1666$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}.

[h] $V^{(0)} = -0.5122$; $V^{(1)} = -0.0424$; $V^{(2)} = 0.0793$; $\sigma(V^E) = 0.0001$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -57.32\ \kappa_S^{(1)} = 1.92$; $\kappa_S^{(2)} = 14.43$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}.

[i] $V^{(0)} = -0.5321$; $V^{(1)} = 0.0670$; $V^{(2)} = 0.0694$; $\sigma(V^E) = 0.0001$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -62.13$; $\kappa_S^{(1)} = -3.46$; $\kappa_S^{(2)} = 6.02$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}; $H^{(0)} = 512.1$; $H^{(1)} = -48.1$; $H^{(2)} = -84.5$; $\alpha\,(H^E) = 1.1$ J mol^{-1}.

[j] $V^{(0)} = -0.4309$; $V^{(1)} = 0.0007$; $V^{(2)} = 0.0219$; $\sigma(V^E) = 0.0001$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -43.33$; $\kappa_S^{(1)} = -2.87$; $\kappa_S^{(2)} = 9.14$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}.

[k] $V^{(0)} = -0.4863$; $V^{(1)} = -0.0047$; $V^{(2)} = 0.0929$; $\sigma(V^E) = 0.0001$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -49.53$; $\kappa_S^{(1)} = -1.35$; $\kappa_S^{(2)} = 4.17$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}.

[l] $V^{(0)} = -0.5067$; $V^{(1)} = -0.0023$; $V^{(2)} = 0.1389$; $\sigma(V^E) = 0.0001$ cm^3 mol^{-1}; $\kappa_S^{(0)} = -56.80$; $\kappa_S^{(1)} = -2.97$; $\kappa_S^{(2)} = 3.83$; $\sigma(\kappa_S^E) = 0.02$ TPa^{-1}; $H^{(0)} = 688.1$; $H^{(1)} = 149.6$; $H^{(2)} = -313.7$; $\alpha\,(H^E) = 1.3$ J mol^{-1}.

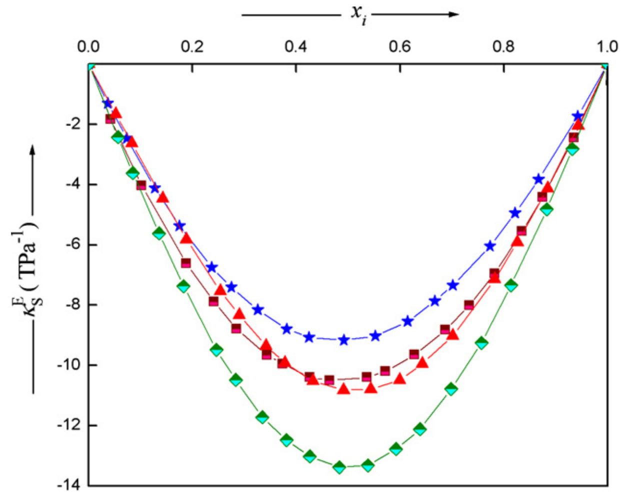


Fig. 4. Excess isentropic compressibilities, κ_S^E at 298.15 K: (I) tetrahydropyran (i) + pyridine (j) (🟥); (II) tetrahydropyran (i) + α-picoline (j) (★); (III) tetrahydropyran (i) + β-picoline (j) (◆); (IV) tetrahydropyran (i) + γ-picoline (j) (▲).

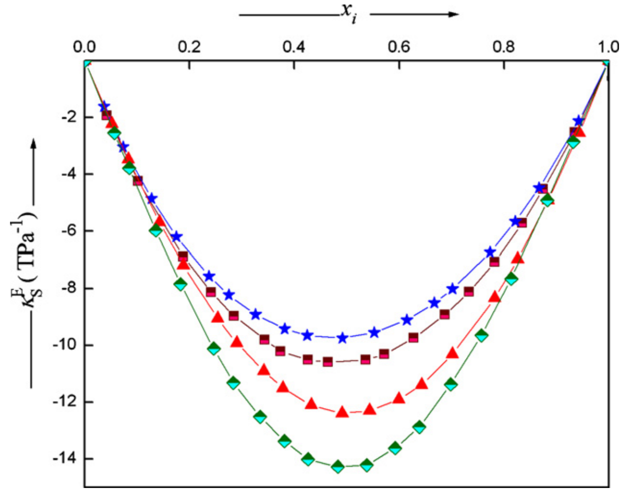


Fig. 5. Excess isentropic compressibilities, κ_S^E at 303.15 K: (I) tetrahydropyran (i) + pyridine (j) (🟥); (II) tetrahydropyran (i) + α-picoline (j) (★); (III) tetrahydropyran (i) + β-picoline (j) (◆); (IV) tetrahydropyran (i) + γ-picoline (j) (▲).

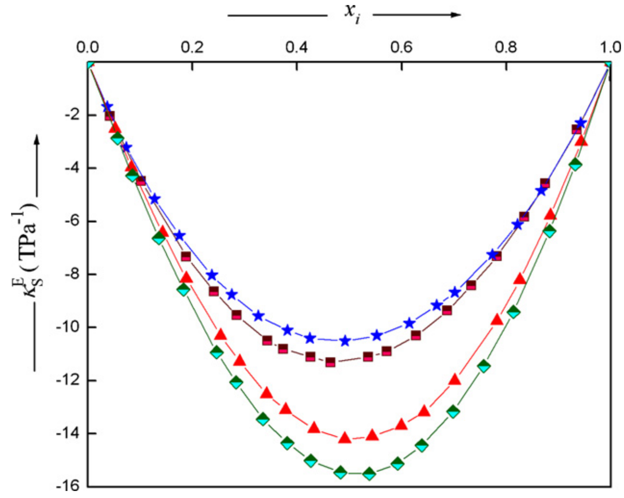


Fig. 6. Excess isentropic compressibilities, κ_S^E at 308.15 K: (I) tetrahydropyran (i) + pyridine (j) (■); (II) tetrahydropyran (i) + α-picoline (j) (★); (III) tetrahydropyran (i) + β-picoline (j) (◆); (IV) tetrahydropyran (i) + γ-picoline (j) (▲).

defined by

$$\sigma(X^E) = \left[\frac{\sum (X^E_{\text{exptl}} - X^E_{\text{calc.Eq.(5)}})^2}{(m-n)}\right]^{0.5} \tag{6}$$

where m is the number of experimental points and n is the number of adjustable parameters in Eq. (5) in Table 2.

4. Discussion

We are unaware of V^E, H^E and κ_S^E data of the studied mixtures with which to compare our results. Excess molar enthalpies, H^E data of (i + j) mixtures are positive over entire composition range and for equimolar composition follow the order: α-picoline ≅ γ-picoline > Py > β-picoline. However, excess molar volumes, V^E and excess isentropic compressibilities, κ_S^E values are negative over entire composition range and for equimolar composition vary in the order: Py > β-picoline > γ-picoline > α-picoline; β-picoline > γ-picoline ≅ Py > α-picoline, respectively. $\partial V^E/\partial T$ and $\partial\kappa_S^E/\partial T$ values of THP (i) + Py or α- or β- or γ-picoline (j) mixtures are positive.

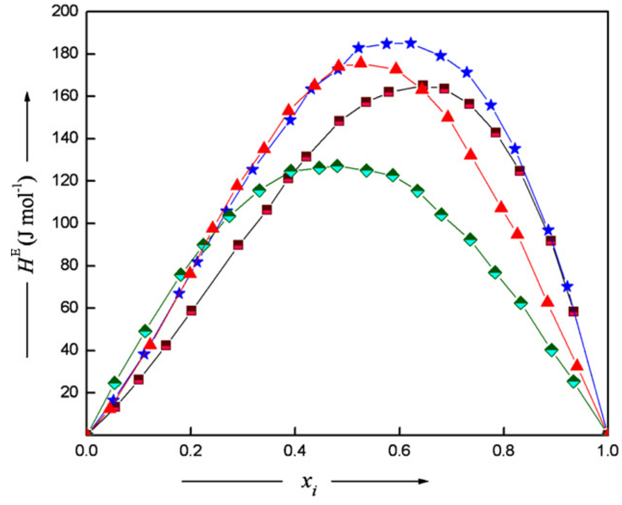


Fig. 7. Excess molar enthalpies, H^E at 308.15 K: (I) tetrahydropyran (i) + pyridine (j); (■); (II) tetrahydropyran (i) + α-picoline (j); (★); (III) tetrahydropyran (i) + β-picoline (j); (◆); (IV) tetrahydropyran (i) + γ-picoline (j); (▲).

The observed V^E, H^E and κ_S^E data of the investigated mixtures can be explained qualitatively, if it is assumed that (i) THP or Py or α-, β- or γ-picoline are associated molecular entities and there is formation of unlike ($\mathrm{i_n}$–$\mathrm{j_n}$) contacts; (ii) unlike contact ($\mathrm{i_n}$–$\mathrm{j_n}$) formation weakens self association of $\mathrm{i_n}$ and $\mathrm{j_n}$ which leads to their depolymerization to form i and j molecules; (iii) molecules of i and j undergo interactions to form i:j molecular complex H^E data of THP (i) + Py (j) mixture suggest that contribution to H^E due to factor (ii) far outweigh the contribution due to factors (i) and (iii) so that over all H^E values for this mixture are positive. The introduction of –CH$_3$ group to Py (as in α- or β- or γ-picoline) would increase π-electron density of nitrogen atom of picolines and thus contribution to H^E due to factor (iii) would be more in THP (i) + α- or β- or γ-picoline (j) mixtures as compared to THP (i) + Py (j) mixture. Consequently, H^E for THP (i) + α- or β- or γ-picoline (j) mixtures should be less than those of THP (i) + Py (j) mixtures. The H^E values of THP (i) + α- or γ-picoline (j) mixtures do not support this view point. This may be due to steric repulsion between THP (i) + α- or γ-picoline (j) mixtures. V^E and κ_S^E data of the studied mixtures suggest that α-picoline gives least packed structure in THP as compared to Py or β- or γ-picoline. This may be due to presence of –CH$_3$ group (adjacent to nitrogen atom in Py) which restrict the approach of α-picoline to THP molecule.

The observed V^E, H^E and κ_S^E data of the studied mixtures have been analyzed in term of (i) Graph theory and (ii) Prigogine–Flory–Patterson theory.

5. Graph theory

5.1. Excess molar volumes

Graph theory deals with the topology of the constituents of mixtures. Topology of the pure (i) and (j) components changes on the addition of i to j or vice versa in (i + j) mixture. Since excess molar volumes, V^E reflects change in topology of the constituents of mixtures, V^E data of (i + j) mixtures were, therefore, analyzed in terms of Graph theory. According to this theory [17], V^E is given by

$$V^E = \alpha_{ij}\left\{\left[\sum x_i({}^3\xi_j)_m\right]^{-1} - \left[\sum x_i({}^3\xi_j)\right]^{-1}\right\} \tag{7}$$

where x_i is the mole fraction of the component (i) and α_{ij} is a constant characteristic of (i + j) mixture. $({}^3\xi_i)$, $({}^3\xi_j)_m$ (i = i or j) are the connectivity parameters of third degree of the components i and j in pure and mixed state and are defined [18] by

$$^3\xi = \sum_{m<n<o<p} (\delta_m^\nu \delta_n^\nu \delta_p^\nu)^{-0.5} \tag{8}$$

where δ_m^ν, etc., reflects the explicitly [19] the valency of mth vertex in molecular graph of component in forming bonds and have been calculated by employing relation [19]: $\delta_m^\nu = Z_m - h_m$, where Z_m is the maximum valency of atom and h_m is the number of hydrogen atoms attached to it. These parameters for the studied mixtures were determined by employing V^E data to Eq. (7). Only those $^3\xi$ values were retained that best reproduced the experimental V^E data. Such $({}^3\xi_i)$, $({}^3\xi_j)_m$ (i = i or j) parameters (which described well experimental V^E data) along with V^E values at other values of mole fraction of (i), x_i are listed in Table 3. Examination of data in Table 3 reveals that V^E values compare well with their experimental values. These $({}^3\xi_i)$, $({}^3\xi_j)_m$ (i = i or j) values were then utilized to extract information about the state of i and j components in their pure and mixed state.

For this purpose it was assumed that THP, Py or α- or β- or γ-picoline exist as molecular entities **I–II**, **III–V**, **VI–IX**, **X–XII** and **XIII–XIV**, respectively (Scheme 1) and their $^3\xi^l$ values were calculated from structural consideration {via Eq. (8)}.

Table 3

Comparison of calculated V^E, H^E (at $T = 308.15$ K) and κ_S^E values from appropriate equations with their corresponding experimental values at temperature of (298.15, 303.15 and 308.15 K) along with their $({}^3\xi_i) = ({}^3\xi_j)_m$ (i = i or j); α_{ij} and χ'_{ij} parameters for the various (i + j) mixtures as a function of x_i, mole fraction of component (i).

Properties	Mole fraction of component (i), x_i								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Tetrahydropyran (i) + pyridine (j)									
$T = 298.15$ K[a]									
V^E (Exptl)	−0.0881	−0.1507	−0.1909	−0.2133	−0.2201	−0.2121	−0.1888	−0.1453	−0.0871
V^E (Graph)	−0.0876	−0.1517	−0.1941	−0.2164	–	−0.2062	−0.1763	−0.1313	−0.0723
V^E (PFP)	−0.0511	−0.0917	−0.1219	−0.1411	−0.1490	−0.1451	−0.1288	−0.0996	−0.0569
κ_S^E (Exptl)	−3.93	−6.94	−9.01	−10.19	−10.51	−9.97	−8.63	−6.50	−3.61
κ_S^E (Graph)	−3.93	−6.93	−9.01	–	−10.51	–	−8.62	−6.49	−3.61
κ_S^E (PFP)	−5.64	−5.99	−6.33	−6.66	−6.99	−7.31	−7.61	−7.92	−8.22
$T = 303.15$ K[b]									
V^E (Exptl)	−0.0908	−0.1548	−0.1970	−0.2207	−0.2282	−0.2202	−0.1962	−0.1539	−0.0902
V^E (Graph)	−0.0909	−0.1574	−0.2014	−0.2245	–	−0.2139	−0.1829	−0.1362	−0.0749
V^E (PFP)	−0.0521	−0.0937	−0.1245	−0.1442	−0.1523	−0.1482	−0.1316	−0.1017	−0.0581
κ_S^E (Exptl)	−4.15	−7.19	−9.23	−10.36	−10.62	−10.07	−8.74	−6.62	−3.72
κ_S^E (Graph)	−4.03	−7.08	−9.18	–	−10.64	–	−8.68	−6.51	−3.60
κ_S^E (PFP)	−5.81	−6.18	−6.53	−6.87	−7.21	−7.53	−7.85	−8.17	−8.48
$T = 308.15$ K[c]									
V^E (Exptl.)	−0.0946	−0.1594	−0.2008	−0.2233	−0.2299	−0.2215	−0.1977	−0.1559	−0.0919
V^E (Graph)	−0.0916	−0.1586	−0.2029	−0.2261	–	−0.2155	−0.1843	−0.1372	−0.0755
V^E (PFP)	−0.0527	−0.0949	−0.1261	−0.1460	−0.1542	−0.1501	−0.1332	−0.1030	−0.0588
H^E (Exptl)	25.8	57.8	92.1	124.1	149.3	163.2	160.7	136.4	84.8
H^E (Graph)	27.0	59.1	92.7	–	149.1	–	161.2	137.6	86.1
H^E (PFP)	54.7	96.1	124.7	140.8	144.9	137.5	118.9	89.6	49.8
κ_S^E (Exptl)	−4.39	−7.64	−9.81	−11.01	−11.24	−10.59	−9.11	−6.83	−3.79
κ_S^E (Graph)	−4.34	−7.60	−9.81	–	−11.26	–	−9.07	−6.75	−3.70
κ_S^E (PFP)	−5.99	−6.37	−6.74	−7.10	−7.45	−7.79	−8.13	−8.46	−8.79
Tetrahydropyran (i) + α-picoline (j)									
$T = 298.15$ K[d]									
V^E (Exptl)	−0.0348	−0.0601	−0.0759	−0.0829	−0.0818	−0.0736	−0.0597	−0.0415	−0.0209
V^E (Graph)	−0.0330	−0.0571	−0.0726	−0.0807	–	−0.0765	−0.0652	−0.0484	−0.0266
V^E (PFP)	−0.0344	−0.0622	−0.0831	−0.0968	−0.1028	−0.1008	−0.0900	−0.0701	−0.0403
κ_S^E (Exptl)	−3.31	−5.95	−7.84	−8.92	−9.19	−8.68	−7.40	−5.46	−2.94
κ_S^E (Graph)	−3.46	−6.09	−7.90	–	−9.17	–	−7.48	−5.61	−3.11
κ_S^E (PFP)	−6.17	−6.44	−6.70	−6.96	−7.22	−7.48	−7.74	−8.01	−8.25
$T = 303.15$ K[e]									
V^E (Exptl)	−0.0357	−0.0622	−0.0793	−0.0874	−0.0869	−0.0789	−0.0644	−0.0452	−0.0230
V^E (Graph)	−0.0351	−0.0605	−0.0772	−0.0857	–	−0.0812	−0.0693	−0.0515	−0.0282
V^E (PFP)	−0.0351	−0.0636	−0.0850	−0.0990	−0.1051	−0.1030	−0.0920	−0.0717	−0.0412
κ_S^E (Exptl)	−3.99	−6.79	−8.60	−9.54	−9.74	−9.23	−8.04	−6.16	−3.51
κ_S^E (Graph)	−3.73	−6.55	−8.47	–	−9.78	–	−7.93	−5.92	−3.26
κ_S^E (PFP)	−6.36	−6.63	−6.90	−7.18	−7.45	−7.71	−7.98	−8.25	−8.51
$T = 308.15$ K[f]									
V^E (Exptl)	−0.0365	−0.0648	−0.0841	−0.0939	−0.0947	−0.0869	−0.0717	−0.0507	−0.0259
V^E (Graph)	−0.0382	−0.0659	−0.0841	−0.0934	–	−0.0885	−0.0755	−0.0561	−0.0308
V^E (PFP)	−0.0357	−0.0646	−0.0863	−0.1005	−0.1068	−0.1046	−0.0934	−0.0728	−0.0419
H^E (Exptl)	34.6	75.8	117.3	153.1	177.8	187.1	176.9	143.9	85.7
H^E (Graph)	40.62	81.67	120.23	–	176.71	–	179.86	150.07	92.19
H^E (PFP)	60.90	108.54	142.81	163.61	170.85	164.42	144.22	110.6	62.12
κ_S^E (Exptl)	−4.20	−7.21	−9.18	−10.24	−10.49	−9.96	−8.69	−6.65	−3.78
κ_S^E (Graph)	−3.98	−7.01	−9.07	–	−10.52	–	−8.58	−6.43	−3.55
κ_S^E (PFP)	−6.54	−6.83	−7.11	−7.39	−7.67	−7.94	−8.22	−8.49	−8.77
Tetrahydropyran (i) + β-picoline (j)									
$T = 298.15$ K[g]									
V^E (Exptl)	−0.0363	−0.0703	−0.0980	−0.1166	−0.1242	−0.1199	−0.1037	−0.0768	−0.0413
V^E (Graph)	−0.0523	−0.0892	−0.1125	−0.1237	–	−0.1151	−0.0973	−0.0717	−0.0391
V^E (PFP)	−0.0567	−0.1030	−0.1382	−0.1617	−0.1725	−0.1697	−0.1523	−0.1192	−0.0689
κ_S^E (Exptl)	−4.23	−7.99	−10.92	−12.76	−13.37	−12.69	−10.79	−7.94	−4.11
κ_S^E (Graph)	−4.83	−8.56	−11.21	–	−13.26	–	−11.06	−8.40	−4.70
κ_S^E (PFP)	−5.60	−5.92	−6.24	−6.56	−6.88	−7.21	−7.53	−7.86	−8.19
$T = 303.15$ K[h]									
V^E (Exptl)	−0.0385	−0.0733	−0.1013	−0.1201	−0.1281	−0.1242	−0.1085	−0.0815	−0.0446
V^E (Graph)	−0.0539	−0.0919	−0.1159	−0.1275	–	−0.1186	−0.1003	−0.0739	−0.0402
V^E (PFP)	−0.0570	−0.1035	−0.1389	−0.1625	−0.1734	−0.1706	−0.1531	−0.1198	−0.0693
κ_S^E (Exptl)	−4.47	−8.52	−11.17	−13.71	−14.33	−13.53	−11.39	−8.16	−4.19
κ_S^E (Graph)	−5.23	−9.24	−12.07	–	−14.19	–	−11.75	−8.88	−4.95
κ_S^E (PFP)	−5.79	−6.12	−6.45	−6.78	−7.11	−7.44	−7.77	−8.11	−8.45
$T = 308.15$ K[i]									
V^E (Exptl)	−0.0391	−0.0747	−0.0381	−0.1238	−0.1331	−0.1303	−0.1151	−0.0876	−0.0487
V^E (Graph)	−0.0561	−0.0955	−0.1205	−0.1325	–	−0.1232	−0.1042	−0.0768	−0.0418
V^E (PFP)	−0.0574	−0.1044	−0.1401	−0.1638	−0.1784	−0.1720	−0.1544	−0.1208	−0.6980
H^E (Exptl)	44.7	81.7	108.7	124.4	128.1	119.8	100.6	72.4	37.7
H^E (Graph)	48.83	85.16	110.66	–	127.27	–	102.58	76.3	41.79
H^E (PFP)	42.43	75.45	99.04	113.18	117.88	113.14	98.96	75.36	42.36

Table 3 (*Continued*)

Properties	Mole fraction of component (i), x_i								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
κ_S^E (Exptl)	−4.99	−9.27	−12.55	−14.69	−15.53	−15.02	−13.14	−9.93	−5.49
κ_S^E (Graph)	−5.35	−9.60	−12.72	–	−15.47	–	−13.30	−10.27	−5.86
κ_S^E (PFP)	−5.98	−6.31	−6.65	−6.99	−7.33	−7.67	−8.01	−8.35	−8.70
Tetrahydropyran (i) + γ-picoline (j)									
T = 298.15 K[j]									
V^E (Exptl)	−0.0376	−0.0677	−0.0898	−0.1032	−0.1077	−0.1032	−0.0897	−0.0676	−0.0375
V^E (Graph)	−0.0458	−0.0779	−0.0981	−0.1075	–	−0.0996	−0.0841	−0.0618	−0.0336
V^E (PFP)	−0.0446	−0.0811	−0.1088	−0.1273	−0.1358	−0.1336	−0.1199	−0.0939	−0.0543
κ_S^E (Exptl)	−3.17	−6.13	−8.55	−10.17	−10.83	−10.45	−9.03	−6.68	−3.58
κ_S^E (Graph)	−3.68	−6.62	−8.79	–	−10.73	–	−9.28	−7.19	−4.11
κ_S^E (PFP)	−5.90	−6.19	−6.48	−6.77	−7.06	−7.35	−7.64	−7.93	−8.22
T = 303.15 K[k]									
V^E (Exptl)	−0.0381	−0.0720	−0.0986	−0.1156	−0.1216	−0.1160	−0.0994	−0.0729	−0.0388
V^E (Graph)	−0.0517	−0.0879	−0.1106	−0.1214	–	−0.1124	−0.0949	−0.0698	−0.0381
V^E (PFP)	−0.0498	−0.0905	−0.1214	−0.1419	−0.1513	−0.1488	−0.1335	−0.1045	−0.0604
κ_S^E (Exptl)	−4.12	−7.56	−10.15	−11.78	−12.38	−11.91	−10.37	−7.81	−4.32
κ_S^E (Graph)	−4.36	−7.78	−10.26	–	−12.34	–	−10.49	−8.04	−4.56
κ_S^E (PFP)	−5.97	−6.28	−6.59	−6.90	−7.21	−7.52	−7.84	−8.15	−8.46
T = 308.15 K[l]									
V^E (Exptl)	−0.0374	−0.0729	−0.1015	−0.1202	−0.1267	−0.1204	−0.1019	−0.0733	−0.0378
V^E (Graph)	−0.0539	−0.0916	−0.1153	−0.1265	–	−0.1171	−0.0989	−0.0727	−0.0396
V^E (PFP)	−0.5460	−0.0991	−0.1328	−0.1552	−0.1665	−0.1627	−0.1460	−0.1141	−0.0659
H^E (Exptl)	33.1	77.7	121.4	154.9	172.0	169.3	146.5	106.4	54.6
H^E (Graph)	51.3	95.1	129.9	–	168.6	–	155.2	124.1	73.4
H^E (PFP)	57.9	103.1	135.5	155.1	161.7	155.4	136.1	103.8	58.4
κ_S^E (Exptl)	−4.68	−8.58	−11.55	−13.45	−14.20	−13.74	−12.05	−9.15	−5.10
κ_S^E (Graph)	−4.91	−8.80	−11.66	–	−14.16	–	−12.17	−9.39	−5.35
κ_S^E (PFP)	−6.04	−6.37	−6.71	−7.03	−7.36	−7.70	−8.03	−8.36	−8.70

[a] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 1.021$; $\alpha_{ij} = 17.4136\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = -22.03\,\text{TPa}^{-1}$; $\chi^* = -4.46\,\text{TPa}^{-1}$; $\chi^*_{ij} = 8.4\,\text{J mol}^{-1}$.

[b] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 1.021$; $\alpha_{ij} = 18.0626\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = -22.64\,\text{TPa}^{-1}$; $\chi^* = -4.05\,\text{TPa}^{-1}$; $\chi^*_{ij} = 8.2\,\text{J mol}^{-1}$.

[c] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 1.021$; $\alpha_{ij} = 18.1972\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = 116.7\,\text{J mol}^{-1}$; $\chi^* = 357.4\,\text{J mol}^{-1}$; $\chi'_{ij} = -24.46\,\text{TPa}^{-1}$; $\chi^* = -3.50\,\text{TPa}^{-1}$; $\chi^*_{ij} = 8.1\,\text{J mol}^{-1}$.

[d] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.991$; $\alpha_{ij} = 5.0572\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = -19.44\,\text{TPa}^{-1}$; $\chi^* = -3.16\,\text{TPa}^{-1}$; $\chi^*_{ij} = 9.4\,\text{J mol}^{-1}$.

[e] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.991$; $\alpha_{ij} = 5.3725\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = -20.98\,\text{TPa}^{-1}$; $\chi^* = -3.01\,\text{TPa}^{-1}$; $\chi^*_{ij} = 9.2\,\text{J mol}^{-1}$.

[f] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.991$; $\alpha_{ij} = 5.8547\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = 197.6\,\text{J mol}^{-1}$; $\chi^* = 326.3\,\text{J mol}^{-1}$; $\chi'_{ij} = -22.3\,\text{TPa}^{-1}$; $\chi^* = -3.6\,\text{TPa}^{-1}$; $\chi^*_{ij} = 9.0\,\text{J mol}^{-1}$.

[g] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.901$; $(_{ij} = 4.0225\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = -26.82\,\text{TPa}^{-1}$; $\chi^* = -4.66\,\text{TPa}^{-1}$; $\chi^*_{ij} = 7.0\,\text{J mol}^{-1}$.

[h] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.901$; $\alpha_{ij} = 4.1456\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = -29.17\,\text{TPa}^{-1}$; $\chi^* = -4.29\,\text{TPa}^{-1}$; $\chi^*_{ij} = 6.9\,\text{J mol}^{-1}$.

[i] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.901$; $\alpha_{ij} = 4.3075\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = 274.8\,\text{J mol}^{-1}$; $\chi^* = 18.6\,\text{J mol}^{-1}$; $\chi'_{ij} = -29.5\,\text{TPa}^{-1}$; $\chi^* = -8.2\,\text{TPa}^{-1}$; $\chi^*_{ij} = 6.8\,\text{J mol}^{-1}$.

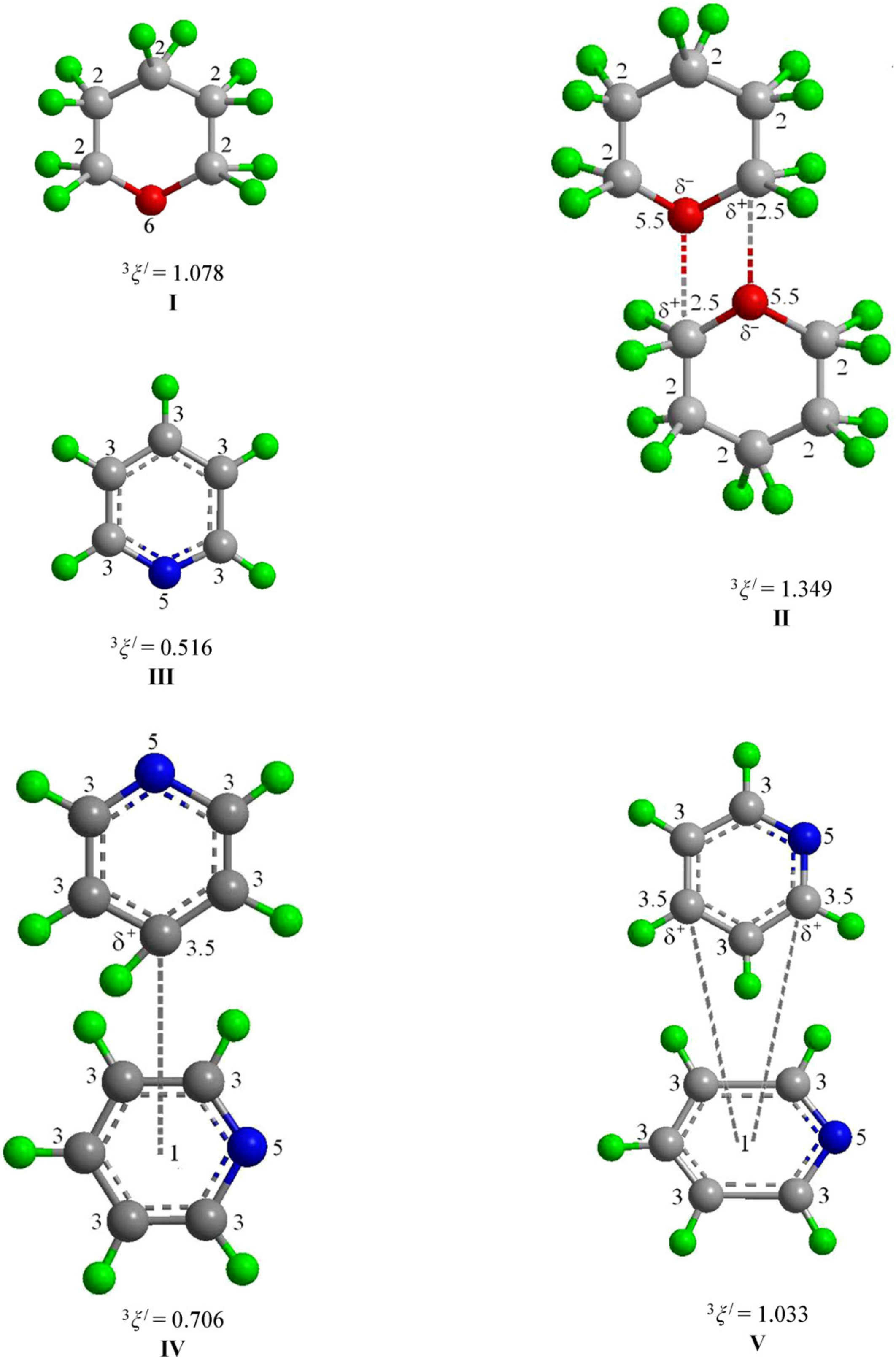
[j] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.882$; $\alpha_{ij} = 3.0843\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = -20.25\,\text{TPa}^{-1}$; $\chi^* = -5.65\,\text{TPa}^{-1}$; $\chi^*_{ij} = 9.1\,\text{J mol}^{-1}$.

[k] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.882$; $\alpha_{ij} = 3.4824\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = -24.11\,\text{TPa}^{-1}$; $\chi^* = -4.36\,\text{TPa}^{-1}$; $\chi^*_{ij} = 9.0\,\text{J mol}^{-1}$.

[l] $({}^3\xi_i) = ({}^3\xi_i)_m = 1.301$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.882$; $\alpha_{ij} = 3.6285\,\text{cm}^3\,\text{mol}^{-1}$; $\chi'_{ij} = 274.3\,\text{J mol}^{-1}$; $\chi^* = 153.9\,\text{J mol}^{-1}$; $\chi'_{ij} = -27.1\,\text{TPa}^{-1}$; $\chi^* = -6.9\,\text{TPa}^{-1}$; $\chi^*_{ij} = 8.9\,\text{J mol}^{-1}$.

These values for the molecular entities **I**–**XIV** were then calculated to be 1.078, 1.349, 0.516, 0.706, 1.033, 0.814, 1.050, 1.184, 1.247, 0.788, 1.371, 1.226, 0.847 and 0.933. ${}^3\xi$ values of 1.301, 1.021, 0.991, 0.901 and 0.882 for THP, Py, α-, β- and γ-picoline (Table 2) suggest that THP (molecular entity **II**; ${}^3\xi' = 1.371$); Py (molecular entity **V;** ${}^3\xi' = 1.033$); α-picoline (mixture of molecular entities **VI**–**VIII**; ${}^3\xi' = 1.016$); β-picoline (mixture of molecular entities **X**–**XII;** ${}^3\xi' = 1.128$); γ-picoline (mixture of molecular entities **XIII**–**XIV**; ${}^3\xi' = 0.890$) exist as associated molecular entities. These observations about the state of Py or α- or β- or γ-picolines are consistent with observations [20] inferred from the *Ab initio* molecular orbital calculations on the structural energetic and electronic properties of Py or α- or β- or γ-picolines.

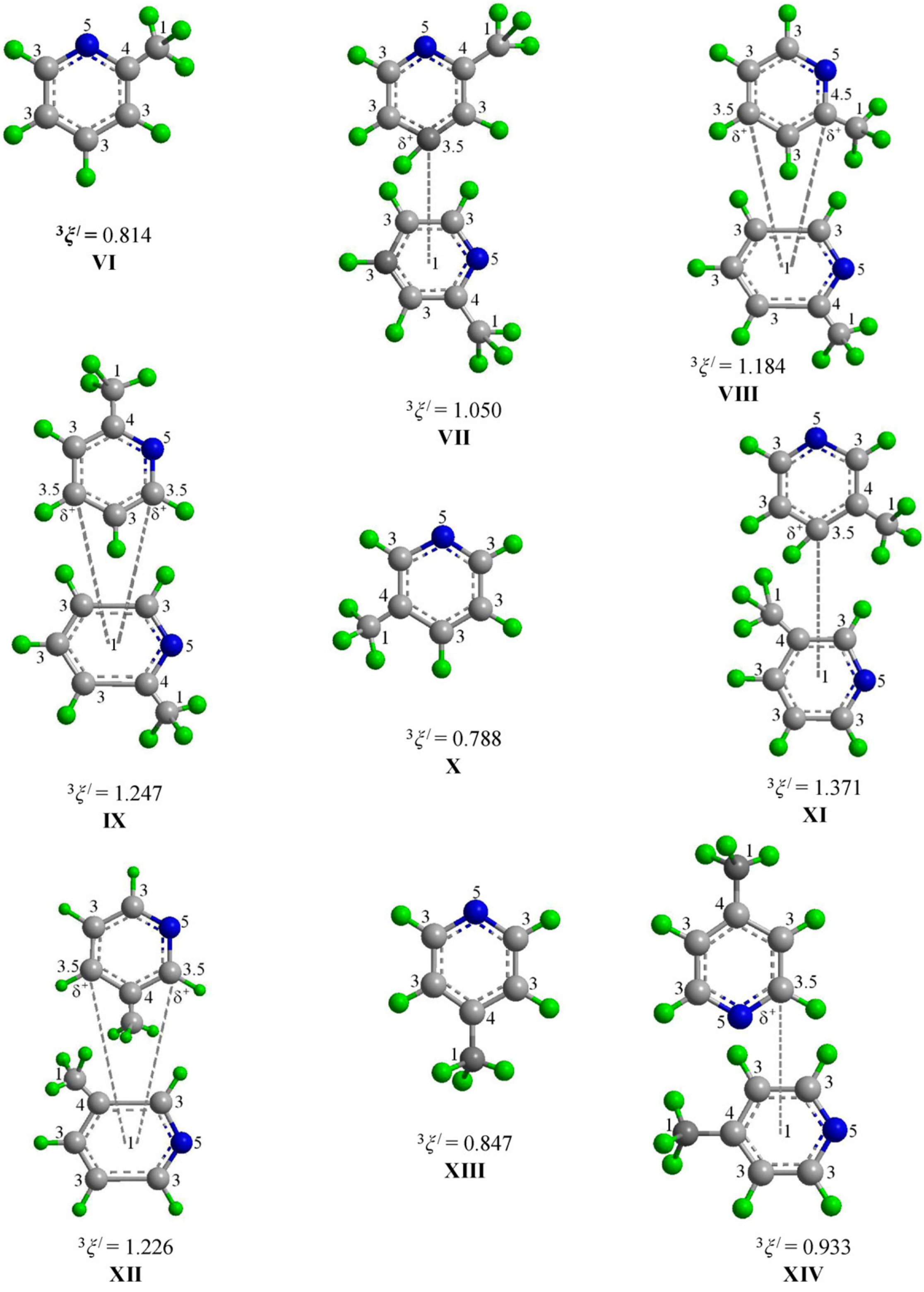
Information about the state of Py or α- or β- or γ-picoline (j) in THP (i) was obtained by evaluating connectivity parameter, $({}^3\xi'_j)_m$ for various i: *j* molecular entities. It was assumed that studied (i + j) mixtures may contain molecular entities **XV**, **XVI**, **XVII** and **XVIII**, respectively. In evaluating $({}^3\xi'_j)_m$ values for these molecular entities it was assumed that nitrogen and carbon atom of Py or α- or β- or γ-picoline are interacting with carbon and oxygen atom of THP (dipole–dipole interactions). The $({}^3\xi'_j)_m$ values for molecular entities **XV**–**XVIII** were then calculated to be 0.880, 1.004, 1.034 and 1.137, respectively. δ_m^v, etc., values for various atoms have also been recorded in various molecular entities. $({}^3\xi_j)_m$ values 1.021, 0.991, 0.901 and 0.882 (Table 2) suggest the presence of molecular entities **XV**–**XVIII** in (i + j) mixtures. The existence of molecular entities **XV**–**XVIII** in these mixtures suggest that addition of *j* to *i* must change C–O–C stretching vibrations of THP and ring vibrations of Py or α- or β- or γ-picolines. To substantiate this, we analyzed IR spectral data of pure THP, α-picoline and equimolar THP (i) + α-picoline (j) mixture. It was observed that characteristic vibrations (C–O–C) at 1090 cm^{-1} in pure THP and 1580, 1490 and 1430 cm^{-1} (ring vibrations) [21] in pure α-picoline shifted to 1130 cm^{-1} (C–O–C) and 1596, 1475 and 1442 cm^{-1} (ring vibrations) in mixed state. The shifting of ring vibrations towards high wave number suggests that interaction between α-picoline with THP through N-atom of α- and γ-picoline [22]. Also C–O–C vibrations of THP are shifted to higher wave number which supports the interaction through oxygen atom of THP with α-picoline. The IR spectral data of THP (i) + α-picoline (j) mixture thus suggest that addition of j to i does change C–O–C vibrations of THP and ring vibrations of α-picoline. This provides additional support to the proposed molecular entities **XV**–**XVIII** in (i + j) mixtures.



Scheme 1. Connectivity parameters of third degree, 3ξ, for various molecular entities.

5.2. Excess molar enthalpies and excess isentropic compressibilities

To analyze the observed H^E and κ_S^E data of the investigated mixtures in terms of Graph theory, it was assumed that $(i+j)$ mixtures formation involve processes; (1) formation of unlike i_n–j_n contacts; (2) unlike contact formation then weakens i_n–i_n; j_n–j_n interactions which leads to their depolymerization to form their monomers; (3) monomers of i and j undergo specific interactions to form i:j molecular complex. If χ_{ij}, χ_{ii}, χ_{jj} and χ_{12} are molar interactions and molar



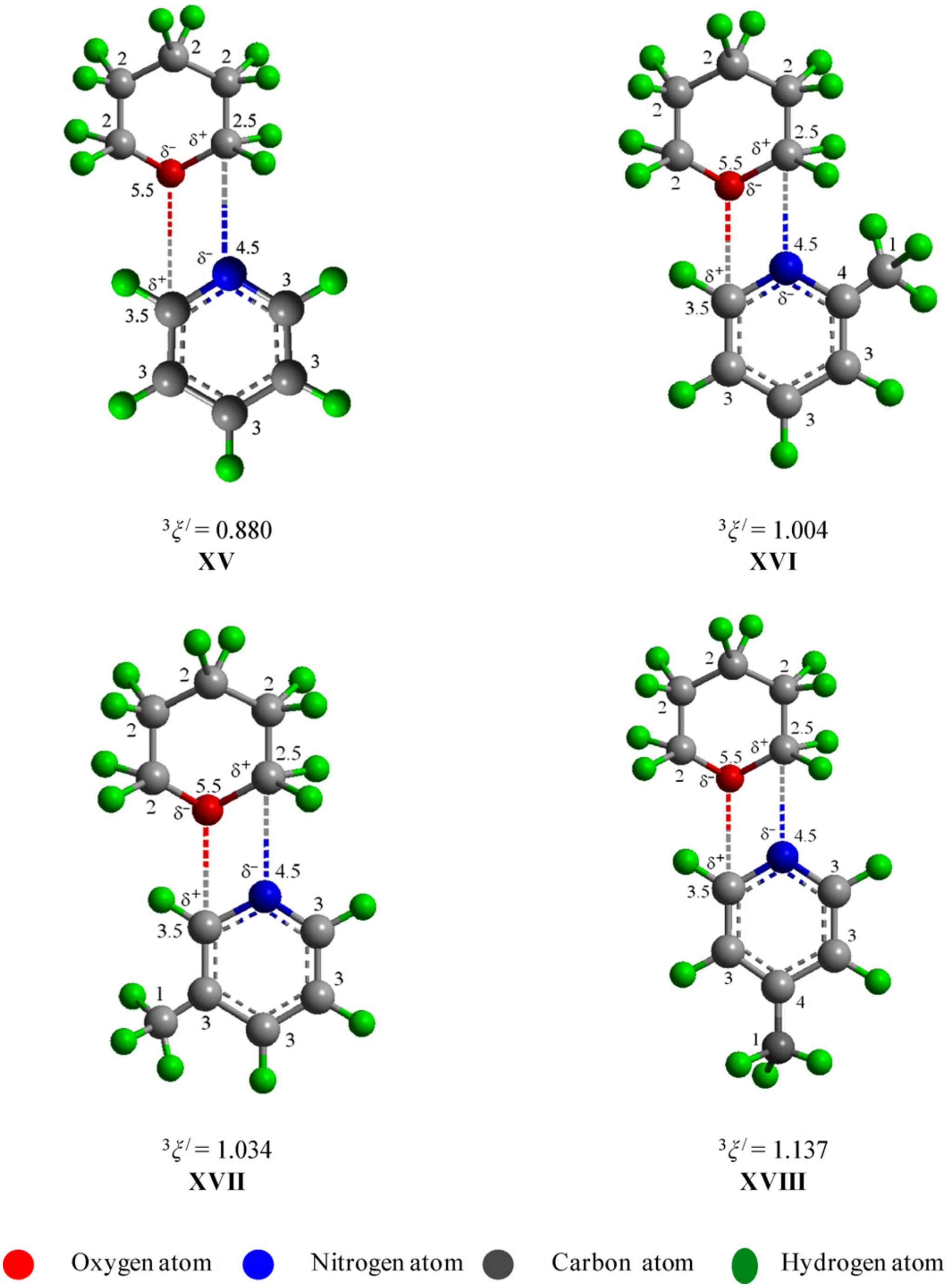
Scheme 1. (*Continued*)

compressibility interactions parameters for *i*–*j*, *i*–*i*, *j*–*j* contacts and specific interactions, respectively, then change in molar thermodynamic properties, ΔX ($X = H$ or κ_S) due to processes {1, 2 and 3} would be given [23–26] by relations:

$$\Delta X_1 = \left[\frac{x_i x_j(^3\xi_i/^3\xi_j)}{x_i + x_j(^3\xi_i/^3\xi_j)}\right]\left[\chi_{ij}\right] \tag{9}$$

$$\Delta X_2 = \left[\frac{x^2 x_j(^3\xi_i/^3\xi_j)}{x_i + x_j(^3\xi_i/^3\xi_j)}\right]\left[\chi_{ii}\right] \tag{10}$$

$$\Delta X_3 = \left[\frac{x^2 x_j(^3\xi_i/^3\xi_j)}{x_i + x_j(^3\xi_i/^3\xi_j)}\right]\left[\chi_{jj}\right] \tag{11}$$



Scheme 1. (*Continued*)

$$\Delta X_4 = \left[\frac{x_i x^2({}^3\xi_i/{}^3\xi_j)}{x_i + x_j({}^3\xi_i/{}^3\xi_j)}\right][\chi_{12}] \tag{12}$$

The overall change in thermodynamic properties, X^E (H or κ_S) due to processes ((1)–(3)) then can be expressed by Eq. (13):

$$X^E = \left[\frac{x_i x_j({}^3\xi_i/{}^3\xi_j)}{x_i + x_j({}^3\xi_i/{}^3\xi_j)}\right]\left[\chi_{ij} + x_i\chi_{ii} + x_i\chi_{jj} + x_j\chi_{12}\right] \tag{13}$$

For the studied mixtures, it is reasonable to assume that $\chi_{ij} \cong \chi_{12} = \chi^{/}_{ij}$ and $\chi_{ii} = \chi_{jj} = \chi^*$, then Eq. (13) can be expressed by

$$X^E = \left[\frac{x_i x_j({}^3\xi_i/{}^3\xi_j)}{x_i + x_j({}^3\xi_i/{}^3\xi_j)}\right]\left[(1 + x_j)\chi^{/}_{ij} + 2x_i\chi^*\right] \tag{14}$$

Eq. (14) contains two unknown parameters. These parameters were predicted by using H^E and κ_S^E data at $x_i = 0.4$ and 0.6 and were then utilized to determine H^E and κ_S^E values of $(i + j)$ mixtures at other values of x_i. Such H^E and κ_S^E values along with $\chi^{/}_{ij}$ and χ^* parameters are recorded in Table 3. Examination of data in Table 3 reveals that H^E and κ_S^E values compare well with their experimental values.

6. Prigogine–Flory–Patterson (PFP) theory

6.1. Excess molar volumes

According to this theory, excess molar volumes [27], V^E is considered to be comprised of three contributions: (i) interaction

Table 4
Properties of pure liquids at various temperatures.

Liquids	Temp./K	$\alpha/\times 10^3\ \mathrm{K}^{-1}$	$V^*/\mathrm{cm}^3\ \mathrm{mol}^{-1}$	$V/\mathrm{cm}^3\ \mathrm{mol}^{-1}$	T^*/K	$P^*/\mathrm{J\ cm}^{-3}$	$C_P/\mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$
THP	298.15	1.170	76.33	97.82	4813.92	545.0	156.5
	303.15	1.179	76.45	98.40	4835.62	545.6	158.3
	308.15	1.186	76.60	98.98	4861.16	546.0	160.2
Pyridine	298.15	1.029	64.42	80.76	5150.27	738.1	135.6
	303.15	1.036	64.50	81.17	5170.45	739.3	137.1
	308.15	1.043	64.58	81.60	5191.53	740.6	138.9
α-Picoline	298.15	0.997	79.35	98.96	5239.75	635.5	159.2
	303.15	1.004	79.44	99.45	5259.23	636.8	160.8
	308.15	1.011	79.53	99.96	5278.83	637.6	162.6
β-Picoline	298.15	0.957	78.86	97.69	5362.42	671.5	159.0
	303.15	0.968	78.88	98.16	5365.94	674.0	161.2
	308.15	0.977	78.93	98.85	5378.23	675.7	163.5
γ-Picoline	298.15	1.003	78.40	89.29	5221.99	674.0	158.9
	303.15	1.008	78.52	89.84	5300.12	670.7	160.8
	308.15	1.013	78.63	90.40	5380.27	667.3	162.9

contribution; (ii) free volume contribution; (iii) the contribution that depends on the difference in both internal pressure and reduced volumes of two components constituting binary mixtures. V^E in terms of these three contributions is expressed as:

$$V^E = V^E_{\text{interaction}} + V^E_{\text{free-volume}} + V^E_{P^*\ \text{effect}} \tag{15}$$

where

$$\frac{V^E_{\text{interaction}}}{\sum x_i v_i^*} = \frac{[(\tilde{v}^{1/3}-1)\tilde{v}\psi_i\theta_j\chi^*_{ij}]}{[(4/3)\tilde{v}^{-1/3}-1]\tilde{v}} \tag{16}$$

$$\frac{V^E_{\text{free-volume}}}{\sum x_i v_i^*} = \left[\left(\tilde{v}_i-\tilde{v}_j\right)^2\left\{\left(\frac{14}{9}\right)\tilde{v}^{-1/3}-1\right\}\right]\frac{\psi_i\psi_j}{[(4/3)\tilde{v}^{-1/3}-1]\tilde{v}} \tag{17}$$

$$\frac{V^E_{P^*\ \text{effict}}}{\sum x_i v_i^*} = \frac{(\tilde{v}_i-\tilde{v}_j)(P_i^*-P_j^*)\psi_i\psi_j}{(P_i^*\psi_j-P_j^*\psi_i)} \tag{18}$$

6.2. *Excess molar enthalpies*

According to PFP theory [28], excess molar enthalpies, H^E is described just for two contributions, namely interactional contribution and free volume contribution. According to this theory H^E are given by

$$H^E = H^E_{\text{interaction}} + H^E_{\text{free-volume}} \tag{19}$$

where

$$\frac{H^E_{\text{interaction}}}{(x_iU_i^*+x_jU_j^*)} = \left(\frac{\chi_{ij}\theta_j\psi_i}{P_i^*}\right)(\tilde{U}\tilde{T}_U+\tilde{T}_U\tilde{C}_P\tilde{T}_U) \tag{20}$$

$$\frac{H^E_{\text{free-volume}}}{(x_iU_i^*+x_jU_j^*)} = \tilde{C}_P(\tilde{T}_U)(\psi_i\tilde{T}_i+\psi_j\tilde{T}_j-\tilde{T}_U) \tag{21}$$

6.3. *Excess isentropic compressibilities*

The isentropic compressibility, κ_S is given [29] by

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \tag{22}$$

where

$$\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial V}{\partial P}\right)_T + TC_P^{-1}\left(\frac{\partial V}{\partial T}\right)_P^2 \tag{23}$$

Flory expressed $\left(\frac{\partial V}{\partial P}\right)_T$ and $\left(\frac{\partial V}{\partial T}\right)_P$ terms by Eqs. (24) and (25), respectively:

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{-\tilde{v}^{7/3}+2\tilde{v}^2-\tilde{v}^{5/3}}{4/3-\tilde{v}^{1/3}}\frac{V^*}{P^*}\frac{1}{\tilde{T}} \tag{24}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\tilde{v}^{4/3}-\tilde{v}}{4/3-\tilde{v}^{1/3}}\frac{V^*}{T} \tag{25}$$

where all the terms in Eqs. (16)–(25) have the same significance as described elsewhere [30,31].

Prediction of V^E, H^E and κ_S^E values by PFP theory requires knowledge of the interactional energy parameter, χ^*_{ij} in addition to the Flory's parameters and isobaric heat capacity of pure liquids and mixtures. Interaction parameter χ^*_{ij} was determined by fitting H^E value of (i + j) mixture at $x_\mathrm{i} = 0.5$ to Eq. (26):

$$H^E = \sum x_iP_i^*\left(U_i^{-1}-U_{\text{cal}}^{-1}\right)+x_iU_i^*\theta_j\chi^*_{ij}U_{cal}^{-1} \tag{26}$$

Various parameters for pure components (reported in Table 4) were determined using isothermal compressibility reported in literature [6,16]. The κ_T values for those liquids that were not available were determined by using their ΔH_v values in the manner suggested by Hildebrand et al. [32]. Such values of V^E, H^E and κ_S^E along with χ^*_{ij} parameters, are recorded in Table 3, where they are also compared with their corresponding experimental values. Examination of Table 3 reveals that PFP theory correctly predicts the sign of V^E, H^E and κ_S^E values for all the studied mixtures. However, quantitative agreement is not so impressive as in case Graph theory. The failure of the theory to correctly predict the magnitude of V^E, H^E and κ_S^E data may be due to various assumptions made in evaluating various parameters which were not reported in the literature but have been determined theoretically and also due to the nature of components of (i + j) mixtures.

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