Volumetric and Ultrasonic Studies of Molecular Interactions in Binary Mixtures of Dimethyl Sulfoxide with Some Aromatic Hydrocarbons at Different Temperatures

Anwar Ali,*[1] **Anil Kumar Nain,**[2] **Dinesh Chand,**[1] **and Rizwan Ahmad**[3]

[1]Department of Chemistry, Jamia Millia Islamia (Central University), New Delhi-110 025, India

[2]Department of Chemistry, Dyal Singh College (University of Delhi), New Delhi-110 003, India

[3]Department of Chemistry, Z. H. College (University of Delhi), Delhi-110 002, India

Received July 21, 2005; E-mail: anwar.ch@jmi.ernet.in

The densities (ρ) and ultrasonic speeds (u) of pure dimethyl sulfoxide (DMSO), benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene, and those of their binary mixtures, with DMSO as the common component, over the whole composition range have been measured at 298.15, 303.15, 308.15, 313.15, and 318.15 K. The excess molar volume (V^{E}), deviation in isentropic compressibility (Δk_{s}), apparent molar volume ($V_{\phi,2}$), apparent molar compressibility ($K_{\phi,2}$), partial molar volume ($\bar{V}^{\circ}{}_{\phi,2}$), and partial molar compressibility ($\bar{K}^{\circ}{}_{\phi,2}$) of aromatic hydrocarbons in DMSO at infinite dilution have been calculated from the experimental data. The variation of these parameters with the composition and temperature of the mixtures indicates that the interaction (DMSO–aromatic hydrocarbons) follows the order: benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene. The effect of the number and position of the methyl groups in these aromatic hydrocarbons on molecular interactions in these mixtures is also discussed. The V^{E} values have also been calculated theoretically by using Flory's statistical theory and the Prigogine–Flory–Patterson theory. The calculated V^{E} values were found to be in good agreement with the experimental V^{E} values for most of the mixtures.

The concentration and temperature dependence of volumetric and acoustic properties of multi-component liquid mixtures have proved to be a useful indicator of the existence of significant effects resulting from intermolecular interactions.[1–3] As a part of our ongoing research focusing on experimental and theoretical studies of volumetric, acoustic, and transport properties of non-aqueous binary liquid mixtures,[4–8] we report here the results of our study on the binary mixtures of dimethyl sulfoxide (DMSO) with six aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene) over the entire composition range at five different temperatures. The objective underlying the present work is to obtain information regarding molecular interactions in the mixtures of a highly polar liquid with non-polar or weakly polar liquids, which is essential for the understanding of many chemical and industrial processes in these media.

DMSO is a versatile compound having a wide range of applications as a solvent in chemical and biological processes involving both plants and animals.[9] It is a highly polar (dipole moment = 3.96 D)[10] and strongly associated aprotic solvent due to the S=O group[11] in the molecule. In their pure state, DMSO molecules associate in chains with parallel dipole moments, while neighboring DMSO molecules from adjacent chains are oriented with anti-parallel dipole moments,[12,13] as reported by Bertagnolli et al.[12] using X-ray and neutron scattering, and confirmed by Vaisman and Berkowitz[13] using molecular dynamics simulation. The aromatic hydrocarbon molecules possess large quadrupole moments, causing an orientational order in these liquids.[14] The orientational order is thought of as a partial alignment of neighboring segments or possibly of whole molecules. The binary mixtures of DMSO with aromatic hydrocarbons are interesting as these systems find applications in the studies of polymer phase diagrams and preferential interaction of polymers in mixed solvents.[15]

A survey of the literature reveals that the thermodynamic studies of the mixtures of DMSO with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene are very few. Aralaguppi et al.[16] reported changes in volume and compressibility of DMSO + benzene/toluene/*m*-xylene/mesitylene mixtures at three temperatures. Wang et al.[17] reported excess molar volumes of DMSO + *o*-/*m*-/*p*-xylene mixtures in the temperature range 293.15 to 353.15 K. Both of these studies were primarily concerned with experimental data and no attempt was made to provide a detailed study of the molecular interactions in these mixtures. Moreover, the trends of the temperature dependence of V^{E}, $(\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T)$, for DMSO + *m*-xylene mixture in these studies[16,17] contradict each other. Therefore, we feel that these systems need to be investigated carefully and in a broader perspective.

In the present paper, we report the densities (ρ) and ultrasonic speeds (u) of pure DMSO, benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene, and those of their 54 binary mixtures, with DMSO as the common component, over the whole composition range at 298.15, 303.15, 308.15, 313.15, and 318.15 K. From the experimental values of ρ and u, the values of excess molar volume, V^{E}, deviation in isentropic compressibility, Δk_{s}, apparent molar volume, $V_{\phi,2}$, apparent molar compressibility, $K_{\phi,2}$, partial molar volume, $\bar{V}^{\circ}{}_{\phi,2}$, and partial molar compressibility, $\bar{K}^{\circ}{}_{\phi,2}$, of aromatic hydrocarbons in DMSO have been calculated. The variations

Published on the web May 12, 2006; DOI: 10.1246/bcsj.79.702

Table 1. Comparison of Experimental Values of Density (ρ) and Ultrasonic Speed (u) of Pure Liquids with the Corresponding Literature Values at Different Temperatures

Liquid	T/K	ρ/kg m^{-3}		u/m s^{-1}	
		Expt.	Lit.	Expt.	Lit.
DMSO	298.15	1095.7	1095.62,[a] 1095.7[c]	1487.3	1489.0,[b] 1485.8[c]
	303.15	1090.0	1091.1[b]	1470.5	1474.0,[b] 1470.4[c]
	308.15	1086.1	1085.9[b],[c]	1454.3	1455.0,[b] 1454.1[c]
	313.15	1081.2	1081.2[c]	1437.6	1437.8[c]
	318.15	1076.3	1076.5[c]	1420.7	1419.8[c]
Benzene	298.15	873.6	873.62,[d] 873.57[e]	1303.5	1304.0[b]
	303.15	868.2	868.1[e]	1281.7	1280.0[b]
	308.15	862.9	862.84[d]	1257.4	—
	313.15	857.6	—	1232.8	—
	318.15	852.2	852.2[d]	1207.2	—
Toluene	298.15	862.3	862.3,[f] 862.2[g]	1310.5	1309.0[b]
	303.15	857.5	857.6[f]	1287.8	1287.0[b]
	308.15	853.0	853.0[g]	1266.2	1264.0[b]
	313.15	848.3	848.3,[h] 848.2[f]	1243.7	—
	318.15	843.6	—	1221.0	—
o-Xylene	298.15	875.7	875.57[a]	1350.3	—
	303.15	871.4	871.36[e]	1335.6	—
	308.15	867.0	867.0[i]	1321.4	1321.4[i]
	313.15	862.7	—	1304.7	—
	318.15	858.4	—	1285.8	—
m-Xylene	298.15	859.9	859.83[a]	1326.6	1326.0[b]
	303.15	855.7	855.87[j]	1305.5	1304.0[b]
	308.15	851.6	—	1281.0	1283.0[b]
	313.15	847.3	—	1264.3	—
	318.15	843.0	—	1243.0	—
p-Xylene	298.15	856.8	856.7[k]	1316.4	—
	303.15	852.4	852.35,[k] 852.39[g]	1288.3	—
	308.15	848.2	848.2,[i] 848.0[l]	1268.0	1268.0[i]
	313.15	843.7	843.64[k]	1248.6	—
	318.15	839.4	—	1230.3	—
Mesitylene	298.15	861.4	861.78,[d] 861.5[b]	1369.8	—
	303.15	857.2	857.3[b]	1348.6	—
	308.15	853.0	852.9[d]	1325.2	—
	313.15	848.8	—	1304.0	—
	318.15	844.6	844.79[d]	1279.0	—

a) Ref. 17. b) Ref. 16. c) Ref. 25. d) Ref. 26. e) Ref. 27. f) Ref. 28. g) Ref. 29. h) Ref. 30. i) Ref. 31. j) Ref. 32. k) Ref. 33. l) Ref. 34.

of these parameters with composition and temperature of the mixtures were found to be useful in understanding the nature and extent of interactions between the component molecules in these mixtures. The effect of the number and position of the methyl group in these aromatic hydrocarbons on molecular interactions in the mixtures is also discussed. The experimental values of V^E were analyzed and compared with the theoretically calculated V^E values by using Flory's statistical theory[18,19] and the Prigogine–Flory–Patterson theory.[19–22]

Experimental

Materials. DMSO (E. Merck, Germany) and benzene (s.d. fine-chem Ltd., India), purities >99.5% (mass percent), were used as such without further purification. Toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene (all s.d. fine-chem Ltd., India, purity >99%) were purified by using the methods described in the literature.[23] Before use, all of the liquids were stored over 0.4 nm molecular sieves to reduce the water content, if any, and were degassed. The mixtures of DMSO with aromatic hydrocarbons were prepared by mass and were kept in special airtight stoppered glass bottles to avoid evaporation. The weighings were done on a Precisa XB-120 (Swiss make) electronic balance with a precision of ±0.1 mg. The probable error in the mole fraction was estimated to be less than ±0.0001.

Instrumental. The densities of pure liquids and their binary mixtures were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of 8×10^{-6} m^3.[4–8] The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triple distilled water. The densities of pure water at the required temperatures were taken from the literature.[24] The reproducibility of density measurements was within ±0.1 kg m^{-3}. The ultrasonic speeds in pure liquids and in their binary mixtures were measured by using a single-crystal variable-path ultrasonic interferometer operating at 3 MHz by a method described elsewhere.[4,24] The ultrasonic speed data were reproducible within ±0.5 m s^{-1}. The temperatures of the test liquids during the measurements were maintained to an accuracy of ±0.02 K in

Table 2. (a) Values of Densities ($\rho/\mathrm{kg\,m^{-3}}$) as Function of Mole Fraction (x_1) of DMSO for the Binary Mixtures at Different Temperatures

x_1	Temperature/K				
	298.15	303.15	308.15	313.15	318.15
DMSO + Benzene					
0.0862	890.6	885.4	880.2	875.0	869.8
0.1578	905.1	899.9	894.8	889.7	884.6
0.2386	921.5	916.4	911.4	906.4	901.4
0.3278	939.8	934.8	929.9	925.0	920.0
0.4241	960.1	955.2	950.3	945.4	940.6
0.5265	982.1	977.3	972.5	967.7	963.0
0.6339	1006.1	1001.3	996.5	991.8	987.1
0.7543	1034.1	1029.3	1024.5	1019.8	1015.2
0.8766	1064.0	1059.3	1054.6	1049.9	1045.2
DMSO + Toluene					
0.1014	879.6	874.8	870.3	865.7	861.1
0.1830	894.4	889.7	885.3	880.8	876.3
0.2725	911.4	906.9	902.5	898.1	893.7
0.3682	930.6	926.2	921.9	917.5	913.1
0.4681	951.8	947.4	943.1	938.7	934.4
0.5706	975.1	970.8	966.5	962.1	957.7
0.6742	1000.4	996.1	991.8	987.3	982.8
0.7858	1030.1	1025.6	1021.1	1016.6	1012.1
0.8946	1061.9	1057.2	1052.5	1047.8	1043.1
DMSO + *o*-Xylene					
0.1134	891.5	887.2	882.8	878.5	874.2
0.2025	905.0	900.7	896.3	892.0	887.7
0.2982	920.7	916.4	912.0	907.7	903.4
0.3980	938.5	934.2	929.8	925.5	921.2
0.4996	958.5	954.1	949.7	945.3	941.0
0.6012	980.5	976.1	971.6	967.2	962.8
0.7013	1004.6	1000.2	995.6	991.1	986.6
0.8063	1033.0	1028.5	1023.9	1019.3	1014.7
0.9059	1063.4	1058.8	1054.1	1049.4	1044.7
DMSO + *m*-Xylene					
0.1153	876.8	872.6	868.5	864.2	859.9
0.2055	891.4	887.2	883.1	878.8	874.5
0.3020	908.3	904.1	899.9	895.6	891.3
0.4023	927.4	923.2	919.0	914.7	910.3
0.5041	948.8	944.6	940.3	935.9	931.5
0.6055	972.4	968.1	963.7	959.3	954.9
0.7051	998.2	993.8	989.4	984.9	980.4
0.8091	1028.5	1024.0	1019.4	1014.8	1010.2
0.9075	1061.0	1056.4	1051.7	1047.0	1042.3
DMSO + *p*-Xylene					
0.1157	874.4	870.1	866.0	861.7	857.5
0.2061	889.4	885.2	881.1	876.8	872.7
0.3028	906.6	902.4	898.3	894.0	889.9
0.4032	926.1	921.8	917.7	913.4	909.2
0.5051	947.9	943.6	939.4	935.0	930.8
0.6064	971.8	967.5	963.2	958.8	954.5
0.7058	997.9	993.5	989.1	984.7	980.3
0.8097	1028.6	1024.1	1019.6	1015.1	1010.6
0.9078	1061.3	1056.7	1052.1	1047.5	1042.9
DMSO + Mesitylene					
0.1045	874.4	870.2	865.9	861.6	857.3
0.2052	888.3	884.0	879.6	875.3	870.9
0.3065	903.9	899.5	895.1	890.7	886.3
0.4036	920.7	916.3	911.8	907.4	902.9
0.5012	939.8	935.3	930.8	926.2	921.7
0.6018	962.3	957.7	953.1	948.5	943.9
0.7068	989.6	985.0	980.3	975.6	970.9
0.8025	1018.7	1014.0	1009.2	1004.4	999.6
0.9043	1055.0	1050.3	1045.4	1040.5	1035.6

Table 2. (b) Values of Ultrasonic Speeds ($u/\mathrm{m\,s^{-1}}$) as Function of Mole Fraction (x_1) of DMSO for the Binary Mixtures at Different Temperatures

x_1	Temperature/K				
	298.15	303.15	308.15	313.15	318.15
DMSO + Benzene					
0.0862	1326.8	1305.6	1281.6	1257.3	1232.0
0.1578	1346.5	1326.1	1302.5	1278.3	1253.7
0.2386	1365.7	1345.8	1322.8	1299.3	1275.3
0.3278	1385.4	1366.1	1344.1	1321.1	1297.9
0.4241	1404.0	1385.3	1364.1	1341.9	1319.5
0.5265	1421.2	1403.1	1382.8	1361.5	1340.0
0.6339	1437.8	1420.2	1400.9	1380.1	1359.4
0.7543	1456.2	1439.1	1420.9	1400.8	1381.2
0.8766	1471.7	1455.6	1438.3	1419.0	1400.7
DMSO + Toluene					
0.1014	1325.4	1303.6	1282.3	1260.2	1238.0
0.1830	1340.9	1319.9	1298.9	1277.2	1255.5
0.2725	1357.9	1336.7	1317.0	1295.7	1275.3
0.3682	1374.5	1354.5	1334.7	1313.8	1292.9
0.4681	1392.0	1372.1	1352.3	1331.8	1311.6
0.5706	1410.1	1391.1	1372.5	1352.4	1332.7
0.6742	1428.9	1410.7	1392.4	1372.7	1353.5
0.7858	1448.3	1431.2	1412.9	1393.5	1374.9
0.8946	1467.7	1451.3	1433.4	1414.7	1396.3
DMSO + *o*-Xylene					
0.1134	1362.0	1347.5	1333.5	1316.8	1298.0
0.2025	1372.5	1357.8	1343.7	1327.0	1308.3
0.2982	1383.0	1368.3	1353.9	1337.4	1318.8
0.3980	1393.8	1379.1	1364.7	1348.2	1329.7
0.4996	1405.5	1390.5	1376.1	1359.3	1340.9
0.6012	1417.5	1402.5	1387.8	1371.0	1352.7
0.7013	1431.1	1415.5	1400.7	1384.2	1366.1
0.8063	1448.4	1432.6	1417.2	1400.4	1383.0
0.9059	1467.8	1451.1	1435.5	1419.0	1401.6
DMSO + *m*-Xylene					
0.1153	1339.3	1318.7	1294.8	1278.5	1257.6
0.2055	1351.8	1331.7	1308.3	1291.7	1271.2
0.3020	1363.9	1344.0	1321.2	1305.0	1284.8
0.4023	1376.6	1357.1	1334.4	1318.1	1298.4
0.5041	1390.5	1371.3	1348.8	1332.3	1313.0
0.6055	1404.7	1386.0	1364.4	1348.2	1328.6
0.7051	1421.1	1402.5	1381.5	1365.2	1346.2
0.8091	1441.3	1423.3	1403.1	1385.9	1367.8
0.9075	1463.1	1446.0	1428.0	1411.5	1393.3
DMSO + *p*-Xylene					
0.1157	1331.4	1304.2	1283.9	1265.1	1248.0
0.2061	1346.4	1318.7	1299.4	1280.7	1263.6
0.3028	1360.7	1333.6	1314.3	1295.6	1278.6
0.4032	1375.2	1349.2	1330.0	1311.3	1293.9
0.5051	1391.1	1366.3	1347.1	1328.4	1311.0
0.6064	1406.2	1382.3	1363.1	1344.4	1327.4
0.7058	1422.3	1400.0	1380.8	1362.1	1345.1
0.8097	1442.4	1422.0	1404.6	1386.0	1369.0
0.9078	1464.3	1446.0	1429.5	1411.5	1394.4
DMSO + Mesitylene					
0.1045	1375.6	1354.8	1331.8	1311.0	1286.4
0.2052	1380.2	1359.8	1337.2	1316.6	1292.4
0.3065	1385.8	1365.6	1343.6	1323.0	1299.4
0.4036	1394.0	1374.2	1352.8	1333.0	1309.4
0.5012	1406.4	1387.0	1366.2	1346.4	1323.8
0.6018	1423.6	1404.4	1383.7	1364.8	1342.8
0.7068	1442.4	1423.2	1403.3	1384.8	1363.2
0.8025	1461.8	1443.2	1424.6	1406.2	1385.4
0.9043	1478.2	1460.2	1443.2	1425.8	1407.2

Table 3. Coefficients (A_i) of Eq. 5 and Standard Deviations $\sigma(Y^E)$ for the Binary Mixtures at Different Temperatures

T/K	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$	T/K	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
DMSO + Benzene							DMSO + *m*-Xylene						
$V^E/10^{-6}$ m^3 mol^{-1}							$V^E/10^{-6}$ m^3 mol^{-1}						
298.15	−1.3795	−0.6897	−0.3931	0.2696	0.5124	0.0029	298.15	−0.6826	−0.0950	0.0204	0.2415	0.3229	0.0014
303.15	−1.5189	−0.7249	−0.1514	0.2336	0.0413	0.0024	303.15	−0.7706	−0.1182	0.1437	0.2529	0.2100	0.0022
308.15	−1.6571	−0.7681	−0.2755	0.3703	0.1174	0.0006	308.15	−0.8255	−0.1200	0.0737	0.2445	0.2450	0.0036
313.15	−1.8074	−0.7318	−0.5352	0.3604	0.4351	0.0017	313.15	−0.9118	−0.1297	0.0587	0.3092	0.2588	0.0028
318.15	−2.0038	−0.7344	−0.4515	0.3498	0.1712	0.0019	318.15	−0.9820	−0.1155	−0.0674	0.3304	0.3873	0.0002
$\Delta k_s/10^{-10}$ m^2 N^{-1}							$\Delta k_s/10^{-10}$ m^2 N^{-1}						
298.15	−1.8208	−0.8588	−0.6505	0.0055	0.5944	0.0017	298.15	−0.8864	−0.3287	−0.6816	−0.0377	0.9582	0.0017
303.15	−1.9819	−0.9273	−0.7573	0.0441	0.6532	0.0021	303.15	−0.9560	−0.3870	−0.7249	0.0189	0.9530	0.0017
308.15	−2.1490	−0.9977	−0.7830	0.0813	0.6975	0.0025	308.15	−1.0055	−0.4059	−0.9299	−0.0465	1.1973	0.0009
313.15	−2.3085	−1.1000	−0.7295	0.0809	0.6790	0.0017	313.15	−1.0673	−0.4224	−0.9487	−0.0898	1.1802	0.0007
318.15	−2.5081	−1.2054	−0.8338	0.1169	0.8306	0.0019	318.15	−1.1466	−0.4960	−1.0025	−0.0874	1.2590	0.0007
DMSO + Toluene							DMSO + *p*-Xylene						
$V^E/10^{-6}$ m^3 mol^{-1}							$V^E/10^{-6}$ m^3 mol^{-1}						
298.15	−1.1775	−0.4183	0.1251	0.3294	0.0637	0.0016	298.15	−1.1048	−0.1429	−0.0077	0.2799	−0.2061	0.0023
303.15	−1.3651	−0.3791	−0.0857	0.2762	0.7703	0.0031	303.15	−1.2310	−0.2330	0.0020	0.3216	−0.2262	0.0024
308.15	−1.5335	−0.3253	−0.1421	0.2498	1.0302	0.0042	308.15	−1.3647	−0.3164	0.0055	0.4064	−0.4165	0.0015
313.15	−1.7166	−0.4071	−0.1842	0.3622	1.1211	0.0043	313.15	−1.5021	−0.3300	−0.4223	0.3189	−0.1594	0.0008
318.15	−1.9262	−0.5187	0.0081	0.5229	0.9008	0.0023	318.15	−1.6555	−0.4453	−0.5679	0.4897	−0.0922	0.0016
$\Delta k_s/10^{-10}$ m^2 N^{-1}							$\Delta k_s/10^{-10}$ m^2 N^{-1}						
298.15	−1.3999	−0.3265	−0.8726	−0.1053	1.6678	0.0014	298.15	−1.1659	−0.5498	−0.7391	0.1532	0.9695	0.0023
303.15	−1.5400	−0.3386	−0.8702	−0.1433	1.7325	0.0015	303.15	−1.2792	−0.6105	−0.4582	0.2759	0.3928	0.0027
308.15	−1.6524	−0.3236	−1.2479	−0.3356	2.3410	0.0031	308.15	−1.3256	−0.6872	−0.7683	0.3737	0.7402	0.0016
313.15	−1.7655	−0.3881	−1.3392	−0.3957	2.5576	0.0032	313.15	−1.3909	−0.7675	−0.7630	0.3470	0.6209	0.0033
318.15	−1.9023	−0.4136	−1.6829	−0.5741	3.1822	0.0049	318.15	−1.4896	−0.8057	−0.7711	0.2055	0.4379	0.0030
DMSO + *o*-Xylene							DMSO + Mesitylene						
$V^E/10^{-6}$ m^3 mol^{-1}							$V^E/10^{-6}$ m^3 mol^{-1}						
298.15	−0.5601	−0.0337	0.1270	0.1199	−0.1855	0.0019	298.15	0.4900	−0.1288	−0.2348	0.0689	0.0597	0.0003
303.15	−0.6060	−0.0272	−0.0669	0.1205	0.1046	0.0003	303.15	0.5473	−0.1158	−0.2498	0.0134	0.0458	0.0021
308.15	−0.6951	−0.0655	0.1420	0.2321	−0.2314	0.0009	308.15	0.5903	−0.1227	−0.3319	0.0272	0.2988	0.0008
313.15	−0.7730	−0.0785	0.0878	0.2964	−0.1741	0.0016	313.15	0.6283	−0.1315	−0.2964	0.0411	0.3924	0.0015
318.15	−0.8788	−0.0998	0.2852	0.3650	−0.4505	0.0007	318.15	0.6568	−0.1411	−0.1939	0.0572	0.4056	0.0015
$\Delta k_s/10^{-10}$ m^2 N^{-1}							$\Delta k_s/10^{-10}$ m^2 N^{-1}						
298.15	−0.7061	−0.3098	−0.4496	0.0853	0.4114	0.0009	298.15	−0.7203	0.5833	0.6479	−0.1426	−1.1384	0.0008
303.15	−0.7455	−0.3475	−0.3955	0.0852	0.3193	0.0001	303.15	−0.7610	0.5413	0.7338	−0.0548	−1.3256	0.0017
308.15	−0.7891	−0.3719	−0.3341	0.1059	0.1642	0.0004	308.15	−0.8137	0.5178	0.7614	0.0700	−1.4720	0.0016
313.15	−0.8236	−0.3594	−0.4566	0.0464	0.3459	0.0002	313.15	−0.8785	0.5275	0.9051	0.1068	−1.7220	0.0026
318.15	−0.8621	−0.3895	−0.4825	0.0609	0.3584	0.0004	318.15	−0.9278	0.5002	0.9626	0.2281	−1.8947	0.0021

an electronically controlled thermostatic water bath (JULABO, Model-MD, Germany). The reliability of experimental measurements of ρ and u were ascertained by comparing the experimental data of pure liquids with the corresponding values, which were available in the literature[16,17,25–34] at the studied temperatures. A comparison is given in Table 1.

Results and Discussion

The experimental values of densities and ultrasonic speeds of binary mixtures of DMSO with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene, over the whole composition range expressed by mole fraction, x_1 of DMSO, at different temperatures are given in Table 2. The values of V^E and Δk_s have been calculated by using the following relations:

$$V^E = x_1M_1(1/\rho - 1/\rho_1) + x_2M_2(1/\rho - 1/\rho_2), \tag{1}$$

$$\Delta k_s = k_s - (\phi_1 k_{s1} + \phi_2 k_{s2}), \tag{2}$$

where x and M are the mole fraction and molar mass, respectively; subscripts 1 and 2 stand for pure components, DMSO and aromatic hydrocarbon, respectively; V and k_s are the molar volume and isentropic compressibility, respectively, and are calculated by using the relations:

$$V = (x_1M_1 + x_2M_2)/\rho, \tag{3}$$

$$k_s = 1/u^2\rho, \tag{4}$$

The values of V^E and Δk_s were fitted to a Redlich–Kister[35] type polynomial equation

$$Y^E = x_1x_2\sum_{i=1}^{5} A_i(1 - 2x_1)^{i-1}, \tag{5}$$

where Y^E is V^E or Δk_s. The values of coefficients, A_i evaluated by the method of least-squares, with all points weighed equally, together with the corresponding standard deviation, $\sigma(Y^E)$ calculated by using the relation

$$\sigma(Y^E) = \left[\sum(Y^E{}_{\text{expt}} - Y^E{}_{\text{cal}})^2/(m - n)\right]^{1/2}, \tag{6}$$

where m is the number of experimental data points and n is the number of coefficients considered ($n = 5$ in the present calculation), are listed in Table 3. $Y^E{}_{\text{cal}}$ has been obtained from

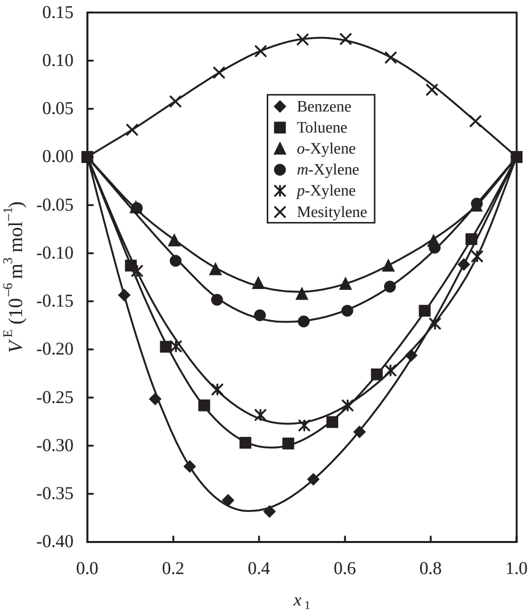

Fig. 1. Variation of excess molar volume (V^E) with mole fraction (x_1) of dimethyl sulfoxide (DMSO) for the binary mixtures at 298.15 K. Points show experimental values and curves show smoothed values using Eq. 5.

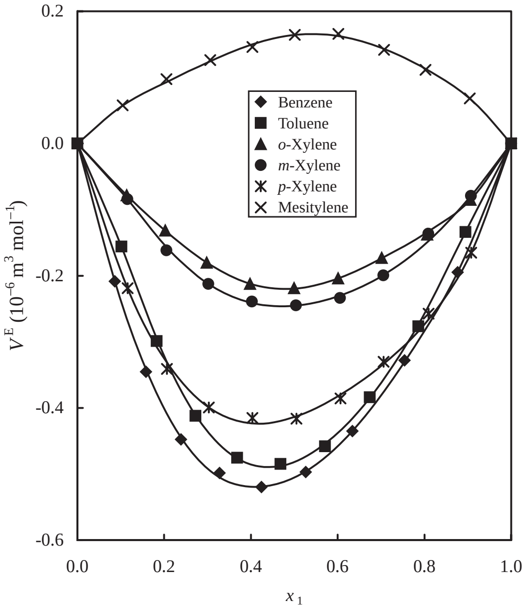

Fig. 2. Variation of excess molar volume (V^E) with mole fraction (x_1) of dimethyl sulfoxide (DMSO) for the binary mixtures at 318.15 K. Points show experimental values and curves show smoothed values using Eq. 5.

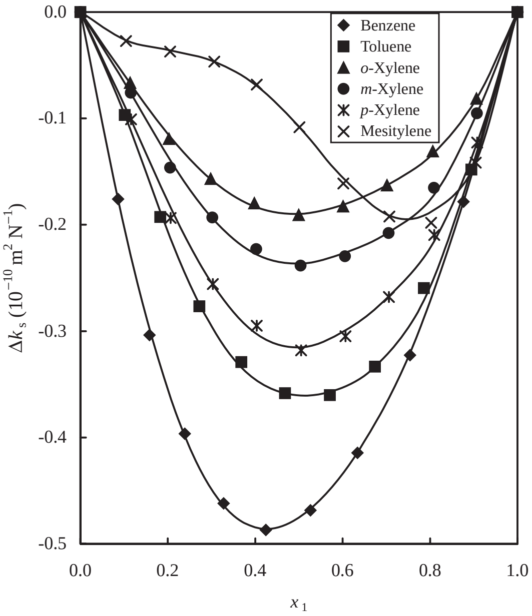

Fig. 3. Variation of deviations in isentropic compressibility (Δk_s) with mole fraction (x_1) of dimethyl sulfoxide (DMSO) for the binary mixtures at 298.15 K. Points show experimental values and curves show smoothed values using Eq. 5.

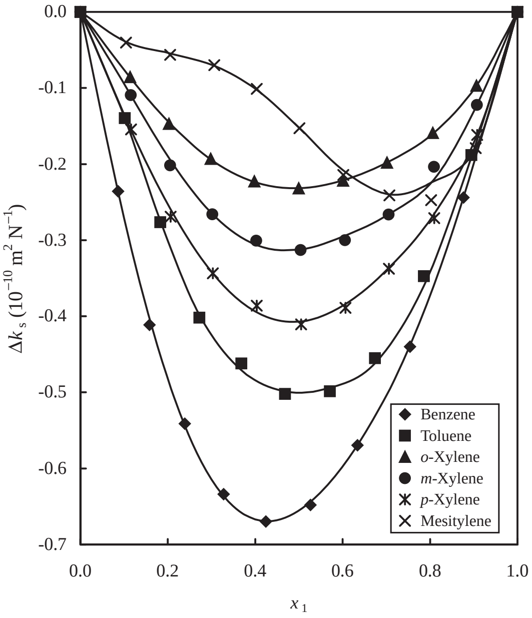

Fig. 4. Variation of deviations in isentropic compressibility (Δk_s) with mole fraction (x_1) of dimethyl sulfoxide (DMSO) for the binary mixtures at 318.15 K. Points show experimental values and curves show smoothed values using Eq. 5.

Eq. 5 by using the best-fit values of coefficient A_i. The variations of smoothed values of V^E and Δk_s with mole fraction, x_1 of DMSO, are shown graphically in Figs. 1–4.

It has been reported[36,37] that the V^E and Δk_s values of the binary mixtures result from the contributions due to the physical, chemical, and structural characteristics of the component liquids. The physical contributions comprise of dispersion forces and non-specific physical (weak) interactions, which lead to positive V^E and Δk_s values. The chemical contributions involve breaking up of the associates present in the pure liquids, resulting in positive V^E and Δk_s values. These contributions also involve specific interactions such as the formation of H-bonding, charge-transfer (donor–acceptor) complexes, and strong dipole–dipole interactions between the component mol-

Table 4. The Values of $\bar{V}^{\circ}_{\phi,2}$, $V^{*}_{\phi,2}$, ΔV, $\bar{K}^{\circ}_{\phi,2}$, $K^{*}_{\phi,2}$, and ΔK of Aromatic Hydrocarbons in DMSO for the Binary Mixtures at Different Temperatures

T/K	$\bar{V}^{\circ}_{\phi,2}$	$V^{*}_{\phi,2}$	ΔV	$\bar{K}^{\circ}_{\phi,2}$	$K^{*}_{\phi,2}$	ΔK
	$/10^{-5}\,\text{m}^3\,\text{mol}^{-1}$		$/10^{-6}\,\text{m}^3\,\text{mol}^{-1}$	$/10^{-14}\,\text{m}^5\,\text{N}^{-1}\,\text{mol}^{-1}$		
			DMSO + Benzene			
298.15	8.844	8.941	−0.97	4.8671	6.0236	−1.1575
303.15	8.891	8.997	−1.06	5.0269	6.3080	−1.2811
308.15	8.933	9.052	−1.19	5.2309	6.6350	−1.4041
313.15	8.974	9.108	−1.34	5.4834	6.9880	−1.5046
318.15	9.014	9.166	−1.52	5.7263	7.3801	−1.6538
			DMSO + Toluene			
298.15	10.599	10.685	−0.87	6.1004	7.2153	−1.1153
303.15	10.646	10.745	−0.99	6.3066	7.5558	−1.2492
308.15	10.689	10.802	−1.13	6.5585	7.8985	−1.3400
313.15	10.733	10.862	−1.28	6.8520	8.2779	−1.4259
318.15	10.778	10.922	−1.44	7.1382	8.6845	−1.5463
			DMSO + *o*-Xylene			
298.15	12.073	12.124	−0.51	6.9418	7.5933	−0.6515
303.15	12.128	12.184	−0.56	7.1556	7.8382	−0.6825
308.15	12.181	12.246	−0.65	7.3616	8.0890	−0.7274
313.15	12.234	12.307	−0.73	7.6102	8.3803	−0.7702
318.15	12.287	12.368	−0.81	7.8974	8.7152	−0.8178
			DMSO + *m*-Xylene			
298.15	12.290	12.347	−0.57	7.3429	8.1588	−0.8159
303.15	12.346	12.407	−0.61	7.6182	8.5076	−0.8894
308.15	12.400	12.467	−0.67	7.9760	8.9214	−0.9454
313.15	12.454	12.530	−0.76	8.2507	9.2518	−1.0010
318.15	12.509	12.594	−0.85	8.5948	9.6695	−1.0755
			DMSO + *p*-Xylene			
298.15	12.289	12.391	−1.02	7.2735	8.3458	−1.0723
303.15	12.344	12.455	−1.11	7.6192	8.8040	−1.1848
308.15	12.393	12.517	−1.24	7.9044	9.1784	−1.2740
313.15	12.443	12.584	−1.41	8.2342	9.5671	−1.3329
318.15	12.493	12.648	−1.55	8.5256	9.9550	−1.4294
			DMSO + Mesitylene			
298.15	13.995	13.954	0.41	7.8033	8.6334	−0.8301
303.15	14.069	14.022	0.47	8.1232	8.9944	−0.8713
308.15	14.144	14.091	0.53	8.4647	9.4068	−0.9421
313.15	14.219	14.161	0.58	8.8064	9.8116	−1.0052
318.15	14.295	14.232	0.63	9.2346	10.3006	−1.0660

ecules of the mixture, resulting in negative V^E and Δk_s values. The structural contributions are due to the geometrical fitting of the molecules of very different molecular sizes into each other's structures resulting in negative V^E and Δk_s values.

The variations of V^E values with x_1 at 298.15 and 318.15 K are shown graphically in Figs. 1 and 2, respectively. For mixtures, DMSO + benzene/toluene/*m*-xylene/mesitylene, our V^E values at 298.15 K compare well with the reported results of Aralaguppi et al.[16] and others.[17,38] The V^E values are negative (Figs. 1 and 2) for DMSO + benzene/toluene/*o*-xylene/*m*-xylene/*p*-xylene mixtures and positive for DMSO + mesitylene mixtures over the whole composition range and at all the investigated temperatures. Thus, the extent of negative deviation in V^E from linear dependence on mole fraction follows the sequence: mesitylene < *o*-xylene < *m*-xylene < *p*-xylene < toluene < benzene. This suggests that there is an expansion in volume of the mixtures as we move from benzene to mesitylene.

The behavior of V^E with the composition of the mixture can be qualitatively examined by considering the nature of the component molecules in the pure state and in the mixture. The molecules of DMSO are associated through strong dipole–dipole interactions[12,13] and those of the aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene) have a large quadrupole moment,[14] which causes molecular order in the pure state. DMSO on mixing with the aromatic hydrocarbons would induce a decrease in the molecular order in the latter, whereas aromatic hydrocarbons would cause disruption of the dipolar association in DMSO molecules in the mixture, resulting in an expansion in volume and, hence, positive V^E values. On the other hand, there is the possibility of electron donor–acceptor type (or charge-transfer) interactions between the highly electronegative oxygen of S=O group of DMSO and the π-electron rich rings of aromatic hydrocarbon molecules, resulting in negative V^E values. The observed negative V^E values suggest the presence of significant donor–acceptor interactions between DMSO and aromatic hydrocarbon molecules in these mixtures. Recently, Ma et al.[27] have also reported a similar type of donor–acceptor interactions between sulpholane and aromatic hydrocarbons (benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene, and *o*-xylene). It is interesting to note that V^E becomes less negative and finally turns positive as the number of $-CH_3$ groups in the ring increases from benzene (devoid of $-CH_3$ group) to mesitylene (with three $-CH_3$ groups). This is contrary to our expectation. The methyl group ($-CH_3$) being an electron-releasing group would enhance the electron density of the benzene ring of the aromatic molecules as we move from benzene to mesitylene, resulting in increased donor–acceptor interaction between unlike molecules. This would cause a decrease in V^E in the sequence: benzene < xylenes < mesitylene; however, the observed V^E values (Figs. 1 and 2) show entirely opposite trend as we move from benzene to mesitylene.

This may be explained by considering the steric hindrance due to the $-CH_3$ groups of the rings. As the number of methyl groups in the ring increases from benzene to mesitylene, the closer approach of a DMSO molecule to the aromatic ring becomes increasingly difficult, resulting in decreased interaction between DMSO and aromatic hydrocarbon molecules. Amongst the xylenes, the magnitude of negative V^E values follows the order: *o*-xylene < *m*-xylene < *p*-xylene; this suggests that the position of $-CH_3$ groups on the aromatic ring plays a substantial role in deciding the magnitude of V^E and, hence, the extent of interaction between the component molecules of the mixtures. The more negative V^E values for DMSO + *p*-xylene may be due to the fact that DMSO molecules could approach more closely to the ring of *p*-xylene from two directions as compared to *o*- and *m*-xylenes, showing maximum interaction of the DMSO molecule with the former xylene than with the latter two xylenes. This is in good agreement with the reported[17] trends in V^E for DMSO + xylenes.

Figures 3 and 4 show the variations of Δk_s values with x_1 at 298.15 and 318.15 K, respectively. The Δk_s values are

Table 5. Physical Constants and Characteristic Parameters of Pure Liquids Used in Flory and PFP Theories

Liquid	C_p /J K^{-1} mol^{-1}	α /10^{-3} K^{-1}	k_T /10^{-10} m^2 N^{-1}	k_s /10^{-10} m^2 N^{-1}	V /10^{-6} m^3 mol^{-1}	$\tilde{V}$	V^* /10^{-6} m^3 mol^{-1}	P^* /10^6 J cm^3	T^* /K
DMSO	153.0	0.887	5.2193	4.1258	71.306	1.2241	58.252	759.31	5599
Benzene	136.78	1.223	9.6490	6.7670	89.412	1.2916	69.224	630.20	4710
Toluene	157.3	1.081	9.1185	6.7525	106.85	1.2640	84.533	564.67	5016
o-Xylene	186.1	0.989	8.1626	6.2630	121.24	1.2454	97.348	560.28	5263
m-Xylene	183.0	0.982	8.5459	6.6080	123.47	1.2439	99.259	529.84	5285
p-Xylene	181.5	1.015	8.8339	6.7351	123.91	1.2509	99.064	536.21	5187
Mesitylene	209.3	0.975	8.0772	6.1870	139.54	1.2426	112.30	555.78	5305

Table 6. Values of χ_{12}, θ_2, Experimental and Calculated V^E (Using Flory and PFP Theories) and Three PFP Contributions for Near Equimolar Composition at 298.15 K

DMSO +	θ_2	χ_{12} /J mol^{-1}	V^E/10^{-6} m^3 mol^{-1}					
			Expt.	Flory	PFP	PFP contributions		
						int.	fv.	ip
Benzene	0.5045	−3.715	−0.3349	−0.3086	−0.3405	−0.0337	−0.1073	−0.1995
Toluene	0.5034	−3.818	−0.2978	−0.2510	−0.2865	−0.0371	−0.0426	−0.2068
o-Xylene	0.5851	−0.278	−0.1421	−0.1354	−0.1378	−0.0029	−0.0130	−0.1219
m-Xylene	0.5847	−2.186	−0.1710	−0.1477	−0.1706	−0.0234	−0.0114	−0.1358
p-Xylene	0.5837	−7.367	−0.2785	−0.1988	−0.2761	−0.0782	−0.0208	−0.1771
Mesitylene	0.6068	22.90	0.1222	−0.1265	0.1224	0.2484	−0.0106	−0.1154

negative for all six binary systems (DMSO + benzene/toluene/*o*-xylene/*m*-xylene/*p*-xylene/mesitylene) studied over the whole composition range and at all of the investigated temperatures. The increase in the magnitude of the negative Δk_s values of DMSO + aromatic hydrocarbon mixtures follow the sequence: mesitylene < *o*-xylene < *m*-xylene < *p*-xylene < toluene < benzene. Like V^E, Δk_s values exhibit a minima, suggesting specific interactions between the component molecules for all the mixtures, except for DMSO + mesitylene, around the middle of the composition scale. However, unlike small positive V^E values over the whole composition range of DMSO + mesitylene, Δk_s exhibits small negative values in the mesitylene-rich region, becoming more negative, with a minimum at $x_1 \approx 0.7$, as the amount of DMSO increases in the mixture. This can be explained by considering the dissociation of the dipolar association in DMSO by mesitylene molecules in the mixture. This dissociation seems to be more pronounced in the mesitylene-rich region than in the DMSO-rich region. Thus, the observed negative Δk_s values suggest that DMSO–mesitylene interaction dominates over the dissociative effect and this interaction is stronger in the DMSO-rich region than in the mesitylene-rich region, thereby, resulting in larger negative values of Δk_s in the former region than in the latter one. However, such a behavior for DMSO + mesitylene is not reflected in the variation of V^E values with x_1. It seems that compressibility is a more powerful thermodynamic parameter in sensing the molecular interactions in liquid mixtures than V^E. A similar view regarding compressibility was also suggested by Wadi and Ramasami.[39]

The apparent molar volume ($V_{\phi,2}$) and apparent molar compressibility ($K_{\phi,2}$) of an aromatic hydrocarbon in DMSO, at all of the temperatures investigated, were calculated by using the relations[40,41]

$$V_{\phi,2} = V^*_{\phi,2} + V^E/x_2, \tag{7}$$

$$K_{\phi,2} = K^*_{\phi,2} + K_s{}^E/x_2, \tag{8}$$

where $K_s{}^E$ [$=(k_s V)^E$] is the excess molar compressibility of the mixture; $V^*_{\phi,2}$ and $K^*_{\phi,2}$ are the molar volume and molar isentropic compressibility of aromatic hydrocarbons, respectively. The partial molar volume ($\bar{V}^\circ_{\phi,2}$) and partial molar compressibility ($\bar{K}^\circ_{\phi,2}$) of aromatic hydrocarbon in DMSO at infinite dilution were obtained by a method described elsewhere.[40,42] The deviations in $V_{\phi,2}$ and $K_{\phi,2}$ at infinite dilution, (ΔV) and (ΔK), respectively, were calculated by using the relations[40]

$$\Delta V = \bar{V}^\circ_{\phi,2} - V^*_{\phi,2}, \tag{9}$$

$$\Delta K = \bar{K}^\circ_{\phi,2} - K^*_{\phi,2}. \tag{10}$$

The values of $\bar{V}^\circ_{\phi,2}$, $V^*_{\phi,2}$, ΔV, $\bar{K}^\circ_{\phi,2}$, $K^*_{\phi,2}$, and ΔK are listed in Table 4. A close look at Table 4 indicates that the deviations ΔV are negative for DMSO + benzene/toluene/*o*-xylene/*m*-xylene/*p*-xylene and positive for DMSO + mesitylene binary mixtures at each investigated temperature. The negative ΔV values clearly suggest that on mixing there is a contraction in volume of the mixture. The deviations in ΔK are also negative (Table 4) for all six binary systems investigated at all of the studied temperatures. This further suggests that the molar compressibilities of aromatic hydrocarbon molecules in the mixture at infinite dilution, $\bar{K}^\circ_{\phi,2}$, are less than their molar compressibilities in the pure state. This, again, suggests a contraction in volume of the mixture. Also, the values of ΔV and ΔK become more negative with increases in temperature (Table 4) for all of the binary mixtures, except ΔV values for DMSO + mesitylene, which show an opposite trend. The observed trends in the values of ΔV and ΔK suggest that DMSO–aromatic hydrocarbon interactions in these mixtures follow the order: benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene. This further supports our earlier conclusion regarding interactions in these mixtures drawn from the composition and temperature dependences of the functions V^E and Δk_s.

Theoretical Analysis of Excess Molar Volume. The Flory statistical theory,[18,19] which is generally valid for non-polar liquids and their mixtures, and its modified form known as the Prigogine–Flory–Patterson (PFP) theory,[20,21] which is applicable to both non-polar and polar liquids and their mixtures, have been successfully employed to estimate and analyze excess thermodynamic functions of binary liquid mixtures by a number of workers in recent years. In the present work, we have applied both theories to predict the excess molar volume, V^E for the mixtures studied. According to the Flory equation of state,[18,19] V^E is given by the equation

$$V^E = \left[\sum_{i=1}^{2} x_i V_i{}^*\right][(\tilde{V}^\circ)^{7/3}/(4/3 - (\tilde{V}^\circ)^{1/3})](\tilde{T} - \tilde{T}^\circ). \quad (11)$$

According to the PFP theory, V^E can be calculated from the equation

$$\begin{aligned}\frac{V^E}{x_1 V_1{}^* + x_2 V_2{}^*} &= \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\psi_1\theta_2\chi_{12}}{[(4/3)\tilde{V}^{-1/3} - 1]P_1{}^*} \\ &\quad - \frac{(\tilde{V}_1 - \tilde{V}_2)^2[(14/9)\tilde{V}^{-1/3} - 1]}{[(4/3)\tilde{V}^{-1/3} - 1]\tilde{V}}\psi_1\psi_2 \\ &\quad + \frac{(\tilde{V}_1 - \tilde{V}_2)}{P_1{}^*\psi_2 + P_2{}^*\psi_1}(P_1{}^* - P_2{}^*)\psi_1\psi_2. \quad (12)\end{aligned}$$

The first term on the right hand side of Eq. 12 represents the interaction contribution, V^E (int.), the second term accounts for the free volume contribution, V^E (fv.), and the third term is the internal pressure contribution, V^E (P^*); ψ, θ, and P^* are the contact energy fraction, surface site fraction, and characteristic pressure, respectively, and are calculated by using the equations

$$\psi_1 = 1 - \psi_2 = \frac{\phi_1 P_1{}^*}{\phi_1 P_1{}^* + \phi_2 P_2{}^*}, \quad (13)$$

$$\theta_2 = 1 - \theta_1 = \frac{\phi_2}{[\phi_2 + \phi_1(V_1{}^*/V_2{}^*)^{1/3}]}, \quad (14)$$

$$P^* = T\tilde{V}^2\alpha/k_T. \quad (15)$$

The notations and terms used in Eqs. 11–15 are the same as given in the literature.[18–21,43–45] The other parameters pertaining to pure liquids and the mixtures are obtained by using the expressions given in the literature[18–21] and are listed in Table 5. The contact interaction parameter, χ_{12}, required for the calculation of V^E from the PFP theory, has been derived by fitting the V^E expression to the experimental equimolar value of V^E for each system studied.

The values of χ_{12}, θ_2, three PFP contributions (V^E (int.), V^E (fv.), and V^E (P^*)), along with the experimental and calculated V^E values by using the Flory and PFP theory (at near equimolar composition) are given in Table 6. It is clear from Table 6 that at near the equimolar composition the calculated values of $V^E{}_{\text{Flory}}$ and $V^E{}_{\text{PFP}}$, by using Flory's statistical theory and the PFP theory, respectively, agree reasonably well with the experimental V^E values for DMSO + benzene/toluene/*o*-xylene/*m*-xylene/*p*-xylene/mesitylene binary mixtures, with the PFP theory providing slightly better results. However, for DMSO + *p*-xylene/mesitylene mixtures, Flory's theory could not predict the V^E values well. It is also clear from Table 6 that all

Table 7. Experimental, Theoretically Calculated (Using Flory and PFP Theory) Values of Excess Molar Volume (V^E) and dV^E/dT as Function of Mole Fraction (x_1) of DMSO for the Binary Mixtures at 298.15 K

x_1	$V^E/10^{-6}\,\text{m}^3\,\text{mol}^{-1}$			dV^E/dT
	Expt.	Flory	PFP	$/10^{-6}\,\text{m}^3\,\text{mol}^{-1}\,\text{K}^{-1}$
		DMSO + Benzene		
0.0862	−0.1336	−0.1027	−0.1096	−0.0031
0.1578	−0.2419	−0.1718	−0.1842	−0.0046
0.2386	−0.3124	−0.2328	−0.2508	−0.0063
0.3278	−0.3479	−0.2794	−0.3029	−0.0072
0.4241	−0.3599	−0.3061	−0.3345	−0.0074
0.5265	−0.3349	−0.3086	−0.3405	−0.0080
0.6339	−0.2856	−0.2834	−0.3162	−0.0071
0.7543	−0.2061	−0.2228	−0.2515	−0.0057
0.8766	−0.1118	−0.1279	−0.1462	−0.0042
		DMSO + Toluene		
0.1014	−0.1129	−0.0911	−0.1022	−0.0022
0.1830	−0.1972	−0.1498	−0.1686	−0.0051
0.2725	−0.2580	−0.1991	−0.2249	−0.0076
0.3682	−0.2970	−0.2341	−0.2656	−0.0088
0.4681	−0.2978	−0.2510	−0.2865	−0.0092
0.5706	−0.2754	−0.2474	−0.2847	−0.0090
0.6742	−0.2260	−0.2220	−0.2580	−0.0079
0.7858	−0.1598	−0.1702	−0.1995	−0.0059
0.8946	−0.0855	−0.0953	−0.1128	−0.0025
		DMSO + *o*-Xylene		
0.1134	−0.0524	−0.0509	−0.0518	−0.0013
0.2025	−0.0868	−0.0831	−0.0844	−0.0023
0.2982	−0.1167	−0.1094	−0.1113	−0.0032
0.3980	−0.1310	−0.1275	−0.1297	−0.0041
0.4996	−0.1421	−0.1354	−0.1378	−0.0039
0.6012	−0.1317	−0.1323	−0.1348	−0.0037
0.7013	−0.1129	−0.1177	−0.1201	−0.0030
0.8063	−0.0872	−0.0894	−0.0914	−0.0026
0.9059	−0.0506	−0.0497	−0.0508	−0.0018
		DMSO + *m*-Xylene		
0.1153	−0.0534	−0.0570	−0.0650	−0.0016
0.2055	−0.1080	−0.0925	−0.1056	−0.0027
0.3020	−0.1483	−0.1210	−0.1386	−0.0031
0.4023	−0.1646	−0.1401	−0.1610	−0.0038
0.5041	−0.1710	−0.1478	−0.1706	−0.0036
0.6055	−0.1597	−0.1433	−0.1665	−0.0036
0.7051	−0.1348	−0.1265	−0.1482	−0.0033
0.8091	−0.0945	−0.0954	−0.1125	−0.0021
0.9075	−0.0487	−0.0526	−0.0624	−0.0015
		DMSO + *p*-Xylene		
0.1157	−0.1185	−0.0769	−0.1037	−0.0052
0.2061	−0.1967	−0.1247	−0.1689	−0.0071
0.3028	−0.2414	−0.1631	−0.2224	−0.0078
0.4032	−0.2679	−0.1886	−0.2592	−0.0075
0.5051	−0.2789	−0.1988	−0.2761	−0.0068
0.6064	−0.2582	−0.1926	−0.2713	−0.0064
0.7058	−0.2216	−0.1700	−0.2433	−0.0055
0.8097	−0.1731	−0.1280	−0.1856	−0.0043
0.9078	−0.1033	−0.0705	−0.1037	−0.0032
		DMSO + Mesitylene		
0.1045	0.0281	−0.0420	0.0330	0.0015
0.2052	0.0577	−0.0754	0.0615	0.0020
0.3065	0.0875	−0.1013	0.0865	0.0019
0.4036	0.1100	−0.1181	0.1066	0.0018
0.5012	0.1221	−0.1265	0.1224	0.0022
0.6018	0.1226	−0.1252	0.1323	0.0021
0.7068	0.1033	−0.1121	0.1292	0.0019
0.8025	0.0698	−0.0885	0.1087	0.0021
0.9043	0.0370	−0.0501	0.0651	0.0016

three contributions of the PFP theory, viz., interactional, free volume, and internal pressure, are negative for both the systems studied, with internal pressure contributing a major part and, hence, playing a dominant role in deciding the sign and magnitude of $V^{\mathrm{E}}{}_{\mathrm{PFP}}$ values. Furthermore, the composition dependence of $V^{\mathrm{E}}{}_{\mathrm{Flory}}$ and $V^{\mathrm{E}}{}_{\mathrm{PFP}}$ values using the χ_{12} value over the entire mole fraction range have been compared with the experimental V^{E} values. The $V^{\mathrm{E}}{}_{\mathrm{Expt}}$, $V^{\mathrm{E}}{}_{\mathrm{Flory}}$, and $V^{\mathrm{E}}{}_{\mathrm{PFP}}$ values as a function of mole fraction, x_1 of DMSO at 298.15 K, have been listed in Table 7 for comparison. Table 7 indicates that both the PFP and Flory theories predict the trend of the dependence of V^{E} on composition quite successfully for all of the binary mixtures investigated.

It is clear from Figs. 1 and 2 that V^{E} values become more negative as the temperature of the mixtures increases from 298.15 to 318.15 K, i.e., the second order thermodynamic mixing volume ($\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$), listed in Table 7, are negative at each mole fraction for all the binary mixtures studied, except for DMSO + mesitylene, which exhibits small positive $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ values. The negative $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ values suggest that there is destruction of order in aromatic hydrocarbons and breaking up of dipolar associates of DMSO in solution when DMSO is mixed with these aromatic hydrocarbons. This is in accordance with the negative $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ values for destruction of *n*-alkane order when mixed with cyclohexane.[14]

One of the authors, AKN, is thankful to the Department of Science and Technology, New Delhi, India for the award of SERC Fast Track Young Scientist Scheme.

References

1 C. M. Kinart, W. J. Kinart, D. Checinska-Majak, A. Cwiklinska, *J. Mol. Liq.* **2004**, *109*, 19.

2 S. L. Oswal, P. Oswal, R. L. Gardas, S. G. Patel, R. G. Shinde, *Fluid Phase Equilib.* **2004**, *216*, 33.

3 B. Gracia, R. Alcalde, J. M. Leal, J. S. Matos, *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1115.

4 A. Ali, A. K. Nain, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 681.

5 A. Ali, A. K. Nain, D. Chand, R. Ahmad, *Phys. Chem. Liq.* **2005**, *43*, 205.

6 A. Ali, A. K. Nain, B. Lal, D. Chand, *Chin. J. Chem.* **2005**, *23*, 377; A. Ali, A. K. Nain, B. Lal, D. Chand, *Int. J. Thermophys.* **2004**, *25*, 1835; A. Ali, A. K. Nain, B. Lal, D. Chand, *Indian J. Chem., Sect. A* **2005**, *44*, 511; A. Ali, A. K. Nain, B. Lal, D. Chand, *Indian J. Pure Appl. Phys.* **2003**, *41*, 928.

7 A. Ali, Abida, A. K. Nain, S. Hyder, *J. Solution Chem.* **2003**, *32*, 865; A. Ali, Abida, A. K. Nain, S. Hyder, *Collect. Czech. Chem. Commun.* **2002**, *67*, 1125.

8 A. K. Nain, A. Ali, M. Alam, *J. Chem. Thermodyn.* **1998**, *30*, 1275.

9 C. Trandum, P. Westh, C. A. Haynes, Y. Koga, *J. Phys. Chem.* **1998**, *102*, 5182.

10 J. A. Dean, *Lange's Handbook of Chemistry*, McGraw-Hill, New York, **1956**.

11 G. A. Krestov, *Thermodynamics of Solvation*, Ellis-Horwood Ltd., England, **1991**.

12 H. Bertagnolli, E. Schulz, P. Chieux, *Ber. Bunsen-Ges. Phys. Chem.* **1989**, *93*, 88.

13 I. Vaisman, M. L. Berkowitz, *J. Am. Chem. Soc.* **1992**, *114*, 7889.

14 D. Patterson, *J. Solution Chem.* **1994**, *23*, 105.

15 J. M. G. Cowie, *J. Polym. Sci., Part C: Polym. Symp.* **1968**, *23*, 267.

16 M. I. Aralaguppi, T. M. Aminabhavi, S. B. Harogoppad, R. H. Balundgi, *J. Chem. Eng. Data* **1992**, *37*, 298.

17 H. Wang, W. Liu, J. Huang, *J. Chem. Thermodyn.* **2004**, *36*, 743.

18 P. J. Flory, R. A. Orwell, A. Vrij, *J. Am. Chem. Soc.* **1964**, *86*, 3507.

19 P. J. Flory, *J. Am. Chem. Soc.* **1965**, *87*, 1833; A. Abe, P. J. Flory, *J. Am. Chem. Soc.* **1965**, *87*, 1838.

20 I. Prigogine, *Molecular Theory of Solution*, North-Holland, Amsterdam, **1957**.

21 D. Patterson, G. Delmas, *J. Polym. Sci., Part C: Polym. Symp.* **1970**, *30*, 1.

22 D. Patterson, *Pure Appl. Chem.* **1976**, *47*, 305.

23 J. A. Riddick, W. B. Bunger, T. Sakano, *Organic Solvents: Physical Properties and Methods of Purification*, Wiley-Interscience, New York, **1986**.

24 F. Kawaizumi, M. Ohno, Y. Miyahara, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2229.

25 A. K. Nain, A. Ali, *Z. Phys. Chem.* **1999**, *210*, 185.

26 L. Maravkova, J. Linek, *J. Chem. Thermodyn.* **2003**, *35*, 1139.

27 C. Yang, P. Ma, Q. Zhou, *J. Chem. Eng. Data* **2004**, *49*, 881.

28 N. C. Exarchos, M. Tasioula-Margar, I. N. Demetropoulos, *J. Chem. Eng. Data* **1995**, *40*, 567.

29 P. S. Nikam, S. J. Kharat, *J. Chem. Eng. Data* **2005**, *50*, 455.

30 R. P. Singh, C. P. Sinha, *J. Chem. Eng. Data* **1985**, *30*, 470.

31 A. Ali, A. K. Nain, D. Chand, R. Ahmad, *J. Mol. Liq.* **2005**, in press.

32 L. Serrano, J. A. Silva, F. Farelo, *J. Chem. Eng. Data* **1990**, *35*, 288.

33 C. Yang, W. Xu, P. Ma, *J. Chem. Eng. Data* **2004**, *49*, 1794.

34 M. I. Aralaguppi, C. V. Jadar, T. M. Aminabhavi, *J. Chem. Eng. Data* **1999**, *44*, 446.

35 O. Redlich, A. T. Kister, *Ind. Eng. Chem.* **1948**, *40*, 345.

36 Y. Marcus, *Introduction to Liquid State Chemistry*, Wiley-Interscience, New York, **1977**.

37 H. Iloukhani, R. Ghorbani, *J. Solution Chem.* **1998**, *27*, 141.

38 C. Pan, Q. Ke, G. Ouyang, X. Zhen, Y. Yang, Z. Huang, *J. Chem. Eng. Data* **2004**, *49*, 1839.

39 R. K. Wadi, P. Ramasami, *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 243.

40 S. K. Mehta, R. K. Chauhan, *J. Solution Chem.* **1997**, *26*, 295.

41 B. Hawrylak, K. Gracie, R. Palepu, *J. Solution Chem.* **1998**, *27*, 17.

42 A. Cipiciani, G. Onori, G. Savelli, *Chem. Phys. Lett.* **1988**, *143*, 505.

43 S. L. Oswal, P. Oswal, P. S. Modi, J. P. Dave, R. L. Gardas, *Thermochim. Acta* **2004**, *410*, 1.

44 G. Camacho, M. A. Postigo, *J. Solution Chem.* **1998**, *27*, 719.

45 T. M. Aminabhavi, V. B. Patil, K. Banerjee, R. H. Balundgi, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1187.