Estimation of Excess Internal Pressure of binary liquid mixtures using two different approaches at temperatures 298.15K and 308.15K

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Abstract

Internal pressure is a measure of how the internal energy changes with expansion or contraction of a system at constant temperature. It is an important tool for studying the intermolecular interactions in liquids and liquid mixtures. Therefore, estimation of internal pressure and its corresponding excess value is very important. In the present work, we have estimated the excess internal pressure of three binary liquid mixtures at two temperatures using different approaches, out of them one is based on mole fraction and other is on volume fraction and a comparative study has been made between them.

Introduction

Internal pressure is a very important parameter in the theory of liquid state in explaining various characteristics of liquids as clustering phenomenon, molecular interactions, ordered structure, internal structure etc. Internal pressure of the liquid mixtures may be defined in terms of the influence of the volume on the internal energy of the liquids and liquid mixtures. For estimation of internal pressure of liquid mixtures thermodynamic methods are very accurate. The importance of internal pressure in liquid mixtures was explained by several workers like Hildebrand[1] etc. Excess internal pressure is a very useful parameter to study the molecular interactions in liquid mixtures. The concept of mole fraction scale in internal pressure, thermal expansivity and compressibility is not suitable because these quantities are volume fraction additive quantities. In this work, a modified approach has been described for the calculation of excess internal pressure and compared with the previous method. In the present study, three binary mixtures viz; Methylbenzene + Hexane-2-ol, Methylbenzene + Heptane-2-ol & Methylbenzene + Octane-2-ol have been put to test at temperatures 298.15K and 308.15K.

Theory

The fundamental thermodynamic equation of state can be derived by using laws of thermodynamics as

$$dU = TdS - PdV \quad (1)$$

where U, V & T are internal energy, volume and temperature respectively.
Differentiating the above equation with respect to volume at constant temperature, we get

$$(\partial U/\partial V)_T = T(\partial S/\partial V)_T - P \quad (2)$$

Using Maxwell's thermodynamic relation, we get

$$(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P \quad (3)$$

Internal pressure is defined as

$$P_i = \left(\partial U / \partial V\right)_T \quad (4)$$

Eqs (3) and (4) give

$$P_i = T(\partial P/\partial T)_V - P \quad (5)$$

where P is the pressure.

Internal pressure can also be expressed in terms of thermal expansion coefficient (α) and isothermal compressibility (K_T)[2] as

$$P_i = \left(\partial U / \partial V\right)_T = \left(\frac{\alpha T}{\kappa_T} - P\right) \quad (6)$$

where all the symbols have their usual meaning.

The excess internal pressure of liquid mixture is given by

$$P_i^{E} = P_i - P_i^{id} = P_i - \sum P_i \ldots x_i \quad (7)$$

where *id* denotes the internal pressure of ideal mixture and x is mole fraction. Excess internal pressure using mole fraction additivity in thermal expansion coefficient and isothermal compressibility calculated using Marczak relation[3] is not accurate because both thermal expansion coefficient and isothermal compressibility are volume fraction additive quantities[4].

For the estimation of P_i^{id}, various authors have assumed [4-7] that

$$P_i^{id} = \sum P_i . x_i$$

In the present work, we have used P_i^{id}

$$P_i^{id} = \left(\frac{\alpha^{id} T}{\kappa_T^{id}} - P\right) \quad (8)$$

where $\alpha^{id} = \sum \phi_i \alpha_i$ & $\kappa_T^{id} = \sum \phi_i \kappa_{T\,i}$

here ϕ_i is volume fraction and can be calculated as

$$\phi_i = \frac{x_i V_i}{\sum x_i V_i}$$

using these parameters in eq(8), we have

$$P_i^{id} = \frac{\sum \phi_i \alpha_i T}{\sum \phi_i \kappa_{T\,i}} - P \quad (9)$$

applying eqs (6) & (9) in eq (7) we get

$$P_i^E = \left(\frac{\alpha T}{\kappa_T} - P\right) - \left(\frac{\sum \phi_i \alpha_i T}{\sum \phi_i \kappa_{T\,i}} - P\right) \quad (10)$$

$$P_i^E = \left(\frac{\alpha T}{\kappa_T} - \frac{\sum \phi_i \alpha_i T}{\sum \phi_i \kappa_{T\,i}}\right) \quad (11)$$

In the present work, thermal expansion coefficient and isothermal compressibility have been calculated through recently developed relations [8-10].

Results and Discussion

Excess internal pressure of Methylbenzene + Hexane-2-ol, Methylbenzene + Heptane-2-ol & Methylbenzene + Octane-2-ol at 298.15K and 308.15K have been calculated using eqs(7) & (11). Necessary data required for the calculation have been taken from the literature[11]. The estimated values of excess internal pressure are given in Table1. The excess internal pressure obtained by the above two approaches have been plotted graphically. In all the systems under investigation, we observed the excess internal pressure values calculated using eq(7) show more deviation when compared with the values calculated using eq(11)

Furthermore, the excess internal pressure values obtained by eq(11) are found to be very close to excess volume and we know that the excess volume indicates correct information about molecular interactions. The literature values further strengthen the validity of the modified and the corrected expression for evaluation of excess internal pressure as compared to the one proposed earlier[3]. It also proves that the excess internal pressure values computed with the volume fraction additivity is more accurate.

References

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Table-1Exess Internal Pressure of binary liquid mixtures at two temperatures

x_1	d(mix) gm cm^{-3}	u(mix) m s^{-1}	P_{int}^E Eq 7 atm	P_{int}^E Eq 11 (atm)
Methylbenzene + Hexane-2-ol at 298.15K				
0.0000	0.8108	1290	0.00	0.00
0.0497	0.8129	1286	-2.06	-1.75
0.1007	0.8151	1284	-3.36	-2.75
0.1588	0.8175	1281	-5.12	-4.22
0.1993	0.8193	1278	-6.69	-5.59
0.2520	0.8215	1274	-8.80	-7.49
0.2999	0.8236	1270	-10.83	-9.36
0.3495	0.8258	1269	-11.72	-10.10
0.4016	0.8282	1267	-12.98	-11.24
0.4468	0.8302	1265	-14.19	-12.38
0.5012	0.8327	1265	-14.70	-12.84
0.5502	0.8351	1264	-15.49	-13.63
0.6003	0.8376	1263	-16.27	-14.44
0.6492	0.8402	1267	-15.00	-13.24
0.7008	0.8431	1268	-14.90	-13.26
0.7476	0.8458	1271	-13.92	-12.42
0.8006	0.8489	1276	-12.11	-10.82
0.8502	0.8521	1280	-10.59	-9.55
0.8945	0.8550	1286	-8.21	-7.43
0.9407	0.8581	1294	-4.97	-4.50
1.0000	0.8622	1306	0.00	0.00
Methylbenzene + Hexane-2-ol at 308.15K				
0.0000	0.8018	1255	0.00	0.00
0.0497	0.8037	1251	-2.14	-1.83
0.1007	0.8059	1245	-5.03	-4.43
0.1588	0.8082	1243	-6.50	-5.60
0.1993	0.8099	1240	-8.14	-7.04
0.2520	0.8120	1237	-9.97	-8.65
0.2999	0.8140	1235	-11.35	-9.86
0.3495	0.8161	1232	-13.16	-11.51
0.4016	0.8183	1230	-14.56	-12.79
0.4468	0.8204	1229	-15.48	-13.63
0.5012	0.8229	1228	-16.45	-14.54
0.5502	0.8253	1228	-16.93	-15.01
0.6003	0.8278	1228	-17.38	-15.48
0.6492	0.8304	1229	-17.36	-15.52
0.7008	0.8333	1230	-17.26	-15.54
0.7476	0.8359	1232	-16.71	-15.13
0.8006	0.8391	1237	-14.78	-13.42
0.8502	0.8423	1242	-12.74	-11.63
0.8945	0.8452	1249	-9.70	-8.86
0.9407	0.8484	1257	-6.11	-5.60

1.0000	0.8528	1270	0.00	0.00

x_1	d(mix) gm cm^{-3}	u(mix) m s^{-1}	P_{int}^E Eq 7 atm	P_{int}^E Eq 11 (atm)
Methylbenzene + Heptane-2-ol at 298.15K				
0.0000	0.8137	1314	0.00	0.00
0.0514	0.81549	1309	-2.09	-1.84
0.1014	0.81727	1303	-4.54	-4.06
0.1469	0.81888	1298	-6.60	-5.93
0.2008	0.82083	1293	-8.66	-7.80
0.2519	0.8227	1288	-10.72	-9.68
0.3007	0.82454	1283	-12.75	-11.58
0.3480	0.82633	1279	-14.40	-13.11
0.4006	0.82845	1276	-15.61	-14.23
0.4526	0.83061	1272	-17.20	-15.74
0.5002	0.83262	1271	-17.60	-16.10
0.5501	0.8349	1269	-18.32	-16.82
0.6011	0.83736	1268	-18.60	-17.12
0.6574	0.84016	1268	-18.45	-17.03
0.7011	0.8425	1269	-17.87	-16.52
0.7560	0.84559	1273	-15.98	-14.77
0.8000	0.84822	1276	-14.47	-13.41
0.8540	0.85169	1283	-11.18	-10.33
0.9009	0.85488	1289	-8.26	-7.64
0.9475	0.85812	1296	-4.88	-4.53
1.0000	0.86218	1306	0.00	0.00
Methylbenzene + Heptane-2-ol at 308.15K				
0.0000	0.8049	1274	0.00	0.00
0.0514	0.80649	1267	-3.05	-2.77
0.1014	0.8082	1261	-5.64	-5.11
0.1469	0.80975	1256	-7.82	-7.09
0.2008	0.81162	1251	-10.02	-9.07
0.2519	0.81337	1246	-12.23	-11.10
0.3007	0.81512	1243	-13.61	-12.33
0.3480	0.81685	1238	-15.77	-14.36
0.4006	0.81886	1235	-17.12	-15.60
0.4526	0.82097	1232	-18.43	-16.83

0.5002	0.82292	1230	-19.32	-17.69
0.5501	0.82513	1229	-19.76	-18.11
0.6011	0.8275	1228	-20.16	-18.53
0.6574	0.83022	1229	-19.71	-18.15
0.7011	0.83253	1230	-19.20	-17.72
0.7560	0.83562	1234	-17.36	-16.03
0.8000	0.83825	1238	-15.49	-14.32
0.8540	0.84171	1243	-13.05	-12.12
0.9009	0.84495	1250	-9.72	-9.04
0.9475	0.8485	1258	-5.82	-5.43
1.0000	0.85279	1270	0.00	0.00

x_1	d(mix) gm cm^{-3}	u(mix) m s^{-1}	P_{int}^E Eq 7 atm	P_{int}^E Eq 11 (atm)

Methylbenzene + Octane-2-ol at 298.15K

0.0000	0.8171	1328	0.00	0.00
0.0494	0.81849	1323	-1.87	-1.70
0.0991	0.81989	1317	-4.14	-3.81
0.1497	0.82139	1313	-5.59	-5.11
0.1999	0.82291	1306	-8.22	-7.60
0.2511	0.82447	1299	-10.84	-10.10
0.2996	0.82603	1294	-12.65	-11.81
0.3540	0.82783	1289	-14.43	-13.49
0.3998	0.82943	1285	-15.81	-14.81
0.4469	0.83112	1279	-17.96	-16.91
0.5000	0.83315	1277	-18.47	-17.38
0.5509	0.83522	1273	-19.73	-18.63
0.5995	0.83733	1271	-20.17	-19.07
0.6486	0.83967	1270	-20.13	-19.06
0.7010	0.84233	1270	-19.60	-18.60
0.7477	0.84488	1271	-18.66	-17.73
0.7989	0.84789	1273	-17.17	-16.37
0.8513	0.85118	1278	-14.38	-13.73
0.9000	0.85446	1286	-10.32	-9.85
0.9511	0.85812	1294	-6.10	-5.84
1.0000	0.86218	1306	0.00	0.00

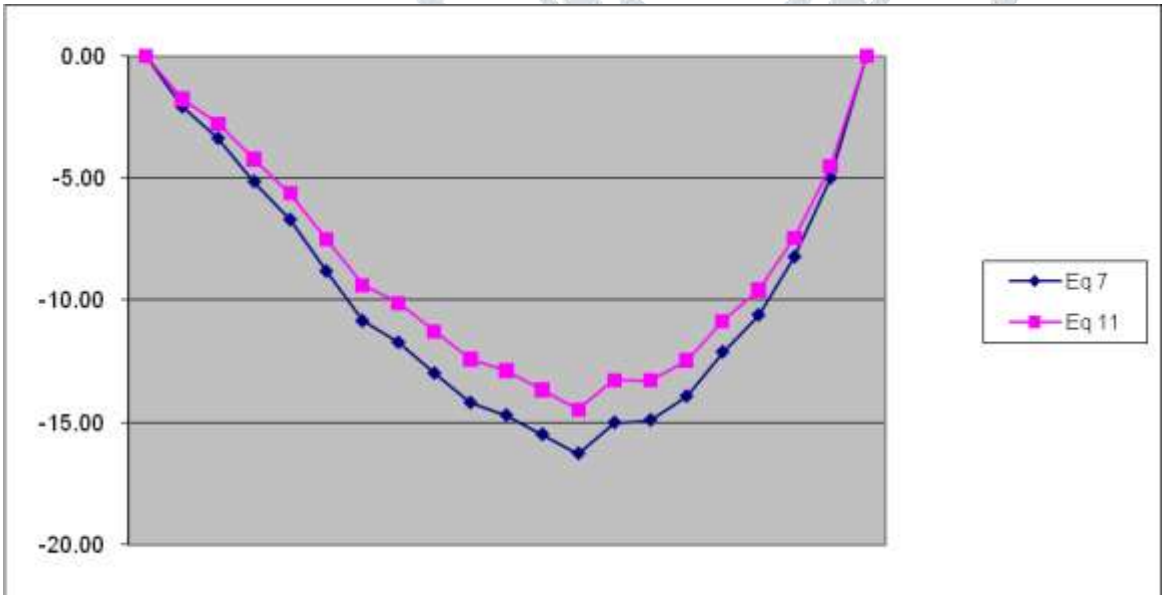
Methylbenzene + Octane-2-ol at 308.15K

0.0000	0.8099	1292	0.00	0.00
0.0494	0.81113	1285	-2.73	-2.58
0.0991	0.8124	1280	-4.65	-4.36
0.1497	0.81376	1274	-6.94	-6.52
0.1999	0.81511	1268	-9.24	-8.69

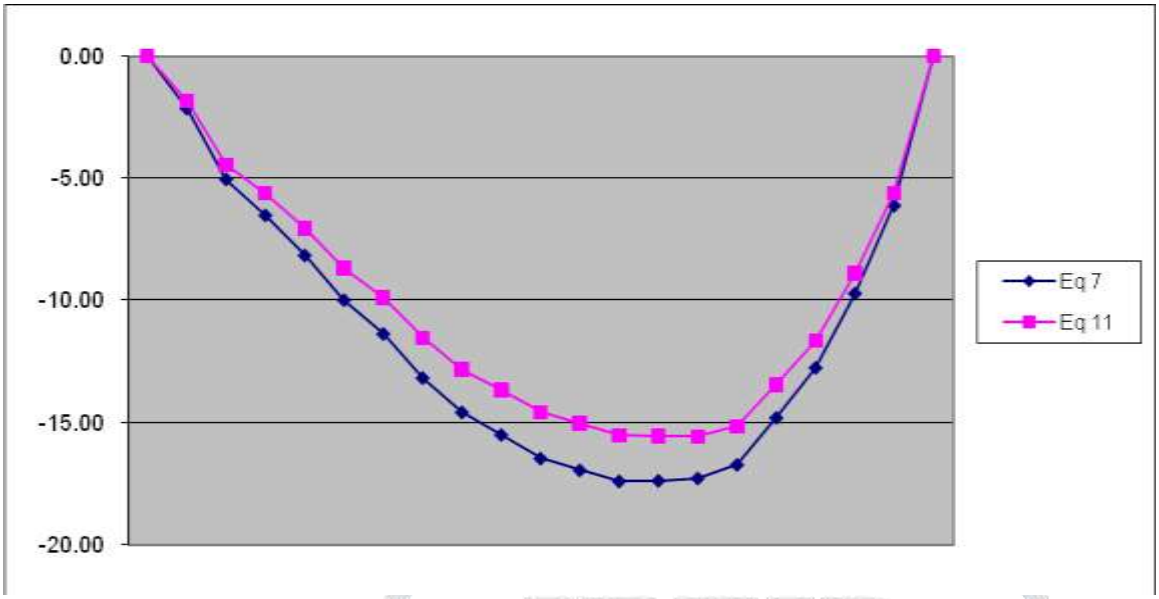
0.2511	0.81648	1261	-11.94	-11.29
0.2996	0.81785	1257	-13.42	-12.67
0.3540	0.81946	1250	-16.06	-15.23
0.3998	0.82091	1247	-17.08	-16.19
0.4469	0.82249	1243	-18.47	-17.54
0.5000	0.82435	1239	-19.81	-18.84
0.5509	0.82629	1235	-21.09	-20.12
0.5995	0.82832	1234	-21.12	-20.16
0.6486	0.83043	1232	-21.53	-20.59
0.7010	0.83294	1233	-20.61	-19.72
0.7477	0.83537	1234	-19.66	-18.84
0.7989	0.83832	1237	-17.72	-17.01
0.8513	0.8416	1241	-15.25	-14.68
0.9000	0.84493	1247	-11.88	-11.46
0.9511	0.84866	1255	-7.52	-7.30
1.0000	0.85279	1270	0.00	0.00

Graph-1Variation of Excess Internal Pressure of binary liquid mixtures

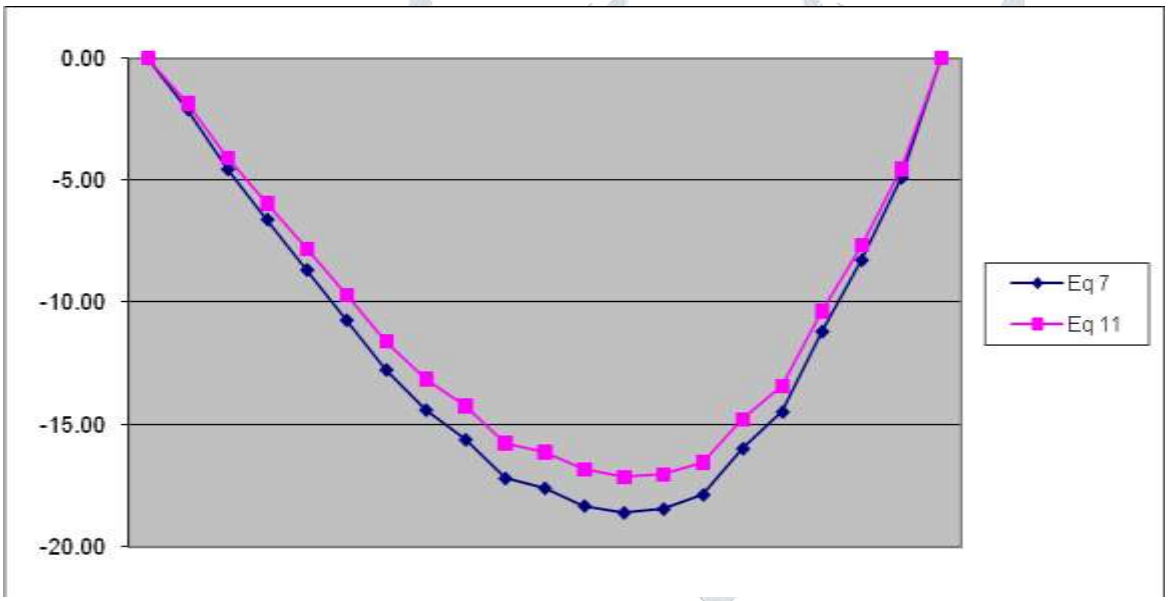
Methylbenzene + Hexane-2-ol at 298.15K



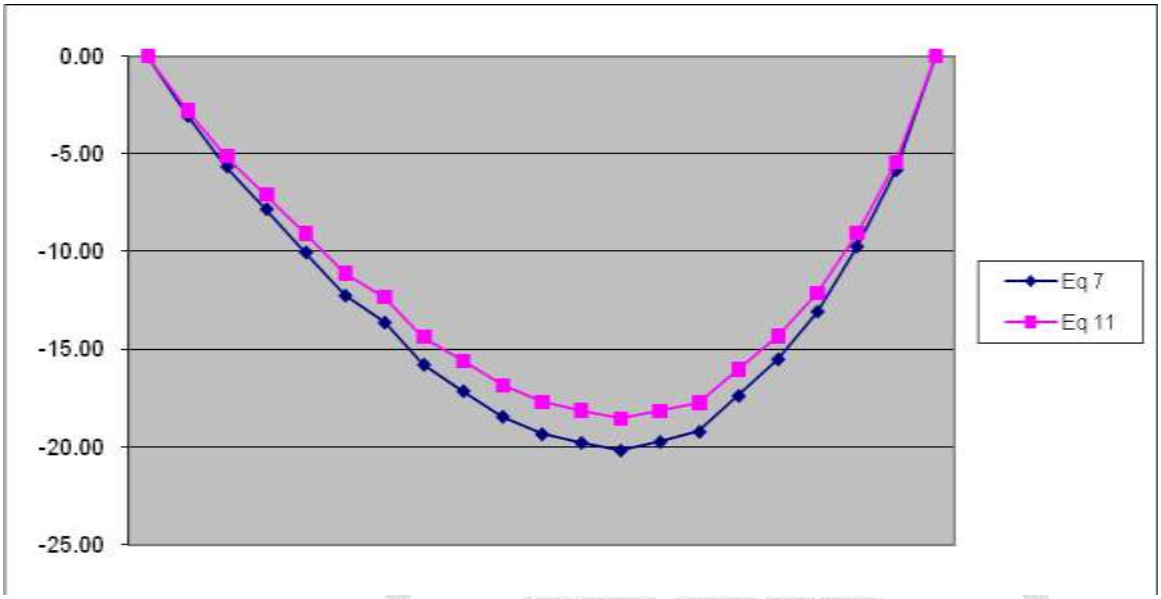
Methylbenzene + Hexane-2-ol at 308.15K



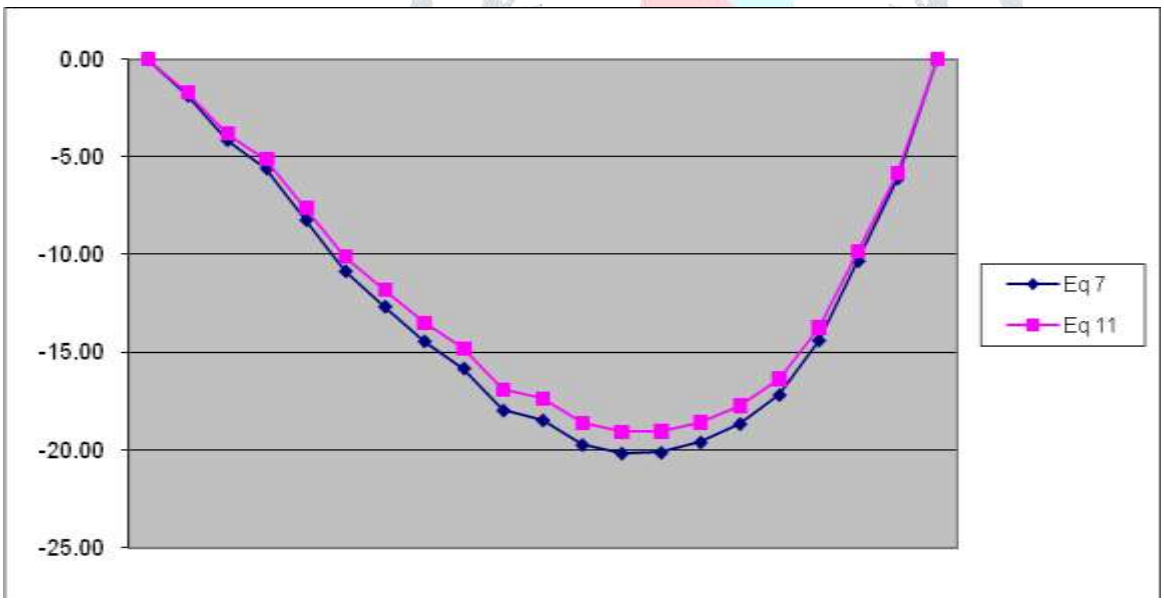
Methylbenzene + Heptane-2-ol at 298.15K



Methylbenzene + Heptane-2-ol at 308.15K



Methylbenzene + Octane-2-ol at 298.15K



Methylbenzene + Octane-2-ol at 308.15K