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PHYSICS

BOILING POINT OF BINARY LIQUID MIXTURES USING ULTRASONIC INVESTIGATION

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Abstract

Ultrasonic velocity is a useful tool to find thermal, physical and chemical parameters. In this work using ultrasonic velocity, the boiling point has been calculated for the following binary mixtures, Toluene+Heptan-1-ol, toluene +Octan-1-ol, toluene +Decan-1-ol, 1,1,1 Trichloroethane +1-propanol, 1,1,1 Trichloroethane+1-Butanol, 1,1,1 Trichloroethane +1-Pentanol, 1,1,1Trichloroethane+1-Hexanol,1,1,1 Trichloroethane +1-Heptanol, Benzonitrile +Butan-1-ol, Benzonitrile+Pentan-1-ol, Benzonitrile+Methylpropan-2-ol and Benzonitrile+ toluene. The results are discussed.

Keywords: Ultrasonic velocity, Density, Boiling point

Introduction

Measurement of ultrasonic velocity in liquid, liquid mixtures and solutions have been employed to find physical, chemical and thermal properties like compressibility, internal pressure, solvation number, heat of enthalpy, Debye temperature etc [1-5]. Various relations connecting ultrasound velocity with surface tension, viscosity, density, refractive index, etc have been suggested and verified very well [6-8].

In the present work boiling point of the following binary mixtures has been calculated. Toluene+Heptan-1-ol, Toluene +Octan-1-ol, Toluene +Decan-1-ol, 1,1,1 Trichloroethane +1-propanol, 1,1,1 Trichloroethane +1-Butanol, 1,1,1Trichloroethane +1-Pentanol, 1,1,1Trichloroethane +1-Hexanol,1,1,1Trichloroethane +1-Heptanol, Benzonitrile + Butan-1-ol, Benzonitrile + Pentan-1-ol, Benzonitrile +Methylpropan-2-ol and Benzonitrile+ Toluene

Theory and Calculations

Maclod [9-10] modified Eyring hole theory and showed that fluidity Φ is related with free volume as

$$\Phi = \frac{1}{\eta} = AV_f \quad (1)$$

Where η is the viscosity of the liquid and Φ is fluidity of the liquid.

Free volume is related with sound velocity as [11]

$$C = \left(\frac{V}{V_f}\right)^{\frac{1}{3}} \left(\frac{RTV}{M}\right)^{\frac{1}{2}}$$
$$V_f = \frac{V}{C^3} \left(\frac{RTV}{M}\right)^{\frac{3}{2}} \quad (2)$$

From equation (1)

$$-\log \eta = \log A + \log V_f \quad (3)$$

And

$$\log V_f = \log \left(\frac{V}{C^3}\right) \left(\frac{V}{M}\right)^{\frac{3}{2}} + \frac{3}{2} \log RT$$

from equation (2) and (3) and Pait's equation¹²

$$\log_{10} \frac{CM^{\frac{1}{2}}\rho^{\frac{1}{2}}}{V^{\frac{1}{2}}} = \frac{m_1}{3}T_B + \frac{m_2}{3} + \frac{\log_{10}A}{3} + \frac{1}{2} \log_{10} RT$$

$$-\log_{10} A - \log_{10} \left(\frac{V}{C^3}\right) \left(\frac{V^{\frac{3}{2}}}{M^{\frac{3}{2}}}\right) - \frac{3}{2} \log_{10} RT = m_1T_B + m_2$$

$$\log_{10} \frac{CM^{\frac{1}{2}}\rho^{\frac{1}{2}}}{V^{\frac{1}{2}}} = \frac{m_1}{3}T_B + B \quad \text{-----}$$

(4)

From equation (4),

$$T_B = \frac{3}{m_1} [\log_{10} c\rho^{5/6} - B]$$

Where,

T_B - Boiling point (K)

c - Ultrasonic velocity in liquid mixtures (m/s)

ρ - Density of liquid mixtures (Kg/m³)

m_1 -constant ($5.2 \times 10^{-3}/c$) for organic liquids

B - constant (4.8595) for organic liquids

The excess boiling temperature can be calculated as

$$T_{EB} = X_1T_{1B} + X_2T_{2B} - T_B \quad (2)$$

Where,

T_{1B} - Boiling temperature of liquid 1 in the liquid mixtures (K)

T_{2B} - Boiling temperature of liquid 2 in the liquid mixtures (K)

T_B - Boiling temperature of liquid mixtures (K)

X_1 - Mole fraction of component 1 in the liquid mixtures

X_2 - Mole fraction of component 2 in the liquid mixtures.

Tables for boiling point and excess boiling point

The symbols and their meaning are used in the following tables are

X – Mole fraction of binary liquid mixtures; Φ – Volume fraction of binary liquid mixtures; c – Ultrasonic velocity in the liquid mixtures (m/s); ρ – Density of liquid mixtures (Kg/m³); T_B – Boiling point of binary liquid mixtures (K); T_{EB} – Excess boiling point of binary liquid mixtures (K).

X	C*	ρ^*	TB	TEB
0	1294	812.52	390.19(449)	0.00
0.0525	1290	814.07	389.81	0.66
0.1014	1287	815.52	389.60	1.14
0.1518	1283	817.05	389.21	1.80
0.1859	1279	818.14	388.71	2.49
0.2489	1274	820.11	388.23	3.31
0.3011	1269	821.80	387.67	4.15
0.3504	1264	823.43	387.09	4.99
0.4006	1260	825.10	386.72	5.63
0.4494	1255	826.86	386.17	6.44
0.5003	1251	828.69	385.83	7.06
0.5486	1248	830.54	385.70	7.46
0.5903	1245	832.19	385.51	7.87
0.6493	1243	834.60	385.71	7.99
0.7011	1242	836.86	386.07	7.90
0.752	1243	839.18	386.85	7.40
0.8041	1245	841.69	387.88	6.65
0.8495	1250	844.02	389.46	5.32
0.9009	1255	846.80	391.15	3.91
0.9487	1260	849.60	392.83	2.48
1	1270	852.79	395.59(383.6)	0.00

Table 1 : Toluene + heptan – 1- ol

Table 2 : Toluene + octan – 1- ol

X	C	ρ	TB	TEB
0	1314	814.57	394.56(468)	0.00
0.0495	1310	815.77	394.10	0.51
0.1104	1303	817.32	393.15	1.52
0.1513	1299	818.35	392.65	2.07
0.1999	1294	819.65	392.01	2.75
0.2517	1288	821.06	391.21	3.61
0.2997	1281	822.41	390.18	4.69
0.356	1274	824.08	389.23	5.69
0.3998	1268	825.36	388.37	6.60
0.4506	1263	827.04	387.81	7.21
0.5001	1259	828.64	387.42	7.66
0.5513	1254	830.48	386.88	8.24
0.6014	1250	832.33	386.55	8.63
0.6495	1248	834.22	386.62	8.61
0.6997	1246	836.39	386.76	8.52
0.7569	1246	838.88	387.38	7.96
0.8012	1245	841.03	387.71	7.67
0.8527	1247	843.69	388.78	6.66
0.9	1251	846.32	390.23	5.26
0.954	1259	846.69	391.92	3.63
1	1270	852.79	395.59(383.6)	0.00

Table 3 : Toluene + decan – 1- ol

X	c	ρ	TB	TEB
0	1352	819.42	402.94(506)	0.00
0.0507	1346	820.28	402.04	0.52
0.1015	1338	821.22	400.79	1.40
0.1473	1332	822.05	399.87	1.98
0.2991	1323	823.27	398.48	2.26
0.2577	1316	824.26	397.41	3.64
0.3006	1310	825.19	396.50	4.23
0.3496	1301	826.26	395.04	5.33
0.4028	1294	827.53	394.01	5.97
0.4516	1286	828.75	392.76	6.86
0.4989	1279	830.05	391.72	7.55
0.5497	1273	831.53	390.92	7.98
0.6009	1266	833.15	389.94	8.58
0.6498	1262	834.80	389.56	8.60
0.7065	1256	836.94	388.90	8.85
0.7524	1256	838.86	389.38	8.03
0.8069	1254	841.28	389.58	7.43
0.8472	1255	843.32	390.29	6.43
0.9063	1259	846.61	391.90	4.38
0.953	1263	849.21	393.33	2.60
1	1270	852.79	395.59(383.6)	0.00

Table 4: 1,1,1 – Tricholoro ethane + 1- Propanol

Φ	c	ρ	TB	TEB
0	1190	795.92	365.44(370)	0.00
0.2174	1119	910.42	378.09	-2.35
0.3419	1077	975.83	382.99	-1.36
0.4499	1043	1032.33	386.71	0.03
0.5454	1018	1082.06	390.45	0.81
0.6293	998	1125.64	393.72	1.51
0.6794	985	1156.78	396.14	1.47
0.7327	977	1179.36	398.13	2.00
0.8514	957	1241.29	403.63	2.12
0.9317	949	1280.34	408	1.55
1	943	1321.02	412.78(347)	0.00

Table 5: 1,1,1 – Tricholoro ethane + 1- Butanol

Φ	c	ρ	TB	TEB
0	1226	801.94	374.48(391)	0.00
0.0807	1192	844.12	378.14	-0.57
0.1947	1149	903.50	383.13	-1.19
0.291	1112	953.51	386.17	-0.54
0.3846	1080	1001.99	389.21	0.00
0.5004	1041	1061.63	392.07	1.58
0.6002	1014	1130.06	395.36	2.11
0.7038	987	1166.36	398.37	3.07
0.7544	975	1192.52	399.93	3.44
0.8383	960	1236.86	403.67	2.92
0.9084	949	1272.61	406.73	2.54
1	943	1321.02	412.78(347)	0.00

Table 6: 1,1,1 – Trichloro ethane + 1- pentanol

Φ	c	ρ	TB	TEB
0	1283	812.12	388.44(411)	0.00
0.0542	1258	839.91	390.54	-0.78
0.1388	1217	882.94	392.67	-0.85
0.2131	1182	920.58	394.07	-0.44
0.3176	1137	973.47	396.07	0.10
0.4152	1097	1022.81	397.36	1.19
0.5104	1063	1071	399.09	1.77
0.6234	1027	1128.29	401.33	2.28
0.667	1014	1150.4	402.19	2.48
0.7888	984	1212.5	405.65	1.99
0.8983	962	1268.63	409.43	0.87
1	943	1321.02	412.80(347)	0.00

Table 7: 1,1,1 – Trichloro ethane + 1- Hexanol

Φ	c	ρ	TB	TEB
0	1252	807.52	381.13(431)	0.00
0.1498	1170	884.29	383.12	2.75
0.2047	1147	912.35	384.67	2.94
0.3501	1091	986.71	388.49	3.72
0.4621	1079	998.87	388.27	7.49
0.5164	1039	1071.26	393.41	4.06
0.6506	1004	1139.85	397.79	3.93
0.7910	974	1211.93	402.99	3.18
0.8955	954	1266.00	406.90	2.57
1	943	1321.02	412.78(347)	0.00

Table8: 1,1,1 – Trichloro ethane + 1- Heptanol

Φ	c	ρ	TB	TEB
0	1228.8	802.4	375.18(449)	0
0.0369	1235.9	810.1	378.61	-0.55
0.1672	1264.5	835.8	390.87	-2.62
0.2355	1278.2	849.4	396.94	-3.35
0.3653	1303.1	874.7	401.35	2.38
0.4372	1314.2	888.5	413.29	-3.94
0.5326	1329.2	906.8	420.39	-3.59
0.6484	1347.1	928.7	428.73	-2.87
0.8078	1373.2	959.0	440.24	-1.92
0.9667	1399.9	989.0	451.50	0.76
1	1402.7	995.4	453.34(347)	0

Table 9: Benzonitrile + Butan – 1 - ol

Φ	c	ρ	TB	TEB
0	1305	815.72	393.68(391)	0.00
0.1169	1245	874.86	396.51	-0.60
0.1515	1227	892.27	396.97	-0.40
0.2807	1165	957.25	398.66	0.38
0.3896	1118	1011.94	399.94	1.18
0.4387	1097	1036.55	400.21	1.85
0.5768	1048	1105.85	402.27	2.43
0.6603	1022	1147.91	403.77	2.52
0.8464	975	1242.19	408.62	1.23
0.9144	960	1276.99	410.37	0.78
1	943	1321.02	412.78(464)	0.00

Table 10: Benzonitrile + Pentan – 1 - ol

Φ	c	ρ	TB	TEB
0	1256	806.8	381.80(411)	0
0.0986	1270.6	825.9	389.59	-0.73
0.1552	1279.1	836.8	393.99	-1.09
0.2926	1301.9	863.3	404.93	-2.19
0.3745	1315.9	878.8	411.33	-2.73
0.4899	1336.8	900.6	420.39	-3.54
0.5959	1354.5	920.3	428.20	-3.77
0.7097	1371.5	941.5	436.08	-3.51
0.812	1383.2	960.4	442.36	-2.47
0.912	1393.8	978.9	448.26	-1.21
1	1402.7	995.4	453.34(464)	0

Table 11: Benzonitrile + 2 – methylpropan – 2 - ol

Φ	c	ρ	TB	TEB
0	1110	775	342.45(381)	0
0.0621	1132.6	788.9	351.21	-1.88
0.1649	1177.6	811.8	366.95	-6.21
0.3002	1220.5	841.7	383.46	-7.72
0.419	1256.5	867.8	397.12	-8.21
0.5123	1279.5	888.3	406.54	-7.28
0.6183	1305.7	911.3	416.96	-5.94
0.7444	1339.3	938.4	429.44	-4.44
0.8394	1364.5	959.1	438.67	-3.14
0.8997	1376.9	972.5	443.83	-1.61
1	1402.7	995.4	453.34(464)	0

Table 12: Benzonitrile + toluene

Φ	c	ρ	TB	TEB
0	1292	856.6	401.39(383.6)	0
0.0974	1304.9	871.8	407.55	-1.1
0.1254	1309.5	876	409.44	-1.53
0.2138	1321.2	888.9	414.72	-2.22
0.3124	1332.5	903.2	420.18	-2.56
0.3844	1340.8	913.5	424.11	-2.75
0.4977	1352.9	928.9	429.85	-2.6
0.6304	1364.9	946.7	436.03	-1.88
0.7278	1374.2	959.6	440.55	-1.35
0.8496	1386.8	975.5	446.27	-0.74
1	1402.7	995.4	453.34(464)	0

* Ref: 2,13,14 and () Exptl values

Figure 1: Boiling temperature for Toluene + heptan – 1- ol, Toluene + octan – 1- ol and Toluene + decan – 1- ol

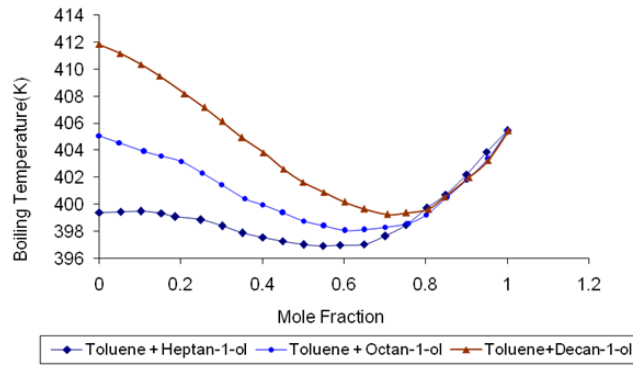


Figure 2: Excess boiling temperature for Toluene + heptan – 1- ol, Toluene + octan – 1- ol and Toluene + decan – 1- ol

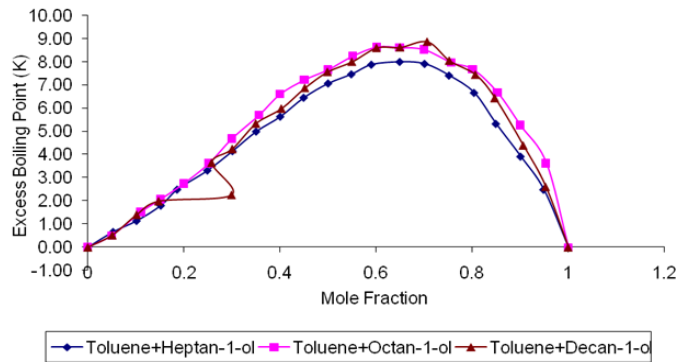


Figure 3: Boiling temperature for 1,1,1 – Trichloro ethane + 1- Propanol, 1,1,1 – Trichloro ethane + 1- Butanol, 1,1,1 – Trichloro ethane + 1- pentanol, 1,1,1 – Trichloro ethane + 1- Hexanol and 1,1,1 – Trichloro ethane + 1- Heptanol.

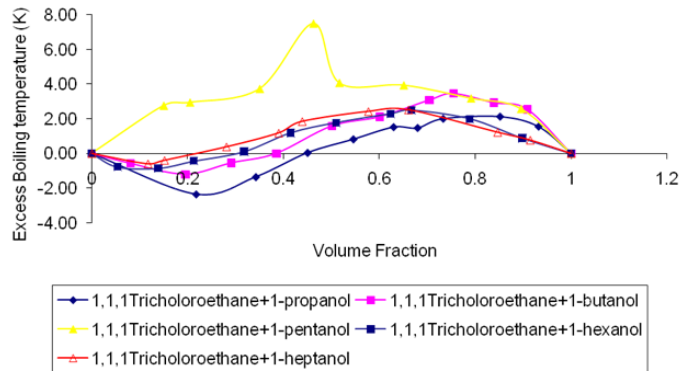


Figure 4: Excess boiling temperature for 1,1,1 – Trichloro ethane + 1- Propanol, 1,1,1 – Trichloro ethane + 1- Butanol, 1,1,1 – Trichloro ethane + 1- pentanol, 1,1,1 – Trichloro ethane + 1- Hexanol and 1,1,1 – Trichloro ethane + 1- Heptanol.

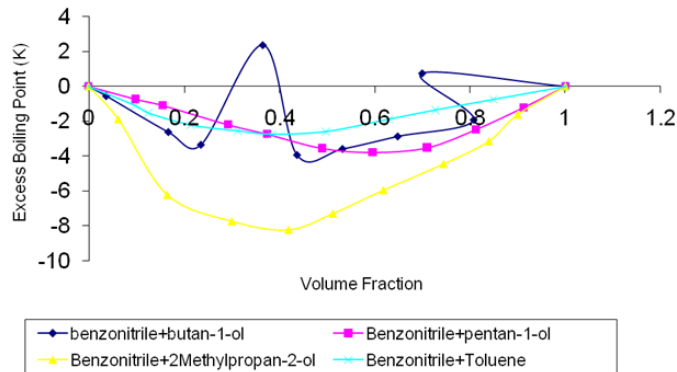


Figure 5: Boiling temperature for Benzonitrile + Butan – 1 – ol, Benzonitrile + Pentan – 1 – ol, Benzonitrile + 2 – methylpropan – 2 – ol and Benzonitrile + toluene

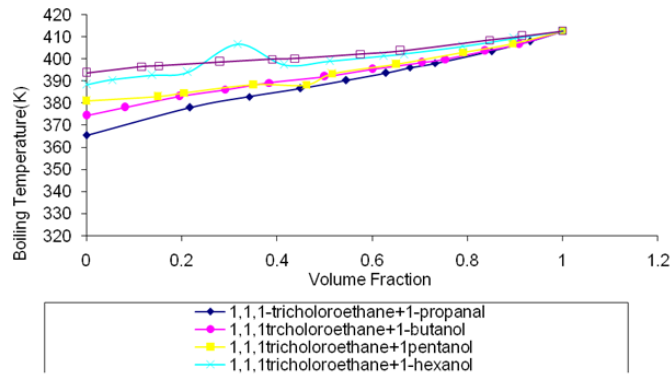
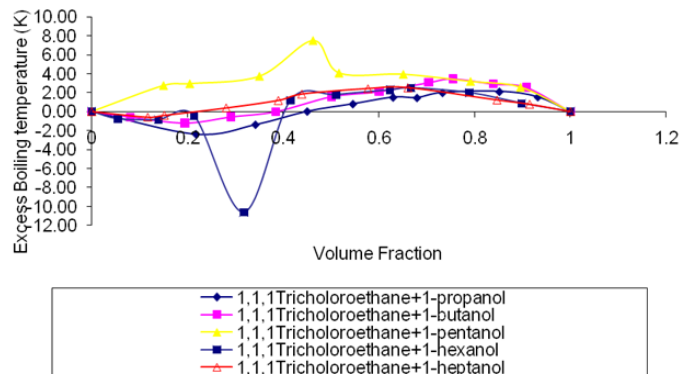


Figure 6: Excess boiling temperature for Benzonitrile + Butan – 1 – ol, Benzonitrile + Pentan – 1 – ol, Benzonitrile + 2 – methylpropan – 2 – ol and Benzonitrile + toluene



Results and Discussion

Table 1-12 gives the boiling point and excess boiling point of organic binary liquid mixtures namely Toluene+heptan-1-ol, Toluene+Octan-1-ol, Toluene+decan-1-ol, Benzonitrile + Butan – 1 – ol, Benzonitrile + Pentan – 1 – ol, Benzonitrile + 2 – methylpropan – 2 – ol, Benzonitrile + toluene, 1,1,1-Trichloroethane+1-propanol, 1,1,1, Trichloroethane+1-Butan-1-ol, 1,1,1, Trichloroethane+1-Pentan-1-ol, 1,1,1 Trichloroethane+Hexan-1-ol and 1,1,1 Trichloroethane+Heptan-1-ol. The calculated values are expected range. The variations of T_B and T_{EB} with mole fraction is shown in graphs 1-6. The calculated values of boiling point for pure liquid is well agreed with literature value. The excess value (T_{EB}) has been calculated using ideal mixing rule. The deviation is used to study strength of interaction of molecules. The order of strength of interaction can be represented as Toluene+decan-1-ol>toluene+octanol>toluene+heptanal. Similarly, the interaction between other combinations can be represented as 1,1,1 - trichloroethane + 1-pentanol>1,1,1 - trichloroethane + 1-butanol>1,1,1 - trichloroethane + 1-heptanol>1,1,1 - trichloroethane + 1-hexanol >1,1,1 – trichloroethane + 1-propanol and Benzonitrile + 2-methyl-2-propanol>Benzonitrile + butanol> Benzonitrile + pentanol> Benzonitrile +toluene.

Conclusion

The prediction of boiling point of organic liquid mixtures using ultrasonic velocity studies, is quite satisfactory. Thus determination of boiling point of

mixtures can be used as another method to study the molecular interactions in liquid mixture.

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