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Theoretical Evaluation of Ultrasonic Velocities in Quaternary Systems

SHIPRA BALUJA* and FALGUNI KARIA
Department of Chemistry, Saurashtra University
Rajkot-360 005, India

Ultrasonic velocity and densities of quaternary systems: chloroform-1,4-dioxane-toluene-cyclohexanone, chloroform-1,4-dioxane-toluene-hexane and chloroform-1,4-dioxane-toluene-heptane have been measured at 298 K as a function of concentration and these experimental values are compared with theoretical values evaluated by using various theories such as Flory Auerback, Nomoto, Van Deal-Vangeal, Rao's specific velocity, collision factor and impedance dependence. The relative applicability of these theories to the present systems has been checked and the results are explained in terms of molecular interactions occurring in these systems.

INTRODUCTION

Literature survey shows that binary and ternary liquid mixtures have been studied extensively to study the ultrasonic and thermodynamic behaviour[1–4]. Scanty work has been done in quaternary systems[5]. Theoretical evaluation of ultrasonic velocity in liquid mixtures and its comparison with the experimental values reflects the molecular interactions in liquid mixtures. Further, ultrasonic velocity and related properties of liquid mixtures are the valuable tools in testing the various theories of liquid state.

In the present investigation, the ultrasonic velocity of three quaternary mixtures: chloroform + 1,4-dioxane + toluene + cyclohexanone (I), chloroform + 1,4-dioxane + toluene + hexane (II) and chloroform + 1,4-dioxane + toluene + heptane (III) have been theoretically evaluated by using various theories at 298 K and these theoretical values are compared with experimental values. Further, acoustical properties like specific impedance and isentropic compressibility are also calculated from experimental data which also helps in understanding the molecular interactions taking part in the mixtures.

EXPERIMENTAL

The liquids used were of AR grade and were purified by standard methods[5]. All the mixtures of different compositions were prepared by volume and were keep in stoppered bottles to minimize the evaporation of components. The densities and ultrasonic velocities (2 MHz) were measured at 298 K by usual procedure as explained before.[6]

Theory

The theoretical values of ultrasonic velocities are calculated from the following relations:

(1) Nomoto relation[7]: $U = (\Sigma x_iR_i/\Sigma x_iV_i)^3$
(2) Flory Auerback (FA) relation[8, 9]: $U = [\sigma/6.3 \times 10^{-4}]^{2/3}$
(3) Impedence relation: $U = (\Sigma x_iZ_i/\Sigma x_id_i)$
(4) VanDeal-Vangeal relation[10, 11]: $U = (\Sigma x_iM_i)/(\Sigma x_i/M_iU_i^2)^{1/2}$
(5) Rao's specific velocity method[12]: $U = (\Sigma x_ir_id)^3$
(6) Collision factor theory[13] (CFT): $U = U_\infty (\Sigma x_iS_i)(\Sigma x_iB_i)/(\Sigma x_iV_i)$

where x_i is mole fraction, U_i is ultrasonic velocity, R_i is molar sound velocity, V_i is molar volume, σ is the surface tension and d is the density of the solution, M_i is molecular weight, r_i is Rao's specific sound velocity = $U_i^{1/3}/d_i$, Z_i is acoustic impedance, S_i collision factor, and B_i is the actual volume of i-th component in the mixture.

Collision factor S_i can be calculated by the equation:

$$S_i = U/U_\infty r_f$$

where r_f is the space filling factor which is given by:

$$r_f = (n_D^2 - 1)/(n_D^2 + 2)$$

where n_D is the refractive index for the sodium D-line. The value for U_∞ is 1600 m/s and Jacobson's constant $K = 2.045 \times 10^{-6}$ in SI units.

B can be calculated by the equation:

$$B = 4\pi r^3N/3$$

where N is Avogadro's number.

Molecular radius r of pure liquids can be evaluated by the equation[14]:

$$r = [(3V/16\pi N)\{1 - (RT/MU^2)(\sqrt{MU^2/3RT}) + 1 - 1)\}]^{1/3}$$

where all the symbols have their usual significance.

The various acoustical parameters were calculated from experimental data by the equations reported earlier[6].

RESULTS AND DISCUSSION

The experimental and theoretical velocities calculated using the above equations are given in Table-1. Table-2 gives the percentage deviation between experimental and theoretical velocities for all the three quaternary liquid mixtures. It is obvious from Table-2 that in system I, at low concentration of cyclohexanone, TABLE-1

EXPERIMENTAL AND THEORETICAL VALUES OF VELOCITIES (in m s^{-1}) IN THE THREE QUATERNARY SYSTEMS AT 298 K

X_4	U_{EXPTL}	U_{FLT}	U_{CFT}	U_{NOM}	U_{IMP}	U_{RAO}	U_{VAN}
Chloroform-1,4-dioxane-toluene-cyclohexanone							
0.0896	1226.4	1065.69	942.75	1205.39	1156.61	1263.05	1146.31
0.2231	1222.5	1109.65	992.66	1219.63	1170.15	1275.39	1168.43
0.3648	1268.3	1160.58	1049.23	1255.67	1208.12	1289.68	1197.28
0.4054	1283.2	1225.14	1077.16	1262.49	1216.32	1384.68	1202.62
0.4722	1113.6	1344.24	1079.82	1285.54	1242.06	1360.70	1224.77
0.5205	1136.2	1242.73	1126.44	1316.80	1285.42	1385.02	1236.99
0.6578	1128.8	1268.97	1152.60	1305.38	1260.55	1376.48	1260.57
0.7701	1337.3	1313.99	1197.88	1338.00	1303.32	1395.69	1292.34
0.8572	1579.0	1403.34	1248.18	1371.57	1352.19	1417.13	1320.51
0.9140	1384.3	1450.27	1271.35	1387.54	1377.02	1428.85	1339.90
Chloroform-1,4-dioxane-toluene-hexane							
0.0723	1164.8	1077.99	931.52	1173.17	1133.00	1275.15	1107.80
0.1474	1260.8	1189.48	1068.60	1252.21	1266.96	1220.60	1073.62
0.1833	1286.0	1029.03	885.41	1069.25	1019.95	1235.43	1082.57
0.3043	1125.2	989.53	997.32	1106.69	1084.80	1269.79	1038.30
0.4089	1126.3	1103.90	1029.98	1125.11	1112.32	1198.31	1009.93
0.5008	1094.2	1115.47	1053.42	1103.15	1091.43	1197.12	985.46
0.6617	1266.3	1115.47	1060.95	1067.51	1037.70	1257.76	950.64
0.7943	1296.3	1137.47	1127.97	1088.90	1088.18	1188.43	910.47
0.8649	1088.0	1133.39	1144.93	1088.06	1091.05	1163.47	892.87
0.8938	1297.2	1198.73	1151.44	1082.71	1083.01	1172.21	886.34
Chloroform-1,4-dioxane-toluene-heptane							
0.1020	1166.7	1025.85	955.85	1171.93	1134.40	1218.26	1128.10
0.1756	1138.6	1069.19	968.67	1153.32	1116.17	1258.02	1128.94
0.2107	1317.2	1030.63	983.81	1176.25	1144.74	1420.31	1132.39
0.3878	1309.0	1030.67	1019.72	1111.52	1073.52	1290.39	1128.65
0.4258	1112.7	1058.78	1046.28	1124.42	1093.95	1259.48	1128.10
0.5398	1120.2	1063.96	1030.16	1102.29	1049.65	1152.21	1134.01
0.6498	1137.2	1131.36	1110.84	1131.27	1118.05	1227.32	1131.18
0.7838	1247.6	1119.39	1146.32	1135.38	1125.72	1241.46	1133.14
0.8569	1334.2	1133.38	1164.94	1137.21	1134.53	1282.94	1134.25
0.9441	1329.9	1145.74	1182.10	1129.52	1122.07	1270.99	1134.33

TABLE-2
PERCENTAGE DEVIATION BETWEEN EXPERIMENTAL AND THEORETICAL VALUES OF VELOCITIES IN THE THREE QUATERNARY SYSTEMS

X_3	Δ_{FT}%	U_{NOM}%	U_{RAO}%	U_{VAN}%	U_{IMP}%	U_{CFT}%
Chloroform-1,4-dioxane-toluene-cyclohexanone						
0.0896	13.10	1.71	–2.99	6.53	5.69	23.13
0.2231	9.23	0.23	–4.33	4.42	4.28	18.80
0.3648	8.49	0.99	–1.69	5.60	4.75	17.27
0.4054	4.52	1.61	–7.91	6.28	5.21	16.05
0.4722	–20.71	–15.44	–22.19	–9.98	–11.54	3.03
0.5205	–9.38	–15.89	–21.90	–8.87	–13.13	0.86
0.6578	–12.42	–15.64	–21.94	–11.67	–11.67	–2.11
0.7701	1.74	–0.05	–4.37	3.36	–2.54	10.43
0.8572	11.42	13.14	10.25	16.37	14.36	20.95
0.9140	–4.77	–0.23	–3.22	3.20	0.53	8.16
Chloroform-1,4-dioxane-toluene-hexane						
0.0723	7.45	–0.72	–9.47	4.89	2.73	20.03
0.1474	5.66	0.68	3.19	14.85	–0.49	15.24
0.1833	19.98	16.85	3.93	15.82	20.69	31.15
0.3043	12.06	1.65	–12.85	7.72	3.59	11.36
0.4089	1.99	0.11	–6.39	10.33	1.24	8.55
0.5008	–1.94	–0.82	–9.41	9.93	0.25	3.73
0.6617	11.91	15.70	0.67	24.93	18.05	16.21
0.7943	12.25	16.00	8.32	29.76	16.06	12.99
0.8649	–4.17	–0.01	–6.94	17.93	–0.28	–5.23
0.8938	7.59	16.54	9.64	31.67	16.51	11.24
Chloroform-1,4-dioxane-toluene-heptane						
0.1020	–12.07	–0.45	–4.42	3.31	2.77	18.07
0.1756	6.10	–1.29	–10.49	0.85	1.97	14.92
0.2107	21.76	10.70	–7.83	14.03	13.09	25.31
0.3878	21.27	15.09	1.44	13.78	17.98	22.10
0.4258	4.84	–1.05	–13.19	–1.38	1.69	5.97
0.5398	5.00	1.58	–2.88	–1.25	6.28	8.02
0.6498	5.14	0.48	–7.92	0.53	2.21	2.32
0.7838	10.28	9.00	0.49	9.17	9.77	8.12
0.8569	15.05	14.76	3.84	14.99	14.97	12.67
0.9441	13.85	15.07	4.43	14.71	15.63	11.11

there is good agreement between experimental and theoretical values calculated by FA,[8, 9] Nomoto,[7] Rao,[12] Van[10, 11] and impedance relations. However, higher deviations are observed at 0.47–0.65 and at 0.85 compositions. The values calculated from CFT give quite high deviations at lower composition range but less deviation in 0.47 to 0.65 range. Comparison of values calculated by CFT and other relations show that CFT values deviate largely in that composition range where other theories agree well or vice versa. In II and III systems, very good agreement is observed between experimental and theoretical values calculated from Rao's relation.[12] In these systems also, in some concentration range, deviations are higher in FA, Nomoto, Van and impedance relations. In hexane system, overall larger deviation is observed in CFT relation whereas in heptane system, in intermediate concentration range, good agreement is observed between experimental and theoretical values calculated from CFT relation but higher deviations are observed at low and higher compositions.

In all the three systems, maximum deviation is observed in certain compositions whereas in other compositions good agreement is observed. Higher deviations in some concentration range suggest the existence of a strong tendency for the association between component molecules in this concentration range[15]. This is further confirmed by acoustical properties like isentropic compressibilities (κ_s) and specific impedance (Z). These values vary nonlinearly with compositions suggesting thereby association in some compositions (Table-3).

TABLE-3
SOME ACOUSTICAL PARAMETERS FOR THE QUATERNARY SYSTEMS

X_4	Z $kg\ m^{-2}$	κ_s Tpa^{-1}	X_4	Z $kg\ m^{-2}$	κ_s Tpa^{-1}	X_4	Z $kg\ m^{-2}$	κ_s Tpa^{-1}
System (I)			System (II)			System (III)		
0.0895	1288.8	632.67	0.0723	1199.9	715.44	0.1019	1190.9	719.74
0.2231	1301.0	628.76	0.1474	1158.7	684.53	0.1756	1149.9	763.80
0.3648	1314.6	599.78	0.1834	1373.5	566.17	0.2107	1299.4	584.25
0.4054	1377.1	565.89	0.3043	1098.5	809.02	0.3691	1266.9	603.02
0.4722	1126.6	797.06	0.4096	974.2	911.33	0.4257	1032.0	870.84
0.5206	1133.2	776.64	0.5007	927.8	985.06	0.5398	963.3	926.86
0.6577	1161.0	763.07	0.6618	1037.7	760.99	0.6497	923.1	952.64
0.7701	1335.2	560.06	0.7945	952.3	810.10	0.7828	950.0	843.68
0.8573	1540.3	411.16	0.8649	766.0	1198.95	0.8575	991.7	755.78
0.9140	1331.7	542.46	0.8938	911.2	846.06	0.9441	962.5	781.26

These results conclude that in spite of good results from statistical theories, these can be improved by considering molecular interactions in polar and non-polar systems.

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