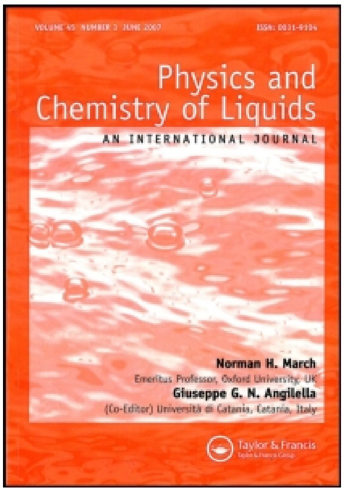

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EVALUATION OF SOUND VELOCITY AND RELATIVE INTERACTION IN BINARY MIXTURES OF *n*-DODECANE + HEXANE ISOMERS

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Sound velocity and relative interaction have been evaluated in binary mixtures of *n*-dodecane + hexane isomers. The results are compared with the excess volume and excess isentropic compressibility studies of Benson *et al.* It has been found that the present studies are useful in understanding the solute solvent interactions in binary liquid mixtures.

KEY WORDS: Sound velocity, liquid mixtures, molecular interactions.

INTRODUCTION

Ultrasonic investigations find extensive applications in probing into physico-chemical behaviour of liquid mixtures such as molecular association and dissociation. Langemann[1] was the first to point out the sound velocity approach for qualitative estimation of interactions in liquids. Later several workers[2–8] studied molecular interactions in binary liquid mixtures. The present paper deals with the evaluation of sound velocity and relative interaction in binary mixtures of *n*-dodecane + hexane isomers. The freelength theory of Jacobson[9] (FLT), Collision factor theory of Schaaffs[10] (CFT) and Kudravtsev theory[11] (KT) have been employed to evaluate sound velocities in liquid mixtures. These results have been interpreted in terms of relative adaptability of each theory and thereby the nature of molecular interactions in liquid mixture has been inferred.

THEORY

(*i*) *Freelength Theory* (*FLT*)

The intermolecular freelength in liquid can be evaluated using Jacobson's equation[9]

$$L_f = \frac{K}{u\rho^{1/2}} \tag{1}$$

Table 1 Intermolecular freelength ($L_f^{M'}$), sound velocity (u) and relative interaction (RI) at different mole fractions of *n*-dodecane + hexane isomers.

X_1	$L_f^{M'} \times 10^{10}$ (m)	u (ms^{-1})				RI
		FLT	CFT	KT	Exp.	
		n-Dodecane + *n*-Hexane				
0.01549	0.712	1118	1080	1083	1082.51	1.0000
0.07322	0.695	1133	1092	1106	1101.08	0.9994
0.12888	0.681	1147	1104	1125	1117.67	0.9990
0.22864	0.659	1169	1125	1155	1144.60	0.9985
0.29240	0.647	1183	1138	1172	1160.21	0.9984
0.40844	0.627	1206	1162	1198	1185.94	0.9984
0.47438	0.618	1218	1175	1210	1199.19	0.9985
0.54845	0.608	1231	1190	1223	1213.03	0.9987
0.61587	0.600	1242	1203	1233	1224.72	0.9988
0.68239	0.593	1252	1216	1243	1235.47	0.9990
0.77707	0.584	1267	1235	1255	1249.70	0.9992
0.88789	0.575	1282	1257	1268	1264.95	0.9996
0.94723	0.570	1290	1269	1274	1272.50	0.9998
		n-Dodecane + 2-Methylpentane				
0.01584	0.739	1085	1045	1049	1047.32	0.9999
0.06700	0.721	1100	1058	1073	1067.18	0.9994
0.12480	0.702	1117	1073	1098	1087.94	0.9989
0.22689	0.675	1145	1098	1134	1120.91	0.9985
0.32084	0.654	1168	1120	1162	1148.05	0.9985
0.35339	0.647	1176	1128	1171	1156.66	0.9984
0.40506	0.637	1188	1140	1183	1169.69	0.9985
0.52969	0.617	1214	1170	1210	1198.25	0.9987
0.61301	0.606	1231	1189	1226	1215.33	0.9989
0.70779	0.594	1248	1211	1241	1233.14	0.9991
0.77327	0.587	1260	1227	1251	1244.51	0.9993
0.83113	0.581	1270	1240	1259	1254.00	0.9995
0.89023	0.576	1280	1254	1266	1263.16	0.9997
0.94633	0.570	1289	1267	1273	1271.42	0.9998
		n-Dodecane + 3-Methylpentane				
0.03139	0.707	1109	1078	1085	1084.05	1.0003
0.08052	0.693	1122	1089	1104	1100.20	0.9998
0.14258	0.677	1138	1103	1126	1119.11	0.9994
0.22072	0.668	1157	1119	1150	1140.50	0.9990
0.33143	0.639	1182	1142	1179	1167.91	0.9988
0.37933	0.631	1192	1152	1189	1178.65	0.9988
0.42082	0.625	1200	1161	1198	1187.66	0.9989
0.55270	0.607	1226	1188	1222	1213.34	0.9991
0.62015	0.600	1238	1202	1233	1225.15	0.9992
0.72576	0.589	1256	1223	1248	1242.08	0.9994
0.81620	0.580	1270	1242	1259	1255.25	0.9996
0.90990	0.573	1284	1261	1270	1267.79	0.9998
0.95513	0.569	1291	1270	1275	1273.48	0.9999

Table 1 (*continued*)

X_1	$L_f^{M'} \times 10^{10}$ (m)	u (ms^{-1})				RI
		FLT	CFT	KT	Exp.	
		n-Dodecane + 2,2-Dimethylbutane				
0.03475	0.763	1061	1009	1020	1015.89	0.9998
0.08547	0.741	1079	1025	1047	1039.00	0.9994
0.11122	0.731	1087	1032	1060	1050.06	0.9993
0.19548	0.701	1114	1057	1098	1083.52	0.9989
0.29373	0.674	1143	1085	1134	1118.03	0.9988
0.37753	0.654	1165	1109	1160	1144.30	0.9980
0.50845	0.628	1198	1145	1194	1180.53	0.9990
0.59540	0.614	1218	1169	1213	1201.43	0.9991
0.68153	0.601	1236	1193	1230	1220.77	0.9993
0.75657	0.592	1252	1213	1244	1235.89	0.9994
0.82240	0.584	1265	1231	1254	1248.77	0.9996
0.88405	0.577	1276	1248	1263	1259.83	0.9998
0.93303	0.572	1285	1261	1270	1267.85	0.9998
		n-Dodecane + 2,3-Dimethylbutane				
0.01658	0.730	1091	1051	1055	1053.53	1.0000
0.05737	0.716	1104	1061	1074	1069.49	0.9998
0.09913	0.703	1016	1071	1092	1084.82	0.9995
0.16032	0.685	1132	1086	1115	1105.67	0.9993
0.25425	0.663	1156	1108	1146	1134.45	0.9991
0.31064	0.651	1170	1122	1162	1150.06	0.9990
0.36026	0.641	1181	1133	1175	1162.90	0.9990
0.40771	0.633	1192	1144	1186	1174.48	0.9990
0.51603	0.616	1214	1169	1209	1199.28	0.9993
0.61454	0.603	1233	1192	1227	1218.84	0.9994
0.73901	0.589	1255	1220	1274	1240.78	0.9996
0.85480	0.578	1275	1246	1262	1258.87	0.9998
0.93594	0.571	1283	1264	1272	1270.31	0.9999

where K is temperature dependent parameter. u and ρ are sound velocity and density respectively.

The freelength in the mixture is evaluated using the relation

$$L_f^{M'} = \frac{K}{u_{\text{mix}}\rho_{\text{mix}}^{1/2}} \tag{2}$$

The surface area per mole of the liquid is given by

$$Y = (36\pi N V_0^2)^{1/3} \tag{3}$$

The ideal freelength can be evaluated using

$$L_f^M = \frac{2V_a}{x_1 y_1 + x_2 y_2} \tag{4}$$

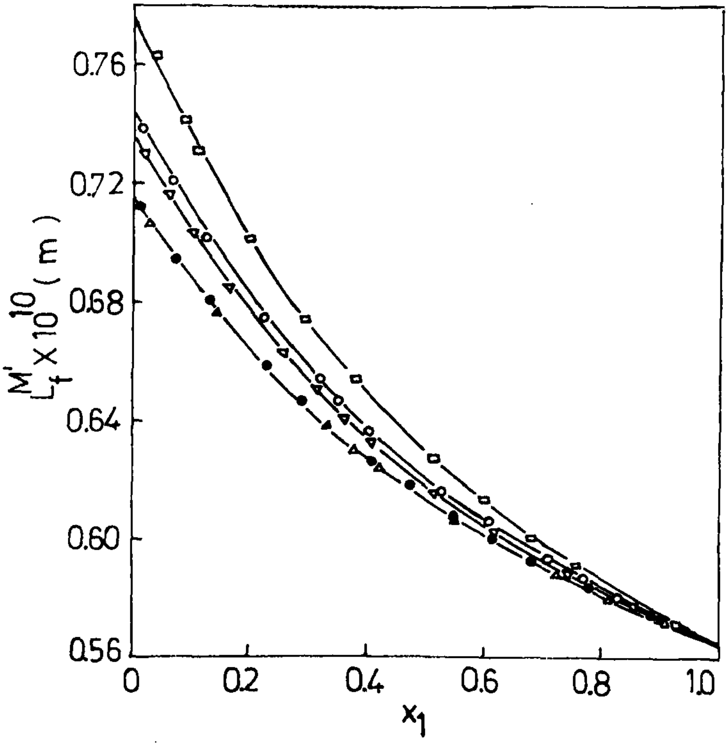

Figure 1 Intermolecular freelength ($L_f^{M'}$) versus mole fracion of *n*-dodecane (X_1) in hexane isomers.

where the available volume is expressed by

$$V_a = (x_1 V_{m1} + x_2 V_{m2}) - (x_1 V_{01} + x_2 V_{02}) \tag{5}$$

V_m and V_0 are molar volumes at temperature T and absolute zero respectively. x_1 and x_2 are the mole fractions of component 1 and component 2 in the mixture respectively.

(*ii*) *Collision Factor Theory* (*CFT*)

Ultrasonic velocity can be evaluated from Schaaffs' Collision Factor Theory[10] via the relation

$$u = u_\infty \frac{SB}{V_m} \tag{6}$$

where S is the Collision factor. B is the actual volume of the molecule per mole and is given by

$$B = 4/3\pi r^3 N \tag{7}$$

Nutsch-Kuhnkies[12] extended the theory to binary mixtures and showed

$$u_{\text{mix}} = \frac{u_\infty(x_1 S_1 + x_2 S_2)(x_1 B_1 + x_2 B_2)}{V_{\text{mix}}} \tag{8}$$

The relative interaction of the two components in a binary liquid mixture has been studied[13,14] in terms of molar sound velocities via the equation

$$RI = \frac{R_{\mathrm{exp}}}{R_{\mathrm{id}}} \tag{9}$$

where $R_{\mathrm{id}} = R_1 x_1 + R_2 x_2$.

(*iii*) *Kudravtsev Theory* (*KT*)

The velocity in the binary liquid mixture due to Kudravtsev[11] is given by the following expression

$$u^2_{\mathrm{mix}} = x_1 \frac{M_1}{M} u_1^2 + x_2 \frac{M_2}{M} u_2^2 + 5.5 \times 10^8 L \tag{10}$$

where M_1 and M_2 are the molecular weights of components 1 and 2 respectively. M is the effective molecular weight of the mixture. L represents the heat capacity of the mixture expressed in cal/g K. u_1 and u_2 represent the velocity of components 1 and 2 respectively.

RESULTS

Various parameters to evaluate sound velocity, freelength and relative interaction in *n*-dodecade + hexane isomer mixtures using the theories of FLT, CFT and KT are taken from the data due to Benson *et al.*[15–17] Since the most accurate data of sound velocity, density and heat capacity of these mixtures are readily available in literature, no attempt has been made to redetermine the same. The results are presented in Table 1. The $L_f^{M'}$ versus x_1 is plotted in Figure 1 for the systems studied.

DISCUSSION

An examination of data presented in Table 1 indicates that KT predicts sound velocities more accurately ($\simeq 1\%$) than CFT and FLT throughout the concentration range. CFT is predicting better in the low and high mole fraction range and the deviation is more near equimolar solution. In general KT predicts accurately for systems which behave ideally.

Table 1 indicates that the relative interaction magnitude change is small for all these systems. It may be mentioned here that RI close to 1, indicates less interaction and if RI = 1, there exist no interaction between the two types of molecules in the mixture and the mixture behaves ideally. The ideal behaviour of these systems was predicted using Flory theory.[17]

The intermolecular freelength versus concentration curves (Figure 1) of *n*-dodecane + hexane isomer systems are in the following order

$$n\text{-}C_6H_{14} > \text{3-MP} > \text{2,3-DMB} > \text{2-MP} > \text{2,2-DMB}$$

Benson *et al.*[15,16] found the same order for these systems from their K_s^E and V^E studies. Hence it may be concluded that the intermolecular freelength and relative interaction studies are very much useful in understanding the solute-solvent interactions in binary liquid mixtures along with V^E and K_s^E studies.

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