Recent Research in Science and Technology 2010, 2(4): 42-45
ISSN: 2076-5061
www.recent-science.com

PHYSICS

STUDY OF MOLECULAR INTERACTIONS IN TERNARY LIQUID SYSTEMS THROUGH THEORETICAL MODELS AT 303K

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Abstract
The theoretical velocity in ternary mixtures of alkyl acetates with butanol and formamide at 303K have been evaluated by using theoretical models of liquid mixtures such as Nomoto's relation, Impedance dependence relation, Ideal mixture relation, collision factor theory and Junjie's method. Ultrasonic velocity of these mixtures has been measured as a function of concentration and the experimental values are compared with theoretical values. U^2_{exp}/U^2_{IMR} has also been evaluated for non-ideality in the mixtures. The results are explained in terms of intermolecular interactions occurring in these ternary systems.

Keywords: Ternary liquid mixtures, ultrasonic study, theoretical models, molecular interaction

Introduction

Ultrasonic study of liquid and liquid mixtures has gained much importance during the last two decades assessing the nature of molecular interactions. The study of molecular interaction in liquid mixture has been extensively carried out from theoretical as well as experimental view points [1-3]. The theoretical evaluation of ultrasonic velocity in liquid mixtures and its comparison with the experimental values reflects the molecular interactions and arrangement in liquid mixtures, which is very much useful to build comprehensive theoretical model for liquids.

In the present investigation, the ultrasonic velocity in ethyl acetate + butanol + formamide, propyl acetate + butanol + formamide and butyl acetate + butanol + formamide ternary mixtures have been theoretically evaluated using Nomoto's relation[4], Impedance dependence relation[5], Ideal mixture relation[6], Collision factor theory[7] and Junjie's method[8] at 303K. The suitability of these theories were checked by comparing theoretical values of ultrasonic speeds with the values obtained experimentally and also the non- ideal behavior of the mixtures are explained in terms of molecular interactions of the mixtures.

Experimental Details

The liquids used were of AR grade and were purified by the standard methods[9]. Liquid mixtures of different compositions were prepared by mixing measured amounts of the pure liquid in cleaned and dried flask. In all the systems, the mole fraction of second component, butanol was kept constant (X_2=0.3) while the concentrations of the remaining two (X_1 and X_3) were varied from 0.0 to 0.7, so as to have the mixtures of different compositions.

The ultrasonic velocity and density were measured using the ultrasonic interferometer [Mittal Enterprises, New Delhi] at fixed frequency of 2 MHz with an accuracy of ± 0.1% and specific gravity bottle respectively.

Theory

The theoretical values of ultrasonic velocity are calculated from the following relations,

Nomoto's Relation [NR]

$$U_{NR} = \left(\frac{\sum_{i=1}^{3} X_i R_i}{\sum_{i=1}^{3} X_i V_i} \right)^3 \quad \ldots (1)$$

Impedance Dependence Relation [IDR]

$$U_{IDR} = \frac{\sum_{i=1}^{3} X_i Z_i}{\sum_{i=1}^{3} X_i \rho_i} \quad \ldots (2)$$

Ideal Mixture Relation [IMR]

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$$U_{IMR} = \left[\frac{1}{\sum_{i=1}^{3} X_i \; m_i} \right]^{1/2} \left[\sum_{i=1}^{3} \frac{X_i}{m_i \; V_i^2} \right]^{-1/2} \quad ...(3)$$

Molecular interaction parameter[α]

$$\alpha = \left(\frac{U_{\exp}^2}{U_{IMR}^2} - 1 \right)$$

Collision Factor Theory [CFT]

$$U_{CFT} = U_{\alpha} \left[\frac{\left(\sum_{i=1}^{3} X_i S_i \right) \left(\sum_{i=1}^{3} X_i B_i \right)}{V_i} \right] \quad \ldots (4)$$

Junjie's method

$$U_{JUN} = \left[\frac{\sum_{i=1}^{3} V_i}{\left(\sum_{i=1}^{3} X_i m_i \right)^{1/2}} \right] \left[\sum_{i=1}^{3} \frac{X_i V_i}{\rho_i U_i^2} \right]^{-1/2} \quad \ldots (5)$$

where ρ_{exp} and U_{exp} are the density and ultrasonic velocity of the mixture. X_i is the mole fraction, U_i is the ultrasonic velocity, R_i and V_i are the molar sound velocity and molar volume, m_i is the molecular weight, Z_i and ρ_i are the acoustic impedance and density, S_i is the 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

$S_i = U/U_{\alpha} Y_f$

where Y_f is the space filling factor, the value of U_{α} … (3) is 1600m/s, B_i can be calculated by the equation,

$B_i = (4/3) \pi r^3 N$

where N is Avogadro's number and 'r' refers to the molecular radius and is given by

$$r = \left(\frac{3b}{16\pi N} \right)^{1/3}$$

where 'b' is van der waals' constant.

Results and Discussion

The theoretical values of ultrasonic velocity obtained by using the relations (1-5) along with the experimental velocity are summarized in Table 1. Table 2 shows the molecular interaction term and the percentage deviation of ultrasonic velocity was calculated using theoretical velocity from experimental velocity values for three systems. The plot of molecular interaction term against mole fraction of alkyl acetates is depicted in Fig. 1.

Fig. 1. Molecular interaction term (α) with mole fraction of alkyl acetates.

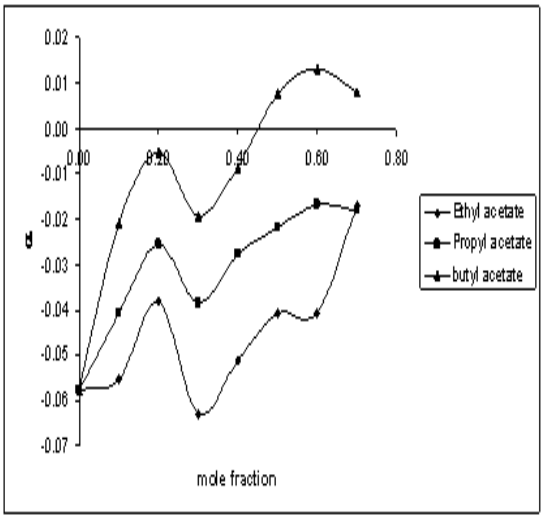

Table 1. Experimental and theoretical values for the ternary mixtures of alkyl acetates at 303K

Mole fraction		U_{expt}	Estimated ultrasonic velocity in ms^{-1}				
X_1	X_3	ms^{-1}	U_{NR}	U_{IDR}	U_{IMR}	U_{CFT}	U_{JUN}
System 1 Ethyl acetate + butanol + Formamide							
0.0000	0.7000	1407.2	1400.5	1502.8	1449.5	1481.5	1328.6
0.0999	0.5999	1354.0	1341.4	1459.7	1393.1	1423.5	1276.0
0.1999	0.5000	1316.8	1293.9	1414.5	1342.6	1391.6	1239.1
0.3000	0.3999	1255.6	1255.0	1367.1	1297.0	1327.3	1211.9
0.4000	0.2999	1223.2	1222.5	1317.3	1255.6	1295.0	1191.0
0.5000	0.1999	1192.8	1194.9	1264.9	1217.8	1241.2	1174.5
0.6000	0.0999	1158.8	1171.2	1209.7	1183.1	1187.8	1161.2
0.7000	0.0000	1141.2	1150.7	1151.5	1151.0	1146.0	1150.2
System 2 Propyl acetate + butanol + Formamide							
0.0000	0.7000	1407.2	1400.5	1502.8	1449.5	1481.5	1328.6
0.1000	0.6000	1360.6	1340.2	1462.3	1389.0	1397.9	1277.0
0.2000	0.5000	1320.2	1294.2	1419.7	1337.4	1367.0	1242.8
0.3000	0.4000	1267.6	1257.8	1375.0	1292.8	1319.5	1218.5
0.4000	0.3000	1236.4	1228.4	1327.8	1253.9	1268.8	1200.4
0.5000	0.2000	1206.4	1204.2	1278.1	1219.8	1221.4	1186.5
0.6000	0.1000	1179.6	1183.8	1225.5	1189.7	1179.9	1175.5
0.7000	0.0000	1152.4	1166.5	1170.0	1162.9	1141.1	1166.5
System 3 Butyl acetate + butanol + Formamide							
0.0000	0.7000	1407.2	1400.5	1502.8	1449.5	1481.5	1328.6
0.1000	0.6000	1367.6	1340.2	1464.6	1382.1	1391.9	1279.2
0.2000	0.5000	1324.0	1296.2	1424.3	1327.6	1341.2	1248.0
0.3000	0.4000	1270.4	1262.7	1381.9	1282.8	1297.7	1226.7
0.4000	0.3000	1240.4	1236.3	1337.2	1245.7	1263.7	1211.3
0.5000	0.2000	1219.6	1215.0	1290.0	1214.9	1215.3	1199.6
0.6000	0.1000	1197.2	1197.5	1240.0	1189.3	1141.9	1190.5
0.7000	0.0000	1172.8	1182.8	1187.0	1168.1	1133.7	1183.2

Table 2. Molecular interaction term and percentage deviation of velocity for the ternary mixtures of alkyl acetates at 303K.

Mole fraction		α	Percentage Deviation				
X_1	X_3		U_{NR}	U_{IDR}	U_{IMR}	U_{CFT}	U_{JUN}
System 1 Ethyl acetate + butanol + Formamide							
0.0000	0.7000	-0.0575	0.48	-6.79	-3.00	-5.28	5.59
0.0999	0.5999	-0.0553	1.40	-7.30	-2.89	-5.13	5.76
0.1999	0.5000	-0.0381	1.99	-7.15	-1.96	-5.68	5.90
0.3000	0.3999	-0.0629	1.00	-7.85	-3.30	-5.71	3.48
0.4000	0.2999	-0.0510	1.13	-6.55	-2.65	-5.87	2.63
0.5000	0.1999	-0.0406	0.95	-4.85	-2.10	-4.06	1.53
0.6000	0.0999	-0.0406	0.71	-2.55	-2.09	-2.50	-0.20
0.7000	0.0000	-0.0169	0.15	0.08	-0.86	-0.42	-0.79
System 2 Propyl acetate + butanol + Formamide							
0.0000	0.7000	-0.0575	0.48	-6.79	-3.00	-5.28	5.59
0.1000	0.6000	-0.0407	1.48	-7.49	-2.10	-2.75	6.13
0.2000	0.5000	-0.0255	1.97	-7.54	-1.30	-3.55	5.87
0.3000	0.4000	-0.0386	0.77	-8.47	-1.99	-4.09	3.87
0.4000	0.3000	-0.0278	0.64	-7.39	-1.42	-2.62	2.91
0.5000	0.2000	-0.0219	0.18	-5.94	-1.11	-1.24	1.65
0.6000	0.1000	-0.0168	-0.36	-3.89	-0.85	-0.03	0.35
0.7000	0.0000	-0.0179	-1.22	-1.52	-0.91	0.98	-1.23
System 3 Butyl acetate + butanol + Formamide							
0.0000	0.7000	-0.0575	0.48	-6.79	-3.00	-5.28	5.59
0.1000	0.6000	-0.0209	2.00	-7.09	-1.06	-1.78	6.46
0.2000	0.5000	-0.0054	2.10	-7.58	-0.27	-1.30	5.74
0.3000	0.4000	-0.0192	0.61	-8.78	-0.98	-2.15	3.44
0.4000	0.3000	-0.0085	0.33	-7.80	-0.43	-1.88	2.35
0.5000	0.2000	0.0077	0.38	-5.77	0.38	0.35	1.64
0.6000	0.1000	0.0133	-0.02	-3.57	0.66	4.62	0.56
0.7000	0.0000	0.0080	-0.85	-1.21	0.40	3.33	-0.88

The deviation in the values of $\frac{U_{\exp}}{U_{IMR}}$ from unity (α) is efficient to state the molecular interactions in the liquid mixtures, especially in those cases where the properties other than the sound velocities are not known. Fig.1. show the variation of molecular interaction term (α) against mole fraction of alkyl acetates at 303K. It can be seen that the α is completely negative for ethyl acetate and propyl acetate systems whereas for butyl acetate exhibit negative deviations over the entire composition range slightly positive deviation in higher mole fraction. This is due to interaction of alkyl acetate with butanol and formamide. The α values clearly indicate the existence of weak H-bond (C=O…H-N) between the proton-acceptor oxygen atom of the C=O group of alkyl acetate and the proton-donor hydrogen atom of the $–NH_2$ group of formamide molecules.

In Table 2, system 1 indicates that Nomoto's relation shows minimum deviations in the range 0.15 to 1.99, which predicts the experimental data well, followed by ideal mixture relation, with deviations in the range -3.30 to -0.86. Junjie's relation, with deviations in the range -0.79 to 5.90 then by collision factor theory with deviation in the range -5.87 to -0.42. The remaining theory, Impedance dependence relation shows maximum deviations in the range -7.85 to 0.08.

In the case of system 2, the percentage deviations for Nomoto's relation, Impedance dependence relation,

ideal mixture relation, Rao's specific velocity method, collision factor theory and Junjie's method respectively, in the range -1.22 to 1.97, -8.47 to -1.52, -3.00 to -0.85, -5.28 to 0.98 and -1.23 to 6.13. Thus, for the above theory and relations, Nomoto's relation seems to predict the experimental data well followed by Ideal mixture relation, Collision factor theory, Junjie's method and Impedance dependence relation respectively.

Table 2 show the percentage deviation of five method for system 3 and the values are given as: for Nomoto's relation (-0.85 to 2.10), which is best suited with the experimental results, followed by ideal mixture relation (-3.00 to 0.66), collision factor theory (-5.28 to 4.62), Junjie's method (-0.88 to 6.46), impedance dependence relation (-8.78 to -1.21).

Among the various theories taken into consideration Nomoto's relation is found to give an excellent prediction of sound velocity for all the systems. Thus the linearity of molar sound speed and additively of molar volumes, as suggested by Nomoto[4] in deriving the empirical relation[10], have been truly observed in the aforementioned ternary liquid mixtures, the success of Nomoto's relation in predicting the experimental ultrasonic speeds for polar – polar mixtures has also been emphasized by others[11-13].

Conclusion

It is concluded that out of the five theories and relations discussed, the Nomoto's relation is found to be best suited with the experimental values. The existence of weak hydrogen bond between the components of the mixture is evident.

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