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Viscosity and Speed of Sound Studies of Binary Liquid Mixtures of Formamide with N,N-Dimethylaniline at Different Temperatures

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Theoretical values of speed of sound in binary liquid mixtures of fomamide with N,N-dimethylaniline have been evaluated at 303.15, 308.15 and 313.15 K. The experimentally determined values of speed of sound have been used to check the applicability of different speed of sound models of Nomoto (NOM), impedance (IMP), ideal mixing relation (IMR), Vandael and Vangeel (VDV), Junjie (JUN) and Rao's specific velocity (RAO) relation. The validity of these theories was checked by applying chi-square test (χ) for goodness of fit and by calculating the average percentage error. Further viscosity data have been used to test the applicability of standard viscosity models of Hind, Grunberg and Nissan, Katti and Chaudhri, Wiki, Tamura and Kurata, after that corresponding interaction terms and standard deviation (σ) of these theories are calculated at various temperatures for the binary liquid systems. The results are interpreted in terms of molecular interaction between the components of the binary mixtures.

Keywords: Speed of sound, Formamide, N,N-Dimethylaniline, Viscosity,

INTRODUCTION

In chemical process industries, materials are normally handled in fluid form and as a consequence the physical, chemical and transport properties of fluids, assume importance. Thus, data on some of the properties associated with the liquids and liquid mixtures like ultrasonic velocity, viscosity and density invention extensive application in solution theory models and molecular dynamics [1,2]. The classification of mixtures through their thermodynamic and transport properties is substantial from the foremost viewpoint of understand their mixing behaviour. The impetus of the present investigation is to compare the experimentally determined speed of sound, viscosity and density with the computed values using different analytical models and empirical relations [1-4].

Such results were obtained by earlier workers [5-8], an increasing variety of research techniques are being employed to get an insight into the molecular behaviour of liquids. In the present stage of development, ultrasonic techniques are yielding fruitful results comparable with those of other methods in the elucidation of molecular mechanisms. Measurement of sound velocity has been used for many years in connection with the determination of elastic and thermodynamic properties of gases, liquids and solids. Intimate relations between the values of sound velocity and chemical or structural characteristics of molecules of liquids or liquid mixtures have been found. This gives sound velocity of the primary quantity in the molecular theory of liquids [5,6]. Theoretical evaluation of ultrasonic velocity in binary liquid mixtures and its comparison with the experimental values reflects the molecular interaction in liquid mixtures, which is very useful to build comprehensive theoretical models for liquids. Several researchers [1,2,7,8] carried out investigations on liquid mixtures and correlated the experimental results of ultrasonic velocity with the theoretical relations of Nomoto (NOM), impedance (IMP), ideal mixing relation (IMR), Vandael and Vangeel (VDV), Junjie (JUN) and Rao's specific velocity (RAO) relation [2]. The validity of these theories was checked by applying chi-square test (χ) for goodness of fit and by calculating the average percentage error (APE) [2,6]. Further, the mixture viscosities were correlated using Hind, Grunberg and Nissan, Katti and Chawdhry, Tamura & Kurata, equations to test their relative applicability with standard deviation (σ) [2,6] for the binary mixture of formamide with N,N-dimethylaniline at different mole fractions [9-11]. The results

are explained and discussed in terms of molecular interactions present in the investigated systems.

EXPERIMENTAL

The ultrasonic velocities were measured at 303.15 to 313.15 K using ultrasonic interferometer (M/s Mittal Enterprises, India) operating at a frequency of 2 MHz with an accuracy of ± 0.1 m/s for the compounds of formamide with N,N-dimethylaniline. The densities were measured by using specific gravity bottle method, while viscosity were measured by using Ostwald's viscometer by the standard procedure.

The following empirical relations are used for the prediction of ultrasonic velocity in the binary liquid mixtures.

Ultrasonic theories

Nomoto's relation:

$$U_{NOM} = [X_1R_1 + X_2R_2/X_1V_1 + X_2V_2] \quad (1)$$

Ideal mixture relation:

$$U_{IMR} = [1/X_1m_1 + X_2m_2]^{1/2}[X_1/m_1U_1^2 + X_2/m_2U_2^2]^{-1/2} \quad (2)$$

Junjie's method:

$$U_{JM} = [X_1V_1+X_2V_2/(X_1m_1 + X_2m_2)^{1/2}][X_1V_1/d_1U_1^2 + X_2V_2/d_2U_2^2]^{-1/2} \quad (3)$$

Imedance relation:

$$U_{IMP} = X_1Z_1 + X_2Z_2/X_1\rho_1 + X_2\rho_2 \quad (4)$$

Vandael and Vangeel relation:

$$U_{VDV} = [1/X_1m_1 + X_2m_2]1/2[X_1/m_1U_1^2 + X_2/m_2U_2^2]^{-1/2} \quad (5)$$

Rao's relation:

$$U_R = (R/V)^3 \quad (6)$$

The validity of the theories is checked by applying Chi-square test and by calculating average percentage error (APE), the relations as follows:

$$APE\ (\%) = [(1/(n)\Sigma 100(U_{exp} - U_{cal})/U_{exp})] \times 100 \quad (7)$$

$$\text{Chi-square } (\chi) = \sum_i^n \left(\frac{(U_{exp} - U_{cal})^2}{U_{cal}} \right) \quad (8)$$

Viscosity theories

Hind proposed the equation:

$$\eta = x_1^2\eta_1 + x^2_2\eta_2 + 2x_1x_2H_{12} \quad (9)$$

Katti and Chaudhri derived the equation:

$$\ln \eta V = x_1 \ln \eta_1V_1 + x_2 \ln \eta_2V_2 + x_1x_2Wvis/RT \quad (10)$$

Wiki expression is:

$$\log \eta_m = x_1^2 \log \eta_1 + x_2^2 \log \eta_2 + 2x_1x_2 \log \eta_{12} \quad (11)$$

Gruenberg-Nissan provided the equation:

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2G_{12} \quad (12)$$

Tamura and Kurata gave the equation:

$$\eta_m = x_1\eta_1\phi_1 + x_2\eta_2\phi_2 + 2(x_1x_2\phi_1\phi_2)^{1/2}T_{12} \quad (13)$$

The standard deviation:

$$\sigma = [(1/(n\text{-}K)\Sigma 100\ (\eta_{exp} - \eta_{cal})/\eta_{exp})^2]^{1/2} \quad (14)$$

RESULTS AND DISCUSSION

The comparison of experimental values of densities (ρ), viscosities (η) and ultrasonic velocities (u) with the literature values are given in Table-1. The experimental values of ultrasonic velocities along with the theoretically evaluated values by using various theories in the binary liquid mixtures of formamide with N,N-dimethylaniline at different temperatures (T = 303.15, 308.15 and 313.15 K) are given in Table-2 and the average percentage error (APE) and chi square test (χ) also included in the Tables.

The average percentage error values are small. On comparison, the Nomoto's relation and impedance relation are found to provide some valuable information on the speed of sound values in these mixtures. The predictive abilities of various speeds of sound theories depend upon the strength of interaction prevailing in a system [2,7]. The extent of deviation may be attributed to the assumptions made in these theories for the non-polar-polar and non-polar-non-polar interaction between the molecules [12,13]. The chi-square value and average percentage error value is minimum for Nomoto's relation and Junjie's method than those obtained by other theories. An important reason for deviation from experimental values of speed of sound is that the molecular association effects are not taken into account in these theories [1,2]. Thus the observed deviation of theoretical values of speed of sound from the experimental values shows that the molecular interaction is taking place between the unlike molecules in the liquid mixtures [14]. Hence, the observed deviation shows that the molecular interaction is taking place between the unlike molecules in the liquid mixture. This suggests the existence of strong tendency for the association between component molecules as a result of hydrogen bonding.

The comparison of viscosity theories at different temperatures (303.15 to 313.15 K) are observed by using of interaction parameter and standard deviation (σ) is given in Table-3. Semi-

TABLE-1
COMPARISON OF EXPERIMENTAL DENSITIES (ρ), VISCOSITIES (η) AND SPEED OF SOUND (U) OF PURE LIQUIDS WITH LITERATURE VALUES

Liquid	Temp. (K)	Density (ρ) (kg m^{-3})		Viscosity (η) (kg m^1 s^{-1})		Speed of sound (U) (m s^{-1})	
		Literature	Experimental	Literature	Experimental	Literature	Experimental
Formamide	303.15	1.1247[a]	1.1281	2.80[b]	2.83	1585.4[c]	1585.0
	308.15	1.1205[a]	1.1208	2.50[b]	2.59	1580.6[c]	1580.0
	313.15	1.1164[a]	1.1110	2.20[b]	2.29	1572.0[c]	1572.0
N-N dimethyl aniline	303.15	0.9481[d]	0.9453	1.173[e]	1.171	1470.5[f]	1470.0
	308.15	0.9439[d]	0.9431	1.078[e]	1.041	1453.4[f]	1453.4
	313.15	0.9397[d]	0.9360	0.989[e]	0.989	1435.2[f]	1435.2

[a,b,c] [Ref. 9,10]; [d,e,f] [Ref. 11]

TABLE-2
SPEED OF SOUND THEORIES FOR THE BINARY MIXTURES OF FORMAMIDE WITH N,N-DIMETHYL ANILINE AT 303.15 K, 308.15K AND 313.15 K

x_1	ρ (kg m^{-3})	U_{EXP} (m s^{-1})	η (kg m^{1} s^{-1})	U_{NOM} (m s^{-1})	U_{IMR} (m s^{-1})	U_{IMP} (m s^{-1})	U_{JM} (m s^{-1})	U_{VDV} (m s^{-1})	U_R (m s^{-1})
303.18 K									
0.0000	1.1281	1585.0	2.8316	1585.0	1585.0	1585.0	1585.0	1585.00	1585.0
0.2629	1.1224	1579.0	2.6323	1568.9	1389.4	1558.5	1562.0	1389.40	1652.7
0.4453	1.1105	1570.4	2.4576	1554.2	1338.6	1538.8	1543.2	1338.58	1689.3
0.5791	1.1015	1565.8	2.2638	1540.7	1330.3	1523.4	1527.7	1330.35	1734.8
0.6816	1.0901	1558.6	2.0326	1528.2	1339.3	1511.2	1514.8	1339.34	1764.8
0.7625	1.0686	1542.8	1.8949	1516.7	1356.3	1501.2	1503.9	1356.30	1740.5
0.8281	1.0396	1533.0	1.7661	1506.0	1377.2	1492.8	1494.7	1377.15	1674.2
0.8822	0.9982	1518.6	1.5397	1496.1	1399.8	1485.8	1487.0	1399.79	1544.9
0.9278	0.9772	1501.6	1.3687	1486.8	1423.2	1479.8	1480.4	1423.23	1508.1
0.9666	0.9627	1490.4	1.2847	1478.1	1446.8	1474.6	1474.8	1446.75	1497.6
1.0000	0.9453	1470.0	1.1712	1470.0	1470.0	1470.0	1470.0	1470.00	1470.0
Average percentage error (APE)				0.0042	0.0302	0.0067	0.0063	0.0302	-0.0320
Chi square test (χ)				0.4489	25.6448	1.1549	1.0060	25.6448	22.4671
308.15 K									
0.0000	1.1208	1580.0	2.5990	1580.0	1580.0	1580.0	1580.0	1580.00	1580.0
0.1461	1.1106	1579.0	2.5320	1562.3	1379.0	1550.8	1555.1	1379.02	1622.9
0.2780	1.0727	1558.0	2.3460	1546.1	1326.5	1529.0	1534.6	1326.54	1539.4
0.3977	1.0519	1537.6	2.1859	1531.3	1317.3	1512.1	1517.7	1317.35	1523.9
0.5066	1.0264	1526.4	2.0018	1517.6	1325.6	1498.6	1503.5	1325.62	1482.6
0.6064	1.0053	1515.2	1.8682	1504.9	1342.0	1487.6	1491.5	1341.97	1455.5
0.6979	0.9816	1509.0	1.7456	1493.1	1362.3	1478.5	1481.3	1362.29	1412.7
0.7823	0.9734	1492.2	1.6431	1482.1	1384.4	1470.7	1472.7	1384.44	1433.3
0.8604	0.9528	1481.6	1.4499	1471.9	1407.4	1464.1	1465.3	1407.43	1396.3
0.9327	0.9480	1472.4	1.2908	1462.3	1430.5	1458.4	1458.9	1430.54	1426.0
1.0000	0.9431	1453.4	1.0417	1453.4	1453.4	1453.4	1453.4	1453.40	1453.4
Average percentage error (APE)				0.0017	0.0286	0.0046	0.0039	0.0286	0.0099
Chi square test (χ)				0.0710	22.3606	0.5120	0.3769	22.3606	2.4528
313.15 K									
0.0000	1.1110	1572.8	2.2958	1572.8	1572.8	1572.8	1572.8	1572.80	1572.8
0.1461	1.1050	1568.8	2.1626	1553.6	1366.9	1541.0	1545.8	1366.87	1631.2
0.2780	1.0962	1557.8	2.0767	1536.0	1312.9	1517.3	1523.7	1312.88	1674.0
0.3977	1.0519	1531.8	1.9689	1519.8	1302.8	1498.9	1505.3	1302.79	1550.7
0.5066	1.0259	1525.8	1.8903	1504.9	1310.4	1484.3	1489.9	1310.36	1504.6
0.6064	1.0057	1509.4	1.7781	1491.1	1326.1	1472.3	1476.9	1326.11	1479.2
0.6979	0.9914	1497.8	1.6041	1478.3	1345.9	1462.4	1465.8	1345.89	1475.8
0.7823	0.9728	1482.6	1.4576	1466.4	1367.5	1454.0	1456.4	1367.55	1449.2
0.8604	0.9648	1477.6	1.3389	1455.3	1390.1	1446.8	1448.3	1390.07	1467.0
0.9327	0.9487	1452.8	1.2253	1444.9	1412.8	1440.6	1441.3	1412.75	1444.9
1.0000	0.9360	1435.2	0.9890	1435.2	1435.2	1435.2	1435.2	1435.20	1435.2
Average percentage error (APE)				0.0030	0.0304	0.0061	0.0054	0.0304	0.0050
Chi square test (χ)				0.2249	25.3327	0.9328	0.7151	25.3327	0.6164

TABLE-3
VISCOSITY THEORIES FOR THE BINARY MIXTURES OF FORMAMIDE WITH N,N-DIMETHYLANILINE AT DIFFERENT TEMPERATURES

Temp. (K)		Hind (H_{12})	Grunberg & Nissan (G_{12})	Wiki ($\log \eta_{12}$)	Katti & Chaudhary (W_{vis}/RT)	Tamura & Kurata (T_{12})
303.15	Interaction parameter	0.8302	0.8828	0.1917	1.6949	4.1407
	Standard deviation (σ)	0.8346	0.6449	0.8346	1.0376	1.2323
308.15	Interaction parameter	0.7790	0.9140	0.1990	1.2030	3.6490
	Standard deviation (σ)	0.7150	1.4360	0.7150	1.0600	1.2350
313.15	Interaction parameter	0.6530	0.8420	0.1830	5.5680	3.3530
	Standard deviation (σ)	0.8710	1.4110	0.8710	1.4410	1.6160

empirical relations have been used to represent the dependence of viscosity on concentration of components in binary liquid mixtures.

It is clear that Tamura and Kurata theory could not give accurate values compared to experimental values. These theories generally fail to predict accurately the values where strong inter-

actions are supposed to exist due to the limitations and approximations incorporated in these theories. Various interaction parameters and their corresponding standard deviations of viscosity computed from different theories in liquid mixture of formamide with N,N-dimethylaniline at different temperatures (303.15, 308.15 and 313.15 K). All the empirical models gave a reasonable fit in all these mixture. The estimated standard deviations are smaller in all cases indicating that the present mixture viscosities are well correlated by these viscosity models.

Plot the variation of evaluated speed of sound theories *viz.*, Nomoto's (nom) relation, ideal mixing relation, impedance dependence relation, Rao's velocity relation (r), Junjie's method (jm) for the formamide with N,N-dimethylaniline system at different temperatures against entire range of mole fraction (X_1). The variation of speed sound theories with respect to the entire mole fraction for formamide with N,N-dimethylaniline ranging from 0 to 1 at 303.15 K (Fig. 1), 308.15 K (Fig. 2) and 308.15 K (Fig. 3) are shown.

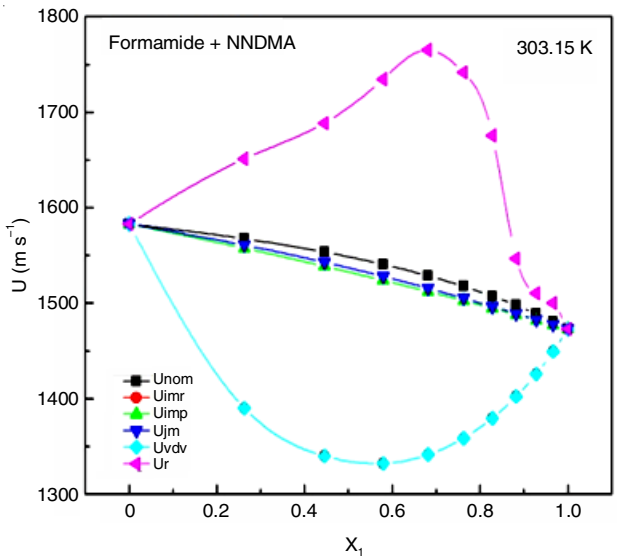

Fig. 1. Variation of speed of sound theories with respect to mole fraction at 303.15 K

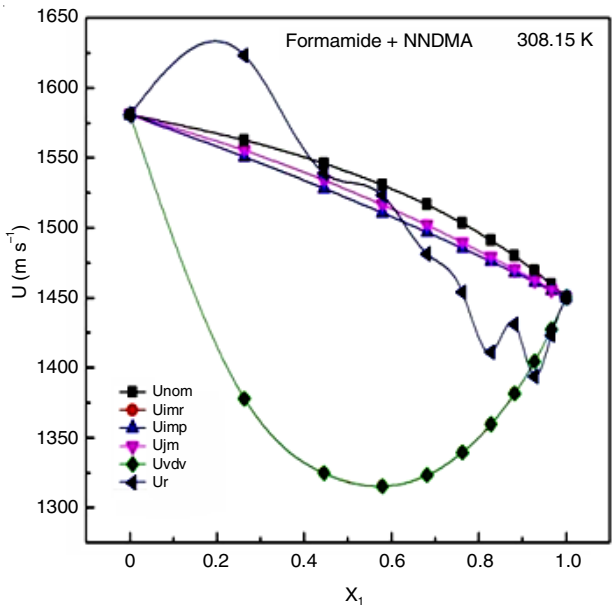

Fig. 2. Variation of speed of sound theories with respect to mole fraction at 308.15 K

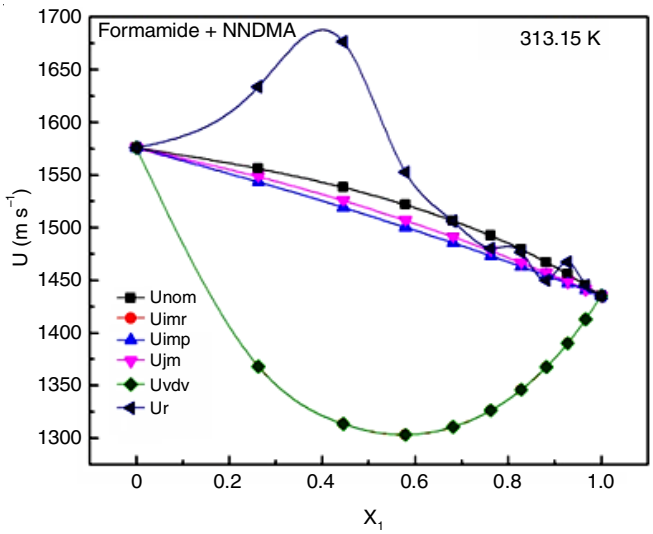

Fig. 3 Variation of speed of sound theories with respect to mole fraction at 313.15 K

It gives an idea of extent of interaction taking place between molecules of the mixtures. The positive deviation for binary systems infers strong interactions between the components. The percentage of deviation in velocity is reflecting both negative and positive magnitudes, indicating non-ideal behaviour of liquid mixtures. The evaluated interaction parameters are positive for all the systems, indicating strong interactions between the mixing molecules. The dynamic viscosities of liquid mixtures have been calculated using several empirical relations *viz.*, Hind, Grunberg and Nissan, Katti and Chaudhri, Wiki, Tamura and Kurata. Figs. 4-6 show the experimental values of viscosity for liquid mixture formamide with N,N-dimethylaniline at different temperatures (303.15, 308.15 and 313.15 K). The non-uniformity values of interaction parameter indicate the dominance of dispersion forces arising from the breakage of hydrogen

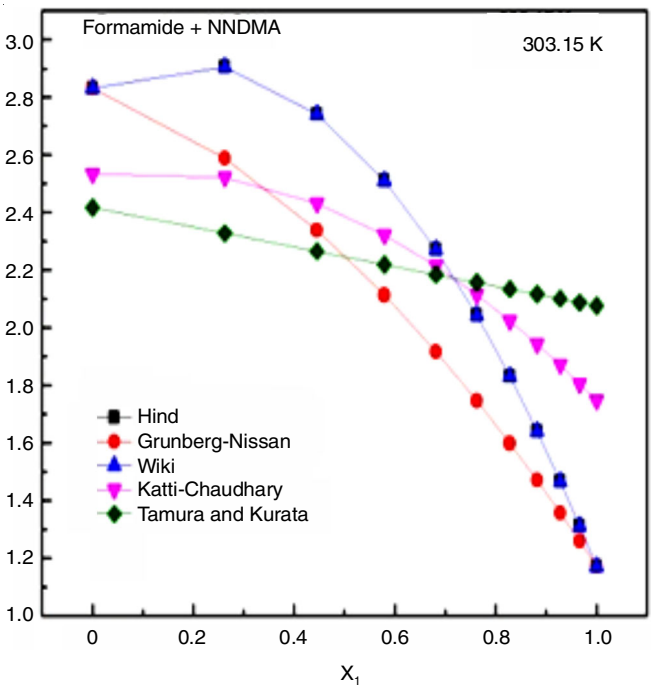

Fig. 4. Variation of viscosity theories with respect to mole fraction at 303.15 K

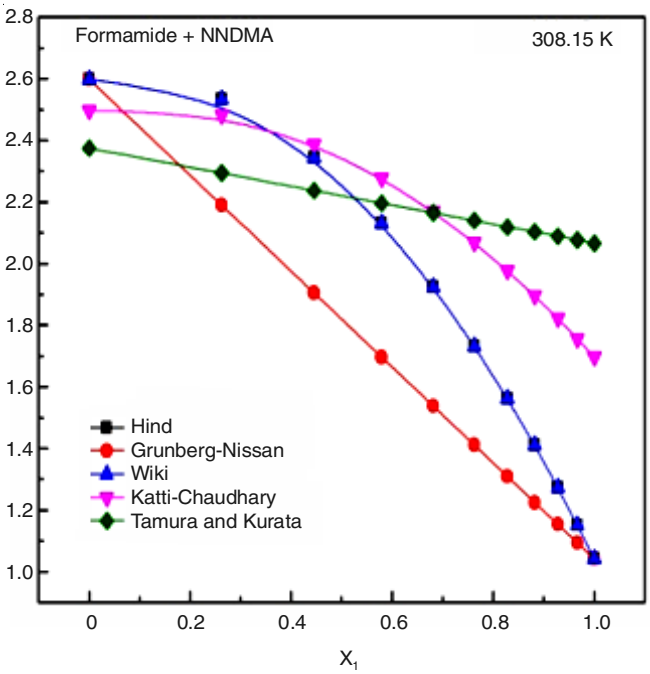

Fig. 5. Variation of viscosity theories with respect to mole fraction at 308.15 K

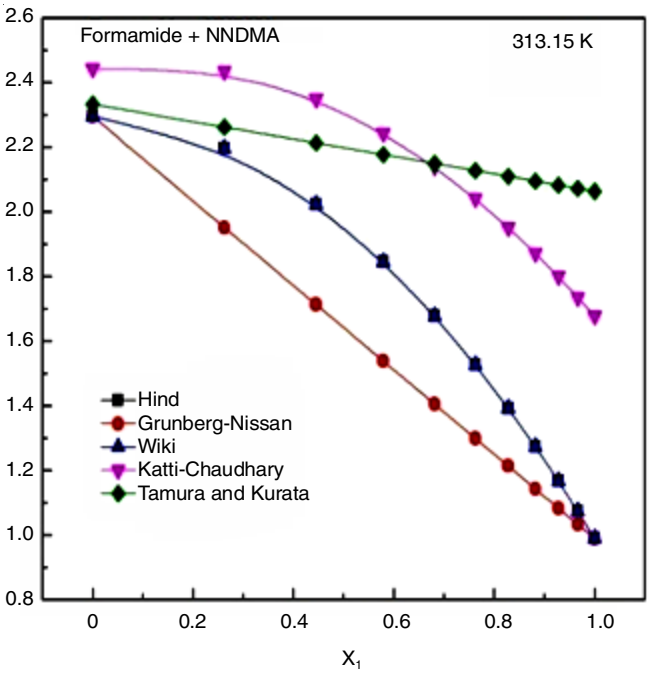

Fig. 6. Variation of viscosity theories with respect to mole fraction at 313.15 K

bonds in the associates. And the higher values of standard deviation at 313.15 K (Fig. 6) indicates the maximum departure of particular theory from experiment at particular concentration, which determines the overall validity of the theory.

Conclusion

The computed speed of sound and viscosity values from different theories have been correlated with the experimentally measured values. Speed of sound values obtained from Nomoto's and Junjie's method relations are in good agreement with the experimental values. It may be concluded that out of these theories, Nomoto's relation is best suited for the liquid mixtures under study. The chi square values also support this theory. The experimental viscosity values are also compared with the viscosity values obtained from different empirical relations and Hind, Grunberg and Nissan are in good agreement with the experimental values. The observed deviation of theoretical values of viscosity and speed of sound from the experimental values is attributed to the presence of intermolecular interactions.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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