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Theoretical Studies of Ultrasonic Velocities in Binary Liquid Mixtures of Quinoline at Different Temperatures

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ABSTRACT

Ultrasonic velocity evaluated from Nomoto's relation, Van Dael ideal mixing relation, impedance relation, Rao's specific velocity relation and Junjie's theory has been compared in the three binary mixtures of quinoline as a common component with o-cresol, m-cresol and p-cresol at 303.15, 308.15, 313.15 and 318.15 K over the entire composition range. A good agreement has been found between experimental and theoretical ultrasonic velocities.U^2_{exp}/U^2_{imx} *has also been evaluated for non-ideality in the mixtures. The relative applicability of these theories to the present systems has been checked and discussed. The results are explained in terms of molecular interactions occurring in these binary liquid mixtures.*

Key words: Ultrasonic velocity, Quinoline, Cresol, Binary liquid mixture.

INTRODUCTION

For better understanding of molecular arrangements in liquids results of theoretical evaluation of ultrasonic velocities are used. Ultrasonic study of liquid and liquid mixtures has been gained much importance during the last two decades in assessing the nature of molecular interactions and investigating the physicochemical behaviour of such systems. Several researchers [1-5] carried out ultrasonic investigations on liquid mixtures and correlated the experimental results of ultrasonic velocity with theoretical relations of Nomoto [6], Van dael and Vangeel [7], impedence relation [8], Rao's specific velocity [9] and Junjie [10] and the results are interpreted in terms of molecular interactions. Velocities in three binary liquid mixtures of quinoline with o-cresol, m-cresol and p-cresol using the above theoretical relations are compared with the experimental values of ultrasonic velocities at four temperatures 303.15, 308.15, 313.15 and 318.15 K. An attempt has been made to study the molecular interaction from the deviation in the values of U^2_{exp}/U^2_{imx} from unity based on the earlier studies.

EXPERIMENTAL SECTION

The chemicals used were of AnalaR grade and obtained from SDFCL chemicals (quinoline) and Merck (cresols). The chemicals were purified by standard procedure [11]. The purity of samples was checked by comparing experimental values of density and ultrasonic velocity with the available literature [12,13] compiled in Table 1. Job's method of continuous variation was used to prepare the mixtures of required proportions. The prepared mixtures were preserved in well-Stoppard conical flasks. After mixing the liquids thoroughly, the flasks were left undisturbed to allow them to attain thermal equilibrium.

The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of ± 0.5%. Weights were measured with an electronic balance (Shimadzu AUY220, Japan) capable of measuring up to 0.1mg. An average of 4-5 measurements was taken for each sample.

The ultrasonic velocities were measured by using single crystal ultrasonic pulse echo interferometer (Mittal enterprises, India; Model: F-80X). It consists of a high frequency generator and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 3MHz. The calibration of the equipment was done by measuring the velocity in carbon tetrachloride and benzene. The results are in good agreement with the literature values [14]. The ultrasonic velocity has an accuracy of ± 0.5 ms^{-1}. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath.

THEORY

Nomoto established an empirical relation for ultrasonic velocity in binary liquid mixtures as

$$U_N = [(x_1R_1+x_2R_2) /(x_1V_1+x_2V_2)]^3 \quad (1)$$

Where R is molar sound velocity, x_1 and x_2 are the mole fractions of 1^{st} and 2^{nd} components of the liquid mixture and V is molar volume.

Van Dael and Vangeel Ideal mixing relation

$$U_{imx} = [(x_1/M_1U^2{}_1 + x_2/M_2U^2{}_2)(x_1M_1+x_2M_2)]^{-1/2} \quad (2)$$

Where U_{imx} is the ideal mixing ultrasonic velocity in liquid mixture. U_1 and U_2 are ultrasonic velocities of individual compounds.

Impedance dependent relation

$$U_{Im} = \Sigma x_iZ_i / \Sigma x_i\rho_i \quad (3)$$

Where x_i is the mole fraction, ρ_i the density of the mixture and Z_i is the acoustic impedance.

Rao's specific velocity

$$U_R= (\Sigma x_i r_i \rho_i)^3 \quad (4)$$

Where x_i is the mole fraction, U_i is the ultrasonic velocity, ρ_i the density of the mixture and r_i is the Rao's specific sound velocity = $U^{1/3}{}_i /\rho_i$ and Z_i is the acoustic impedance.

Jungie equation

$$U_J = (x_1M_1/\rho_1 + x_2M_2/\rho_2)/ [\{x_1M_1+x_2M_2\}^{1/2} \mathbf{x} \{x_1M_1/\rho_1U^2{}_1+x_2M_2/\rho_2U^2{}_2\}]^{1/2} \quad (5)$$

Where M_1, M_2 are molecular weights of constituent components, ρ_1 and ρ_2 are the densities of constituent components.

RESULTS AND DISCUSSION

Comparison of theoretical values of ultrasonic velocities with those obtained experimentally in the present binary liquid mixtures is expected to reveal the nature of interaction between the component molecules in the mixture. Such theoretical study is useful in building the comprehensive theoretical model for the liquid mixtures.

Table-1 Experimental and literature values of density and ultrasonic velocity of pure liquids at 303.15K

Liquids	ρ / ($kg.m^{-3}$)		U / ($m.s^{-1}$)	
	Expt.	Lit.	Expt.	Lit.
Quinoline	1085.45	1085.82[a]	1554	1547[a]
o-Cresol	1036.20	1036.2[b]	1485.26	1485.3[b]
m-Cresol	1025.80	1025.8[b]	1464.21	1464.2[b]
p-Cresol	1026.50	1026.5[b]	1461	1468.4[b]

Expt. – Experimental; Lit. – Literature; [a]Ref. 12; [b]Ref.13

The theoretical evaluation of sound velocity based on different models in liquid mixtures has been used to correlate with the experimental findings. The theoretical values of ultrasonic velocities calculated by using the equations (1-5) along with the experimental values for all the three mixtures at temperatures of 303.15, 308.15, 313.15 and 318.15K are given in Tables 2-4.

It can be seen from Tables 2-4 that the theoretical values of ultrasonic velocity calculated by using various theories show deviation from experimental values. The limitations and approximation incorporated in these theories are responsible for the deviations of theoretical values from experimental values. In Nomoto's theory, it is supposed that the volume does not change on mixing. But on mixing two liquids, the interaction between the molecules of the two liquids takes place because of the presence of various types of forces such as dispersive forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions. The deviations of experimental values from theoretical values calculated using van Dael and Vangeel equation might be due to the compressibility of the component liquids in the present mixtures. The deviations of experimental values and values calculated from impedance relation and Rao's relation imply non-additivity of acoustic impedance and Rao's velocity in the liquid mixtures. Large deviations are observed in case of Junjie's relation. Thus, the observed deviation of theoretical values of velocity from the experimental values shows that the molecular interactions are taking place [15-19] between the unlike molecules in the liquid mixture.

Table-2 Experimental and theoretical values of velocities ($m.s^{-1}$) in quinoline + o- cresol system at different temperatures

X_1	U_{exp}	U_N	U_{imx}	U_{Im}	U_R	U_J
303.15 K						
0.0000	1485.26	1485.26	1485.26	1485.26	1485.26	1459.09
0.0888	1500.00	1492.01	1490.07	1491.60	1491.25	1461.94
0.1798	1509.47	1498.78	1495.23	1498.04	1497.41	1464.87
0.2732	1515.79	1505.57	1500.78	1504.59	1503.75	1467.88
0.3690	1525.26	1512.38	1506.74	1511.25	1510.27	1470.97
0.4672	1531.58	1519.22	1513.16	1518.02	1516.97	1474.15
0.5681	1534.21	1526.07	1520.07	1524.91	1523.88	1477.40
0.6717	1537.89	1532.94	1527.53	1531.92	1531.00	1480.74
0.7782	1544.21	1539.83	1535.58	1539.05	1538.33	1484.16
0.8876	1550.53	1546.75	1544.27	1546.30	1545.89	1487.67
1.0000	1553.68	1553.68	1553.68	1553.68	1553.68	1491.28
308.15K						
0.0000	1466.84	1466.84	1466.84	1466.84	1466.84	1444.62
0.0888	1493.68	1475.07	1473.07	1474.62	1474.16	1448.69
0.1798	1506.16	1483.33	1479.67	1482.52	1481.69	1452.87
0.2732	1512.63	1491.63	1486.69	1490.56	1489.44	1457.16
0.3690	1518.95	1499.97	1494.14	1498.72	1497.41	1461.57
0.4672	1522.42	1508.33	1502.08	1507.03	1505.63	1466.10
0.5681	1528.57	1516.73	1510.54	1515.47	1514.09	1470.76
0.6717	1534.21	1525.17	1519.58	1524.05	1522.82	1475.55
0.7782	1543.00	1533.64	1529.24	1532.78	1531.82	1480.46
0.8876	1546.21	1542.14	1539.58	1541.65	1541.10	1485.51
1.0000	1550.68	1550.68	1550.68	1550.68	1550.68	1490.69
313.15K						
0.0000	1452.11	1452.11	1452.11	1452.11	1452.11	1433.59
0.0888	1487.37	1461.42	1459.36	1460.96	1460.41	1438.53
0.1798	1503.16	1470.79	1467.01	1469.95	1468.94	1443.60
0.2732	1507.59	1480.19	1475.10	1479.09	1477.73	1448.83
0.3690	1509.47	1489.65	1483.65	1488.37	1486.79	1454.20
0.4672	1513.63	1499.15	1492.71	1497.81	1496.12	1459.73
0.5681	1515.79	1508.70	1502.32	1507.39	1505.73	1465.43
0.6717	1519.79	1518.29	1512.53	1517.14	1515.65	1471.29
0.7782	1525.26	1527.94	1523.40	1527.05	1525.89	1477.32
0.8876	1535.89	1537.63	1534.99	1537.12	1536.45	1483.53
1.0000	1547.37	1547.37	1547.37	1547.37	1547.37	1489.92
318.15K						
0.0000	1437.06	1437.06	1437.06	1437.06	1437.06	1422.13
0.0888	1481.05	1447.20	1445.08	1446.74	1446.10	1427.71
0.1798	1493.68	1457.39	1453.52	1456.56	1455.40	1433.46
0.2732	1500.00	1467.64	1462.42	1466.54	1464.99	1439.38
0.3690	1503.16	1477.95	1471.80	1476.68	1474.86	1445.49
0.4672	1506.32	1488.32	1481.71	1486.98	1485.05	1451.79
0.5681	1509.47	1498.75	1492.20	1497.45	1495.55	1458.28
0.6717	1516.00	1509.23	1503.32	1508.08	1506.38	1464.97
0.7782	1520.10	1519.78	1515.13	1518.89	1517.56	1471.87
0.8876	1528.42	1530.39	1527.68	1529.88	1529.12	1478.99
1.0000	1541.05	1541.05	1541.05	1541.05	1541.05	1486.33

Table-3 Experimental and theoretical values of velocities ($m.s^{-1}$) in quinoline + m- cresol system at different temperatures

X_1	U_{exp}	U_N	U_{imx}	U_{Im}	U_R	U_J
303.15K						
0.0000	1464.21	1464.21	1464.21	1464.21	1464.21	1445.68
0.0896	1488.00	1472.84	1470.85	1472.49	1471.94	1449.48
0.1813	1495.84	1481.50	1477.87	1480.88	1479.88	1453.41
0.2752	1509.47	1490.19	1485.30	1489.37	1488.03	1457.47
0.3713	1518.95	1498.92	1493.17	1497.97	1496.41	1461.65
0.4697	1528.42	1507.68	1501.52	1506.69	1505.02	1465.97
0.5706	1532.00	1516.47	1510.39	1515.51	1513.89	1470.42
0.6740	1544.21	1525.30	1519.81	1524.46	1523.00	1475.01
0.7799	1547.37	1534.17	1529.85	1533.52	1532.39	1479.75
0.8886	1549.00	1543.07	1540.56	1542.70	1542.05	1484.63
1.0000	1552.00	1552.00	1552.00	1552.00	1552.00	1489.66
308.15K						
0.0000	1456.00	1456.00	1456.00	1456.00	1456.00	1440.60
0.0896	1484.00	1465.21	1463.20	1464.88	1464.26	1444.86
0.1813	1487.00	1474.47	1470.80	1473.86	1472.75	1449.26
0.2752	1494.00	1483.77	1478.81	1482.96	1481.48	1453.81
0.3713	1500.00	1493.10	1487.28	1492.18	1490.45	1458.51
0.4697	1513.00	1502.48	1496.24	1501.51	1499.67	1463.36
0.5706	1522.00	1511.90	1505.73	1510.96	1509.16	1468.36
0.6740	1533.00	1521.37	1515.79	1520.53	1518.92	1473.53
0.7799	1540.00	1530.87	1526.49	1530.23	1528.97	1478.86
0.8886	1544.21	1540.41	1537.87	1540.05	1539.33	1484.36
1.0000	1550.00	1550.00	1550.00	1550.00	1550.00	1490.03
313.15K						
0.0000	1444.00	1444.00	1444.00	1444.00	1444.00	1431.88
0.0896	1481.00	1453.97	1451.92	1453.64	1452.95	1436.75
0.1813	1484.00	1463.99	1460.24	1463.40	1462.15	1441.78
0.2752	1491.00	1474.06	1469.00	1473.28	1471.61	1446.99
0.3713	1497.00	1484.19	1478.23	1483.28	1481.33	1452.36
0.4697	1503.00	1494.36	1487.98	1493.41	1491.34	1457.92
0.5706	1516.00	1504.59	1498.27	1503.66	1501.63	1463.66
0.6740	1521.00	1514.86	1509.16	1514.05	1512.23	1469.60
0.7799	1528.00	1525.19	1520.71	1524.56	1523.15	1475.73
0.8886	1538.00	1535.57	1532.97	1535.21	1534.40	1482.06
1.0000	1546.00	1546.00	1546.00	1546.00	1546.00	1488.60
318.15K						
0.0000	1433.00	1433.00	1433.00	1433.00	1433.00	1423.42
0.0896	1475.00	1443.45	1441.36	1443.12	1442.38	1428.73
0.1813	1478.00	1453.95	1450.14	1453.35	1452.02	1434.21
0.2752	1481.00	1464.51	1459.36	1463.72	1461.93	1439.88
0.3713	1487.00	1475.12	1469.07	1474.21	1472.13	1445.75
0.4697	1497.00	1485.79	1479.30	1484.84	1482.62	1451.81
0.5706	1506.00	1496.52	1490.10	1495.59	1493.42	1458.07
0.6740	1514.00	1507.31	1501.51	1506.48	1504.55	1464.55
0.7799	1519.00	1518.15	1513.59	1517.51	1516.01	1471.24
0.8886	1532.00	1529.04	1526.40	1528.69	1527.82	1478.16
1.0000	1540.00	1540.00	1540.00	1540.00	1540.00	1485.31

On increasing the temperature, the ultrasonic velocity values decrease in the three binary liquid mixtures. This is probably due to the fact that the thermal energy activates the molecule, which would increase the rate of association of unlike molecules [20].

Plots of U^2_{exp}/ U^2_{imx} against mole fraction of quinoline for all the three mixtures at different temperatures are given in Figures 1 to 4, respectively. It is observed from figures that as the temperature increases, the value of U^2_{exp}/U^2_{imx} increases in all the systems. The ratio U^2_{exp}/U^2_{imx} is used to measure the non-ideality in liquid mixtures, especially in those cases where the properties other than sound velocity are not known.

Table-4 Experimental and theoretical values of velocities (m.s^{-1}) in quinoline + p- cresol system at different temperatures

X_1	U_{exp}	U_N	U_{imx}	U_{Im}	U_R	U_J
303.15K						
0.0000	1461.00	1461.00	1461.00	1461.00	1461.00	1442.02
0.0896	1472.00	1469.74	1467.75	1469.39	1468.83	1445.98
0.1812	1491.00	1478.52	1474.88	1477.88	1476.87	1450.07
0.2751	1500.00	1487.33	1482.42	1486.48	1485.13	1454.29
0.3711	1505.00	1496.18	1490.41	1495.20	1493.62	1458.65
0.4696	1514.00	1505.06	1498.87	1504.03	1502.36	1463.14
0.5704	1522.00	1513.98	1507.86	1512.98	1511.34	1467.76
0.6738	1533.00	1522.93	1517.41	1522.05	1520.58	1472.53
0.7798	1541.05	1531.92	1527.58	1531.24	1530.10	1477.45
0.8885	1547.37	1540.94	1538.42	1540.56	1539.90	1482.52
1.0000	1550.00	1550.00	1550.00	1550.00	1550.00	1487.74
308.15K						
0.0000	1449.00	1449.00	1449.00	1449.00	1449.00	1433.32
0.0896	1458.00	1458.79	1456.73	1458.43	1457.77	1438.13
0.1812	1470.00	1468.62	1464.87	1467.99	1466.79	1443.10
0.2751	1486.00	1478.51	1473.44	1477.66	1476.06	1448.23
0.3711	1500.00	1488.44	1482.48	1487.46	1485.60	1453.52
0.4696	1506.00	1498.41	1492.02	1497.38	1495.40	1458.99
0.5704	1516.00	1508.43	1502.12	1507.44	1505.50	1464.63
0.6738	1528.42	1518.50	1512.80	1517.62	1515.89	1470.46
0.7798	1534.89	1528.62	1524.14	1527.94	1526.60	1476.47
0.8885	1541.05	1538.79	1536.18	1538.40	1537.63	1482.67
1.0000	1549.00	1549.00	1549.00	1549.00	1549.00	1489.07
313.15K						
0.0000	1436.00	1436.00	1436.00	1436.00	1436.00	1423.18
0.0896	1446.00	1446.74	1444.61	1446.38	1445.63	1428.80
0.1812	1462.00	1457.54	1453.65	1456.89	1455.53	1434.60
0.2751	1476.00	1468.39	1463.14	1467.54	1465.72	1440.60
0.3711	1494.00	1479.30	1473.13	1478.32	1476.20	1446.80
0.4696	1500.00	1490.27	1483.65	1489.24	1486.98	1453.21
0.5704	1506.00	1501.30	1494.75	1500.30	1498.08	1459.83
0.6738	1516.00	1512.39	1506.48	1511.50	1509.52	1466.67
0.7798	1525.00	1523.53	1518.89	1522.85	1521.31	1473.74
0.8885	1535.00	1534.74	1532.04	1534.35	1533.46	1481.05
1.0000	1546.00	1546.00	1546.00	1546.00	1546.00	1488.60
318.15K						
0.0000	1424.00	1424.00	1424.00	1424.00	1424.00	1414.21
0.0896	1440.00	1435.11	1432.96	1434.77	1433.97	1420.12
0.1812	1456.00	1446.29	1442.36	1445.67	1444.23	1426.24
0.2751	1472.00	1457.52	1452.22	1456.70	1454.77	1432.57
0.3711	1484.00	1468.83	1462.59	1467.88	1465.63	1439.11
0.4696	1494.00	1480.19	1473.50	1479.20	1476.80	1445.88
0.5704	1497.00	1491.62	1485.01	1490.66	1488.31	1452.88
0.6738	1512.00	1503.12	1497.15	1502.26	1500.17	1460.13
0.7798	1517.00	1514.68	1509.99	1514.02	1512.39	1467.62
0.8885	1528.42	1526.31	1523.58	1525.93	1525.00	1475.37
1.0000	1538.00	1538.00	1538.00	1538.00	1538.00	1483.39

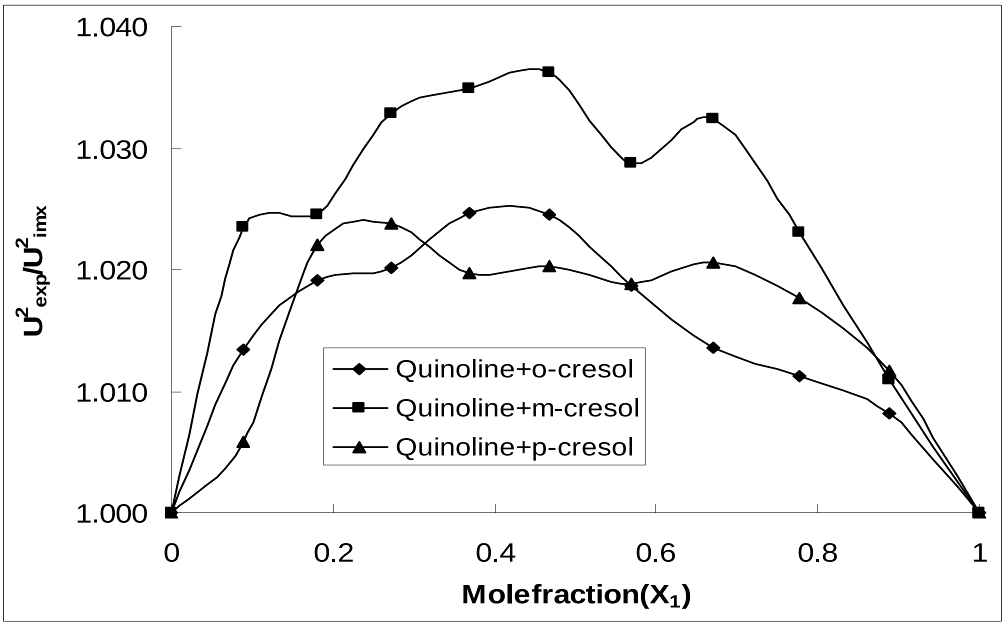

Fig.1 Variation of U^2_{exp}/U^2_{imx} at temperature 303.15 K for different systems.

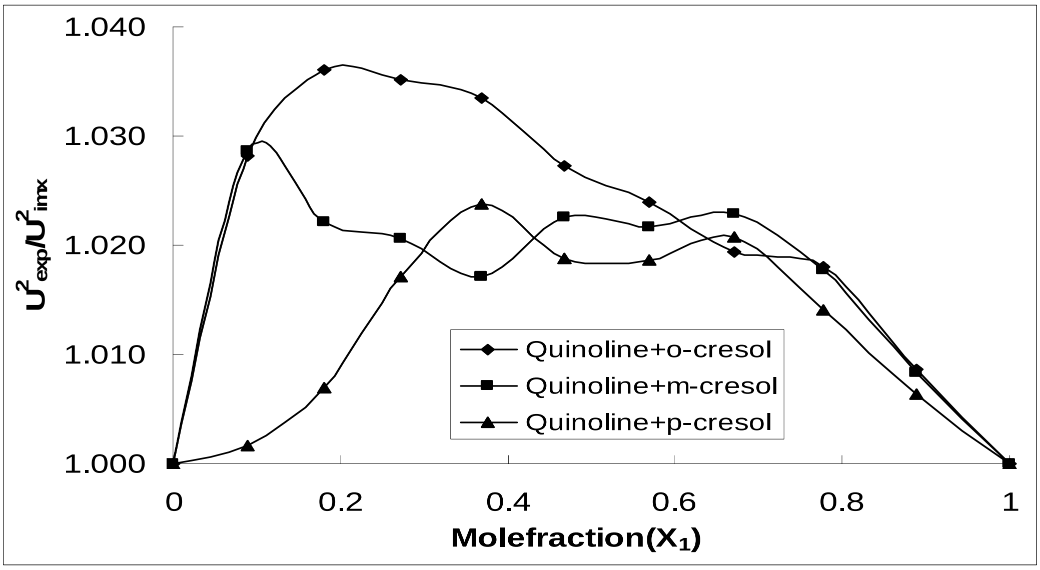

Fig. 2 Variation of U^2_{exp}/U^2_{imx} at temperature 308.15 K for different systems.

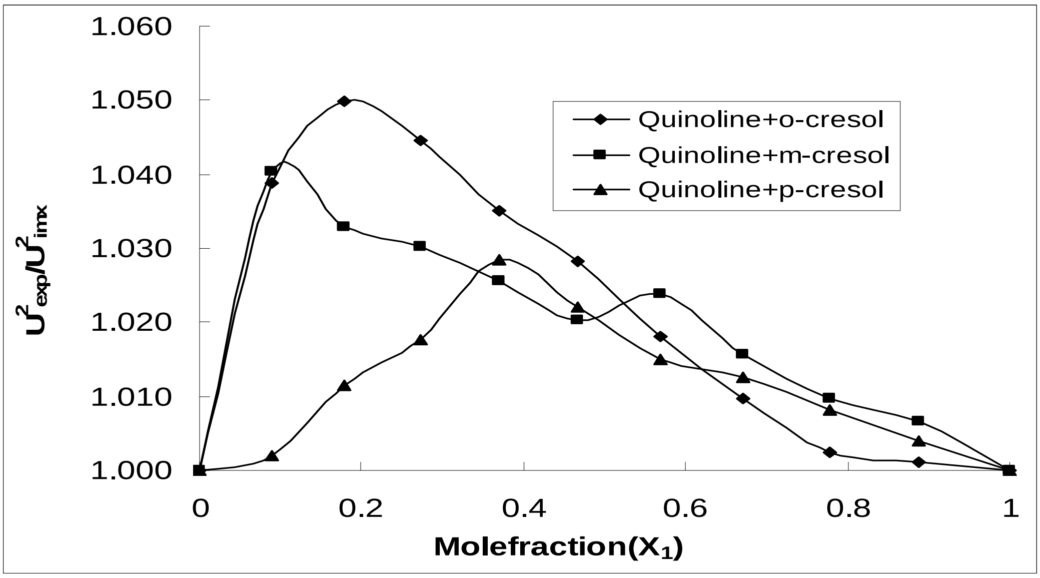

Fig. 3 Variation of U^2_{exp}/U^2_{imx} at temperature 313.15 K for different systems.

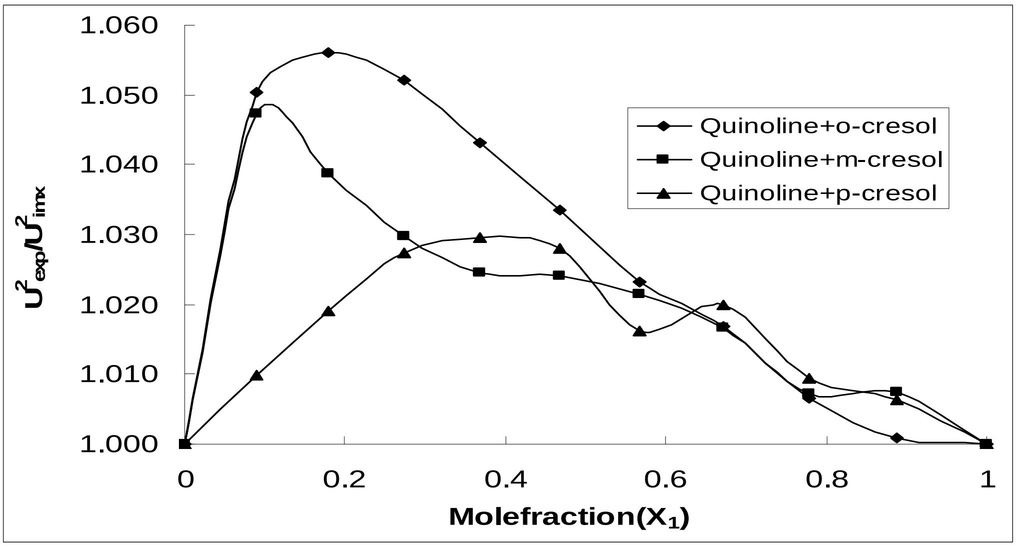

Figure-4 Variation of U^2_{exp}/U^2_{imx} at temperature 318.15 K for different systems.

CONCLUSION

Theoretical evaluations of ultrasonic velocities in three binary liquid mixtures are determined, and the validity of different theories is checked. It is observed that out of all the theories Nomoto's theory gives best results followed by Impedance dependence relation in all the systems studied.

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