THEORETICAL EVALUATION OF ULTRASONIC VELOCITIES IN BINARY LIQUID MIXTURES OF PYRROLIDINONE WITH PROPANE-1, 2-DIOL AT DIFFERENT TEMPERATURES

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ABSTRACT

Ultrasonic velocities and densities of the binary liquid mixtures of pyrrolidinone and propane-1, 2-diol have been measured at temperatures (303.15, 308.15, 313.15 and 318.15) K over the entire mole fraciton range. The theoretical values of ultrasonic velocity were evaluated using Nomoto's relation (u_{NR}), Impedance relation (u_{IR}), Ideal mixing relation (u_{IMR}), Junjie's relaiton (u_{JR}) and Rao's specific velocity relation (u_R). The theoretical values have been compared with the experimental values. The molecular association (α) has been evaluated from the values of experimental and theoretical speeds.

KEYWORDS: Pyrrolidinone, Propane-1,2-diol, Theoretical velocities

INTRODUCTION

Ultrasonic velocity data is very important in determining the Physico-chemical behaviour of liquid mixtures, and it have many applications in industry. Ultrasonic velocity investigations has been carrying by many researchers from several years and correlating the experimental results with the theoretical relations of Nomoto, impedance, ideal mixing relation, Junjie and Rao's specific velocity. Due to its nondestructive nature, ultrasonic velocity of liquid mixtures has been extensively carrying out in the last two decades in different branches of science to measure the thermodynamic properties to predict the nature of molecular interaction between the molecules in a mixture.

Here we report the experimental values of ultrasonic velocities along with theoretical values calculated using Nomoto's relation, ideal mixing relation, impedance relation, Rao's specific velocity relation and Junjie's relation for diethyl carbonate and aniline at temperatures (303.15, 308.15, 313.15 and 318.15) K over the entire mole fraciton range. The relative applicability of these theories to the present system has been checked and discussed.

MATERIALS AND METHODS

The chemicals used in the present investigation were obtained from Aldrich Chemicals with purity >99% and were used as such without further purification. The purity of the samples was checked by comparing the observed values of densities and speeds of sound with those reported in the literature.

Anton Paar DSA 5000 density and sound analyser provided with two Pt 100 platinum thermometers are used for measuring the densities and speeds of sound of pure liquids and liquid mixtures. The density is extremely sensitive to temperature, so the apparatus was controlled to ±0.001 K by a built in solid state thermostat. The stated accuracy in density and speed of sound are $5x10^{-3}$ kgm^{-3} and 0.5 m/s respectively.

The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight-stoppered bottles to minimize evaporation losses. The weighings were done with an electronic balance with a precision of ±0.01mg.

Theory: Nomoto's relation: Nomoto established the following relation for speed of sound of binary liquid mixtures on assuming the addivity of molar sound speed (R) and no volume change on mixing:

$$R = M/\rho u^{1/3} \quad (1)$$

Where u and ρ are determined experimentally, and M is the mean molecular weight in a binary mixture.

$$M = (x_1M_1 + x_2M_2) \quad (2)$$

Where x_1, x_2, M_1 and M_2 are mole fractions and molecular weights of constituent components.

$$u_{NR} = [(x_1R_1 + x_2R_2)/(x_1V_1+x_2V_2)]^3 \quad (3)$$

Where V_1 and V_2 are the molar volumes of 1st and 2nd components of the liquid mixture.

Impedance relation: $u_{IR} = \Sigma x_iZ_i / \Sigma x_i\rho_i$ (4)

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

Junjie equation: $u_J = (x_1M_1/\rho_1 + x_2M_2/\rho_2)/[\{x_1M_1 + x_2M_2\}^{1/2} \{x_1M_1/\rho_1u_1^2 + x_2M_2/\rho_2u_2^2\}^{1/2}]$ (5)

Rao's specific velocity: $u_R = (\Sigma x_ir_i\rho_i)^3$ (6)

where x_i is the mole fraction, ρ_i the density and r_i is the Rao's specific sound velocity of the mixture.

Ideal Mixing relation: $1/(x_1M_1 + x_2M_2)*u^2_{imx} = x_1/M_1u_1^2 + x_2/M_2u_2^2$ (7)

The degree of molecular interaction given as interaction parameter, α is calculated using the relation,

$$\alpha = (u_{exp}^2/u_{imx}^2) - 1 \quad (8)$$

RESULTS AND DISCUSSION

The experimental values of ultrasonic velocity for the binary system along with theoretical values at different temperatures are presented in table-1. Data reveals that the ultrasonic velocities calculated from Rao's relation (R) exhibit more

satisfactory agreement with the experimental values in all the temperatures studied than other approaches in the binary system. From table-2 it is observed that there is a deviation between experimental and theoretical values which confirms the existence of molecular interactions. Higher variation is observed at some intermediate concentrations suggesting the existence of strong tendency of association between component molecules as a result of hydrogen bonding.

Table.1.Experimental and theoretical values of speeds of sound for Pyrrolidinone + propane-1,2-diol at different temperatures

x_1	u_{expt}	u_{NR}	u_{IR}	u_{IMR}	u_{JR}	u_R	u_{expt}	u_{NR}	u_{IR}	u_{IMR}	u_{JR}	u_R
	303.15 K						308.15 K					
0.0000	1495.63	1495.63	1495.63	1495.63	1495.63	1495.63	1481.49	1481.49	1481.49	1481.49	1481.49	1481.49
0.0994	1507.74	1507.96	1508.57	1504.66	1505.94	1505.47	1493.15	1493.60	1494.20	1490.35	1491.63	1491.03
0.1962	1525.27	1519.94	1521.01	1514.02	1516.35	1525.08	1510.29	1505.36	1506.41	1499.56	1501.85	1510.33
0.3038	1543.19	1533.20	1534.63	1525.12	1528.34	1544.90	1527.83	1518.39	1519.78	1510.46	1513.63	1529.84
0.4148	1559.96	1546.85	1548.47	1537.39	1541.19	1563.18	1544.28	1531.79	1533.37	1522.50	1526.25	1547.82
0.5021	1571.91	1557.53	1559.19	1547.64	1551.65	1575.96	1556.03	1542.28	1543.90	1532.57	1536.53	1560.40
0.5951	1583.47	1568.90	1570.48	1559.20	1563.17	1588.06	1567.42	1553.45	1554.99	1543.92	1547.84	1572.30
0.6891	1593.90	1580.35	1581.74	1571.56	1575.19	1598.65	1577.72	1564.68	1566.04	1556.06	1559.64	1582.72
0.7994	1604.54	1593.73	1594.77	1587.01	1589.82	1609.00	1588.28	1577.83	1578.83	1571.22	1574.00	1592.89
0.8908	1612.06	1604.79	1605.41	1600.63	1602.39	1615.87	1595.77	1588.68	1589.29	1584.60	1586.33	1599.65
1.0000	1617.97	1617.97	1617.97	1617.97	1617.97	1617.97	1601.62	1601.62	1601.62	1601.62	1601.62	1601.62
	313.15 K						318.15 K					
0.0000	1467.85	1467.85	1467.85	1467.85	1467.85	1467.85	1453.16	1453.16	1453.16	1453.16	1453.16	1453.16
0.0994	1478.77	1479.70	1480.29	1476.53	1477.78	1477.06	1463.96	1464.88	1465.45	1461.74	1462.98	1462.12
0.1962	1495.39	1491.22	1492.24	1485.54	1487.80	1495.99	1480.30	1476.26	1477.27	1470.64	1472.88	1480.76
0.3038	1512.45	1503.98	1505.33	1496.21	1499.33	1515.12	1497.08	1488.87	1490.21	1481.19	1484.28	1499.62
0.4148	1528.52	1517.09	1518.63	1508.01	1511.70	1532.76	1512.91	1501.84	1503.36	1492.85	1496.50	1517.04
0.5021	1540.04	1527.37	1528.94	1517.86	1521.75	1545.10	1524.28	1511.99	1513.54	1502.59	1506.44	1529.23
0.5951	1551.26	1538.29	1539.80	1528.97	1532.83	1556.77	1535.37	1522.79	1524.27	1513.58	1517.39	1540.79
0.6891	1561.47	1549.29	1550.62	1540.85	1544.38	1566.99	1545.49	1533.66	1534.97	1525.32	1528.80	1550.94
0.7994	1572.01	1562.16	1563.14	1555.70	1558.42	1576.98	1555.98	1546.38	1547.34	1539.99	1542.69	1560.88
0.8908	1579.58	1572.78	1573.37	1568.79	1570.49	1583.60	1563.53	1556.88	1557.46	1552.93	1554.62	1567.52
1.0000	1585.44	1585.44	1585.44	1585.44	1585.44	1585.44	1569.39	1569.39	1569.39	1569.39	1569.39	1569.39

Table.2.Percentage deviations and interaction parameters (α) for Pyrrolidinone + propane-1,2-diol at different temperatures

x_1	u_{expt}	u_{NR}	u_{IR}	u_{IMR}	u_{JR}	u_R	u_{expt}	u_{NR}	u_{IR}	u_{IMR}	u_{JR}	u_R
	303.15 K						308.15 K					
0.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00	0.0000
0.0994	-0.01	-0.06	0.20	0.12	0.15	0.0041	-0.03	-0.07	0.19	0.10	0.14	0.0038
0.1962	0.35	0.28	0.74	0.58	0.01	0.0149	0.33	0.26	0.71	0.56	0.00	0.0144
0.3038	0.65	0.56	1.17	0.96	-0.11	0.0238	0.62	0.53	1.14	0.93	-0.13	0.0231
0.4148	0.85	0.74	1.45	1.20	-0.21	0.0296	0.82	0.71	1.41	1.17	-0.23	0.0288
0.5021	0.92	0.82	1.54	1.29	-0.26	0.0316	0.89	0.79	1.51	1.25	-0.28	0.0309
0.5951	0.93	0.83	1.53	1.28	-0.29	0.0314	0.90	0.80	1.50	1.25	-0.31	0.0307
0.6891	0.86	0.77	1.40	1.17	-0.30	0.0286	0.83	0.75	1.37	1.15	-0.32	0.0280
0.7994	0.68	0.61	1.09	0.92	-0.28	0.0222	0.66	0.60	1.07	0.90	-0.29	0.0218
0.8908	0.45	0.41	0.71	0.60	-0.24	0.0143	0.45	0.41	0.70	0.59	-0.24	0.0141
1.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00	0.0000
	313.15 K						318.15 K					
0.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00	0.0000
0.0994	-0.06	-0.10	0.15	0.07	0.12	0.0030	-0.06	-0.10	0.15	0.07	0.13	0.0030
0.1962	0.28	0.21	0.66	0.51	-0.04	0.0133	0.27	0.20	0.65	0.50	-0.03	0.0132
0.3038	0.56	0.47	1.07	0.87	-0.18	0.0218	0.55	0.46	1.06	0.86	-0.17	0.0216
0.4148	0.75	0.65	1.34	1.10	-0.28	0.0274	0.74	0.64	1.33	1.08	-0.27	0.0271
0.5021	0.83	0.73	1.44	1.19	-0.33	0.0294	0.81	0.71	1.42	1.17	-0.32	0.0291
0.5951	0.84	0.74	1.44	1.19	-0.36	0.0294	0.83	0.73	1.42	1.17	-0.35	0.0290
0.6891	0.79	0.70	1.32	1.09	-0.35	0.0269	0.77	0.69	1.31	1.08	-0.35	0.0266
0.7994	0.63	0.57	1.04	0.86	-0.32	0.0211	0.62	0.56	1.03	0.85	-0.32	0.0209
0.8908	0.43	0.39	0.68	0.58	-0.25	0.0138	0.43	0.39	0.68	0.57	-0.26	0.0137
1.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00	0.0000

The assumption in Nomoto's theory is that the volume does not change on mixing, so no interaction between the components of liquid mixtures has been taken into consideration. In ideal mixing relation, the ratio of specific heats of ideal mixtures and the volumes are also equal; again no molecular interactions are taken into consideration. But on mixing, interactions between the molecules occur because of the presence of various types of forces such as charge transfer, hydrogen bonding, dispersion forces, dipole-dipole and dipole-induced dipole interactions. Thus, the observed deviations of theoretical values of ultrasonic velocity from the experimental values shows that molecular interactions are taking place between the unlike molecules.

The negative and positive magnitudes of percentage deviations in ultrasonic velocities indicate non ideal behavior of liquid mixtures. The positive value of α at all temperatures clearly indicates the existence of strong tendency for the formation of association in mixture through dipole-dipole interactions. All the theoretical models fairly predicted the speeds of sound are reasonably close to the experimental values.

CONCLUSION

Ultrasonic velocity and density values are measured at temperatures 303.15, 308.15, 313.15 and 318.15 K. Using various theoretical models ultrasonic velocity is evaluated. Experimental values are compared with the theoretical results and it is observed that Rao's relation provides good results when compared to other relations.

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