

Densities and Volumes of Mixed Hexamethyl Phosphor Triamide (HMPT) – Water at 298.15K

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Keywords

Densities, Dielectric Constant, Molar Volume, Van der Waals Volume, Electrostriction Volume, Crystal Volume, (HMPT) - Water Mixtures

In this paper The densities and dielectric constants for mixed, hexamethyl phosphor triamide (HMPT) – water solvents at 298.15K were accurately measured using densimeter DMA-58 and decameter DK-300 respectively. These values are necessary for further thermodynamic and solution parameters evaluation. Different volumes (molar volume V_M , Van der Waals volume V_W , electrostriction volume V_e and crystal volume V_C) for mixed (HMPT) – H_2O solvents were evaluated from density measurements.

Introduction

Study of dielectric behavior of polar and nonpolar molecules and their mixtures under varying conditions of compositions has evoked considerable interest. There have been several investigations on the dielectric behavior of solvent mixtures in which dielectric spectra were used to examine molecular orientations, hydrogen bonded networks and micro dynamics of these systems. Excess properties depend on the composition and temperature, are of great importance for the study of the interaction between mixing components. Density measurements of solvent mixtures are expected to shed some light on the solvent-solvent interaction and configuration of their mixtures. When a binary mixture is formed, the excess properties like dielectric parameters do not vary linearly with composition. The deviation from linearity of these parameters is termed as excess parameters and is helpful to understand the nature of intermolecular interactions and bonding between the two liquids. As a result many workers have studied the excess parameters in liquid mixtures.

Solvents miscible in water has important role on the effect of hydrogen bonds of water which plays vital role in chemical, physical and biological processes.

The aim of this work is to measure accurately the density and dielectric constants of mixed (HMPT- H_2O) solvents which are necessary for further thermodynamic calculations which explain the general behavior in liquid state.

The increase in densities, decrease of volumes and decrease of dielectric constants with decrease of mole fraction of HMPT in the mixture were discussed in view of the relation between dipole moment and square diameter of solvent parameter.

Experimental Details

Materials

Hexamethyl phosphor triamide (HMPT) is obtained from Merck Co.

These chemicals were used without further purification as the supplier claims their purity is more than 99%. The solutions are prepared with different volume fractions of respective chemicals.

These volume fractions are converted to mole fractions for further calculations.

Double distilled water was used for preparation of solution mixtures (with conductivity less than 5 $\mu\text{S/cm}$).

Instruments

Densimeter DMA-58 and dekameter (decimeter) DK-300 were used for measuring both density and dielectric constant respectively. The temperature was maintained constant using a thermostate (INSREF-India make) with an accuracy of $\pm 0.1\text{K}$ to maintain the temperature at 298.15K.

Results and Discussion

The densities of mixed HMPT- H_2O at 298.15K were evaluated from the measured oscillation parameter (T) and β parameter as given in equations (1-3).

$$D = A(T^2 - \beta) \quad (1)$$

$$A = \frac{d_{\text{H}_2\text{O}} - d_l}{T^2_{\text{H}_2\text{O}} - T^2_l} \quad (2)$$

$$\beta = T^2_l - \frac{d_l}{A} \quad (3)$$

Where (T) is the oscillation period measured by densimeter, $d_{\text{H}_2\text{O}}$ is the density of water and d_l is the density of air ($d_{\text{H}_2\text{O}}$ at 298.15 = 0.99707, d_l at 298.15 = 0.001185 measured at 760 Torr).

The densities of mixed HMPT – H_2O are given in Table (1) with calculated molecular weights for used mixtures from equation (4).

$$M = X_{s(\text{H}_2\text{O})} \cdot M_{(\text{H}_2\text{O})} + X_{s(\text{O.S})} \cdot M_{(\text{O.S})} \quad (4)$$

Where (M) is the molecular weight of the mixed solvent, $M_{(\text{H}_2\text{O})}$ is the mole fraction of water, $X_{(\text{H}_2\text{O})}$ is the mole fraction of organic solvent, $M_{(\text{O.S})}$ is the molecular weight of water and $M_{(\text{O.S})}$ is the molecular weight of organic solvent.

The molar volumes (V_M) were obtained from density measurements. The V_M as calculated by dividing the molecular weight by exact solution densities.

The packing density (ρ) as explained by Kim ^[7, 8] the relation between Van der Waals volumes (V_W) and the molar volumes (V_M) for relatively large molecules was found to be constant ^[9] and equal to 0.661.

$$\rho = V_W / V_M = 0.661 \pm 0.017 \quad (5)$$

The electrostriction volumes (V_e) which is the volume compressed by the solvent can be calculated by using equation (6) as follows ^[10-30]:

$$V_e = V_W - V_M \quad (6)$$

The solvated radii of the organic-aqueous mixtures (HMPT- H_2O) were calculated using equation (7) by considering the spherical form of the solvated molecules ^[31-49].

$$V = \frac{1}{6} \pi N \sigma^3 \quad (7)$$

Where V is the molar volume calculated from the densities as described before and σ is the solvated diameter.

The molar volume (V_M), Van der Waals volume (V_W), and electrostriction volume (V_e) for mixed HMPT- H_2O solvents at 298.15K are tabulated in Table 2.

The packing density for crystal was evaluated from the mean values of many readings and found to be 0.6482.

Dividing the Van der Waals volume (V_W) by crystal volume (V_C) equation (8):

$$P_C = \frac{V_W}{V_C} = 0.6482 \quad (8)$$

The calculated crystal volumes for mixed HMPT-H₂O mixtures are listed in table 2.

The dipole moments evaluated from the literature values of pure solvent dipole moments by applying equation (9) ^[9-49]:

$$\mu_s = X_1\mu_1 + X_2\mu_2 \quad (9)$$

Where μ_1 , μ_2 are the dipole moments for both HMPT and water at 298.15K, and X_1 , X_2 are the mole fractions of both mixtures.

Relaxation μ_s/σ^2 were evaluated and tabulated in table 3.

From results It is observed that density increases with increase in mole fraction of HMPT in the mixture.

Also it is observed that different volumes are increased by the addition of HMPT solvent.

Table (1). Oscillation period (*T*) and density (*D*) values for (HMPT-H₂O) mixtures at 298.15K.

vol. %	$X_S(FA)$	<i>T</i>	<i>D</i> (g/cm ³)	<i>M.Wt</i>
100	1	3.9154	1.0202	179.2
95	0.6615	3.9231	1.0282	124.6
90	0.4807	3.9279	1.0332	95.49
85	0.3682	3.9326	1.0381	77.37
80	0.2915	3.9359	1.0416	65
75	0.2358	3.9387	1.0445	56.02
70	0.1935	3.9395	1.0453	49.2
65	0.1603	3.9400	1.04597	43.86
60	0.1336	3.9401	1.04595	39.56
55	0.1116	3.9384	1.0442	36.01
50	0.0932	3.9362	1.0418	33.04

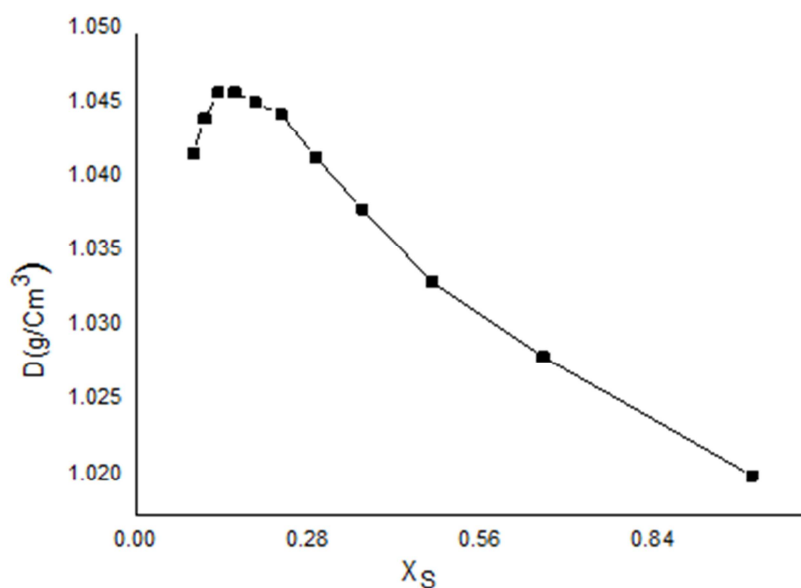


Fig (1). Relation between mole fraction of HMPT (X_S) and density at 298.15K.

Table (2). Different volumes of mixed (HMPT – H₂O) solvents at 298.15K.

$X_S(FA)$	V_M (cm ³ /mole)	V_W (cm ³ /mole)	V_e (cm ³ /mole)	V_c (cm ³ /mole)
1	175.640	116.09	-59.55	179.09
0.6615	121.175	80.09	-41.085	123.55
0.4807	92.416	61.08	-31.336	94.23
0.3682	74.526	49.26	-25.266	75.995
0.2915	62.400	41.24	-21.16	63.622
0.2358	53.630	35.44	-18.19	54.67
0.1935	47.066	31.11	-15.956	47.99
0.1603	41.930	27.71	-14.76	42.74
0.1336	37.822	25	-12.822	38.568
0.1116	34.489	22.79	-11.699	35.158
0.0932	31.711	20.96	-10.75	32.335

Table (3). Diameter (σ), dipole moment (μ s), (μ s/ σ^2) and dielectric constant (ϵ) of mixed (HMPT – H₂O) solvents at 298.15K.

Xs(FA)	σ (Å ⁰)	μ s (10 ¹⁸ esu)	μ s/ σ^2	ϵ
1	3.47	179.2	14.88	29.6
0.6615	3.069	124.6	13.22	46.15
0.4807	2.8	95.49	12.1	54.99
0.3682	2.6	77.37	11.44	60.49
0.2915	2.46	65	10.7	64.24
0.2358	2.33	56.02	10.31	66.96
0.1935	2.23	49.2	9.89	69.03
0.1603	2.155	43.86	9.44	70.65
0.1336	2.08	39.56	9.14	71.96
0.1116	2.01	36.016	8.91	73.03
0.0932	1.96	33.04	8.6	73.93

Conclusion

The density of HMPT-H₂O solutions have been measured experimentally at 298.15K. From density data the different volumes (molar volume, Van der Waals volume, electrostriction volume, crystal volume) are determined. The dielectric parameter shows systematic changes with concentration conclude that these mixtures have intermolecular interactions. Also the values of different volumes indicating the presence of intermolecular interaction between mixtures components. ■



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