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Accurate Solvent – Solvent Densities, Dielectric Constants and Volumes of Mixed N, N-Dimethylformamide (DMF) – Water at 298.15K

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Abstract: In this paper the densities and dielectric constants for mixed (DMF) – water solvents at 298.15K were accurately measured using densimeter DMA-58 and decameter DK-300 respectively. Different volumes (molar volume V_M, Van der Waals volume V_W, electrostriction volume V_e and crystal volume V_C) for mixed (DMF) – H_2O solvents were evaluated from density measurements.

Keywords: Densities; Dielectric constant; Molar volume; Van der waals volume; Electrostriction volume; Crystal volume; (DMF) – Water Mixtures.

1. Introduction

The thermodynamic properties of a binary mixture such as dielectric constant and density are important from practical andtheoretical points of view to understand liquid theory. Their properties are extremely useful for the design of process equipment in chemical industries. Binary liquid mixtures due to their unusual behavior have attracted considerable attention.Thus data on some of the properties associated with the liquids and liquid mixtures like density and viscosity find extensive application in solution theory and molecular dynamics. Such results are necessary for interpretation of data obtained from thermochemical, electrochemical, biochemical and kinetic studies [1-8]. Amides of (R1, R2)-NCHO type (R1, R2 = H and/or an alkyl group) possess a large dipole moment and a hydrophilic property, so that they mix well with water.

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.

Studiesofdensities, viscosities, and dielectric constant of mixed solvents are of great use in characterizingthe structure and properties of these solvents.

The aim of this work is to measure accurately the density and dielectric constants of mixed (DMF-H_2O) solvents which are necessary for further thermodynamic calculations.

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

2. Experimental Details

(DMF) are obtained from Merk 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 µs/cm).

Densimeter DMA-58 and decameter DK-300 were used for measuring both density and dielectric constant respectively. The temperature was maintained constant using a thermostat (INSREF-India made) with an accuracy of ±0.1K to maintain the temperature at 298.15K.

3. Results and Discussion

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

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

$$A = \frac{d_{H_2O} - d_l}{T^2{}_{H_2O} -} \qquad (2)$$

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

Where (T) is the oscillation period measured by densimeter, d H_2O is the density of water and d_L is the density of air (d H_2O at 298.15 = 0.99707, d_L at 298.15 =0.001185 measured at 760 Torr) .

The densities of mixed DMF – H_2O are given in Table (1) and Fig.1, with calculated molecular weights for used mixtures by equation (4).

$$M = X_{s_{(H_2O)}} . M_{(H_2O)} + X_{s_{(O.S)}} . M_{(O.S)} \qquad (4)$$

Where (M) is the molecular weight of the mixed solvent, $X_{s_{(H_2O)}}$is the mole fraction of water, $X_{s_{(O.S)}}$is the mole fraction of organic solvent, $M_{(H_2O)}$ is the molecular weight of water and $M_{(O.S)}$ 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 [9-11] and equal to 0.661.

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

The electrostriction volumes (V_e) which is the volume compressed by the solvent can be calculated by using equation (6) as follows:

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

The solvated radii of the organic–aqueous mixtures (DMF-H_2O) were calculated using equation (7) by considering the spherical form of the solvated molecules [12-20].

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

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 DMF-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):

$$P_C = \frac{V_w}{V_c} = 0.6482 \qquad (8)$$

The calculated crystal volumes for mixed DMF-H_2O mixtures are listed in table 2.

The dipole moments taken from the literature [7, 8] values of pure solvent dipole moments by applying equation (9):

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

Where μ_1, μ_2 are the dipole moments for both DMF 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.

Most values in Table 3 are increased with increase of DMF mole fractions indicating more solvent- solvent interactions.

From results drawn in Figs.1 and 2, it is observed that density increases with increase in mole fraction of DMF in the mixture.

Also it is observed that different volumes are increasing by the addition of DMF solvent.

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

vol. %	X_S(FA)	T	D (g/cm^3)	M.Wt
100	1	3.8414	0.9439	73.10
95	0.8162	3.8511	0.9538	62.97
90	0.6774	3.8598	0.9628	55.32
85	0.5694	3.8677	0.9709	49.38
80	0.4831	3.8742	0.9776	44.62
75	0.4121	3.8791	0.9826	40.71
70	0.3528	3.8838	0.9874	37.44
65	0.3026	3.8869	0.9907	34.68
60	0.2595	3.8894	0.9933	32.30
55	0.2221	3.8910	0.9949	30.24
50	0.1894	3.8921	0.9960	28.44

Fig-1. Relation between mole fraction of DMF (X_S), V_M and (μ_s/σ^2).

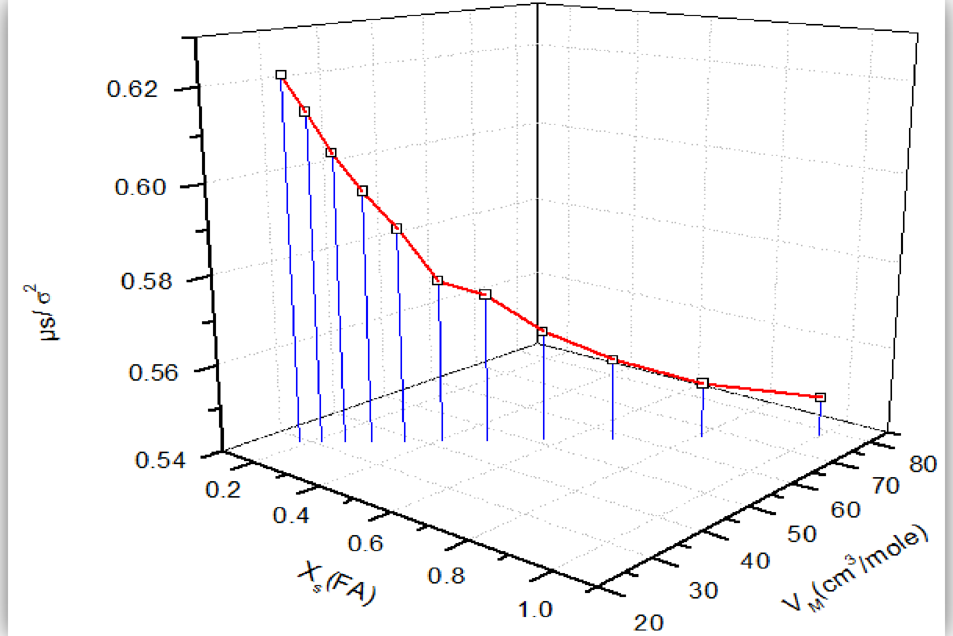

Fig-2. Relation between mole fraction of DMF (X_S), Density and oscillation period (T).

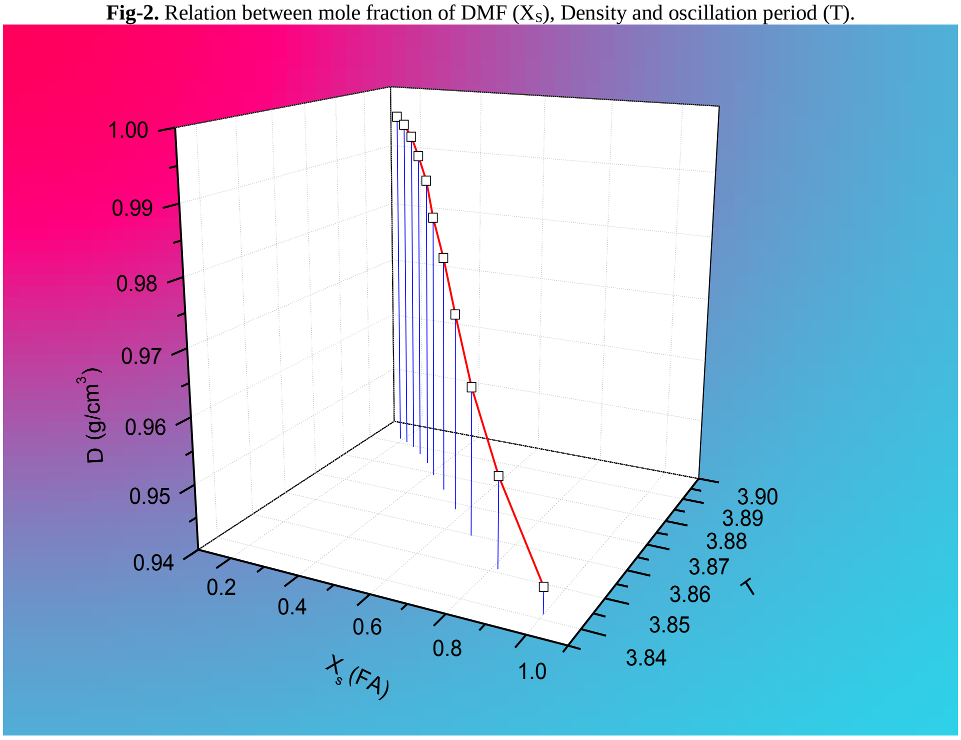

Table-2. Different volumes of mixed (DMF – H_2O) solvents at 298.15K.

X_S(FA)	V_M(cm^3/mole)	V_W(cm^3/mole)	V_e(cm^3/mole)	V_C(cm^3/mole)
1	77.439	51.187	-26.252	78.967
0.8162	66.015	43.635	-22.28	67.317
0.6774	57.455	37.977	-19.478	58.588
0.5694	50.858	33.617	-17.241	51.862
0.4831	45.647	30.172	-15.475	46.547
0.4121	41.433	27.387	-14.046	42.250
0.3528	37.923	25.067	-12.855	38.671
0.3026	35.008	23.140	-11.868	35.699
0.2595	32.529	21.501	-11.028	33.170
0.2221	30.403	20.096	-10.307	31.002
0.1894	28.559	18.877	-9.681	29.122

Table-3. Diameter (σ), dipole moment (μ_s), (μ_s/σ^2) and dielectric constant (ϵ) of mixed (DMF – H_2O) solvents at 298.15K.

X_S(FA)	σ (A^0)	μ_s (10^{18}esu)	μ_s/σ^2	ϵ
1	2.644	3.84	0.5493	36.6
0.8162	2.507	3.4767	0.5531	40.0
0.6774	2.393	3.2012	0.5590	42.6
0.5694	2.298	2.9874	0.5657	45.1
0.4831	2.216	2.8165	0.5742	48.2
0.4121	2.146	2.6759	0.5774	50.3
0.3528	2.084	2.5585	0.5891	53.2
0.3026	2.029	2.4591	0.5973	56.0
0.2595	1.980	2.3738	0.6055	57.8
0.2221	1.935	2.2997	0.6142	60.1
0.1894	1.896	2.2350	0.6217	62.5

4. CONCLUSION

The density of DMF-H_2O solutions have been accurately measured experimentally at 298.15K. From density data the different volumes (molar volume, Van der Waals volume, electrostriction volume, and crystal volume) are determined. The dielectric constant parameters show 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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