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Accurately Densities, Dielectric Constants and Volumes of Mixed Formamide (FA) – Water at 298.15K

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Keywords

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he densities and dielectric constants for mixed formamide – water solvents at 298.15K were accurately measured using densimeter DMA-58 and decameter DK-300 respectively. Different volumes (molar volume $V_{\rm M}$, Van der Waals volume $V_{\rm W}$, electrostriction volume $V_{\rm e}$ and crystal volume ($V_{\rm C}$) for mixed FA – H_2O solvents were evaluated from density measurements . Accurately values of densities and dielectric constants are needed for further thermodynamic parameters evaluation.

Introduction

The mixing of different solvents results in the formation of a solution that is different from ideal.

The thermodynamic properties of multi component liquid mixtures and their analysis in terms of interpretative models constitute a very interesting subject. The practical need for thermodynamic data for teaching and research aswell as for design and set up of industrial processes continue to drive research in the study of multi component systems. The characterization of mixtures through their thermodynamic and transport properties is important from the fundamental viewpoint of understand their mixing behavior. A thorough knowledge of transport properties of non-aqueous solutions is essential in many chemical and industrial applications .Densities and dielectric constants are necessary parameters for solution thermodynamic and statistical thermodynamics and their accurate determination is the target of this work.

Studies on density and dielectric constant of binary mixtures along with other thermodynamic properties are being increasingly used as a tool for investigation of the properties of pure components and the nature of intermolecular interaction between liquid mixtures constituents. [1,2]

Also volumes, excess volumes and heat capacities give good information about solvent – solvent interactions [3], also these studies find direct applications in chemical and biochemical industry [4].

Density and viscosity are important properties for characterizing liquid flow through a channel, as well as heat and mass transfer in many food processing processes.[5]

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Experimental

Materials

Formamide (FA) of the highest purity available and was purchased from Merck Company.

Mixture Preparation

Binary mixtures were prepared by weighing appropriate amounts of formamide and water on an electronic balance. An AE Adam balance (Adam Equipment Inc. USA) model PW124 with a maximum capacity of 120 g, a readability range 0.0001 g and repeatability (S.D.) of 0.00015 g, linearity 0.0002 g, operating temperature +10°C to 40°C was used in all measurements.

Density and Dielectric Constant Measurements

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 make) with an accuracy of ± 0.1 K. The dielectric constants were measured experimentally by the use of Decameter of the type DK 300(WTW).

Results and Discussion

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

$$D = A(T^2 - \beta) \tag{1}$$

$$A = \frac{d_{H_2O} - d_l}{T^2_{H_2O} - T^2_l} \tag{2}$$

$$\beta = T^2_{l} - \frac{d_l}{A} \tag{3}$$

Where (T) is the oscillation period measured by densimeter, d H_2O is the density of water and dl is the density of air. The densities are increased with increase FA mole fractions (Fig.1). The densities of mixed FA – H_2O are given in Table (1) with calculated molecular weights for used mixtures from equation (4).

$$M = X_{S(H_2O)} \cdot M_{(H_2O)} + X_{S(O,S)} \cdot M_{(O,S)}$$
(4)

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 in literature [6-8] the relation between Van der Waals volumes (V_M) and the molar volumes (V_M) for relatively large molecules was found to be constant [9-20] and equal to 0.661.

$$\rho = V_W / V_M = 0.661 \pm 0.017 \tag{5}$$

The electrostriction volumes (V_e) [20-27] which is the volume compressed by the solvent can be calculated by using equation (6) as follows:

$$V_e = V_W - V_M \tag{6}$$

The solvated radii of the organic-aqueous mixtures (FA-H₂O) were calculated using equation (7) by considering the spherical form of the solvated molecules.

$$V = \frac{1}{6}\pi N\sigma^3 \tag{7}$$

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

All different volumes evaluated are tabulated in Table 2 with increase in their values with decrease in FA percentages in the mixture.

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The dielectric constants (ε) are measured exactly by using the above mentioned dekameter and their values are listed in Table with decrease in them by decrease formamide mole fraction in the mixture.

The dipole moments and diameters (σ) for mixed FA-H₂O were estimated by the sum of the dipole moments (ref.7) for each solvent multiplied by their mole fractions. The estimated dipole moments together with the ratio μ_s/σ^2 are also cited in Table 3.

All different values in Table 3 are decreased with decrease of FA mole fractions indicating less solvation.

Table 1. Oscillation	neriod (T	and density (D) values for	(FA-H ₂ O) mixtures at 298.15K.

vol. %	X _S (FA)	T	D (g/cm ³)	M.Wt
100	1	4.0179	1.1282	45.04
95	0.8958	4.0128	1.1227	42.22
90	0.8628	4.0071	1.1167	38.63
85	0.7194	4.0018	1.1110	37.45
80	0.6441	3.9963	1.1052	35.42
75	0.5758	3.9908	1.0994	33.57
70	0.5136	3.9853	1.0935	31.89
65	0.4566	3.9799	1.0878	30.35
60	0.4043	3.9746	1.0822	28.94
55	0.3566	3.9677	1.0749	27.65
50	0.3115	3.9622	1.0691	26.43

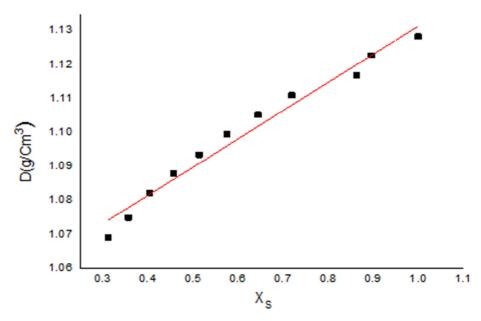


Fig 1. Relation between mole fraction of formamide (X_S) and density at 298.15K.

Table 2. Different volumes of mixed ($FA - H_2O$) solvents at 298.15K.

$X_{S}(FA)$	V _M (cm ³ /mole)	Vw(cm³/mole)	V _e (cm ³ /mole)	V _C (cm ³ /mole)
1	39.92	26.38	-13.54	40.69
0.8958	40.11	26.51	-13.60	40.89
0.8628	40.33	26.65	-13.68	41.11
0.7194	40.53	26.79	-13.74	41.32
0.6441	40.75	26.93	-13.82	41.54
0.5758	40.96	27.07	-13.89	41.76
0.5136	41.18	27.21	-13.91	41.97
0.4566	41.40	27.36	-14.04	42.20
0.4043	41.61	27.50	-14.11	42.42
0.3566	41.90	27.69	-14.21	42.71
0.3115	42.12	27.84	-14.28	42.94

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X _S (FA)	$\sigma(A^0)$	μ _s (10 ¹⁸ esu)	μ_s / σ^2	ϵ	
1	2.120	3.410	0.75	109.7	
0.8958	2.120	3.240	0.72	106.448	
0.8628	2.121	3.190	0.70	103.549	
0.7194	2.130	2.910	0.65	100.947	
0.6441	2.134	2.850	0.62	98.598	
0.5758	2.138	2.150	0.60	96.465	
0.5136	2.140	2.650	0.57	94.524	
0.4566	2.146	2.560	0.55	92.748	
0.4043	2.149	2.520	0.52	91.116	
0.3566	2.150	2.410	0.51	89.627	
0.3115	2 158	2 3 4 0	0.50	88 221	

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

Conclusion

The density of aqueous formamide solutions have been accurately measured experimentally at 298.15K. The different volumes (molar volume, Van der Waals volume, electrostriction volume , crystal volume) are determined. Also the dielectric constrants for mixed FA-H₂O solvents were experimentally measured.■



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