Research Article

Volumetric and Viscometric Study of MCM-41 in the Presence of Nicotinamide (A Hydrotropic Agent) in Ethanol

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ABSTRACT

Mesoporous MCM-41 was synthesized by using cetylhexadecyltrimethyl-ammoniumbromide (CTAB) and tetraethylorthosilicate (TEOS). The synthesized MCM-41 was characterized by XRD, Fourier Transformed-Infrared spectroscopy (FT-IR), high resolution transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The characterized showed that MCM-41 possessed high crystallinity, mesospheric morphology and porous structure to be potentially used as a catalyst, drug delivery system. Since no physico-chemical properties like density and viscosity data are available for MCM-41, the present work has been undertaken to carry out the density and viscosity measurements of the solutions of MCM-41 in the presence of nicotinamide, a hydrotropic agent in ethanol at temperatures ranging from 298.15 K to 313.15 K at an interval of 5K.The results have been discussed in the light of molecular interactions.

Keywords: MCM-41, Ethanol, nicotinamide, Partial molar properties, viscosity co-efficient.

INTRODUCTION

The discovery of ordered mesoporous silica materials in 1992 by Mobil Oil Corporation, Taiwan[1] has lead to a variety of applications in diverse areas, such as catalysis, biomolecule separations, adsorption, photo catalysis, sensing etc.[2,3] Recently, research has been focused on the application of these materials as a potential drug delivery system for hydrophobic drugs due to their partial solubility in water, biocompatibility, non-toxic nature, high surface area, porous interiors and adjustable pore diameter.[4-6] It has been documented that the ordered hexagonal mesoporous MCM-41, can be used as a vehicle to overcome the insolubility problem of the hydrophobic drugs.[7]

In recent years, there has been an increasing interest in the measurement of the physico-chemical properties like density, viscosity, conductance and ultrasonic velocity that provide insight into the molecular interactions taking place in the system.[8-10] It is due to the fact that these interactions are the key to understand structural and characteristics properties of the molecules. Well documented reports are available that use viscometric and ultrasonic measurements to access into thermodynamic parameters of biological molecules and interpreted the molecular interactions.[11,12] However, thermodynamic studies of mesoporous silica materials are seldom reported. Hence, the present work aims at studying the physico-chemical properties of mesoporous MCM-41 from density and viscosity measurements in solutions of ethanol + nicotinamide (a hydrotropic agent) at different temperatures ranging from 298.15K to 313.15K at an interval of 5K that will provide better scope to use the mesoporous materials for carriers of partially soluble drugs. The results have been discussed in terms of molecular interactions in presence of a hydrotropic agent in ethanol.

MATERIALS AND METHODS

Materials

Cetylhexadecyltrimethylammoniumbromide (CTAB) used as structure directing agent, Tetraethylorthosilicate (TEOS) used as the silica source, ammonia solution used as mineralizing agent, and nicotinamide used as hydrotropic agent respectively, were purchased from Merck. Ethanol was of AnalaR grade and used after dehydration with molecular sieve over night. Deionized water (Sp. Cond. ~10^{-6} S cm^1) was used throughout the experiment.
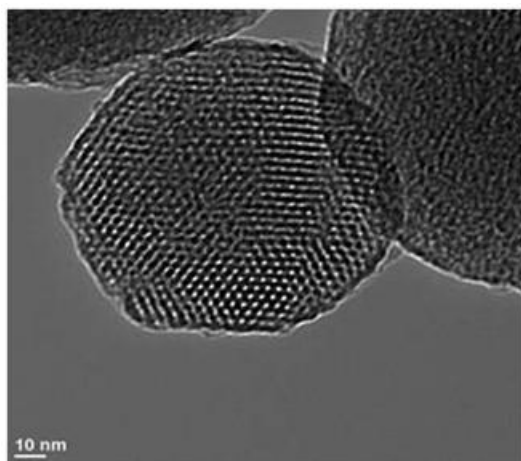
Synthesis of mesoporous MCM-41

2.4 g of CTAB was dissolved in 120ml of water at 25^0C and after complete dissolution 8 ml of NH_3 solution was added with stirring. 10ml of TEOS was added to the solution under vigorous stirring (300rpm). The hydrolysis of TEOS took place during first minute at room temperature. The solution became milky and slurry, whereas, the condensation of mesoporous hybrid material was achieved after 1 hour of reaction. The material was then filtered and allowed to dry under static air at 80ºC for 12 hours. The final mesoporous material was simply obtained by calcinations of the hybrid structure at 550ºC for 5 hours.[3]

Preparation of solution of MCM-41

The solutions of MCM-41 were prepared by using 0.1 M solution of nicotinamide in ethanol as solvent. The concentration of the solutions ranges from 40 ppm to 140 ppm and the solutions were used on the same day.
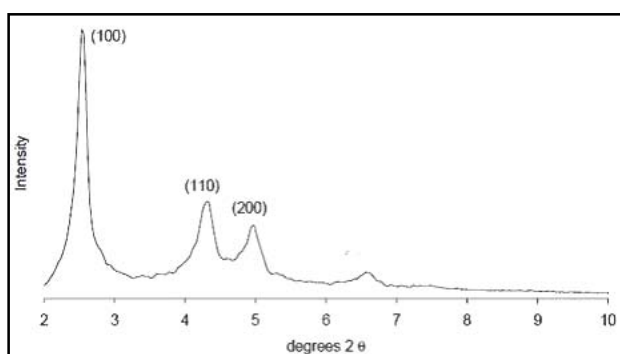
Figure 2: TEM image of mesoporous MCM-41

The X-ray diffraction of MCM-41 depicts the long-range highly ordered mesopores in the amorphous material. The limited three peaks appear at low angle because of the nanometer scale of parameters. Three peaks corresponding to (100), (110) and (200) diffractions are shown in Fig 3.

Figure 3: X-ray diffractogram of MCM-41 showing (100), (110) and (200) reflections assigned to the hexagonal lattice of the mesoporous material.

FTIR investigations

At room temperature MCM-41 exhibits a sharp absorption peak at 3738 cm^{-1} ascribed to free silanol (SiOH) groups. A broad band at 3222 cm^{-1} assigned to hydrogen bonded SiOH groups is perturbed by physically adsorbed water. All the silanol groups should be pendant to the internal surface of MCM-41. The band obtained at

3738 cm^{-1} is also assigned to the geminal silanol groups coming from external surfaces or internal lattice defects. The band at 1640 cm^{-1} ascribed to Si-OH vibration, a broad band at 1090cm^{-1} for symmetric and 808 cm^{-1} at symmetric Si-O stretching vibrations are also given by IR measurements. The pendant hydroxyl groups of SiOH play an important role during functionalization and modification of various precursors onto MCM-41.

Densiometric study

The density of solvent (0.1M nicotinamide in ethanol) and those of the solutions of MCM-41 of different concentrations have been determined at four different temperatures varying from 298.15K to 313.15K. The values of densities are given in Table 1. From the Table, it is evident that the densities of solutions are greater than that of solvent and the density values increase with increase in concentration and decrease with increase in temperature.

A typical plot of density of solution (d) vs. $c^{1/2}$ at 298.15K is given in fig 4.
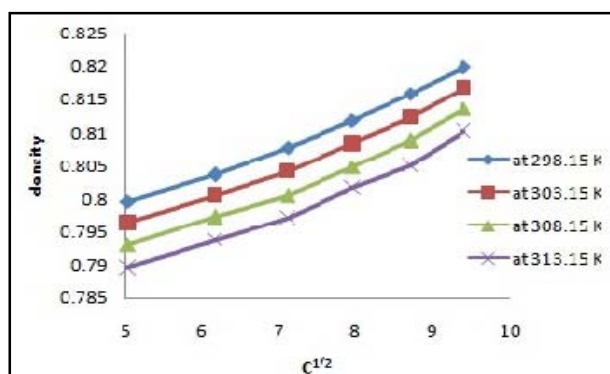
Figure 4: Plot of density vs. $c^{1/2}$ of solutions of MCM-41.

Using the density values (d) of the solutions and solvent (d_0) in Equation (1), the apparent molar volume (V_ϕ) was calculated at each concentration(c) of the solutions. The concentration was changed from ppm scale to molar scale. The molecular weights of the solutions were determined by Equation (3) and then average molecular weight was calculated. Then molecular weight of MCM-41 was calculated which was found to be 158232. The values of V_ϕ^0 and S_v as obtained by Equation(2) are given in Table 2.

Table 1: Values of densities, d (Kg/m^3) of MCM-41 different concentrations in 0.1 M solution of Nicotinamide at four different temperatures

Temp (K)	Solvent	d (Kg/m^3) of MCM-41 at different Conc.c×10^7 (mol dm^{-3})					
		2.5278	3.792	5.056	6.320	7.584	8.848
298.15	0.7958	0.7996.	0.8036	0.8077	0.8118	0.8159	0.8199
303.15	0.7926	0.7964	0.8005	0.8042	0.8083	0.8123	0.8168
308.15	0.7892	0.7931	0.7973	0.8006	0.8049	0.8088	0.8136
313.15	0.7858	0.7896	0.7938	0.7972	0.8017	0.8051	0.8103

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Table 2: Values of V_ϕ (m^{3}mol^{-1}), V_ϕ^0 (m^{3}mol^{-1}), S_v (m$^{9/2}$mol$^{3/2}$), E_ϕ (m^{3}mol^{-1}K^{-1}), E_ϕ^0 (m^{3}mol^{-1}K^1) and S_E (m$^{9/2}$mol$^{-3/2}$K^{-1}) for solutions of MCM-41 at different temperatures.

Temp (K)	c×10^7 mol dm^{-3}	V_ϕ×10^{-7}	V_ϕ^0×10^{-6}	S_v×10^{-10}	E_ϕ×10^{-4}	E_ϕ^0×10^{-7}	S_E×10^{-10}
298.15	2.528	-1.869	-3.496	-3.414	-9.260	0.782	-1.066
	3.792	-2.564			-12.767		
	5.056	-2.937			+0.170		
	6.320	-3.161			-6.445		
	7.584	-3.310			+1.043		
	8.848	-3.402			-11.102		
303.15	2.528	-1.876	-3.872	-3.343	-9.266	0.780	-1.064
	3.792	-2.608			-12.805		
	5.056	-2.874			+0.224		
	6.320	-3.114			-6.405		
	7.584	-3.257			+1.088		
	8.848	-3.430			-11.125		
308.15	2.528	-1.934	-4.856	-3.245	-9.316	0.783	-1.068
	3.792	-2.686			-12.871		
	5.056	-2.837			+0.255		
	6.320	-3.127			-6.416		
	7.584	-3.254			+1.091		
	8.848	-3.474			-11.163		
313.15	2.528	-1.892	-3.934	-3.369	-9.280	2.486	-3.391
	3.792	-2.664			-12.853		
	5.056	-2.849			+0.245		
	6.320	-.3.181			-6.462		
	7.584	-3.218			+1.122		
	8.848	-3.503			-11.188		

Table 3: Values of viscosities η (poise) for solvent (0.1 M solution of Nicotinamide in ethanol), viscosities η (poise) and relative viscosities (η$_r$), A (dm$^{3/2}$mol$^{-1/2}$), B (dm^{3}mol^{-1}), $\Delta\mu_1^{0*}$(KJ mol^{-1}) and $\Delta\mu_2^{0*}$(KJ mol^{-1}) for different solutions of MCM-41 in ethanol + nicotinamide at different temperatures.

Temp (K)	Solvent η×10^3 (poise)	Conc. c×10^7 (mol dm^{-3})	η×10^3 (poise)	η$_r$	A	B×10^{-4}	$\Delta\mu_1^{0*}$	$\Delta\mu_2^{0*}$ × 10^{-7}
298.15 K	9.8290	2.528	9.9810	1.0155	-49.378	15.284	67.309	1.477
		3.792	10.0779	1.0253				
		5.056	10.2348	1.0413				
		6.320	10.3928	1.0574				
		7.584	10.5519	1.0735				
		8.848	10.7107	1.0897				
303.15 K	8.858	2.528	8.9998	1.0155	-35.044	12.450	68.172	1.215
		3.792	9.0958	1.0268				
		5.056	9.1878	1.0372				
		6.320	9.2848	1.0481				
		7.584	9.4317	1.0647				
		8.848	9.5853	1.0821				
308.15 K	7.985	2.528	8.1659	1.0226	-27.004	13.420	69.028	1.326
		3.792	8.2563	1.0339				
		5.056	8.3379	1.0441				
		6.320	8.4779	1.0616				
		7.584	8.6147	1.0788				
		8.848	8.7621	1.0972				
313.15 K	7.148	2.528	7.2703	1.0171	-54.867	17.891	69.857	1.830
		3.792	7.3967	1.0348				
		5.056	7.5171	1.0516				
		6.320	7.6485	1.0700				
		7.584	7.7702	1.0870				
		8.848	7.9104	1.1066				

The negative values of S_v at the experimental temperatures indicate that there are less less solute-solute interactions. In other words once MCM-41 dissolved in the solvent in the presence of nicotinamide (a hydrotropic agent) the cluster of MCM-41 breaks down and the individual MCM-41 particles get solvated without regenerating the cluster. The V_ϕ value varies linearly with $C^{1/2}$ at the experimental temperatures which suggests that the overall structural order is enhanced in ethanol solution. As observed (Table 2) the values of limiting apparent molar volume V_ϕ^0 are negative in all solutions at the experimental temperatures. Since V_ϕ^0 is a measure of solute-solvent interaction, negative value suggests that there is less solute-solvent interaction i.e., MCM-41 particles once saturated with solvent molecules exhibit no further tendency toward interaction with solvent in the presence of nicotinamide.[14] As observed; the V_ϕ^0 values show an irregular trend as the temperature increases. The values of E_ϕ and S_E as obtained from Equation (4) are also given in Table 2. As observed, E_ϕ values show an irregular trend with increase in concentration of MCM-41. From Table 2 it was found that the E_ϕ^0 values are positive in all cases. Since E_ϕ^0 gives an indication of caging or packing effect[15], the positive values of E_ϕ^0 suggest that the structure making effect of MCM-41 is favored in ethanol solvent satisfying the contention that the interaction between the solvated MCM-41 particles and the solvent molecules is favored.

Viscometric study

The experimentally determined values of viscosity (η) for solvent as well as solutions at 298.15, 303.15, 308.15, and 313.15K are represented in Table 3. The relative viscosities (η_r), values of viscosity co-efficient A and B, $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ have been evaluated by means of Equations 6, 7 and 8 and are presented in the same Table.

A perusal of Table 3 shows that the viscosity and relative viscosity values increase with increase in concentration and the viscosity decreases with increase in temperature. The plot of $[((\eta_r/\eta)-1))/c^{1/2}]$ vs. $c^{1/2}$ is shown in figure 5. From the plot, it was shown that viscosity increases with increasing concentrations of MCM-41.
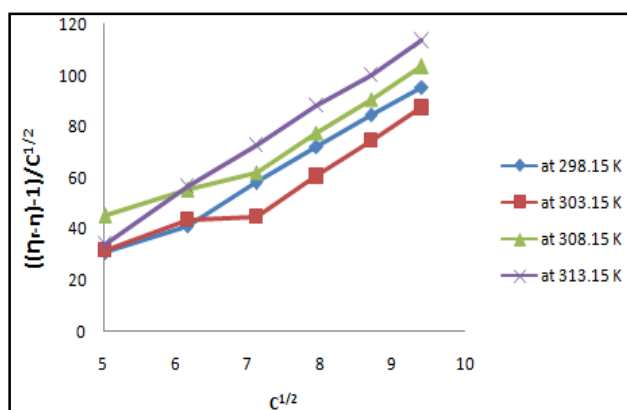

Figure 5: Plot of $[((\eta_r/\eta)-1))/c^{1/2}]$ vs. $c^{1/2}$ of solutions of MCM-41 at different temperatures.

The values of A are negative in all cases. Since A is considered to be a measure of solute-solute interaction, the negative A values may indicate the presence of weak solute-solute interactions in the solutions concerned. The B-coefficient is a measure of the effective solvodynamic volume of the solvated molecules, and is governed by the solute-solvent interactions, i.e., the structural effect of the solvent in solution.[15,16] It is a fact that when a solute dissolves in a solvent, some of the solvent molecules are attached to the solute molecules because of solute-solvent interactions, and this causes an increase in viscosity of solution(a positive contribution to the B - coefficient). On the other hand, these solvent molecules have to be wrenched out of the bulk solvent and this breaking of the solvent structure causes a decrease in viscosity of the solution (a negative contribution B-coefficient).

As observed, the values of B are positive at all temperatures indicating the presence of solute-solvent interactions which is in agreement with the contention corroborative to the negative S_v values stated earlier. Moreover, the values of B are larger as compared to A values. This shows that the solute-solvent interactions dominate over solute-solute interactions i.e., no formation of clusters of MCM-41 particles do not interact further. The viscosity data were also analyzed on the basis of the transition state theory. The values of $\Delta\mu_1^{0*}$ are found to be positive at all temperatures showing positive contribution per mole of the solvent to free energy of activation for viscous flow of solution. The positive values of $\Delta\mu_2^{0*}$ show greater contribution per mole of solute to free energy of activation for viscous flow of the solution and are good agreement with the values of B-coefficient. Again positive and large values of $\Delta\mu_2^{0*}$ indicate the formation of the transition state accompanied by the rupture and distortion of the intermolecular forces in solvent structure.

CONCLUSION

The density and viscosity values were found to increase with concentration and decrease in temperature. The negative value of limiting apparent molar volume (V_ϕ^0) is the indicative of the less solute-solvent interaction. The negative value of A indicates that there is no formation of clusters of MCM-41 after dissolution in the solvent, ethanol in the presence of the hydrotropic agent, nicotinamide.

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