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Research Article

STUDY OF MOLECULAR INTERACTIONS OF NH_2-MCM-41 IN PRESENCE OF NICOTINAMIDE (A HYDROTROPIC AGENT) IN ETHANOL FOR PARTIALLY SOLUBLE DRUGS

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ABSTRACT

Objectives: To study the density, viscosity, and conductance of the solutions of Amine modified MCM-41(NH_2-MCM-41) in the presence of nicotinamide as hydrotropic agent in ethanol solvent at different temperatures ranging from 25 °C to 40 °C at an interval of 5 °C.

Methods: 5 and 10 weight percentages of Amine modified MCM-41(NH_2-MCM-41) were synthesized via co-condensation method using cetyltrimethyl ammonium bromide (CTAB) as structure directing agent, tetra ethyl ortho silicate (TEOS) as silica source, and 3-aminopropyl triethoxy silane (APTES) as amine source. The samples were characterized by scanning electron micrograph (SEM), X-ray powder diffraction (XRD), and Fourier-transfer infrared spectroscopy (FTIR). The density, viscosity and conductance of Amine modified MCM-41 (NH_2-MCM-41) (5 and 10 weight %) have been measured in the concentration range of 40 ppm-140 ppm in ethanolic solution of hydrotropic agent nicotinamide at different temperatures ranging from 25 °C to 40 °C at an interval of 5 °C. The density and viscosity data have been analyzed for the evaluation of limiting apparent molar volume (V_φ^0), limiting apparent expansibility (E_φ^0), Falken-Hagen co-efficient (A), Jones-Dole co-efficient (B). The conductance data have been analyzed by Shedlovsky method to obtain limiting molar conductance (Λ_0) and association constant(K_A). The thermodynamic parameters like change in enthalpy (ΔH^0), entropy (ΔS^0), free energy (ΔG^0), Walden product ($\Lambda_m{}^0\eta_0$) for the ion pair formation have been calculated from the value of ion association constant at constant temperature.

Results: Characterization result indicated that Amine modified MCM-41(NH_2-MCM-41) retained the mesoscopic morphology and porous structure. The results of density and viscosity measurements have been discussed in the light of molecular interactions. The values of limiting apparent molar volume (V_φ^0), Jones-Dole co-efficient (B), activation energy (Es), free energy change, ΔG^o is positive for all the samples in the solvent.

Conclusion: The findings suggest that amine modification increases the solvation of MCM-41 in ethanolic solution of hydrotropic agent nicotinamide.

Keywords: NH_2--MCM-41, Ethanol, Nicotinamide, Apparent molar volume, Partial molar properties, Viscosity co-efficient.

INTRODUCTION

Mesoporous materials have attracted much attention in the field of pharmaceutical science because of their potential application in drug delivery of water insoluble drugs. After their discovery in the 1990s, these materials have been used in other fields. The modification of mesoporous silica materials increase their applications towards adsorption, catalysis, photocatalysis, sensing, biomedical use, etc [1,2,3-5,6]. The chemical modification of the mesoporous matrix with appropriate functional groups is found to be essential for effective delivery of water insoluble drugs than the conventionally used other delivery systems [7,8]. MCM-41(Mobil Composition of Matter number forty one) is probably the most investigated material for this type. Amine functionalized MCM-41 has proved itself useful for so many applications including drug delivery of hydrophobic drugs.

Study of thermophysical properties gives valuable information regarding molecular interactions of a solute in different solvents through various parameters such as limiting apparent molar volume (V_φ^0), limiting apparent expansibility (E_φ^0), Falken-Hagen co-efficient (A_F), and Jones-Dole co-efficient (B_J). Much work has been done on the determination of these parameters for amino acids, electrolytes, drugs, hydrotropic agents, etc., in both aqueous and non-aqueous solvents but less focus has been fetched toward mesoporous materials. In continuation to our previous work [9-11], in this study, we have attempted to study the density, viscosity and conductance of amine modified MCM-41 in the solvent (ethanol) in the presence of a hydrotropic agent (nicotinamide) [16,17] at four different temperatures ranging from 25 °C to 40 °C at an interval of 5°C .The main purpose of this work is to elucidate the molecular interactions taking place in the system [9-15] which will provide a better scope for structural elucidation, characteristic properties, drug delivery activity, mechanism of action, and hydrotropic solubilization of these materials to act as potential carriers for most of the hydrophobic drugs.

MATERIALS AND METHOD

Materials

Cetyltrimethyl ammonium bromide (CTAB), Tetraethyl ortho silicate (TEOS), ammonia solution, and nicotinamide were purchased from Merck, and 3-Aminopropyl triethoxy silane (APTES) and sodium hydroxide were purchased from Sigma-Aldrich. Methanol and ethanol were of Analar grade and used after dehydration with a molecular sieve overnight. Deionized water (Sp. cond. $\sim 10^{-6}$ S cm^{-1}) was used throughout the experiment.

Synthesis

The mixture of Cetyltrimethyl ammonium bromide (CTAB) (2.0 g), 2M sodium hydroxide NaOH (7 ml), and water (480 ml) was heated at 80°C for 30 minutes to attain a pH ≈ 12.3. To this clear solution, various amounts of Tetraethyl ortho silicate (TEOS) (10.04 ml and 5 ml) and 3-Aminopropyl triethoxy silane (APTES) (1.09 ml) were added sequentially and rapidly via injection. Following the injection, a white precipitate was observed after 3 minutes of stirring at 550 rpm. The reaction temperature was maintained at 80°C for 2 hrs. The products were isolated by a hot filtration, washed with an excess amount of water and methanol and dried under vacuum (oven) for 8 hrs at 110°C, and powdered. Calcination was done by acid extraction for which a mixture of methanol (200 ml), concentrated hydrochloric acid (conc. HCl) and as made materials were heated at 60°C for 6 hrs. The resulting surfactant

removed solid products were filtered and washed with water and methanol and dried in oven for 8 hrs at 110°C. The amine modified MCM-41 was synthesized (Fig. 1). The samples are designated as NH_2-MCM-41 (xx) where xx stands for 5 and 10 weight % of the samples.

Preparation of solution of NH_2-MCM-41

The solutions of NH_2-MCM-41(xx) were prepared using 0.1 M solution of nicotinamide in ethanol as solvent. The concentration of the solutions ranges from 40 to 140 ppm, and the solutions were used on the same day.

Measurement of density, viscosity and conductance

The density, viscosity, and conductance values of the solutions were measured as described elsewhere [9,10] at different temperatures ranging from 25 °C to 40 °C at an interval of 5°C.

THEORETICAL ASPECTS

From the density (d), viscosity coefficient (η) and conductance data, the following parameters have been determined.

1. Apparent molar volume, V_φ was calculated by Equation (1) [19].

$$V_\varphi = 1000\ (cd_0)^{-1}\ (d_0\text{-}d)+Md_0^{-1} \quad (1)$$

Where c is the molar concentration, d_0 is the density of the solvent, d is that of the solution and M is the molecular mass of the MCM-41.

2. Limiting apparent molar volume, V_φ^0 was determined by least squares method [19] by fitting the V_φ data to the Masson equation.

$$V_\varphi = V_\varphi^0+S_v\ c^{1/2} \quad (2)$$

Where S_v is the slope of the plot of V_φ versus $c^{1/2}$ plot.

3. Apparent molar expansibility, E_φ was calculated by using equation (3) [19].

$$E_\varphi = E_\varphi^0+(\alpha\text{-}\alpha_0)\ 1000\ c^{-1} \quad (3)$$

Where α and α_0 are the coefficient of thermal expansion of the solution and solvent, respectively, and were obtained from the usual relation [19].

4. Limiting apparent expansibility E_φ^0 was determined by least squares method [19] by fitting the E_φ data to the Masson equation by Equation (4).

$$E_\varphi = E_\varphi^0+S_E\ c^{1/2} \quad (4)$$

Where S_E is the slope of the E_φ versus $c^{1/2}$ plot.

5. The average molecular weight of MCM-41 solution was determined by Equation (5).

$$M = (d\eta/\eta)\times10^6 \quad (5)$$

Where n=40-60.

Then, the molecular weight of MCM-41 was determined by substracting molecular weights of ethanol and nicotinamide from it.

6. The relative viscosity of the solution was determined by Jones and Dole [21] empirical equation as follows:

$$\eta_r = \eta/\eta_0 = 1+Ac^{1/2}+Bc \quad (6)$$

Where η_r is the relative viscosity, η is the viscosity coefficient of the solution, η_0 is that of the solvent, A is Falken-Hagen coefficient and B is Jones-Dole coefficient.

The constants A and B are the intercept and slope of the linear plots of $(\eta/\eta_0\text{-}1)/c^{1/2}$ versus $c^{1/2}$, respectively.

7. The viscosity data have been analyzed on the basis of transition state theory from the relation [20].

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*}+(RT/\ \bar{V}_1^0)1000B\text{-}(\ \bar{V}_1^0\text{-}\ \bar{V}_2^0) \quad (7)$$

Where $\Delta\mu_2^{0*}$ is the contribution per mol of the solute to free energy of activation for viscous flow of the solution.

$$\Delta\mu_1^{0*} = 2.303\ R\ T\ \log\ (\eta_0\ \bar{V}_1^0/hN) \quad (8)$$

Where h and N are Planck's constant and Avogadro number, respectively.

$\Delta\mu_2^{0*}$ is the contribution per mol of the solvent to free energy of activation for viscous flow of the solution.

$$\bar{V}_1^0 = M_{solvent/d} \quad (9)$$

$$\bar{V}_1^0 = V_\varphi^0$$

8. The molar conductance is calculated from the specific conductance value by the relation.

$$\Lambda = 1000\ k/c \quad (10)$$

Where ʌ is molar conductance, k is the specific conductance and c is the concentration of the solution.

9. The approximate limiting molar conductance (Λ0) is obtained from the intercept of the plot between Λ and c1/2 by least squares method [17] using the equation.

$$\Lambda = \Lambda_0 - S\ c^{1/2} \quad (11)$$

Where S is the slope and Λ_0 is the intercept of the plot of Λ versus $c^{1/2}$.

10. The dielectric constant of the solvent is found out using the relation.

$$S = 82.4/\eta_0\ (DT)1/2+8.2\times105/(DT)3/2\ \Lambda_0 \quad (12)$$

Where η_0, D are the coefficients of viscosity, and dielectric constant of the solvent, respectively, at temperature T.

11. The experimental data of conductance measurements of the solution were analyzed using the Fuoss and Shedlovsky extrapolation technique [18].

$$1/\Lambda\ S(Z) = 1/\Lambda_0+K_A/\Lambda_0^2\ c\Lambda S(Z)$$

Where $S(Z) = 1+Z+Z^2/2+Z^3/8$

$$\text{And } Z = S(\Lambda c)^{1/2}/\Lambda_0^{3/2} \quad (13)$$

From the linear plot between $1/\Lambda S$ (Z) and cΛS (Z), Λ_0 and K_A were evaluated from the intercept and slope, respectively. The procedure was repeated till constant values of Λ_0 and K_A are obtained.

12. The standard free energy change, ΔG^0 for the association process is calculated from the following relation [22],

$$\Delta G^0 = -RT\ \ln\ K_A \quad (14)$$

The heat of association ΔH^0 is calculated from the slope of the plot of ln K_A versus 1/T and the entropy change, ΔS^0 from Gibbs-Helmholtz equation,

$$\Delta G^0 = \Delta H^0\text{-}T\Delta S^0 \quad (15)$$

13. The activation energy of the transport process is determined from the relation [25].

14. Λ_0 = A e−Es/RT or log Λ_0=log A-Es/2.303 RT (16)

Where A is the frequency factor, R is the gas constant and Es is the Arrhenius activation energy. From the plot of log Λ_0 versus 1/T, the Es values have been computed from the slope (=−Es/2.303 R).

15. The Walden product ($\Lambda_0\eta_0$) is calculated for the solutions using the coefficients of viscosity of the solvent (η_0) at temperature T.

RESULTS

Characterization of materials

The scanning electron microscopy indicated the two-dimensional hexagonal long range mesoscopic morphology of NH_2-MCM-41 (5 and 10 weight %) (Figs. 2 and 3). The uniform distribution of spherical particles representing the outer surface shows the typical siliceous material.

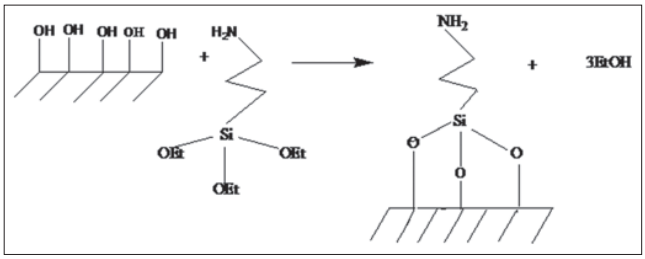

Fig. 1: Mechanism for amine loading

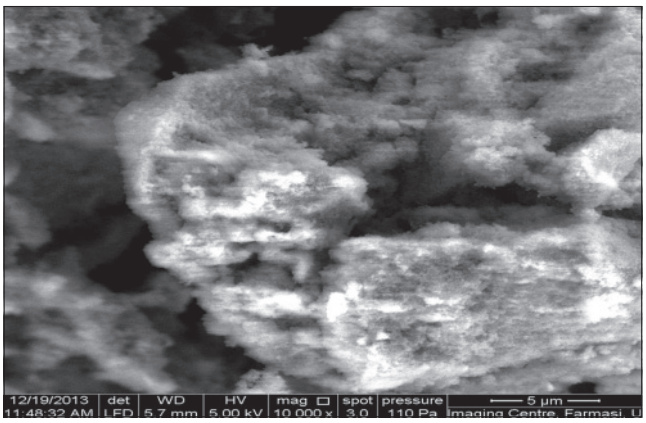

Fig. 2: Scanning electron microscopy image of mesoporous NH_2-MCM-41 (5)

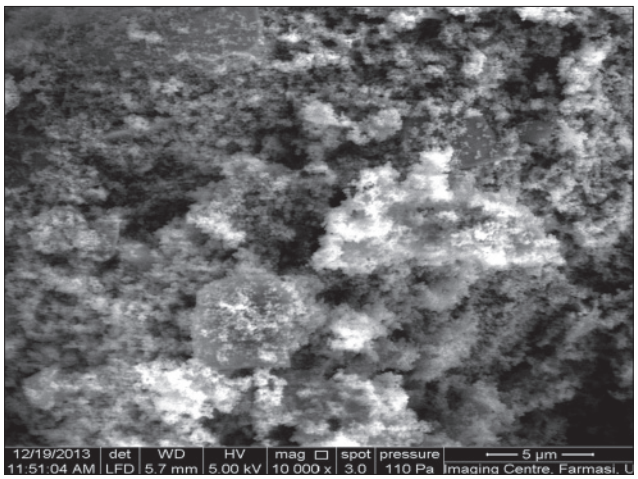

Fig. 3: Scanning electron microscopy image of mesoporous NH_2-MCM-41 (10)

The deflections at d (100) at 2.4°, d (110) and d (200) at 4.2° and 4.4°, respectively, given by the X-ray diffraction of NH_2-MCM-41 are similar to the parent MCM-41. This confirms that the ordered hexagonal symmetry was retained after amine fictionalization.

The Fourier transform infrared spectroscopy spectra of MCM-41 and amine modified MCM-41 are shown in Fig. 5. The absorption bands at 1080-1090, 1620-1640 and 3100-3600/cm are due to Si-O stretching, H-O-H bending and adsorbed water molecules,

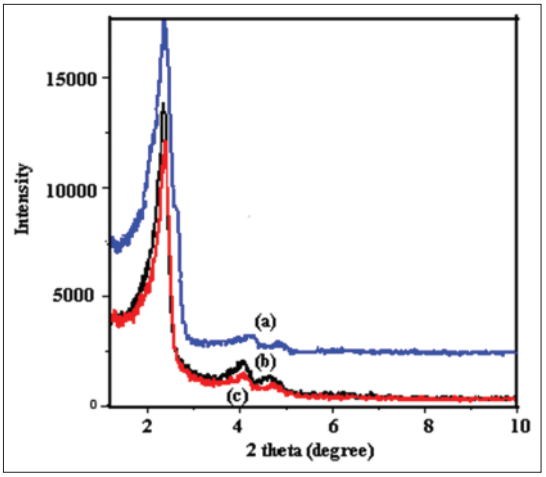

Fig. 4: X-ray diffraction image of mesoporous, (a) MCM-41, (b) NH_2-MCM-41 (5), and (c) NH_2-MCM-41 (10)

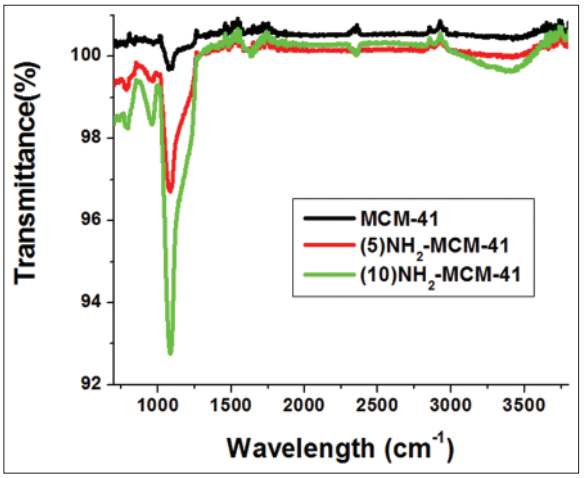

Fig. 5: Fourier transform infrared image of mesoporous MCM-41 and NH_2-MCM-41 (5 and 10)

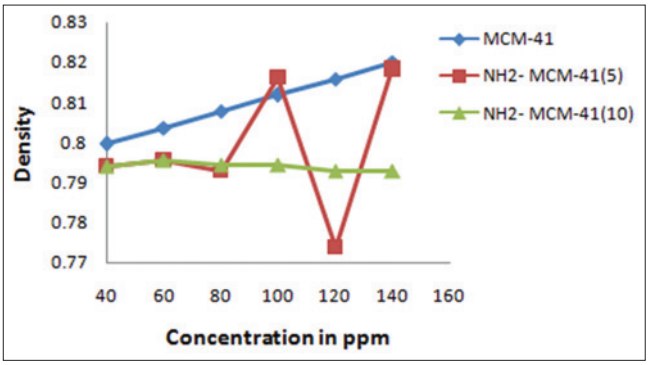

Fig. 6: Plot of density versus concentration of solutions of MCM-41, NH_2-MCM-41 (5), and NH_2-MCM-41 (10) at 25°C

respectively. The presence of N-H bending vibration at 690/cm NH_2 symmetric bending vibration at 1532/cm which is absent in neat MCM-41, indicates the successful functionalization of an amine group on MCM-41.

Densiometric study

The density of solvent (0.1 M nicotinamide in ethanol) and those of the solutions of NH_2-MCM-41 of different concentrations have been determined at four different temperatures varying from 25 °C to 40 °C.

Table 1: Values of densities d (kg/m^3) of solvent, NH_2-MCM-41 (5), NH_2-MCM-41 (10) of different concentrations in 0.1 M solution of nicotinamide at four different temperatures

Density (d) of solvent (0.1 M nicotinamide in ethanol)						
Temp (°C)	25 °C	30 °C	35 °C	40 °C		
d	0.7958	0.7926	0.7892	0.7858		
Density (d) of NH_2-MCM-41 (5) in 0.1 M nicotinamide in ethanol						
Temp (°C)	40 ppm	60 ppm	80 ppm	100 ppm	120 ppm	140 ppm
25	0.7940	0.7955	0.7728	0.8162	0.7738	0.8183
30	0.7914	0.7921	0.7678	0.8149	0.7695	0.8142
35	0.7882	0.7896	0.7640	0.8116	0.7661	0.8124
40	0.7861	0.7872	0.7589	0.8073	0.7617	0.8055
Density (d) of NH_2-MCM-41 (10) in 0.1 M nicotinamide in ethanol						
Temp (°C)	40 ppm	60 ppm	80 ppm	100 ppm	120 ppm	140 ppm
25	0.7940	0.7956	0.7944	0.7945	0.7928	0.7929
30	0.7907	0.7913	0.7902	0.7904	0.7892	0.7893
35	0.7863	0.7889	0.7869	0.7871	0.7851	0.7852
40	0.7841	0.7855	0.7538	0.7842	0.7827	0.7828

Table 2: Values of parameters 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} °C^{-1}), E_φ^0 (m^{3}mol^{-1} °C^{-1}), S_E (m$^{9/2}$mol$^{-3/2}$ °C^{-1}) for solutions of NH_2-MCM-41 (5), NH_2-MCM-41 (10) of different concentrations and temperatures NH_2-MCM-41 (5) in 0.1 M nicotinamide in ethanol

Temp (°C)	c×10^7 moldm^{-3}	V_φ×10^{-7}	V_φ^0×10^{-7}	S_V×10^{-10}	E_φ×10^{-5}	E_φ^0×10^{-6}	S_E×10^{-9}
25	2.558	0.903	4.789	−5.725	−6.742	−0.910	1.108
	3.837	0.117			−3.694		
	5.117	5.667			7.536		
	6.396	−3.988			−2.066		
	7.675	3.621			2.971		
	8.955	−3.137			2.027		
30	2.558	0.611	4.440	−5.166	−6.814	−0.680	0.690
	3.837	0.184			−3.699		
	5.117	6.134			7.664		
	6.396	−4.379			−2.135		
	7.675	3.817			−3.020		
	8.955	−3.023			−2.056		
35	2.558	0.515	4.269	−5.108	−6.839	−1.417	1.907
	3.837	−0.112			−3.748		
	5.117	6.260			7.732		
	6.396	−4.417			−2.142		
	7.675	3.833			3.042		
	8.955	−3.262			2.026		
40	2.558	−0.129	2.589	−2.784	−6.985	−1.515	2.054
	3.837	−0.444			−3.829		
	5.117	6.709			7.851		
	6.396	−4.257			−2.134		
	7.675	4.015			3.085		
	8.955	−2.779			2.767		
NH_2-MCM-41 (10) in 0.1 M nicotinamide in ethanol							
25	2.534	0.904	0.796	−0.498	−0.180	−0.016	0.057
	3.801	0.085			0.233		
	5.068	0.363			0.722		
	6.335	0.275			0.443		
	7.603	0.511			0.195		
	8.870	0.426			0.165		
30	2.534	0.957	1.145	−0.753	−0.172	−0.288	0.355
	3.801	0.447			−2.957		
	5.068	0.611			0.767		
	6.335	0.453			0.474		
	7.603	0.578			0.207		
	8.870	0.484			0.175		

(*Contd...*)

Table 2: ***(Continued)***

Temp (°C)	c×10^7 moldm^{-3}	V_φ×10^{-7}	V_φ^0×10^{-7}	S_V×10^{-10}	E_φ×10^{-5}	E_φ^0×10^{-6}	S_E×10^{-9}
35	2.534	1.456	1.437	−1.067	−0.069	−0.002	0.045
	3.801	0.119			1.142		
	5.068	0.589			0.776		
	6.335	0.436			0.481		
	7.603	0.696			0.234		
	8.870	5.859			0.199		
40	2.534	0.865	0.776	−0.414	−6.967	−1.545	2.103
	3.801	0.119			−3.817		
	5.068	0.517			7.397		
	6.335	0.338			−1.761		
	7.603	0.534			2.815		
	8.870	0.446			3.069		

The values of densities are given in Table 1. From the Table 1, it is evident that the densities of solutions of NH_2-MCM-41 (both) show no regular gradation with concentration. From 40 to 60 ppm, it increases then it suddenly decreases at 80 ppm then increases at 100 ppm. Again it increases at 140 ppm after decreasing at 120 ppm. Again density value of NH_2-MCM-41 (5) is greater than that of NH_2-MCM-41 (10) at all concentrations except in 80 and 120 ppm. It is also seen that density of solutions of NH_2-MCM-41 (5) is the highest at 80 ppm among MCM-41, NH_2-MCM-41 (5), NH_2-MCM-41 (10). The density values for all the solutions decreased with increase in temperature. A typical plot of density (d) versus concentration (C) is shown in Fig. 6.

Using the density values (d) of the solutions and solvent (d_0) in equation (1), the apparent molar volume V_φ, and apparent expansibility E_φ were calculated at each concentration(c) of the solutions. The concentration was changed from ppm scale to molar scale. The values of V_φ^0 and S_v as obtained by equation (5) are given in Table 2.

Viscometric study

The experimentally determined values of viscosity (η) for solvent as well as solutions at 25 °C -40 °C are presented in Table 3. The relative viscosities of solutions are shown in the same table for the corresponding temperature. As found from the table, the viscosity values follow no regular trend with concentration. Comparing with our previous work [9] it is found that the viscosity coefficient is highest for MCM-41except at 60 ppm and 100 ppm.

Conductometric study

It is evident from Table 5 that the values of specific conductance (k), molar conductance (Λ), and limiting conductance ($Λ_0$) increase regularly with increase in temperature for NH_2-MCM-41 (5 weight %, and 10 weight %), indicating less solvation or higher mobility of the ions in the solvent systems studied. This is due to the fact that the increased thermal energy results in greater bond breaking and also variation in vibrational, rotational and translational energy of molecules lead to higher frequency and higher mobility of ions. Between NH_2-MCM-41 (5 and 10), the conductance value of former is more than that of later except for 40 ppm which shows that the conductivity decreases with amine loading.

DISCUSSION

From our previous work [9, 11] we have found that MCM-41 as well as its titania modification (TiO_2-MCM-41) show low solubility due to weak solute-solvent interaction. However the positive values of V_φ^0 mean strong solute-solvent interaction. Negative values of S_V mean weak solute-solute interaction. Negative value of E_φ^0 means no caging effect. The negative values of Sv means there is poor solute-solute interaction for both the weight % i.e. there is no solute-co solute association. The caging effect is absent in amine modified samples as shown by the negative values. The negative values of coefficient A indicate the presence of weak solute-solute interaction, which may be attributed

Table 3: Values of viscosities η (poise) for solvent (0.1 M solution of nicotinamide in ethanol, viscosities η (poise) and relative viscosities ($η_r$) for solutions of NH_2-MCM-41 (5), NH_2-MCM-41 (10) at different temperatures

	NH_2-MCM-41 (5) (15) TiO_2-MCM-41			NH_2-MCM-41 (10)		
Temp (°C)	c×10^7 moldm^{-3}	η×10^3 poise	$η_r$	c×10^7 moldm^{-3}	η×10^3 poise	$η_r$
25	2.558	9.811	0.998	2.534	9.650	0.107
	3.837	10.243	1.042	3.801	10.244	0.114
	5.117	9.849	1.002	5.068	10.124	0.112
	6.396	10.510	1.069	6.335	10.282	0.114
	7.675	10.375	1.055	7.603	10.052	0.111
	8.955	10.116	1.029	8.870	10.157	0.113
30	2.558	8.952	1.010	2.534	8.666	0.978
	3.837	9.574	1.080	3.801	9.217	1.040
	5.117	9.136	1.031	5.068	9.056	1.022
	6.396	9.798	1.106	6.335	9.256	1.044
	7.675	9.739	1.099	7.603	9.094	1.026
	8.955	9.397	1.060	8.870	9.293	1.049
35	2.558	7.976	0.998	2.534	7.721	0.966
	3.837	8.652	1.083	3.801	8.313	1.041
	5.117	8.234	1.031	5.068	8.151	1.020
	6.396	8.844	1.107	6.335	8.389	1.050
	7.675	8.707	1.090	7.603	8.226	1.030
	8.955	8.486	1.062	8.870	8.462	1.059
40	2.558	6.952	0.972	2.534	6.757	0.945
	3.837	7.582	1.060	3.801	7.300	1.021
	5.117	7.181	1.004	5.068	7.196	1.006
	6.396	7.730	1.081	6.335	7.465	1.044
	7.675	7.214	1.009	7.603	7.319	1.023
	8.955	7.422	1.038	8.870	7.540	1.054

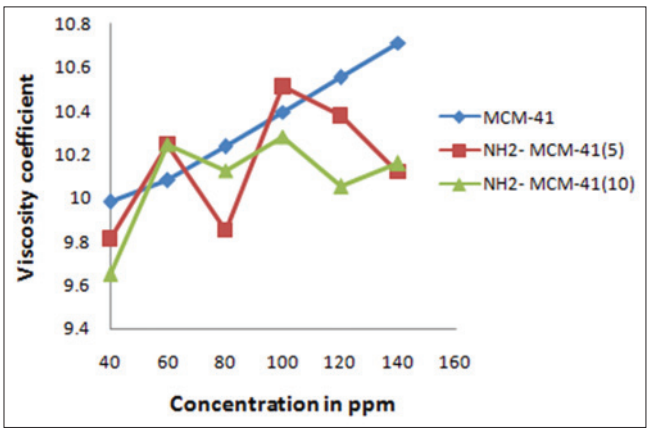

Fig. 7: Plot of viscosity coefficient (η) versus concentration of solutions of MCM-41, NH_2-MCM-41 (5), and NH_2-MCM-41 (10)at 25°C

Table 4: Values of parameters A ($dm^{3/2}\ mol^{-1/2}$), B ($dm^3\ mol^{-1}$), $`V_1^0$(m^3), $\Delta\mu_1^{0*}$(kJ mol^{-1}), $\Delta\mu_2^{0*}$ (KJ mol^{-1}) for solutions of MCM-41, NH_2-MCM-41 (5), NH_2-MCM-41 (10) of different concentrations at different temperatures

Parameters	NH_2-MCM-41 (5)				NH_2-MCM-41 (10)			
	25 °C	30 °C	35 °C	40 °C	25 °C	30 °C	35 °C	40 °C
A	−23.81	−1.71	−24.93	−43.00	−38.09	−72.55	−120.11	−206.97
$B\times10^{-4}$	9.26	11.49	14.05	10.40	9.52	14.15	20.54	29.70
Δμ10*	67.30	68.17	69.02	69.85	67.30	68.17	69.02	69.85
$\Delta\mu2_0\times10^{-7}$	1.39	1.60	1.87	1.35	1.02	1.54	2.25	3.17
B/V_φ^0	0.0019	0.00260	0.0032	0.004	0.0119	0.0123	0.0142	0.0381

Table 5: Values of specific conductance (k) (Scm^{-1}), molar conductance ($Scm^2\ mol^{-1}$) and limiting molar conductance (Λ_0) ($Scm^2\ mol^{-1}$) for different concentrations of NH_2-MCM-41 (5 and 10) at different temperatures

Temp (°C)	Conc. (ppm)	Specific conductance (k)		Molar conductance (Λ)		Limiting molar conductance (Λ_0)	
		NH_2-MCM-41 (5)	NH_2-MCM-41 (10)	NH_2-MCM-41 (5)	NH_2-MCM-41 (10)	NH_2-MCM-41 (5)	NH_2-MCM-41 (10)
25	40	1.287	1.425	5031.274	5623.520	545.55	465.89
	60	1.345	1.146	3505.343	3014.996		
	80	1.323	1.109	2585.348	2188.240		
	100	1.267	1.096	1980.926	1730.071		
	120	1.263	0.696	1645.603	915.4281		
	140	1.330	0.767	1485.204	864.7125		
30	40	1.488	1.698	5817.045	6700.868	249.68	584.88
	60	1.543	1.300	4021.371	3420.153		
	80	1.485	1.253	2901.921	2472.376		
	100	1.423	1.119	2224.828	1766.377		
	120	1.400	0.994	1824.104	1307.379		
	140	1.452	1.023	1621.441	1153.326		
35	40	1.632	1.893	6379.984	7470.403	440.15	688.98
	60	1.739	1.428	4532.187	3756.906		
	80	1.634	1.308	3193.090	2580.900		
	100	1.497	1.275	2340.525	2012.628		
	120	1.403	1.128	1828.013	1483.625		
	140	1.519	1.236	1696.259	1393.461		
40	40	1.848	2.023	7224.394	7983.425	524.19	709.40
	60	1.927	1.598	5022.153	4204.157		
	80	1.793	1.437	3503.801	2835.438		
	100	1.591	1.380	2487.492	2178.374		
	120	1.500	1.234	1954.392	1623.044		
	140	1.603	1.327	1790.061	1496.054		

Table 6: Thermodynamic parameters K_A ($dm^3\ mol^{-1}$), $\Lambda_0\eta_0$, ΔG^0 (J mol^{-1}), ΔH^0 (J mol^{-1}), ΔS^0 (J $mol^{-1}\ K^{-1}$) and E_s (J mol^{-1}) at different temperatures

	Temp (K)							
Parameters	NH_2-MCM-41 (5)				NH_2-MCM-41 (10)			
	25 °C	30 °C	35 °C	40 °C	25 °C	30 °C	35 °C	40 °C
KA	−31,800	−15,378	−23,422	−25,066	−31,636	−33,432	−34,654	−33,562
$\Lambda_0\eta_0$	5.36	2.21	3.51	3.74	4.57	5.18	5.50	5.07
ΔG^0	31411	30107	31681	32372	31398	32064	32685	32372
ΔH^0	4839.25				10082.09			
ΔS^0	−89.12	−83.35	−87.10	−87.92	−71.49	−72.51	−73.35	−73.60
E_s	6564.06				22141.99			

to the formation of a sheath of ethanol molecules around the solute resulting in the weakening of solute-solute interaction. The positive value of B in NH_2-MCM-41 may be ascribed to the structure making tendency of the solute in the solvent. $\Delta_\mu20$, the Gibbs free energy of activation for viscous flow of solution is positive and also larger than the free energy of activation for viscous flow of solvent ($\Delta_\mu10$) for net structure makers. This suggests that there is strong interaction between the solute and solvent molecules in the transition state than in the ground state. Hence, in the transition state, the solvation of the solute molecules is more favored in the free energy terms.

The solvation can be judged from the hydration number (B/V_φ^0) as given in table 4.These values are indicatives of solvated or unsolvated solute molecules. The B/V_φ^0 values are higher in NH_2-MCM-41(10) which indicates that NH_2-MCM-41(10) is more solvated. This may be due to formation of hydrogen bonding of amine group with the solvent molecules.

A perusal of table 6 shows that association constant (K_A) shows no regular trend with increase in temperature. As the weight percentage of amine increases, there is a variation trend observed in Walden product values. From this value it is found that NH_2-MCM-41(5) is highly solvated in the solvent. It is evident that the activation energy, Es, is positive for all the samples in the solvent. The free energy change, ΔG^o, values are positive for all the systems studied. This shows that the dissociation process is favored over the association process in the

solvent. The positive values of ΔH^{o} show that the association process is endothermic in nature and the negative values of ΔSo indicates that randomness is decreased in the solvent system.

CONCLUSION

The positive values of V_{φ}^{0} and B indicate that solution of amine modified MCM-41 is favored in ethanol. The caging effect is absent in both weight % NH_2-MCM-41, which was present in neat MCM-41 as shown by the positive value of E_{φ}^{0} [9]. The negative values of coefficient A indicate the presence of weak solute-solute interaction, which may be attributed to the formation of a sheath of ethanol molecules around the solute resulting in the weakening of solute-solute interaction. The transition state treatment of viscosity data indicates that there is strong interaction between the solute and solvent molecules in the transition state than in the ground state. The association process is endothermic in nature and dissociation process is favored over the association process in the solvent.

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Author Queries???

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