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Pre-requisite physico-chemical studies of 1,3,5 triazine for micro mixing with wax emulsion + 4-nonyl phenol ethoxylate, estimated with SEM technique

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Density ($\rho/10^3 \text{ kg m}^{-3}$), apparent molar volume ($V_2/10^6 \text{ m}^3 \text{ mol}^{-1}$) and viscosity ($\eta, \text{ g cm}^{-1} \text{ s}^{-1} = \text{poise}$, P; $\text{P} = 0.1 \text{ kg m}^{-1} \text{ s}^{-1}$, SI unit) for 5.0–60.0 mmol kg^{-1} 1,3,5 triazine (melamine) at interval of 5.0 mmol kg^{-1} were determined. The calculated data were regressed and extrapolated to infinite dilution ($m \rightarrow 0$) and used to calculate free energy of activation ($\Delta\mu_2^0/k\text{J mol}^{-1}$). The latter three functions illustrate feasibility of micromixing of melamine with paraffin wax emulsifier + 4-nonyl phenol ethoxylate, a nonionic surfactant in aqueous solution.

Keywords: Intrinsic viscosity; Activation energy; Surfactant; Melamine; poly(acrylic acid)

1. Introduction

Currently triazine has become an elegant core material for resin and macromolecule preparations [1]. Recently, Singh [2] and Yadav [3] used it for developing an adhesive force on the cellulosic paper strip for impregnation of transitional metals and salts for adsorption of toxic gases. Melamine does show a positive response for reactions of surfactants, biomolecules and other additives, due to 3 amino ($-\text{NH}_2$) functional groups at 1, 3 and 5 positions in the ring. It has been chosen to develop new microstructure with wax and nonyl phenol ethoxylate. The N^+ ionic atoms of it induce intra/intermolecular interactions causing torsional forces and disruption of electron distribution forming dipoles. It can deform, stress or strain solutions depicted by density and viscosity data, thus interactions are of fundamental significance [2,3] for biochemical sciences. Furthermore, a treatment of transition state theory including partial molal volume and intrinsic viscosity B together resolve the structure breaking and making actions. Free energy of activation for structural changes has been of thermodynamic interest for linkages with medium. Thus the ethoxylate surfactant

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interacts with melamine and wax surfaces through electrostatic and van der Waal's forces. Hence dispersion stability of the solid particles [4] like wax become the subject of investigations. The 4-nonyl phenol ethoxylate is electrically dispersed dishwashing product and with different concentrations has been noted for the stability of coal suspensions [5]. Notably use of a free high molecular mass hydroxyethylcellulose for depletion of flocculation of the polymerically stabilized polystyrene [6] and application of neutral surfactants to agglomerate ink particles during paper de-inking has been reported [7]. Thus, an aqueous solution of ethoxylate surfactants is chosen for micromixing for effective homogenous mixing of melamine and wax. First, dispersion of the particles in an individual dispersion for subsequent mixing of the two dispersions has been illustrated along with their flocculation in homogenous mixture. Such a mechanism is subjected for studies with triazine stabilized by poly(acrylic acid), and wax particles, stabilized by 4-nonyl phenol ethoxylate. The hydrogen bondings that occur between acrylic acid and ethoxylate surfactant are assumed to facilitate a formation of melamine–wax linkages with subsequent flocculation. Since poly(acrylic acid) acts as polyelectrolyte and absorbs water almost two times its own weight, it is taken as an ideal stabilizer. Present studies illustrate a role of the molecular functions of melamine with objectives that it interacts [8,9] with wax molecules + 4-nonyl phenol ethoxylate solutions. Physico-chemical characterization [10–12] decides the nature of micromixing of melamine with the chosen additives and enhances applicability [13] for better micromixing methods and selection of surfactant to facilitate the phenomenon.

2. Experiments and procedure

2.1. Materials and methods

Melamine (AR, E. Merck, 99.99%) and water-based paraffin wax emulsifier (Gujchem, India) were used as received and 0.1% aqueous 4-nonyl phenol ethoxylate (Gujchem, India) prepared. Poly(acrylic acid, 4500 g mol⁻¹, E Merck) was diluted to 10% w/w aqueous solutions. Melamine and 4-nonyl phenol ethoxylate were dried at 420 K and 320.15 K under vacuum for 24 h, stored over P₂O₅ in desiccators and re-dried before use, respectively. Dryness was checked by mixing a small quantity of them separately with a small amount of silica gel plus anhydrous CuSO₄ salt. The latter did not respond to colour change. Demineralized triple distilled water over acidified potassium dichromate and then alkaline permanganate was used. Dissolved air is boiling off, conductivity was found to be 10⁻⁶ Ω⁻¹ cm⁻¹ and used for solution prepared w/w by same day to avoid hydrolysis. Weighings were made with 0.01 mg Dhona balances model DX100. Distilled water deionized by passing through two Cole–Parmer mixed bed ion exchange column, vacuum corrections were applied to all weighing.

2.2. Density and viscosity measurements

Densities and viscosities were measured with bicapillary pycnometer of 20 × 10⁻³ dm³ and survismeter [14] (calibration number-06070582/1.01/C-0395, NPL, Govt. of India, New Delhi) thermostated to better than ±0.01°C for 20 min, read by Beckman thermometer. Temperature was maintained by electric relay encircuited with contact thermometer and 25 W immersion rod along with circulation of cold water by

circulatory pump through copper coil immersed in a water bath. The solutions in an apparatus were thermostated for about 30 min. The pycnometer and survismeter at 298.15 K were calibrated with aqueous sodium chloride solution and water, respectively. An absolutely dried empty pycnometer was filled with water and solution separately was weighed with 1×10^{-5} g reproducibility and similar solutions were taken in viscometer for their flow times noted with electronic racer with ± 0.01 s. Errors in density and viscosity were calculated from weights and flow times, respectively.

2.3. Melamine dispersion

The 8% melamine dispersions were prepared w/w by using an increasing amount of poly(acrylic acid) dispersant for a stable dispersion. The prepared dispersion was gently mixed in an end over end tumbler for 45 h for melamine reaction with the poly(acrylic acid). Additionally, a control was prepared without acrylic acid, dispersant to ensure inherently no interaction of melamine with wax. The micromixing was based on a 1:1 ratio of melamine and wax v/v and wax emulsion added to the melamine dispersion, afterwards centrifuged for 25 min at 3500 rpm. The supernatant is removed and sediment obtained from the micromixing, dried and prepared for analysis.

2.4. Analysis technique

The wax, melamine and sediment were viewed with a scanning electron microscope (SEM). The wax emulsions were placed on graphite stubs and were subsequently frozen and dried in liquid propane at -180°C with a Reichert KF 80 freeze plunger. The frozen samples were transferred under liquid nitrogen into slots in copper block ($63 \times 63 \times 15 \text{ mm}^3$) completely immersed in liquid nitrogen in a plastic container. Nitrogen prevented the condensation of the moisture onto the sample. The copper block thereafter was transferred to a Fission high vacuum unit with immediate evacuation. Freezing and drying were carried out for 48 h, over which the temperature steadily increased back to room temperature. The samples were coated with chromium in an ion beam coater, model 681 and melamine and sediments were placed on the polished side of the graphite stubs using double-sided carbon tape removing an excess particles. Changing of the particles was observed and thereafter the samples coated with ruthenium tetroxide and processed particles were viewed with Stereoscan 360 Cambridge scanning electron microscope.

3. Result and discussion

The ρ values were calculated from $w/w_0 + 0.0012[1 - (w/w_0)]$ relation, the w and w_0 are weights of solution and solvent filled pycnometer, and ρ , ρ_0 and $0.0012 \text{ kg mol}^{-1}$ are solution, solvent and air density, respectively. The $(1 - w/w_0)$ is buoyancy correction to weights, standard deviation in ρ was calculated [13] and the ρ values were used to calculate V_2 as under

$$V_2 = 1000 \frac{\rho_0 - \rho}{m\rho_0\rho} + \frac{M}{\rho} \quad (1)$$

Here M is the molar mass of melamine, an error in V_2 , calculated from $\pm\Delta\rho 1000 m^{-1}$. The V_2 values on regression with m extrapolated to $m \rightarrow 0$, will be termed limiting apparent molal or partial molal volumes, \bar{V}_2^0 . The V_2 with m show a polynomial relation with S_v and S'_v slope values. The \bar{V}_1^0 of water is calculated from $18.01/\rho_0$ relation. The \bar{V}_2^0 values denote melamine–water while S_v and S'_v melamine–melamine are known as pair-wise interactions, respectively. The η values of the solutions are calculated from the $\eta = \rho t / (\rho_0 t_0) \eta_0$ and relative viscosity $\eta_r = \eta / \eta_0$ relations, the t flow time of solution and t_0 of solvent. Here, η and η_0 represent the viscosities of the solution and solvent, respectively. Concentration dependence of pair-wise interactions is expressed by fitting η_r values in an empirical relation given by Jones-Dole [15] as follows

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm. \quad (2)$$

Falkenhagen *et al.* [16] demonstrated long large interionic forces with $m^{1/2}$ and coefficient A could be calculated from the Debye–Huckel Onsager equation, measuring molecular interactions. B in equation (2) is Jones–Dole coefficient depicting water-melamine interactions and could be fitted to Huggins equation depicting similar effects on hydrodynamic volume. Martin, Tyrell [17] and Phang [18] modified equation (2) for aqueous salts, and coefficient A for a nonelectrolyte like melamine is almost zero. Thus an extended Jones–Dole equation given below is fitted

$$\frac{\eta_r - 1}{m} = B + Dm + D'm^2. \quad (3)$$

The D and D' are slope values representing pair-wise interactions and their values for melamine show opposite orders. The B values represent the values of intrinsic viscosity or the absolute values at $m=0$ concentration. The values of B are known as Jones–Dole coefficient. The melamine with heterocyclic benzene ring having the three $-\text{NH}_2$ and 3π conjugations if dissolved in water to obtain the aqueous solutions, and their viscous flow (through fine capillary of viscometer) requires some amount of activation energy (E^*). The E^* is calculated from the B values with Arrhenius equation given as follows

$$\ln(B) = \ln F - \frac{E^*}{RT}. \quad (4)$$

The $\ln B$ against $1/T$ plot gives F as intercept and is referred to as frequency factor and $-E/R$ is slope, $R = 8.314 \text{ kJ mol}^{-1}$. The E^* values are calculated and independent of temperature and represent the minimum thermal energy for interactions and micromixing. The η data are examined for transition state theory of η_r as per Feakins *et al.* [19] as follows

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} - \bar{V}_1^0 \left[\frac{(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})/RT}{1000} \right]. \quad (5)$$

The B , \bar{V}_1^0 and \bar{V}_2^0 are as usual, $\Delta\mu_2^{0*}$ and $\Delta\mu_1^{0*}$ contributions mol^{-1} of melamine and water to the free energies of activation for viscous flow and $\Delta\mu_1^{0*}$ is calculated as follows

$$\Delta\mu_1^{0*} = RT \ln \left(\frac{\eta_0 \bar{V}_1^0}{hn} \right). \quad (6)$$

Table 1. Densities $\rho/10^3 \text{ kg m}^{-3}$, viscosities $\eta/0.1 \text{ kg m}^{-1} \text{ s}^{-1}$, apparent molal volumes $V_2/10^{-6} \text{ m}^3 \text{ mol}^{-1}$, reduced viscosities $(\eta_r - 1)/m$ (in kg mol^{-1}), with standard errors in the data for aqueous melamine. Activation energy $E^*/\text{kJ mol}^{-1}$ and frequency factor F .

mmol kg^{-1}	$\rho \pm 1 \times 10^{-5}$	V_2	$\eta \pm 1 \times 10^{-5}$	$(\eta_r - 1)/m$	E^*	F
293.15 K						
5.02	0.99810 ± 4.3	146.90 ± 8.72	0.92414 ± 14.90	-15.46165	-5.637	-0.14
10.56	0.99810 ± 4.3	136.06 ± 4.14	0.90968 ± 15.04	-8.71619	-2.362	-0.09
14.98	0.99922 ± 4.3	57.62 ± 2.92	0.89024 ± 15.23	-7.43995	8.455	0.11
17.98	0.99934 ± 4.3	62.29 ± 2.43	0.88685 ± 15.26	-6.38663	4.822	0.03
30.17	0.99989 ± 4.3	69.94 ± 1.44	0.89683 ± 15.18	-3.47612	13.560	0.19
32.19	1.00009 ± 4.3	67.28 ± 1.35	0.89575 ± 15.19	-3.29121	1.172	-0.02
35.48	1.00031 ± 4.3	66.53 ± 1.23	0.89445 ± 15.20	-3.02270	-14.084	-0.30
298.15 K						
5.02	0.99704 ± 4.3	129.25 ± 8.73	0.81868 ± 14.90	-16.14737		
10.56	0.99745 ± 4.3	88.41 ± 4.14	0.80078 ± 15.09	-9.57937		
14.98	0.99786 ± 4.3	71.78 ± 2.92	0.78779 ± 15.23	-7.72598		
17.98	0.99815 ± 4.3	64.63 ± 2.43	0.7742 ± 153.8	-7.28510		
30.17	0.99877 ± 4.3	69.00 ± 1.45	0.81221 ± 149.8	-2.92778		
32.19	0.99831 ± 4.3	86.88 ± 1.36	0.80024 ± 151.0	-3.16142		
35.48	0.99831 ± 4.3	90.53 ± 1.23	0.78642 ± 152.4	-3.30543		
303.15 K						
5.02	0.99572 ± 4.3	112.33 ± 8.74	0.73074 ± 149.2	-16.85755		
10.56	0.99587 ± 4.3	105.60 ± 4.15	0.72119 ± 150.2	-9.14682		
14.98	0.99599 ± 4.3	103.59 ± 2.93	0.71621 ± 150.8	-6.86479		
17.98	0.99610 ± 4.3	101.12 ± 2.44	0.71001 ± 151.5	-6.15138		
30.17	0.99731 ± 4.3	71.00 ± 1.45	0.72635 ± 149.8	-2.98755		
32.19	0.99755 ± 4.3	66.83 ± 1.36	0.71346 ± 151.3	-3.30156		
35.48	0.99779 ± 4.3	65.56 ± 1.23	0.6979 ± 153.10	-3.54473		

The h and N are Planck's constant and Avogadro number, respectively, the $\Delta\mu_2^{0*}$ are calculated from a relation given as follows

$$\Delta\mu_2^{0*} - \Delta\mu_1^{0*} = -\left(\frac{RT}{\bar{V}_1^0}\right)[1000B - (\bar{V}_1^0 - \bar{V}_2^0)]. \quad (7)$$

The $\Delta\mu_2^{0*}$ values are higher than those of $\Delta\mu_1^{0*}$ which predicts the viscous flow as a difficult process with complex of melamine due to interactions with water. The values of ρ and \bar{V}_2 ; and η and $(\eta_r - 1)/m$; and E^* and F are given table 1, and of the \bar{V}_2^0 and B along with the first- and second-order slope values in table 2. The $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$, and $\Delta\mu_2^{0*} - \Delta\mu_1^{0*}$ values are given in table 2. The values of the ρ and η are plotted in figure 1(a), along with \bar{V}_2 in figure 1(b) and $(\eta_r - 1)/m$ against m in figure 1(c), similarly B and \bar{V}_2 in figure 2(a), and S_v and S'_v values in figure 2(c) while D and D' in figure 2(c). The figure 2(d-f) depict structures of melamine, nonyl phenol ethoxylate and poly(acrylic acid), respectively. The SEM micrographs for wax + nonyl phenol ethoxylate, melamine + poly(acrylic acid) along with their mixed dispersion in figure 3. Likewise the mechanistic view of the 4-nonyl phenol ethoxylate and poly(acrylic acid) is shown in figure 4. The wax emulsions in figure 5(a) and (b), and of melamine in figure 6(a) and (b) while melamine is without and with poly(acrylic acid) in figure 7(a) and (b), and the figure 8(a) and (b) represent melamine treated with poly(acrylic acid) followed by wax emulsion. Figure 1(a) represents trend of the ρ and η values with a regular increments with m at each temperature except 303.15 K.

Table 2. The coefficients of regression analysis of reduced viscosity and molal volume \bar{V}_2^0 of melamine, and free energies of activation of water, $\Delta\mu_1^{0*}$ and melamine $\Delta\mu_2^{0*}$, in solutions.

Temperature (K)	B	D	D'	\bar{V}_2^0	S_v	S'_v
293.15	-19.73112	1093.322	-17923.73	208.89	-12069.72	234250.27
298.15	-20.74970	1127.203	-17966.79	171.48	-9894.53	218143.50
303.15	-22.53559	1401.094	-24731.00	125.34	-1717.16	0.00
	$\Delta\mu_1^{0*}$	$\Delta\mu_2^{0*}$	$\Delta\mu_2^{0*} - \Delta\mu_1^{0*}$			
293.15	-21.9646	-2667.6183	-23.174			
298.15	-22.2158	-2850.1994	-18.2173			
303.15	-22.4697	-3149.2501	-11.8118			

Units: $B/\text{kg mol}^{-1}$, $D/(\text{kg mol}^{-1})^2$, $D'/(\text{kg mol}^{-1})^3$; $\bar{V}_2^0/10^{-6} \text{ m}^3 \text{ mol}^{-1}$, $S_v/10^{-6} \text{ m}^3 \text{ kg}^{-1} \text{ mol}^{-2}$, $S'_v/10^{-6} \text{ m}^3 \text{ kg}^{-2} \text{ mol}^{-3}$. The $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$, in kJ mol^{-1} .

Such order of η values depicts a regular Newtonian flow of melamine. A regular increment in ρ values at 303.15 K represents slightly stronger pair wise interactions and remains effective at 298.15 K around 0–0.03 mol kg^{-1} melamine (figure 1a). Afterwards a decrease in ρ values and further slight increment by 8.76 kg m^{-3} , illustrate a disruption in pair-wise interactions attributed to micelle formation and instantaneous disruption followed by a quick reorganization. Thus, it becomes inevitable to study physico-chemical characterization of melamine prior to micromixing with poly(acrylic acid) and 4-nonyl phenol ethoxylate and regulate micromixing and dispersion dynamics. Thus interaction mechanism of melamine with poly(acrylic acid) and nonyl phenol ethoxylate stabilizers give an insight of action. Unlike the order of ρ at 298.15 K, the trends at 293.15 K is noted to be reverse and ρ values from 0 to 0.0138 mol kg^{-1} increase with slightly larger magnitude than those of 298.15 K and 303.15 K do. Afterwards the ρ values show a linear increase at 293.15 K (figure 1a). It depicts slightly stronger pairwise interactions at around lower concentration, which normalized for higher concentrations. It denotes a stronger activity of melamine in micromixing and dispersion processes, as the ρ values are directly proportional to the intermolecular forces a sole player for an action mechanism. The η values unlike ρ show a regular decrease by 0.01446, 0.0179 and 0.00955/ $0.1 \text{ kg m}^{-1} \text{ s}^{-1}$ at 293.15 K, 298.15 K and 303.15 K, respectively, a minimum decrease in η values is evident at higher temperature. It depicts a mild concentration effect at higher temperature, or stability in pair-wise interactions with concentration at 303.15 K. Thus micromixing and dispersion may be more effective at higher temperature, however a decrease in η values with temperature is observed to be 0.10546 from 293.15 K to 298.15 K and 0.08794/ $0.1 \text{ kg m}^{-1} \text{ s}^{-1}$ from 298.15 K to 303.15 K. Comparably these show larger decrease in η values with temperature rather than concentration and a substantial micromixing and dispersion. Thus the thermal energy rather than concentration gradient weaken intermolecular forces making melamine accessible for mixing and dispersing. Unlike a 2% decrease in η with temperature, the melamine reports a 5.535/ $0.1 \text{ kg m}^{-1} \text{ s}^{-1}$ decrease in η per degree. However melamine restricts to a Newtonian flow and $(\eta_r - 1)/m$ values show an increase with concentration and a net water structure breaker due to stronger interactions with water with a larger size hydrodynamic sphere (figure 1c). The higher $(\eta_r - 1)/m$ with temperature prove structure-breaking action and activation energy of viscous flow (table 2) do not show any fixed order of values and prove that during flow the symmetry of melamine does not remain fixed. Thus melamine occupy many conformational states, some out of them require low energy of optimization and the

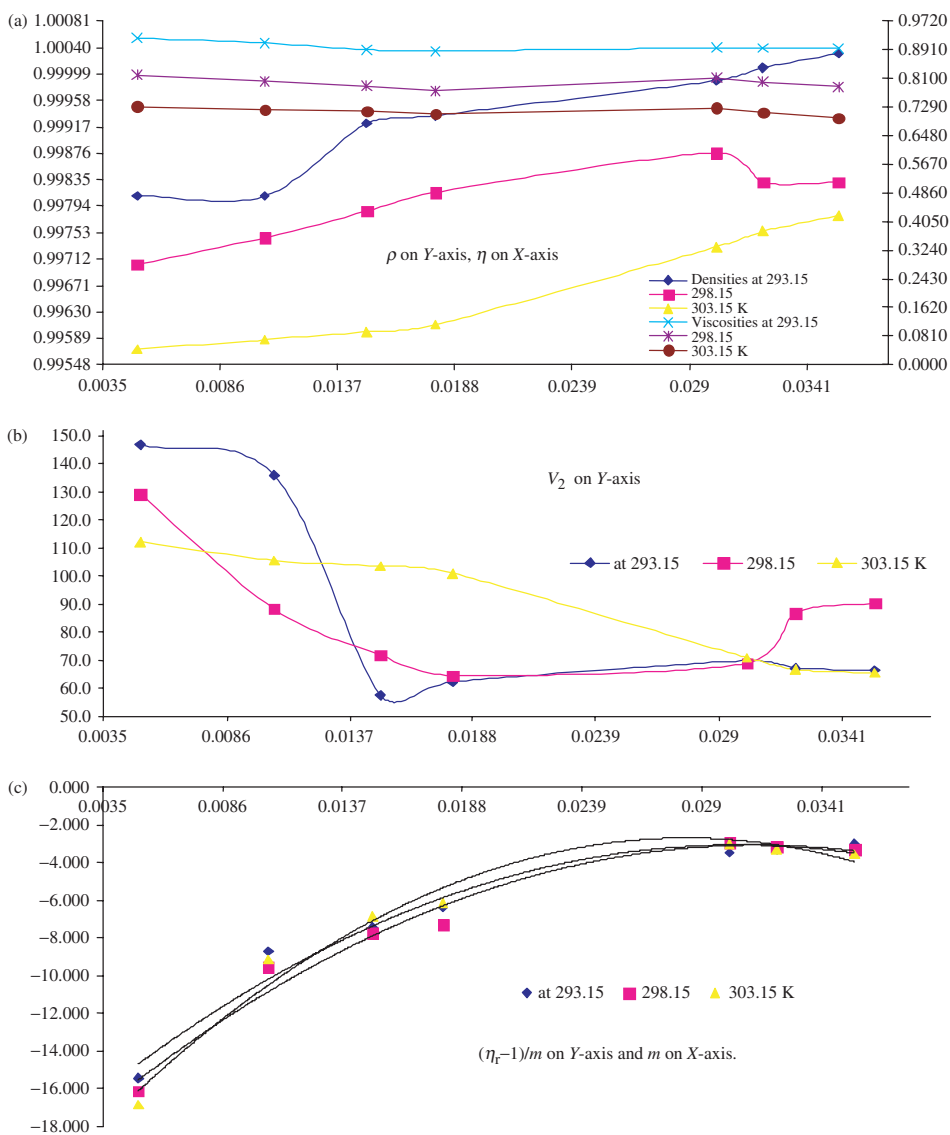


Figure 1. (a) Y-axis at left hand side represents densities and on right hand side the viscosities, the molalities are plotted on X-axis, of aqueous melamine solutions at three temperatures. Likewise the, (b) Y-axis represents the V_2 and the X-axis the values of the m , (c) Y-axis $(\eta_r - 1)/m$, the reduced viscosities and the molalities are on X-axis.

others higher. The E^* values results a disorderliness and frequency factor F seems associated to the conformational states with a low value (table 1) with no fixed trends. It could be amounted to the changing states of the molecule. Contrary to a regular increase in $(\eta_r - 1)/m$ against m (figure 1c), the V_2 versus m show a continuous decrease at around $5.02 \text{ mmol kg}^{-1}$. The 17.65 decrease (figure 1b) from 293.15 K to 298.15 K and $16.92/10^{-6} \text{ m}^3 \text{ mol}^{-1}$ from 298.15 K to 303.15 K (table 1) supports a lowering in size of hydrodynamic sphere. However, with concentration the ρ values and V_2 at 303.15 K

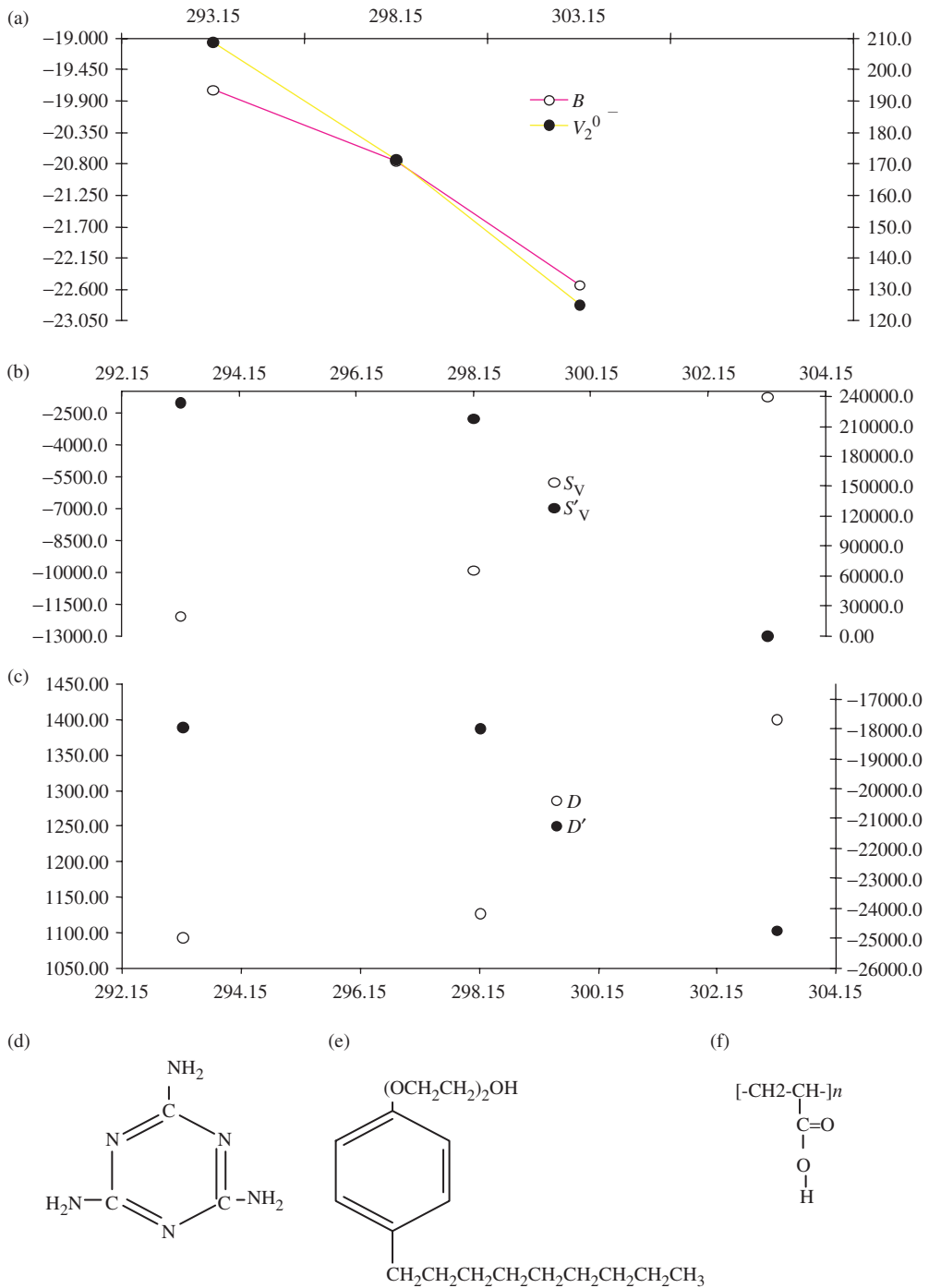


Figure 2. (a) Y-axis on the left hand-side represents the B values and on the right hand side the V_2^0 . (b) Y-axis S_v on the left-hand side and S'_v on the right side, (c) Y-axis D on the left hand side and D' on the right side; the X-axis for (a-c) depict the values of the molalities, of melamine in aqueous solutions at three temperatures. (d) Melamine structure. (e) 4-Nonyl phenol ethoxylate. (f) Poly(acrylic acid).

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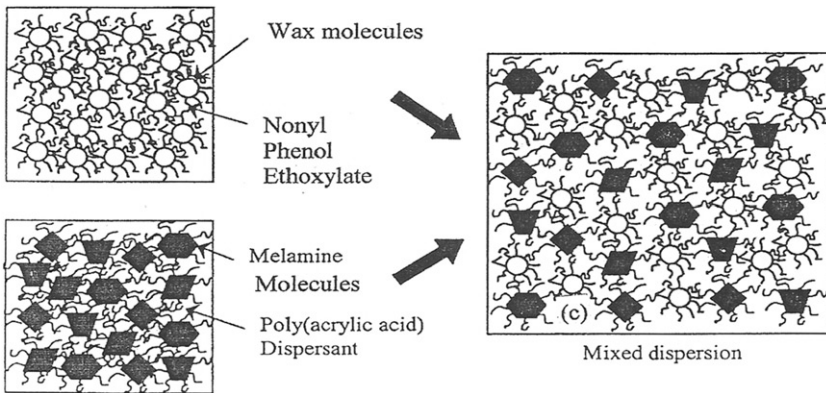


Figure 3. SEM micrographs of nonyl phenol ethoxylate, a nonionic surfactant, supported micromixing of melamine.

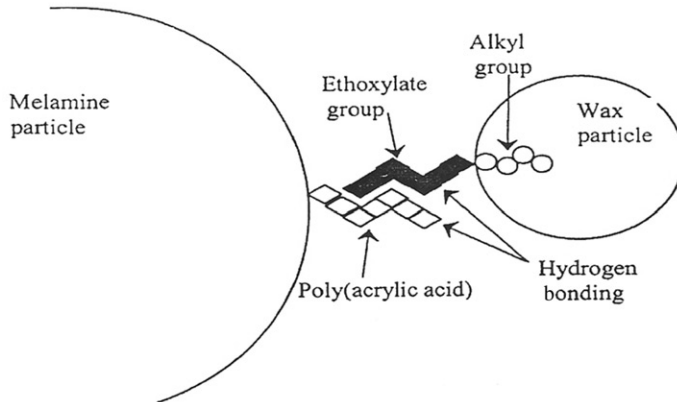


Figure 4. Interaction between the poly(acrylic acid) and ethoxylate functional group of surfactant.

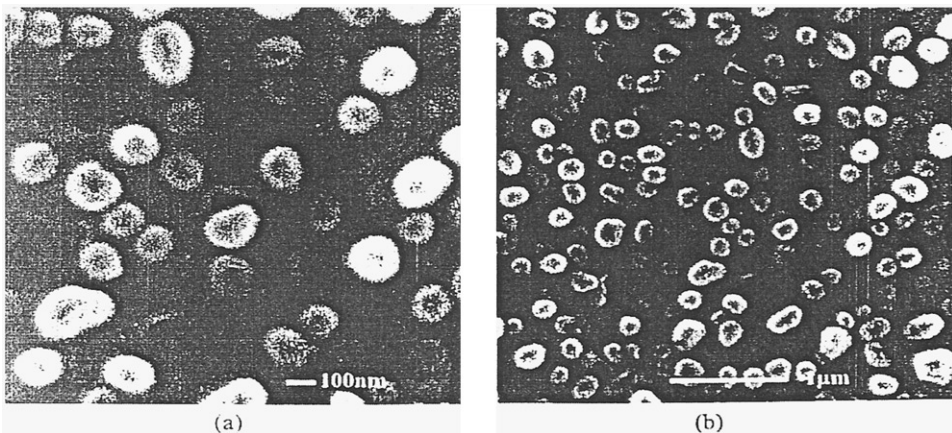


Figure 5. SEM micrographs of (a) wax emulsions and (b) stabilized by surfactant.

show a linear decrease (figure 1b) and higher increase at around $30.0 \text{ mmol kg}^{-1}$ at 298.15 K and 303.15 K with sharp decrease at around 9.0 mmol kg^{-1} at 298.15 K, afterwards a slight and regular increase. These changes in values highlight volumetric interaction in micromixing and dispersion with concentration.

3.1. Interaction at infinite dilution

The B and \bar{V}_2^0 constants along with slope values are plotted in figure 2(a–c), and is evident that both B and \bar{V}_2^0 decrease with temperature by 1.01858 and $1.78589 \text{ mol kg}^{-1}$ and 34.41 and $46.14/10^{-6} \text{ m}^3 \text{ mol}^{-1}$ from 293.15 K to 298.15 K and 298.15 K to 303.15 K , respectively. These illustrate an effect of temperature on structural reorientation weakening of water–melamine interaction as thermal energy weakens the intermolecular forces. A magnitude of the S_v and S'_v , and of D and D' are plotted in figure 2(a–c) showing opposite trends with an intersection at almost same concentrations proving stronger pair-wise interactions around higher concentrations. Free energy of activation (table 2) with a continuous decrease reveals less energy for micromixing and dispersion at higher temperature. The \bar{V}_2^0 and B functions [1] denote disruption of water structure and conformational transition due to hydrophilic and hydrophobic interactions. The $-\text{NH}_2$ groups weaken water structure in two ways [3,4] (a) indirectly surrounding water to destabilize (b) directly replacing water partially from hydration shell of melamine. Thus melamine destabilizes the water-water bonds developing interactions water acting water structure breaker [5,8]. Computer simulations find negligible effect on water structure while electron-spin resonance spectroscopy confirms replacement and notches up the direct action. An increase and decrease in ρ with concentration and temperature, respectively (table 1), attributes to disruption of water with a decrease or an increase in intermolecular free length [13]. It increases hydrophobic (structure making) and hydrophilic (breaking, due to $-\text{NH}_2$) interaction (figure 2d), partial occupation of melamine in interstitial cavities of water contributes to density changes. The η_r decreases at each temperature and higher viscosity coefficient B values are obtained for lower concentration, an increase in η_r concludes breaking of cluster formation of water that surround melamine terming it as structure maker. The both B and \bar{V}_2^0 values decrease with temperature (figure 2a) proving effective activity of melamine. The positive and negative values of D and D' , respectively (figure 2c) measure hydrodynamic solvation of pairwise complex with an element of order or disorderliness caused by $-\text{NH}_2$ in the water structure. A positive D values at 293.15 K supports stronger pair-wise interactions terming melamine as structure maker whereas negative D' weakly breaker. The \bar{V}_2^0 values support making and breaking actions [13,19] e.g. a decrease in \bar{V}_2^0 with temperature at around lower concentration implies weakening due to $-\text{NH}_2$ groups. A larger decrease in S_v at 298.15 K illustrates weaker pair-wise interactions, which strengthen with concentration due to stronger interactions with desolvating effect. An increase in E^* values with concentration proves a consumption of an additional energy for pair-wise interaction. Melamine at around $32.2 \text{ mmol kg}^{-1}$ has the least E^* forming most stable conformational state. The $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$, and $\Delta\mu_2^{0*} - \Delta\mu_1^{0*}$ values (table 2), show a decrease by about 264 kJ mol^{-1} in $\Delta\mu_2^{0*}$ depicting mixing, which enhances with temperature, the $\Delta\mu_2^{0*} - \Delta\mu_1^{0*}$ support a mixing. The SEM micrographs depicted in figures 3 and 4 infer melamine interaction (figure 2d) with wax particles. Figures 5(a) and (b) show the wax micromixed emulsion in a matrix

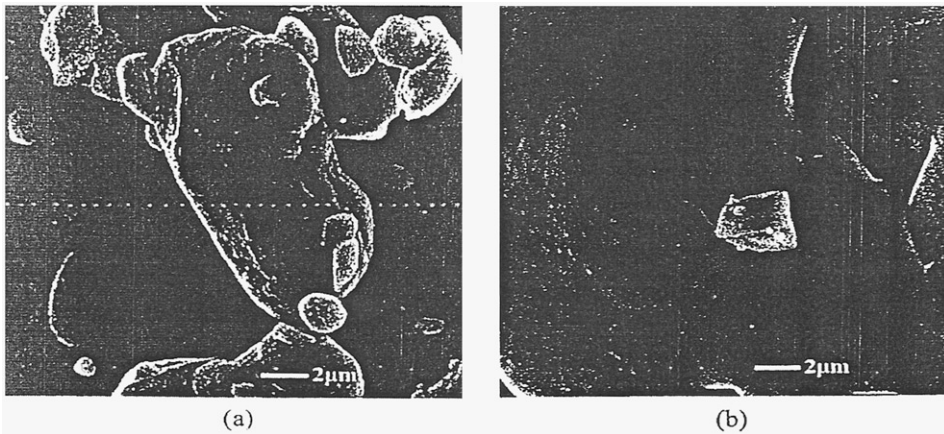


Figure 6. Micrographs of (a) melamine before micromixing and (b) melamine dispersion not stabilized by poly(acrylic acid).

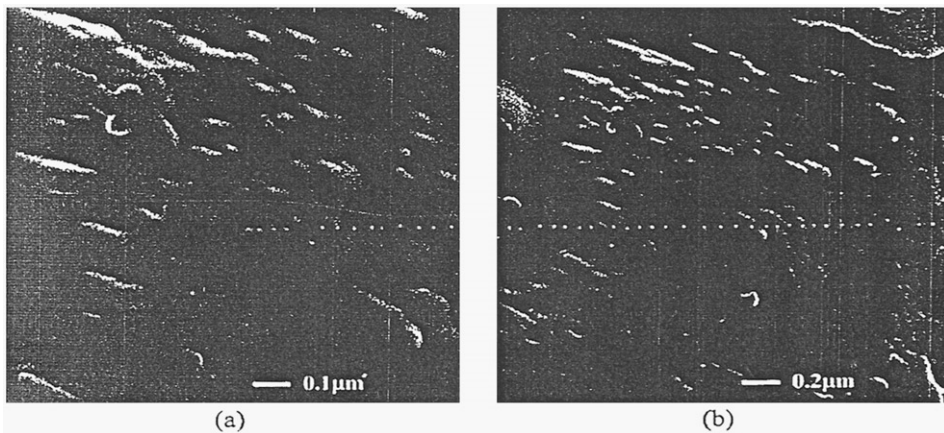


Figure 7. Micrographs of (a) melamine processed with acrylic acid (b) micromixed with wax, wax molecules maintain identity on melamine surface.

of continued phase and figure 6(a) and (b) the melamine surface prior micromixing with nonyl phenol ethoxylate (figure 2e). The melamine surfaces along with a control experiment (figure 7a and b) are noted with characteristic humps proving close contact of melamine and wax without physico-chemical interaction. But poly(acrylic acid), stabilizer (figure 2f) facilitates such interaction, (figure 8a and b) highlights melamine surface processed with 8% poly(acrylic acid) on a mass basis. The wax particles are seen on the processed surface of melamine indicating occurrence of interactions between the poly(acrylic acid) and ethoxylate group of surfactant with the wax emulsion surfaces due to hydrogen bonding [20,21]. The wax becomes attached to the melamine surface along with sedimentation of particles. Figures 7 and 8(a) and (b) display an absence of wax particles on an area of a treated melamine surface. However, no comparison of figure 7(a) and (b) with figure 8(a) and (b) is possible, the melamine surface show distinct difference with respect to surface texture. The humps in figure 7(a) and (b) are not discernable in figure 8(a) and (b), and possibly amounted to an influence of

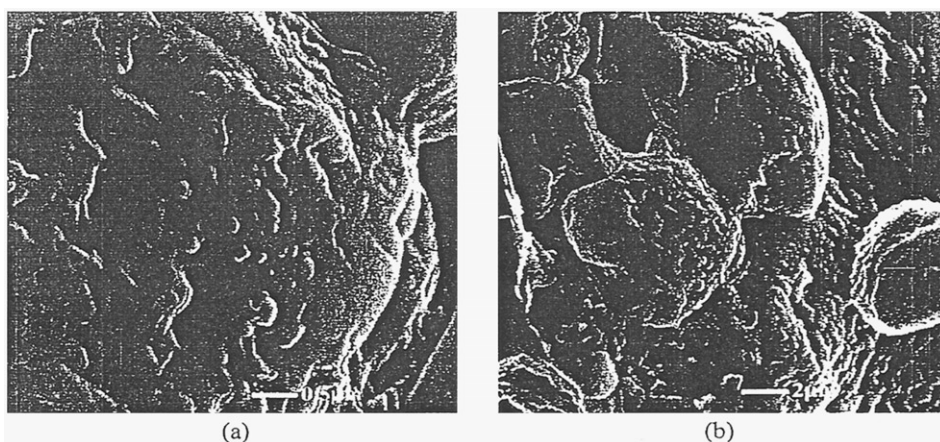


Figure 8. Micrographs of (a) melamine processed with poly (acrylic acid) (b) micromixed with wax, wax molecules lose identity.

free 4-nonyl phenol ethoxylate that is found in the matrix of the continuous phase (figure 5a and b). The interactions of the poly(acrylic acid) treated melamine with the matrix film results in a change in melamine surface texture. An evidence of surfactant supported micromixing opens the possibility of using polymeric surfactants such as, amphiphilic block copolymer [22], in the novel application especially in situations that require good particle-particle interactions [23].

4. Conclusion

Physico-chemical properties of melamine solutions become ready reckoners for predicting an intermingling with neutral macromolecules like wax. These are interesting interactions at molecular level where the $\Delta\mu_2^{0*}$ of melamine have been a pre-required condition. For mixing process the residual forces of melamine are the foundation, thus density, volume and viscosity and $\Delta\mu_2^{0*}$ have been found to be a great help for micromixing in emulsion. SEM micrographs prove an effective mixing of melamine and wax in the presence of nonionic surfactant.

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