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Tensiometric and Fluorescence Study of Cationic Gemini Surfactant with Some Special Alcohols

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ABSTRACT

Special alcohols have been used as additives to study interfacial properties of cationic Gemini surfactant pentanediyl-*1*, *5*-bis (dimethyldodecylammonium bromide) (12-5-12). As these branched chain alcohols (in comparison with linear chain alcohols) are playing a measure roll in creating a microemulsion with Gemini surfactants. The surface tension values were measured by using ring detachment method. During the experiments, the ring was cleaned well by heating it in alcohol flame. The critical micelle concentration (*cmc*) values were obtained from surface tension (γ) versus $\log C_t$ plots. The γ values decreased continuously and then become constant along a wide concentration range. The point of break, when the constancy of surface tension begins, was taken as the *cmc* of the system. Calculated Parameters are *cmc*, Γ_{max} (maximum surface excess concentration), A_{min} (minimum surface area per molecule), C_{20} (the concentration of surfactant where the surface tension of the solvent is being reduced by 20 mN.m^{-1}), $G_{\min}^{(s)}$ (free energy of the given air/water interface), and the standard Gibbs energy of adsorption, ΔG^0_{ads}. An important property of micelle formation is the mean aggregation number which provides direct information about the general size and shape of the aggregates formed by amphiphiles in solution, and how these properties are related to the molecular structure of the amphiphiles**.** Mixed micellization behavior has been shown by these parameters. The mean aggregation number (N_{agg}) of mixed micelles has been obtained by using the steady state fluorescence quenching method. Some other concerned parameters including dielectric constant (*D*), binding constant (K_{SV}) were calculated in this study by using the ratio of intensity of peaks.

Keywords: Alcohols, critical micelle concentration, dielectric constant, Gemini surfactant

INTRODUCTION

Surfactants are the molecules having lyophilic and lyophobic parts and show very interesting properties of both adsorption and absorption on surface and interfaces both at very low concentrations. Surfactants are very useful as detergents, foaming agents, and they have many industrial applications.

The lyophilic part of the surfactants is soluble in water while lyophobic part is water insoluble. When water is used as solvent then these parts are called namely hydrophilic and hydrophobic. The charge bearing portion is called hydrophilic and long chain (tail) is called hydrophobic. Conventional surfactants have long carbon chain that may be linear or branched, and the charge bearing part may be ionic. The hydrophilic part of the surfactants interacts strongly with the polar part of the water molecule.

Surfactants have many applications in our daily life as well as in the industrial field. Gemini surfactants are much superior in comparison with conventional surfactants. These surfactants (Gemini surfactants) have two hydrophilic and two hydrophobic parts, with their hydrophilic parts being connected with a spacer.

Mitsui Okahara and his colleagues (Okahara *et al*., 1988), have first prepared gemini or dimeric surfactants. These surfactants show more efficient wetting properties (Rosen, 1993) than conventional surfactants and possess very low critical micelle concentration (*cmc*). They show specific rheological and specific aggregation properties (Zana & Talmon, 1993; Alami *et al.*, 1993; Frindi *et al.*, 1994; Talmon, 1999). In comparison with convention surfactants, Gemini surfactants form micelles at very low concentrations and also have score of better properties. Gemini surfactants are mostly used in the presence of additives. Among various additives, alcohols hold a very special place as they are the common co-surfactants used with surfactant and oil systems to generate microemulsions. Alcohols played multiple roles in microemulsions. First, it delays the occurrence of liquid crystalline phases. Second, it decreases the binding modulus and increases the fluidity of the mixed surfactant and alcohol interfacial layers separating oil and water.

A structural presentation of Gemini surfactant pentanediyl- *1, 5*-bis (dimethyldodecylammonium bromide) (12-*5*-12) is shown in Figure 1.

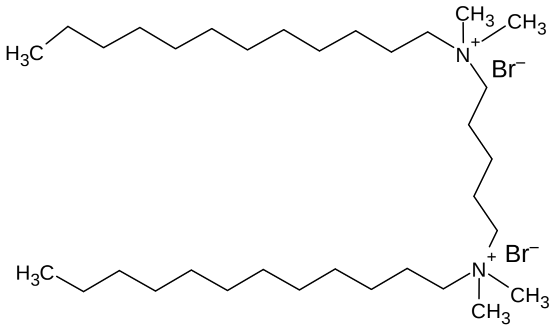


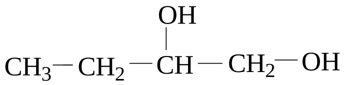
Figure 1. Structural presentation of Gemini surfactant

Due to their superior surface activity, Gemini surfactants possess many applications in various fields. These surfactants play major role in spreading aids, cleaning processes and etc. These surfactants are used in gene therapy as well as bioimaging because of their ability to interact with DNA (Ahmed *et al*., 2016). Gold, silver and gold-silver alloy nanoparticles can be prepared by using Gemini surfactants with the help of seed mediated method (Tiwari *et al*., 2015). The special alcohols have been chosen here in this work as additives to study the mixed micellization behaviour of Gemini surfactant (12-*5*-12), because these alcohols potentially show advanced properties when compared to simple linear chain alcohols. This is the first attempt so far to study the aggregation number of cationic Gemini surfactant in the presence of special alcohols. In the preparation of microemulsion, mainly alcohols are used as co-surfactants with surfactants and oil systems. There is very important role of alcohol in microemulsion, as it deacreaes the binding modulus (Binks *et al*., 1989; Strey & Jonstromer, 1992) and increases the fluidity (Lianos *et al*., 1982) of the system.

MATERIALS AND METHODS

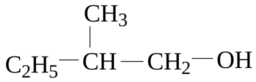
The special alcohols 1,2-butanediol (≥98.2%, Sigma-Aldrich, Germany), 2-methyl-1-butanol (≥99.3%, Sigma-Aldrich, Germany), 2-ethyl-1-butanol (≥98.2%, Sigma-Aldrich, Germany), and 2-butene-1,4-diol (≥95.5%, Sigma-Aldrich, Germany) were used. The chemical structures of special alcohols are given in Figure 2.

(a) 1,2-butanediol



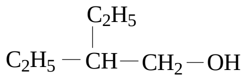
$$CH_3-CH_2-\overset{\overset{OH}{|}}{CH}-CH_2-OH$$

(b) 2-methyl-1-butanol



$$C_2H_5-\overset{\overset{CH_3}{|}}{CH}-CH_2-OH$$

(c) 2-ethyl-1-butanol



$$C_2H_5-\overset{\overset{C_2H_5}{|}}{CH}-CH_2-OH$$

(d) 2-butene-1,4-diol

$$HO-CH_2-CH=CH-CH_2-OH$$

Figure 2. Special alcohols used for the synthesis of gemini surfactant

The Gemini surfactant 12-*5*-12 was synthesized by using 1,5-Dibromopentane (≥98.3%, Merck, Germany), and *N, N*-dimethyldodecylamine (≥95.5%, Fluka, Germany) in dry alcohol at 80.15 °C till 48 h with continuous stirring. Thin layer chromatography (TLC) technique was used to monitor the progress of the reaction. Recrystallization process was used to remove solvent. ^1H NMR and Fourier Transform Infrared Chromatography (FT-IR) techniques were used to check the purity of the Gemini surfactant.

The *cmc* values of the Gemini surfactants (with and without additives) in aqueous media were determined by measuring the surface tension of the pure Gemini as well as of 12-5-12/additive (alcohol) solutions of various mole fractions at 303.15 K, whereas surface tension was measured by S. D. Hardson tensiometer (Kolkata, India). The surface tension (γ) values decrease continuously and then become constant along a wide concentration range. The point of break, when the constancy of surface tension begins, was taken as the *cmc* of the system. The uncertainties on the *cmc* are estimated to be in the (0.1 – 0.3) $\times 10^{-5}$ mol.dm^{-3} range.

Steady-state fluorescence quenching have been used to determine the micellar aggregation numbers (N_{agg}) of pure Gemini surfactant and mixed systems. The fluorescence measurements were taken on a Hitachi F-2500 fluorescence spectrometer (Japan) with excitation and emission slits widths of 2.5 nm. All the spectra was recorded at the room temperature i.e., 298.15 K. Herein cetylpridinium chloride and pyrene were used as quencher and probe respectively. Excitation was done at 337 nm and emission was recorded at 350 – 450 nm.

N_2 gas was used to evaporate the solvent. By keeping pyrene concentration constant at 2×10^{-6} mol/L, the surfactant solution was added into the volumetric flask.

RESULTS AND DISCUSSION

Different mole fractions of special alcohols (additives) was used to find out the variable change in the surface tension of Gemini surfactant (12-5-12) (Figure 3). The obtained results showed that the surface tension decreases as the concentration of additive increases. At low concentrations, the molecules of the surfactant adsorb at the liquid/air interface until the solution surface is occupied completely. As a result, the excess molecules become self-associate in the solution to form micelles, and surface tension becomes constant. The concentration where break in the curve take place represents the *cmc* of the system. Table 1 shows all the *cmc* values obtained at different mole fractions of additives. The values of other parameters like C_{20}, cmc/C_{20}, Γ_{max}, A_{min}, Π_{cmc} (the pressure that created at the *cmc*), $G^{(s)}_{\min}$ (free energy of the given air/water interface), and the standard Gibbs energy of adsorption, ΔG^0_{ads}, were calculated (Table 1).

The value of Γ_{max} (in mol/m) and A_{min} (in Å^2), were calculated by applying the following Eq. (1) and Eq. (2) (Rosen, 2004)

$$\Gamma_{\max} = -\frac{1}{2.303n\mathrm{RT}}(\mathrm{d}\gamma/\mathrm{d}\log C_{\mathrm{t}})_{\mathrm{T}} \qquad \text{Eq. (1)}$$

$$A_{min} = 10^{20}/\,N_A\,\Gamma_{max} \qquad \text{Eq. (2)}$$

Where R = Gas constant N_A = Avogadro's number, and T = absolute temperature. The value of n in the above equation represents the number of species whose concentration at the interface alters with changes in the surfactant concentration in the solution. In the present case, the value of n has been set as 2 to calculate the $\Gamma_{max.}$ (Li *et al.*, 1999). Due to the presence of alcohols more Gemini surfactant molecules can be accommodated at the interface, because the repulsion among head groups decreases and hence, the value of Γ_{max} increases with increase in the additive (alcohol) concentration (Table 1). The values of A_{min} decrease as the concentration of additives increases. Low values of A_{min} indicate that the air/water interface is packed closely and, the orientation of the surfactant molecules at the interface is almost perpendicular to the interface.

The standard Gibbs energy of micellization, ΔG^0_m, and the standard Gibbs energy of adsorption, ΔG^0_{ads}, were calculated by using the following Eq. (3) and Eq. (4)

$$\Delta G^0_m = RT \cdot \ln C_{12}{}^m \qquad \text{Eq. (3)}$$

where $C_{12}{}^m$ is the *cmc* of the mixture of the two components at a given mole fraction.

$$\Delta G^0_{ads} = \Delta G^0_m - \Pi_{C_{12}}{}^m/\Gamma_{max} \qquad \text{Eq. (4)}$$

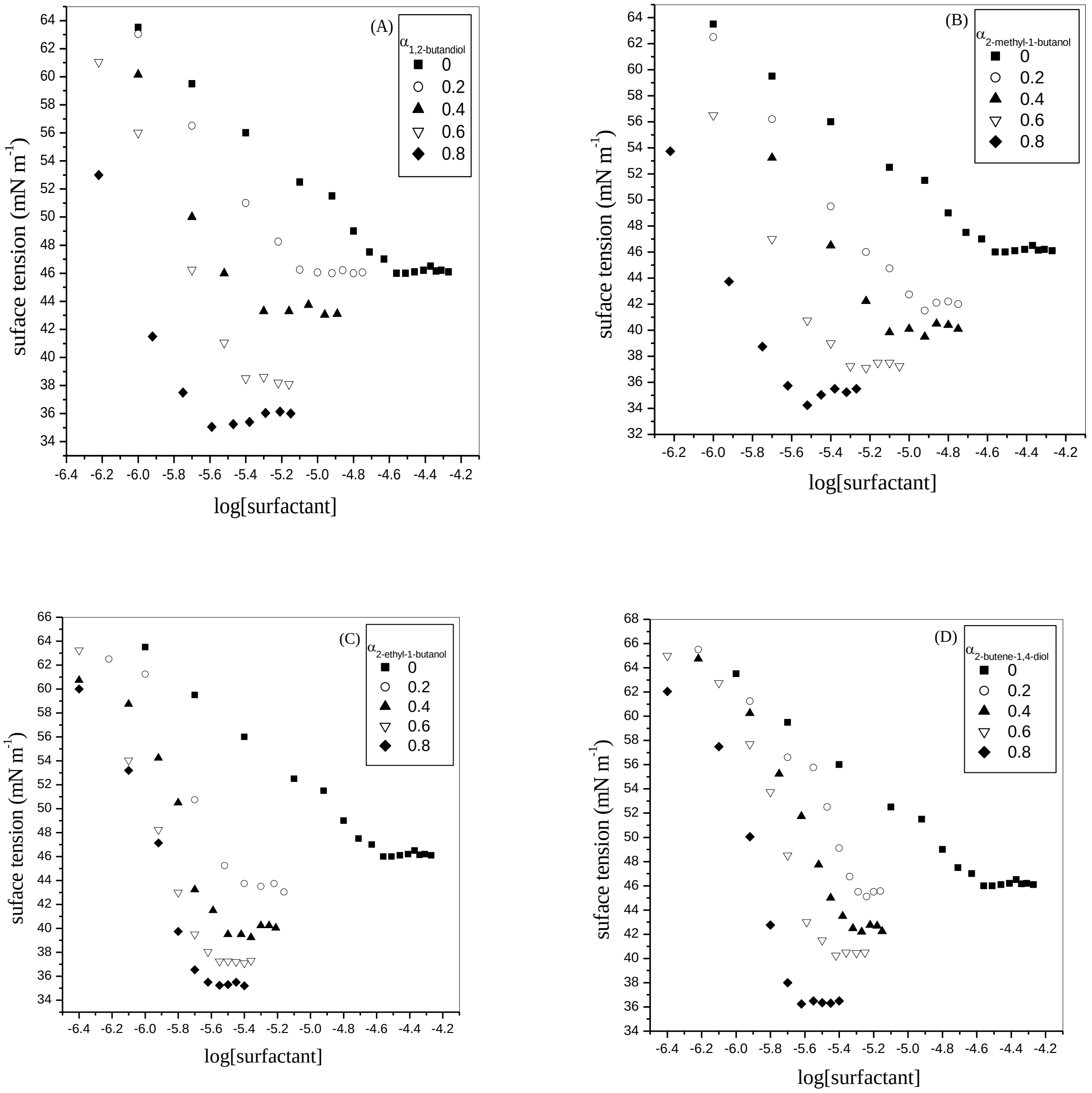


Figure 3. The variation of surface tension (γ) with logarithm of Gemini surfactant (12-5-12) concentration (log C_t) at different mole fraction of alcohols [1, 2-butanediol (A), 2-methyl-1-butanol (B), 2-ethyl-1-butanol (C), and 2-butene-1, 4-diol (D)]

The values of $\Delta G^0{}_{ads}$ (Table 1) decrease with increasing the alcohol concentrations. The standard state for the adsorbed surfactant is a hypothetical monolayer at its minimum surface area per molecule, but at zero surface pressure. The last term in Eq. (4) represents the work involved in transferring the surfactant molecule from a monolayer at a zero-surface pressure to the micelle. In Eq. (4), the last term is very small as compared to ΔG^0_m, which indicates that the work involved in transferring the surfactant molecule from a monolayer at zero surface pressure to the micelle is negligible. Negative values of $\Delta G^0{}_{ads}$ (Table 1) show that the adsorption of the surfactants at the air/mixture interface takes place spontaneously. The $\Pi_{C_{12}}{}^m$ values were calculated by Eq. (5)

$$\Pi_{C_{12}}{}^m = \gamma_0 - \gamma_{C_{12}}{}^m \qquad \text{Eq. (5)}$$

where, $\gamma_{0,}$ and $\gamma_{C_{12}}{}^{m}$ represents the surface tension of the pure solvent and of the mixture at the *cmc*. As the concentration of alcohols increases, the values of $\Pi_{C_{12}}{}^{m}$ increase, this indicates that the efficiency of the system increases (Table 1).

Sugihara and co-workers (Sugihara *et al*., 2003) found the thermodynamic quantity for obtaining the synergism in mixing, which is the free energy $G^{(s)}_{\min}$ of the given air/water interface, as defined in Eq. (6)

$$G^{(s)}_{\min} = A_{\min} \cdot \gamma_{C_{12}}{}^{m} \cdot N_A \qquad \text{Eq. (6)}$$

where, the obtained $G^{(s)}_{\min}$ values, decrease with increasing the additive (alcohol) concentration (Table 1). The $G^{(s)}_{\min}$ is regarded free energy change accompanied by the transition from the bulk phase to the surface phase of the solution components. In other words, the lower the value of $G^{(s)}_{\min}$, the more thermodynamically stable surface is formed.

The values of mean aggregation number provide the information about the dimensions of the micelles formed by surfactant in the solution. The mean aggregation number may be defined as amount of surfactant molecules that occupy together to form a spherical structure called micelle. Mainly their shape looks like a bubble. Force of attraction into the micellar solution depends on hydrocarbon chain of the monomer. From geometric point of view, the aggregation number (N_{agg}) increased rapidly in aqueous media if the length of the hydrophobic group (l_c) of the surfactant molecule is increased while it decreased when there was increase in the intersection area (a_0) of the lyophilic group.

Fluorescence quenching is the best method for calculating the micellar aggregation numbers (N_{agg}) of pure and mixed system. It is a more competent method. The Micellar aggregation numbers (N_{agg}) was calculated by applying the following Eq. (7) (Turro *et al*., 1978)

$$\ln I_0 = \ln I_Q + \frac{N_{agg}[Q]}{[S] - cmc} \qquad \text{Eq. (7)}$$

where, $[Q]$ and $[S]$ have their own meaning representing quencher concentrations and total surfactant concentration, respectively, while I_o represent the intensity of fluorescence when quencher is absent and I_Q represents the intensity of fluorescence when quencher is present.

Spectra had been recorded at different mole fractions of alcohols (data are given in the Table 2). High values of N_{agg} were obtained for mixtures rather than of pure solution (when no additive was added). The obtained results are well matched with the literature (Mohammad, 2019). Due to high concentration of the alcohols, the repulsion among head groups will decrease so the compact micelles with higher aggregation number will form.

The intensity ratio of the first (I_1) and third (I_3), vibronic peaks represent the micropolarity index of the system in the presence of surfactant; i. e., it provides a view on the microenvironment of the micelle. The smaller value of this ratio (<1) represents that pyrene has nonpolar surrounding, whereas greater value (>1) represents that the pyrene has polar surrounding (Kalyanasundram & Thomas, 1977). The following Eq. (8) has been used for calculating the apparent dielectric constant (Maeda, 1995).

$$\frac{I_1}{I_3} = 1.00461 + 0.01253\, D \qquad \text{Eq. (8)}$$

The local polarity is measured by calculating the values of D from Eq. (8) where, the probe is present. If all the molecules are present into the regions of micelle, it means that the size of the probe is large. Then obtained D values are average. This is due the complementary effect, which was created due to the separation of the ionic head groups of Geminis. The dielectric constant is reduced in water on polar surfaces when the surface electrical potential is increased; this is due to the orientation of water molecules by the electric field (Ferchmin, 1995; Lamm & Pack, 1997). The intercalation of alcohol species between the charge bearing part of the surfactant should increase the value of D with respect to that in the pure surfactant micelles.

Stern-Volmer binding constant, (K_{SV}) (Rohatgi-Mukherjee, 1992), was calculated by applying the following Eq. (9)

$$\frac{I_1}{I_3} = 1 + K_{SV}[Q] \qquad \text{Eq. (9)}$$

where, K_{SV} represents as the ratio of the bimolecular quenching constant to the unimolecular decay constant. If one got the higher value of K_{SV} values, it means that the pyrene having longer lifetime in micellar solutions and quenching is more efficient.

CONCLUSION

The interaction of cationic Gemini surfactant pentanediyl- *1, 5*-bis (dimethyldodecylammonium bromide) (12-*5*-12) with special alcohols showed that the trend of the increase/decrease of Γ_{max}, *cmc* and A_{min} are due to formation of mixed micelles with the Gemini surfactant. The values of ΔG^0_{ads} indicated that the adsorption of the surfactant at the air/solution interface takes place spontaneously.

As the concentration of alcohols increase the values of N_{gem} and $N_{alcohol}$ also increases. This indicated the strong synergism between Gemini surfactant and additives (alcohols). When micelles are formed from more than one chemical species, then there is a formation of mixed micelle. Mixed micelle has very important application in pharmaceutical and biological fields, due to their superior performance than pure micelles (Holland & Rubingh, 1992). Alcohols are very good co-surfactants and they can be used in microemulsion formulation (Lianos *et al.*, 1984). There are very few studies available using alcohols as co-surfactants so they are potential candidates for such formulations (Wormuth & Kaler, 1987).

Table 1. At different mole fraction of alcohols the value of *cmc*, C_{20}, *cmc*/C_{20}, Π_{cmc}, Γ_{max}, A_{min}, G^s_{min} , and ΔG^0_{ads} at 303.15 K

α_1	10^5 *cmc* (mol.dm^{-3})	10^5 C_{20} (mol.dm^{-3})	*cmc*/C_{20}	Π_{cmc} (mN.m^{-1})	10^6 Γ_{max} (mol.m^{-2})	A_{min} (Å^2)	G^s_{min} (kJ.mol^{-1})	$-\Delta G^0_{ads}$ (kJ.mol^{-1})
				System: 1,2-butanediol/12-*5*-12				
0	5.68	2.00	2.84	25.5	0.87	90.8	53.43	32.76
0.2	0.70	0.55	1.27	26.0	1.75	4.8	26.27	34.95
0.4	0.62	0.40	1.55	30.0	2.63	3.1	15.97	32.25
0.6	0.45	0.21	2.14	32.0	3.50	7.4	11.42	31.04
0.8	0.32	0.12	2.67	34.0	4.38	7.8	8.65	29.89
				System: 2-methyl-1-butanol/12-*5*-12				
0.2	2.27	0.63	3.60	28.5	0.96	172.9	45.29	-25.03
0.4	2.10	0.53	3.96	29.5	1.05	158.1	40.20	-25.23
0.6	0.90	0.22	4.09	32.0	2.63	63.1	15.21	-27.33
0.8	0.44	0.13	3.38	33.0	3.50	47.4	11.14	-29.1
				System: 2-ethyl-1-butanol/12-5-12				
0.2	0.85	0.32	2.66	29.0	1.92	86.4	22.37	-27.47
0.4	0.55	0.21	2.62	31.0	2.80	59.3	14.65	-28.55
0.6	0.43	0.15	2.86	34.5	3.68	45.1	10.19	-29.16
0.8	0.32	0.10	3.20	38.5	4.29	38.6	7.79	-29.89
				System: 2-butene-1,4-diol/12-*5*-12				
0.2	0.70	0.45	1.55	25.5	2.32	71.5	20.02	-27.95
0.4	0.45	0.21	2.14	28.0	2.42	68.6	18.18	-29.04
0.6	0.39	0.19	2.05	33.5	2.74	60.6	14.05	-29.4
0.8	0.26	.011	2.36	39.0	3.23	51.3	10.20	-30.4

α_1 = mole fraction of the alcohol.

Table 2. The value of mean aggregation number and other related parameter calculated by fluorescence measurements

α_1	N_{agg}	N_{gem}	$N_{alcohol}$	$K_{SV}/10^4$ (mol^{-1} dm^3)	I_1/I_3	D
System: 1,2-butanediol /12-5-12						
0	42	36	12	6.7	1.98	77
0.20	120	89	28	5.7	1.82	65
0.40	130	90	55	3.6	1.52	41
0.60	172	53	102	4.6	1.67	53
0.80	300	75	218	6.1	1.88	69
System: 2-methyl-1-butanol /12-5-12						
0.20	62	49	14	2.8	1.42	33
0.40	89	62	38	3.8	1.55	43
0.60	99	36	54	4.3	1.63	49
0.80	152	30	125	1.3	2.86	148
System: 2-ethyl-1-butanol /12-5-12						
0.20	50	42	15	3.7	1.55	43
0.40	64	31	25	4.4	1.65	51
0.60	82	28	50	5.1	1.74	58
0.80	112	15	92	8.4	2.22	96
System: 2-butene-1,4-diol /12-5-12						
0.20	52	42	12	3.0	1.44	34
0.40	55	32	22	3.8	1.56	44
0.60	74	24	40	5.7	1.84	66
0.80	89	18	74	6.7	1.98	77

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