Critical Micelle Concentration of Surfactant Using Hadkar Factor

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ABSTRACT

Critical micelle concentration is an important characteristic property of a surfactant and various methods such as osmotic pressure, surface tension, interfacial tension, UV-Visible spectrophotometry have been reported to determine it. The drop weight method was used to determine the Hadkar factor H_1 for organic liquid lighter than water and Hadkar factor H_2 was used for organic liquid heavier than water. The plot of H_1 or H_2 vs concentration of the aqueous surfactant solution was used to determine the critical micelle concentration of the surfactant. Interfacial tension between the aqueous surfactant solution and the organic liquid was also determined using Hadkar factors H_1 and H_2.

Key words: Drop weight method, Hadkar factors, Interfacial tension, critical micelle concentration, surfactant, pipette.

INTRODUCTION

Surfactants are surface active agents and a surfactant molecule has both hydrophilic part and hydrophobic (lipophilic) part and as a result the surfactant molecules are adsorbed at the interface of immiscible phases, and thereby reduce the interfacial tension.[1] As the concentration of surfactant is increased, the surface tension goes on decreasing and at a certain concentration, the monomer surfactant "n" molecules associate to form aggregates called micelles.[2,3] The process of formation of micelles is termed as micellization. The minimum concentration at which micelle formation takes place is called the critical micelle concentration (cmc) and is temperature dependent. The methods such as pendant drop method, Withelmy plate method, have been reported to determine interfacial tension between two liquids.[4] The cmc of a surfactant can be determined by various methods such as osmotic pressure, surface tension, interfacial tension, conductivity method.[5] The plot of the physical quantity vs the surfactant solution concentration shows a sudden change in the measured physical quantity at the cmc of the surfactant and this fact is used to determine the critical micelle concentration.[6] The method reported here to determine the Interfacial Tension between organic liquid and surfactant solution is the drop weight method same as that reported by Hadkar U.B. and Ravindra R.P.[7] The drop weight method was used to determine Hadkar Factor H_1 for two different systems, namely, the aqueous surfactant Tween-20 solution-butanol system and cetyl trimethyl ammonium bromide (CTAB) aqueous surfactant solution-butanol system. Also Hadkar Factor H_2 was determined for two different systems, namely, CCl_4- Tween-20 aqueous solution and CCl_4 – CTAB aqueous solution.

MATERIAL AND METHOD

Carbon tetrachloride and butanol:-AR grade, S.D. Fine Chemicals.

Tween-20 and cetyl triammonium bromide (CTAB):- Central Drug House (CDH)

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Method for organic liquids heavier than water (or aqueous surfactant solution)

CCl_4 and aqueous solution of Tween-20

The lighter liquid Tween-20 aqueous solution was taken in a 100 ml beaker placed in a petri dish. A volumetric pipette (inner radius r=0.062 cm) filled with CCl_4 (heavier liquid) was held in a vertical position and the tip of the pipette was just dipped into the aqueous solution. The number of drops of CCl_4 in the aqueous solution was determined for a fixed volume (3.5 ml). The drop rate was about 8-10 drops per minute. The volume of the liquid could be measured accurately by pasting a strip of graph paper on the upper and lower stem of the pipette. The number of drops of CCl_4 in the aqueous solution of surfactant was determined for various concentrations of Tween-20 (0 mg /100 ml to 16 mg/100 ml). The number of drops per 3.5 ml of CCl_4 in air and that of the aqueous solution of Tween-20 in air were also determined. The data is given in Table1.

CCl_4 and aqueous solution of CTAB

The number of drops of CCl_4 in the aqueous CTAB solution was determined per 3.5 ml using the same pipette (r=0.062 cm) used in the part (A). The number of drops of CCl_4 in aqueous solution of surfactant was determined for various concentrations of CTAB (0 mg/100 ml to 50 mg/100 ml). The number of drops of aqueous solution of CTAB in air were also determined using the same pipette and for the same volume (3.5 ml). The data is given in the Table 2.

Method for organic liquids lighter than water (or aqueous solution of surfactant)

Aqueous Tween- 20 solution and butanol

The procedure followed was the same as in the part (A). The heavier liquid (aqueous Tween-20 solution, concentration 0 mg/100 ml – 16 mg/100 ml) was taken in the pipette (radius r=0.026 cm) and the number of drops per 4 ml in butanol was determined. The number of drops of butanol per 4 ml in air as well as the number of drops per 4 ml for each aqueous Tween- 20 solution in air was also determined, using the same pipette. The data is given in the Table 3.

Aqueous solution of CTAB and butanol

The method used was the same as in the part (A). The heavier liquid (aqueous CTAB solution, concentration 0 mg/100 ml – 50 mg/100 ml) was taken in the pipette (r =0.062 cm) and the number of drops per 3.5 ml in butanol was determined. The number of drops of butanol per 3.5 ml in air as well as number of drops per 3.5 ml of each aqueous CTAB solution in air was also determined, using the same pipette. The data is given in the Table 4.

Calculation for the Hadkar Factor H_1 (Organic liquid lighter than the aqueous solution):

The Hadkar factor H_1 is given by

$$H_1 = \frac{(n^{org.\ air})}{(n^{aqueous.air})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where, $n^{org.\ air}$ = number of drops of organic liquid in air for a given volume V.

$n^{aqueous\ \ air}$ = number of drops of aqueous solution in air for the same volume V, using the same pipette (same radius).

Calculation for the Hadkar Factor H_2 (Organic liquid heavier than aqueous solution):

The Hadkar factor H_2 is given by

$$H_2 = \frac{(n^{org.\ aqueous})}{(n^{org.\ air}) - (n^{aqueous.air})} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where, $n^{org.\ aqueous}$ = number of drops of organic liquid in aqueous solution for the given volume V.

$n^{org.\ air}$ = number of drops of organic liquid in air for the same volume V.

$(n^{\ aqueous\ .air})$ = number of drops of aqueous solution in air for the same volume V, using the same pipette (same radius)

Calculation for interfacial tension between the surfactant solution and the immiscible organic liquid:

When the drop of the heavier liquid is about to detach from the tip of the pipette inside the lighter liquid,

that is, at the equilibrium,

$$mg = 2\pi\ r\gamma_{int}\ H_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

$$mg = 2\pi\ r\gamma_{int}\ H_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

where,

m = apparent mass of the drop inside the liquid.[8]

Note: The apparent mass of heavier liquid drop is less than the true mass of the liquid drop because of the up-thrust of the lighter liquid.

g = acceleration due to gravity = 980 cm/sec^2

r = radius of the tip of the pipette in cm.

$\gamma_{int\ =}$ Interfacial tension between the two liquids

$H_{1\ =}$ Hadkar factor when the aqueous solution is heavier than the organic liquid

(Given by equation 1)

H_2 = Hadkar factor when the aqueous solution is lighter than the organic liquid.

Table 1: Hadkar factor H_2 and the Interfacial tension between CCl_4 and Tween-20 aqueous solutions at 28°C ± 1°C

C mg/100 ml	n^{T20} in air per 3.5 ml	n^{CCl_4} in T20 per 3.5 ml	H_2	v (ml)	m_o (gm)	m (gm)	γ_{int} dyn/cm	SD ±
0	54	127	0.709	0.0275	0.04364	0.01609	57.08	0.56
2	60	130	0.751	0.0269	0.04265	0.01572	52.60	0.55
4	60	133	0.768	0.0263	0.04168	0.01537	50.32	0.56
6	65	147	0.875	0.0238	0.03771	0.01319	39.99	0.56
8	67	154	0.928	0.0227	0.0360	0.01327	35.99	0.57
10	71	160	0.988	0.0218	0.03465	0.01278	32.54	0.56
12	71	175	1.080	0.0200	0.03168	0.01168	27.23	0.57
14	71	175	1.080	0.0200	0.03168	0.01168	27.23	0.56
16	72	178	1.106	0.0197	0.03115	0.01148	26.13	0.54

The values of γ_{int} are the average values of 5 readings.
r = Radious of the tip the pipette = 0.062 cm

Hadkar factor, $H_2 = \frac{(n^{CCl_4} \text{ in T-20})}{(n^{CCl_4} \text{ in air} - n^{T\text{-}20} \text{ in air})}$

n^{CCl_4} in air = number of drops of CCl4 in air per 3.5 ml =233
$n^{T\text{-}20}$ in air = number of drops of aqueous solution of Tween-20 in air.
n^{CCl_4} in T-20 = number of drops of CCl4 in aqueous Tween-20 solution.
γ_{int} = Interfacial tension between CCl4 and the aqueous Tween-20 solution = (m2/H2) (g/2πr)
C = Concentration of aqueous Tween-20 solution in mg/100ml
g = acceleration due to gravity = 980 cm/sec^2
v = Vol. in cc of 1 drop of CCl_4 in Tween-20 solution = 3.5 / n^{CCl_4} in T-20
m = m_o (ρ - ρ')/ ρ = apparent mass of CCl_4 drop in the aqueous Tween-20 solution in gm.
m_o = true mass of the CCl4 drop in gm = v ρ
ρ = density of the heavier liquid CCl4 = 1.584 gm/cc.
ρ' = density of the lighter liquid (aqueous T-20 solution) = 1 gm/cc.
Note: The density of aqueous Tween-20 solution (being dilute) is considered the same as the density of water.

Table 2: Hadkar factor H_2 and the Interfacial tension between CCl_4 and CTAB aqueous solutions at 28°C ± 1°C

C mg/100 ml	n^{CTAB} air per 3.5 ml	n^{CCl_4} in CTAB per 3.5 ml	H_2	v (mL)	m_o (gm)	m (gm)	γ_{int} dynes/cm	SD ±
0	54	133	0.743	0.0263	0.04168	0.015369	49.5	0.92
5	66	154	0.922	0.0227	0.0360	0.01327	36.2	0.89
10	71	179	1.105	0.0196	0.0309	0.01142	26.0	0.92
15	80	229	1.497	0.01528	0.0242	0.00893	15.0	0.85
20	84	343	2.302	0.01020	0.0162	0.00596	6.5	0.84
25	94	768	5.525	0.00456	0.00722	0.002662	1.2	0.75
30	101	1877	14.219	0.001865	0.00295	0.001089	0.19	0.77
35	104	1828	14.171	0.0019147	0.00303	0.001118	0.19	0.78
40	105	1849	14.445	0.001893	0.002998	0.001105	0.19	0.68
45	105	1768	13.813	0.001979	0.00314	0.001156	0.21	0.62
50	105	1946	15.203	0.001799	0.002849	0.00105	0.17	0.65

The values of γ_{int} are the average values of 5 readings.
r = radious of the tip the pipette = 0.062 cm

Hadkar factor $H_2 = \frac{(n^{CCl_4} \text{ in CTAB})}{(n^{CCl_4} \text{ in air} - n^{CTAB} \text{ in air})}$

n^{CCl_4} in air = number of drops of CCl4 in air per 3.5 ml = 233
n^{CTAB} in air = number of drops of aqueous solution of CTAB in air.
n^{CCl_4} in CTAB = number of drops of CCl4 in aqueous CTAB solution.
γ_{int} = Interfacial tension between CCl4 and the aqueous CTAB solution = (m/H2).(g/2πr)
C = Concentration of aqueous CTAB solution in mg/100ml
g = acceleration due to gravity = 980 cm/sec^2
v = vol. in c.c. of 1 drop of CCl4 in CTAB solution = 3.5 / n^{CCl_4} in CTAB
m = m_o (ρ - ρ')/ ρ = apparent mass of CCl4 drop in the aqueous CTAB solution.
m_o = True mass of the CCl4 drop in gm = v. ρ
ρ = density of the heavier liquid CCl_4 = 1.584 gm/cc
ρ' = density of the lighter liquid (aqueous CTAB solution) = 1 gm/c.c
Note : The density of aqueous CTAB solution is considered the same as the density of water.

(Given by equation 2)

RESULTS AND DISCUSSION

Hadkar factor H_2 was calculated for CCl_4 and the aqueous surfactant solution of Tween-20 and is given in Table 1 and Hadkar Factor H_2 calculated for CCl_4 and the aqueous surfactant solution of CTAB is given in Table 2.

Hadkar factor H_1 calculated for aqueous surfactant solution of Tween-20 and butanol is given in the Table 3 and Hadkar Factor H_1 calculated for the aqueous surfactant solution of CTAB and butanol is given in Table 4.

Table 3: Hadkar factor H_1 and the Interfacial tension between aqueous tween-20 solution and butanol at 28°C ± 1°C

C mg/100ml	$n^{Tween-20}$ air per 4 ml	$n^{Tween-20}$ in butanol per 4 ml	H_1	v (ml)	m_o (gm)	m (gm)	γ_{int} dynes/cm	SD ±
0	86	828	2.616	4.83×10^{-3}	4.83×10^{-3}	0.918×10^{-3}	2.10	0.02
2	90	934	2.50	4.283×10^{-3}	4.283×10^{-3}	0.8139×10^{-3}	1.95	0.021
4	90	940	2.50	4.255×10^{-3}	4.255×10^{-3}	0.8085×10^{-3}	1.93	0.019
6	103	965	2.184	4.145×10^{-3}	4.145×10^{-3}	0.7876×10^{-3}	2.16	0.02
8	107	1029	2.103	3.887×10^{-3}	3.887×10^{-3}	0.7386×10^{-3}	2.10	0.023
10	109	1182	2.064	3.841×10^{-3}	3.841×10^{-3}	0.64298×10^{-3}	1.86	0.024
12	109	1195	2.064	3.347×10^{-3}	3.347×10^{-3}	0.63598×10^{-3}	1.84	0.02
14	110	1186	2.0455	3.373×10^{-3}	3.373×10^{-3}	0.6408×10^{-3}	1.87	0.022
16	110	1190	2.0455	3.361×10^{-3}	3.361×10^{-3}	0.6386×10^{-3}	1.87	0.022

The values of γ_{int} are the average values of 5 readings.
r = radious of the tip of the pipette = 0.026 cm

$$\text{Hadkar factor } H_1 = \frac{(n^{butanol} \text{ in air})}{(n^{Twee-20} \text{ in air})}$$

$n^{butanol}$ in air = number of drops of butanol in air per 4 ml = 225
$n^{Tween-20}$ in air = number of drops of aqueous Tween-20 solution.per 4 ml
$n^{Tween-20}$ in butanol = number of drops of aqueous Tween-20 solution in butanol
γint = Interfacial tension between aqueous Tween-20 solution and butanol = (m/H1).(g/2πr)
C = Concentration of aqueous Tween-20 solution.
g = acceleration due to gravity = 980 cm/sec^2
v = vol. in c.c. of 1 drop of Tween-20 solution in butanol = 4 / $n^{Tween-20}$ in butanol
m = mo (ρ - ρ')/ ρ = apparent mass of Tween-20 solution drop in butanol.
m_o = True mass of Tween-20 solution drop in gm = v. ρ
ρ = density of the heavier liquid Tween-20 solution = 1gm/cc.
ρ' = density of the lighter liquid butanol = 0.81 gm/cc
Note : The density of aqueous Tween-20 solution is considered the same as the density of water = 1gm / cc.

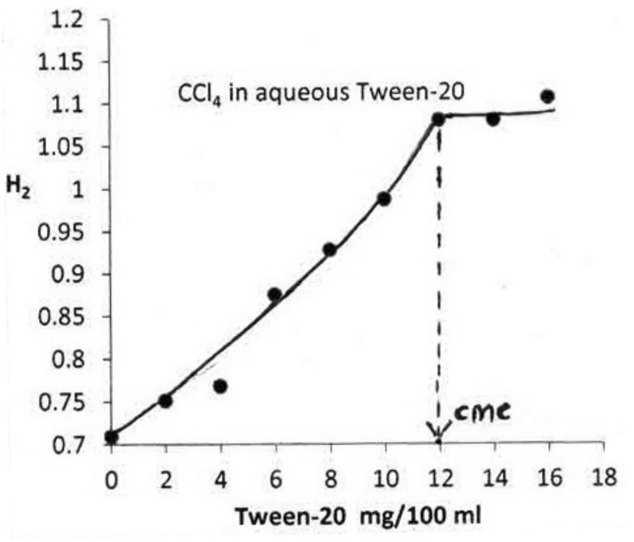

Figure 1: Plot of Hadkar Factor H_2 vs concentration of aqueous Tween-20 solutions

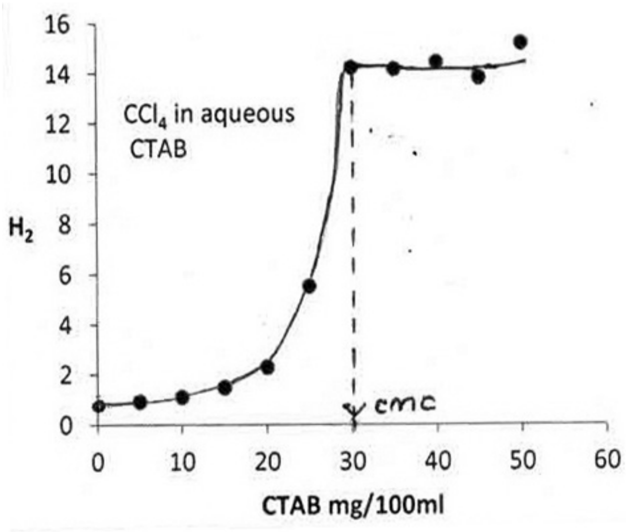

Figure 2: Plot of Hadkar Factor H_2 vs concentration of aqueous CTAB solutions

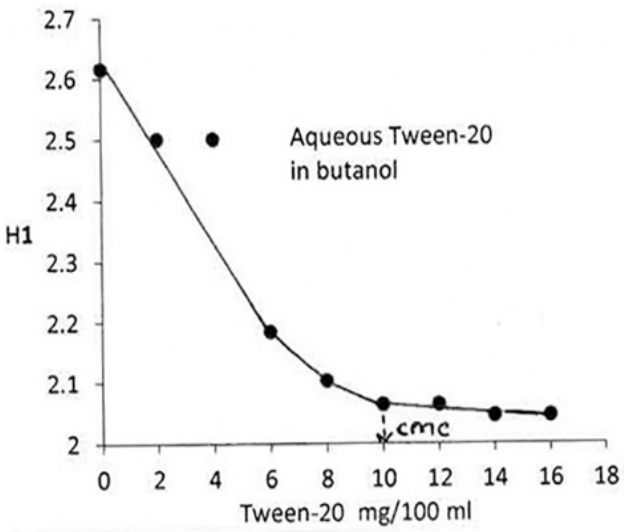

Figure 3: Plot of Hadkar Factor H_1 vs concentration of aqueous Tween-20 solutions

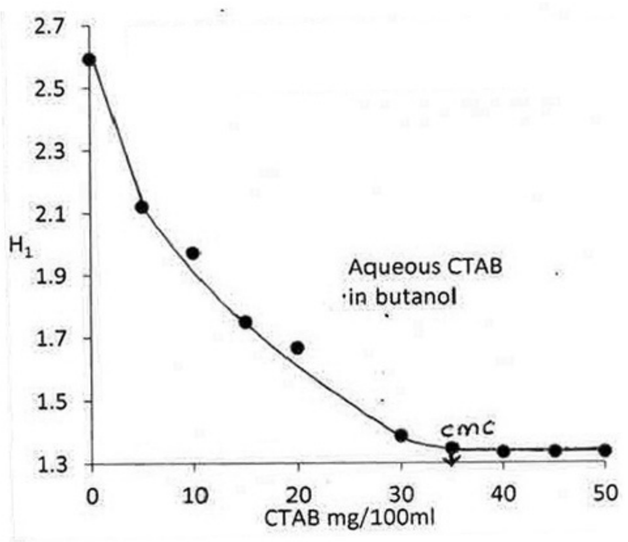

Figure 4: Plot of Hadkar Factor H_1 vs concentration of aqueous CTAB solutions

Table 4: Hadkar factor H_1 and the Interfacial tension between aqueous CTAB solution and butanol at 28°C ± 1°C

C mg/100 ml	nCTAB air per 3.5 ml	nCTAB in butanol per 3.5 ml	H_1	v (ml)	m_o (gm)	m (gm)	γ_{int} dynes/cm	S ±
0	54	397	2.5926	8.8161×10^{-3}	8.8161×10^{-3}	1.6751×10^{-3}	1.62	0.021
5	66	571	2.1212	6.1296×10^{-3}	6.1296×10^{-3}	1.1646×10^{-3}	1.38	0.022
10	71	647	1.9718	5.4096×10^{-3}	5.4096×10^{-3}	1.0278×10^{-3}	1.31	0.020
15	80	692	1.75	5.0578×10^{-3}	5.0578×10^{-3}	0.9609×10^{-3}	1.38	0.022
20	84	722	1.6667	4.8476×10^{-3}	4.8476×10^{-3}	0.9219×10^{-3}	1.39	0.023
30	101	761	1.3861	4.5992×10^{-3}	4.5992×10^{-3}	0.8738×10^{-3}	1.58	0.024
35	104	846	1.3462	4.1371×10^{-3}	4.1371×10^{-3}	0.7861×10^{-3}	1.46	0.020
40	105	870	1.3333	4.0229×10^{-3}	4.0229×10^{-3}	0.7644×10^{-3}	1.44	0.022
45	105	852	1.3333	4.1079×10^{-3}	4.1079×10^{-3}	0.7801×10^{-3}	1.47	0.022
50	105	852	1.3333	4.1079×10^{-3}	4.1079×10^{-3}	0.7805×10^{-3}	1.47	0.021

The values of γ_{int} are the average values of 5 readings.
r = radious of the tip of the pipette = 0.062 cm

$$\text{Hadkar factor H1} = \frac{(n^{butanol} \text{ in air})}{(n^{CTAB} \text{ in air})}$$

$n^{butanol}$ in air = number of drops of butanol in air per 3.5 ml = 140
n^{CTAB} in air = number of drops of aqueous CTAB solution.
n^{CTAB} in air = number of drops of aqueous CTAB solution in butanol per 3.5 ml.
γ_{int} = Interfacial tension between aqueous CTAB solution and butanol =(m/H1).).(g/2πr)
C = Concentration of aqueous CTAB solution in mg/100 ml
g = acceleration due to gravity = 980 cm/sec^2
v = vol. in c.c. of 1 drop of CTAB solution in butanol = 3.5 / nCTAB in butanol
m = mo (ρ - ρ')/ ρ = apparent mass of CTAB solution drop in butanol.
m_o = True mass of CTAB solution drop in gm = v . ρ
ρ = density of the heavier liquid CTAB solution = 1gm/cc.
ρ = density of the lighter liquid butanol = 0.81 gm/cc
Note : The density of aqueous CTAB solution is considered the same as the density of water = 1gm/cc

The interfacial tension (γ_{int}) between organic liquid and the aqueous surfactant solution was calculated using equations (3) and (4) and are reported in the tables 1 to 4. It was found that the Hadkar factor as well as the interfacial tension remains practically constant after the cmc of the surfactant. The plots of Hadkar factor H_1 or H_2 vs the concentration of the surfactant solution are given in the Figure. 1 to 4 and were used to determine the cmc of the surfactant. The cmc values of the surfactants Tween-20 and CTAB determined were in close agreement with the reported values and are given in the Table 5.The general equation for the determination of surface tension γ, of the liquid by drop weight method is

$$mg = 2\pi r \gamma \cos\theta \text{ ------------- } (5)$$

Table 5: Comparison between the cmc values of the surfactant.

Surfactant	cmc mg/100 ml	
	Determined Average value	Reported
Tween-20	11	9.865 (Note 1)
CTAB	32.5	33.48 (Note 2)

Note 1: The cmc for Tween-20 obtained from Wikipedia.com
The molecular formula of Tween-20 is $C_{58}H_{114}O_{26}$(mol.wt.1227)
cmc = 8.04×10^{-5} moles/litre = $8.04 \times 10^{-5} \times 1227$ gm/litre
=9.865 mg/100 ml.

Note2 : The cmc of CTAB (mol.wt.364) is reported by Sigma Aldrich and is obtained from, www.sigmaaldrich.com
The cmc of CTAB = 0.92 milli moles / litre
= $0.92 \times 10^{-3} \times 364$ gm / litre
= 33.48 mg/100 ml

where, m is the mass of the liquid drop about to detach from the tip of the pipette of inner radius r and θ is the angle of contact between the liquid and the glass. The equations (3) and (4) used to determine the interfacial tension, replace cosθ by Hadkar Factor H_1 and H_2 in the equations (5). The comparison of the equations (3), (4) with equation (5) indicates that Hadkar Factor H_1 and H_2 depend on the angle of contact between heavier and lighter liquids and the glass and also probably on the angle of contact between the two liquids. This however has to be proved. The exact physical significance of the Hadkar Factors H_1 and H_2 is not yet clear.

CONCLUSION

The plot of γ_{int} vs concentration of surfactant solutions is normally used to obtain cmc of the surfactant because the value of γ_{int} remains practically constant after the cmc. Since Hadkar factor H_1 (or H_2) is also found to remain constant after the cmc of the surfactant, the plot of H_1 or H_2 vs the surfactant solution concentration was used to obtain the cmc of the surfactant. The cmc values obtained from these plots are in good agreement with the reported values (Table 5).

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