Physiochemical evaluation of mixed newly mined biosurfactant with synthetic surfactants

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Abstract

Biosurfactants are surface-active molecules produced by microorganisms. Biosurfactant activity was tested on 30 random isolates. Oil displacement and drop collapse experiments proved biosurfactant production. Tensiometer and conductometer measure CMC and surface tension decrease. Isolate No. 3 had a CMC of 0.91 mg/L and reduced water surface tension by 34 mN/m. The significance of investigating mixed micellization comes in the ability to adjust the bending performance of an amphiphile by varying the stoichiometry of the mixture. Tensiometry and conductometry were used in this investigation to investigate the binary mixed systems of cetylpyridinium chloride (CPC), dodecylpyridinium chloride (DPC), and Isolate 3 at a temperature of 37.5°C. In the majority of cases, the cmc seen from either technique is comparable; however, in CPC/DPC mixtures, the tensiometric cmc is slightly attenuated to that of the conductometric. This might be because the mixed solution has a smaller stoichiometric mole fraction of CPC, resulting in a lesser extent of counterion binding at the interface of the micelle.

Keywords: Biosurfactants, surface tension, critical micelle concentration, micellization

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INTRODUCTION:

Biosurfactants are organic amphiphilic molecules containing both hydrophobic (head) and hydrophilic (tail) components [1,2]. An interfacial boundary exists between two immiscible phases [3]. Recently, interest in biosurfactants has increased because of their diversity, selectivity, flexibility in operation, higher ability to produce foam, less toxicity, greater stability under extreme conditions, and are more ecofriendly than chemical surfactants [4–12]. Biosurfactants are produced by a wide range of microorganisms, mostly bacteria, fungus, and yeast, and have a wide range of chemical compositions and characteristics. In terms of decreasing the surface tension of aqueous solutions [12–14], mixed aqueous surfactant systems often work better than the individual parts. So, these systems have a better ability to clean and dissolve insoluble substances in water. They are frequently used in the sectors of suspension, wetting, emulsifying agents, and many other technical, biological, and medicinal applications [15]. Surfactants, because of their amphiphilic nature, tend to become adsorbed interfacially in the low concentration zone. However, once the concentration is raised above a specific critical level, they begin to self-aggregate and form assembled structures. The size, form, and content of these aggregated structures are controlled by factors such as concentration of amphiphile, temperature, and salt amount, etc. The critical micelle concentration is the surfactant concentration above which micelles develop and any further surfactants added to the solution are converted into micelles. Due to the fact that micelles conduces a distinct phase inside a solution, ultimately affecting physicochemical characteristics to a significant extent depending upon the amount of surfactant. When you measure these properties with different concentrations of surfactant, you get a break in the profile, which lets you figure out the cmc of the surfactant. Most of the time, properties like surface tension and conductance are used to figure out the cmc. The variations in these attributes occur across a limited concentration range. In addition, the concentration-dependent variations in these characteristics in the pre-and post-micellar regions may be represented by two distinct linears, the intersection of which can be interpreted as the cmc of the surfactant. Investigations into the ways in which the surfactants in a mixture interact with one another might give useful information on the self-aggregation and association thermodynamics of this kind of system [16]. Researchers have invested a lot of attention analysing the self-aggregation and related thermodynamics of a wide variety of mixed surfactant combinations [17]. In this paper, we have looked at the physicochemical properties of three biosurfactants, including CPC, DPC, and Isolate number 3[18] in both unblended and blended states. DPC and CPC contain the identical head group but differ in hydrophobic tail as 12 and 16 Carbon respectively. Three binary permutations, CPC/isolate 3, DPC/isolate 3 and CPC/DPC, have been investigated. The cmc of each combination was determined by both the methods. "Using these two methods, it is possible to determine thermodynamic properties such as Gibbs adsorption energy ($\Delta \boldsymbol{G}^{\mathbf{0}}_{\boldsymbol{ad}}$) and Gibbs micellization energy ($\Delta \boldsymbol{G}^{\mathbf{0}}_{\boldsymbol{m}}$). Other variables, including cmc, Gibbs surface excess (Γ_{max}), minimum area of exclusion per surfactant monomer at the air/solution interface (A_{min}), pC_{20} (where C_{20} is the surfactant concentration required to reduce the surface tension of the liquid by 20 units), and degree of counterion binding (g), are also considered" [19].

1. Materials and Methods

Isolate 3 was extracted from contaminated soil and it was used without further purification. Experiments were conducted at a temperature of 310.65±0.4 K and solutions were prepared in double-distilled water.

*2.1 Suface tension determination:*Using the drop weight method, the surface tension of different solutions was measured. An equal volume of aliquot was added from the micropipette to a 50ml water sample in the beaker. Each experiment was done several times to make sure the results were accurate. Harkins and Jordon's approach was employed to correct the surface tension (γ) values that were measured with a precision of 0.1 mNm^{-1}.

*2.2 Conductometric:*The CMC of surfactant was measured by observing conductance measurementsusing a microprocessor-based conductometer (model-1601), make Electronic India (EI). Conductometer with cell constant 1.04 cm-1 at 37.5 (± 0.1)°C. Equal volume of aliquot was added from the micropipette to a 50ml water sample in the beaker**.** The precision of the measurements was within ±1% [19, 20].

2. RESULTS AND DISCUSSION

3.1 CMC evaluation(tensiometerically)

Using a tensiometer, the surface tension of these various dilutions was determined. In order to calculate the CMC, we plotted the surface tension versus the surfactant concentration [21,22]. We were able to get a value for the CMC by analysing the breakpoint in the generated curve. The surface tension (γ) remains relatively constant after this point. Tensiometrically, The CMC of the extracted biosurfactant can be calculated from the graph. The surface tension dropped significantly as the concentration of biosurfactants increased, reaching a minimum value of 34,00 mN/m. Surface tension could not be decreased further even after the addition of more biosurfactants to it. CMC refers to the surfactant concentration at which the the straight lines of plots of Surface tension vs log (concentration) intersection (Figure 1). (Biosurfactant concentrations above the CMC were incapable of further reducing the surface tension, suggesting that biosurfactant molecules had begun to assemble).

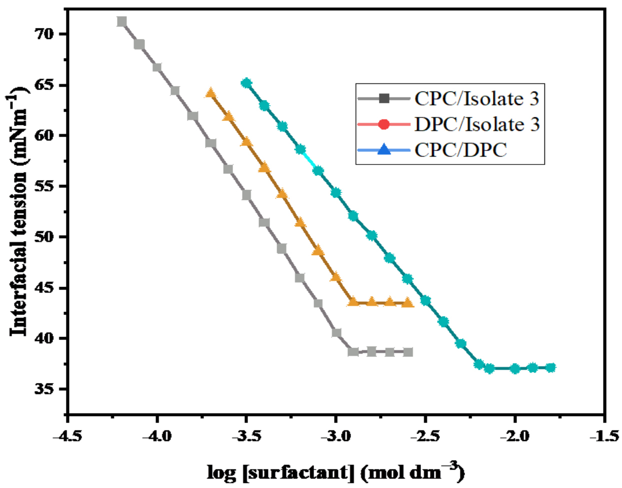

Fig 1. Tensiometric plot: Interfacial tension with log [surfactant] of binary mixtures

(1) CPC/Isolate 3,α_{CPC}=0.50;(*2*)DPC/Isolate 3,α_{DPC}=0.60;(*3*)CPC/DPC,α_{CPC}=0.90 at 311K.

From a physical perspective, this cmc is the same as the saturation of interfacial adsorption. Above this concentration, the additional surfactants have very little ability to change the interfacial morphology. Instead, they are forced to aggregate in the thick of the solution in the form of micelles. The arrangememt of monomer in micelle is like that all the hydrophobic part of monomer is engulfed by hydrophilic part of monomer [19,20]. The graph predicated the pure isolate 3, DPC and CPC to be 34.1 mNm−1 39.4 mNm−1 and 44.3 mNm−1 respectively.

3.2.CMC evaluation (conductometerically)

The conductance of the pure and mixed surfactant was determined by the same procedure as followed in the case of tensiometry. This allowed for the measurement of the conductance of the surfactant solution at varying concentrations. CMC determination through conductivity measurement is carried out by plotting the specific conductance (*k*) versus the surfactant concentration. Conductometrically, CMC is to be seen in conductivity measurements; and the conductivity of any solution is directly proportional to the concentration of its ions.

Conductivity measurement reveals characteristic plots and discontinuities of specific conductivity (*k*) versus surfactant concentration. When aggregation begins, the counterions, because of their smaller size, have very high mobility and get adsorbed in the interface region of micelle and solution [23]. This behaviour significantly change in the electrical conductivity, obviously due to the reduction in the number of ionic charge carriers in the solution. This indicates a clear split in the solution's specific conductance (κ) against the surfactant concentration isotherm (Figure 2). So, the conductometric cmc is the same as the point at which ionic surfactants in bulk solution start to stick together on their own.

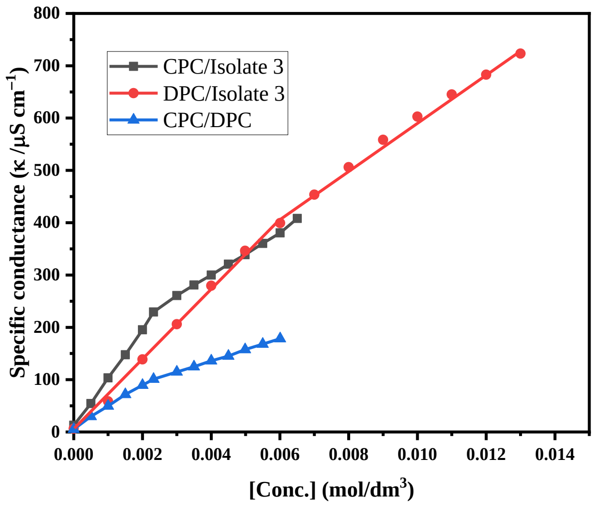

Fig 2. The plot of specific Conductance with [conc.] of binary mixture (*1*)CPC/Isolate 3,α_{CPC}=0.25;(*2*)DPC/Isolate 3,α_{DPC}=0.40; (*3*)CPC/DPC,α_{CPC}=0.90 at 311K.

If the processes of interfacial saturation and bulk association are consistent with one another, the values of cmc that are detected using either approach will corroborate one another and vice versa. Both methods yield the cmc value of the pure surfactants, which are quite close to one another (Table 1 to 3). The cmc values have a reciprocal relationship with the length of the tail [24, 25]. Their cmcs differ by almost a 1:19 ratio. This shows that in the micellization process, the hydrophobic interaction is stronger than the electrostatic interaction.

Table 1:CMC valueofisolate 3(pure) and a binary mixture of CPC and Isolate 3 (10^3cmc,mol/L) at 311K.

α_{CPC}	Tensiometric cmc	Conductometric cmc	Averagecmc
0.00	3.715	3.524	3.620
0.10	2.564	2.716	2.640
0.25	1.556	2.255	1.906
0.50	1.247	1.562	1.404
0.75	0.998	1.250	1.124
0.90	0.920	1.313	1.026
1.00	0.910	1.036	0.973

Table 2: CMC value of isolate 3 (pure) and a binary mixture of DPC and Isolate 3(10^3cmc,mol/L) at 311K.

α_{DPC}	Tensiometric cmc	Conductometric cmc	Averagecmc
0.00	3.715	3.524	3.620
0.10	3.908	3.992	3.950
0.25	4.645	4.731	4.688
0.40	5.297	5.781	5.539
0.50	5.929	6.435	6.182
0.60	7.211	7.131	7.171
0.75	9.453	9.387	9.420
0.90	11.695	12.414	12.054
1.00	17.132	17.608	17.370

Table 3: CMC valueofDPC (pure) and a binary mixture of CPC and DPC (10^3cmc,mol/L) at 311K.

α_{CPC}	Tensiometric cmc	Conductometric cmc	Averagecmc
0.00	17.132	17.608	17.370
0.10	4.291	8.631	6.461
0.25	3.254	7.764	5.509
0.40	2.218	5.190	3.704
0.50	1.527	3.950	2.739
0.60	1.465	2.775	2.120
0.75	1.445	2.469	1.957
0.90	1.096	2.296	1.696
1.00	0.910	1.036	0.973

Among the binary mixes, the cmc values obtained from either approach are quite similar to one another for the CPC/Isolate 3 and DPC/Isolate 3 systems. On the other hand, for CPC-DPC binary mixtures, the CMC calculated tensiometrically is significantly less in comparison to conductometrically. indicating a shift in concentration for saturation of interface and micelle formation. It can be deduced that for any mixture the CMC is near to the value of component that has a longer tail length and this value become more close with an increase of ratio of that component.

3.2. Interfacial adsorption and energetic of micellization

3.2.1. Interfacial adsorption:

When surfactants are introduced to water, their surface-active qualities cause them to first collect at the interface between the air and an aqueous medium. As a result, that disrupts the water molecule arrangement on the surface, thus decreasing the water at the surface. When the process of interfacial saturation by the surfactant is finished, the molecules of the surfactant begin 1046
to assemble in the thick of the solution on micelles. The commencement of interfacial saturation is indicated by a sudden jerk in the graph of γ vs. log [concentration], after which the interfacial tension becomes independent of concentration. The efficacy of any pure and mixed amphiphile may be evaluated in the form of Gibbs surface excess ($\Gamma_{\max}$). This value is determined by using equation no. 2 [19,20, 26-29].

$$\Gamma_{\max} = -\frac{1}{2.303nRT}\underset{C-cmc}{Lt}\frac{d\gamma}{d\log C} \quad (2)$$

Where, γ, R and T bear their usual significance, while n denotes the mean number of ions per surfactant monomer. In this scenario, n is assumed to be equal to one for pure surfactants as well as for their binary mixes. Its estimation based on the fact of counterion trapping in the interface region seems to be a rough estimation. On a molarity scale [20], C represents the overall concentration of surfactant. Using equation 3, we can figure out the (A_{min}) and provide a list of all abbreviations for every in a fully saturated interface near the critical micelle concentration.

$$A_{min} = \frac{10^{18}}{N_A\Gamma_{max}} \quad (3)$$

Where 10^{18} is the factor that results from converting metres to nanometers and N_A is the Avogadro number. By using conductometry, we are able to determine the percentage of counterion binding (g) that occurs on the surface of the micellar aggregate [19,27-29]. The proportion of counterion dissociation (*f*) was evaluated by the quotient of slopes of the post micellar and pre micellar regions of the graph of the specific conductance v/s. [conc.]. From the *f* (counterion dissociation); the factor g (counterion binding) is calculating by using formula g = 1 – *f* [30, 31]. C_{20} is the concentration of surfactant that is necessary to reduce the surface tension by 20 mNm^{-1}. pC_{20} is-log [C_{20}]. The C_{20} concentration is inversely proportional to the activity of the surfactant. The ratio of cmc to C_{20} determines the preference of a surfactant mixture for micellization over interfacial adsorption [30, 31].

According to Table 4 to 5, the maximum valueΓ_{max} rises as the tail becomes longer, whileA_{min}it falls with time. The pC_{20} values exhibit the same trend as Γ_{max}, as predicted, as shown in the table, as isotherms are linear. The proportionate relationship ofΓ_{max} and pC_{20} with tail length is owed to the increased surface activity resulting from the surfactant's increasing hydrophobicity. The decrease means that the surfactant-saturated monolayer is getting closer together because the van der Waals forces between the hydrophobic ends are getting stronger. The ratio of cmc/C_{20} rises with decreasing chain length, indicating that the shorter-chained surfactant prefers micellization over interfacial adsorption. The degree to which counterions condense onto the membrane interface is greatest for Isolate 3 and decreases from CPC to DPC. This is because Isolate 3 has the highest concentration of counterions at the interface. The decrease in g with decreasing hydrophobic length may be due to a change in the size of the micellar. Nevertheless, the larger "g" value for Isolate 3 indicates a stronger zeta potential.

Table 4: Physiochemical properties (Π_{cmc}, Γ_{max}, A_{min}, g, pC_{20}) and free energy (interfacial andmicellization)of isolate 3and CPC mixtureat311K.

α_{CPC}	$(\Pi_{cmc})10^3$, J/m^2	$(\Gamma_{max})10^6$ mol/m^2	A_{min}, nm^2/molecule	g	$-\Delta G_m^\circ$, kJ/mol	$-\Delta G_{ad}^\circ$, kJ/mol	pC_{20}	$\frac{cmc}{C20}$
0.00	37.9	4.52	0.37	0.645	39.94	48.33	3.09	4.41
0.10	36.1	4.63	0.36	0.583	39.70	47.50	3.19	4.09
0.25	35.7	4.89	0.34	0.564	40.50	47.81	3.36	4.38
0.50	34.0	4.97	0.33	0.557	41.52	48.36	3.38	3.38
0.75	31.5	5.19	0.32	0.602	43.62	49.69	3.36	2.59
0.90	29.2	5.50	0.30	0.615	44.34	49.65	3.34	2.23
1.00	27.7	5.99	0.28	0.601	44.17	48.79	3.28	1.84

In the case of the CPC/Isolate 3 mixes, bothγ_{cmc} and Γ_{max} rise with an increasing composition of CPC, butA_{min}value follows the opposite pattern. There is a noticeable decline in the value of 'g' of pure Isolate 3 micelle due to the simple presence of CPC; this value decreases to its lowest point at α_{CPC} = 0.5 and then begins to rise again. At the same time, pC_{20} achieves its highest value at α_{CPC} = 0.5.

Table 5: Physiochemical properties (Π_{cmc}, Γ_{max}, A_{min}, g, pC_{20}) and free energy (interfacial and micellization)of isolate 3and the DPC mixtureat311K.

α_{DPC}	$(\Pi_{cmc})10^3$, J/m^2	$(\Gamma_{max})10^6$ mol/m^2	A_{min}, nm^2/molecule	g	$-\Delta G_m^\circ$, kJ/mol	$-\Delta G_{ad}^\circ$, kJ/mol	pC_{20}	$\frac{cmc}{C20}$
0.00	37.9	4.52	0.37	0.645	39.94	48.33	3.09	4.45
0.10	37.4	4.29	0.39	0.710	41.14	49.86	3.07	4.62
0.25	37.6	4.48	0.37	0.639	38.73	47.11	3.01	4.85
0.40	37.2	5.13	0.32	0.606	37.27	44.52	2.86	3.97
0.50	36.6	4.25	0.39	0.592	36.51	45.12	2.91	5.07
0.60	35.7	3.47	0.48	0.579	35.62	45.92	2.93	6.14
0.75	34.6	3.30	0.51	0.542	33.73	44.21	2.80	5.94
0.90	33.7	3.12	0.53	0.500	31.88	42.67	2.67	5.66
1.00	32.6	2.6	0.64	0.554	31.59	44.14	2.48	5.29

In the case of the DPC/Isolate 3 mixes, the value of γ_{cmc} reaches a minimum when α_{DPC} equals 0.4 and then gradually grows after that Γ_{max} achieves another maximum value when α_{DPC} is equal to 0.4.

However, the pC_{20} readings do not follow any regular pattern. The difference in 'g' represents the stoichiometric proportion of DPC.

Table 6: Physiochemical properties (Π_{cmc}, Γ_{max}, A_{min}, g, pC_{20}) and free energy (interfacial and micellization)of DPCand the CPC mixtureat311K.

α_{CPC}	$(\Pi_{cmc})^{*}10^3$, J/m^2	$(\Gamma_{max})10^6$ mol/m²	A_{min}, nm²/molecule	g	$-\Delta G^\circ_m$, kJ/mol	$-\Delta G^\circ_{ad}$, kJ/mol	pC_{20}	$\frac{cmc}{C_{20}}$
0.00	32.6	2.60	0.64	0.554	31.59	44.14	2.48	5.29
0.10	31.6	2.27	0.73	0.338	29.56	43.48	3.20	10.24
0.25	30.7	2.51	0.66	0.371	30.65	42.88	3.24	9.57
0.40	29.8	2.75	0.60	0.37	33.19	44.03	3.28	7.13
0.50	29.6	3.74	0.44	0.355	33.85	41.76	3.24	4.73
0.60	28.7	3.96	0.42	0.521	38.98	46.23	3.23	3.61
0.75	28.1	4.14	0.40	0.509	38.98	45.77	3.25	3.47
0.90	27.6	4.51	0.37	0.503	39.36	45.48	3.24	2.97
1.00	27.7	5.99	0.28	0.601	44.17	48.79	3.28	1.84

$^{*}\Pi_{cmc}$ = Surface pressure at cmc

In the case of the CPC/DPC mixes, when α_{CPC} value is increased, the γ_{cmc} of the CPC/DPC system gradually lowers while the Γ_{max} value gets higher. The most significant finding is that there is a precipitous drop in the value of 'g' for pure DPC when CPC is present at concentrations up to 0.5 times its normal level. This shows that there is a decline in charge density at the surfaceofthe head group of surfactant. This is likely due to the pile up interaction between the pi-electron cloud, which is possible only if the chain length varies. This results in a reduction in the degree of counterion condensation, which in turn destabilises the micellar structure. This destabilisation may be responsible for the concentration lag that exists between interfacial saturation and bulk micellization in certain compositions.

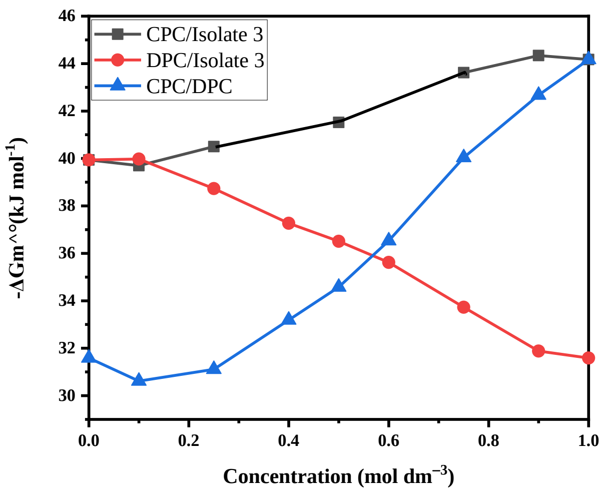

Fig 3.The plot of the standard free energy of micellization with concentration at 311K.

3.3 EnergeticsofMicellization

It is possible to calculate the $\Delta G^o_m$for micellization with the use of the value as given by the equation.

$$\Delta G^o_m = (1 + g)R\,T\ln x_{cmc} \quad (4)$$

Where x_{cmc} denote cmc in term of mole fraction and factor (1 + g) in equation 4 is the contribution to ΔG_m^o resulting from the condensation of counterions on the micellar surface. The equation to determine the $\Delta G_{ad}^o$is givenas follows:

$$\Delta G_{ad}^o = \Delta G_m^o - \left(\Pi_{\text{cmc}}/\Gamma_{\text{max}}\right) \quad (5)$$

Where $\Pi_{\text{cmc}}$is denotion for pressure at the surface at the cmc value, which is defined by $\Pi_{\text{cmc}} = \gamma_{\text{water}} - \gamma_{\text{cmc}}$, where γ_{water} is the surface tension of pure water at a given temperature and the latter is the surface tension of the solution at the cmc value. Changes in free energy caused by micellization and interfacial adsorption. Tables 4 to 6 list the ΔG_m^o and ΔG_{ad}^o for binary surfactant combinations CPC/Isolate 3, DPC/Isolate 3 and CPC/DPC, respectively. The counterion condensation (g) values for the CPC/Isolate 3 and DPC/Isolate 3 binary blends are greater than the binary CPC/DPC system. The corresponding$\Delta G_m^o$for the CPC/Isolate 3 and CPC-DPC mixture both rise with the mole fraction of CPC (Fig. 3), which shows that the micelle formation becomes more thermodynamically feasible with CPC. On the other hand, the DPC/Isolate 3 system exhibits the opposite pattern. The values adhere to the same pattern as that of $\Delta G_m^o$for binary mixes CPC/Isolate 3, DPC/Isolate 3, but ΔG_{ad}^odo not adhere to any regular trend when it comes to CPC/DPC.

Conclusion

From a thermodynamic point of view, this study uses tensiometry and conductometry to study how three surfactants with different lengths of tails behave when mixed. The fact that the cmc value goes up as the length of the tail gets shorter shows that hydrophobic interactions are the most important factor in micelle formation behaviour. The strong agreement of cmc values by both methods strongly suggests that saturation at the surface and the formation of micelle in bulk occur simultaneously. The discrepancy in critical micelle value for CPC/DPC by both methods (Table-3) may be due to lower charge density at the interface. Owing to the pi to pi bond interaction of the pyridinium head group with varying hydrophobic lengths, The fact that there was a negative difference in the empirical value of CMC for binary suggests that the surfactant head groups with similar charges are involved in van der Waals attractive forces.

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