Induced Alterations in the Aggregation Behavior and Thermodynamic Properties of Anionic Surfactant Sodium Tetradecl Sulfate (STS) in presence of Imidazolium Based Ionic Liquid in Aqueous Media: A Conductometric Study

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Abstract. Surfactants can be considered as an important class of chemical species having a polar head and non-polar tail, which make it capable to be utilized in many industrial formulations such as coatings, paints, lubricants, and cosmetics, etc. Also, ionic liquids, which are actually molten salts, are also having many useful properties such as negligible vapor pressure, high thermal stability, etc. They can modify the physiological as well as aggregation properties of conventional surfactants according to our desire. The mixtures of ionic liquids with a surfactant are found to be better systems for many industrial applications than individual ones. Thus the micellization behavior of sodium tetradecl sulfate STS is investigated in the presence of 1-propyl-3-methylimidazolium bromide [C₃mim][Br] in aqueous media. For this, ionic liquid 1-propyl-3-methylimidazolium bromide [C₃mim][Br] is synthesized in our lab. Then the conductivity measurement is done to determine the critical micelle concentration (CMC) of sodium tetradecyl sulfate STS in the absence and presence of (0.02, 0.05 and 0.1) wt. %, of 1-propyl-3-methylimidazolium bromide [C₃mim][Br] in aqueous medium at three different temperatures i.e. (298.15, 303.15 and 308.15) K. The results are then utilized to find the thermodynamic parameters of micellization such as, standard free energy of micellization, standard enthalpy of micellization, and standard entropy of micellization, which are important to understand the driving force behind the process of micellization.

1. Introduction

Amphiphilic compounds such as surfactants have the capability to aggregate in the aqueous medium due to the presence of a hydrophobic tail group and a hydrophilic polar head group in their structures. The aggregation of surfactant monomers happens through the delegate balance between hydrophobic and hydrophilic interactions occurring within the molecule after the addition of a specific concentration of them in the aqueous medium. These aggregates of surfactant monomers are referred to as micelles and the specific concentration above which formation of micelle starts is known as critical micelle concentration (CMC) [1]-[4]. The self-assembly of surfactant monomers is the unique property of surfactants, which makes them capable to be used in various applied fields such as detergents, paints, cosmetics, biotechnology, and petroleum industry, etc.[5], [6]. The aggregation of surfactant monomers can be altered by the addition of additives, thereby changing the critical micelle concentration of surfactants. These additives can be ionic liquids, electrolytes, drugs or amino acids, etc. [7]-[9]. In this report, the ionic liquid is taken as an additive which altered the aggregation behavior of anionic surfactant. Ionic liquids are basically molten organic salt having specific...
physicochemical properties, which make them to be utilized in biodegradable composite materials, medicine and separation processes of various compounds [10]-[13]. Thus the investigation of various alterations induced in the aggregation behavior of anionic surfactant by the addition of ionic liquids is important from the fundamental point of view and due to the practical significance of such systems [14], [15]. For this, the conductometric technique is employed, which can be considered as a very reliable method to determine the critical micelle concentration [16], [17]. The value of critical micelle concentration obtained for sodium tetradecyl sulfate (STS) at different temperatures as well as in the presence of (0.02, 0.05 and 0.1) wt. %, of 1-propyl-3-methylimidazolium bromide [C₃mim][Br], is further utilized to find various thermodynamic parameters of micellization, which gives insight to the process of micellization.

![Figure 1. Structures of (a) sodium tetradecyl sulfate (b) 1-propyl-3-methylimidazolium bromide](image-url)

2. Experimental

2.1. Materials

1-methylimidazole and 1-bromopropane purchased from HIMEDIA Laboratories Pvt. Ltd having purity >0.99 and >0.98 respectively were used to synthesize the ionic liquid 1-propyl-3-methylimidazolium bromide [C₃mim][Br]. For the reaction, acetonitrile purchased from LOBA Chemie Pvt. Ltd Mumbai having purity >0.995 was used as a solvent. Hexane having purity >0.96 was procured from TCI Pvt. Ltd. The anionic surfactant sodium tetradecyl sulfate (STS) purchased from SIGMA ALDRICH, which was then dried under vacuum and stored over P₂O₅ in vacuum desiccators for at least 48h before its use. Table 1 incorporates the details of all the chemicals used in the study.

| Chemicals               | Source                                | CAS No | Purification Method       | Mass Fraction Purity* |
|-------------------------|---------------------------------------|--------|---------------------------|-----------------------|
| 1-methylimidazole       | HIMEDIA Laboratories Pvt. Ltd          | 616-47-7 | No further purification   | >0.99                 |
| 1-bromopropane          | HIMEDIA Laboratories Pvt. Ltd          | 106-94-5 | No further purification   | >0.98                 |
| Acetonitrile            | LOBA Chemie Pvt. Ltd Mumbai           | 75-05-8 | No further purification   | >0.995                |
| Hexane                  | TCI Pvt. Ltd                          | 110-54-3 | No further purification   | >0.96                 |
| Sodium tetradecyl sulfate | SIGMA ALDRICH                        | 1191-50-0 | Vacuum drying             | >0.95                 |

*As declared by the supplier

2.2. Synthesis of [C₃mim][Br]
Ionic Liquid [C₃mim][Br] has been synthesized by adding 1-bromopropane into 1-methylimidazole taken in a round bottom flask. Acetonitrile is taken as a solvent to dissolve the reaction mixture. Then the above mixture is refluxed at about 80-84°C for 48 hours. Thin Layer Chromatography (TLC) technique is used to monitor the progress of the reaction. Then the solvent is evaporated by using a rotary evaporator. The product obtained was then washed using hexane in a separatory funnel to remove the impurities. The stock solutions are prepared only after drying the ionic liquid under vacuum for a few days. The ¹H NMR and FT-IR spectra of synthesized ionic liquid [C₃mim][Br] have been shown in figure S1 and figure S2 given in supporting information.

2.3. Conductivity measurements

Systronics 306 digital conductivity meter with a cell having unit cell constant is employed to carry out conductivity measurements. For this, the stock solution of (0.02, 0.05 and 0.1) wt. % of 1-propyl-3-methylimidazolium bromide [C₃mim][Br] has been prepared using Sartorius CPA 225 D (precision = ±0.00001g). Doubly distilled deionized water obtained from Millipore, Milli-Q Academic water purification system has been utilized to prepare the samples. The conductivity of the test solution is measured after each addition of the surfactant solution. The conductivity is calibrated using an aqueous KCl solution before the measurement of conductivity. The temperature of the test solution is maintained using a refrigerated circulated water thermostat having an accuracy of ±0.1 K.

3. Results and discussions

3.1. Effect of adding[C₃mim][Br]on the critical micelle concentration (CMC) of STS

The conductivity, κ, of anionic surfactant STS is measured in the absence and presence of [C₃mim][Br] in aqueous medium at different temperatures i.e. (298.15, 303.15, 308.15) K.

Table 2. Specific conductivity κ (µS cm⁻¹) of STS in the absence and presence of 0.02 wt.% of [C₃mim][Br] at (298.15, 303.15, 308.15) K temperatures.

| Concentration (mM) | 0.00 wt.% [C₃mim][Br] | 0.02 wt.% [C₃mim][Br] |
|-------------------|------------------------|------------------------|
|                   | 298.15K  | 303.15K  | 308.15K  | 298.15K  | 303.15K  | 308.15K  |
| 0.196             | 22.58    | 32.62    | 47.43    | 102.8    | 119.7    | 135.3    |
| 0.291             | 30.45    | 40.33    | 54.61    | 107.3    | 125.2    | 139.5    |
| 0.385             | 37.93    | 49.21    | 61.52    | 112.7    | 130.2    | 144.5    |
| 0.476             | 46.13    | 54.15    | 68.42    | 117.6    | 134.3    | 148.1    |
| 0.566             | 52.55    | 62.04    | 75.19    | 122.5    | 138.9    | 152.7    |
| 0.654             | 59.16    | 68.69    | 80.93    | 126.2    | 143.4    | 155.5    |
| 0.741             | 66.43    | 74.81    | 87.56    | 130.5    | 147.2    | 159.1    |
| 0.826             | 73.44    | 81.13    | 93.39    | 133.9    | 150.7    | 163.1    |
| 0.909             | 80.44    | 85.45    | 98.89    | 139.1    | 154.5    | 166.9    |
| 0.991             | 84.79    | 91.96    | 104.3    | 142.2    | 158.4    | 170.4    |
| 1.071             | 88.79    | 97.28    | 110.5    | 146.4    | 161.5    | 173.2    |
| 1.150             | 93.31    | 103.2    | 116.0    | 148.3    | 165.0    | 175.8    |
| 1.228             | 97.10    | 106.8    | 121.6    | 151.3    | 168.2    | 179.1    |
| 1.304             | 100.0    | 111.7    | 126.5    | 153.1    | 171.1    | 182.2    |
| 1.379             | 103.2    | 114.7    | 131.5    | 155.8    | 174.1    | 184.5    |
| 1.453             | 107.5    | 118.2    | 136.1    | 157.6    | 176.7    | 187.1    |
| 1.525             | 111.4    | 123.4    | 140.6    | 160.3    | 179.1    | 190.0    |
| 1.597             | 114.6    | 128.2    | 144.7    | 162.1    | 181.1    | 192.6    |
| 1.667             | 118.2    | 131.1    | 149.2    | 164.2    | 183.1    | 195.1    |
| 1.736             | 121.1    | 135.2    | 153.1    | 166.3    | 186.6    | 197.0    |
| 1.803             | 124.7    | 138.3    | 156.5    | 168.1    | 189.1    | 199.7    |
| 1.870             | 127.3    | 142.3    | 160.1    | 170.8    | 190.7    | 201.8    |
| 1.935             | 130.8    | 145.2    | 163.2    | 173.6    | 193.6    | 204.4    |
Table 3. Specific conductivity $\kappa$ ($\mu$S cm$^{-1}$) of STS in the presence of 0.05 wt.% and 0.10 wt.% of [C$_3$mim][Br] at (298.15, 303.15, 308.15) K temperatures.

| Concentration (mM) | $0.05$ wt.% [C$_3$mim] [Br] | $0.10$ wt.% [C$_3$mim] [Br] |
|--------------------|-----------------------------|-------------------------------|
|                    | 298.15K | 303.15K | 308.15K | 298.15K | 303.15K | 308.15K |
| 0.196              | 194.9   | 214.8   | 236.9   | 382.5   | 415.1   | 444.8   |
| 0.291              | 196.5   | 216.7   | 238.9   | 384.3   | 417.3   | 446.5   |
| 0.385              | 198.4   | 218.4   | 240.5   | 386.5   | 418.9   | 448.2   |
| 0.476              | 199.9   | 220.7   | 242.3   | 387.8   | 421.4   | 449.7   |
| 0.566              | 201.7   | 222.6   | 244.1   | 389.8   | 423.3   | 450.9   |
| 0.654              | 203.2   | 224.8   | 246.4   | 391.1   | 425.1   | 452.4   |
| 0.741              | 205.1   | 226.1   | 248.5   | 392.8   | 426.3   | 453.9   |
| 0.826              | 206.2   | 227.8   | 250.4   | 394.1   | 428.7   | 455.2   |
| 0.909              | 207.7   | 229.9   | 252.2   | 395.7   | 430.6   | 456.8   |
| 0.991              | 209.2   | 231.8   | 254.1   | 397.2   | 432.3   | 458.2   |
| 1.071              | 210.2   | 233.3   | 255.3   | 398.5   | 433.8   | 459.4   |
| 1.150              | 211.7   | 234.6   | 256.9   | 399.9   | 435.7   | 460.9   |
| 1.228              | 212.5   | 236.2   | 258.4   | 400.8   | 437.1   | 462.4   |
| 1.304              | 213.2   | 237.7   | 259.8   | 401.4   | 438.2   | 463.4   |
| 1.379              | 214.3   | 238.9   | 261.7   | 402.7   | 439.4   | 464.3   |
| 1.453              | 214.8   | 240.1   | 262.9   | 403.4   | 440.6   | 465.5   |
| 1.525              | 215.6   | 241.2   | 264.4   | 404.2   | 441.7   | 466.3   |
| 1.597              | 216.4   | 242.4   | 265.6   | 405.5   | 442.9   | 467.5   |
| 1.667              | 217.2   | 243.7   | 266.5   | 406.6   | 444.2   | 468.6   |
| 1.736              | 218.3   | 244.8   | 267.6   | 407.3   | 445.3   | 469.7   |
| 1.803              | 219.1   | 245.8   | 269.1   | 407.9   | 446.5   | 470.6   |
| 1.870              | 219.8   | 246.9   | 270.5   | 408.5   | 447.8   | 471.5   |
| 1.935              | 220.7   | 247.9   | 271.8   | 409.3   | 449.1   | 472.4   |
| 2.000              | 221.9   | 249.3   | 273.2   | 410.4   | 450.5   | 473.6   |

The values of conductivity, $\kappa$, in the absence and presence of [C$_3$mim][Br]. at (298.15, 303.15, 308.15) K has been shown in table 2 and table 3. The critical micelle concentration (CMC) has been determined by utilizing this data.
The plots of conductivity versus concentration of STS has been shown in figure 2 and figure 3. In the plots, two linear regions having different slopes have been observed indicating that the rate of change of conductivity with the concentration of STS varies after the micellization of STS. The value of conductivity rises rapidly before micelle formation due to the presence of more charge carriers whereas this rise becomes less rapid after micelle formation due to slow mobility of micelles [18], [20]. Thus the critical micelle concentration is obtained at the breakpoint as shown in Figure. The value of CMC has been found in good agreement with the literature [21].

Table 4. Critical micelle concentration (CMC), degree of counter ion dissociation ($\alpha$) of STS in (0.00, 0.02, 0.05, 0.10) wt.% of [C$_3$ mim] [Br] at (298.15, 303.15, 308.15) K temperatures.

| [C$_3$ mim] [Br] (wt.%) | CMC (mM) | $\alpha$ |
|-------------------------|----------|----------|
| **$T = 298.15$ K**      |          |          |
| 0.00                    | 0.98     | 0.608    |
| 0.02                    | 1.03     | 0.625    |
| 0.05                    | 1.07     | 0.660    |
| 0.10                    | 1.14     | 0.683    |
| **$T = 303.15$ K**      |          |          |
| 0.00                    | 1.04     | 0.739    |
| 0.02                    | 1.08     | 0.764    |
| 0.05                    | 1.11     | 0.788    |
| 0.10                    | 1.18     | 0.802    |
| **$T = 318.15$ K**      |          |          |
| 0.00                    | 1.09     | 0.823    |
| 0.02                    | 1.13     | 0.835    |
| 0.05                    | 1.16     | 0.867    |
| 0.10                    | 1.22     | 0.872    |

Standard uncertainties s are $s(T) = \pm 0.1 \text{ K}$, $s(\text{CMC}) = \pm 0.0001 \text{ mM}$
The ratio of slopes in the post- micellar region ($S_2$) and pre-micellar region ($S_1$) gives the degree of counter-ion dissociation ($\alpha$) indicated by equation (1).

$$\alpha = \frac{S_2}{S_1}$$ (1)

The critical micelle concentration (CMC) and degree of counter-ion dissociation ($\alpha$) of system constituting STS and [C$_3$mim][Br] has been reported in table 4 at different temperatures. The value of critical micelle concentration (CMC) as well as the degree of counter-ion dissociation ($\alpha$) increases with the increase in the concentration of [C$_3$mim][Br]. The increase in the CMC of STS can be explained by using the fact that the hydrophobic interactions dominate on the addition of [C$_3$mim][Br], which can lead to solubilization of surfactant monomers leading to delay in process of aggregation [22].

3.2. Effect of increasing temperature on the critical micelle concentration (CMC) of STS

The value of critical micelle concentration (CMC) of STS increases with the increase in temperature of the system. This may be due to the reason that the increase in temperature leads to the disruption of H-bonds existing in water structure, which contributes to delay in process of micellization. Thus at a higher temperature, self-assembly of STS becomes poorer giving rise to an increase in the value of CMC.

3.3. Determination of thermodynamic parameters of micellization

Temperature dependence of conductivity has been utilized to determine different thermodynamic parameters of micellization such as standard Gibbs free energy of micellization $\Delta G^0_m$, standard enthalpy of micellization $\Delta H^0_m$, standard entropy of micellization $\Delta S^0_m$. Determination of these parameters is important to find the driving force behind the process of micellization. Table 5 incorporates the values of these parameters obtained for STS in the presence of different concentrations of [C$_3$mim][Br] at different temperatures.

3.3.1. The standard Gibbs’ free energy of micellization ($\Delta G^0_m$)
The standard Gibbs free energy of micellization, $\Delta G_m^0$, can be determined by using the equation (2) given below based upon charged pseudo-phase model of micelle formation [1].

$$\Delta G_m^0 = (2-\alpha) RT \ln X_{CMC}$$ (2)

where, $R$ is universal gas constant, $T$ is absolute temperature, $X_{CMC}$ is the value of CMC obtained from conductivity concentration plots and expressed in mole fraction units, $\alpha$ is the degree of counterion dissociation. The value of $\Delta G_m^0$ come out to be negative for all the concentrations of [C$_3$ mim] [Br] as well as temperatures indicating the spontaneity of the process of micellization. These negative values become less negative by the addition of [C$_3$ mim] [Br] as well as with the increase in temperature. This indicates that the process of micellization become less feasible by the addition of [C$_3$ mim] [Br] and with the increase in temperature.

**Table 5.** The standard Gibbs’ free energy of micellization ($\Delta G_m^0$), the enthalpy of micellization ($\Delta H_m^0$), and the entropy of micellization ($\Delta S_m^0$) of STS in (0.00, 0.02, 0.05, 0.10) wt.% of [C$_3$ mim] [Br] at (298.15, 303.15, 308.15) K temperatures.

| [C$_3$ mim] [Br] (wt.%) | $\Delta G_m^0$ (kJ mol$^{-1}$) | $\Delta H_m^0$ (kJ mol$^{-1}$) | $\Delta S_m^0$ (J mol$^{-1}$ K$^{-1}$) |
|-------------------------|-------------------------------|------------------------------|-------------------------------------|
|                         | $T = 298.15$ K                |                              |                                     |
| 0.00                    | -37.77                        | -10.94                       | 89.97                               |
| 0.02                    | -37.14                        | -9.42                        | 92.97                               |
| 0.05                    | -36.06                        | -8.00                        | 94.12                               |
| 0.10                    | -35.25                        | -6.60                        | 96.08                               |
|                         | $T = 303.15$ K                |                              |                                     |
| 0.00                    | -34.60                        | -10.25                       | 80.33                               |
| 0.02                    | -33.78                        | -8.75                        | 82.59                               |
| 0.05                    | -33.06                        | -7.48                        | 84.38                               |
| 0.10                    | -32.48                        | -6.21                        | 86.67                               |
|                         | $T = 318.15$ K                |                              |                                     |
| 0.00                    | -32.69                        | -9.89                        | 74.00                               |
| 0.02                    | -32.25                        | -8.52                        | 77.00                               |
| 0.05                    | -31.29                        | -7.23                        | 78.09                               |
| 0.10                    | -31.01                        | -6.04                        | 81.01                               |

The negative values of $\Delta H_m^0$ obtained by utilizing conductivity data indicate that the micellization process is exothermic in nature. The value of $\Delta H_m^0$ becomes less negative by the addition of ionic liquid and with the increase in temperature as observed from the data given in table 5.

**3.3.2. The enthalpy of micellization ($\Delta H_m^0$)**

For the determination of the enthalpy of micellization, $\Delta H_m^0$, the following equation (3) has been utilized [1].

$$\Delta H_m^0 = -RT^2 (2-\alpha) [d(ln X_{CMC})/dT]$$ (3)

**3.3.3. The entropy of micellization ($\Delta S_m^0$)**

The entropy of micellization, $\Delta S_m^0$ can be calculated by using the equation (4) given below [1].

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0)/T$$ (4)

The large positive values of $\Delta S_m^0$ obtained indicates that the process of micellization is driven by entropy. This large positive value can be explained by considering the fact that the three-dimensional structure of water around the hydrophobic tails of the surfactant gets disrupted by the aggregation of surfactant monomers in solution. This results in the release of water molecules from the hydrophobic pocket of micelle to bulk leading to increased entropy of the system. But the value of entropy is
decreased by the increase in temperature of the system as observed in table 5. Figure 6, figure 7 and figure 8 shows the effect of the addition of [C₃mim] [Br] and increasing temperature on the thermodynamic parameters of micellization of anionic surfactant STS in an aqueous medium.

**Figure 6.** Plot of Gibbs' free energy of micellization ($\Delta G^0_m$) of STS in (0.00, 0.02, 0.05, 0.10) wt.% of [C₃mim] [Br] at (298.15, 303.15, 308.15) K temperatures.

**Figure 7.** Plot of enthalpy of micellization ($\Delta H^0_m$) of STS in (0.00, 0.02, 0.05, 0.10) wt.% of [C₃mim] [Br] at (298.15, 303.15, 308.15) K temperatures.

**Figure 8.** Plot of the entropy of micellization ($\Delta S^0_m$) of STS in (0.00, 0.02, 0.05, 0.10) wt.% of [C₃mim] [Br] at (298.15, 303.15, 308.15) K temperatures.

4. Conclusion
A detailed conductivity study of the system constituting anionic surfactant sodium tetradecyl sulfate STS and ionic liquid [C₃mim][Br] has been carried out to examine the aggregation behavior of STS in presence of ionic liquid at different temperatures in an aqueous medium. It is observed that the aggregation behavior of STS in aqueous medium gets modified by the addition of [C₃mim][Br] at all temperatures of the system. The increase in the value of CMC is observed for STS by the addition of ionic liquid [C₃mim][Br] and with increasing the temperature. Also, the negative value of $\Delta G^0_m$ and $\Delta H^0_m$ observed in all the cases indicates the process of micellization is spontaneous as well as exothermic in nature. The higher values of $\Delta S^0_m$ as compared to $\Delta H^0_m$ indicates that the process of micellization is predominantly entropy-driven in nature. From the data, it is concluded that the
tendency of micellization of sodium tetradecyl sulfate (STS) decreases by the addition of ionic liquid [C<sub>3</sub>mim][Br] and with the increase in temperature as depicted in figure 9 summarizing the results obtained.

Figure 9. Schematic diagram indicating the aggregation behavior of sodium tetradecyl sulfate (STS) in the presence of (0.00, 0.02, 0.05, 0.10) wt.% of [C<sub>3</sub>mim][Br] at (298.15, 303.15, 308.15) K temperatures in aqueous medium.

5. References

[1] Rosen M J 2004 Surfactants and Interfacial Phenomena (New York: John Wiley & Sons)
[2] Attwood D and Florence A T 1983 Surfactant Systems, Their Chemistry, Pharmacy and Biology (New York: Chapman and Hall)
[3] Kumar D and Rub M A 2018 J. Mol. Liquids 250 329
[4] Azum N, Rub M A and Asiri A M 2014 Colloids Surf. B 121 158
[5] Cutler W G and Kissa E 1987 Detergency: Theory and Practice (New York: Marcel Dekker)
[6] Reiger M M 1985 Surfactants in Cosmetics (New York: Marcel Dekker)
[7] Kumar D, Hidayathulla S and Rub M A 2018 J. Mol. Liquids 271 254
[8] Patel R, Khan A B, Dohare N, Ali M M and Rajor H K 2015 J. Surfact. Deterg. 18 719
[9] Harutyunyan L R and Harutyunyan R S 2017 Tenside Surfactant Deterg. 54 141
[10] Greaves T L and Drummond C J 2015 Chem. Rev. 115 11379
[11] Mahmood H, Moniruzzaman M, Yusup S and Welton T 2017 Green Chem. 19 2051
[12] Egorova K S, Gordeev E G and Ananikov V P 2017 Chem. Rev. 117 7132
[13] Ventura S P M, Silva F A, Quental M V, Mondal D, Freire M G and Coutinho J A P 2017 Chem. Rev. 117 6984
[14] Chauhan S, Kaur M, Singh K, Chauhan M S and Kohli P 2017 Colloids Surf. A 535 232
[15] Chahda C, Singh G, Singh G, Kumar H and Kang T S 2016 RSC Adv. 6 38238
[16] Molla M R, Rana S, Rub M A, Ahmed A and Hoque M A 2018 J. Surfact. Deterg. 21 231
[17] Hoque M A, Patoary M O F, Rashid M M, Molla M R and Rub M A 2017 J. Solut. Chem. 46 682
[18] Kumar H, Katal A and Rawat P 2018 J. Mol. Liquids 249 227
[19] Dominguez A, Fernandez A, Gonzalez N, Iglesias E and Montenegro L 1997 J. Chem. Educ. 74 1227
[20] Del Castillo J L, Suárez-Filloy M J, Castedo A and Svitova T 1997 J. Phys. Chem. B 101 2782
[21] Kumar V and Gilbert T W 1972 J. Electroanal. Chem. Interfacial Electrochem. 40 419
[22] Markarian S A, Harutyunyan L R and Harutyunyan R S 2005 J. Solution Chem. 34 36

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