# Thermodynamic Study of the Sulphonation of Polystyrene-Butadiene Rubber with Chlorosulphonic Acid for Proton Exchange Membrane Fuel Cell

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**ABSTRACT:** The thermodynamic study of the sulphonation of polystyrene-butadiene rubber (PSBR) with chlorosulphonic acid for fuel cell application was carried out. This was done to understand the properties of the sulphonation process in terms of the change in enthalpy ($\Delta H$), entropy ($\Delta S$), and the Gibbs free energy ($\Delta G$) relative to product stability. The $\Delta H^0$, $\Delta S^0$, and $\Delta G^0$ were found to be 40.708 kJ, 64.22 J K$^{-1}$, and 22.916 kJ, respectively, indicating that the reaction is not thermodynamically favorable (though non-sponteneous) where products are less favored compared to reactants which thus required energy. However, at elevated temperature (>328 K), a phase change from liquid to solid was encountered which suggests that the optimum temperature to carry out the sulphonation of PSBR in chlorosulphonic acid should be within 328 K. Results obtained also revealed that the sulphonation time influenced the qualities such as, proton conductivity, degree of sulphonation, and methanol permeability of the sulphonated PSBR. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1766–1771, 2010

**Key words:** polystyrene-butadiene rubber; chlorosulphonic acid; enthalpy; entropy; Gibbs free energy

## INTRODUCTION

The high cost of fuel cell especially, proton exchange membrane fuel cell (PEMFC) despite its recognition as the most efficient alternative to fossil fuel energy sources is mainly due to the high cost of the ionic membrane, which is the heart of the PEMFC. This has caused fuel cell to lag behind from full scale commercialization.[1,2] Beside the high cost of the state-of-the art membrane (perflourinated Nafion®), other major disadvantages includes; fuel (methanol) permeability, dehydration at high temperature (>80°C) and therefore loss of properties.[3] Serious efforts are now being geared towards getting an alternative proton exchange membrane (PEM) for fuel cell application.

Going by the great effort of getting a possible alternative PEM, the sulphonation of a glassy poly-ether ether ketone at 80°C was carried out in 96% H$_2$SO$_4$ and was found to have low water adsorption capacity. Although, a calculated specific conductivity of about $1.7 \times 10^{-2}$ S/cm was achieved but the membrane was found to achieve only 14% water uptake and this is an important property for the proton transport through dense membrane during fuel cell operation.[4] Sulphonated polystyrene-poly(ethyelene-butylene)-polystyrene triblock polymer that was prepared from a low cost material by sulphonating the styrene blocks of the polymer using chlorosulphonic acid was found to achieve proton conductivity of $10^{-1}$ S/cm, however, the thermal analysis of the membrane using differential calorimetric analysis (DSC) and thermographic analysis (TGA) showed that the thermal stability of the polymer decreases due to sulphonation.[5] Sulphonated poly(phthalazinones) with different degrees of sulphonation ranging from 1 to 1.37 has also been prepared from poly(phthalazinones) using dilute fuming sulphuric acid as both the solvent and the sulphonating agent. Although the membranes were able to achieve conductivity in the order of $10^{-2}$ S/cm but the thermal analysis showed that the membranes were losing sulphonic acid groups in two steps followed by degradation of the polymer main chain.[3] In the same vein, sulphonated polystyrene by Smitha et al.[6] showed that the resulting membrane exhibited a steep fall in glass transition temperature to a level which does not comply with requisite operating conditions in PEM fuel cells. However this drawback was suggested to be overcome by crosslinking or copolymerization with other suitable polymers.[6] Nevertheless, it is now recognised that Homopolymer, random

copolymers and block, as well as graft copolymers containing aromatic rings or double bonds, are suitable materials for PEMs in fuel cell application.[6]

The sulphonation of polystyrene-butadiene rubber (PSBR) was earlier carried out for PEM synthesis by this group, and the thermal analysis of the PEM synthesised using DSC and TGA showed that the synthesised membrane is thermally stable for fuel cell application, as it exhibited a glass transition temperature ($T_g$) of about 200°C. The proton conductivity was found to be in the range of $10^{-3}$–$10^{-2}$ S/cm,[7] ideal for fuel cell application. The water uptake of the membrane which is very vital for ionic transport across the membrane was found to be moderate with low methanol permeation making the synthesised membrane to be efficient for fuel cell application has also been reported earlier.[8] The kinetic study of the chlorosulphonation of the PSBR has been submitted to this very journal. This article therefore presents the thermodynamic study of the sulphonation of PSBR using chlorosulphonic acid. This study appears to be novel as there is no literature currently on the thermodynamic study on polymer sulphonation especially, the aromatic sulphonation of PSBR.

## EXPERIMENTAL

### Materials

98.5% of 1,2-dichloroethane (MERCK, RSA), 98.8% of hydrochloric acid (FLUKA, RSA), 98% ethanol (MERCK, RSA), 98% chlorosulphonic acid (Sigma-Aldrich, RSA), while PSBR was donated by KARBO-CHEM (RSA).

### Sulphonation of PSBR with chlorosulphonic acid

A known weight (10 g) of PSBR was dissolved in 250 mL of 1,2-dichloroethane. This was followed by the gradual addition of 1.6 M of chlorosulphonic acid that was initially chilled in 1,2-dichloroethane solution in an ice bath to eliminate heat released into a vigorously stirred solution of PSBR in a four-neck round bottom flask reactor. This was carried out under argon atmosphere at different temperatures. The sulphonation reaction was allowed to proceed for varying time. The reaction was later terminated by adding ethanol where the precipitated sulphonated PSBR was recovered, washed with deionised water until the pH of wash reached values of 6–7. The product was then dried in an oven at 80°C for 2–3 h. The degree of sulphonation (DS) was obtained from the IEC calculated using eq. (1),[9] which is the function of the percentage of sulfur present in the dry sample of the sulphonated polystyrene-butadiene rubber (SPSBR) by elemental analysis.

$$IEC = \frac{1000 S_c}{MW_s} \tag{1}$$

where $S_c$ is the sulfur content (percentage weight rate), $MW_s$ is the molecular weight of sulfur and 1000 is the multiplying factor in obtaining the IEC value in mmol/g. The DS of SPSBR was thus obtained using the relationship shown in eq. (2)[10]:

$$DS = \frac{IEC \times M_{PSBR}}{1 - (IEC \times MW_{SO_3H})} \tag{2}$$

where IEC is the ion exchange capacity (IEC) (mmol/g), $M_{PSBR}$ is the molecular weight of the polystyrene- butadiene (g/mol) and $MW_{SO_3H}$ is the molecular weight of $SO_3H$ (g/mol).

### Casting of SPSBR into a thin film membrane

Ten gram of SPSBR which was dissolved in 200 mL of 1,2-dichloroethane was used to form a casting solution of about 15–30% wt, and cast onto a clean polymer paper support using a laboratory doctor blade casting machine. It is important to know that before the casting, the doctor blade was set to a known thickness with the aid of feeler gauges of the appropriate thickness. The casting was carried out by dragging the head of the casting blade along the length of the substrate, and cured for 4 days. The cast membrane was then dried further in oven at 75°C for 4–5 h and finally vacuum dried for 4 h to remove the residual solvent.

### Measurement of proton conductivity

Measurement of the proton conductivity of the membrane was carried out using alternating current impedance over a frequency range of $1$–$10^6$ Hz in 1 $M$ $H_2SO_4$ as an electrolyte. The membrane resistance was obtained from the value at the intersection of the high frequency impedance curve against the real axis and the proton conductivity was thus calculated using eq. (3):

$$\sigma = \frac{T}{RS} \tag{3}$$

where $\sigma$ is the proton conductivity (S/cm), $T$ (cm), $S$ (cm$^2$), and $R$ is the thickness, surface area of the membrane samples and the resistance determined from the impedance plane, respectively.

### Heat measurement of PSBR and sulphonated PSBR

The heat measurement of both the unsulphonated PSBR and sulphonated PSBR were carried out using the differential scanning calorimetric (DSC) machine

**TABLE I**
**Properties of the Synthesised Membrane Sulphonated at 22°C**

| Sulphonation time (Hrs) | Sulfur content (%) | IEC (mmol/g) | DS (%) | Proton conductivity (S/cm) | Methanol permeability (mol/cm$^2$s) |
|---|---|---|---|---|---|
| 3 | 1.41 | 0.44 | 7.21 | 0.0051 | $5.01 \times 10^{-8}$ |
| 6 | 2.11 | 0.66 | 10.99 | 0.0055 | $4.94 \times 10^{-8}$ |
| 9 | 3.01 | 0.94 | 16.08 | 0.0067 | $4.41 \times 10^{-8}$ |
| 12 | 3.34 | 1.04 | 17.99 | 0.0069 | $4.41 \times 10^{-8}$ |
| 15 | 3.64 | 1.14 | 19.79 | 0.0071 | $4.38 \times 10^{-8}$ |
| 18 | 3.94 | 1.23 | 21.6 | 0.0075 | $4.37 \times 10^{-8}$ |
| 21 | 4.45 | 1.39 | 25.75 | 0.0078 | $4.33 \times 10^{-8}$ |
| 24 | 4.77 | 1.49 | 26.8 | 0.0081 | $4.31 \times 10^{-8}$ |

(822E DSC analyzer). Measurements were performed over the range of 20–80°C at a heating rate of 5°C/minute under nitrogen atmosphere (flushed at 75 mL/min).

## RESULTS AND DISCUSSION

Various analyses such as IEC, DS, Proton conductivity, methanol permeability, and morphology of the SPSBR were investigated and the results obtained are presented.

IEC which is the number of milli-equivalent of ions in 1 g of the dry polymer of the membrane was calculated using eq. (1) and the results obtained as presented in Table I shows that the sulphonation time influences the IEC of the SPSBR. For instance, at the sulphonation time of 3 hrs, the IEC value is 0.44 mmol/g while at the sulphonation time of 24 h the IEC value becomes 1.49 mmol/g translating to about 70.47% increment. The DS represents the average number of sulphonic groups present in the sulphonated polymer and the results obtained are presented in Table I. Results of the sulphonation carried out at 22°C show that sulphonation time influences the DS such that, for sulphonation time of 3 h the DS obtained is 7.21% while the sulphonation time of 24 h results in membrane with DS to be 26.8%. Also investigated is the effect of sulphonation time on the methanol permeability of the synthesized membranes. Methanol crossover is considered as the capacity of the membrane to block the fuel from going through the membrane to avoid fuel oxidation, and it is considered as a major characteristic of the membrane that determines its performance in fuel cell application.[11] The implication of fuel crossover through the membrane is that it encourages decrement in the cathode potential and energy efficiency.[12] Hence, it is important to synthesized membrane with low methanol permeability. Results obtained on the effect of sulphonation time on the methanol permeability are also presented in Table I. Results show that as the sulphonation time increases, the permeability of methanol across the membrane decreases. This is expected as increase in sulphonation time increases the DS, it in turn results in equivalent weight reduction, which leads to more ionic sites for the distribution of methanol in the membrane matrix. Results obtained on the methanol permeability reveals that the methanol permeability of the synthesized membrane is lower that of the Nafion ($3.15 \times 10^{-6}$ cm$^2$/s), being the commercially available membrane.

Also investigated is the proton conductivity of the synthesised membrane. But before the proton conductivity was measured, the membrane samples were soaked in distilled water until full hydration of the membranes was attained. Hydration is essential for membrane that relies on sulphonic acid to conduct protons before it can attain a desirable level of proton conductivity. Results obtained in Table I on the effects of sulphonation time on the proton conductivity of the synthesized membranes reveal that proton conductivity of the synthesized membrane is in the order of $10^{-3}$ S/cm.

The morphology of the unsulphonated and sulphonated PSBR was carried out using the scanning electron microscopy (SEM). Result (Fig. 1) shows that the unsulphonated PSBR is a coarse and a porous material, however, after sulphonation the morphology of the PSBR changes from a porous base material to a dense material. The sulphonation process also enhances the pores of the polymer and with a uniform distribution after sulphonation. This gives flexibility to the rubber and also helps to overcome related problem brittleness.

### Thermodynamic study

The thermodynamic study of the PSBR sulphonation is carried out to understand the properties of the sulphonation reaction in terms of the enthalpy, entropy and the Gibbs free energy of the sulphonation process. From thermodynamic relation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (4)$$

and

**TABLE II**
**Heats of Different Reactants and Products at Different Temperatures of 298, 318, 328, 338, and 348 K, Respectively**

| Temp. (K) | $H_A$ (J) | $H_B$ (J) | $H_C$ (J) | $H_D$ (J) |
|---|---|---|---|---|
| 295 | −17.3349 | 44976.9994 | −9759.47 | 44960.06 |
| 308 | −1888.36 | 47262.4852 | −5303.77 | 46941.35 |
| 318 | −4046.85 | 49046.1836 | −3218.16 | 48465.42 |
| 328 | −6178.19 | 50852.9113 | −1205.85 | 49989.49 |
| 338 | −8306.95 | 52683.341 | 99.20316 | 51513.56 |
| 348 | −10426 | 54538.1456 | 43.00952 | 53037.63 |

$$\Delta G^0 = -RT \ln K \qquad (5)$$

This becomes

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (6)$$

where $K$ is the equilibrium constant; $\Delta H^0$ and $\Delta S^0$ are the standard enthalpy and standard entropy change, respectively and $R$ is the gas constant. A plot of the natural logarithm of the equilibrium constant versus the reciprocal temperature (not shown) is used to obtain the $\Delta H^0$ and $\Delta S^0$, respectively. The results give $\Delta H^0$ and $\Delta S^0$ to be 40.708 kJ and 64.22 J K$^{-1}$, respectively, while $\Delta G^0$ gives 22.916 kJ. This implies that the positive value of $\Delta G^0$ indicates that the reaction is not thermodynamically favorable and thus products are less favored compared to reactants. This follows that the reaction is nonspontaneous and thus requires energy; hence the $\Delta H^0$ value is high. This should be expected since the material under consideration is a polymeric rubber with high molecular weight (106,100 g/mL MW) and viscosity, having a repeat unit weight of 158 g/mol. The low $\Delta S^0$ value shows that the system is relatively less disordered and the implication of the positive $\Delta S^0$ is that the product has more tendency to be disordered than the reactant. However, temperature dependence of entropy of reaction may warrant us to ascertain product stability with temperature. The below expression is the chemical equation for the sulphonation process as;

$$PSBR + ClSO_3H \rightarrow PSBRSO_3H + HCl \qquad (7)$$

The heats of reaction of the different reactants and products are obtained as;

$$H_B = M \times C_p(T) \qquad (8)$$

where $H_B$, $M$, $C_p$ and $T$ represent heat for ClSO$_3$H, mass, specific heat capacity and temperature, respectively.

But $C_p$ is a function of temperature $= 1.204 + 1.402 \times 10^{-4}\ T - 2.887 \times 10^{-6}\ T^2$ (J k$^{-1}$ g$^{-1}$)[13]

$$H_D = M \times C_p T \qquad (9)$$

where $H_D$ represents heat for HCl

But $C_p = 4.186$ (J k$^{-1}$ g$^{-1}$) ($C_p$ of HCl is constant in the range of temperature between 295 and 348 K)

$H_A$ and $H_C$ (being heat for PSBR and PSBRSO$_3$H) were obtained calorimetrically using the differential calorimetry curve (DSC) machine. Table II shows the heat of the different reactants and products at different temperatures.

The sensible heat change of each of the reactant is obtained as shown below;

$$\Delta H_B = M \int_{298}^{348} C_p dT \qquad (10)$$

$$\Delta H_D = H_D^T - H_D^0 \qquad (11)$$

**TABLE III**
**The Heat Change of the Different Reactants at Different Temperatures. These were Obtained Using Eqs. (7)–(10), Respectively**

| Temp. (K) | $\Delta H_A$ | $\Delta H_B$ | $\Delta H_C$ | $\Delta H_D$ |
|---|---|---|---|---|
| 298–295 | 71.35581 | −524.144 | −2268.96 | −457.221 |
| 298–308 | −1799.67 | 1761.342 | 2186.747 | 1524.07 |
| 298–318 | −3958.16 | 3545.041 | 4272.357 | 3048.14 |
| 298–328 | −6089.5 | 5351.768 | 6284.664 | 4572.209 |
| 298–338 | −8218.26 | 7182.198 | 7589.716 | 6096.279 |
| 298–348 | −10337.3 | 9037.002 | 7533.522 | 7620.349 |

**TABLE IV**
**Calculated Values of $\Delta G_R$, $\Delta H_R$, and $\Delta S_R$ at Different Temperatures. These were Obtained Using Eqs. (14)–(16), Respectively**

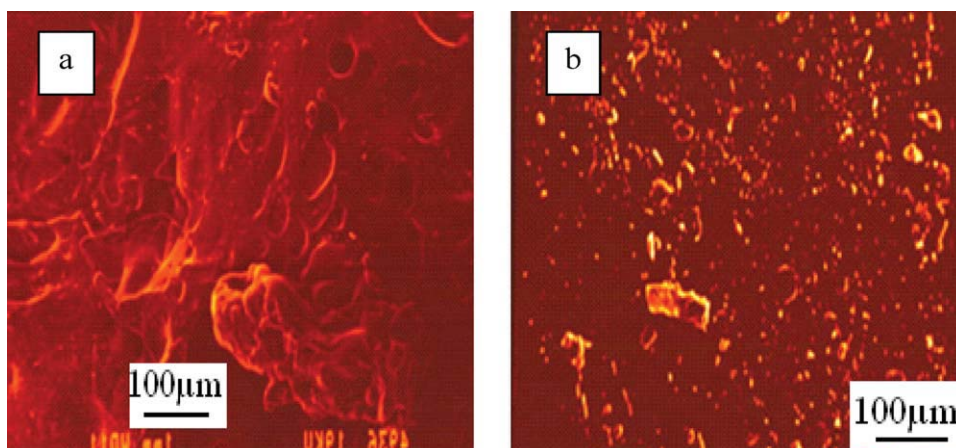| Temp. (K) | $\Delta G_R$ | $\Delta H_R$ | $\Delta S_R$ |
|---|---|---|---|
| 295 | 22589.56 | 38434.61 | 53.71204 |
| 308 | 20771.8 | 44457.14 | 76.90046 |
| 328 | 20230.41 | 52302.61 | 97.78108 |
| 338 | 19411.7 | 55430.05 | 106.5632 |
| 348 | 18812.89 | 57162.13 | 110.199 |

**Figure 1** SEM images of PSBR. Image (a) is the unsulphonated and (b) is the sulphonated using 1 g of sample each with the Jeol 840 SEM machine. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com.]

$$\Delta H_A = H_A^T - H_A^0 \tag{12}$$

$$\Delta H_C = H_C^T - H_C^0 \tag{13}$$

Table III shows the heat change of the different reactants and products at different temperatures, where the heat is found to increase as temperature increases.

The enthalpy change, entropy change and the free Gibbs energy of the reaction at different temperature are finally obtained from the following relation;

$$\Delta H_R^T = \Delta H_R^0 + \Delta H_{\text{products}}^T - \Delta H_{\text{reactants}}^T \tag{14}$$

$$\Delta S_R^T = -\frac{\Delta G_R^T - \Delta H_R^T}{T} \tag{15}$$

$$\Delta G_R^T = RT \ln K \tag{16}$$

Table IV shows the $\Delta G_R^T$, $\Delta H_R^T$, and $\Delta S_R^T$ and at different temperatures. Result shows that, as $\Delta H_R^T$, and $\Delta S_R^T$ increase as temperature increases, $\Delta G_R^T$ decreases with temperature which indicates that the reaction is becoming more feasible as temperature increases, and thus product formation or rather forward reaction is favored. The increase of $\Delta S_R^T$ with temperature will increase the level of disorderness of the reaction. The nature of the entropy of the reaction as temperature changes can be seen in Figure 2.

The reaction involving PSBR and chlorosulphonic acid is nonspontaneous, the particles of the system is expected to exhibit relatively low degree of randomness. This is shown in the low value of $\Delta S^0$

obtained. But as the solution gets warm with temperature, the particles start to move, generating some disorderness, as a result of increase in the entropy of the system with temperature and as such, the average kinetic energy of the particles increases.

However at above 328 K the degree of disorderness of the system can be seen to be reducing gradually and which will thus decrease the randomness of the system. This is the point where the solutions is becoming a solid and hence decrease in the average kinetic energy of the particles. This phenomenon is actually encountered during the experiment as reaction carried out above 328 K, the viscosity of the solution gets so high and solution resulting into a solid with time. Therefore, this indicates that the optimum temperature to carry out sulphonation of PSBR in chlorosulphonic acid should be within 328 K.
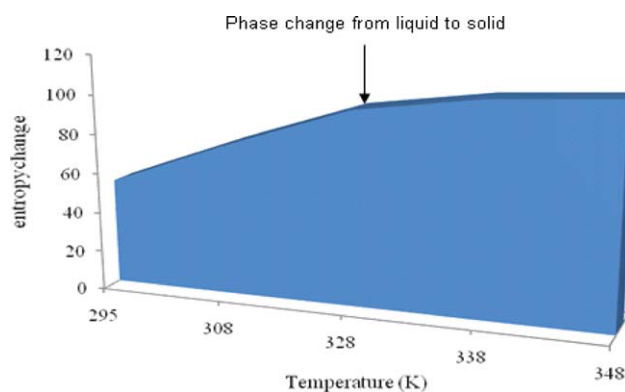


**Figure 2** Entropy plot against temperature. The point of phase change from liquid to solid is when the reaction is carried out at above 328 K. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

## CONCLUSION

The thermodynamic study of the sulphonation of PSBR was carried out and results show that the reaction is nonspontaneous, and as temperature increases the reaction system experienced phase change from liquid to solid state at temperature above 328 K, as the entropy of the system started reducing gradually with increasing temperature. This indicates that the optimum temperature to carry out the sulphonation of PSBR in chlorosulphonic acid should be within 328 K.

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