



# Crosslinked poly(vinyl alcohol)/sulfonated poly(ether ether ketone) blend membranes for fuel cell applications—Surface energy characteristics and proton conductivity

P. Kanakasabai, P. Vijay, Abhijit P. Deshpande, Susy Varughese\*

Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600 036, India

## ARTICLE INFO

### Article history:

Received 7 May 2010

Received in revised form 27 July 2010

Accepted 20 August 2010

Available online 6 September 2010

### Keywords:

Surface energy

Contact angle

Ionic polymer blends

Membranes

Proton conductivity

## ABSTRACT

Ionic polymers, their blends and composites are considered potential candidates for application as electrolytes in fuel cells. While developing new materials for membranes, it is important to understand the interactions of these electrolytic materials with electrodes/catalysts and with reactants/products. Some of these interactions can be understood by estimating the surface energy and wettability of the membrane materials. In this work, polyvinyl alcohol with varying degrees of sulfonation and its blend with sulfonated poly(ether ether ketone) are prepared and studied for their wettability characteristics using goniometry. The surface energy and its components are estimated using different approaches and compared. Properties such as the ion-exchange capacity, the proton conductivity and the water sorption/desorption behaviour are also investigated to understand the relationship with wettability and surface energy and its components. Among the different methods, the van Oss acid–base and the modified Berthelot approaches yield comparable estimates for the total surface energy.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydrogen and direct methanol fuel cells (DMFCs) are among several types of fuel cell that utilize proton-conducting electrolyte membranes [1]. Most of the commercially available polymer electrolyte membranes are based on perfluorosulfonic acid (PFSA) polymers due to their good proton conductivity, mechanical strength, and chemical/thermal stability. Nafion and other flourinated polymer based membranes, however, have disadvantages such as high cost, limited operating temperature, high methanol crossover and environmental problems that limit their widespread application [2].

Alternative membranes based on poly(vinyl alcohol) (PVA) show good proton conductivity with low methanol permeability [1,3,4], but have poor mechanical properties and thermal stability. Among non-flourinated membrane materials, sulfonated poly(ether ether ketone) (SPEEK) is another ionic polymer that has high mechanical and thermal stability along with good proton conductivity [5]. Some of the properties of individual polymers can be used as a basis to devise novel membranes, with desirable overall performance, by blending [6]. In addition to developing novel fuel cell membranes, understanding their interactions with

electrodes/catalysts and with reactants/products are also important. These interactions are crucial in determining membrane behaviour in terms of water sorption–desorption, proton conductivity and interfaces in membrane–electrode assembly. They can be understood by examining wettability characteristics and, more specifically, by determining surface energies of the membrane materials. Wettability of solid materials such as membranes can be quantified by estimating solid–vapour and solid–liquid interfacial energies. The wetting characteristics of proton conducting membranes, especially with water, are important in understanding the water uptake behaviour of the membranes, as well as their performance under varying humidity conditions in the fuel cell. It is difficult to measure the surface energies directly. There are several indirect approaches for estimating the surface energy of solids [7–10]. In this work, some of these approaches are used to arrive at estimates of the surface energies of the PVA–SSA/SPEEK blend membranes.

Among the various methods, contact angle measurement is considered to be the simplest [11]. The contact angle ( $\theta$ ) is related to the solid–vapour ( $\gamma_{sv}$ ), the solid–liquid ( $\gamma_{sl}$ ) and the liquid–vapour ( $\gamma_{lv}$ ) surface energies (or surface tensions) and can be obtained from Young's equation:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

This equation contains two measurable quantities,  $\theta$  and  $\gamma_{lv}$ . In order to determine  $\gamma_{sv}$  and  $\gamma_{sl}$ , an additional equation relating

\* Corresponding author. Tel.: +91 44 2257 4172; fax: +91 44 2257 4152.  
E-mail address: [susy@iitm.ac.in](mailto:susy@iitm.ac.in) (S. Varughese).

### Nomenclature

*M* water uptake  
*W* weight (g)

#### Greek letters

$\beta$  fitting parameter ( $\text{m}^2 \text{mN}^{-1}$ )  
 $\gamma$  surface tension ( $\text{mN m}^{-1}$ )  
 $\theta$  contact angle ( $^\circ$ )

#### Subscripts

dry dry membrane  
*l* liquid  
*lv* liquid–vapour interface  
*s* solid  
*sl* solid–liquid interface  
*sv* solid–vapour interface  
 wet water sorbed membrane

#### Superscripts

– base component  
 + acid component  
 1,2 phases  
 12 interphase  
 AB acid–base component  
*d* dispersive component  
*i* liquid or solid  
 LW Lifshitz–van der Waals component  
*p* polar component

these quantities is needed. According to Fowkes [12], the total surface energy of a solid can be expressed as the sum of the dispersive and non-dispersive components. It has been found from earlier studies [11] that the surface energy components determined according to Fowkes' approach may not correspond to the exact nature of molecular interactions that exist in a solid, especially, in the case of ionic solids and acid–base materials. Nevertheless, it has been used frequently to estimate the surface energies of surface modified polymers such as plasma modified polyacrylonitrile, polyester and polyolefins [13–15] and in the case of conducting polymers such as polyaniline, polythiophene and polypyrrole [16–18]. The van Oss acid–base approach is a generalization of the Fowkes' approach, as it takes into account the acid–base interactions at the interface [19]. Combinations of different test liquids are required for the estimation of surface energy using the above two methods. Equation-of-state approaches such as Berthelot's and modified Berthelot's [20] for estimating solid surface energy are based on molecular interactions of like–pairs, the London theory of dispersion, and the long-range dispersion function. The advantage of the equation-of-state approach is that it is capable of estimating the solid surface energy from contact angle data using a single test liquid. In the modified Berthelot's approach, contact angle data obtained using different test liquids are used to fit and estimate the surface energy. Most of the studies on the wettability of gas-diffusion layers, membranes and membrane–electrode assemblies use the contact angle method [21,22]. The wetting properties of Nafion were investigated by Zawodzinski et al. [23] using contact angles of water on the surface of dry and humidified membranes. They found that the equilibrium contact angle of water on Nafion membranes decreased as the water content in the membrane increased. Ramdutt et al. [24] studied the effect of plasma treatment on Nafion and found better wettability for the modified Nafion (based on a reduction in contact angle from  $120^\circ$  to  $50^\circ$ ). Brack et al. [25]

estimated the surface energy of radiation-grafted ion-exchange membranes based on poly(ethylene-*alt*-tetrafluoroethylene) and poly(tetrafluoroethylene-*co*-hexafluoropropylene) blends using contact angle data and the van Oss acid–base approach. In summary, the Fowkes and van Oss acid–base approaches are the only methods reported for the estimation of the surface energy of ionic and conducting polymers.

The present work reports results of the estimation of the surface energy and the wettability characteristics of a novel, ionic polymer blend system based on crosslinked PVA and SPEEK. The surface energies of the membranes are estimated from contact angle data obtained using paraffin, ethylene glycol, formamide and de-ionized water as test liquids. The Fowkes approach using the Wu harmonic mean method, the van Oss acid–base and the equation-of-state methods are employed to estimate the surface energy and its components. The relationships between the estimated surface energy, their components and the ion-exchange capacity (IEC), water uptake and proton conductivity of the membranes are also investigated.

## 2. Materials and methods

### 2.1. Materials

Polyvinyl alcohol (PVA) ( $M_w = 125\,000$ , degree of hydrolysis of 88%) and formamide were purchased from Sd fine Chemicals Limited (India). Poly(ether ether ketone) (PEEK) with an average molecular weight of 45 000 was purchased from Victrex (UK). Sulfosuccinic acid (SSA, 70 wt.% solution in water) used as the crosslinking agent was purchased from Aldrich Chemical (USA). Sulfuric acid (98 wt.%) was obtained from RFCL Limited (India). Glycerol, paraffin and N-methyl-2-pyrrolidone (NMP) were purchased from Sisco Research Laboratories Limited (India). All the polymers and chemicals were used as received. All solutions were prepared with distilled water. Distilled water also served as the test liquid in contact angle measurements.

### 2.2. Membrane preparation

For various measurements including contact angle, conductivity and IEC, polymer membranes of PVA, SPEEK and their blends were required. This section describes the preparation of PVA–SSA, SPEEK and PVA–SSA/SPEEK blend membranes.

All the PVA membranes referred hereafter are crosslinked using sulfosuccinic acid (SSA). To prepare these membranes, PVA (10% w/w) was dissolved in water at  $90^\circ\text{C}$  for 6 h [4]. SSA solution (in water) was added to the PVA solution at room temperature and stirred for 24 h. The homogenous solutions thus obtained were poured into Petri dishes and allowed to dry at  $60^\circ\text{C}$  in an air oven for 24 h. The membranes were further heated for 1 h at  $120^\circ\text{C}$  in an air oven to complete the crosslinking. PVA–SSA membranes with varying SSA content (10, 20 and 30 wt.%) were prepared. PVA–SSA/SPEEK blend membranes were obtained by mixing PVA and SPEEK solutions followed by crosslinking of the PVA phase with SSA. For this, SPEEK with 70% degree of sulfonation (DS) was prepared by sulfonating PEEK using sulfuric acid [26]. The prepared SPEEK was dissolved in water at  $70^\circ\text{C}$  by stirring for 4 h. The required amounts of PVA and SPEEK solutions were blended at  $70^\circ\text{C}$  by stirring for 30 min. 20% SSA (with respect to weight fraction of PVA) was added to the PVA/SPEEK solution for crosslinking the PVA phase. Since PVA crosslinked with 20 wt.% SSA showed optimum properties, PVA/SPEEK blends were prepared with 20 wt.% SSA. By this process, it is expected that PVA chains are crosslinked with SSA in the presence of SPEEK chains. Therefore, in the blend membranes, sulfonic acid groups are present in the crosslinked PVA

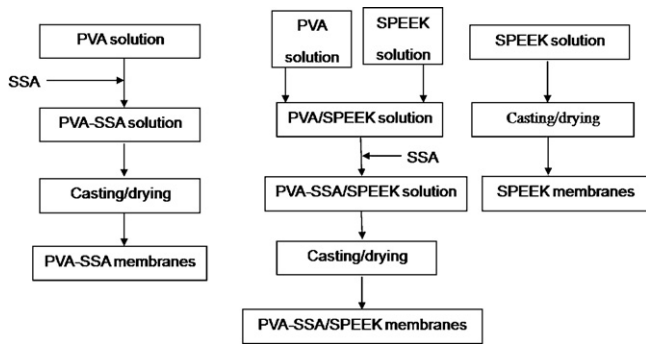


Fig. 1. Schematic representation of membrane preparation.

network, as well as on the SPEEK chains. These blend membranes are expected to have advantages of both PVA–SSA and SPEEK, for proton conducting applications. A schematic diagram showing the preparation of the membranes is given in Fig. 1.

For comparison, pure SPEEK membranes were also prepared. For this, SPEEK was dissolved (10 wt.%) in NMP [27]. The solutions were then poured into Petri dishes and dried in stages (8 h at 40 °C, 8 h at 60 °C, 8 h at 80 °C and 48 h at 100 °C) to evaporate the NMP completely from the membranes. The thickness of the prepared membranes was in the range of 150–200 μm. The membranes were stored in distilled water at room temperature to keep them hydrated.

### 2.3. Sorption and desorption of water

For the sorption/desorption studies, circular samples of 30 mm diameter were punched out from the membranes. The water sorption in the membranes was determined after immersing these samples in distilled water at 25 °C for 24 h. The samples were taken out (the surface water was removed carefully using tissue paper) and weighed immediately on a microbalance. The water uptake ( $M$ ) in the membrane was estimated by means of the gravimetric method, i.e.,

$$M = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (2)$$

To determine the desorption rate, membranes saturated in distilled water were taken out (the surface water was removed carefully using tissue paper) and weighed at specific intervals. During the desorption test, the membranes were kept in a controlled atmosphere, at 25 ± 2 °C and 55 ± 3% relative humidity (RH). The ion-exchange capacity of the membranes was determined using methods given in the literature [4].

### 2.4. Conductivity measurements

Proton conductivities of the membranes were estimated using through-plane impedance measurements under a fully hydrated condition by the two-probe electrode method. The impedances of membranes were measured with an impedance analyzer in combination with an electrochemical interface (GILL ACM Instrument) using two circular silver electrodes of area 1.13 cm<sup>2</sup> in the frequency range of 1–300 kHz. The resistance ( $R$ ) of the membrane was estimated from the low intersection of the high-frequency semi-circle on a complex impedance plane with the Re ( $Z$ ) axis.

The proton conductivity of the membrane (S cm<sup>-1</sup>) is given by:

$$\sigma = \frac{l}{RS} \quad (3)$$

where  $R$  is the bulk resistance or ohmic resistance of the membrane sample;  $l$  is the thickness and;  $S$  is the cross-sectional area of the sample (cm<sup>2</sup>).

Measurements were repeated on samples taken from three different membranes of the same composition. The error in the reported values is in the range of ±5%.

### 2.5. Contact angle measurements

The contact angles of various test liquids (paraffin, ethylene glycol, formamide, and distilled water) on the membranes were obtained using a Goniometer (GBX Digidrop Contact angle meter). A single drop of the test liquid (drop volume ~3 μl) was placed on the polymer membrane via a microlitre syringe that was rinsed with the test liquid in advance. Dynamic contact angles were measured at 25 ± 2 °C and 55 ± 3% RH for 2 min. For each membrane, the contact angle was determined six times at different positions on the membranes and the average values are reported. The variation in contact angle during the measurements was found to be within ±1.5°.

The rate and extent of wetting are significantly different, not only for different liquids but also for different substrates [28]. Hence, a dimensionless contact angle is used, i.e.,

$$\text{Normalized contact angle } \phi = \frac{\theta - \theta_e}{\theta_0 - \theta_e} \quad (4)$$

where  $\theta_0$  is the contact angle at time  $t=0$ ;  $\theta$  is the contact angle at any time  $0 < t < t_e$ , where  $t_e$  is the time to reach equilibrium values and,  $\theta_e$  is the equilibrium contact angle taken from Table 2.

## 3. Theory and calculation

### 3.1. Surface energy of membranes

The surface energy of the membranes was estimated from contact angle data using various methods, namely, the Fowkes' approach using Wu harmonic mean; the van Oss acid–base approach, and the equation-of-state approaches such as the Berthelot's and the modified Berthelot's.

#### 3.1.1. Fowkes approach using Wu harmonic mean

Fowkes postulated that the total surface energy of a solid can be expressed as the sum of two different surface energy components that arising from specific types of intermolecular forces. Accordingly, the total surface energy,  $\gamma$ , of a solid is given by [19]:

$$\gamma = \gamma^d + \gamma^p \quad (5)$$

where  $\gamma^d$  is the dispersive component and  $\gamma^p$  is the polar component.

The Fowkes' approach using the geometric mean, however, is not considered suitable for materials with low surface energies like polymers [11,25,29,30]. Instead, Wu proposed a harmonic mean relationship [29] for estimating the surface energy of solids from, namely:

$$(1 + \cos \theta)\gamma_l = 4 \left( \frac{\gamma_s^d \gamma_l^d}{\gamma_s^d + \gamma_l^d} + \frac{\gamma_s^p + \gamma_l^p}{\gamma_s^p + \gamma_l^p} \right) \quad (6)$$

Eqs. (5) and (6) are coupled with Eq. (1) for estimating the surface energy.

#### 3.1.2. van Oss acid–base approach

The van Oss acid–base approach [11] is a generalization of the Fowkes' approach taking into consideration the acid–base interactions at the surface. It is used in many special cases to estimate the surface energies of modified surfaces or in cases where strong ionic interactions exist. According to this approach, the total surface energy ( $\gamma_i$ , where  $i$  stands for solid, liquid or vapour phase) is composed of a Lifshitz–van der Waals component ( $\gamma_i^{LW}$ ) and a Lifshitz

acid–base component ( $\gamma_i^{AB}$ ) [25]

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (7)$$

where  $\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-}$  and  $\gamma_i^+$  is the acid and  $\gamma_i^-$  is the base component. With this approach, the interfacial tension for a solid–liquid system [19] is given by:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^{LW} \gamma_l^{LW})^{1/2} - 2(\gamma_s^+ \gamma_l^-)^{1/2} - 2(\gamma_s^- \gamma_l^+)^{1/2} \quad (8)$$

Combining Eqs. (8) and (1) yields [11]:

$$\gamma_l(1 + \cos \theta) = 2(\gamma_l^{LW} \gamma_s^{LW})^{1/2} + 2(\gamma_l^+ \gamma_s^-)^{1/2} + 2(\gamma_l^- \gamma_s^+)^{1/2} \quad (9)$$

Using Eq. (8), the surface energy components ( $\gamma_s^{LW}$ ,  $\gamma_s^+$  and  $\gamma_s^-$ ) of solids can be obtained by means of three simultaneous equations and the contact angles determined for the three test liquids.

This approach requires a highly polar liquid and a highly non-polar liquid for obtaining a reasonable estimate of the surface energy. There are few drawbacks in using this approach [11], e.g., the Lewis acid–base interaction components calculated using different test liquids may not be the same. Despite these flaws, this approach has been used to examine and to understand variations in the surface energy of ionic substrates [25,31].

There are two degrees of freedom to describe the independent variables ( $\gamma_{lv}$ ,  $\gamma_{sl}$  and  $\gamma_{sv}$ ) as per the Young equation (Eq. (1)). In the case of the Wu harmonic mean method and the van Oss acid–base approach, the degrees of freedom are three ( $\gamma_l$ ,  $\gamma_l^d$  and  $\gamma_l^p$ ) and six ( $\gamma_l^{LW}$ ,  $\gamma_s$ ,  $\gamma_l$ ,  $\gamma_s^+$ ,  $\gamma_l^+$  and  $\gamma_s^{LW}$ ), respectively [20]. This is reported to lead to inconsistent values of the surface energy and its components. Therefore, approaches based on an equation-of-state that has less degrees of freedom was proposed in the literature.

### 3.1.3. Equation-of-state approach: Berthelot combining rule

In this approach, the geometric mean of the combination rule is used and the solid–liquid interfacial tension  $\gamma_{sl}$  can be obtained as:

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2\sqrt{\gamma_{lv}\gamma_{sv}} \quad (10)$$

Combining Eq. (10) with Young's equation (Eq. (1)) yields the Berthelot equation:

$$\cos \theta = -1 + 2\sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} \quad (11)$$

Contact angle data obtained with a single test liquid are sufficient to estimate the surface energy via the Berthelot equation. It has been shown, however, that this leads to different estimates when different test liquids are used [32]. Additionally, the Berthelot equation, which is based on geometric mean combination rule (Eq. (10)), over-estimates the surface energy, for large differences of  $|\gamma_{lv} - \gamma_{sv}|$  [11]. Therefore, modifications to the Berthelot equation were suggested and an example is discussed below.

### 3.1.4. Equation-of-state approach: modified Berthelot rule

A modification factor has been introduced in Eq. (10) to reduce the effect of overestimation of the surface energy due to the geometric mean method:

$$\gamma_{sv} = \gamma_{lv} + \gamma_{sv} - 2\sqrt{\gamma_{lv}\gamma_{sv}} \exp(-\beta(\gamma_{lv} - \gamma_{sv})^2) \quad (12)$$

Combining Eq. (12) with the Young equation (Eq. (1)) gives a modified Berthelot equation for determining the surface energy of solids, where  $\beta$  is a constant.

$$\cos \theta = -1 + 2\sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} \exp(-\beta(\gamma_{lv} - \gamma_{sv})^2) \quad (13)$$

Contact angles ( $\theta$ ) are measured for different test liquids on the substrate.  $\gamma_{sv}$  and  $\beta$  can be obtained from the best fit of Eq. (13) with experimental data ( $\gamma_{lv}$  and  $\theta$ ) [33].

**Table 1**

IEC values of PVA–SSA and PVA–SSA/SPEEK blend membranes.

Samples	IEC (mmol g <sup>-1</sup> )	IEC by rule of mixtures
Nafion	1.02	–
PVA–10% SSA	0.70	–
PVA–20% SSA	1.51	1.51
PVA–30% SSA	1.41	–
PVA–SSA/SPEEK-70/30	1.23	1.65
PVA–SSA/SPEEK-50/50	1.32	1.74
PVA–SSA/SPEEK-30/70	1.59	1.83
SPEEK	1.97	1.97

## 4. Results and discussion

The water uptake, desorption and wetting characteristics of various membranes based on PVA–SSA, SPEEK and blends of PVA–SSA and SPEEK are discussed in the following sections. For comparison, Nafion membranes were also studied.

### 4.1. Water uptake and IEC

Membrane–water interactions are important in the bulk as well as on the surface of the membranes. Conductivity, water uptake and IEC of the membranes are inter-dependent. The extent of water uptake depends upon the degree of crosslinking and the amount of sulfonic acid groups present in the membranes. Hence, the water uptake of the membrane changes with the amount of sulfonic acid groups present in the membrane. In this section, the water uptake and the water desorption characteristics of PVA (with varying SSA content), SPEEK and PVA–SSA/SPEEK blend membranes (different blend ratios, 20% SSA content) are discussed. The IEC values for the membranes are given in Table 1. With the high degree of sulfonation (70%), SPEEK shows the highest IEC values. The IEC value obtained for Nafion (1.02 mmol g<sup>-1</sup>) is comparable with a value reported in the literature [25]. The IEC values of PVA–SSA systems and their blends show unusual trends. PVA with 10% SSA content shows the lowest IEC value, but almost doubles on increasing the SSA content to 20%. On further increasing the SSA content to 30%, however, the IEC remains almost the same. This may be due to the higher initial concentration of SSA, which causes the crosslinking reaction to proceed at a faster rate initially, and then restricting further diffusion of SSA molecules into the network polymer. Even though the IEC values are similar for the 20% and 30% PVA–SSA, their crosslink densities are different, as discussed later.

In the case of PVA–SSA/SPEEK blends, the IEC is higher for blends with higher SPEEK content. It should be noted that the same amount of SSA (20%, with respect to PVA) was used in all the blends. Individual components, PVA–20% SSA and SPEEK (70 – degree of sulfonation) have higher IEC values, when compared to with blends. The blends show negative deviation for the IEC values from the additive rule for blends (Table 1). This could be due to the lower sulfonation of the PVA phase in the presence of SPEEK that hinders the PVA–SSA reaction. The IEC is an important parameter in determining the water uptake behaviour, as discussed below.

In the case of PVA–SSA membranes, water uptake due to swelling decreases with an increasing amount of SSA (Fig. 2). Though the IEC values of 20% and 30% SSA–PVA membranes are similar, the water uptake values are much lower in the case of PVA–30% SSA. These results indicate that the crosslink density is higher in the case of PVA–30% SSA though the IEC is similar to that of PVA–20% SSA. SPEEK, even though it has the highest IEC, swells less in water due to the hydrophobic nature of the PEEK backbone. Similarly, Nafion also swells less in water. The water uptakes of the blend membranes are found to be between those of the pure components. The behaviour is different when compared with the variation of IEC with the blend ratio. The IECs of the blends are found to be lower

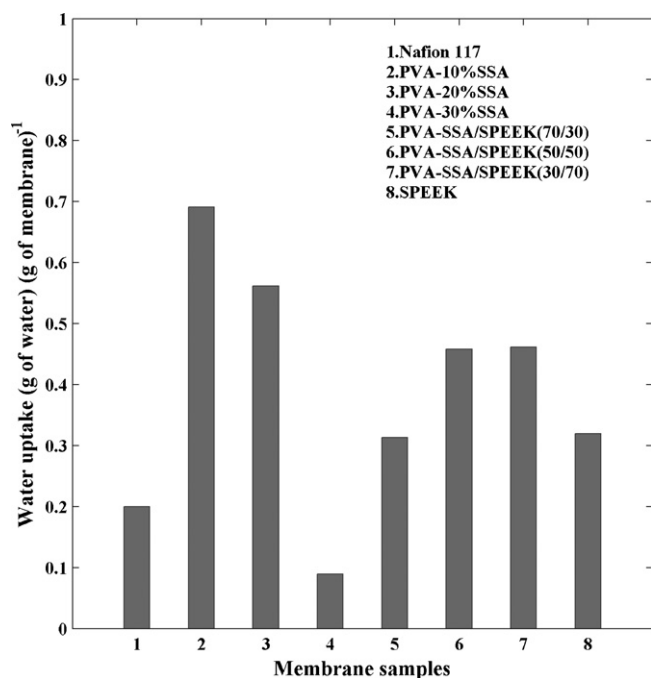


Fig. 2. Water uptake in different membranes.

than those of the pure components. In pure SPEEK, the water uptake is dictated by the sulfonation level [26], whereas, in the case of the hydrophilic polymer PVA–SSA the water uptake is determined by the crosslink density. The water uptake in the blends would depend on the relative amounts of SPEEK as well as the crosslink density of the PVA–SSA network. Lower IEC values (lower than the additive rule) in the case of blends imply a lower level of SSA incorporation, i.e., the presence of SPEEK hinders the crosslinking of PVA with SSA and therefore a lower degree of crosslinking. Hence, a higher water uptake for the blend membranes would be expected.

To study the water desorption characteristics, membranes saturated with water were exposed to a controlled atmosphere (25 °C and 55% RH). These membranes lost water with time, and eventually attained equilibrium with the ambient humidity. The initial desorption rates for various membranes are shown in Fig. 3; the rates were estimated from the slope of the initial linear portion (first 30 min) of the desorption curve. Nafion shows a higher desorption rate compared with the other membranes, possibly due to its highly hydrophobic PTFE backbone. The desorption rate for PVA–30% SSA was higher than that for PVA–10% SSA and PVA–20% SSA. SPEEK membranes exhibit very low rates of desorption. With increase in the SPEEK content in the blend, the rate of desorption decreases. An important feature of these results is the non-monotonic variation of the properties as a function of the composition of blends.

#### 4.2. Contact angle

The effect of varying SSA content on the contact angle of water drops on PVA–SSA membranes, as a function of time, is shown in Fig. 4. With increase in the SSA content, the equilibrium contact angle decreases. Increase in the sulfonic acid groups in the membrane increases the hydrophilic nature of the membranes and reduces the contact angle [4]. This is contrary to the dependence of water uptake on SSA content which decreases with increasing SSA content due to the higher degree of crosslinking (Fig. 2). It should be noted that membranes saturated with water are used for the measurement of the contact angle. As can be seen from the data in Fig. 4, the initial rate of change of the contact angle is more for PVA–10% SSA than for PVA–20% SSA and PVA–30% SSA membranes.

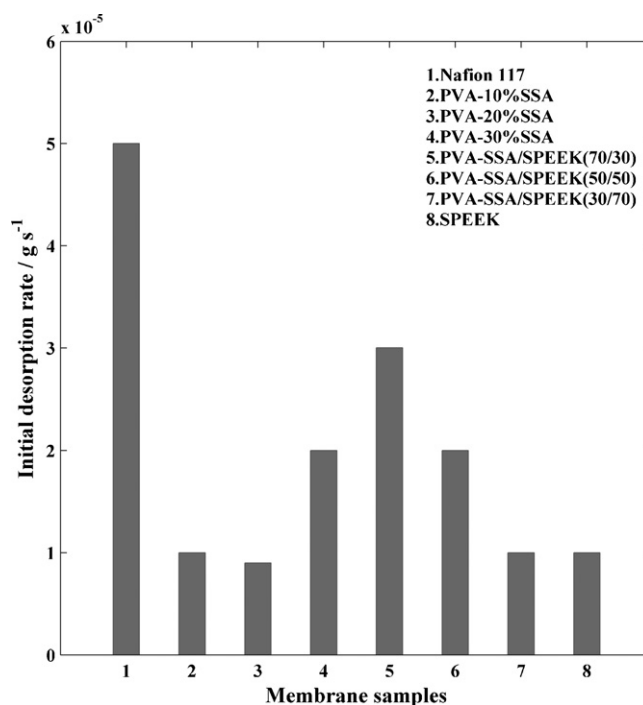


Fig. 3. Initial water desorption rates for different membranes.

The variation of the contact angle of water on Nafion is also shown in Fig. 4. Wetting and spreading behaviour of a liquid on a solid surface would depend on the molecular nature and microstructural features of the surface. Due to the large differences in the molecular interactions (highly hydrophobic backbone with strong ionic groups), Nafion is known to be heterogeneous at the mesoscopic scale [34]. These variations could lead to a slower rate of spreading of water on the Nafion surface.

The equilibrium contact angle of water on blend membranes decreases with increase in SPEEK content (Fig. 5). Even though the water uptake of the SPEEK membrane is lower than that of PVA–20%

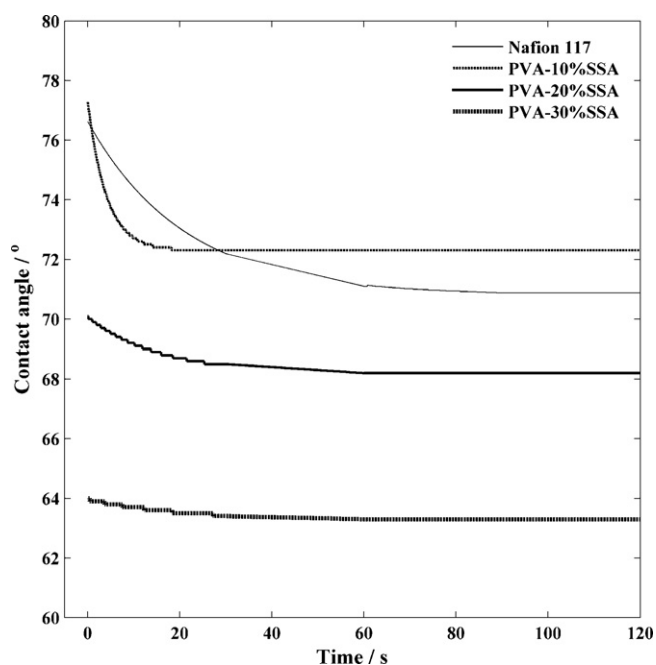


Fig. 4. Dynamic contact angle for PVA–SSA and Nafion membranes using water.

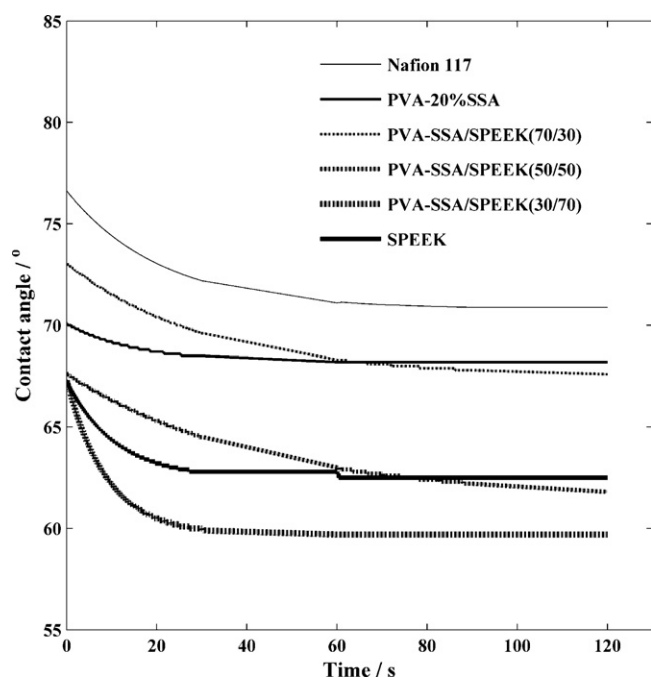


Fig. 5. Dynamic contact angle for PVA-SSA/SPEEK blends and Nafion membranes using water.

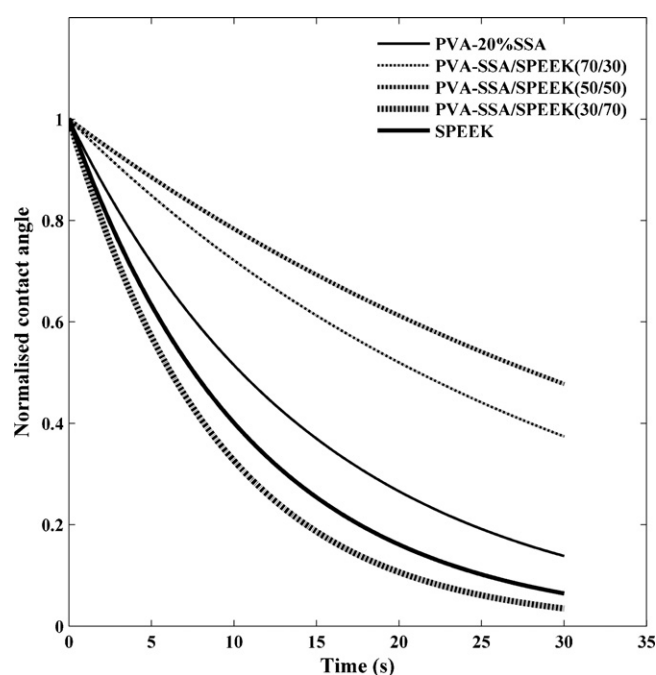


Fig. 6. Normalized contact angle for PVA-SSA/SPEEK blend membranes.

SSA, the wettability, as determined from the contact angle of water, is higher for the SPEEK membrane. The equilibrium contact angle of water on SPEEK was found to be comparable with that on PVA-30% SSA membranes. The contact angle on a PVA-SSA/SPEEK-30/70 blend is lower than that on SPEEK. The blend morphology, surface roughness, microstructure and the distribution of sulfonic acid groups are among the factors that affect the contact angle.

The rate of change of contact angle on the PVA-SSA/SPEEK-30/70 blend is similar to that for SPEEK (Fig. 6). By contrast, the contact angle changes far more slowly on the PVA-SSA/SPEEK-70/30 and 50/50 blends. These observations provide a qualitative insight into the surface wettability and the dynamics of wetting of the membranes. To obtain quantitative estimates of the surface energy of these membranes, however, contact angles were measured using different test liquids.

Table 2

Equilibrium contact angles for PVA-SSA and PVA-SSA/SPEEK blend membranes with different test liquids.

Samples	Contact angle (°)			
	Paraffin	Ethylene glycol	Formamide	Water
Nafion	19 ± 0.68	74 ± 1.14	82 ± 1.48	71 ± 1.31
PVA-10% SSA	12 ± 0.80	64 ± 0.86	65 ± 0.94	72 ± 0.75
PVA-20% SSA	11 ± 0.63	50 ± 1.00	55 ± 0.78	68 ± 1.45
PVA-30% SSA	13 ± 1.17	51 ± 1.33	52 ± 1.21	63 ± 1.10
PVA-SSA/SPEEK-70/30	11 ± 0.93	47 ± 1.03	41 ± 1.19	68 ± 1.00
PVA-SSA/SPEEK-50/50	17 ± 0.67	52 ± 1.48	45 ± 1.44	62 ± 1.23
PVA-SSA/SPEEK-30/70	14 ± 0.91	56 ± 1.41	50 ± 0.93	60 ± 0.65
SPEEK	06 ± 1.00	50 ± 0.75	44 ± 0.82	62 ± 0.98

Table 3

Total surface energy and its components of test liquids in [mN m<sup>-1</sup>] [31].

Test liquids	Total surface tension $\gamma_{lv}$	Polar component $\gamma^p$	Dispersive component $\gamma^d$	$\gamma^{LW}$	Lifshitz acid-base component $\gamma^{AB}$	$\gamma^+$	$\gamma^-$
Paraffin	28.9	0	28.9	28.9	0	0	0
Ethylene glycol	48.0	19.0	29.0	29.0	19.0	1.92	47.0
Formamide	58.0	19.0	39.0	39.0	19.0	2.28	39.6
Water	72.8	51.0	21.8	21.8	51.0	25.50	25.5

The equilibrium contact angles for different test liquids on various membranes are given in Table 2. Among the test liquids, paraffin is highly non-polar and water is highly polar. Ethylene glycol and formamide have surface tension between that of paraffin and water (Table 3). The contact angles of paraffin drops do not vary significantly with increasing SSA content or crosslinking in PVA. By contrast, the changes in contact angles for ethylene glycol and formamide were large for PVA-20% SSA in comparison with PVA-10% SSA. More interestingly, a non-monotonic variation in the contact angles for the blends, i.e., larger contact angles than either of the pure components, was observed (Table 2) especially for paraffin. The contact angles with both formamide and water (high surface tension liquids) on blend membranes are between those on PVA-SSA and SPEEK. The contact angle of water on Nafion was similar to that of PVA-10% SSA membranes. On blending PVA-SSA with SPEEK, as well as on increasing the crosslinking of PVA, a lower contact angle and an increase in wetting are observed. The surface

**Table 4**

Surface energy of Nafion and PVA–SSA/SPEEK–50/50 membranes estimated using Fowkes' approach using Wu harmonic mean (Eq. (5)).

Liquid combinations	Surface energy [mN m <sup>-1</sup> ]					
	Nafion			PVA–SSA/SPEEK–50/50		
	$\gamma^d$	$\gamma^p$	$\gamma_s$	$\gamma^d$	$\gamma^p$	$\gamma_s$
Paraffin–ethylene glycol	78.8	0	78.8	–949.6	0	–949.6
Paraffin–formamide	126.5	0	126.5	–81.8	0	–81.8
Paraffin–water	45.8	0	45.8	56.2	0	56.2
Formamide–water	33.0	5.0	38.0	22.4	23.0	45.4
Ethylene glycol–water	37.1	3.0	40.1	32.8	9.9	42.6
Ethylene glycol–formamide	5.4	18.0	23.4	–2.4	92.8	90.5

energy components of the liquids used for the determination of the surface energy of the membranes are given in Table 3 [31].

### 4.3. Surface energy analysis

#### 4.3.1. Fowkes approach using Wu harmonic mean

Contact angles were measured using four test liquids, and therefore six combinations of liquid pairs could be used for the surface energy estimation using the Fowkes method. It is generally observed that combinations of highly non-polar and highly polar test liquids result in better estimations of surface energies. The surface energies of various membranes calculated using paraffin–ethylene glycol and paraffin–formamide combinations are negative. On the other hand, the surface energies estimated using paraffin–water, formamide–water, ethylene glycol–water and ethylene glycol–formamide combinations are positive. For a given membrane, the total surface energy and its components are widely different for different combinations of test liquids. Example results for Nafion and PVA–SSA/SPEEK–50/50 are listed in Table 4. For the blend membrane, ethylene glycol–formamide and ethylene glycol–water pairs give similar total surface energy. The estimated surface energy components are, however, quite different. Similar observations are made for all the other membranes. Therefore, it may be concluded that the Fowkes approach using Wu harmonic mean may not be suitable for estimating the surface energy and its components for these types of ionic material [25]. Hence, the van Oss acid–base approach which includes the acid–base balances were considered in further analysis.

#### 4.3.2. van Oss acid–base approach

The van Oss acid–base approach is used to estimate the total surface energy ( $\gamma_s$ ) and the Lewis acid–base components of the surface energy ( $\gamma^{LW}$ ,  $\gamma^+$ ,  $\gamma^-$ , and  $\gamma^{AB}$ ) for the membranes. The results are given in Tables 5 and 6. The total surface energy calculated by this approach is positive for all combinations of liquids. The surface energy estimated using a paraffin–ethylene glycol–formamide combination seems to be erroneous as the total

**Table 5**

Surface energy of membranes estimated using van Oss acid–base approach (Eq. (7)) with paraffin, ethylene glycol and water as test liquids.

Samples	Surface energy [mN m <sup>-1</sup> ]				
	Paraffin–ethylene glycol–water				
	$\gamma^{LW}$	$\gamma^+$	$\gamma^-$	$\gamma^{AB}$	$\gamma_s$
Nafion	28.6	0.1	18.7	1.7	30.3
PVA–10% SSA	28.6	0.9	12.0	6.5	35.1
PVA–20% SSA	28.6	2.9	10.0	10.8	39.4
PVA–30% SSA	28.6	2.3	15.4	11.9	40.4
PVA–SSA/SPEEK–70/30	28.6	3.6	8.9	11.3	39.8
PVA–SSA/SPEEK–50/50	28.6	2.0	17.0	11.7	40.3
PVA–SSA/SPEEK–30/70	28.6	1.3	21.6	10.4	39.0
SPEEK	28.6	2.4	16.0	12.3	40.9

**Table 6**

Surface energy of membranes estimated using van Oss acid–base approach (Eq. (7)) with paraffin, formamide and water as test liquids.

Samples	Surface energy [mN m <sup>-1</sup> ]				
	Paraffin–formamide–water				
	$\gamma^{LW}$	$\gamma^+$	$\gamma^-$	$\gamma^{AB}$	$\gamma_s$
Nafion	28.6	0.4	15.3	4.8	33.3
PVA–10% SSA	28.6	5.6	4.2	9.6	38.2
PVA–20% SSA	28.6	9.8	3.0	10.8	39.4
PVA–30% SSA	28.6	10.3	5.0	14.4	42.9
PVA–SSA/SPEEK–70/30	28.6	17.9	0.4	5.4	34.0
PVA–SSA/SPEEK–50/50	28.6	13.9	3.3	13.5	42.1
PVA–SSA/SPEEK–30/70	28.6	10.7	6.2	16.3	44.9
SPEEK	28.6	14.5	3.1	13.3	41.9

surface energy and the individual components vary greatly among different membranes. The surface energy of Nafion estimated using paraffin–ethylene glycol–water and paraffin–formamide–water is comparable with the results reported earlier by Brack et al. [25]. Interestingly, the estimation based on the paraffin–ethylene glycol–water combination leads to comparable surface energies for all the membranes, except for Nafion and PVA–10% SSA. The individual components of the surface energy, however, vary greatly among these membranes. Moreover, for all the membranes, the contribution from the basic component ( $\gamma^-$ ) is much higher than from the acidic component ( $\gamma^+$ ) which is counter-intuitive, since the membranes are acidic. Though this approach gives better total surface energy values than the Wu harmonic mean method, the estimation based on van Oss acid–base approach also does not lead to consistent values of overall surface energy and its components for all the membranes and for all combinations of test liquids. Therefore, the equation-of-state approaches were used in further analysis.

#### 4.3.3. Equation-of-state approach: Berthelot combining rule

The total surface energies of the membranes were estimated using the Berthelot equation (Eq. (10)) and are given in Table 7. Estimation using the Berthelot approach gives positive values of surface energy for all the test liquids. The estimated surface energies of the membranes are lower than those of the test liquids. Also, different test liquids report different surface energies for the same membrane. For example, the estimated surface energy for Nafion is in the range 18.82 (formamide) to 31.92 (water) mN m<sup>-1</sup>. The surface energies estimated with paraffin and water are in agreement with the surface energies estimated using the van Oss acid–base approach (using a test liquid combination with the largest range of  $\gamma_{lv}$ ). This estimate is also in agreement with the values reported for Nafion [25,31]. As mentioned in Section 2.5, however, the Berthelot approach can lead to overestimation of the surface energy, and therefore analysis using the modified Berthelot equation was attempted.

**Table 7**

Surface energy of membranes estimated using Berthelot equation (Eq. (10)) with paraffin, ethylene glycol, formamide and water as test liquids.

Samples	Surface energy [mN m <sup>-1</sup> ]			
	Paraffin	Ethylene glycol	Formamide	Water
	Nafion	27.4	19.5	18.8
PVA–10% SSA	28.3	24.8	29.4	31.2
PVA–20% SSA	28.4	32.4	35.9	34.4
PVA–30% SSA	28.2	31.9	37.9	38.5
PVA–SSA/SPEEK–70/30	28.4	34.0	44.7	34.4
PVA–SSA/SPEEK–50/50	27.7	31.3	42.3	39.3
PVA–SSA/SPEEK–30/70	28.1	29.2	39.1	41.0
SPEEK	28.7	32.4	42.9	39.3

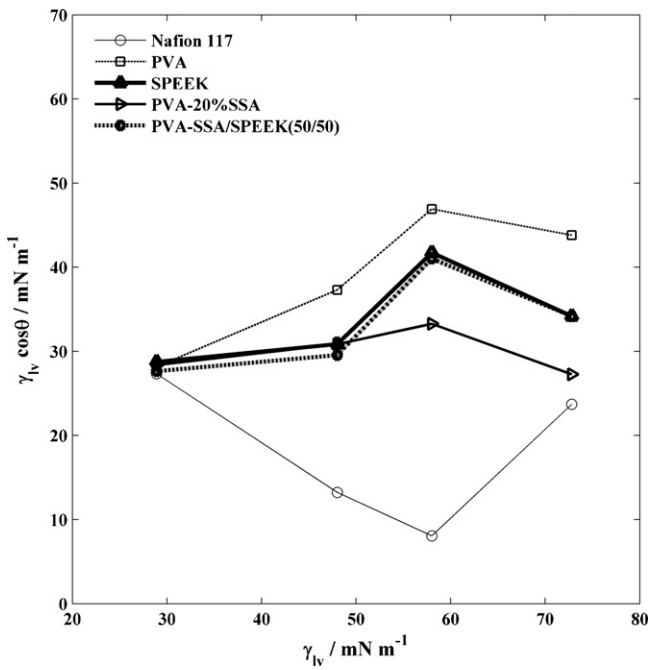


Fig. 7.  $\gamma_{lv} \cos \theta$  variation with  $\gamma_{lv}$  for different membranes.

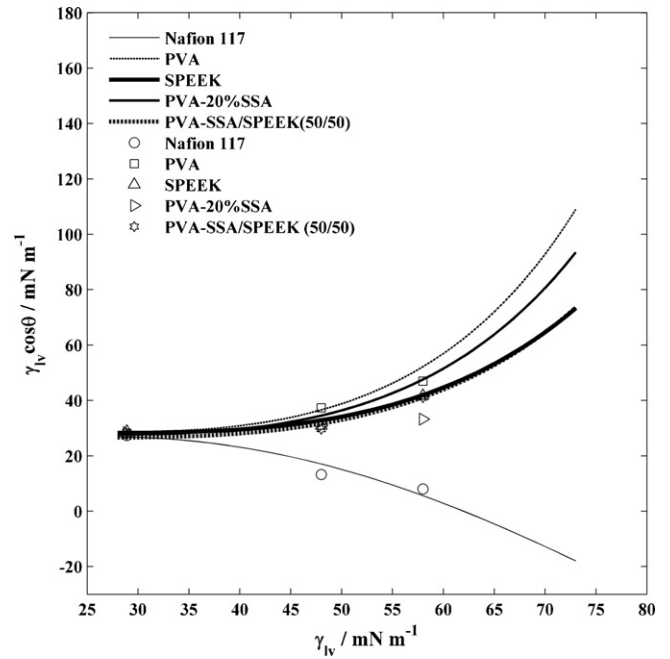


Fig. 8.  $\gamma_{lv} \cos \theta$  vs.  $\gamma_{lv}$  fit using Eq. (11) for different membranes.

4.3.4. Equation-of-state approach: modified Berthelot rule

Eq. (13) implies that  $\gamma_{lv}$  and  $\theta$  for different test liquids on a given surface can be related to each other. In the modified Berthelot approach, this relationship is usually expressed using the plot of  $\gamma_{lv} \cos \theta$  and  $\gamma_{lv}$ . For numerous polymeric substrates, such as polystyrene and polyacrylates, it has been shown that  $\gamma_{lv} \cos \theta$  decreases with increasing  $\gamma_{lv}$  [11,20,32]. Plots of  $\gamma_{lv} \cos \theta$  vs.  $\gamma_{lv}$  for Nafion, PVA-SSA and SPEEK membranes investigated in this work are presented in Fig. 7. An interesting feature of these results is that data with water do not follow the trend observed in the case of other test liquids. This could be due to physico-chemical interactions of water with the ionic polymer membranes. Similar observations were made with a PVA membrane. Such deviations from expected trends were reported for test liquids which interact with solid surfaces [11]. Therefore, the data with water are excluded from the estimation of surface energy using the modified Berthelot approach.

The qualitative trend for Nafion is similar to the reported trend of  $\gamma_{lv} \cos \theta$  decreasing with increasing  $\gamma_{lv}$ . For PVA, PVA-SSA and SPEEK (as well as for other crosslinked and blend membranes), however,  $\gamma_{lv} \cos \theta$  increases with increasing  $\gamma_{lv}$ . There are no other reports of using the modified Berthelot approach for ionic polymers and therefore, the significance of the observed trends requires further investigation.

The surface energy and the parameter,  $\beta$  are obtained from the best fits of Eq. (13), using surface tensions of test liquids and

their contact angles on membranes. The best-fit curves for selected membranes are presented in Fig. 8. The corresponding surface energy and the  $\beta$  values, for the different membranes are given in Table 8. Due to the difference in the qualitative trend,  $\beta$  is positive for Nafion and negative for other membranes. This may be due to the fact that perfluorosulfonic polymers like Nafion combine the high hydrophobicity of the perfluorinated backbone with the high hydrophilicity of sulfonic acid groups [34] in one macromolecule. Particularly, in hydrated membranes, this gives rise to the formation of hydrophobic/hydrophilic nano-domains. In the case of hydrocarbon-based membranes, hydrophilic/hydrophobic differences in the macromolecule are less prominent and the higher flexibility of the polymer backbone reduces the possibilities of separation into a hydrophilic and a hydrophobic domain. The surface energies of the blend membranes are found to be marginally lower than the surface energy of SPEEK and PVA membranes. The contact angles of water on the blend membranes also show similar trends. PVA-SSA/SPEEK-30/70 blend has the lowest contact angle and the highest surface energy among the blend membranes.

A larger concentration of sulfonic acid groups (higher IEC) in the membrane leads to an increase in the surface energy of the pure component as well as the blend membranes, as shown in Fig. 9. As observed earlier, Nafion does not follow this trend. Therefore, it may be concluded that in addition to the concentration of the sulfonic acid groups, their distribution at the microscopic level may play a role in determining the surface energy.

Table 8

Surface energy of membranes estimated using modified Berthelot equation (Eq. (13)) (paraffin, ethylene glycol and formamide were used for estimation, except for PVA-SSA/SPEEK-30/70 for which paraffin, formamide and water were used).

Samples	Surface energy [mN m <sup>-1</sup> ]	$\beta \times 10^4$ [m mN] <sup>2</sup>	Error band for the fit [mN m <sup>-1</sup> ]
Nafion	26.9	1.12	±1.74
PVA-10% SSA	26.8	-0.38	±0.84
PVA-20% SSA	27.7	-1.50	±1.40
PVA-30% SSA	28.7	-1.50	±0.62
PVA-SSA/SPEEK-70/30	25.8	-1.34	±1.41
PVA-SSA/SPEEK-50/50	26.6	-1.18	±1.92
PVA-SSA/SPEEK-30/70	27.8	-0.50	±0.83
SPEEK	28.3	-1.19	±1.70



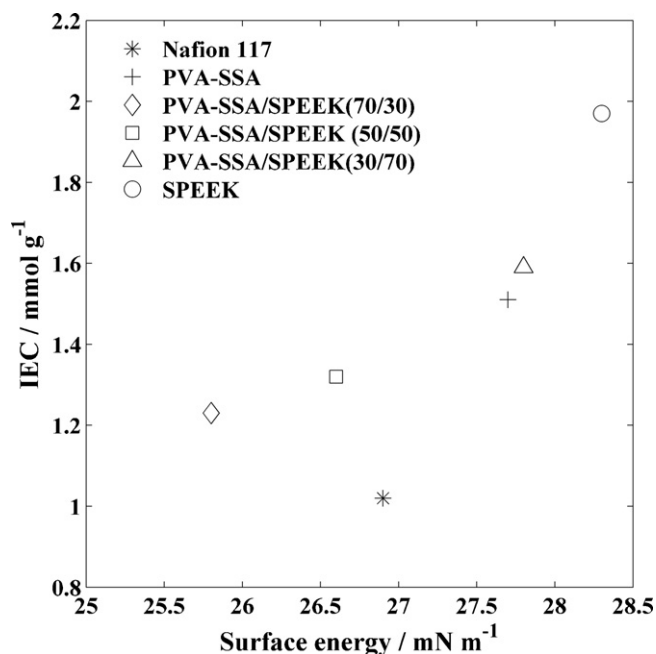


Fig. 9. Variation of IEC with surface energy for different membranes.

For a particular ionic membrane, higher IEC implies higher proton conductivity up to a certain level. Beyond this level, the change in IEC does not affect the conductivity significantly. Given that the IEC correlates well with the surface energy for different membranes (Fig. 9), it is interesting to observe the variation of conductivity with surface energy (estimated using the modified Berthelot equation). This variation is shown in Fig. 10 and it is seen that membranes with higher surface energy have lower conductivity, except in the case of Nafion. It should be noted that conductivity is plotted using the log scale. Nafion has a higher conductivity at relatively lower surface energy. Again, this may be explained based on the unique surface domain morphology of Nafion. The variation of conductivity with  $\gamma_i^+$  and  $\gamma_i^-$  estimated using the van Oss acid–base approach

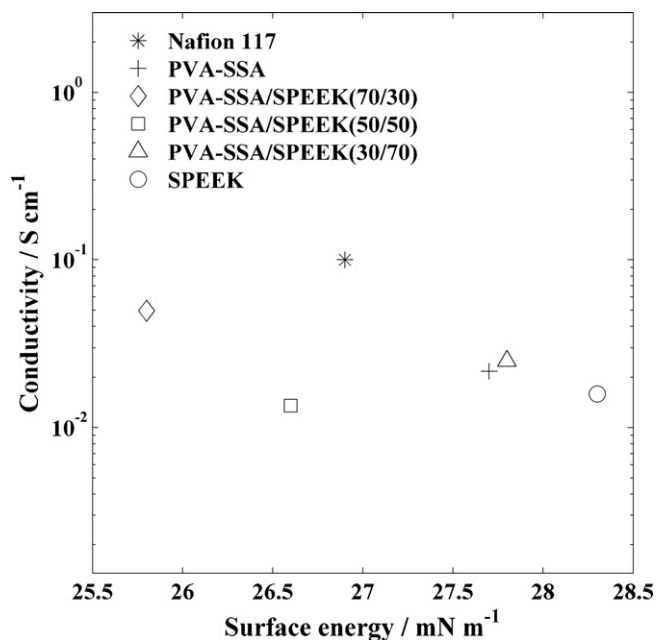


Fig. 10. Variation of conductivity with surface energy (estimated using modified Berthelot equation (Eq. (11))) for different membranes.

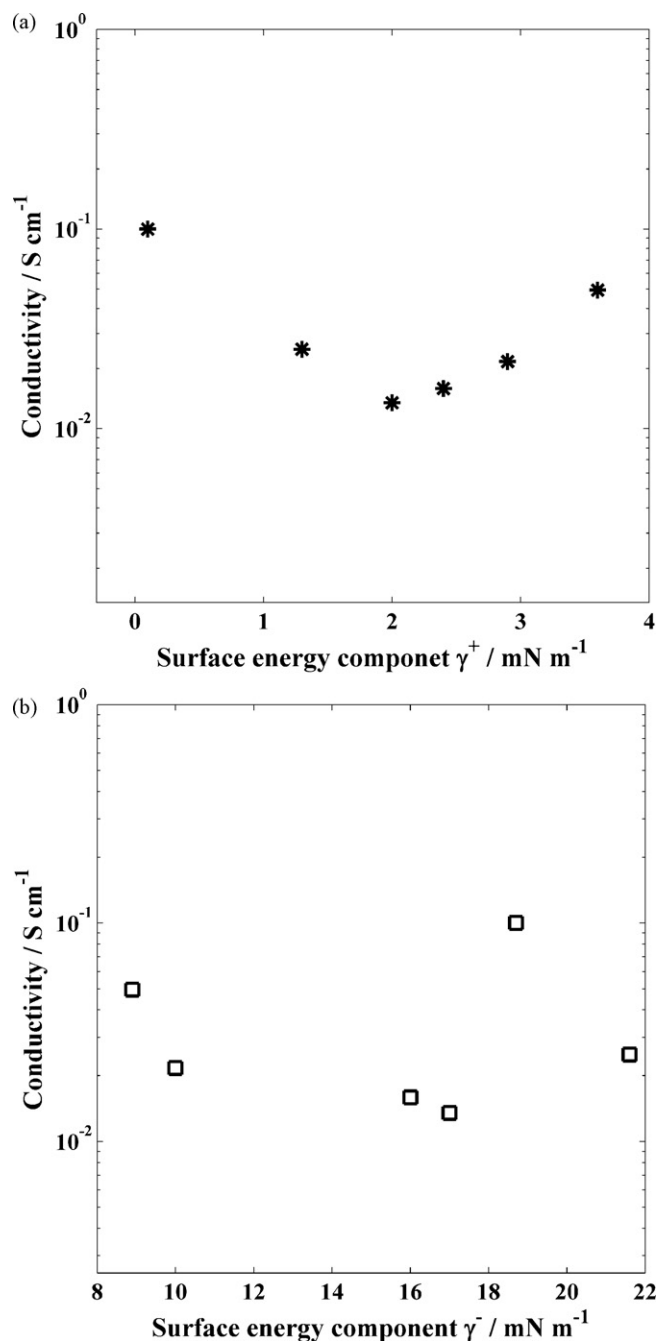


Fig. 11. Conductivity as function of surface energy components (a)  $\gamma_i^+$  (b)  $\gamma_i^-$  (estimated using van Oss approach Eq. (5) and test liquids paraffin, ethylene glycol and water).

(using paraffin, ethylene glycol and water as test liquids) is shown in Fig. 11(a) and (b), respectively. As expected, there is no correlation between the surface energy components and the conductivity. This reinforces the observation that the van Oss approach, though it gives reasonable total surface energy values, fails to capture the individual contributions to the total surface energy.

## 5. Conclusions

Various methods to estimate the surface energy of ionic polymers were applied to determine the surface energy and its components of novel, ionic polymer blend membranes based on crosslinked polyvinyl alcohol (PVA–SSA) and sulfonated poly(ether

ether ketone) (SPEEK). The total surface energies estimated using the van Oss acid–base and the modified Berthelot approaches are found more reasonable in comparison with the Fowkes approach using Wu harmonic mean method. On the other hand, the surface energy components estimated using the van Oss acid–base approaches do not seem to be reliable. The ion-exchange capacity, the proton conductivity and the water sorption characteristics of the membranes have also been studied and compared with the surface energy and wettability characteristics of the membranes. Good correlation is found between the surface energy estimated using the modified Berthelot approach and the ion-exchange capacity of the membranes. All the PVA–SSA and SPEEK based membranes have higher surface energy compared with Nafion. The micro-domain morphology of Nafion which is entirely different from other polymer membranes may be the reason for the observed difference. The proton conductivity of each membranes is found to be a decreasing function of the total surface energy. Results obtained using the modified Berthelot approach suggest that it could be used to obtain better estimates of the surface energy of ionic, proton conducting membranes.

### Acknowledgement

The authors are grateful to the Naval Research Board, India, for financial support.

### References

- [1] C.E. Tsai, C.-W. Lin, B.-J. Hwang, *J. Power Sources* 195 (2010) 2166–2173.
- [2] T.A. Sherazi, M.D. Guiver, D. Kingston, S. Ahmad, M. Akram Kashmiri, X. Xue, *J. Power Sources* 195 (2010) 21–29.
- [3] D.S. Kim, H.B. Park, J.W. Rhim, Y.M. Lee, *Solid State Ionics* 176 (2005) 117–126.
- [4] J.W. Rhim, H.B. Park, C.S. Lee, J.H. Jun, D.S. Kim, Y.M. Lee, *J. Membr. Sci.* 238 (2004) 143–151.
- [5] M.M. Hasani-sadrabadi, E. Dashtimoghadam, K. Sarikhani, F.S. Majedi, G. Khanbabaee, *J. Power Sources* 195 (2010) 2450–2456.
- [6] N.Y. Arnett, W.L. Harrison, A.S. Badami, A. Roy, O. Lane, F. Cromer, L. Dong, J.E. McGrath, *J. Power Sources* 172 (2007) 20–29.
- [7] A. Fogden, L.R. White, *J. Colloid Interface Sci.* 138 (1990) 414–430.
- [8] R.M. Pashley, P.M. McGuiggan, R.G. Horn, B.W. Ninham, *J. Colloid Interface Sci.* 126 (1988) 569–578.
- [9] A.W. Neumann, R.J. Good, C.J. Hope, M. Sejjal, *Colloid Interface Sci.* 49 (1974) 291–304.
- [10] D.K. Owens, R.C. Wendt, *J. Appl. Polym. Sci.* 13 (1969) 1741–1747.
- [11] D.Y. Kwok, A.W. Neumann, *Adv. Colloid Interface Sci.* 81 (1999) 167–249.
- [12] F.M. Fowkes, *Ind. Eng. Chem.* 56 (1964) 40–52.
- [13] Y.C. Liu, D.N. Lu, *Plasma Chem. Plasma Process.* 26 (2006) 119–126.
- [14] R.D. Peters, X.M. Yang, T.K. Kim, B.H. Sohn, P.F. Nealey, *Langmuir* 16 (2000) 4625–4631.
- [15] R. Smith, R. Pitrola, *J. App. Polym. Sci.* 83 (2002) 997–1008.
- [16] M.J. Liu, K. Tzou, R.V. Gregory, *Synth. Met.* 63 (1994) 67–71.
- [17] B. Bergmann, T.W. Hanks, *Macromolecules* 33 (2000) 8035–8042.
- [18] E.K. Lee, S.Y. Choi, *Korean J. Chem. Eng.* 23 (2006) 1055–1062.
- [19] C.J. van Oss, M.K. Chaudhury, R.J. Good, *Chem. Rev.* 88 (1988) 927–941.
- [20] D.Y. Kwok, D. Li, A.W. Neumann, *Eng. Aspects* 89 (1994) 181–191.
- [21] J. Zhang, G.P. Yin, Q.-Z. Lai, Z.-B. Wang, K.-D. Cai, P. Liu, *J. Power Sources* 168 (2007) 453–458.
- [22] E.C. Kumbur, K.V. Sharp, M.M. Mench, *J. Power Sources* 161 (2006) 333–345.
- [23] T.A. Zawodzinski, S. Gottesfeld, S. Shoichet, T.J. McCarthy, *J. Appl. Electrochem.* 23 (1993) 86–88.
- [24] D. Ramdutt, C. Charles, J. Hudspeth, B. Ladewig, T. Gengenbach, R. Boswell, A. Dicks, P. Brault, *J. Power Sources* 165 (2007) 41–48.
- [25] H.P. Brack, M. Wyler, G. Peter, G.G. Scherer, *J. Membr. Sci.* 214 (2003) 1–19.
- [26] F.G. Wilhelm, I.G.M. Punt, N.F.A. Vejt, H. Strathmann, M. Wessling, *J. Membr. Sci.* 199 (2002) 167–176.
- [27] S. Kaliaguine, S.D. Mikhailenko, K.P. Wang, P. Xing, G. Robertson, M. Guiver, *Catal. Today* 82 (2003) 213–222.
- [28] K.N. Prabhu, P. Fernandes, G. Kumar, *Mater. Des.* 30 (2009) 297–305.
- [29] S. Wu, *J. Polym. Sci., Part C* 34 (1971) 19–30.
- [30] N.H. Jalani, P. Choi, R. Datta, *Solid State Ionics* 175 (2004) 815–817.
- [31] T. Caykara, S. Demirci, S.M. Eroglu, O. Guven, *J. Polym. Sci., Part B: Polym. Phys.* 44 (2006) 426–430.
- [32] D. Li, A.W. Neumann, *J. Colloid Interface Sci.* 148 (1992) 190–200.
- [33] C. Lipson, N.J. Sheth, *Statistical Design and Analysis of Engineering Experiments*, McGraw-Hill Publishing Co., New York, 1973.
- [34] K.D. Kreuer, *J. Membr. Sci.* 185 (2001) 29–39.