CHAPTER IV

ALKYL UROCANATES AS PROTON TRANSFER SPECIES IN MOLTEN STATE: AN ACCESS TO PROTON CONDUCTIVITY IN THE LONG RANGE OF OPERATING TEMPERATURE

4.1 Abstract

A series of alkyl urocanates with different chain lengths as proton transfer species in sulfonated poly (ether ether ketone) (SPEEK) for polymer electrolyte membrane fuel cell are focused. The detailed studies of proton conductivity and the changes of hydrogen bond network as well as the activation energy regarding to the temperature lead us to an understanding of the proton transfer steps and mechanism. Alkyl urocanates which are in liquid molten state in a long range of temperatures based on their low melting temperatures and high degradation temperatures (for example, butyl urocanate; T_m 46 °C, T_d 220 °C) apply their molecular motion to transfer the proton under the protonation and hydrogen bond and as a result, the proton conductivity can be maintained even the operating temperature is varied from 60 °C to as high as 170 °C. In addition, as SPEEK contains a certain amount of water molecules, both water and imidazole synchronize the proton transfer regarding to its favorable molecular motion during heat treatment. Although the role of water clusters in those Nafion® and SPEEK membranes is well clarified, the movement of water as liquid species in the membrane to perform proton conductivity is not that much raised as a model of effective proton transfer condition. The present work, for the first time, shows how alkyl urocanates perform the similar proton transfer mechanism to water and the proton transfer species in liquid or molten state effectively initiate proton conductivity. Hence, we can easily obtain the high proton transfer efficiency in the long range of the operating temperatures if the proton transfer species are stable in molten state to offer the proton transfer clusters.

4.2 Introduction

Proton exchange membrane fuel cell (PEMFC) is an alternative energy which can be applied in several practical systems, such as, automotives, portable devices and power generators [1]. In PEMFC, the polymer electrolyte membrane (PEM) is the essential component where proton transfer occurs. Nowadays, sulfonated polymers such as Nafion®, and SPEEK are well accepted [2]. The sulfonyl group plays an important role in maintaining the water as clusters inside the polymer matrices so that the proton can transfer through the hydrogen bond network of hydranium ions (H_3O^+) [3]. A fully hydrated SPEEK membrane shows the highest proton conductivity approximately 10^{-2} S cm^{-1} at 90 °C [4, 5]. In fact, the sulfonated membranes have some limitations, especially a significant decrease in proton conductivity at high temperature due to the evaporation of water [1, 6].

PEMFC operation at the high temperature (above 80 °C) has its own merits, which are related to the acceleration of proton transfer, the increase of proton conductivity efficiency, and the desorption of CO on Pt catalysts. The traditional proton transfer via water clusters is, therefore, difficult to gain those merits as mentioned above.

Heterocycles, especially imidazole-based compounds, are known for their resonance structure which hydrogen atom can be alternated on both nitrogen atoms N-C=N leading to the proton movement. When imidazoles are in the hydrogen bond networks where the molecular reorientation is possible, proton transfer among different molecules can be achieved [7]. Several reports have demonstrated how heterocycles initiate the proton conductivity along the polymer matrices for PEMFC at high temperature [8].

Heterocycles can be introduced into the polymer matrices via many approaches such as polymer blend [9-11], copolymerization [12], and side chain modification [13, 14]. For example, poly(4,5-vinylimidazole) doped with phosphoric acid was reported to enhance the proton conductivity to 10^{-4} S cm^{-1} at 150 °C [9]. Copolymers of 4,5-vinylimidazole and acrylic acid with a proton donor and acceptor in a single polymer chain exhibited the proton conductivity around 10^{-4} S cm^{-1} at 150 °C [12]. Pangon *et al.* proposed the synthesis of multibranched benzimidazole, as well as the blend with poly(vinyl alcohol) (PVA), and demonstrated its multi-directional hydrogen bond networks to achieve the proton conductivity for 10^{-3} S cm^{-1}at 190 °C [14]. Other reports about polymer blends with heterocycles such as polyacid/ heterocycles[15-17], Nafion®/ poly(1-vinyl-1, 2 ,4-triazole) [18], Nafion®, and poly (vinylphosphonic acid)/ 1H-1,2,3-benzotriazole [19] showed proton conductivity in the range of 10^{-3} S cm^{-1} – 10^{-4} S cm^{-1} at 80 °C – 120 °C.

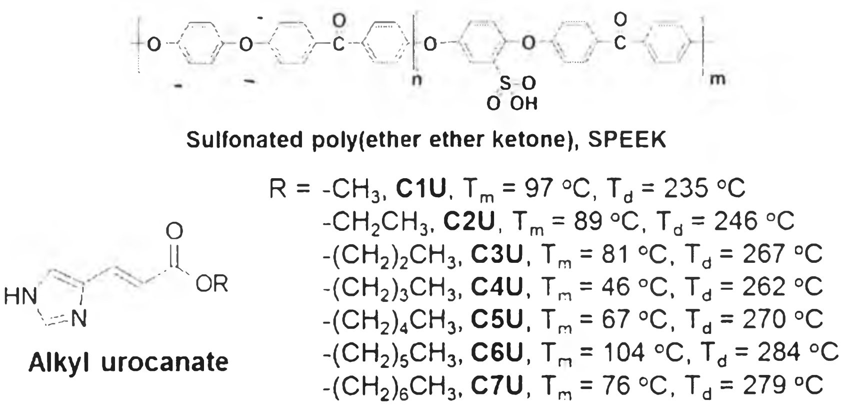
At present, most research works focus on the key factors to maintain or induce proton conductivity in the long range of operating temperatures by applying heterocycles as proton transfer species instead of water molecules. To our viewpoint, if we consider the heterocycles in the polymer matrices similar to water clusters, highly efficient proton conductivity might not only be relied on the hydrogen bond networks and the molecular motion, but also can be achieved at high temperature due to the thermal stability of the heterocyclic molecules as well as their clusters formation. The molecular motion and thermal stability including the cluster formation can be traced by the glass transition temperature (T_g), the melting temperature (T_m), and the degradation temperature (T_d). In fact, the hydrogen bond network is a consequence of molecular packing or alignment, which is dynamically changed under the variation of temperatures. However, the clarification about how heterocycles form the clusters by hydrogen bond networks along with their molecular motion in the molten state has not yet been clarified.

It is important to note that water clusters either in perfluoro-sulfonated membrane or SPEEK membrane tend to be destroyed, when the temperature of PEMFC system was increased during operation, resulting in a short range of efficient operating temperature (40 °C – 80 °C). Therefore, if the water clusters were substituted by heterocycles, it is possible that we may be able to obtain PEMFC system with a long range of operating temperatures, especially when those heterocycles in the system show the low melting temperature (as low as 40 °C) and high degradation temperature (much higher than 80 °C). To our question, if the performance of the water is the model, we should be able to clarify the efficient operating temperature related to the properties of heterocycles in terms of T_m and T_d.

In our previous work, we focused on a series of alkyl urocanates with variable chain lengths to find that by esterifying urocanic acid with different alkyl chain lengths, it is possible to prepare a series of alkyl urocanates with different thermal properties (Scheme 4.1) [20]. Ideally, if the imidazole derivatives possess T_m much lower than the operating temperature as well as the T_d much higher than the operating temperature (for example, high operating temperature of 120 °C), they are in their molten state without degradation in the membrane matrices. As a result, the favorable thermal motion of the molecules for proton transfer can be expected in a long range of temperatures.

Combining our success in preparing alkyl urocanates under the points yet to be done as mentioned above, the present work aims to clarify (i) the performances of alkyl urocanates, especially at the temperatures in between their T_m and T_d, as proton transfer species in the polymer membrane, (ii) the detailed structural analyses on the hydrogen bond and chain mobility of alkyl urocanates under the variation of temperatures, and (iii) the proton transfer steps and mechanism comparing with those belong to water clusters. The success of this work will be a guideline to obtain the high proton transfer efficiency in the long range of the operating temperatures.

Scheme 4.1 Sulfonated poly (ether ether ketone), **SPEEK**, and alkyl urocanates, **CxU**.



R = $-CH_3$, **C1U**, $T_m = 97$ °C, $T_d = 235$ °C
$-CH_2CH_3$, **C2U**, $T_m = 89$ °C, $T_d = 246$ °C
$-(CH_2)_2CH_3$, **C3U**, $T_m = 81$ °C, $T_d = 267$ °C
$-(CH_2)_3CH_3$, **C4U**, $T_m = 46$ °C, $T_d = 262$ °C
$-(CH_2)_4CH_3$, **C5U**, $T_m = 67$ °C, $T_d = 270$ °C
$-(CH_2)_5CH_3$, **C6U**, $T_m = 104$ °C, $T_d = 284$ °C
$-(CH_2)_6CH_3$, **C7U**, $T_m = 76$ °C, $T_d = 279$ °C

4.3 Experimental

4.3.1 Materials

All chemicals were reagent grade and used without further purification. Urocanic acid and deuterated dimethylsulfoxide (DMSO-*d*$_6$) were purchased from Aldrich, Germany. Sodium hydroxide (NaOH), and methanol were bought from Carlo Erba, Italy. DMSO, sulfuric acid (H_2SO_4), 35% hydrochloric acid (HCl), isopropanol, and butanol were bought from Labscan, Ireland. Hexanol, 1-propanol, Potassium bromide (KBr), and heptanol were purchased from Merck, Germany. Poly ether ether ketone (PEEK) was a gift from JJ Degussa Chemical (Thailand) Ltd., Thailand.

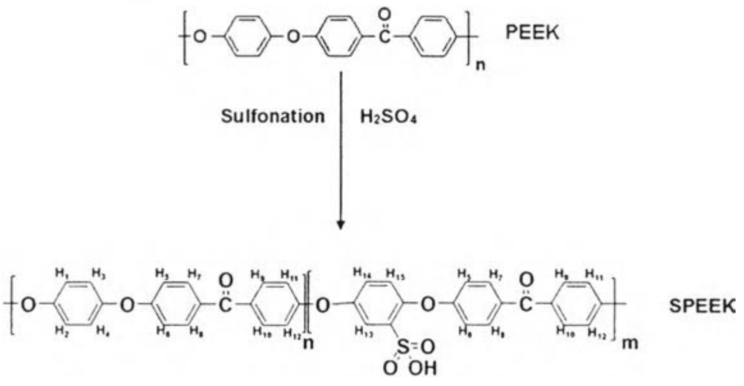
4.3.2 Synthesis of Alkyl Urocanates

A series of alkyl urocanates (Scheme 4.1) were prepared as reported previously [20-22]. In brief, urocanic acid (1 g, 7.24 mmol) was dissolved in methanol (60 mL) with HCl as a catalyst. The solution was refluxed for a day to obtain a yellowish solution. The insoluble part was filtrated before evaporating the yellowish solution to obtain solid particles (0.5 g). The particles were dissolved in deionized (DI) water followed by a few drops of potassium carbonate solution (5 mol L^{-1}) and stirred in a cold water bath to obtain the suspension. The precipitates were filtrated and washed several times with cold DI water before drying at room temperature to obtain the yellowish powder, methyl urocanate, **C1U** (43 % yield). Other alkyl urocanates were synthesized in similar way to obtain ethyl urocanate (**C2U**, 45 % yield), iso-propyl urocanate (**C3U**, 35 % yield), butyl urocanate (**C4U**, 37 % yield), pentyl urocanate (**C5U**, 40 % yield), hexyl urocanate (**C6U**, 45 % yield), and heptyl urocanate (**C7U**, 42 % yield).

4.3.3 Preparation of SPEEK and SPEEK Membrane

The preparation of SPEEK was carried out as reported by Vetter et *al.*, 2005 [5]. In brief, PEEK (4.0 g) was dried in a hot air oven for 2 days and then dissolved in concentrated sulfuric acid (400 mL). The yellow solution was continuously stirred for 1 day at room temperature. The brownish solution was precipitated in an iced-water bath (4 L) to obtain white precipitates. The white precipitates were filtrated and washed several times by DI water until neutral pH. The white precipitates obtained were dried in vacuo at 60°C for 1 day to get yellowish powder (Scheme 2). The molar quantity of the sulfonic acid group in the yellowish powder, SPEEK, was 57 %. SPEEK powder (0.5 g) was dissolved in DMSO (5 mL) and left drying at 80 °C for 2 days to obtain SPEEK membrane. The ion exchange capacity of the SPEEK membrane was 1.654 mol $(l \cdot g)^{-1}$ (Appendix D).

Scheme 4.2 Preparation of SPEEK.



4.3.4 SPEEK-CxU Blend Membranes

Compound **C1U** (0.5 mmol L^{-1}) was recrystallized in chloroform before use. The crystals obtained were dissolved in 5% (wt/v) of SPEEK solution (5 mL) and cast on a 3.5 cm × 1 cm glass mold. The mold was left at 80 °C for 2 days and at room temperature for a day to obtain **SPEEK-C1U** membrane (2 wt% of **C1U**). Other **SPEEK-CxU** membranes were prepared in similar way.

4.3.5 Characterization

Fourier transform infrared (FTIR) spectra of the **SPEEK** and **SPEEK-CxU** membrane systems were clarified by a Bruker Alpha FTIR spectrometer at a resolution of 2 cm^{-1} and number scan of 32. Structural characterization of the alkyl urocanates was confirmed by a Bruker 500 MHz Avance III nuclear magnetic resonance (NMR) spectrometer operated at Larmor frequency of 500.13 MHz. The solvent wasDMSO-*d6*. Electrospray ionization mass spectra (ESI-MS) were analyzed by using a Bruker Micro TOF II equipped with Bruker Compass Data Analysis 4.0 software operating in positive ion mode.

Thermal analyses were observed by using a Perkin Elmer Pyris Diamond thermogravimetric analysis (TGA) at a heating rate of 10 $Kmin^{-1}$ under nitrogen atmosphere from 30 °C to 800 °C, and a NETZCH 200 F3 Maia differential scanning calorimeter (DSC) at a heating rate of 10 K min^{-1} and cooling rate of 2 K min^{-1}. The scanning temperature was in the range -90 °C to 230 °C under nitrogen atmosphere.

An in-house sealed-off teflon impedance cell was used. Proton conductivity was analyzed by the complex impedance method using a μAUTOLAB Type III potentiostat/galvanostat in a frequency range of 5×10^5 Hz to 1 Hz and AC signal amplitude of 0.05 V from 30 °C to 170 °C under dry conditions. Proton conductivity (σ) was calculated from impedance data based on$\sigma = L/RA$, where L is the membrane thickness (cm), A is the cross-sectional area of the electrode (cm^2) and R is the membrane resistance (Ω) derived from the intersection of the Nyquist plot on the zero x axis.

Temperature dependence FTIR was carried out by a Bruker Alpha FTIR spectrometer with a deuterated trigylcine sulfate (DTGS) detector in the transmission mode equipped with an in-house designed hot stage. The temperature was controlled from 30 °C to 170 °C during the 32 number of scan at a resolution of 2 cm^{-1}.

4.4 Results and Discussion

Structural characterizations of all alkyl urocanates were analyzed by using FTIR, NMR, ESI-TOF and single crystal analysis as reported previously [20]. The neat SPEEK membrane (DS = 57 %) and **SPEEK-CxU** were primarily characterized by FTIR spectra (Appendix E). Compared to the neat SPEEK membrane, the **SPEEK-CxU** showed a significant characteristic peak of C=O (ester) at 1717 cm^{-1} referring to **CxU**. It is important to note that the inter- and intra-hydrogen bond networks of the imidazole ring in 2400 cm^{-1}– 3500 cm^{-1} were observed. In addition, CH stretching (2800 cm^{-1} – 2900 cm^{-1}) of the hydrophobic chain was clearly identified especially for the long chain length of the alkyl urocanates. This is the basic information to discuss (in the later part) about proton transfer based on the chain mobility and hydrogen bond network of **CxU**.

4.4.1 Thermal Properties of **SPEEK-CxU**

Thermal stabilities of **SPEEK-C4U** and **SPEEK-C6U** are essential information to identify the temperature that the membranes show the high performance without degradation. In general, SPEEK membrane shows dehydration of water (T_{dH2O}) at 80 °C – 100 °C and membrane degradation ($T_{d\ membrane}$) at ~ 365 °C, and at ~ 530 °C (Figure 4.1a) [23, 24]. It is natural to think that by adding **CxU** in the membrane, degradation of CxU can be observed (T_{dCxU}).This can be confirmed by the peak at 295 °C ~ for T_{dC4U} and at 293 °C for T_{dC6U}. However, it should be noted that apart from the abovementioned peaks, an extra peak was identified. For example, in the cases of **SPEEK-C4U**, and **SPEEK-C6U** (Figures 4.1b, and 4.1c), the peaks are at 233 °C, and 235 °C, respectively. It comes to the question that what this extra peak of **SPEEK-CxU** is referred to. Further analysis by using temperature dependence FTIR gives us the answer that the peak represents the loss of hydrogen bond between imidazole and sulfonic acid group, $T_{d\ Imz\text{-}SO3H}$ (see more details in 3.4 Confirmation of possible proton channels in **SPEEK-CxU** via temperature dependence FTIR). Other **SPEEK-CxU** showed the similar trends in terms of T_d (Appendix F).

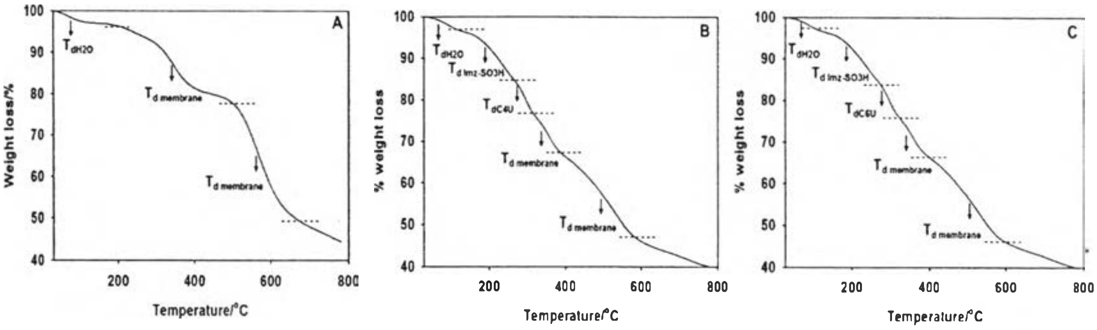


Figure 4.1 Degradation temperatures of (a) SPEEK, (b) **SPEEK-C4U** and (c) **SPEEK-C6U**.

4.4.2 Proton Conductivity of **SPEEK-CxU**

Proton conductivity of **SPEEK-CxU** was traced from 30 °C – 170 °C (Figure 4.2) without acid doping in order to evaluate precisely the performance of **CxU**. For the temperature lower than 100 °C, the proton conductivity gradually increases with the temperatures. The fact that the membrane contains moisture for ~ 3 wt% – 6 wt% (Appendix F), the water molecules might participate, especially when the operating temperature was below the boiling point, in proton transfer resulting in the similar proton conductivity for all **SPEEK-CxU** for 10^{-5} S cm^{-1}.

For the temperature above 100 °C, the proton conductivity was as high as 10^{-4} S cm^{-1}– 10^{-5} S $cm^{-1}$and surprisingly, it was maintained at the similar level for up to 170 °C. It should be noted that all **CxU** are existed in their molten state when the operating temperature was above 90 °C and might perform the flow behavior as liquid which is similar to water. It is possible that the molecular motion in liquid molten state is significant. In addition, all **CxU** are stable up to above 200 °C as indicated from their T_d (Figure 4.1, and Appendix F). The stability of **CxU** might be the key factor to maintain proton conductivity even the temperature was as high as 170 °C. Among all membranes, **SPEEK-C4U** shows the most significant conductivity (~ 10^{-4} S cm^{-1}) even the operating temperature was as high as 170 °C.

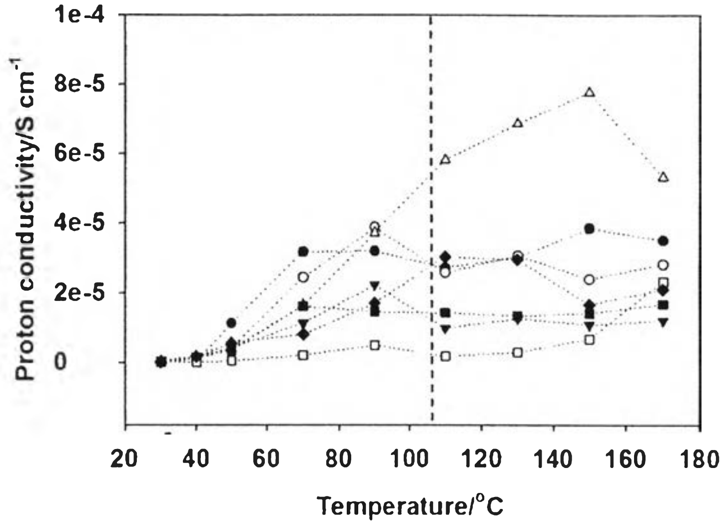


Figure 4.2 Proton conductivity of SPEEK blended with **C1U** (-●-), **C2U** (-○-), **C3U** (-▼-), **C4U** (-△-), **C5U** (-□-), **C6U** (-■-), and **C7U** (-◆-).

4.4.3 Proton Transfer Mechanism Based on Activation Energy Evaluation

Generally, the mechanism of proton transfer can be classified into two types, Grotthuss and vehicle mechanism [25]. The Grotthuss mechanism is for the proton hopping from one imidazole ring to another via hydrogen bond network and reorientation [26, 27]. The vehicle mechanism refers to the direct proton transfer between the thermally active molecules.

For **SPEEK-CxU**, the vehicle mechanism might be dominant since the molecular motion in the system was mainly relied on the state of water molecules and the alkyl urocanates. This mechanism was evaluated by the Vogel-Tammann-Fulcher (VTF) equation (eq. 1) [28-30].

$$\text{Log}(\sigma) = \text{Log}(\sigma_0) - E_a / R\,(T - T_0) \qquad (1)$$

where σ is proton conductivity at various temperatures (S cm^{-1}), E_a is activation energy (KJ mol^{-1}), R is constant value of gas which is 8.134 J K^{-1} mol^{-1}, T_0 is Vogel temperature, which can be replaced by T_g of alkyl urocanates (K) [20], and T is the observed temperature (K). The slope of this equation can be calculated by using the linear curve fitting and it represents E_a.

Here, the proton conductivities of **SPEEK**, **SPEEK-C4U** and **SPEEK C6U** were plotted with the VTF equation (Figure 4.3). As described earlier, the decrease of proton conductivity of the neat **SPEEK** membrane at the high temperature (10^{-8} S cm^{-1} at 130 °C) was mainly due to the loss of water (Figure 4.3a).The proton conductivities of **SPEEK-C4U** and **SPEEK-C6U** are found to increase with an increase of temperature until 100 °C. For the temperature above 100 °C, the proton conductivities are maintained at a certain value even the temperature was as high as 170 °C (Figures 4.3b, and 4.3c). Other **SPEEK-CxU** exhibited the similar trends (Appendix G). It should be noted that all **SPEEK-CxU** show the conductivities retaining for 10^{-4} S cm^{-1} in a wide range of temperatures, i.e. 110 °C-170 °C. This reflects the role of alkyl urocanates. Judging from the thermal properties of alkyl urocanates (Scheme 4.1, and Figure 4.3), it is reasonable to refer the proton transfer at high temperature to their high thermal motion.

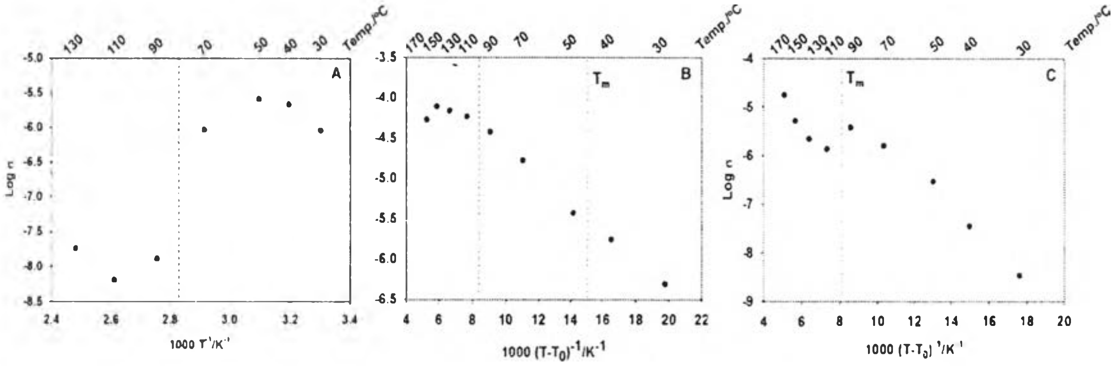


Figure 4.3 Proton conductivity of (a) SPEEK, (b) **SPEEK-C4U**, and (c) **SPEEK-C6U** by VTF equation.

It is important to note that water molecules also performed as proton transfer species in SPEEK membrane via hydrogen bond formation with sulfonic acid groups. In fact, the water molecules are in liquid state and their performances are referred to the high molecular motion. This makes our SPEEK (without fully dehydration) shows the proton conductivity at the range of 10^{-5} S cm^{-1} at 30 °C – 70 °C (Figure 4.3a).

For **SPEEK-CxU**, the alkyl urocanates could form an interaction with the sulfonic acid group and/or water molecules. As discussed in our previous work, as the temperature increases, the alkyl urocanates turn to the molten state in which the molecular thermal motion becomes dominant. At that time, the significant proton transfer to obtain the proton conductivity can be expected [20]. Here, it is clear that the proton conductivity is maintained in a long range of temperatures (40 °C – 170 °C) to be as high as 10^{-4} S cm^{-1}.

The activation energy (E_a) of all blends was calculated via the slope of the VTF equation. In general,-activation energy refers to how a proton can easily transfer in the system. Therefore, the low E_a means the high efficient proton transfer. Considering the **SPEEK-CxU**, E_a should be evaluated between 30 °C and 100 °C as the linear relationship was satisfied (Figures 4.3b, 4.3c and Appendix G). However, at above 100 °C, the E_a determination is not possible because of the constant proton conductivity (~10^{-4} S cm^{-1}). In other words, the VTF plot becomes a straight line without slope. Therefore, E_a at above 100 °C was neglected.

The activation energy of all blends were plotted (Figure 4.4) to clarify the effectiveness of proton transfer of **CxU** above their melting. **C4U** shows the lowest melting temperature (46 °C) and at that time the activation energy of **SPEEK-C4U** is as less as 1.5 KJ mol^{-1}. In contrast, **C6U** which shows the high melting temperature (106 °C) exhibits the highest activation energy for 2.7 KJ mol^{-1}. Regarding to all **CxU**, it is clear that the low melting temperature compounds (lower than 90 °C) induce more proton transfer resulting in low E_a. In addition, the activation energy values of **SPEEK-CxU** (averagely below 5 KJ mol^{-1}) are much lower than the activation energy of the **SPEEK** membrane (72 KJ mol^{-1}) [31]. The comparison of **SPEEK** and **SPEEK-CxU** led us understand how the alkyl urocanates can promote proton transfer more effectively than the water molecules in the SPEEK matrix at the high temperatures.

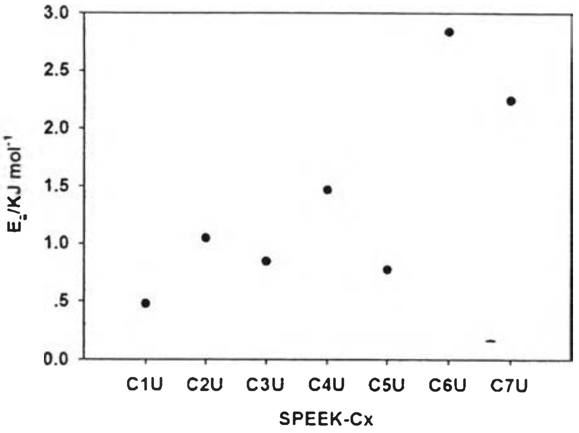


Figure 4.4 Activation energy of **SPEEK-CxU**.

4.4.4 Confirmation of Possible Proton Channels in **SPEEK-CxU** via Temperature Dependence FTIR

It is known that the proton transfer mechanism in the **SPEEK** membrane is satisfied with the function of the water cluster to transfer the proton via the hydrogen bond network of the hydranium ions [32]. In the cases of **SPEEK-CxU**, the proton transfer might come from the hydrogen bond networks such as the hydranium ions (H_3O^+--H_2O), the hydranium ion and the imidazole ring (H_3O^+--N), and among imidazole rings (NH--N). Therefore, the temperature dependence FTIR is useful to follow the hydrogen bond network, especially at 2500 cm^{-1} – 3500 cm^{-1} (inter-and intra-hydrogen bond networks of imidazole rings and sulfonic acid groups). However, it was difficult to follow hydrogen bond network of sulfonic acid group in this range due to an interference of the imidazole ring. Therefore, symmetric sulfonic acid peak (1228 cm^{-1}) was used to refer the hydrogen bond network. The characteristic peaks of the sulfonic acid group were observed around 1000cm^{-1}- 1400 cm^{-1} (Figure 4.5a). After the sample was heated, the peak at 1228 cm^{-1} shifts to a lower wavenumber at 1225 cm^{-1} which shows an isosbestic point at 1221 cm^{-1} (Figure 4.5b). It is important to note that other **SPEEK-CxU** displayed a similar pattern (Appendix H). This highlights that all **SPEEK-CxU** perform proton transfer from room temperature to moderate temperature (<100 °C) via hydrogen bond network based on the sulfonic acid group and molecular motion of **CxU** as soon as the **CxU** reached its melting temperature. When the temperature was continuously increased, the next stage of proton transfer via the molecular motion of urocanate becomes the main contribution.

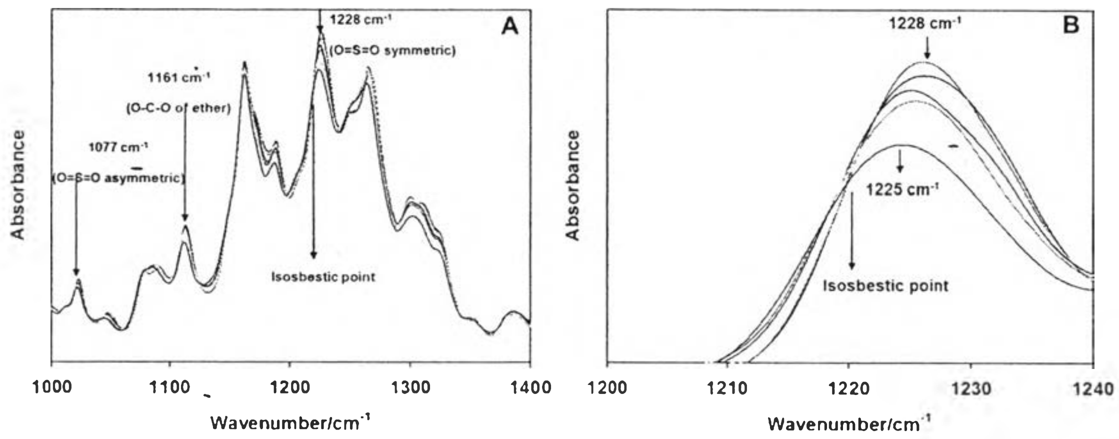


Figure 4.5 Temperature dependence FTIR spectra of **SPEEK-C4U;** (a) in range of wavenumber 1000 cm^{-1} – 1400 cm^{-1}, and (b) in range of wavenumber 1200 cm^{-1}.– 1240 cm^{-1}.

The curve fitting technique for temperature dependence FTIR was carried out to find hydrogen bond network formed with sulfonyl groups. It comes to the questions about proton channel required for protonated species to transfer the proton. As the main matrices contain sulfonyl groups, the observation of sulfonyl peak by FTIR at different temperatures enables us to evaluate the change of hydrogen bond networks. Mikhaylovaet. *al.* reported the evaluation of hydrogen bond networks between phenolic group and aromatic polyester by using full width half maximum (FWHM) of the hydrogen bond peak of interest [33]. Here, the peak at 1228 cm^{-1} referring to sulfonyl groups was applied. And the curve fitting using OPUS 5.5 program of this peak was carried out. At that time, the FWHM of sulfonyl groups could be identified. The changes of FWHM occur exactly at the melting temperature of each compound (**C4U**, and **C6U**) (Figure 4.6). In addition, the FWHM of other **CxU** were also showed the significant changes at their T_m (Appendix I). This implies that at low temperatures, water inside the membrane can transfer protons. However, at the high temperature, the alkyl urocanates in the molten state, instead of water molecules, provided a new proton channel (SO_3**H**--N or/and N**H**--N) for proton conductivity. It should be noted that at the high temperature, the interaction of sulfonic acid with water started to be weakened and at that time, another type of interaction, especially SO_3**H**--N or/and N**H**--N of imidazole rings in addition to the molecular thermal motion in the molten state of the alkyl urocanates is formed. This leads us to a concept of the synchronized effect of water and imidazole molecules.

In fact, this result is relevant to that of TGA which showed a degradation peak at relatively high temperature (at 233 °C for **C4U**, and at 235 °C for **C6U**). As this peak could not be observed in the case of SPEEK without **CxU**, it is reasonable to conclude that the peak is for thermal decomposition of imidazole and sulfonic acid groups (when the hydrogen bonds were destroyed).

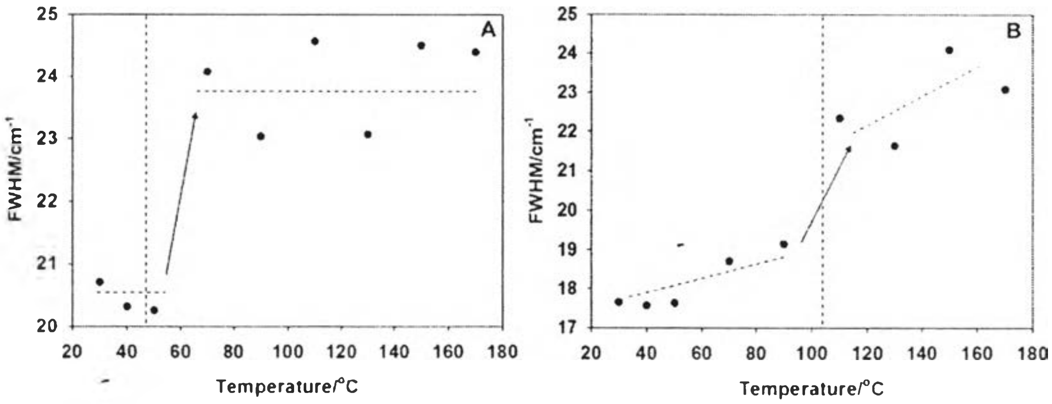


Figure 4.6 FWHM of sulfonic acid group as a function of temperatures of (a) **SPEEK-C4U**, and (b) **SPEEK-C6U**.

4.4.5 Clarification of Proton Transfer via Synchronized Effect of Water and Imidazole

It is the fact that the water molecules and imidazole rings are co-existed in the membrane and both of them function as proton transfer species.

The proton conductivity of **SPEEK** decreases with an increase in temperature (Figure 4.7a). The decrease is significant starting from 70 °C which reflects the water evaporation. When dehydration occurred, hydronium ion could not form resulting in a decrease in proton conductivity.

In the case of **SPEEK-C4U**, the result in the range of 30 °C – 90 °C is contrast to that of SPEEK. That is to say, the proton conductivity increases with an increase of the temperature even the water was evaporated. This implies the role of **C4U** in the membrane. In fact, when the temperature reached 46 °C (T_m of **C4U**), **C4U** started to be in its molten state. At that time, it is reasonable to mention that **C4U** formed urocanate clusters under thermal motion in the **SPEEK** matrices to compensate the proton conductivity during water dehydration.

It should be noted that even the temperature was above 100 °C, the proton conductivity of **SPEEK-C4U**, instead of decreasing, is still maintained at 10^{-4} S cm^{-1}. This implies the function of **C4U** as proton transfer species at its molten state. In fact, a careful observation on water dehydration of **SPEEK** and **SPEEK-C4U** suggests us that **C4U** also retarded the water evaporation. For example, **SPEEK** at 90 °C, shows the water content 0.5 wt% (Figures 7a) whereas **SPEEK-C4U** shows 2 wt% (Figure 4.7b). The retardation of water dehydration might come from the hydrogen bond between imidazole rings and water molecules. This can be further confirmed by the existence of inter- and intra-hydrogen bond network of imidazole ring even the temperature was above 100 °C (Appendix J).

At the high temperature range (110 °C – 170 °C), the proton conductivity of **SPEEK-C4U** shows much higher conductivity than the neat **SPEEK** membrane by 10^4 times (Figure 4.7b). This suggests the role of **C4U** leads us to a scheme that the imidazole forms cluster in molten state (when temperature was above its T_m (46 °C)) and moves along the **SPEEK** matrices similar to the water clusters.

The overall performance of **SPEEK-C4U** leads to the possible mechanism including synchronized effect of water and imidazole molecules to represent **SPEEK-CxU** as follows (Figures 4.7c and 4.7d). At below T_m of **CxU**, the proton transfer is based on the water molecules. In addition, **CxU** molecules forms the hydrogen bond with water to retard the dehydration and prolong the conductivity at the temperature above the boiling point of water. At the temperature above T_m of **CxU**, the molecule was in high thermal motion under the molten state and as a result, the conductivity is initiated by the resonance structure of **CxU** with a good balance of its thermal motion and hydrogen bond network. As all **CxU** show high T_d (above 200 °C), their molecular motions are maintained and consequently, the proton conductivity at the high temperature range is possible.

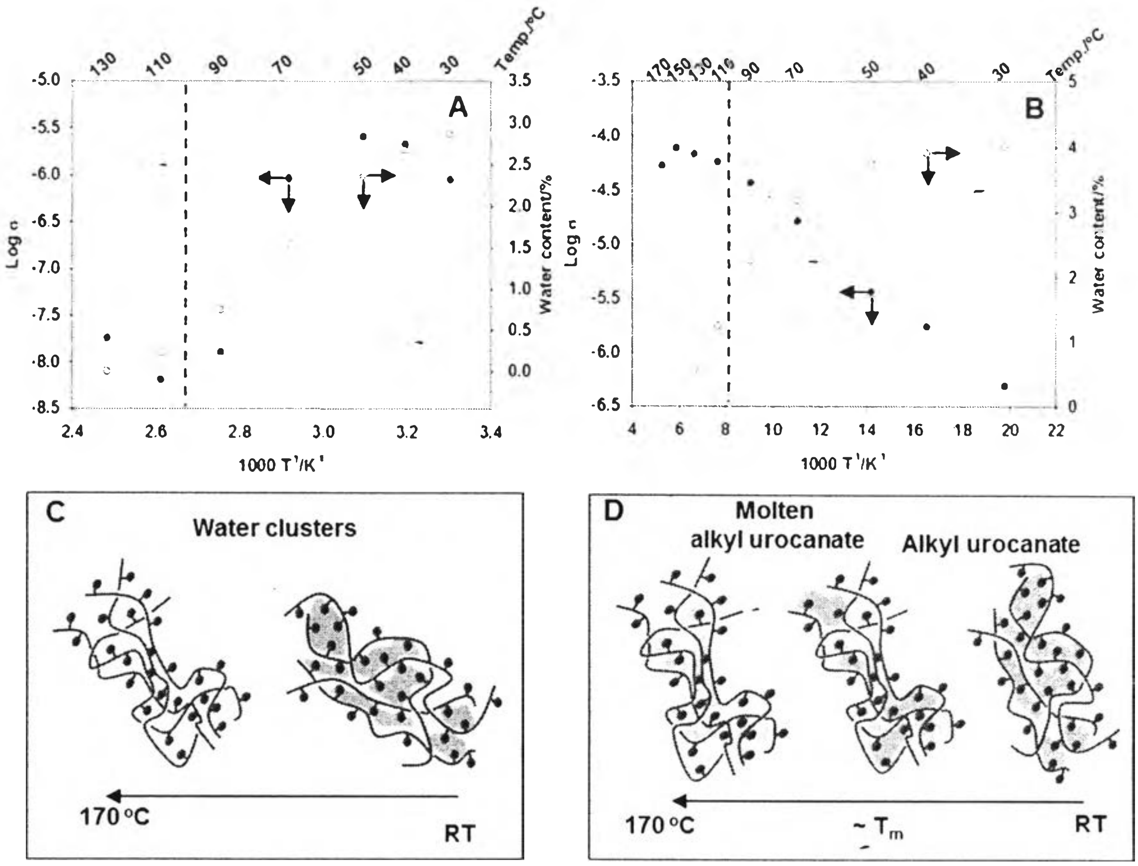


Figure 4.7 Proton conductivity of (a) SPEEK, (b) **SPEEK-C4U** as a function of temperatures based on VTF equation, and schematic proton transfer mechanism of (c) SPEEK, and (d) **SPEEK-CxU** with synchronized effect of water and imidazole molecules related to different temperatures.

It comes to the questions about water and imidazole clusters (of **C6U**) during an increase of temperature function as proton transfer species under synchronized manner. The **SPEEK-C6U** also exhibited a similar behavior as **SPEEK-C4U.** In fact, there was a shift of proton conductivity in the case of

SPEEK-C6U at temperatures near its melting point, i.e. **C6U** at 106 °C. It is important to note that the melting temperature of **C6U** is above the boiling point of water. That is to say, **C6U** started to function in a molten state after water clusters were almost destroyed which can be observed by a sudden drop of conductivity (Appendix K). When the temperature reached 106 °C, a recover of conductivity is observed. This shift of conductivity leads us to the concept of the synchronized proton transfer mechanisms of water clusters and imidazole clusters.

4.5 Conclusions

Alkyl urocanates were the promising molecules for proton transfer species based on not only for the hydrogen bond and proton resonance structures but also for the possibility to prepare with different the methylene chain lengths to vary the degradation and melting temperature. By adding alkyl urocanates for 2 wt% into **SPEEK** membrane, the **SPEEK-CxU** membrane obtained significantly enhanced the proton conductivity over a long range of the operating temperature. The hydrogen bond networks as clarified by the temperature dependence FTIR, as well as the activation energy as calculated by the VTF equation insisted that hydrogen bonded water molecules and alkyl urocanate molecules synchronized the role of proton transfer. Figure 4.8 summarizes the proton transfer steps and mechanism which can be explained as follows. In **SPEEK-CxU** membranes, the proton transfer species are water and imidazoles. At closed to the boiling temperature of water, the hydrogen bonded water clusters were significantly mobilized to promote the proton transfer before they evaporated completely. At the same time, when the temperature reached the melting point of alkyl urocanates, the alkyl urocanates form as clusters while their molten state provide the significant proton transfer along imidazole units. The fact that the melting points of alkyl urocanates are below boiling point of water whereas the degradation temperatures are far higher than the high operating temperature (usually 120 °C – 150 °C). The synchronized function between water and alkyl urocante occurs accordingly. Although most research works focus on the water clusters under hydrogen bond functioning as proton transfer species, the present work emphasizes the movement of water clusters in highly activated liquid form as another important characteristic. Here, imidazole clusters under molten state is somewhat similar to water clusters to transfer the proton since the molecules are highly active under the thermal motion.

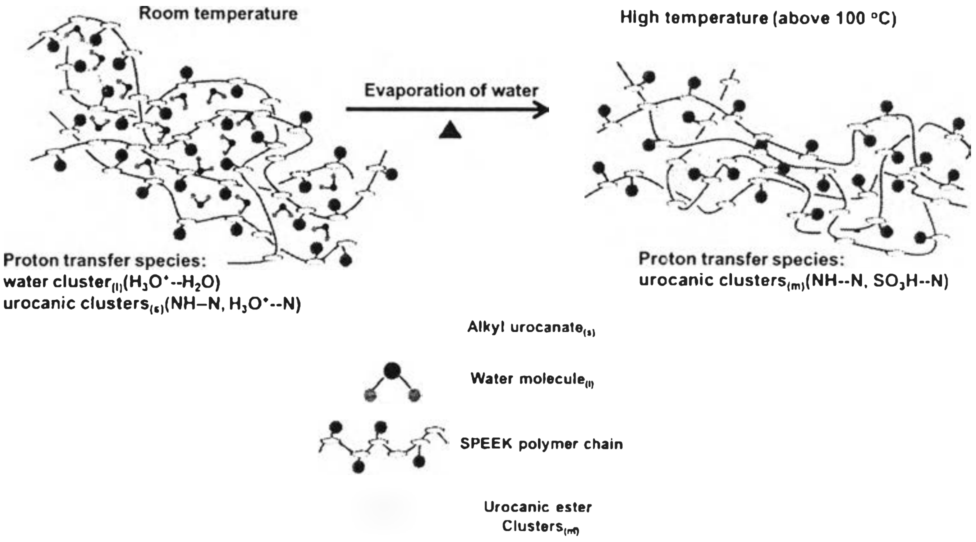


Figure 4.8 Schematic of **SPEEK-CxU** at different operating temperatures.

4.6 Acknowledgements

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