CHAPTER IV

RESULTS AND DISCUSSION

Hydrogen permeation through sandwich membranes made of two types of Derakane® resin, Derakane® 470-300 and Derakane® 8084, in non-reactive and reactive gas atmosphere was studied. Firstly, hydrogen permeability coefficients in non-reactive gas atmosphere of both types of membranes at 25, 50 and 80°C were determined. Chlorine permeability coefficients were measured in pure chlorine atmosphere to study the ability of membranes with a thin active layer to withstand chlorine. The determination of both permeability coefficients was described in chapter 3. The selectivity of the two types of sandwich membranes for hydrogen was calculated. Then, the type of membrane that possessed higher selectivity for hydrogen at 80°C was studied for hydrogen permeation in reactive gas atmosphere. The experiments were done using 1%, and 5% H_2 in Cl_2 gas mixture.

4.1 Hydrogen Permeability Coefficient in Hydrogen-Argon Atmosphere

Experiments to determine hydrogen permeability coefficients were done on Derakane® 470-300 at 25 and 80°C and Derakane®8084 sandwich membranes in 5% hydrogen/95% argon atmosphere at 25, 50, and 80°C. The average permeability coefficients of the membranes at each temperature are shown in Tables 4.1 and 4.2.

Table 4.1 Hydrogen permeability coefficient of Derakane® 470-300 sandwich membranes at 25, and 80°C.

Temperature (°C)	Average active layer thickness* (mm)	Hydrogen permeability coefficient (cm^3(STP) cm / cm^2 min atm)
25	0.07	1.35E-6
80	0.06	9.12E-6

* The average active layer thickness is the average thickness of all membranes tested at the indicated temperature.

Table 4.2 Hydrogen permeability coefficient of Derakane® 8084 sandwich membranes at 25, 50 and 80°C.

Temperature (°C)	Average active layer thickness* (mm)	Hydrogen permeability coefficient (cm^3(STP) cm / cm^2 min atm)
25	0.02	1.52E-6
50	0.07	6.55E-6
80	0.04	3.74E-5

* The average active layer thickness is the average thickness of all membranes tested at the indicated temperature.

As can be seen from the two tables, the permeability coefficients of both types of Derakane® sandwich membrane increase with increasing temperature. The thickness of the membranes developed does not exceed 0.10 mm which is the range of interest in this study. When comparing the permeability coefficients of the two types of Derakane® sandwich membranes, sandwich membranes made of Derakane® 8084 show higher hydrogen permeability in the range of temperature studied.

4.2 Chlorine Permeability Coefficient in Pure Chlorine Atmosphere

Chlorine permeability coefficients of two types of Derakane® sandwich membrane were determined using pure chlorine by the following method using a detector tube in conjunction with the standard method ASTM F739-91 described in chapter 3. Three samples of each type of Derakane® sandwich membrane were tested at each temperature and the results are shown in Table 4.3 for Derakane® 470-300 and Table 4.4 for Derakane® 8084. The thickness of the membrane in the table is the average thickness of the three sample membranes.

The permeation rate of chlorine seemed to increase with time so, to confirm that, an experiment using two detector tubes connected in series was conducted. The plot of chlorine permeation versus time is shown Figure 4.1. The slope of the plot represents the permeation flux of chlorine. From the graph, the slope obtained from data set of tube #2 is higher than that of tube #1.

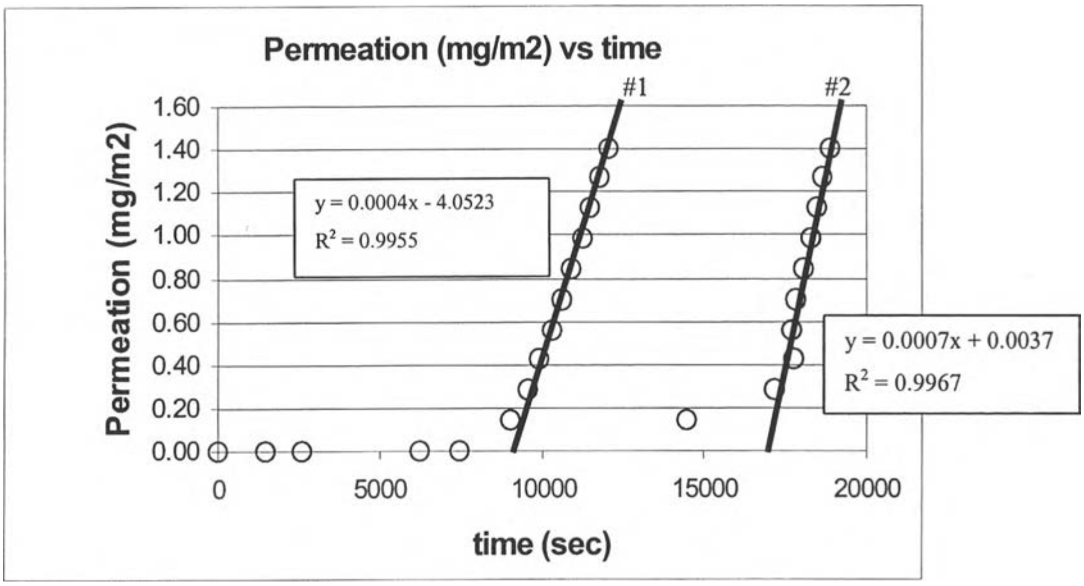

Figure 4.1 The permeation of chlorine versus time in the experiment using two tubes connected in series.

The increase of the slope of the graph indicates that the permeation flux of chlorine through the membrane increases with time. The reason might be either that the steady state of chlorine permeation had not been reached when chlorine first broke through the membrane or chlorine degrades the membrane gradually so the properties of the membrane change with time. Hence, it is important to note that the permeability coefficients shown in the tables are the permeability coefficients when chlorine was first detected.

Table 4.3 Chlorine permeability coefficient of Derakane® 470-300 sandwich membranes at 25, 50 and 80°C.

Temperature (°C)	Average active layer thickness (mm)	Chlorine permeability coefficient (cm^3(STP) cm / cm^2 min atm)
25	0.04	3.03E-9
50	0.03	8.97E-9
80	0.03	2.12E-8

Table 4.4 Chlorine permeability coefficient of Derakane® 8084 sandwich membranes at 25, 50 and 80°C.

Temperature (°C)	Average active layer thickness (mm)	Chlorine permeability coefficient (cm^3(STP) cm / cm^2 min atm)
25	0.02	1.32E-9
50	0.05	7.41E-9
80	0.03	4.95E-8

Chlorine can permeate through both types of Derakane® sandwich membranes and the permeation rate increases with increasing temperature.

4.3 Selectivity of The Sandwich Membranes

The selectivity for hydrogen of each membrane was calculated using the permeability ratio of hydrogen (in section 4.1) and chlorine (in section 4.2).

Table 4.5 Hydrogen selectivity of the membranes.

Temperature (°C)	Material	
	Derakane® 470-300	Derakane® 8084
25	446	1148
50	-	884
80	430	755

According to Table 4.5, the selectivity for hydrogen of both types of Derakane® sandwich membranes decreases with increasing temperature. However, Derakane® 8084 membranes show higher selectivity than Derakane® 370-400 membranes. Also, we can see that temperature affects the selectivity of Derakane® 8084 membranes more than Derakane® 470-300 membrane. To study the effect of temperature on the selectivity of the membranes, an Arrhenius plot of the permeability data was accomplished as illustrated in Figure 4.2.

From the Arrhenius law (Eq 33), the permeability coefficient (P) is related to the temperature (T) as follows:

$$P = P_0 \exp(-\Delta E_P/RT) \qquad (33)$$

where P_0 is the pre-exponential constant

ΔE_P is the activation energy of permeation

R is the gas constant

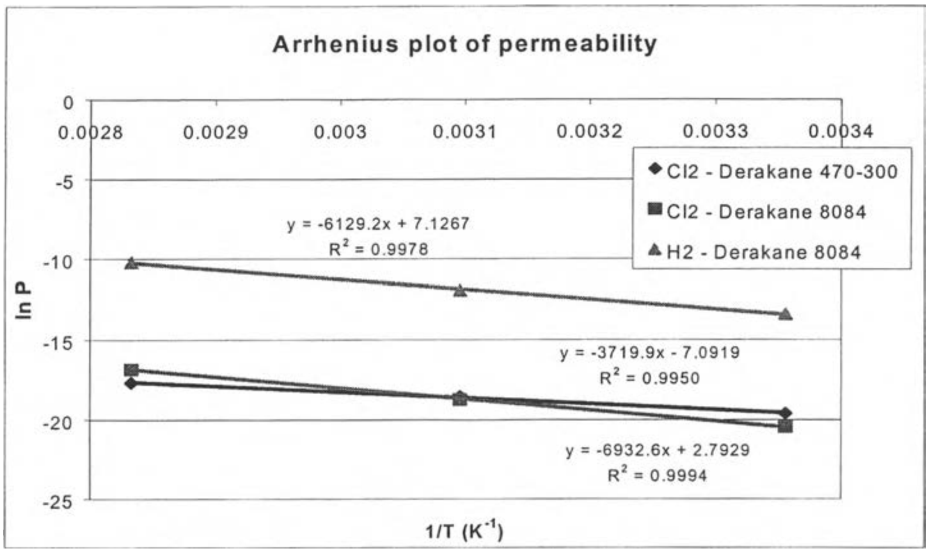

Figure 4.2 Arrhenius plots of the permeability data of Derakane® 470-300 and Derakane® 8084 membranes.

By plotting the natural logarithm of permeability versus reciprocal temperature, the activation energy of permeation can be calculated using the slope of the graph. Table 4.6 shows the activation energy in the two types of membrane studied. Good correlation of the parameters indicates the consistency of the properties of the membranes tested.

The activation energy of permeation of both types of Derakane® shows that the permeation of both hydrogen and chlorine is an endothermic reaction, which means that the permeation would increase with increasing temperature. The magnitudes of ΔE_P indicate how much the transport of the gas depends on the operating temperature. ΔE_P of Derakane® 8084 for chlorine is higher than that of Derakane® 470-300. In addition, Derakane® 8084 transports hydrogen better at each temperature studied (section 4.1). From the study of the activation energy of permeation, the selectivity of Derakane® 8084 is more temperature dependent.

Table 4.6 Activation energy of permeation.

Gas	ΔE_P (kJ/mole)	
	Derakane® 470-300	Derakane® 8084
Hydrogen	-	5.10E+4
Chlorine	3.09E+4	5.76E+4

4.4 Hydrogen and Chlorine Permeability Coefficients in H_2/Cl_2 Mixed Gas System

Since Derakane® 8084 possesses higher selectivity for hydrogen than Derakane® 470-300, it was chosen to be tested in the mixed gas system. The experiments of 1% and 5% hydrogen in chlorine mixed gas at 80°C, which is the temperature in the electrolytic cell of the Chlor-Alkali plant were carried out. Two membranes were tested in each system. The results of the experiments at 5% hydrogen in chlorine and argon were compared to determine the effect of the presence of chlorine on the transport of hydrogen. The average values of the permeability coefficients obtained were shown in Table 4.7.

Table 4.7 Hydrogen and chlorine permeability coefficients of Derakane® 8084 sandwich membranes in mixed gas systems at 80°C.

Gas Mixture	Permeability coefficients (cm^3(STP) cm / cm^2 min atm)	
	H_2	Cl_2
1% H_2 and 99% Cl_2	9.90E-6	1.95E-8
5% H_2 and 95% Cl_2	3.67E-6	6.86E-8
5% H_2 and 95% Ar	3.74E-5	-

As can be seen from the table, the presence of chlorine affects the transport of hydrogen to permeate through the membrane when comparing the results obtained from the experiments at 5% hydrogen in reactive (chlorine) and non-reactive (argon) gas. The hydrogen permeability coefficient in reactive gas mixture is lower for about an order of magnitude. The different contents of hydrogen in the gas mixture give interesting results on the permeability coefficients of both hydrogen and chlorine. The permeability coefficient of hydrogen in the mixed gas containing 1% of hydrogen is higher than that of the gas containing 5% of hydrogen. When comparing chlorine permeability coefficients of different contents of hydrogen in the gas mixture, the higher permeability coefficient was found at higher content of hydrogen. It is probably due to the reaction to produce hydrogen chloride (Eq. 34) to occur at 80°C.

$$H_2 + Cl_2 \rightarrow 2HCl \tag{34}$$

It is believed that hydrogen chloride might affect the transport of hydrogen and chlorine in mixed gas system by altering the properties of the membrane to transport both gases. So it is interesting to study further about the permeability coefficients of hydrogen and chlorine in the mixed gas to determine the effect of the content of hydrogen in the gas mixture on the permeation of the two gases.

4.5 Measurements of Hydrogen Concentration in Non-Reactive and Reactive Gas

The sandwich membrane developed has been attached with the amperometric sensor proposed for measuring hydrogen concentration in the presence of moist chlorine. The measurement of hydrogen concentration in non-reactive and reactive gas was done by another research group at CNER. Figures 4.3 and 4.4 report the responses of the sensor on a change in hydrogen concentration in argon atmosphere and chlorine atmosphere, respectively.

The sensor showed smooth and quick responses in non-reactive gas atmosphere. In reactive gas atmosphere, the sensor responded slowly and there was a lot of noise present in the response signal of the sensor. Also, the response current of the sensor testing is lower in reactive gas mixture than in the non-reactive gas mixture. As the current was described by Eq.(35), this agreed well with the result in the previous section observed for which there was lower permeability coefficient of hydrogen in reactive gas than in the non-reactive gas.

$$I = \frac{zFAP_{H_2}}{l} p_{H_2} \tag{35}$$

The heights of the response in each system are not proportional to the partial pressure of hydrogen. This supports the results obtained from the previous section that the permeability coefficients of different contents of hydrogen in the gas mixture are different.

In addition, the difference in peak heights of the response signal with the change of hydrogen concentration in chlorine gas is smaller than that of the response signal of the sensor in argon atmosphere. It means that the sensitivity of the sensor in reactive gas mixture is lower.

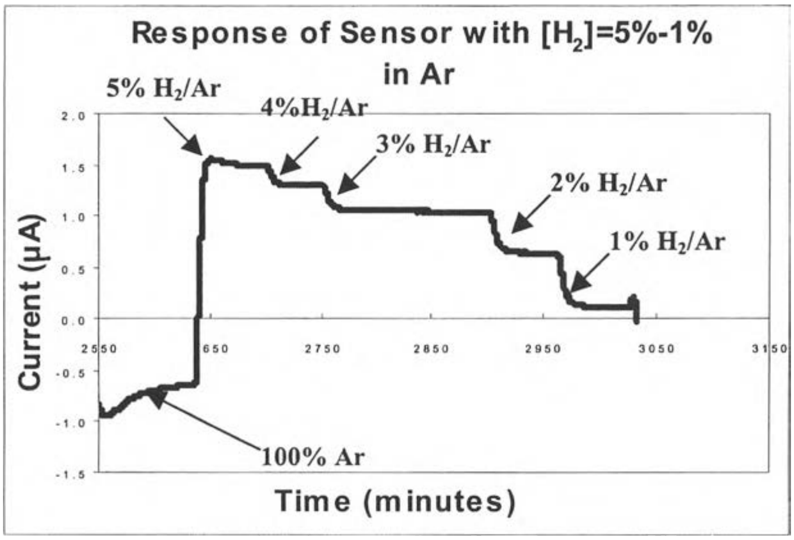

Figure 4.3 The response of amperometric sensor attached with Derakane® sandwich membrane in non-reactive gas atmosphere.

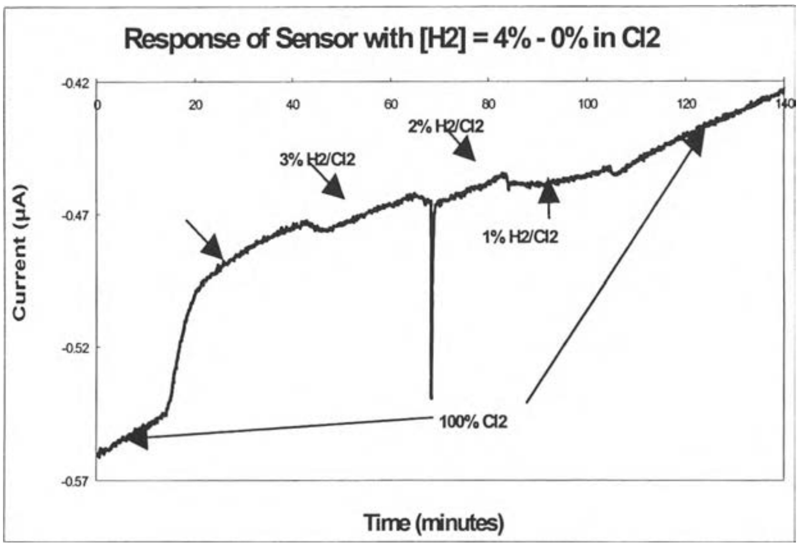

Figure 4.4 The response of amperometric sensor attached with Derakane® sandwich membrane in reactive gas atmosphere.