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Effect of Feed Temperature and Solution Concentration on Pervaporation for separation of Azeotropic Mixtures

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Abstract

In present work reports the Pervaporative separation of azeotropic mixtures using PVA and PVA-PES membrane. The membranes were tested for separation of ethanol/water and Acetonitrile/water system. Flux of membrane has been studied and analyzed as a function of feed composition and temperature where as permeate pressure kept constant for all the experiments as 740 mmHg. In present study comparative experimental results has been presented over a wide range of temperature of 45-75 ^{0}C and water concentration varies from 6.25- 14.34 wt%. The experimental results of ethanol/water and Acetonitrile /water system were compared with model data. It was observed that PVA-PES membrane has higher flux and lower separation factor than PVA membrane. A good agreement is shown in between model data and experimental data.

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Keywords: Pervaporation; PVA; PVA-PES ; Flux; selectivity;

1. Introduction

Pervaporation process is an effective membrane separation process in chemical industries in which parameters are isolated from the liquid mixture. Separation of azeotropic mixtures, organic mixtures and aqueous mixtures is very well known examples of Pervaporation separation process [1-2]. The Pervaporation membrane process, in which a liquid feed contacts one side of a membrane and a vacuum, is drawn on the other side of the membrane to produce a permeate vapor [3]. Pervaporation is an effective, emerging, separation technique for

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separation of azeotropic mixture. In this process, the membrane permeates one component preferentially to the other in the feed.[4-6] Many researchers have reported Pervaporation process principle and experimental results with different polymeric materials. In their study separation of a variety of binary mixtures such as azeotropic mixtures, organic mixtures and aqueous mixtures etc. have been investigated [7].

The objective of this work is to study how the operating parameters are affecting the performance of Pervaporation process for separation of ethanol/water and Acetonitrile/water system. This work reports experimental results on the Pervaporative flux of membrane using a PVA and PES-PVA composite membrane, the behavior of the membrane to changes in feed conditions namely feed composition and temperature. It is also analyzed and compared with both membranes.

2. Experimental

2.1. Material

Poly vinyl alcohol (PVA) and PVA-PES composite membrane was used in membrane test cell for comparative study of Pervaporation system obtained from Shivom membrane Pvt.ltd Ichalkaranji, Sangali. All the experiments were conducted at different temperature range varies from 45 ^{0}C to 75 ^{0}C and concentration of water in feed varies from 6.25 wt% to 14.34wt%. The membrane effective area is 0.026 m^2 and thickness of membrane is about 30 μm for PVA and 3 μm for PVA-PES membrane.

2.2. Pervaporation experiments

The experiments were carried out using PVA and PVA-PES membrane for separation of azeotropic mixture such as ethanol/water and Acetonitrile/water. A schematic representation of Pervaporation apparatus is as shown in fig. 1. PVA dense membrane and PVA-PES composite membrane was used in PV cell to measure the performance of Pervaporation system. In the Pervaporation experiments, the heated feed mixture was continuously circulated over the membrane using circulating feed pump from the feed tank.

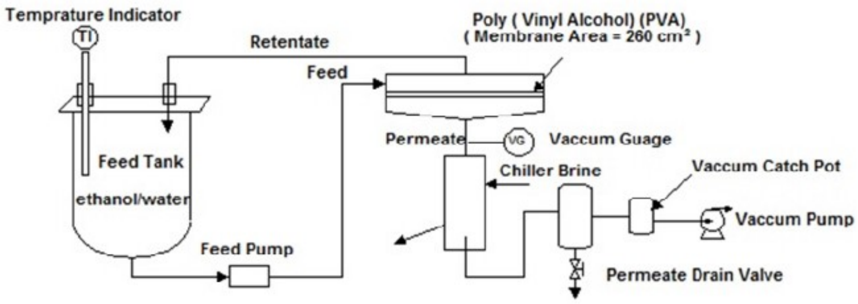


Fig.1. Schematic diagram of the Pervaporation set up

The temperature was kept constant throughout the experiment. In the membrane cell the membrane effective membrane area was 260 cm2. A Vacuum was applied on permeate side is 740 mmHg by using vacuum pump. The permeate vapours are condensed using heat exchanger and collected at drain valve. Permeate sample was collected and analyzed by Karl Fischer Titration. The PVA and PVA-PES membrane performance was evaluated by performance parameters such as flux of membrane, separation factor, Permeate separation index (PSI) and enrichment factor. The total flux was determined from the amount of permeate sample collected for a given time of period. The individual flux of each component was obtained from total flux and the concentration of components in the permeate.

The membrane performance was evaluated by flux and separation factor of membrane which were calculated by following equations;

$$J = \frac{M}{A \times t} \qquad (1)$$

Where, J is flux of membrane , M represent mass of the permeate (kg), A is the effective membrane area (m^2) and t is time (hr)

$$\alpha = \frac{\left(y1/y2 \right)_P}{\left(x1/x1 \right)_F} \qquad (2)$$

Where y1,y2, x1 and x2 represent the weight fraction of component 1 and 2 in permeate and feed respectively.

3. Results and Discussion

3.1. Swelling of PVA and PVA-PES membrane in ethanol/water mixture

In this section results of the swelling measurements in ethanol/water and Acetonitrile/water azeotropic mixture are presented in fig. 2. Degree of swelling of PVA and PVA-PES membrane was measured as a function of water concentration. The swelling of the membrane measured on digital weighing microbalance. The membranes were dipped in different concentration samples up to 72 hours. The increment of weight in membrane is considered as sorption of water and ethanol by the membrane. According to solubility parameter theory the component which has a solubility parameter (water) closer to that of membrane rather than other component. Result shows that the amount of absorption increases with increasing water concentration in feed. As a result more water permeates through the membrane when treating ethanol/water and Acetonitrile/water mixtures as water concentration increases.

The degree of swelling is calculated by relation given in equation 3

$$DOS = \frac{W_S - W_D}{W_D} \qquad (3)$$

Where W_S and W_D denotes the weight of swollen membrane and weight of dry membrane

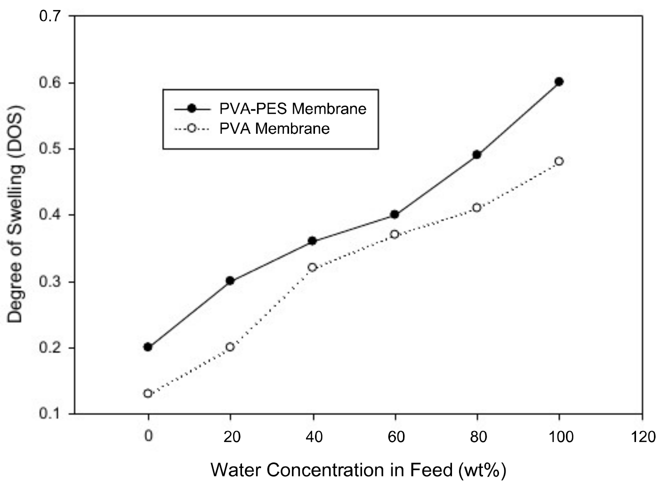


Fig 2. Degree of swelling of PVA and PVA-PES membrane in ethanol/water mixture

3.2 Comparison between the membrane flux and selectivity of PVA dense membrane and PVA-PES membrane

For comparative study of Pervaporation system PVA dense membrane and PVA-PES membrane were used for separation of ethanol/water and Acetonitrile/water azeotropic mixture. As seen in Fig. 3 (a)(b)& (c) (d) it shows that the effect of temperature on flux of PVA dense membrane and PVA-PES membrane for separation of ethanol/water and Acetonitrile/water azeotropic mixture. It is observed that in figures 3 PVA-PES membrane has higher flux than PVA membrane with the concentration of water in feed increases in both the system. Temperature enhancement increases side chain mobility in the PVA and PVA-PES membrane and this can results in enlarge ment of free volume inside the both the membranes. Therefore, permeation rate of the constitutes increases. This cause more water molecule pass through the membrane and thus ethanol selectivity decreases.

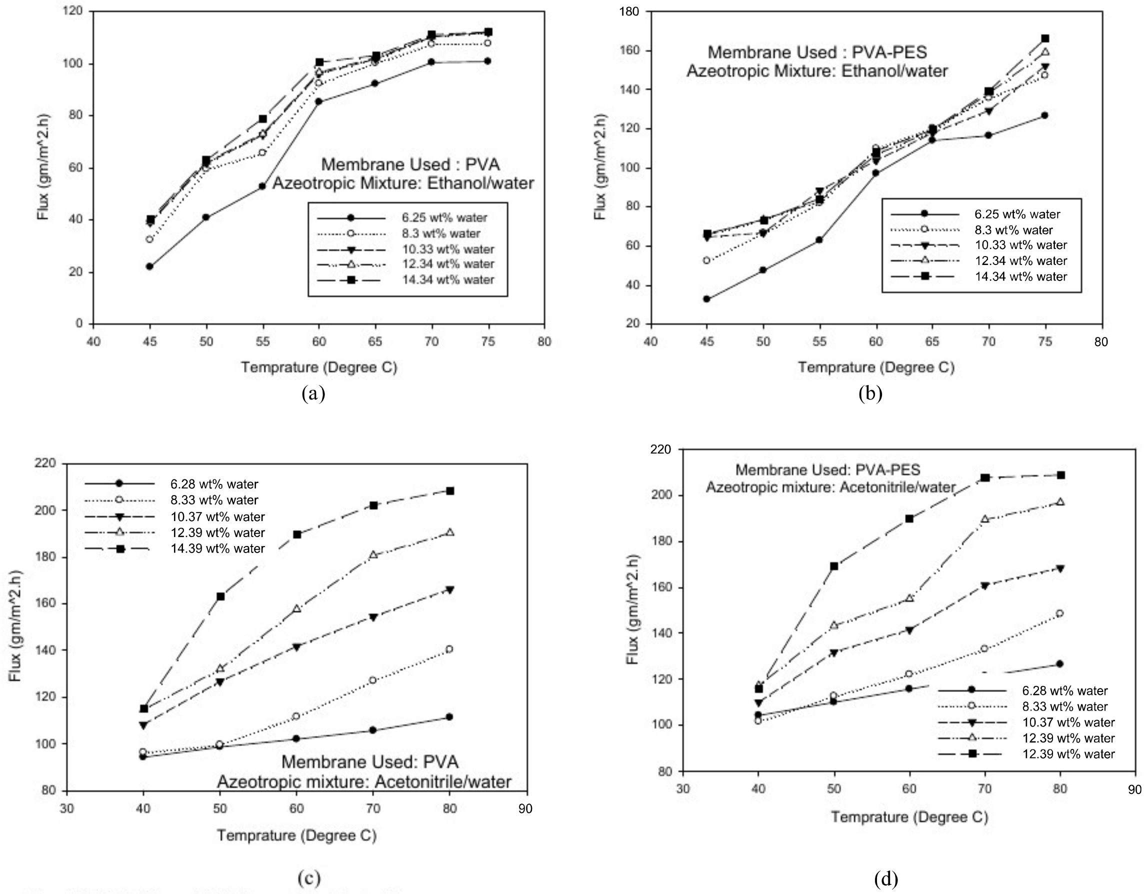
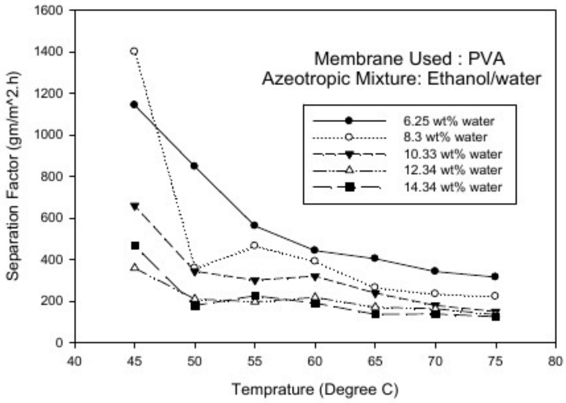


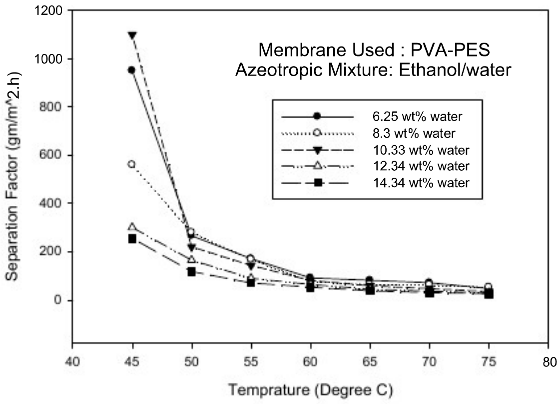
Fig. 3 (a) (b) (c) and (d) shows the effect of temperature on flux of PVA dense membrane and PVA-PES membrane for separation of ethanol/water and Acetonitrile/water azeotropic system.

The driving force, which is on the basis of concentration difference, is created by partial vapor pressure difference of permeating components in the feed and permeate sides. With increase in temperature of feed, the vapor pressure of feed side increases but permeate side vapor pressure does not change significantly. This cause the driving force of mass transfer increases.

Fig 4 (a) (b) (c) and (d) shows the effect of temperature on flux of PVA dense membrane and PVA-PES membrane for separation factor of ethanol/water and Acetonitrile/water azeotropic system. Fig 4(a) and (b) is for ethanol-water system while (c) and (d) is for Acetonitrile-water system. In figure 4 variation of separation factor with water concentration in feed can be observed. It's seen that, separation factor decreases with increase in water concentration in feed. As seen in figure the PVA-PES membrane has lower separation factor obtained than PVA membrane for both the systems. The results of both the systems were similar trend observed. The effect of temperature and feed concentration on the membrane performance were found to be similar. Increasing temperature and feed concentration increase both the membrane flux while selectivity decreases.



(a)



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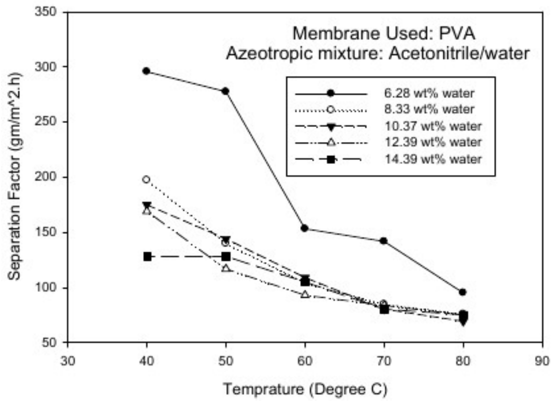
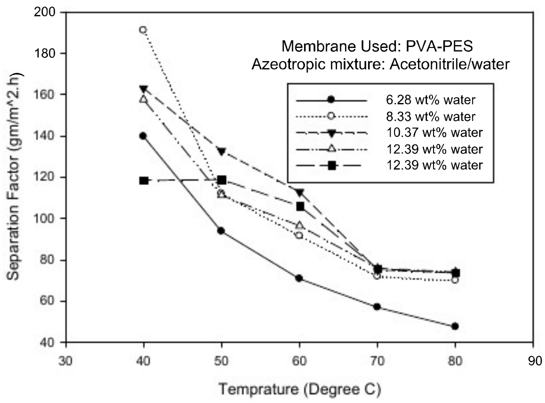


(c)



(d)

Fig.4 (a) (b) (c) and (d) shows the effect of temperature on flux of PVA dense membrane and PVA-PES membrane for separation factor of ethanol/water and Acetonitrile/water azeotropic system.

3.3 Comparison of experimental and model values of total flux and selectivity

The comparison of experimental data and model data of total flux and selectivity is shown in table 1 and 2. The data in table 1 and 2 indicate that flux and selectivity of PVA and PVA-PES membrane along with the model for ethanol-water system and Acetonitrile-water system respectively. It shows that the experimental data is good agreement with model data. The PVA-PES membrane was found to high performance for dehydration of ethanol containing smaller amount of water. The model data is obtained by single and multiple regression analysis technique using Polymath 6.0 software. This predicted data is verified by Numerical technique such as least square method. The azeotropic composition of ethanol-water and acetonitrile-water was easily broken by Pervaporation system. For ethanol/water system has obtained higher flux value 112.11 gm/m^2.h for PVA membrane and 165.97 gm/m^2.h for PVA-PES membrane at 14.34 wt% water content in feed, while as For Acetonitrile/water system has obtained higher flux value 207.42 gm/m^2.h for PVA membrane and 208.57 gm/m^2.h for PVA-PES membrane at 14.39 wt%

Table 1 Experimental and model values of total flux and selectivity for Ethanol-water system

Temp. (℃)	Water Content of Feed (wt%)	PVA Membrane				PVA-PES Membrane			
		Experimental Data		Model Data		Experimental Data		Model Data	
		Total Flux (gm/m^2 h)	α_{Sep}	Total Flux (gm/m^2 h)	α_{Sep}	Total Flux (gm/m^2 h)	α_{Sep}	Total Flux (gm/m^2 h)	α_{Sep}
75		100.71	316.67	100.54	316.67	126.50	47.50	125.75	53.29
70		100.35	343.37	100.50	343.37	116.38	71.25	119.14	50.09
65		92.13	405.14	94.02	405.14	113.86	81.43	111.34	100.33
60	6.25	85.15	443.91	79.62	443.91	96.99	91.48	94.52	111.63
55		52.65	562.96	59.05	562.96	62.75	171.00	68.98	121.88
50		40.77	848.21	37.31	848.21	47.40	266.00	43.15	299.25
45		21.89	1143.39	22.62	1143.39	32.56	950.00	33.56	942.19
75		107.62	224.00	107.19	242.75	147.08	53.20	147.15	54.57
70		107.37	235.79	108.62	163.40	135.62	63.00	134.96	58.55
65		100.15	265.82	100.37	346.60	120.27	64.00	122.52	65.67
60	8.3	92.27	392.00	87.51	417.90	109.81	77.78	105.99	88.16
55		65.62	466.67	72.54	347.04	81.98	168.00	85.46	150.76
50		59.46	360.00	55.35	447.93	66.63	280.00	64.99	290.68
45		32.30	1400.00	33.21	1378.66	52.29	560.00	52.60	557.59
75		111.84	151.25	111.75	153.85	152.14	34.83	152.27	43.25
70		110.19	180.40	110.12	168.66	129.21	46.75	128.83	15.14
65		101.62	240.43	103.26	260.13	117.74	58.67	117.73	90.44
60	10.33	96.12	321.20	91.99	307.80	103.71	80.30	105.00	100.94
55		72.54	302.50	77.10	302.91	88.39	143.00	86.47	80.27
50		61.77	344.67	59.36	348.36	66.63	220.00	67.78	263.99
45		38.97	660.00	39.47	658.74	64.61	1100.0	64.35	1089.52
75		111.97	135.82	111.87	138.45	159.06	29.51	159.06	29.41
70		110.32	165.00	110.33	153.18	138.14	36.00	137.79	36.09
65		102.12	172.13	103.65	191.70	118.75	45.00	120.44	46.01
60	12.34	96.62	219.00	92.52	206.20	106.78	64.29	103.43	61.32
55		73.04	198.00	77.66	197.63	82.99	90.00	86.33	93.45
50		62.28	211.50	59.81	215.64	73.55	165.00	71.88	163.13
45		39.22	360.00	39.73	358.65	65.62	300.00	65.95	300.39
75		112.11	126.44	112.29	133.63	165.97	25.65	166.00	26.14
70		110.96	139.65	109.85	111.55	139.29	29.79	138.83	27.79
65		103.02	137.18	105.79	169.81	119.39	38.09	121.28	40.77
60	14.34	100.47	191.81	96.77	198.47	108.56	52.31	105.05	51.80
55		78.95	227.14	81.73	184.52	84.14	70.47	87.51	68.55
50		62.92	179.82	61.81	211.92	73.41	117.90	71.76	119.59
45		40.25	469.43	40.44	461.57	66.26	254.90	66.58	254.46

water content in feed. Here in both the membranes the flux of membrane is very closer at high concentration of water content in feed i.e. 14.39 wt%. The experimental data is fitted with the fifth degree polynomial relationship given in equation 4 and 5 respectively. As shown in equation flux and selectivity are dependent variables while as temperature is independent variable.

Table 2 Experimental and model values of total flux and selectivity for Acetonitrile-water system

Temp. (°C)	Water Content of Feed (wt%)	PVA Membrane				PVA-PES Membrane			
		Experimental Data		Model Data		Experimental Data		Model Data	
		Total Flux (gm/m^2 h)	α_{Sep}	Total Flux (gm/m^2 h)	α_{Sep}	Total Flux (gm/m^2 h)	α_{Sep}	Total Flux (gm/m^2 h)	α_{Sep}
80	6.28	111.27	95.00	111.26	100.24	126.38	47.50	126.39	47.37
70		105.59	141.55	105.64	120.59	121.35	57.00	121.31	57.51
60		102.02	153.06	101.95	184.51	115.67	70.78	115.73	70.02
50		98.63	277.40	98.68	256.44	109.99	93.73	109.95	94.24
40		94.28	295.56	94.27	300.80	104.31	139.65	104.32	139.52
80	8.33	139.43	76.00	140.32	75.84	148.36	70.00	148.36	68.94
70		130.50	84.00	126.95	84.64	133.02	72.00	133.01	76.24
60		106.23	105.00	111.55	104.05	122.07	91.54	122.08	85.18
50		103.07	139.07	99.52	139.71	112.64	112.00	112.63	116.24
40		95.42	197.40	96.31	197.24	101.70	190.91	101.70	189.85
80	10.37	165.57	70.28	166.23	69.12	168.28	73.86	168.90	72.68
70		157.15	75.63	154.51	80.27	160.86	75.00	158.39	79.72
60		137.78	115.79	141.74	108.83	141.49	112.75	145.20	105.67
50		129.35	139.33	126.71	143.97	131.78	132.69	129.31	137.41
40		107.60	176.00	108.26	174.84	110.03	163.00	110.65	161.82
80	12.39	189.20	75.94	190.28	74.91	196.62	74.12	197.86	73.24
70		184.99	79.50	180.66	83.61	189.20	75.94	184.24	79.47
60		151.10	99.00	157.59	92.83	154.81	96.43	162.25	91.14
50		136.27	112.50	131.94	116.61	143.18	111.18	138.22	114.71
40		113.51	170.00	114.59	168.97	117.22	157.50	118.46	156.62
80	14.39	207.42	75.71	208.59	75.25	208.57	73.52	209.20	72.81
70		206.92	78.33	202.26	80.15	207.42	75.71	204.92	78.56
60		182.65	107.59	189.64	104.86	189.56	106.00	193.31	101.72
50		167.81	126.19	163.15	128.01	168.96	118.78	166.46	121.63
40		114.01	128.71	115.18	128.25	115.80	118.39	116.43	117.68

In table 3 its shows that estimated coefficients from the regression models of flux and selectivity for ethanol-water, Acetonitrile-water. The R^2 values varies from 0.9883327 to 0.9999804 for flux model equation and for Selectivity model varies from 0.9389314 to 0.9999959. For all these two models R^2 value close to one hence the developed model equations are correct. The large value of variance indicates that the data are noisy. In table 3 the variance value is large for selectivity model i.e. 937.7508 and 1922.87 it indicates that for respective model the data are noisy but for all the models Rmsd values are smaller. From those results we can say that the predicted model equations are correct. The developed model equations are as follows

$$Flux= a_0 + a_1T + a_2 T^2 + a_3T^3 + a_4T^4 + a_5T^5 \quad (4)$$

$$Selectivity= a_0 + a_1T + a_2 T^2 + a_3T^3 + a_4T^4 + a_5T^5 \quad (5)$$

The experimental data is also regretted using multiple linear Regressions including a free parameter in polymath 6.0 software. Here in multiple linear Regressions we got correlation coefficient 0.9090736 and 0.9590219 for ethanol -water system and 0.8926773 and 0.8845644 for Acetonitrile system. In multiple regression analysis smaller values of Rmsd obtained. Figure 5 (a) (b) & (c) (d) shows the multiple linear regression analysis. The experimental flux and calculated flux is compared.

Table 3 Estimated coefficients from the regression models of flux and selectivity

System	Membrane used		Model equation coefficients		R^2	Varience	Rmsd
			Flux	Selectivity			
Ethanol-water	PVA	a_0=	-32990	-2798000	0.9883327	70.60539	1.200386
		a_1=	2900.035	234500			
		a_2=	-101.1527	-7790.618			
		a_3=	1.748124	128.2855			
		a_4=	-0.014944	-1.047771	0.9999959	2.302062	0.2167507
		a_5=	0.00005053	0.0033971			
	PVA-PES	a_0=	-62770	686500	0.998306	14.13164	0.5370296
		a_1=	5545.692	-55930			
		a_2=	-194.1873	1817.584			
		a_3=	3.367093	-29.42444			
		a_4=	-0.028887	0.2372253	0.998493	937.7508	4.374674
		a_5=	0.00009809	-0.0007618			
Acetonitrile-water	PVA	a_0=	34.65014	-508.765	0.9999473	0.0089157	0.0188846
		a_1=	2.841988	51.83638			
		a_2=	-0.04402	-1.02706	0.9389314	1922.87	8.770109
		a_3=	0.000256	0.005928			
	PVA-PES	a_0=	89.67786	718.1641	0.9999804	0.0060357	0.015538
		a_1=	0.099845	-25.5312			
		a_2=	0.008821	0.338929	0.9997901	1.134116	0.2129897
		a_3=	-0.00005	-0.00156			

Multiple Linear Regression polymath report shows that R^2 and R^2adj values are close to one and smaller the Rmsd value. Here flux is dependent variable and temperature and wt% of water in feed is independent variables. From the multiple regression analysis we get the model equation as follows

$$Flux = a_0 + a_1T + a_2WC \quad (6)$$

Where, a_0, a_1 and a_2 are the coefficients of model equation, T is the temperature and WC is the water content in feed in wt%

For multiple regression analysis we considered 35 data points to develop the model equation having two independent parameters such as temperature and water content in feed. In this regression analysis we get the large the variance but smaller the Rmsd value. Fig. 4 shows the graphical representation of model flux and experimental flux. A good agreement is shows in both the data and graphical representation and shown in below table 4.

Table 4 Estimated coefficients from Multiple Linear Regression models of flux

System	Membrane used	Model equation coefficients		R^2	R^2adj	Varience	Rmsd
Ethanol-water	PVA	a_0= a_1= a_2=	-89.60617 2.535829 1.847268	0.9090736	0.9033907	73.4001	1.384699
	PVA-PES	a_0= a_1= a_2=	-118.4673 3.228614 2.495636	0.9590219	0.9564608	51.09637	1.155319
Acetonitrile-water	PVA	a_0= a_1= a_2=	-45.01288 1.45232 9.214111	0.8926773	0.8829207	153.0437	2.321021
	PVA-PES	a_0= a_1= a_2=	-27.75875 1.4872 7.969237	0.8845644	0.8740702	143.0697	2.244115

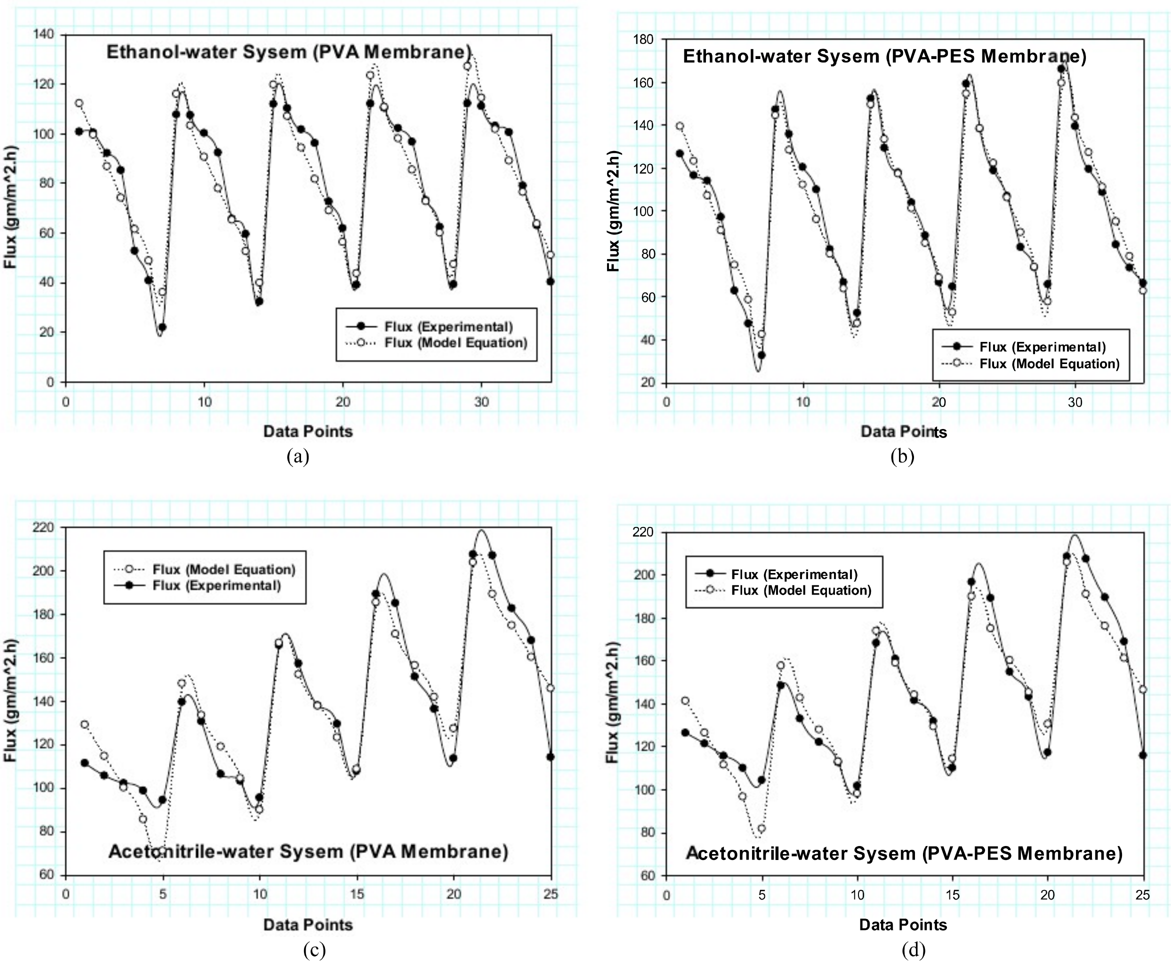


Fig. 5 Multiple Linear Regression including a free parameter for ethanol-water and Acetonitrile-water system

4. Conclusion

Separation of azeotropic mixture such as ethanol-water and Acetonitrile-water was carried out by using PVA and PVA-PES membrane in Pervaporation system. The effect of feed temperature and feed concentration on flux and separation factor were investigated for both the system. The results of both the systems are presented and compared with model data. Increasing feed temperature and feed concentration increases the flux of both the membranes. It's shown in experimental data Acetonitrile-water system has higher flux observed than the ethanol-water system but lower the separation factor. For 14.34 wt% of water in feed and temperature is 75 ^{0}C has obtained higher flux value up to 165.97 gm/m^2.h in ethanol water system and for 14.39 wt% of water in feed and temperature is 80 ^{0}C flux is obtained up to 208.57 gm/m^2.h in Acetonitrile-water system. Both the higher flux is obtained by using PVA-PES membrane in PV. As a result, it can be said that PVA-PES membrane has higher flux than PVA membrane while separation factor is lower.

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