

Solvent-Coating Powder Interaction and Permeability of Coated Clay-Alumina Membrane

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Abstract

The present study deals with membrane-solvent interaction using two types of oxide ceramic coating namely alumina and zirconia over clay alumina tubular support to study the effect of transmembrane pressure on solvent transport under crossflow microfiltration condition. Physical properties of solvents and membrane materials viz. viscosity of solvents, particle size of ceramic powders used for coating as membrane layers, contact angle between ceramic powders and solvents, and apparent porosity of ceramic tubes were determined to find out their role on solvent permeability. Permeability constant was calculated using regression analysis for different membranes and solvents. An attempt was made to correlate the membrane-solvent interaction parameter determined using regression analysis of time variation of flux with contact angle between respective membrane coating powder and solvent.

Key words – Contact Angle, Viscosity, Permeability, Membrane, Solvent, Regression Analysis.

I. Introduction

Several models are available to explain pressure driven solvent permeation process using porous membrane [1-7]. Using MF/UF membranes, one can safely assumed that the membrane pore size is much bigger than the solvent molecule size, so viscous flow will predominate. Most of those models consider viscosity as the only solvent property. These equations do not consider the interaction between solvent and membrane layer which may be one of the controlling factors for transport of solvent through the membrane. The change in volumetric flow rate with transmembrane pressure for pure solvent follows Darcy's equation [8,9] :

$$Q = (KA\Delta P)/(\eta L) \quad (1)$$

where, Q, ΔP , L, A, K and η are volumetric flow rate (m^3/s), transmembrane pressure (Pa), thickness of membrane (m), filtration area of membrane (m^2), permeability constant (m^2) and viscosity of solvent (Pa.s) respectively.

Time variation of flux at constant transmembrane pressure may be solved using the relation [10] :

$$J_{v,0}/J_{v,t} = (a+kt)^n \quad (2)$$

where, $J_{v,0}$ is the initial flux ($t=0$), $J_{v,t}$ is the flux at time 't', k is defined as the kinetic constant of the solvent-membrane

surface interaction process and 'n' has different values according to the prevailing fouling mechanism. For standard blocking, intermediate blocking and cake formation, the values of 'n' are 2, 1 and 0.5 respectively.

None of the models explains the interaction between solvent and surface of the membrane layer in term of contact angle. Since contact angle (θ^0) is a measure of solid-liquid interaction, the present investigation was aimed to study the relation between contact angle and the kinetic constant (k).

II. Materials and Method

Water obtained from Millipore India (Milli-Q) instrument was of 18.2 M Ω at 25°C, Hexane (fraction from petroleum) and Methyl ethyl ketone (MEK) were procured from s d Fine-Chem Limited (India) and used without further modification. Ceramic oxide powders viz zirconia (Z18) from M/s. Tosoh, Japan, alumina (A37) from M/s. Condea, Germany and low purity alumina (B11) from M/s. Indal, India were procured. Surface area of zirconia and alumina powders was determined to be 15 m^2/g and 1.2 m^2/g respectively, using BET pore volume analyzer (Model: AS-1-MP, Quantachrome Corporation, USA). Alumina (B11) powder was screened through mesh #200 (74 μm) and used for contact angle measurement. This alumina (B11) powder was used as clay-alumina tubular support.

Particle size distribution of ceramic powders used for membrane preparation were determined using Mastersizer-Hydro 2000(A), Malvern Instruments, UK. Contact angle between coating powder and solvent were determined using Tensiometer-DCAT11, Dataphysics, Germany.

Membrane permeability experiments were conducted in laboratory scale set up.

III. Membrane Characterization

Zirconia and alumina coated membranes were developed [11] over clay-alumina support tube and were analyzed using FESEM (Leo S430i, UK) and BET surface area & pore volume analyzer. Figure 1a & 1b show the crack free surface feature of zirconia and alumina coated membranes respectively.

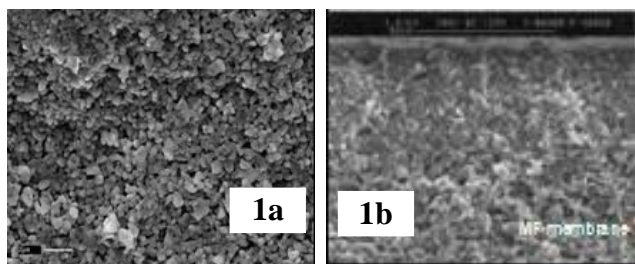


Figure 1a & 1b: FESEM micrograph of zirconia coated (1a) and alumina coated (1b) membrane.

Unsupported zirconia and alumina membranes were calcined at 700°C and 500°C for 2 hrs, respectively. BET surface area & pore volume analysis of calcined unsupported membranes are shown in figures 2a & 2b. Pore size distribution curves show 0.002-0.11 µm pore diameter of zirconia membrane and 0.002 – 0.07 µm of alumina membrane.

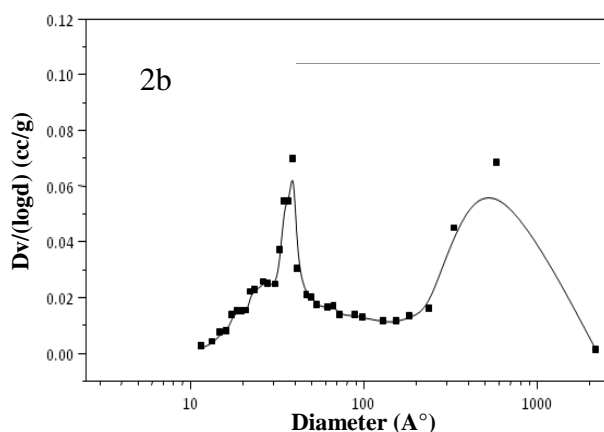
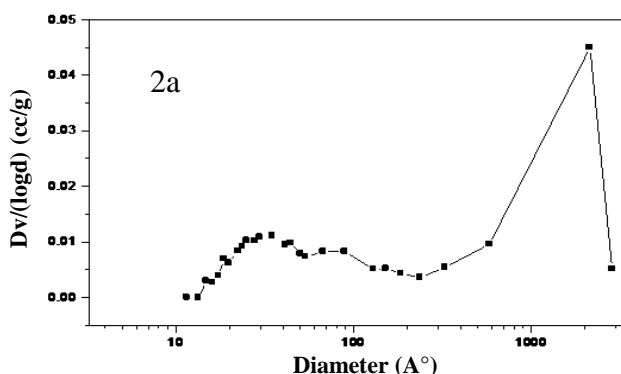


Figure 2a & 2b: BET pore volume analysis of calcined unsupported membrane (2a) zirconia at 700°C/2hr & (2b) alumina at 500°C/2hr.

IV. Experimental The permeation characteristics of a typical polar (water) and two non-polar (Hexane and MEK) solvents through alumina and zirconia powder coated membranes were conducted in cross-flow membrane filtration (CMF) mode at 1 bar transmembrane pressure (TMP) and 14°C. Initial flux of pure solvents at various

TMPs was calculated from slope of time variation of flux at respective TMPs.

V. Results and Discussions

Surface feature of FESEM micrographs of zirconia and alumina membranes as shown in Figures 1a & 1b and found crack free. Average membrane thickness was determined from cross-section view of the micrograph to be 6.6 µm and 3.6 µm for alumina and zirconia layer respectively. Particle size of oxide powders (d_{50}) in aqueous media using Mastersizer was analyzed and it was 0.74 µm for alumina (A37) and 1.69 µm for zirconia (Z18) powders. Particle size analysis of coating powder and BET surface area & pore volume analysis of unsupported membrane (Figures 2a & 2b) show that membrane pore diameter is lower for finer coating powder as in case of alumina. Apparent porosity of membranes determined using buoyancy method were 36.1%, 36.8% and 36.5% for alumina coated and zirconia coated membrane tubes and support tube respectively.

Experimental curves of initial flux versus trans-membrane pressure (Figures 3-5) show that hexane and MEK permeate at a much faster rate compared to water besides similar apparent membrane porosity which may be attributed to the lower viscosity (Table 1) and lower contact angles (Table 2) for hexane and MEK [12-14]. Zirconia coated membrane shows higher flux for water, hexane and MEK compared to alumina coated membrane, may be due to lower contact angle in the former case. Permeability constants calculated using Eq. (1) is shown in Table-3 and the plot of permeability constant vs. contact angle (θ^0) is shown in Figure-6. It appears that there exists a linear correlation between the two parameters in case of alumina coated membrane only. Analysis of flux data using Eq. (2) is given in Table-4 and the relation with 'k' (solvent – membrane surface interaction parameter) calculated from Eq. (2) and contact angle (θ^0) is shown in Figure-7. It transpires that while there exists a linear correlation between the two parameters in case of zirconia coated sample, such relation does not exist for clay-alumina support and alumina coated

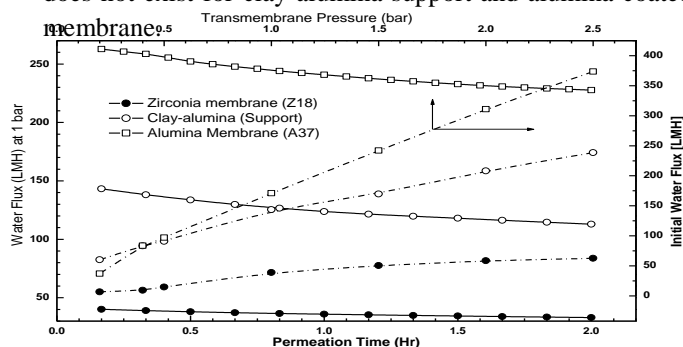


Figure 3 : Effect of permeation time (solid line) and transmembrane pressure (broken line) on permeation of prefiltered tap water using crossflow method through different tubular ceramic membranes at 14°C

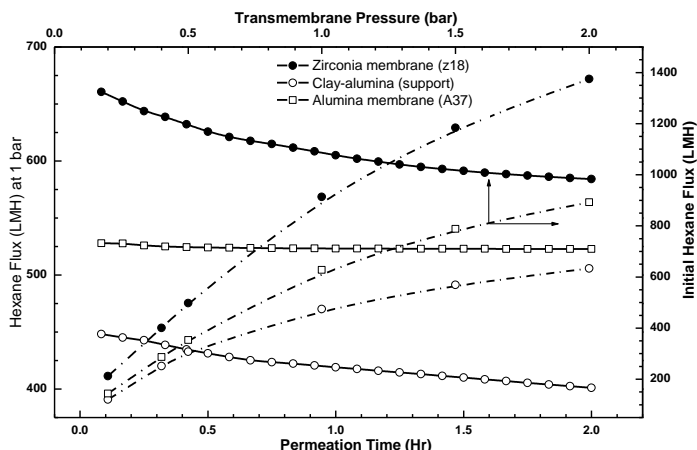


Figure 4 : Effect of permeation time (solid line) and transmembrane pressure (broken line) on permeation of hexane using crossflow method through different tubular ceramic membranes at 14°C

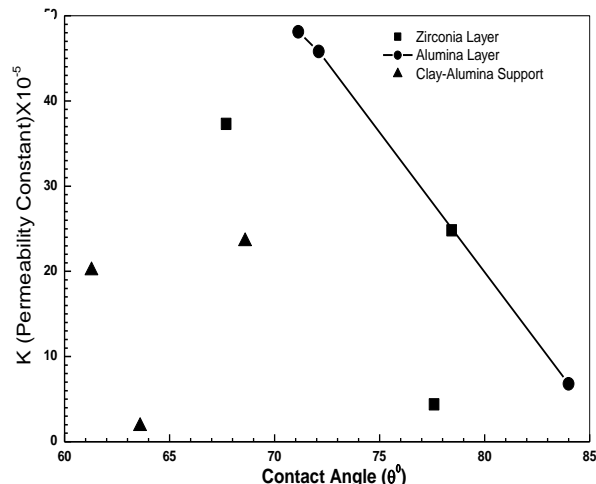


Figure 6: Relation between contact angle (θ^0) and 'K' for clay-Alumina support, Alumina and Zirconia coated membrane

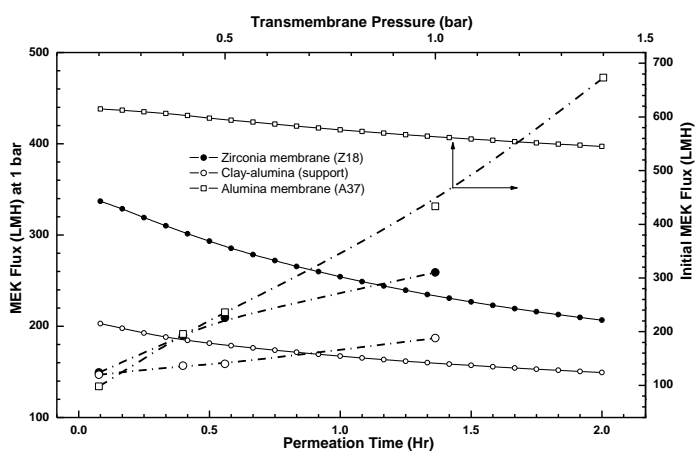


Figure 5 : Effect of permeation time (solid line) and transmembrane pressure (broken line) on permeation of MEK using crossflow method through different tubular ceramic membranes at 14°C

Table 4 : Results of solving equation $Y = (a+kt)^n$, where $Y = J_{v,0}/J_{v,t}$

Solvent	Membrane layer	$Y=(a+kt)^n$		
		a	k	n
Hexane	Alumina (A37)	0.89	0.45	0.06
	Zirconia (Z18)	0.70	3.21	0.06
	Support	0.87	1.34	0.09
Water	Alumina (A37)	0.97	0.13	0.69
	Zirconia (Z18)	0.89	0.74	0.23
	Support	0.75	1.46	0.18
MEK	Alumina (A37)	0.98	0.15	0.38
	Zirconia (Z18)	0.93	0.66	0.60
	Support	0.89	1.44	0.23

Table 1 : Viscosity of solvents at various temperature

Solvent	Viscosity (cp, at 14°C)
Water	1.171
Hexane	0.374
MEK	0.436

Table 2 : Contact angle between solvents and coating powders

Coating powder	Contact Angle (θ^0)		
	Water	Hexane	MEK
Z18	77.6	67.7	78.43
A37	84.0	72.1	71.13
B11(-200#)	63.6	61.28	68.60

Table 3 : Membrane Characteristics and Darcy constant

Membrane	K, Permeability Constant (m^2) $\times 10^{-5}$		
	Water	Hexane	MEK
Coating Layer			
Alumina (A37)	6.78	45.8	48.1
Zirconia (Z18)	4.39	37.3	24.8
Support (B11)	1.81	20.1	23.5

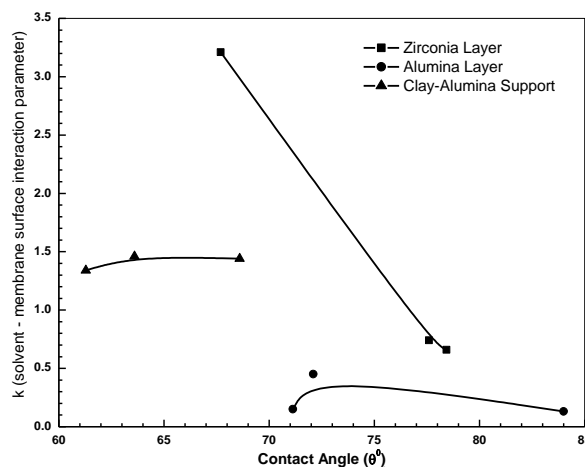


Figure 7: Relation between contact angle (θ^0) and 'k' for clay-Alumina support, Alumina and Zirconia coated membrane

VI. Conclusion

Flux is higher for solvent having lower contact angle irrespective of the nature of coating material. Lower contact angle implies better wetting of liquid and thus facilitate transport through porous membrane. Contact angle may be a

controlling parameter for solvent transport through membrane.

VII. References

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