01-7990556 c.1
CPOB

PREFERENTIAL ADSORPTION AND SELECTIVE PERMEATION OF ALCOHOL/HYDROCARBON MIXTURES IN REVERSE OSMOSIS

B.A. Farnand and H. Sawatzky
SYNTHETIC FUELS RESEARCH LABORATORIES

OCTOBER 1987

ERL 87-016 (OPJ) c.1
ERL 87-16 (OPJ)

ENERGY RESEARCH LABORATORIES
DIVISION REPORT ERL 87-16(OPJ)

This document was produced by scanning the original publication.

Ce document est le produit d'une numérisation par balayage de la publication originale.

PREFERENTIAL ADSORPTION AND SELECTIVE PERMEATION OF ALCOHOL/HYDROCARBON MIXTURES IN REVERSE OSMOSIS

BY

B.A. Farnand* and H. Sawatzky*

ABSTRACT

In binary mixtures of alcohols and hydrocarbons there are two types of reverse osmosis performances. These are selective permeation of the alcohol and selective permeation of the hydrocarbon. This work deals with the regulation of the selective permeation of both the hydrocarbon and the alcohol. As expected, the selective permeation of the alcohol appears to be a function of the polarity of the membrane. This has been demonstrated in the case of polyethylene and cellulose ester membranes with methanol and pentane solutions. These results are of interest for the production of oxygenated fuel blending agents where specifications require the removal of unreacted methanol for further processing and distillation is not viable because of azeotropes. These selective permeation results are compared

with the selective adsorption of methanol and hydrocarbons on membrane material as determined by liquid chromatography. The liquid chromatography results can be used to predict the performance of reverse osmosis membranes where the membranes may be difficult to fabricate as well as to determine performance limits in terms of separation.

---

*Hydrocarbon Separation Section, Synthetic Fuels Research Laboratory, Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa, K1A 0G1.

INTRODUCTION

The reduction of the amount of lead permitted in gasoline has created problems for oil refiners. To maintain existing quality specifications, i.e. gasoline octane ratings, refiners add mixtures of benzene, toluene and xylenes (BTX), reformer gasoline, and other blending agents found in refineries. However, there is concern that these in-refinery products will become limited. For this reason, oxygenates are being considered for blending into gasoline because of their ability to improve the octane number, and also because of their adequate supply. Alcohols were among the first to be considered but technical difficulties may preclude their large-scale use. For example, methanol needs an expensive cosolvent and its high vapour pressure requires a reduction of inexpensive high octane number butanes from the final gasoline product. An alternative is to produce light methyl ethers from refinery olefins and methanol.

The reactions needed to produce methyl tertiary butyl ether (MTBE)and methyl tertiary amyl ether (TAME) are shown in Fig. 1. The reactions are equilibrium limited (1), and only the iso-olefins will react. The remaining unreacted non iso-olefins should be removed from the reactor product

before they are blended into the gasoline pool. Also, the unreacted methanol and the oxygenates must be removed from the remaining olefins to allow their processing in alkylation or other existing refinery operations that use strong acid catalysts (2). It is this removal of methanol that is the object of our study, since distillation cannot be used because of azeotropes. Cost estimates indicate that one-sixth of the cost of MTBE production from refinery olefins is for the removal of methanol from the remaining olefins by existing technology such as solid adsorption and liquid extraction (3,4). The goal of this study is to consider the removal of methanol by reverse osmosis as an alternative to existing technology.

Since the extent of reaction is limited by equilibrium, it is desired to improve the yields by using an excess of methanol. This strategy puts an even greater capacity requirement on the methanol removal process than would be anticipated from stoichiometry. Since the etherification reactor product consists mainly of hydrocarbons, the separation of methanol from methanol and pentane mixtures was studied. This requires the assumption that the pentane behaves in the same manner as the C_4 and C_5 olefins, and that the ethers also behave as hydrocarbons. Results from

experiments using simulated etherification reactor product demonstrated the validity of these simplifications (5).

The degree of separation of different compound types by reverse osmosis depends upon the difference of affinity that the membrane exhibits for these components. These differences can be assessed by liquid chromatography experiments which have also been included in this study (6). The effect of concentration of methanol on membrane performance was also investigated.

EXPERIMENTAL

LIQUID CHROMATOGRAPHY

A schematic of the liquid chromatography apparatus is shown in Fig. 2. The chromatography columns were filled with 38-53 μm sieve size candidate membrane polymers. Pure pentane was pumped through the column and both methanol and deuterated pentane were injected separately to determine their retention volumes for each of the polymer materials. Deuterated pentane was chosen because of its different refractive index compared to the natural pentane carrier. It is assumed that the deuterated pentane behaves in the same manner as natural pentane so that its retention volume would simulate that of natural pentane.

REVERSE OSMOSIS

A schematic of the reverse osmosis apparatus is shown in Fig. 3. The reservoir tank was fitted with a condenser to reduce the loss of light components to the atmosphere. The membrane permeates were collected through septa capped bottles. Prior to sample collection, these bottles were partly filled with toluene to reduce the vapour pressure of the contents, to reduce the volume of permeate sample needed and to suppress the formation of bubbles in

subsequent analysis by automated capillary gas chromatography. The weight increase of these samples was used to determine the permeation rate.

The temperature was maintained at 23^{o}C and the circulation rate over the membranes was 1 L/min. Thus, even the large separation experiments did not change the concentration of the feed solution from the first membrane through to the last membrane of the series. The feed solution samples were also collected through a septum into a bottle partly filled with toluene.

RESULTS AND DISCUSSION

LIQUID CHROMATOGRAPHY

The liquid carrier inside the column is considered to consist of two phases: a mobile phase that flows through the column; and a stationary or adsorbed phase which is in the region of the surface of the particles as well as inside the pores of the packing (Fig. 4). After solutes are injected, their distribution between the mobile phase and the stationary phase determines the retention time. A longer retention time is indicative of a longer residence time in the stationary phase. Solutes that are not preferentially adsorbed do not enter the stationary phase and are eluted very quickly. An important assumption is that the relation of the mobile phase to the stationary phase is the same as the relation of the interfacial region to the bulk solution as found in reverse osmosis. This leads to the use of liquid chromatography to describe the preferential adsorption of solutes in the membrane-solution interfacial region.

The candidate membrane materials investigated for preferential adsorption of pentane and methanol were polyethylene (PE) supplied by BDH Chemicals, cellulose acetate (CA), and cellulose acetate butyrate (CAB), both supplied by the Eastman Kodak Company. The average retention

volumes for these polymers are shown in Table 1. It is further assumed that the surface areas of the three columns packed with polymer powder is similar. On the basis of these results, membranes of polyethylene would be expected to preferentially adsorb pentane and to pass a pentane-rich permeate whereas the CA and CAB membranes should preferentially adsorb methanol and pass a methanol-rich permeate. As well, the CAB should be expected to show a greater separation than CA, all other factors considered equal. The assumption that the surface areas of the three polymers tested in the liquid chromatography are similar may be erroneous given the results of Matsuura and Sourirajan (6) for surface areas in aqueous conditions for CA and CAB. Results were unattainable with methanol concentrations of 1% and greater because of the high vapour pressure of methanol-pentane mixtures and the difficult operating conditions.

REVERSE OSMOSIS

Membranes of the above materials were tested in reverse osmosis experiments with various methanol-pentane mixtures along with a commercial membrane. The PE membranes used for these experiments were pieces of commercially available domestic food wrappers, namely, Handiwrap (Dow Chemical) and

Glad Wrap (Union Carbide). They possibly contain plasticizers, typically polyvinyl acetate. The CA and CAB membranes were cast in the laboratory by established methods (7,8). Two Filmtec SW-30 thin film composite membranes that were developed for the reverse osmosis treatment of sea water were also tested. They have surface layers of aromatic polyamides that are in the same range of polarity as cellulose acetate (9). These membranes were placed in random order in the apparatus.

The results of the reverse osmosis separations are expressed in terms of methanol separation factor, α, defined as

$$\alpha = \frac{(x/(1-x))}{(y/(1-y))} \qquad (2)$$

where x and y are the mole fractions of methanol in the permeate and feed samples. Where α is greater than 1, there is selective permeation of the methanol from the membrane !!permeate. Where α is less than 1, there is selective rejection of the methanol. Separation factors have been plotted with concentration of methanol in the feed solution for all of the membranes in Fig. 5 to 10.

Contrary to what was expected from the liquid chromatography results, the CA membrane had the greatest separation factors -almost 50 for low concentrations and about 15 for high concentrations. The separation factors for the CAB and the SW-30 membranes were considerably lower than those for CA. Also, the SW-30 membranes' separation factor decreased towards unity as the methanol concentration was reduced. The separation factors for the PE membranes were less than unity which indicates a selective permeation of pentane. Similar to the SW-30 membranes, their separation factors approached unity as the methanol concentration was reduced.

A simulated etherification reactor effluent containing methanol, pentane and TAME was tested with CA, CAB, and PE membranes as shown in Table 2. The pentane was assumed to behave similarly to the unreacted iso-pentanes. At lower methanol concentrations, the CA membranes showed the greatest separation factors, but this decreased with increasing methanol concentration. The pentane was rejected whereas the average separation factor for TAME is approximately unity. As expected, the permeation rate decreases as the separation factor increases. The CAB membrane showed considerably lower separation factors for both methanol and pentane and selectively permeated TAME.

The Glad Wrap PE membrane selectively permeated pentane and rejected methanol with a separation factor for TAME in the region of unity. The Handiwrap PE membrane had performed similarly but with separation factors closer to unity.

To compare these results requires an assumption concerning the relative pore sizes of these membranes. The CA, CAB, and SW-30 membranes would give salt separations in excess of 95% from aqueous solutions. However, there is no evidence that the pore sizes of the membranes would not be modified by the presence of nonaqueous solutions. The PE membranes do not have any permeate in aqueous reverse osmosis. This may not necessarily be an indication of the absence of porosity, since capillary pressure to force water through a pore in the PE membranes could be quite large. Further, the presence of a nonaqueous solution may cause the PE membranes to have different porosity than in the aqueous experiments. Thus a comparison of the membrane experiment results is not definitive; the relative results regarding the selective permeation and rejection of components by a given membrane are more valid. The same limitations must also be applied to the liquid chromatography results. The absence of information regarding the effective surface area of the polymer in pentane, and the absence of an estimate of "dead" volume for the apparatus with the columns attached

limits the direct comparison of the polymers. However, the basic observation of the relative retention volume for pentane compared to methanol for a given membrane material is valid.

For the process of removing methanol from etherification reactor effluent, the membrane with the highest separation factor, CA, is the obvious candidate. The removal as permeate of the minor component, methanol, is desirable in that less surface area would be required for a separation process. Future work shall consider the modification of the membrane surface to improve the selective permeation of methanol and to increase the permeation rate.

CONCLUSIONS

Polar membranes can selectively permeate methanol from mixtures of unreacted olefins and the ether product formed during the production of MTBE and TAME. Non polar membranes selectively permeate the hydrocarbons from the same mixtures. For most of the cases except cellulose acetate membranes, the separations decreased as the methanol content decreased. Of the membranes tested,the cellulose acetate membranes also had the greatest separation factors for methanol.

REFERENCES

1. Chase, J.D. (1984) Synthesis of High Octane Ethers From Methanol and Iso-Olefins. In: Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals, Edited by R.G.Herman, p.307, Plenum Pub., USA.

2. Chase, J.D.; Galvez, B.; Kennedy, B.W. (1980) A Method For Processing Etherified Light Hydrocarbon Mixtures To Remove Methanol. US Patent 4,218,569.

3. Bitar, L.S.; Hazbun, E.A.; Piel, W.J. (1984) MTBE Production and Economics. Hydrocarbon Processing, October, 1984, p.63

4. Chase, J.D.; Galvez, B.B. (1981) Maximize Blend Ethers With MTBE and TAME. Hydrocarbon Processing, March, 1981, p.89.

5. Farnand, B.A.; Sawatzky, H. (1986) Reverse Osmosis and The Selective Permeation and Rejection of Methanol From Hydrocarbon Mixtures. In: Proceedings of the International Membrane Conference on the 25th Anniversary of Membrane

Research in Canada, Sept 24-26, 1986, National Research Council Canada, Ottawa, Canada.

6. Matsuura, T.; Sourirajan, S. (1981) Reverse Osmosis Transport Through Capillary Pores Under The Influence of Surface Forces. Ind.Eng.Chem.,Process Des.Dev., 20, p.273.

7. Pageau, L.; Sourirajan,S. (1972) Improvement of Porous Cellulose Acetate Reverse Osmosis Membranes By Change of Casting Conditions. J. Appl. Polym. Sci., 16, p.3185.

8. Sourirajan, S.; Kunst, B. (1977) Cellulose Acetate and Other Cellulose Ester Membranes. In: Reverse Osmosis and Synthetic Membranes, Edited by S. Sourirajan, National Research Council Canada, Ottawa, Canada, p.129.

9. Kesting, R.E. (1985) Synthetic Polymeric Membranes. Wiley Interscience, New York, USA, p.279.

Figure 1 Reactions of Iso-Olefins and Methanol To Produce MTBE and TAME

Figure 2 Schematic of Liquid Chromatography Apparatus

Figure 3 Schematic of Reverse Osmosis Apparatus

PI is the pressure indicator
TI is the temperature indicator
PC is the pressure controller

Figure 4 Schematic of Liquid Chromatography Mobile and Stationary Phases

Figure 5 Reverse Osmosis Separation Factors for CA Membrane

Figure 6 Reverse Osmosis Separation Factors for SW30-1 Membrane

Figure 7 Reverse Osmosis Separation Factors for SW30-2 Membrane

Figure 8 Reverse Osmosis Separation Factors for CAB Membrane

Figure 9 Reverse Osmosis Separation Factors for GladWrap (PE) Membrane

Figure 10 Reverse Osmosis Separation Factors for Handiwrap (PE) Membrane

Table 1 Average Liquid Chromatography Retention Volumes for PE, CA, and CAB

	Retention Volume, mL		
	PE[a]	CA[b]	CAB[c]
Methanol	2.81	2.15	3.76
C_5D_{12}	2.91	2.01	2.44

---

[a] 0.3820 g of 38-53 μm sieve size powder in a 2mm ID column.

[b] 1.219 g of 38-53 μm sieve size powder in a 2 mm ID column.

[c] 1.250 g of 38-53 μm sieve size powder in a 2 mm ID column.

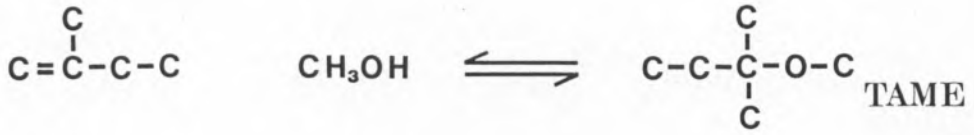
Table 2 Reverse Osmosis Results for Synthetic Etherification Reactor Effluent[a]

Run No.	Memb	Feed Concn, wt% MeOH	Feed Concn, wt% n-C5	Feed Concn, wt% TAME	Perm[b] Rate	Separation Factor MeOH	Separation Factor n-C5	Separation Factor TAME
1	Glad	4.38	94.72	0.08	n/a	n/a	n/a	n/a
	CA-1				0.82	8.166	0.130	1.244
	CA-2				0.72	10.37	0.103	1.127
	CAB				5.23	2.201	0.471	1.612
	CA-3				0.61	15.27	0.070	0.931
	Handi				1.17	0.752	1.296	1.873
2	Glad	10.54	83.41	5.46	0.96	0.478	1.782	1.122
	CA-1				1.117	3.892	0.298	0.883
	CA-2				1.170	3.713	0.298	0.760
	CAB				6.072	1.506	0.723	n/a
	CA-3				0.878	4.953	0.220	0.850
	Handi				0.798	0.582	1.667	n/a
3	Glad	9.57	84.56	5.21	1.117	0.520	1.712	0.997
	CA-1				0.971	5.697	0.193	0.857
	CA-2				1.144	4.180	0.262	0.941
	CAB				6.782	1.222	0.808	1.217
	CA-3				0.997	5.868	0.183	1.038
	Handi				n/a	0.704	1.233	1.437

[a] operating pressure of 2 MPa, operating temperature of 25°C.

[b] permeation rate in $kg/h/m^2$


C=C-C
CH3OH
C-C-O-C
C
MTBE


C=C-C-C
CH3OH
C-C-C-O-C
C
TAME

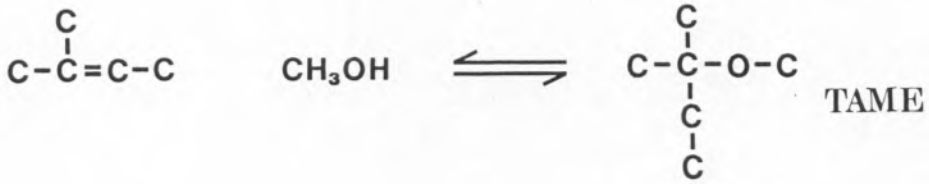

C-C=C-C
CH3OH
C-C-O-C
C
C
TAME

Fig 1

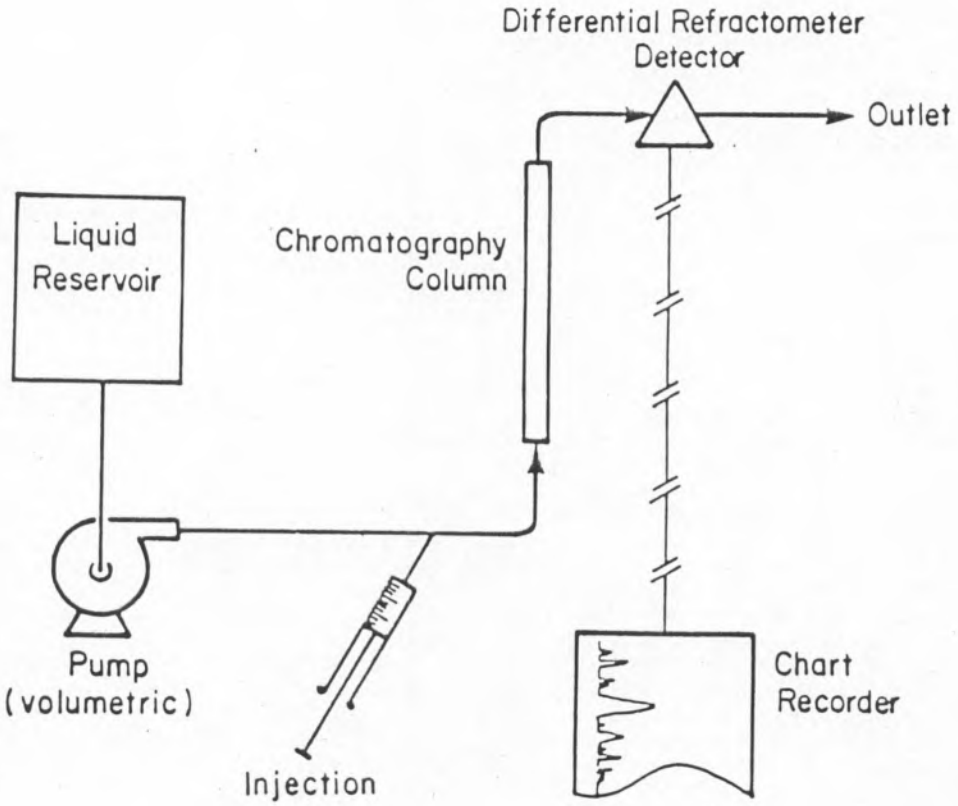

Differential Refractometer
Detector
Outlet
Liquid
Reservoir
Chromatography
Column
Pump
(volumetric)
Injection
Chart
Recorder

Fig 2

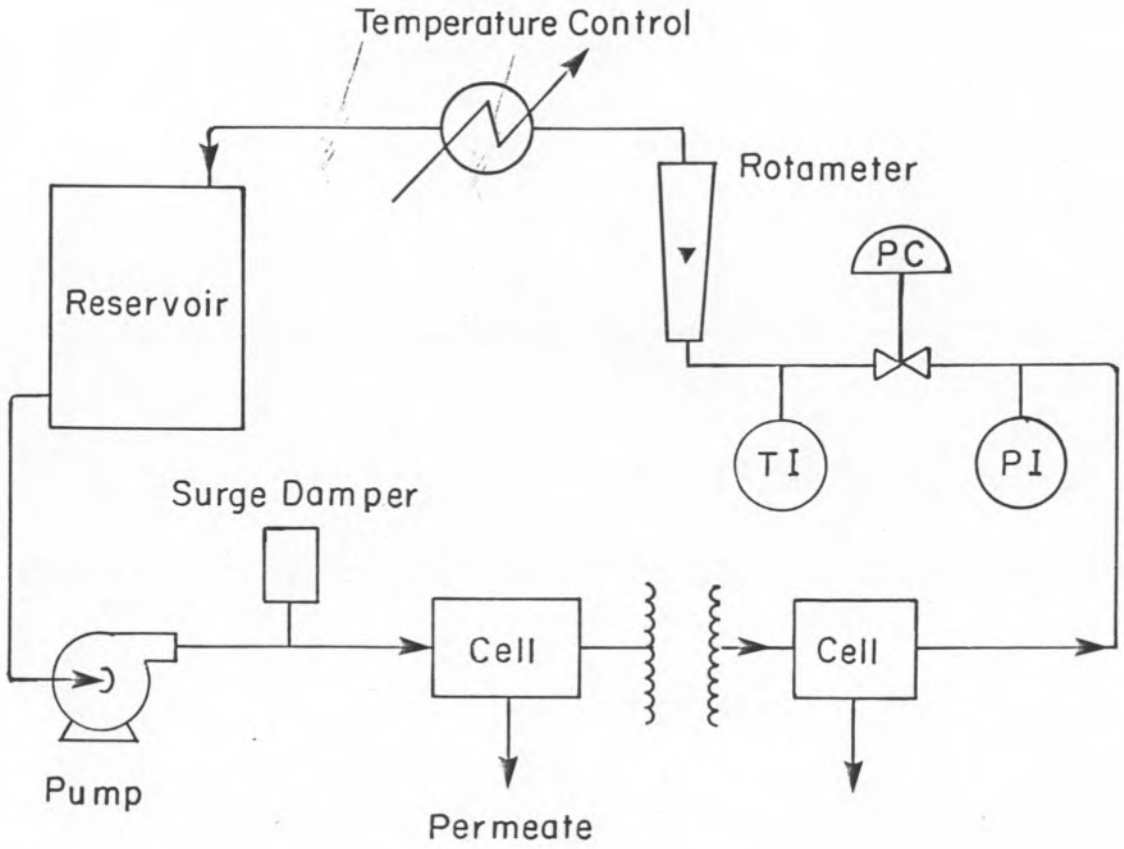

Temperature Control
Rotameter
Reservoir
PC
TI
PI
Surge Damper
Cell
Cell
Pump
Permeate

Fig 3

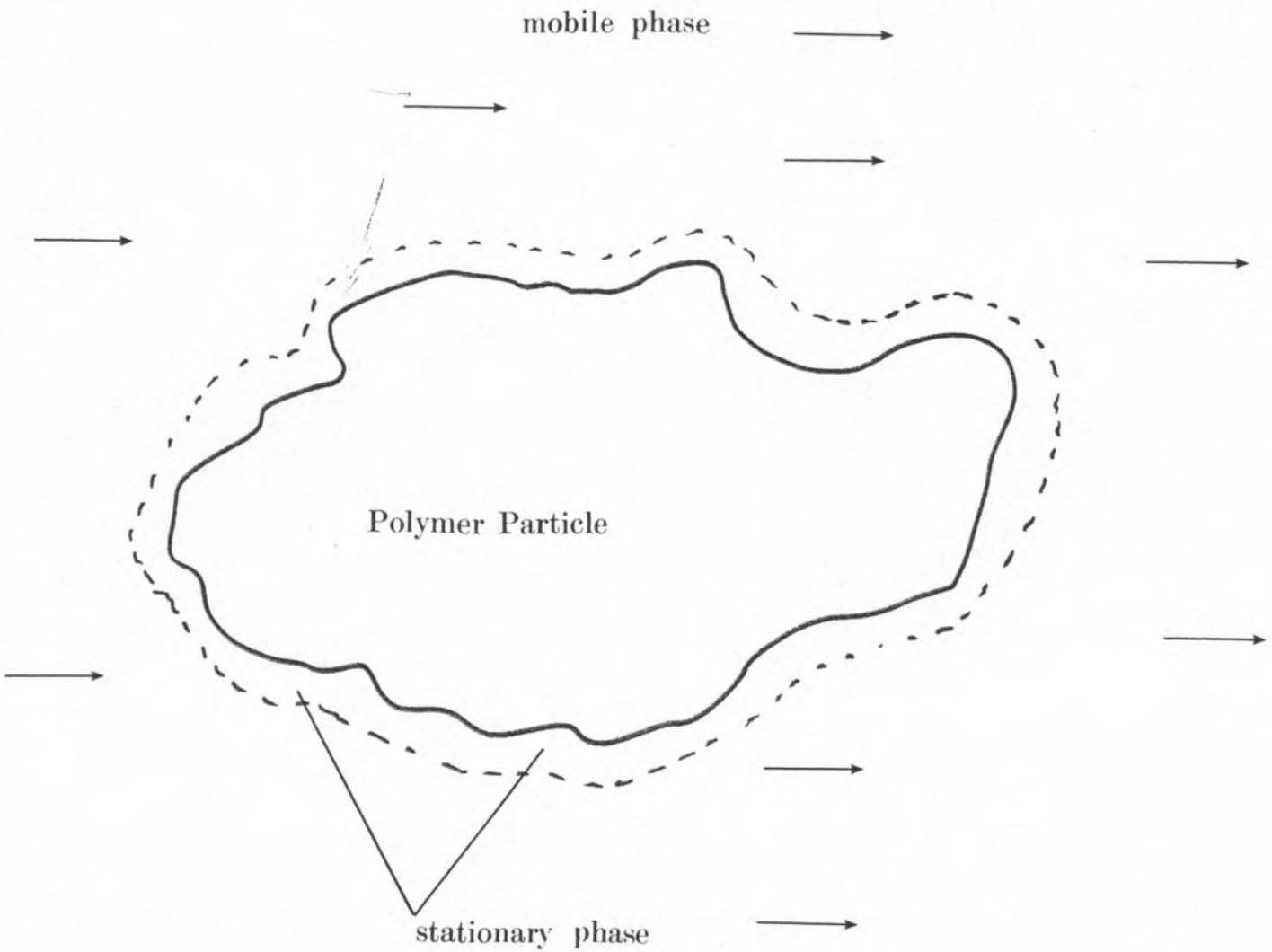


Fig 4

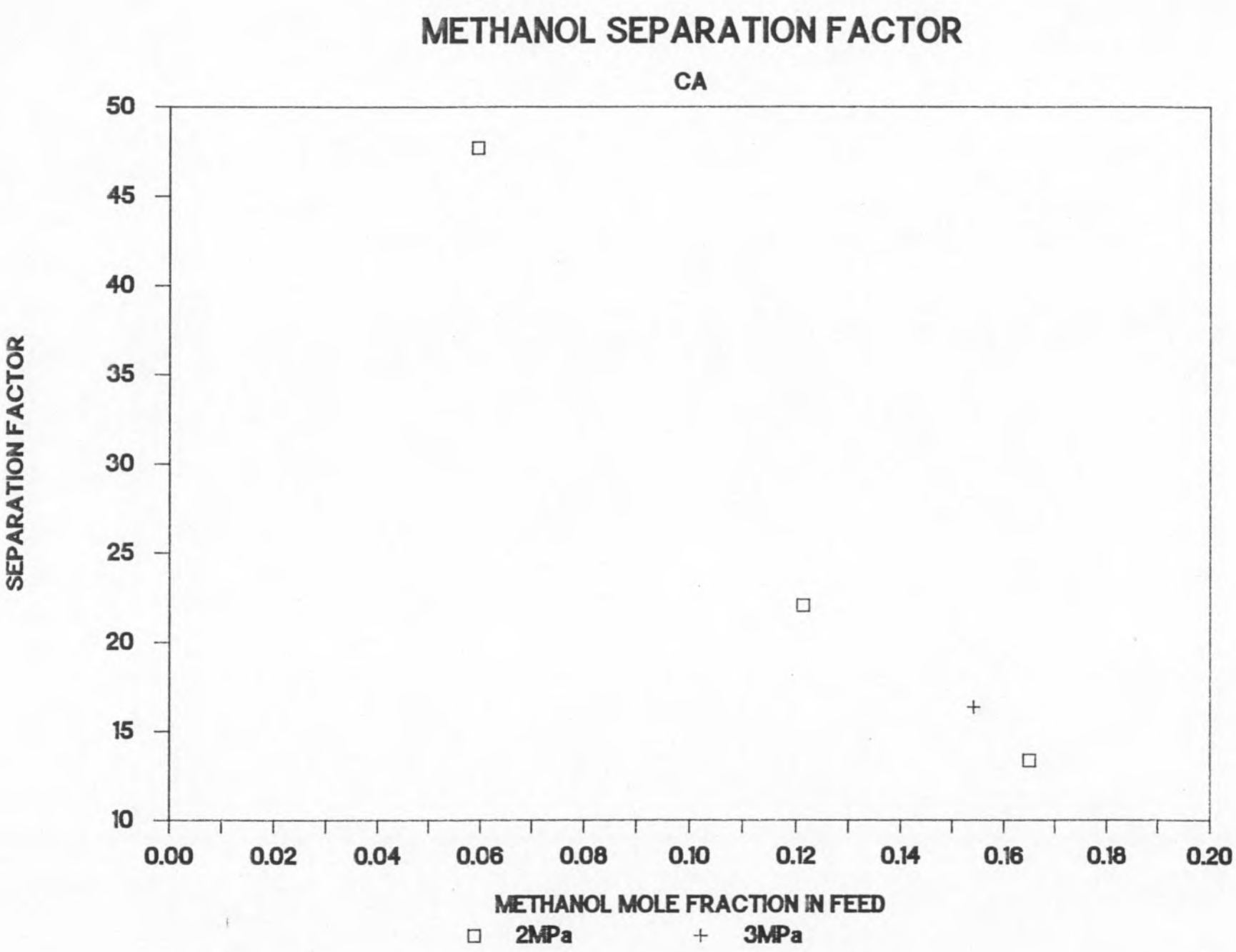

METHANOL SEPARATION FACTOR
CA
SEPARATION FACTOR
50
45
40
35
30
25
20
15
10
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
METHANOL MOLE FRACTION IN FEED
2MPa
3MPa

Fig 5

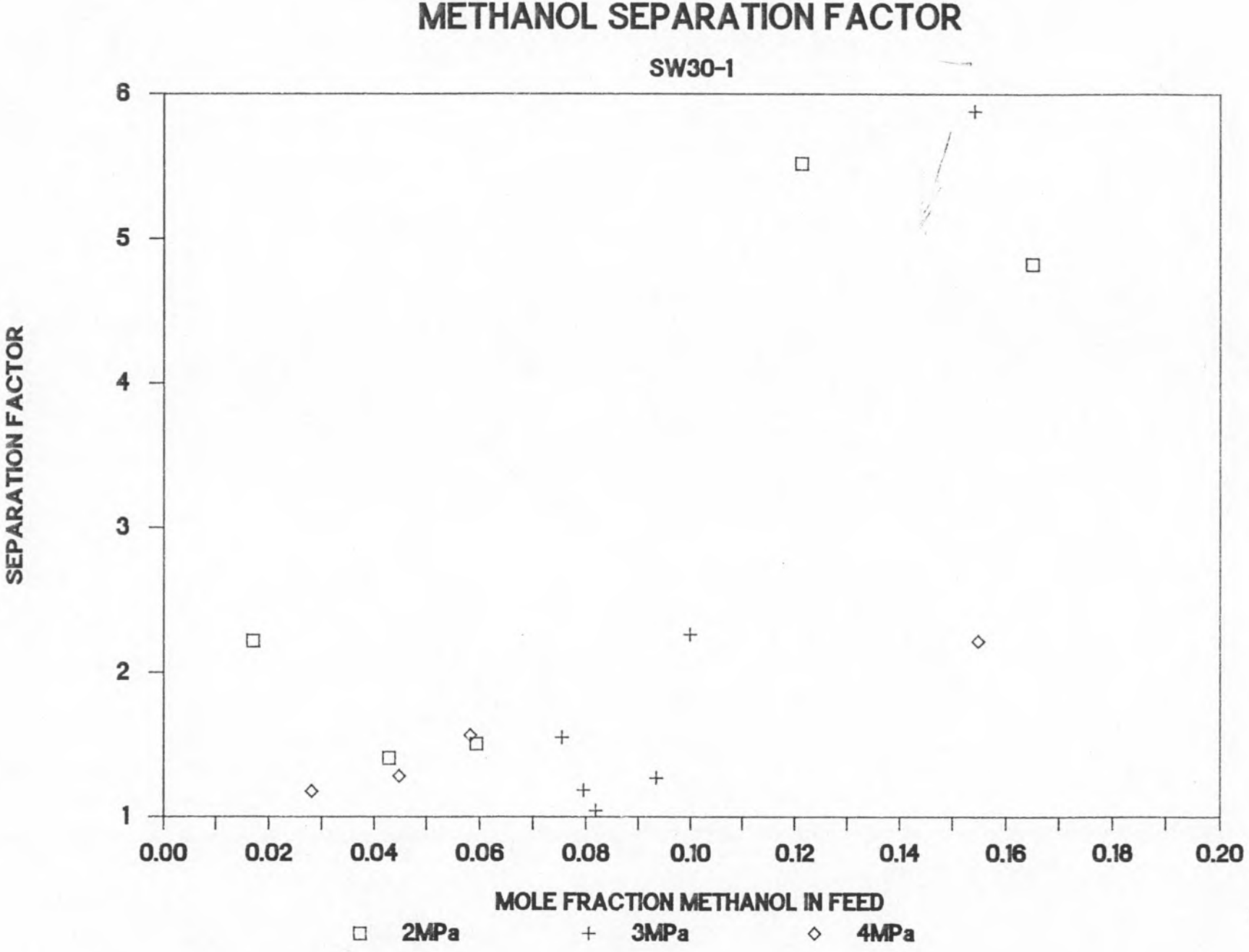

METHANOL SEPARATION FACTOR
SW30-1
SEPARATION FACTOR
6
5
4
3
2
1
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
MOLE FRACTION METHANOL IN FEED
2MPa
3MPa
4MPa

Fig 6

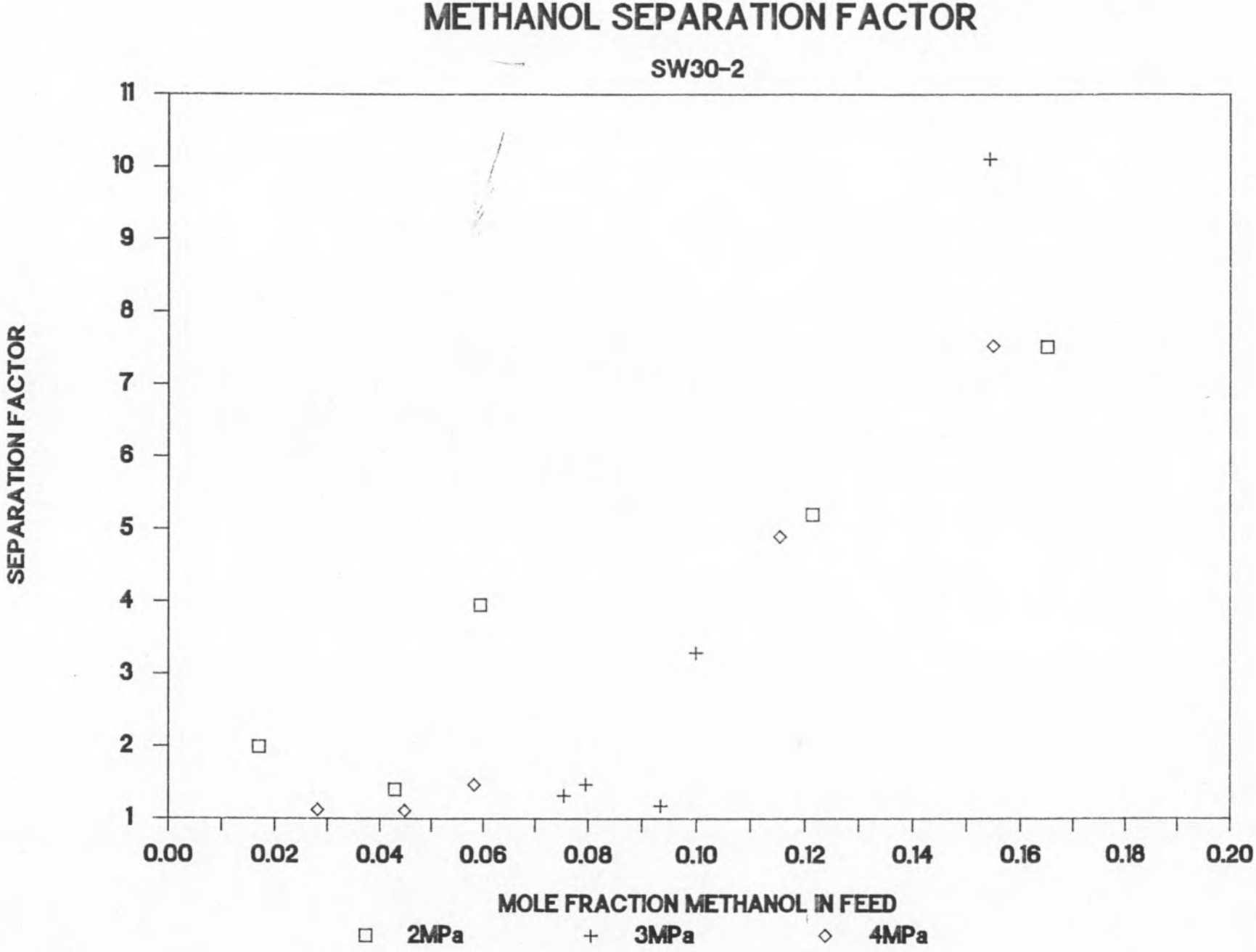

METHANOL SEPARATION FACTOR
SW30-2
SEPARATION FACTOR
11
10
9
8
7
6
5
4
3
2
1
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
MOLE FRACTION METHANOL IN FEED
2MPa
3MPa
4MPa

Fig 7

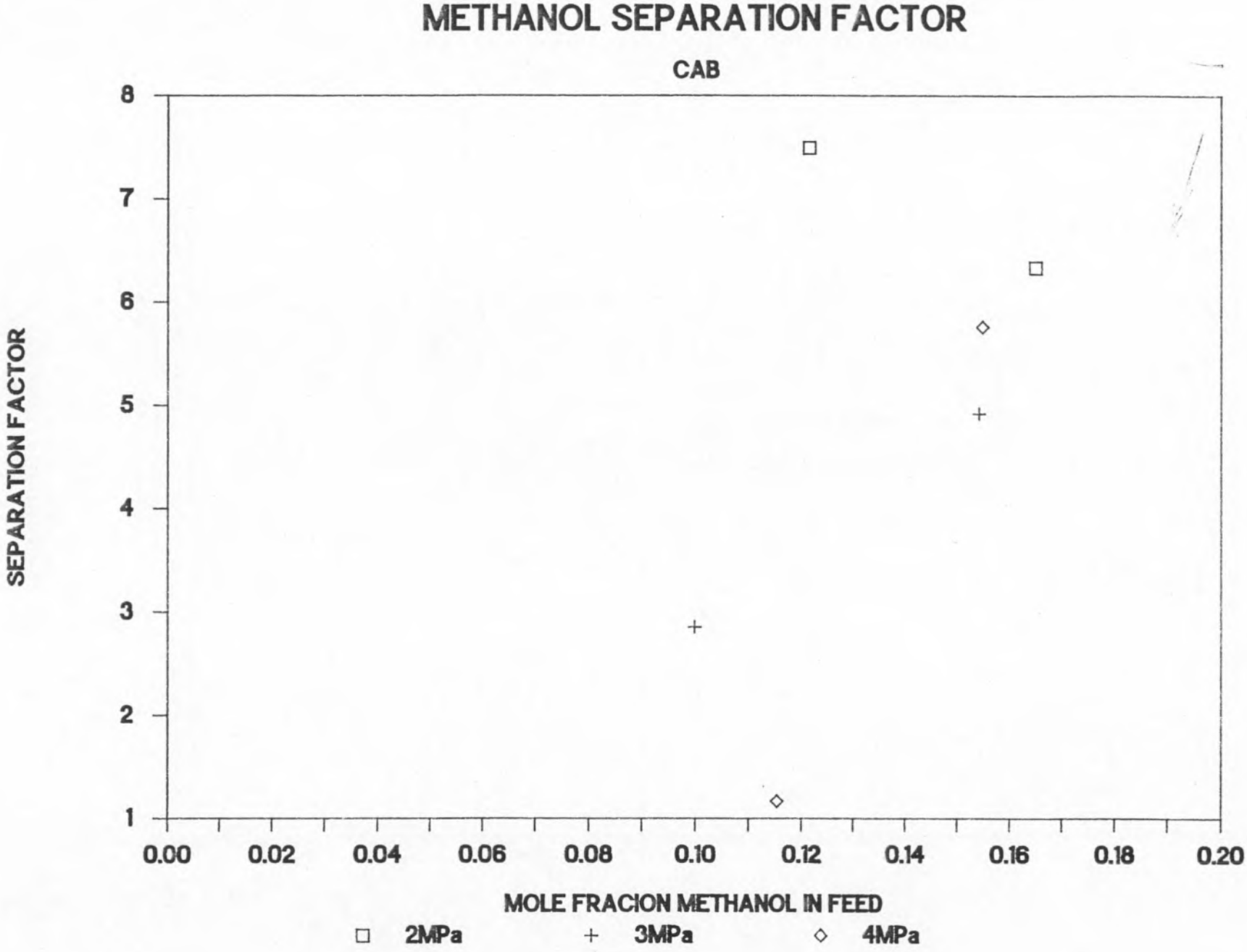

METHANOL SEPARATION FACTOR
CAB
SEPARATION FACTOR
8
7
6
5
4
3
2
1
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
MOLE FRACION METHANOL IN FEED
2MPa
3MPa
4MPa

Fig 8

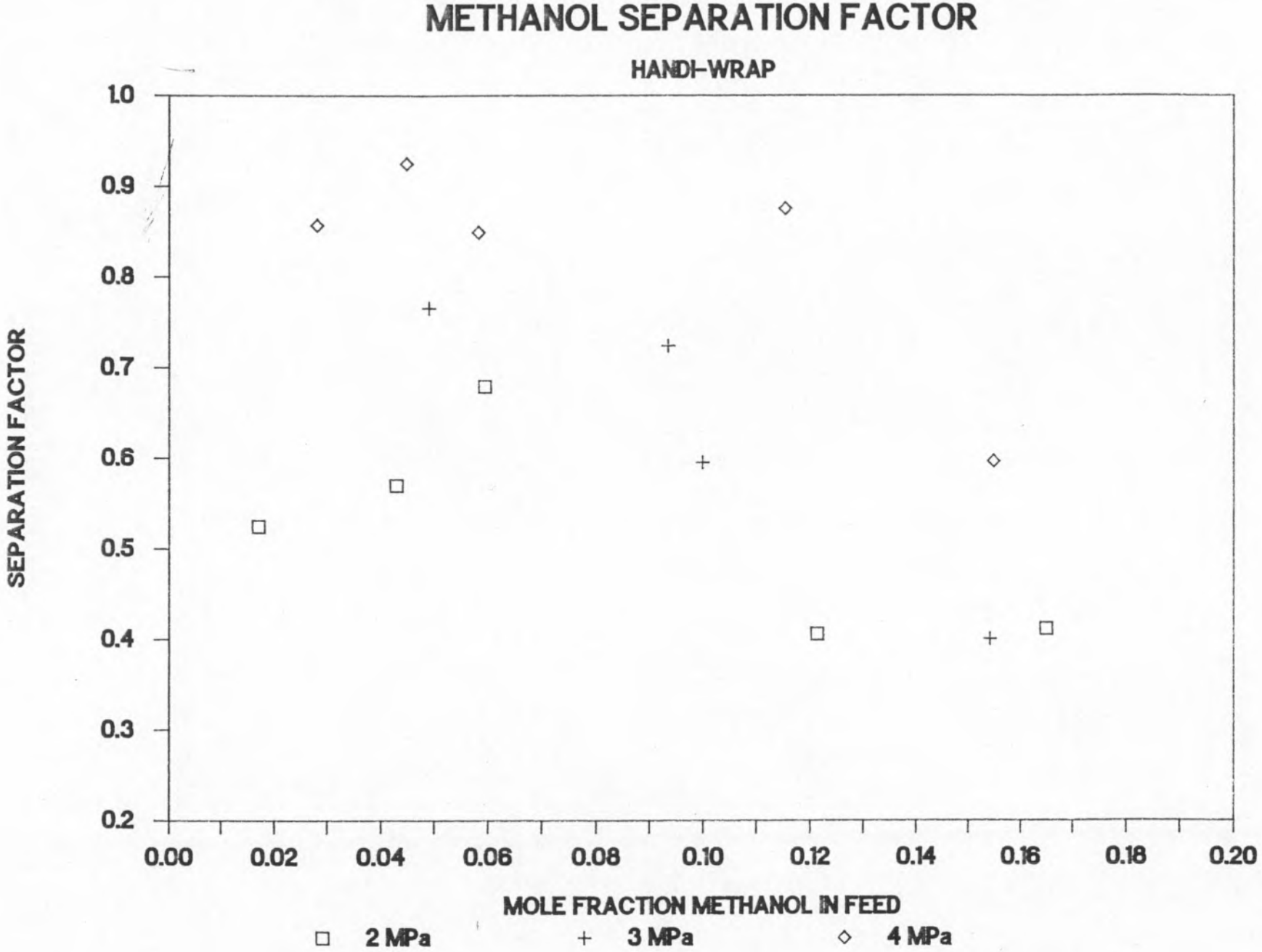

METHANOL SEPARATION FACTOR
HANDI-WRAP
SEPARATION FACTOR
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
MOLE FRACTION METHANOL IN FEED
□ 2 MPa
+ 3 MPa
◇ 4 MPa

Fig 9

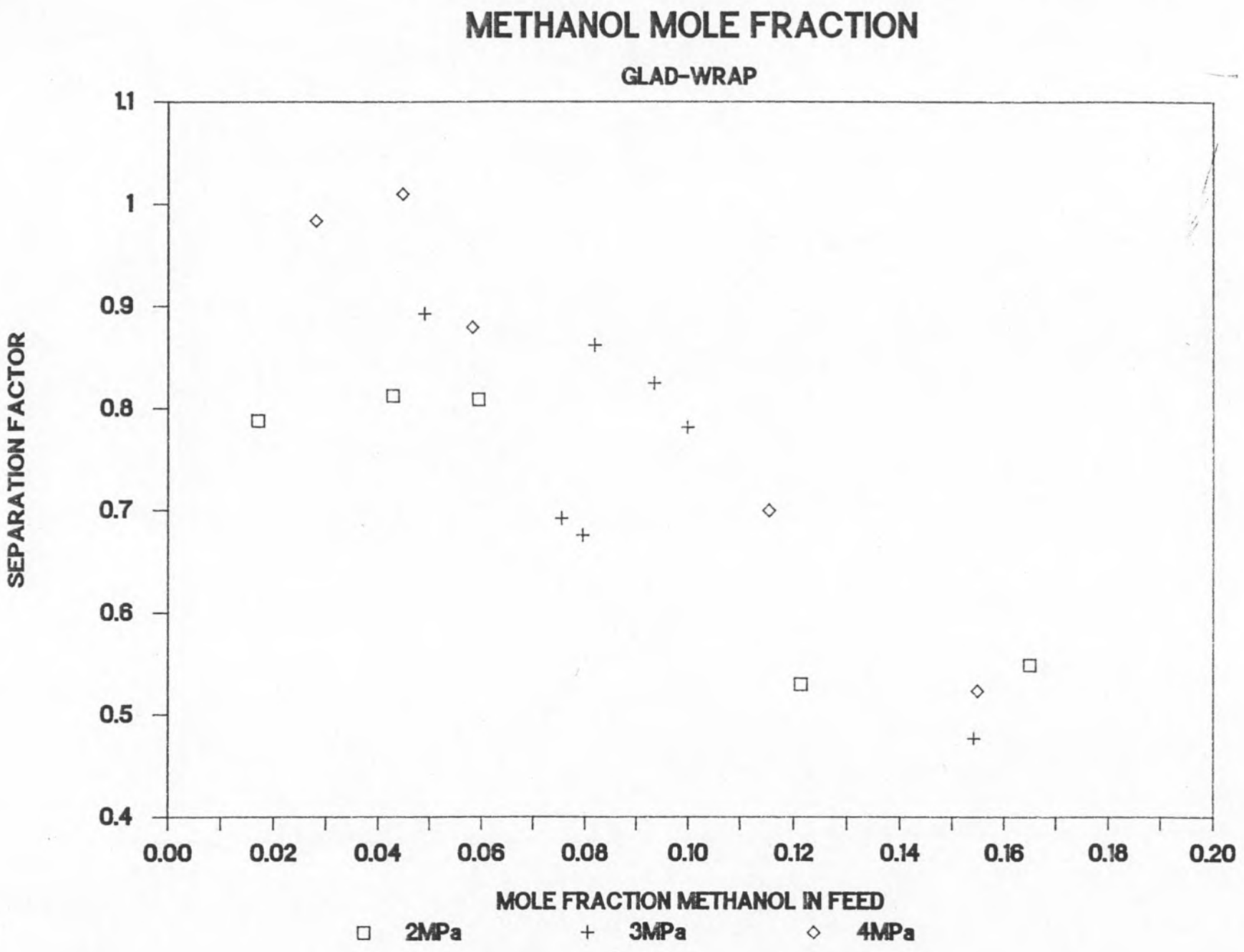

METHANOL MOLE FRACTION
GLAD-WRAP
SEPARATION FACTOR
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
MOLE FRACTION METHANOL IN FEED
2MPa
3MPa
4MPa

Fig 10