EVALUATION OF VARIOUS POLYMERS AS MEMBRANES FOR THE REVERSE OSMOSIS
UPGRADING OF LIGHT PETROLEUM DISTILLATES

Brian A. Farnand, Colette Nader and Henry Sawatzky, Energy
Research Laboratories, c/o 555 Booth Street, Ottawwa, CANADA, K1A OG1

INTRODUCTION

We have undertaken the development of membrane technology for the
upgrading of naphtha streams, and this report is a preliminary statement of
the results of a study concerning the selection of promising polymeric mater-
ials for membranes.

Naphtha streams from synthetic crudes have poor octane ratings,
usually based upon their low aromatic content (1). As well, refining of these
streams is complicated by the presence of problematic compounds, usually con-
taining nitrogen and sulphur or other heteroatoms. The primary goal of the
membrane work is the improvement of the octane rating of naphtha by producing
an aromatic rich stream and an aromatic lean stream. The latter would be
available for catalytic upgrading. A secondary goal is the removal of nitro-
gen and sulphur containing components from the naphtha streams, also by using
membranes.

Previous experience with the development of reverse osmosis in aque-
ous as well as non-aqueous solutions has demonstrated the utility of affinity
chromatography for the qualitative and quantitative prediction of reverse
osmosis and ultrafiltration performance (2,3,4,5). This work extends these
principles, simplified by the use of pure solvents (toluene and heptane) as
the carrier liquid to represent aromatic and aliphatic naphtha to the naphtha
case. Because of this simplification, prediction of reverse osmosis perform-
ance cannot be made. However, speculation as to the nature of reverse osmosis
performance can be inferred from these experiments.

The probes used in this work were chosen on the basis that they
represent specific group contributions, extremes in size, or were found to be
present in significant quantities in synthetic naphtha streams (6,7). The
candidate membrane materials were: cellulose (CE); cellulose acetate E-398
(CA); cellulose acetate butyrate (CAB, 17% butyrated); cellulose triacetate
(CTA); cellulose acetate hydrogen phthalate (CAHP); low density polyethylene
(PE); and Teflon[R]. With the exception of the latter two materials, reverse
osmosis membrane fabrication details are available in the literature.

EXPERIMENTAL

A schematic diagram of the apparatus used for affinity chromato-
graphy is shown in Fig. 1. Single solute probe solutions of approximately 1%
by weight of solute in carrier solvent were injected into the carrier stream
and their retention times were reported. When the entire set of solutions was
injected, the carrier solvent was changed. The new carrier solvent was passed
through the column to remove residual traces of the previous carrier. When a
stable baseline for the refractive index detector was obtained, the second set
of probes was injected.
The columns were filled with candidate membrane materials in powder
form, usually in the 38-53 μm size range (sieved). In the case of Teflon[R]
and PE powder, they were already supplied in a powder finer than the 38-53 μm
size range. As well, because of the large amount of swelling of PE in
toluene, "toluene pre-swollen" PE powder was used in the column. All of the
columns were filled by dry powder methods.

The retention volume was determined for each probe,
according to

$$V_R = t_R \cdot Q \qquad (1)$$

where V_R is the retention volume, t_R is the retention time, and Q is the carrier solvent's volumetric flow rate through the column. These are shown in Table 1 for the heptane carrier solvent case, and Table 2 for the toluene carrier case.

DISCUSSION

Because the candidate membrane materials' surface areas are unavailable and the solvent retention volumes were not determined, direct comparison between the data for the different materials in Tables 1 and 2 cannot be made. However, the relative ability to retain aromatic components can be compared. This can be quantified by calculating the ratios of retention volumes for various compounds and comparing these directly for the different candidate materials. These pairs were chosen on the basis of similar carbon atom content to minimize diffusion and steric exclusion effects. These are shown in Table 3 for the heptane carrier case and in Table 4 for the toluene carrier case.

On the basis of the information of Tables 3 and 4, the selection of materials for further study can be made. The CAB and CTA materials show the greatest selectivities for aromatics with respect to aliphatic compounds. Pyridine was also retained with respect to the aliphatic compounds for both materials, which may be taken as an indication of the preferential adsorption of polar compounds on these two materials. This shows promise for compounds heteroatoms, since they are also considered to be polar in nature. Further, the values of the ratios of Tables 3 and 4 for common pairs indicate the preferential adsorption of aromatic components is more pronounced in heptane than in toluene. This is understandable as the toluene carrier would compete with the aromatic probes for preferential adsorption. It is also an indication that the preferential adsorption of aromatic and polar components will be more pronounced in aliphatic rich naphthas.

CONCLUSIONS AND RECOMMENDATIONS

An indication of the different affinities of membrane materials for probe compounds chosen from naphtha components can be determined by affinity chromatography. Work of this nature should be continued with candidate membrane materials to determine their suitability for naphtha upgrading. Of the materials tested, cellulose triacetate and cellulose acetate butyrate demonstrate affinity for aromatic probes when compared with aliphatic probes. A test of their performance for the upgrading of naphtha should be made, since methods for reverse osmosis membrane fabrication with these two materials are available in the literature.

REFERENCES

1.   Steere, D.E., MacDonald, W.A., Stone, D.H., Hydrocarbon Process 263;
     September 1981.
2.   Farnand, B.A., Talbot, F.D.F., Matsuura, T., Sourinajon, S., Ind Eng Chem
     Process Des Dev 22: 179; 1983.
3.   Farnand, B.A.; Talbot, F.D.F., Matsuura, T., Sourirajan, S., Sep Sci
     Tech, (in press).
4.   Farnand, B.A., Ph.D. Thesis, Chap. 4, U. of Ottawa, (Canada); 1983.
5.   Matsuura, T., Taketani, Y., Sourirajan, S., J Colloid Interface Sci 95:
     10; 1983.
6.   George, A.E., Smiley, G.T., Sawatzky, H., CANMET Report No. 79-17; CANMET
     Energy, Mines and Resources Canada; 1979.
7.   Whittemore, I.M. in Chromatography in Petroleum Analysis, Altgelt, K.H.,
     Gown, T.H., editors, Chromatographic Science, 11: 41; 1979.

TABLE 1

RETENTION VOLUMES FOR THE HEPTANE CARRIER CASE

	CF	CA	CTA	CAB	CAHP	PE	Teflon
Cycloheptane	1.34	1.60	2.68	2.60	1.70	2.61	1.04
Methylcycloheptane.	1.39	1.56	2.68	2.57	1.78	2.70	1.10
Cyclohexane	1.36	1.56	2.60	2.60	1.52	2.76	1.12
Benzene	1.40	1.64	-	4.38	1.55	2.78	1.12
Toluene	1.36	1.64	-	3.73	1.57	2.73	1.12
p-Xylene	1.36	1.61	3.04	3.55	1.58	2.67	1.10
Ethylbenzene	1.34	1.58	3.09	3.56	1.52	2.64	1.10
Propylbenzene	1.36	1.56	3.06	3.38	1.81	2.70	1.10
Cumene	1.38	1.54	2.87	3.37	1.51	2.76	1.12
Mesitylene	1.42	1.57	2.85	3.35	1.59	2.70	1.05
Butylbenzene	1.34	1.58	2.82	3.18	1.51	2.64	1.03
Naphthalene	1.40	1.66	2.69	6.48	1.56	2.78	1.16
Methylnaphthalene	1.38	1.60	3.33	5.85	1.51	2.73	1.09
bis-Phenol	1.36	1.65	4.41	7.03	1.67	2.76	1.05
di-Butylbenzene	1.43	1.56	2.58	2.69	1.62	2.67	1.04
2,2-Dimethylbutane	1.32	1.58	2.68	-	-	2.73	-
Hexane	1.38	1.73	-	-	1.69	2.76	1.19
Heptane	-	-	-	-	-	-	-
i-Octane	1.35	1.81	-	2.56	1.79	2.32	1.13
Hexadecane	1.36	1.54	2.52	2.27	1.46	2.47	0.99
Tetratetracontane (C44)	1.31	1.53	-	2.15	1.39	-	-
1-Hexene	1.35	1.83	-	-	-	2.75	1.08
1-Nonene	1.35	1.58	2.60	2.50	1.51	2.64	1.09
Pyridine	1.48	1.81	npk	npk	npk	2.78	1.28
Toluenethiol	-		-	-	-	2.67	1.08
Material Weight, g	0.586	0.688	0.622	1.250	0.913	0.382	0.471
Average Flowate, mL/min.	0.267	0.288	0.271	0.294	0.222	0.273	0.270

npk = peak was not eluted or visible, equivalent to a large value.

TABLE 2

RETENTION VOLUMES FOR THE TOLUENE CARRIER CASE

	CE	CA	CTA	CAB	CAHP	PE	Teflon
Cycloheptane	1.47	1.59	3.30	2.14	1.74	2.74	1.20
Methylcycloheptane	1.49	1.63	2.89	2.68	1.62	2.71	1.19
Cyclohexane	1.43	1.64	3.21	2.16	-	2.71	1.24
Benzene	1.51	1.97	-	-	1.81	2.74	1.14
Toluene	-	-	-	-	-	-	-
p-Xylene	1.49	1.90	3.74	3.27	1.73	2.71	-
Ethylbenzene	1.52	1.90	-	-	1.83	-	1.16
Propylbenzene	1.52	1.85	3.36	2.41	1.81	2.68	1.14
Cumene	1.49	1.90	-	2.16	1.78	2.71	-
Mesitylene	1.52	1.84	-	-	1.83	2.74	-
Butylbenzene	1.49	1.89	3.64	2.55	1.77	2.71	-
Naphthalene	1.47	1.75	3.02	3.06	1.87	2.62	-
Methylnaphthalene	1.49	1.74	3.06	2.35	1.84	2.59	1.11
bis-Phenol	1.49	1.67	2.78	2.32	1.83	2.56	1.13
di-Butylbenzene	1.52	1.86	-	1.98	1.93	2.74	1.26
2,2-Dimethylbutane	1.49	1.67	3.73	2.19	1.81	2.65	1.18
Hexane	1.49	1.72	3.15	-	1.74	2.80	1.15
Heptane	1.44	1.64	3.15	2.11	1.78	2.68	-
i-Octane	1.47	1.63	3.04	2.09	1.71	2.59	-
Hexadecane	1.49	1.67	3.06	2.35	1.42	2.59	1.15
Tetratetracontane (C44)	1.49	1.88	-	-	.80	-	-
1-Hexene	1.49	1.74	3.34	2.74	1.78	2.74	-
1-Nonene	1.49	1.67	3.06	2.05	1.75	2.71	-
Pyridine	1.49	1.90	3.67	npk	1.77	2.77	1.27
Toluenethiol	-	-	-	-	-	2.56	1.12
Material Weight, g	0.586	0.688	0.662	1.250	0.913	0.382	0.471
Average Flowate, mL/min.	0.293	0.322	0.306	0.297	0.297	0.188	0.293

npk = peak was not eluted or visible, equivalent to a large value.

TABLE 3

RATIOS OF RETENTION VOLUMES WITH HEPTANE AS THE CARRIER SOLVENT

Solute A/Solute B	$V_{R,A}/V_{R,B}$						
	CE	CA	CTA	CAB	CAHP	PE	Teflon
toluene/i-octane	1.01	0.91	-	1.46	0.88	1.17	0.99
benzene/hexane	1.01	0.95	-	-	0.92	1.01	0.94
ethylbenzene/i-octane	1.00	1.05	-	1.57	0.85	1.14	1.11
toluene/methylcyclohexane	1.01	1.05	-	1.45	0.88	1.01	1.02
benzene/cyclohexane	1.02	1.05	-	1.68	1.02	1.01	1.00
bisphenol/hexadecane	1.00	1.07	1.75	3.10	1.14	1.12	1.06
propylbenzene/1-nonene	1.01	0.99	1.17	1.35	1.20	1.02	1.01
pyridine/2,2-dimethylbutane	1.12	1.14	a	a	a	1.02	-
Average, Aromatic/Aliphatic	1.01	1.01	-	1.85	0.95	1.08	1.02

a No peak for pyridine was eluted, which implies a large value for $(V_{R,A}/V_{R,B})$.

b The inverse of 0.85 is 1.18. This can also be used to compare with the other values in this table.

TABLE 4

RATIOS OF RETENTION VOLUMES WITH TOLUENE AS THE CARRIER SOLVENT

| Solute A/Solute B	$V_{R,A}/V_{R,B}$						
	CE	CA	CTA	CAB	CAHP	PE	Teflon[R]
benzene/hexane	1.01	1.15	-	-	1.04	0.98	0.99
ethylbenzene/i-octane	1.03	1.17	-	-	1.07	-	-
benzene/cyclohexane	1.06	1.20	-	-	-	1.01	0.92
bisphenol/hexadecane	1.00	1.00	0.91	0.99	1.29	0.99	0.98
p-xylene/heptane	1.00	1.16	1.18	1.55	0.97	1.01	-
propylbenzene/1-nonene	1.02	1.14	1.10	1.18	1.03	0.99	-
pyridine/2,2-dimethylbutane	1.00	1.14	0.98	-	0.98	1.04	1.08
Average, Aromatic/Aliphatic	1.02	1.14	1.05	1.27	1.09	1.00	0.96
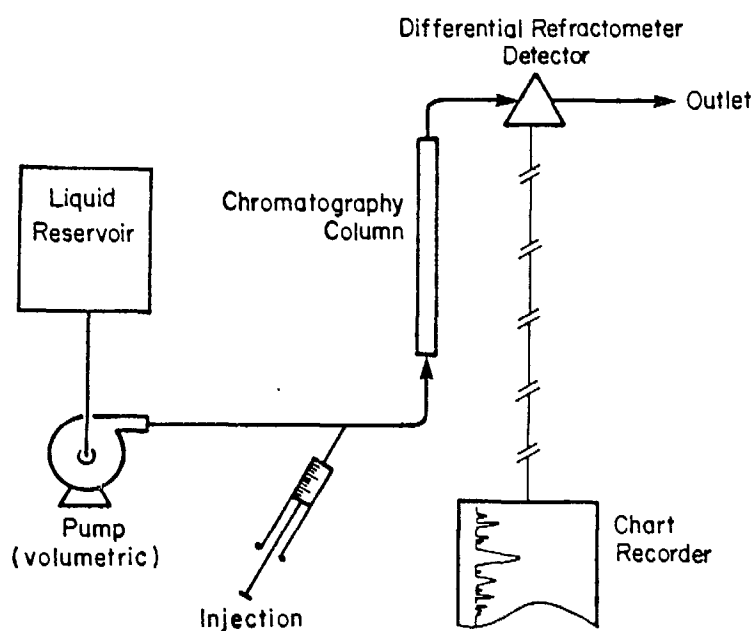
Figure 1. Schematic Diagram of Liquid Chromatographic Apparatus.

ERL/CAT 84/85 058