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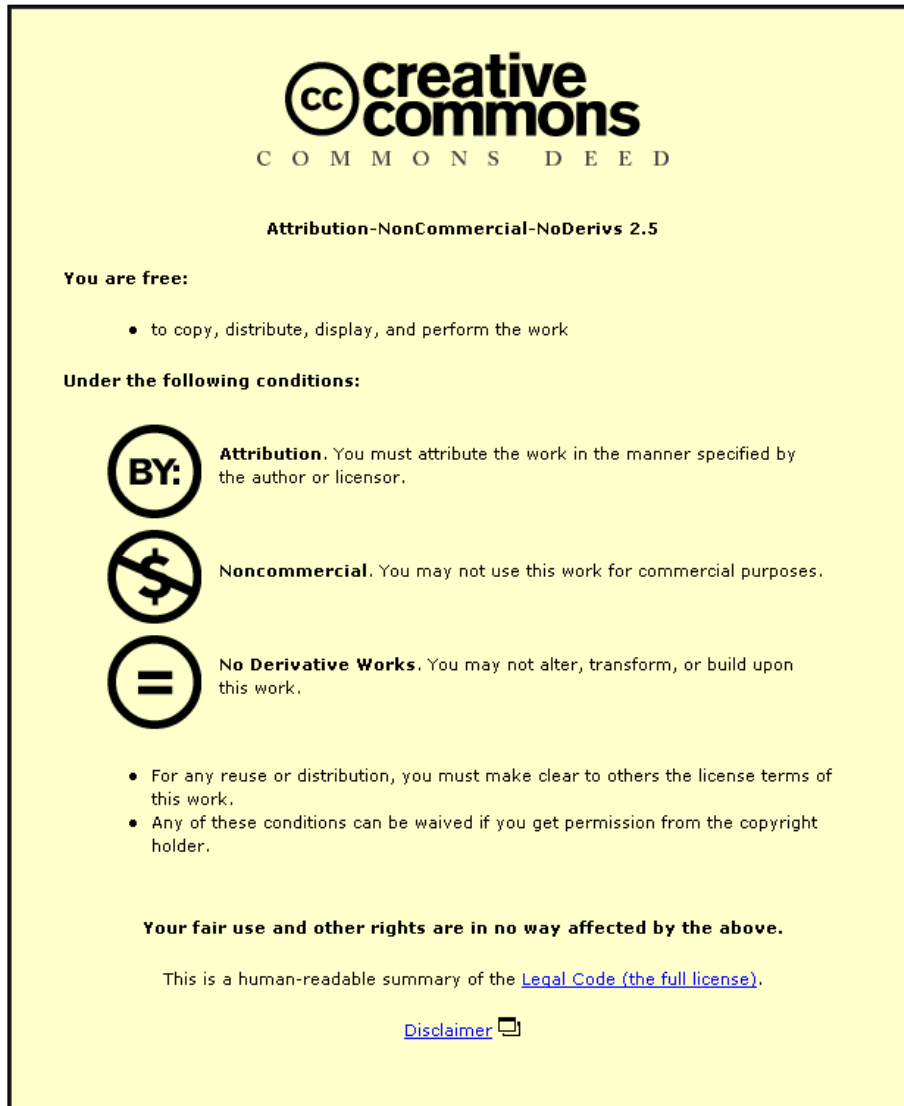
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NANOFILTRATION – A METHOD FOR SOLUTE REMOVAL FROM FUEL SIMULANTS

E.S. Tarleton¹ (e.s.tarleton@lboro.ac.uk) and J.P. Robinson²

¹ Advanced Separation Technologies Group, Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK.

² now at School of Chemical, Environmental and Mining Engineering, University of Nottingham, Nottingham, NG7 2RD, UK.

ABSTRACT

The separation characteristics of a dense polydimethylsiloxane (PDMS) membrane were studied using alkyl and aromatic solvents and low-polarity, sulphur bearing, organometallic (OM) and polynuclear aromatic (PNA) solute compounds. Rejection was found to be dependent on trans-membrane pressure, crossflow rate (hydrodynamic conditions), solute size and the degree of swelling induced by the solvent. Rejection increased progressively with pressure whilst a threshold condition was observed above which further increases in crossflow had a negligible influence on rejection. Measurements over the molecular weight range 84-612 g/mol showed the membrane to have a cut-off in the region 350-400 g/mol to all but one of the tested PNA compounds (rubrene). An additional correlation using molecular dimensions instead of molecular weight showed the cut-off size to be in the region of 1-2 nm, with all data falling on a well defined rejection/size curve.

Solvent type influenced membrane swelling to an extent dependent on the relative magnitude of the solubility parameters for the solvent and PDMS; similar values led to more swelling, higher fluxes and lower rejections. Results support the concept of viscous solvent flow whilst solute transport could be either predominantly viscous or a combination of viscous and diffusive. With larger molecules a size exclusion mechanism was dominant.

KEYWORDS

Nanofiltration; Membranes, PDMS; Organic solvents; Separation; Solvent resistant membranes; Fuel simulants

INTRODUCTION

In recent years the possibility of using polymeric nanofiltration (NF) membranes for non-aqueous separations has been explored, examples include the recovery of organometallic catalysts from organic solvents¹ and the de-acidification of vegetable oils². There is, however, limited understanding of the fundamental mechanisms involved. The literature favoured concept for non-aqueous NF systems is solution-diffusion where permeation takes place by a substance dissolving in the membrane material and subsequently diffusing through it. An alternative approach is the pore flow model, where even a dense membrane is considered to behave as if it had an appreciable free volume and pores through which viscous permeation takes place. In this study low-polarity solvents and low, but representative, concentrations of solute were used to both enhance the understanding of non-aqueous NF processes and assess the potential for applying the technology in (liquid) hydrocarbon processing; see also³⁻⁷.

EXPERIMENTAL

All experiments used a polyacrylonitrile (PAN)/polydimethylsiloxane composite membrane supplied by GKSS Forschungszentrum. The PAN substrate was inactive³ whilst the radiation crosslinked and selective PDMS layer exhibited a nominal thickness of 2 μm . A single membrane was used to

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obtain the reported data. No preconditioning of the membrane was required prior to an experiment and no appreciable deterioration in flux/rejection performance was observed over the duration of the study. The solvent induced swelling of the composite membrane layers was completely reversible⁷.

The solvent/solute systems were studied in the crossflow membrane filtration apparatus shown schematically in Figure 1. The solvent/solute mixture was added to reservoir (A) from which an air-driven pump (B) delivered the fluid to the membrane module (C) via a variable area flow meter (F), a flow control valve (V6) and a 15 μm rated pre-filter (D). The permeate could either be circulated back to the reservoir or collected separately for subsequent sample analysis. The retentate stream returned to the reservoir through a cooler (E). Trans-membrane pressure and crossflow rate were controlled primarily by the back-pressure regulator (V7) and the air-regulator to the pump (V2). The maximum pressure and crossflow obtainable with this apparatus were 800 kPa and 0.7 l min^{-1} respectively. A second apparatus was also available on a limited basis which facilitated filtration pressures up to 2000 kPa and crossflow rates of 4 l min^{-1} . In both apparatus the circular, flat sheet membrane was mounted in a standard, and un-modified, Osmonics DESAL membrane module to give a wetted surface area of 75 cm^2 .

n-heptane, cyclohexane and xylene solvents were used in the experiments as fuel simulants, all of which were supplied by Sigma-Aldrich. n-heptane is a straight chain alkane, whilst cyclohexane and xylene are respectively cyclic alkane and aromatic compounds. The two solute compounds forming the main focus of the study were iron (III) acetylacetonate (an organometallic, OM) and 9,10-diphenylanthracene (a poly-nuclear aromatic, PNA). A few data were also obtained with other representative PNA, organometallic and sulphur bearing compounds (see Table 1). Solute concentrations up to 75 ppm were used and determined by UV/vis spectroscopy. All the experiments were performed using one litre of the chosen solvent/solute mixture and a 10% stage cut. Prior to an experiment the test solution was circulated for several minutes with no permeation to remove any trapped air in the system. With the pressure and crossflow set to the desired values, the permeate was circulated back to the reservoir for 10 mins. in order to establish equilibrium conditions. The permeate was then diverted and collected in a separate vessel, this sample being used to determine the flux and solute concentration.

RESULTS AND DISCUSSION

Experiments addressed the influence of the principal operating parameters on solute rejection, namely crossflow rate, trans-membrane pressure, solute concentration, solute size and membrane swelling. The latter is interlinked with the effects of the other operational parameters and presented accordingly.

Effects of Crossflow Rate (Hydrodynamics)

The rejection of 9,10 diphenylanthracene was determined at a fixed pressure of 500 kPa. Three pure solvents and one solvent mixture were employed with crossflow rates ranging from 0.1–4 l/min ; in the case of cyclohexane and the n-heptane/xylene mixture the crossflow was limited to 0.7 l/min due to operational difficulties with the second, up-rated apparatus.

In all cases rejection increased as crossflow was raised, an effect also observed with the other tested solutes (Figure 2). Above a threshold value of $\sim 0.5 \text{ l/min}$, little increase in rejection was noted for n-heptane and xylene solvents up to the highest available crossflow of 4 l/min . The rejection behaviour of the cyclohexane solvent was intermediate between these two pure solvents and the n-heptane/xylene mix, whose composition gave a solubility parameter of $\delta = 16.8 \text{ MPa}^{0.5}$, showed marginally improved rejection. A potential reason for the threshold is a transition in the hydrodynamic flow regime above the membrane surface as characterised by the Reynolds Number (Re). The module design prevented the calculation of Re as the flow velocity and flow diameter

are unknown. However, as the module dimensions were the same in each test, and the flow velocity is proportional to crossflow rate, $Q\rho/\mu$, a similar expression to Re , can be used to compare rejection behaviour (see Figure 3); Q is the crossflow rate, ρ is solvent density and μ is solvent viscosity.

As intuitively expected, the data in Figure 3 are similar in form to those presented in Figure 2. Whilst an absolute value of $Q\rho/\mu$ is only valid for the DESAL module, the results are significant as they show how hydrodynamics can influence separation in NF, and that an optimum crossflow rate (in terms of rejection) is just above the threshold value. Figures 2 and 3 also clearly show that solute rejection is dependent on solvent type and is a consequence of the degree of solvent induced swelling in the selective PDMS layer of the membrane. Previous work by the authors^{3,4} showed that the level of solvent flux can be directly related to membrane swelling and the relative magnitude of δ for the permeating solvent and membrane. The current work extends this finding where solvents inducing a larger amount of swelling yield lower solute rejection than poorer-swelling solvents. The solubility parameters of xylene, cyclohexane and n-heptane are 18.2, 16.8 and 15.3 MPa^{0.5} respectively, which is consistent with the order in which the rejection data appear in Figure 3 (i.e. $\delta_{n\text{-heptane}} \approx \delta_{PDMS}$ to give the greatest swelling and lowest rejection). Further evidence that solute rejection is strongly dependent on the solvent induced swelling was obtained by testing a solvent mixture; no separation of solvents was detectable on passage through the membrane; measurement resolution = 0.2%. Xylene and n-heptane, respectively aromatic and straight chain alkane compounds, were added together to give a mixture with a solubility parameter the same as cyclohexane, a cyclic alkane compound. Figure 3 shows that solute rejection for cyclohexane and the n-heptane/xylene mixture overlap, not only confirming that the degree of swelling affects solute rejection, but also that solubility parameters for low-polarity solvents can be used to characterise the degree of swelling of a PDMS composite membrane.

Over the ranges tested, crossflow velocity had a limited effect on permeate flux. Given the low levels of solute present in the feed solutions, and the lack of a surface fouling layer on the membrane, this result is not surprising. Moreover, the reversibility of the membrane in terms of performance indicators infers that any internal fouling of the PDMS layer is non-permanent.

Effects of Pressure

The effects of pressure on rejection for two solute compounds was determined in a xylene solvent with the two experimental apparatus. Rejections at pressures up to 800 kPa were determined at a crossflow rate corresponding to $Q\rho/\mu \approx 10$ m which is above the threshold noted in Figure 3. Experiments at higher pressures were performed using the up-rated apparatus with $Q\rho/\mu = 45$ m. Figure 3 suggests that operating with such different $Q\rho/\mu$ values has a negligible influence on solute rejection and thus the results in Figures 4 and 5 are the sole effects of pressure.

For both solutes the rejection improved as filtration pressure increased, with the largest gains being achieved at lower pressures. The data suggest that the rejection of 9,10 diphenylanthracene lies below that recorded for iron (III) acetylacetonate; molecular weights are 330 and 353 respectively. The rejection of 9,10 diphenylanthracene was further studied in a range of solvents and the results are compared in Figure 5. In all cases the rejection improved as pressure increased, with rejection from the n-heptane/xylene mixture being comparable to that recorded using cyclohexane; in both these cases $\delta = 16.8$ MPa^{0.5}. Rejection levels with n-heptane were consistently the lowest whilst experiments with xylene displayed the highest rejections. The results confirm the indications from Figure 3 and strengthen the argument that low-polarity solute rejection is uniquely dependent on the degree of solvent induced swelling. It is noted that the data in Figure 5 are similar to those reported by Scarpello *et al.*¹ who suggest how limiting rejection with pressure is caused by compaction of the membrane that leads to a corresponding drop in flux. Whilst compaction with pressure was recorded for the PDMS layer⁷, the measured flux/pressure relationships exhibited linearity over the tested pressure range, with the slope being determined by

the chosen solvent. Hence, increased rejection with pressure is apparently not solely a consequence of a change in membrane structure.

Effects of Concentration

The rejection of 9,10 diphenylanthracene was investigated with a xylene solvent at a range of concentrations normally found in the process of interest. Figure 6 shows that for practical purposes rejection is independent of concentration. It is unlikely that concentrations in the ppm range are sufficient to influence the degree of solvent induced membrane swelling. Figure 7 shows that solvent flux is essentially unaffected by solute concentration over the range tested.

Effects of Solute Size

Experiments with additional PNA, organometallic and sulphur bearing solutes were used to examine the influence of solute size (see Table 1). Referring to Figure 8, with the exception of rubrene which gave a rejection lower than expected, the membrane exhibits a molecular weight cut-off in the region of 350-400 g/mol. Such behaviour is indicative of the selective PDMS layer rejecting low-polarity, minimally interacting solutes on the basis of size-exclusion. The data in Figures 2-5, and other data^{4,6}, suggest viscous solvent transport to an extent dependent on the degree of swelling induced porosity. A size-exclusion mechanism seems unlikely for dense membranes like PDMS as solute (and solvent) transport is intuitively diffusive. Although larger molecules can be expected to have very low diffusion rates, and thus high rejections, smaller molecules would not be expected to give zero rejections as observed in Figure 8. At least three scenarios are possible here:

- Solvent is transported via viscous flow and solute flux is diffusive (i.e. same rate)
- Solvent and solute fluxes both occur via a diffusive mechanism at identical rates
- Solvent and solute transport via a viscous flow mechanism at the same rate.

In the authors' opinion, the most feasible explanation is the latter where the solvent swells the membrane to effectively induce an ill-defined porous structure in the PDMS, and the zero rejections are due to the solvent and solute moving through the membrane structure 'as one' under viscous flow with no separation occurring. Using a more limited range of solutes, very similar behaviour to that shown in Figure 8 was measured for an n-heptane solvent, albeit with rejections ~5% below those recorded for xylene due to the increased membrane swelling.

The outlying rejection for rubrene in Figure 8 questions the validity of using molecular weight to characterise solute rejection. Due to the fine length scales involved in NF, the dimensions of the solute molecule are likely to be an important factor in determining rejection behaviour. Although there are inevitable approximations, representative sizes of the solute molecules were calculated using bond lengths and covalent radii and, where necessary, by resolving bond angles to a single plane. By way of example, the limiting rejection in xylene as a function of maximum molecule length is shown in Figure 9; the tested solvents had estimated maximum molecular dimensions of 0.8 nm or less. The data in Figure 9 give a relatively sharp transition in the region of 1-2 nm and the result for rubrene follows the data for the other solutes closely. The data in Figures 8 and 9 could be interpreted using solution-diffusion concepts as the solute diffusion coefficient will decrease with increasing solute size. Although this mechanism can't be completely dismissed, in the authors opinion the sharpness of the profile in Figure 9 is more indicative of a size exclusion/sieving mechanism. Considerable coincidence would be required for the solute sorption and diffusion coefficients to align and produce the results shown.

In Figure 9 it is likely that three distinct regions exist. In *Region A* the solvent induced swelling of the membrane causes sufficiently small solutes to translate directly with the solvent flow. In *Region C* the solute molecules are sufficiently large for high rejection to occur predominantly via a size exclusion mechanism. In *Region B* it is envisaged that a mixture of viscous flow and diffusion

could exist. Other modelling work by the authors^{5,6} supports these types of behaviour for the GKSS membrane, although when more crosslinked PDMS membranes are considered the solution-diffusion model also appears to fit adequately.

CONCLUSIONS

The rejection of low-polarity organic solute compounds in organic solvents has been shown to be dependent on solute size, hydrodynamic conditions, operating pressure and solvent induced swelling. A hydrodynamic threshold is considered to exist, above which solute rejection plateau's. For crossflow rates above the threshold, the swelling effect of the solvent was found to be the predominant factor governing solute rejection. The concept of viscous flow is supported by the observation that the rejection of low-polarity solutes is predominantly one of size exclusion. Poor-swelling solvents yield a lower flux and higher solute rejection than good-swelling solvents. It is postulated that swelling increases the free volume within the membrane, which can be interpreted as an induced pore-like structure, and that the Hildebrand solubility parameter is a good indicator of swelling potential for PDMS membranes as well as a good predictor of their likely flux/rejection behaviour.

ACKNOWLEDGEMENTS

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TABLES AND FIGURES

Designation	Solute name	Classification	M.W. (g/mol)
1	thiophene	thiophene	84
2	1-butanethiol	mercaptan	90
3	acenaphthene	PNA	154
4	anthracene	PNA	178
5	phenanthrene	PNA	176
6	ferrocene	OM	186
7	pyrene	PNA	202
8	coronene	PNA	300
9	9,10 diphenylanthracene	PNA	330
10	1,1,2,2 tetraphenylethylene	PNA	332
11	iron (III) acetylacetonate	OM	353
12	iron (III) naphthenate	OM	373
13	rubrene	PNA	532
14	copper (II) naphthenate	OM	612

Table 1: Details of test solutes (PNA \equiv poly-nuclear aromatic; OM \equiv organometallic).

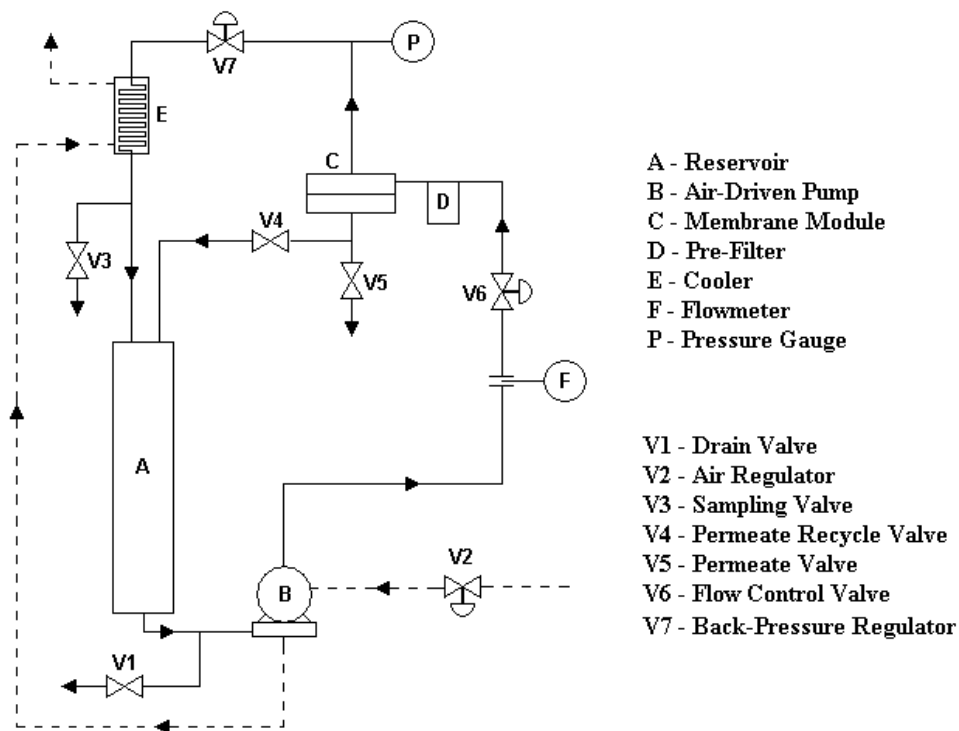


Figure 1: Schematic of the crossflow membrane filtration apparatus.

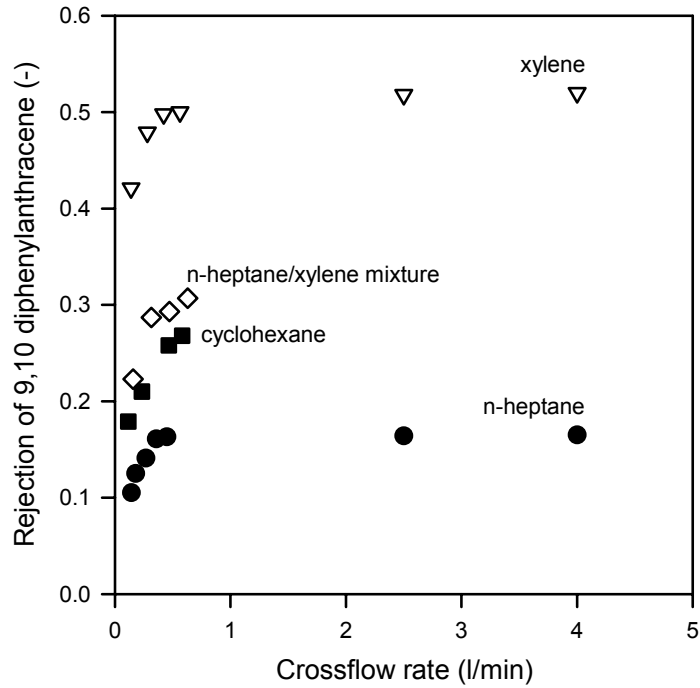


Figure 2: Effects of crossflow rate on the rejection of 9,10 diphenylanthracene at 20 ppm from four solvents.

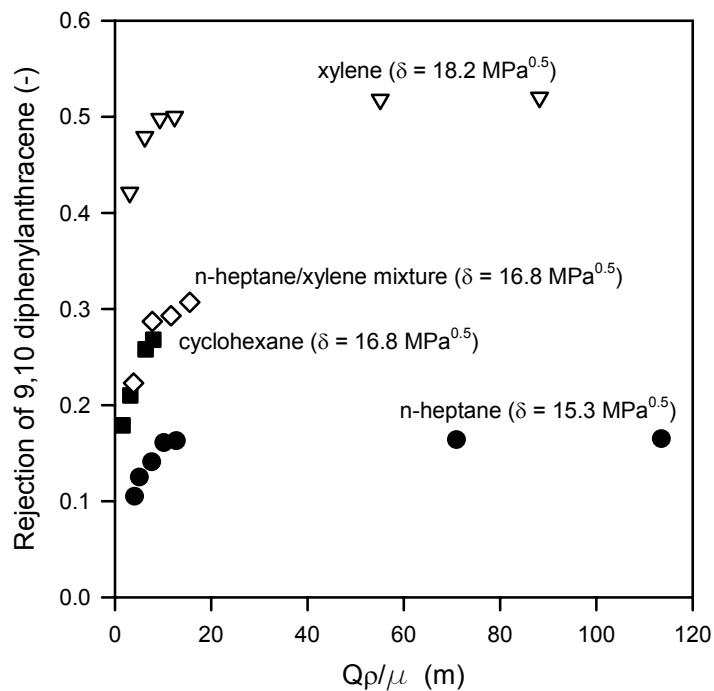


Figure 3: Effects of Reynolds Number (equivalent) on the rejection of 9,10 diphenylanthracene at 20 ppm from four solvents.

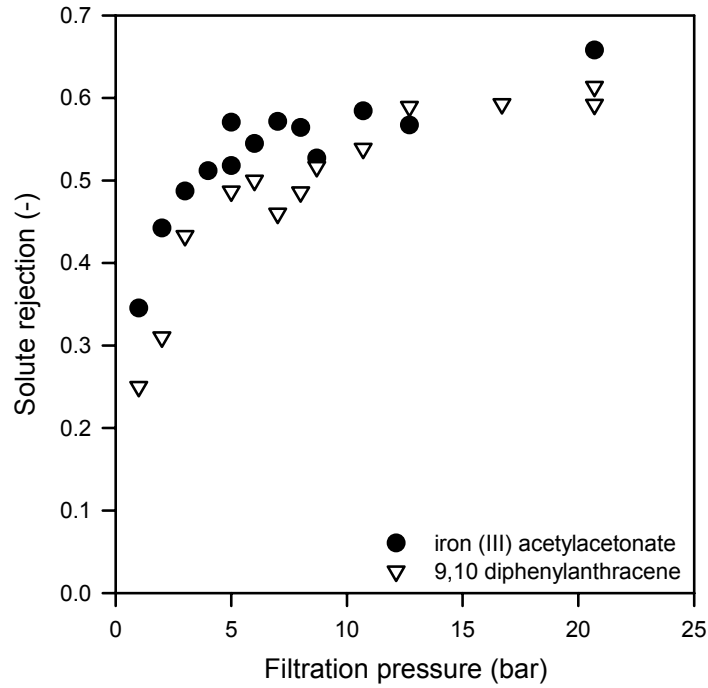


Figure 4: Effects of pressure on solute rejection from pure xylene.

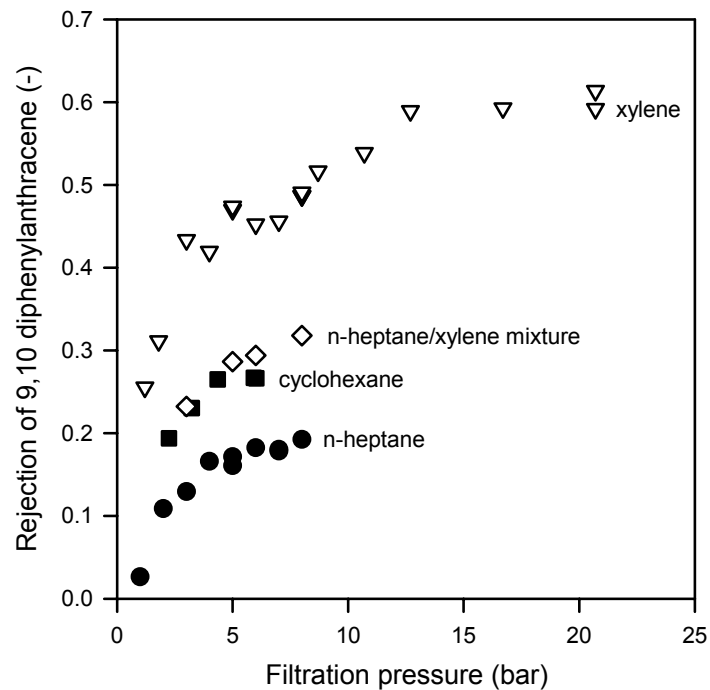


Figure 5: Effects of pressure on solute rejection from four solvents.

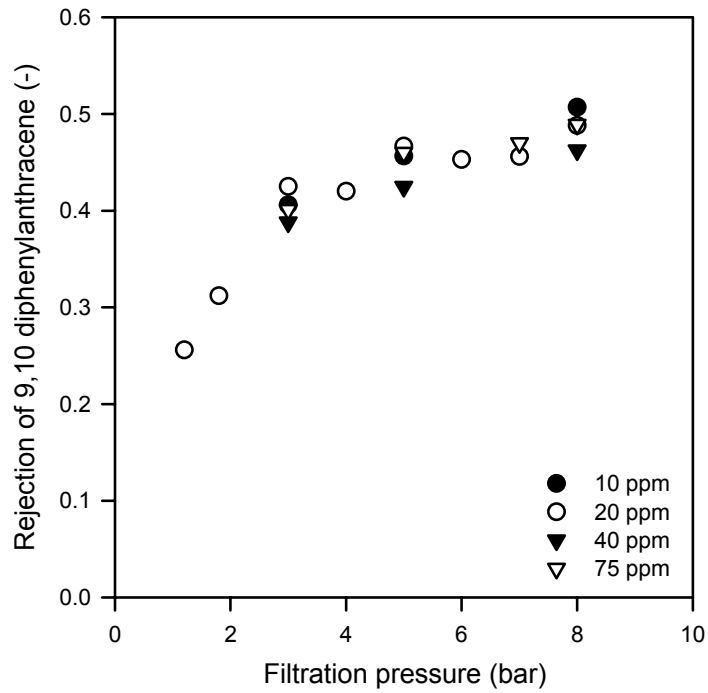


Figure 6: Effects of solute concentration on the rejection of 9,10 diphenylanthracene.

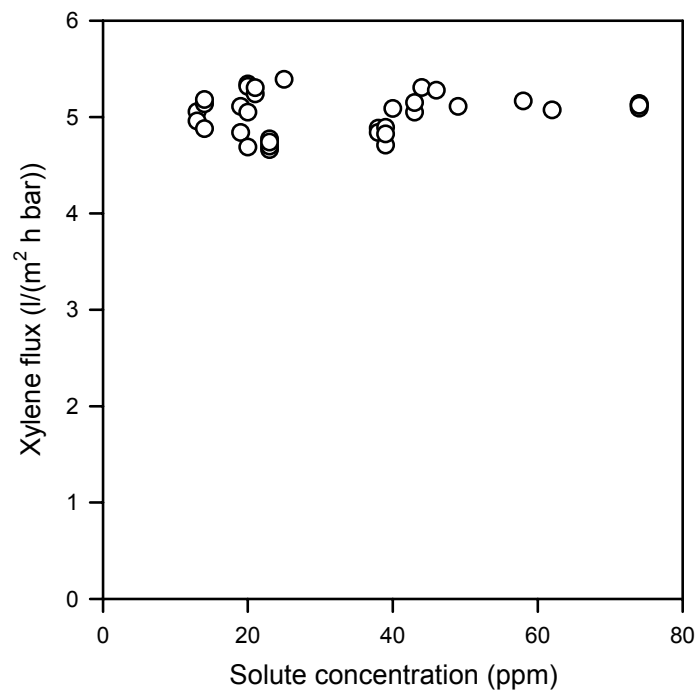


Figure 7: Effects of solute concentration on xylene flux.

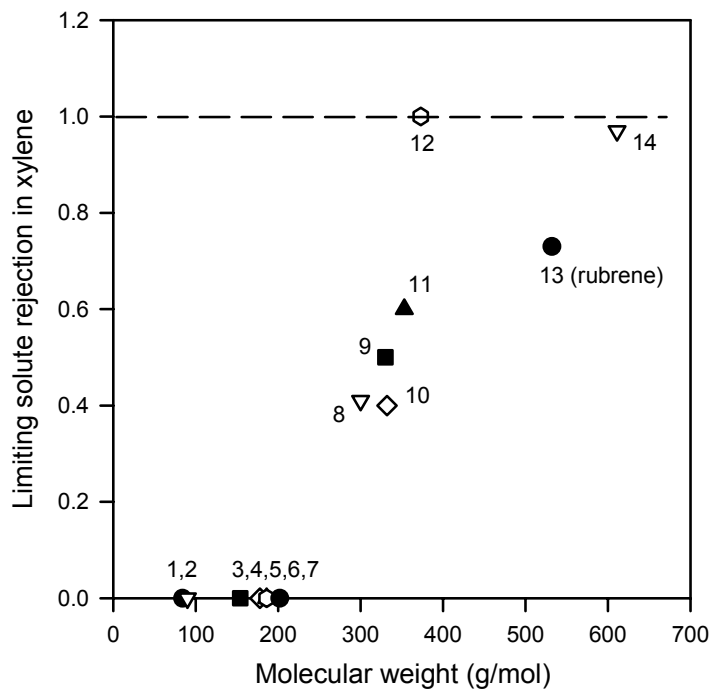


Figure 8: Effects of solute molecular weight on solute rejection from a xylene solvent.

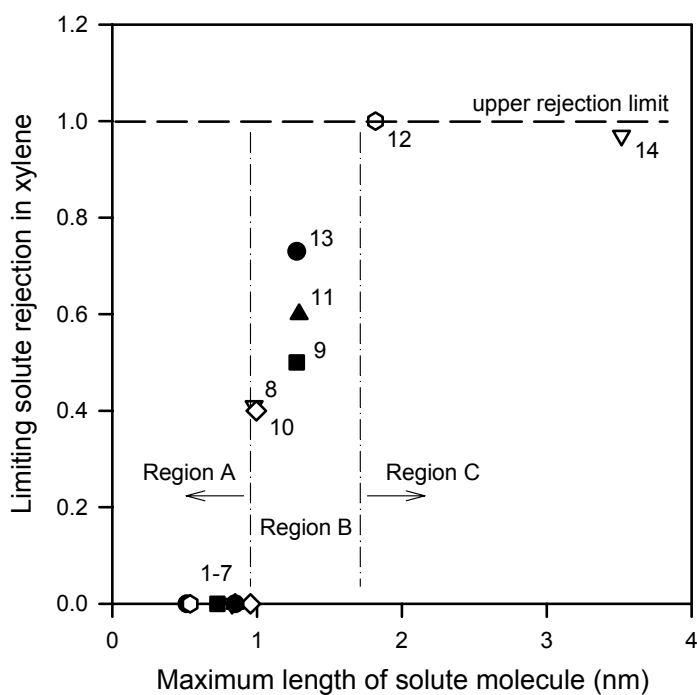


Figure 9: Effects of maximum molecular dimension on solute rejection from a xylene solvent.