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NONAQUEOUS SOLUTIONS

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ABSTRACT

The physicochemical parameters that are used to describe reverse osmosis behaviour are successful in aqueous as well as nonaqueous solutions. Independent determinations of solute-membrane interactions can be made and compared with the physicochemical parameters that describe reverse osmosis performance. This has been used to demonstrate the independence of the reverse osmosis mechanism with regard to membrane material as well as solvent. Thus, reverse osmosis can be made to perform in any solvent system with any membrane material, excluding the cases where the membrane is soluble in the solvent. Further, independent determinations of membrane-solute interactions can be used to estimate membrane performance.

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INTRODUCTION

The use of membrane processes in aqueous solutions for the separation of various components is well known and commercial installations exist for the treatment of industrial wastes and for the removal of salt from sea water. Other applications in the production of food and dairy products use membranes, but these are aqueous conditions as well. Early work with membranes indicated that they could also be used for separation of components in nonaqueous media as well as in gases. The commercial success of the treatment of water has overshadowed the use of membranes in nonaqueous media until recent developments with gas separations and the use of pervaporation for the processing of some petrochemicals. The use of ultrafiltration and reverse osmosis for the treatment of nonaqueous media has also been considered for application to industrial separations in nonaqueous media.

This work is concerned with the performance of reverse osmosis in nonaqueous solutions and demonstrating that this mechanism is independent of solvent. The description of reverse osmosis performance in nonaqueous solutions can be described by the same physicochemical parameters as in aqueous reverse osmosis, and this forms the basis for

demonstrating that they are controlled by the same mechanism. Results from experimental studies in water, methanol and ethanol solutions with the same solutes in dilute concentrations were used. These experimental results had been used to determine the physicochemical parameters of the surface force - pore flow model, and it is these parameters that can be successfully compared.

Liquid chromatography experiments can be used to determine the solute-solvent-membrane material interactions where the chromatography column packing used is made from the same polymer as the membrane. These interactions are then compared with the physicochemical parameters that were obtained from reverse osmosis experiments. Because the same interaction for several solvents including water were obtained, this demonstrates that the reverse osmosis mechanism is independent of solvent. As well, the performance of different membrane materials follows the same trend, and the reverse osmosis mechanism can be considered to be independent of membrane material.

SURFACE FORCE - PORE FLOW MODEL

This model describes reverse osmosis performance by representing the simultaneous velocity distribution and concentration distribution inside the pores of a membrane. It has been successful in describing the separation of organic solutes in dilute solutions, including permeate enrichment that occurs with aqueous solutions of phenols. Computational details of the model have been reported elsewhere, and only a brief description is presented in this work.

Israelachvili and Tabor (1973) described the interaction of an organic molecule with an infinite polar surface with a modified Sutherland intermolecular interaction potential. This includes the assumption that the organic molecule behaves as a hard sphere. In terms of membrane performance, the hard sphere behaviour of the solute molecule inside the pore represents the effect of steric hindrance. Inside the pore, the solute is assumed to be distributed as described by the Boltzmann equation. The pore is assumed to be cylindrical, and the flow of liquid through the pore is modelled by the Poiseuille equation. It is these two distributions that are combined to describe the permeation of solvent and solute through the membrane pores. The results reported in this work were obtained after

assuming that the pores were all of the same size.

The parameters that describe membrane performance for a solute are the size parameter, D , and the surface potential parameter, B . The size parameter is determined to be the distance of closest approach of the solute to the walls of the membrane pore. The surface potential parameter describes the attraction and repulsion of the solute from the walls of the pore, with negative values describing attraction to the pore surface. The surface potential energy equation is written as follows.

$$\phi(x) = \begin{cases} \infty & ; x < D \\ -BRT/x^3 & ; x > D \end{cases} \quad (1)$$

The distance of the solute molecule from the pore wall is x , and the surface potential is assumed to approach infinity as the solute (hard sphere) comes into direct contact with the pore surface.

SURFACE EXCESS CONCENTRATION AND LIQUID CHROMATOGRAPHY

The interaction of solutes with a surface can be modelled by the use of liquid chromatography. Several experiments have been performed with various carrier solvents, polymer packings and probe solutes, all chosen to represent the membrane-solution system. The concentration gradient at the polymer surface is represented by the Boltzmann distribution as

$$c_A(x) = c_{A,bulk} \exp(-\phi(x)/RT) \tag{2}$$

where c_A is the solute concentration at distance x and $c_{A,bulk}$ is the concentration of the bulk of the solution. The surface excess concentration, Γ_A , is defined as:

$$\Gamma_A = \int_0^{\infty} (c_A(x) - c_{A,bulk}) dx \tag{3}$$

The integration limits in eq 3 are from the surface of the polymer ($x=0$) to the point where the bulk concentration prevails (large x). If the hard sphere surface potential of eq 1 is used in eq 2 to describe the concentration distribution of the solute, and then substituted in eq 3 along with the hard sphere model of the solvent, eq 3 can be rearranged to

$$\Gamma_{A/c_{A,bulk}} = D - D_{\text{solvent}} + \int_D^{\infty} [\exp(-\phi/RT) - 1] dx \quad (4)$$

Chuduk et al. (1981) and Huber and Gerritse (1971) related the surface excess concentration to chromatography retention volume, $[V]$, by

$$\Gamma_A = 1/A_P \int_0^{c_A} ([V]_A - [V]_{\text{solvent}}) dc_A \quad (5)$$

where A_P is the surface area of the solid phase in the chromatography experiment and c_A is the solute concentration in the mobile phase. Chuduk et al. (1981) simplified eq 5 by demonstrating that Γ_A/c_A was constant at low concentrations so that

$$\Gamma_A/c_A = ([V]_A - [V]_{\text{solvent}})/A_P \quad (6)$$

By assuming that Chuduk et al.'s solute concentration in chromatography, c_A , is the same as the bulk solute concentration, $c_{A,bulk}$, of the surface potential energy/Boltzmann equation, eq 3 and eq 6 can be equated to give the relation of liquid chromatography and reverse osmosis performance. By obtaining the surface excess concentration of eq 6 from liquid chromatography, the surface potential parameters of D

and B can be directly related. Further, by assuming that variations caused by steric hindrance is the same for all cases, a unique relation between liquid chromatography and reverse osmosis performance can be demonstrated. The success of this relation to describe aqueous and nonaqueous performance demonstrates the universal mechanism of reverse osmosis. It should be noted that equating eq 3 and 6 requires that the membrane material used in the reverse osmosis experiments is the same as that used in the liquid chromatography experiments.

COMPARISON OF REVERSE OSMOSIS AND LIQUID CHROMATOGRAPHY

To determine the surface excess concentration, liquid chromatography data were obtained from the literature for organic solutes in water (Matsuura et al. (1981)), methanol (Farnand et al. (1983)) and ethanol (Farnand et al. (1987)). The surface potentials ^{were calculated} ~~was also determined~~ for ^{the solutes in the same} ~~these~~ solutions ^{using data} from reverse osmosis experiments and ~~the data were~~ obtained from the same references as ^{and} well as from Farnand et al. (1988). It should be noted that the surface potentials for aqueous solutions were for polar organic solutes only, because of solubility limitations. Most of the same solutes were used in the experiments with the alcohol solutions, with the limitation on analysis of organic solutes in an organic solvent. These were also polar organic solutes since their analysis was based upon their ultraviolet absorption (~~as~~ for the aromatics) and their heteroatomic content. These have been compared in Fig 1 for the three solvents and for cellulose acetate membranes.

For an exact relation of surface excess concentration from liquid chromatography to the surface potential, the size of both the solute and the solvent must be considered as shown in eq 4. Further, the assumption of a hard sphere for both the solute and the solvent may also be imprecise, especially for the case of water where organic solutes tend

to have limited solubility. For the case of limited solubility in combination with mass transfer effects at the surface of the membrane, there is a possibility that the solute may coalesce or agglomerate and behave as if the solute size was much larger than expected, with a subsequent modification to the surface potential determined in the experiment. This effect would not occur in the liquid chromatography experiments.

The relation of liquid chromatography surface excess concentration and the surface potential as demonstrated in Figure 1 suggests that the mechanism for the three solvent cases evaluated are identical. While only one type of membrane ^{material} has been included in this relation, evidence that the performance of other membranes will be identical is shown in Figure 2, where the liquid chromatography surface excess concentration and the reverse osmosis determined surface potential have been compared for cellulose, cellulose acetate and PPPH 8273, an aromatic polyamide membrane. This shows that for different membrane materials in a given solvent, the same relation shall be obtained as for a given membrane ^{material} in different solvents. It can then be assumed that all reverse osmosis cases can be described in the same manner, independent of solvent, membrane material, and solute, with the limitations of the assumptions

described above.

CONCLUSIONS

The relation of liquid chromatography results and reverse osmosis physicochemical parameters has been used to demonstrate that the reverse osmosis mechanism is independent of both the membrane material and the solvent. Reverse osmosis is controlled by the solute-membrane interactions which can be predicted by liquid chromatography or some other method. Providing that the assumptions of consistent solute and solvent size are valid, the physicochemical nature of reverse osmosis performance can be estimated by these methods.

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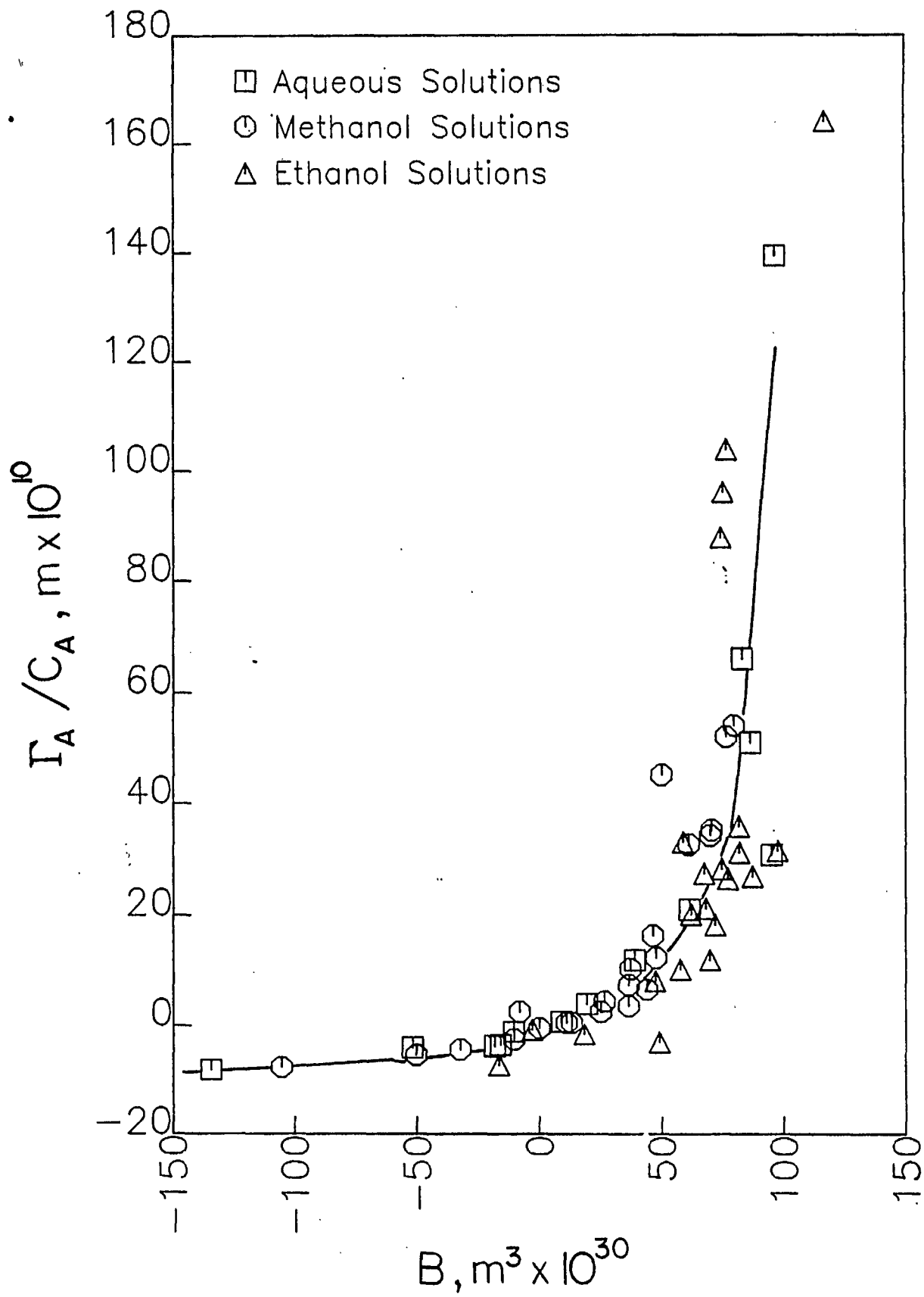
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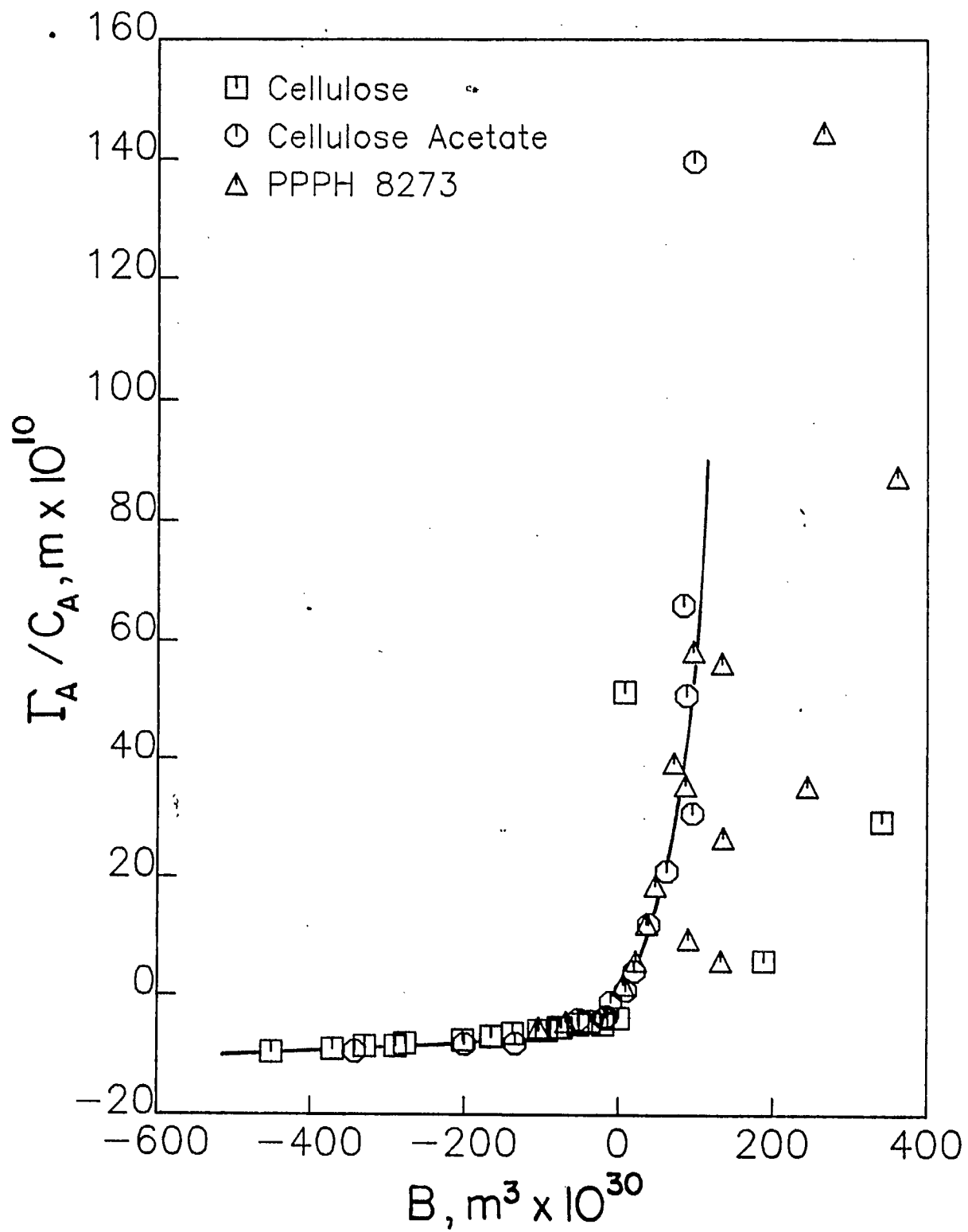
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Figure 1 Comparison of Surface Potential with Surface Excess Concentration for Methanol, Ethanol, and Water for Cellulose Acetate Membranes.

Figure 2 Comparison of Surface Potential with Surface Excess Concentration for Cellulose, Cellulose Acetate, and Polyamide Membranes in Aqueous Solutions.





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