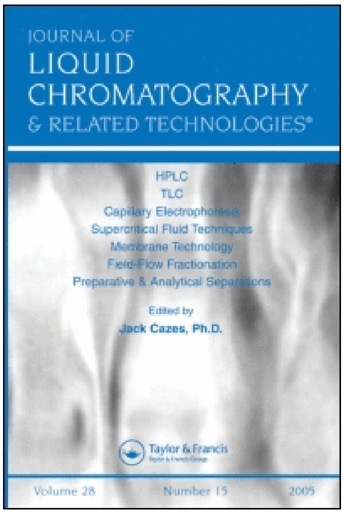

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RETENTION CHARACTERISTICS OF INORGANIC SALTS AND POLYETHYLENE GLYCOLS ON POLYSULFONES

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Abstract

Polysulfone interfacial properties were determined using HPLC. The equilibrium distribution coefficients for a series of inorganic salts as well as a series of poly-ethylene glycols with different molecular weights are presented. The difference in solute-polymer interactions are explained in terms of differences in the polymer structure. Hansen's solubility parameter was used to quantify this difference in polymer structure.

Introduction

Membrane separations are governed in part by the surface interactions occuring between the polymer-solute-solvent system. Matsuura *et al.* [1,2] have proposed that an analogy can be drawn between the retention behaviour of a solute under liquid chromatography conditions and the physiochemical interactions at the solute-membrane interface. Membrane materials can therefore be characterized based on liquid chromatography data. Surface properties of membrane materials such as cellulose acetate have been throughly studied based on such liquid chromatography techniques [3,4,5].

Polymers other than cellulose acetate are also made into membranes. Aromatic polysulfones are another type of material commonly used for commercial membranes. Aromatic polysulfones have good film forming properties as well as excellent mechanical, chemical and thermal characteristics. Polysulfones are therefore preferrable to cellulose acetate for some applications. Although a great deal of work has been done on the mechanism of membrane formation and the separation characteristics of polysulfone membranes [6], relatively little data is available concerning the interfacial properties of these polymers.

In this work, retention behaviour for a series of salts as well as polyethylene glycols (PEG) of different molecular weight is reported for three types of polysulfones. The retention behaviour for polysulfones are compared to that of cellulose acetate. The difference in the distribution coefficient is attributed to basic changes in polymeric structure. This difference in polymer structure and the subsequent change in interfacial property is related using Hansen's solubility parameters. Such determination of surface interactions is important for the characterization of membrane materials.

Theory

Distribution Coefficient

The relationship between the LC-system and the membrane-solution interface can best be visualized in Figure 1. In the LC system, as water flows past the polymer surface, a stationary phase is formed. This phase can be considered to be similar to the interfacial layer in the case of the membrane system. The mobile phase in the LC system can be considered to be equivalent to the bulk solution in the membrane system.

For the LC system, a distribution coefficient (K_a) is defined as the ratio of the concentration of a solute in the moble phase (c_m) and the concentration of the solute in the surface influenced stationary phase (c_s), so that

$$K_a = \frac{c_s}{c_m}. \tag{1}$$

Based on a mass balance of the solute in the chromatography system, a capacity factor (k'_a) relates the retention volume of the solute (V_r) to a retention

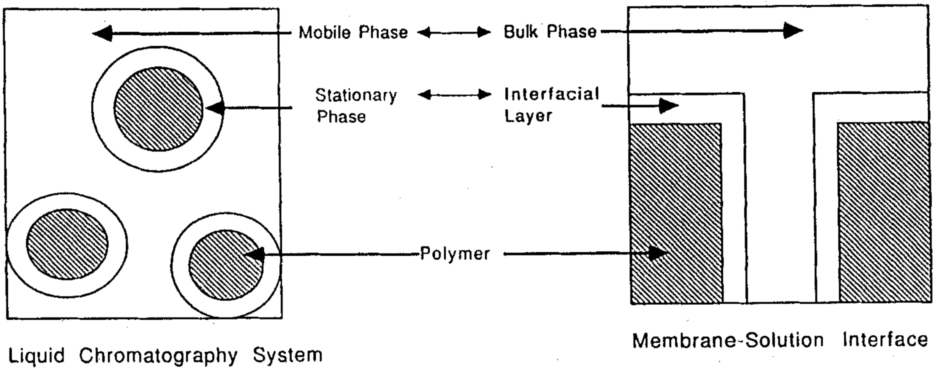


Figure 1: Relationship between LC system and Membrane-Solution Interface.

volume of a mobile phase (V_m),

$$V_r = V_m + k_a' V_m. \tag{2}$$

The capacity factor by definition is the mole ratio of solute in the stationary phase and in the mobile phase. This capacity factor can be related to the distribution coefficient by

$$k_a' = \frac{V_s}{V_m} K_a \tag{3}$$

where V_s is the retention volume for the stationary phase. Rewritting Equation 2 in terms of the distribution coefficient yields,

$$V_r = V_m + V_s K_a. \tag{4}$$

The minimum retention volume (V_{min}) for a particular solute and the retention volume (V_{D_2O}) for deuterated water are introduced in order to solve for K_a in Equation 4. The minimum retention volume includes both the dead volume as well as the volume of the mobile phase. V_{min} can best be visualized as the volume that one would obtain if a designated reference solute travels the same path as the mobile phase without the influence of the polymer surface. Therefore, the value is a direct measure of both the dead volume as well as the retention volume of the mobile phase. The stationary volume is obtained from the injection of deuterium oxide (D_2O) into the system. D_2O is assumed to experience the same interaction as water in the column. The difference between the retention volume of D_2O and the volume due to the mobile phase (V_{min}) will then be the stationary phase volume (*ie.* $V_s = V_{D_2O} - V_{min}$).

The distribution coefficient as a function of the retention volume of the solute can therefore be obtained,

$$K_a = \frac{V_r - V_{min}}{V_s} \tag{5}$$

$$= \frac{V_r - V_{min}}{V_{D_2O} - V_{min}} \tag{6}$$

A simple application of liquid chromatography data to membrane material characterization is to consider retention data as a measure of the strength of affinity between the material and the solute. A distribution coefficient that is greater than one means there is strong attraction of the solute for the packing material. Similarly, a K_a value less than one indicates a rejection of the solute. Thus, chromatography data can be used to choose the appropiate membrane material. If the separation requires transport of the solute throught the membrane (preferential sorption of the solute) then a material that have a distribution coefficient of greater than one should be chosen. When the separation requires the transport of the solvent through the membrane (rejection of the solute) than the material required should have a distribution coefficient that is less than one. An extermely large K_a value indicates extremely strong attraction between the material and solute and increases the possibility of fouling during membrane operations.

Polymer Solubility Parameters

The concepts represented by Hansen's solubility parameters can be used as a quantative description of the differences in the polymer. Hansen [7] subdivided molecular interactions into three basic parameters. The dispersive parameter, δ_d, describes the attractive force resulting from random fluctuations of the electron clouds. The polar parameter, δ_p, describes the strength of attraction as a result of fluctuating atomic dipoles. The hydrogen bonding parameter, δ_h, describes the hydrogen bonding ability of the polymer. The total solubility parameter, δ_t, is defined as

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}. \tag{7}$$

δ_t is by definition a measure of the cohesive energy density of the polymer per unit volume. Solubility parameters are frequently used in choosing the appropriate solvent for a polymer. The choice for best solvent being a substance that have similar solubility parameter as the polymer. Since solubility

Table 1: Solubility Parameters for Various Substances.

Polymer	V cm^3/mol	δ_d $MPa^{\frac{1}{2}}$	δ_p $MPa^{\frac{1}{2}}$	δ_h $MPa^{\frac{1}{2}}$	δ_t $MPa^{\frac{1}{2}}$	Reference
CA-398	816.2	15.6	15.9	11.9	19.0	[18]
CA-398	816.2	18.5	12.7	11.0	25.0	[8]
Victrex	172.8	18.7	2.5	9.8	21.3	a
Radel	313.8	18.7	1.9	7.9	20.4	a
Udel	366.2	18.1	1.2	7.3	19.5	a
Udel	-	18.1	4.7	5.5	19.4	[16]
EG	-	-	-	-	32.9	[8]
PEG 600	-	-	-	-	20.5	[15]
PEG 1000	-	-	-	-	20.1	[15]
PEG 4000	-	-	-	-	19.4	[15]
PEG (MW = 36)	-	17.7	11.1	9.2	22.8	b
PEG 200	-	-	-	-	21.4	b
PEG 300	-	-	-	-	21.1	b
PEG 400	-	-	-	-	20.8	b
PEG 600	-	-	-	-	20.5	b
Water	18.0	15.6	16.0	42.3	48.1	[8]

a - calculated from group contributions.

b - calculated from regression equation : $\delta_p = \delta_s - \sqrt{500.78 + 40.415 \ln Mw}$.

parameters ultimately measures the intermolecular attractions of the polymer repeating group, they are related to the molecular actions at interfaces. Hansen solubility parameters have been used to describe interactions at interfaces [8], and has been related to liquid chromatography data [9].

Experimentally determined solubility parameter for polysulfones are not available but can be calculated based on the group contribution method proposed by Van Krevelen [10]. The values for cellulose acetate can be obtained from the literature. The calculated solubility parameters as well as literature data for the substances under discussion are summarised in Table 1.

The physio-chemical difference of cellulose acetate (CA-398) can be compared to polysulfones based on solubility parameters. CA-398 has larger values of δ_p than the polysulfones. The dispersive solubility parameter for the cellulose acetate is similar to the values for the polysulfones. Victrex can be considered to be the base structure for the family of polysulfones. Victrex has low values for δ_p but high values for δ_d. In Udel, the addition of a carbon and two methyl groups to the basic Radel repeating unit, reduce its solubility parameter. The estimates based on group contributions are reasonable approximations to the actual solubility parameter of the polymer. Table 1 shows a comparision between the value calculated from group contributions for Udel and reported values.

The solubility parameter for polyethylene glycols (PEG) is estimated by another method. The solubility parameter varies with the molecular weight of the substance. A relationship between solubility parameter and molecular weight can be derived by first considering the variation of intrinsic viscosity with the solubility parameter and then consider the change in intrinsic viscosity with the molecular weight.

Mangaraj *et al.* [11] proposes the following relationship relating intrinsic viscosity ($[\eta]$) to solubility parameters.

$$[\eta] = [\eta]_{max} \cdot \exp(\frac{V_s}{RT}(\delta_s - \delta_p)^2) \tag{8}$$

where V_s is the molar volume for the solvent, $[\eta]_{max}$ is the maximum intrinsic viscosity for various solvents, R is the gas constant, δ_s and δ_p is the solubility parameter for the solvent and polymer respectively.

The intrinsic viscosity for a polymer solution varies with the polymer molecular weight (Mw) according to Mark-Houwink-Kahn-Sakurada (MHKS) [17] equation , so that,

$$[\eta] = KMw^{\alpha}, \tag{9}$$

where K and α are the MHKS constants.

Combining Equation 8 and 9, the change in solubility parameter with the molecular weight can be obtained.

$$[\eta]_{max} \cdot \exp(\frac{V_s}{RT}(\delta_s - \delta_p)^2) = KMw^{\alpha} \tag{10}$$

therefore,

$$(\delta_s - \delta_p)^2 = \frac{RT}{V_s}(\alpha \ln Mw + (\ln K - \ln[\eta]_{max})). \tag{11}$$

Based on Equation 11 and data listed in Kawakami *et al.* [15], the variation of the solubility parameter with the molecular weight for PEG can then be obtained.

Figure 2 is a plot of the natural logarithm of Mw and the square of the solubility parameter difference between water and PEG. The solubility parameter for the test solutes (PEG 200, PEG 300, PEG 400 and PEG 600) are calculated from this fitted equation. The result is tabulated in Table 1. The regression coefficient for the equation is 0.98. The MHKS exponent (α) can be calculated from the slope of the fitted equation as a further check on the validity of Equation 11. The slope of the line is the value $\frac{\alpha RT}{V_s}$. The slope obtained from the fitted equation is 40.42. Given that the molar volume for

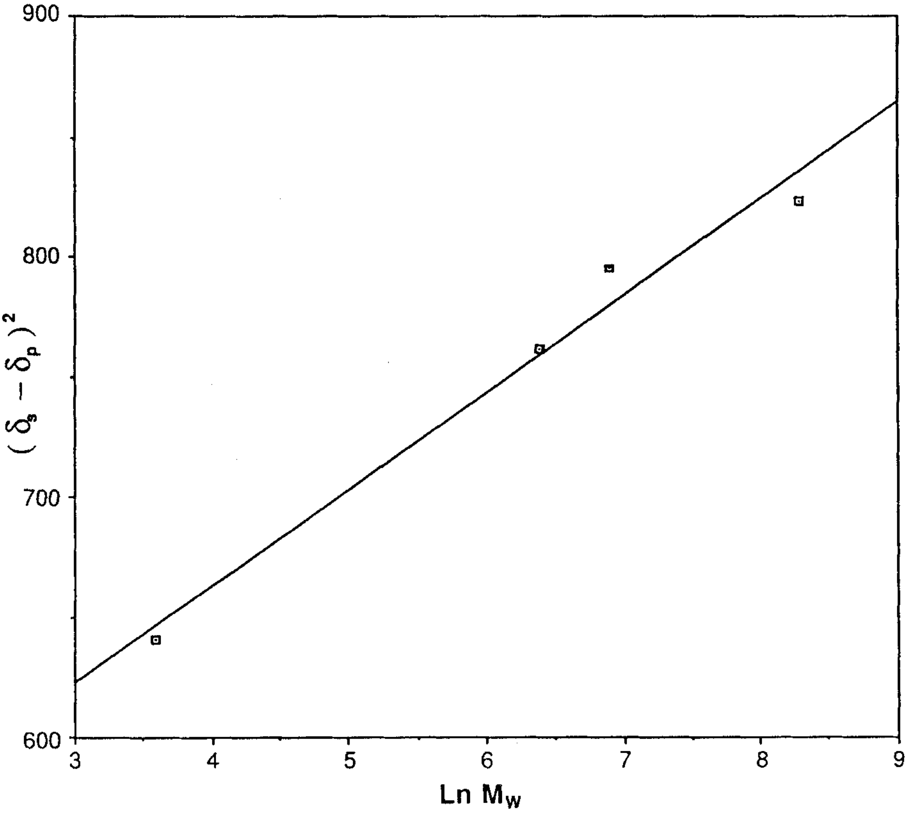
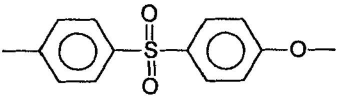


Figure 2: Relationship Between the Square of the Solubility Parameter Difference between Water and PEG ($(\delta_s - \delta_p)^2$) and the Natural Logarithm of Molecular Weight of PEG.

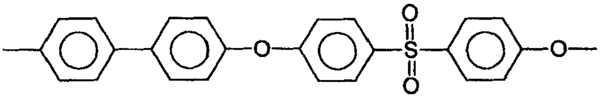
water is 18.0, the MHKS constant for polyethylene glycol is estimated to be 0.3. This α value compares reasonably well with the literature value of 0.5 [12].

Experimental

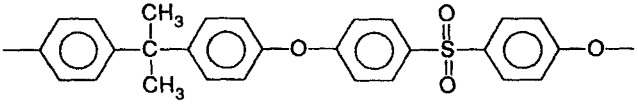
Three types of polysulfones used in this study were polyether sulfone (Victrex), bis-phenol-A-polysulfone (Udel), and polyphenylsulfone (Radel). All



Victrex Polyethersulfone



Radel Polyphenyl Sulfone



Udel Polysulfone

Figure 3: Polysulfone Structures.

three polymers contain a polyether sulfone group in their repeating unit. Their structures are shown in Figure 3. Polymers used for the chromatography experiments were obtained directly from the supplier. Udel was obtained from Amoco Performance Products; Victrex was purchased from ICI America Inc.; and Radel was acquired from Union Carbide.

Column packing was made by spray - atomizing a twenty weight percent polymer-solvent (1-methyl 2- pyrrolidone) solution into open air and precipating the fine droplets into water [13]. The final polymer beads were spherical as observed under an optical microscope. The particles were sieved to obtain a narrow particle size distribution between 38-53 μm. The polymers were bounced packed into a 60 cm (1/8" OD.- 0.020 Wall 304 SS) chromatography column.

Solutes were all analytical grade reagents and were used without further purification. The inorganic salts were obtained from Aldrich Chemical Company, and the PEG's were purchased from Fluka Chemical Corp. . The mobile phase (water) was processed through a Millipore ultrapure water system (Milli-Q) to ensure water purity.

The liquid chromatography system consisted of a Waters Associate liquid chromatography pump (model M510) fitted with the Waters R4000 differential refractometer. The data was stored directly on an IBM compatible

Table 2: Inorganic Salts Distribution Coefficients for Various Polysulfones and Cellulose Acetate

Solute	Victrex	Radel	Udel	CA-398 [14]
LiCl	1.13	1.18	0.00	0.25
NaCl	1.29	0.84	0.35	0.30
KCl	0.80	1.00	0.25	0.34
RbCl	1.14	0.98	0.69	0.34
NH_4Cl	2.62	0.72	0.01	0.24
NaF	1.22	2.28	0.35	0.21
NaCl	1.29	0.84	0.35	0.30
NaBr	0.83	1.77	1.48	0.42
NaI	1.57	0.66	0.41	0.43
$MgCl_2$	0.00	0.00	0.21	0.09
$CaCl_2$	0.57	1.30	0.39	0.16
$BaCl_2$	0.67	0.77	0.42	0.16
$SrCl_2$	0.00	0.92	0.71	0.18
KCl	0.80	1.00	0.25	0.34
KBr	0.61	0.52	0.31	0.45

micro-computer. The solvent flow rate was set at 0.3 cm^3 per minute. The concentration of the solute was 1g solute / 100 g water. The column and refractometer was maintened at a constant room temperature (25 °C) by a circulator bath. The time between the injection of the solute and the appearance of the maximum detector response was defined as the retention time for the solute. At least three 50 μL injection was made for each solute. An average value for the retention volume was used to calculate the distribution coefficient.

Results and Discussions

Table 2 summarizes the iorganic salts distribution coefficients obtained for the three polysulfones. The values for CA-398 were calculated using the data from Kiso and Kitao [14]. The distribution coefficients data shows that inorganic salts were rejected by both cellulose acetate and Udel (ie. $K_a < 1$). Victrex has K_a values that is close to one. This means that interactions between Victrex and inorganic salts were similar to the interactions between

Table 3: Polyethylene Glycols Distribution Coefficients for Various Polysulfones and Cellulose Acetate

Solute	Victrex	Radel	Udel	CA-398 [18]
Ethylene Glycol	1.10	1.50	0.83	-
PEG 200	2.18	4.99	3.25	-
PEG 300	3.57	13.84	9.71	-
PEG 400	8.48	73.39	34.16	-
PEG 600	31.59	1.57	1.00	0.53
PEG 1000	1.48	-	-	0.50
PEG 1530	0.98	-	-	0.52

Victrex and water. The same observation can also describe the behaviour of Radel.

Kiso and Kitao [14] reported that the distribution coefficient increases with the increase in the ionic size of the salts for CA-398. No such trend was evident for the polysulfones even though both cationic and anionic size were varied. Retention data therefore indicates that polysulfone-solute interactions are not affected by increases in charge density. Polysulfone interfaces are less electrically active than cellulose acetate interfaces. This conclusion is supported by the calculated solubility parameters of celulose acetate and the polysulfones. δ_p for polysulfone is much less than that of CA-398 and consequently the polar forces for polysulfones could be considered to be much lower than for cellulose acetate.

Table 3 lists the distribution coefficients generated for various molecular weights of polyethylene glycols. The distribution coefficients for polyethylene glycol are greater than one which indicated there is an affinity between polyethylene glycols and polysulfones. This attraction increases with the PEG molecular weight up to a certain molecular weight then the K_a value decreases. This sudden drop in K_a is attributed to the effect of size exclusion of the packing material. Size exclusion occurs when the PEG molecule is too large to travel the same path as the other smaller molecules (such as the

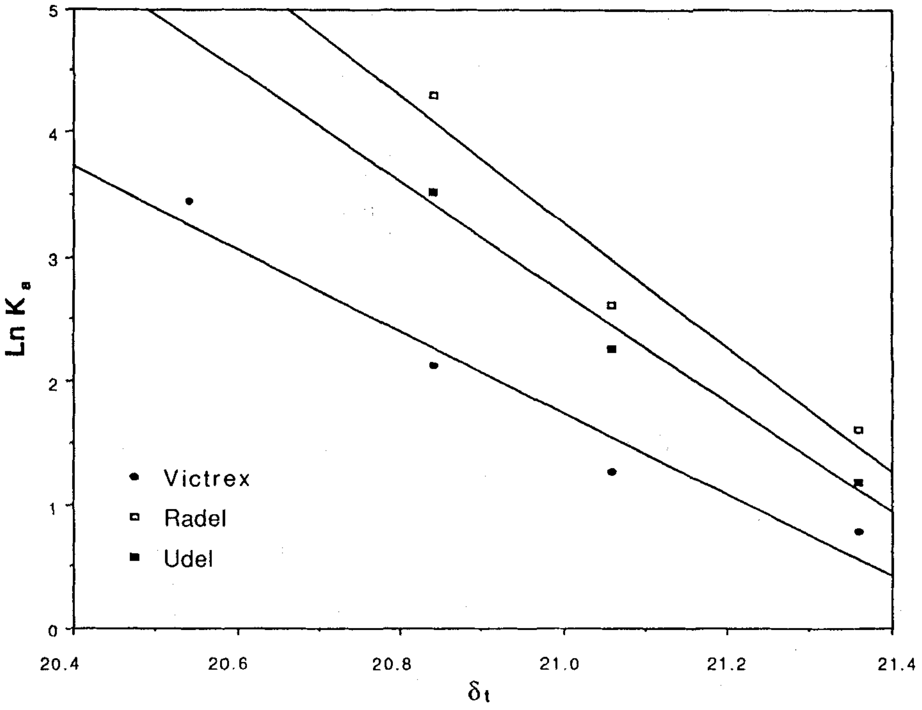


Figure 4: Plot $\ln K_a$ vs. δ_t for PEG and Various Polysulfones.

solvent). Consequently, the molecule can travel faster throught the column. The end result for large PEG molecules is a smaller retention time and a lower value of K_a. The K_a value for such high molecular weight PEG's are no longer measuring surface forces.

Figure 4 shows the linear relationship between the natural logarithm of K_a and the solubility parameter for polyethylene glycol. This relationship can be explained by considering the solubility parameter of PEG and the polymer. The total solubility parameter for the polysulfones ranges from 19.5 $\mathrm{MPa}^{\frac{1}{2}}$ (Udel) to 21.3 $\mathrm{MPa}^{\frac{1}{2}}$ (Victrex). The total solubility for PEG decreases from 21.4 $\mathrm{MPa}^{\frac{1}{2}}$ (PEG 200) to 20.5 $\mathrm{MPa}^{\frac{1}{2}}$ (PEG 600). As the total solubility parameter for the PEG decreases, there is a tendency for the PEG to be in the stationary water phase. This increase in K_a is an illustration of the increase in attraction between substances of similar solubility parameter.

Table 4: Slope and Regression Coefficient for $\ln Ka$ vs. δ_t for PEG.

Polymer	Slope	r^2
Victrex	-3.3	0.96
Radel	-5.1	0.95
Udel	-4.5	0.98

Forces of attraction are strongest for substances of similar solubility parameter. This result follows the same reasoning as using solubility parameter for choosing the "best" solvent for a polymer. The criteria for best solvent being the solvent with similar solubility parameter as the polymer and thus implying that the polymer-solvent interactions are strongest. The same underlining concept exists in this case. The attraction between PEG and the polysulfone increases as the PEG solubility parameter approaches that of the polysulfones.

Retention data can also determine the difference in interfacial properties between the three types of polysulfones. Table 4 lists the slope and the regression coefficient for the three polysulfones. The slope obtained from the linear regression equation describes the strength of interaction between polyethylene glycol and polysulfone. The slope represent the change in $\ln K_a$ (a measure of interfacial forces) with the change in solubility parameter (a measure of solute cohesive forces). A large value for the slope indicates a stronger interactions between the polymer and the PEG. The strength of interaction increase in the order of

$$\text{Udel} \simeq \text{Radel} > \text{Victrex}.$$

Udel and the Radel polymer have similar strength of interaction for PEG because of their similar solubility parameter. Victrex have less interaction with PEG.

Conclusion

The inorganic salt distribution coefficient for cellulose acetate and Udel polysulfones were experimentally determined to be less than one while distribution coefficient for Victrex and Radel is close to one. There was no significant change in the distribution coefficient for polysulfones as the ionic size of the solute was varied. The results was interpreted as a difference in the polar solubility parameter of the cellulose acetate and the polysulfones. Cellulose acetate is more polar as a material and thus retention behaviur is affected by the charge of the solute. Polysulfones are less polar, and consequently, solute charge does not play as important a role in their retention behaviour. There was strong attraction between PEG's of various molecular weights and polysulfones. This strength of interactions was measured by the slope of the $\ln K_a$ vs. $\ln \delta_t$ graph.

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