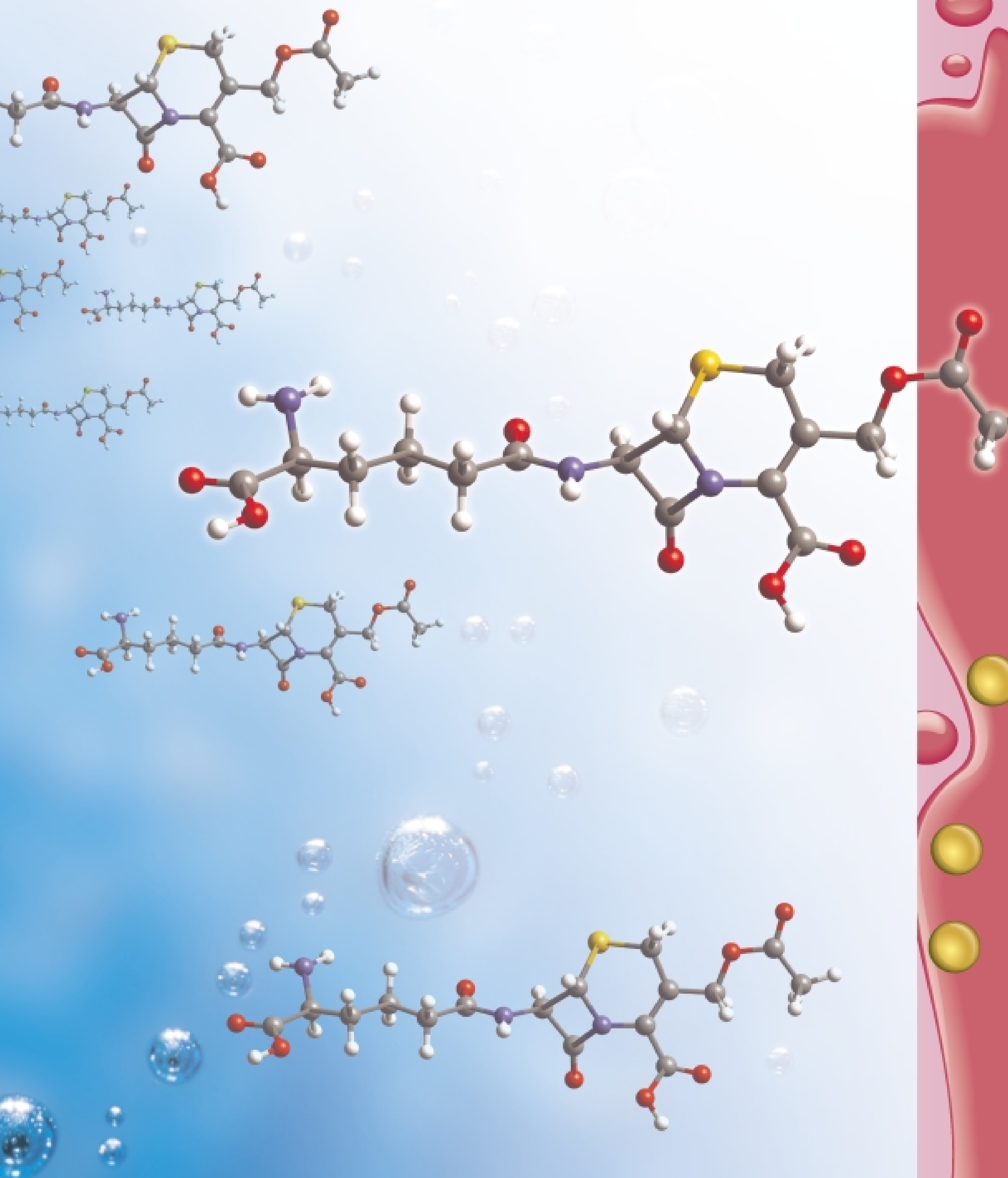
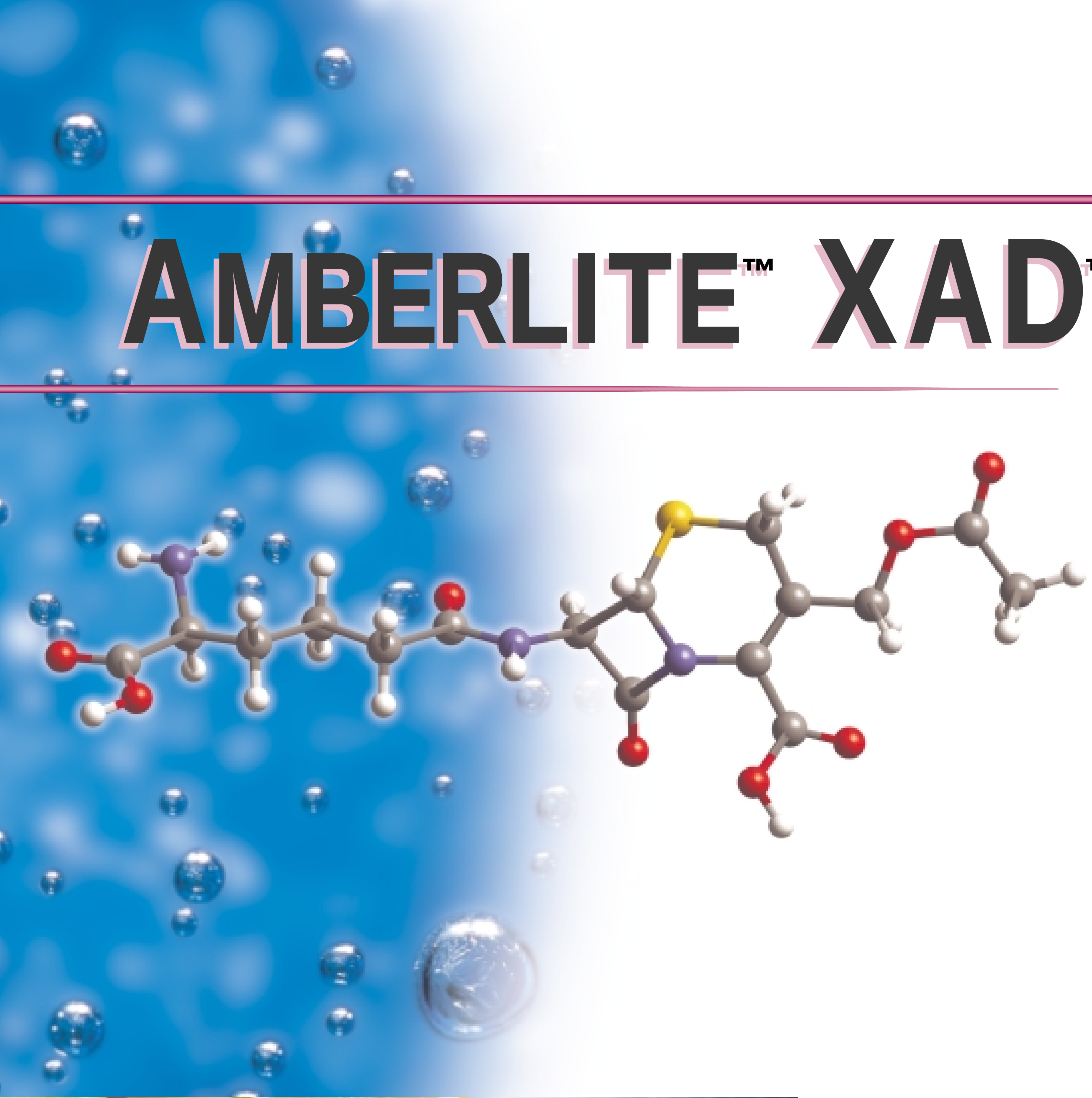
ROHM AND HAAS

AMBERLITE™ XAD™

POLYMERIC ADSORBENTS



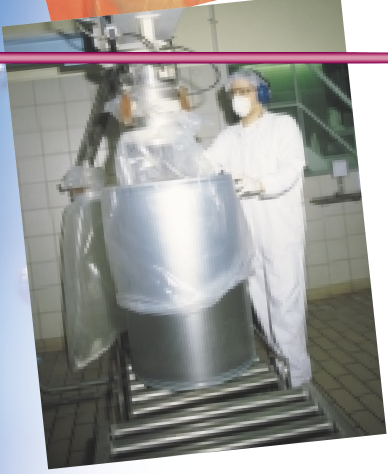
AMBERLITE™ XAD™



Polymeric adsorbents can be thought of as highly porous structures whose internal surfaces can adsorb and then desorb a wide variety of different species depending on the environment in which they are used. For example, in polar solvents such as water, polymeric adsorbents exhibit non-polar or hydrophobic behaviour and so can adsorb organic species that are sparingly soluble. This hydrophobicity is most pronounced with the styrenic adsorbents (dipole moment = 0.4 debye).

In non-polar solvents, such as hydrocarbons, etc. most adsorbents exhibit slightly polar or hydrophilic properties and so will adsorb species with some degree of polarity. This polarity is most pronounced with the acrylic adsorbents (dipole moment = 1.83 debye) and the phenolic adsorbents (dipole moment = 1.63 debye).

The adsorption of a particular species can also depend upon its similarity to a particular polymeric adsorbent on the basis that “like attracts like” - hence acrylic and phenolic adsorbents also have important applications in aqueous media. In many cases, it is the product of interest that is adsorbed onto the resin and so the elution of the product is also important and is considered in a separate section.



DECIDING ON WHICH ADSORBENT

The following is a brief description of one type of methodology that can be used to determine which type of polymeric adsorbent could be useful in a particular application. It is by no means exhaustive or very detailed since many other factors can influence whether a particular species will be adsorbed onto a polymeric adsorbent. As such, it is hoped that it will serve as a useful guide to some initial experimental work in this area.

A summary of the decision steps taken is given below :

- Nature of the solvent
- Functionality of solute
- Polarisation
- Size of solute.

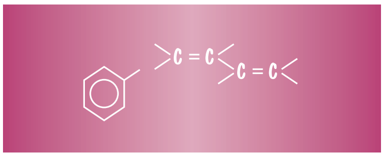
NATURE OF THE SOLVENT

Since the majority of the known applications for polymeric adsorbents are in the aqueous phase, this will be taken as the example. Hence the first decision, that of the nature of the solvent, is to move towards polar solvent on the diagram (see page 4-5). The next decision is related to the bulk properties of the solute itself. For this, the solutes can be divided into two arbitrary classes "I" and "II" as explained below.

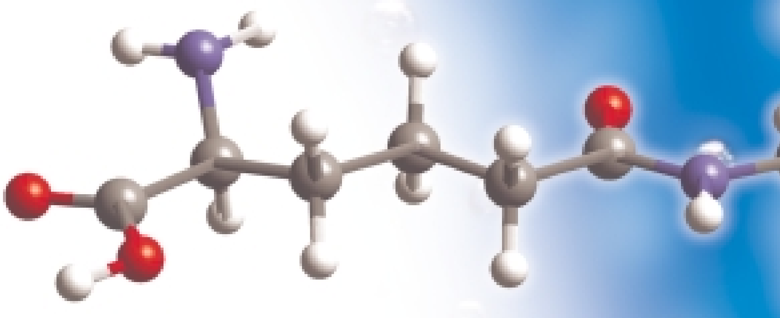
FUNCTIONALITY OF SOLUTE

"Class I" solute can be thought of as having one or more of the following characteristics :

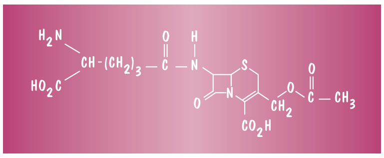
- Aromatic groups such as : Examples include benzene, toluene, xylene and molecules such as carotene.



- High local electron density due to the presence of atoms within the molecular structure such as nitrogen, sulphur, chloride or bromide. If these atoms are oxidised to any degree then the solute could also be recovered by means of ion exchange.



There are many examples of this type of molecule but perhaps one of better known is that of Cephalosporin C.



Simpler molecules include all of the chlorinated hydrocarbons such as MDC, EDC, etc.

“Class II” solutes can be regarded as those whose structure contains predominately saturated C-C bonds with few areas of high electron density. Examples of these types of solutes include proteins/peptides, amino-acids, vitamins and hydrocarbons such as cyclohexane.

POLARISATION

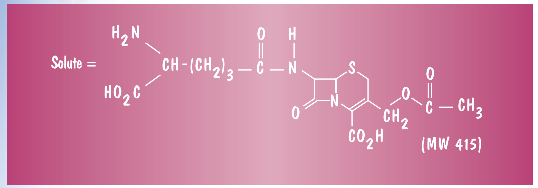
A further subdivision can be made by determining whether the solute has groups that can be easily polarised or not. This is an arbitrary decision but can be related to the dipole moment or dielectric constant of a particular species.
For example, - CO_2H and - NH_2 groups can be regarded as easily polarisable and capable of hydrogen bonding, whereas groups such as $>C=O$ or ethers, whilst they can be polarised under extreme conditions, are not normally so.

This type of classification is intended only as a guide to the points to note in certain applications and not as a definitive approach.

SIZE OF SOLUTE

The next important parameter that then needs to be considered is that of the size of the target molecule. One useful definition is that small molecules are defined as having a molecular weight < 1000 D whilst large molecules have a molecular weight > 10,000 D.
To demonstrate this type of decision tree, there now follows a number of worked examples based on the above methodology.

① CEPHALOSPORIN C FROM AN AQUEOUS FERMENTATION MEDIA



Solvent = water

Decision [1] Polar solvent.

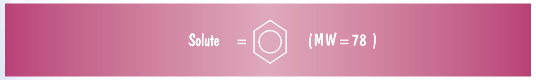
Decision [2] “Class I” due to the presence of the S and N groups but also due to the many C=O groups.

Decision [3] Polarisable due to the - CO_2H and - NH_2 groups.

Decision [4] Small molecular weight <1000 D.

Hence suitable resins for an initial trial would be AMBERLITE XAD4 and AMBERLITE XAD16.

② BENZENE FROM AN AQUEOUS WASTE STREAM



Solvent = water

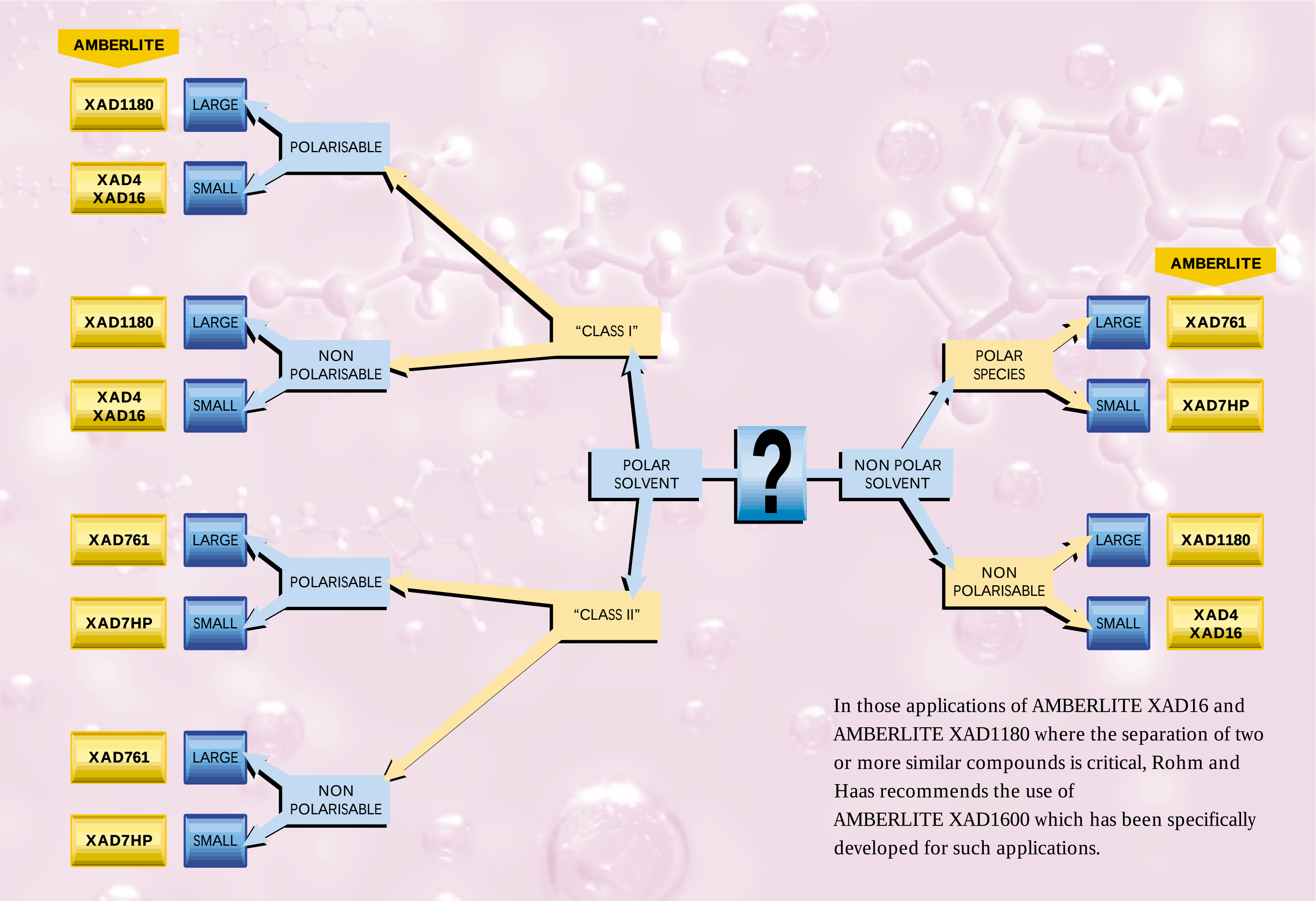
Decision [1] Polar solvent.

Decision [2] “Class I” due to its aromatic nature.

Decision [3] Non polarisable.

Decision [4] Small molecular weight <1000 D.

Hence, AMBERLITE XAD16 and AMBERLITE XAD4 should be studied.



In those applications of AMBERLITE XAD16 and AMBERLITE XAD1180 where the separation of two or more similar compounds is critical, Rohm and Haas recommends the use of AMBERLITE XAD1600 which has been specifically developed for such applications.

ELUTION AND REGENERATION

Both the elution and regeneration of polymeric adsorbents can be thought of as the same basic process in which the attractive forces between the solute and the polymer are sufficiently weakened so that the solute is removed from the resin. In the cases where the solute is the product of interest, then careful elution is required to obtain a purified product. For regeneration, the solutes are considered as impurities and the most important criteria is to return the polymeric adsorbent to its original state without due regard to the solute.

THERMAL DISSOCIATION

The interaction between the solute and the polymer is relatively weak when compared to pure ionic or covalent bonding. In some cases, the attractive forces can be disrupted simply by raising the temperature and there are examples where steam and even hot water (60°C) can be used to either elute or regenerate polymeric adsorbents.

However, many of the applications of polymeric adsorbents involve the isolation of products that are sensitive to temperature. This is particularly true of some of the important antibiotics and enzymes of the pharmaceutical and biotechnological industries. In this type of application, other methods of weakening the solute-polymer interaction need to be developed and these can be divided into two broad categories depending on whether the solute itself is modified or the environment.

SOLVENT / SOLUTE INTERACTIONS

A solute can also be desorbed from a polymeric adsorbent by changing the solvent so that the new solvent has a higher affinity for the polymer matrix. For example, if a solute was originally adsorbed from a purely aqueous medium, then the use of a solvent, such as acetone, could disrupt the interaction by better solvating the solute. In some cases a solvent / aqueous mixture may be sufficient to remove the solute and the use of a gradient can give selective desorption of certain species.

CHANGES IN THE SOLUTES

If the solute contains either a weakly ionic or a polarisable functionality then this can also be used to either adsorb and then desorb the product. Some of the important applications of polymeric adsorbents involve the isolation of weakly acidic or basic compounds. Adsorption usually takes place at a pH where the product has no net charge. The subsequent desorption step takes place at another pH where the solute exists as a weakly charged entity. The technique has been found useful in some application particularly where a buffer is used to elute a product and some very selective separations have been demonstrated.

In all cases, the chemical and physical stability of the polymeric adsorbents themselves allows for a wide range of conditions to be studied in order to determine the optimum absorption and desorption conditions in any application.

EXPERIMENTAL NOTES

ADSORPTION ISOTHERM DETERMINATION

One of the best methods to compare different polymeric adsorbents on the laboratory scale for a given application is to perform batch adsorption isotherms. In this case, the capacity of the polymeric adsorbent for a particular solute is determined by contacting a known amount of polymeric adsorbent with a number of different solute concentrations and then plotting the results on a log-log graph using a derivation of the following equation :

$$x/m = K\,C^{1/n}$$

$$\log x/m = \log K + 1/n \log C$$

where

x/m = Quantity of solute adsorbed / Quantity of polymeric adsorbent

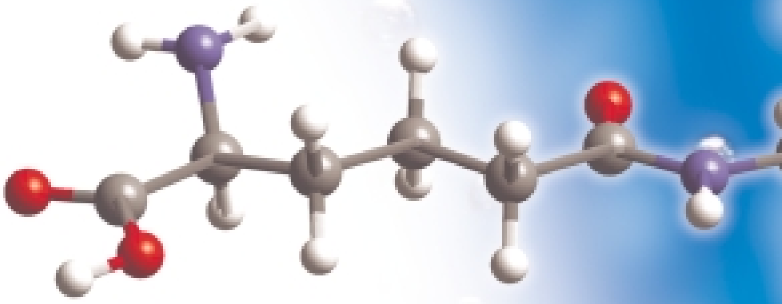
C = Residual concentration of adsorbed solute

$1/n$ = Slope of the isotherm

EXPERIMENTATION

There are two types of experiments that can be performed to determine which polymeric adsorbent could be most suited to a particular application.

The simplest of these is the batch stir where a volume of polymeric adsorbent is contacted with a particular solution for a certain length of time. This allows the adsorption isotherm to be determined as indicated above and hence an equilibrium capacity of the polymeric adsorbent. This approach is particularly suited to applications where the polymeric adsorbent is to be used to concentrate a single solute. In terms of an expected capacity then typically for a small molecule such as an antibiotic or peptide, a capacity of 30 - 100 mg / ml of polymeric adsorbent should be attainable. This depends on the application itself but as a guide, initial experiments should lead to use these figures.



Example : A 100 ml solution contains a solute of 5 mg/ml concentration. The solute is relatively small and so with an expected capacity of 50 mg/ml of resin, it is suggested that 10 ml of resin be contacted with the solution for 24 hours with small aliquots being taken at 15 mins, 30 mins, 1 hr, 2 hr, 4 hr, 8 hr and 24 hr to determine the rate of adsorption. On a practical note, magnetic stirrer should not be used in a batch stir and the preferred method of ensuring intimate contact is to either use a shaker table or an overhead stirrer.

In most applications, a separation of two or more species will be required and in this type of application the batch stir experiments will not give clear results; it will give very poor results. In these cases, it is advisable to use small columns in order to evaluate the selectivity of the polymeric adsorbent. A detailed outline for this column methodology is contained within the booklet “Laboratory column procedures for testing AMBERLITE and DUOLITE polymeric resins” which can be supplied upon request. In the past, a polymeric adsorbent bed depth of at least 50 mm was required to accurately evaluate the polymeric adsorbent performance. With the laboratory equipment available today, satisfactory results can be obtained with much smaller columns containing as little as 100 ml of polymeric adsorbents. This is particularly important when highly valuable solutes are being studied and the solution volume available for testing is typically restricted.

On a practical note; polymeric adsorbents swell between the aqueous and pure solvent phases. When using such systems for regeneration and/or elution, care should be taken, particularly in glass columns, to avoid breaking the polymeric adsorbents or the column itself. In these cases, consideration should be given to performing the operation counter-current or upflow through the polymeric adsorbent bed.

LIST OF AVAILABLE ADSORBENTS

Product	Surface area (m2/g)	Porosity (ml/ml)	Particle size (mm)	Pore envelope (Å)
Aromatic				
AMBERLITE XAD4	750 (min)	≥ 0.50	0.3 - 1.2	55 - 80
AMBERLITE XAD16	800 (min)	≥ 0.55	0.3 - 1.2	200 - 250
AMBERLITE XAD16HP	800 (min)	≥ 0.55	0.3 - 1.2	200 - 250
AMBERLITE XAD1180	500 (min)	≥ 0.60	0.2 - 1.9	400 - 450
AMBERLITE XAD1600(1)	800 (min)	≥ 0.55	0.4	80 - 120
Acrylic				
AMBERLITE XAD7HP	380 (min)	≥ 0.50	0.3 - 1.2	450 - 500
Phenolic				
AMBERLITE XAD761(2)	150 - 250	0.95 - 1.18	0.3 - 1.2	55 - 80

(1) AMBERLITE™ XAD™1600 is specially targetted at chromatographic separations on the industrial scale.
(2) AMBERLITE™ XAD™761 is a granular product.

Rohm and Haas is a leading manufacturer of ion exchange and adsorbent resins and is committed to the on-going development both of new polymeric adsorbent resins and new applications for our products.

The product process in European plants has obtained the ISO 9002 quality assurance certification and the ISO 14001 environmental certification.

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CAUTION

Ion exchange resins and polymeric adsorbents, as produced, contain by-products resulting from the manufacturing process. The user must determine the extent to which organic by-products must be removed for any particular use and establish techniques to assure that the appropriate level of purity is achieved for that use. The user must ensure compliance with all prudent safety standards and regulatory requirements governing the application. Except where specifically otherwise stated, Rohm and Haas Company does not recommend its ion exchange resins or polymeric adsorbents, as supplied, as being suitable or appropriately pure for any particular use. Consult your Rohm and Haas technical representative for further information.

Acidic and basic regenerant solutions are corrosive and should be handled in a manner that will prevent eye and skin contact. Nitric acid and other strong oxidising agents can cause explosive type reactions when mixed with Ion Exchange resins.

Proper design of process equipment to prevent rapid buildup of pressure is necessary if use of an oxidising agent such as nitric acid is contemplated. Before using strong oxidising agents in contact with Ion Exchange Resins, consult sources knowledgeable in the handling of these materials.

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