SOLVENT SWELLING, SORPTION KINETICS AND DIFFUSION ENERGETICS IN UNTREATED AND OXIDIZING ACID ETCHED POLYPROPYLENE FILM SAMPLES.

BY

ISA, ABDULLAHI BALA.

A DISSERTATION SUBMITTED TO THE DEPARTMENT OF CHEMISTRY, IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD

OF

M. TECH IN ANALYTICAL CHEMISTRY

JUNE, 1998

DECLARATION

I hereby declare that this dissertation has been written by me and it is a record of my own research work. Information are derived from the published and unpublished work of others and they are specifically acknowledged by means of references.

ABDULLAHI BALA ISA.

CERTIFICATION

The research has been carefully read through and approved as meeting the requirement of the department of chemistry, Federal University of Technology, Minna, for the award of M.Tech in Analytical chemistry.

DR. T.C UZOMAH

SUPERVISOR

PROF. J. OLAYEMI

(EXTERNAL EXAMINER)

DR.A.A. FARUK

HEAD OF DEPARTMENT

PROF.J. M. BABA

DEAN, S.S.S.E.

DATE------------------

DEDICATION

This work is fondly dedicated to my late friend, Dalhatu (Dantala) Hassan Kwali, on whose counsel and judgement I frequently called.

ACKNOWLEDGEMENTS

It is impossible to complete a work such as this without the help of a great many people.

My supervisor, Dr T.C Uzomah was decisive factor in the completion of the work, His vision, simplicity, tolerance, good disposition, constructive criticism, suggestions, guidance, unfailing kindness and excellent supervisory role defy estimation.

I am also grateful to the head of department, Dr. A.A. Faruk, Prof. O.A Olatunji, Dr. M.A.T Sulaiman, P.A.E Ako, Dr.Reju, G.O. Adesina for moulding me into what I'm aspiring to become. My profound gratitude also goes to the chief technologist Mrs M.A Akinbode, B.Y Emmanuel, B.A. Bala, J.A. Abdullahi, and J.A. Aje for their technical assistance and co-operation throughout the study.

The invaluable contribution of my family members to the successful completion of this programme is most appreciated and it will remain as an indelible mark in my memory. Special mention must be made of my parent(s); Alhaji Muhammadu Isa Agaie, Hajiya Ramatu and Salamatu Isa, for their financial and moral support throughout the study.

During the course of this study, a very heavy burden fell on my friends and coursemates who avowed interest in my progress. To them I owe immense gratitude.

Finally, I am most grateful to almighty Allah.

ABSTRACT

In view of the intensifying interest in the application of polymeric membranes in mixture separation processes, gravimetric sorption of six solvents into polypropylene(PP) films at different temperatures 28^0C ,40^0C, and 60^0C have been studied. The solvents used include non-polar solvents (tetrachloromethane, toluene,n-hexane and dioxane) and polar solvents (benzylchloride and acetone) with large differences in dipole moments, and calculated interaction parameters.

The swelling data defined by the swelling quotient was used according to Gee's theory in two different forms to estimate the solubility parameters of PP. The values obtained respectively agreed reasonably with the experimental solubility parameter most frequently quoted. The solvent uptake data for each solvent was taking at different time intervals until equilibrium was obtained. The equilibrium sorption was found to be attained at a smaller time intervals for polar solvents ($60s^{½}$) and higher range for non-polar solvents (60-$85s^{½}$). This indicates that non-polar solvents are preferentially sorbed more than the polar solvents in PP, a non-polar polymer. Also, the diffusivity was found to be of the order of $10^{-8}cm^2s^{-1}$ as predicted for polymers. Solubility,S, and permeability,P, were found to depend primarily upon the molar volume of the solvent. The data on permeability for each solvent at different temperatures were used to calculate the permselectivity Z given by $Z=P_i/P_j$. The magnitude Z showed that out of the thirteen penetrant pairs, only five, exhibited a decrease in Z with

increase in temperature. However, seven penetrant pairs showed an increase in perm-selectivity with temperature especially for polar molecules in which case shows the reluctance of non-polar PP, chains to interact with polar organic molecules. The mechanism of swelling was studied by fitting the swelling data obtained into well known expressions from which the mode of transport defined by the value of n and the extent of interaction between PP polymer chain and the various values K were estimated graphically. It was observed that the kinetics of liquid sorption in every case deviate from the regular Fickian trend, only in a few cases e.g tetrachloromethane was there a tendency toward Fickian diffusion at 60^0C. n values decrease with increase in temperature while K values increase with increase in temperature. The activation energy of sorption, enthalpy, entropy and the PP-solvent interaction parameter were evaluated for the six solvents. The positive values obtained for enthalpy (ΔH), shows that the process is endothermic while the negative values obtained for entropy change , ΔS (with exception of dioxane), shows that PP polymers retains some liquid solvent even when dried. The critical dissolution time (CDT) and the apparent crystallinity (AC) developed in PP films at equilibrium liquid sorption at different temperatures were also investigated. The CDT were found to be higher for non-polar solvents and lower for the polar solvents.

Chemical etching has been used to change the surface properties of the PP films through the removal of the amorphous phase surfaces. Chromic acid was observed to be a more efficient etchant than nitric acid judging from the weight loss. Data from sorption studies on the etched films were not reproducible so that sorption studies on these etched films were not continued.

TABLE OF CONTENTS

CHAPTER ONE

CHAPTER TWO

CHAPTER THREE

CHAPTER FOUR

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS, GLOSSARIES AND SYMBOLS

1.	PP	Polypropylene
2.	Tg	Glass transition temperature
3.	PAN	Polyacrylonitrile
4.	Mc	Molecular weight between crosslink
5.	Vs	Molar volume
6.	Q	junction functionality
7.	J	mass flux of permeant
8.	D	diffusion coeficient
9.	dc/dx	concentration gradient of permeant
10.	Mt	amount of permeant sorbed at equilibrium
11.	δ	solubility parameter
12.	$M\infty$	quantity of penetrants sorbed at equilibrium
13.	Mw	molecular weight
14.	Qt	swelling ratio
15.	Q	swelling quotient
16.	ΔE	enthalpy of vapourization
17.	X	interaction constant
18.	β	entropic constant
19.	Pi/Pj	permeability ratio
20.	S	solubility
21.	P	permeability
22.	E_D	activation energy of diffusion
23.	E_s	activation energy of solution
24.	E_p	activation energy of permeation
25.	k_s	equilibrium sorption constant

26. PET	polyethyleneteraphthalate
27. AC	apparent crystallinity
28. CDT	critical dissolution time

CHAPTER ONE

1.0 INTRODUCTION

1.1 Polypropylene (PP) is the lightest major plastic, with a density of 0.905 g/cm^{-3}. It's high crystallinity impart to its high tensile strength, stiffness and hardness. The resulting high strength-to-weight is an advantage in many applications. Finished articles usually have good gloss and high resistance to marring. The high melting point of PP allow well molded parts to be stabilized, and the polymer retains high tensile strength at elevated temperature(1).

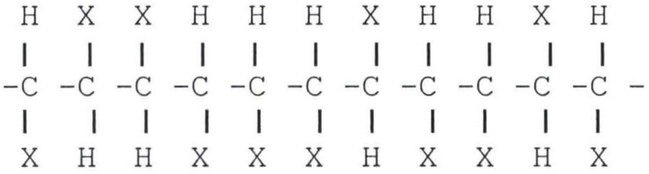
The low-temperature impact strength of PP is some what sensitive to fabrication and test conditions. This sensitivity results from the presences of dominating α-transition in PP at about 0^0C, resulting in marked lost in stiffness near this temperature. In high-density polyethene (HDPE), the dominant transition is the lower-temperature β-transition. Thus, the restriction, of molecular motion leading to brittle behavior takes place not far below room temperature in PP, but at a much lower temperature in PE. PP has excellent electrical properties and the chemical inertness and moisture resistance typical of hydrocarbon polymers. It is completely free from environmental stress cracking. However, it is inherent less stable than PE to heat, light, and oxidative attack (presumably because of the presence of tertiary hydrogens) and must be stabilized with antioxidant and ultraviolet light absorbers for satisfactory, even for such application as indoor-outdoor carpeting, but are more expensive(1).

1.2 STRUCTURE, MANUFACTURE AND APPLICATION

With the commercial utilization of co-ordination polymerization in 1957, the production of PP became possible. In the intervening decade, this has become one of the world's major plastic . The PP molecules is presence in the polymer in the three fold helix form. Three PP monomers units complete a helix form. A uniaxial drawn PP is describe for simplicity as an assemble of long thin cylinder rather like a packet of spaghetti, with their long axes all parallel in drawn direction. The direction of molecular orientation is therefore the same as that of fibre films axis. The implication of such alignment is that the molecules packed in a more ordered manner, thereby improving the crystallinity; molecular slippage is enhanced unless there is high degree of cross-linking. Very few experimental techniques however can help in the determination of the orientation and thermodynamic equilibrium component.

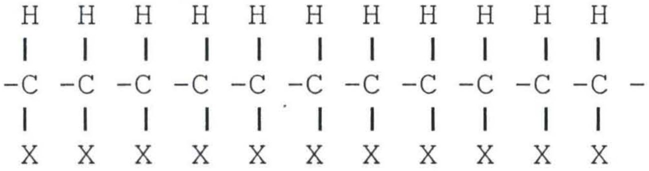
Polymers are not wholly crystalline, as for example salt or simple organic substance might be. The crystalline regions are surrounded by a matrix of less ordered amorphus material. They are above the Tg of the amorphus material, at ambient temperature, an hence derived their hardness from the crystalline region. Below the Tg of the amorphus polymer they become brittle and glassy (2).

PP can be made in isotactic or atactic form. The most regular arrangement, with all the `R' groups on one side is the isotactic configuration, the arrangement in which the `R' and the 'H' groups alternate is the syndiotactic and where the groups are randomly disposed, the arrangement is called atactic. The older methods for making addition polymers, usually at high temperature and pressure, lead to atactic products, but newer methods using the process originated by Ziegler and Natta produce stereoregular polymers. This process run at low temperature and pressure and rely on specially developed catalyst for their success (2). When attempt to produce PP by the high pressure methods, the results was atactic polymers which is very unsatisfactory material, soft and without useful mechanical properties. It was only with the advent of Ziegler-Natta catalyst that isotactic PP became a practical possibility. The crystalazability of isotactic PP make it the sole form with properties of commercial interest. Isotactic PP is an essentially linear, highly crystalline polymer, with a melting point of 165^{0}C (2).



$$\begin{array}{cccccccccccc} H & X & X & H & H & H & X & H & H & X & H & \\ | & | & | & | & | & | & | & | & | & | & | & \\ -C & -C & -C & -C & -C & -C & -C & -C & -C & -C & -C & - \\ | & | & | & | & | & | & | & | & | & | & | & \\ X & H & H & X & X & X & H & X & X & H & X & \end{array}$$

ATACTIC



$$\begin{array}{cccccccccccc} H & H & H & H & H & H & H & H & H & H & H & \\ | & | & | & | & | & | & | & | & | & | & | & \\ -C & -C & -C & -C & -C & -C & -C & -C & -C & -C & -C & - \\ | & | & | & | & | & | & | & | & | & | & | & \\ X & X & X & X & X & X & X & X & X & X & X & \end{array}$$

ISOTACTIC

FIG 1: Atactic and stereoregular polymers.

The tough, leathery or horny polymers like PE and PP and the harder tough "engineering" polymers like polyacetal are not brittle at ordinary temperatures, although they may become so at low temperature. They would thus seem to be above there Tg.

Why then are they not soft and rubbery? The reason is that they have appreciable crystalline, ordered regions which impact rigidity to the structure. Such ordered regions are possible when the fundamental chemical structure of the molecules is sufficiently regular. This is why stereoregular PP is a valuable hard plastic, where atactic polymers is soft and of no practical value. The isotactic or syndiotactic structures allows crystalline regions to be formed, the chain are packed together in regular way (2).

The isotactic PP made by Ziegler-Natta polymerization is about 70% crystalline. Even though the stereoregular structure ease crystallization, the crystal unit cell adopts a spacious spiral which gives the polymer it's low density (2). Also, interestingly, amorphous PP, previously an unwanted by products of isotactic PP manufacture, is also becoming increasingly important particularly, for modifying asphalt roofing compounds(3) Typical properties of PP is shown in Table (1)

Ethylene, PP, and other alpha-olefins can be polymerized in the same equipment with very little modification, leading to highly flexible operation. Catalyst and operation condition must be selected with care to ensure that isotactic PP is produced.

Processing methods are largely determined by the rheological properties of the polymer in question. A primary consideration is whether the material is thermoplastic, i.e. retain the ability to flow at elevated temperature for relatively long time, or thermosetting, i.e. subject to (controlled) cross-linking reactions at the temperatures necessary to induce flow, so that the ability to flow is rather quickly lost in favour of form stability. Other considerations of importance in selecting fabrication methods are softening temperature, stability and, of course, the size and shape of the end product. Methods of processing include the following:-

Calendering: This is the process used for the continuous manufacturing of sheet or film.

Casting: In this process, a liquid material is poured into a mould and solidified by physical (e.g. cooling) or chemical (e.g. polymerization) means, and the solid object is removed from the film.

Film casting: These are produced by flowing a solution of the polymer into an extremely smooth surface in the form of a large polished wheel, or, occasionally, a metal belt or band.

Compression molding: The polymer is put between stationary and movable members of a mold. The mould is closed, and heat and pressure are applied so that the material become plastic, flows to fill the mold, and become a homogenous mass.

Injection molding:The polymer is preheated in a cylindrical chamber to a temperature at which it will flow and then is forced into a relatively cold, closed mold cavity by means of quite high pressure applied hydraulically, traditionally through a polymer.

Blow molding: A section of molten polymer tubing (parison) is extruded into an open mold. By means of a compressed air or steam the plastic is then blown into the configuration of the mold. This technique is widely used for the manufacture of bottles and similar articles.

Rotational molding:In this technique the powdered polymer is loaded into a relatively inexpensive closed mold, which is intensively heated while being rotated biaxially.

Polypropylene hinge:The PP hinge is integrally molded with the rest of the appliance.The most common application for the device is in lidded boxes, e.g. for card index storage, instruments, e.t.c. Other uses include disposable surgical forceps and car accelerator pedals. The hinge is a thin web of material, usually 0.2 to 0.6 mm thick, but can be up to 1mm thick when there is restricted movement e.g. in the car accelerator pedal. There are radii on either side which minimize restriction during molding and shapely defined the hinge line. The hinge must be straight or it buckles in use. The hinge works uniquely in PP, because this polymer has a spiral crystal unit cell, compared with the orthorhombic structure found in PE, other polymers also form rigid crystalline structure(2).

The interest in the study of sorption and transport properties of small organic molecules into propylene films is based on it's numerous application for packaging and as molded containers for various solids and liquids. During use this materials are in contact with different organics and their vapuors which permeate at different rates that they may alter their morphological features. With use therefore these films may suffer some deterioration of useful properties. In some other cases, these membranes may exhibit some degree of selectivity to these organic molecules (4).

1.3 DIFFUSION AND PERMEABILITY OF VAPUORS INTO FILMS

Permeation is the rate at which a gas or vapuor passes through a polymer. The mechanism by which permeation takes place involves three steps:

* Absorption of the permeating species into the polymer.

* Diffusion of the permeating species through the polymer, travelling on average, along the concentration gradient and

* Desorption of the permeating species from the polymers surface and evaporation or removal by other mechanisms.

Factors affecting permeability include the solubility and diffusivity of the penetrant into the polymer, polymer packing, and side group complexity, polarity, crystallinity, orientation, fillers, humidity and plastilazation. For example, polymers with high crystallinity usually are less permeable because their ordered structure has fewer holes through which gases may pass.

It must be emphasized that holes in materials are required for all types of molecular motions beyond simple vibrational and rotational states. The holes and the molecules are transposed, so the hole is where the molecules was before the action started (5). It is recognized that transport of matter is dependent on properties of the permeant and the medium and it is important in such processes as drying of textiles, passage of moisture and air in soil, migration of plasticizers, food materials into and out of polymer films, permselectivity of polymer films to liquid/vapour molecules, concentration of proteins, deminerazation of seawater, treatment of effluent water, and separation of mixture of close boiling liquid (4).

Also, it is well known that the composition of liquid mixture can be altered by allowing a portion of the mixture to permeate through a polymeric membranes (6). This phenomenon thus provide a basis for the separation process, so as a result motivated a substantial amount of a research and development effort which has intensified in recent years(6). In many cases the commercialization of these processes is limited by interaction of membrane permselectivity-permeation rate. It is therefore of interest to find methods for rendering polymer structures more and/or permeable to component of liquid mixtures.

However, crystalline polymers are considered as composites(7), consisting of impermeable microcrystalline islands embedded in permeable amorphous phase. The solubility of permeants in perfectly crystalline regions of polymers is expected to be zero, since they act as barriers. The diffusivity of the vapour in glassy polymer is dependent on the inertness and swelling tendency. Thus, for inert gases and non-swelling vapour in glassy polymers the diffusion process is generally well described by the "dual mode" sorption model (8). The model provides a good quantitative representation of gas solubility (sorption) isotherms i.e. isothermal plots of concentration, C, of the permeant dissolved in the polymer as a function of permeant pressure, P, at solution equilibrium. It thus also described the independence of the effective (measured) gas diffusion and permeability coefficient in pressure and concentration. This dependence becomes more complex when the solubility of the permeant is sufficiently large to plasticize the polymer. The original "dual-mode" sorption model assumed negligible plasticizing effect of the permeant. Extension of this model by Stern and co-workers (9,10) took into account the plasticizing effect of the permeant gas/vapour as it has been applied satisfactorily to the solution and transport (diffusion and permeation) of water in polyacrylonitrile(PAN); methanol, acetone and benzene in ethyl cellulose. Another extension of this model which introduces partial immobilization assumed the existence of two different penetrants population with different mobility and examined the effect on penetrants transport in the Henry's law (concentration) and Langmuir (pressure) domains separately (11).

The mutual diffusion coefficient Dd and Dh which characterized the penetrants transporting the domains are exponential function of the penetrants concentration (11).

A second original model that include the plasticizing (swelling) effect of the penetrants into the polymer is based on the "free-volume" model of Cohen and Turnbull (12), adopted by Kreitus and Frisch (13), but has being modified by Fujita and other workers (14). The theory considers semicrystalline polymers as an

heterogenous material in which mass transport was described as the result of the super-position of two mechanisms:

* In the crystalline phase the diffusion coefficient is considered to be zero.

* In the amorphous(non-crystalline) or rubbery phase, the modified "free-volume" model applies.

The practical implication of these two theories : `dual mode' and `free volume' models is that diffusion of small molecules in polymers is strongly dependent on the physical structure of the polymer matrix. The motion of the permeant are determined by three dimensional network formed by the polymer chains. Associated with this network are crosslinks entanglements, crystallites e.t.c and these determine the molecular weight between crosslinks, degree of crystallinity, size of crystallite chain rigidity and degree of swelling. The `mesh' size of the network is determined by the hydrodynamics radius of gyration so that the diffusion coefficient of the penetrants is affected by the `mesh size' which acts as barrier to transport and the factors which increase the mobility of the polymer chain or the distance between them, enhances the transport of molecules (15).

A direct consequence is that gaseous diffusion into a polymer material is affected by :

* molecular size of the penetrants
* the temperature
*. the wetting property of the gaseous penetrant
*. the molecularity regularity of the polymer

These studies are important because of the wide application of polypropylene products as containers for water, liquid detergents, vegetable oils, petroleum products e.t.c. These products may undergo weathering with usage. Therefore it is important to asses the resistance of the products to environmental stress cracking by physical actions, the accelerated craze initiation, craze growth and failure were interpreted by the wetting of the polymer surface by the liquid, it's diffusion into the polymer and swelling due to it's sorption by the polymer (16). Other interpretations of the environmental stress cracking were based on solubility parameters and plasticization (17). The relations between the sorption of liquid or vapour by the polymer, the swelling and the plasticization of the polymer by this sorption, the reduction of the surface energies and the solubility parameters means that several explanations are possible and that the fundamental origin of environmental stress cracking is obscured (16).

The investigation of the swelling equilibrium and kinetics can help to elucidate the structure of the PP network. It is assumed that the change in total free energy is the direct sum of the elastic free energy and the free energy of mixing. Flory and Rehner relations were developed for a network deforming affinely, i.e., the components of each chain vector transform linearly with macroscopic deformation and the junction points are assumed to be embedded in the network without fluctuation. Then the molecular weight between crosslinks (Mc) for the affine limit of the model [Mc(aff)] was calculated by the formula (18).

$$Mc(aff) = \frac{\rho V_s \mu^{2/3} 2c\ V^{1/3} 2m\ (1-\mu/v\ V_{2m}{}^{1/3})}{-(\mathrm{In}\ (1-V_{2m}) + V_{2m} + X\ V^{2}{}_{2m})} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where V_s is the molar volume of the solvent ,μ and V are called the number of effective chain and junctions, V_{2m} is the polymer volume fraction during crosslinking and ρ is the polymer density. In the phantom network model proposed by James and Guth [(19)], chains may move freely through one another, the junction points fluctuate over time around their mean position without been hindered by the presence of the neighboring chains and are independent of deformation. The instantaneous end-to-end vector of each chain is not affine in the strain because it is the sum of a mean vector, which is affine, and a fluctuation, which is independent of the strain. According to the theory, the molecular weight between crosslinks for the phantom limits of the model ($M_{c(ph)}$) was calculated by

$$M_{c(ph)} = \frac{(1-2/Q)\,P \quad V_s \quad V_{2c}^{2/3} \quad V_{2m}^{1/3}}{-(\ln(1-V_{2m}) \;+\; V_{2m} \;+\; XV_{2m}^{2})} \cdots\cdots\cdots\cdots(2)$$

where Q is the junction functionality.

1.4 FREE-VOLUME THEORY

Diffusion of small molecules in polymers is strongly affected by the physical structure of the polymer matrix. The motions of the penetrants are restricted by the three dimensional network formed by the polymer chains associated with the network, which may be formed by crosslink, entanglement or crystallite is a characteristic correlation length of the `Mesh size' which is affected by molecular weight between crosslinks, degree of crystallinity, size of crystallite, rigidity of chains, and degree of swelling. When the mesh size approaches the size of the penetrants, as described by a characteristic measure such as equivalent stakes hydrodynamic radius or the radius of gyration, the solute coefficient becomes strongly dependent on the mesh size (20-22).

The essential feature of diffusion in polymers is that the macromolecular chains act as barriers to transport, and the factors which increase either the mobility of the chains or the distance between them enhance the transport of small molecule in polymers is described by the free volume theory. The theory was developed by Cohen and Tumbull and generalized by Fugita and Vrentas and Duda (23). The theory has been extended by Peppas and Reinhart (22) to include the effects of crosslinking. Perhaps one of the most interesting case of the polymer behaviour as the solvent has to do with permeating of water and glass. Often polymers, in form of films, are used as barriers to keep out water and air. In the case of food wrappers, it is often described to keep in water but keep out oxygen. One of the more recent application is the use of amorphous poly(ethylene terephthalate) for soft drinks bottles. The major requirements are to keep carbon(IV)oxide and water in and to keep oxygen out. One must realize that this gases are continuously being transported across the plates even if at a low rate causing the soft drink to go `flat'. Thus these drinks have a "shell-life" after which they must be discarded if not sold (15).

The steady state activated transport of a fluid through a polymeric membrane may be described be Fick's law:

$$J=-D(dc/dx) \qquad (3)$$

where J is the mass flux of the permeant, D is the diffusion coefficient, and dc/dx is the concentration gradient of the permeant . For the case of a liquid in contact with upstream face of a membrane(of thickness l) and with the concentration of the penetrant kept negligible at downstream face, Fick's law may be integrated to yield:

$$Q=Jl=\int_{o}^{c1} Ddc \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The product, Jl, represents the flux rate normalized to unit membrane thickness and is denoted by Q.

By defining an integral diffusivity ($Đ$) to represent the average difussivity across the membrane, as:

$$Đ=(1/c_1) \int_{o}^{c1} Ddc \text{---------------------------} (5)$$

One obtain the following expression for Q:

$$Q=Đc_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

This relation is a major significance, since it underlined the two primary factors which affect the steady-state permeation flux: the diffusivity of a molecule in a membrane and its equilibrium concentration (c_i), or sorption, in the polymer. Q values can be obtained from a steady-state liquid permeation experiment: equilibrium vapour sorption data (at $p/p_o=1$) yield C_1 values, and a combination of two enabled calculation of integral diffusivity (ĐQ). Other estimates of diffusivity can be derived from unsteady state sorption data as described below.

As shown by Crank$^{(24)}$, the differential equation expressing Fick's second law can be solved for the condition prevailing during the early phase of a diffusion experiment ($t \rightarrow 0$), yield the expression

$$M_t / M_\infty = 4(\text{Đ}_t / l^2\pi)^{1/2} \text{ .... } (7)$$

where M_t is the amount of permeant sorbed (or desorbed) in time t, M_∞ represents the quantity of penetrant in the film at equilibrium, Đ is integral diffusivity, and l is film thickness. The slope of a plot of M_t / M_∞ versus $t_{1/2}$, therefore, can be used to estimate the integral diffusivity during sorption, D_s, or during desorption, D_d Crank indicate that the average of D_s and D_d (denoted by Đ_{av}) for time independent diffusion, corresponds reasonably well to diffusivity as estimated by the combining the permeation flux rate of a compound with its equilibrium concentration in the polymer (ĐQ) = Q/C under the equivalent boundary conditions. Thus, this Đ_{av} values, representing the kinetics of sorption and desorption between the terminal states of vacuum and saturated vapour, were compare to ĐQ values.

With regards to polymer mophorlogical features which governs permeant transport, it is worthy of emphasis that previous studies have established that transport takes place previous studies have established that transport takes place primarily in the non-crystalline regions of polymeric membranes(6).

A structural features of this amorphus regions that is important in determining transport behaviour is the degree of constraint of "tightness" of the amorphus polymer change segments comprising these regions, which acts as "tie-links" between crystallites (25). It can readily be appreciated that transport of penetrant molecules would be more hindered when passing among stiff and immobile tie-chains (i.e. in a highly constrained matrix) than when diffusion through relatively flexible chains.

Independent examination of the solubility and behaviour of the various permeants in PP provided insight into the effect of permeant properties on transport rates(since $Q=DC_1$). Sorption behaviour is governed primarily by the relative magnitude of molecular forces acting between polymer segments and penetrant molecules, i.e. thermodynamic factors control sorption. In this study, the compatibility of a solvent and polypropylene film were expressed through the use of solubility parameter (σ), were σ equals the square root of cohesive energy density, C.E.D. (internal energy of vapourization divided by molar volume).

Diffusion through the matrix of a polymer may be related to the frequency with which a dissolve molecule can find, or creat, a space between adjacent polymer chains large enough to accommodate it. Thus, the higher diffusivity of a smaller molecule (e.g.toluene) may be attributed to the higher probability of finding an appropriate "gap-size" for the passage of this molecule. Brandt(26) has shown that for a polymer with limited chain segmental mobility, the activation energy for transport (and therefore diffusivity) would depend on the square of the molecular diameter of the permeant. The apparent d^2 dependency of transport of relatively large permeant found in PP is probably a reflection of the rigidity imparted to the backbone of PP by the pendant methyl group. This chain stiffness suggested by the diffusion data is also reflected in the relatively high glass transition temperature of PP (263K) compared to that of polyethylene (148K). This difference in diffusivity suggests the existence of more direct diffusion on paths in polypropylene, which could result from differences in the crystalline habit of these polymers(6).

1.5 SOLVENT INDUCED CRYSTALLIZATION (SINC)

Amorphous polymers, been metastable with respect to their crystalline forms, can be induced to crystallized in several ways:

* thermally induced crystallization, by increasing the, temperature above Tg to decrease the viscosity and allow the re-arrangement.

* strain-induced crystallization

* solvent-induced crystallization.

It is this third process which is of particular interest from the point of view of the cohesion parameters. When such crystallization of amorphous region of fibre occurs there is subsequent shrinkage. Most studies have used poly(ethyleneteraphthalate) since it can be easily quenched from the melt to a glass without complication of the presence of crystallinity before exposure to solvent. Although some discrepancies are noted in the correlation of solvent-induced crystallization with hildebrand parameters, particularly because the bimodal distribution of such properties of poly(ethyleneteraphthalate) (27). When partial cohesion parameters such as Hansen parameters are used the agreement is better (27). Crystallization most occur between Tg and Tw, although solvents depress Tm, this melting point lowering is not as great as the depression of Tg.

Sheldom and Co-worker (28-30) measured densification of 0.02-0.04 can thick PET films, immersed in benzene and in ketones. They concluded that the penetrant transport controlled the extent of induced crystallization since the penetrant uptake and the sample density were linearly related, and the density increased linearly with the square root of contact time between the liquid and the sample activation energy.

Theoretical investigation of solvent induced crystallization focussed in the nucleation and growth of crystallization. The observation of small,uniformly sized spherulites in solvent-crystallized polymer suggest that thermal (heterogenous) nucleation occurs since such spherulites result from the simultaneous initiation of crystallites from a fixed number of nuclei (31).

The effects of the various solvents sorption on the mechanical properties of PP were studied and analyzed as a consequence of plasticization and solvent-induced crystallization.

1.6 ETCHING

The ultrahigh specific strength, ultra-high specific modulus, and extra ordinary impact resistance make them fibres of interest for advanced aerospace, military, automotive, and biomedical applications.

The greatest drawback to using these fibre in composite materials application have been their poor adhesion to polymer matrices (32).Whether the properties of a fibre can effectively be imparted to the composite depends on the adhesion between reinforcement and matrix. However, for the PP structures, the adhesion with most materials is poor, due to chemical inertness and a smooth surface preventing chemical as well as mechanical adhesion (33).

Over the last thirty years several methods to modify polyolefins surfaces have been developed, most of them with the aim to improve metal plating and/or printability. Examples are etching ,flame, plasma, corona, and ozone treatment (33).

It is assumed that this treatment improved the adhesion in a two fold manner; firstly the surface free energy is increase to improve wettability and secondly and most importantly functional groups are introduced at the surface, giving rise to a large increase in the chemical interaction at the surface (33).

Chemical etching is a popular method of surface modification that changes both surface chemistry and surface roughness. The modification mechanism consist of the abstraction of hydrogen atoms from the polymer backbone and their replacement with polar groups from the oxidizing etchants (33). Composite properties are dependent on stress transfer through the fibre matrix interface (33). Enhanced interfacial adhesion improves stress transfer and is expected to improve composite properties. The single-fibre strength and failure strain, however, may be altered by the polymer degradation associated with adhesion-enhancing surface treatments. Chemical etching can embrittle the polymer and create flaws on the fibre surface. The etching process is expected to diminish fibre strength and failure strain. Surface treatments for composite application must strike a balance between adhesion enhancement and single fibre property degradation (33).

End-use physical properties of polymers depend strongly on crystallinity and morphology. Correlations between the physical properties and crystallinity of PE are well known (34). Morphology is more difficult to determined quantitatively, and the effects of morphology are less well understood. No single method gives a complete characterization and a combination of a complementary methods is desirable. Electron miscrocopy, small angle light scattering, small angle x-ray scattering, thermal analysis, and Raman spectroscopy are all useful, but each has limitations associated with sampling requirements and reliability for some types of samples(35).

Chromic acid(36) and potassium parmanganate(37) has been used as etchants for PE. Perhaps the most generally applicable methods for characterizing morphology is aqueous nitric acid etching, followed by characterizing of the residues(34). The principle of the aqueous nitric acid etching method is that the reaction with solid polyolefins selectively destroys the amorphous phase and the chain folds at the surfaces of the crystallites. There is a progressive decrease in the percent residues and molecular weight, an increase in the percent crystallinity, and other changes. It has been established that the residues consist of fragments of the crystallites initially present in the sample(34). Thus characterization of the residues provides useful information about the crystalline morphology, particularly the distribution of lamellar thickness.

The effects of morphology or the degree of crystallinity on oxidation of solid polyolefins by O_2 were observed by Hawkins et al(38), who concluded that reaction with O_2 occurs only in the amorphous phase,Bobalek et al(39) observed similar effects on the oxidation of solid polyethylene with aqueous nitric acid and also suggested that the amorphous phase was preferentially attacked. Palmer and Cobbold(40) first used nitric acid etching (also referred to as oxidation, digestion or nitration) for characterizing morphology. The method has been applied widely to the characterization of PE in all forms, i.e., nascent polyethylenes,bulk specimens,films, fibre, and single crystals(41) Illers(42) made a systematic study of etching conditions and characterized the residues by several techniques. Most workers have used only one or two characterizations of the etched residues, e.g. weight loss and molecular weight. However, comparison of the results of different laboratories, with allowance for differences in samples and procedures, have led to a qualitative understanding of the etching process and an interpretation of the properties of the residues.

It has been generally assumed that the residues from nitric acid etching are mildly modified polyethylene, such that polyethylene calibrations can be used in estimating molecular weights and percent crystallinity. Infrared spectroscopy and elemental analysis(43), indicated the presence of COOH and NO_2 groups in the residues. Additional physical and chemical evidence indicated that the residues were probably nitrated alkanedioic acids, but the locations of the substituents groups were not established. More extensive chemical characterizations by Melby(44) have established that the products from linear polyethylene are nitrated α, ;-alkane dioic acids; the nitro groups are secondary and located near the chain ends. Carboxyl to nitro groups ratios depend on etching conditions, ranging from 1.6 : 1 to 11 : 1.

Chromic acid, and nitric acid are the etchants studied in this research.

1.7 AIMS AND OBJECTIVES OF THE STUDY

The sorption and transport of molecules either gases or liquids into polymeric films and membranes has been the object of many research work(45-47). It is in pursuit of such studies that this research project was embarked upon. The aims and objectives of this study were therefore to generate enough data on the sorption and diffusion of organic liquid molecules into polypropylene film. Such information on diffusivity, solubility, permeability of these organic molecules into PP films at different temperatures would be sought. It was also intended to generate information on the mode of transport (whether the diffusion process was Fickian or non-Fickian) and extent of polymer solvent interactions in these systems, the entropy, the enthalpy and free energy of solution solvent molecules into PP films.

The study also sought to compare the effect of solvents treatment of PP films with regard to those properties enumerated above. Sorption involving some selected solvents will also be performed on different PP films at different temperatures. The crystallinity develop in PP films at maximum sorption in different solvents would also be estimated.

The changes in the properties: sorption and diffusion, energetics, and as a result of solvent treatment and crystallinity developed be studied in terms of changes in molar volume, molar mass, dipole moment and interactions constants of the liquid used.

These studies are important because of the wide application of PP products as container for water, liquid detergents, packaging organic materials, vegetable oils, petroleum products, and as container of liquids which may exhibit vapours. These products may undergo weathering with usage. It is therefore necessary to know how PP materials are permselective to organic liquids and vapours and to asses the resistance of the products to environmental stress cracking agents.

CHAPTER TWO

2.0 EXPERIMENTAL

2.1 MATERIALS

The polypropylene film used in this work was supplied by BAGCO (Nig) Ltd., Lagos. It's molecular weight Mw ≈ 3.2×10^5, and 48% crystallinity and density is $0.905cm^{-3}$, film thickness (=0.32).

Reagents grade organic solvents were used in this study. These solvents were used without further treatment. Some properties of these solvents used as permeant are shown in Table II.

The chromic acid etching solution was prepared by mixing potassium dichromate (IV) $K_2Cr_2O_7$, sulphuric acid (H_2SO_4) and distilled water in a ratio of 7 : 150 : 12 mass ratio. The nitric acid used was the red fuming (>90%) HNO_3. All solvents and reagents were obtained from the chemistry laboratory store.

2.2 METHODS

2.2.1 SORPTION STUDIES:

Swelling measurements(18) were performed by immersing the cut polymer film (≈ 0.10g) in test tubes containing 25-30 cm^3 of solvents contained at 28^0C, 40^0C and 60^0C at different times. The film thickness (≈ 0.32mm) was measured at several points in the film using a micrometer screw gauge with an accuracy of ± 0.01mm. After immersion period, the samples were blotted with filter paper to remove surface liquid and weighed. A possible source of error in this method arises from reproducibility of the "blotting" procedure, i.e., blotting can some time remove "not all" and some time "more than" the solvents adhering on the surface of the film depending on the pressure applied and the absorptivity of the paper. Because weighing was done between 30-40 sec, the error owing to evapouration of other than surface absorbed liquid is considered insignificant. The procedure was continued until the film attained maximum swelling and this generally took atleast 60 minutes. After equilibration, the mole percent swelling ratio, Qt, was defined by (48)

$$Qt = \frac{(\text{ weight of the liquid sorbed at time t})/(\text{molecular mass of the liquid})}{\text{Initial weight of PP sample}} \times 100 \quad \ldots.(8)$$

For the determination of solubility parameter PP, Swelling quotient, after equilibration was defined by the expression(18)

$$Q = \frac{m - m_o}{m_o} \times \frac{1}{\rho_s} \times 100\% \quad \ldots\ldots..(9)$$

were m is the weight of the swollen samples, m_o is the dry weight, and ρ_s is the density of the swelling agent. The on the swelling quotient for all the solvents used and at different times are recorded in Table III while the data for mole percent swelling are recorded in Table IV.

2.3 CHEMICAL ETCHING

PP films were immersed in chromic acid, i.e., $K_2Cr_2O_7/H_2O/H_2SO_4$ (7:12:150 by weight) or concentrated nitric acid etchants solutions at 28^0C for exposure time of 72hrs. Next all films were rinsed in distilled water. Finally all films were rinsed with acetone, dried and stored in a desiccator. The etching solution and rinsing procedure were as reported earlier(32).

2.4 CRITICAL DISSOLUTION TIME (CDT)

Treated samples from the equilibrium swelling films for each solvent and untreated PP films were cut to suitable sizes (1 x 0.5cm) and separately immersed in hot toluene ($110^{0}C$) with constant stirring. The time taking for immersed PP sample to dissolve was noted. The mean of the five experiments was recorded in each case. The untreated PP films serve as the control.

The apparent crystallinity (AC) was determined from the expression (49)

$$\text{Apparent Crystallinity}(\%) = \frac{CDT_{treated} - CDT_{control}}{CDT_{treated}} \times 100 \quad \ldots.(8)$$

The data on CDT and AC are recorded in Table (IX);

CHAPTER THREE

3.0 RESULTS AND DISCUSIONS

3.1 SOLUBILITY PARAMETER

The square root of the cohesive energy density is widely known as the solubility parameter σ

$$\sigma = (\Delta E/V)^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

Where ΔE and V are enthalpy of vapourization and molar volume respectively. The solubility parameter was first proposed to be a useful quantity to characterize the strength of interaction in simple organic liquids. Gee proposed that while solubility of a polymer depends on its molecular weight, the temperature and so on, the interaction and swelling ratio will be a maximum where the solubility parameter of the polymer matches that of the solvent(σ_s). This idea can be used to calculate the cohesive energy density of a variety of synthetic polymers. The conventional methods of vapourization by direct calorimetric experiment or from the temperature dependance of vapour pressure, using the Clausius-Clapeyron equation are unsuitable because they decompose at high temperatures before passing to the vapour

state(50).

The theory of Gee was represented by equation (12)(51)

$$[\ V^{-1} . \ln Q_\infty/Q\ ] = [a^{1/2}\ (\ \sigma_s - \sigma_p)] \ldots\ldots\ldots(12)$$

where Q_∞ and Q are the equilibrium swelling quotient and at time t. By plotting $[\ V^{-1} . \ln Q_\infty/Q\ ]^{1/2}$ against σ_s, $a^{1/2}$ and σ_p

can be determined from the slope and the intercept of the horizontal axis respectively. The solubility parameter σ_p of lightly vulcanized rubbers(50), have been calculated by this method. A modification of this method have been described earlier for natural rubber and of a number of synthetic rubbers(52).

Figure 1 shows the relationship between the percent swelling quotient of the PP and the solubility parameter of the various solvents. With the data in Table III for 13 solvents are plotted in figure 1, an envelope is drawn through the innermost points, the maximum of which corresponds to the solubility parameter of PP. The PP film exhibited the largest swelling in carbon tetrachloride (σ = 17.8MPa$^{1/2}$) among the solvents used while the swelling data correlated with a linear relationship between

$[V^{-1}.\ln Q_{max}/Q]^{1/2}$ and σ_s (figure 2) yielding a value of 19.4MPa$^{1/2}$, both values reasonably close to 18.8MPa$^{1/2}$, a value obtained by Hayes(53). It has been suggested that the scatter of swelling data within the envelope probably reflects the inadequacy of σ_s as a correlation parameter for polymer swelling both in polar liquids and in liquids of differing molecular shape and size(54). Moreover the polymer crystallization produced by these liquids certainly reduces the solubilities subtentially from what their level would be in totally amorphous polymer(54). Thus some of the swelling scatter may arise from variations from liquid to liquid in the degree of solvent rejection with occurrence of crystallization. Recently, this method has been used to determine solubility parameters of some other polymer networks (55)

Also, solubility parameters was also calculated based on the knowledge of the chemical structure of PP (small's group contribution method)(56). Use was made of the group molar attraction , G, for each repeating unit group, using the following relationships:

$$\sigma = \frac{p \, \Sigma G}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

Where ρ represent the density and M is the formula weight of the polymer repeating unit and ΣG is the sum of the small's group contribution (i.e. molar attraction constant). Using the values of G for CH_3-(=214),-CH_2(=133) and -CH(=28) respectively , a value of 8.04 $cal/cm^{3\ 1/2}$ equals to 16.45 $Mpa^{1/2}$ was obtained for PP.

Liao et al(18) showed that analysis of the swelling equilibrium behaviour of polymer networks in solvents can determine the molecular weight between crosslinks and also the solubility parameters of the bismaleimide rubbers. The equilibrium absorption depends on the activity of the component that is absorbed and on the interaction between this component and the polymer. The equilibrium volume-fraction of a liquid or a vapour in an amorphous polymer can be obtain in first approximation from(58)

$$\text{Ina} = \text{InV} + (1-V) + X(1-V)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

Where a is the activity of the component in the environment, V the equilibrium volume of this component in the polymer matrix and X the interaction constant. The activity of a vapour is given by(57)

$$a = \frac{p}{p_o} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

Where P is the actual vapor pressure and p_0 the vapor pressure at saturation. Equation(14) is based on the Flory-Huggins theory(58), in which the influence of the entanglement network is neglected. This is permitted at low equilibrium absorptions. However, at higher absorption values, the neglect of this influence result in wrong values of V.

As a result, X for the PP films in the various solvents was calculated according to the solubility parameter theory(59)

$$X = \beta \quad \frac{V^S}{RT} \quad (\sigma_P - \sigma_s)^2 \ldots\ldots\ldots\ldots (16)$$

where V_2 is the molar volume of the solvent, R is the gas constant, T is the absolute temperature, and the constant entropy term β was taken as 0.34(60) p and s represent polymer and solvent respectively .

The value of X obtained are also included in Table II.

3.2 SORPTION OR SOLVENT UPTAKE

Sorption behavior is governed primarily by the relative magnitude of molecular forces acting between polymer segments and penetrants molecules, i.e. thermodynamic factors control sorption(18).

The result of sorption experiment are expressed as mole percent of penetrants sorbed by unit mass of the polymer. The mole percentage swelling (Qt) were expressed as in the Unnikishnan and Thomas method (48)

$$Qt = \frac{\text{weight of the liquid sorbed at time t/molar mass of the liquid}}{\text{initial weight of PP sample}} \times 100$$

The mole percentage swelling at time t, Qt, and at equilibrium, Qm for the PP film provided the data for sorption or solvent uptake (Table III). The Qt values obtained thereby were plotted against the square root of the total time of immersion. Figures 3-8, shows the diffusion curve of PP films at different temperatures 28^0c, 40^0c and 60^0c. Organic liquid transport rate through PP films are enhanced as the temperature of permeation is increased. This behavior is to be expected in a system in which activated transport takes place, i.e., the higher thermal energy associated with increased temperatures facilitates the movement of the permeant molecules. The increase in the solubility of liquid hydrocarbons in PP at increasing temperatures, suggest yet another reason for enhanced permeation, since fluid transport is exponentially dependent on concentration(6).

In Table III and IV and in figure 3-8 it is evident that the permeation rate increase with increase in temperature for any particular liquid : comparison of the data in Table III and plots on figures 9-11 shows that at a particular temperature the order of liquid sorption ccl_4 > toluene > n-Hexane > dioxane > benzylchloride > acetone. This can be explained by combination of factors: molar volume, dipole moment of liquids. For non-polar liquid n-hexane, toluene, tetrachloromethane and dioxane, the major factors that determines sorption into PP, are hydrocarbon polymer is the molar volume. Hence, with the exception of dioxane, the order is ccl_4 > toluene > n-Hexane. However, for polar liquids into non-polar PP, the over-riding factor is the polarity of the solvent the less the sorption; hence the sequence for benzylchloride > acetone. Such reports have been previously reported for other polymer - solvent system(6). Further more the higher sorption rate at the initial time was attributed to the rapid cavitation which exposed a greater surface area, allowing penetration of the solvent. At longer times, there would exist a finite gradient of concentration near the interface between the penetrated outer region and the unpenetrated inner core. Makerewicz and Wilkes(62) reached the same conclusion. Comparison of figures 9-11 shows that equilibrium sorption is reached at about $\sqrt{t} = 60s^{1/2}$ for benzyl chloride and acetone (i.e. polar solvent). However for n-hexane, ccl_4, toluene and dioxane (non polar solvent), equilibrium sorption is attained at about

$\sqrt{t} = 60 - 84.85^{1/2}$. This observation suggests that non-polar solvents are sorbed for longer time before attainment of equilibrium than the polar solvent by PP films swells more with ccl_4 and least with dioxane. For polar solvent, PP swells more with benzyl chloride. The time of attainment of equilibrium for any particular solvent is largely independent of the temperature(62).

3.3 DIFFUSION COEFFICIENTS

The solvent transport in a polymer membrane has been described by Fick's second law of diffusion.Crank(62) has shown that the differential form of Ficks second law equation for the initial diffusion into films can be expressed as

$$Qt/Qm = 4(Dt/h^2 \pi) \ldots\ldots\ldots\ldots (17)$$

where Qt and Qm are the amount of penetrant sorbed at time t and at equilibrium respectively, h is the film thickness and D is the integral diffusivity. For the case of the kinetic parameter, diffusion coefficient $D(cm^2S^{-1})$ in the samples, the following relations was used(63)

$$D = \pi(hq/4Q_\infty)^2 \ldots\ldots\ldots\ldots (18)$$

where h is the samples thickness, Q is the slope of the linear portion of the sorption curves before attaining 50% equilibrium , and $Q\alpha$ is the mol % increase in sorption at equilibrium.

3.3.1 DIFFUSIVITY

The data on diffusivity of solvent vapours in PP obtained using equation (17) are given in Table V.

It is interesting to see that though n-hexane shows lower Q_∞ values compared to toluene and ccl_4 , the values are higher than for both, supporting the concept of inverse dependency of diffusion coefficient on the molecular weight of solvents. For polar liquids (acetone and benzyl chloride), the D-values for benzyl chloride is higher. This is due to the established interaction between chlorohydrocarbons and PP(1). Michael et al(6) noted that chain `tightness' influence the diffusive behaviour of a polymer to a greater extent than it affects the polymer sorptive capacity. Figure 12 which is the Arrhenius plots of log D V_S I/T for PP is exponentially dependent on concentration.

The diffusion of vapour molecules through polymer membranes is related to the frequency of finding or creating a cavity between neighbouring polymer chains which they can pass(6). It is therefore expected and confirmed by the higher diffusivity of small molecules (toluene and n-hexane) through suitable small size cavities for their passage. Michael et al(6) has shown that the diffusivity of vapour on untreated PP film is proportional to the absolute difference in the solubility parameter of polymer and solvent, the apparent cross sectional area (representing the molecular dimensions of the diffusing molecules). The result on the increase in diffusivity with decrease in the interaction constants of a liquids are corroborated by these reports.

Michael et al(6) compared the transport and selective properties of PP films with respect to p- and O-xylene to those of PE films. The data indicated that the permeation flux of xylene is higher (by about 50%) in PP films than in linear PE. Solubility of xylene in the two polymers are not expected to be appreciably different in view of the fact that the solubility parameters of PE, 16.16 $Mpa^{1/2}$, is quite close to that of PP, 16.57$Mpa^{1/2}$. On the other hand the integral diffusivities appear to be higher in PP, De Filippi(4) reported the diffusivity of p- and o-xylene (at 40^0C, in 60% crystalline untreated PE) to be $1.87x10^{-7}$ and $1.0x10^7$ cm^2 /sec respectively; while the comparible value in 65% crystalline , untreated polypropylene are $2.8x10^{-7}$

and 1.4 x 10^{-7} cm^2/sec. This difference in diffusivity suggest that the existence of more direct diffusion paths in polypropylene, which could result from difference in the crystalline habit of these polymers . Comparison of the data in Table V Shows that at 60^0C , the values of the diffusion coefficient is in the order n-hexane > ccl_4 > toluene > dioxane.

3.3.2 SOLUBILITY

Solubility relations in polymer systems are more complex than those among low molecular weight compounds because of the size difference between polymers and solvent molecules, the viscosity of the system, and the effects of the texture and molecular weight of the polymer. In turn, presence or absence of solubility as conditions (such as the nature of the solvent or the temperature) are varied and can give more information about the polymer(3).

The sorption or solvent uptake, calculated by the mole percentage swelling at time t, Qt, and at equilibrium Q_∞ have been expressed earlier in section 3.2. The solubility S in the film was determined from the constant maximum mole percentage swelling attained per unit mass of film. In Table V is reported the data on S.

Organic liquids transport rates through PP films are enhanced as the temperature of permeation is increased. This behaviour is to be expected in the system in which activated transport takes place, i.e. the higher the energy associated with increased temperature facilitates the movement of the permeant molecules. The increase in the solubility of the liquid hydrocarbons in PP at increasing temperature, suggest yet another reason for enhanced permeation, since fluid transport is exponentially dependent on concentrations(6). These results are in agreement with Michael et al view(6), since for all the solvents studied, the solubility increases with increasing temperature. It is evident that the solubility of solvent increases as the interaction parameter X, molar volume and the molar mass of vapour molecules decreases. However enhanced higher solubilities exhibited by tetrachloromethane, a non-polar solvent can be explained by the reported specific interaction exhibited by PP in chlorosolvents(64). Acetone exhibited the least solubility. This may be associated with the higher dipole moment and interaction constant which together contribute to having low solubility.

As shown in Table V, for non-polar solvents, solubility is seen to be more controlled by the molar mass of the solvent, hence the order of solubility ccl_4 > toluene > n-Hexane > dioxane. Generally non-polar solvents are more soluble in PP than polar solvents. Comparing the data for polar solvents, solubility decreases with increase in the dipole movement constant. Hence benzyl chloride is more soluble in PP than acetone, this is in agreement with the old rule of thumb that "like dissolves like", since PP is a hydrocarbon non-polar polymer and this class of solvents exhibit high degree of polarity.

3.3.3 PERMEABILITY

The permeability, P, is defined as the volume of vapour passing per unit time through unit area of polymer having unit thickness, with a unit pressure difference across the sample(1).

The solubility, S, determines the concentration. For the simplest case,

$$P = D.S \qquad (19)$$

which express the permeability interms of solubility, S and diffusivity, D. In Table V are reported the data for permeability for different solvents at different temperatures.

For organic liquids, the permeability and/or difussivity have been related to various polymer penetrants interactions. Sweeney and Rose(65) found that for liquid mixture the component whose polarity must closely match that of the membrane preferentially permeated the membrane; polar compounds tended to permeate polar membranes faster than non-polar compounds, and vice versa. Hang and lin(66) and Micheal et al came to the same conclusion.

The value obtained in this study are in agreement with the above observations. CCl_4 has the highest permeability value among all the solvents used. This is attributed to the non-poler PP film tending to be preferentially permeated by CCl_4, a non-polar solvent. Added to this is the reported preferential interaction of PP films in chloro solvents. For the polar solvent used, the higher permeability of benzyl chloride over acetone could be attributed to the strong interaction reported to PP with chloro hydrocarbons(64).

For other non-polar solvents the permeability order n-Hexane > toluene > dioxane seems to be explained by an increases in the molar volume of the solvents. In the case of polar solvents permeability, the order seems to apparently dependent on molar volume since the order is benzyl chloride > acetone as the molar volume decreases. But the true situation is probably due to the reported preferential contact between chloro-solvents and PP(64).

3.3.4 SELECTIVITY

Selectivity of a membrane to solvent molecules is defined by the permeability ratio or ratio of product of permeability and solubility. The basis of membrane separation is the selective permeation of the permeating molecule through the membrane. Usually, the ideal permselectivity of a membrane (as reflected by the permeation flux ratio of two pure permeants) is lower in films exhibiting high flux rates. This is reasonable since low permeation rate can be related to polymer morphology characterized by a higher degree of interlamellar amorphus chain ties. In such a constrained structure, some regions may be accessible to the smaller molecules (e.g. toluene, acetone and n-hexane). Micheals et al(6) presented a model based on the polymer acting as a molecular sieve or screen, where in the amorphous region constituted the holes and the interconnecting crystalline regions constituted the mesh. They suggested that if selectivity $P_s >> 1$, an increase in permeability will reduce the area requirements for separation even if selectivity decreases appreciably, while if $P_s \approx 1$, a slight decrease in selectivity will significantly impair rather than a large increase in permeability. The data on selectivity as defined by the permeability ratio p_i/p_j for penetrant pairs at different temperatures are represented in Table IV.

It follows from Table IV that there is a regular trend with respect to types of solvents pairs, of the thirteen solvent pairs five solvent pairs seem to exhibit a decrease in Z with increase in temperature, while seven solvents pairs show an increase in Z value. Perm-selectivity for these solvents pairs Tol./Hex., Tet./Hex., are impaired at higher temperatures. Such results have been reported earlier(6). However with non-polar/polar solvents pairs e.g. Tol./ Acet., the trend is an increase with temperature suggesting that these solvents pairs can be separated at higher temperatures. Similar trend is observed for polar/polar solvents pair e.g. Benz./acet.

been reported earlier(6). However with non-polar /polar solvent pairs e.g. Tol./Acet., Benz./ Acet., the trend is an increasing temperature suggesting that these solvents pair can be separated at higher temperature. Similar trend is observed for polar/polar solvents pair e.g. benz/acet, the trend is an increase with increasing temperature suggesting that these solvent pairs can be separated at higher temperatures.

It is interesting to note that, the increase in selectivity with increasing temperature (e.g. from $P_i/P_j \approx 4.4$ at 28^{0}c to $p_i/p_j \approx 7.5$ at 40^{0}C, and 128 at 60^{0}C for toluene-acetone pair) is consistent with the postulated relief of constraint occuring at higher temperatures. It has been reported that the changes in polymer morphology resulting from solvent treatment also influence the selectivity of the PP films towards various organic liquids(6). It should be pointed out that selectivity values reported for these work are "theoretical" since they were calculated by taking a ratio of the measured permeation rates for the pure components. Although this theoretical value is indicative of the separation capacity of the films, the actual selectivity in the case of liquid mixtures would be expected to be different.

3.4 MODE OF TRANSPORT

In order to find the mechanism of transport phenomenon, the dynamic swelling data have been fitted to the expression (68)

$$\text{Log } Qt/Qm = \text{Log } K + n \text{ Logt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (20)$$

Where Qt and Qm are the mole % increase in sorption/solvent uptake at time t and at equilibrium time, m, respectively. The parameters K and n have been determined from a least squares fit of the experimental Log(Qt/Qm) values against Logt. Plots for all the solvents studied are given in figures 13-19. The estimated values of k and n are listed in Table V. k is a constant depending on the structural characteristics of the polymer in addition to it's interaction with the solvent. The magnitude of n denote the transport mode . n values are diagnostic of the mode of transport into the membrane. For Fickian transport n=0.5 while n=1 shows case II (relaxation controlled) transport, the values of n in between 0.5 and 1 suggest an anomalous behaviour of transport. There has also been reports of n>1, which is called supercase II(48)

The magnitude of n for PP in different solvents generally varied from 0.2 to 1.17, suggesting the deviation of transport mechanism from normal Fickian mode and hence, can be classified as anomalous(48). Only in the case of toluene and acetone at 40^{0}C and 60^{0}C and dioxane at 28^{0}C is there some tendency towards Fickian model. It can also be seen that the values of n generally decrease with rise in temperature, for all systems (except in the case of tetrachloromethane and dioxane). Alfrey et al(68) summarized the mass transport in glassy polymers as follows: if the penetrated concentration is low, or the penetrant molecule (or atom) is small, swelling is not important so that the transport is controlled by the Fickian law which often is named as case I. On the other hand, if the penetrated concentration is high or penetrant molecule is large, swelling is pronounced, so that transport is controlled by stress relaxation which is frequently called case II. When the kinetics is dominated by case II, the amount of penetrant is linearly proportional to time t, whereas when the kinetics is dominated by case I, the sorption is proportional to $t^{1/2}$. Anomalous transport which is mixed case I with case II is also frequently observed and the exponent of time is between 0.5 and 1.It is worth mentioning that the direction of case II transport is controlled by the sign of velocity $\dot{V}$, for transport from the center to the outer surface. If V is positive, the transport is from the center to the outer surface. Otherwise the negative sign corresponds to the opposiet direction(69).

The constant k of equation (20) describes the structural characteristics of the film and extent of the polymer-solvent interaction. The low values of k suggest low polymer-solvent interaction. In Table V, it is clear that, for non-polar solvents (n-hexane,toluene,tetrachloromethane and dioxane) at any particular temperature, k values at low temperature 28°C increase with decreasing molar volume. At higher temperatures no such generalization can be made. Furthermore, it is seen that the values of k increase with increase in temperature for all solvents(with the exception of dioxane) suggesting the increase in PP-penetrant interaction with temperature. This increase in k values may be associated to decrease in interaction constant X (equ. 16) of a polymer-solvent system with increase in temperature.

3.5 ACTIVATION ENERGY

The values of diffusivity D, solubility S, and permeability P at different temperatures (Table V) were used to calculate the activation energies of diffusion, E_D, solubility E_s, and permeability E_p from the Arrhenius type expression$^{(49)}$

$D=D_0 \exp(- E_D/RT)$ ....(21)

$S=s_0 \exp(-E_s/RT)$ ....(22)

$P=P_0 \exp(-E_p/RT)$ ....(23)

Where R and T are the gas constant and absolute temperature respectively. These expression can be reduced to the form

$\mathrm{Log}D=\mathrm{Log}D_0-E_D/2.303RT$ ....(24)

$\mathrm{Log}S=\mathrm{Log}s_0-E_s/2.303RT$ ....(25)

$\mathrm{Log}P=\mathrm{Log}P_0-E_p/2.303RT$ ....(26)

Hence plot of Log D against 1/T is a straight line from which E_D can be obtained from the slope. Similarly plot of LogS and LogP, against 1/T separately can be used to estimate E_s and E_p respectively . Typical Arrhenius plots of above relationships are given in figures 12,19 and 20. The calculated values of E_D,E_s and E_p are given in Table VII. For the non-polar solvents used for this work, the activation energy values are found to be higher for benzyl chloride respectively. This indicate the higher temperature sensitivity of PP to their solvents. For the non-polar solvents (that include four classes of solvents) used, the E_D is in the order n-Hexane > CCL_4 > toluene > dioxane. This seems to be explained by a decrease in interaction constant in the same order. For the polar-solvents used, the E_D is in the order benzyl chloride > acetone. This seems to be explained by a decrease in molar volume in that order. Also from, the temperature dependence on flux rates, the activation energies for solubility (fig 19) and permeation (fig 20) were calculated and were found to be in the range 0.90-17.96KJmol^{-1} and 14.9-82.97KJ mol^{-1} respectively.

The low E_s for toluene and tetrachloromethane are consistent with the high solubility of these solvents in PP film arising from the low interaction constant. The relative lower value of E_D for acetone relative to n-Hexane, toluene and tetrachloromethane may be explained by the small size (molar volume = 74cm mol^{-1}), in addition to its high polarity leading to very low solubility. Both factors add up to result into low E_D ,E_s and E_p values . That the magnitudes of E_D ,E_s and E_p for benzyl chloride a polar solvent with high polarity lead to the higher observed values relative to the non-polar solvents.

3.6 ENERGETICS

The energetics of any thermodynamic system is governed by the well known Gibb's free energy expression

$$\Delta G=\Delta H - T\Delta S \qquad (27)$$

Where ΔG is the change in the free energy of system and has a negative value for spontaneous change; ΔH is the enthalpy change, is the entropy change and T is the Kelvin temperature.

For the sorption organic molecules, the equilibrium amount sorbed by a given mass of polymer, denoted by equilibrium sorption constant, K_s was calculated from the expression(49)

$$K_s = \frac{\text{moles of penetrants sorbed}}{\text{unit mass of polymer}} \ldots\ldots\ldots\ldots\ldots(28)$$

The Van't Hoff's equation is useful in obtaining the entropy change ΔS and enthalpy ΔH and given by

$$\mathrm{Log}K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303R} \cdot 1/T \ldots\ldots\ldots\ldots\ldots(29)$$

Plot of $\log K_s$ against 1/T(K) is a straight line and ΔH can be calculated from the intercept. These plots are shown in figure 21 and values of ΔH, ΔS then ΔG calculated for 28□C from equation (27) are reported in Table VIII.

The ΔS values are negative in most cases except for dioxane sorption suggested the retainment of liquid structure of solvent molecules even in the sorbed state. Such explanation had been reported before(49). Except for dioxane which have a positive

ΔS value ($+5.36 \mathrm{Jmol}^{-1}\mathrm{k}^{-1}$) all the non-polar solvents have higher negative ΔS values. The ΔS values for solvents are positive, the lowest value been observed in tetrachloromethane and toluene which have been reported here as having the largest solubility in PP. In fact considering only n-Hexane, toluene and tetrachloromethane ΔS and ΔH are shown to increase with increase in molar volume of solvent. Except in the case of n-hexane which has negative ΔG value (-6.12KJ mol^{-1}), the free energy of solubility is positive for the other solvents studied; being largest for acetone and benzyl chloride which are polar solvents. From the positive values of ΔG it is implicit that these solvents do not spontaneously dissolve PP in the range of temperature studied; as it is found experimentally. The negative values of ΔG for n-hexane though suggests solubility but experimental results show that this does not happen in the temperature range studied.

Thus thermodynamic prediction did not explain the experimental insolubility of PP in n-hexane.

3.7 CRITICAL DISSOLUTION TEMPERATURE (CDT) AND APPARENT CRYSTALLINITY (AC)

The data on CDT and AC of PP filma are presented in Table IX. The CDT technique assumes that

(i) The treated films consist of two phases: the impermeable crystalline embedded in an amorphous region

(ii) The solvent molecules permeate the amorphous phase only

(iii) The crystallites take longer time to dissolve than the smaller crystallites(50).

In Table IX, it is evident that films treated at higher temperatures have higher apparent crystallinity than those treated at lower temperatures. This implies that the larger

CDT and AC result from high temperature solvent annealing. It has been shown that larger crystallites take longer time to dissolve than smaller crystallites(50). Johnson and Popoola(50) have shown that heat treatment of polyethyleneterephthalate (PET) fibre gave rise to larger CDT and AC than solvent treatment. This they explained in terms of fewer but larger crystallites produced by heat treatment when compared to large number of smaller crystallites produced by solvent treatment. The usefulness of this simple experimental method of monitor changes on the morphology of polymer films is that apparent crystallinity data have also been corroborated with infrared(IR) crystallinity data(50).

3.8 STUDIES ON ETCHED SAMPLES

Originally it was intended to study the effects of different etching media-chromic acid and nitric acid, on the physical (weight loss) morphological (density, crystallinity etc) and chemical microstructure (functional groups, elemental analysis) on some PP samples. When the instrumental methods of analysis e.g. infrared(IR), nuclear magnetic resonance (nmr) were finally confirmed unavailable, attention was then turned towards the changes in the swelling sorption and energetics as a result of the etching and then to compare these with those of the unetched PP films.

First,a change in the thickness of PP films resulted from the etching, with chromic acid-etched showing a percent thickness decrease of 65.6 ± 1.45% while the nitric acid etched film exhibited a percent thickness decrease of 53.1 ± 8.45%.

The greater variation of thickness decrease in the latter case may be due to changes in the concentrated acid solution with time. The weight loss % recorded were 0.0643g and 0.0253g for chromic acid and nitric acid etching respectively. These values of percent thickness decrease and % weight loss are in conformity with the reports that chromic acid is a more efficient etching medium than nitric acid(32).

3.8.1 SORPTION IN ETCHED PP FILMS

The data on the swelling in mole percent sorbed at different time intervals and different temperatures in n-hexane are recorded in Table X and plotted in figures 22 & 23. In addition to the problems of reproducibility recorded in section 3.8, etched PP films present a more serious reproducibility problem. This arises from the fact that etching by these oxidizing media remove a skin on the polymer film. This skin is made up of amorphous/atactic polymer materials, oligomers originally present or resulting from chain cleavages. Because these materials are inhomogeneously packed in the film, some positions will contain more and others less, so that the PP film at different locations contain different amounts of crystalline materials and this will affect the sorption properties.Numerous attempts to obtain swelling data that will give the usual curves as with the untreated films failed. The data in Table X and plotted in figures 22 and 23 are about one of the best that could be obtained.

Generally, in Table X, one finds that the swelling data are larger for the nitric acid etched film than chromic acid etched film at 28^0c and 40^0c in agreement with the finding that nitric acid is a less efficient etchant and therefore left more polymer materials on the PP film than the chromic acid etchant.Since the data from the etched films are so unpredictable, studies on diffusion coefficients, mode of transport, activation energy and energetics were not pursued further.It is therefore concluded that the etching treatments at these acid concentrations and temperatures may not be suitable for improving the selectivity of PP films/membrane to various organic solvent mixtures.The first attempt to improve the adhesion of ultra drawn PE structures was undertaken by Ladizesky and Ward(70) who investigated the effect of plasma and chromic acid treatment on the adhesion of melt-spun/drawn PE films to an epoxy matrix.Both treatments markedly improved the adhesion, although plasma treatment was far more effective.This was attributed to the pitted surface produced by the plasma treatment, providing excellent mechanical interlocking.Similar results following air or oxygen plasma treatment were reported by Nguygen et al(71), Nardin and Ward(72) and Kaplan et al.(73). A marked increase in wettability and adhesion was observed after ammonia plasma treatment, although scanning electron microscopy showed no changes in surface structure(74). Recently, Postema et al(75) reported a five fold increase in the adhesion of gel-spun PE fibre to gypsum plaster after chlorosulphonation. According to the authors this improvement could be related to surface roughening of the fibres.

Traditionally, permanganic etching has been employed to study representative internal morphologies in a whole range of semi crystalline polymers(76). The techniques works by selectively removing particular morphological elements. In general, amorphous region are etched away more rapidly than the crystalline parts, resulting in the development of a relief at the development of a relief at the specimen surface which is directly related to the underlying microstructure (i.e. the local reaction kinetics depend upon the molecular organization). In multicomponent systems many reactions may occur and, by suitably tailoring the etching reagents, many different effect may be generated(77).

CHAPTER FOUR

SUMMARY CONCLUSION AND SUGGESTION FOR FURTHER STUDIES

Gravimetric Sorption studies of six solvents into polypropylene (PP) films at different temperatures 28^0c, 40^0c and 60^0c have been studied. The six solvents used include non polar hydrocarbon solvents (tetrachloromethane, toluene, n-hexane and dioxane) and polar solvents (benzylchloride and acetone) with large differences in dipole moments, and with varying molar masses/volumes and calculated interaction parameters. These were chosen to illicit information on how change in solvent polarity, molar volume and interaction parameters of solvents will affect the properties of interest.

First the swelling data defined by the swelling quotient was used according to Gee's theory in two different forms (1) plot of $[v^{-1} \text{In } Q_\infty/Q]^{1/2}$ against solubility parameter δ_2 of solvent and (2) plot of swelling ratio against solubility parameter δ_s of solvent to obtain the maximum in the swelling envelope and the X-intercept respectively, the solubility parameter of solvent at this points respectively being equal to the solubility parameter of PP. The values obtained respectively were 19.4 and 17.5 and these agreed reasonably with the experimental solubility parameter $\delta_p = 18.80\text{MPa}^{1/2}$ most frequently qouted. In addition, the solubility parameter of PP, δ_p , obtained from small's group molar attraction constant was $16.4\text{MPa}^{1/2}$ lower than the values quoted above.

The solvent uptake data for each solvent was taken at different time intervals until equilibrium sorption was attained, and the square root of time $t^{1/2}$ $(S^{1/2})$ for this to occur generally was found to be lower for polar solvents $t^{1/2} =$ $60S^{1/2}$

but $t^{1/2} = 60 - 85\ S^{1/2}$ for the non polar solvents. This was explained as a clear indication of the non-polar solvents having been sorbed more than the polar solvents in PP, a non-polar polymer. The plots of mole percent swelling at time t, Qt against square root of time $t^{1/2}(S^{1/2}$) provided the profiles for obtaining the slope of the kinetic region. The slope was fitted into the well known Crank's expression for the calculation of diffusivity D, of organic molecules into polymer films and membranes. For each solvent, it was apparent that the initial slope increase with increase in temperature of solvent sorption and thus followed the data on the diffusivity. The diffusivity was of the order of $10^{-8}cm^{2}\ S^{-1}$ as predicted for polymers. The solubility S, was defined by maximum mole percent solvent sorbed by the polymer film, while the permeability P, was defined by the product of diffusivity and solubility (P = DS). It was also shown that for any particular solvent the solubility S and the permeability increased with increase in sorption temperature. Generally non-polar solvents in particular aromatic solvents exhibited higher values of diffusivity, solubility and permeability and for this group of solvents determines the values of these properties since the smaller the molar volume the larger the values of D, S, and P, hence the order n-hexane > toluene > CCl_4 > dioxane. However, for the polar solvents, the solvent polarity and interaction constant X come into importance, since the more polar the solvents and the more the interaction constant X the less these diffusion coefficients. The dipole moment of acetone (=2.88) is higher than that of benzyl chloride (=1.70).it is also apparent that for a homologous series of solvent e.g. esters, the inverse dependence of these properties on molar volume shows up. The high values of D, P, S for the chlorosolvents is probably due to the specific interaction of PP with this family of solvents. The data on permeability for each solvent at different temperatures were used to calculate the permselectivity Z given by $Z = P_i/P_j$.

The magnitude Z showed that out of the thirteen penetrant pairs, five e.g. tol./hex. exhibited a decrease in Z with increase in temperature, the result of which has been explained in terms of the loss of selectivity due to partial melting of crystalline and amorphous zones that can now allow 'holes' for the penetrants to pass through and move to the advantage of larger molecules. However seven penetrant pairs showed an increase in perm-selectivity with temperature especially for polar molecules in which case the reluctance of non-polar PP chains to interact with polar organic molecules, and this effect is expected to be more at higher temperatures.

The mechanism of swelling was studied by fitting the swelling data into well-known expression from which the mode of transport defined by the value of n and the extent of interaction between the PP polymer chain and the various values were estimated graphically. The values of n largely between 0.5 and 1.0 which were described as non-fickian but rather anomalous were characteristics of the diffusion of these organic molecules into PP. Only in a few cases e.g. tetrachloromethane was there a tendency towards Fickian diffusion and at 60^0c temperature.

A typical example of the super case II n >1.0 was exhibited by n-hexane at 28^0c . The n values were generally found to decrease with increase in temperature. The polymer-solvent interaction described by K values for any particular solvent is shown to increase with increasing sorption temperature. This is expected as the partial melting of polymer material with temperature will led to greater polymer-solvent interaction. The k values are high for non-polar solvents and chlorosolvents and these have been explained by "like-dissolves like" type of interaction and the preferential interaction of PP with chlorosolvents.

The activation energies of diffusion, E_D , solubility E_s and permeability E_p were calculated from the slopes Arrhennius plots of logD, logS, logP separately with reciprocal absolute temperature 1/T. Similarly the entropy Δs and ΔH of solubility were calculated from the intercept and slopes of logarithm of maximum solubility (mole) log k_s versus reciprocal Kelvin temperature with the finding that the mode of transport was the case I diffusivity and case II velocity. The activation energies calculated were in all cases positive, ranging from 4.79KJmol^{-1} to 73.40KJmol^{-1} for E_D ; 0.90KJmol^{-1} to 17.96KJmol^{-1} and 14.90KJmol^{-1} to 82.97KJmol^{-1} for E_p. The E_s value was found to increase with decrease in molecular weight for non-polar solvents while for polar solvents, an increase in molar volume, molecular weight and interaction constant lead to an increase in E_s value. The negative values of entropies for practically all the solvents is an indication that these solvents still remains in the liquid state in sorbed state. The positive values of the enthalpy of solution implies an endothermic process for solvent transport into PP.

The critical dissolution time (CDT) and the apparent crystallinity developed in PP films at equilibrium liquid sorption at different temperatures were also investigated. It was shown that CDT and the AC were also higher for non-polar solvents while they were lower for the polar solvents. This was expected since solvent induced crystallization (SINC) apparently depended on the plasticizing effect of the difference in the solubility parameter of polymer and solvent $/\Delta\delta/$. The low value CDT and AC for n-hexane compared to other non-polar solvents was dependent on the large $/\Delta\delta/$ value.

Chemical etching is a popular method of surface modification that changes both surface chemistry and surface roughness. Composite properties are dependent on stress transfer through the fibre-matrix interface. Enhanced interfacial adhesion improves stress transfer and is expected to improve composite properties. The single fibre strength and failure strain, however, may be altered by the polymer degradation associated with adhesion-enhancing surface treatments. Chemical etching can embrittle the polymer and create flaws on the fibre surface. The etching process is expected to diminish fibre strength and failure strain.

Based on the results from gravimetric sorption studies of solvents in PP films, one may now conclude as follows:

(1) The Gee's theory on solubility parameter can be used effectively to estimate within experimental errors the solubility parameter of PP.

(2) Solvent uptake by PP and solubility, diffusivity and permeability into PP increase with increase in temperature.Generally non-polar solvents have higher values of these properties for chlorosolvents though polar solvents are explained by prefential contacts between PP and this class of solvents. Polar solvents took shorter $t_{1/2}$ to attain saturation level ($\approx 60S^{1/2}$) while non-polar solvents took longer time $t_{1/2} = 60 - 85S^{1/2}$.

(3) The mode of transport as described by the value of n is shown generally to be non-fickian, but rather anomalous being made up of Case I and II velocity. The n values for each solvents were shown to decrease with increase in temperature.

(4) Perm-selectivity for most solvents pairs studied decrease with increase in temperature.

(5) The activation energies of diffusion, solubility and permeability are all positive and the profiles are consistent with the fact that the diffusion into PP is a combination of case I diffusion and case II velocity in the same way as the Vant's Hoff plots for enthalpy of

solution.

(6) The negative values of the changes and the positive values of ΔH are implicit that the solvents molecules are still in the liquid state in the PP matrix and that enthaply of solution is endothermic respectively.

(7) The positive sign of the free energy of solution implies that the solubility of these solvents at the temperatures studied is not spontaneous

(8) CDT and AC increase with increase in temperature, being high for non-polar solvents e.g. carbontetrachloromethane but low for polar acetone.

(9) Chromic acid is a more powerful etchant and can remove the weak, boundary layers and oxidize PP films than fuming nitric acid.

(10) The etched PP films may not be suitable for sorption studies.

A lot of work need to be further done on PP films like the effects of heat treatment, natural weathering, strain induced crystallization and how these affect the sorption energetics and selectivities. The use of different scanning calorimetry (DSC), differential thermal analysis (DTA), thermal gravimetry analysis (TGA), electro scanning spectroscopy (ESR), infrared spectroscopy (IR) to determine change in crystallinity and characterization should be employed.

Also further studies on etched PP films need to be studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), wide angle X-ray scattering and birefrigence to monitor the changes in surface topography, polymer microstructures and molecular orientation of crystalline regions, also a combination of Fourier transform-infrared spectroscopy (FTIR) and electro spectroscopy for chemical analysis (ESCA) to examine surface composition.

REFERENCES

1. Bilmeyer F.W:"Text Book of Polymer Science" 2nd Ed. John Wiley, New York(1976).
2. Morton - Jones D.H:"Polymer Processing"1st Ed. C&H (1989)
3. Stevens M.P:"Polymer Chemistry (An Introduction)" 2nd Ed. Oxford University Press, Inc New York (1992)
4. De Fillipi R.P, Sc.D Thesis, Massachusetts Institute Technology,Cambridge, Massachusetts (1962).
5. Sperling L.H:"An introduction to physical polymer Science" 2nd Ed. John Willey, New York (1992)
6. Michael A.S, Vieth W., Hoffman A.S, Alcalay H.A: J. ApplPolym.Sci., 13,577 (1969)
7. Horas, J.A and Rizzotto, M.G: J. Polym. Sci.,*27*,175 (1989)
8. Vieth W.R, Howell, J.M, and Hsieh, J.H: J. Member.Sci.,*1*, (1976).
9. Mauze, G.R, and Stern, S.A: J. Member. Sci.,*12*,51 (1982)
10. Mauze, G.R, and Stern, S.A: J. Polym. Eng. Sci.,*23*,548(1983)
11. Zhous, S and Stern, S.A: J. Polym. Sci, part B, Polym. Phys; *27*,205 (1989)
12. Cohen, M.H and Tunbull, D : J. Chem. Phys.,*31*,1164 (1959)
13. Kreituss, A and Frisch, H.L: Polym. Phys. Ed. *19*,889 (1989)
14. Fujita, H : Fortschr, Hoch Polym. Fors *3* ,1 (1961)
15. Kormerer, R.W, Meerwall, E.V and Peppas, N.A:J. Polym. Phys Ed.*24*,409 (1986)
16. Breen. J:J. Mater. Sci *28*,3769 (1983)
17. Mai Y.W: J. Mater. Sci, *21*,904 (1986)

18. Liai, D.C, Chern, Y.C, Han, J.L, and Hsieh K.H: J. Polym. Sci, Part B, Polym. Phys, *35*,1747 (1997)

19. James,H.M and Guth .E : J. Chem. Phys, *15*,669 (1947)

20. de Gennes P.G :Scaling concepts in polymer physics, Cornell, Theca, N. York (1979)

21. Yasuda H. and Lamaze.C: J. Macromal. Sci. Phys *135*,111 (1971)

22. Peppas,N.A and Reinhart C.T:J.Member. Sci. *15*,275(1983)

23. Vrentas J.S and Duba J.L:J. Polym. Sci.,Polm.Phys. Ed, *15*, 417(1977)

24. Crank J :"The mathematics of Diffusion", Oxford Univ. Press, London (1956)

25. Hausslein R.W; Ph.d Thesis, Massachusetts Institute Of Technology, Cambridge, Massachusetts, 1964.

26. Brant W.W:J.Phys.Chem.,*63*,1080 (1959)

27. Weast R.C (Ed):CRC Handbook of chemistry and physics, 1st student Ed.,CRC Pres.Inc,Boca Raton,Florida(1987)

28. Sheldon R.P :Polymer, *3*,27 (1962)

29. Moore W.R and Sheldon R.P : Polymer, *2*,315 (1961)

30. Cottarn L. and Sheldon R.P: Adv. Polym. Sci. Technol.*26*,65 (1966)

31. Desai A.D and Wilkes G.L :J. Polym. Scic., *46*,291 (1974)

32. Silverstein M.S and Breuer O.J : J. Mater Sci., *46*,4153-58 (1993)

33. Merex F.P, Benzina A.,Van Langeveld A.D and Lemstra P.J: J. Mater Sci.,*28*,753 (1993)

34. Raymond C.F, Henry T.S, Yau W.W and Harrey H.H :"
Estimation of polyethelene morphology by nitric
acid etching and gel permeation
chromatography",J.Appl.Polm.Sci.,21,1911(1977). 35.
Wunderlich B.:Macromolecular physics, Academic, New
York, Vol.1 chap.*4*,1973.

36. Briggs D, Borewis and Konieczo M.B, Ibd.11 (1976) 1270

37. Olley R.H, Hodge A.M and Bassett D.C :Polym. Sci.,Polym. Phys. Ed, *17*,627 (1979)

38. Hawkins W.L, Matregek W. and Winslow F.H : J Appl. Polym. Sci.,*4*,431(1959)

39. Bobalek E.G., Henderson J.N, Serafini T.T and Sheldon J.R: J. Appl. Polym. Sci, *2*,210 (1959)

40. Palmer R.P and Cobbold A.J:Makromol.Chem.,74,174(1964)

41. Williams T. Udagawa. Y. Keller. A. and Ward I.M: Polym. Sci., Part A,8,35(1970)

42. Illers K.H : Makromol. Chem.,*118*,88 (1968)

43. Winslow F.H and Matreyk W.:Am. Chem. Soci.,Div. Polym. Chem., Prepr., 7, 540 (1966)

44. Melby B.R :Macromolecules,*11*,50 (1978)

45. Paul D.R and Ebra-Lima: J. Appl. Polym. Sci.19,275(1975)

46. Renner N. and Oppermann. W:Colloid Polym. Sci., *270*, 527 (1992)

47. Andreopoulos A.G, Polyzois G.L and Evangelatou. M: J. Appl. Polym. Sci.*50*,729 (1993)

48. Unnikrishnan G. and Thomas S.:J. Polym. Sci. B, polym. Phys, Ed,*35*,725 (1975)

49. Johnson A., and Popoola,A.V : J. Appl. Polym. Sci.,*42*,2703 (1991)

50. Tager A.A and Kalmakova, L.K Polym. Sci. (USSR) *22*,533 (1981)

51. Gee G.:"Thermodynamics of rubber solutions and gels in advances in colloid state ", Vol II, interscience, New York (1946)

52. Scott R.L and Magat M : J Polym. Sci.,*4*,555 (1949)

53. Hayes R.A : J. Appl. Polym. Sci.,*5*,318 (1961)

54. Kambour R.P, Gruner C.L and Romagosa E.E: Macromolecules, 7,2 (1974)

55. Yagi Y.,Inomata .H., Saito S : Macromolecules, *25*,2997 (1997)

56. Small P.A :J. Appl. Chem., *3*,71 (1953)

57. Berens A.R and Hoppenberg, H.I:J. Membrane *10*,283 (1982)

58. Flory P.J :"Principles of polymer chemistry" Cornell theca,495, (1953)

59. Hildebrand J.H and Scott R.L:"The solubility of non-electrolytes,3rd Ed., Reinhold, New York, 1949.

60. Grulke E.A :Polymer Handbook, 2nd .Ed.,J. Brandup and E.H Immergut, eds.,Interscience, New York, 1975, VII, p.521

61. Makarewicz P.J and Wilkes G.L: J. Polym. Sci.,Polym. Phys. Ed.,*16*,1529 (1978)

62. Crank J.:The mathematics of diffusion, 2nd ed.,oxford University, London, 1975

63. Cassidy P.E, Aminabhavi T.M and Thompson C.M : Rubber chem.

Technol. Rubber per. *56* 594 (1983)

64. Rodridguez, F:"Principles of polymer systems", 2nd ed. Graw Hill, London, 523 (1983)

65. Sweeny R.F and Rose A.:Ind. Eng. Chem., Prod. Res. Develop., *4* ,248 (1965)

66. Li N.N, Long R.B and Henley E.T : Ind. Eng. Chem.,*57*,18 (1965)

67. Lucht L.M and Peppas N.A : J. Appl. Polym. Sci.,*33*,1557 (1987)

68. Alfrey. T., Gurnee E.F and Lloyd W.G : J.Polym. Sci.(C),*12*,249(1966)

69. Onyang H. chen .C., Lee .S. and Yang.H.:J.Polym. Sci.B.PP.*36*,163(1998)

70. Ladizesky N.H and Ward I.M.: J.Mater. Sci. *18*,533 (1983)

71. Nguygen H.X, Riahi.G. and Poursatip .A.:"Proceedings of 38th International SAMPE symposium". Anaheim (1988) pp 1721-9

72. Nardin M. and Ward I.M:J.Mater. Sci. Technol. *3*,814 (1987)

73. Kaplan S.L, Rose P.W, Nguygen H.X and Chang H.W:SAMPE Q. *19*,455,(1988)

74. Holmes S. and Schwartz. P: comp. Sci. Technol. *38*,1,(1990)

75. Postema A.R, Doornkamp A.T, Meijer J.G and Vlekkert H.V:Polym. Bull. 16 (1986)

76. Vaughan A.S and Bassett D.C: Polymer *20*,1397 (1988)

77. Sutton S.J and Vaughan A.S: J.Mater. Sci.*28*,4662 (1993)

78. Barton A.F.M:"Handbook of solubility parameters and other cohesion parameters" CRC, Boca Raton, Florida (1983)

TABLE I: PROPERTIES OF POLYPROPYLENE

PROPERTIES	VOLUME RANGE
Specific gravity, g/cm^3	0.902 - 0.906
Refractive index, $n_o^{2.5}$	1.49
Tensile strength, Psi	4300 - 5500
Elongation, %	200 - 700
Tensile modulus, 10^5 Psi	1.6 - 2.3
Impact strength, ft-lb/in, of notch	0.5 - 2.0
Heat-deflection temp, ^{0}F, 264 Psi	125 - 140
Dielectric constant, 1000 cycles	2.2 - 2.6
Dielectric loss, 1000 cycles	$<$ 0.0005 - 0.0018
Water absorption, 1/8lb.bar,24hrs,%	$<$ 0.01
Burning rate	Slow
Effect of sunlight	Requires protection
Effect of strong acids or bases	Resistance
Effect of organic solvent	Resist. (below 80^0C)
Clarity	Opaque

TABLE II: SOLVENTS BY BOILING POINT (BP^t), DIPOLE MOMENT (□), MOLAR VOLUME (V_s), MOLAR MASS (M_s), SOLUBILITY PARAMETER (δ) AND CALCULATED INTERNAL CONSTANT X

PERMEANT	B.pt^a (∞)	μ^a	V_s^b	SOLUBILITYPARAMETER (δ) (MPa$^{1/2}$)^b	X	M_s
Acetone	56.2	2.88	74.0	20.0	0.38	58.08
Acetonitrite	81.6	3.92	52.6	24.4	0.44	41.05
Benzylchloride	179.3	1.70	115.0	20.3	2.06	126.6
n-Butanol	117.2	1.66	91.5	23.1	1.02	74.12
Chloroform	61.0	1.01	80.7	19.0	0.34	119.4
Cyclohexane	80.7	0	108.7	16.8	0.52	84.16
1,4-Dioxane	101	0	85.7	20.5	0.40	88.11
Ethyl acetate	77.1	1.78	98.5	18.1	0.36	88.1
n-Hexane	69	0	131.6	14.9	1.15	86.18
Methylacetate	57	1.72	79.7	18.7	0.34	74.1
Tetrachloro methane	76.5	0	97.1	17.8	0.38	153.4
Toluene	110.6	0	106.8	18.2	0.36	92.14
Xylene	144.4	0	121.2	18.0	0.37	106.2

(a) from Ref[27]   (b) from Ref[59]

TABLE III: PERCENT SWELLING AT 10min (Q_t) AND AT EQUILIBRIUM (Q') FOR PP IN DIFFERENT SOLVENTS AND SOLUBILITY PARAMETER OF SOLVENTS

LIQUID	T (^{0}C)	Q_t (mol %)	Q_∞ (mol%)	δ_s[a] (MPa$^{1/2}$)
n-Haxane	28	0.108	0.162	14.9
	40	0.146	0.240	
	60	0.207	0.260	
Toluene	28	0.158	0.300	18.2
	40	0.196	0.300	
	60	0.241	0.350	
Tetrachloro methane	28	0.184	0.420	17.8
	40	0.260	0.430	
	60	0.262	0.440	
Acetone	28	0.011	0.046	20.0
	40	0.012	0.053	
	60	0.014	0.063	
Dioxane	28	0.038	0.08	20.5
	40	0.066	0.13	
	60	0.090	0.16	
Benzylcholoride	28	0.017	0.053	
	40	0.049	0.062	
	60	0.069	0.110	20.3

(a) Ref.[1]

TABLE IV: VARIATION OF WEIGHT INCREASE $\Delta w_{(g)}$ AND THE MOLE PERCENT SWELLING % Q_t OF POLYPROPYLENE (PP) AT DIFFERENT TIMES $t_{(min)}$ AND DIFFERENT TAMPERATURE T, IN DIFFERENT SOLVENTS

	28°C		n-Hexane 40°C		60°C	
Time	Δw	Q_t	Δw	Q_t	Δw	Q_t
2	0.0022	0.024	0.1147	0.594	0.0098	0.111
5	0.0046	0.051	0.0096	0.104	0.0147	0.161
7	0.0088	0.100	0.0126	0.140	0.0155	0.191
10	0.0093	0.108	0.0134	0.146	0.0189	0.207
15	0.0100	0.111	0.0144	0.168	0.0184	0.213
20	___		0.0164	0.185	0.0175	0.222
30	0.0108	0.112	0.0167	0.201	0.0206	0.230
45	0.0123	0.142	0.0208	0.228	0.0212	0.236
60	0.0133	0.147	0.0198	0.228	0.0210	0.251
120	0.0144	0.161	0.0223	0.244	0.0219	0.256
180	___	___	___	___	0.0233	0.260
240	0.0135	0.163	0.0214	0.237	0.0220	0.259
300	0.0134	0.162	0.0228	0.0231	0.0210	0.248
360						

TABLE IV: Continue

	28°C		Toluene 40°C		60°C	
Time	Δw	Q_t	Δw	Q_t	Δw	Q_t
2	0.0044	0.048	0.0063	0.066	0.0120	0.128
5	0.0076	0.082	0.0128	0.138	0.0150	0.154
7	0.0155	0.125	0.0152	0.177	0.0204	0.202
10	0.0146	0.158	0.0182	0.196	0.0218	0.241
15	0.0209	0.210	0.0217	0.221	0.0239	0.267
20	—	—	0.0235	0.240	0.0264	0.280
30	0.0200	0.224	0.0265	0.276	0.0265	0.297
45	0.0212	0.248	0.0270	0.292	0.0277	0.298
60	0.0277	0.287	0.0277	0.314	0.0317	0.338
120	0.0282	0.303	0.0324	0.331	0.0314	0.345
180	—	—	—	—	—	—
240	0.0293	0.304	0.0314	0.331	0.0312	0.346
300	0.0296	0.320	—	—	0.0299	0.346
360						

TABLE IV: Continue

	28°C		CCl_4 40°C		60°C	
Time	Δw	Q_t	Δw	Q_t	Δw	Q_t
2	0.0109	0.067	0.0120	0.076	0.030	0.188
5	0.0166	0.106	0.0257	0.169	0.033	0.208
7	0.0254	0.156	0.0403	0.259	0.036	0.226
10	0.0298	0.184	____	____	0.0407	0.262
15	____	____	0.0453	0.283	0.0470	0.312
20	0.0330	0.208	0.0482	0.293	____	____
30	0.0397	0.266	0.0499	0.312	0.0584	0.377
45	0.0509	0.317	0.0573	0.358	0.068	0.427
60	0.0614	0.385	0.0643	0.414	0.066	0.429
120	0.0675	0.418	0.0667	0.421	____	____
180	0.0671	0.419	0.0669	0.420	0.067	0.427
240	0.0680	0.416	0.0677	0.431	0.065	0.403
300	0.0663	0.428	639	0.422		
360						

TABLE IV: Continue

	28°C		Acetone 40°C		60°C	
Time	Δw	Q_t	Δw	Q_t	Δw	Q_t
2	0.0006	0.011	0.0009	0.012	0.0008	0.014
5	0.0008	0.014	0.0011	0.019	0.0012	0.021
7	0.0012	0.021	0.0013	0.023	0.0015	0.026
10	0.0013	0.023	0.0016	0.028	0.0018	0.031
15	0.0017	0.030	0.0020	0.034	0.0023	0.039
20	____	____	____	____	____	____
30	0.0021	0.036	0.0025	0.043	0.0030	0.051
45	0.0026	0.045	0.0028	0.048	0.0036	0.063
60	0.0027	0.046	0.0031	0.053	0.0034	0.063
120						
180	0.0027	0.046	0.0031	0.053	0.0034	0.063
240	____	____	0.0031	0.0.54	____	____
300						
360						

TABLE IV: Continue

	28°C		Dioxane 40°C		60°C	
Time	Δw	Q_t	Δw	Q_t	Δw	Q_t
2	0.0014	0.016	0.0020	0.023	0.0025	0.029
5	0.0023	0.026	0.0029	0.033	0.0043	0.049
7	0.0027	0.031	0.0051	0.058	0.0049	0.057
10	0.0033	0.038	0.0058	0.066	0.0079	0.090
15	0.0037	0.042	0.0063	0.071	0.0076	0.087
30	0.0053	0.061	0.0076	0.088	0.0102	0.116
45	0.0063	0.072	0.0090	0.105	0.0101	0.116
60	0.0071	0.081	0.0113	0.128	0.0138	0.161
120	0.0070	0.080	0.0110	0.124	0.0137	0.160
180	0.0072	0.083	0.0109	0.125	0.0138	0.161
240	_____	_____	0.0114	0.130	0.0145	0.165

TABLE IV: Continue

	Benzyl chloride					
	28°C		40°C		60°C	
Time	Δw	Q_t	Δw	Q_t	Δw	Q_t
2			0.0018	0.015	0.0059	0.047
5	0.0011	0.008	0.0016	0.013	0.0074	0.059
7	0.0013	0.031	0.0050	0.041	______	0.069
10	0.0022	0.010	0.0006	0.049	0.0088	0.075
15	0.0032	0.017	0.0066	0.052	0.0095	0.087
30	0.0038	0.025	0.0068	0.055	0.0116	0.095
45	0.0071	0.030	0.0065	0.051	0.0119	0.101
60	0.0069	0.055	0.0080	0.061	0.0310	0.106
120	______	______	0.0080	0.062	0.0134	0.1084
180	______	0.053	0.0079	0.063	0.0137	______
240	______	______			______	______

TABLE V: VARIATION OF DIFFUSIVITY D, SOLUBILITY S, PERMEABILITY P AND n AND K OF EQUATION AT DIFFERENT SORPTION TEMPERATURES T

LIQUID	T(°C)	D x10^{-8} (cm^2S^{-1})	S mol%	Px10^{-8} (mol.S^1)	n	K
n- Hexane	28	4.8	0.162	0.78	1.17	0.001
	40	9.0	0.237	2.13	0.68	0.008
	60	27.7	0.256	7.10	0.42	0.050
Toluene	28	4.3	0.309	1.33	0.78	0.004
	40	9.0	0.331	2.98	0.50	0.008
	60	18.5	0.346	6.40	0.46	0.035
Tetrachloromenthane	28	3.4	0.420	1.40	0.71	0.006
	40	5.5	0.424	2.30	1.00	0.004
	60	18.6	0.428	7.90	0.22	0.126
Acetone	28	6.1	0.046	0.30	0.60	0.020
	40	7.2	0.053	0.50	0.54	0.022
	60	7.3	0.063	0.60	0.47	0.025
Dioxane	28	6.0	0.081	0.50	0.50	0.017
	40	6.1	0.126	0.80	0.65	0.007
	60	6.4	0.162	1.00	0.58	0.006
Benzylechloride	28	1.7	0.054	0.09	1.09	0.008
	40	13.8	0.061	0.80	0.72	0.010
	60	28.1	0.107	3.0	0.23	0.126

TABLE VI: SELECTIVITY Z_i/Z_j OF PP FILMS AT DIFFERENT TEMPERATURE

LIQUID PAIRS	TEMPERATURE °C			
	28	40	60	TREND
Tol/Hex	1.7	1.4	0.9	d
Tol/Tet	1.0	1.3	0.8	*
Tol/acet	4.4	7.5	12.8	i
Tol/Diox	2.7	3.7	6.4	i
Tet/Hex	1.8	1.1	1.1	d
Tet/acet	4.7	5.8	15.8	i
Tet/Diox	2.8	2.9	7.9	i
Diox/acet	1.7	2.0	2.0	i
Tol/Benz	2.5	0.7	0.7	d
Tet/Benz	2.0	0.4	0.7	d
Diox/Benz	3.5	0.4	0.2	d
Hex/Diox	0.8	1.5	4.3	i
Benz/acet	0.3	1.9	3.8	i

KEYS:

Hex= n-hexane, Tol=Toluene, Acet=Acetone,

Diox=Dioxine ,Benz=Benzylchloride, d=decrease

i=increase, x=Irregular

TABLE VII:VARIATION OF ACTIVATION ENERGIES OF DIFFUSION E_D, SOLUBILITY E_S AND PERMEABILITY E_P FOR LIQUID SORPTION INTO PP FILMS.

LIQUID	E_D(KJmol^{-1})	E_S(KJmol^{-1})	KJmol^{-1})
n-Hexane	64.76	14.1	38.33
Toluene	39.42	1.24	44.65
Tetrachloromethane	49.24	0.90	47.89
Acetone	4.79	8.40	14.90
Dioxane	9.57	17.96	18.53
Benzylchloride	73.40	17.95	82.97

TABLE VIII: VARIATION OF ENTROPY ΔS, ENTHALPY ΔH,AND FREE ENERGY ΔG OF SORPTION INTO PP FILMS AT 28°C.

LIQUID	ΔS(Jmol^{-1}K^{-1}	ΔH(KJmol^{-1})	ΔG, (KJmol^{-1})
n-Hexane	-13.79	+10.27	-6.12
Toluene	-36.95	+3.83	+7.30
Tetrachloromethane	-44.42	+0.48	+12.90
Acetone	-38.29	+8.38	+19.91
Dioxane	+ 5.36	+19.15	+17.54
Benzylchloride	-0.97	+17.95	+18.24

TABLE IX: MOL. PERCENT SWELLING AT EQUILLIBRIUM (Q_y),CRITICAL DISSOLUTION TIMES(CDT),AND PERCENT APPARENT CRYSTALLINITY (%AC) IN DIFFERENT SOLVENTS OF POLYPROPYLENE(PP).

SOLVENT	T (°C)	Q_y (mol%)	CDT (sec)	%AC
n- Hexane[a]	28	0.162	16.3	20.25
	40	0.220	17.6	26.14
	60	0.260	20.4	36.30
Toluene[a]	28	0.310	17.30	24.90
	40	0.330	18.30	28.96
	60	0.350	23.00	43.50
Tetrachloro-menthane[a]	28	0.420	18.00	27.80
	40	0.430	18.75	30.60
	60	0.430	25.00	48.00
Acetone[b]	28	0.046	16.30	11.04
	40	0.053	16.70	14.00
	60	0.063	18.30	21.00
1,4-Dioxane[b]	28	0.092	17.90	19.00
	40	0.130	19.30	24.80
	60	0.162	21.70	33.18
Benzyle-chloride[b]	28	0.054	17.40	16.70
	40	0.062	18.10	19.90
	60	0.110	20.60	29.61

[a] $CDT_{control}$ =13seconds
[b] $CDT_{control}$ =14.5seconds
%AC=0

TABLE X: VARIATION OF WEIGHT INCREASE $\Delta w_{(g)}$ AND THE MOLE PERCENT SWELLING % Q_t OF ETCHED POLYPROPYLENE (PP) AT DIFFERENT TIMES $t_{(min)}$ AND DIFFERENT TEMPERATURE T, IN CHLOROFORM

	28°C		Nitric Acid 40°C		60°C	
Time	Δw	Q_t	Δw	Q_t	Δw	Q_t
2	0.0032	0.052	0.0071	0.118	0.0072	0.121
5	0.0045	0.105	0.0084	0.139	0.0062	0.124
7	0.0079	0.124	-	-	0.0075	0.124
10	0.0082	0.133	0.0094	0.149	0.0081	0.133
15	0.0095	0.152	0.0085	0.143	0.0085	0.141
30	-	-	0.0085	0.137	0.0088	0.145
45	0.0100	0.160	0.0084	0.133	0.0090	0.147
60	0.0110	0.174	0.0086	0.138	0.0091	0.147
120	-	-	-	-	0.0069	0.111

TABLE X CONTINUES:

	28°C		Chromic Acid 40°C		60°C	
Time	Δw	Q_t	Δw	Q_t	Δw	Q_t
2	0.0022	0.036	0.0048	0.078	0.0049	0.083
5	0.0029	0.048	0.0050	0.088	-	-
7	0.0041	0.066	0.0051	0.091	0.0090	0.089
10	0.0075	0.116	0.0066	0.109	0.0090	0.161
15	0.0078	0.121	0.0070	0.112	0.0160	0.275
30	0.0073	0.117	0.0064	0.105	0.0092	0.168
45	0.0076	0.117	0.0064	0.101	0.0110	0.200
60	0.0078	0.122	0.0058	0.101	0.0110	0.197
120	-	-	0.0066	0.108	0.0102	0.168

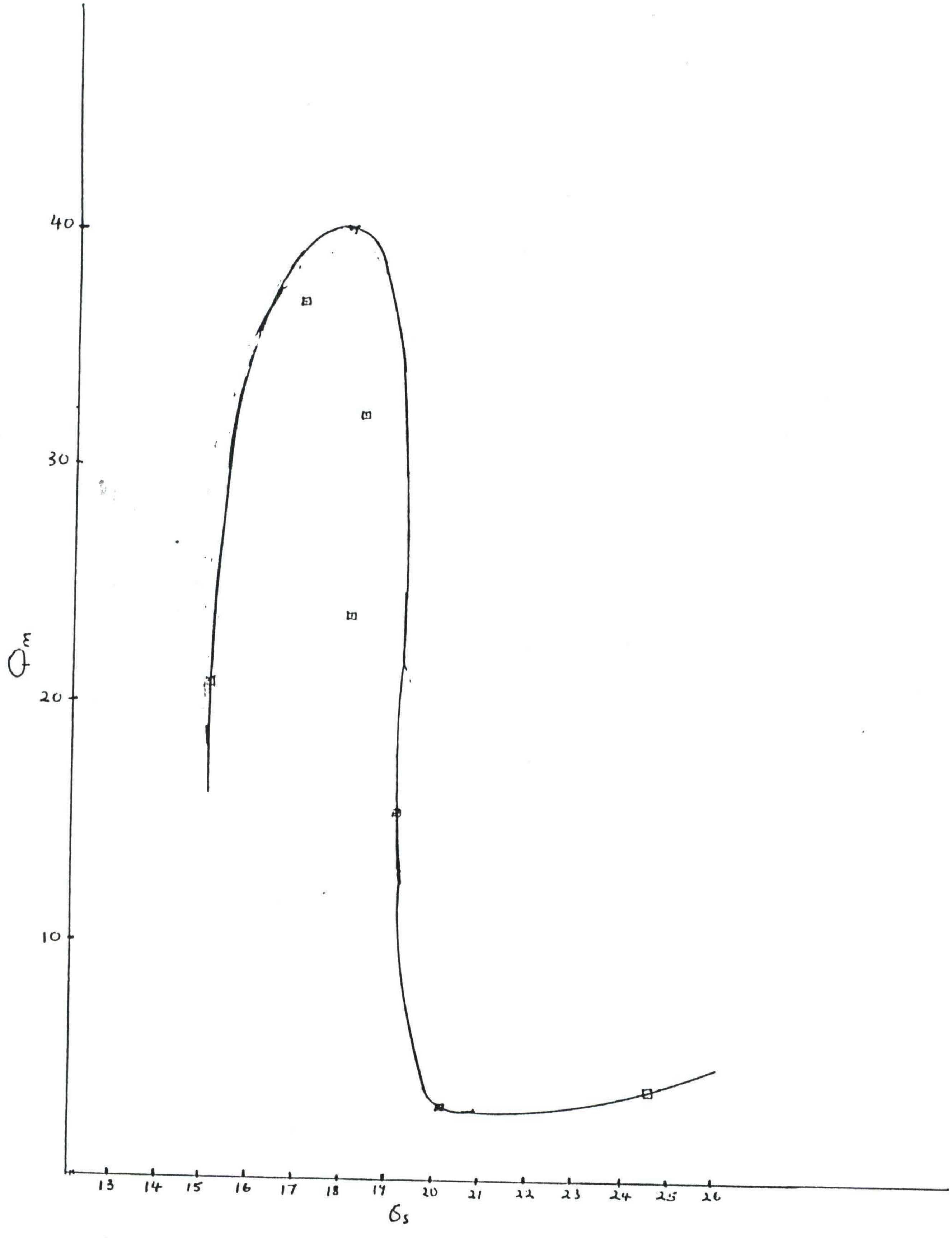


FIG 1: GRAPH OF THEORETICAL REPRESENTATION OF THE RELATIONSHIP BETWEEN THE SWELLING RATIO OF THE PP FILM AND THE SOLUBILITY PARAMETER OF THE VARIOUS SOLVENTS.

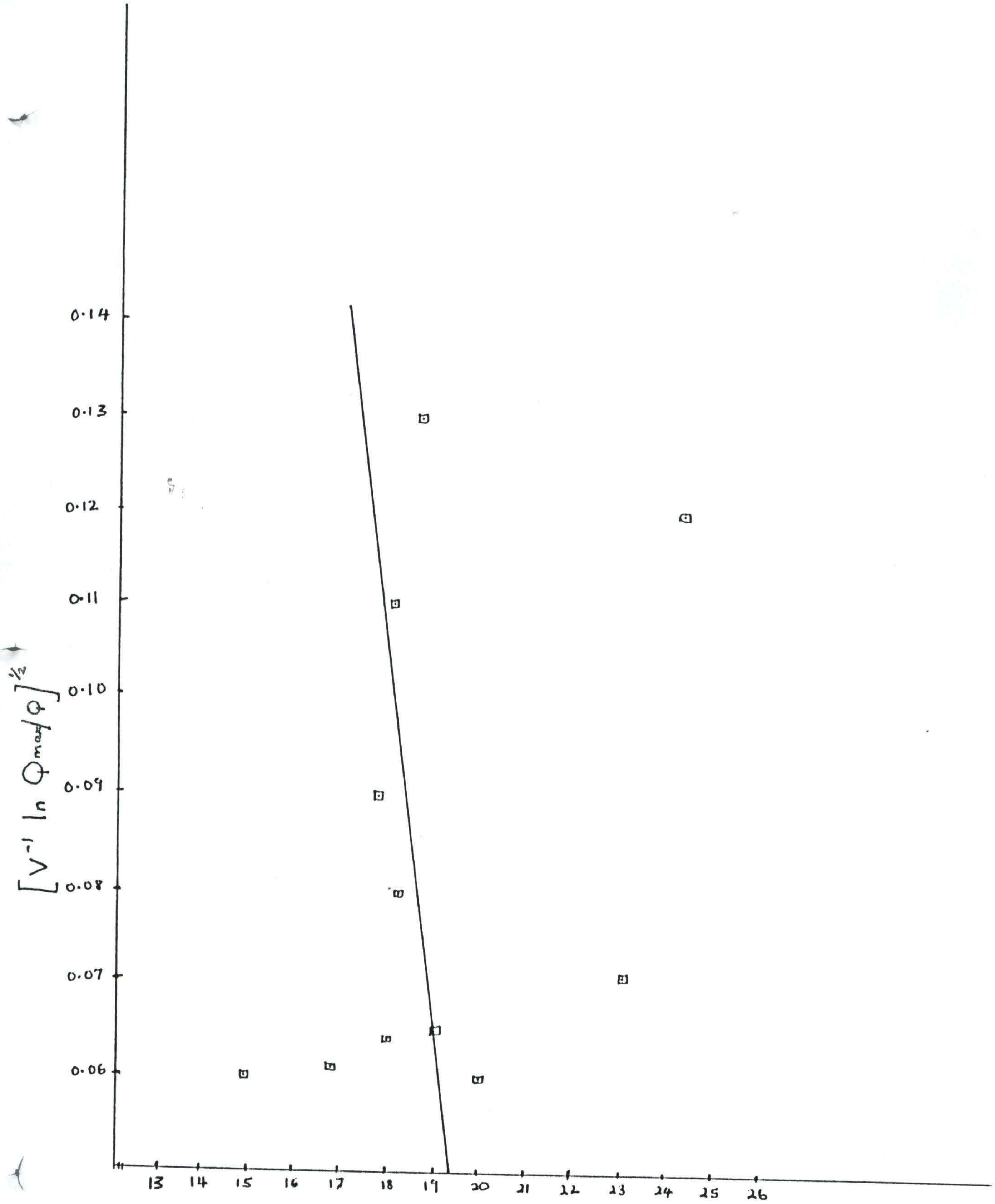


FIG 2: GRAPH OF PLOTS OF $[V^{-1}. \ln Q_{max}/Q]^{1/2}$ OF THE PP FILM VERSUS THE SOLUBILITY PARAMETER OF THE VARIOUS SOLVENTS.

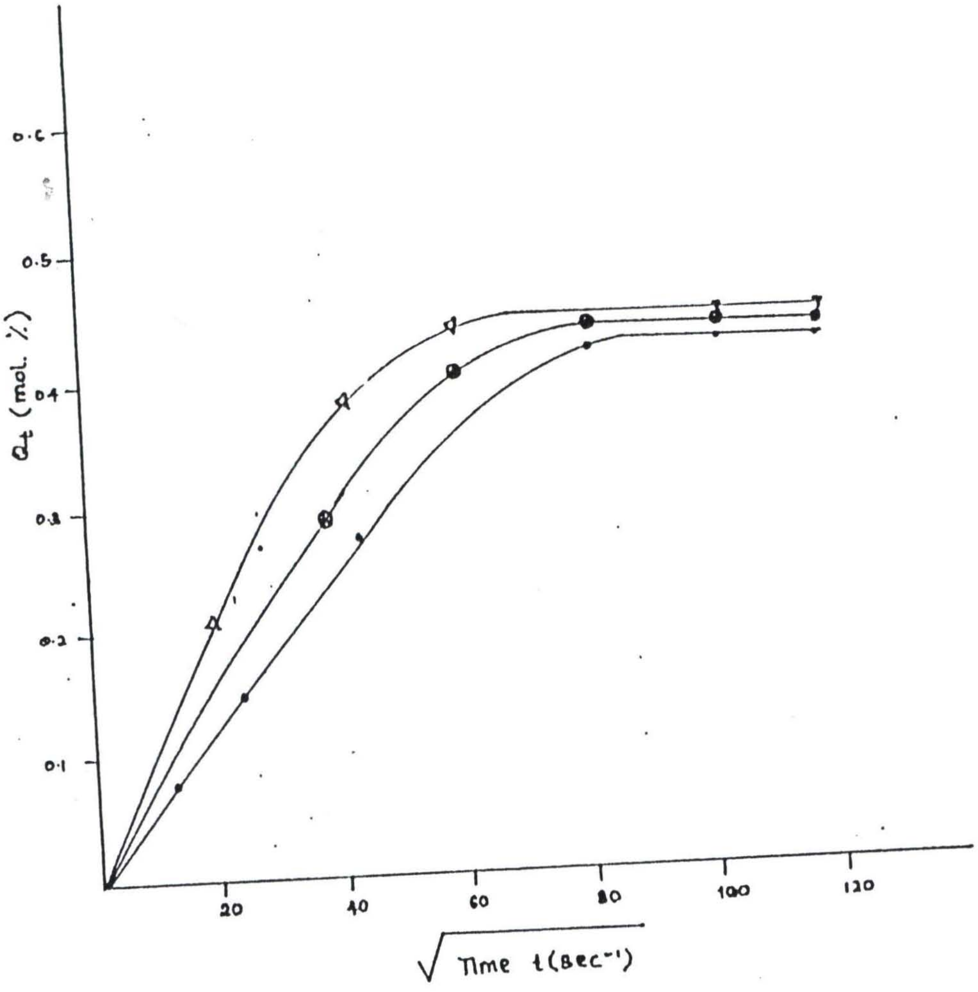


FIG. 3: MOL. PERCENT CCl_4 UPTAKE OF PP AT DIFFERENT TEMP.
60°C (▽), 40°C (⊗), 28°C (•)

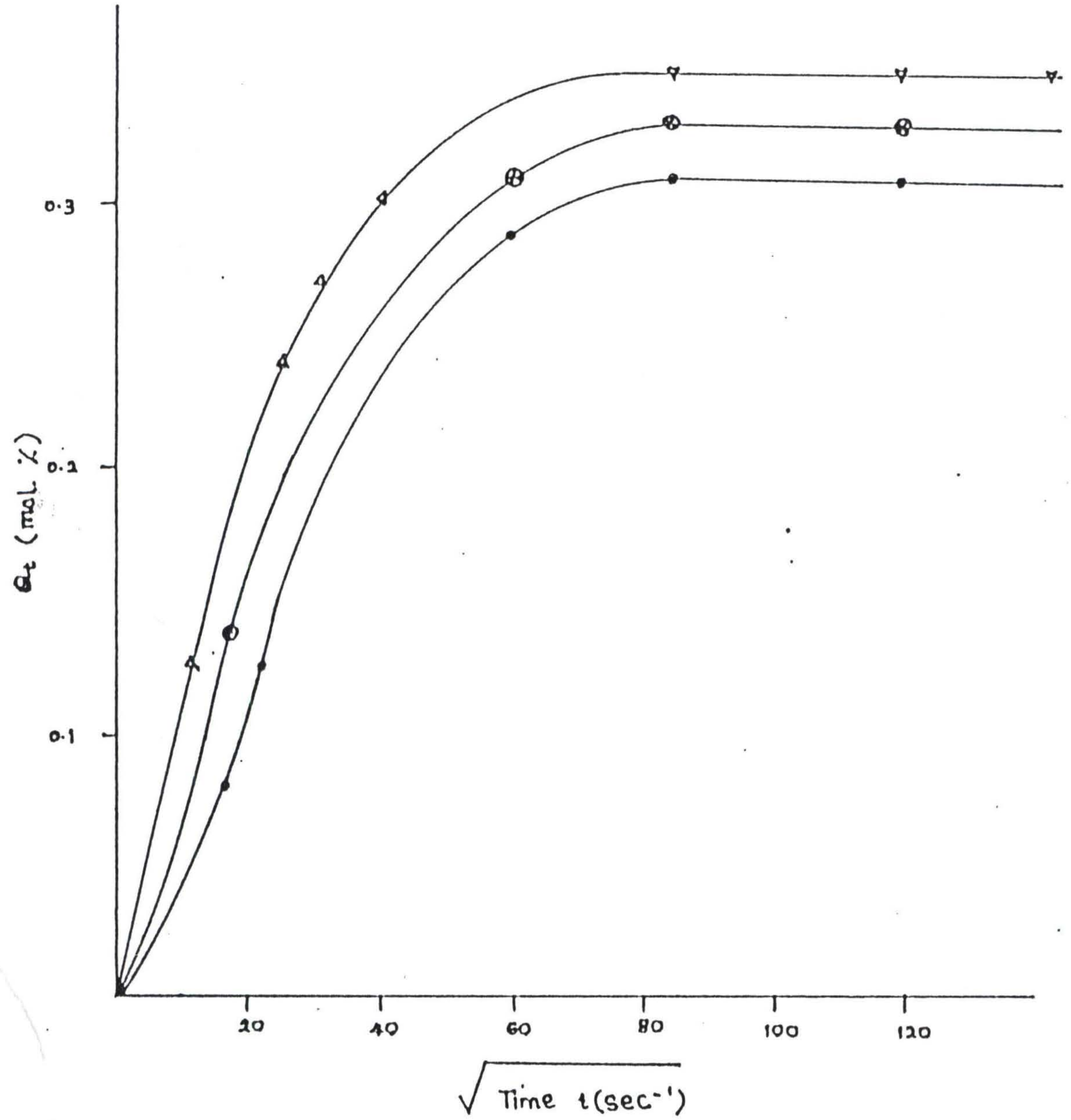


FIG. 4: MOL. PERCENT TOLUENE UPTAKE OF PP AT DIFFERENT TEMP.
60°C (▽), 40°C (⊕), 28°C (•)

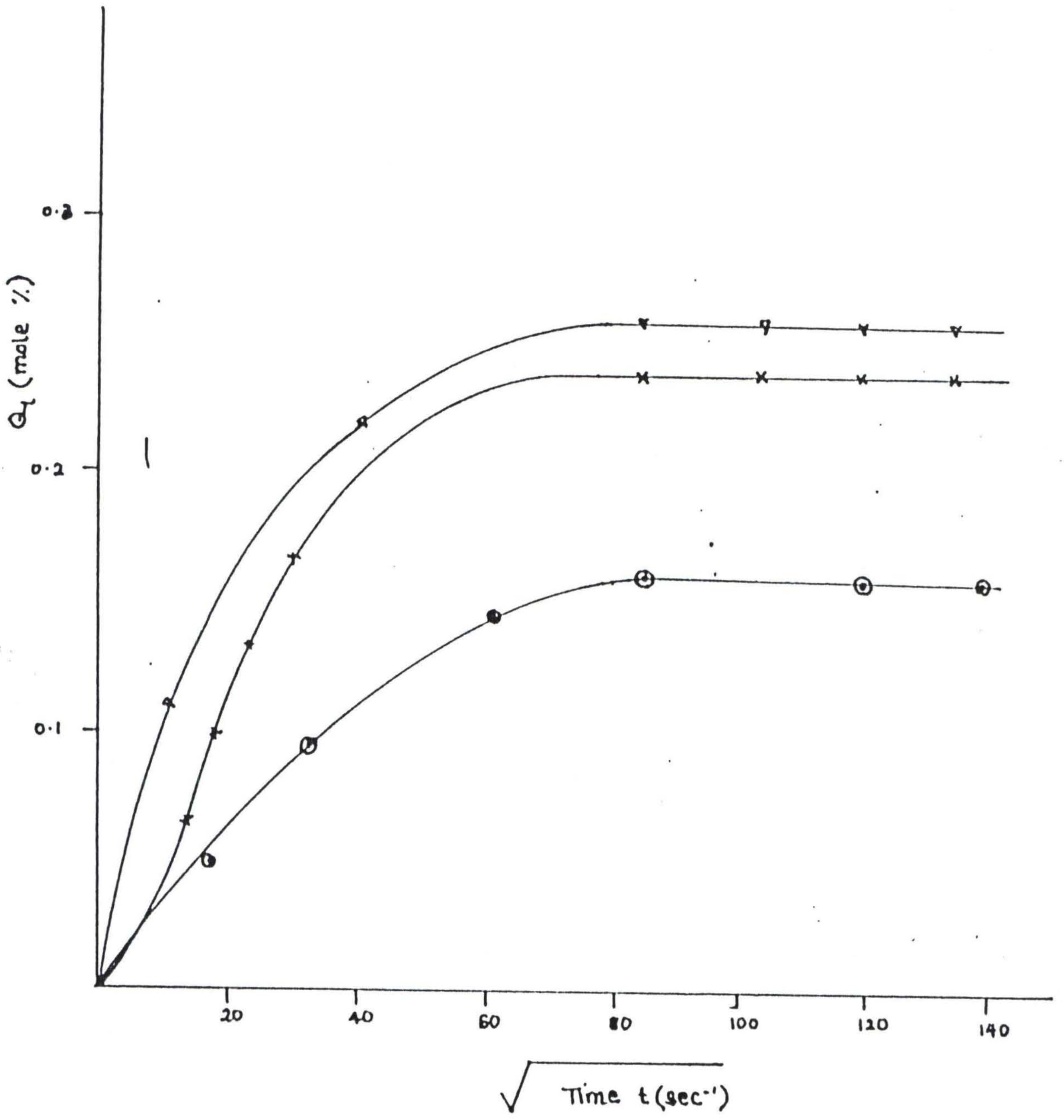


FIG.5: MOL. PERCENT n-HEXANE UPTATE OF PP AT DIFFERENT TEMP. 60°C (▽), 40°C (×), 28°C (⊙)

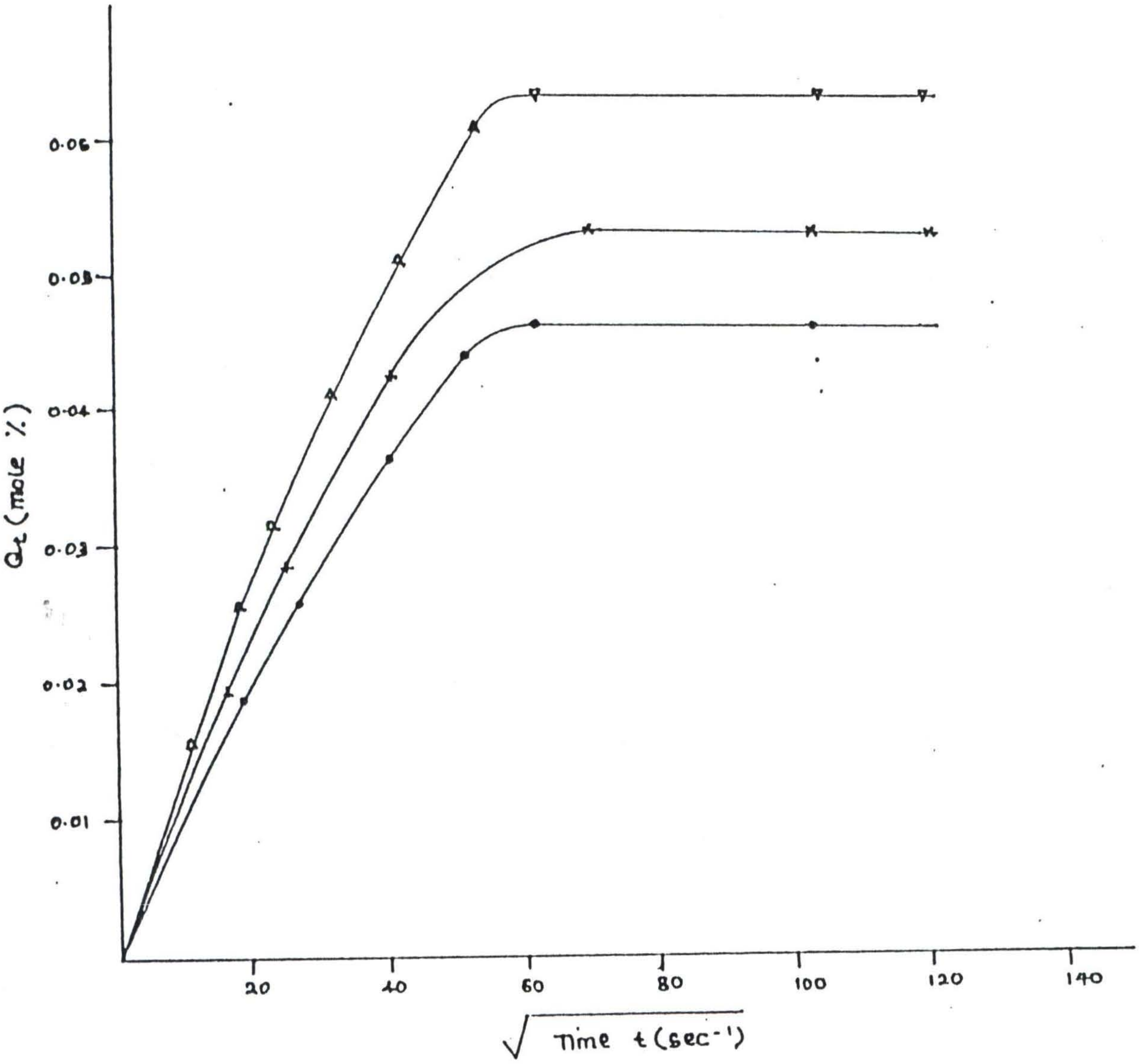


FIG. 6: MOL. PERCENT ACETONE UPTAKE OF PP AT DIFFERENT TEMP.
60°C (∇), 40°C (×), 28°C (•)

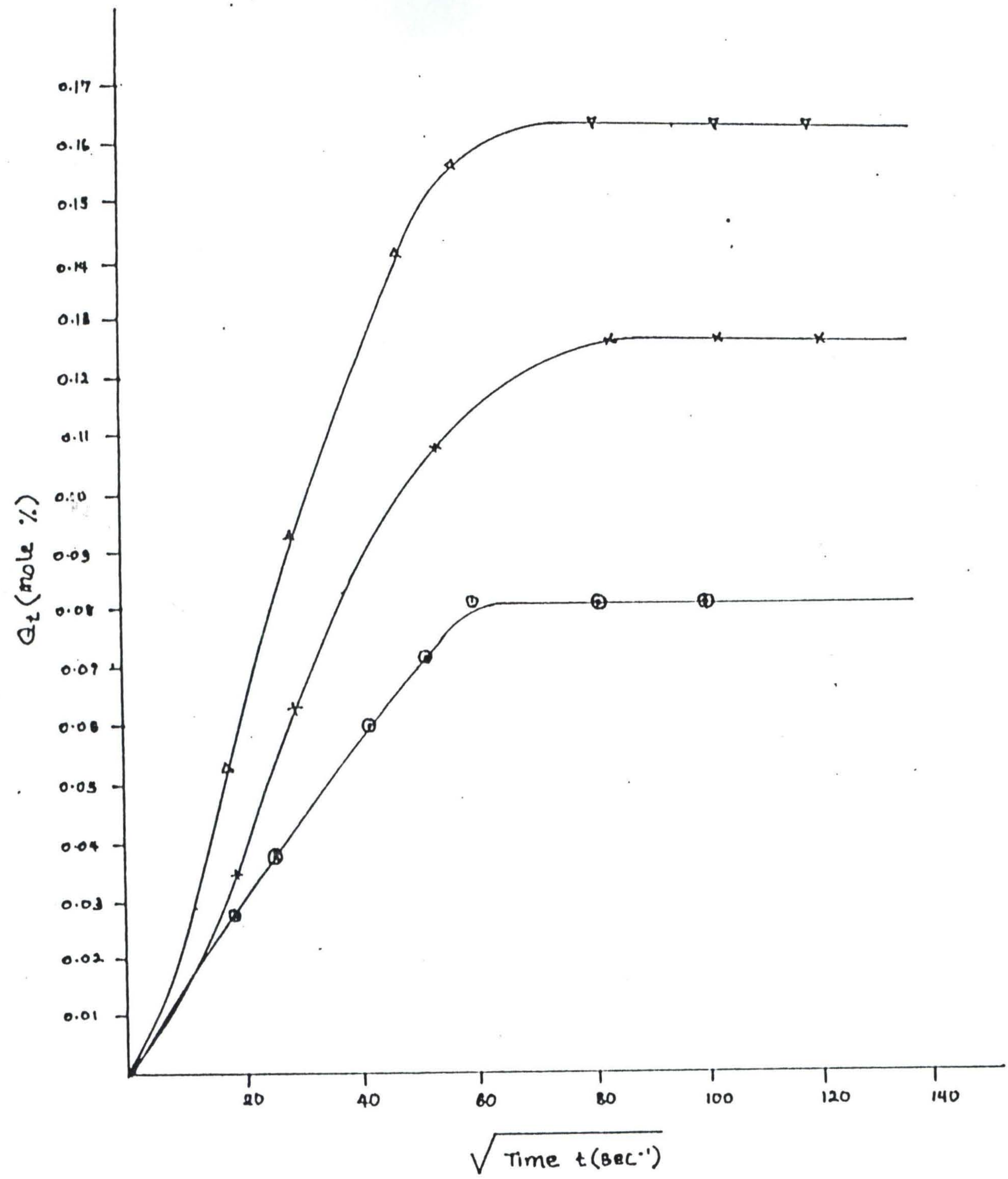


FIG. 5: MOL. PERCENT DIOXANE UPTAKE OF PP AT DIFFERENT TEMP. 60°C (▽), 40°C (×), 28°C (⊙)

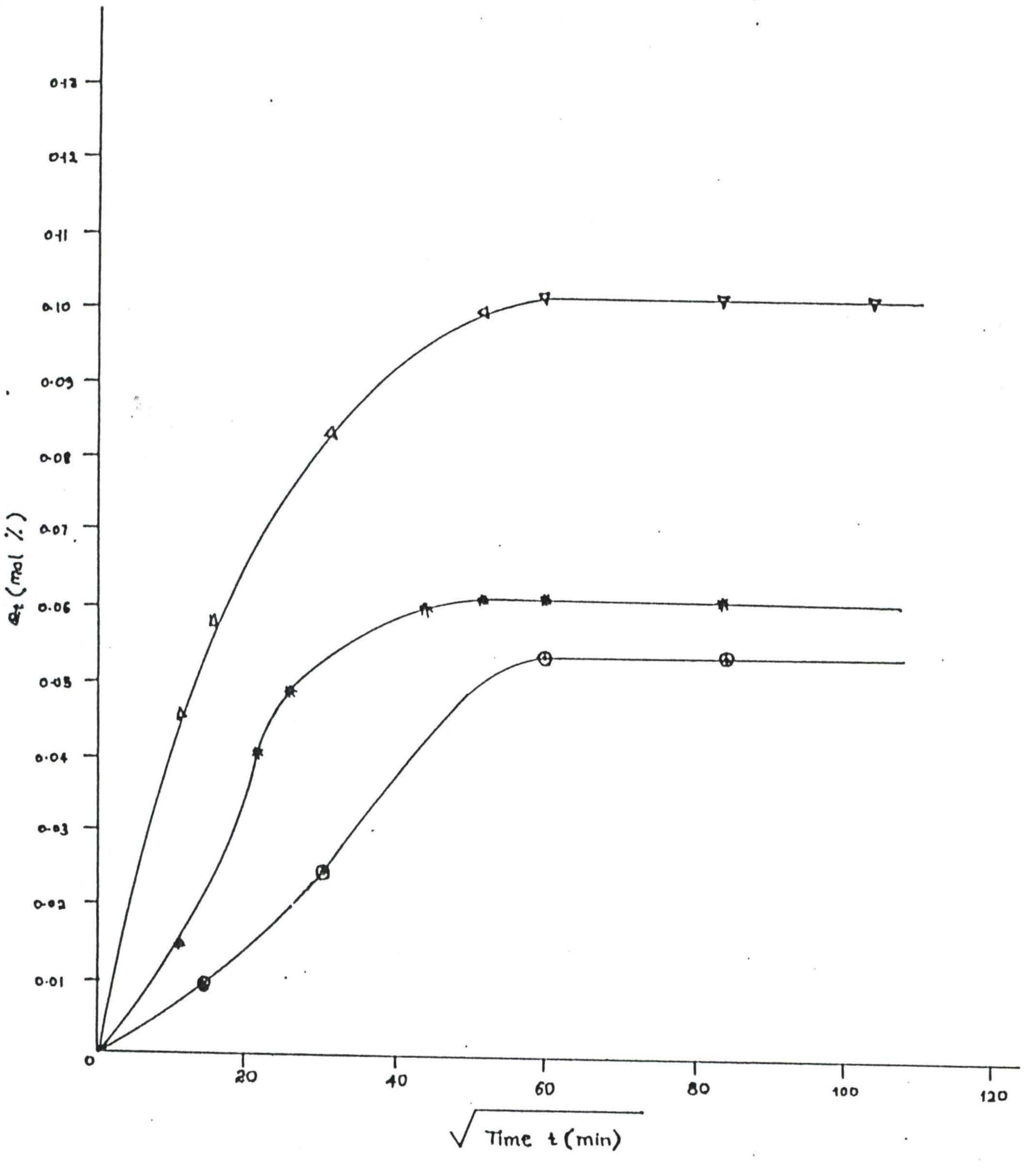


FIG. 8: MOL. PERCENT BENZYL CHLORIDE UPTAKE OF PP AT DIFFERENT TEMP.
60°C (▽), 40°C (✱), 28°C (⊕)

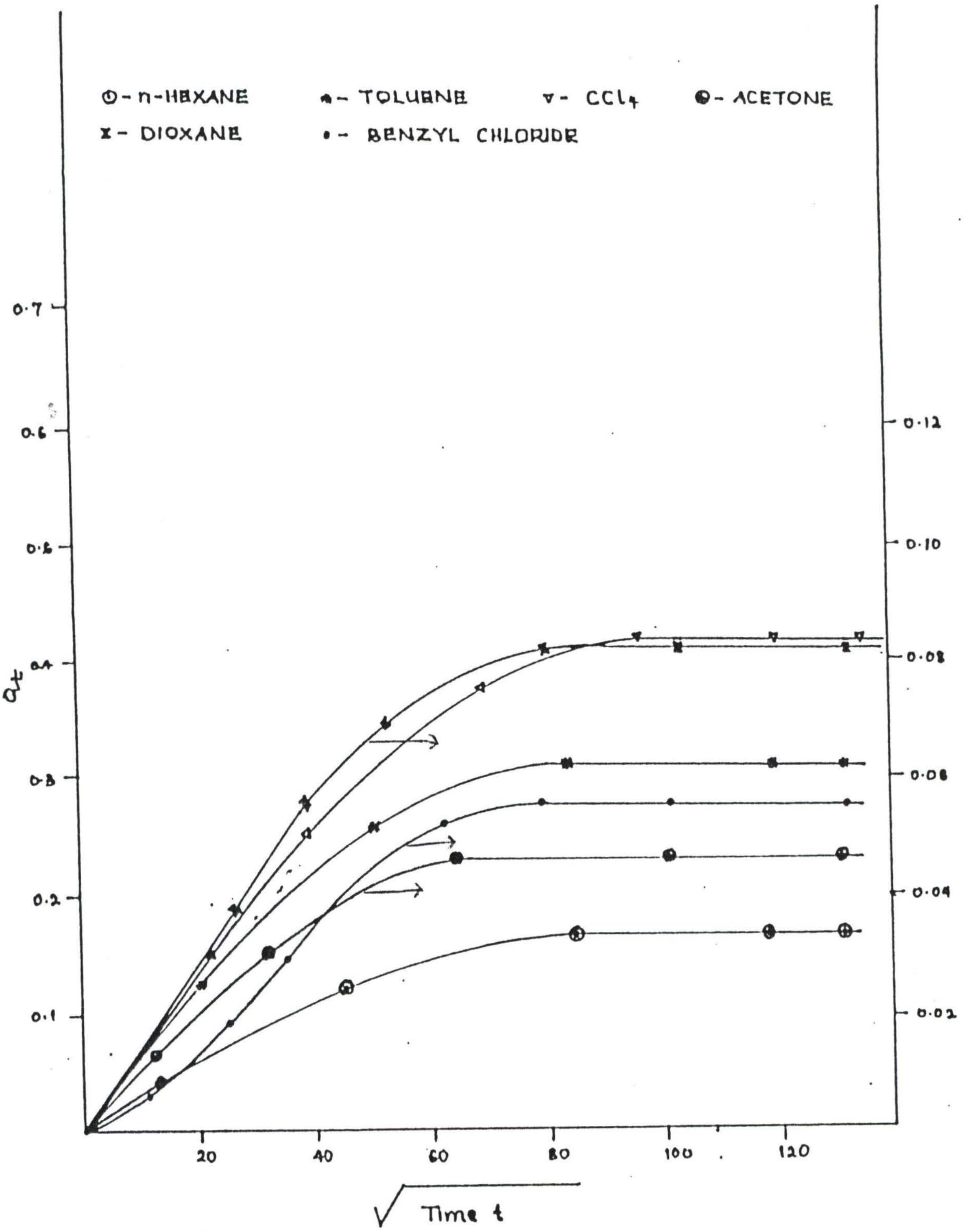


FIG. 9: MOL. PERCENT SOLVENT UPTAKE OF PP AT 28°C

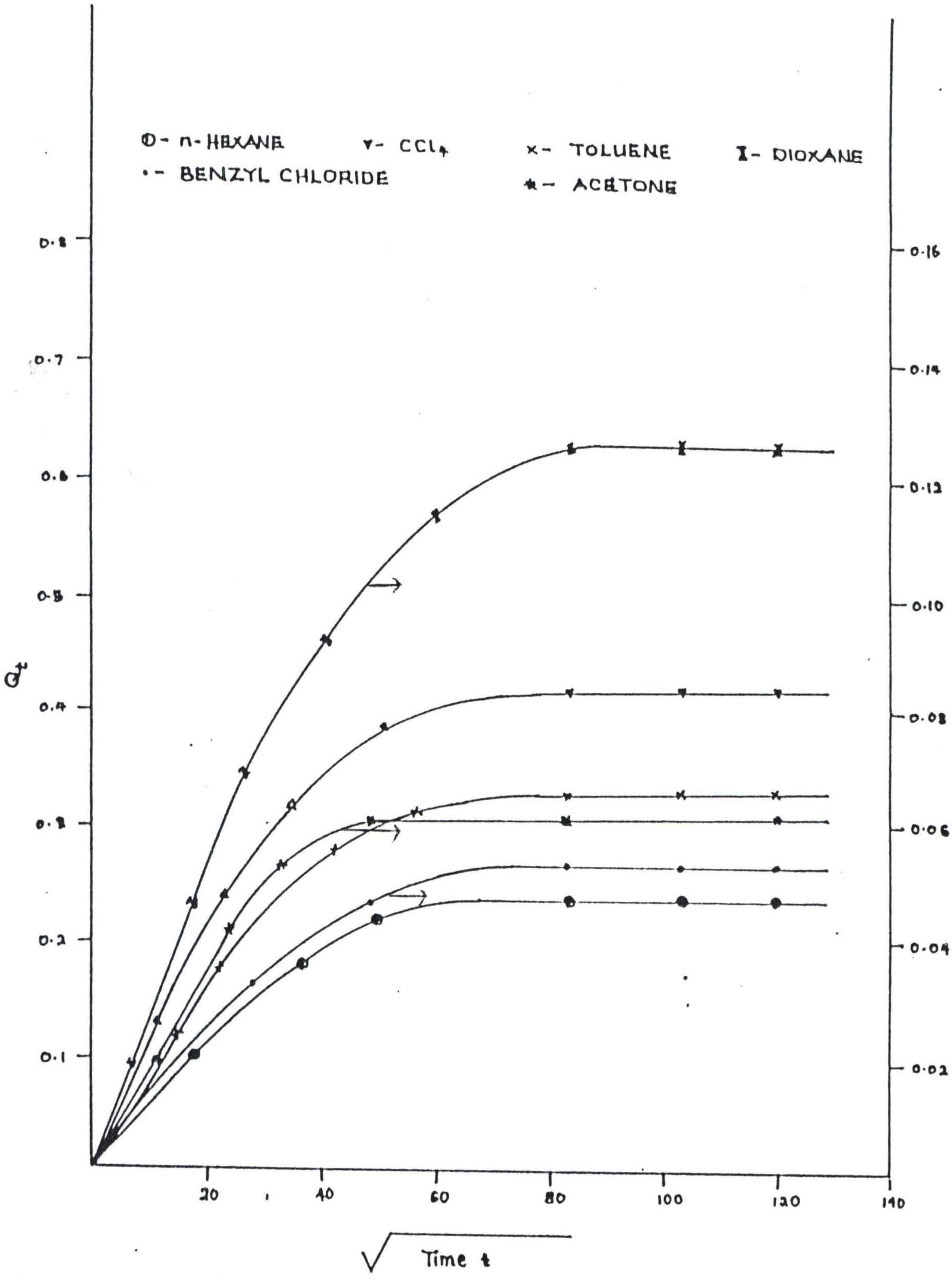


FIG. 10: MOL. PERCENT SOLVENT UPTAKE OF PP AT 40°C

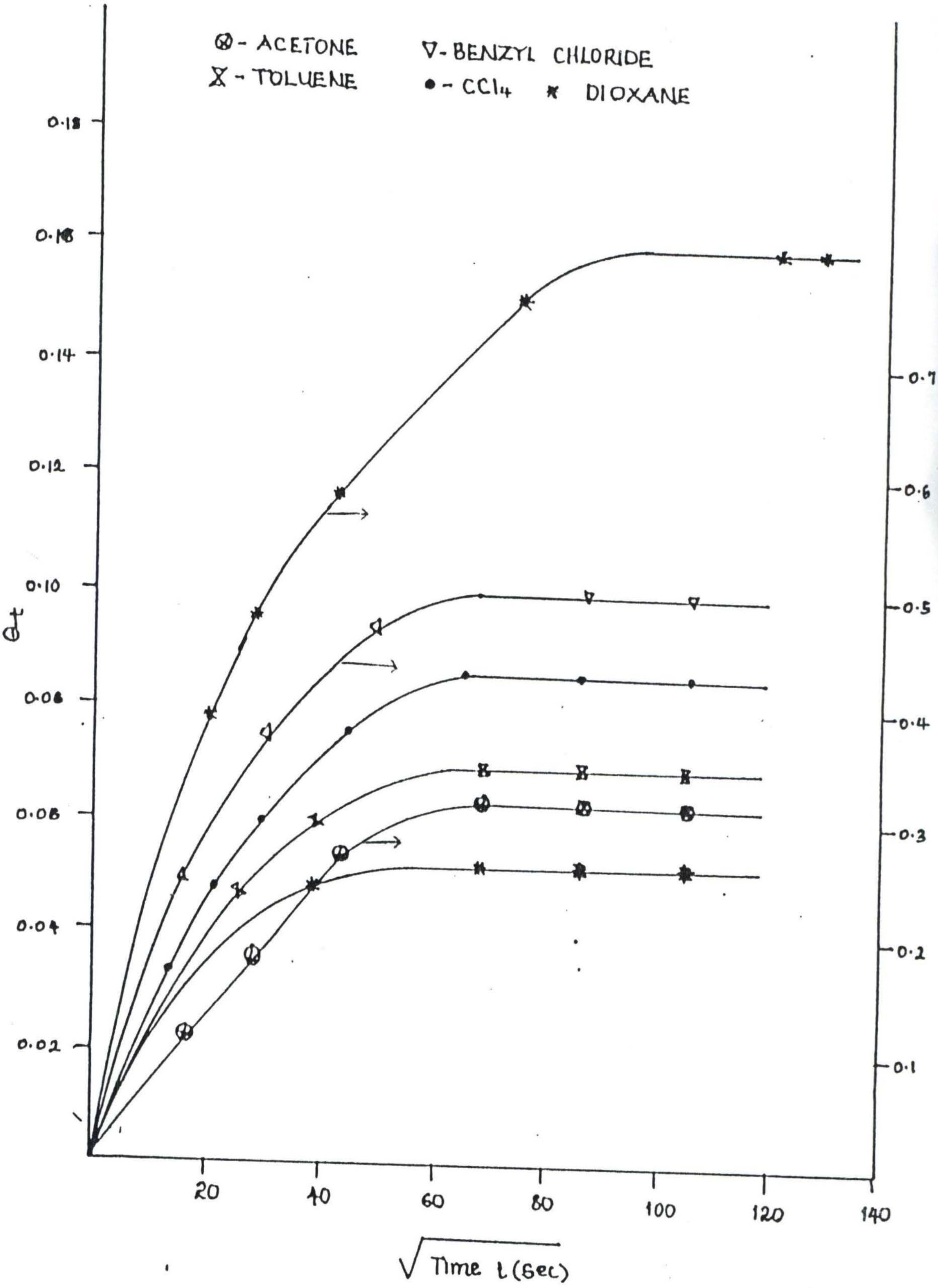


FIG. 11: MOL. PERCENT SOLVENT UPTAKE OF PP AT 60°C

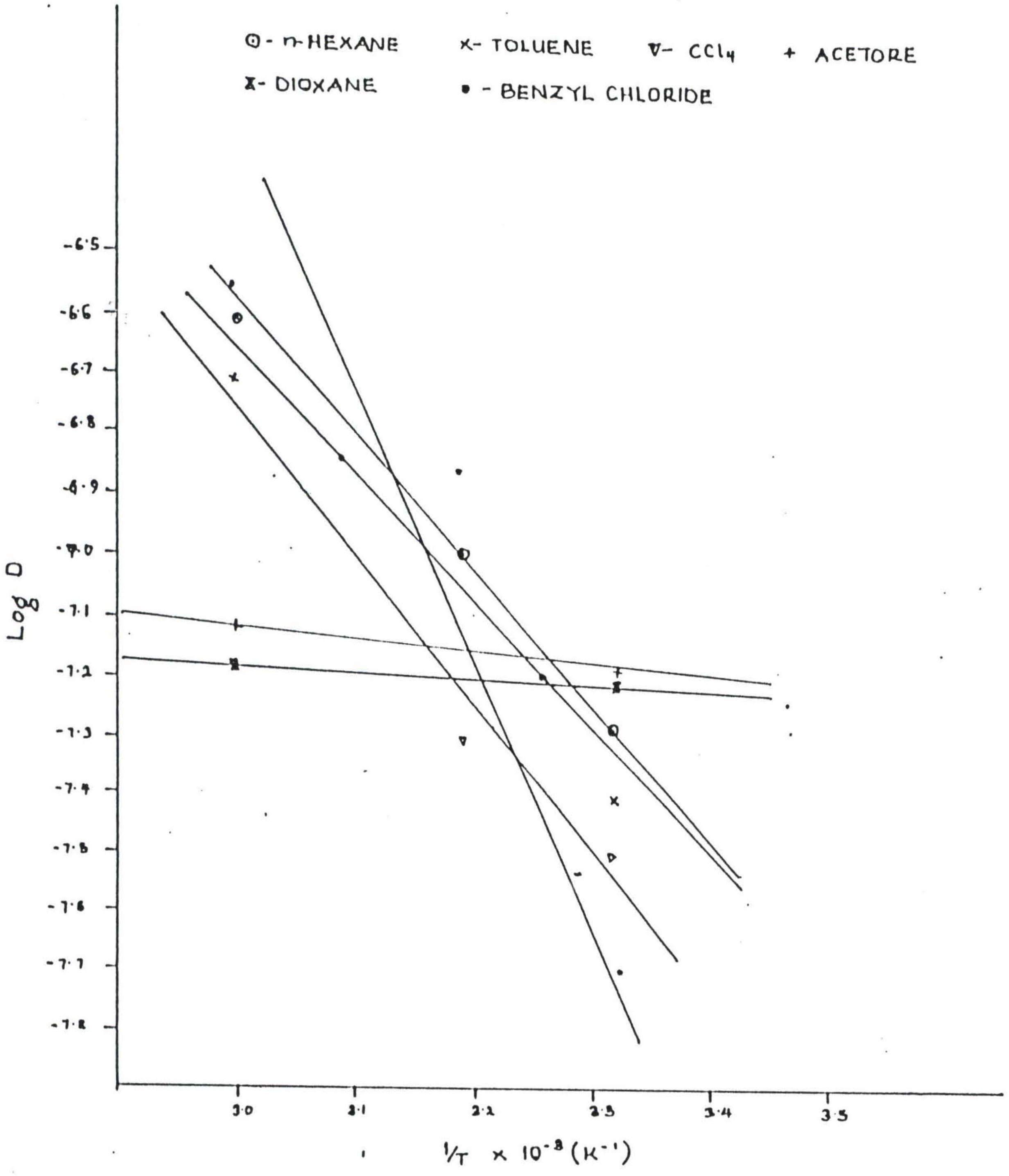


FIG. 12: ARRHENIUS PLOTS OF LOG D Vs 1/T FOR PP IN DIFFERENT SOLVENTS

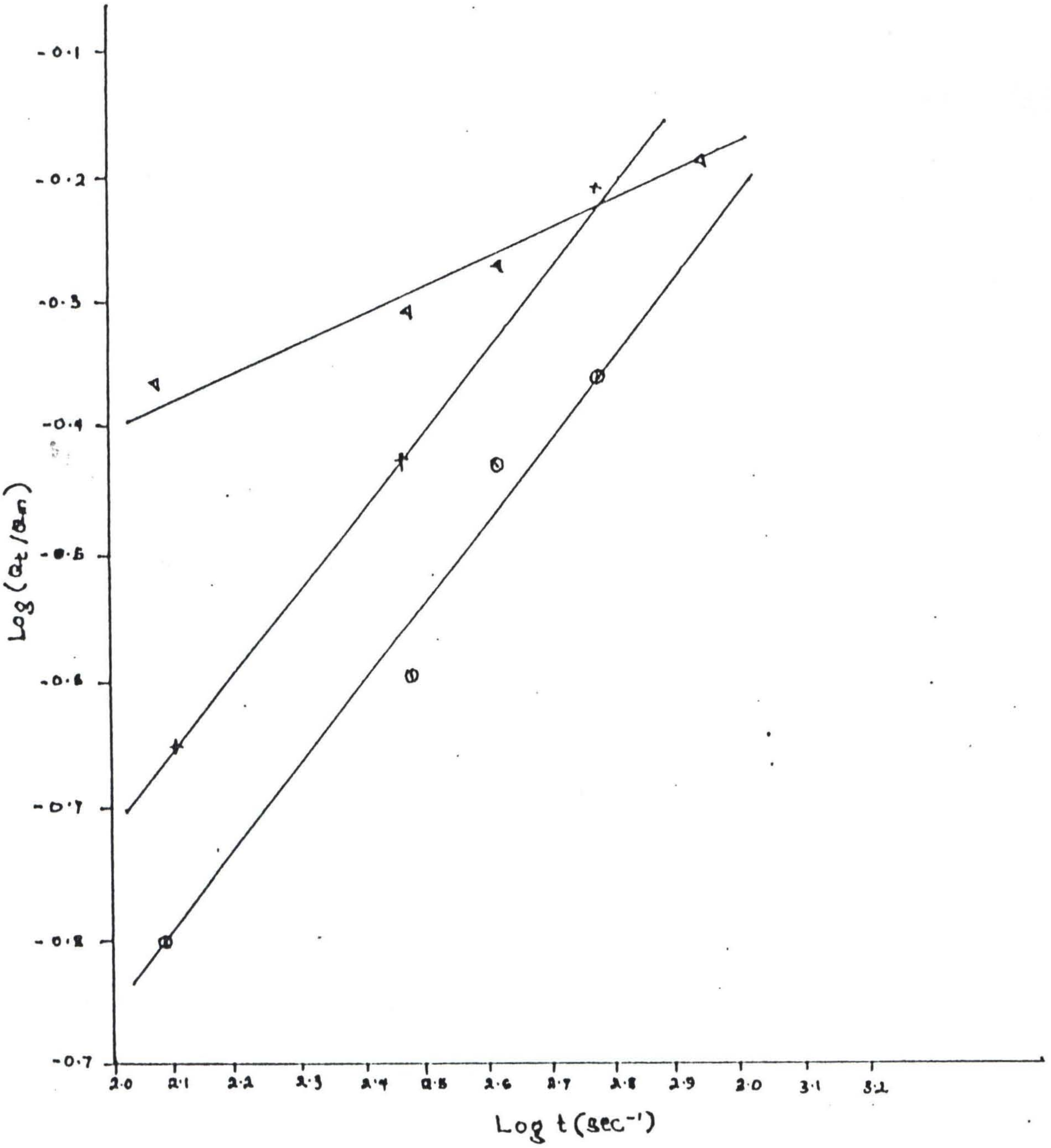


FIG. 13: LOG (a_t/a_m) Vs LOG t CURVES FOR PP IN CCl_4 AT 60°C (∇), 40(×), 28°C (⊘)

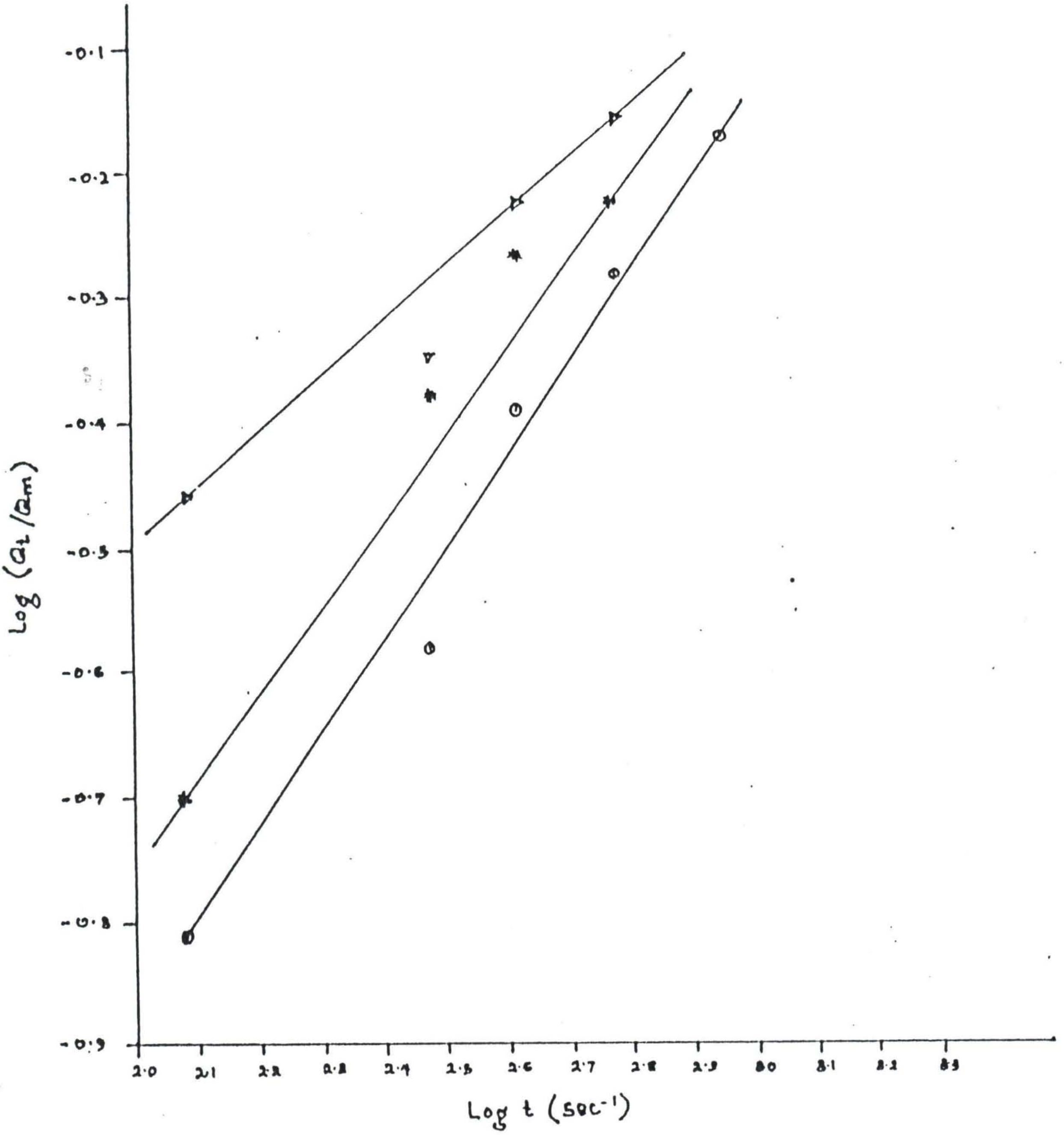


FIG. 14: LOG (Q_t/Q_m) Vs t CURVES FOR PP IN TOLUENE AT 60°C (∇), 40°C (*), 28°C (⊙)

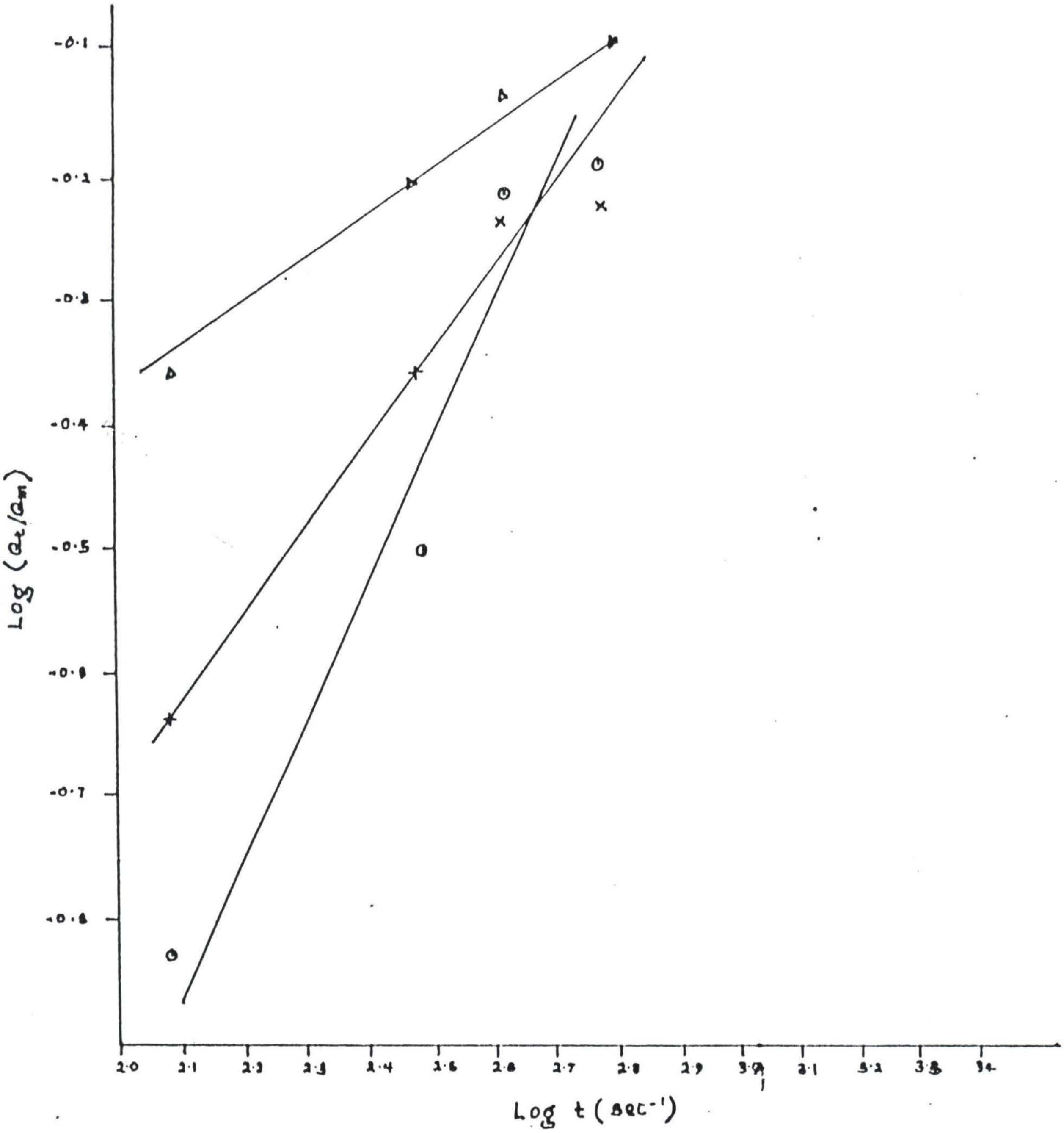


FIG. 15: LOG (Q_t/Q_m) Vs LOG t CURVES FOR PP IN n-HEXANE AT 80°C (∇), 40 (×), 28°C (⊙)

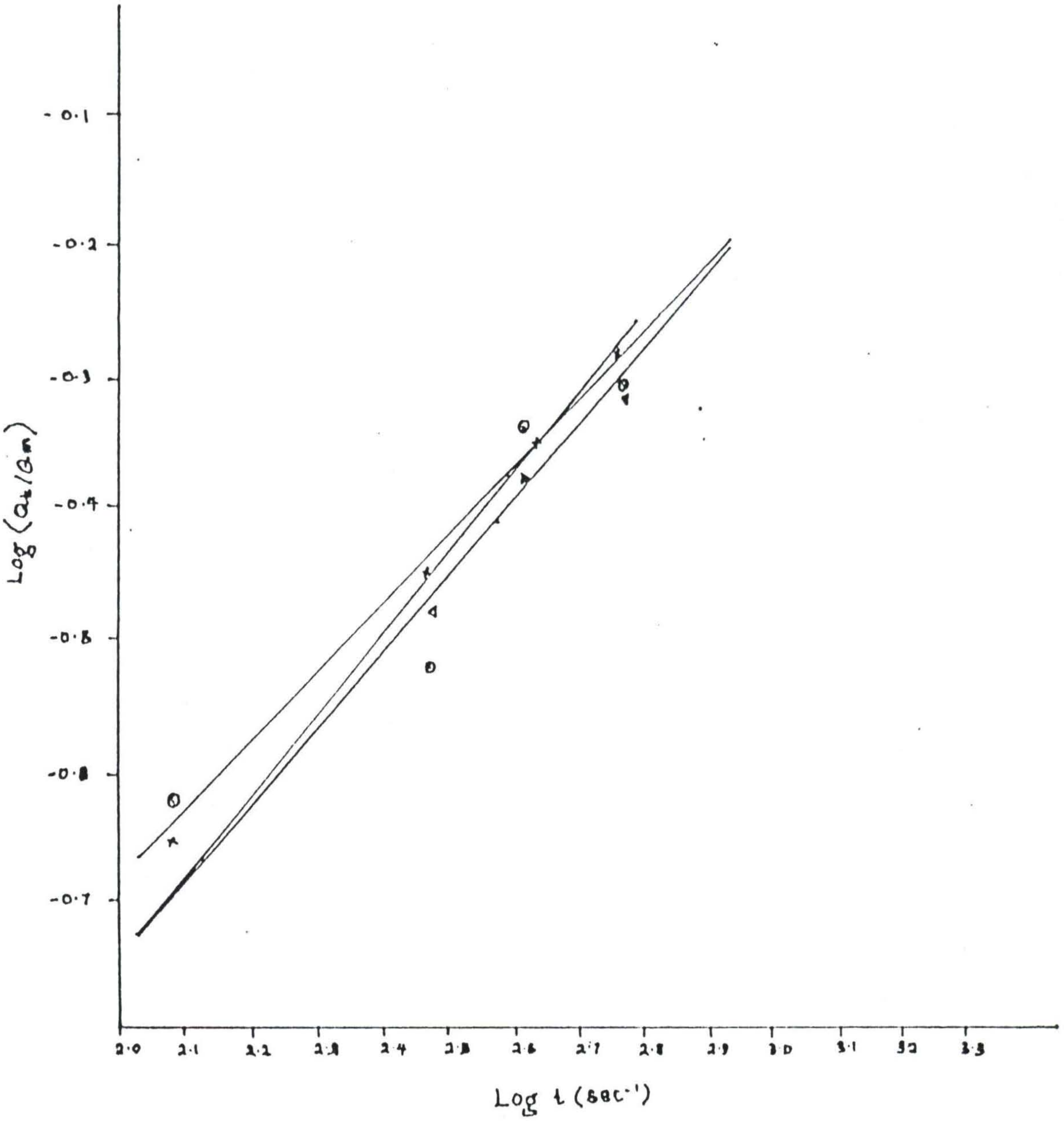


FIG. 18: LOG (Q_t/Q_m) Vs LOG t CURVES FOR PP IN ACETONE AT 60°C(▽), 40°C(×), 28°C(o)

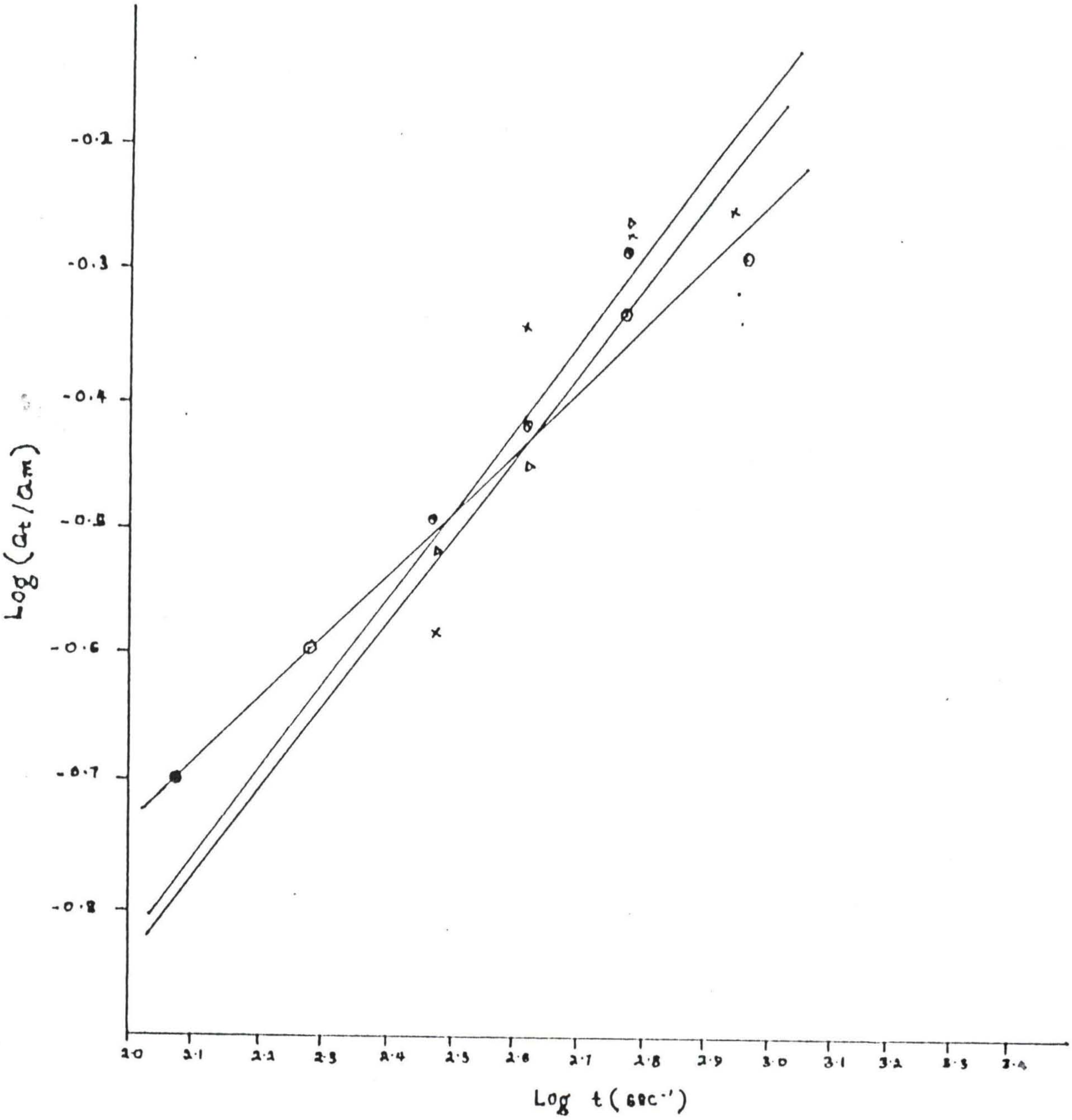


FIG. 17: LOG (Q_t/Q_m) Vs LOG t CURVES FOR PP IN DIOXANE AT 60°C (▼), 40°C (×), 28°C (⊙)

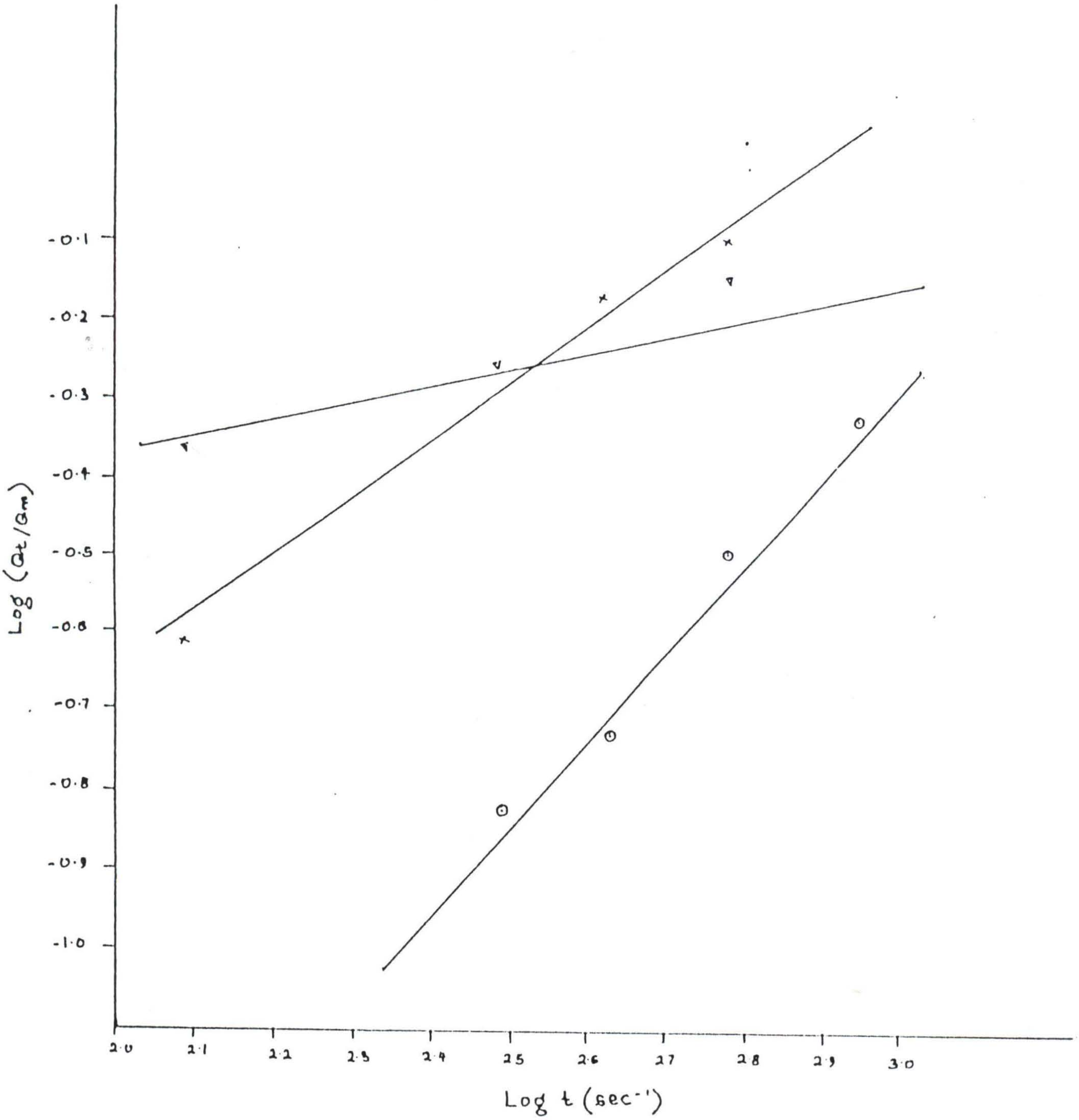


FIG. 18: LOG (Q_t/Q_m) Vs LOG t CURVES FOR PP IN BENZYL CHLORIDE AT 60°C (▽), 40°C (×), 28°C (⊙)

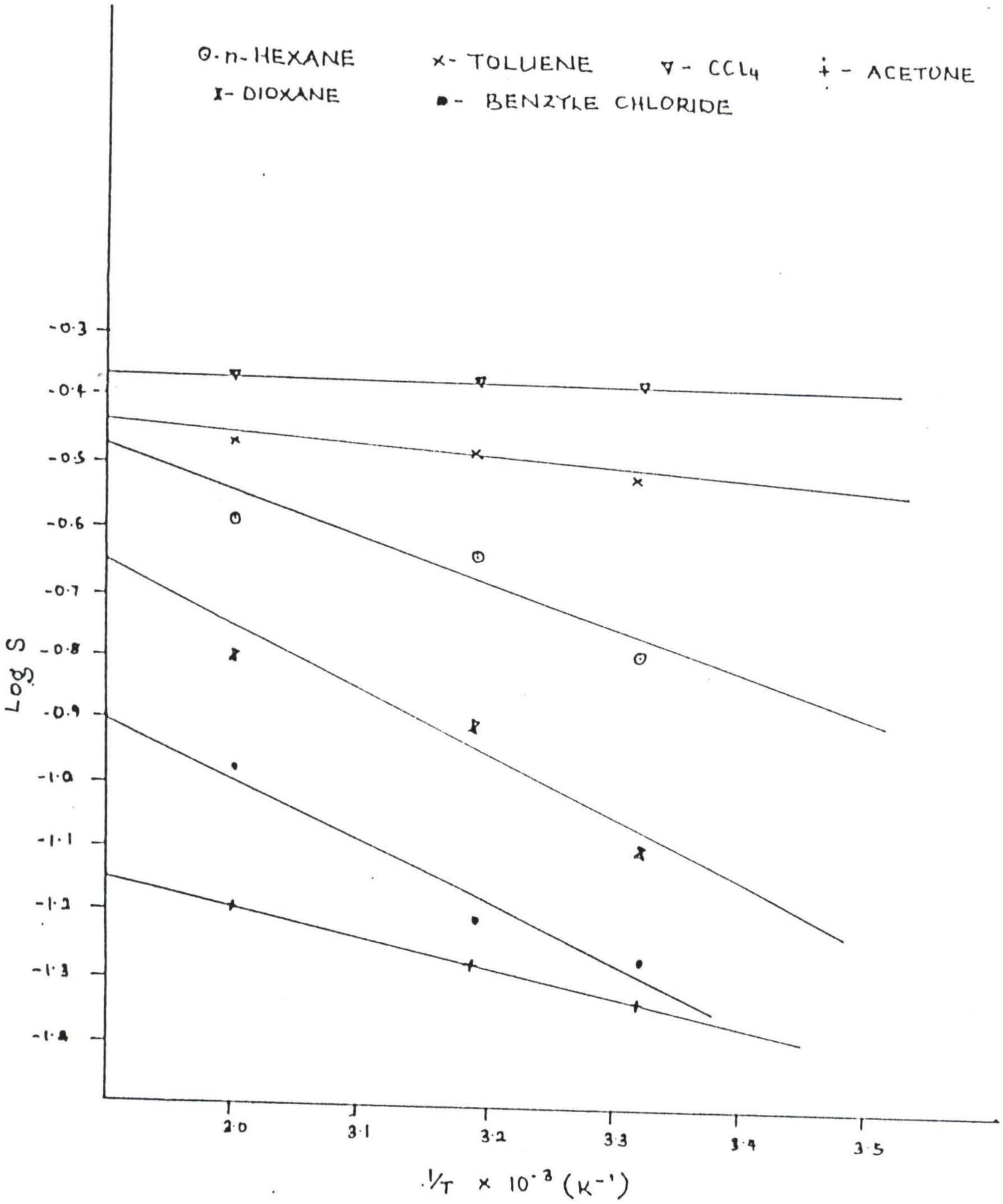


FIG. 19: ARRHENIUS PLOTS OF LOG S Vs 1/T FOR PP IN DIFFERENT SOLVENTS

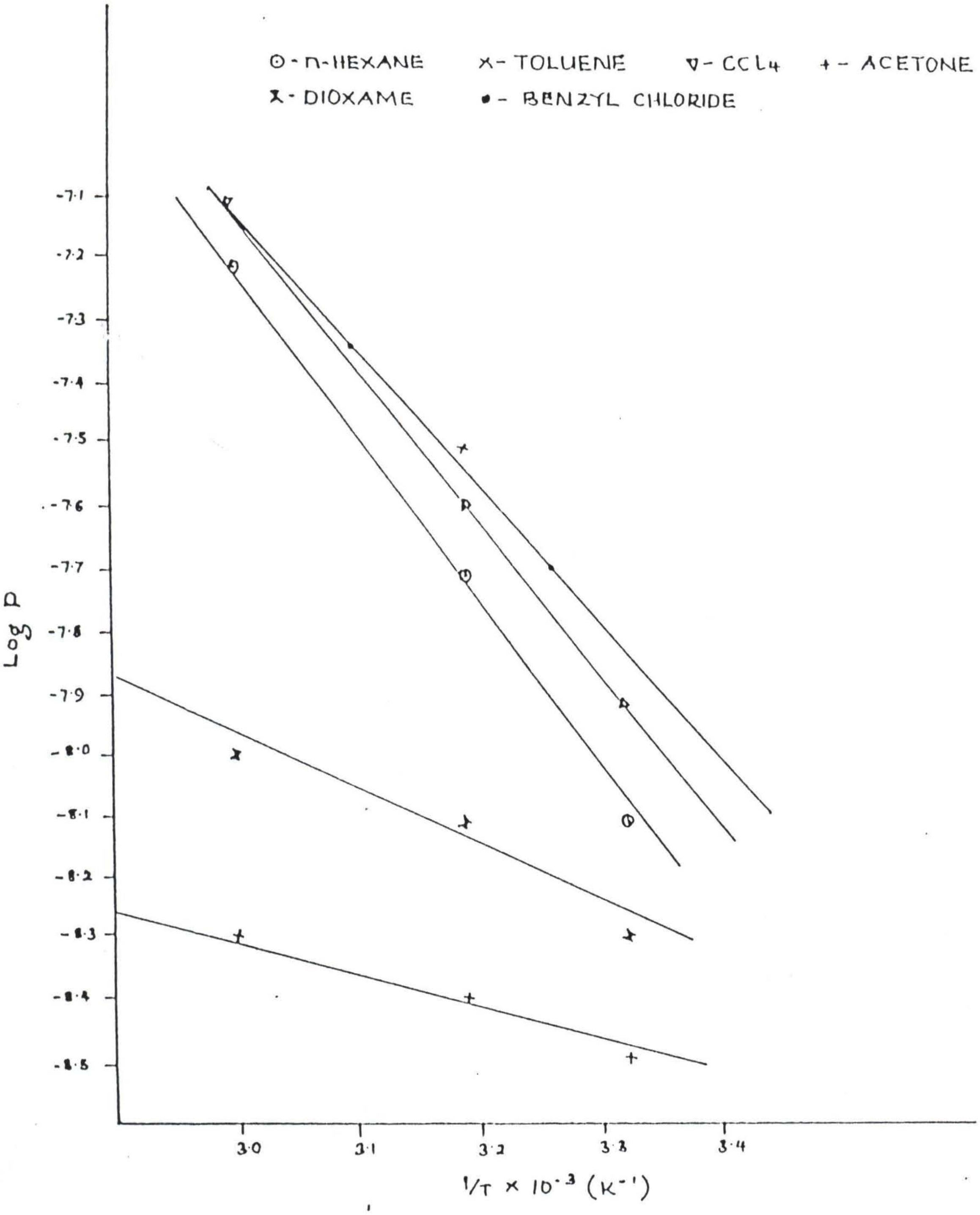


FIG. 20: ARRHENIUS PLOTS OF LOG P Vs 1/T FOR PP IN DIFFERENT SOLVENTS

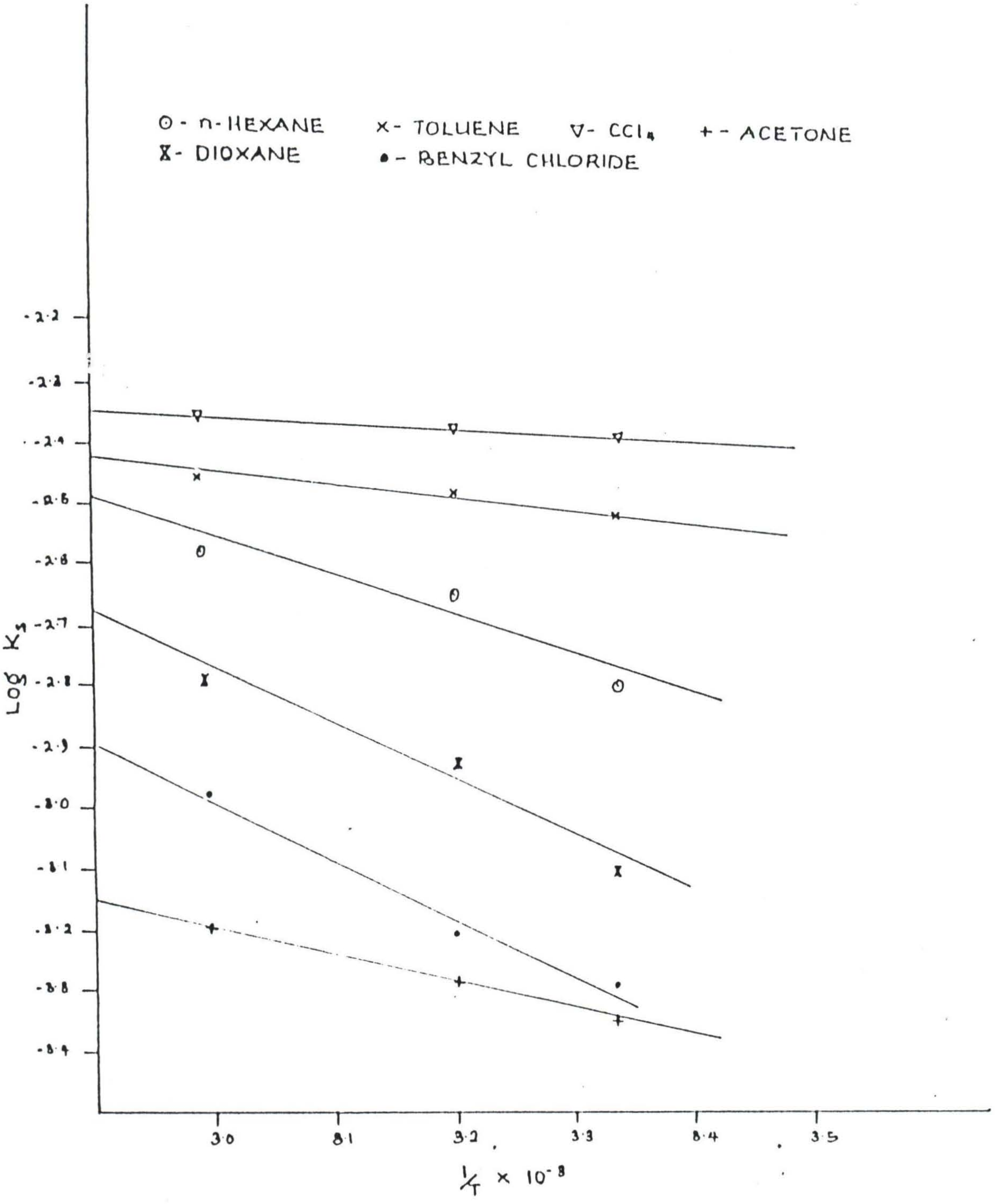


FIG. 21: LOG K_s Vs 1/T FOR PP IN DIFFERENT SOLVENTS

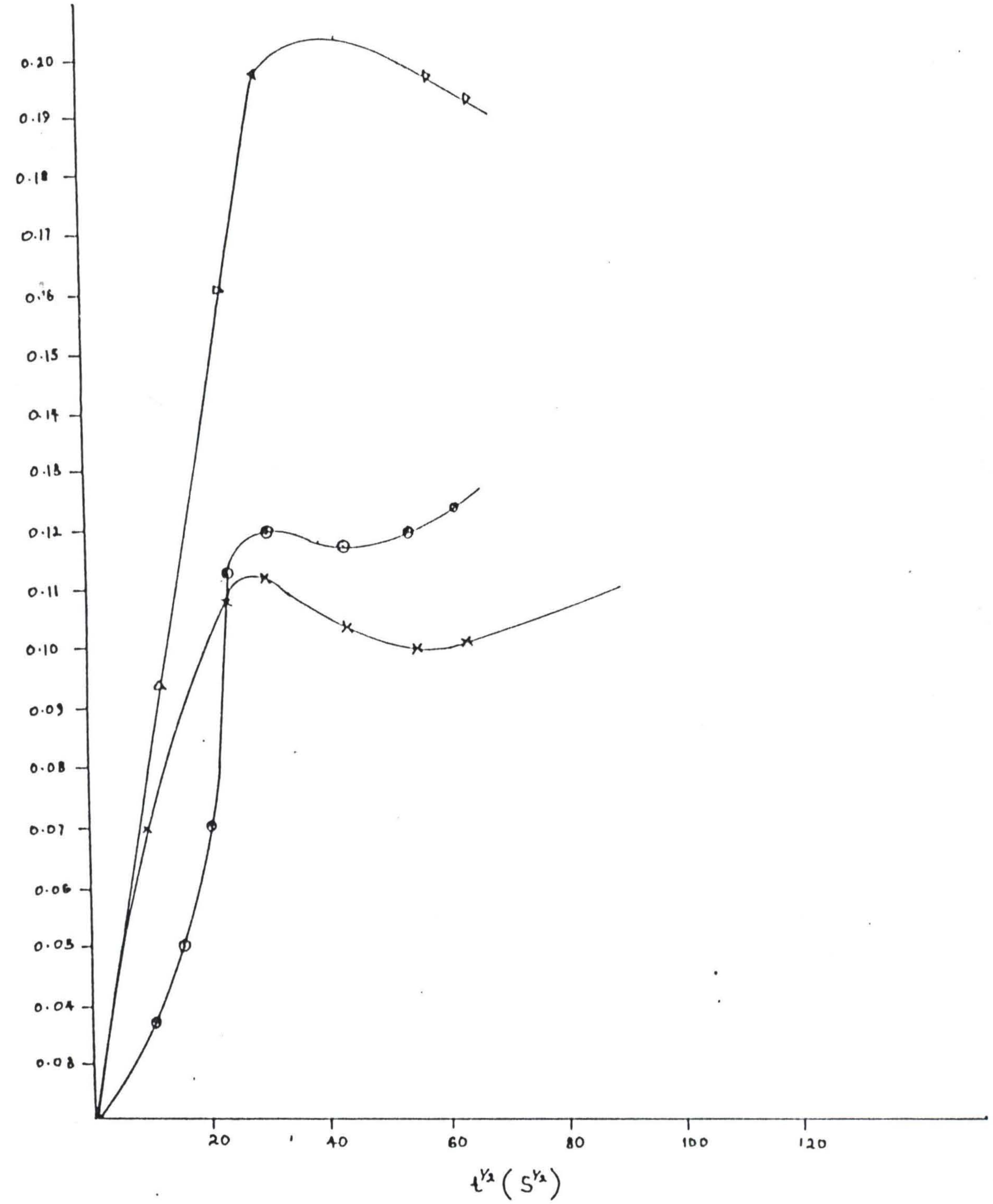


FIG.22: MOL. PERCENT CHLOROFORM UPTAKE OF CHRONIC ACID ETCHED PP AT DIFFERENT TEMP. 60°C (▽), 40°C (×), 28°C (⊖)

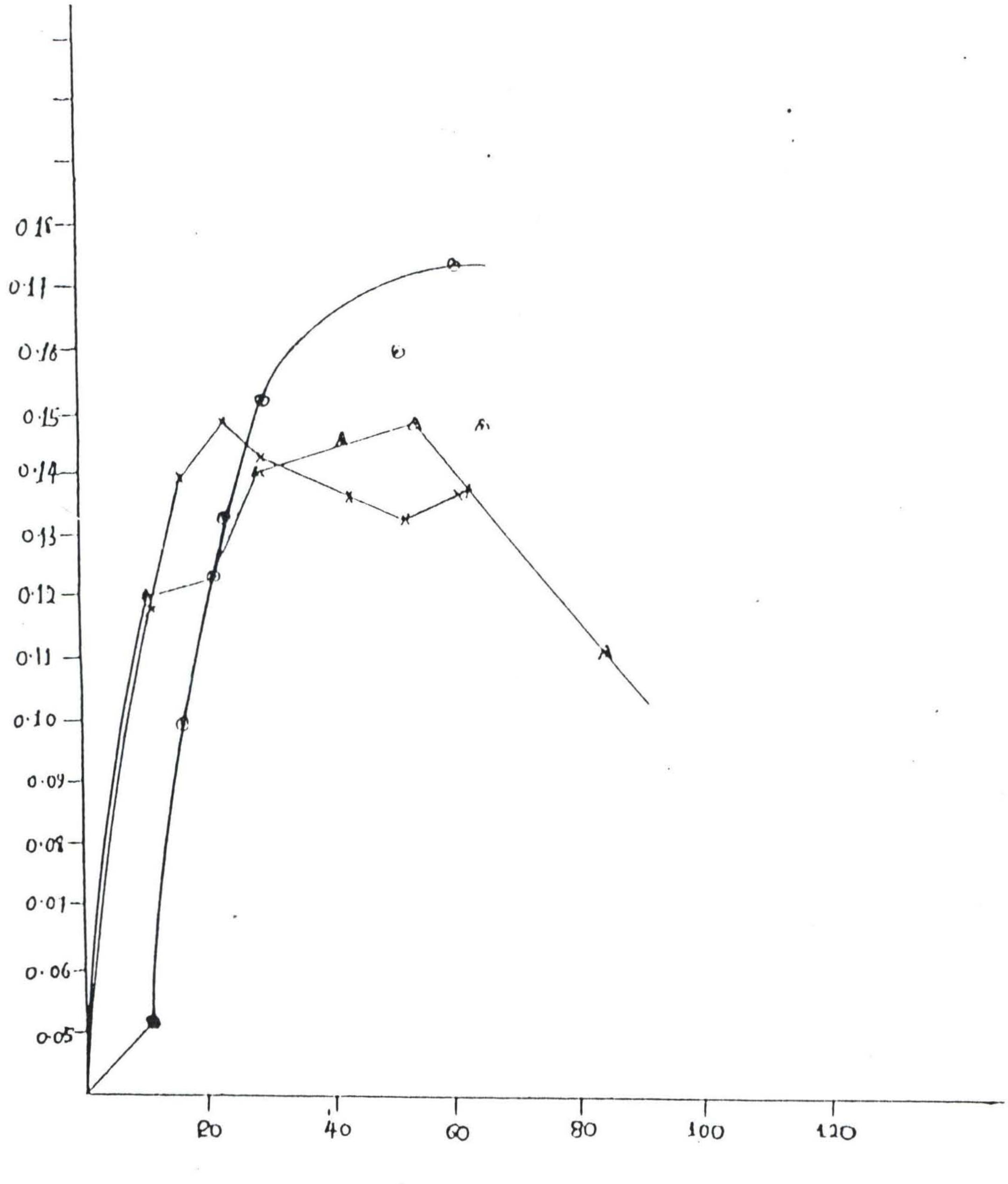


Fig 23: mol percent chloroform uptake of Nitric Acid etched pp at different Temperature 60°c (Δ), 40°c (x), 28°c (o)