SWELLING, SORPTION KINETICS AND SORPTION ENERGETICS IN UNTREATED AND SOLVENT TREATED POLYPROPYLENE FILM SAMPLES.

BY

IBRAHIM, ISAH LAKAN

A DISSERTATION SUBMITTED TO THE DEPARTMENT OF CHEMISTRY, IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF M.TECH IN ANALYTICAL CHEMISTRY.

JUNE, 1998

DECLARATION

I here by declare that this thesis 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 Information are derived from the published and unpublished work of others and they are specifically acknowledged by means of references.

Ibrahim Isah Lakan

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
(project supervisor)

EXTERNAL EXAMINER

DR.A A FARUK
HEAD OF DEPARTMENT

Prof. M . BABA
DEAN, S.S.S.E

DATE____________

DEDICATION

To my mother Hajiya Aisha Moh'd for her unflinching support and To my father Alhaji Moh'd Usman for his understanding.

ACKNOWLEDGEMENT

Glory be to Allah, the most beneficent and merciful. I will run short of words to be able to express my gratitude to God sent,tolerable, tireless, examplary, free minded, very hardworking Dr T. c. Uzomah my supervisor, without whose help, understanding and regard, the production of this thesis would have been impossible at this material time. I am indebted to Dr. A.A. Faruk, the Head of chemistry department,Dr.M.A.T Suleiman, Dean student affairs and other members of academic staff of chemistry department for your co-operation.

Iam very grateful to the chief technologist Mrs M.A Akinbode, and the technical staffs; B.Y. Emanuel, B.A.Bala, J.A.Abdullahi and J.A.Aje for you Assistance.I also acknowledge with gratitude the entire Alh Usman's family, well wishes, and my children, Ibrahim Ibrahim and Aisha Ibrahim and my dear wives Salamatu Isah and Hauwa Isah for your understanding and encouragement during this programme.

ABSTRACT

The swelling/sorption kinetics and diffusion co-efficient of solvent treated and untreated polypropylene films samples were investigated in nine solvents. the solvents are grouped into polar and non-polar chlorosolvents, esters and non-polar hydrocarbon solvents. Swelling ratio was used in two forms in accordance to Gee's theory:

1. a plot of $\left[Qt^{-1}\,\mathrm{In}\,\frac{Q}{Qt}\right]^{\frac{1}{2}}$ against the solubility parameter [δs [$mPa^{\frac{1}{2}}$]] of solvent to obtain the maximum in the swelling envelop.

2. a plot of Q_t against solubility parameter δs of the solvent to obtain the intercept of abscissa at the value of (δs) equal solubility parameter of the polymer δ_p [8,9].

The values obtained are 19.05 $mPa^{\frac{1}{2}}$ and 18.65 $mPa^{\frac{1}{2}}$ respectively. By small's group contribution constant method the solubility parameter was calculated as δ_p =16.4 $mPa^{\frac{1}{2}}$.

Sorption Kinetics study shows that polar solvents attained equilibration at t ($s_{\frac{1}{2}}$) = 60 ($s_{\frac{1}{2}}$), while non- polar solvents at t ($s_{\frac{1}{2}}$) = 60 - 85 ($s_{\frac{1}{2}}$). Diffusion coefficients; diffusivity was computed with the use of Crank's expression and from which, permeability and solubility were calculated. These parameters were shown to increase with increasing sorption temperature. Basically, non- polar solvents, particularly aromatic solvents, exhibited higher values of diffusion coefficients hence, the order tetrachloromethane > benzene > xylene > toluene for non-

polar solvents, and for polar solvents benzylchoride > chloroform > chlorobenzene > ethylacetate > Methylacetate. Similarly, the order of dipole moments for polar solvents is chloroform < chlorobenzene < benzylchloride < Methylacetate < ethylacetate.

Perm-selsectivity Z was computed for each solvents pair at respective temperatures. The result shows out of 30 pairs of penetrant investigated, 13 pairs showed a decrease, 14 pairs as increase and 3 pairs as irregular behaviour of Z with increase in temperature.

The mechanism of transport were obtained from the mode of transport n and extent of interaction k and were computed graphically with values ranging between 0.5 to 1.0 that is anomalous behaviour. The mode of transport n generally decreases with increase in temperature. The polymer-solvent interaction k however increases with increase in sorption temperature.

Arhenius plots of log D, logs S and log P against the reciprocal of absolute temperature $^1/_T$ were used to calculate activation energies of diffusion E_D , solubility E_S and permeability E_P respectively. Similarly, the entropy Δ_S and enthalpy Δ_H of solubility (mol) were determined, from the plot of log K_s against reciprocal of absolute temperature $(_1/_T)$. The negative sign of Δ_S indicates PP polymer retains some liquid solvents even when dried, while the enthalpy was positive hence the process is endothermic.

The critical dissolution time (CDT) and Apparent crystallinity (AC) were calculated and found to increase with increasing sorption temperature. The non-polar solvents exhibited lower CDT hence AC than the polar solvents.

Mode of transport /sorption Kinetics of treated PP films samples shows that solvent treatment played significant effect on the sorption characteristics. No solvent exhibited Fickian behaviour as well and also ' values decreases with increase in temperature, while K values increases with increase in temperature. Sorption/Solvent uptake increases for instance,benzene from 0.378 mol% to 0.44 mol% while chloroform 0.486 mol% to 0.592 mol% all at 28°c. Similarly, at 40°c and 60°c sorption / solvent uptake increases; when compared with untreated film samples. The date on diffusivity D, solubility S, and permeability P were used to estimate energies of diffusion E_D, solubility E_s and permeability E_p also for toluene - treated PP film samples and the Magnitudes shows that the parameters were greater than those untreated PP film samples.

Comparison of selectivity data of treated and untreated films samples shows general increase in selectivity although marginal as well but greater for treated sample than those untreated film sample.

Critical dissolution time (CDT) and Apparent crystallinity (AC) data of PP film swollen to equilibrium for treated PP film sample shows that the values obtained seem to be larger than those obtained for untreated film samples.

TABLE OF CONTENTS

Chapter One

Chapter Two

Chapter Three

Chapter Four

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS, GLOSSARIES AND SYMBOLS

PP	Polypropylene
Q_t	Swelling ratio
Q	Swelling quotient
E_D	Activation energy of diffusion
E_s	Activation energy of solution
E_p	Activation energy of permeability
K_s	Equilibrium sorption constant
PET	Polyethyleneterephthalate
PAN	polyacrylonitrile
AC	Apparent crystallinity
CDT	Critical dissolution time
S	Solubility
P	Permeability
M_t	Amount of permeant sorbed in time t
M_c	Molecular weight between cross links
V_s	Molar volume
Φ	Junction functionality
M_∞	Quantity of penetrant sorbed at equilibrium
δ	Solubility parameter
β	Entopic constant
χ	Interaction constant
ΔE	Enthalpy of vaporization
D	Diffusion constant
dt/dx	Concentration gradient of permeant
P_i/P_j	Permeability ratio
M_w	Molecular weight

CHAPTER ONE

1.0 INTRODUCTION

Coordination polymerization makes the commercial production of polypropylene possible. Polypropylene is the lightest plastic known. Its high crystallinity imparts to it high tensile strength, stiffness and hardness. The resulting strength to weight ratio is an advantage in many applications (77).

1.1.0 POLYPROPYLENE POLYMER

Polypropylene is high molecular weight and highly crystalline polymer similar in properties to high density polyethylene [1]. Polypropylene (PP) can be in three forms. The forms are differentiated by the way the methyl groups are attached to the chains. The one in which carbon atoms are in the same plane is called isotactic (2). Other forms includes syndiotactic and atactic.

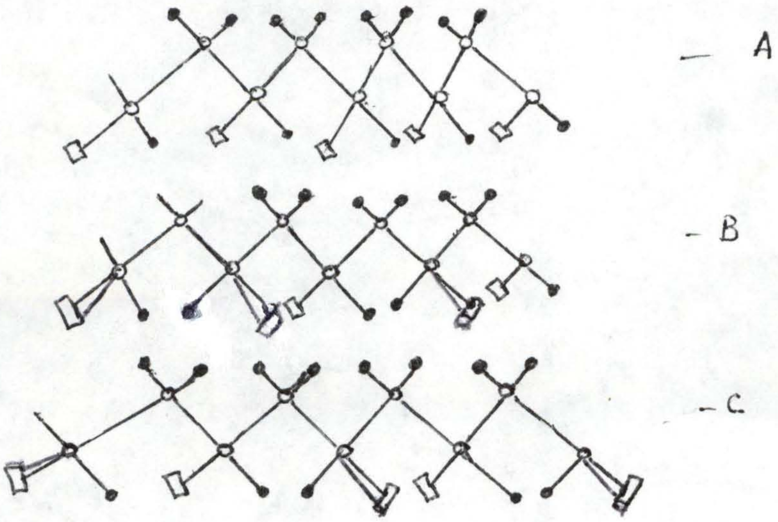


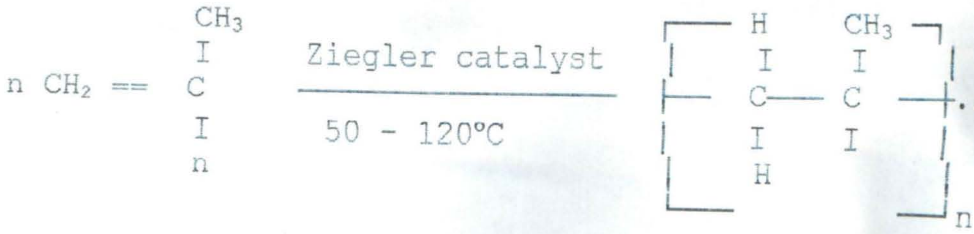
Fig. A. is isotactic, B is syndiotactic and c is atactic

● **Hydrogen**

○ **Carbon**

☐ **Methyl**

Isotactic polypropylene is harder, stronger than and at about 160°C softens. Polypropelene is available at low cost in large quantities from cracking of petroleum hydrocarbons. High-molecular weight isotactic polymers are formed in the presence of the stereo specific catalysts such as titaniumtrichloride and tetramethylaluminum, other wise called Ziegler catalyst used on ethlene polymerization as shown below:



$$n\ CH_2 == \overset{CH_3}{\underset{n}{C}} \xrightarrow[50\ -\ 120^{\circ}C]{\text{Ziegler catalyst}} \left[\underset{H}{\overset{H}{C}} - \overset{CH_3}{C} \right]_n \ldots.(1)$$

The crystalline products which are about 90-95% isotatic have an unusual combination of properties: high strength, exceptional resistance to flexing, resistance to stress cracking and the lowest density of any commercially available thermoplastic ($0.9-5\ gcm^{-3}$). The morphology is especially important in determining physical properties and may be controlled by varying the rate of cooling from melt during processing or by incorporating nuclcating agents. Application in moulded and extruded articles, films, and fibres have increased very rapidly.

In order to reduce the tendency toward embrittlement at low temperature or to enhance the dyebility of fibres, copolymerization with ethylene or other monomers is frequently advantageous. The wide range of possible copolymer compositions makes it possible to tailor particular compositions and for mutation for specific uses. Reinforcing materials such as asbestos or glass fibres may be used to improve properties such as stiffness. The discovery of stereo-specific catalyst was a major break through in production of polymer with specified orientation in such a way, that the catalyst acts as a kind of molecular jig or template turning each propylene molecule in the right direction before allowing its addition to the polymer chains [2]. The distinct use of stereospecific catalysts confers on the polymer a strong durable fibre with excellent resistance to chemical attack although liable to damage by oxidising agents. A wide range of application is possible because of some of its special features. These include, in automobiles and appliances parts, wire insulation is required pipe and protective liners. The usual flex resistance makes it possible to mould polypropylene as an interesting hinge. Ease of electroplating has led to considerable use for decorative items.

The use of both unoriented and oriented films of homopolymers and copolymers has grown rapidly in such applications as packaging for textile and food, liners for bags, and treat - shrinkable wraps, raps records and other articles. Many types of fibre products are available and their high tenacity and good abrasion resistance have led to acceptance for such uses as indoor - outdoor and nets. The low molecular weight polypropylene oils formed in the presence of acid catalysts such as boron trifluoride or phosphoric acid are useful in the manufacture of gasoline and synthetic detergents but are not employed in plastic technology.

1.2.0 STRUCTURE OF POLYPROPYLENE

The polypropylene molecule is ordinarily present in the polypropylene film in a three-fold helix form i.e four of the helix is completed in three monomer repeat unit [3]. In a simplified view, therefore, the one-way drawn polypropylene film may be thought of as an assembly of long thin cylinder rather like packet of spaghetti, with their long axes all parallel and in the draw (machine) direction.

There are three well known crystalline structure namely: monoclinic (α), hexagonal (β) and triclinic (γ) associated with polypropylene. The crystallization conditions for these structure have been discussed extensively (11). Among these three structures monoclinic (α) structure is the most common; being found in normal melt crystallised or solution crystallised samples. Also of concern is a "quenched form" which can be obtained when polypropylene is rapidly quenched from the melt. The infrared (I.R) spectra reveal that the quenched and the monoclinic structures are similar implying same three similar helical conformation in this quenched state [13,14]. The density of quenched foam has a value between values for the amorphous and crystalline structure [13,15]. All the above result tend to suggest that the quenched structure is organised in a state intermediate between amorphous and crystalline states. This structure is described as "Smectic" [14] and said to be composed of parallel three perpendicular helices, but that disorder exist in the packing of the chains perpendicular to their axis [13]. It was suggested that, the quenched form is "para crystalline. i.e a disordered structure [16].

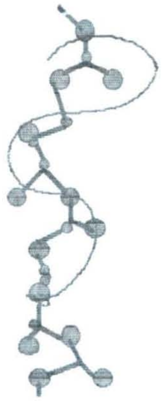


Fig B possible type of helices for isotactic chairs with various lateral groups [31].

1.3.0 **FACTORS FROM THE ENVIRONMENT**

It has been recorded that the energy needed to break PP bonds in molecules is Ca 210 - 420 KJ. This compares with the energy of 344.4KJ/mole associated with radiation wave-length .3500 A° which is the mid-point of the radiation comprising 5% of natural sunlight of the earth surface. Combination of ultra-violet (u.v) radiation, water, infra-red will often result in more advanced levels of degradation than ultra-violet radiation by itself [5]. This is because heat moisture and oxygen can modify the polymer or its additive so as to shift the ultra-violet absorption to those wave-length at which photochemical degradation can occur.

Temperature increase can affect the degradation process as reported [5], a 10°C increase in temperature will double the speed of the degradative reaction. The effect of alternating the thermal state of a plastic material can give rise to the development of surface crazing owing to excessive expansion and contraction and is even more pronounced if the material contains "frozen in" stresses resulting from fabrication. Reactions between polymers and oxygen are very slow at normal ambient temperatures. The more serious problem would appear to be the synergistic effect with moisture and ultra-violet radiation at elevated temperature [4]. A very real and important phenomenon affecting not only this, but other stabilization systems particularly in polypropylene has been illustrated [6,9]. This phenomenon is the rejection of additives by the growing crystal front, causing their redistribution and localised concentration during the crystallisation of an initially homogeneous polymer melt.

Computer simulation and prediction of the growth/rejection process has been carried out [7]. Basically the overall result of this phenomenon is a greater or less degree of rejection of the additives to the spherullites boundaries. The degree of rejection is dependant upon the ability of the additive molecules within the polymer, the rate of crystallisation, the weight species) to areas where they become the dominant component.

1.4.0 **SOLVENT INDUCED CRYSTALLIZATION (SINC)**

This focuses on crystallization in interacting liquids polymer films of moderate thickness. It has been established that penetrant transport controls the crystallization process. Density measurements were employed to monitor the crystallization. Change in sample density reflects a change in volume average crystallinity. Sheldom and co-workers [17,18,19] measured the densification of 0.02 - 0.04an thick polyethylene terephthalate (P.E.T.) films immersed in benzene and in ketones. They concluded that the penetrant transports controlled the extent of induced crystallisation, since the penetrant uptake and the sample density were linearly related. The density increases linearly with the square root of the contact time between the liquid and the sample activation energy.

Theoretical investigation of solvent induces crystallisation focused on nucleation and growth of crystallites. The observation of small uniformly sized spherulite in solvent crystallised polymer suggests that a thermal (heterogenous) nucleation occurs, since such, spherulitc results from the simultaneous initiation of crystallite from a fixed number of nuclei.

1.5.0 FREE VOLUME THEORY

Generally, molecular motion can not take place without the presence of holes. These holes are collectively called free volumes. Studies have shown that molecular motion in the bulk state depends on the presence of holes, or places where there are vacancies or voids [41]. When a molecule moves into a hole, the hole of course exchange with the molecule as shown below.

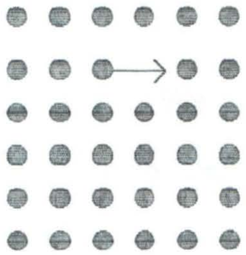


fig. C. A quaiscrystalline lattice exhibiting vacancies or holes. Circle represent molecules; arrow indicate molecules motion.

plasticizing effect of the permeant gas/vapour and it has been applied satisfactorily to the solution and transport (diffusion and permeation) of water polyacrylonitrile ((PAN) [44,46]; methanol, acetone and benzene in ethylcellulose [45]. Another extension of this model which introduces partial immobilization assumes the existence of two different penetrant population with different mobilities and examines the effects on penetrant transport in the Henry's law (concentration) and langmuir (pressure) domains separately. The mutual diffusion coefficient Dd and Dh which characterise the penetrant transport in the domains are exponential functions of the penetrant concentration [47]. A second original model that includes the plasticizing (swelling) effect of the penetrant into the polymer is based on the "free volume" model of cohen and Turn bull [48], adopted by Kreituss and Frisch [49], but has been modified by Fujita and other workers [50,51]. The theory considers a semi-crystalline polymer as an heterogenous material in which mass transport was described as the result of the super-position of two mechanisms:

(i) In the crystalline phase, the diffusion coe-fficient is considered to be zero.

(ii) In the amorphous (non-crystalline) or rubbery phase, the modified " free volume" model applies. Peppas and Reintrart [52] have included the effect of cross-linking to this theory.

The practical implication of these two theories; "dual mode" and" free volume" models is that diffusion of small molecules polymers is strongly dependent on the physical structure of the polymers matrix. The motions of the permeant are determined by the three dimensional network formed by the polymer chains. Associated with this network are cross-link, entanglements, Crystallites, etc and are affected by degree of crystallinity, size of crystallite, chain rigidity and degree of swelling. The "Mesh size" of the network is determined by the hydrodynamic radius or radius of gyration so that the diffusion coefficient of the penetrant is affected by the"mesh size" [20, 22] This diffusion in polymers is determined by the "Mesh size" which act barriers to transport and the factors which increase the mobility of the polymer chain or the distance between them, enhances the transport of molecules [53].

1.6.0 **POLYPROPYLENE- SOLVENT SYSTEM**

The load-extension curves of polypropylene yarn in the dry state as well as after inhibition in several liquids shows that the solvent effects are relatively minor which is probably due to the fact that the polypropylene yarns have a high crystallinity and a high molecular weight [25] . These two factors would be expected to obscure or eliminate interactions of solvent with the amorphous region in the filament structure. The application of the solubility parameter principle to the polypropylene solvent interaction shows the variation of modulus with the total solubility parameter of solvent. The modulus is shown to be highest with solvents whose solubility parameter are close to that of polypropylene. This reflects the fact that, the major contributions to intermolecular bonding in polypropylene arises from dispersion forces. There is a definite trend in the experimental points towards increasing interactions as the solubility parameter of polypropylene is approached. However, a few points indicate interactions with solvent that have considerable contributions from polar and hydrogen- bonding forces indicating more complexity in the intermolecular bonding [25].

1.7.0 **SOLVENT /VAPOUR DIFFUSION**

The steady-state activated transport of a fluid through a polymeric membrane may be described by Ficks law:

$$J = -D(d_c/d_x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where J is the mass flux of the permeant, D is the diffusion coefficient and d_c/d_x is the concentration gradient of the permeant for the case of a liquid in contact with the up stream face of a membrane of thickness L, Ficks law may be integrated to yield:

$$Q = JL = \int_{0}^{G} D dc \quad \ldots\ldots\ldots (3)$$

The product, JL represent the flux rate normalized to unit membrane thickness and is denoted by Q. By defining an integral diffusivity D, to represent the average diffusivity across the membrane as:

$$D \quad = L/c_1 \int_{o}^{c1} \text{........}4$$

One obtains the following for Q:

$$Q \quad = \quad D\ C_1 \text{.........}5$$

The relation is of a major significance, since, it underlines the two primary factors which affect the steady state. Permeation flux: the diffusivity of a molecule in a membrane and its equilibrium concentration C_1, or sorption in the polymer.

Crank [24] solved for differential equation expressing ficks second law using early phase prevailing condition in diffusion experiment ($t \longrightarrow o$) to obtain. equation (6);

$$Q_t\ /Q_\infty \quad = \quad 4 \left[\frac{D \quad t}{l^2 \quad \Lambda}\right]^{1/2} \text{........}(6)$$

Where Q_t is the amount of permeant sorbed or desorbed in time t, Q_∞ represents the quantity of the penetrant in the film at equilibrium, D is the integral diffusivity and is film thickness. The slope of a plots of Q_t/Q_∞ versus $t^{1/2}$, therefore can be used to estimate the integral diffusivity during sorption, D_s

or during desorption D_t. Crank [24] indicates that the average of D_s and D_d denoted by Dav for time independent diffusion, corresponds reasonably well to the diffusivity as estimated by combining the permeation flux rate of a compound with its equilibrium concentration in the polymer; $D_Q = Q/_G$ Under equivalent boundary conditions. Thus Dav Values representing the kinetics of sorption and desorption between the terminal states of vacuum and saturated vapour were compared to D_Q values.

It has been established, that permeant transport of polymeric membrane [25]. A structural feature of these amorphous region that is important in determining transport behaviour is the degree of constraint of "tightness" of the amorphous polymer chain segments comprising these regions, which act as "tie-links" between crystallites [26]. It can readily be appreciated that transport of penetrant molecule would be more hindered when passing among stiff and immobile tie chains that is a highly constrained matrix than when diffusing through relatively flexible chains. However, crystalline polymers are considered as composites [30], consisting of impermeable micro crystalline islands embed in impermeable amorphous phase. The solubility of permeant in perfectly crystalline regions of the polymer is expected to be zero, since they act as barriers.

1.8.0 **Sorption Behaviour**

This is governed primarily by the relative magnitude of molecular forces acting between polymer segments and penetrant molecules, ie thermodynamic factors. It has been found that compatibility of a solvent and a polymer is expressed through the use of solubility parameter (δ), where δ equal the square root of the cohesive energy density [CED] which is the internal energy of vaporization divided by molar volume [27]. Furthermore, it has also been observed [27] that, there is increase in permeation rate subsequent to solvent treatment which can be partially attributed to changes in the sorptive capacity of the polymer. In addition, it is recognised that transport of matter is dependent properties of the permeated and the medium.

1.9.0 **Permeability and Diffusivity**

Permeability is the rate at which a gas or vapour passes through an object polymer. The mechanism by which permeation takes place involves three steps:

(a) Absorption of the permeating species into the polymer,

(b) Diffusion of the permeating species through the polymer, travelling, on average, along the concentration gradient and

(c) Desorption of the permeating species from the polymer surface and evaporation or removal by other mechanism [33].

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

It must be emphasised that holes in materials are required for all types of molecular motion beyond simple vibrational and rotational states. Generally, when a molecule moves from position A to B, it is believed that A moves into a hole. The hole and molecule are transposed, so that hole is where the molecule was before action started.

In elastomers, concerted movement of several adjacent chains segment take place to provide rapid transport. Such motions are restricted in glassy polymers [37]. Also, free volume is much less in glasses than in plastics.The size of the permeant is critical in determining its diffusion rates in polymers. Sizes range from 2 to 5°A for many molecules. The larger the molecule, the smaller the diffusion rate.

In general, permeability decreases from elastomers to amorphous plastics to semi crystalline plastics. One of the more recent application is the use of amorphous

poly-(ethylene terephthalate) for soft drink bottles. The major requirements are to keep carbon (iv) oxide and water in and to keep oxygen out. One must realise these gases are continuously being transported across the plastic even if at a low rate causing the soft drink eventually to go "flat". Thus, these drinks have a "Shelf life" after which they must be discarded if not consumed.

The permeability coefficient, P is defined as the volume of vapour passing per unit time through unit area of polymer having thickness with unit pressure difference across the sample. The solubility coefficient, S determines the concentration for the simplest case;

$$\overline{P} = \overline{D}.\ \overline{S} \ \ldots\ldots\ldots\ldots (7)$$

Which express the permeability in terms of solubility and diffusivity. The temperature dependence of the solubility obeys the clausius - claperon equation written in the form [34].

$$\Delta H_S = \frac{-R\ d.\ \mathrm{In}\ S}{d(^I/_T)} \ \ldots\ldots\ldots\ldots (8)$$

A study of vapour solubility as a function of temperature allows the heat of solution ΔH_S to be evaluated. Since, the size of the diffusing molecules per second is important. It turns out that the logarithm of the diffusion coefficient depends inversely on the molar volume [35,36]. However, permeability coefficients depend on the temperature according to the Arrhenius equation;

$$\bar{P} = \bar{P}_o e^{\frac{-\Delta E_p}{RT}} \qquad \text{..........(9)}$$

Where, ΔE_p is the activation energy for permeation [37], similar relation hold for solubility and diffusivity. Similar expressions can be written for activation energy of solubility ΔE_s and diffusivity ΔE_D as in equation (10) and (11)

$$\bar{S} = \bar{S}_o e^{\frac{-\Delta E_s}{RT}} \qquad \text{.......(10)}$$

$$\bar{D} = \bar{D}_o e^{\frac{-\Delta E_D}{RT}} \qquad \text{..........(11)}$$

1.10.0 **SELECTIVITY**

Selectivity is defined as the ratio of permeability of one solvent to the permeability of the other.

$$Z = P^i / P_j \qquad \text{.............(12)}$$

Where P_i is the permeability of solvent i, P_j is permeability of another solvent j. The changes in polymer morphology resulting from solvent treatment also influence the selectivity of polypropylene films towards various organic solvents. Usually, the ideal permselectivity of a membrane is lower in films exhibiting high flux rates Michael etal [27] have shown in sorption of PP film that low permeation rate can be related to polymer morphology characterized by a high degree of interlamellar amorphous chain ties. In such a constrained structure, there exist [27] some regions that may be accessible only to the smaller molecule (eg toluene). Solvent annealing promotes "loosening" of the polymer matrix and thus transport is facilitated, especially for the larger molecules eg Iso-octane, whose size restricts their movements to a greater extent in the unmodified membrane. Furthermore, it has also been shown that there exist inverse relationship between flux rate and log of selectivity [27]. This mean selectivity decreases with increasing temperature. As in effect at higher temperature transport rate of larger molecules are affected more than those of smaller size.

However, in considering values of solvent modification with respect to the potential use of membranes in separation processes,the changes of both permeation flux (Q) and selectivity _ _

(P S) are taken in to account. For a given overall enrichment, the number of states required is roughly inversely proportional to the log of selectively, while the area required per state for a given through put is inversely proportional to the

— —

permeability. Thus if $P\ S >> I$ and increase in flux will decreases appreciably. On the other hand, if $P\ S$ or 1, a slight loss in selectivity will be far more damaging than a large gain in permeability.

1.11 **ENERGETICS**

The energetics of any thermodynamic system is expressed generally by the well-known Gibb's free energy equation;

$$\Delta G = \Delta H - T \Delta S \quad \ldots\ldots\ldots\ldots\ldots(13)$$

Where ΔG is the change in the free energy of system and has a negative value for a spontaneous process, ΔH is the enthalpy change, ΔS is the entropy change and T is the Kelvin temperature. For the sorption of organic molecules, the equilibrium amount sorbed by a mass of polymer denoted by the equilibrium sorption constant K_s was calculated from the expression [54]:

$$K_s = \frac{\text{Moles of penetrant sorbed}}{\text{Unit mass of the polymer}} \quad \ldots\ldots\ldots(14)$$

The van't Hoff's is used to obtain the entropy change Δs and enthalpy change ΔH as shown below:

$$\text{Log}K_s = \frac{\Delta s}{2.303R} - \frac{\Delta H}{2.303R} \frac{I}{T} \quad \ldots\ldots\ldots(15)$$

A plot of logs K_s against 1/T (K^{-1}) is a straight line and ΔH can be calculated from the slope while Δs is obtained from the intercept.

1.12. AIMS AND OBJECTIVES

Research works have been reported on sorption and transport of gases or liquid molecules into polymeric films and membranes [24,27, 30, 40, 66, 71, 72]. In corroboration of the above, this research project was embarked upon. The aims and objectives of this study, basically, is to generate enough date on the sorption and diffusion of organic liquid molecules into polypropylene (PP) film. Such information on the diffusivity, solubility, permeability of these organic molecules in to pp films at different temperatures would be sought. Information about mode of transport (whether the diffusion process was fickian or non- fickian) and the extent of polymer solvent interaction in these systems, the entropy, enthalpy and free energy of molecules into PP films were targeted.

This study aims at comparing the effects of solvent sorption into treated PP films and untreated PP films with regard to those properties enumerated above. Sorption studies involving some selected solvents would also be performed on the treated PP films at the different temperatures. The crystallinity developed in PP films at maximum sorption in different solvents would also be estimated. The changes in the properties: sorption

/diffusion,solvent treatment and crystallinity developed will be studied in terms of changes in molar volume, molar mass, dipole moment and interaction constants of the liquid used.

In view of wide application of PP; being used as packaging organic materials, food and containers of liquids which may emit vapours, in the concentration of proteins, demineralization of sea water, treatment of effluent waters and the separation of mixture of close-boiling liquids necessitates research studies of this nature. Having discussed the aims and objectives, theoretical basis and literature associated with the study, various parameters that may affect the sorption characteristics, mode of transport and energetics are now highlighted. The variation of polarity,molar volumes, molar mass and the interaction constant of the nine solvent used for the study and the degree to which those correlate with the properties of interest will be discussed. The effect of temperature of sorption and changes in properties of interest when solvent treated PP films are investigated will also be discussed.

The layout of the project is in parts:Introduction and literature review, the experimental section and figure finally the finding of the research project are summarised. condition are drawn and an attempt is made at suggesting some related areas for further investigation .

CHAPTER TWO

2.0 EXPERIMENTAL

2.1 MATERIALS

The solvents used: Benzene, Benzylchloride, Xylene mixture, chloroform,Tetrachloromethene, chlorobenzene, Methylacetate, Ethylacetate, n-Hexane, and Toluene were reagents grade from chemistry laboratory store. These solvents were used without further purification.

Water bath, thermometer (0 to 360°C), Mettler balance AT 400 with precision of ± 0.1mg, micrometer screw gauge.

The polypropylene films used in this study were of weight average molecular weight, 3.2×10^5, average thickness 0.32mm, density $0.9ghcm^3$ and percent crystallinity 48%. They were supplied by Nigeria bag manufacturing company Lagos limited [BAGCO].

2.2 Method

2.2.1 Sorption/swelling

A sample of polypropylene film (0.1g) was weighed into a sample bottle and $10cm^3$ of solvent was poured into the sample bottle just to cover the film.\]The stoppered sample bottle was then immersed in a water both maintained at 28°C. In each case, the sample of film under study was kept in the solvent of choice for 2,5,7,10,15,20,30,60,120,180 and 240 minutes or until maximum absorption of solvent had occurred to obtain data for amount of swelling Qt at time t and at infinity Q_w. After, each swelling procedure, the solvent was decanted and sample of film was carefully blotted, dry and weighed on a mettler balance AT 400 with precision of ± 0.1mg to obtain the weight of the swollen polymer. The sorption/swelling data were obtained from measurement in triplicates [54]:

$$Q_t == \frac{\dfrac{\text{Wt of the solvent sorbed at a given time}}{\text{Mol Wt of the solvent}}}{\text{Initial Wt of the rubber specimen}} \text{ x } 100 \ldots (16)$$

Where Q_t is expressed as moles of liquid sorbed by polypropylene (PP) film at time t. The swelling experiment was repeated for each solvent at higher temperatures; 40°C and 60°C.

Data for the swelling envelope were however, computed from the swelling quotient given by:

$$Q_t = \frac{M_t - M_o}{M_o} \text{ x } \frac{1}{\rho_s} \text{ x } 100 \ldots\ldots\ldots\ldots (17)$$

Where M_t and M_o are masses of swelling and dry polymers, ρ_5 is the density of solvent [57].

A likely draw back in this method may be:

(i) As a result of the paper used for blotting, which is possible too remove more than expected solvent on the film sample depending on the pressure applied and absorptivity of the paper. Since, blotting was done in 20 - 30 seconds, essentially, error due to evaporation other than surface adsorbed liquid is assumed in significant [54].

(ii) At higher temperature of solvent sorption in particular, at the early time, for example, 2 minutes error may arise, since, the film may not have equilibrated at the higher temperature [54]. The result is that the amount of solvent sorbed if the film had assumed the higher temperature. This may affect the value of initial slope for graph of log (Q_t/Q_w) V_s $t^{½}$ needed for the calculation of diffusivity D of film and hence the permeability P.

2.2.2 **SOLVENT TREATMENT**

The PP film sample of known thickness and weight was immersed into conical flask containing the treatment liquid (toluene) and left at 28°C for 24 hr. The treated sample was left in the open laboratory to dry to constant weight. After the sample had assumed constant weight, the same sorption studies as in section [2.2.1] were carried out.

2.2.3 **CRITICAL DISSOLUTION TIME (CDT) [71]**

The treated films that assumed equilibration were used for critical dissolution time experiment. Basically, this was done by heating toluene suspended in paraffin oil contained in a beaker. The paraffin oil was heated to 110°C, PP films (1 x 1cm) cut from the films which had assumed maximum swelling in different liquids were dropped separately into hot toluene with stirring. Time taken for complete dissolution of the samples were taken. The untreated PP film was also similarly dissolved in the hot toluene. A mean of the dissolution times for three separate experiments for PP samples was recorded as the critical dissolution time. The data on CDT were used for the calculation of percent apparent crystallinity developed by the various solvent treated PP film according to the equation [71].

$$\% \text{ Apparent crystallinity (AC)} = \frac{CDT_{treated} - CDT_{control}}{CDT_{treated}} \times 100$$

$CDT_{treated}$ and $CDT_{control}$ are the critical dissolution time for the solvent- treated films and that for the untreated films respectively.

CHAPTER THREE

3.0.0 RESULT AND DISCUSSION

3.1.0 SOLUBILITY PARAMETERS

Solubility parameter (δ) is defined as square root of the cohesive energy density [CED]. Earlier, solubility parameter was thought to be a quantity that expresses strength of interaction in simple liquids [32]. It is related to fundamental thermodynamic properties of polymers and was extended to polymer-solvent system. Solubility parameter (δp) of a polymer can be determined by experiment or by calculation [75].

However, assumptions of theory of regular solution forms the basic of all the experimental methods and according to the theory the best mutual solubility is obtained when the solubility parameters are the same. Hence, the correctness of this concept is assumed before this has been justified. Therefore various properties of polymer solutions associated with polymer-solvent interaction, are studied in a series of solvents with different solubility parameters δs. The value of δs corresponding to the highest value of the property being is equated to δp of the polymer.

The methods that have found widest use are those of determination of degree of swelling and intrinsic viscosity. According to Gee [72] the dependence of the equilibrium degree of swelling of a polymer in low-molecular liquids, on the value of δs of the later, is expressed by a curve with a maximum, the abscissa of which is equal to δp of thew polymer. For more accurate determination of δp, the degree of swelling Q_t is represented in the form of the equation [75];

$$Q_t = Q_\infty e^{-Vs(\delta s - \delta p)2} \;...............(19)$$

Where Q_∞ is the degree of swelling corresponding to the maximum in the curve and Vs is the molar volume of the solvent, where;

$$\delta p = \delta s \pm \_ \frac{1}{Vs} \; \mathrm{In} \; \frac{Q_\infty}{Q_t} ....(20)$$

The data on δs and Vs are presented in table 1, which these experimental data of Q_t and Q_w are listed in Table 2. From equation (17) the graph of

against δs gives a straight line, intercepting the abscissa at the value of δs equal δp of the polymer.

In addition Gee [8] proposed that the interaction and swelling ratio will be a maximum when the solubility parameter of the polymer δp matches that of the solvent (δs). This idea can be used to calculate the cohesive energy density of a variety of synthetic polymer [55]. The theory of Gee was also represented as follows [8,56].

$$\frac{Q_t}{Q_\infty} = e^{-a.Q_t(\delta s - \delta p)2} \text{ ....}(21)$$

Where Q_t is the swelling ratio, Q_w is the maximum swelling ratio and a is constant. Equation (21) can be rearranged as;

$$\left[Q_t^{-1} \text{ In} \left[\frac{Q_t}{Q_w} \right] \right]^{1/2} = a^{1/2} (\delta s - \delta p) \text{ ....}(22)$$

A graph of $\left[Q_t^{-1} \text{ In} \quad \frac{Q_t}{Q_w} \right]$ against δs gives $a^{1/2}$ and δp as the slope and the intercept of the horizontal axis respectively [57]. From the plot, the solubility parameter of PP δp is 19.05 mPa$^{1/2}$ as shown in figure I. This value is comparable with that obtained by Hayes. The plot of % Q against δs is shown in figure 2. The value of δs corresponding to maximum value of Q in the

The plot of % Q against δs is shown in figure 2. The value of δs corresponding to maximum value of Q in the swelling envelope is equal to the δp of the polymer PP. This equals 18.68 mPa$^{\frac{1}{2}}$ from the plot. This is reasonably close to Hayes value of 18.8 mPa$^{\frac{1}{2}}$ [77]. Solubility parameters of samples could also be calculated by Small's group contribution method [58], using the relation.

$$\delta_p = \frac{\rho\Sigma F}{M} \ldots\ldots\ldots\ldots\ldots\ldots (23)$$

Where ΣF is the sum of Small's group contribution, that is molar attraction constant, M the formula weight of the polymer repeat unit and ρ the polymer density. The molar attraction for CH_3, CH_2 CH- are ;214, 133, and 28 respectively [31]. Using these data, δp calculated is 16.45mPa$^{\frac{1}{2}}$ a value reasonably close to Hayes value 18.8mPa$^{\frac{1}{2}}$ [77].

However, analysis of the swelling equilibrium behaviour of polymer networks in solvents could also be used to determine the molecular weight between crosslink (Mc) [59,61,62,63]. Specifically, Flory-Huggin's interaction parameter χ for the polymer- solvent system is expressed by solubility parameter theory [55].

$$\chi = \beta + \frac{V_s}{RT}\left[\delta s - \delta p\right]^2 \ldots\ldots\ldots\ldots\ldots(24)$$

Where Vs is the molar volume of the solvent, R is the gas constant, T is the absolute temperature and constant entropy term β taken as 0.34 [57].

Table I shows variation of physical properties of the liquid used for this work and their calculated interaction parameter χ. The calculated values χ show that n-hexane with largest difference between the solubility parameters of the solvent and polymer $I\Delta\delta I$ equal to $3.9mPa^{1/2}$ and largest χ value (0.876), while methylacetate with smallest $I\Delta\delta I$ value = $0.1mPa^{1/2}$ and smallest $V_s = 79.7\ cm^2\ mol^{-1}$ has the least χ value 0.34. These value are consistent with Flory - Huggins equation above equation [24].

3.2.0 **SORPTION & SOLVENT UPTAKES**

After the equilibration the amount of solvent sorbed Q_t is expressed as in reference [54]:

$$Q_t = \frac{\dfrac{\text{Weight of the solvent at a given time}}{\text{mol weight of the solvent}}}{\text{Initial weight of the polymer specimen}} \times 100 \ldots.(25)$$

The Q_t values obtained were plotted against square root of time of immersion in figures 3-7 and 8-10. The figures 3-7 are plots of Q_t against $\sqrt{t}$ (s) for solvents at different temperatures while figures 8-10 compare the profiles of nine chosen solvents at the three different temperatures of sorption.

Generally, profiles of Q_t (% moles) against $\sqrt{t}$ (s) are divided into two distinct parts. For clarity; the initial slope for diffusivity which is part of the kinetic region and saturation or equilibrium level. From the figures 3-10 of Q_t against $\sqrt{t}$, inverse relationship between Q_t and $\sqrt{t}$ was observed at initial slope for diffusivity and kinetic region, until at saturation level where the profile assumes plateau horizontally showing the polymer has taken much of what to sorb.

Figures 8-10 show clearly that the initial slope and maximum swelling mol % increase with increase in temperature. This is expected as increased temperature of sorption results in partial melting of the polymer contributing to more polymer matrix that is available for solvent permeation. Comparison of figure 8-10 shows that equilibrium is reached at about _t = $60^{\frac{1}{2}}$min for methyl acetate, ethylacetate, chlorobenzene, benzylchloride all polar molecules with the exception of chloroform. But for benzene, xylene and toluene (non polar solvents) equilibriums sorption is attained at about _t=(65-$85)^{\frac{1}{2}}$min.

This seems to suggest that non polar liquids with exception of tetrachloromethane are sorbed for longer time before the attainment of equilibrium than the polar or chloro solvents by PP films.

At 28°C, 40°C and 60°C out of the solvents choosen, ethylacetate exhibited lowest uptake and chloroform the highest. Explanation for this findings have been above. Apparently, from figure 8-10, Q_w at any particular temperature for the non polar solvent increases in the order xylene to benzene, in agreement with decrease in molar volume and decrease in interaction parameter X. However, for polar solvents factors to be considered are dipole moment, molar volume and interaction parameter. The increase in solvent uptake seems to correlate with the earlier factors. Hence, the order of increasing Q_∞ is ethylacetate, tetrachloromethane, chlorobenzene and chloroform The increased sorption of chloro-solvents lies in the fact that these solvents exhibit specific interaction with PP [70].

For finer details, one finds that figures 3-7 show also that equilibrium sorption Q_{max} is higher for methylacetate compared to ethylacetate, chloroform compared to tetrachloromethane, chlorobenzene compared to benzylchloride, benzene compared to xylene and toluene respectively.

Apparently; in figures 3-7 it is evident that for each solvent Q_t and Q_w increase with increase in sorption temperature. This is expected as increase in temperature leads to partial melting of some crystalline polymer material and loosening of amorphous zone and this allow greater solvent sorption.

3.3.0 DIFFUSION PROPERTIES

In polymeric membranes, it has been reported that transport is accomplished via three steps [66]: Solution or absorption of the permeating molecule at one surface of the membrane,activated diffusion of the penetrant molecules through the membrane, and desorption from the membrane surface. Furthermore, transport takes place primarily in the non-crystalline regions of polymeric membrane[25]. A structural feature of these amorphous regions that is important in determining transport behaviour is the degree of polymer chain segment comprising these regions which act as (tie links) between crystallites [26]. It can be readily appreciated that transport of a penetrant molecule would be more hindered when passing among stiff and immobile tie-chains [that is in highly constrained matrix] than when diffusion is through relatively flexible chains

3.3.1 DIFFUSIVITY

This is a parameter that expresses steady state permeation flux. The kinetic parameter, diffusion coefficient D in the sample is expressed as [54]:

$$D = \pi \left[\frac{h\Theta}{4\ Q_{\infty}} \right]^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (26)$$

where h is the sample thickness, θ is the slope of the linear portion of the sorption curve before attaining 50% equilibrium and Q_∞ has the same meaning as mol% swelling at maximum level or equilibrium.

The data on diffusivity are listed in table 4. Non-polar solvents; benzene, toluene, xylene and tetrachloromethane seem to exhibit higher diffusivity than polar molecules especially esters; methylacetate and ethylacetate in non-polar PP film. The relatively high D values for other chloro solvents may be explained by the reported high preferential interaction in these solvents [57]. This preferential interaction effect also explains the high diffusivity of tetrachloromethane among the non-polar solvents. For polar solvents,the diffusivity seems to be controlled by the solvent polarity and interaction parameter generally, though for a homologous series of esters an inverse dependence on molar volume of solvent results. Direct relationship between diffusivity and temperature has been reported [72]; increase in treatment temperature has a consequent increase on diffusivity. This report is corroborated by our result since, for any particular solvent the diffusivity increase with increase temperature. High temperature reduces the amorphous chains constraints consequent upon partial melting and leads to an increase in diffusivity.

3.3.2 **SOLUBILITY**

Solubility is defined here as the number of moles of liquid Qt sorbed by 100g of polymer. The data on solubility of different solvents into PP at different temperature are listed in table iv.

Solubility of PP in hydrocarbons is believed to increase with increasing temperature, which means permeation is enhanced since, fluid transport is exponentially dependent on concentration [72]. Our results seen to support this view since for all the solvents studied, the solubility increase with increasing temperature. Chloroform (polar molecule) and benzene (non-polar molecule) exhibiting the largest solubility of all the solvents studied. The high solubility of chloroform (polar molecule) with small molar volume into PP a hydrocarbon polymer can be explained by the reported specific interaction exhibited by PP [57]. However, ethylacetate and benzylchloride exhibited relatively the 'lowest solubility value compared with other solvents. This may be associated with the high dipole moment, large molar volume and interaction constant all together contributing to having low solubility. Comparing the non-polar solvents, Table 4 shows clearly that solubility increases with decrease in molar volume and molecular weight. Thus, the order of increasing solubility found is for non-polar solvent; xylene at all temperatures are benzene > tetrachloromethane > toluene > xylene in the same order as increasing molar volume. Similar results have been reported [72].

3.3.4 **SELECTIVITY**

Selectivity is defined as the ratio of permeability of one solvent p_i to the permeability P_j of the other.

$$Z = {}^{Pi}/_{Pj} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (27)$$

For this work Z calculated employs the use of P_i for non-polar or less polar solvent, while P_j is for the more polar solvent for a non-polar or less polar- polar solvent pair. The data on selectivity are given in table 5. Out of a total of 30 solvent pairs, 13 solvent pairs exhibited a decrease in permeability with increase in temperature, 14 solvent pairs exhibited an increase in permeability with increase in temperature, while 3 solvent showed some irregular dependence on temperature. Table V also reveals that the solvent pairs involving toluene and polar solvent, non-polar solvents and non-polar solvent/benzylchloride pairs generally exhibited increase in permeability trend with increase in temperature. The decrease in permeability trend with increase in temperature can be explained by the inability of film at higher temperature to discriminate over the different molecules at different molar volumes. For the increase in permeability trend with increase in temperature may be accounted for by the reluctance of hydrocarbon polymer to attract polar molecules or complex molecular structure and larger molecular volume of benzyl chloride.

3.4.0 **MODE OF TRANSPORT/SORPTION KINETICS**

Essentially, transport of solvents through polymer films is affected by polymer-polymer structure, cross-linking density, mode of cross-linking, pressure of fillers, penetrant size and treatment temperature [57].

In order, to find the mechanism of transport phenomenon, the dynamic swelling data were fitted into the equation [54, 57];

$$\text{Log } Q_t/Q_\infty = \text{Log}K + \text{Log } t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (28)$$

Where Q_t and Q_∞ are the mole % increase in sorption at time t and equilibrium respectively, K is a constant depending on the structural characteristics of the polymer, in addition to its interaction with the solvent, the magnitude of m denote the transport mode. For fickian transport $n = 0.5$. where $n = 1$, shows relaxation controlled transport. The values of n is between 0.5 and 1.0 suggest an anomalous behaviour of transport. However, values of n can be greater than 1 revealing super relaxation controlled transport.

Figure 11-15 are plots of log Q_t/Q_∞ against log t (s) for the nine different solvents studied and the magnitudes of n and

K are listed in Table 4. The n values range from 0.21 to 1.14: no solvent have the mode of transport fickian while toluene, xylene and methylacetate all at 28°C exhibited the special super relaxation controlled transport. All other solvent uptake processes tended to be anomalous. One in addition reports that n values decrease with increase in temperature. Generally, K values increase with increases in sorption temperature. This implies increase in PP-penetrant interaction with temperature. These results of both n and K values exhibited are in the same trend as those obtained by earlier workers [54, 57].

However, non-polar solvents with the exception of tectrachloromethane have k values larger than those of polar counterparts. These larger values are in agreement with the old empirical principles: "Like dissolves like". The non-polar solvents are expected to have greater interaction with PP a non-polar than the polar solvents would have.

3.5 **ENERGETICS**

The energetics of any thermodynamic system was described by J. Willard Gibbs expressions at constant pressure.

$$\Delta G = \Delta H - T\Delta s \qquad \text{.....................(29)}$$

Where ΔG is the change in the free energy of system, ΔH is the enthalpy change; Δs is the entropy change and T is the kelvin temperature. Enthalpy change ΔH is a measure of total change in the exception of tetrachloromethane, ΔS is negative implying liquid solvent retainment in the polymer structures even after being dried. Table 7 shows that ΔG values increase with increase in molecular weight of the penetrant. Positive value of ΔG showing non spontaneity of the process.

3.6.0 Sorption Studies of Solvent treated PP Film

3.6.1 Sorption /Solvent uptake

The date on mol.% swelling at different time intervals and at different temperatures are presented in table 8 and plots are in figures 20 to 24. In table 8 and figures 20 to 24, It is evident that solvent that solvent -uptake increases with increase in temperature of sorption.

Comparison of the date in table 3, the sorption of untreated PP films and those in table 8; those treated PP films sample data, it is evident that solvent treatment has a significant effect on the sorption characteristic of PP films. For instance the time for attainment of equilibrium for benzene and chloroform remains $V_t = 120^{½}$ but sorption/solvent uptake increases from 0.370% o.378mol.% to o.44mol.% at 28°c for benzene.

While for chloroform sorption/solvent uptake increases from o.486 mol.% to o.592mol.% at 28°c. Similarly, at 40°c and 60°c than of the earlier. This is explained from the extent of transport enhancement increasing with increasing treatment temperatures, under conditions of reduced amorphous chains constraint, prevalent in treated samples, movement of polymer chains segments is facilitated and penetration enhanced. Michaels etal [27] have reported similar result.

Hence,plots of logD, log S and log P separately against $^1/_T$ were used to estimate energies of diffusion E_D, Solubility E_s and permeability E_p. Theses plots are given in figures 28 - 30 and the calculated values of E_D, and E_s and E_p are listed in table 11. The result shows that E_D and E_p are of the order; benzene > chloroform > n-hexane.

Apparently, the gradation might not be unrelated to the general decrease in the interaction parameter and molar volume. However, E_s varies in the order, n-hexane > chloroform > benzene. Increasing molar volumes and interaction parameters χ are responsible for the above trend. Unnikrishnan and Thomas [54] obtained similar result.

3.8.0 **Selectivity**

The definition and method of computation of selectivity Z have been given in section 3.3.4 the data are presented in tables for the toluene treated PP films. The three pairs; benzene/chloroform, benzene/n-hexane and chloroform/n-hexane in comparison with those of untreated films shows general increase in selectivity with increase in temperature, though the increase in Z for the toluene - treated PP films is only marginal. Thus Solvent -treatment of PP films apparently reduces the selectivity to the same solvent pairs.

3.9.0 Mode of transport/sorption Kinetic of treated PP film sample

Mechanism of transport and method of estimation of the parameters n and k have been described in section 3.4.0. figures 25 to 27 are profiles of logs Q_t/Q_w against log t of three solvents.

Magnitudes of n and k are shown in table 9. The n value range from 0.18 to 0.45. No solvent exhibited Fickian behaviour but all exhibited n < 0.5 values decreasing with increase in temperature.

The low values of n obtained may be due to residual solvent in the treated film impending the flow of incoming solvents. The low values of k obtained is explained by the fact that the residual solvent molecules already in contact with the PP tend to reduce further contacts by the in-coming solvent molecules.

3.10.0 Critical dissolution time (C.D.T) [71]

The data for the mean of dissolution time of PP films in hot toluene were recorded as critical dissolution time C.D.T. Percent apparent crystallinity (AC) were also computed for both treated and untreated PP films at respective temperatures as shown in table 14 Tables (14A and 14B) shows CDT of PP films swollen to equilbrum for untreated and treated samples respectively.

Generally, it was observed that CDT and AC increases with increase in temperature for PP films both treated and untreated films, swollen to equilibrium in solvents. Comparison of PP samples treated and untreated shows that the values of CDT and AC obtained for the treated samples seem to be larger than those obtained for untreated samples.

This is as a result of larger size of the crystallite developed by solvent treatment which lead to larger percent apparent crystallinity. It was also observed that solvent with low interaction parameter exhibited high (A C) in view of the fact that larger crystallites were developed.
Johnson and Popoola [71] have shown that heat treatment of polyethylene terephthalate fibres gave rise to larger C D T and A C than solvent treatment. This was explained interms of fewer but larger crystallites produced by heat treatment when compared with solvent treatment. The usefulness of this simple experimental method to monitor changes in the morphology of polymer films is that apparent crystallinity data have also been corroborated with infra-red IR crystallinity.

non-polar solvents, particularly aromatic solvents exhibited higher values of diffusivity, solubility and permeability and for this set of solvents it was evident that the molar volume of the solvent determines the values of these properties since the smaller the molar volume the larger the values of D, S and P, that is tetrachloromethane > benzene > xylene > toluene for non - polar solvents, and for polar solvents benzylchloride > chlorobenzene > ethylacetate > methylacetate.

However, for polar solvents polarity and interaction constant χ play vital role, as the more polar the solvent the more interaction constant χ, and the less these diffusion coefficients. The order of dipole movement for polar solvents is chloroform < chlorobenzene < benzylchloride < methyllcucetate < ethylacetate. It is also apparent that for a homologous series of solvents for example esters, the inverse dependence of these properties on molar volume shows high values of D,S, and P for the chloro-solvents which is probably due to the specific interaction of PP with this family of solvents. The data of permeability for each solvent at different temperature were used to calculate the perm-selectivity Z given by Z = p^i/p_j. The Magnitude Z showed that out of the 30 pairs of penetrants studied 13 pairs showed a decrease, 14 pairs a increase and 3 pairs on irregular behaviour of Z with increase in temperature, the result of which has been explained in terms of the loss of

The activation energies of diffusion E_D solubility E_s, and permeability E_p were calculated from the slope Arrhenius plots of log D, log S and log p separately with reciprocal of absolute temperature $^I/_T$ .Similarly, the entropy ΔS and enthalpy ΔH of solubility (mol) were determined. Log Ks versus reciprocal kelvin temperature $^I/_T$. The shapes of these curves are in agreement with the finding that the mode of transport was the case I diffusivity and case II velocity. The activation energies computed were in all case of solvent positive, varying from 4.461 kJ/mol to 45.595 KJ/mol for E_D, 3.59 KJ/mol to 14.360 for E_s and 9.899 KJ/mol to 57.440 KJ/mol for E_p. The negative sign of entropies for practically all the solvents is an indication that these solvents still remain as liquids in the sorbed state. The positive values of enthalpy of solution implies an endothermic process for solvents transport into PP. The critical dissolution time [CDT] and the apparent crystallinity [AC] developed in PP films at equilibrium liquid sorption an temperature were studied. It was shown that the CDT and AC increase with increasing temperature. This was expected since solvent induced crystallization (SINC) is apparently dependent on the plasticization process which has been expressed as the difference between the solubility parameter of polymer and solvent IΔδI. The low value for CDT and AC for n-hexane compared to other non-polar solvents was dependent on the larger $I\Delta\delta I$ value. Base on the results, from gravimetric sorption studies of solvent in PP films, one may now conclude as follows:-

(1) The Gee 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 by PP increases with increase in sorption temperature. Generally, non-polar solvents have higher values of these properties than polar solvents because of favourable compatibility in these cases. The high values of these properties for chloro-solvents through polar solvents are explained by the preferential constants between PP and this set of liquids. Polar solvents took shorter time to attain saturation level ≈ 60 $(s^{½})$ while non-polar solvents took longer time $\approx 60\text{-}85$ $(s^{½})$.

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

(4) Perm- selectivity for most solvent pairs investigated decreased with increase in temperature.

sorption /solvent uptake increase when comparing treated and untreated PP film.

Also, the equilibrium mol.% swelling of n-hexane has same $\sqrt{t} = 60^{1/2}$. However, weight increase or sorption/solvent uptake increases for treated PP films compared with untreated PP. films [76].

Generally, the above is explained from the increase in permeation rates, subsequent to solvent treatment as a result of changes in sorptive capacity of the polymer. Michael et obtain similar result [27].

3.7.0 **Diffusion Coefficients**

The diffusion Coefficient; diffusivity D, Solubility S, and permeability P, have been defined in section 3.3.1, and methods of calculation were also given. The data on the diffusivity D, Solubility S and permeability P for toluene - treated PP film for the non-hexane, benzene and chloroform at deferent temperatures are given in table 9. In table 9 it is clear that D, S, and P for benzene, chloroform and n-Hexane sorption by toluene-treated PP also increases with increased in sorption temperature. However, comparison of data in table 4 with respect to benzene, chloroform and n-Hexane's data from obtained privately from Abdullahi B.I. 1998 M.Tech for untreated PP film with those in table 8 for the toluene -treated PP films shows that the magnitude of these parameters for the later are greater energy for the process or reaction and the TΔs term is a measure of change which results from the rearrangement of atoms during the reaction or process. Therefore, ΔG has its rudimentary meaning as energy available to do work. Experiments have shown that reaction proceed spontaneously in the direction for which the free energy change is negative [74].

The amount of penetrant sorbed by a given mass of polymer, the equilibrium sorption constant Ks can be calculated as follows [54].

$$K_s = \frac{\text{No of mol of penetrant sorbed}}{\text{Unit mass of the polymer}} \quad \ldots\ldots\ldots\ldots (30)$$

From the values of K_s, the entropy Δs and enthalpy ΔH of sorption can be estimated using van't Hoff's equation [54];

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots (31)$$

Where values of ΔH and Δs are enthalpy change and entropy change of the system respectively. R is gas constant and T is absolute temperature scales.

The plot of logs K_s against $^1/_T$ is given in figure 19. The ΔH and Δ_s values are given in table 7. The ΔH values follow the order toluene < xylene < benzene < Tetrachloromethane for non-polar solvents while for polar solvents methylacetate < ethylacetate < chlorobenezene < benzlchloride. In all cases with

(5) The activation energies of diffusion, solubility and permeability are all positive and the profiles are in agreement with the mode of diffusion into PP as a combination of case I diffusion and case II velocity in the same way as the van't Hoff's plots for enthalpy of solution.

(6). The negative values of the ΔS and positive values of ΔH are indications that polymer matrix still retains solvent molecules and that enthalpy of solution is endothermic respectively.

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

(8) CDT and AC increased with increase in temperature; being low for non-polar solvent for example benzene, xylene, toluene, but high for polar solvent eg chloroform and benzlchloride.

(9) The sorption/solvent uptake gas a significant effect on the sorption characteristics of PP films.

(10) Sorption in to toluene-treated PP also increases with increase in sorption temperature hence the magnitude of diffusion coefficients; diffusivity, solubility and permeability are greater for the treated compared to untreated PP sample.

(11) There is general increase in selectivity with increase in sorption temperature.

(12) n values decreases with increase in temperature while K increases with increase in sorption temperature

(13) Values of CDT and AC obtained for the treated sample seem to be larger than those obtained for untreated PP samples.

Finally, in view of the wide application of PP polymer, much research is needed to further corroborate the present ones, particularly on effect of surface characteristics and degradation. Hence, the use of ultraviolet (UV), Infrared (IR), x-ray diffraction crystallography, Thermal gravimetry analysis (TGA), Differential scanning calorimetry (DSC), Osmometry and viscometry methods are suggested for study.

REFERENCES

1. Charles, A.C; Hancock, E.G (Ed): Exxon Research and engineering company, Encyclopedia of science and Technology 10 647 Mc-Graw Hill, Floriham park NJ (1973).
2. Tooley, P: Chemistry in industry," High polymers" 1st ed 36, John murray Albemarle street London (1977).
3. Natta, G; Corradini, P and Cessari,M: Atti, Acad, Nazlincei, classe sci fis, Mat Nat 21 , 365 (1956).
4. Achhammer, B.G: report in IUPAC international symp of "Aging of plastic" Dussel dozf copy 370-374, 378-379 (1959).
5. Melchose, J: A.I.E, prod Res I.D 1, 232 (1962).
6. Curson, A.D: " Distribution of additives in polymers by UV Microscopy " unpublished presentation "Micro 72" Oxford (1972).
7. Tergue, F.H and Blumberg, M: Appl polym symp in Ed Musa, R. Kamal, weatheribility of material Wiley Newyork 4, 175 (1965).
8. Crank, J: The mathematics of Diffusion claredon press, Oxford (1976).

9 Frank, H.P and Lehner, H: J. Polym sci. 31, 193 (1970).

10. Hsu,C.C; Geil, P.H; Miyaji, H and Asai, K: J. polym. sci. part B. 24, 1009 (1986).

11. Hsu, C.C; Geil, P.H; Miyaji, H and Asai, K: J. polym. sci. part B.24, 2379 (1986).

12. Morris, D.R: J. Macromol. sci. phy. B 1, 53 (1969).

13. Miller,R.L: polymer 1 , 135 (1960).

14. Natta,G: S.P.E.J. 373 (1959).

15. Boye, C.A.Jr; Watson, M.T;and patton, H.W: J.polym. sci. 39, 534 (1959).

16. Hoseman, R: Acta. crysta 4 , 520 (1951)

17. Sheldon, R.P: polmer 3 , 27 (1962).

18. Moore, W.R and sheldon, R.P: polymer 2 , 315 (1961).

19. Cottan, L and sheldon, R.P. Adr. polym. sci. Technol 26, 65 (1966).

20. Desai, A.D and Wilkes, G.C:J. polym.sci. sym 46, 291 (1974).

21. De Gemmes, P.G: Scaling concepts in polymer physics, cornel thiaca New york (1979).

22. Yasuda, H and Lamaze, C:J. Macromal. sci. phys,135, 111 (1971).

23. Valko, E.I and shawali, A.S: Absorption of organic liquids by polypropylene ACS symbosium of " interaction of fibre systems with organic liquid" Chicago illinous september 14 (1970).

24. Crenk, J: The Mahtematics of diffusion oxford univ press, London (1956).

37. Koros, W.J and Hellums, M.W: Encyclopedia of polymer science and Engineering 2nd ed. Supplement Volume, Wiley, New York 724 (1989).

38. Arizzi, S and Suter, U.W: polym, Matter sci. Eng. prepr. 61, 481 (1989).

39. Reinhart, C.T; Korsmeyer, R.W and Peppas: Int.J. Pharm. Tech. prod. Mfr 2 (2) 9 (1981).

40. Mark,J.E; Eisenberg, A; Graesseley, W.W; Mandelkern, L; and Koening, J.L: "Physical properties of polymers," American chemical society, Washington DC, (1984).

41. Eyring, H: J. chem. phys.4, 283 (1936).

42. Veith, W.R; Howell, J.M and Hseieh , J.H: J.Membr. sci. 1,177 (1976).

43. Roggers, C.E: " Physics and chemistry of the organic solids states" D. Fox M.M. Label and A. Weissberger (eds); Interscience Publishers New York 11 , 509 (1965).

44. Mauze, G. R. and Stern, S.A: J. Member. sci. 12,51 (1982).

45. Mauze, G.R. and Stern, S.A:J. Member. sci. 18,99 (1984).

46. Mauze, G.R. and Stern, S.A:J. polym. Eng. sci, 23, 548 (1983).

47. Zhou, S and Stern, S.A: J. polym. sci, part B. polym. phys, 27, 205 (1989).

48. Cohen, M.H and Turnbull, D: J. chem. phys. 31, 1164 (1959).

61. Flory, P.J: " principles of polymer chemistry" cornell University press, Hhaca (1953).

62. Treloar, "The physics of Rubber Elasticity", Clarendon press oxford (1975).

63. Mark, J. E: Rubber chem. Technol 55, 591 (1994).

64. Grulke, E.A: Polymer Handbook, 2nd Brand up, Jand Immergent, E.H eds Interscience, New York Vii 521 (1975).

65. Scoll, R.L and Magat, E:J. polym. sci. 4, 555 (1949).

66. Schneier, B: J. Appl. polym.sci 16, 2343 (1972).

67. Krewinghaus, A.B: ph.D, Thesis massachussets Institute of Technology, Cambridge, Massachssets (1966).

68. Keith, H. O. and Radden, F. J. Jr. J. Appl. phys. 35, 1270, 1280. 1286 (164).

69. Park, G. S.: Trans Faraday Soc. 48, 11 (1952).

70. Weiighmann, h. g. AND Rebruck, A. S.: Text. Res. J. 165 (1974.

71. Johnson, A. and Popoola, A. V.: J. Appl. Polym. Sci. 43, 2703 (1991).

72. Gee, G.: Trans, Faraday Soc., 38 269 (1942).

73. Robert, C.W (ed): Handbook of chemistry and physics, CRC press, Inc. Boca Raton Florida (1987).

74. Heys, H.L: Physical chemistry 3rd ed, Geoge G. Harrap & co Ltd London 344 (1966).

TABLE 1

Comparison of dipole moment μ, molar volume Vs, molar Mass M, solubility parameters δs, density ρ_S, and interaction parameter χ at 28°C of different solvents.

Liquids	$\mu^{(a)}$ (D)	$\delta_S^{(b)}$ mpa$^{\frac{1}{2}}$	$V_S^{(b)}$(c m^{3}mol-1	M^s glmd	$\rho_S^{(a)}$ (gkm^{-3})	χ $^{(c)}$
Hexane	0.0	14.9	131.0	86	0.659	0.876
Benzene	0.0	18.6	89.4	78	0.874	0.342
Toluene	1.3	18.2	106.8	92	0.867	0.357
Xylene	1.3	18.0	121.2	106	0.86	0.374
Methyl acetate	1.72	18.7	79.7	74	0.932	0.340
Ethyl acetate	1.78	18.1	98.5	88	0.902	0.361
Tetrachloromethane	0.0	17.8	97.1	154	1.594	0.382
chloro Bezene	1.69	19.6	102.1	112.5	1.106	0.369
benzyl chloride	1.70	20.3	115	126.5	1.1002	0.416
chloroform	1.01	19.0	80.7	119.5	1.492	0.341

(a) From Ref 75, (b) From Ref 75, (c) Calculation χ δ_p = 18.8 mPa$^{\frac{1}{2}}$

TABLE [2]

Comparison of Swelling Quotient at 10 minutes Q_t and at Maximum sorption Q_∞ and solubility parameter of the solvants used.

Liquids	Q_t (cm^3.g^{-1})	Q_∞ (cm^3 g^{-1})	δ_s (mPa$^{\frac{1}{2}}$)	$\left[Q_{-1} \text{ In } \frac{Q_\infty}{Q_t}\right]^{1/2}$
Benzene	0.208	0.352	18.6	1.59
Toluene	0.190	0.331	18.2	1.71
Xylene	0.172	0.35	18.0	2.07
Methylacetate	0.083	0.221	18.7	3.43
Ethylacetate	0.051	0.091	18.1	3.37
Tetrachloro	0.152	0.272	17.7	1.96
Methanechloro	0.130	0.316	19.6	4.32
BenzeneBenzyl Chloride	0.092	0.170	20.3	4.48
chloroform	0.182	0.415	19.0	2.13

75. Tager, A.A and Kolmakova, L.K: polym. sci (USSR) 22, 533 (1981).

76. Billmeyer, F.W.Jr: "Text book of polymer science", 2nd ed 371. A wiley- Interscience, New York (1962).

77. Hayers, R.A: J. Appl. polym sci. 5,318 (1961).

49. Kreituss, A and Frish, H.L: J. polym. sci, polym. phys. Ed 19, 889 (1989).

50. Fujita, H: Fortschr. Hochpolym. Fors 3 ,1 (1961).

51. Vrentas, J.S and Duba, J. L: AICHE> J 25,1 (1979).

52. Peppas, N.A and Reinhart, C.J: J. Member, sci. 15, 275 (1983).

53. Korsmever, R.W; meer wall, E.V and Peppas, N.A: J. Polym. sci, polym. phys. Ed 24, 409 (1986).

54. UnniKrishnan, G and Thomas, S: J. polym. sci. B. polym. phys. 35, 725 (1997).

55. Me. Hattie, J. S; koros, W. J and paul, D.R: polymer 33, 1701 (1992).

56. Schutt, K.A and Paul, D.R: J. Polym. sci, part B. polym phys, 34, 2805 (1996).

57. Liao, D.C; chern, Y.C; Han, J; Hsieh, K.H: Department of Chemical Engineering Nat. Inst. of Agric and Technology, 1-Lan Taiwan (1997).

58. Okamoto, K; Tanihara, N; Watanabe, H; Tanak, K; kita, H; Nakamura, A; Kusuki, Y and Nakagaw, K: J. Polym. sci. part B: polym phys 30, 1223 (1992).

59. Mark, J.E and Erman, B: Rubberlike Elasticity, a molecular primer, Wiley- NNew York (1988).

60. Hoy, K.L: J. paint. Technol 42, 76 (1970).

25. Michaels, A.S and Brixler, H.J: J polym.sci. 50, 393 (1961).

26. Hausslein, R.W: Ph.D, Thesis Massachuessetts institute of Technology cambridge massachuessetts (1964).

27. Alan, S; Michaels, W. V; Allans, H and Alealary Alealary, H. M:J Appl. Polym. sci. 13 , 577 (1969).

28. Li, N. N; Long , R.B and Henley, E:J. ind. chem.57, 18 (1965).

29. De phillipi, R.P: Sc D . Thesis Massachuessetts institute of Technology, Cambridge, Massachuessetts (1962).

30. Horas, J.A and Rizzoto, M.G: J. polym. sci part B polym. phys. Ed. 27 , 175 (1989).

31. Sperling, L.H : "introduction to physical polymer science" 2nd ed. 66, 146, 334, A Wiley- interscience, New york.

32. Hildebrand, J and scott, R: The solubility of Non-electrolyte, 3rd ed, Reinhold New York (1949).

33. Cambellick, W.A: Encyclopedia of polymer science and Engineering, Vol 2 Wiley, New York 176 (1985).

34. Meares, P:" polymers, structure and bulk properties", Van Nostrand, New York chap 12, (1965).

35. Amerongen, G.V: J. Appl. phys. 17, 972 (1946).

36. Amerongen, G.V: J. polym. sci. 5, 307 (1950).

TABLE 3

Comparison of Weight increase Δw, and mole of Liquids Q_t sorbed by Polypropylene (PP) at Different Times t and Different Temperature T In Different Solvents.

28°C Benzene			40°C		60°C		28°C Toluene		40°C		60°C	
t(min)	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt
2	0.0091	0.117	0.0108	0.138	0.0119	0.153	0.0054	0.055	0.0057	0.065	0.0133	0.148
5	0.0132	0.169	0.0156	0.200	0.018	0.231	0.0071	0.084	0.0116	0.128	0.0114	0.201
7	0.0147	0.188	0.0180	0.231	0.0214	0.274	0.0127	0.0132	0.0163	0.182	0.0229	0.271
10	0.0168	0.215	0.0199	0.255	0.0246	0.315	0.0164	0.184	0.0192	0.206	0.0249	0.288
15	0.0195	0.250	0.0232	0.297	0.0261	0.335	0.0192	0.217	0.0202	0.219	0.0258	0.295
20	0.0216	0.277	0.0258	0.331	0.0275	0.353	0.0204	0.230	0.0214	0.228	0.0275	0.308
30	0.0238	0.305	0.0283	0.363	0.0310	0.397	0.0242	0.259	0.0272	0.299	0.0275	0.318
60	0.0259	0.332	0.0331	0.424	0.0377	0.483	0.0290	0.292	0.0297	0.324	0.078	0.342
120	0.0292	0.374	0.0341	0.440	0.0394	0.505	0.0308	0.312	0.0302	0.330	0.0301	0.352
180	0.0298	0.382	0.0371	0.476	0.0394	0.505	0.0286	0.312	0.0304	0.331	0.0296	0.351
240	0.0294	0.377	0.0370	0.476	0.0395	0.506	0.0282	0.312	0.0301	0.332	0.0293	0.350

TABLE 3

28°C Xylene			40°C		60°C		28°C Chloroform		40°C		60°C	
t(min)	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt
2	0.0081	0.076	0.0100	0.094	0.0113	0.107	0.0138	0.115	0.0164	0.137	0.0196	0.164
5	0.0099	0.093	0.0126	0.119	0.0138	0.130	0.0201	0.168	0.0233	0.195	0.0245	0.205
7	0.0101	0.095	0.0150	0.142	0.0168	0.158	0.0245	0.205	0.0263	0.220	0.0294	0.246
10	0.0141	0.133	0.0173	0.163	0.0201	0.190	0.0275	0.230	0.0296	0.248	0.0305	0.255
15	0.0183	0.173	0.0198	0.187	0.0228	0.215	0.0342	0.286	0.0346	0.290	0.0405	0.339
20	0.0212	0.200	0.0244	0.230	0.0270	0.255	0.0389	0.326	0.0423	0.354	0.0434	0.363
30	0.0238	0.225	0.0297	0.280	0.0335	0.316	0.0558	0.467	0.0555	0.464	0.0558	0.467
60	0.0264	0.249	0.0336	0.317	0.0368	0.347	0.0575	0.481	0.0636	0.532	0.0612	0.512
120	0.0300	0.283	0.0360	0.340	0.0377	0.356	0.0561	0.468	0.0675	0.565	0.0705	0.590
180	0.0305	0.288	0.0361	0.341	0.0370	0.349	0.0596	0.499	0.0663	0.555	0.0704	0.589
240	0.0306	0.289	0.0362	0.342	0.0377	0.356	0.0594	0.497	0.0665	0.556	0.0699	0.585

28°C Tetrachloro Methane			40°C		60°C		28°C Chloro-benzene		40°C		60°C	
t(min)	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt
2	0.0094	0.061	0.0200	0.1299	0.0443	0.288	0.0078	0.069	0.0095	0.084	0.0258	0.210
5	0.0150	0.091	0.0269	0.1747	0.0514	0.334	0.0087	0.077	0.0109	0.097	0.0281	0.250
7	0.0180	0.117	0.0355	0.2305	0.0542	0.352	0.0092	0.082	0.0162	0.144	0.0321	0.285
10	0.0219	0.173	0.0377	0.2448	0.0594	0.386	0.0134	0.119	0.0189	0.168	0.0341	0.303
15	0.0281	0.182	0.0407	0.2643	0.0664	0.431	0.0178	0.158	0.0221	0.198	0.0393	0.349
20	0.0341	0.221	0.0432	0.2805	0.0686	0.445	0.0219	0.195	0.0249	0.221	0.0420	0.373
30	0.0379	0.246	0.0468	0.3039	0.0698	0.453	0.0252	0.224	0.0278	0.247	0.0473	0.420
60	0.0405	0.263	0.0513	0.3331	0.0755	0.470	0.0319	0.284	0.0354	0.315	0.0511	0.454
120	0.0412	0.266	0.0557	0.3617	0.0734	0.477	0.0322	0.286	0.0350	0.311	0.0505	0.449
180	0.0412	0.266	0.0539	0.3500	0.0731	0.475	0.0322	0.286	0.0358	0.318	0.0513	0.456
240	0.0412	0.266	0.0539	0.3500	0.0731	0.475						

28°C Methyl- Acetate			40°C		60°C		28°C Ethyl- acetate		40°C		60°C	
t(min)	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt
2	0.0019	0.012	0.0025	0.034	0.0043	0.058	0.0031	0.013	0.0019	0.0216	0.0048	0.055
5	0.0039	0.053	0.0061	0.082	0.0079	0.107	0.0028	0.032	0.0038	0.0432	0.0054	0.060
7	0.0052	0.070	0.0076	0.103	0.0099	0.134	0.0037	0.420	0.0043	0.0489	0.0063	0.072
10	0.0070	0.095	0.0095	0.128	0.0129	0.174	0.0043	0.049	0.0054	0.0614	0.0071	0.081
15	0.0108	0.146	0.0131	0.177	0.0162	0.219	0.0051	0.580	0.0061	0.0693	0.0079	0.090
20	0.0134	0.181	0.0158	0.214	0.0181	0.245	0.0063	0.072	0.0068	0.077	0.0091	0.103
30	0.0162	0.219	0.0194	0.262	0.0211	0.285	0.0073	0.083	0.0078	0.089	0.0094	0.107
60	0.0200	0.270	0.0216	0.292	0.0256	0.346	0.0075	0.085	0.0086	0.098	0.0093	0.106
120	0.0201	0.272	0.0223	0.301	0.0244	0.330	0.0079	0.088	0.0089	0.0101	0.0099	0.113
180	0.0202	0.273	0.0232	0.314	0.0246	0.332	0.0078	0.089	0.0088	0.0100	0.0104	0.118

28°C Benzyl- Chloride			40°C		60°C	
t(min)	Δw	Qt	Δw	Qt	Δw	Qt
2	0.0049	0.388	0.0068	0.058	0.0068	0.538
5	0.0077	0.609	0.0096	0.759	0.0108	0.854
7	0.0084	0.664	0.0108	0.854	0.0122	0.964
10	0.0093	0.735	0.0129	0.1020	0.0148	0.1170
15	0.0115	0.909	0.0150	0.1186	0.0171	0.1352
20	0.0137	0.1083	0.0182	0.1439	0.0200	0.1581
30	0.0155	0.1225	0.0213	0.1684	0.0242	0.1913
60	0.0173	0.270	0.0216	0.292	0.0294	0.2324
120	0.0201	0.1368	0.0256	0.2024	0.0294	0.2324
180	0.0171	0.1352	0.0260	0.2055	0.0285	0.2253
240	0.0174	0.1355	0.0259	0.2055	0.0285	0.2253

TABLE 4

Comparison of Diffusivity D, Solubility S, Permeability P, and n and K of equation 28 at different liquid sorption Temperature T.

Liquid	T °C	$Dx10^{-8}$ ($cm^2 S^{-1}$)	S (mol%)	$Px10^{-8}$ ($molcm^2 S^{-1}$)	n	K
Benzene	28	13.20	0.378	5.00	0.75	0.05
	40	14.20	0.476	6.71	0.72	0.055
	60	16.10	0.506	8.15	0.62	0.072
Toluene	28	3.10	0.312	1.00	1.10	0.013
	40	6.20	0.331	2.05	0.76	0.050
	60	31.50	0.367	11.56	0.70	0.068
Xylene	28	5.70	0.287	1.64	1.14	0.006
	40	8.10	0.341	2.73	0.92	0.025
	60	9.80	0.352	3.45	0.83	0.035
Methyl acetate	28	1.30	0.272	0.40	1.13	0.0006
	40	1.90	0.302	0.60	0.83	0.0033
	60	4.50	0.336	1.50	0.68	0.0081
Ethyl acetate	28	3.70	0.086	0.30	0.88	0.0048
	40	7.60	0.100	0.80	0.68	0.0100
	60	18.40	0.112	2.10	0.40	0.1072
Tetra chloro Methane	28	8.10	0.266	2.10	0.64	0.0032
	40	22.40	0.348	7.80	0.40	0.0457
	60	55.20	0.481	26.5	0.23	0.2138

Chloro	28	4.70	0.284	1.30	0.54	0.0110
benzene	40	6.80	0.315	2.20	0.40	0.0457
	60	25.00	0.453	11.3	0.21	0.1584
Benzyl	28	14.00	0.136	1.90	0.38	0.038
chloride	40	11.30	0.204	2.30	0.40	0.0437
	60	12.80	0.230	3.00	0.48	0.0490
Chloroform	28	7.00	0.518	3.60	0.45	0.027
	40	9.90	0.567	5.60	0.37	0.041
	60	12.10	0.592	7.20	0.30	0.069

TABLE 5

Selectivity Z: P_i/P_j of PP films at different temperature.

Penetraint pairs	Temperature T °C 28	40	60	Trend
Bz/MAC	10.20	7.40	3.60	d
Bz/EtAC	3.60	1.90	0.90	d
Bz/ClBz	2.80	2.10	0.60	d
Bz/BnzCl	0.90	1.20	1.30	i
TOL/MAC	2.40	3.30	7.00	i
TOL/EtAC	0.80	0.80	1.70	i
TOL/ClBz	0.70	0.90	1.30	i
TOL/BnzCl	0.20	0.50	2.50	i
XYL/MAC	4.40	4.20	2.20	d
XYL/EtAC	1.50	1.10	0.50	d
XYL/ClBz	1.20	1.20	0.20	d
XYL/BnzCl	0.40	0.70	0.80	i
Bz/TOL	4.30	2.30	0.50	d
Bz/XYL	2.30	1.80	1.60	d
Bz/Tet	1.60	0.60	0.30	d
TOL/XYL	0.50	0.80	3.20	i
TOL/Tet	0.40	0.30	0.60	*
MAC/EtAC	0.40	0.30	0.20	d
ClBz/BnzCl	0.30	0.60	2.00	i
Tet/ClBz	1.70	3.30	2.20	*
Tet/BnzCl	0.60	2.00	4.30	i

BnzCl/ClBz	3.0	1.70	0.50	d
Bz/Cl	1.90	1.40	1.30	d
TOL/Cl	0.40	0.60	2.60	i
XYL/Cl	0.80	0.82	0.81	*
Tet/Cl	1.20	2.20	4.60	i
MAC/Cl	0.20	0.20	0.40	i
EtAC/Cl	0.50	0.80	1.50	i
ClBz/Cl	0.70	0.70	2.10	i
BnzCl/Cl	2.00	1.10	1.10	d

Bz = benzene, Tol= Toluene, Xyl =Xylene, MAC = Methylacetate, EtAC =Ethylacetate, Tet =Tetrachloromethane, Cl= Chloroform, ClBz = Chlorobenzene, BnzCl = Benzylchloride, d = decrease, i = increase, * = Irregular.

TABLE 6

Comparison of Activation energies of Diffusion E_D, Solubility E_s and permeability E_p for liquid sorption into PP films.

Liquid	E_D (KJ/mol)	E_s (KJ/mol)	E_p (KJ/mol)
Benzene	9.574	6.836	16.505
Toluene	35.271	12.580	39.654
Xylene	4.461	5.744	9.899
Methylacetate	32.32	5.802	24.890
Ethylacetate	41.28	7.774	36.380
Tetrachloromethane	38.294	14.634	49.412
Chloroform	15.318	3.590	19.417
Chlorobenzene	45.595	11.967	57.440
Benzylchloride	9.574	12.771	11.967

TABLE 7

Entropy ΔS, Enthalpy ΔH and free energy of sorption into polyprolene film at 28°C.

Liquid	ΔS (J/mol/K)	ΔH (KJ/mol)	ΔG (KJ/mol)
Benzene	-24.9	11.488	18.987
Toluene	-32.2	4.188	13.885
Xylene	-28.7	5.319	13.962
Methylacetate	-32.2	5.984	15.681
Ethylacetate	-36.8	6.582	17.664
Tetrachloromethane	-22.0	14.959	21.584
Chlorobenzene	-14.9	14.959	19.446
Benzylchloride	-9.6	17.95	20.814
Chloroform	-31.8	-2.90	13.167

TABLE 8

Comparison of weight increase Δw and mole of liquids Q_t sorbed by PP at different times (t) and different temperature T, in different solvents.

28°C Benzene			40°C		60°C		Chloroform 28°C		40°C		60°C	
t(min)	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt	Δw	Qt
2	0.0057	0.176	0.0089	0.228	0.0108	0.277	0.0098	0.164	0.0162	0.271	0.0194	0.325
5	0.0073	0.187	0.0104	0.267	0.0124	0.318	0.0159	0.266	0.0234	0.292	0.0243	0.407
7	0.0089	0.207	0.0111	0.285	0.0146	0.374	0.0172	0.0288	0.0223	0.373	0.02453	0.473
10	0.0099	0.254	0.0117	0.300	0.0156	0.408	0.0194	0.325	0.0234	0.392	0.0274	0.459
15	0.0118	0.303	0.0145	0.372	0.0174	0.446	0.0229	0.383	0.0257	0.430	0.0294	0.492
20	0.0131	0.336	0.0151	0.387	0.0177	0.454	0.0243	0.407	0.0256	0.429	0.0332	0.556
30	0.0139	0.356	0.0161	0.428	0.0191	0.490	0.0275	0.460	0.0306	0.512	0.0369	0.618
60	0.0152	0.390	0.0201	0.515	0.0210	0.538	0.0298	0.499	0.0358	0.599	0.0398	0.651
120	0.0172	0.441	0.0209	0.536	0.0212	0.544	0.0345	0.577	0.0373	0.624	0.0447	0.748
180	0.0171	0.439	0.0208	0.533	0.0221	0.567	0.0354	0.592	0.0384	0.643	0.0447	0.748
240	0.0171	0.439	0.0208	0.533	0.0221	0.567	0.0354	0.592	0.0384	0.643	0.0447	0.748

28°C Hexane			40°C		60°C	
t(min)	Δw	Qt	Δw	Qt	Δw	Qt
2	0.0035	0.082	0.0048	0.112	0.0058	0.121
5	0.0057	0.132	0.0067	0.156	0.0068	0.158
7	0.0062	0.144	0.0070	0.162	0.0074	0.172
10	0.0065	0.152	0.0078	0.182	0.0084	0.195
15	0.0075	0.174	0.0084	0.190	0.0090	0.216
20	0.0078	0.182	0.0094	0.218	0.0096	0.219
30	0.0079	0.184	0.0099	0.230	0.0100	0.240
60	0.0083	0.194	0.0107	0.248	0.0124	0.288
120	0.0089	0.206	0.0110	0.256	0.0113	0.270
180	0.0088	0.204	0.0104	0.236	0.0114	0.271

TABLE 9

Comparison of Diffusivity D, Solubility S, Permeability P and of n and K in equation (28) for solvent- treated PP films at different temperature: T,

Liquids	(T°C)	Dx^{-9} (cm^2s^{-1})	S (mol%)	$Px10^{-8}$ (mol% cm^2s^{-1}	n	K
Benzene	28	13.9	0.44	6.1	0.32	0.0437
	40	29.6	0.534	15.8	0.18	0.1380
	60	50.3	0.567	28.5	0.29	0.1122
Chloroform	28	13.3	0.592	7.9	0.44	0.0151
	40	26.0	0.642	16.7	0.30	0.0550
	60	36.9	0.748	27.6	0.22	0.1202
n-Hexane	28	22.3	0.205	4.6	0.45	0.0794
	40	29.4	0.247	7.3	0.30	0.0955
	60	32.1	0.276	8.9	0.29	0.1000

TABLE .10

Comperrison of selectivity $Z = P_i/p_j$ for solvent-Treated PP films at different Temperatures.

Perietraint Pairs	28°	40°	60°C	Trend
Bz/Ch	0.77	0.95	1.03	¿
Bz/Hex	1.33	2.16	3.20	¿
Ch/Hex	1.72	2.29	3.10	¿

B_z = benzene, He x = n - hexane, ch = chloroform.

TABLE .11

Comparison of Activation energy of Diffusion E_D, solubility E_s, permeability E_p for solvent treated PP film at 28°C.

Liquids	E_D ($KJmol^{-1}$)	E_s ($KJmol^{-1}$)	E_p ($KJmol^{-1}$)
Benzene	35.103	6.382	40.149
Chloroform	29.917	6.103	32.909
n-Hexane	9.574	7.659	17.950

TABLE 12

Entropy Δs, Enthalpy ΔH and Free energy ΔG of sorption into solvent treated PP film at 28°C.

Liquid	ΔS (Jmol^{-1} R^{-1})	ΔH (KJmol^{-1})	ΔG (KJmol^{-1})
Benzene	-0.957	6.382	6.670
Chloroform	-2.872	6.103	6.968
n-Hexane	6.702	7.659	9.677

TABLE 13

Comparison of permeability Ratio for the same solvent in treated P^t and untreated p^0PP films at Different temperatures.

P^t/P^0 at temperature (°C)

Liquid	28	40	60	Trend
Benzene	1.22	2.35	3.50	¿
Chloroform	2.19	2.98	3.83	¿
n - Hezene	5.90	3.42	1.25	d.

TABLE 14

Comparison of Critical dissolution time (CDT) and percent Apparent Crystallinity (AC) for some solvent used at different temperature for PP untreated Table (A) and treated Table (B).

Note: CDT control = 12.0s.

Table 14A

Liquid	Temperature °C	CDT s	AC
Chloroform	28	16.2	26.0
	40	18.0	33.0
	60	20.2	40.6
Benzene	28	14.0	14.3
	40	19.0	36.8
	60	20.4	41.2
Toluene	28	14.2	15.5
	40	15.0	20.0
	60	17.0	29.4
Xylene	28	14.5	17.2
	40	16.0	25.0
	60	18.0	33.0
Methylacetate	28	14.2	15.5
	40	19.0	36.8
	60	21.2	43.4
Ethylacetate	28	18.5	35.1
	40	20.5	41.5
	60	21.0	42.9

Tetrachloromethane	28	15.0	20.0
	40	16.2	26.0
	60	19.5	38.5
Chlorobenzene	28	16.5	27.3
	40	18.0	33.0
	60	22.2	46.0
Benzylchloride	28	16.5	27.3
	40	19.2	37.5
	60	23.0	47.8

Table 14B

Benzene	28	15.5	22.6
	40	20.2	40.6
	60	22.5	46.7
Chloroform	28	17.5	31.4
	40	19.2	37.5
	60	22.2	46.0
n-Hexane	28	13.0	7.70
	40	17.0	29.4
	60	20.8	42.3

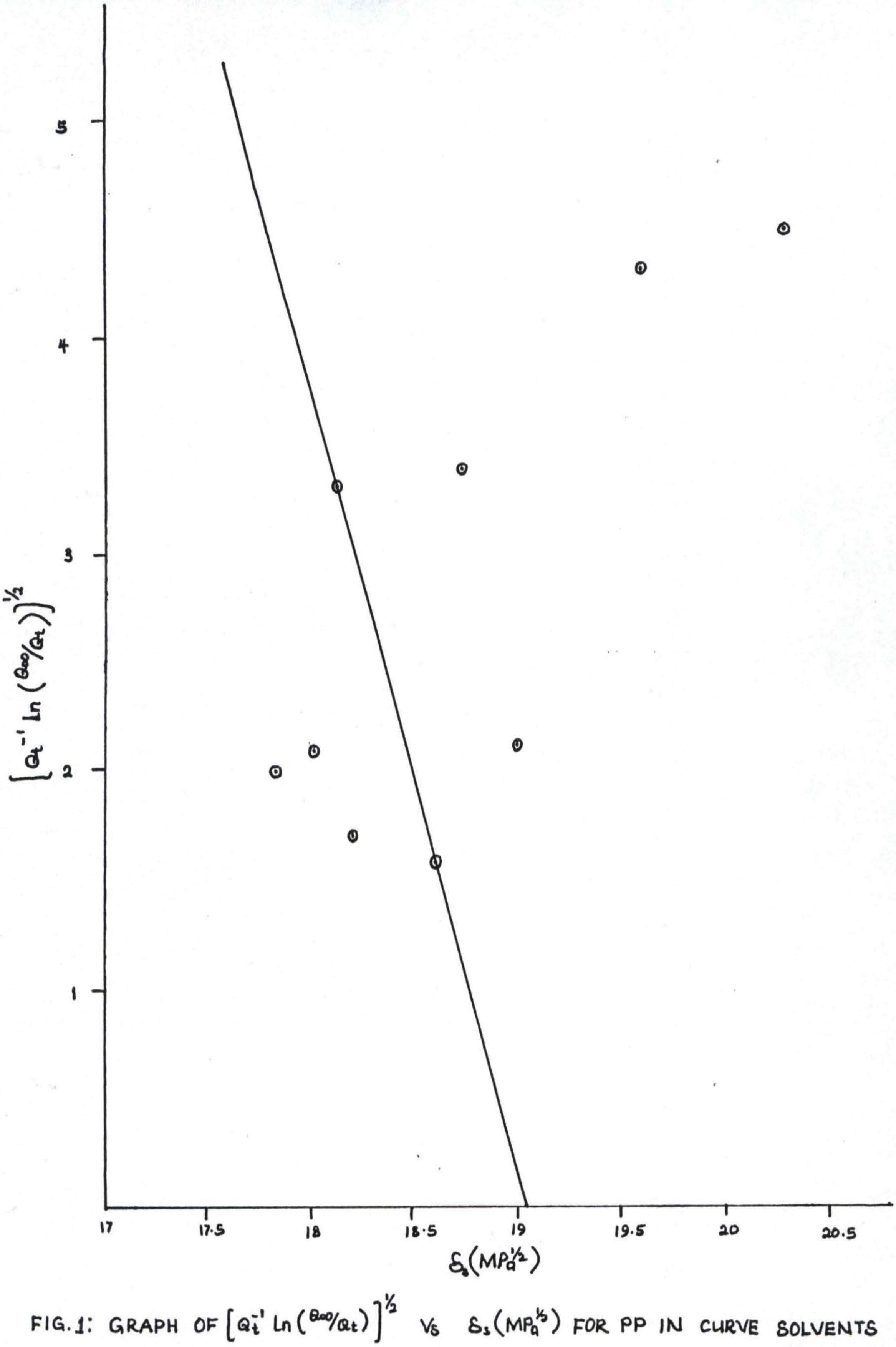


FIG.1: GRAPH OF $\left[Q_t^{-1}\ln\left(Q_\infty/Q_t\right)\right]^{1/2}$ Vs $\delta_s(MPa^{1/2})$ FOR PP IN CURVE SOLVENTS

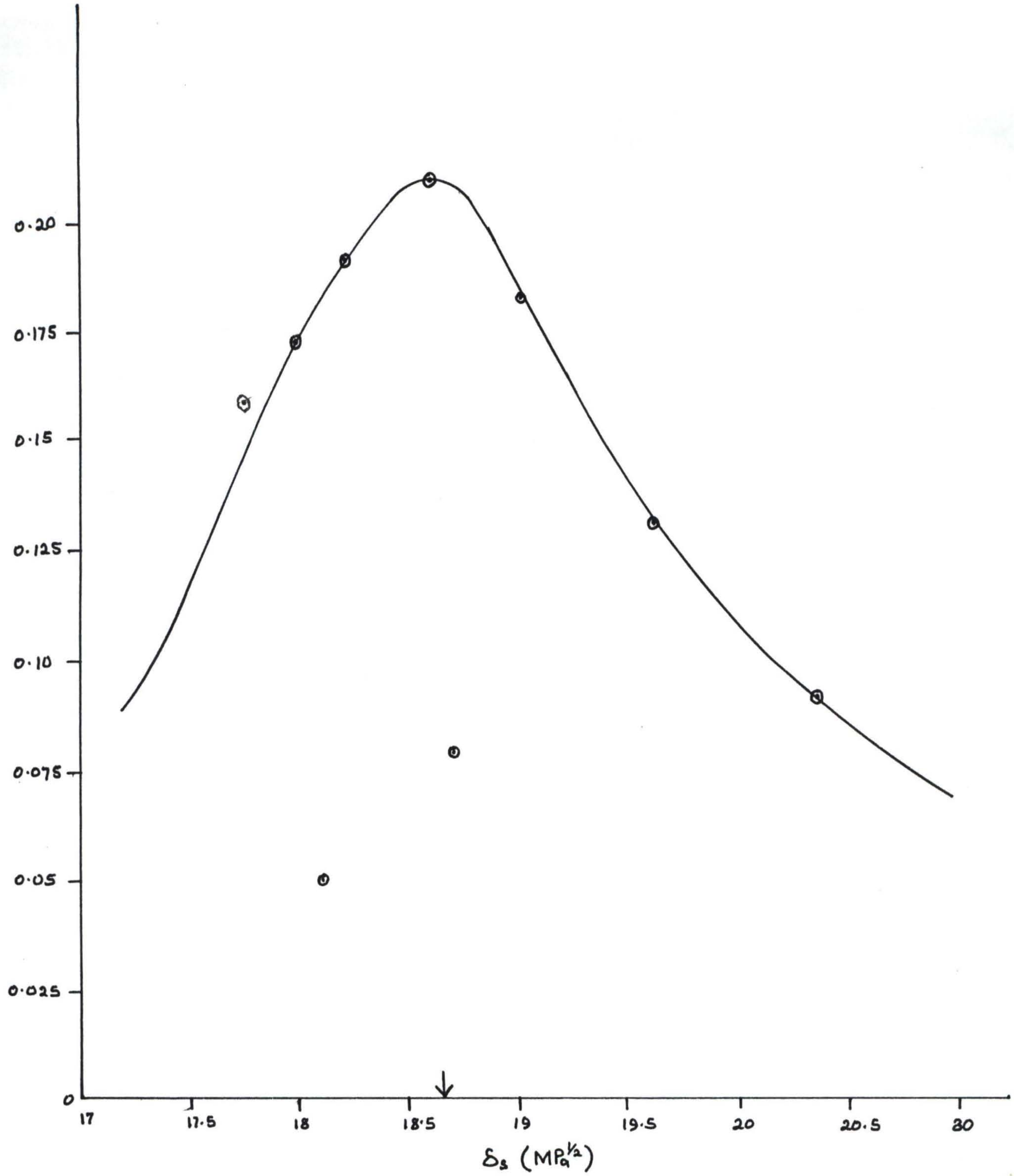


FIG. 2: GRAPH OF Qt AT 10 Min Vs δ (MPa½) FOR PP IN NINE SOLVENTS

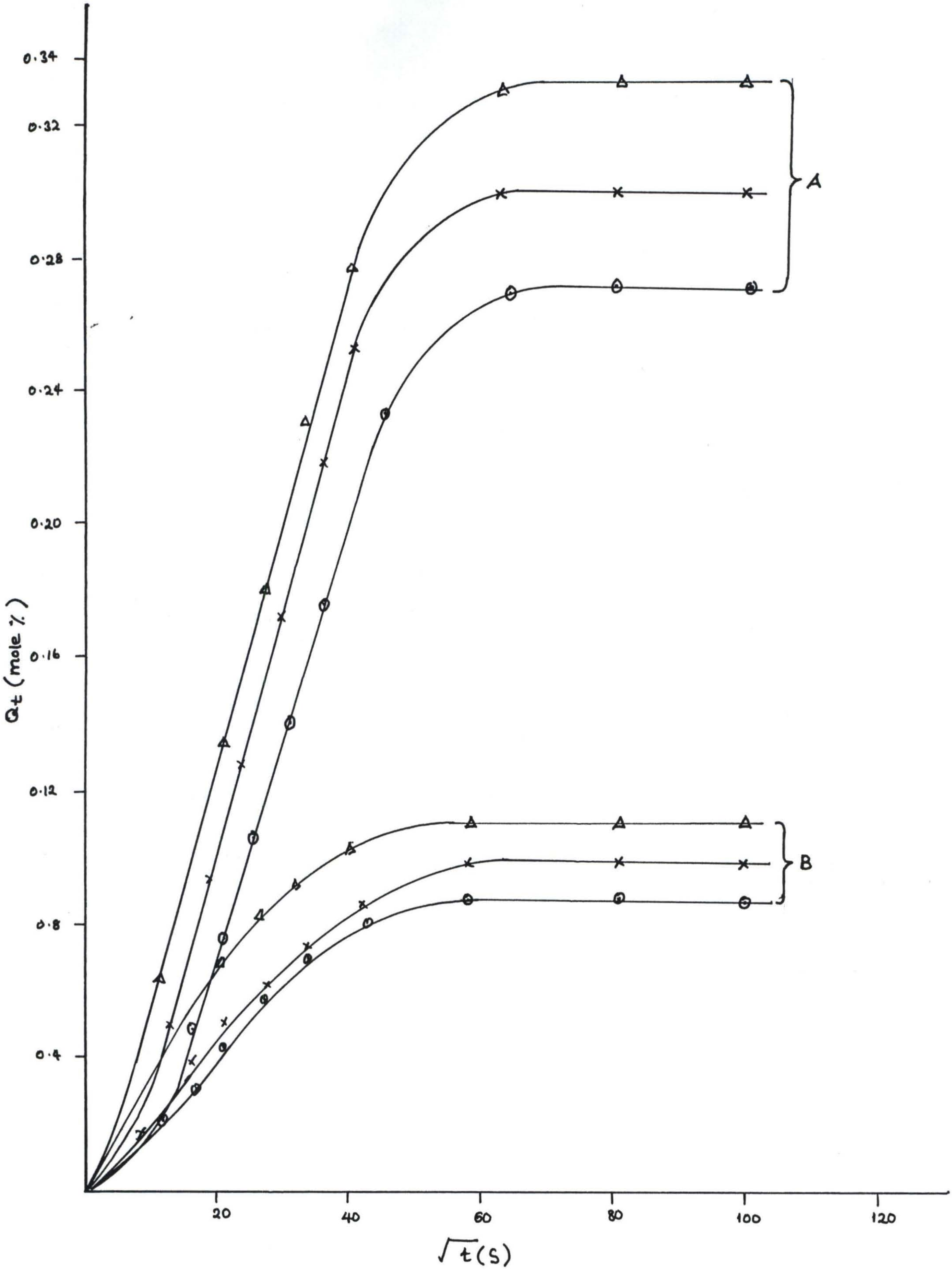


FIG. 3: GRAPH OF MOL. % OF LIQIUDS (Q_t) SORBED Vs $\sqrt{t}$ (S), (⊖) 28°C, (x) 40°C, (Δ) 60°C FOR PP IN METHYL ACETATE (A) & ETHYL ACETATE (B)

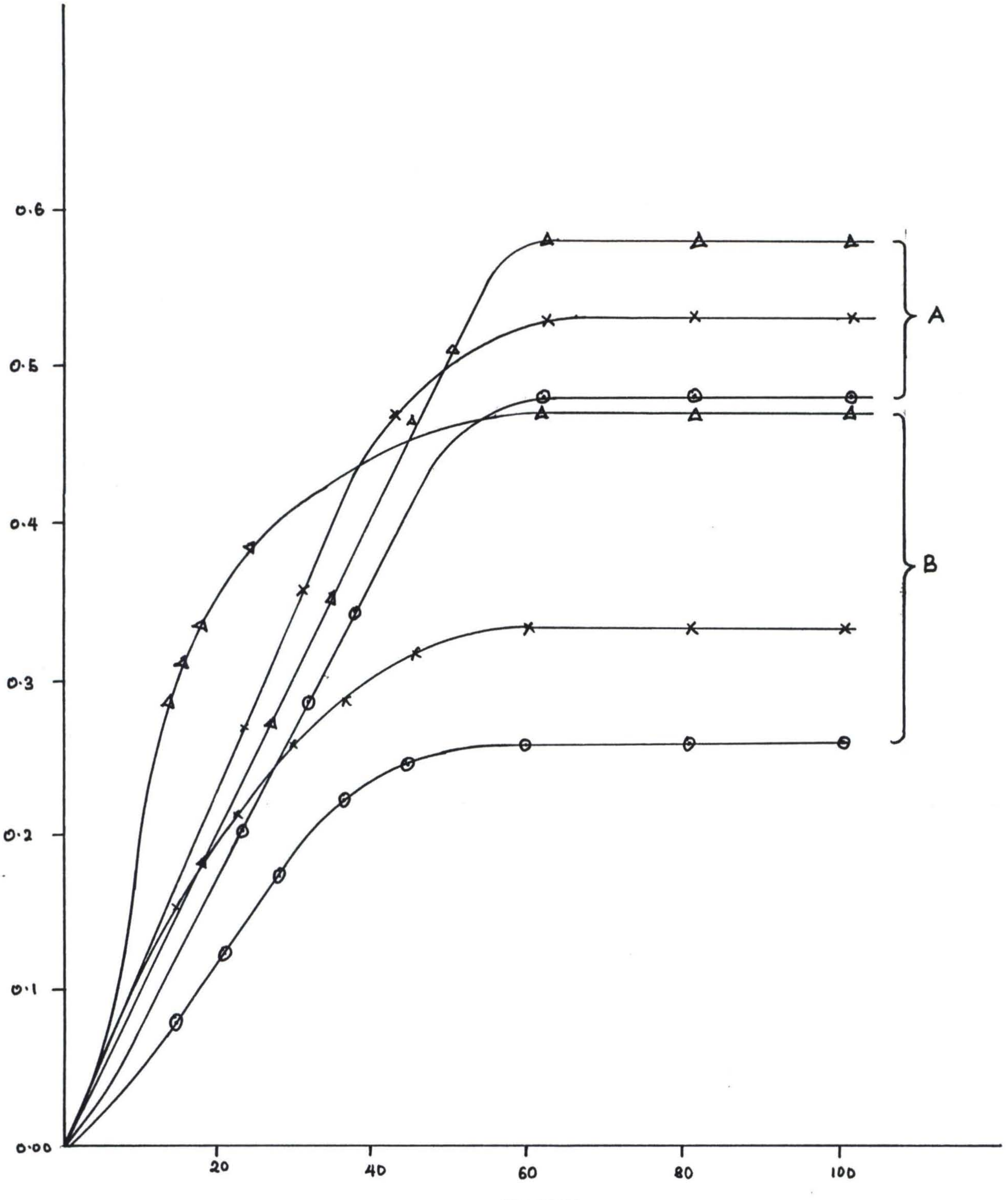


FIG. 4: GRAPH OF MOl. PERCENT OF LIQUIDS (Q_t) SORBED Vs $\sqrt{t}$ (S), (⊙) 28°C, (×) 40°C, 60°C FOR PP IN CHLOROFORM (A) & CCl_4 (B)

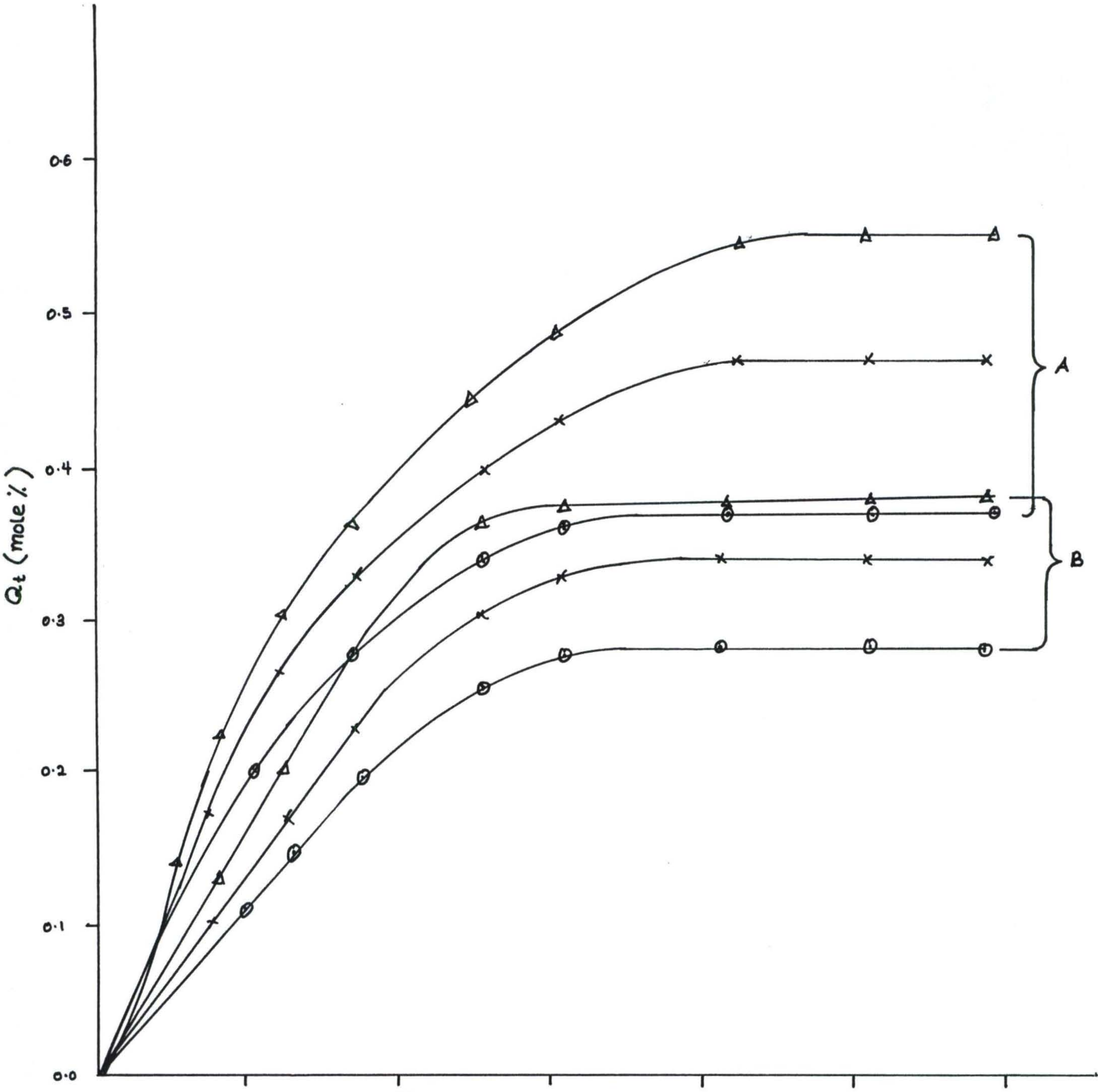


FIG. 5: GRAPH OF MOLE PERCENT OF LIQUIDS(Q_t) SORBED Vs $\sqrt{t}$(S), (⊙) 28°C, (×) 40°C, (△) 60°C FOR PP IN BENZENE (A) & XYLENE (B)

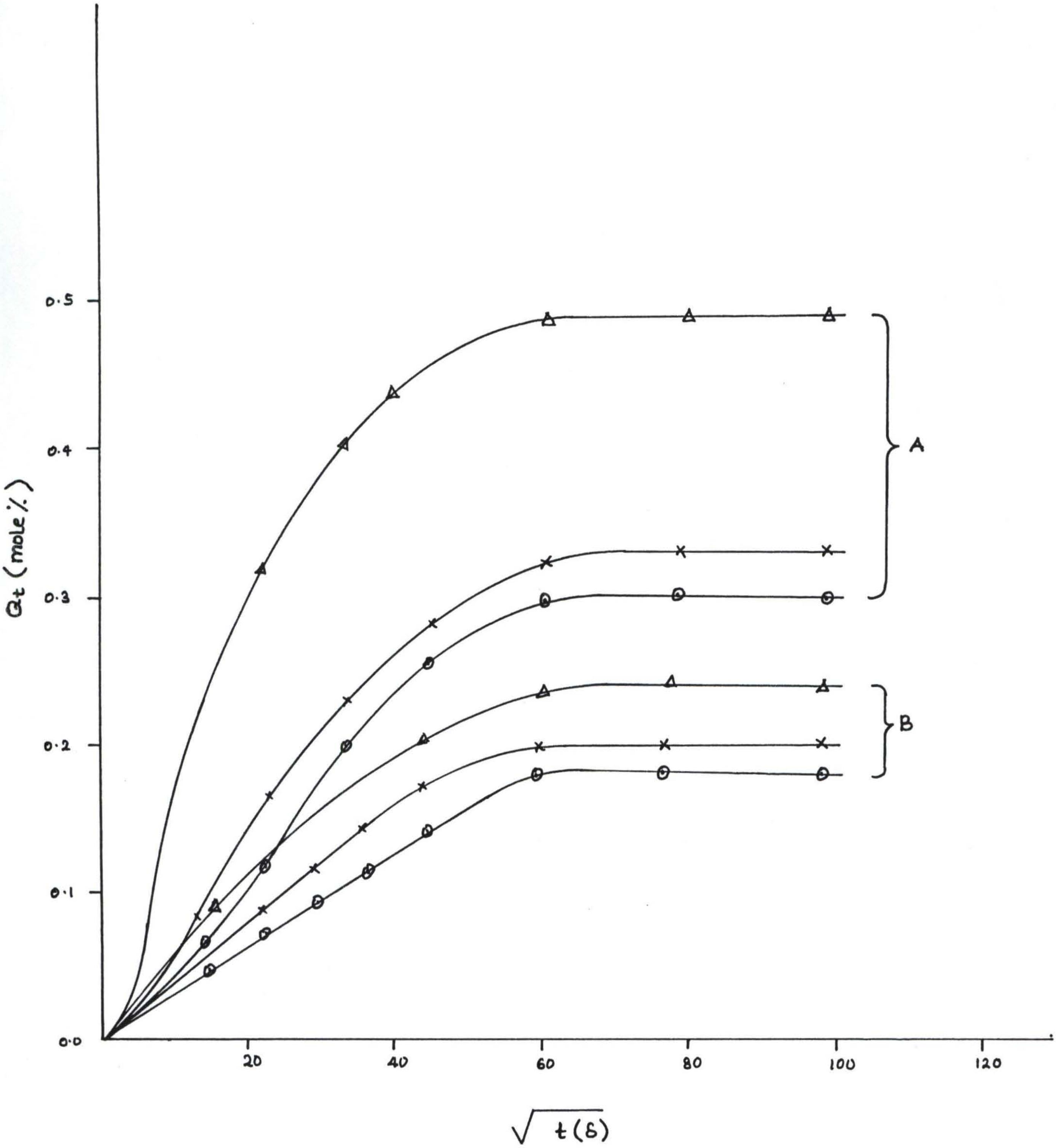


FIG. 6: GRAPH OF MOL. PERCENT OF LIQUIDS(Qt) SORBED Vs $\sqrt{t}$ (S), (⊙) 28°C, (x) 40°C, (Δ) 60°C FOR PP IN CHLORO BENZENE (A) & BENZYL CHLORIDE (B)

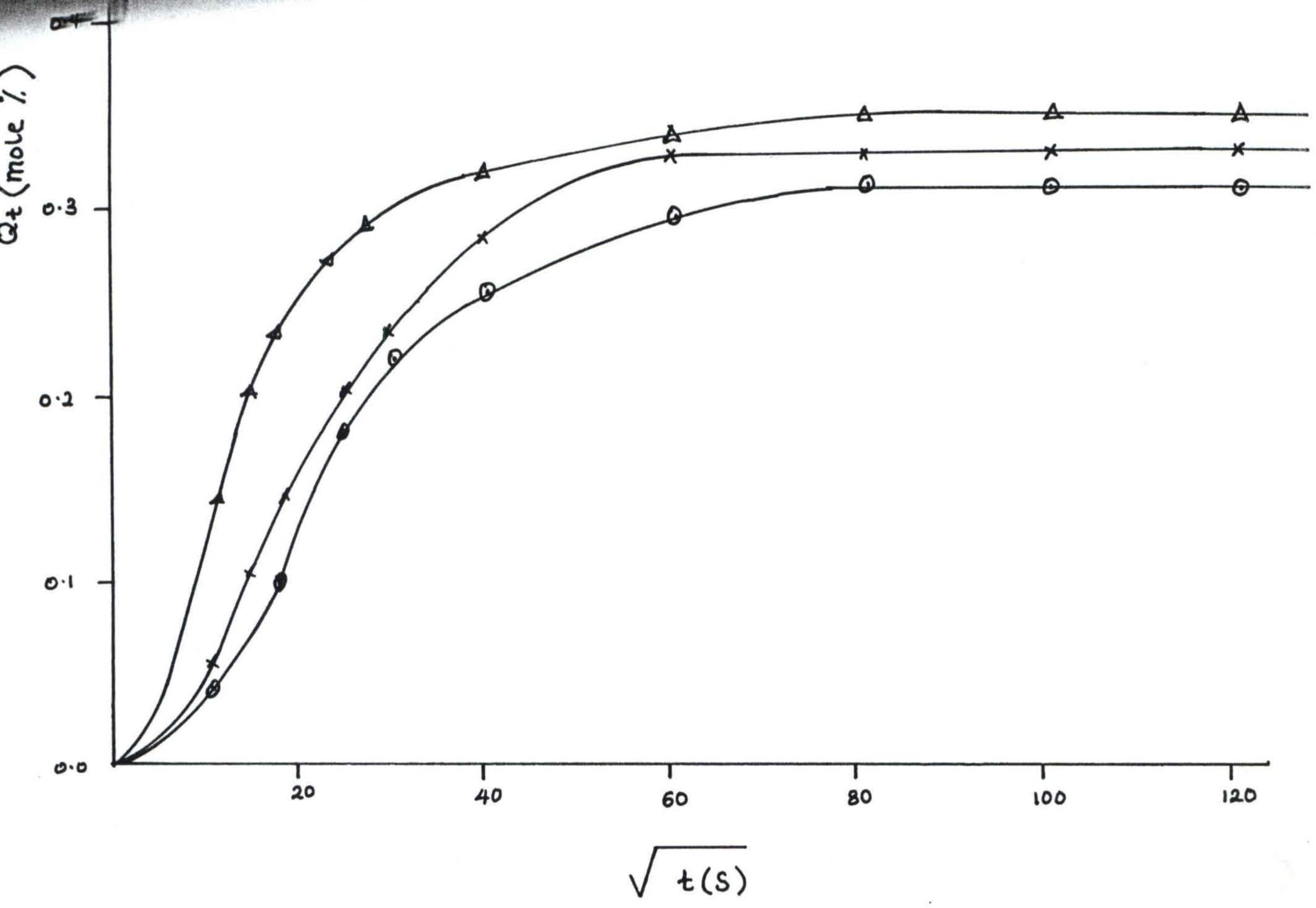


FIG. 7: GRAPH OF MOL. PERCENT OF LIQUIDS (Q_t) SORBED Vs $\sqrt{t}$ (S), (o) 28°C, (x) 40°C, (Δ) 60°C FOR PP IN TOLUENE

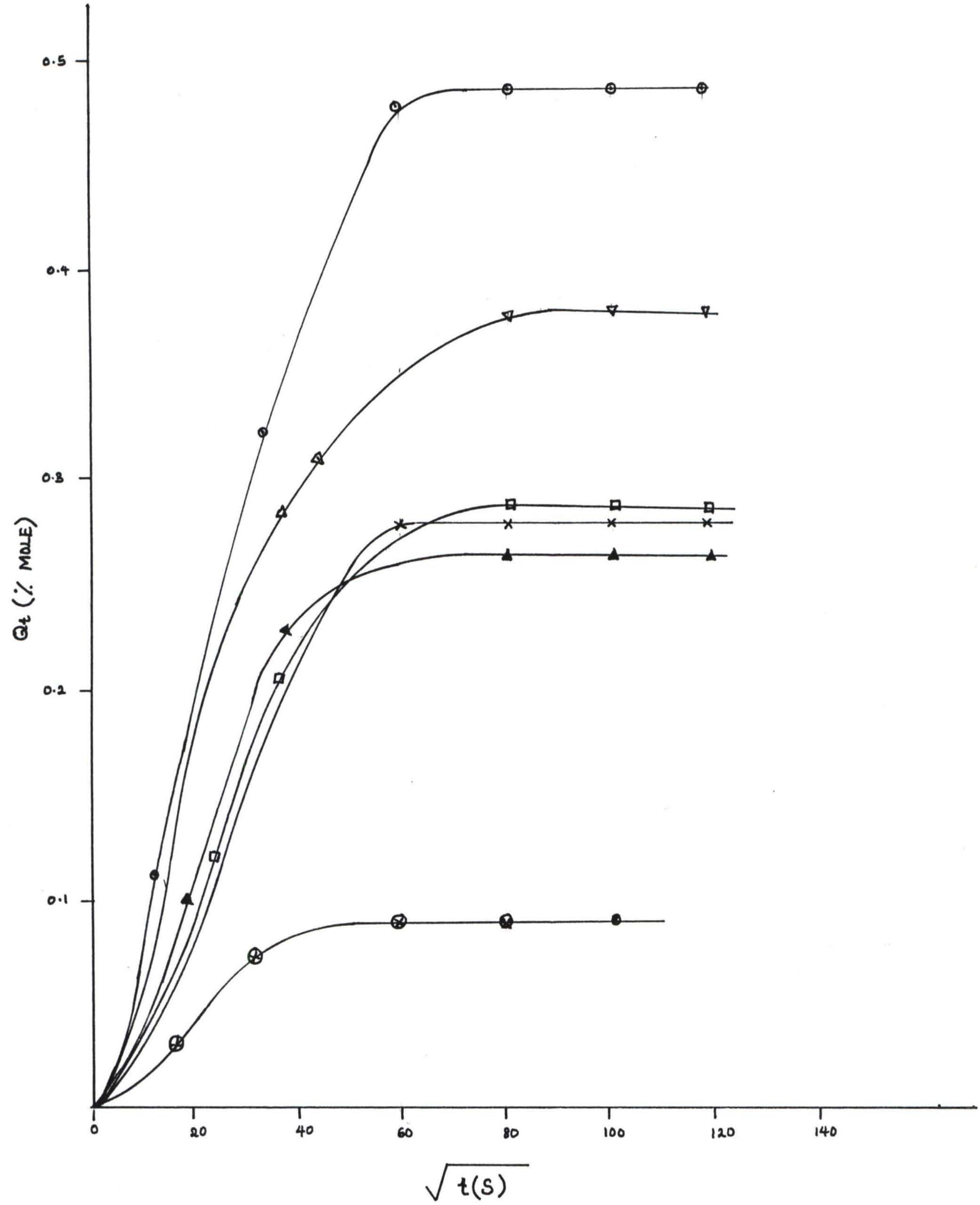


FIG. 8: GRAPH OF Q_t Vs $\sqrt{t}$(S) AT 28°C OF PP IN (△) BENZENE, (□) XYLENE (⊙) CHLOROFORM, (×) CHLORO BENZENE, (⊗) ETHYLE ACETATE, (▲) CCl_4

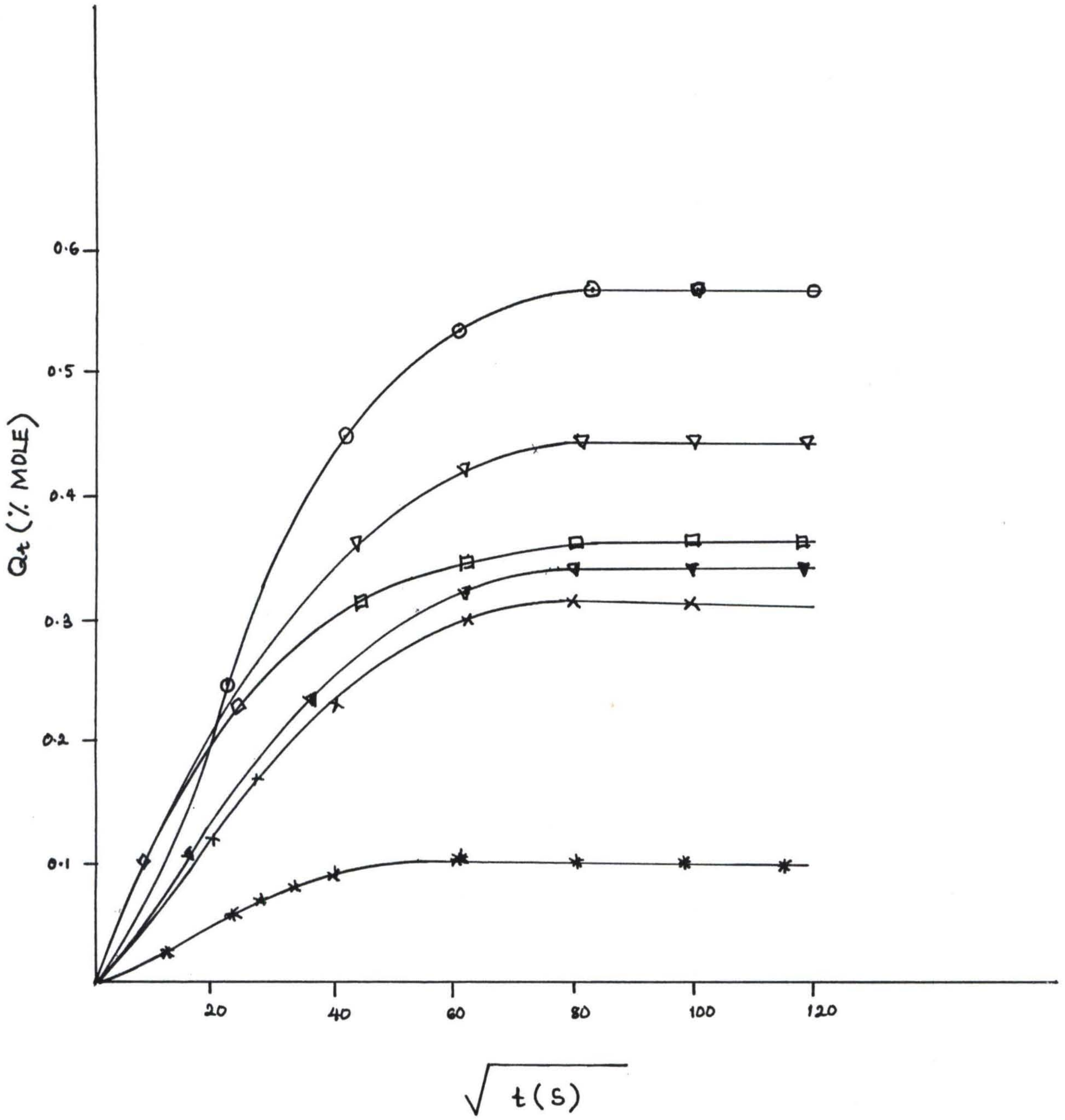


FIG. 9: GRAPH OF MOL. PERCENT Vs $\sqrt{t}$(S) AT 40°C OF PP IN (⊙) ETHYL ACETATE, (×) CHLORO BENZENE, (Δ) BENZENE, (▼) XYLENE, (□) CCl_4, (*) CHLOROFORM

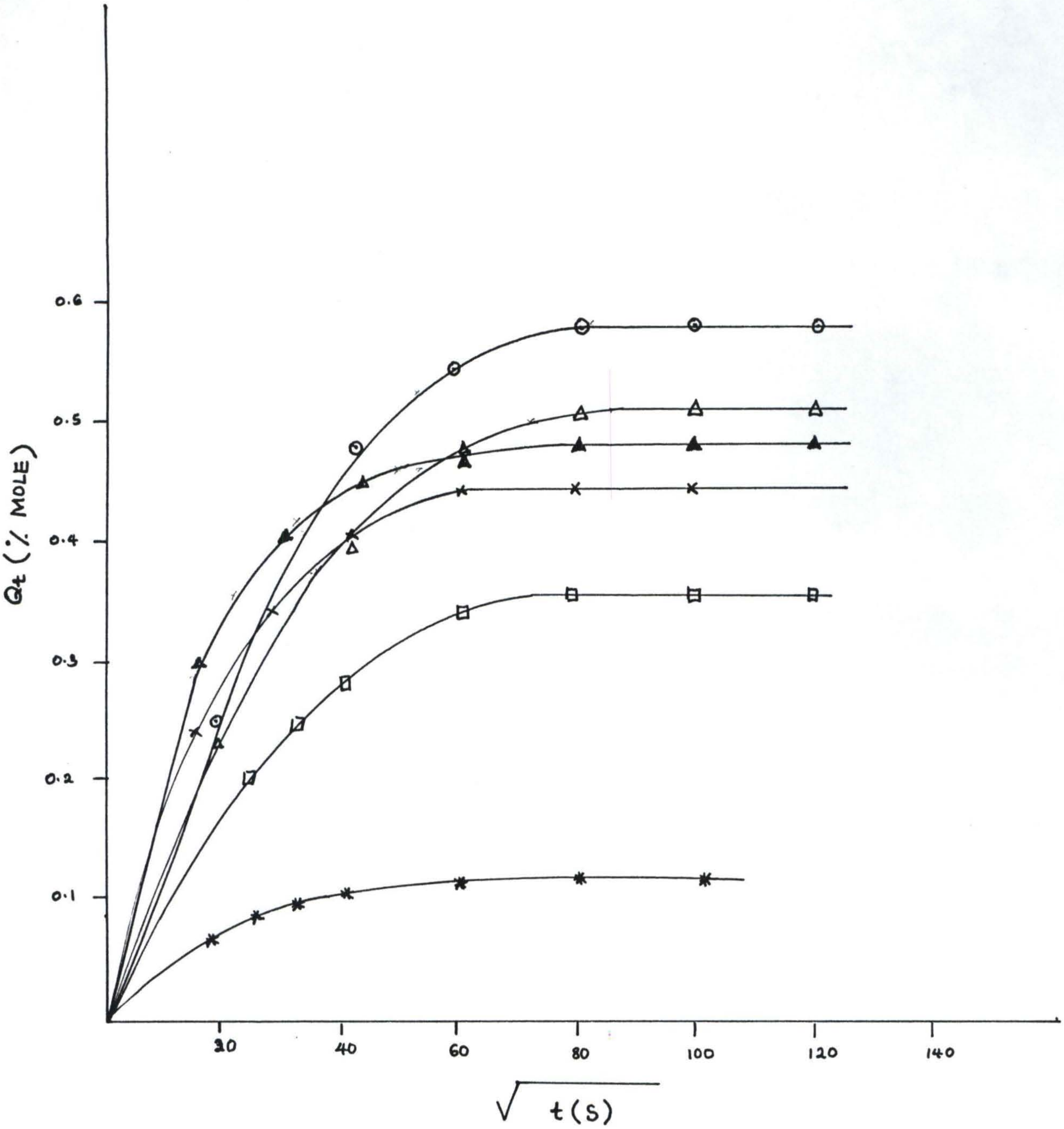


FIG. 10: GRAPH OF Q_t Vs $\sqrt{t}$ (S) AT 60°C OF PP IN ETHYL ACETATE (×), CHLORO BENZENE (△), XYLENE (▲), CCl_4 (✱), CHLOROFORM (⊙).

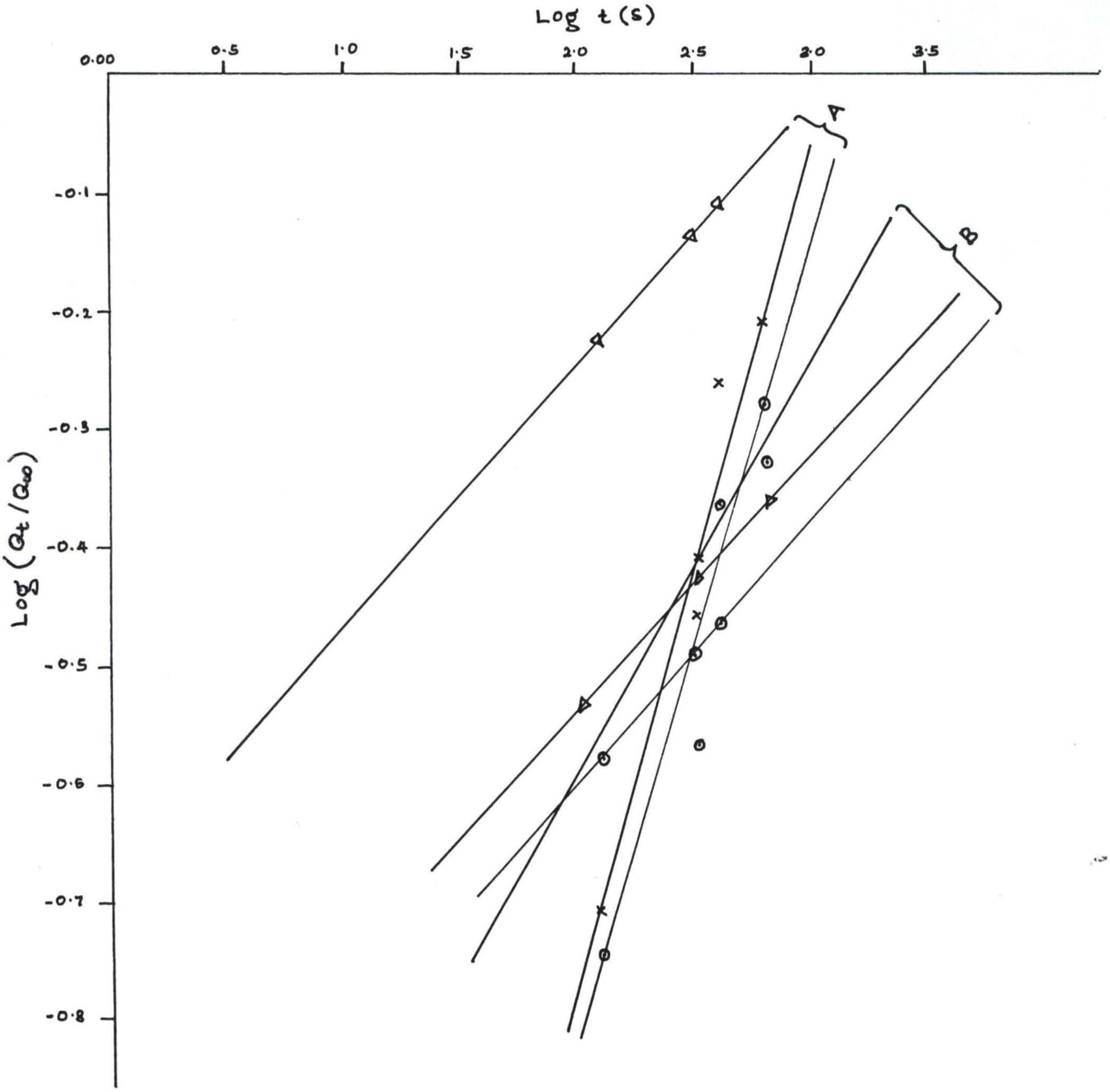


FIG.11: GRAPH OF LOG(Q_t/Q_∞) Vs LOG t(S), (⊙) 28°C, (×) 40°C & (▽) 60°C FOR PP IN TOLUENE (A) & XYLENE (B)

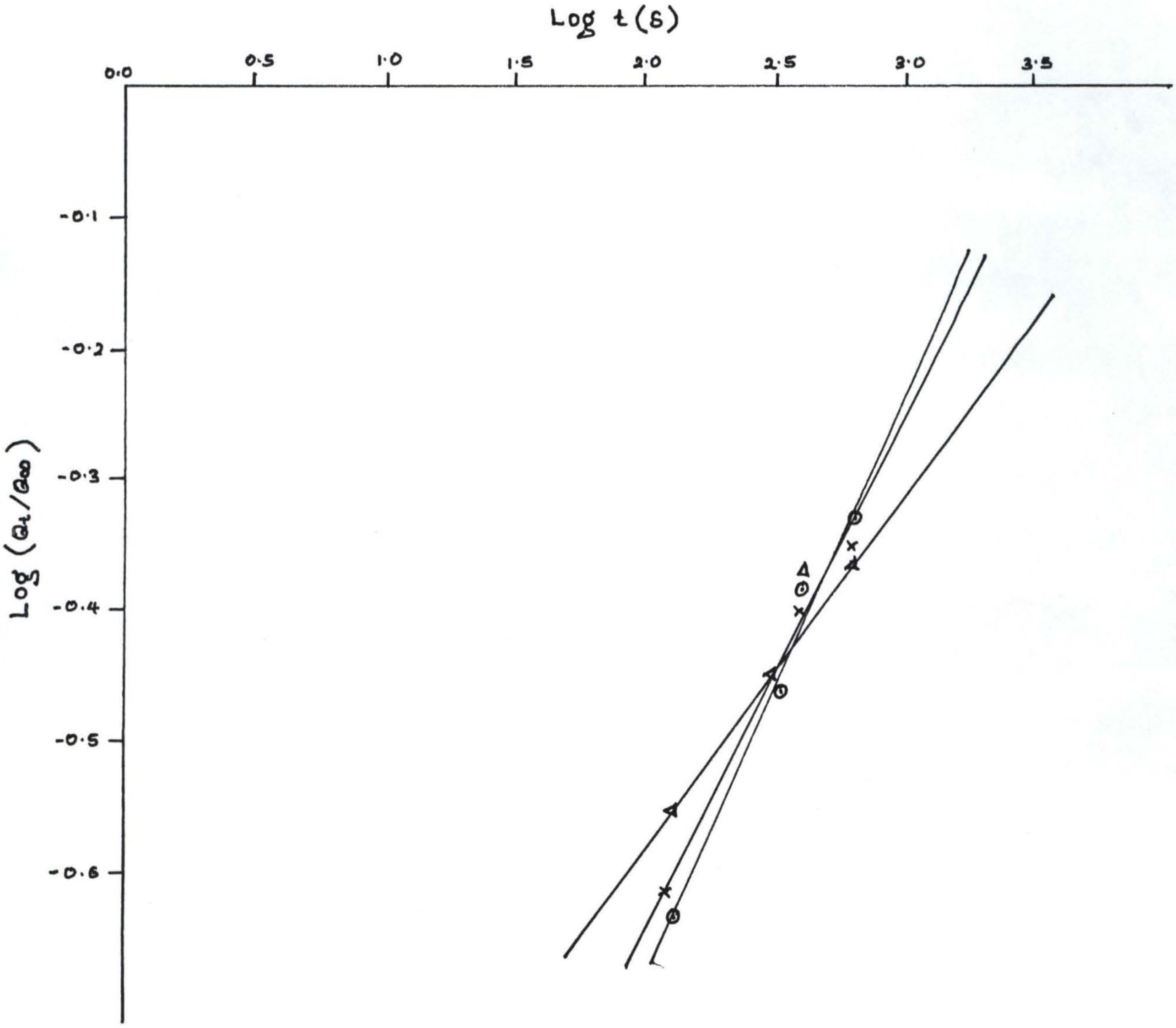


FIG.12: GRAPH OF LOG (Q_t/Q_∞) Vs LOG t(S), (⊙) 28°C, (x) 40°C & (Δ) 60°C
FOR PP IN CHLOROFORM

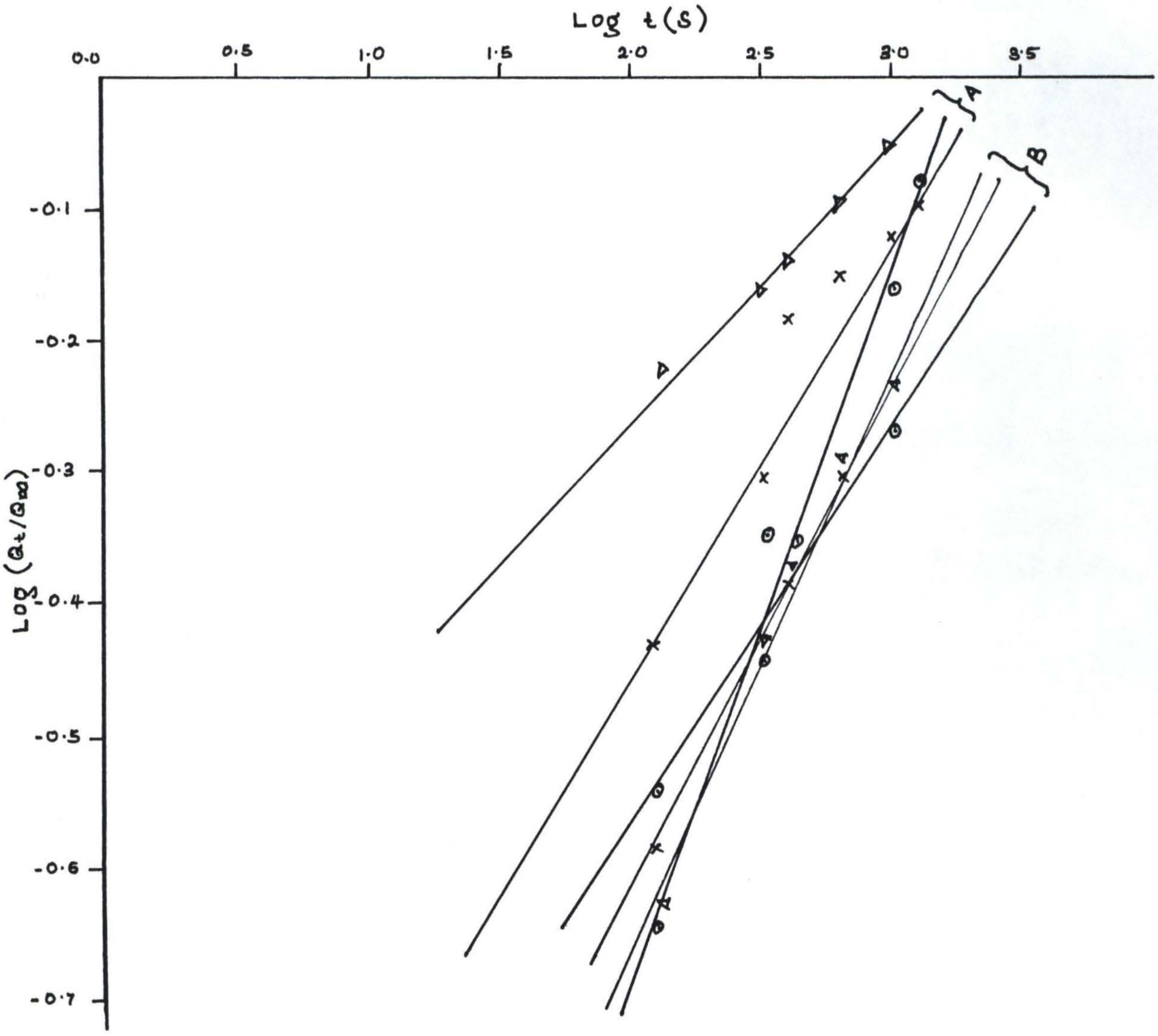


FIG. 13: GRAPH OF LOG (Q_t/Q_∞) Vs LOG t(S), (⊙) 28°C, (x) 40°C & (▽) 60°C FOR PP IN CCl_4 (A) & BENZYL CHLORIDE (B)

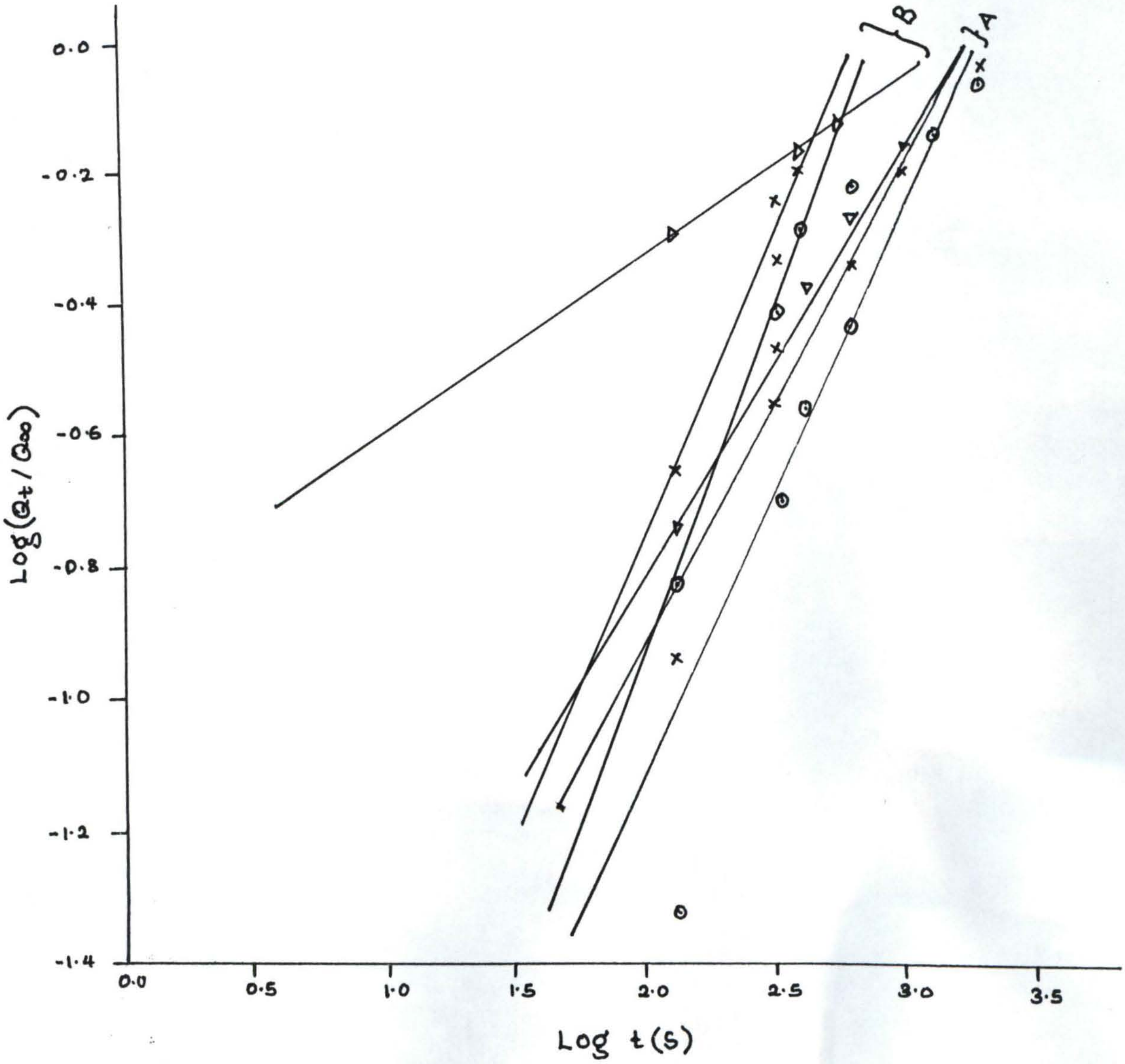


FIG. 14: GRAPH OF LOG (Q_t/Q_∞) Vs LOG t(s), (⊙) 28°C, (×) 40°C & (▽) 60°C FOR PP IN METHYL ACETATE (A) & ETHYLE ACETATE (B)

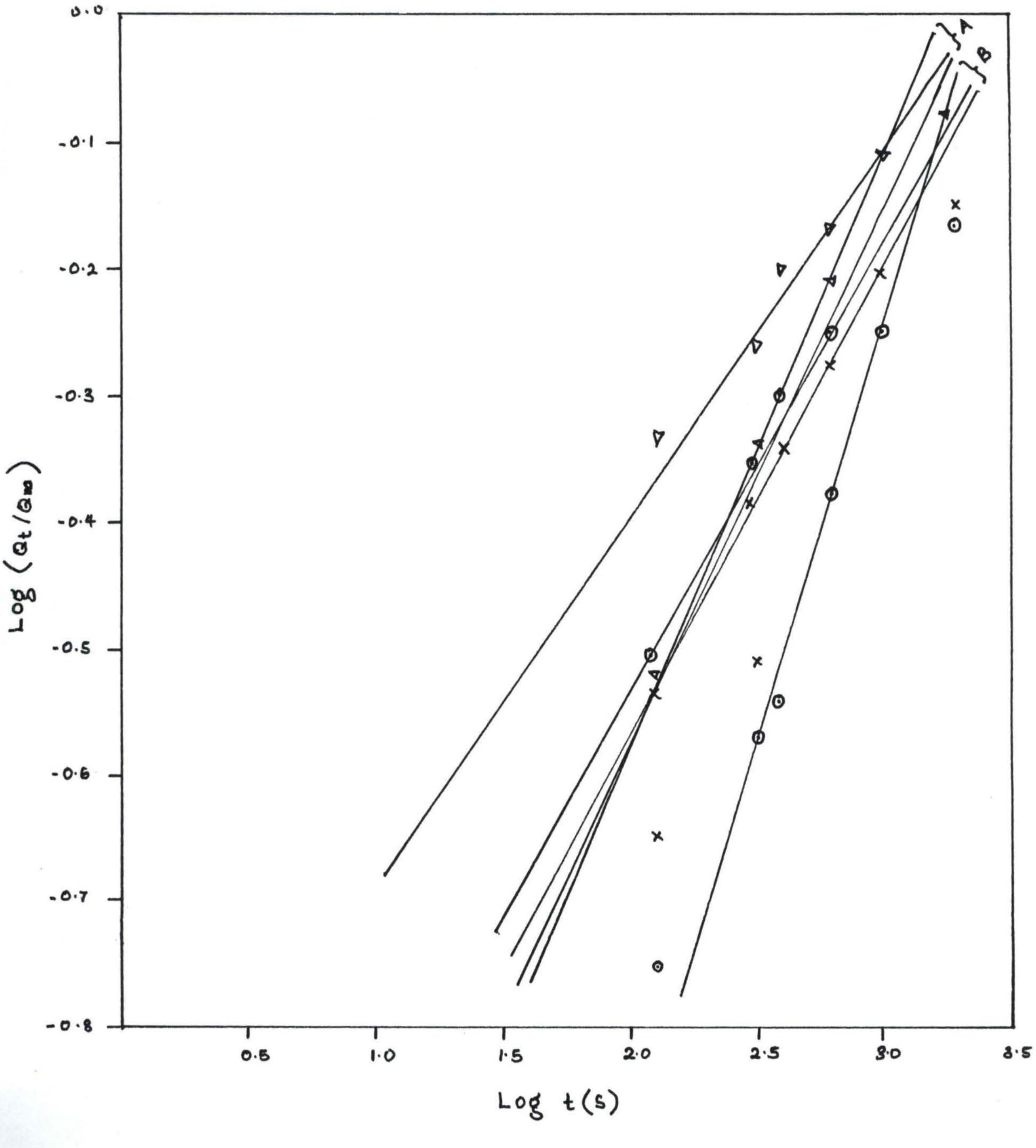


FIG. 15: GRAPH OF LOG (Qt/Q∞) Vs LOG t(s), ⊙ 28°C, (×) 40°C & (▽) 60°C FOR PP IN CHLOROBENZENE (A) & BENZENE (B)

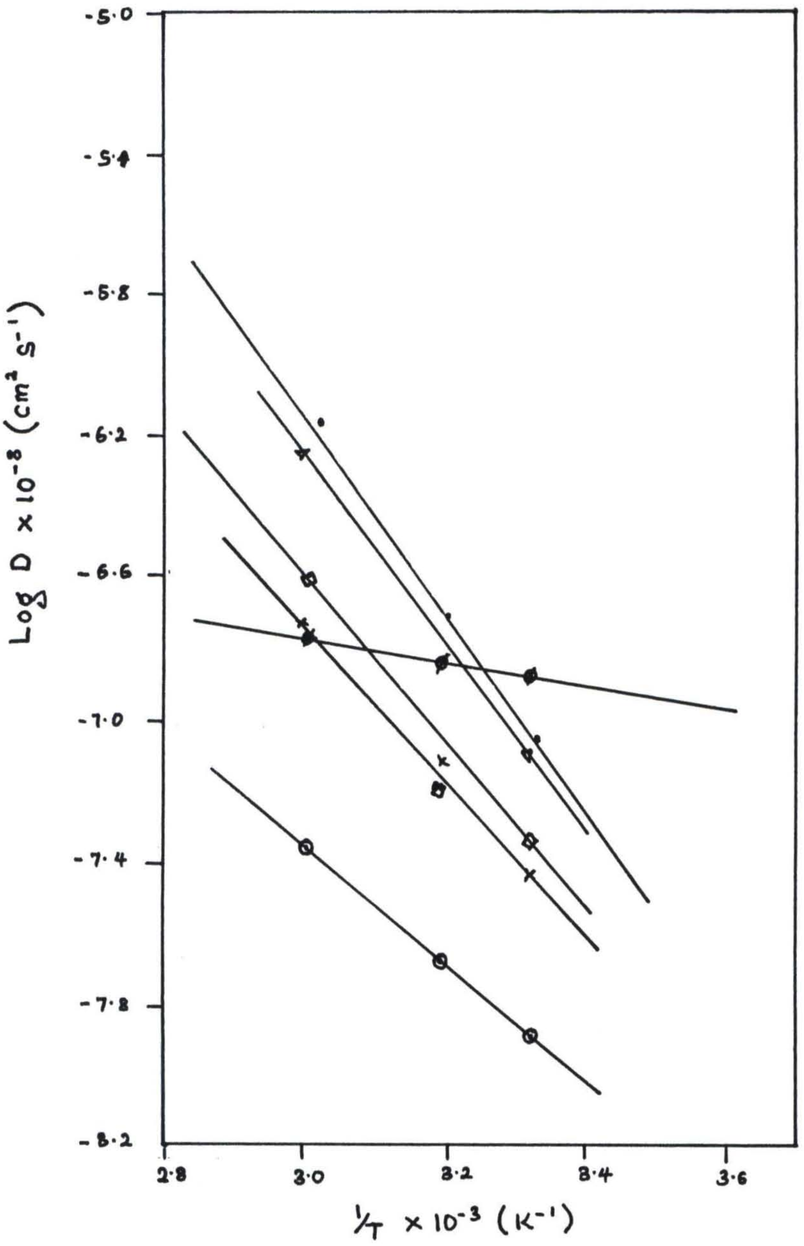


FIG. 16: ARRHENIUS PLOTS OF LOG D Vs 1/T FOR PP IN (⊕) METHYL ACETATE, (×) ETHYL ACETATE, (∇) CCl_4, (□) CHLOROFORM, (•) BENZYL CHLORIDE, (ø) BENZENE

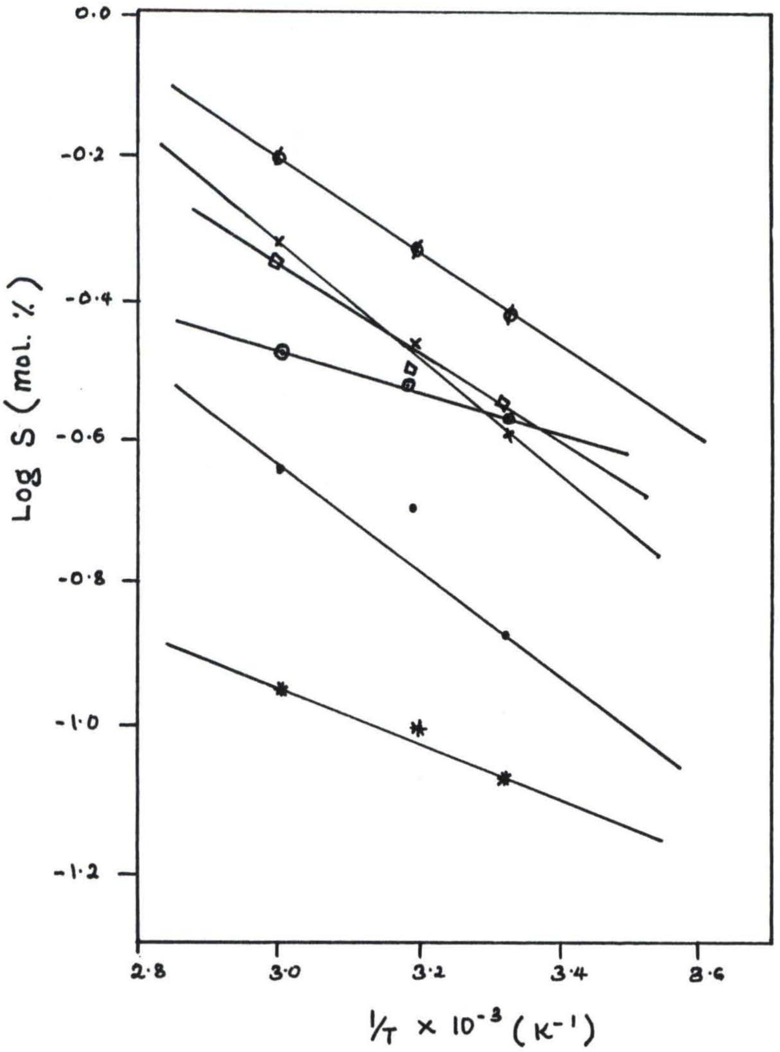


FIG. 17: GRAPH OF ARRHENIUS PLOT OF LOG S Vs 1/T FOR PP, (⊙) METHYL ACETATE, (×) ETHYL ACETATE, (▿) CCl4, (□) CHLORO BENZENE, (·) BENZYL CHLORIDE, (ø) BENZENE

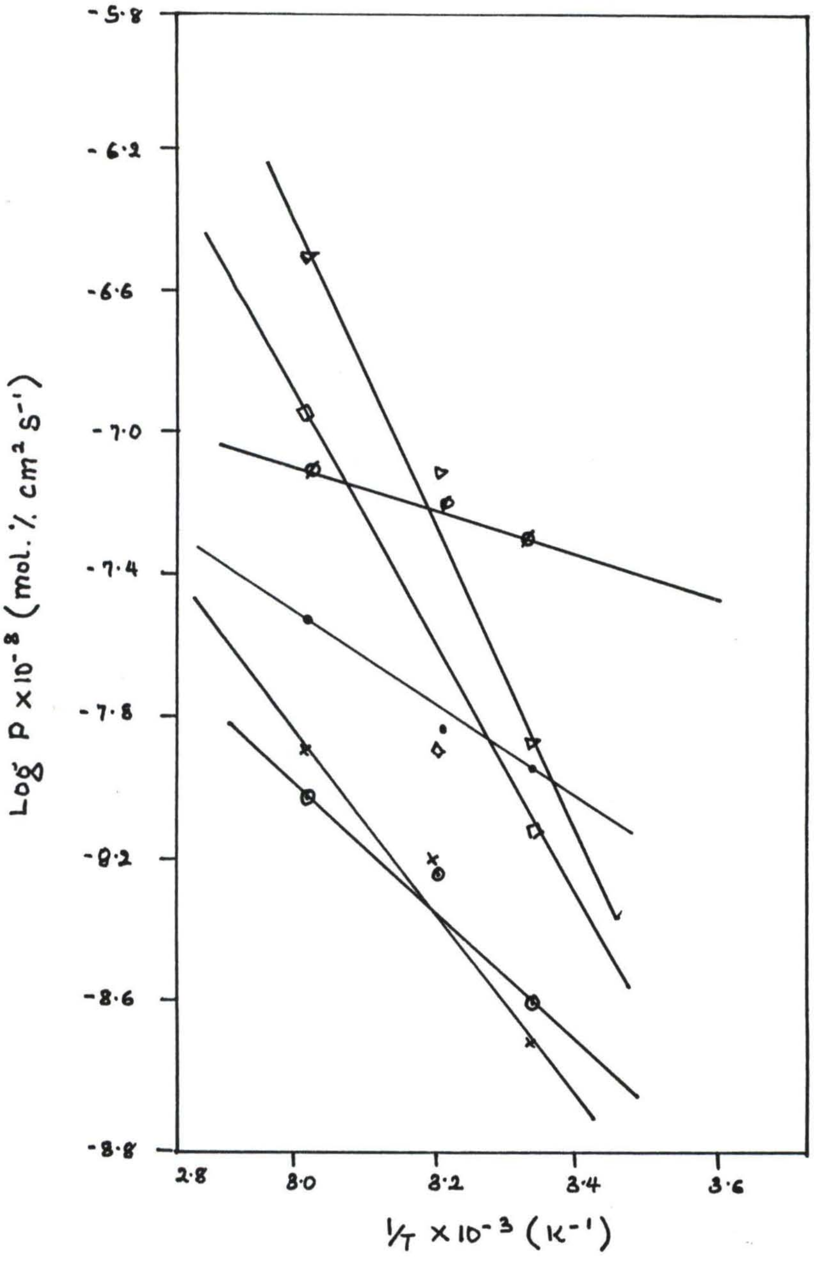


FIG. 18: ARRHENIUS PLOTS OF LOG P Vs 1/T FOR PP IN (⊙) METHYL ACETATE, (x) ETHYLACETATE, (▽) CCl_4, (□) CHLOROBENZENE, (•) BENZYL CHLORIDE, (ø) BENZENE

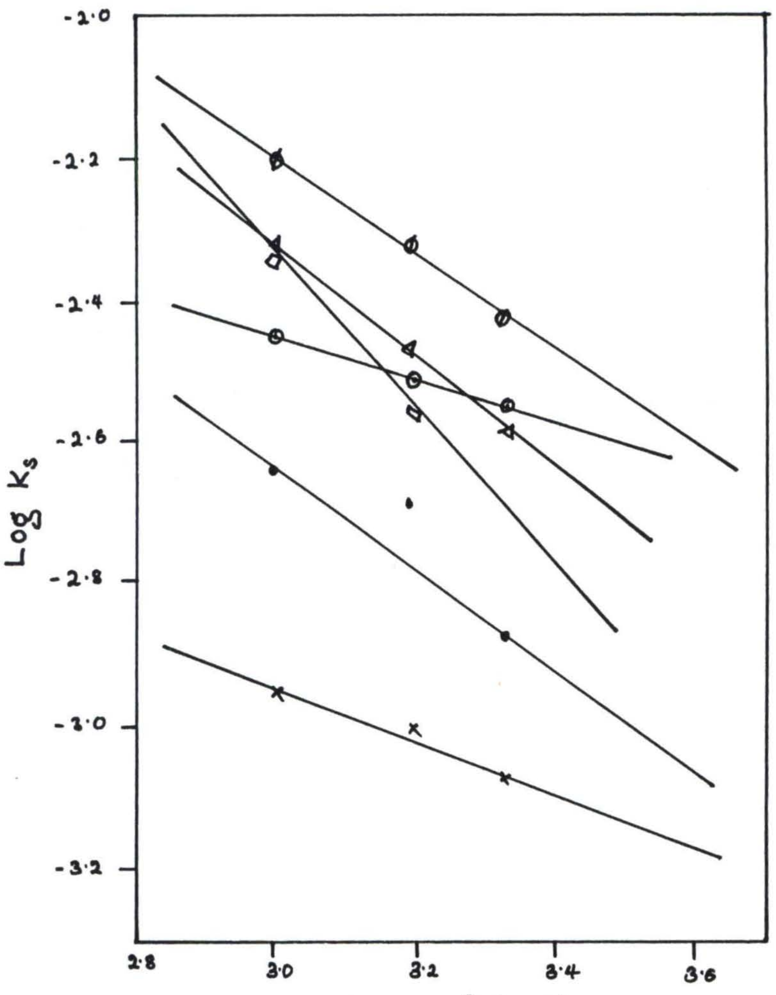


FIG. 19: GRAPH OF LOG K_s Vs $^1/_T$ FOR PP IN (⊙) METHYL ACETATE, (×) ETHYL ACETATE, (▽) CCl_4, (□) CHLORO BENZENE, (⊖) BENZYL CHLORIDE, (∅) BENZENE

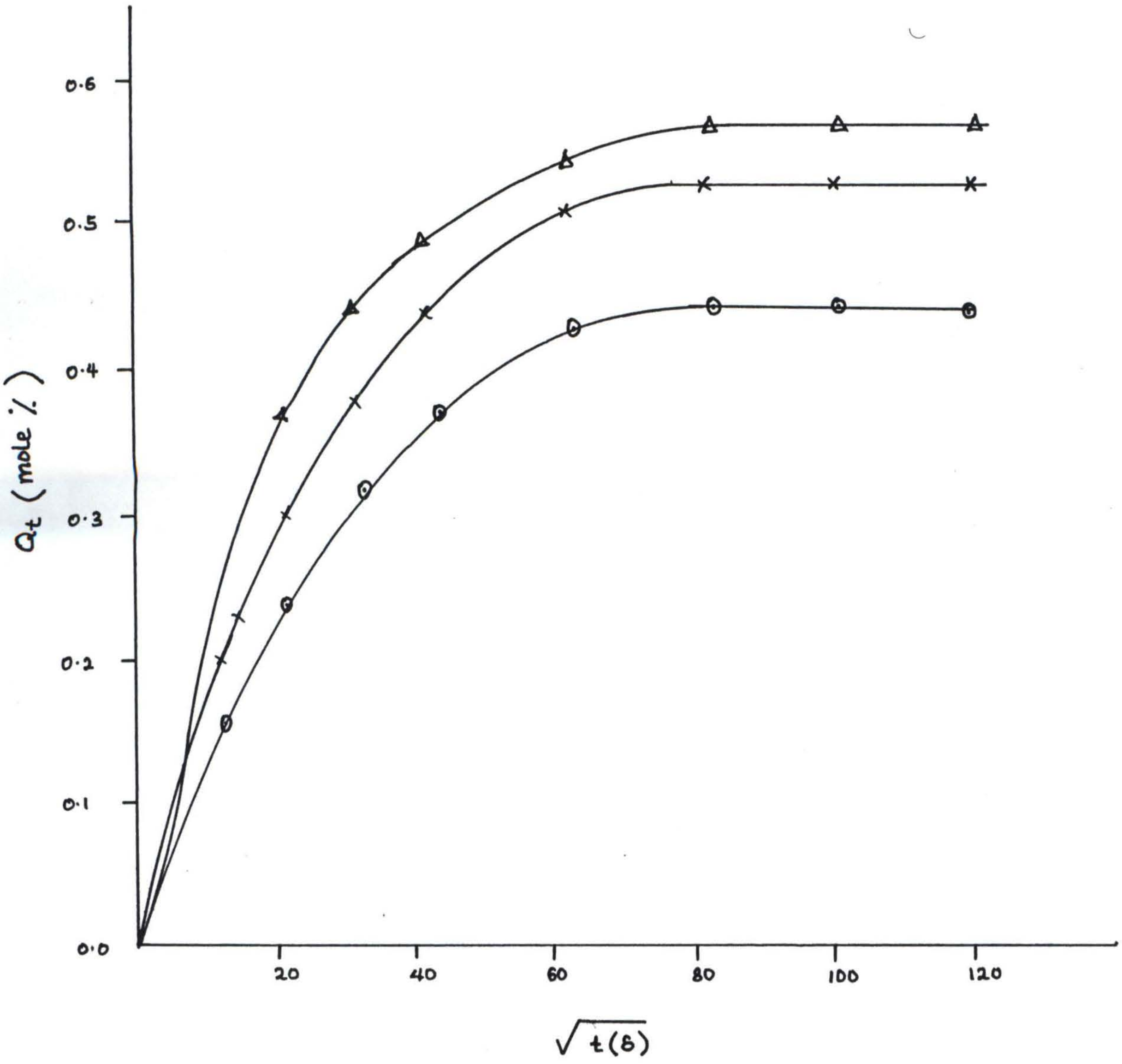


FIG. 20: GRAPH OF Q_t Vs $\sqrt{t}$ ($) OF TREATED PP IN BENZENE, (o) 28°C, (x) 40°C, (Δ) 60°C

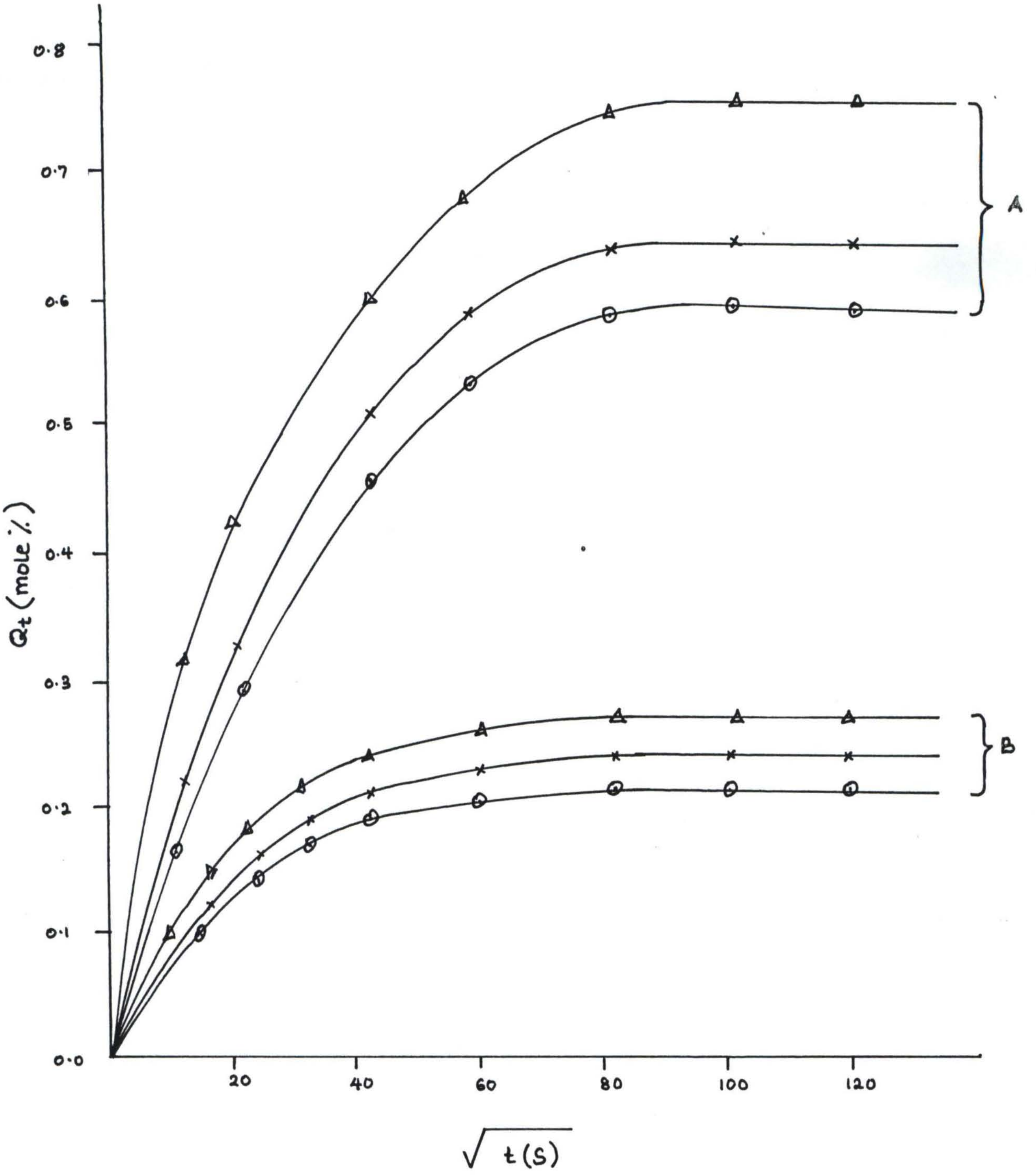


FIG. 21: GRAPH OF MOL. PERCENT Q_t Vs $\sqrt{t}$ (S) OF TREATED PP IN CHLOROFORM (A) & n-HEXANE (B), (⊙) 28°C, (×) 40°C AND 60°C

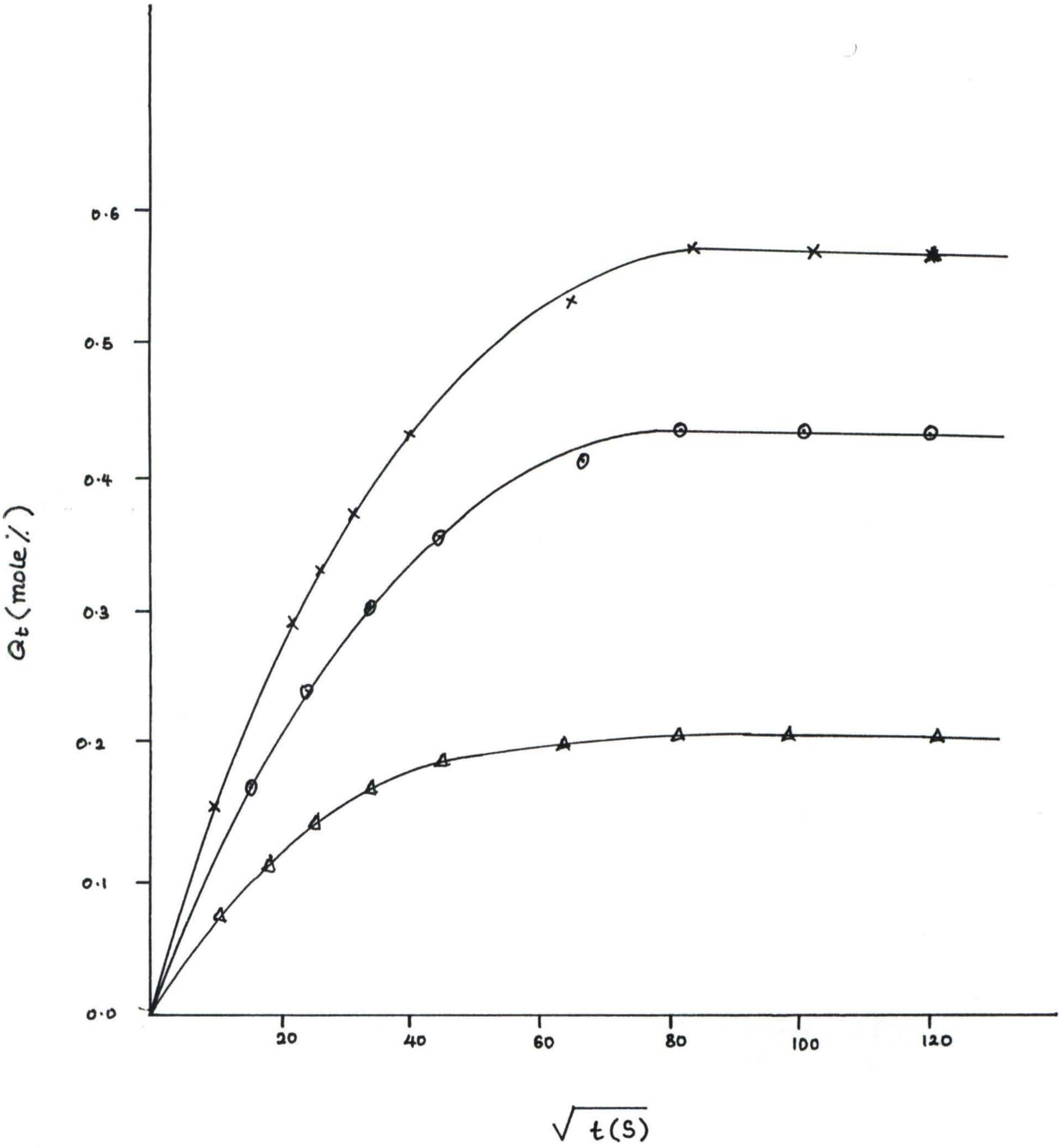


FIG. 22: GRAPH OF Q_t Vs $\sqrt{t}$ (S) OF TREATED PP AT 28°C, (⊙) BENZENE, (x) CHLOROFORM, (Δ) n-HEXANE

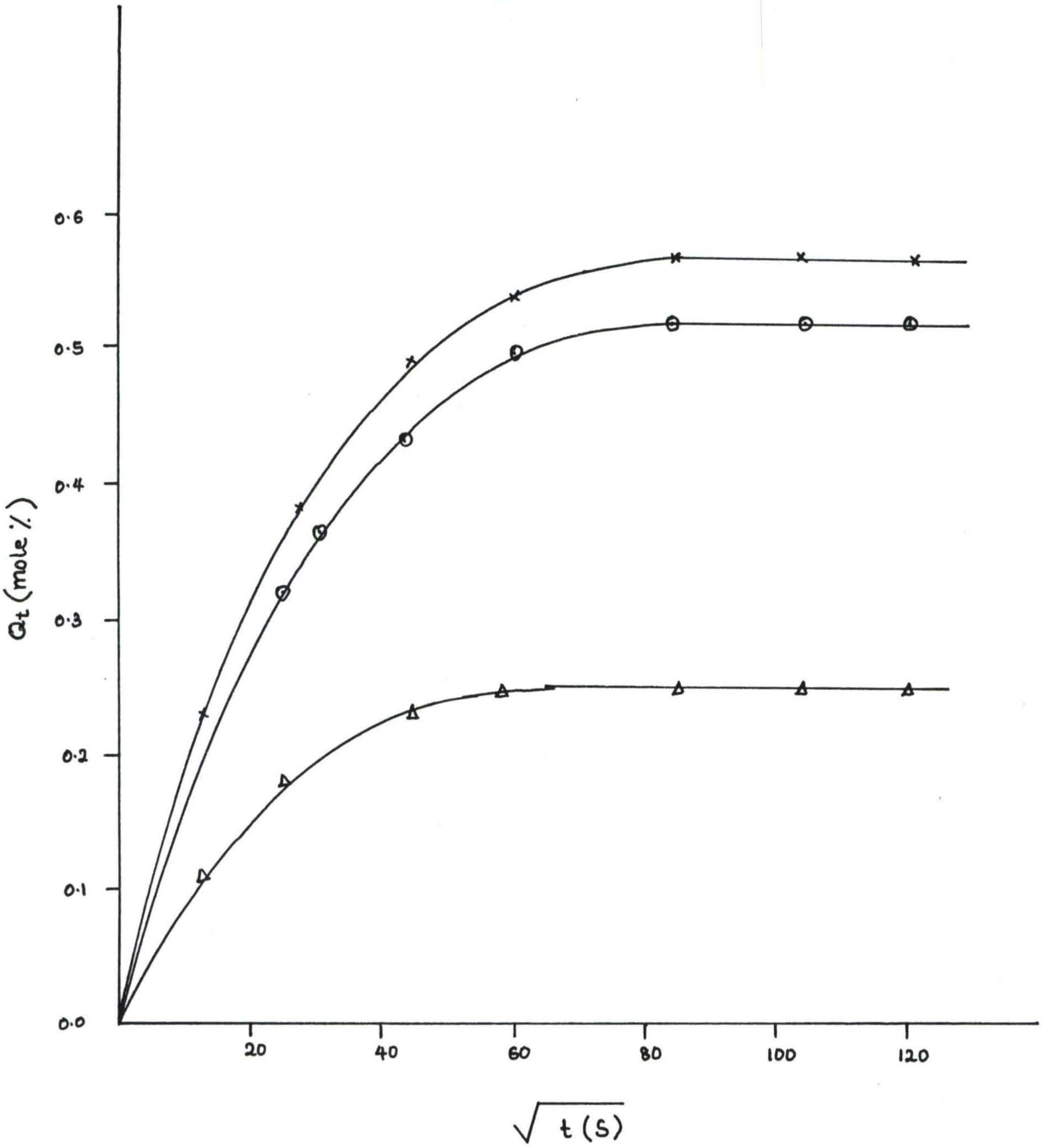


FIG. 23: GRAPH OF MOL. PERCENT √t (S) OF TREATED PP AT 40°C, (O) BENZENE, (X) CHLOROFORM & (Δ) n-HEXANE

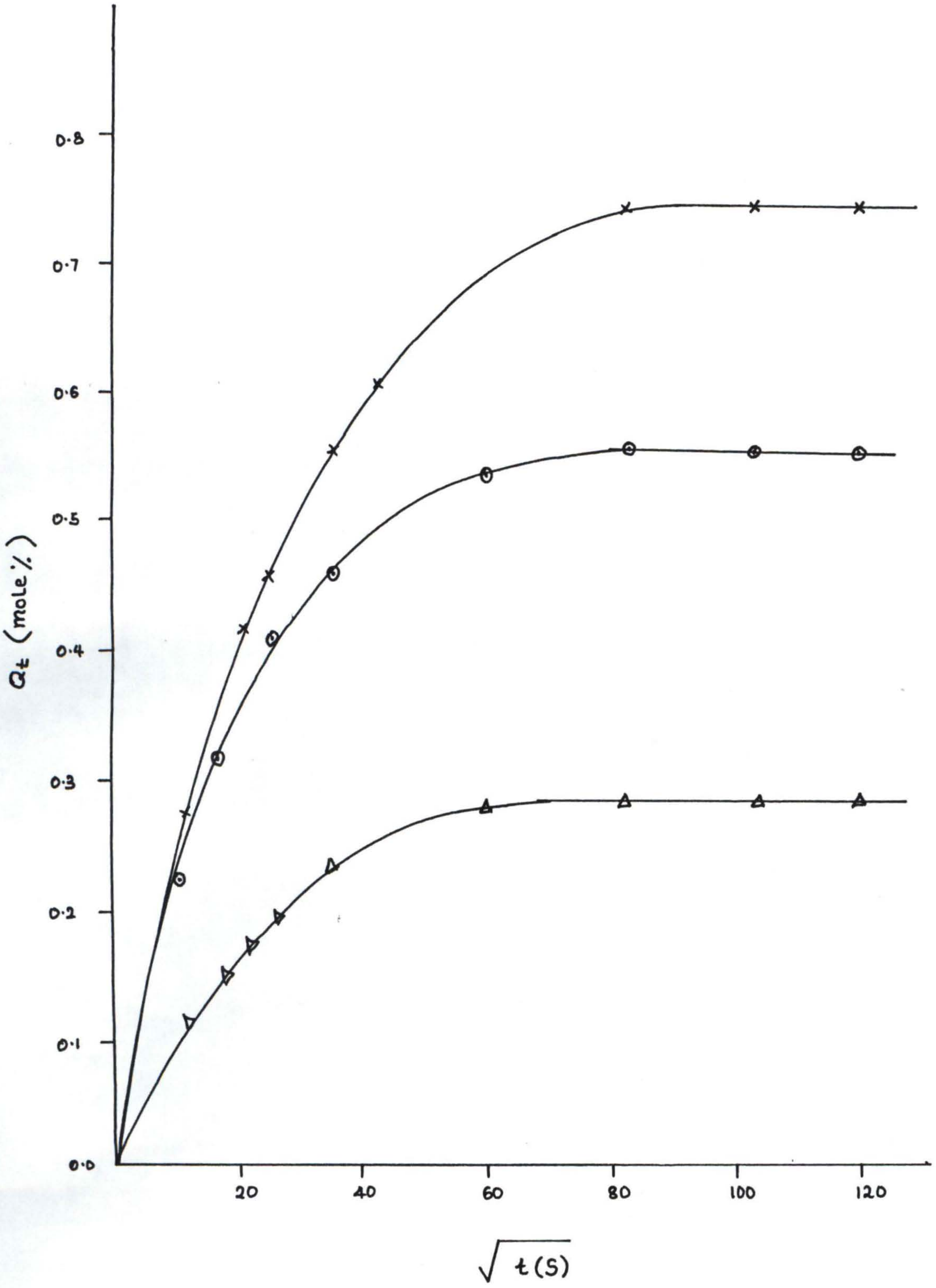


FIG. 24: GRAPH OF Q_t Vs $\sqrt{t}$(S) OF TREATED PP AT 60°C, (⊙) BENZENE, (x) CHLOROFORM & (Δ) n-HEXANE

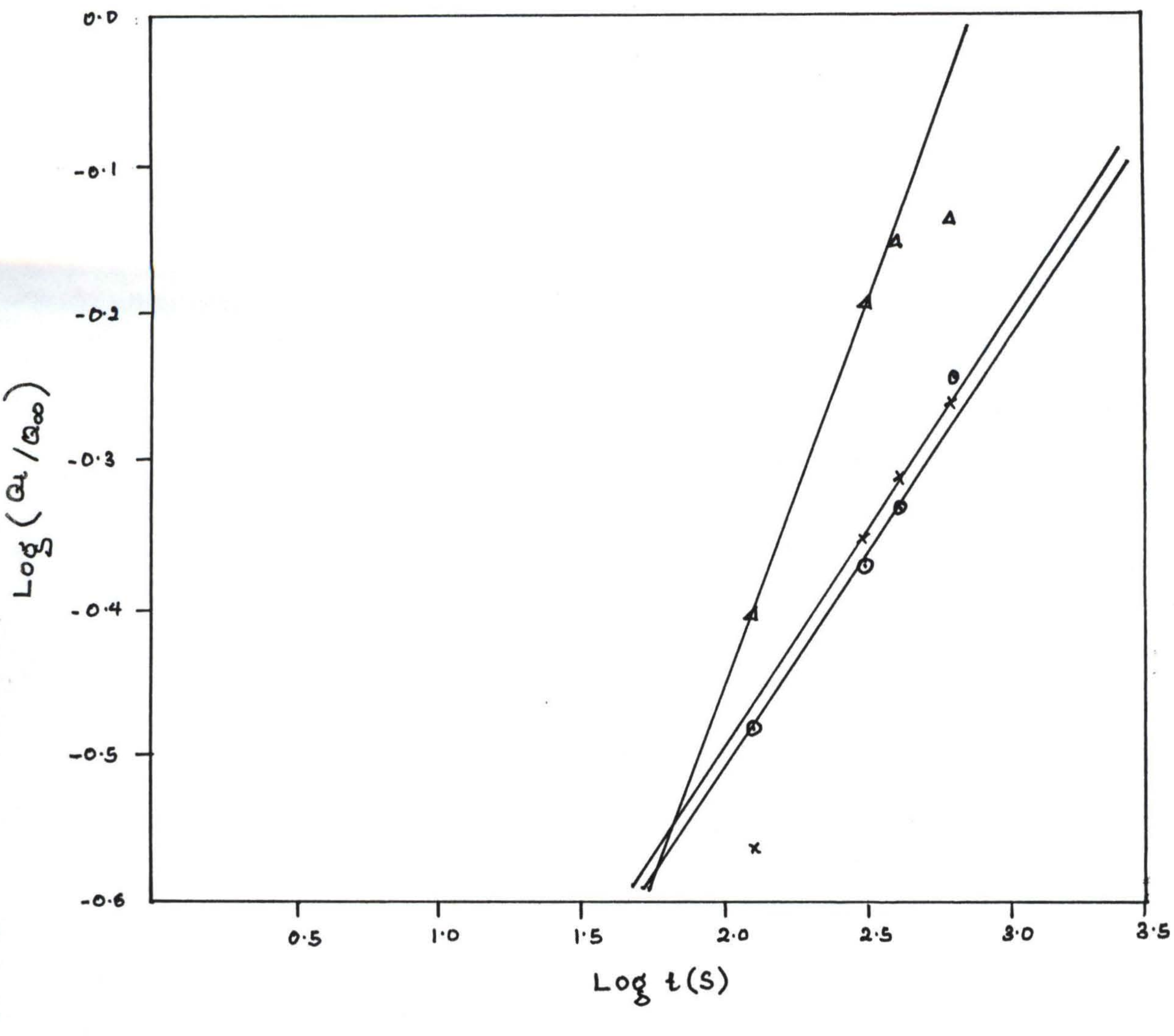


FIG. 25: GRAPH OF LOG Qt/Q∞ Vs LOG t(S) FOR PP AT 28°C IN (⊙) BENZENE, (x) CHLOROFORM & n-HEXANE

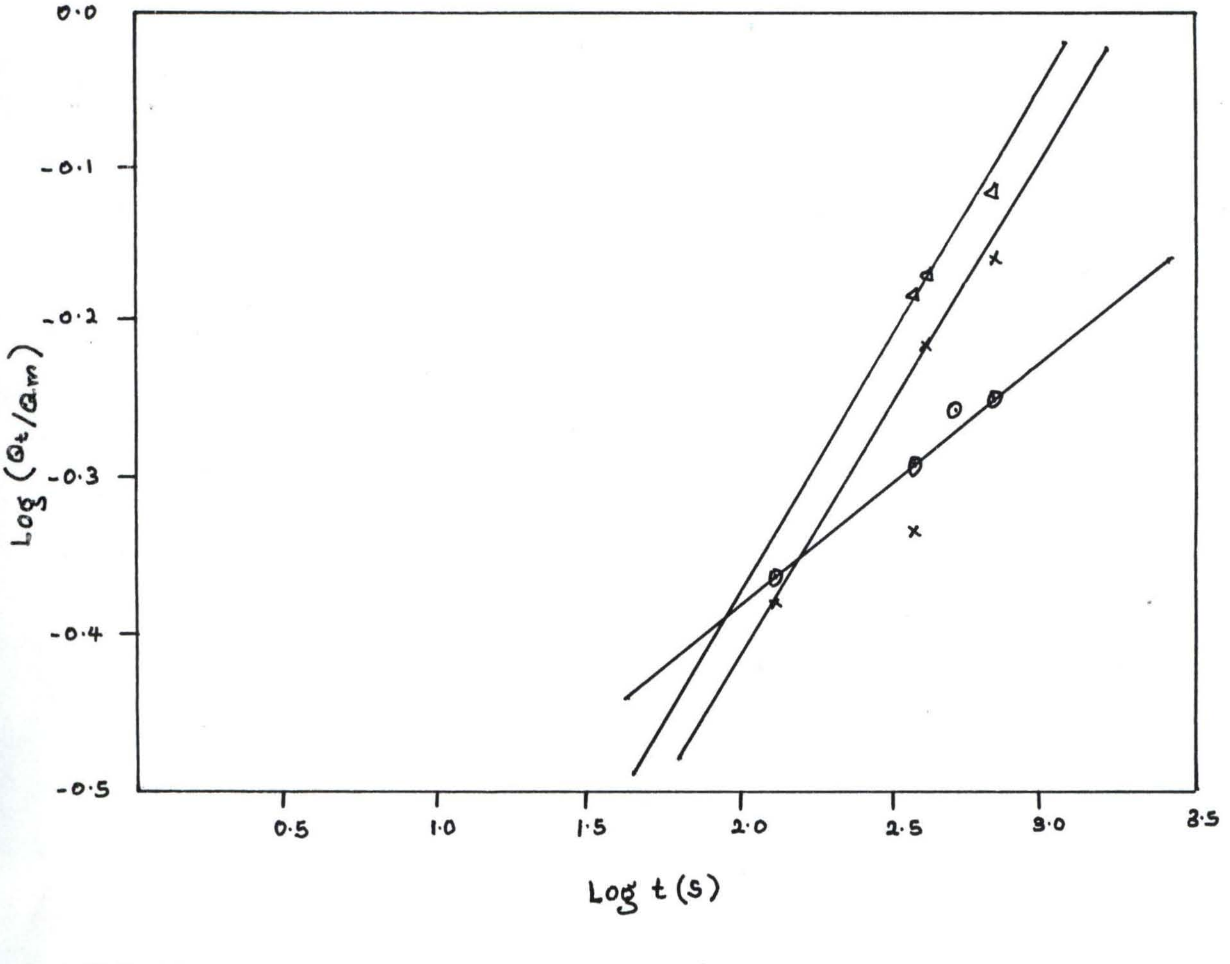


FIG. 26: GRAPH OF LOG Q_t/Q_∞ Vs LOG t(S) FOR TREATED PP AT 40°C, (⊙) BENZENE, (×) CHLOROFORM & n-HEXANE

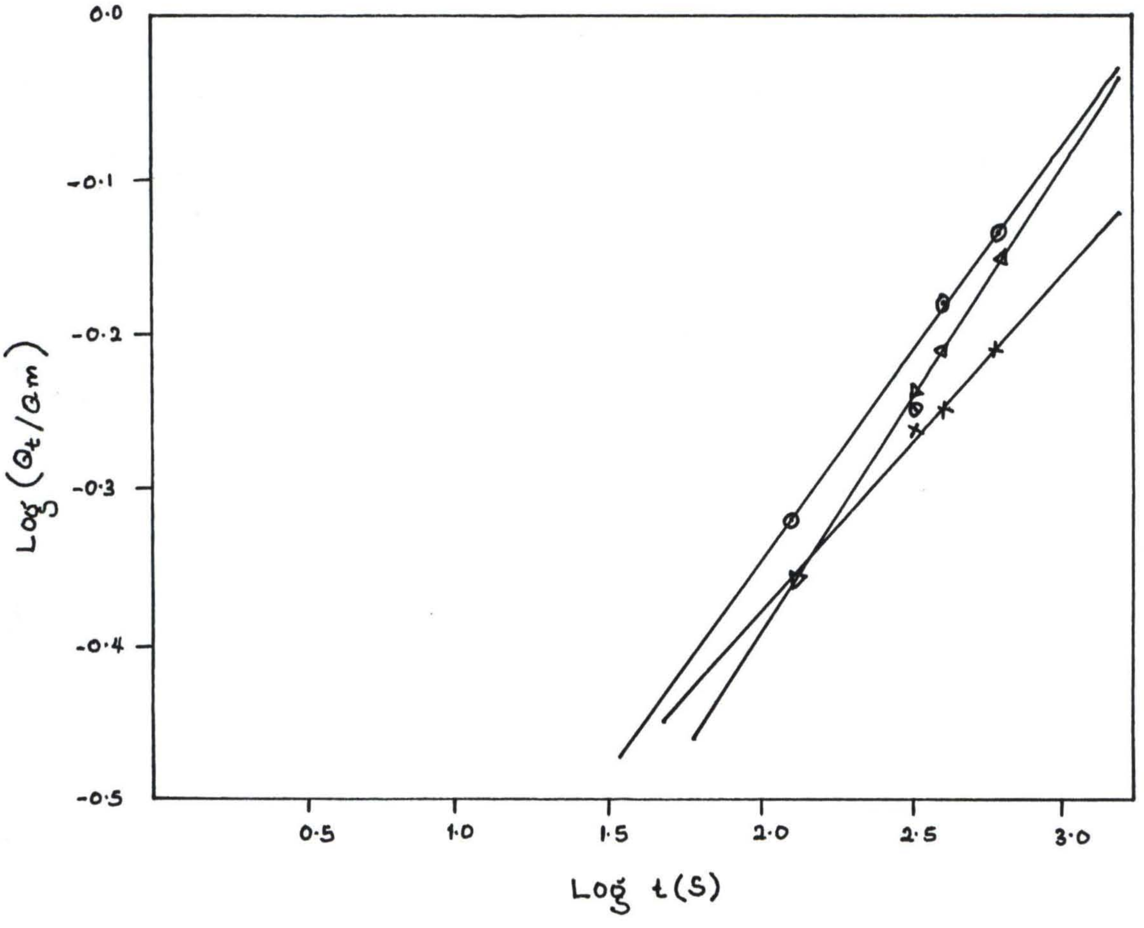


FIG. 27: GRAPH OF LOG Qt/Q∞ Vs LOG t(S) FOR TREATED PP AT 60°C, (⊙) BENZENE, (×) CHLOROFORM & (Δ) n-HEXANE

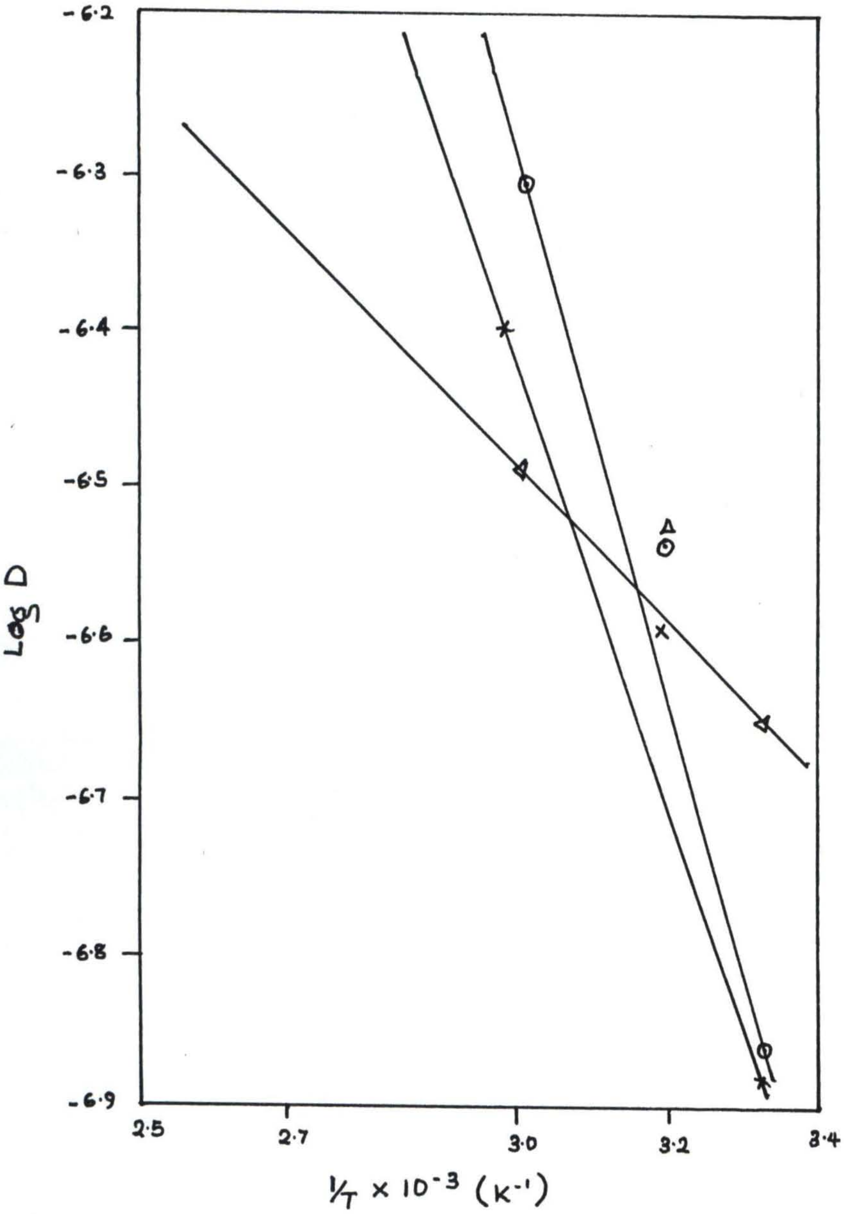


FIG. 28: GRAPH OF LOG D Vs 1/T (K⁻¹) OF PP IN (⊙) BENZENE, (Δ) n-HEXANE & (×) CHLOROFORM

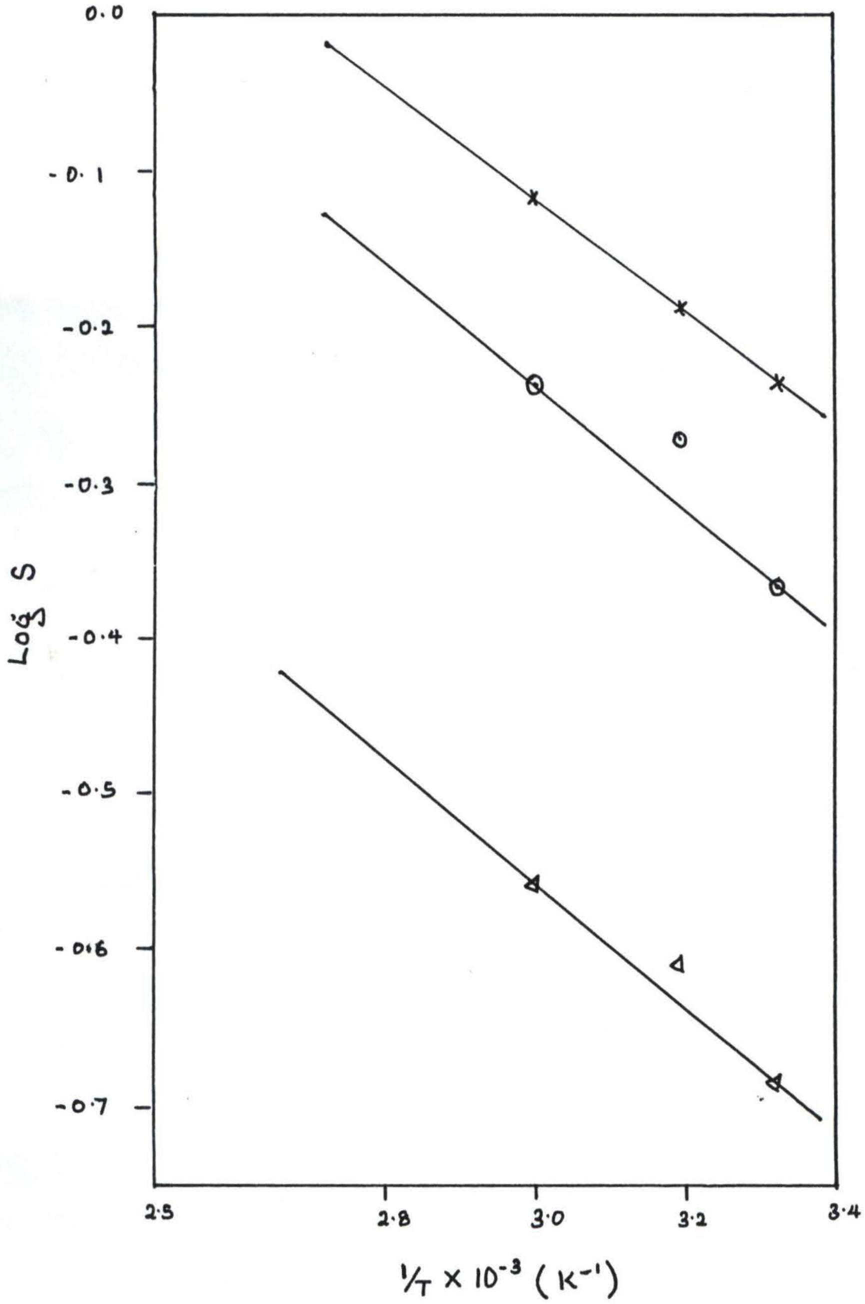


FIG. 29: GRAPH OF LOG S Vs 1/T (K^{-1}) OF PP IN (⊙) BENZENE, (×) CHLOROFORM, & (Δ) n- HEXANE (TREATED FILM)

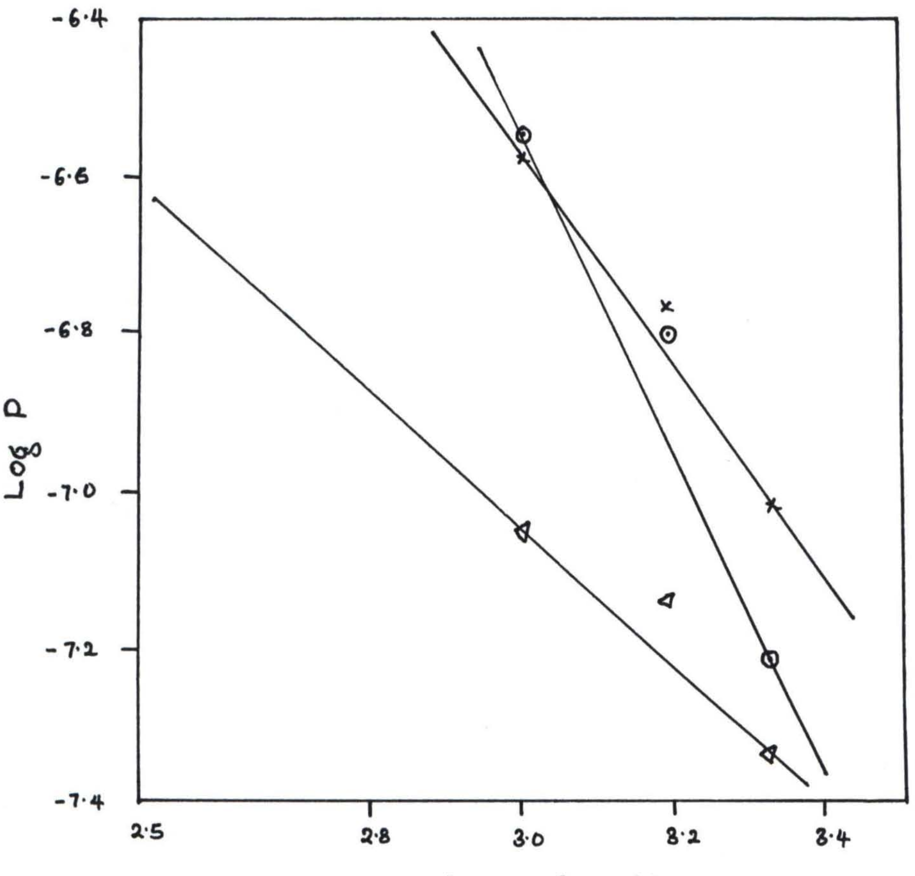


FIG. 30: GRAPH OF LOG P Vs 1/T (K⁻¹) OF PP (⊙) BENZENE, (x) CHLOROFORM & (Δ) n- HEXANE (TREATED FILM)

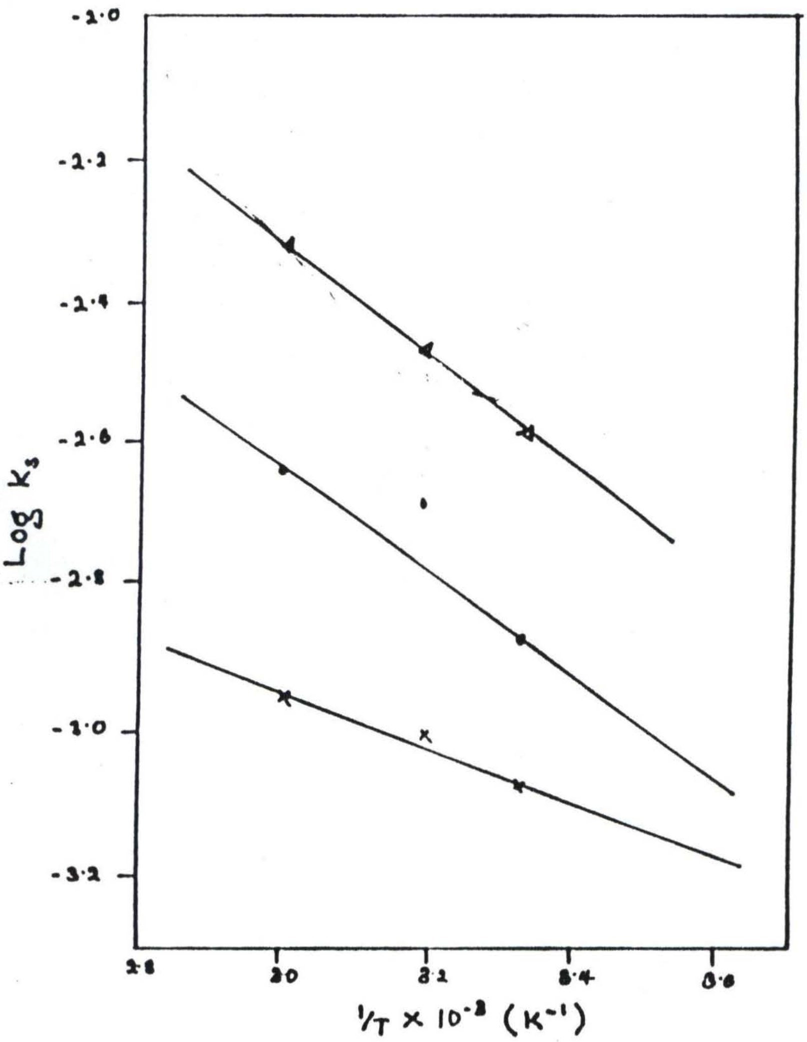


Fig 31 Graph of log ks aganst $\frac{1}{T}$ (K-1) of PP (O) benzene (x) chloroform and ( ) n-hexane (treated film).