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An experimental study of the diffusion of organic vapors in cellulose acetate films.

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AN EXPERIMENTAL STUDY OF THE DIFFUSION OF ORGANIC VAPORS IN CELLULOSE ACETATE FILMS

by

© Hussein Mahmoud Achkar

A Thesis
submitted to the
Faculty of Graduate Studies and Research
through the Department of
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of Master of Applied Science at
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ABSTRACT

AN EXPERIMENTAL STUDY OF THE DIFFUSION OF ORGANIC VAPORS IN CELLULOSE ACETATE FILMS

by

Hussein Mahmoud Achkar

The diffusion of methanol, ethanol, and benzene in cellulose acetate films at 25, 35 and 45°C has been investigated at different penetrant activity levels.

The sorption of the penetrants were generally found to be Fickian. Therefore, the sorption curves obtained in this study were utilized to obtain the integral (experimental) diffusion coefficients for the systems involved. The differential diffusivities were calculated from the integral values using the method reported by Crank (1979).

The dependence of the diffusion coefficients on concentration for the systems investigated has been determined. Also, diffusivities at zero penetrant concentration have been evaluated. These have been utilized to assess the effect of penetrant size and temperature on diffusivities.

The intrinsic and thermodynamic diffusion coefficients for the systems under investigation have been calculated and were found to change in an exponential manner with penetrant activity within the concentration range investigated in this work.

The predictions of free volume model suggested by

Wilken and Long (1957) appear to be in close agreement with the experimental results obtained in this study.

DEDICATION

TO MY PARENTS

ACKNOWLEDGEMENTS

Primarily, I wish to declare my honest gratitude to ALMIGHTY GOD for His help, inspiration and guidance.

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At last, but by no means least, I feel very grateful to my parents for their invaluable sacrifices and encouragements.

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Chapter I

INTRODUCTION

1.1 General

Diffusion is a process by which matter is transported from one point to another under a concentration gradient. Fick's first law has usually been employed for describing steady state diffusion. It is given by the following expression for one dimensional diffusion:

$$J_A^c = -D_F \frac{dC_A}{dx} \qquad (1.1)$$

where, J_A^c is the flux of component A in a coordinate fixed frame of reference, C_A is the concentration of the diffusing species, x is the space coordinate, and D_F is a proportionality constant which is known as the Fickian diffusion coefficient.

Unsteady state diffusion in one dimension, can be described by Fick's second law, which is given by:

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2} \qquad (1.2)$$

where $\partial C_A/\partial t$ is the rate of change of concentration of the diffusing species.

Diffusion in polymers is a process by which matter is transported from one part of a piece of polymer to another part. Van Amerongen (1965) pointed out that this subject is important because polymers are always used in contact with foreign molecules which may be gases, liquids, or solids, which can diffuse into it. This starts with the processes for the manufacture of polymers which often involve diffusion of reactants or products to or from the site of the polymerization reaction. The absorption of larger quantities of liquids and gases is highly undesirable as it may lead to weakening or even disintegration of the polymer. Many technical applications of polymers are based on their property of being a medium for diffusion of foreign molecules.

Furthermore, diffusion in polymers is of interest to chemical engineers because thin polymer membranes may be employed in separation processes. The separation processes include hydrocarbon separation, dialysis, reverse osmosis, and blood oxygenators.

Diffusion of water vapor and solvents in general, presents problems in the manufacture of commercial polymers and the spinning of these to produce textile fibers.

The wide use of plastic films for packaging has created the need for measuring vapor transfer rates through these polymeric films. The packaging industry requires low vapor and liquid permeability in the polymeric films used to package food.

A special subject which is closely connected with diffusion and solubility is permeation. This process is concerned with the crossing by foreign molecules of a polymer membrane that separates two reservoirs containing these foreign molecules at different concentrations or pressures. The main qualitative features concerning permeation of the movement (diffusion) of gases through polymer membranes were described in the classic paper of Graham published in 1866. The process was described as the condensation and solution of gas at one surface of the membrane film followed by diffusion through in the form of a liquid, to the other face of lower concentration where finally, they evaporate to the gaseous state or are extracted (desorbed). Accordingly, the process of permeation is divided into several independent processes, those of solution and evaporation being governed by Henry's law and that of diffusion by the diffusion equation (Fick's law).

1.2 Terminology

Mutual diffusion coefficient, D_{AB}

The behaviour of a system consisting of two components A and B interdiffusing into each other, satisfying the condition of zero volume change on mixing, may be described in terms of a single diffusion coefficient. This coefficient has been termed the mutual diffusion coefficient.

Integral Diffusion Coefficient, $\overline{D}$

The integral diffusivity can be considered as some mean value of the diffusion coefficient for the concentration range over which diffusion takes place.

Differential Diffusion Coefficient, D

The differential diffusivity can be considered as the instantaneous value of the diffusion coefficient at a certain concentration.

Fickian Diffusion Coefficient, D_F

It is the kind of diffusivity which is associated with the process of diffusion of a penetrant gas in a polymeric film when such a process is governed by Fick's law. The characteristics of the Fickian diffusion curves are:

i) the sorption curves are linear in the initial stage. The linear region extends over 60% or more of M_∞ where M_∞ is the amount of vapor absorbed per gram of dry polymer until the sorption equilibrium is reached,

ii) above the linear portions, the sorption curves are concave to the abscissa.

1.3 Objectives

The objectives of this work are to:

i) Design and build a computer-controlled vapor-sorption experimental set-up, and

ii) Measure the diffusion coefficients of methanol, ethanol, and benzene in cellulose acetate films at different penetrant activity levels and at 25, 35, and 45°C.

1.4 Significance

The results obtained in this project are expected to contribute to the data base required for obtaining a generalized correlation for the dependence of distribution coefficients on concentration. Such a correlation is needed for designing pervaporation modules.

Chapter II

LITERATURE SURVEY

2.1 General

The earliest studies on the transport of gases and vapors in polymeric membranes were concerned with natural polymers. Stannette (1978) reviewed briefly some of these studies.

The first observations were apparently those of Thomas Graham in 1829. He observed that a wet bladder inflates to the bursting point when placed in an atmosphere of carbon dioxide.

In 1831 a systematic study of the rates of permeation of ten different gases through natural rubber was reported by Mitchell. The rate of collapse of small rubber balloons in air when filled with each gas was used as the method of measurement. The rates of permeation were found to vary by one hundredfold with carbon monoxide being the slowest and ammonia the most rapid. Mitchell also observed that natural rubber absorbed its own volume of carbon dioxide and correctly associated this high solubility with its high permeation rate.

Graham (1866) published a paper which truly laid the foundations for today's membrane science and technology. Graham devised and tested a permeability rate measuring device using flat membranes with a vacuum on one side. Graham also postulated the mechanism of the permeation process as the solution of the gas in the upstream surface of the membrane, diffusion through the membrane, followed by evaporation from the downstream membrane surface. This is the basis for the so called "solution-diffusion" model which is used in various forms and modifications in the handling of most membrane problems today. Other observations which are still useful and tenable today are that the more easily condensed and the more soluble in water and other liquids a gas is, the more it is soluble in rubber and the more rapidly it permeates. Graham pointed out that the permeability increased with increasing temperature even though the solubility decreased. This increase was attributed to the increasing softness and more liquid nature of the rubber at higher temperatures, thus facilitating the permeation process.

Fick (1855) had proposed his law of diffusion by analogy with Fourier's law of heat conduction.

Exner (1875) and Stefan (1878) showed experimentally that the permeation of gases through soap films was proportional to the product of the solubility of the gas in water and the Fickian diffusion coefficient. These results were extended and applied to rubber by Von Wroblewski in 1879.

Kayser (1891) provided further support for the solution-diffusion theory by demonstrating the validity of Henry's law for the absorption of carbon dioxide by rubber over a wide range of pressures and temperatures.

A series of studies performed between 1917 and 1920 by Shakespear supported Graham's observations. Shakespear also found that the temperature dependence of the gas permeability was independent of the pressure difference across the membrane.

Edwards (1918) found a highly non-linear effect of temperature on measured permeabilities of hydrogen in rubbers. He also measured or estimated errors due to sorption of water vapor in the membrane, evolution of volatile substances in the membrane, and effects of gas flow rate across the membrane surface.

Dewar (1930) measured the permeabilities of several gases in rubbers over a range of temperatures, and found that a plot of the logarithm of the pressure (P) of the penetrant, versus the temperature (T) for a given gas consisted of two straight lines which intersected at 0°C. He attributed the discontinuity to the presence of water in the membranes.

Barrer (1939) demonstrated that the permeabilities and diffusivities follow an Arrhenius type equation.

Desultory (1948) studied in detail gases, gelatin and some cellulose films. In addition, some organic vapors and water vapor studies were made with these polymers and with rubber, but fundamental advances with these penetrants began after this period.

Mandelkern and Long (1949) conducted a detailed study of the take-up of vapors of methylene chloride and acetone by films of cellulose acetate as a function of vapor pressure, film thickness, and temperature. In their study, the previously suspected complexity of the sorption mechanism for cellulose acetate was confirmed. They reported an inversion in slope of the take-up time curves in such a way that sometimes an increase of the temperature results in a lower diffusion rate, which is unexpected. These investigators failed to give any explanation for such unexpected behaviour.

Prager and Long (1951) reported the diffusion coefficients of six hydrocarbons (propane, n-butane, isobutane, n-pentane, iso-pentane and neopentane) in polyisobutylene from sorption data at 35°C. The investigators found that all the diffusion coefficients increase exponentially with increasing concentration of the hydrocarbon in the polymer. Furthermore, they found that an increase in both the degree of branching and the size of the diffusing molecules lowers the diffusion coefficient. The degree of branching was found to have a much greater effect on the diffusion coefficient than does molecular size. The results were accounted for on the basis of Eyring's "hole" theory of diffusion. According to this theory, there are in any solid a number of holes, arising from thermal fluctuations; diffusion takes place by a molecule leaving its current position and jumping into one of these holes.

Wilkens and Long (1957) reported a model for the diffusion of small molecules. An assumption was made that diffusion takes place in polymers only when local configurations of high free volume occur. It was proposed that the rate of diffusion is directly proportional to the probability of the occurrence of these local configurations. A model which shows the dependence of the diffusion coefficient on the volume fraction of the penetrant was derived. The model proposed agreed with the experimental results for diffusion of organic vapors into polymers.

Rogers et al. (1960) investigated the diffusion and penetration of several organic vapors in polyethylenes over wide ranges of vapor pressures. The integral diffusion coefficients were estimated. The integral diffusion coefficients were found to be exponential functions of vapor pressures.

Newns (1963) used the sorption technique to study the diffusion of benzene in polymethyl acrylate at 25, 35, and 45°C, and for different concentrations of benzene. He reported that the diffusion coefficient increased rapidly and approximately exponentially with the concentration of benzene. The activation energy for diffusion was found to decrease with increasing benzene concentration.

Kishimoto and Matsumoto (1964) studied the absorption and desorption of organic vapors in polymers in a wide temperature range, as a function of film thickness. The systems chosen for this study were polyvinyl acetate (PVAc)/allychloride at 40°C and polymethyl acrylate(PMA)/methyl acetate at 15 and 35°C. The absorption curves for different film thicknesses at relatively high penetrant concentrations were apparently normal, but the initial slopes of the plots increased with increasing film thickness (ℓ). The investigators found that these processes are controlled by a purely Fickian diffusion mechanism.

Schneider et al. (1968) carried out sorption measurements of water vapor over the temperature range 27-40°C on a polyurethane polymer film. The results presented in their paper serve to clarify the nature of the water vapor transport process in polyurethane. The mutual diffusion coefficient was determined from the initial slope of M_t/M_∞ versus $t^{1/2}$, where M_t and M_∞ are the weight increases at time t and at equilibrium, respectively.

Prosser (1970) reported an experimental technique for the simultaneous determination of the amount of vapor absorbed and desorbed by a polyethylene terephthalate film (Mylar film). For Mylar film at 40°C, it was found that the amount of water vapor absorbed was about 10^{-7} g/cm^2. Prosser found that sorption plots of M_t/M_∞ versus ($t^{1/2}$) using water vapor as the penetrant do not rise linearly from the origin as they should, but generally intercept the abscissa on the positive side giving the impression that there is a short time lag before the start of sorption. This delay is usually attributed to the time required for the admission of the water vapor and to the fact that the amount adsorbed is not negligible compared with the amount adsorbed.

Dollimore and Holt (1973) examined the rates of sorption of water vapor and of methanol vapor in cellulose films by stepwise increments of vapor pressure. In addition, the rates of sorption of the series of vapors (water, methanol, ethanol, n-propanol, and n-butanol) were studied at different pressures. The investigators confirmed the idea that the diffusion of water vapor and the vapors of organic solvents by cellulose is non-Fickian.

Berens et al. (1974-1982) conducted comprehensive investigations of the sorption of vinyl chloride monomer (VCM) vapor by polyvinyl chloride (PVC). Berens' studies initially were undertaken to help design processes for removing residual monomer from the polymer. The sorption process appears to consist of two stages:

i) Relatively rapid attainment of diffusion equilibrium, and
ii) Much slower relaxation to equilibrium.

The gravimetric sorption-rate data for vinyl chloride in PVC powders were found to obey the Fickian model over limited ranges of vinyl chloride pressure increments. The main difference between Berens' work and this work is that this work deals with polymeric films rather than polymer powders. The mathematical treatment is completely different.

Felder (1977) pointed out that experimental methods for studying the transport of vapors in polymers may be divided into three categories: integral permeation rate measurement, in which the cumulative amount of a penetrant that has passed through a membrane is determined; differential permeation rate measurement, in which the rate of penetration through a membrane is measured instantaneously, and sorption rate measurement, or determination of the cumulative amount of penetrant absorbed in a polymer sample. In his paper, Felder reviewed commonly used techniques for estimating diffusion coefficients from transport data of all three types. Several new estimation formulae were postulated, and the merits of different measurements were discussed.

Hopfenberg (1978) realized the effect of a characteristic dimension of a polymeric specimen on the kinetic mechanism controlling unidirectional absorption of organic vapors and liquids in polymers. He showed that effect by comparing n-alkanes absorption experiments in films, microspheres, spheres, and sheets of polystyrene. It was found that absorption in submicron micorspheres is controlled by Fickian diffusion where, under otherwise identical boundary conditions, films (75 μm thick) and spheres (184 μm in diameter) sorb according to non-Fickian diffusion absorption kinetics. Thinner films (35 μm thick) sorb by super non-Fickian diffusion kinetics, and relatively thick sheets (2000 μm thick) sorb initially by non-Fickian diffusion kinetics.

Roussis (1981a, 1981b, 1983) investigated the concentration dependence of the diffusion coefficient of water in cellulose acetate. Aspects of the non-Fickian behaviour of the system were reported and the data were treated in alternative ways. Roussis also investigated the mechanism of sorption of water vapor in polymethyl methacrylate (PMMA). Typical non-Fickian features were discerned in differential absorption kinetics on membranes of different thicknesses.

Saxena and Stern (1982) investigated the sorption and transport of acetone, benzene, and methanol vapors in ethyl cellulose which have been studied previously by Barrer, Barrie and Slater (1957a, 1957b) over a range of temperatures and penetrant concentrations. The sorption curves for the three penetrants as well as the diffusivity and permeability data for acetone reported by these investigators were analyzed in terms of the "solution-diffusion" model, assuming that the diffusion coefficient is concentration dependent. These investigators gave comprehensive clarification of the "solution-diffusion" model which is called dual-sorption model. The model postulates that a gas dissolves in a polymer by two simultaneous mechanisms. These are:

i) Ordinary dissolution, and

ii) Diffusion in pre-existing cavities or holes in the polymer matrix.

Stannett et al. (1982) reported permeabilities and sorption/desorption kinetics for water vapor in polyacrylonitrile (PAN) films. A wide range of vapor pressures was studied at 15, 30 and 45°C. Permeation behaviour at low and intermediate upstream vapor pressures suggested that Fickian transport occurred under most of the conditions studied. Integral sorption/desorption kinetics at low and intermediate vapor pressures also appeared to be Fickian with a concentration-dependent diffusion coefficient. Deviations from Fickian behaviour may occur during permeation at high penetrant concentrations.

Odani et al. (1983) studied the diffusion behaviour of methanol vapor into two copolymer films: poly(2 vinylpyridine) polyisoprene and poly(2 vinylpyridene)/polystyrene, at 25°C. The rate of absorption or desorption of methanol was measured gravimetrically. A quartz spring balance was used for this purpose. For both copolymer systems, absorption and desorption processes of non-Fickian type were observed. However, the magnitude of the deviations from purely Fickian behaviour was small, and the integral diffusion coefficient, $\overline{D}$, was obtained with reasonable accuracy. At low and medium concentrations, $\overline{D}$, for methanol in poly(2 vinylpyridine)/ polyisoprene was greater than that for poly(2 vinylpyridine) polymer; on the contrary, $\overline{D}$, for methanol in poly(2 vinylpyridine)/polystyrene copolymer was lower than that for poly(2 vinylpyridine). The authors tried to explain this diffusion behaviour by comparing the size of a methanol molecule with the size of the repeating unit of the copolymers studied.

2.2 Factors Influencing the Diffusion of Liquids and Gases in Polymers

Extensive studies of diffusion of organic penetrants in polymers and the factors influencing diffusion of liquids and gases in polymer solids such as penetrant concentration, temperature, and the type of penetrant molecules have been made, by several research groups. A brief account on these factors is in order:.

2.2.1 Effect of penetrant concentration

The effect of concentration on diffusion coefficients has been investigated on a number of penetrant-polymer systems. It was observed that diffusion coefficients for penetrant gases in polymers are essentially independent of concentration. This can be attributed to the low solubility of gases in polymers. The diffusivity of vapors and liquids were found to vary strongly with concentration. Natural rubber and polyisobutylene have been subjected to extensive vapor diffusion measurements by several investigators, e.g., Hayers and Park (1955); Aitken and Barrer (1955), Barrer and Ferguster (1950)..

King (1945); Hartley (1946); Robinson (1950); Kishimoto and Enda (1963); found that at low concentrations, the diffusion coefficient of liquids and vapors often increases considerably with concentration. Furthermore, Park (1950, 1951); Prager and Long (1951); Kokes et al. (1952); Kokes and Long (1953) and Prager et al. (1953); found that for a number of systems, diffusion coefficients increase exponentially with concentration.

2.2.2 Effect of temperature

Barrer and Skirrow (1948); Van Amerongen (1950); Kokes and Long (1953); Hayes and Park (1955); Fujita et al. (1960) showed that for many systems, the temperature dependence of the diffusion coefficients for limited ranges of temperature may be represented by the Arrhenius type of equation:

$$D = D^{o} e^{-E_d/RT}$$

where D^{o} is a constant; E_d is the activation energy of diffusion, R is the universal gas constant, and T is the absolute temperature. Measurements made over extended ranges of temperature have shown that E_d decreases as the temperature increases for a number of systems.

2.2.3 Effect of the penetrant molecular size

Park (1950) reported that the diffusion coefficient for the system halomethane-polystyrene, varied experimentally with the size of the penetrant molecule.

Prager and Long (1951) and Prager et al. (1953), pointed out that for the diffusion of hydrocarbons in polyisobutene, the branching of the hydrocarbon chain was more important than the molecular size of the penetrant used.

Chapter III

THEORY

The mathematical theory of diffusion is based on the hypothesis that the rate of transfer of a diffusing substance is proportional to the concentration gradient. For one dimensional diffusion we have:

$$J_A^C = -D \frac{dC_A}{dx} \tag{3.1}$$

where J_A^C is the rate of transfer per unit area in the co-ordinate fixed frame of reference, C_A is the concentration of the diffusing substance A, x is the space coordinate, and D is called the diffusion coefficient (which has dimensions length ^{2} time^{-1}).

Considering the mass balance around an element of volume, $\Delta x \Delta y \Delta z$, it is easy to show that the fundamental differential equation of diffusion takes the form:

$$\frac{\partial C_A}{\partial t} = D\left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right) \tag{3.2}$$

provided D is constant. In many polymer systems, D depends markedly on the concentration. Consequently, Equation (3.2) becomes:

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C_A}{\partial x}\right) + \frac{\partial}{\partial y}\left(D \frac{\partial C_A}{\partial y}\right) + \frac{\partial}{\partial z}\left(D \frac{\partial C_A}{\partial z}\right) \tag{3.3}$$

where D may be a function of x, y, z and C_A. Frequently, diffusion occurs effectively in one direction only, e.g., there is a gradient of concentration only along the x-axis; in such cases Equations (3.2) and (3.3) reduce respectively, to:

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2} \tag{3.4}$$

and

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C_A}{\partial x}\right) \tag{3.5}$$

Equations (3.1) and (3.4) are commonly referred to as Fick's first and second laws of diffusion, respectively. The film is kept at a constant concentration, C_{A_o}, the initial concentration being zero throughout the film. The following initial and boundary conditions apply:

$C_A = 0, \quad x > 0, \quad t = 0$ I.C.

$C_A = C_{A_o}, \quad x = 0, \quad t > 0,$ B.C.

C_A remains finite as x becomes very large B.C.

Multiplying both sides of Equation (3.4) by e^{-st} and integrating with respect to t from 0 to ∞, it follows that:

$$\int_0^\infty e^{-st} \frac{\partial^2 C_A}{\partial x^2} dt - \frac{1}{D} \int_0^\infty e^{-st} \frac{\partial C_A}{\partial t} dt = 0 \qquad (3.6)$$

Interchanging the orders of differentiation and integration, it can be shown that:

$$\int_0^\infty e^{-st} \frac{\partial^2 C_A}{\partial x^2} dt = \frac{\partial^2}{\partial x^2} \int_0^\infty C_A e^{-st} dt = \frac{\partial^2 \overline{C}_A}{\partial x^2} \qquad (3.7)$$

where

$$\overline{C}_A = \int_0^\infty C_A e^{-st} dt \qquad (3.8)$$

$\overline{C}_A$ is the Laplace transform of C_A.

Integrating by parts the second term in Equation (3.6):

$$\int_0^\infty e^{-st} \frac{\partial C_A}{\partial t} dt = [C_A e^{-st}]_0^\infty + s \int_0^\infty C_A e^{-st} dt = s\overline{C}_A \qquad (3.9)$$

since the term in the square brackets vanishes at t=0 by virtue of the initial condition stated above, and at t=∞ through the exponential factor. Thus, Equation (3.4) reduces to:

$$D \frac{d^2 \overline{C}_A}{dx^2} = s\, \overline{C}_A \qquad (3.10)$$

The solution of Equation (3.10) is:

$$\overline{C}_A = M\, e^{qx} + N\, e^{-qx} \qquad (3.11)$$

where M and N are constants and $q^2 = \frac{s}{D}$.

On using the boundary conditions stated earlier, one obtains:

$$\overline{C}_A = \frac{C_{A_o}}{s} e^{-qs} \tag{3.12}$$

where we have used the relationship:

$$\overline{C}_A = \int_o^\infty C_{A_o} e^{-st} dt = \frac{C_{A_o}}{s} \tag{3.13}$$

Taking the inverse Laplace transform of Equation (3.12) gives:

$$C_A = C_{A_o} \text{ erfc } \frac{x}{2\sqrt{Dt}} \tag{3.14}$$

where erfc Z = 1 - erf Z.

Using Equation (3.14), one determines:

$$\left(\frac{dC_A}{dx}\right)_t = C_{A_o} \left(\frac{\text{derfc } \frac{x}{2\sqrt{Dt}}}{dx}\right) \tag{3.15}$$

$$\left(\frac{dC_A}{dx}\right)_t = C_{A_o} \frac{1}{2\sqrt{Dt}} \left(\frac{\text{derfc } \frac{x}{2\sqrt{Dt}}}{d\, \frac{x}{2\sqrt{Dt}}}\right) \tag{3.16}$$

Since

$$\text{erfc}\,\frac{x}{2\sqrt{Dt}} = 1 - \int_{0}^{\frac{x}{2\sqrt{Dt}}} \frac{2}{\sqrt{\pi}}\, e^{-\eta^2}\, d\eta = 1 - E \tag{3.17}$$

where E is the normal error function. Hence:

$$\frac{d\,\text{erfc}\,\frac{x}{2\sqrt{Dt}}}{d\,\frac{x}{2\sqrt{Dt}}} = \frac{-2}{\sqrt{\pi}}\, e^{-\frac{x^2}{4Dt}} \tag{3.18}$$

it follows that:

$$\left(\frac{dC_A}{dx}\right)_t = -\, C_{A_o}\, \frac{1}{\sqrt{\pi Dt}}\, e^{-\frac{x^2}{4Dt}} \tag{3.19}$$

Now, at x=0

$$\left(\frac{dC_A}{dx}\right)_t\Bigg|_{x=0} = -\, C_{A_o}\, \frac{1}{\sqrt{\pi Dt}} \tag{3.20}$$

Thus,

$$J = -\, D\left(\frac{dC_A}{dx}\right)_t = D\, C_{A_o}\, \frac{1}{\sqrt{\pi Dt}} \tag{3.21}$$

Now, 1/2 M_t, the mass of penetrant vapor absorbed through one boundary by the polymer sheet at time t, is given by:

$$\frac{1}{2} M_t = A \int_0^t J dt = A \frac{DC_{A_o}}{\sqrt{\pi D}} 2\sqrt{t} = 2AC_{A_o} \sqrt{\frac{Dt}{\pi}} \qquad (3.22)$$

where A is the surface area of the polymer film.

For a finite sheet of thickness ℓ, the total mass of vapor absorbed by one side of the polymer film at infinite time is given by:

$$\frac{1}{2} M_\infty = A\ C_o \frac{\ell}{2} \qquad (3.23)$$

Hence,

$$\frac{M_t}{M_\infty} = \frac{4}{\ell} \sqrt{\frac{Dt}{\pi}} \qquad (3.24)$$

where D is the integral diffusivity.

In this experimental work, Equation (3.24) has been utilized in the following way:

i) Measurements of the uptake of penetrant vapor at equal intervals of the square root of time are taken.

ii) For every sorption experiment, a plot of M_t/M_∞ vs. $t^{1/2}$ is prepared. The slope of the straight line portion of the curve is $\frac{4}{\ell}\sqrt{\frac{D}{\pi}}$, from which the diffusivity can be calculated.

Chapter IV

EXPERIMENTAL

4.1 General

The simplest method for studying sorption involves direct weighing of the polymer under investigation. A specimen of known shape and size is kept in an atmosphere of constant penetrant vapor pressure and is withdrawn and weighed from time to time. The kinetics of sorption and desorption of water vapor by several materials has been investigated using this method (e.g., A. Kovacs, 1948). However, there has been little application to organic vapors, except for some studies by Crank and Park (1949) and by Park in (1950, 1951) of diffusion in polystyrene. In this simple technique, the errors due to the presence of an air barrier can be large in the more rapid experiments and the interruption of the sorption process at each weighing results in erroneous measurements.

These errors can be overcome by measuring the polymer mass directly by suspension from a quartz spring (Mac Bain and Baker, 1926; King, 1945; Prager and Long, 1951). The errors due to air barrier can be reduced by using vacuum methods.

4.2 Description of Experimental Set-Up

The experimental set-up used in this study consists of a recording electrobalance (CAHN 2000) which was put in a glass vacuum-enclosure and mounted in a temperature controlled

Figure 4.1: Schematic Diagram of the Experimental Set-Up

EXPERIMENTAL SET-UP

Key

A	Electrobalance beam
B	Electrobalance vacuum bottle
C	Jacketed sample hangdown tube
D	Middle hangdown tube
E	Counter weight hangdown tube
F	Polymer film
G	Counter weight
H	Temperature controlled chamber
J	Thermometer
K	Thermocouple 1
L	Thermocouple 2
T1 T2 T3	Valves

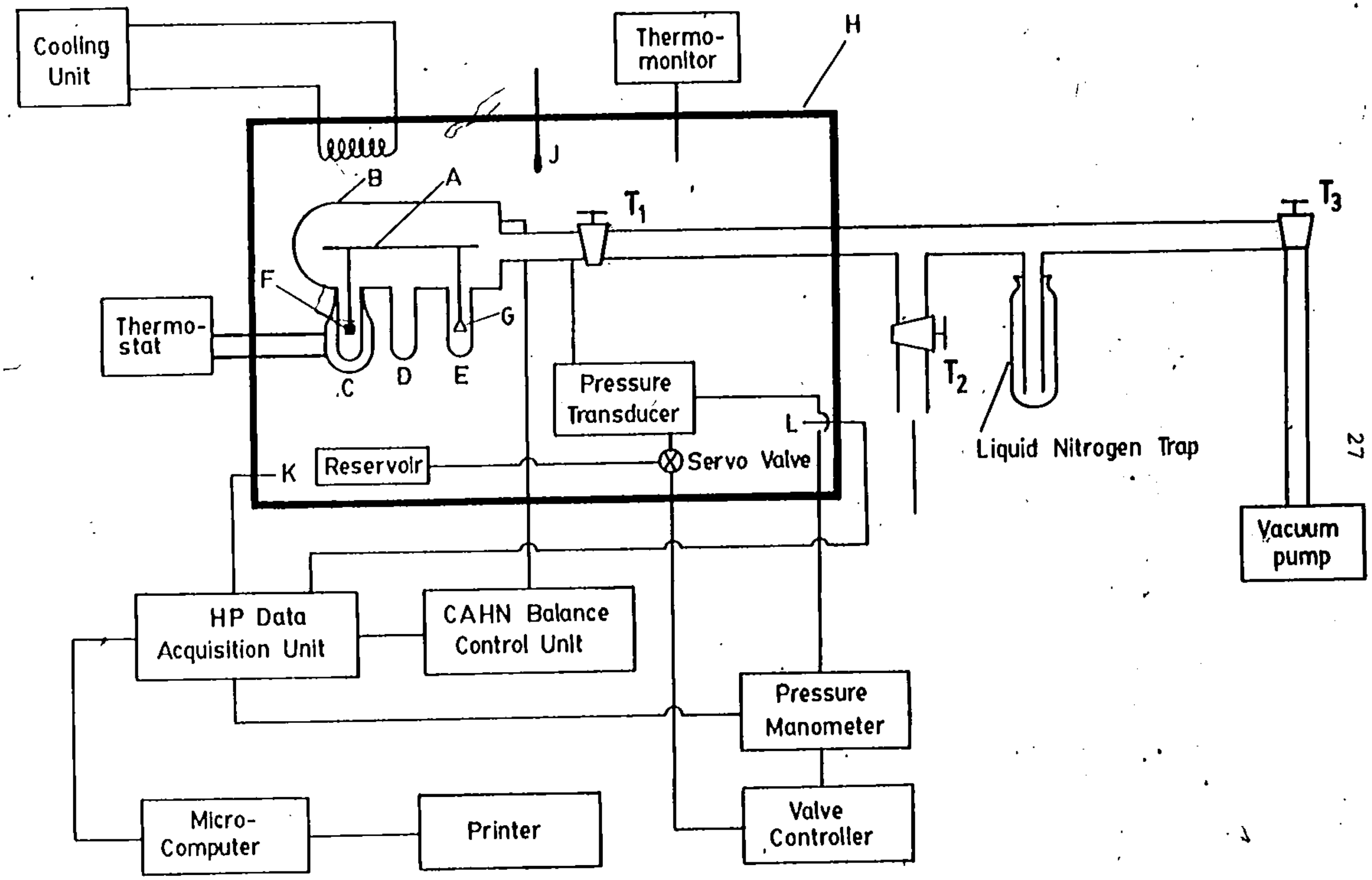

Figure 4.1 : A Schematic Diagram of the Experimental Set-up.

chamber (± 0.05°C) by a heating and cooling arrangement and a Sargent Welch temperature controller. The glass vacuum-enclosure of the balance is connected to a source of the penetrant vapor, and to a vacuum pump (Sargent Welch - Model 1400) which was used to evacuate the system overnight, and the pressure of the vacuum system was measured with a Datametrics Type 590 vacuum/pressure transducer and a type 1400 digital electronic manometer. In addition, the sample hangdown tube of the balance is fitted with a water jacket that kept the sample temperature fluctuations to within ± 0.02°C. Vapor at a certain pressure was admitted into the chamber using a Brooks servo-valve and Datametrics type 1404 servo valve controller for automatic pressure control. The take-up of vapor was monitored by a microcomputer interfaced to the CAHN electrobalance. The computer is programmed to take the balance's readings at equal time intervals. This represents a substantial improvement over previous designs because:

i) more accurate weight change readings can be obtained,

ii) more data points can be recorded during an experimental run,

iii) temperature control in this case is better than that in previously reported studies.

Figure 4.1 depicts a schematic diagram of the experimental set-up used in this study.

4.2.1 Materials

Cellulose acetate sheets of 0.025 mm thickness were employed in this study. The acetyl content of cellulose acetate is 39.8 ± 0.5%.

Gold label grade methanol, ethanol, and benzene were purchased from Aldrich Chemical Co. and were used without further purification.

4.2.2 Procedure

The following is a description of the experimental procedure adopted in this study.

i) The electrobalance was zeroed and calibrated at the start of each experiment.

ii) rectangular specimens of cellulose acetate (35x 16x 0.025 mm) with a hole at the top were cut and suspended on the hangdown of the balance.

iii) The temperature controller was set to the required temperature.

iv) The whole system was evacuated overnight, before any sorption experiment was begun.

v) The solvent to be used was degassed by repeated freezing and melting.

vi) The controller to the servo valve was set to the required pressure and put on (close) mode of operation.

vii) An auxilliary valve was used to help the servo valve stay active all the time, thus maintaining the pressure within ± 0.5 mmHg.

viii) The sampling time is specified to the computer program.

ix) The controller to the servo valve was then put on the (Automatic) mode of operation; and immediately the computer started taking data of the weight, pressure, and temperature according to the sampling time specified.

x) the vapor-sorption through the membrane was allowed to proceed for enough time to assure attainment of steady state.

Chapter V

RESULTS AND DISCUSSION

5.1 Description of the Sorption Processes in Cellulose Acetate

Using the experimental technique for integral sorption described earlier, measurements were taken for the uptake of penetrant vapors, viz.; methanol, ethanol, and benzene at different temperatures and pressures. Consequently, the gathered data have been used in preparing plots of M_t/M_∞ versus $t^{1/2}$. Where M_t is the mass of vapor taken up at time t, and M_∞ is the mass taken up at equilibrium. Data used in preparing such plots are contained in Appendix A. A family of curves of M_t/M_∞ versus $t^{1/2}$ have been drawn for each (polymer/penetrant) system at 25, 35, and 45°C and at different activity levels of the penetrant. These are depicted in Figures 5.1 to 5.3 for the systems investigated at 25°C.

The M_t/M_∞ versus $t^{1/2}$ graphs for the systems methanol-cellulose acetate and ethanol-cellulose acetate at 25°C are depicted in Figures 5.1 and 5.2, respectively. Figures for the same systems at 35°C and 45°C are given in Appendix B. All these plots indicate a Fickian behaviour. The initial parts of these curves are linear which enables one to determine the value of the diffusion coefficient as described earlier.

Some time lags have been observed in the case of the

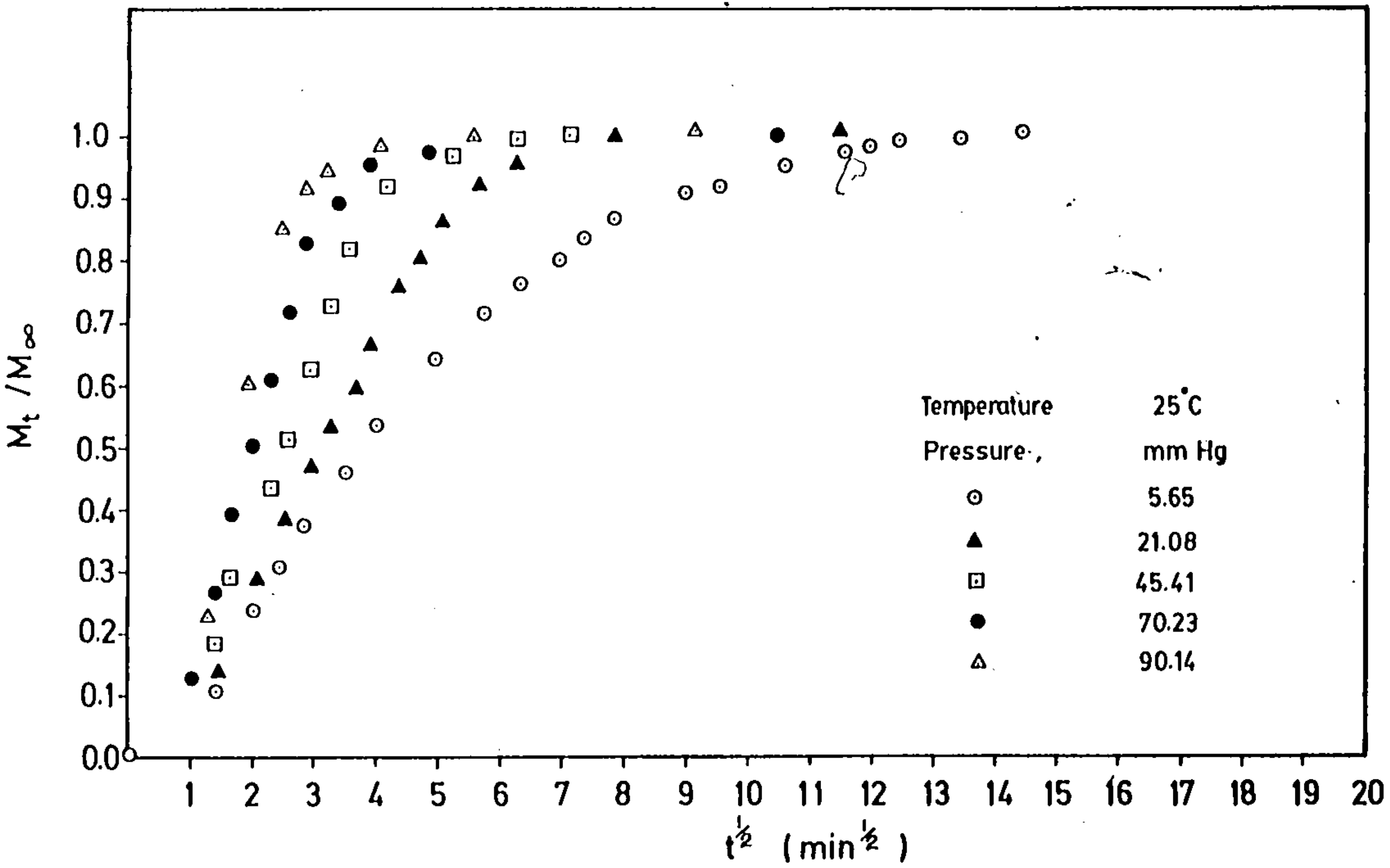

Figure 5.1 : Sorption of Methanol in Cellulose Acetate

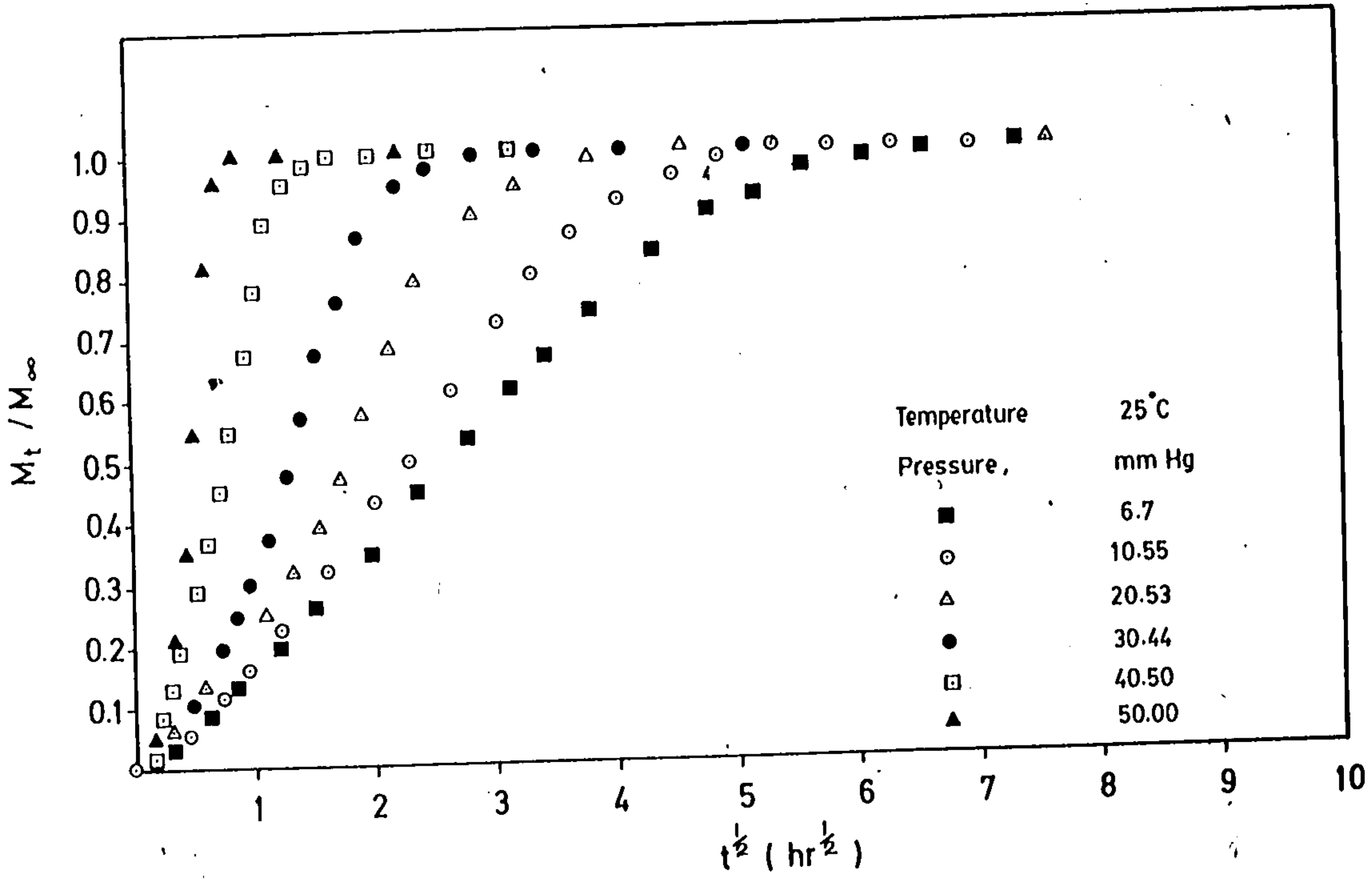

Figure 5.2 : Sorption of Ethanol in Cellulose Acetate

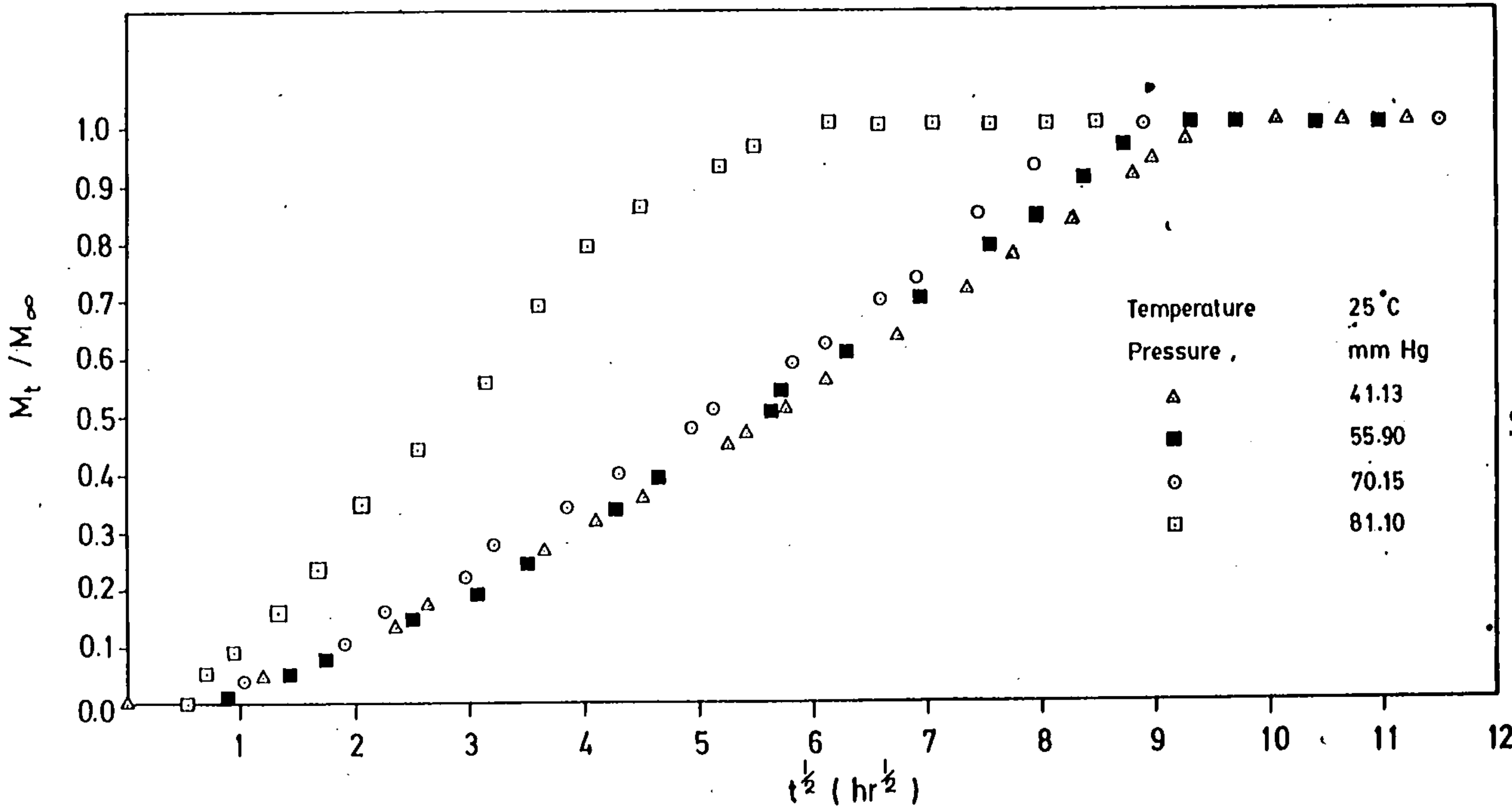

Figure 5.3 : Sorption of Benzene in Cellulose Acetate

cellulose acetate-benzene system before any observable vapor uptake takes place. These time lags become shorter when the temperature is increased probably because the polymer becomes less glassy.

Furthermore, these time lags become shorter as the operating pressures increase. This may be attributed to the increase of the activity of the penetrant vapor. Such a behaviour can be observed in Figure 5.3 which reports sorption data obtained at 25°C. Similar behaviour can be observed from inspecting benzene-cellulose acetate data at 35°C and 45°C, which are depicted in Figures B.5 and B.6 in Appendix B. However, it should be noted that the time lags become shorter as the temperature is increased.

Due to the physical limitations of the experimental set-up, the maximum vapor pressure which could be employed is 100 mmHg. Consequently, the work reported in this thesis has been carried out at very close penetrant activity levels, even when the temperature was raised to 45°C. On that basis, one can notice that the sorption curves obtained get closer to each other as the temperature is increased.

5.2 Calculation of the Integral Diffusion Coefficient, $\bar{D}$

As can be seen from Figures 5.1 to 5.3 and B.1 to B.6, the initial portion of each plot is linear, and the slopes of the plots increase steadily with increasing penetrant concentration. This indicates that the diffusion coefficient is concentration dependent.

For sorption in a plane sheet, the solution of the diffusion equation derived previously is given by:

$$D = \frac{\ell^2 \pi}{16} \left(\frac{M_t/M_\infty}{t^{1/2}} \right)^2 \qquad (5.1)$$

where D is the mutual diffusion coefficient as defined previously, and ℓ is the thickness of the polymer film.

Equation (5.1) has been derived for the case where D does not depend on concentration. When the diffusion coefficient is dependent upon concentration, Equation (5.1) yields some mean value, $\overline{D}$, of the variable diffusion coefficient averaged over the appropriate concentration range. $\overline{D}$ is called the integral (experimental) diffusivity.

5.3 Calculation of Differential Diffusivities, D, from Integral Diffusivity Values, $\overline{D}$

The differential diffusion coefficient, D, can be obtained from the integral diffusion coefficient, $\overline{D}$. The method adopted in this work is the one reported by Crank and Park (1979). The relation between the differential and integral diffusivity is given by:

$$\overline{D} = \int_{C_{n-1}}^{C_n} \frac{D dC}{(C_n - C_{n-1})} \qquad (5.2)$$

where C_{n-1} and C_n are the equilibrium concentrations at the start and at the end of the nth sorption interval. Now, it is possible to calculate an average diffusion coefficient which is defined by:

$$D_{av} = \frac{1}{C_i} \int_{o}^{C_i} DdC \qquad (5.3)$$

where C_i is the equilibrium concentration at the end of a sorption interval.

Equation (5.2) can be rewritten in the following way:

$$\int_{C_{n-1}}^{C_n} DdC = \overline{D}(\Delta C)_n \qquad (5.4)$$

using Equation (5.3) it is possible to write:

$$\int_{o}^{C_i} DdC = D_{av}C_i = \overline{D}_1(C_1-C_0)+\overline{D}_2(C_2-C_1)+\ldots+\overline{D}_i(C_i-C_{i-1})$$

$$= \Sigma\ \overline{D}_n(\Delta C)_n \qquad (5.5)$$

also from Equation (5.3) it follows that:

$$d(D_{av}C_i)/dC_i = D$$

It is possible to draw a graph of $\Sigma\ \overline{D}(\Delta C)_n$ versus C_i. Numerical or graphical differentiation of the curve with respect to C_i will give the relationship between D and C_i.

It is more convenient to plot ln $\Sigma\ \overline{D}(\Delta C)_n$ versus C_i. The slope of this plot gives $d[\int_{o}^{C_i} DdC]/dC_i$ at each value of C_i. The differential diffusivity, D, can then be obtained as a function of C. Detailed manual calculations of the differential diffusivities from the integral values are given in Appendix C for a cellulose acetate-ethanol

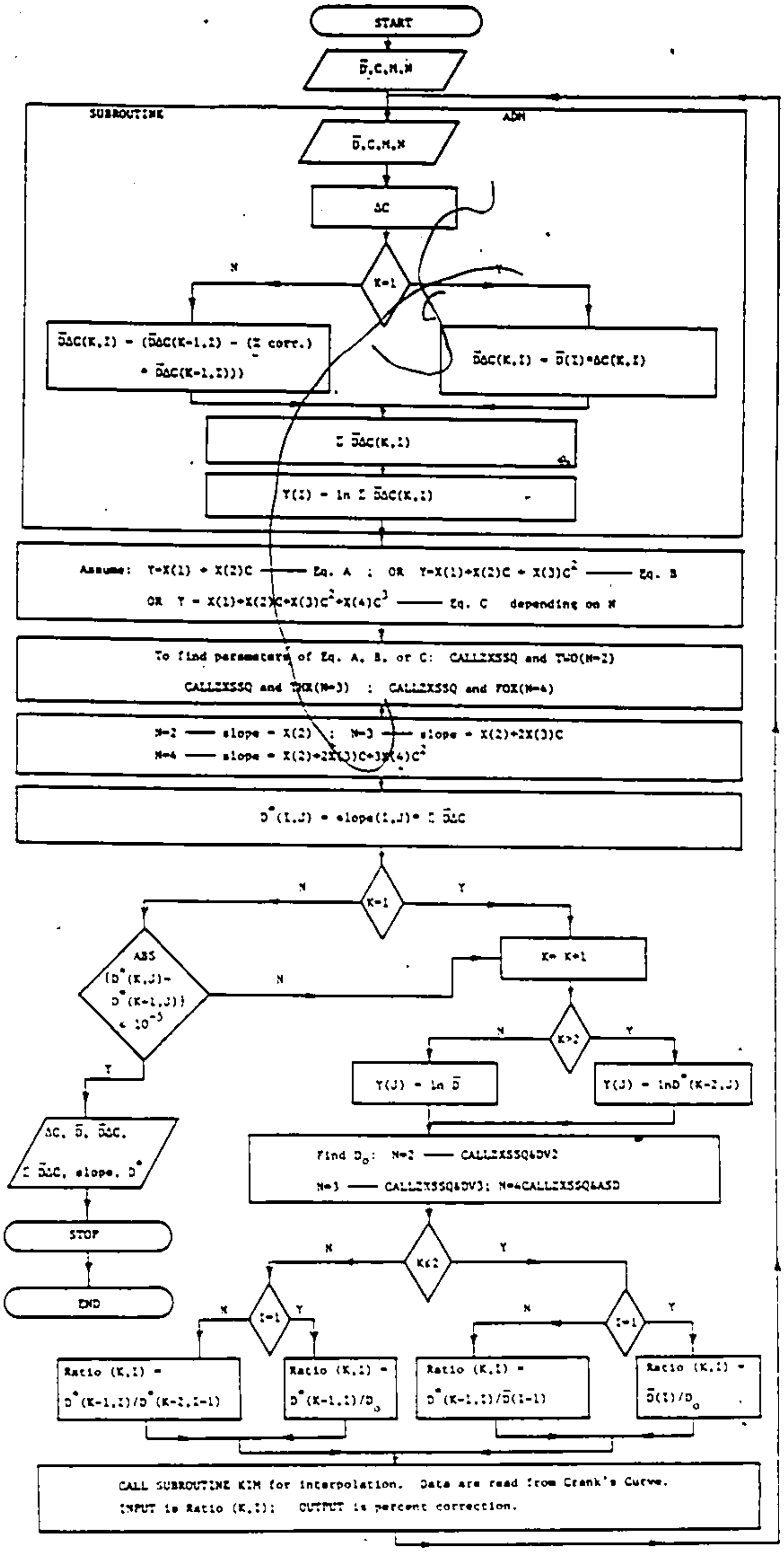

Figure 5.4: Flow Chart of the Computer Program Used to Calculate the Differential Diffusivities from the Integral Values.

system at 45°C.

The quantity $\overline{D}(C_n - C_{n-1})$ is only approximately equal to $\int_{C_{n-1}}^{C_n} D\,dC$. Crank (1956) has given corrections to this approximation for a range of values of $\overline{D}/D(C_s)$. Where, $D(C_s)$ is the value of D at the concentration C_s, at the beginning of the sorption interval.

$\overline{D}/D(C_s)$ can be calculated and used with Crank's correction graphs (Crank, 1956) to obtain better values for D. An example of the correction used to give the second approximation of D is given in Appendix C for a cellulose acetate-ethanol system at 45°C.

A computer program which serves to calculate the differential diffusivity, D, from integral values, $\overline{D}$, is also provided in Appendix D. A flow chart of the computer program is described in the next section and is shown in Figure 5.4. The results of the computer calculations for all the systems investigated are provided in Appendix E as well.

5.3.1 Description of the flow chart of the computer program used to calculate the differential diffusivities from the integral values

As mentioned earlier, a computer program has been prepared to calculate the differential diffusivities from the integral values. The following is a description of the flow chart given in Figure 5.4:

i) The input data include values of the integral (experimental) diffusivities, $\overline{D}$, and the corresponding concentrations, C. The number of the experimental data points (M) has to be provided.

ii) Subroutine ADM is called to perform the following calculations:

   a) Calculate ΔC.

   b) Calculate $\Sigma\ \overline{D}\Delta C$.

   c) Calculate $\ln\ \Sigma\ \overline{D}\Delta C$.

iii) The relation between $\ln\ \Sigma\ \overline{D}\Delta C$ (denoted by Y) and the concentration is assumed to be of the form:

$$Y = \alpha + \beta C + \gamma C^2 + \delta C^3 \qquad (5.6)$$

iv) The library subroutine ZXSSQ together with subroutine FOX are called to calculate the coefficients α, β, γ, and δ using the least squares technique.

v) Differentiation of Equation (5.6) with respect to C_i yields:

$$\frac{dY}{dC_i} = \beta + 2\gamma C + 3\delta C^2$$

vi) The differential diffusivity (denoted by D*) is then calculated as follows:

$$D^* = \left(\frac{dY}{dC_i} \right) * \Sigma\ \overline{D}\Delta C$$

vii) The value of the diffusivity at zero concentration, D_o, is calculated according to the following procedure:

a) For the first correction (K = 2) assign $Y = \ln \overline{D}$, otherwise $Y = \ln D^*$.

b) The library subroutines ZXSSQ and ASD are called to calculate the coefficients on the following equation:

$$Y = \theta + \psi C + \mu C^2 + \eta C^3$$

viii) The ratio $\overline{D}/D(C_s)$ is calculated. Where $D(C_s)$ is the value of D at the concentration, C_s, at the beginning of the sorption interval.

ix) Subroutine KIM is called. Input to KIM is the ratios $\overline{D}/D(C_s)$ and output is the percentage correction read from Crank's corrective curve (Crank, 1956) by interpolation. This percentage correction has to be subtracted from $\overline{D}\Delta C$ calculated earlier. Now, a corrected value of $\overline{D}\Delta C$ is obtained.

x) Repeat steps 2 to 6 to find the improved or corrected value of the differential diffusion coefficient (denoted by D**).

xi) Compare the first calculated value of the differential diffusivity (D*) with the corrected value (D**); if the two values within a specified tolerance, then the program prints all the value calculated and comes to a stop. Otherwsie, another iteration is needed, i.e. K = K+1 and proceed from step 7.

Table 5.1

Diffusivity–Concentration Data for the System Cellulose Acetate/Methanol

Concentration $\frac{\text{mg penetrant}}{\text{mg polymer}}$	Integral Diffusivity $\bar{D}$, cm^2/sec	Differential Diffusivity D, cm^2/sec
Temperature = 25°C		
0.146×10^{-1}	0.284×10^{-9}	0.1398×10^{-9}
0.336×10^{-1}	0.912×10^{-9}	0.7786×10^{-9}
0.588×10^{-1}	0.191×10^{-8}	0.2152×10^{-8}
0.916×10^{-1}	0.383×10^{-8}	0.6095×10^{-8}
0.1244	0.6273×10^{-8}	0.1254×10^{-7}
Temperature = 35°C		
0.83×10^{-2}	0.44×10^{-9}	0.2161×10^{-9}
0.22×10^{-1}	0.912×10^{-9}	0.897×10^{-9}
0.39×10^{-1}	0.176×10^{-8}	0.2465×10^{-8}
0.49×10^{-1}	0.315×10^{-8}	0.4139×10^{-8}
0.66×10^{-1}	0.597×10^{-8}	0.9404×10^{-8}
Temperature = 45°C		
0.55×10^{-2}	0.59×10^{-9}	0.2729×10^{-9}
0.145×10^{-1}	0.155×10^{-8}	0.1292×10^{-8}
0.24×10^{-1}	0.2063×10^{-8}	0.276×10^{-8}
0.35×10^{-1}	0.317×10^{-8}	0.5247×10^{-8}
0.414×10^{-1}	0.469×10^{-8}	0.7411×10^{-8}

Table 5.2

Diffusivity-Concentration Data for the system Cellulose Acetate/Ethanol

Concentration $\frac{\text{mg penetrant}}{\text{mg polymer}}$	Integral Diffusivity $\bar{D}$, cm^2/sec	Differential Diffusivity D, cm^2/sec
	Temperature = 25°C	
0.29×10^{-1}	0.141×10^{-10}	0.13×10^{-10}
0.35×10^{-1}	0.251×10^{-10}	0.1855×10^{-10}
0.54×10^{-1}	0.738×10^{-10}	0.6551×10^{-10}
0.81×10^{-1}	0.1127×10^{-9}	0.1693×10^{-9}
0.12	0.296×10^{-9}	0.5322×10^{-9}
	Temperature = 35°C	
0.2×10^{-1}	0.229×10^{-10}	0.2416×10^{-10}
0.26×10^{-1}	0.39×10^{-10}	0.367×10^{-10}
0.36×10^{-1}	0.712×10^{-10}	0.7379×10^{-10}
0.44×10^{-1}	0.1486×10^{-9}	0.1356×10^{-9}
0.52×10^{-1}	0.192×10^{-9}	0.2191×10^{-9}
0.72×10^{-1}	0.2938×10^{-9}	0.5112×10^{-9}
	Temperature = 45°C	
0.97×10^{-2}	0.62×10^{-10}	0.2713×10^{-10}
0.15×10^{-1}	0.653×10^{-10}	0.4418×10^{-10}
0.23×10^{-1}	0.81×10^{-10}	0.7471×10^{-10}
0.33×10^{-1}	0.1064×10^{-9}	0.1225×10^{-9}
0.41×10^{-1}	0.131×10^{-9}	0.1691×10^{-9}
0.47×10^{-1}	0.1773×10^{-9}	0.2161×10^{-9}
0.91×10^{-1}	0.958×10^{-9}	0.1771×10^{-8}

Table 5.3

Diffusivity-Concentration Data for the system Cellulose Acetate/Benzene

Concentration $\frac{\text{mg penetrant}}{\text{mg polymer}}$	Integral Diffusivity $\bar{D}$, cm^2/sec	Differential Diffusivity D, cm^2/sec
	Temperature = 25°C	
0.154×10^{-1}	0.447×10^{-11}	0.2847×10^{-11}
0.27×10^{-1}	0.719×10^{-11}	0.6184×10^{-11}
0.32×10^{-1}	0.889×10^{-11}	0.8029×10^{-11}
0.65×10^{-1}	0.1626×10^{-10}	0.2714×10^{-10}
	Temperature = 35°C	
0.76×10^{-2}	0.134×10^{-10}	0.1207×10^{-10}
0.94×10^{-2}	0.211×10^{-10}	0.165×10^{-10}
0.127×10^{-1}	0.204×10^{-10}	0.2448×10^{-10}
0.148×10^{-1}	0.2090×10^{-10}	0.2948×10^{-10}
	Temperature = 45°C	
0.63×10^{-2}	0.332×10^{-10}	0.21×10^{-10}
0.7×10^{-2}	0.353×10^{-10}	0.2348×10^{-10}
0.97×10^{-2}	0.302×10^{-10}	0.3167×10^{-10}
0.122×10^{-1}	0.272×10^{-10}	0.3816×10^{-10}

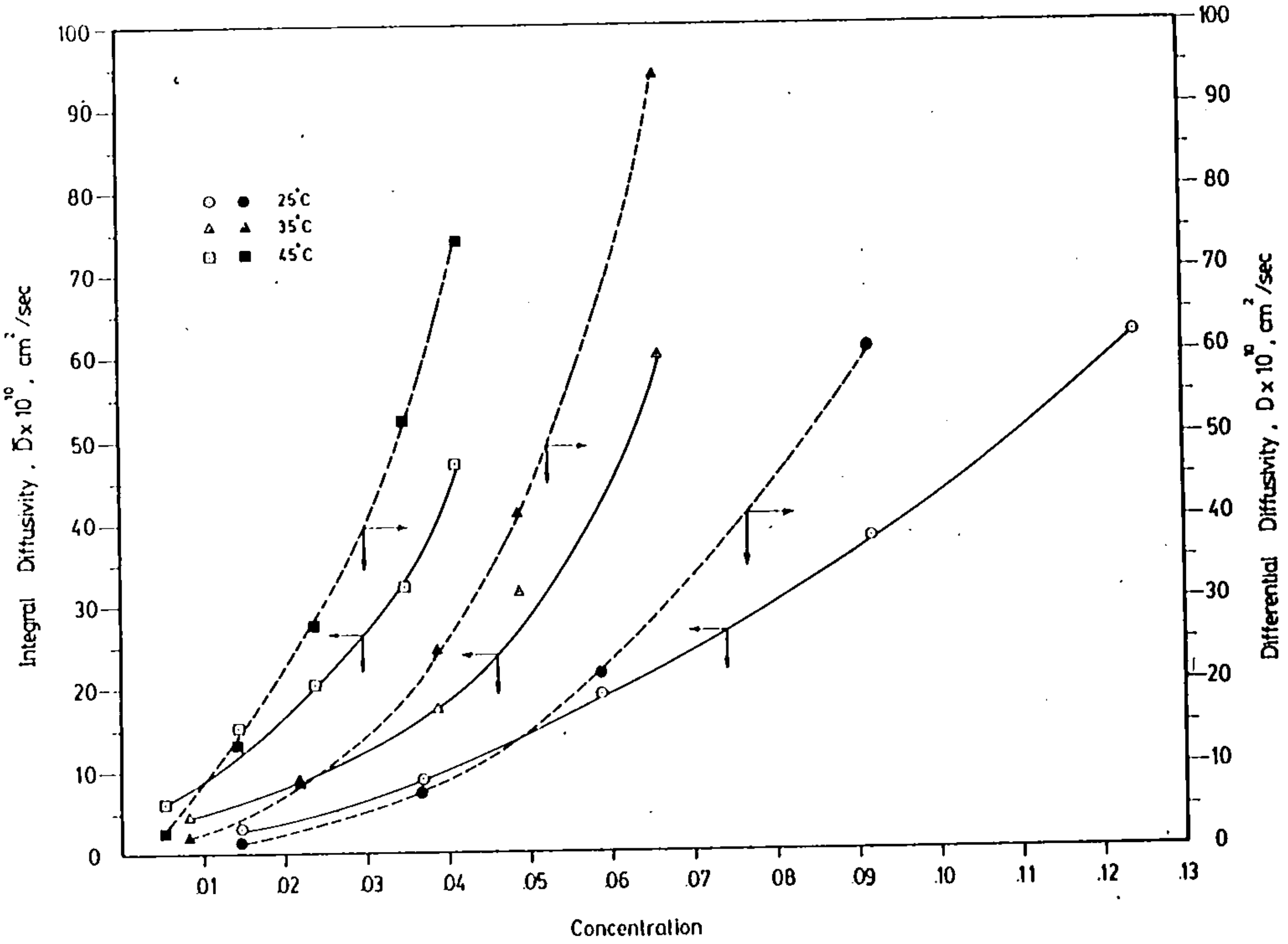

Figure 5.5 Dependence of Diffusivity on Concentration for the System Methanol-Cellulose Acetate.

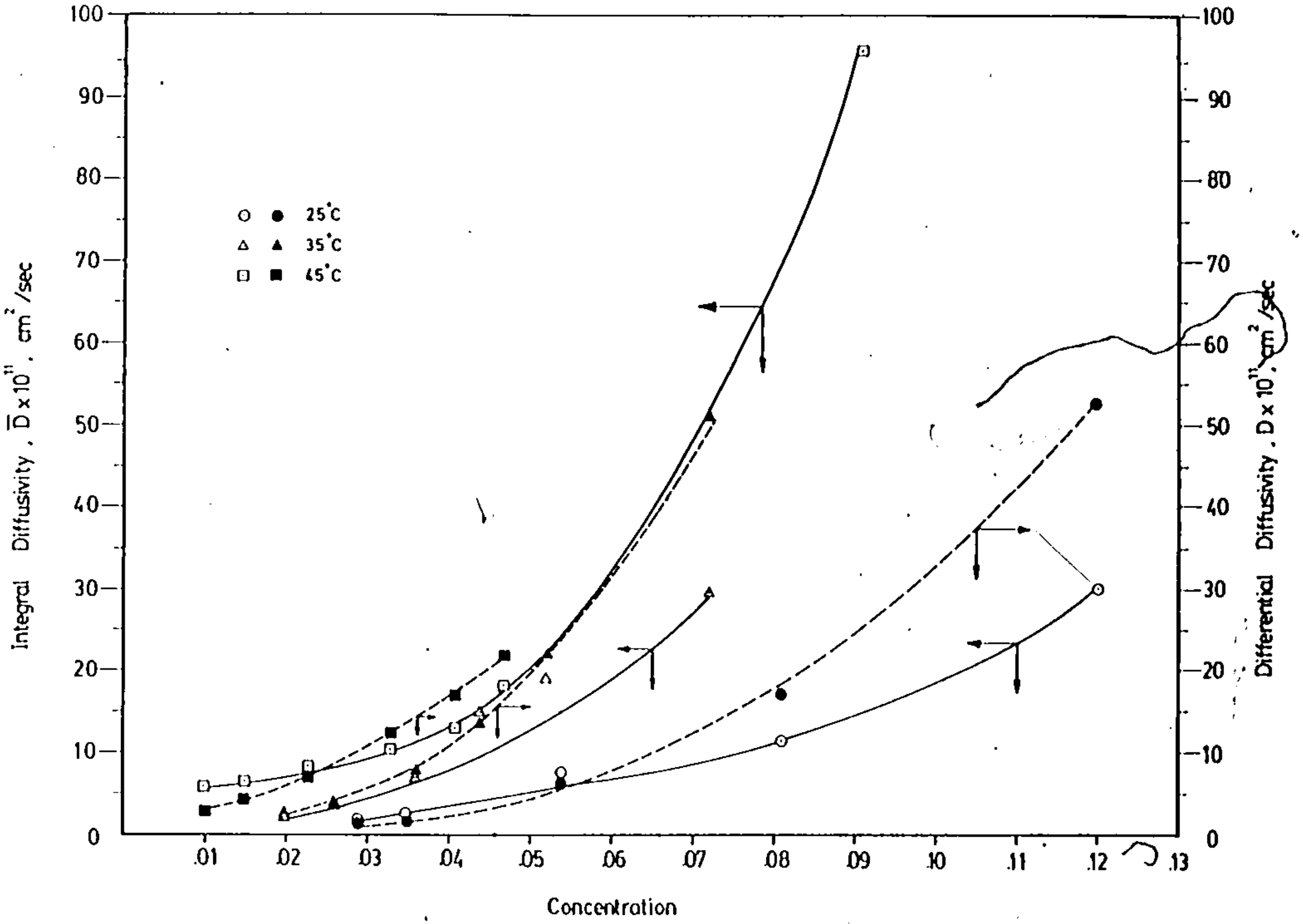

Figure 5.6 Dependence of Diffusivity on Concentration for the System Ethanol-Cellulose Acetate

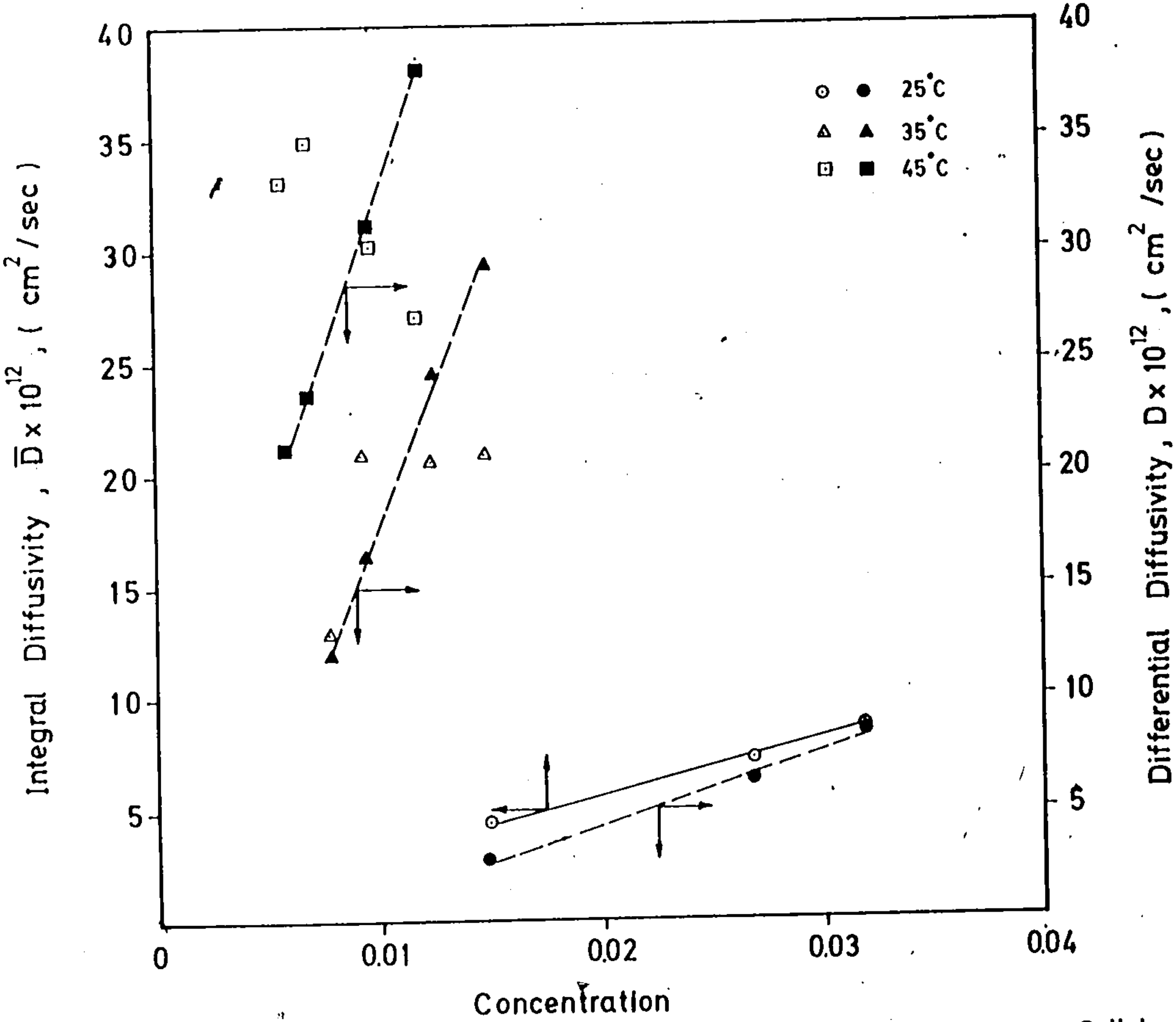

Figure 5.7 : Dependence of Diffusivity on Concentratration for the System Benzene-Cellulose Acetate

The flow chart described above is applicable when the concentration dependence of the diffusion coefficient is represented by a non-linear polynomial of the third degree.

If a quadratic or straight line model is assumed to represent the concentration dependence of the diffusivity, the computer program can still be used. The required number of parameters (N) has to be specified. Subroutines TW0 and DV2 take care of the straight line model while subroutined THR and DV3 take care of the quadratic case.

5.4 Concentration Dependence of Diffusion Coefficients

The values of the integral and differential diffusivities at different concentrations for all the systems investigated at 25, 35, and 45°C are given in Tables 5.1 to 5.3.

Figures 5.5 to 5.7 show the change of both the integral and the differential diffusivities with concentration. In the case of methanol and ethanol, the increase of diffusivity with concentration is non-linear. However, in the case of benzene the differential diffusivities change linearly with concentration within the narrow concentration range studied. As far as integral diffusivities of benzene are concerned, linear behaviour is only clear at 25°C. At 35°C and 45°C the data do not seem to follow any particular pattern. This can probably be attributed to the narrow vapor activity levels employed in this study. The narrow activity levels have been dictated by the physical limitations of the

Table 5.4

Diffusion Coefficients at Zero Penetrant Concentration, D_o, and Penetrant Molar Volumes

System	Temperature °C	Molar Volume of Penetrant $*10^6$, m^3/mol	D_o cm^2/sec
Cellulose acetate/methanol	25	40.8	0.5173×10^{-10}
	35	41.3	0.181×10^{-9}
	45	41.85	0.27×10^{-9}
Cellulose acetate/ethanol	25	59.9	0.3×10^{-11}
	35	60.6	0.854×10^{-11}
	45	61.1	0.173×10^{-10}
Cellulose acetate/benzene	25	89.3	0.174×10^{-11}
	35	90.5	0.513×10^{-11}
	45	91.7	0.1128×10^{-10}

experimental system.

Inspection of Figure B.6 indicates that the straight line portions of the M_t/M_∞ versus $t^{1/2}$ curves at different temperatures come very close together since the vapor activity levels are very close. This resulted in obtaining very close diffusivity values for benzene in cellulose acetate at the three temperatures employed. Such behaviour has not been detected in the cases of methanol and ethanol since the vapor activity levels employed have been relatively much larger than those in the case of benzene.

5.5 Diffusion Coefficient at Zero Concentration, D_o

The diffusion coefficient is concentration-dependent. Therefore, such diffusion coefficients cannot be considered characteristic of the polymer unless evaluated at zero penetrant concentration. Furthermore, evaluating the diffusion coefficient at zero penetrant concentration provides a very important tool for investigating the effect of the different variables such as penetrant size and temperature.

In this study, D_o, has been determined by extrapolating the plot of D versus concentration to zero concentration.

Values of D_o for the systems investigated in this study are given in Table 5.4. A discussion of the effect of penetrant size and temperature follows.

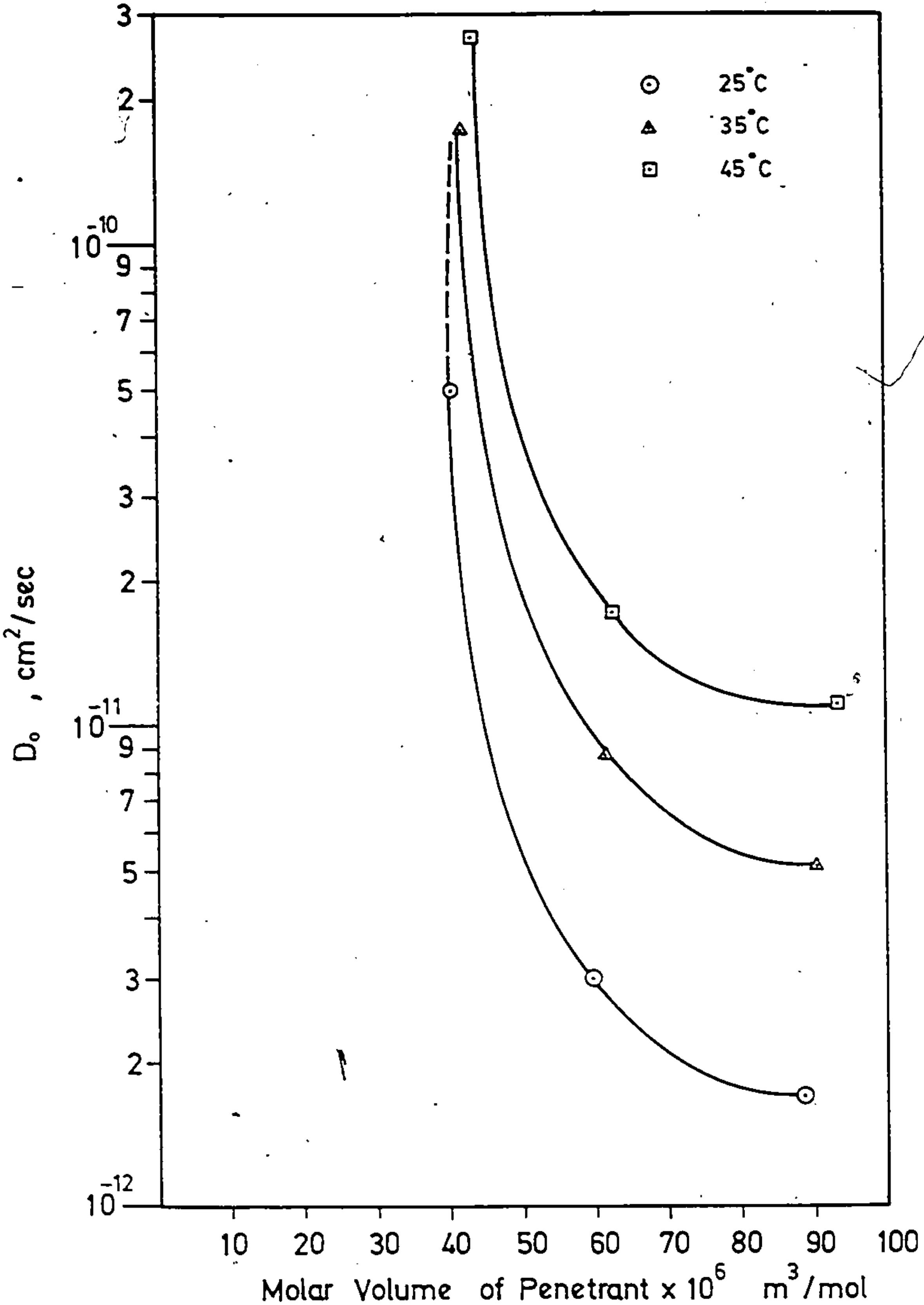

Figure 5.8 : Variation of D_o with the Molar Volume of the Penetrant.

5.5.1 Effect of the size of the penetrant molecule

The molar volumes at 25, 35, and 45°C of the penetrants used in this study are reported in Table 5.4. A plot of the diffusion coefficient at zero concentration versus the molar volume of the penetrant for all the systems studied at 25, 35, and 45°C is shown in Figure 5.8.

Figure 5.8 indicates that the diffusion coefficient, D_o, as expected decreases with increasing penetrant size. This behaviour has been reported in several studies for other systems, e.g., Prager and Long (1951).

Prager and Long (1951) explained this behaviour assuming that the diffusion process occurs when the penetrant molecule leaves its current position and jumps into one of the local free volumes (best pictured as holes) resulting from thermal fluctuations. Usually, the free volumes or holes are not the size of the entire penetrant molecules, therefore, several jumps must occur in the same direction before the penetrant molecule can be admitted to the free volume. For a hole to be created, a certain number of secondary valence bonds (Van der Waals bonds) must be broken and this in turn gives rise to sites of higher energy. So, the creation of a larger hole requires the breakage of more bonds, the result is that there are fewer of these large holes. Thus, molecules with a large size diffuse more slowly.

40

Table 5.9

Examples for Systems which show a Decrease in the Diffusivity Upon Increasing the Temperature

System	Temperature °C	Pressure mm Hg	Activity	Integral Diffusivity $\bar{D}$, cm^2/sec
Cellulose acetate/methanol	25	45.41	0.36	$.191 \times 10^{-8}$
	35	45.38	0.22	$.176 \times 10^{-8}$
Cellulose acetate/methanol	25	70.23	.56	$.383 \times 10^{-8}$
	35	70.29	.34	$.315 \times 10^{-8}$
Cellulose acetate/methanol	25	90.14	.72	$.628 \times 10^{-8}$
	35	90.08	.43	$.597 \times 10^{-8}$
	45	90.67	.27	$.469 \times 10^{-8}$
Cellulose acetate/ethanol	25	20.53	.33	$.738 \times 10^{-10}$
	35	20.7	.19	$.71 \times 10^{-10}$
Cellulose acetate/ethanol	25	30.24	.29	$.15 \times 10^{-9}$
	35	30.53	.17	$.106 \times 10^{-9}$
Cellulose acetate/ethanol	25	40.5	0.67	$.296 \times 10^{-9}$
	35	40.38	0.39	$.192 \times 10^{-9}$
	45	41.8	0.23	$.131 \times 10^{-9}$

5.5.2 Effect of temperature

Increasing the temperature results in softening the polymer, which in turn has been found to result in increasing penetrant diffusivity.

The explanation of this phenomenon becomes very easy once one understands ~~that~~ a penetrant molecule can only move from one place to another when the local amount of empty space (it is called free volume as will be discussed later) around the penetrant molecule reaches a certain critical value. The volume fraction of 'empty space' is called the fractional free volume, and this fractional free volume of any system increases with increasing temperature. Thus increasing the probability of finding sufficient local free volume which in turn results in increasing penetrant diffusivity.

In the case of methanol and ethanol it was found that an increase in the temperature may result in a decrease in the value of the experimental diffusivity. An example of this phenomenon is the case of the system (cellulose acetate-methanol); it was found that the diffusivities at 25, 35, and 45°C and at penetrant pressure of 90 mm Hg are as follows: $0.62x \times 10^{-8}$, 0.597×10^{-8} and 0.469×10^{-8} cm^2/sec. Table 5.5 gives more examples of the systems which behaved similarly.

The effect of temperature on diffusivity has been determined by preparing Arrhenius type plots for $\ln D_o$

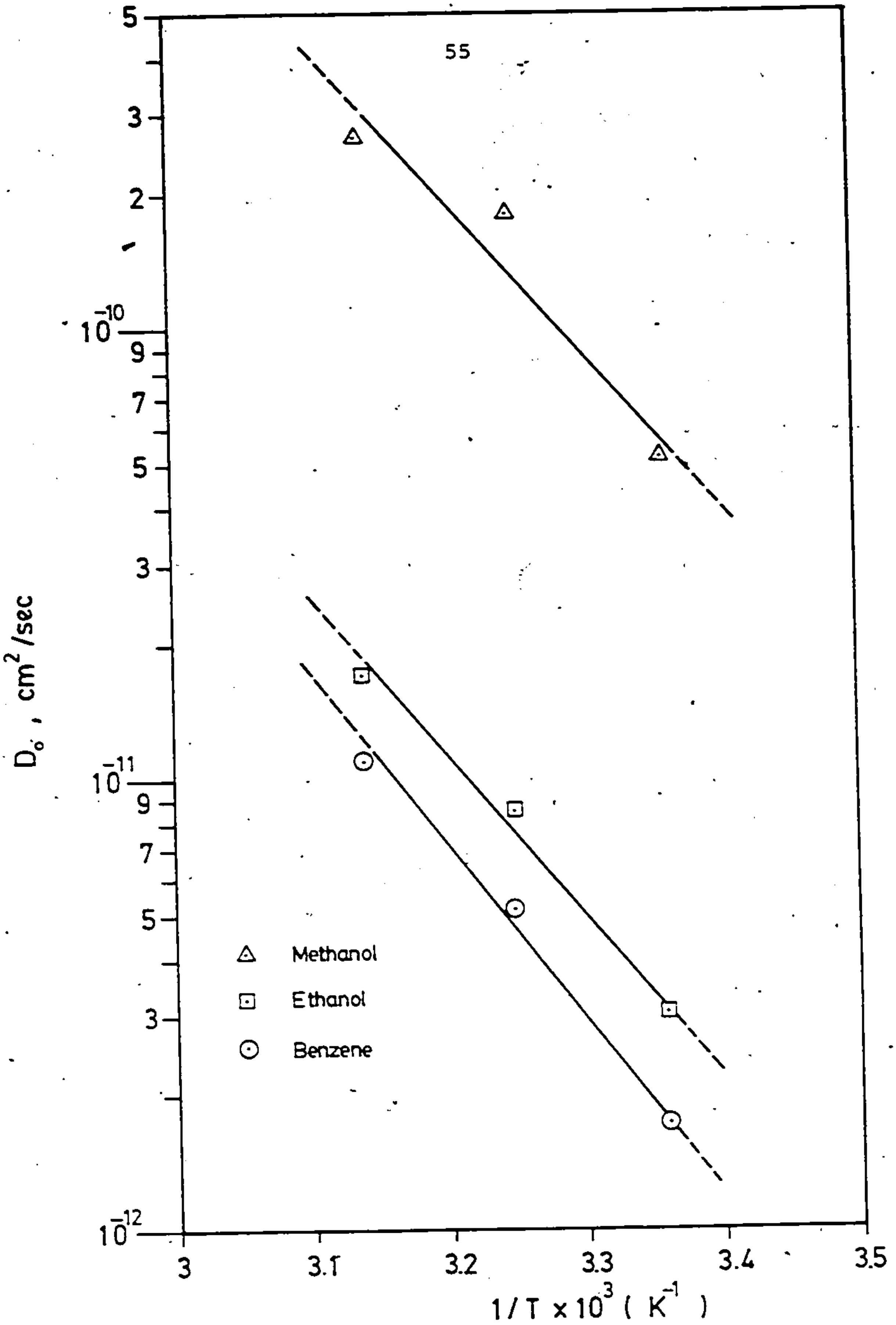

Figure 5.9 : Arrhenius Type Plot for the Determination of the Activation Energy of Diffusion

Table 5.6

Activation Energies for Diffusion, E_d, for the Penetrants Studied in Cellulose Acetate at 25°C

Penetrant	Activation Energy, E_d, in KJ/mol
Methanol	65.42
Ethanol	69.11
Benzene	73.7

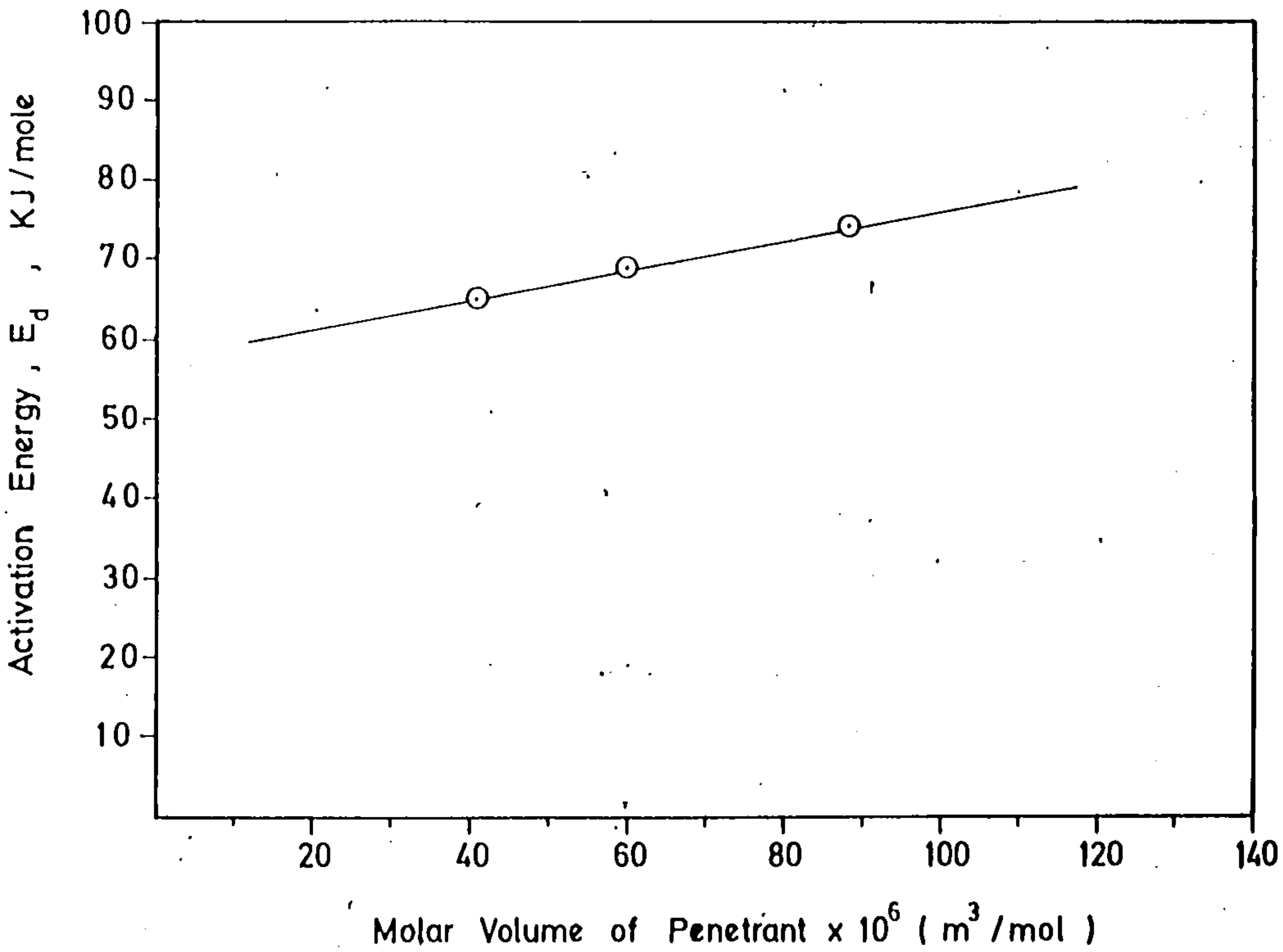

Figure 5.10 : Change of Activation Energy of Diffusion with Molar Volume of Penetrant.

against 1/T. Such plots are depicted in Figure 5.9. The plots are linear within the temperature range employed in this study.

Since it has been assumed that the diffusion coefficient changes with temperature according to the relationship:

$$D = D^{o} e^{-E_d/RT} \tag{5.7}$$

the slope of the plots given in Figure 5.9 have been utilized in calculating values of the activation energy of diffusion, E_d, in the temperature range 25-45°C. These activation energies are reported in Table 5.6.

A plot of the activation energy versus penetrant molar volume is given in Figure 5.10. The relationship is linear and indicates that the activation energy increases with increasing penetrant molar volume.

Kokes and Long (1953) reported similar behaviour and confirmed the fact that the activation energy of diffusion increases with penetrant size until a critical value of the activation energy is reached, after which it stays constant.

On the basis of the postulation given by Prager and Long (1951) which was described earlier, it is possible to explain the increase in the activation energy of diffusion with the penetrant size in the following way: the activation energy of diffusion, E_d, is presumably related to the energy required to create a large enough hole in the polymer for the penetrant molecule to pass through it. So, a larger amount of energy is required to create a large hole in the polymer to allow a large penetrant molecule to diffuse.

Table 5.5 gives examples for systems which showed a decrease in the experimental diffusivities upon increasing the temperature. Similar behaviour was reported by other investigators, e.g. Mandelkern and Long (1949).

The investigators studied the sorption results obtained at 30°C and 40°C with both methylene chloride and acetone. For pressures of 100 mm Hg of methylene chloride, and cellulose acetate films of the same thickness, the investigators found that at 40°C the sorption process is more rapid than the one at 30°C, which is expected. However, complications arised when methylene chloride was used at higher pressure (204 mm Hg). When plotting M_t/M_∞ versus $t^{1/2}$ for both temperatures, it was found that the two curves cross each other and that there was a region in which the 40°C take-up is slower than that at 30°C.

Furthermore, Mandelkern and Long (1949) found that for methylene chloride at 400 mm Hg, the inflection of slopes of the take-up curve appeared again, with the result that the rate of take-up at 40°C is always slower than the one at 30°C. Similar results were obtained when acetone was used as the diffusant.

Those investigators tried to attribute this phenomenon to variations in the true temperature of the polymer film

Table 5.7

Intrinsic Diffusion Coefficient Data for the System Cellulose Acetate/Methanol

Activity, a	Volume Fraction of Penetrant, ϕ	Intrinsic Diffusion Coefficient $\mathcal{D}$, in cm^2/sec
	Temperature = 25°C	
0.045	0.024	0.148×10^{-9}
0.169	0.036	0.85×10^{-9}
0.363	0.09	0.268×10^{-8}
0.562	0.13	0.84×10^{-8}
0.721	0.17	0.193×10^{-7}
	Temperature = 35°C	
0.027	0.014	0.223×10^{-9}
0.099	0.036	0.977×10^{-9}
0.219	0.061	0.286×10^{-8}
0.34	0.076	0.498×10^{-8}
0.435	0.1	0.12×10^{-7}
	Temperature = 45°C	
0.017	0.0092	0.279×10^{-9}
0.062	0.024	0.137×10^{-8}
0.136	0.039	0.3×10^{-8}
0.212	0.056	0.6×10^{-8}
0.274	0.065	0.867×10^{-8}

Table 5.8

Intrinsic Diffusion Coefficient Data for the System Cellulose Acetate/Ethanol

Activity, a	Volume Fraction of Penetrant, ϕ	Intrinsic Diffusion Coefficient $\mathcal{D}$, in cm^2/sec
	Temperature = 25°C	
0.11	0.046	0.145×10^{-10}
0.177	0.054	0.211×10^{-10}
0.344	0.082	0.8×10^{-10}
0.51	0.12	0.228×10^{-9}
0.678	0.165	0.81×10^{-9}
	Temperature = 35°C	
0.063	0.033	0.261×10^{-10}
0.102	0.041	0.405×10^{-10}
0.199	0.055	0.842×10^{-10}
0.291	0.07	0.161×10^{-9}
0.389	0.08	0.267×10^{-9}
0.484	0.11	0.67×10^{-9}
	Temperature = 45°C	
0.037	0.016	0.281×10^{-10}
0.061	0.025	0.469×10^{-10}
0.119	0.038	0.818×10^{-10}
0.176	0.053	0.139×10^{-9}
0.241	0.065	0.198×10^{-9}
0.29	0.073	0.258×10^{-9}
0.547	0.133	0.247×10^{-8}

Table 5.9

Intrinsic Diffusion Coefficient Data for the System Cellulose Acetate/Benzene

Activity, a	Volume Fraction of Penetrant, ϕ	Intrinsic Diffusion Coefficient $\mathcal{D}$, in cm^2/sec
	Temperature = 25°C	
0.43	0.022	0.3×10^{-11}
0.59	0.038	0.677×10^{-11}
0.738	0.045	0.894×10^{-11}
0.853	0.088	0.336×10^{-10}
	Temperature = 35°C	
0.274	0.011	0.124×10^{-10}
0.373	0.014	0.171×10^{-10}
0.473	0.019	0.256×10^{-10}
0.541	0.022	0.311×10^{-10}
	Temperature = 45°C	
0.182	0.0096	0.215×10^{-10}
0.247	0.01	0.24×10^{-10}
0.314	0.015	0.33×10^{-10}
0.358	0.018	0.4×10^{-10}

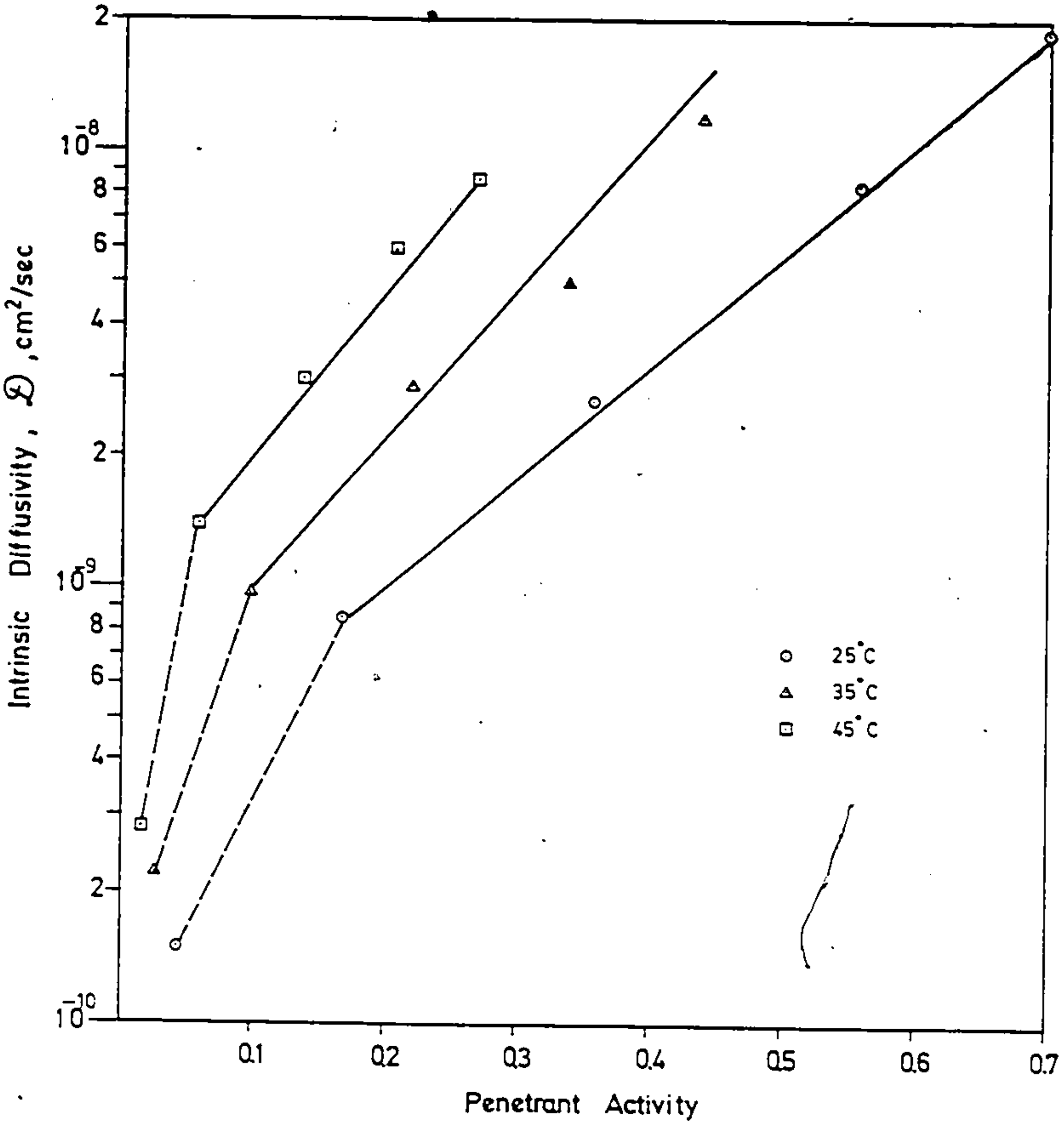

Figure 5.11 : Dependence of the Intrinsic Diffusion coefficient on Penetrant Activity for the System Methanol-Cellulose Acetate.

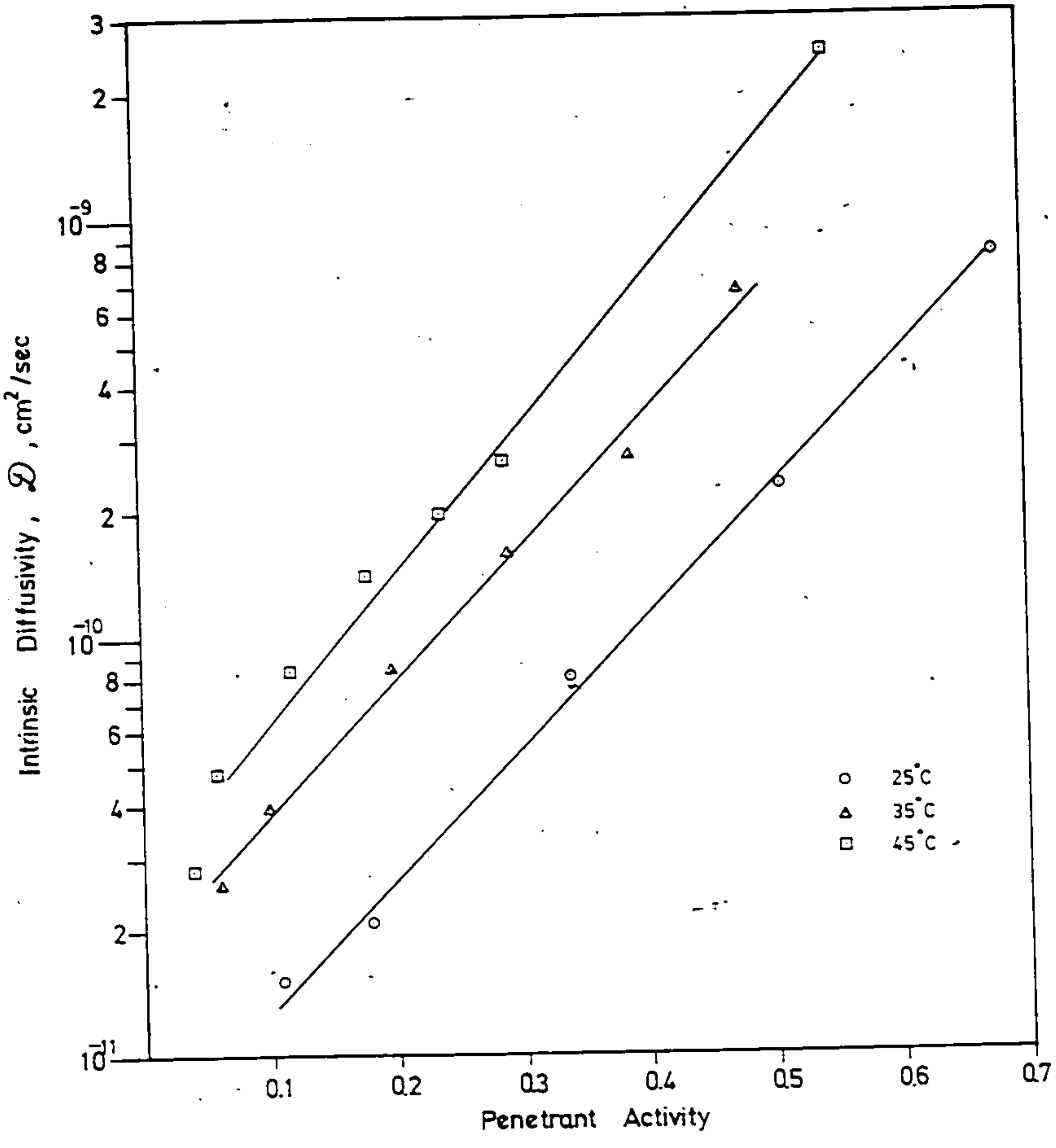

Figure 5.12 : Dependence of the Intrinsic Diffusion coefficient on Penetrant Activity for the System Ethanol-Cellulose Acetate.

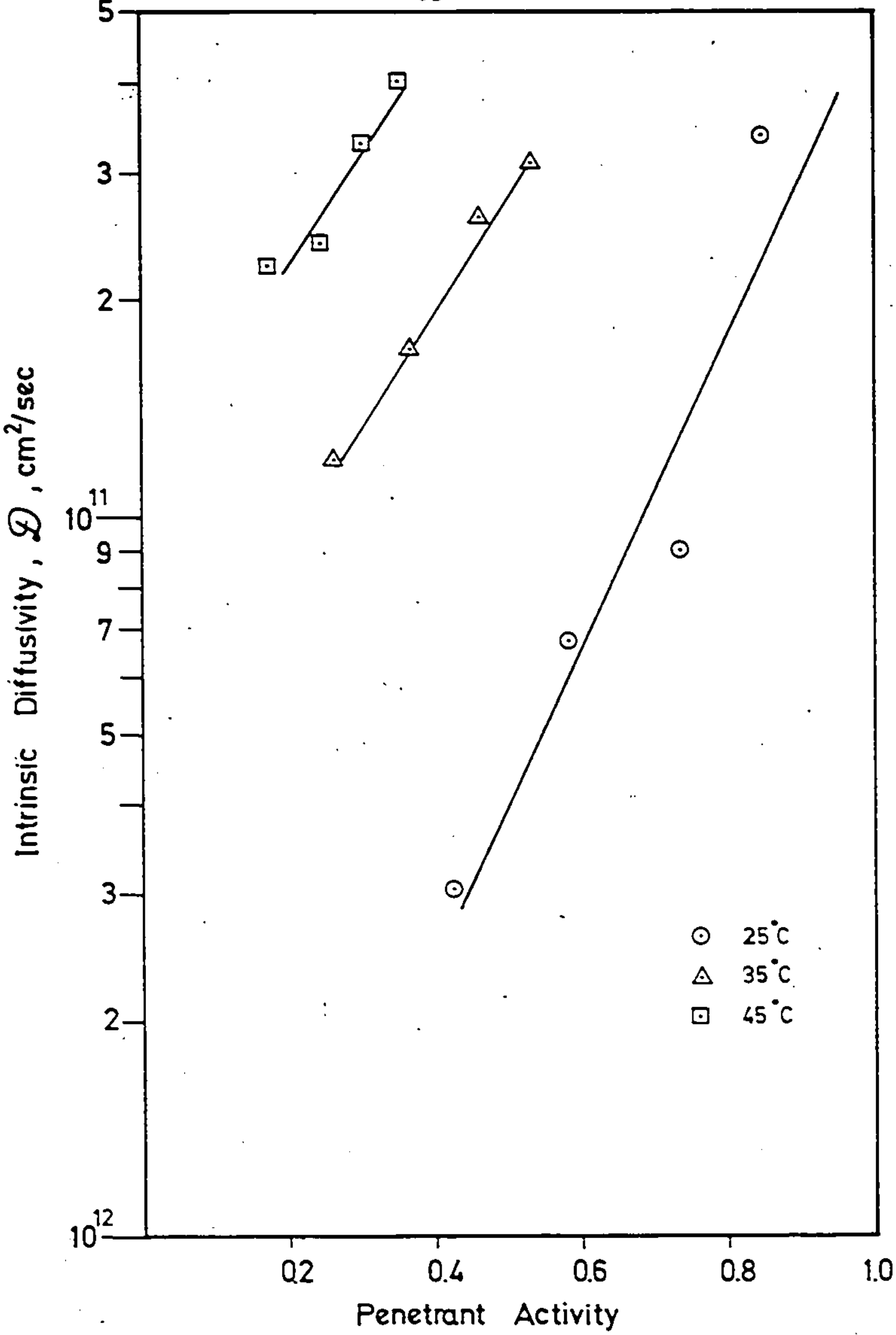

Figure 5.13 : Dependence of the Intrinsic Diffusion Coefficiet on Penetrant Activity for the System Benzene-Cellulose Acetate.

caused by the heat evolved during sorption. Experimental work and calculations enabled these investigators to conclude that the temperature rise is not the cause of these inflections. They could not give any interpretation for the complex sorption behaviour for cellulose acetate. This phenomenon has not been explained yet.

5.6 Intrinsic Diffusion Coefficient, $\mathcal{D}$

A method has been described earlier for obtaining the differential diffusion, D, from the integral value, $\bar{D}$. Such a method ignores the swelling that occurs to the polymer sample as sorption takes place. An allowance can be made for this, and the intrinsic diffusion coefficient, $\mathcal{D}$, can be calculated as well by using the following expression which was suggested by Garrett and Park (1965):

$$\mathcal{D} = \frac{D}{(1-\phi)^{\frac{7}{3}}} \qquad (5.8)$$

where ϕ is the volume fraction of the penetrant. Tables 5.7 to 5.9 show the values of the intrinsic diffusion coefficients, $\mathcal{D}$, calculated from the differential diffusion coefficient, D, at different activity levels and volume fractions of the penetrants for all the systems involved in this study at 25, 35, and 45°C.

Figures 5.11 and 5.13 show the change of the intrinsic diffusion coefficient, $\mathcal{D}$, with the activity level of the penetrant in semi-log plots. The straight lines obtained

Table 5.10

Constants of Equation (5.9)

System	Temperature °C	$\mathcal{D}_o$ cm^2/sec	α
Cellulose acetate/Methanol	25	3.3×10^{-10}	5.68
	35	5.13×10^{-10}	7.13
	45	8.55×10^{-10}	8.8
Cellulose acetate/Ethanol	25	6.43×10^{-12}	7.12
	35	1.82×10^{-11}	7.34
	45	2.66×10^{-11}	8.297
Cellulose acetate/Benzene	25	2.99×10^{-13}	5.19
	35	4.7×10^{-12}	3.49
	45	1.06×10^{-11}	3.64

indicate that the relation between the intrinsic diffusion coefficient, $\mathcal{D}$, and the activity level of the penetrant, a, is of the form:

$$\mathcal{D} = \mathcal{D}^{o} e^{\alpha a} \qquad (5.9)$$

The coefficients $\mathcal{D}^{o}$ and α in Equation (5.9) are given in Table 5.10.

5.7 Thermodynamic Diffusion Coefficient, $\mathcal{D}^{*}$.

The concentration gradient has long been considered the driving force for any diffusional processes. However, the development of the diffusion equation by using arguments based on irreversible thermodynamics indicated that the chemical potential gradient is the true driving force of diffusion. On that basis, the diffusivity value obtained from Fick's law has to be corrected to reflect the change in the driving force.

It has been shown by several investigators, e.g. Park (1961) that:

$$\mathcal{D}^{*} = \mathcal{D}/\beta \qquad (5.10)$$

where

$$\beta = \partial \ln a / \partial \ln \phi$$

where β is generally called the thermodynamic correction factor and, $\mathcal{D}^{*}$, is the thermodynamic diffusion coefficient. Experimental evidence to show that the chemical potential gradient is the true driving force of diffusion and not concentration gradient was reported by Cullinan and Lenczyk (1969).

Park (1983) reported that the solubility of gases in polymer membranes is low enough to ensure that Henry's law is obeyed in which the concentration of gas in a polymer sample is directly proportional to the gas pressure. As far as organic vapors are concerned, their solubility in polymers is much greater than that of gases. This results in deviations from Henry's law; and a very common method of representing the relationship between the volume fraction of the organic vapor, ϕ , and the vapor pressure, P, is given by the Flory-Huggins relationship:

$$\ln \frac{P}{P^o} = \ln \phi + (1-\phi) + \chi(1-\phi) \qquad (5.11)$$

or

$$\ln a = \ln \phi + (1-\phi) + \chi(1-\phi) \qquad (5.12)$$

where P^o is the saturation vapor pressure. In this study, the values of the saturation vapor pressures for the penetrants studied were calculated using Antoine's equation. In Equation (5.11) and (5.12), χ is the Flory-Huggins interaction parameter, and is characteristic for a given system. According to Park (1960), this parameter is small

Table 5.11

The Flory-Huggins Interaction Parameter, χ, Data for all the Systems Investigated

System	Temperature °C	Flory-Huggins Interaction Parameter, χ
Cellulose acetate/Methanol	25	-0.037
	35	-0.064
	45	-0.1177
Cellulose acetate/Ethanol	25	0.184
	35	0.18
	45	0.09
Cellulose acetate/Benzene	25	1.879
	35	2.313
	45	2.099

Table 5.12

Thermodynamic Diffusivity, $\mathcal{D}^*$, – Activity Data for the System Cellulose Acetate/Methanol

Activity, a	Thermodynamic Diffusivity, $\mathcal{D}^*$ cm^2/sec
Temperature = 25°C	
0.045	0.15×10^{-9}
0.169	0.88×10^{-9}
0.363	0.29×10^{-8}
0.562	0.95×10^{-8}
0.721	0.23×10^{-7}
Temperature = 35°C	
0.027	0.22×10^{-9}
0.099	0.1×10^{-8}
0.219	0.3×10^{-8}
0.34	0.54×10^{-8}
0.435	0.13×10^{-7}
Temperature = 45°C	
0.017	0.28×10^{-9}
0.062	0.14×10^{-8}
0.136	0.31×10^{-8}
0.212	0.62×10^{-8}
0.274	0.91×10^{-8}

Table 5.13

Thermodynamic Diffusivity, $\mathcal{D}^*$, – Activity Data

for the System

Cellulose Acetate/Ethanol

Activity, a	Thermodynamic Diffusivity, $\mathcal{D}^*$ cm^2/sec
Temperature = 25°C	
0.11	0.154×10^{-10}
0.177	0.227×10^{-10}
0.344	0.9×10^{-10}
0.51	0.27×10^{-9}
0.678	0.1×10^{-8}
Temperature = 35°C	
0.063	0.273×10^{-10}
0.102	0.43×10^{-10}
0.199	0.91×10^{-10}
0.291	0.18×10^{-9}
0.389	0.3×10^{-9}
0.484	0.79×10^{-9}
Temperature = 45°C	
0.037	0.29×10^{-10}
0.061	0.48×10^{-10}
0.119	0.86×10^{-10}
0.176	0.15×10^{-9}
0.241	0.215×10^{-9}
0.29	0.28×10^{-9}
0.547	0.29×10^{-8}

Table 5.14

Thermodynamic Diffusivity, $\mathcal{D}^*$, – Activity Data for the System Cellulose Acetate/Benzene

Activity, a	Thermodynamic Diffusivity, $\mathcal{D}^*$ cm^2/sec
Temperature = 25°C	
0.43	0.33×10^{-11}
0.59	0.82×10^{-11}
0.738	0.11×10^{-10}
0.853	0.55×10^{-10}
Temperature = 35°C	
0.274	0.13×10^{-10}
0.373	0.19×10^{-10}
0.473	0.28×10^{-10}
0.541	0.35×10^{-10}
Temperature = 45°C	
0.182	0.226×10^{-10}
0.247	0.25×10^{-10}
0.314	0.36×10^{-10}
0.358	0.44×10^{-10}

when the polymer and organic penetrant liquid are completely miscible and is large when the organic vapor and the polymer are incompatible. The data reported in Table 5.11 confirm such a behaviour.

Values of $\partial \ln a/\partial \ln\phi$ are obtained by differentiation of the Flory-Huggins relationship given by Equation (5.12):

$$\frac{\partial\ \ln a}{\partial\ \ln\phi} = 1 + [\phi(-1)] + 2\chi(1-\phi)\{\phi(-1)\}$$

$$= 1 - \phi(1+2\chi) + 2\chi\ \phi^2 \qquad (5.13)$$

For all the systems studied, data for the activity of the penetrant, a, and the volume fraction of the penetrant, ϕ, were fitted to Equation (5.12) to calculate the value of the interaction parameter, χ . The values of $\partial \ln a/\partial \ln\phi$ are then obtained by substituting the values of χ in Equation 5.13). The values of the thermodynamic diffusion coefficients are calculated by dividing the intrinsic diffusion coefficient, $\mathcal{D}$, values by the thermodynamic correction factor $\partial \ln a/\partial \ln\phi$. Typical manual calculations of $\mathcal{D}^*$ from $\mathcal{D}$ are included in Appendix F.

The obtained values of the Flory-Huggins interaction parameter, χ , are given in Table 5.11. Similarly, the calculated values of the thermodynamic diffusion coefficients at different activity levels of the penetrant are reported in Tables 5.12 to 5.14.

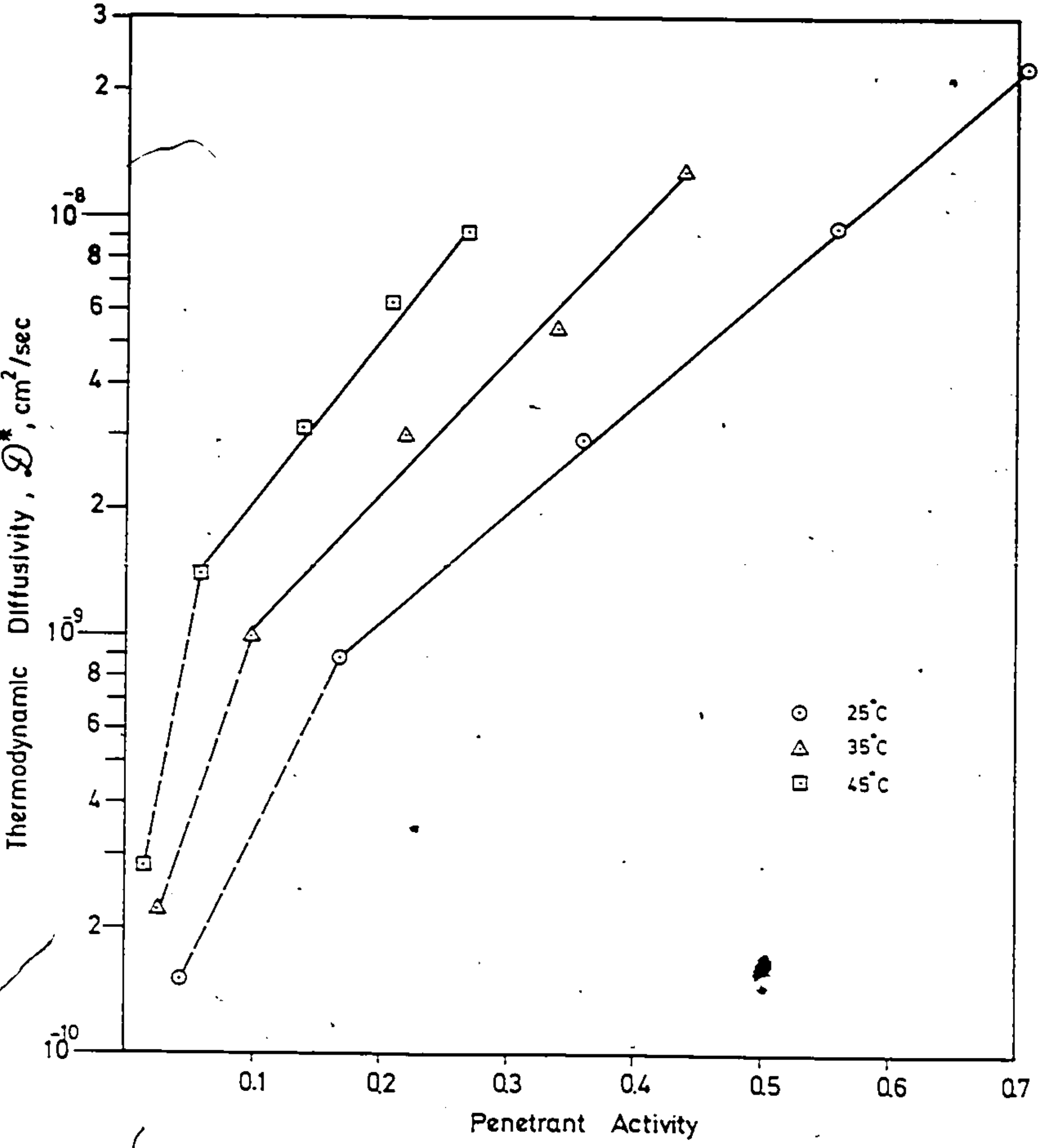

Figure 5.14 : Dependence of the Thermodynamic Diffusion Coefficient on Penetrant Activity for the System Methanol - Cellulose Acetate.

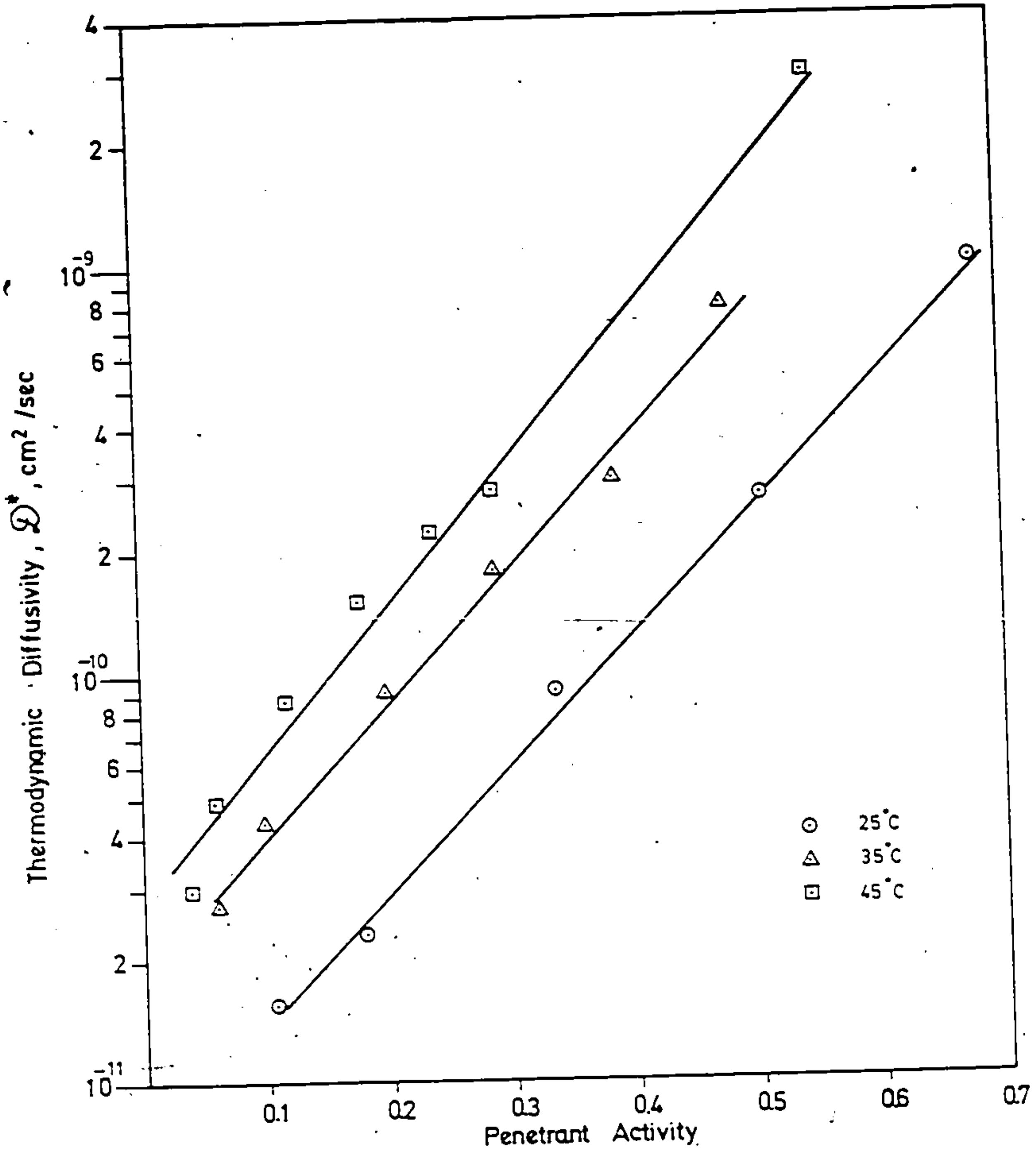

Figure 5.15 : Dependence of the Thermodynamic Diffusion Coefficient on Penetrant Activity for the System Ethanol-Cellulose Acetate.

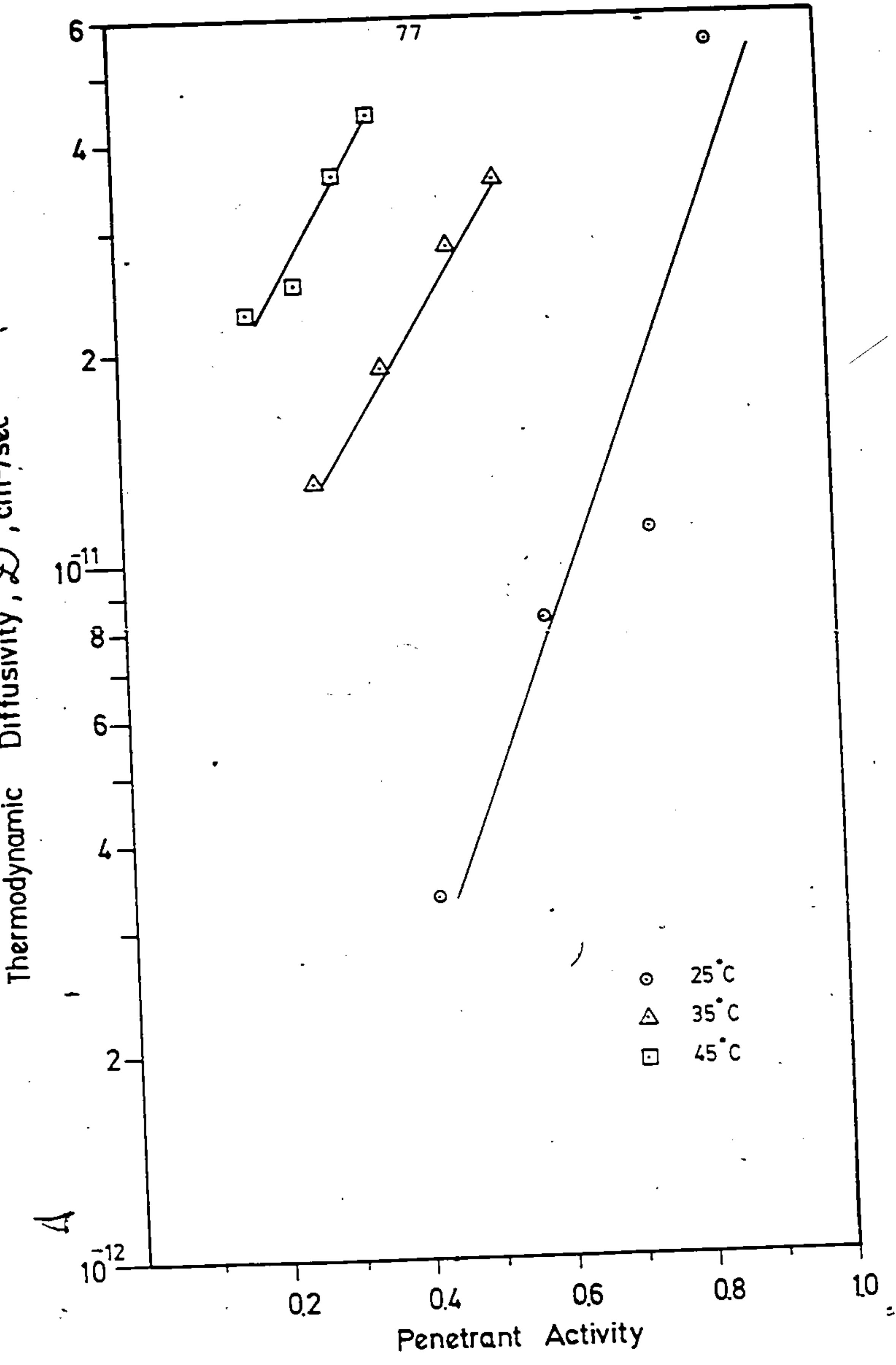

Figure 5.16 : Dependence of the Thermodynamic Diffusion Coefficient on Penetrant Activity for the System Benzene-Cellulose Acetate.

Table 5.15

Constants of Equation (5.14)

System	Temperature °C	$\mathcal{D}_o^*$ cm^2/sec	β
Cellulose acetate/Methanol	25	1.76×10^{-10}	7.05
	35	5.18×10^{-10}	7.3
	45	8.55×10^{-10}	8.96
Cellulose acetate/Ethanol	25	6.6×10^{-12}	7.38
	35	1.87×10^{-11}	7.59
	45	2.71×10^{-11}	8.57
Cellulose acetate/Benzene	25	2.19×10^{-13}	6.05
	35	4.67×10^{-12}	3.75
	45	1.07×10^{-11}	3.85

Also, plots of ln $\mathcal{D}^*$ versus the activity of the penetrant vapor were prepared and shown in Figures 5.14 to 5.16. The linearity of these plots indicates that the relation between $\mathcal{D}^*$, and, a, is of the form:

$$\mathcal{D}^* = \mathcal{D}_o^* \, e^{\beta' a} \qquad (5.14)$$

The coefficients $\mathcal{D}_o^*$ and β' in Equation (5.14) are given in Table 5.15 for all the systems investigated at 25, 35, and 45°C.

5.8 A Free-Volume Model for Diffusion in Polymers

Wilkens and Long (1957) reported a model for the diffusion of penetrant molecules in polymers. The derivation of the model depends on the major assumption that the diffusion process takes place when local configurations of high free volume occur. Garrett (1965) defined free volume as the difference between the volume taken up by a molecule and the volume of the molecule itself.

On this basis, free volume could be pictured as 'holes' opened up in the polymer configuration by thermal fluctuations. Furthermore, the rate of the diffusion process is proportional to the probability of occurrence of regions in which the free volume exceeds a certain critical value; after reaching this critical value, the diffusion rate becomes independent of the free volume of the polymer. The investigators then derived an expression for this probability and related it to the diffusion coefficient.

The dependence of the diffusion coefficient on volume fraction of the penetrant molecule was found to be of the form:

$$\ln \mathcal{D}^* = \ln \mathcal{D}_o^* + A\phi + B\phi^2 \qquad (5.15)$$

where $\mathcal{D}^*$ is the thermodynamic diffusion coefficient, $\mathcal{D}_o^*$ is its value at zero penetrant concentration, and A and B are constants.

Table 5.16

Constants of Equation (5.15)

System	Temperature °C	ln $\mathcal{D}_o^*$	A	B	B/A
Cellulose acetate/Methanol	25	-23.25	51.37	-109.14	- 2.12
	35	-23.088	70.153	-210.72	- 3.00
	45	-22.938	117.84	-782.15	- 6.64
Cellulose acetate/Ethanol	25	-27.36	59.63	-118.85	- 1.99
	35	-26.527	73.39	-206.42	- 2.81
	45	-24.83	41.58	- 21.5	- 0.52
Cellulose acetate/Benzene	25	-27.74	65.88	-216.7	- 3.29
	35	-26.79	191.41	-3125.0	-16.32
	45	-25.57	133.59	-2126.5	-15.92

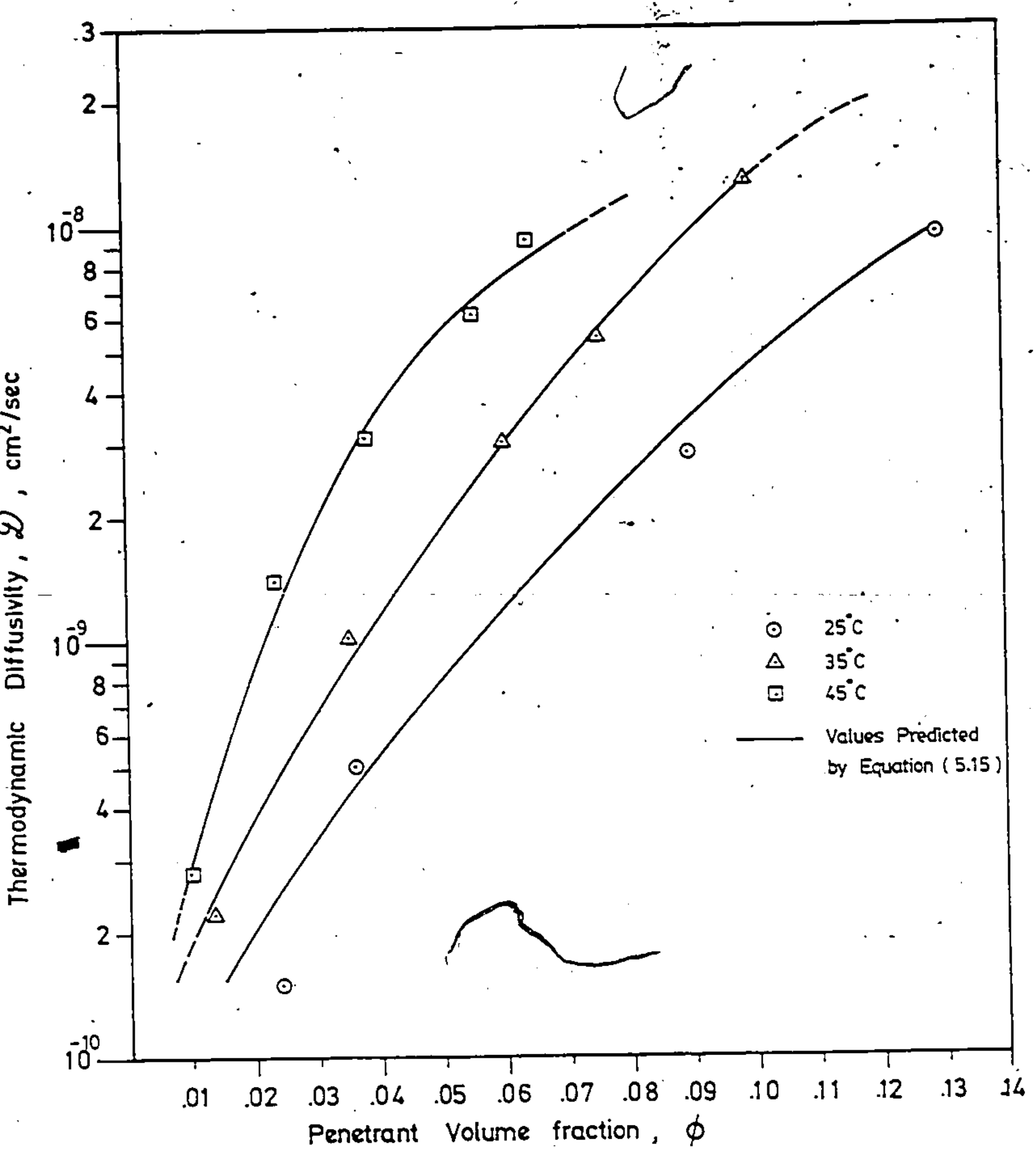

Figure 5.17 : Comparison Between the Experimental Thermodynamic Diffusion coefficients and Predictions of Equation (5.15), for the System Methanol-Cellulose Acetate.

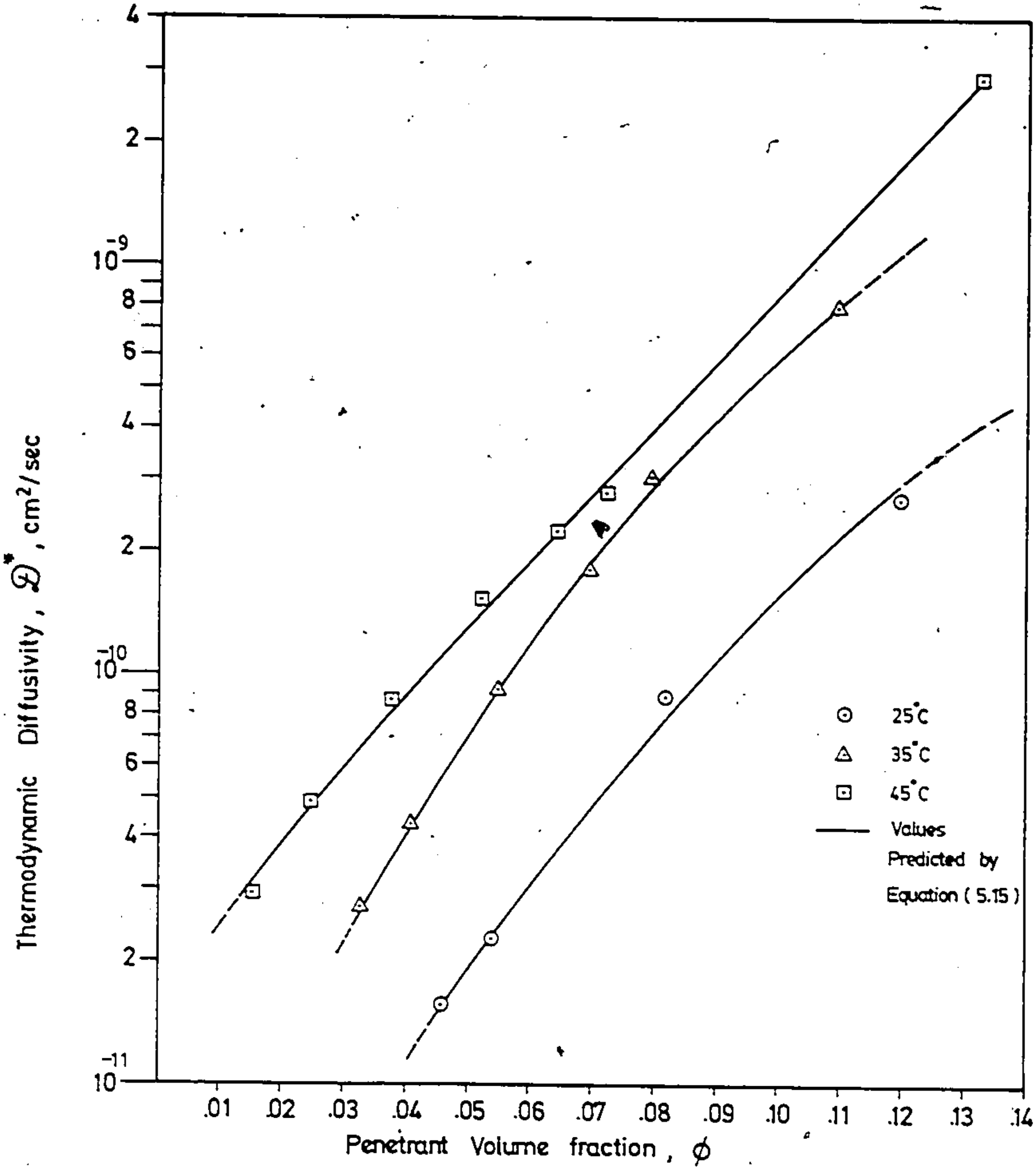

Figure 5.18 : Comparison Between the Experimental Thermodynamic Diffusion coefficients and Predictions of Equation (5.15) for the System Ethanol-Cellulose Acetate.

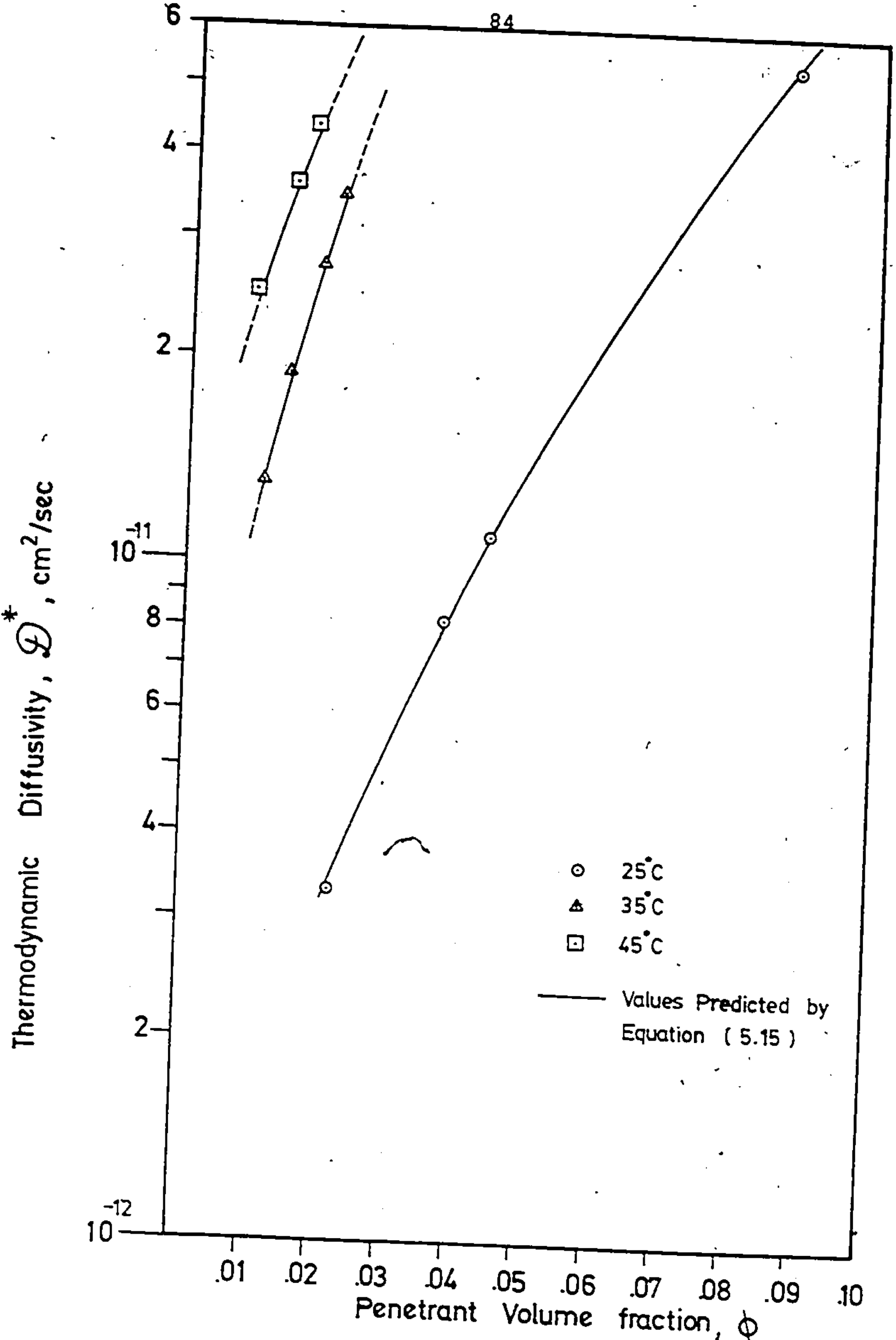

Figure 5.19 : Comparison Between the Experimental Thermodynamic Diffusion coefficients and Predictions of Equation (5.15) for the System Benzene-Cellulose Acetate.

Data for the thermodynamic diffusivities and the volume fractions of the penetrants involved in this study were fitted to Equation (5.15). The values of the constants ln $\mathcal{D}_o^*$, A, B, were obtained and are reported in Table 5.16 along with the values of B/A.

It can be observed from the data reported in Table 5.16 that the values of B/A show no definite trend upon increasing the temperature. On the other hand, the values of $\mathcal{D}_o^*$ increase with temperature as expected.

Equation (5.15) indicates that at very low values of penetrant volume fraction, the relationship between the thermodynamic diffusion coefficient and the volume fraction of the penetrant becomes exponential.

Knowing the constants of Equation (5.15), it is possible to predict the values of the thermodynamic diffusion coefficients at any value of the volume fraction of the penetrant. The values of the thermodynamic diffusivities determined both experimentally and by using Equation (5.15) with the appropriate constants are plotted against the volume fraction of the penetrant for all the systems investigated. Figures 5.17 to 5.19 show such plots.

Figure 5.17 to 5.19 indicate that the experimental results of the thermodynamic diffusion coefficients agree with the ones calculated by using Equation (5.15) for diffusion of methanol, ethanol, and benzene into cellulose acetate at 25, 35 and 45°C.

Chapter VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The most relevant findings of the present work can be summarized as follows:

i) The sorption of methanol, ethanol, and benzene in cellulose acetate films is Fickian in nature, in the range of operating temperatures and activity levels of the penetrants used.

ii) The integral diffusion coefficients for the systems studied can be calculated from the slope of the straight line portions of the take-up time curves.

iii) The diffusion coefficients were found to be concentration dependent.

iv) The diffusion coefficients of the organic penetrants studied in cellulose acetate were found to decrease with increasing penetrant size, which agrees with previous findings for other polymer/penetrant systems.

v) The temperature dependence of the diffusion coefficients were found to follow an Arrhenius type equation.

vi) Plots of ln D_o against 1/T were found to be linear within the temperature range employed. The slopes of such plots have been ~~utilized~~ in calculating values of the activation energies of diffusion.

vii) The activation energies of diffusion were found to be independent of temperature in the temperature range 25-45°C employed.

viii) The activation energy of diffusion was found to increase with increasing penetrant molar volume in a linear fashion, which supports previous findings in the literature.

ix) Some unexpected results were obtained in the case of diffusion of methanol and ethanol, represented by the inversion of the slopes of the take-up time curves at higher pressures. The same phenomenon was reported in the literature.

x) The intrinsic and thermodynamic diffusion coefficients were found to depend exponentially on the activity level of the penetrant.

xi) The experimental results obtained in this study were found to agree very much with the results predicted by the free-volume model for diffusion in polymers suggested by Wilkens and Long.

6.2 Recommendations for Further Work

The following are suggestions for further studies:

i) Some modifications have to be introduced in the design of the experimental set-up to enable higher activity levels of the penetrants to be used.

ii) Different thicknesses of the polymer film can be employed to study the effect of thickness.

iii) The glass transition temperature of the polymer film has to be determined. This will permit comparing experimental data with the predictions of Fujita's free volume theory.

NOMENCLATURE

The meanings of all important and frequently used symbols are described below. The meanings of other symbols are described in the text as they are used.

A = constant

a = activity of the penetrant

B = constant

C = concentration (mg penetrant/mg polymer)

D = differential diffusion coefficient

D_{AB} = mutual diffusion coefficient

D_F = Fickian diffusion coefficient

$\overline{D}$ = integral diffusion coefficient

D_o = diffusivity at zero penetrant concentration

$\mathcal{D}$ = intrinsic diffusion coefficient

$\mathcal{D}^*$ = thermodynamic diffusion coefficient

E_d = activation energy of diffusion

ℓ = thickness of the polymer film

M_t = amount of penetrant sorbed at time t

M_∞ = amount of penetrant sorbed at equilibrium

P = vapor pressure of the penetrant

P^o = saturation vapor pressure of the penetrant

R = universal gas constant

T = temperature

t = time

J_A^c = flux of component A in a coordinate frame of reference

β = thermodynamic correction factor

ϕ = volume fraction of the penetrant molecule

χ = Flory-Huggins interaction parameter

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APPENDICES

APPENDIX A

Experimental Data

TABLE A.1

Sorption Data for the System:
Cellulose Acetate - Methanol

<u>Conditions</u>:

Temperature = 25°C, Penetrant vapor pressure = 5.65 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
2.0	0.0435
4.0	0.0861
6.0	0.115
8.0	0.1384
12.0	0.1688
16.0	0.1988
24.0	0.2339
34.0	0.2675
40.0	0.2831
48.0	0.3
54.0	0.3093
60.0	0.3206
80.0	0.3367
110.0	0.3535
130.0	0.3624
140.0	0.3672
216.0	0.38 = M_∞

TABLE A.2

Sorption Data for the System:
Cellulose Acetate - Methanol

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 21.08 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
2.0	0.1265
4.0	0.2666
6.0	0.3582
10.0	0.4976
12.0	0.5583
14.0	0.6131
16.0	0.6627
18.0	0.7078
22.0	0.7765
24.0	0.8024
26.0	0.8242
32.0	0.866
40.0	0.8967
60.0	0.9238
196.0	0.9509 = M_∞

TABLE A.3

Sorption Data for the System:
Cellulose Acetate - Methanol

<u>Conditions</u>:

Temperature = 25°C, Penetrant vapor pressure = 45.41 mm Hg

Time, t, minutes	Amount sorbed, mg
0.0	0.0
2.0	0.2927
3.0	0.4443
5.0	0.659
7.0	0.845
9.0	1.0117
11.0	1.1573
13.0	1.2674
17.0	1.3908
21.0	1.4392
27.0	1.4711
40.0	1.5
50.0	1.5111
75.0	1.5208
140.0	1.5241
200.0	1.5296 = M_∞

TABLE A.4

Sorption Data for the System:
Cellulose Acetate - Methanol

<u>Conditions</u>:

Temperature = 25°C, Penetrant vapor pressure = 70.23 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
1.0	0.275
2.0	0.622
3.0	0.911
4.0	1.16
5.0	1.4
7.0	1.8
9.0	2.0
12.0	2.15
15.0	2.21
24.0	2.27
31.0	2.2832
34.0	2.2889
75.0	2.3218
120.0	2.351
178.0	2.3811 = M_∞

TABLE A.5

Sorption Data for the System:

Cellulose Acetate - Methanol

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 90.14 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
2.0	0.74
4.0	1.93
6.0	2.70
8.0	2.94
10.0	3.026
12.0	3.067
14.0	3.0877
16.0	3.1
20.0	3.128
26.0	3.15
32.0	3.175
42.0	3.201
64.0	3.2318
70.0	$3.2335 = M_\infty$

TABLE A.6

Sorption Data for the System:

Cellulose Acetate - Methanol

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 5.59 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
2.0	0.032
4.0	0.052
6.0	0.0674
8.0	0.0799
10.0	0.0906
15.0	0.1104
20.0	0.1296
25.0	0.1446
30.0	0.1607
40.0	0.1808
50.0	0.1949
60.0	0.205
70.0	0.2078
90.0	0.2167 = M_∞

TABLE A.7

Sorption Data for the System: Cellulose Acetate - Methanol

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 20.55 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
2.0	0.1284
4.0	0.2081
6.0	0.264
8.0	0.3113
10.0	0.3532
15.0	0.4358
20.0	0.494
25.0	0.5242
30.0	0.544
40.0	0.5663
50.0	0.5752
60.0	0.5783
72.0	$0.583 = M_\infty$

TABLE A.8

Sorption Data for the System:
Cellulose Acetate - Methanol

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 45.38 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
2.0	0.2577
4.0	0.441
6.0	0.5786
8.0	0.6987
10.0	0.7944
12.0	0.8623
14.0	0.9086
16.0	0.9381
18.0	0.9587
20.0	0.973
25.0	0.9943
30.0	0.9996
50.0	1.0184 = M_∞

TABLE A.9

Sorption Data for the System:
Cellulose Acetate - Methanol

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 70.29 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
2.0	0.3291
3.0	0.4825
4.0	0.6156
5.0	0.7382
6.0	0.8515
8.0	1.0327
9.0	1.0973
12.0	1.2051
15.0	1.245
20.0	1.2679
32.0	1.2811
38.0	1.2827 = M_∞

TABLE A.10

Sorption Data for the System:
Cellulose Acetate - Methanol

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 90.08 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
2.0	0.4805
3.0	0.7926
4.0	1.0494
5.0	1.2774
6.0	1.4411
8.0	1.5981
9.0	1.6352
12.0	1.6838
15.0	1.7073
18.0	1.717
23.0	1.7211
30.0	1.7285 = M_∞

TABLE A.11

Sorption Data for the System:
Cellulose Acetate - Methanol

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 5.63 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
1.0	0.0173
2.0	0.0305
3.0	0.0417
4.0	0.048
7.0	0.064
9.0	0.068
10.0	0.0741
13.0	0.0867
16.0	0.0957
23.0	0.1109
30.0	0.1228
40.0	0.1307
68.0	$0.1418 = M_\infty$

TABLE A.12

Sorption Data for the System:
Cellulose Acetate - Methanol

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 20.63 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
1.0	0.0536
2.0	0.1028
3.0	0.1348
4.0	0.1561
5.0	0.1841
6.0	0.2217
7.0	0.243
8.0	0.2537
11.0	0.295
13.0	0.3103
17.0	0.3313
21.0	0.3458
25.0	0.3546
38.0	0.3774 = M_∞

TABLE A.13

Sorption Data for the System:
Cellulose Acetate - Methanol

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 45.2 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
1.0	0.1118
2.0	0.216
3.0	0.2855
4.0	0.3304
5.0	0.376
6.0	0.4155
7.0	0.4484
8.0	0.4816
11.0	0.5429
14.0	0.5725
16.0	0.5837
20.0	0.5982
22.0	0.6049
27.0	$0.6153 = M_\infty$

TABLE A.14

Sorption Data for the System:
Cellulose Acetate - Methanol

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 70.24 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
1.0	0.1228
2.0	0.3116
3.0	0.446
4.0	0.5551
5.0	0.6422
6.0	0.7103
7.0	0.7613
8.0	0.7987
9.0	0.8267
10.0	0.8472
11.0	0.8598
13.0	0.8794
16.0	0.8934
19.0	0.9018
22.0	0.906
27.0	0.911 = M_∞

TABLE A.15

Sorption Data for the System:
Cellulose Acetate - Methanol

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 90.67 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
1.0	0.1201
2.0	0.38
3.0	0.57
4.0	0.7214
5.0	0.84
6.0	0.9205
7.0	0.97
8.0	1.0029
11.0	1.0435
15.0	1.0617
24.0	1.076

TABLE A.16

Sorption Data for the System:

Cellulose Acetate - Ethanol

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 6.7 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.1	0.035
0.5	0.08
0.7	0.1
1.6	0.16
2.1	0.19
3.9	0.27
5.5	0.33
8.0	0.41
10.0	0.47
12.0	0.515
14.0	0.56
19.0	0.64
22.0	0.68
27.0	0.71
37.0	$0.752 = M_\infty$

TABLE A.17

Sorption Data for the System:
Cellulose Acetate - Ethanol

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 10.55 mm Hg

Time, t, hours	Amount sorbed, mg
0.0	0.0
0.2	0.045
0.53	0.10
0.93	0.15
1.5	0.21
2.0	0.25
4.0	0.39
5.5	0.48
7.5	0.575
9.0	0.65
11.0	0.72
12.0	0.74
14.0	0.79
16.0	0.825
20.0	0.86
23.0	0.88
28.0	0.90 = M_∞

TABLE A.18

Sorption Data for the System:

Cellulose Acetate - Ethanol

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 20.53 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.20	0.05
0.40	0.1
1.25	0.35
1.75	0.45
2.5	0.6
3.0	0.7
3.5	0.8
4.5	0.95
6.0	1.15
8.0	1.28
10.0	1.32
14.0	1.38
16.0	$1.4 = M_\infty$

TABLE A.19

Sorption Data for the System:
Cellulose Acetate - Ethanol

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 30.44 mm Hg

Time, t, minutes	Amount Sorbed, mg
0.0	0.0
0.2	0.23
0.5	0.45
0.7	0.55
0.9	0.65
1.4	0.9
1.7	1.1
2.1	1.3
2.3	1.4
3.0	1.7
3.9	1.9
4.8	2.0
6.1	2.05
7.0	2.1 = M_∞

TABLE A.20

Sorption Data for the System:

Cellulose Acetate - Ethanol

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 40.5 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.067	0.4
0.13	0.6
0.2	0.75
0.33	1.0
0.53	1.42
0.67	1.7
0.93	2.3
1.0	2.43
1.33	2.85
1.67	2.98
2.0	3.05
2.53	$3.1 = M_\infty$

TABLE A.21

Sorption Data for the System:
Cellulose Acetate - Ethanol

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 50.0 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.01	0.07
0.04	0.35
0.09	0.85
0.16	1.4
0.25	2.1
0.36	3.15
0.49	3.7
0.64	3.85 = M_∞

TABLE A.22

Sorption Data for the System:
Cellulose Acetate - Ethanol

<u>Conditions</u>:

Temperature = 35°C, Penetrant vapor pressure = 6.57 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.17	0.0473
0.5	0.0847
1.0	0.1198
1.67	0.1725
3.0	0.2332
4.17	0.2876
5.0	0.3143
8.0	0.3785
10.0	0.4213
13.3	0.5081
17.75	0.5386 = M_∞

TABLE A.23

Sorption Data for the System:

Cellulose Acetate - Ethanol

<u>Conditions:</u>

Temperature = 35°C, Penetrant vapor pressure = 10.6 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.17	0.0713
0.5	0.1288
0.83	0.171
1.67	0.2547
2.67	0.3428
3.33	0.3936
4.17	0.4482
5.0	0.4911
6.0	0.541
8.0	0.5988
11.17	0.6735 = M_∞

TABLE A.24

Sorption Data for the System:
Cellulose Acetate - Ethanol

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 20.7 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.03	0.066
0.2	0.134
0.8	0.299
1.1	0.365
1.6	0.459
2.17	0.5486
3.17	0.6814
3.5	0.7212
4.0	0.7674
5.0	0.8455
6.52	$0.9 = M_\infty$

TABLE A.25 .

Sorption Data for the System:
Cellulose Acetate - Ethanol

<u>Conditions</u>:

Temperature = 35°C, Penetrant vapor pressure = 30.24 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.17	0.1517
0.25	0.1977
0.5	0.322
0.83	0.4713
1.17	0.591
1.5	0.717
2.0	0.8517
2.33	0.921
2.67	0.9913
3.0	1.055
4.0	1.1328
4.13	1.142 = M_∞

TABLE A.26

Sorption Data for the System:

Cellulose Acetate - Ethanol

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 40.39 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.08	0.2125
0.167	0.295
0.333	0.4366
0.42	0.498
0.5	0.5476
0.67	0.662
0.83	0.763
0.92	0.812
1.0	0.861
1.33	1.0457
1.83	1.2912
2.0	1.348 = M_∞

TABLE A.27

Sorption Data for the System:

Cellulose Acetate - Ethanol

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 50.27 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.08	0.357
0.167	0.5121
0.25	0.633
0.333	0.7432
0.67	1.1445
0.83	1.347
0.92	1.447
1.0	1.5373
1.17	1.689
1.33	1.8011
1.5	1.87 = M_∞

TABLE A.28

Sorption Data for the System:

Cellulose Acetate - Ethanol

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 90.0 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.048	0.2
0.084	0.46
0.1T56	0.72
0.168	1.22
0.2	1.6
0.23	2.0
0.25	2.2
0.281	2.67
0.336	3.32
0.372	3.52
0.422	3.67
0.518	3.7456 = M_∞

TABLE A.29

Sorption Data for the System:
Cellulose Acetate - Ethanol

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 10.59 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.083	0.0462
0.33	0.0704
0.42	0.0788
0.67	0.1093
1.0	0.1305
1.67	0.184
2.08	0.2035
2.92	0.2483
3.33	0.2738
4.58	0.3269
5.0	0.3343
5.83	0.3582
6.67	0.3715
7.55	$0.39 = M_\infty$

TABLE A.30

Sorption Data for the System:

Cellulose Acetate - Ethanol

Conditions:

Temperature = 45°C,   Penetrant vapor pressure = 20.73 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.17	0.1067
0.5	0.1831
0.833	0.2416
1.5	0.3383
2.08	0.4076
2.92	0.4788
3.75	0.5425
4.58	0.5848
4.97	0.6092 $\Rightarrow M_\infty$

TABLE A.31

Sorption Data for the System:

Cellulose Acetate - Ethanol

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 30.53 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.05	0.1081
0.1	0.1333
0.17	0.1631
0.42	0.2585
0.667	0.3291
0.833	0.3752
1.17	0.4717
1.5	0.5525
2.08	0.6657
2.5	0.7296
2.92	0.7833
3.33	0.8243
4.06	0.8659 = M_∞

TABLE A.32

Sorption Data for the System:

Cellulose Acetate - Ethanol

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 41.8 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.17	0.2155
0.333	0.3101
0.42	0.3579
0.5	0.3963
0.83	0.528
1.17	0.6464
1.5	0.7617
1.67	0.8056
2.5	0.9697
2.92	1.013
3.62	1.0653 = M_∞

TABLE A.33

Sorption Data for the System:

Cellulose Acetate - Ethanol

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 50.35 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.05	0.163
0.1	0.2286
0.25	0.3559
0.333	0.42
0.5	0.5227
0.833	0.7078
1.0	0.7996
1.5	1.0038
1.67	1.0492
2.08	1.1342
2.5	1.1809
3.28	1.2151 = M_∞

TABLE A.34

Sorption Data for the System:
Cellulose Acetate - Ethanol

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 94.91 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.048	0.326
0.0676	0.45
0.133	0.834
0.152	0.9202
0.2025	1.1625
0.23	1.3221
0.372	1.892
0.436	2.0639
0.504	2.169
0.67	2.2811
0.828	2.3236
1.322	2.3706 = M_∞

TABLE A.35

Sorption Data for the System:
Cellulose Acetate - Benzene

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 41.13 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
1.5	0.015
5.5	0.055
6.5	0.065
13.0	0.105
17.0	0.125
21.0	0.145
27.0	0.175
30.0	0.19
33.0	0.205
37.0	0.222
46.0	0.258
60.0	0.315
70.0	0.345
88.0	$0.405 = M_\infty$

TABLE A.36

Sorption Data for the System:
Cellulose Acetate - Benzene

<u>Conditions</u>:

Temperature = 25°C, Penetrant vapor pressure = 55.9 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.5	0.0
2.0	0.035
3.0	0.05
6.0	0.09
9.0	0.125
12.0	0.16
18.0	0.225
21.0	0.255
33.0	0.36
39.0	0.4
48.0	0.47
57.0	0.53
63.0	0.565
69.0	0.605
84.0	0.695 = M_∞

TABLE A.37

Sorption Data for the System:
Cellulose Acetate - Benzene

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 70.15 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
1.0	0.03
4.7	0.13
10.0	0.23
18.0	0.33
26.0	0.43
36.0	0.53
46.0	0.63
54.0	0.73
64.0	0.85 = M_∞

TABLE A.38

Sorption Data for the System:
Cellulose Acetate - Benzene

Conditions:

Temperature = 25°C, Penetrant vapor pressure = 81.1 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.3	0.0
0.5	0.1
0.8	0.15
2.0	0.3
3.5	0.5
4.2	0.6
5.7	0.8
10.7	1.05
12.7	1.15
16.7	1.38
20.7	1.48
26.7	1.58
29.7	1.65
37.7	1.7 = M_∞

TABLE A.39

Sorption Data for the System:
Cellulose Acetate - Benzene

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 40.55 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.167	0.0029
0.333	0.0077
1.17	0.0246
1.67	0.0334
2.5	0.0549
4.17	0.0737
5.0	0.0801
10.0	.1042
11.67	.1056
16.7	.1429
23.33	.1586
26.7	.1859
29.83	.1965 = M_∞

TABLE A.40

Sorption Data for the System:
Cellulose Acetate - Benzene

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 55.27 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.5	0.0237
0.67	0.0303
0.83	0.0337
1.5	0.0489
1.67	0.0565
3.33	0.0908
4.17	0.0987
6.67	0.1212
10.0	0.1706
11.67	0.1853
15.0	0.2037
16.7	0.2187
19.67	0.2454 = M_∞

TABLE A.41

Sorption Data for the System:
Cellulose Acetate - Benzene

Conditions:

Temperature = 35°C,   Penetrant vapor pressure = 70.0 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.67	0.0189
1.67	0.0473
2.5	0.0592
3.33	0.0832
5.0	0.1225
6.67	0.1468
8.33	0.1609
10.0	0.1876
11.67	0.2113
13.33	0.2324
16.7	0.2924
20	0.3294 = M_∞

TABLE A.42

Sorption Data for the System:
Cellulose Acetate - Benzene

Conditions:

Temperature = 35°C, Penetrant vapor pressure = 80.16 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.5	0.0144
1.17	0.0498
1.33	0.0557
2.5	0.084
3.33	0.1073
6.67	0.1958
8.33	0.2129
10.0	0.2436
11.67	0.2739
13.33	0.3116
15.00	0.3375
16.7	0.3856 = M_∞

TABLE A.43

Sorption Data for the System:
Cellulose Acetate - Benzene

<u>Conditions</u>:

Temperature = 45°C, Penetrant vapor pressure = 40.68 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
1.17	0.0251
1.33	0.0303
2.5	0.0445
4.17	0.0644
6.67	0.0998
8.33	0.1083
11.67	0.1444
13.33	0.1545
14.17	0.1585
15.08	0.1645 = M_∞

TABLE A.44

Sorption Data for the System:

Cellulose Acetate - Benzene

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 55.17 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.333	0.0051
0.666	0.0161
1.83	0.0472
2.5	0.0557
3.25	0.064
3.6	0.0723
5.0	0.0823
5.5	0.1136
7.42	0.1322
8.42	0.1423
11.42	0.1548
12.7	0.1644
12.92	0.1829 = M_∞

TABLE A.45

Sorption Data for the System:

Cellulose Acetate - Benzene

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 70.20 mm Hg

Time, t, hours	Amount Sorbed, mg
0.0	0.0
0.167	0.002
0.333	0.0176
0.83	0.0353
1.5	0.0516
2.5	0.0736
4.17	0.1066
6.67	0.1418
8.33	0.1864
10.0	0.2037
13.33	0.2355
15.67	0.253 = M_∞

TABLE A.46

Sorption Data for the System:

Cellulose Acetate - Benzene

Conditions:

Temperature = 45°C, Penetrant vapor pressure = 79.97 mm Hg

Time, t, hours	Amount Sorbed, g
0.0	0.0
0.25	0.0045
0.833	0.0321
1.0	0.0397
1.5	0.0609
3.0	0.1068
3.67	0.1265
4.17	0.1366
5.17	0.1552
5.83	0.1663
6.67	0.1801
9.17	0.2146
10.0	0.2278
11	0.2433
11.83	0.255
14.75	0.294
16.67	0.3166 = M_∞

APPENDIX B

Sorption Curves for the Systems Investigated in this Study at 35 and 45°C

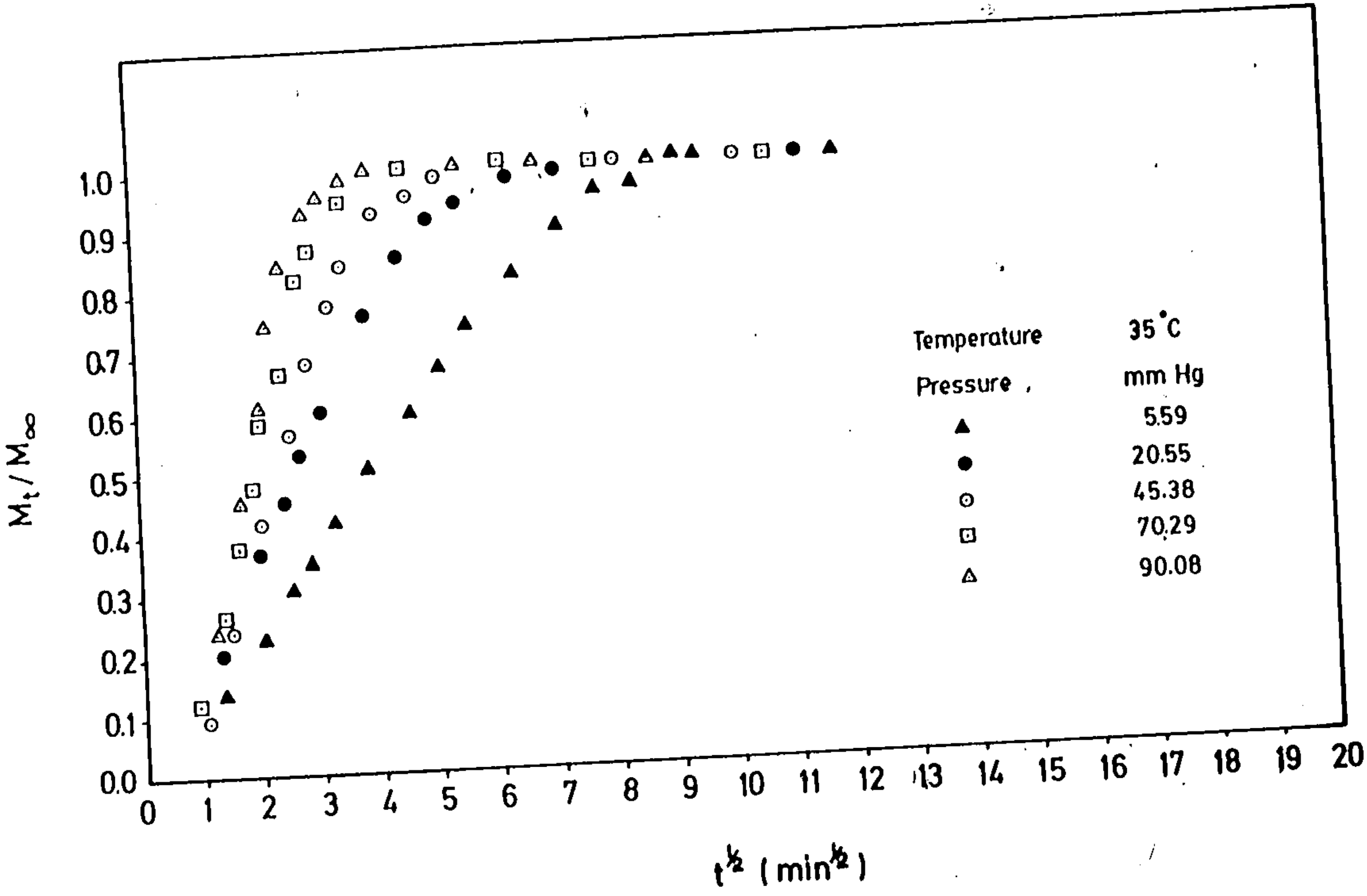

Figure B.1 : Sorption of Methanol in Cellulose Acetate

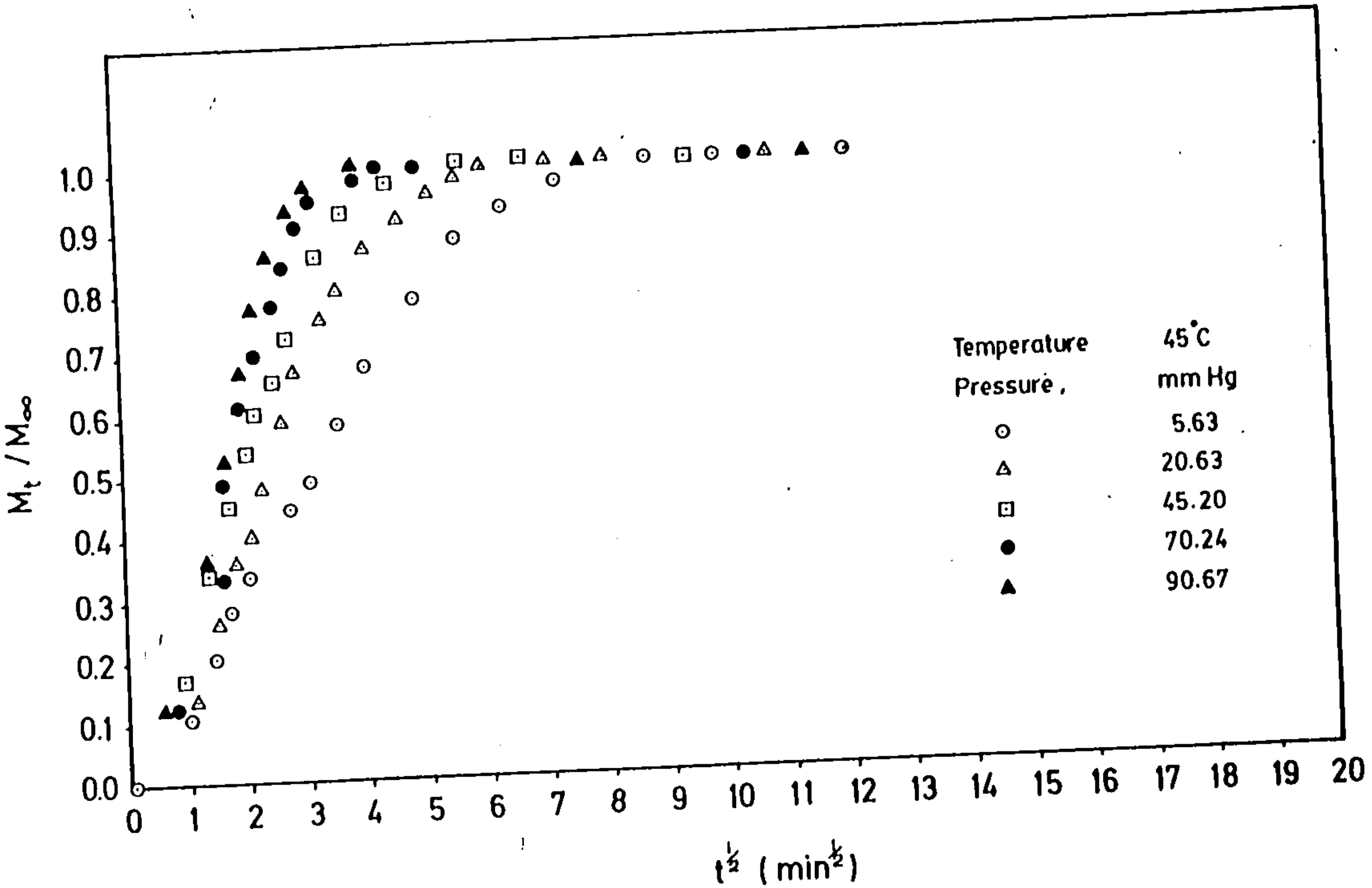

Figure B.2 :Sorption of Methanol in Cellulose Acetate

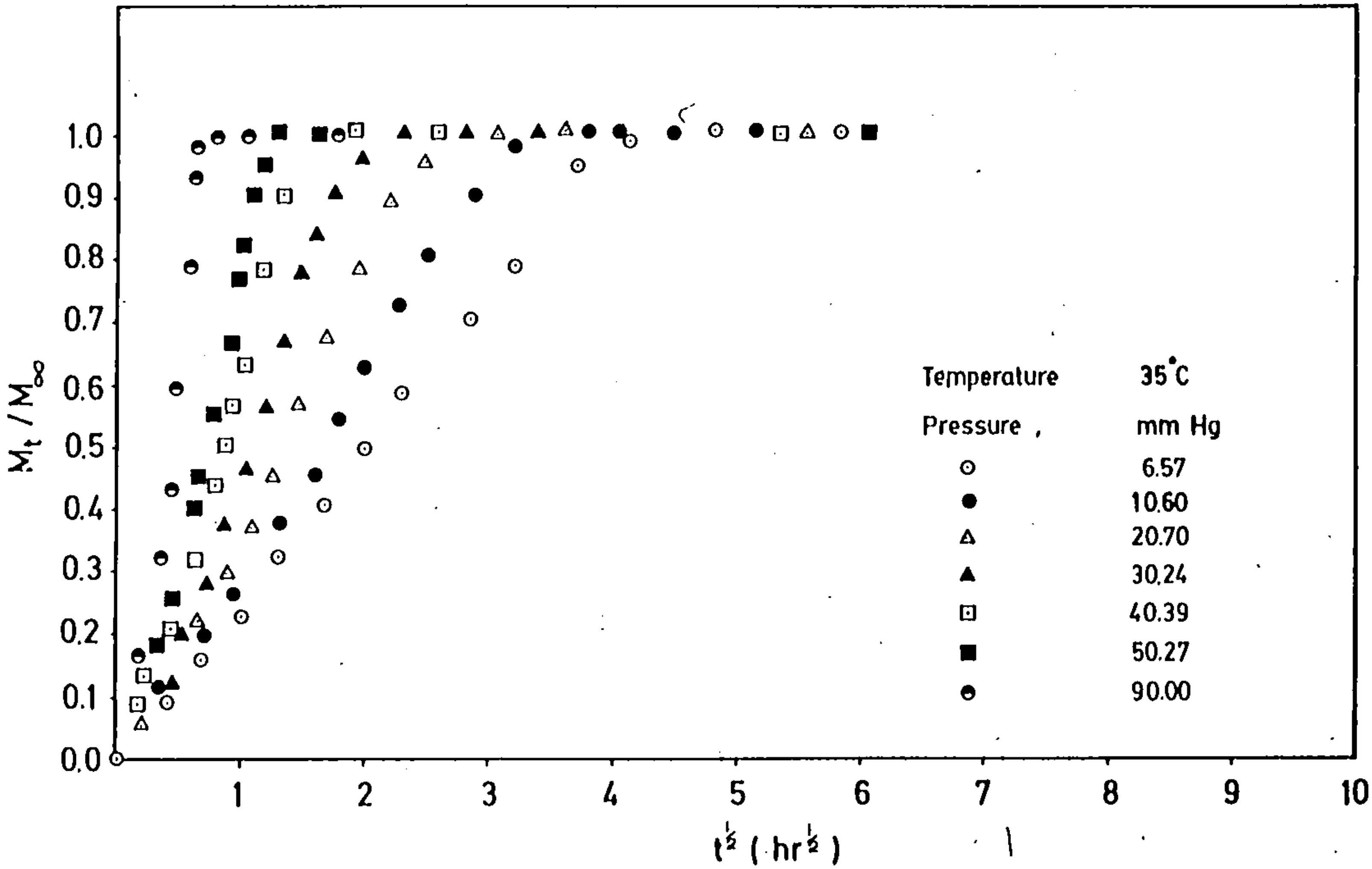

Figure B.3 : Sorption of Ethanol in Cellulose Acetate

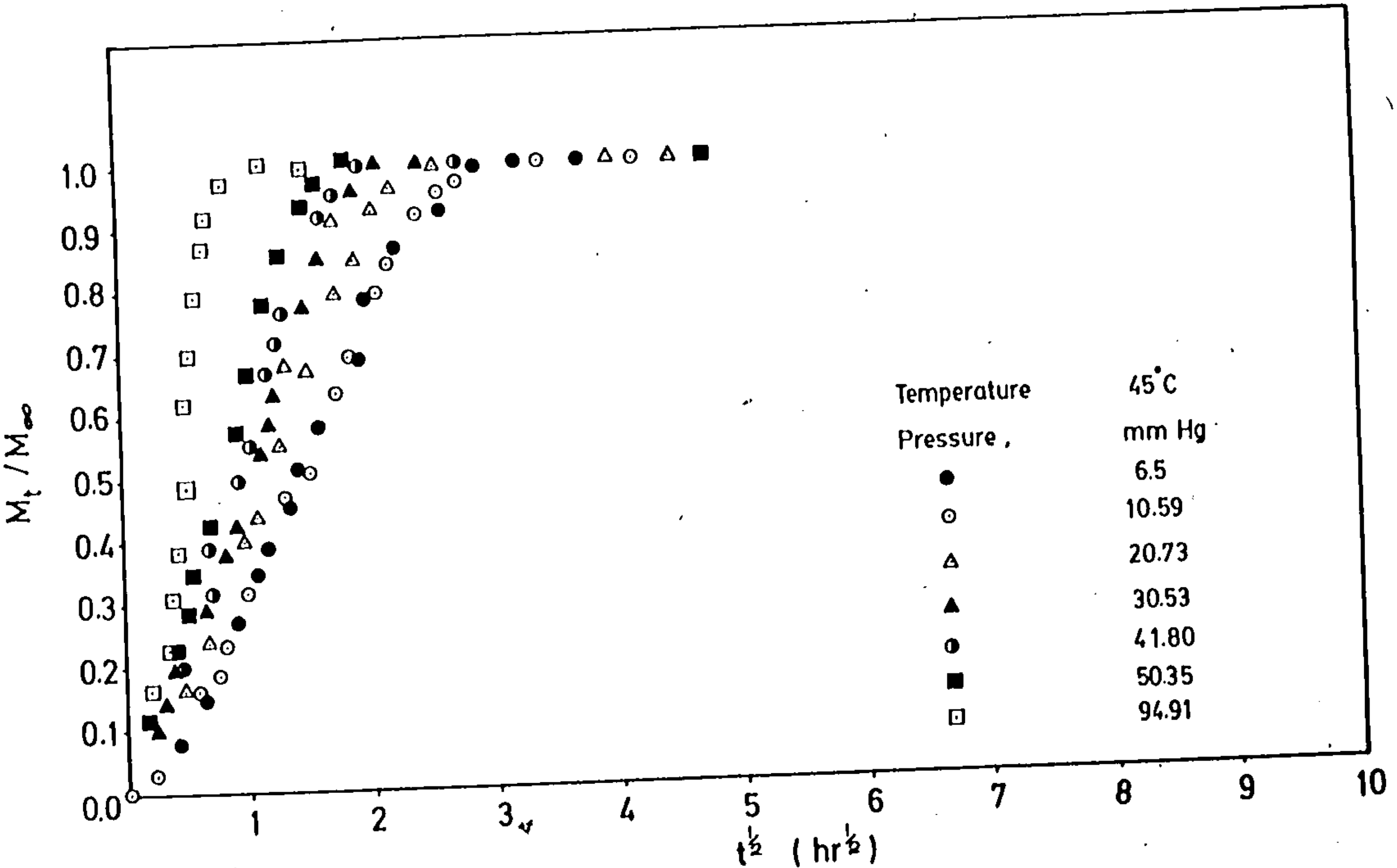

Figure B.4 : Sorption of Ethanol in Cellulose Acetate

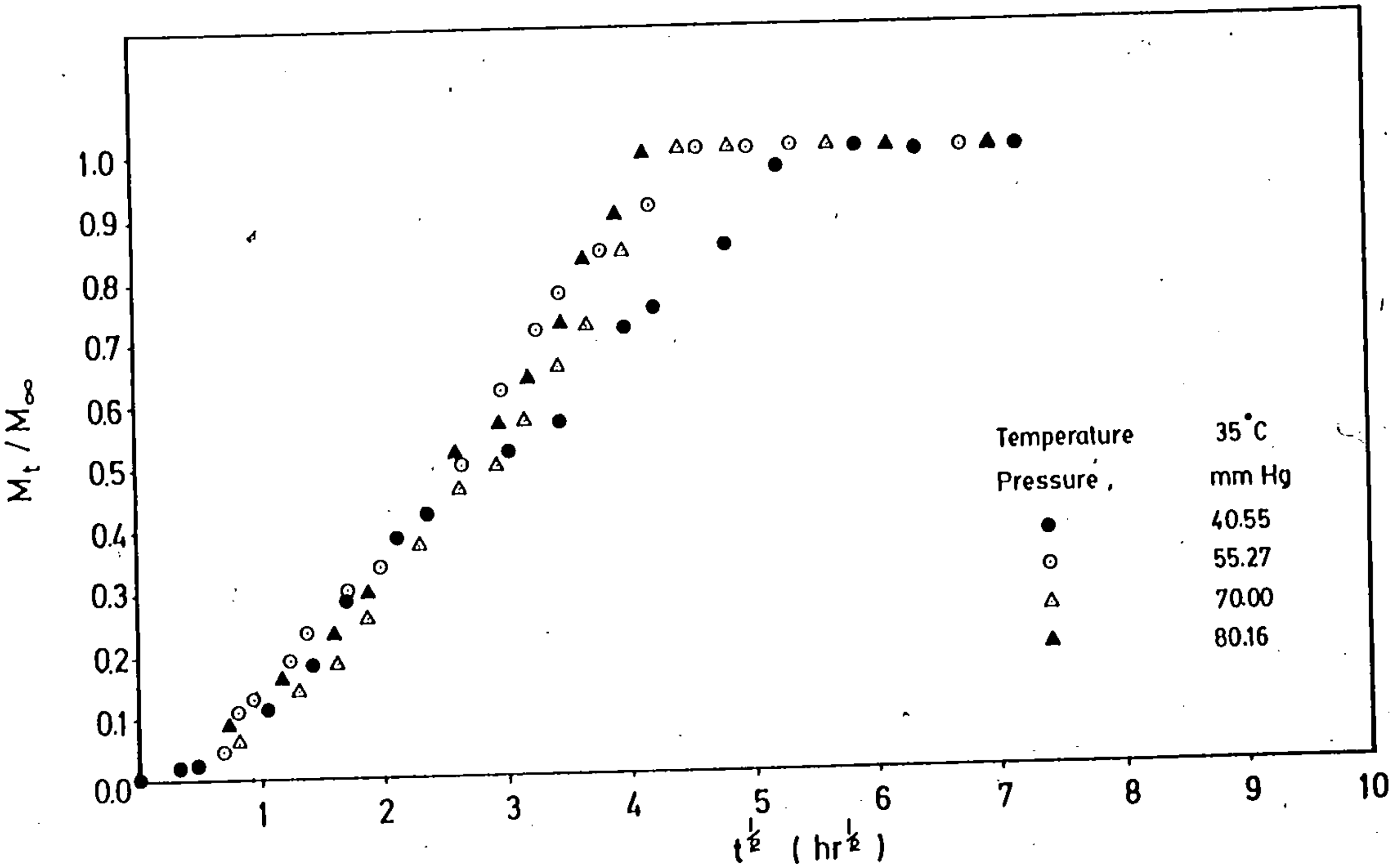

Figure B.5 : Sorption of Benzene in Cellulose Acetate

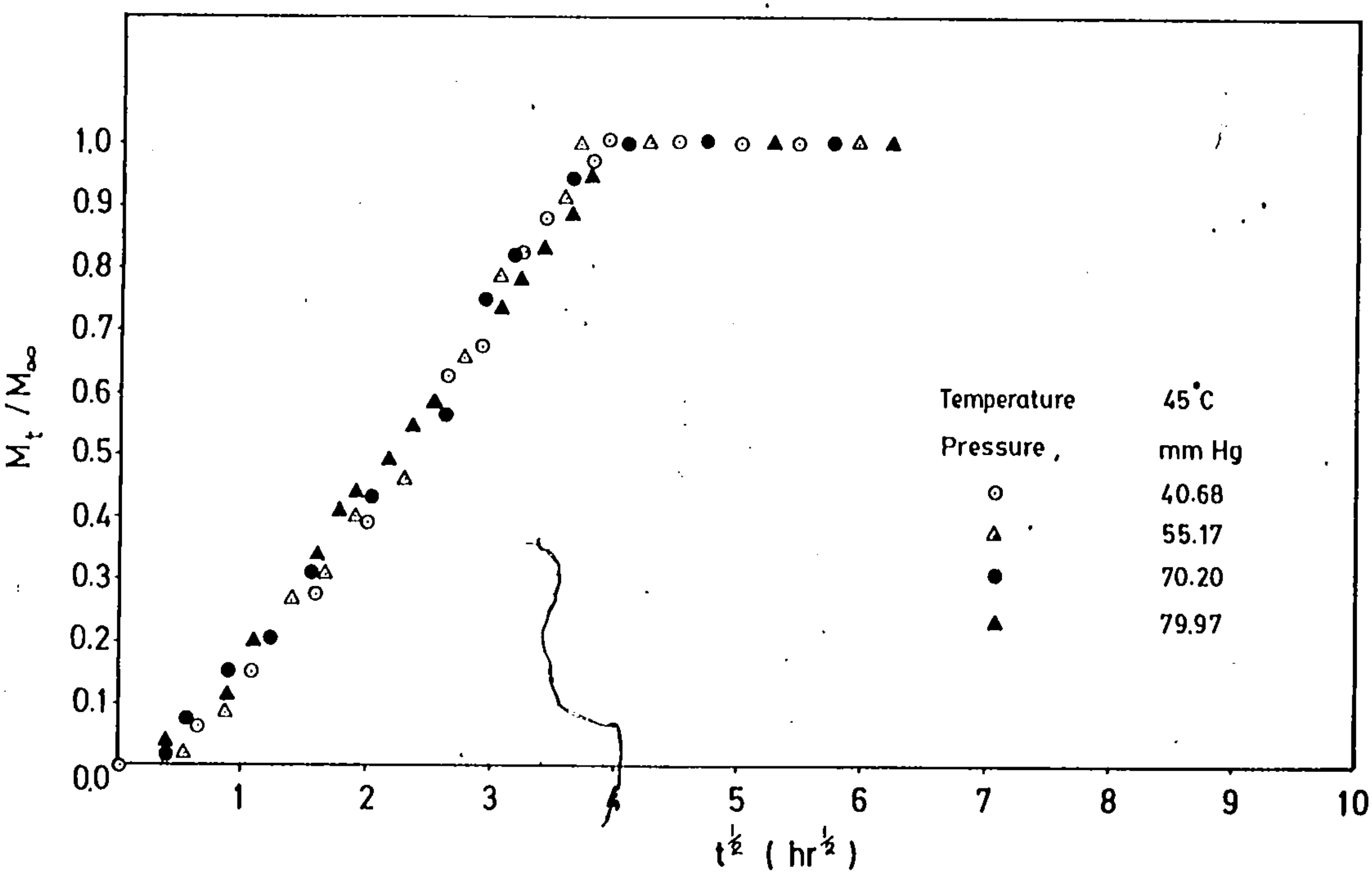

Figure B.6 : Sorption of Benzene in Cellulose Acetate

APPENDIX C

Detailed Manual Calculations of the Differential Diffusivities from the Integral Values for the System Cellulose Acetate/ Ethanol at 45°C

Table C.1

An Example of the Calculation of the Differential Diffusivities
from the Integral Values for the System
Cellulose Acetate/Ethanol
at 45°C

P mm Hg	C x 10	ΔC	$\bar{D} \times 10^{12}$ cm^2/sec	$\bar{D}\Delta C = \int_{C_{n-1}}^{C_n} D dC$	$\Sigma \bar{D}\Delta C = \int_{o}^{C_i} \bar{D}\Delta C$	$\frac{d \ln \Sigma \bar{D}\Delta C}{dC}$	First Approximation $D * 10^{12}$
6.5	0.097	0.097	62.0	6.014	6.014	5.1316	30.86
10.59	0.15	0.053	65.3	3.461	9.475	5.1316	48.622
20.73	0.23	0.08	81.0	6.48	15.955	5.1316	81.87
30.53	0.33	0.1	106.4	10.64	26.595	5.1316	136.475
41.8	0.41	0.08	131.0	10.48	37.075	5.1316	190.254
50.35	0.47	0.06	177.3	10.638	47.713	5.1316	244.844
94.91	0.91	0.44	958.0	421.52	469.23	5.1316	2407.9

Table C.2

Corrections Applied to the First Approximate Value of D, in Table C.1 to Give the Second Approximation

$D \times 10^{12}$ cm^2/sec	$\frac{\bar{D}}{D_o}$	Percent Correction	Corrected Diffusion Coefficient, cm^2/sec			
			$\bar{D}\Delta C$	$\Sigma\ \bar{D}\Delta C$	$\frac{d \ln \Sigma\ \bar{D}\Delta C}{dC}$	2nd approx. $D \times 10^{12}$
30.86	1.66	6	5.65	5.65	5.075	28.67
48.622	2.1	11.5	3.08	8.73	5.075	44.30
81.87	1.66	6	6.09	14.82	5.075	75.212
136.475	1.3	4	10.21	25.03	5.075	127.03
190.254	0.96	0	10.48	35.51	5.075	180.21
244.844	0.93	0	10.638	46.148	5.075	234.201
2407.9	0.4	0	421.52	467.668	5.075	2373.415

APPENDIX D

Computer Program for Calculating the Differential Diffusivities from the Integral Values

This program was prepared and it has been used for the calculation of the differential diffusivities for the systems investigated in this study from the integral diffusivities obtained experimentally.

```
//JOBNAME  JOB  (R060,E7C),'HUSSEIN',CLASS=Z
//       EXEC  FORTVCLG
//FORT.SYSIN  DD  *
C *********************************************************************
C THIS PROGRAM IS FOR DETERMINING DIFFERENTIAL DIFFUSIVITIES FROM
C       INTEGRAL(EXPERIMENTAL)DIFFUSIVITIES
C *********************************************************************
      EXTERNAL ADM
      EXTERNAL TWO
      EXTERNAL THR
      EXTERNAL FOX
      EXTERNAL DV2
      EXTERNAL DV3
      EXTERNAL ASD
      EXTERNAL KIM
      INTEGER M,N,IXJAC,NSIG,MAXFN,IOPT,I,INFER,IER
      DIMENSION Y(22),DLTC(100,9),SP1(100,9),SOP(100,9),
     @AP1(100,9),SSP1(100,9),RT(100,9),PER(100,9),Q(100,20),QP(100,10
     #),DCOR(100,10),V(22),DD(9),A(100,10),XZ(15),YZ(15),VP(10)
      REAL PARM(8),X(8),F(22),XJAC(22,8),XJTJ(72),WORK(94),
     *EPS,DELTA,SGN,SSQ
      COMMON/ZSQ/Y,V
      M=5
C     M = NUMBER OF DATA POINTS.
      NN=15
C     NN = NUMBER OF DATA POINTS FROM CRANK'S CORRECTION CURVE.
      L=0
C      L= COUNTER
      K=1
C     K= ITRATION NUMBER
      DO 505 I=1,M
      READ(5,502) VP(I)
502   FORMAT(F5.2)
C     VP = OPERATING VAPOR PRESSURE
505   CONTINUE
      DO 11 I=1,M
      READ(5,55) V(I),DD(I)
55    FORMAT(G10.4,G19.4)
C     V= CONCENTRATION
C     DD= INTEGRAL(EXPERIMENTAL)DIFFUSIVITY
11    CONTINUE
      DO 19 I=1,NN
      READ(5,79)XZ(I),YZ(I)
79    FORMAT(2F10.2)
19    CONTINUE
      READ(5,507)N
507   FORMAT(I1)
C     N=NUMBER OF PARAMETERS (N.B. THERE IS 2 REGRESSION SUBROUTINES)
960   CALL ADM(V,K,DD,DLTC,QP,SP1,SSP1,Y)
      IXJAC=10
      NSIG=3
      EPS=0.0
      DELTA=0.0
      MAXFN=500
      IOPT=1
```

```
C     THE INITIAL VALUES OF THE PARAMETERS ARE TO BE PROVIDED
      IF(N.EQ.4)GO TO 508
      IF(N.EQ.6)GO TO 509
      IF(N.GE.8)GO TO 510
508   X(1)=0.1
      X(2)=0.2
      X(3)=0.15
      X(4)=0.004
      GOTO 511
509   X(1)=0.1
      X(2)=0.2
      X(3)=0.15
      X(4)=0.004
      X(5)=0.35
      X(6)=0.17
      GO TO 512
510      X(1)=0.7500
      X(2)=0.8
      X(3)=0.01
      X(4)=0.00
      X(5)=2.5
      X(6)=0.821
      X(7)=-0.2554
      X(8)=0.082
C     ASSUME THE RELATION BETWEEN Y AND V TO BE OF THE FORM :
C              Y=X(1)+X(2)*V+X(3)*V**2+X(4)*V**3
C     THE COEFFICIENTS X(1),X(2),X(3),X(4) ARE TO BE DETERMINED
C     USING THE LIBRARY SUBROUTINE ZXSSQ AS FOLLOWS :
       CALL ZXSSQ(FOX,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,
     * PARM,X,SSQ,F,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
C     NOW A POLYNOMIAL OF Y .VS. V IS KNOWN
C     ANALYTICAL DIFFERENTIATION IS PERFORMED TO DETERMINE THE SLOPES.
      DO 7 I=1,M
      SOP(K,I)=X(2)+2.0*X(3)*V(I)+3.*X(4)*V(I)**2
C     SOP=SLOPE(VALUE OF THE DERIVATIVE EVALUATED AT A CERTAIN CONC.
7     CONTINUE
      GO TO 517
511       CALL ZXSSQ(TWO,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,
     * PARM,X,SSQ,F,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
      GO TO 513
512       CALL ZXSSQ(THR,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,
     * PARM,X,SSQ,F,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
      GO TO 515
513   DO 514 I=1,M
      SOP(K,I)=X(2)
514   CONTINUE
      GO TO 517
515   DO 516 I=1,M
      SOP(K,I)=X(2)+2.0*X(3)*V(I)
516   CONTINUE
517      DO 8 J=1,M
       AP1(K,J)=SOP(K,J)*SSP1(K,J)
8     CONTINUE
C     AP1 = FIRST APPROXIMATION OF THE DIFFERENTIAL DIFFUSIVITIES
C          A CORRECTION IS NEEDED TO FIND 2nd APPROXIMATION USING
C          CRANK'S CORRECTION CURVE.
```

```
      IF(K.EQ.1) GO TO 225
      IF(K.EQ.2) GO TO 93
225   WRITE(6,223)
223   FORMAT(23X,'System: Cellulose Acetate/Methanol')
      WRITE(6,224)
224   FORMAT(/,31X,'Temparature= 45 C')
      WRITE(6,227)
227   FORMAT(//,33X,'First Iteration')
      WRITE(6,228)
228   FORMAT(//,12X,'VP',9X,'C',8X,'DLTC',10X,'DD',8X,'SSP1',7X,
     @'D*',/)
      DO 230 I=1,M
      WRITE(6,229) VP(I),V(I),DLTC(K,I),DD(I),SSP1(K,I),AP1(K,I)
229   FORMAT(11X,F5.2,2X,G10.4,2X,G10.4,2X,G10.4,2X,G9.2,2X,G10.4)
230   CONTINUE
      S=SQRT((SSQ/3))
      WRITE(6,250)S
250   FORMAT(//,15X,'Standard deviation=',G13.4)
      WRITE(6,234)
234   FORMAT(//,15X,'These abbreviations have been used above',/)
      WRITE(6,9781)
9781  FORMAT(15X,'VP   =Operating vapor pressure(mmHg)',/)
      WRITE(6,9782)
9782  FORMAT(15X,'C    = Concentration',/)
      WRITE(6,235)
235   FORMAT(15X,'DLTC = Delta concentration: Cn-Cn-1',/)
      WRITE(6,236)
236   FORMAT(15X,'DD   = Experimental diffusivity in cm2/s',/)
      WRITE(6,237)
237   FORMAT(15X,'SSP1 =Summation(DD*DLTC)',/)
      WRITE(6,238)
238   FORMAT(15X,'D*   =First approximation(differential diffusivity
     *in cm2/s')
      WRITE(6,300)
300   FORMAT('1')
      GO TO 290
93    WRITE(6,251)
251   FORMAT(23X,'System: Cellulose Acetate/Methanol')
      WRITE(6,252)
252   FORMAT(/,31X,'Temperature= 45 C')
      WRITE(6,253)
253   FORMAT(//,33X,'Second Iteration')
      WRITE(6,254)
254   FORMAT(//,15X,'D*',10X,'DD/D ',4X,'% CORREC.',7X,
     *'SLOPE',7X,'D**',/)
      DO 255 I=1,M
      WRITE(6,256) AP1(K-1,I),RT(K,I),Q(K,I),SOP(K,I),AP1(K,I)
256   FORMAT(12X,G10.4,3X,G10.4,3X,G9.3,2X,F9.6,2X,G13.4)
255   CONTINUE
      S=SQRT((SSQ/3))
      WRITE(6,257)S
257   FORMAT(//,15X,'Standard deviation=',G13.4)
      WRITE(6,350)DI
350   FORMAT(/,15X,'Diffusivity at zero concentration=',G12.4,' cm2/s')
      WRITE(6,360)
```

```
360    F0RMAT(//,15X,'These abbreviations have been used above',/)
        WRITE(6,362)
362    FORMAT(15X,'% CORREC.= %Correction to be subtracted from (DD*DLTC
     *)',/)
       WRITE(6,9783)
9783   FORMAT(15X,'Slope    =dln(Sum(DD*DLTC))/dc',/)
        WRITE(6,363)
363     FORMAT(15X,'D**       =2nd approximation (Differential Diffusivity
     *) in cm2/s')
302    FORMAT('1')
290    IF(K.EQ.1)GOTO 2010
       DO 1958 J=1,M
       IF(ABS(AP1(K,J)-AP1(K-1,J)).GT.0.00001)GOTO 1958
       L=L+1
1958   CONTINUE
       IF(L.EQ.M)GOTO 91
2010   K=K+1
       IF(K.GT.2)GOTO 1938
       DO 1895 J=1,M
       Y(J)=ALOG (DD(J))
1895   CONTINUE
       GOTO 7019
1938   WRITE(6,3091)
3091   FORMAT('          ')
       DO 3391 J=1,M
       Y(J)=ALOG (AP1(K-2,J))
3391   CONTINUE
7019   WRITE(6,7029)
7029   FORMAT('                   ')
       IF(N.EQ.4)GO TO 518
       IF(N.EQ.6)GO TO 520
       IF(N.GE.8)GO TO 530
518    CALL ZXSSQ(DV2,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,X,SSQ,F,
     @XJAC,IXJAC,XJTJ,WORK,INFER,IER)
       DI=EXP (X(3))
        GO TO 519
520    CALL ZXSSQ(DV3,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,X,SSQ,F,
     @XJAC,IXJAC,XJTJ,WORK,INFER,IER)
       DI=EXP (X(4))
       GO TO 519
530    CALL ZXSSQ(ASD,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,X,SSQ,F,
     @XJAC,IXJAC,XJTJ,WORK,INFER,IER)
       DI=EXP (X(5))
C      DI= INITIAL DIFFUSIVITY WHEN CONCENTRATION EQUALS ZERO.
C      DI IS FOUND FROM THE INTERCEPT OF A PLOT OF lnDD .VS. V
519       IF(K.LE.2) THEN
       I=1
       RT(K,I)=DD(I)/DI
       ELSE
       I=1
       RT(K,I)=AP1(K-1,I)/DI
       END IF
       IF(K.EQ.2)THEN
       DO 1001 I=2,M
       RT(K,I)=AP1(K-1,I)/DD(I-1)
```

```
1001  CONTINUE
C     RT= RATIO(DD/Do)
      ELSE
      DO 1007 I=2,M
      RT(K,I)=AP1(K-1,I)/AP1(K-2,I-1)
1007  CONTINUE
      END IF
      DO 833 J=1,M
      A(K,J)=RT(K,J)
833   CONTINUE
      CALL KIM(A,K,M,XZ,YZ,Q)
      DO 707 J=1,M
      QP(K,J)=Q(K,J)/100
707   CONTINUE
C     Q = PERCENTAGE CORRECTION NEEDED
      GO TO 960
91    STOP
      END
      SUBROUTINE ADM(V,K,DD,DLTC,QP,SP1,SSP1,Y)
      DIMENSION X(5),Y(22),DLTC(100,9),SP1(100,9),SOP(100,9),
     @AP1(100,9),SSP1(100,9),RT(100,9),PER(100,9),Q(100,20),QP(100,10
     #),DCOR(100,10),V(22),DD(9),A(100,10),XZ(15),YZ(15)
      INTEGER K
      M=5
      I=1
      DLTC(K,I)=V(I)
C     DLTC= DIFFERENCE BETWEEN TWO CONSECUTIVE CONCENTRATIONS
      DO 3 I=2,M
      DLTC(K,I)=V(I)-V(I-1)
3     CONTINUE
      IF(K.EQ.1)THEN
      DO 9990 I=1,M
      SP1(K,I)=DD(I)*DLTC(K,I)
C     SP1=ACCUMULATIVE SUMMATION OF DD*DLTC
9990  CONTINUE
      ELSE
      DO 7766 I=1,M
      SP1(K,I)=(SP1(K-1,I)-(QP(K,I)*SP1(K-1,I)))
7766  CONTINUE
      END IF
      J=1
      SSP1(K,J)=SP1(K,J)
C     SSP1=ACCUMULATIVE SUMMATION OF SP1
      DO 5 J=2,M
      SSP1(K,J)=SSP1(K,J-1)+SP1(K,J)
5     CONTINUE
      DO 6 I=1,M
      Y(I)=ALOG(SSP1(K,I))
6     CONTINUE
C     Y= LOGARITHM TO THE BASE e OF SSP1
      RETURN
      END
      SUBROUTINE TWO(X,M,N,F)
      INTEGER M,N,I
      REAL X(N),F(M),Y(22),V(22)
```

```
      COMMON/ZSQ/Y,V
      DO 29 I=1,M
      F(I)=(Y(I)-(X(1)+X(2)*V(I)))/(Y(I))
29    CONTINUE
      RETURN
      END
      SUBROUTINE THR(X,M,N,F)
      INTEGER M,N,I
      REAL X(N),F(M),Y(22),V(22)
      COMMON/ZSQ/Y,V
      DO 29 I=1,M
      F(I)=(Y(I)-(X(1)+X(2)*V(I)+X(3)*V(I)**2))/(Y(I))
29    CONTINUE
      RETURN
      END
      SUBROUTINE FOX(X,M,N,F)
      INTEGER M,N,I
      REAL X(N),F(M),Y(22),V(22)
      COMMON/ZSQ/Y,V
      DO 29 I=1,M
      F(I)=(Y(I)-(X(1)+X(2)*V(I)+X(3)*V(I)**2+
     *X(4)*V(I)**3))/(Y(I))
29    CONTINUE
      RETURN
      END
      SUBROUTINE DV2(X,M,N,F)
      INTEGER M,N,I
      REAL X(N),F(M),Y(22),V(22)
      COMMON/ZSQ/Y,V
      DO 9229 I=1,M
      F(I)=(Y(I)-(X(3)+X(4)*V(I)))/(Y(I))
9229  CONTINUE
      RETURN
      END
      SUBROUTINE DV3(X,M,N,F)
      INTEGER M,N,I
      REAL X(N),F(M),Y(22),V(22)
      COMMON/ZSQ/Y,V
      DO 9229 I=1,M
      F(I)=(Y(I)-(X(4)+X(5)*V(I)+X(6)*V(I)**2))/(Y(I))
9229  CONTINUE
      RETURN
      END
      SUBROUTINE ASD(X,M,N,F)
      INTEGER M,N,I
      REAL X(N),F(M),Y(22),V(22)
      COMMON/ZSQ/Y,V
      DO 9229 I=1,M
      F(I)=(Y(I)-(X(5)+X(6)*V(I)+X(7)*V(I)**2+X(8)*V(I)**3))/Y(I)
9229  CONTINUE
      RETURN
      END
C     THE FOLLOWING IS AN INTERPOLATION SUBROUTINE
C     DATA ARE READ FROM CRANK'S CORRECTION CURVE
      SUBROUTINE KIM(A,K,M,XZ,YZ,Q)
```

```
      DIMENSION Q(100,20),A(100,10),XZ(15),YZ(15)
      INTEGER M,NN,I,N
      NN=15
      DO 1983 J=1,M
      I=1
      IF(A(K,J).LE.XZ(I))GO TO 2
      IF(A(K,J).GT.XZ(I).AND.A(K,J).LT.XZ(I+1))GOTO 152
      GOTO 1983
152   Q(K,J)=((A(K,J)-XZ(I))/(XZ(I+1)-XZ(I))*(YZ(I+1)-YZ(I)))+YZ(I)
      GOTO 1983
2     Q(K,J)=YZ(I)
1983  CONTINUE
      DO 703 J=1,M
      DO 704 I=2,NN
      IF(A(K,J).EQ.XZ(I))GOTO 222
      IF(A(K,J).GT.XZ(I).AND.A(K,J).LT.XZ(I+1))GO TO 733
      GO TO 704
222   Q(K,J)=YZ(I)
      GO TO 703
733   Q(K,J)=((A(K,J)-XZ(I))/(XZ(I+1)-XZ(I))*(YZ(I+1)-YZ(I)))+YZ(I)
      GO TO 703
704   CONTINUE
703   CONTINUE
      RETURN
      END
/*
//GO.SYSIN  DD  *
05.63
20.63
45.20
70.24
90.67
  0.83E-02          2.23E-10
  2.20E-02          9.77E-10
  3.90E-02          2.86E-09
  4.90E-02          4.98E-09
  6.60E-02          1.20E-08
      0.0      0.0
      1.0      0.0
      1.1      2.0
      1.2      3.0
      1.3      5.0
      2.0     11.5
      3.0     16.0
      4.0     18.0
      5.0     20.5
      6.0     21.5
      7.0     22.5
      8.0     23.0
     10.0     24.0
     20.0     27.0
     30.0     28.0
8
//
```

APPENDIX E

Values of the Differential Diffusivities for the Systems Investigated, Calculated Using the Computer Program Provided in Appendix D.

System: Cellulose Acetate/Methanol

Temparature= 25 C

First Iteration

VP	C	DLTC	DD	SSP1	D*
5.65	0.1460E-01	0.1460E-01	0.2840E-09	0.41E-11	0.1594E-09
21.08	0.3660E-01	0.2200E-01	0.9120E-09	0.24E-10	0.9302E-09
45.41	0.5880E-01	0.2220E-01	0.1910E-08	0.67E-10	0.2558E-08
70.23	0.9160E-01	0.3280E-01	0.3830E-08	0.19E-09	0.7379E-08
90.14	0.1244	0.3280E-01	0.6278E-08	0.40E-09	0.1528E-07

Standard deviation= 0.2136E-01 cm^2 / sec

These abbreviations have been used above

VP =Operating vapor pressure(mmHg)

C = Concentration

DLTC = Delta concentration: Cn-Cn-1

DD = Experimental diffusivity in cm^2/sec

SSP1 =Summation(DD*DLTC)

D* =First approximation(differential diffusivity in cm^2/s

System: Cellulose Acetate/Methanol

Temperature= 25 C

Second Iteration

D*	DD/D	% CORREC.	SLOPE	D**
0.1594E-09	2.029	11.6	38.153137	0.1398E-09
0.9302E-09	3.275	16.6	38.153564	0.7786E-09
0.2558E-08	2.805	15.1	38.154022	0.2152E-08
0.7379E-08	3.863	17.7	38.154678	0.6095E-08
0.1528E-07	3.988	18.0	38.155334	0.1254E-07

Standard deviation= 0.2073E-01 cm^2 / sec

Diffusivity at zero concentration= 0.1400E-09 cm^2/sec

These abbreviations have been used above

% CORREC.= %Correction to be subtracted from (DD*DLTC)

Slope =dln(Sum(DD*DLTC))/dc

D** =2nd approximation (Differential Diffusivity) in cm^2/s

System: Cellulose Acetate/Methanol

Temparature= 35 C

First Iteration

VP	C	DLTC	DD	SSP1	D*
5.59	0.8300E-02	0.8300E-02	0.4400E-09	0.37E-11	0.2359E-09
20.55	0.2200E-01	0.1370E-01	0.9120E-09	0.16E-10	0.1043E-08
45.38	0.3900E-01	0.1700E-01	0.1760E-08	0.46E-10	0.2976E-08
70.29	0.4900E-01	0.1000E-01	0.3150E-08	0.78E-10	0.5011E-08
90.08	0.6600E-01	0.1700E-01	0.5970E-08	0.18E-09	0.1157E-07

Standard deviation= 0.1196E-01 cm^2 / sec

These abbreviations have been used above

VP =Operating vapor pressure(mmHg)

C = Concentration

DLTC = Delta concentration: Cn-Cn-1

DD = Experimental diffusivity in cm^2/sec

SSP1 =Summation(DD*DLTC)

D* =First approximation(differential diffusivity in cm^2/s

```
System: Cellulose Acetate/Methanol

      Temperature= 35 C

        Second Iteration

  D*            DD/D       % CORREC.      SLOPE          D**

0.2359E-09     1.380         5.74       62.763351     0.2161E-09
0.1043E-08     2.371        13.2        62.763626     0.8970E-09
0.2976E-08     3.263        16.5        62.763977     0.2465E-08
0.5011E-08     2.847        15.3        62.764175     0.4139E-08
0.1157E-07     3.673        17.3        62.764511     0.9404E-08
```

Standard deviation= 0.1109E-01 cm^2 / sec

Diffusivity at zero concentration= 0.3189E-09 cm^2/sec

These abbreviations have been used above

% CORREC.= %Correction to be subtracted from (DD*DLTC)

Slope =dln(Sum(DD*DLTC))/dc

D** =2nd approximation (Differential Diffusivity) in cm^2/s

```
          System: Cellulose Acetate/Methanol

                   Temparature= 45 C

                    First Iteration

  VP          C          DLTC          DD          SSP1        D*

  5.63  0.5500E-02  0.5500E-02  0.5900E-09   0.32E-11  0.2864E-09
 20 63  0.1450E-01  0.9000E-02  0.1550E-08   0.17E-10  0.1518E-08
 45.20  0.2400E-01  0.9500E-02  0.2063E-08   0.37E-10  0.3248E-08
 70.24  0.3500E-01  0.1100E-01  0.3170E-08   0.72E-10  0.6326E-08
 90.67  0.4140E-01  0.6400E-02  0.4690E-08   0.10E-09  0.8975E-08

     Standard deviation=   0.1663E-01 cm2 / sec

     These abbreviations have been used above

     VP    =Operating vapor pressure(mmHg)

     C      = Concentration

     DLTC  = Delta concentration: Cn-Cn-1

     DD    = Experimental diffusivity in cm2/sec

     SSP1  =Summation(DD*DLTC)

     D*    =First approximation(differential diffusivity   in cm2/s
```

```
              System: Cellulose Acetate/Methanol

                    Temperature= 45 C

                     Second Iteration

    D*             DD/D       % CORREC.        SLOPE         D**

 0.2864E-09        1.055        1.10        85.044815     0.2729E-09
 0.1518E-08        2.572        14.1        85.044998     0.1292E-08
 0.3248E-08        2.095        11.9        85.045181     0.2760E-08
 0.6326E-08        3.066        16.1        85.045395     0.5247E-08
 0.8975E-08        2.831        15.2        85.045532     0.7411E-08

      Standard deviation=   0.1522E-01 cm2 / sec

      Diffusivity at zero concentration=  0.5593E-09 cm2/sec


      These abbreviations have been used above

      % CORREC.= %Correction to be subtracted from (DD*DLTC)

      Slope     =dln(Sum(DD*DLTC))/dc

      D**       =2nd approximation (Differential Diffusivity) in cm2/s
```

System: Cellulose Acetate/Ethanol

Temparature= 25 C

First Iteration

VP	C	DLTC	DD	SSP1	D*
6.70	0.2900E-01	0.2900E-01	0.1410E-10	0.41E-12	0.1638E-10
10.55	0.3500E-01	~~0.6000E-02~~	~~0.2510E-10~~	~~0.56E-12~~	~~0.2241E-10~~
20.53	0.5400E-01	0.1900E-01	0.7380E-10	0.20E-11	0.7857E-10
30.44	0.8100E-01	0.2700E-01	0.1127E-09	0.50E-11	0.2004E-09
40.50	0.1200	0.3900E-01	0.2960E-09	0.17E-10	0.6628E-09

Standard deviation= 0 1089E-01 cm^2 / sec

These abbreviations have been used above

VP =Operating vapor pressure(mmHg)

C = Concentration

DLTC = Delta concentration: Cn-Cn-1

DD = Experimental diffusivity in cm^2/sec

SSP1 =Summation(DD*DLTC)

D* =First approximation(differential diffusivity in cm^2/s

System: Cellulose Acetate/Ethanol

Temperature= 25 C

Second Iteration

D*	DD/D	% CORREC.	SLOPE	D**
0.1638E-10	5.029	20.5	39.990005	0.1300E-10
0.2241E-10	1.589	7.69	39.990112	0.1855E-10
0.7857E-10	3.130	16.3	39.990494	0.6551E-10
0.2004E-09	2.716	14.7	39.991043	0.1693E-09
0.6628E-09	5.881	21.4	39.991821	0.5322E-09

Standard deviation= 0.1172E-01 cm^2 / sec

Diffusivity at zero concentration= 0.4014E-11 cm^2/sec

These abbreviations have been used above

% CORREC.= %Correction to be subtracted from (DD*DLTC)

Slope =dln(Sum(DD*DLTC))/dc

D** =2nd approximation (Differential Diffusivity) in cm^2/s

System: Cellulose Acetate/Ethanol

Temparature= 35 C

First Iteration

VP	C	DLTC	DD	SSP1	D*
6.57	0.2000E-01	0.2000E-01	0.2290E-10	0.46E-12	0.2744E-10
10.60	0.2600E-01	0.6000E-02	0.3900E-10	0.69E-12	0.4146E-10
20.70	0.3600E-01	0.1000E-01	0.7120E-10	0.14E-11	0.8412E-10
30.24	0.4400E-01	0.8000E-02	0.1486E-09	0.26E-11	0.1554E-09
40.39	0.5200E-01	0.8000E-02	0.1920E-09	0.41E-11	0.2474E-09
50.27	0.7200E-01	0.2000E-01	0.2938E-09	0.10E-10	0.5995E-09

Standard deviation= 0.6892E-02 cm^2 / sec

These abbreviations have been used above

VP =Operating vapor pressure(mmHg)

C = Concentration

DLTC = Delta concentration: Cn-Cn-1

DD = Experimental diffusivity in cm^2/sec

SSP1 =Summation(DD*DLTC)

D* =First approximation(differential diffusivity in cm^2/s

System: Cellulose Acetate/Ethanol

Temperature= 35 C

Second Iteration

D*	DD/D	% CORREC.	SLOPE	D**
0.2744E-10	1.957	11.1	59.341095	0.2416E-10
0.4146E-10	1.811	9.74	59.341217	0.3670E-10
0.8412E-10	2.157	12.2	59.341415	0.7379E-10
0.1554E-09	2.182	12.3	59.341568	0.1356E-09
0.2474E-09	1.665	8.39	59.341736	0.2191E-09
0.5995E-09	3.122	16.2	59.342133	0.5112E-09

Standard deviation= 0.7188E-02 cm^2 / sec

Diffusivity at zero concentration= 0.1520E-10 cm^2/sec

These abbreviations have been used above

% CORREC.= %Correction to be subtracted from (DD*DLTC)

Slope =dln(Sum(DD*DLTC))/dc

D** =2nd approximation (Differential Diffusivity) in cm^2/s

System: Cellulose Acetate/Ethanol

Temparature= 45 C

First Iteration

```
  VP        C           DLTC          DD           SSP1         D*

  6.50  0.9700E-02  0.9700E-02  0.6200E-10   0.60E-12   0.3114E-10
 10.59  0.1500E-01  0.5300E-02  0.6530E-10   0.95E-12   0.4907E-10
 20.73  0.2300E-01  0.8000E-02  0.8100E-10   0.16E-11   0.8263E-10
 30.53  0.3300E-01  0.1000E-01  0.1064E-09   0.27E-11   0.1377E-09
 41.80  0.4100E-01  0.8000E-02  0.1310E-09   0.37E-11   0.1920E-09
 50.35  0.4700E-01  0.6000E-02  0.1773E-09   0.48E-11   0.2471E-09
 94.91  0.9100E-01  0.4400E-01  0.9580E-09   0.47E-10   0.2430E-08
```

Standard deviation= 0.5007E-02 cm^2 / sec

These abbreviations have been used above

VP =Operating vapor pressure(mmHg)

C = Concentration

DLTC = Delta concentration: Cn-Cn-1

DD = Experimental diffusivity in cm^2/sec

SSP1 =Summation(DD*DLTC)

D* =First approximation(differential diffusivity in cm^2/s

System: Cellulose Acetate/Ethanol

Temperature= 45 C

Second Iteration

D*	DD/D	% CORREC.	SLOPE	D**
0.3114E-10	1.664	8.38	49.242950	0.2713E-10
0.4907E-10	0.7914	0.000E+00	49.243057	0.4418E-10
0.8263E-10	1.265	4.31	49.243225	0.7471E-10
0.1377E-09	1.700	8.72	49.243423	0.1225E-09
0.1920E-09	1.805	9.68	49.243576	0.1691E-09
0.2471E-09	1.886	10.4	49.243698	0.2161E-09
0.2430E-08	13.71	25.1	49.244583	0.1771E-08

Standard deviation= 0.6383E-02 cm^2 / sec

Diffusivity at zero concentration= 0.3726E-10 cm^2/sec

These abbreviations have been used above

% CORREC.= %Correction to be subtracted from (DD*DLTC)

Slope =dln(Sum(DD*DLTC))/dc

D** =2nd approximation (Differential Diffusivity) in cm^2/s

System: Cellulose Acetate/Benzene

Temparature= 25 C

First Iteration

VP	C	DLTC	DD	SSP1	D*
41.13	0.1540E-01	0.1540E-01	0.4470E-11	0.69E-13	0.3131E-11
55.90	0.2700E-01	0.1160E-01	0.7190E-11	0.15E-12	0.6924E-11
70.15	0.3200E-01	0.5000E-02	0.8890E-11	0.20E-12	0.8946E-11
81.10	0.6500E-01	0.3300E-01	0.1626E-10	0.73E-12	0.3335E-10

Standard deviation= 0.4652E-02 cm^2 / sec

These abbreviations have been used above

VP =Operating vapor pressure(mmHg)

C = Concentration

DLTC = Delta concentration: Cn-Cn-1

DD = Experimental diffusivity in cm^2/sec

SSP1 =Summation(DD*DLTC)

D* =First approximation(differential diffusivity in cm^2/s

System: Cellulose Acetate/Benzene

Temperature= 25 C

Second Iteration

D*	DD/D	% CORREC.	SLOPE	D**
0.3131E-11	1.261	4.22	43.174683	0.2847E-11
0.6924E-11	1.549	7.31	43.174911	0.6184E-11
0.8946E-11	1.244	3.88	43.175003	0.8029E-11
0.3335E-10	3.752	17.5	43.175674	0.2714E-10

Standard deviation= 0.4966E-02 cm^2 / sec

Diffusivity at zero concentration= 0.3545E-11 cm^2/sec

These abbreviations have been used above

% CORREC.= %Correction to be subtracted from (DD*DLTC)

Slope =dln(Sum(DD*DLTC))/dc

D** =2nd approximation (Differential Diffusivity) in cm^2/s

System: Cellulose Acetate/Benzene

Temparature= 35 C

First Iteration

VP	C	DLTC	DD	SSP1	D*
40.55	0.7600E-02	0.7600E-02	0.1340E-10	0.10E-12	0.1259E-10
55.27	0.9400E-02	0.1800E-02	0.2110E-10	0.14E-12	0.1729E-10
70.00	0.1270E-01	0.3300E-02	0.2040E-10	0.21E-12	0.2561E-10
80.16	0.1480E-01	0.2100E-02	0.2090E-10	0.25E-12	0.3104E-10

Standard deviation= 0.1604E-02 cm^2 / sec

These abbreviations have been used above

VP =Operating vapor pressure(mmHg)

C = Concentration

DLTC = Delta concentration: Cn-Cn-1

DD = Experimental diffusivity in cm^2/sec

SSP1 =Summation(DD*DLTC)

D* =First approximation(differential diffusivity in cm^2/s

System: Cellulose Acetate/Benzene

Temperature= 35 C

Second Iteration

D*	DD/D	% CORREC.	SLOPE	D**
0.1259E-10	1.217	3.34	122.59256	0.1207E-10
0.1729E-10	1.290	4.81	122.59261	0.1650E-10
0.2561E-10	1.214	3.28	122.59267	0.2448E-10
0.3104E-10	1.522	7.06	122.59271	0.2948E-10

Standard deviation= 0.1612E-02 cm^2 / sec

Diffusivity at zero concentration= 0.1101E-10 cm^2/sec

These abbreviations have been used above

% CORREC.= %Correction to be subtracted from (DD*DLTC)

Slope =dln(Sum(DD*DLTC))/dc

D** =2nd approximation (Differential Diffusivity) in cm^2/s

```
              System: Cellulose Acetate/Benzene

                      Temparature= 45 C

                        First Iteration

 VP          C          DLTC          DD          SSP1        D*

40.68  0.6300E-02  0.6300E-02  0.3320E-10   0.21E-12  0.2130E-10
55.17  0.7000E-02  0.7000E-03  0.3530E-10   0.23E-12  0.2381E-10
70.20  0.9700E-02  0.2700E-02  0.3020E-10   0.32E-12  0.3212E-10
79.97  0.1220E-01  0.2500E-02  0.2720E-10   0.38E-12  0.3904E-10

     Standard deviation=   0.1056E-02 cm2 / sec

     These abbreviations have been used above

     VP   =Operating vapor pressure(mmHg)

     C    = Concentration

     DLTC = Delta concentration: Cn-Cn-1

     DD   = Experimental diffusivity in cm2/sec

     SSP1 =Summation(DD*DLTC)

     D*   =First approximation(differential diffusivity   in cm2/s
```

```
System: Cellulose Acetate/Benzene

          Temperature= 45 C

             Second Iteration

   D*              DD/D       % CORREC.        SLOPE          D**

0.2130E-10    0.7471         0.000E+00     100.39532     0.2100E-10
0.2381E-10    0.7173         0.000E+00     100.39534     0.2348E-10
0.3212E-10    0.9098         0.000E+00     100.39539     0.3167E-10
0.3904E-10     1.293          4.85         100.39543     0.3816E-10

   Standard deviation=   0.1132E-02 cm^2 / sec

   Diffusivity at zero concentration=  0.3044E-10 cm^2/sec

   These abbreviations have been used above

   % CORREC.= %Correction to be subtracted from (DD*DLTC)

   Slope     =dln(Sum(DD*DLTC))/dc

   D**       =2nd approximation (Differential Diffusivity) in cm^2/s
```

APPENDIX F

Calculation of the Thermodynamic Diffusivities from the Intrinsic Values for the System: Cellulose Acetate/Ethanol at 25°C

Activity of Penetrant. a	Volume Fraction of Penetrant, ϕ	$\frac{\partial \ln a}{\partial \ln \phi}$	$\mathcal{D}$, cm^2/sec	$\mathcal{D}^*$, cm^2/sec
0.1	0.046	0.94	0.145×10^{-10}	0.154×10^{-10}
0.177	0.054	0.93	0.211×10^{-10}	0.227×10^{-10}
0.344	0.082	0.89	0.8×10^{-10}	$0.9 \quad 10^{-10}$
0.51	0.12	9.84	0.228×10^{-9}	0.27×10^{-9}
0.678	0.165	0.784	0.81×10^{-9}	0.1×10^{-8}

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