Migration of Novel Epoxidized Neem Oil as Plasticizer from PVC: Experimental Design Approach

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ABSTRACT: Migration behavior of epoxidized neem oil (ENO) from poly(vinyl chloride) (PVC) plasticized with ENO to acrylo nitrile butadiene rubber (NBR) was investigated. Central composite rotatable design (CCRD) for three variables at five levels was chosen as the experimental design. Concentration of Neem oil in PVC matrix, acrylo nitrile (ACN%) content in NBR matrix, and peroxide content used in NBR formulation were selected as three independent variables. Other parameters pertinent to migration phenomena such as partition coefficient, activation energies, rate constants, and diffusion coefficients were evaluated and these properties were fitted to a distinctive response equation generated by CCRD. Proposed response equations for most parameters were considered as having sufficient explanatory power and "good fit" in the statistical sense. Partitioning of ENO as a plasticizer between PVC and NBR follows first order equilibrium kinetics, and the forward reaction is found to be endothermic. The percentage migration of plasticizer at 296 K at equilibrium is well below 25% for the majority of cases irrespective of other pertinent factors. Parameters such as forward, backward, and overall rate constants and their respective activation energies and enthalpy change related to the partitioning phenomenon are influenced to different degrees by plasticizer concentration in PVC, ACN% in NBR and crosslink density of NBR. The influence caused by plasticizer concentration and ACN% was found to be the most significant. Diffusion of plasticizer through PVC matrix is the rate determining step for the overall migration process. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 823–838, 2011

Key words: poly(vinyl chloride); activation energy; plasticizer migration; diffusion; design experiment

INTRODUCTION

PVC is a versatile material with an extensive range of applications.[1] A plasticizer is a substance incorporated into PVC to increase its flexibility, softness, distensibility, or workability.[2] The most commonly used plasticizers are the phthalate plasticizers, which are esters of ortho phthalic acid. These petroleum-derived plasticizers are subjected to several significant limitations. First, it is processed from nonrenewable source, and hence they are often expensive. Second, these plasticizers are suspected to disrupt human endocrine activity.[3] As a large quantity of PVC products produced is consumed by the food industry as packing materials, there is a growing concern about the toxicity and the migration of small plasticizer molecules from the polymeric packaging material to foodstuff.[4–7]

Permanence is an important characteristic of a good plasticizer evaluating an efficiency of it. The property of "permanence" relates to the ability of a polymer to retain plasticizer under different environmental conditions.[8] Migration is the transfer of plasticizer from plasticized PVC material into another material when the two materials are in surface contact. This is considered as a diffusion process in which plasticizer migrates from a specimen of higher concentration to lower concentration at some point of contact. This may adversely affect the properties of the recipient material especially if the material is a vastly dissimilar polymer. Various studies on migration of plasticizers from food contact materials can be found in the literature.[4,5,7,9-11] Migration of di-2-(ethylhexyl)phthalate (DOP) from excessively plasticized PVC into water/ethanol mixture and acetonitrile was analyzed using gas chromatography (GC) by Jung et al.[12] and estimated the diffusion coefficient using Fick's law. Use of different analytical techniques such as GC, FTIR, AAS, and DSC to study the interaction between packaging and food was reported.[4] A similar study to evaluate the extents of contaminants migrating from polymer

into the food simulants was carried out by Boussoum et al. with PVC stabilized with epoxidized sunflower oil. Their results were quantified by gravimetric, atomic absorption, and FTIR analysis.[13] An attempt to reduce plasticizer migration by alloying of PVC has been reported by Thomas[5]; this alloying is considered a novel aspect of mitigating the plasticizer migration. A detailed study of migration of plasticizers from flexible PVC to paraffin oil and unplasticized PVC was carried out by Henriksen[14] showing the importance of diffusion rates on rate of migration of plasticizers. According to Ritchie,[8] Knappe has investigated some of the plasticizer migration into polymeric substances like PVC, polystyrene (PS), polyolefines, and cellulose acetate and found that loss of plasticizer is proportional to $t^{1/2}$ up to 30% weight loss. Equation (1) was used to calculate the apparent diffusion constant by Knappe.

$$D = \frac{(\Delta m)^2 \pi}{F^2 (\Delta C_0)^2 t} \quad (1)$$

where, D = Diffusion coefficient;

Δm = increasing in weight of specimen with low initial concentration;

F = surface area perpendicular to direction of diffusion;

ΔC_0 = difference between the initial concentrations;

t = time.

Papakonsstantinou and Papaspyrides[15] investigated the phenomena of migration of DOP from plasticized PVC to unplasticized PVC at 64°C using a model system in which the plasticizer-containing polymer was sandwiched between two unplasticized polymers. The workers found that a linear relationship between M_t/M_∞ and $t^{1/2}$ was observed as predicted by eq. (2). Using this linear relationship, Papakonsstantinou and Papaspyrides were able to characterize the migration kinetics for a solid/solid system.

$$\frac{M_t}{M_\infty} = \left(\sqrt{\frac{4D}{\pi l^2}} \right) \sqrt{t} \quad (2)$$

where M_∞ is the amount migrated at equilibrium and M_t is the amount loss at time t.

Plasticizer loss involves three basic steps: diffusion of plasticizer to an interface; transfer across the interface; and diffusion away from the surface. In these steps, the first and the latter are considered to be the most significant in most systems.[8] One of these three processes will be the rate determining step in terms of permanence of plasticizer in a given environment. According to Penn[16] structural parameters such as polarity, molecular weight, aromaticity,

and linearity of a plasticizer play an important role in permanence of a plasticizer in a PVC matrix. On the other hand, physical parameters such as boiling point and vapor pressure of plasticizers also have a positive impact on volatile loss of plasticizers; for an example boiling point of about 400°C or higher at atmospheric pressure is suggested for a good plasticizer. It was also reported that loss of plasticizer from plasticized PVC into air is influenced by exposed surface area, sample thickness, plasticizer concentration, and temperature and air flow over the sample.[8]

We have previously reported[17] on the potential stabilizing effect engendered by epoxidized neem oil (ENO) in a PVC matrix. This study investigates pertinent factors related to the migration of ENO as a secondary plasticizer from PVC plasticized with DOP and ENO to NBR with particular reference to the effect of polarity and crosslink density of the receiving or recipient polymer. In addition, the effect of the level of plasticizer in the donor polymer on the extent of migration was investigated. A central composite rotatable design (CCRD) for a three-factor variable at five levels were chosen as the experimental design for investigating quantitative relationships between response functions and process variables. CCRD overcomes the major pitfalls that are manifest in the conventional "screening variables" approach. All responses in terms of CCRD obtained for parameters which are related to the migration phenomena were fitted to their distinctive response equations by regression analysis.

EXPERIMENTAL

Materials

The suspension homopolymer of PVC with ICI-K value of 65 (ISO viscosity 125) was purchased from European vinyl corp. UK. The standard plasticizer, DOP was technical grade and obtained from CIBA-Geigy (UK) Limited. Technical grade calcium stearate, zinc stearate, and dibasic lead phthalate were acquired from fisher scientific UK. Uncured nitrile rubber samples with ACN contents 22.8% (hot polymerized), 32% (low temperature polymerized), and 41%(low temperature polymerized) were obtained from James Walkers, UK. To study systems containing a wider range of ACN contents two further samples of NBR were prepared containing 26.6% and 37.3% ACN by blending. Dicumylperoxide (E-DCP-40p) from Umaya-UK was used as the curing agent for nitrile rubber.

Neem oil was obtained from D. Peiris and Co. Ltd., Colombo, Sri Lanka and was epoxidized with peroxymethanoic acid as described in our previous report.[17]

TABLE I
Real Values Assigned to Variables in Design Experiment

Code	Code conversion	Real values		
		Plasticizer- ENO (phr) (PLC) $C = 30$, $DS = 11.9$	ACN content (wt %) (ACN) $C = 31.9$, $DS = 5.4$	Peroxide (wt %) (PRX) $C = 1.75$, $DS = 0.45$
−1.68 (star point)	$C-1.68DS$	10	22.8	1.00
−1 (factorial points)	$C-DS$	18	26.5	1.30
0 (centre point)	C	30	31.9	1.75
+1 (factorial points)	$C + DS$	41.9	37.3	2.20
+1.68 (star points)	$C + 1.68DS$	50	41	2.50

Design experiment

Three independent variables (or factors) were selected, namely, plasticizer level (PLC), ACN content (wt %) (ACN), and peroxide content % (PRX) which influences the crosslink density of NBR. Various parameters characterizing the process of migration were studied using CCRD; these parameters are usually designated dependent variables in terms of the terminology used in typical CCRD design. In an orthogonal design, five levels are assigned to each factor or variable which are rotatable around a design center point. The levels are identified by codes as shown below:

$$- a, -1, 0, 1, a$$

a, is determined from the expression:

$$a = 2^{k/4}$$

where, k is the number of independent variables. Thus for a three factor design $a = 2^{3/4} = 1.68$.

These five levels (codes) indicate different positions in reference to spatial arrangement and the expressions used to convert codes to real values are indicated in Table I. The design step (DS) and the central point value (C) were determined for each independent variable based on their limiting values.

Combination mixes for three-factor design in terms of design codes and entries in terms of substituted real values are shown in Table II. In reference to Table II, each particular setting of the factors is termed a "Run." Further it should be noted that a certain pattern emerges with respect to the way in which the codes are placed. For instance concerning the factorial points it can be seen that in the PLC column the signs alternate between positive and negative. It is also noted that the center point runs are repeated and this is important to allow errors to be assessed. The number of replicates is decided by the

TABLE II
The Mixes with Their Appropriate Design Codes and Assigned Real Values

	Run	PLC (X)		ACN (Y)		PRX (Z)	
		Code	Real value	Code	Real value	Code	Real value
Factorial points	1	−1	18	−1	26.5	−1	1.30
	2	+1	41.9	−1	26.5	−1	1.30
	3	−1	18	+1	37.3	−1	1.30
	4	+1	41.9	+1	37.3	−1	1.30
	5	−1	18	−1	26.5	+1	2.20
	6	+1	41.9	−1	26.5	+1	2.20
	7	−1	18	+1	37.3	+1	2.20
	8	+1	41.9	+1	37.3	+1	2.20
Axial points	9	−1.68	10	0	31.9	0	1.75
	10	+1.68	50	0	31.9	0	1.75
	11	0	30	−1.68	22.8	0	1.75
	12	0	30	+1.68	41	0	1.75
	13	0	30	0	31.9	−1.68	1.00
	14	0	30	0	31.9	+1.68	2.5
Centre points and replicates	15	0	30	0	31.9	0	1.75
	16	0	30	0	31.9	0	1.75
	17	0	30	0	31.9	0	1.75
	18	0	30	0	31.9	0	1.75
	19	0	30	0	31.9	0	1.75
	20	0	30	0	31.9	0	1.75

TABLE III
Analysis of Variances

Source	Sum of squares (SS)	Degrees of freedom (df)	Mean Squares (SS/df)
Response Equation	$\sum(Y_F - \overline{Y})^2$	$V_1 = R - 1$	RGMS
Residuals	$\sum(Y_E - Y_F)^2$	$V_2 = N^a - R^b$	RSMS
Lack of fit	$\sum(Y_F - \overline{Y})^2 - \sum(Y_{EC} - \overline{Y}_{EC})^2$	$V_1 = N - R - C^C + 1$	LFMS
Pure Error	$\sum(Y_{EC} - \overline{Y}_{EC})^2$	$V_2 = C - 1$	PEMS

N^a = Number of runs in the experiment design.
R^b = Number of terms in the response equation.
C^C = Number of centre point replicates.
Y_F = Fitted value.
$\overline{Y}$ = Means of the observations.
Y_E = Experimental value.
Y_{EC} = Experimental values for the centre point replicates.
$\overline{Y}_{EC}$ = Mean of the experimental values for the centre point replicates.

number of independent variables and for a three factor design the number of replicates is normally six.

The data generated by CCRD is fitted to a quadratic response equation. Thus, by way of example, for a three-factor design in which the partition coefficient (K_D) is the independent variable our response equation has the following form:

$$K_D = B_0 + B_1 X + B_2 Y + B_3 Z + B_{11} X^2 + B_{22} Y^2$$
$$+ B_{33} Z^2 + B_{12} XY + B_{13} XZ + B_{23} YZ \quad (3)$$

In eq. (3), K_D is the partition coefficient being measured, X, Y, Z are the independent variables of PLC, ACN%, and PRX respectively, and B with various appended subscripts represents the coefficients of the quadratic response equation. Regression analysis was performed to relate the experimental K_D values to either of three variables under consideration. The validity of the response equation was assessed by an F ratio for the response equation (F_{eq}) which can be tested for significance by reference to standard statistical tables according to eq. (4):

$$F_{eq} = \text{RGMS/RSMS} \quad (4)$$

where RGMS is the regression mean square and RSMS is the residual mean square. With the degrees of freedom for both numerator and denominator, F_{eq}

can be compared with the values in the F distribution tables. If the ratio exceeds the upper 5% point of the distribution, it is almost certain that the response equation has some explanatory power.[18] To test the lack of fit of the experimental results to the response surface an F ratio for lack of fit (F_{LF}) was determined as defined by eq. (5).

$$F_{LF} = \text{LFMS/PEMS} \quad (5)$$

where LFMS is lack of fit mean square and PEMS is pure error mean square. If the response fits the results adequately then the calculated F_{LF} ratio will be less than the entry at the 5% level in the F distribution tables. Table III illustrates the formulae used for calculating the mean squares in eqs. (4) and (5). The degree of freedom associated with each sum of squares are also shown in Table III and are a function of the total number of experiments (N) in the design including replicates, the number of terms in the response equation (R), and the number of center point replicates(C).

Preparation of nitrile rubber samples

As suggested by the design, nine samples (A–I) of nitrile rubber were prepared with different ACN% and peroxide% as given in Table IV. In the preparation of the samples, appropriate weights of nitrile

TABLE IV
Prepared Nitrile Rubber Samples with Varying Amount of Peroxide

Sample	ACN %	Batch size/g	Peroxide %	Mass of DCMP-40 per 100 g	Half life (min)	Curing time (min)
A	26.5	300	1.30	3.25	7.6	53
B	37.3	300	1.30	3.25	5.4	38
C	26.5	300	2.20	5.5	6.5	46
D	37.3	300	2.20	5.5	4.1	29
E	31.9	300	1.75	4.375	4.5	31
F	22.8	300	1.75	4.375	5.6	39
G	41.0	300	1.75	4.375	6.3	44
H	31.9	300	1.00	2.5	7.4	52
I	31.9	300	2.50	6.25	5.2	37

rubber were masticated on a two-roll mill (at 50–60°C) until it was observed to be coherent and homogeneous; having attained this condition, the mix was removed from the mill as a thin sheet. The masticated sheets were placed on a flat surface and allowed to cool; when sufficiently cooled the required level of peroxide (E-DCP-40p) was sprinkled over the sheets. The sheets were then rolled into a "sausage-like" form to encapsulate the peroxide and returned to the mill for further homogenization to attain uniform dispersion of the peroxide. To transform the rubber mixes containing various levels of peroxide into a fully cured vulcanisate, it was necessary to determine the half-lives of the rubber mixes. An Oscillating Disc Rheometer was used to determine the half lives of nitrile rubber mixes. Rate constants for curing process were obtained from the slopes of the straight lines produced by plotting $\ln\left[\frac{R_H - R_L}{R_H - R_t}\right]$ versus $(t - t_i)$ according to the eq. (6).

$$\ln\left[\frac{R_H - R_L}{R_H - R_t}\right] = k(t - t_i) \tag{6}$$

where, R_H is the maximum torque attained, R_L is the minimum torque, and t_i is the time of induction. R_t is the torque measured at an general time t and k is the rate constant. An ODR trace produced for the rubber mix at 160°C for 60 min was utilized to evaluate R_H, R_L, R_t, and t_i. Having evaluated the rate constants the half-lives, $t_{0.5}$, were calculated by using eq. (7):

$$t_{0.5} = \frac{\ln 2}{k} + t_i \tag{7}$$

Samples were then cured in an electric press at 160°C; cure times used were those corresponding to seven half lives. At the end of each curing cycle a vulcanized sheet was produced of dimensions $152.4 \times 152.4 \times 1.14$ mm^3.

Preparation of PVC specimens with ENO

Samples were prepared using the following ingredients (parts by weight):
  PVC: 100 parts;
  DOP: 30 parts;
  Dibasic lead phthalate (Dblp): 5 parts;
  Calcium stearate: 0.5 parts;
  ENO: 10/18/30/42/50 parts.
  Batches based on 300 g of PVC were prepared. Ingredients were weighed to the nearest gram and hand mixed. The mixture was processed on a conventional laboratory-sized two-roll mill operating at 140°C until a coherent melt was obtained; the duration of

this procedure was about 10 min. The fused PVC mixture was removed from the mill as a continuous sheet or as pieces of broken crumb and subsequently compression-molded using a temperature and pressure of 150°C and 9266.5 kPa, respectively, to form sheets of nominal dimensions $152.4 \times 152.4 \times 1.14$ mm^3.

Determination of crosslink densities of NBR

Dumb-bell shaped test specimens were punched from cured NBR sheets using a metal cutter. Two reference lines were drawn 40 mm apart normal to the parallel sides of the dumb-bell specimens. For any given dumb-bell specimen one end was fixed and standards weights were applied to the free end in a step-wise manner. The corresponding increases in length between the reference lines on application of each load were measured using a Cathetometer. In carrying out this procedure care was taken to ensure that the overall strain did not exceed 50%; all measurements were carried out at room temperature of 25°C ± 1°C. The shear moduli (G) were calculated from the slopes of the straight lines obtained according to eq. (8). The network chain densities were subsequently determined by using eq. (9).[19]

$$\sigma = G(\lambda - \lambda^{-2}) \tag{8}$$

where,
  σ = nominal stress (Force per unit unstrained area),
  G = Shear modulus,
  λ = extension ratio (Stretched length/initial length).

$$G = nRT \tag{9}$$

where n is the network chain density, R is the universal gas constant, and T is the temperature in Kelvin.

Determination of partition coefficient

Circular test specimens ($\sim$ 45 mm diameter) were punched from prepared nitrile rubber sheets and plasticized PVC sheets. After recording the accurate mass of each specimen, two specimens, PVC and NBR specimen, were pressed firmly together according to the combinations given in the design experiment. Each pair was wrapped with aluminum foil and placed on a metal plate. To ensure uniform and effective contact between paired sheets a metal plate was placed over the samples that had already been arranged on a flat separate metal plate. The arrangement was kept at temperature 23°C ± 2°C, and the mass of each specimen were recorded with time over an extensive period ($\sim$ 6 months). Experiments

were carried out in triplicate. The partition coefficients of ENO between NBR and PVC were calculated using eq. (10). The same process was carried out but keeping the paired specimens in a circulating air oven at 50°C ± 1°C to determine the partition coefficient at 50°C.

$K_D = \frac{[\text{Plasticiser}]_{\text{NBR}}}{[\text{Plasticiser}]_{\text{PVC}}}$; [Plasticizer] is the plasticizer concentration at equilibrium in NBR and PVC, phases respectively. The apparent partition coefficient (K_t) at any time (t) was calculated using the eq. (10).

$$K_t = \left(\frac{\Delta m}{m_0 - m_t}\right)\left(\frac{V_{\text{PVC}}}{V_{\text{NBR}}}\right) \qquad (10)$$

where Δm = increase in mass of NBR specimen;

m_0 = mass of oil derivative in the PVC specimen before pairing;

m_t = mass loss of PVC specimen at time t;

V_{PVC} = volume of PVC specimen (calculated from the dimensions);

V_{NBR} = Volume of NBR specimen (calculated form the dimensions);

The value of K_t at equilibrium is equal to the partition coefficient (K_D).

By knowing the value for K_D, the mass ENO that has migrated to the NBR phase can be calculated using eq. (11).

$$m_{\text{eq}} = \frac{m_0 K_D}{\left(\frac{V_{\text{PVC}}}{V_{\text{NBR}}} + K_D\right)} \qquad (11)$$

Then the percentage migration is given by eq. (12).

$$\frac{100 m_{\text{eq}}}{m_0} = \frac{100 K_D}{\left(\frac{V_{\text{PVC}}}{V_{\text{NBR}}} + K_D\right)} \qquad (12)$$

where m_{eq} is the mass of plasticizer migrated to the NBR phase at equilibrium.

RESULTS AND DISCUSSION

Partition coefficients

Partition coefficient (K_D) can generally be defined as the ratio of concentrations of a compound in the two phases of a mixture of immiscible solvents at equilibrium. Hence K_D values are a measure of differential solubility of a compound between two solvents and it is constant for a given system at constant temperature. The concept of partitioning can be applied in the phenomena of migration of plasticizers from plasticized PVC. Therefore the partition coefficient could be used to evaluate the extent of migration of plasticizer.

However, given the nature of the diffusion process, it is clear that the partitioning of plasticizer between two solid phases will take an appreciable period of time to reach a state of equilibrium. Therefore, an apparent partition coefficient (K_t) was determined for each set as defined by the CCRD analysis was calculated as described in "Determination of Partition Coefficient" section at regular intervals. Variation of K_t with time is illustrated in Figure 1. It is clear from the Figure 1 that the equilibrium value for K_D cannot be extrapolated directly. Therefore, the K_D value was determined using a mathematical concept primarily used for determining asymptotic values. Equilibrium partition coefficients obtained at two temperatures are given in Table V.

It was assumed that the change in masses of both PVC and NBR specimens were only due to the plasticizer migration when calculating K_D. Nevertheless there is a possibility of volatile loss of plasticizer, especially at temperature 50°C, over a long period of time. In an attempt to confirm that the volatile loss at 50°C is negligible; respective PVC specimens with similar dimensions were kept at 50°C and variation of mass was monitored. Figure 2 illustrates that the volatile loss of plasticizer is insignificant at 50°C, over the time frame used in the analysis.

Kinetics of partitioning

The form of the relationship shown in the variation of K_t with time (Fig. 1) suggests a first order trend of K_t behavior. There appears to be direct proportionality between the slopes at any point on the K_t versus time curve and the difference between K_D and K_t at the point at which the slope is taken.

That is,

$\frac{dK_t}{dt} \propto K_D - K_t$, by introducing a constant k, we obtain

$$\frac{dK_t}{dt} = k(K_D - K_t) \qquad (13)$$
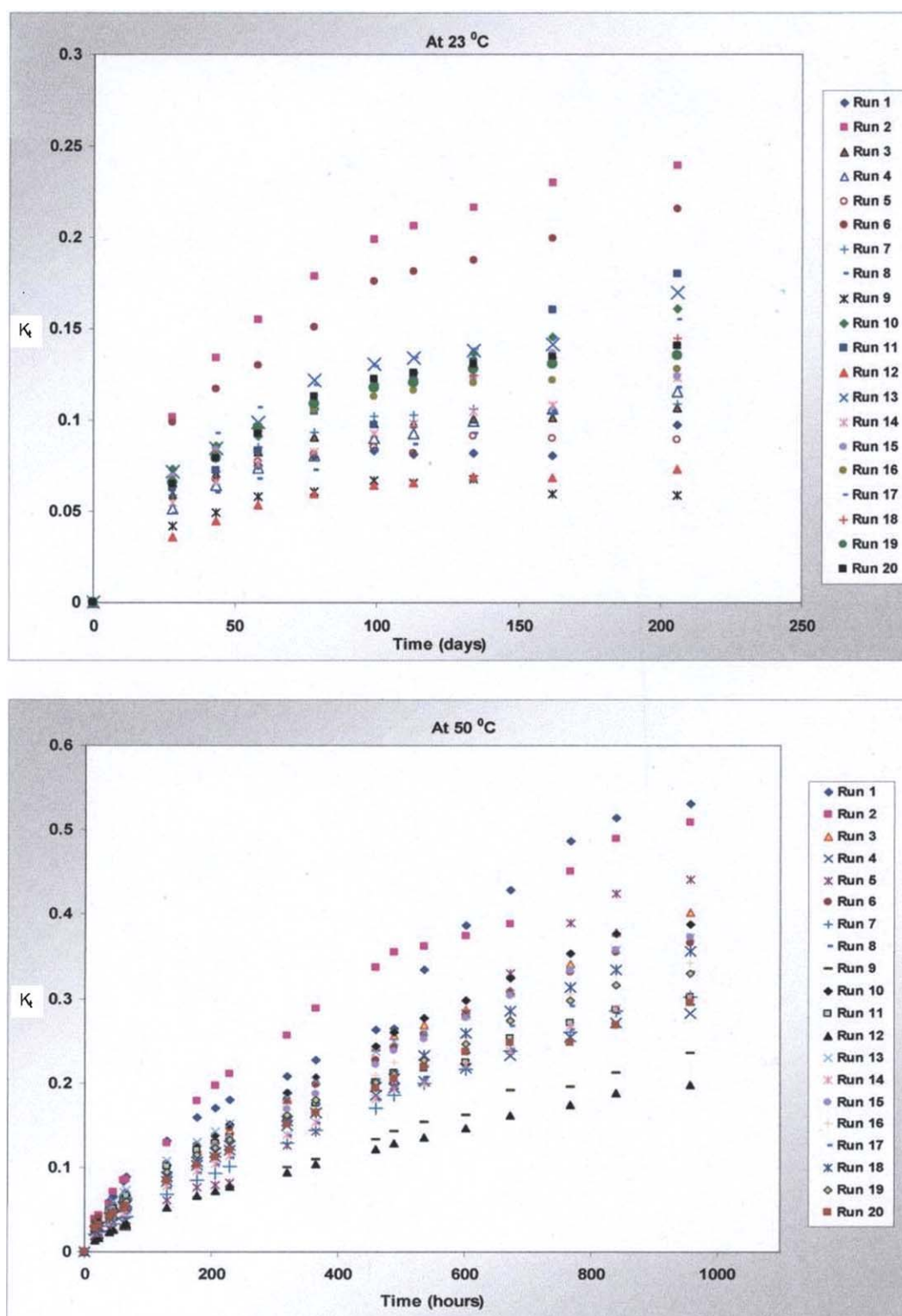
Rearrangement and integration of the eq. (13) gives,

$$-\ln(K_D - K_t) = kt + C, \qquad (14)$$

where, C is the constant of integration.

At $t = 0$, $K_t = 0$ so that $C = -\ln K_D$, by substituting C and rearranging eq. (14), we get

$$\ln\left(1 - \frac{K_t}{K_D}\right) = -kt \qquad (15)$$

Equation (15) indicates that a plot of $\ln\left(1 - \frac{K_t}{K_D}\right)$ against time (t) should be linear with the gradient k which is the observed rate constant for

Figure 1 Variation of K_D with time at 23 and 50°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

partitioning. All plots constructed showed excellent agreement with eq. (15) at both temperatures. Linear equations thus obtained together with respective R^2 values and observed rate constants are given in the Table V.

The rate equation for a simple equilibrium reaction close to equilibrium is also found to be first order[20] and resembles eq. (15).

Thus, observed rate constant, $k_{obs} = k_f + k_b$; also $K_{eq} = \frac{k_f}{k_b}$ where, k_f and k_b are forward and backward

TABLE V
Partition Coefficients, Rate Equations with Their R^2 Values, and Observed Rate Constants for the Series of Runs at 296 and 323 K

	At 296 K				At 323 K			
Run	K_{Dat23}	Rate equation	R^2	k_{obs}	K_{Dat50}	Rate equation	R^2	k_{obs}
1	0.0832	$Y = -0.0428X$	0.9971	5.0	0.3091	$Y = -0.0042X$	0.9980	11.7
2	0.2243	$Y = -0.0204X$	0.9943	2.4	0.5942	$Y = -0.0018X$	0.9983	5.0
3	0.1024	$Y = -0.0286X$	0.9948	3.3	0.5592	$Y = -0.0013X$	0.9988	3.6
4	0.1005	$Y = -0.0229X$	0.9954	2.7	0.2765	$Y = -0.0027X$	0.9754	7.5
5	0.0864	$Y = -0.0365X$	0.9769	4.2	0.1414	$Y = -0.0043X$	0.9956	11.9
6	0.1846	$Y = -0.0242X$	0.994	2.8	0.4467	$Y = -0.0017X$	0.9985	4.7
7	0.112	$Y = -0.0234X$	0.9958	2.7	0.4892	$Y = -0.001X$	0.9997	2.8
8	0.0933	$Y = -0.023X$	0.996	2.7	0.3990	$Y = -0.0014X$	0.9995	3.9
9	0.0735	$Y = -0.0253X$	0.9825	2.9	0.3934	$Y = -0.0009X$	0.9996	2.5
10	0.1441	$Y = -0.0176X$	0.9983	2.0	0.4840	$Y = -0.0017X$	0.9976	4.7
11	0.1534	$Y = -0.0146X$	0.9977	1.7	0.3588	$Y = -0.0019X$	0.9982	5.3
12	0.0678	$Y = -0.0258X$	0.9934	3.0	0.2600	$Y = -0.0015X$	0.9995	4.2
13	0.1324	$Y = -0.0267X$	0.9954	3.1	0.4712	$Y = -0.0016X$	0.9991	4.4
14	0.0984	$Y = -0.0261X$	0.9807	3.0	0.4044	$Y = -0.0014X$	0.9992	3.9
15	0.1265	$Y = -0.0257X$	0.9914	2.6	0.5264	$Y = -0.0013X$	0.9996	3.6
16	0.1261	$Y = -0.0227X$	0.9935	2.6	0.4316	$Y = -0.0016X$	0.9986	4.4
17	0.1461	$Y = -0.0219X$	0.9994	3.0	0.4035	$Y = -0.0017X$	0.9974	4.7
18	0.1232	$Y = -0.026X$	0.998	3.0	0.4167	$Y = -0.0011X$	0.9996	4.8
19	0.138	$Y = -0.0201X$	0.9886	2.3	0.3970	$Y = -0.0017X$	0.9978	4.7
20	0.1345	$Y = -0.0229X$	0.9945	2.7	0.3323	$Y = -0.002X$	0.9976	5.6

k_{obs} is the observed rate constant in s^{-1} ($\times 10^7$).

rate constants respectively; k_{eq} is the equilibrium constant. The equilibrium constant for the process of partitioning is equal to the partition coefficient K_D.

Values for k_f and k_b were calculated with the aid of observed rate constants and K_D values. These calculated rate constants for two temperatures were
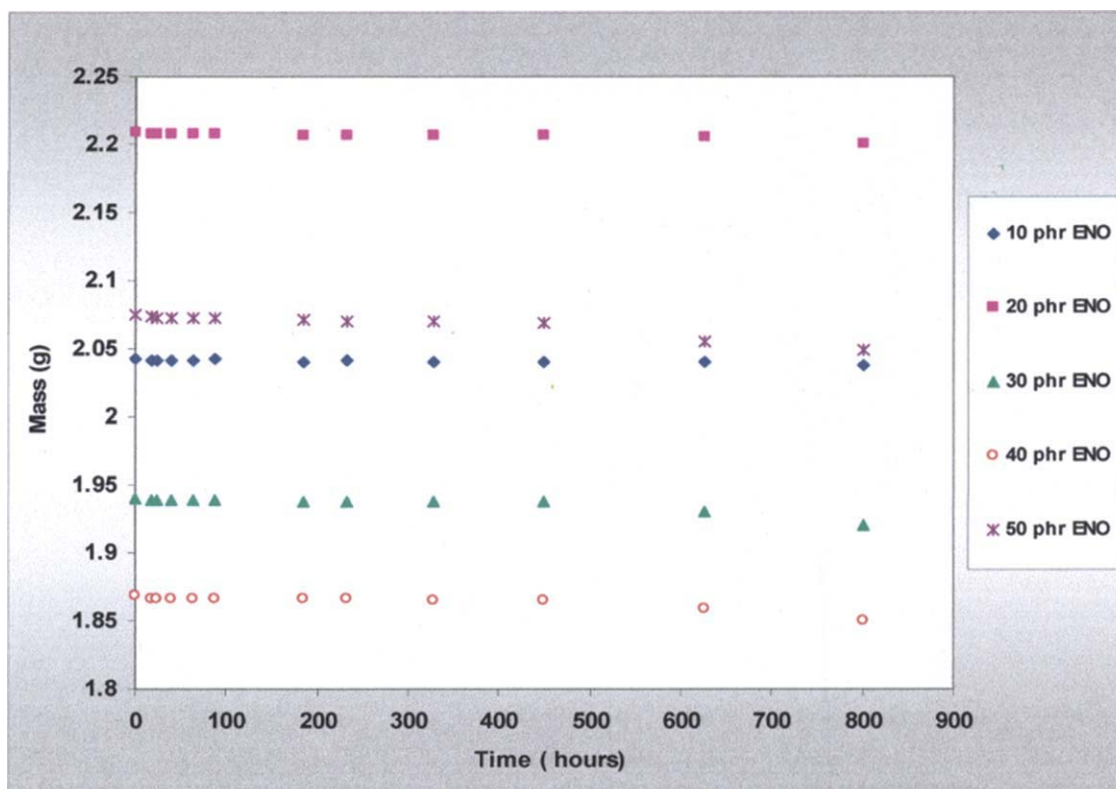

Figure 2 Variation of mass of PVC specimens with varying amount of ENO kept at 323 K for an extended period of time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VI
Rate Constants (Overall, Forward, and Backward Reactions) at Temperatures 296 K and 323 K, Respective Activation Energies, Enthalpy Changes, Diffusion Coefficients, and Activation Energies for Diffusion

				Partition											Diffusion				
				Rate constant at 293 K ($s^{-1} \times 10^{-7}$)			Rate constant at 323 K ($s^{-1} \times 10^{-7}$)			Activation energy (kJ/mol)			ΔH (kJ/mol)	PVC Phase			NBR Phase		
Run	ACN% in NBR	PLC% in PVC	CLD in NBR	k_{obs}	k_f	k_b	k_{obs}	k_f	k_b	E_{aobs}	$E_{a\,f}$	$E_{a\,b}$		D_{293}	D_{323}	E_a	D_{23}	D_{50}	E_a
1	26.5	18	146	4.95	0.38	4.57	11.67	2.75	8.91	25.0	58.3	19.6	38.6	5.0	67.4	76.5	39.6	329.7	62.4
2	26.5	42	146	2.36	0.43	1.93	5.00	1.86	3.14	21.6	43.0	14.3	38.7	5.6	66.5	72.6	44.6	343.2	60.1
3	37.3	18	134	3.31	0.31	3.00	3.61	1.30	2.32	2.6	42.3	−7.6	50.0	1.4	44.5	102.1	14.7	147.3	67.9
4	37.3	42	134	2.65	0.24	2.41	7.5	1.62	5.88	30.1	56.1	26.3	29.8	1.5	32.9	90.4	14.1	152.9	70.1
5	26.5	18	215	4.22	0.34	3.89	11.94	1.48	10.46	30.7	43.6	29.1	14.5	1.6	30.7	86.4	3.9	76.1	87.7
6	26.5	42	215	2.80	0.44	2.36	4.72	1.46	3.26	15.4	35.5	9.5	26.0	4.3	47.9	70.9	33.6	223.1	55.7
7	37.3	18	161	2.71	0.27	2.44	2.78	0.91	1.87	0.9	35.5	−7.9	43.4	1.2	30.3	95.1	12.4	75.9	53.4
8	37.3	42	161	2.66	0.23	2.43	3.89	1.11	2.78	10.8	46.4	3.9	42.8	1.0	25.2	95.1	8.2	93.6	71.7
9	31.9	10	171	2.93	0.20	2.73	2.50	0.71	1.79	23.3	37.1	−12.3	49.4	0.4	32.2	130.9	7.2	55.7	60.1
10	31.9	50	171	2.04	0.26	1.78	4.72	1.54	3.18	25.3	52.8	17.1	35.7	2.2	42.4	86.5	21.6	229.0	69.5
11	22.8	30	239	1.69	0.22	1.47	5.28	1.39	3.88	33.4	53.7	28.7	25.0	2.3	52.9	92.8	28.4	299.6	69.4
12	41.0	30	125	2.99	0.19	2.80	4.17	0.86	3.31	9.7	44.5	4.9	39.6	0.5	18.9	107.7	5.7	53.3	65.7
13	31.9	30	129	3.09	0.36	2.73	4.17	1.33	2.83	10.6	38.5	1.1	37.4	3.3	55.1	82.6	31.9	317.4	67.7
14	31.9	30	224	3.02	0.27	2.75	3.89	1.12	2.77	7.6	41.8	0.2	41.6	1.5	36.9	95.1	16.0	152.5	66.3
15	31.9	30	171	2.97	0.33	2.64	3.61	1.25	2.37	9.7	38.7	−3.2	42.0	2.2	44.7	88.8	22.1	199.3	64.8
16	31.9	30	171	2.63	0.29	2.33	4.44	1.34	3.10	15.8	44.6	8.4	36.2	2.0	40.4	87.8	21.4	188.4	64.0
17	31.9	30	171	2.53	0.32	2.21	4.72	1.36	3.36	13.3	42.3	12.4	29.9	2.5	41.3	83.0	25.4	201.2	61.0
18	31.9	30	171	3.01	0.33	2.68	4.80	2.68	2.12	13.8	42.8	6.9	35.9	2.1	38.7	85.2	22.3	180.5	61.6
19	31.9	30	171	2.33	0.28	2.04	4.72	1.34	3.38	21.2	45.9	14.8	31.1	2.0	46.9	92.9	19.7	206.1	69.1
20	31.9	30	171	2.65	0.31	2.34	5.56	1.39	4.17	21.5	43.7	17.1	26.6	1.9	38.4	88.1	24.1	176.0	58.5

Processing parameters are also included for easy comparison.
Diffusion constants were given in cm^2/s ($\times 10^9$); Activation energies are given in kJ/mol.

utilized to calculate respective activation energies according to the eq. (16) derived from Arrhenius equation. Enthalpy change for the process was subsequently calculated with forward and backward activation energies.

$$E_a = R\left(\frac{T_1 T_2}{T_1 - T_2}\right) \ln\left(\frac{k_1}{k_2}\right) \qquad (16)$$

Values thus obtained are delineated in Table VI and likely energy profile is given in Figure 3.

Diffusion of plasticizers

Perusal of literature indicates that the variation of mass due to plasticizer migration could be used as a diagnostic for diffusion controlled process, if the mass change is linear against square root of time. Figures 4 and 5 authenticate this relationship for both PVC and NBR matrices. Linear relationships thus obtained could be fixed to eqs. (17) and (18) for PVC and NBR phases, respectively. Therefore, gradients of these linear plots were utilized to estimate diffusion coefficients for PVC and NBR phases.

$$\Delta m = \left(2FC_0\sqrt{\frac{D}{\pi}}\right)\sqrt{t} \qquad (17)$$

where, D is total mass loss of PVC specimen at time t and F is the surface area of the specimen. D is the diffusion coefficient; C_0 is the initial concentration of ENO in the PVC specimen.
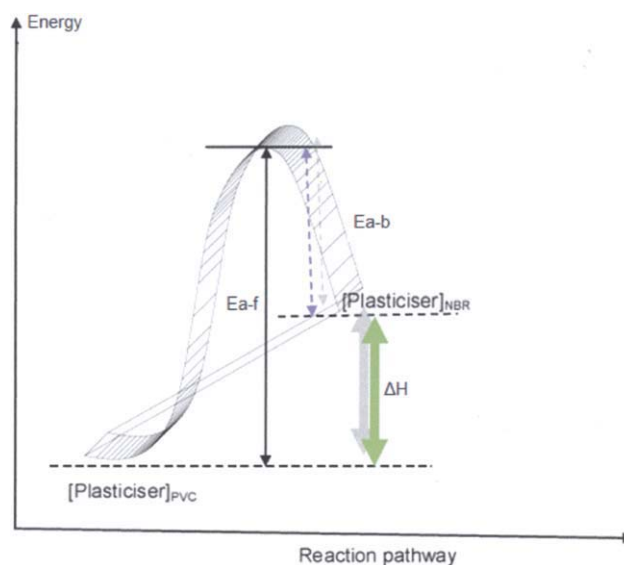
Figure 3 Energy profile for plasticizer migration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
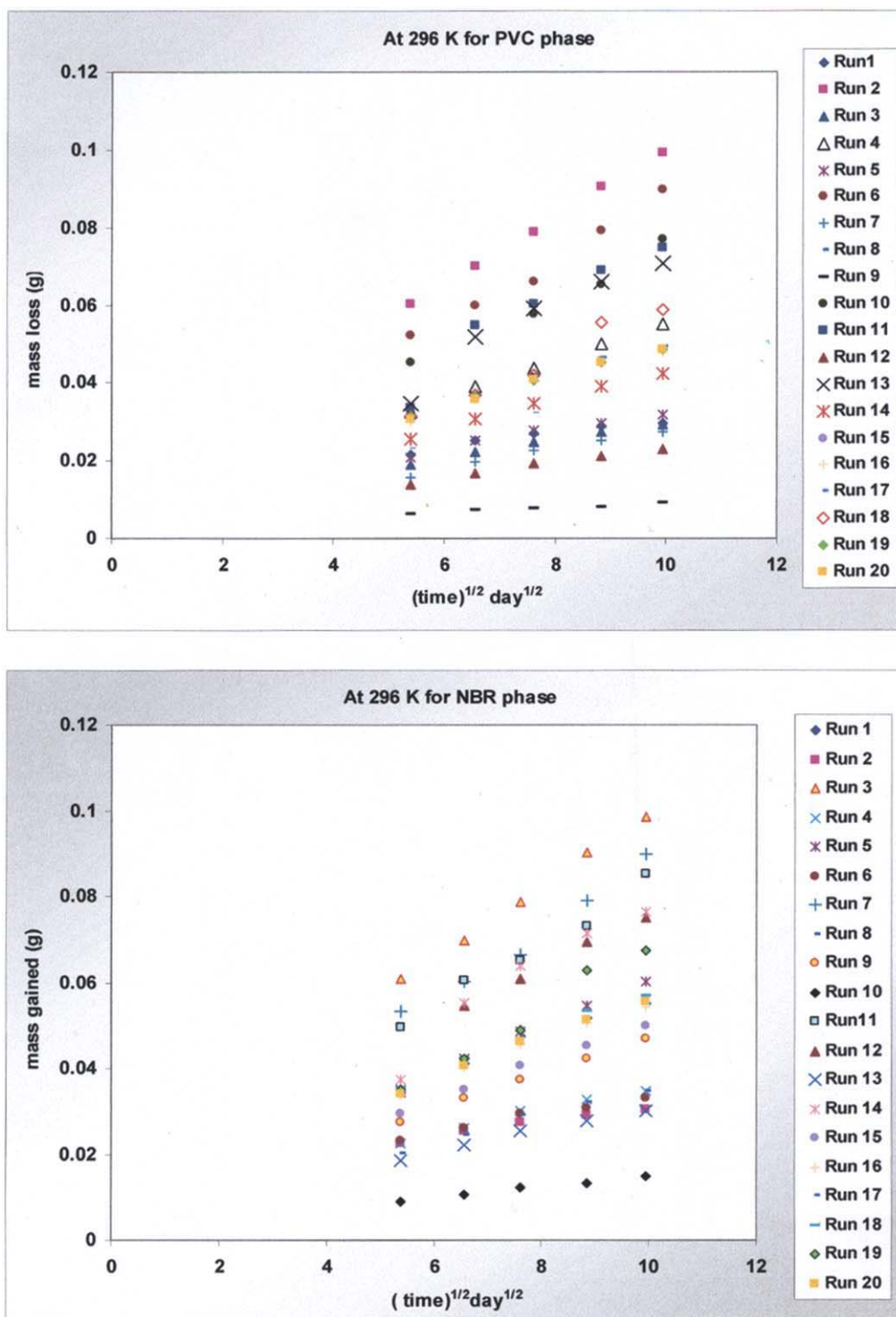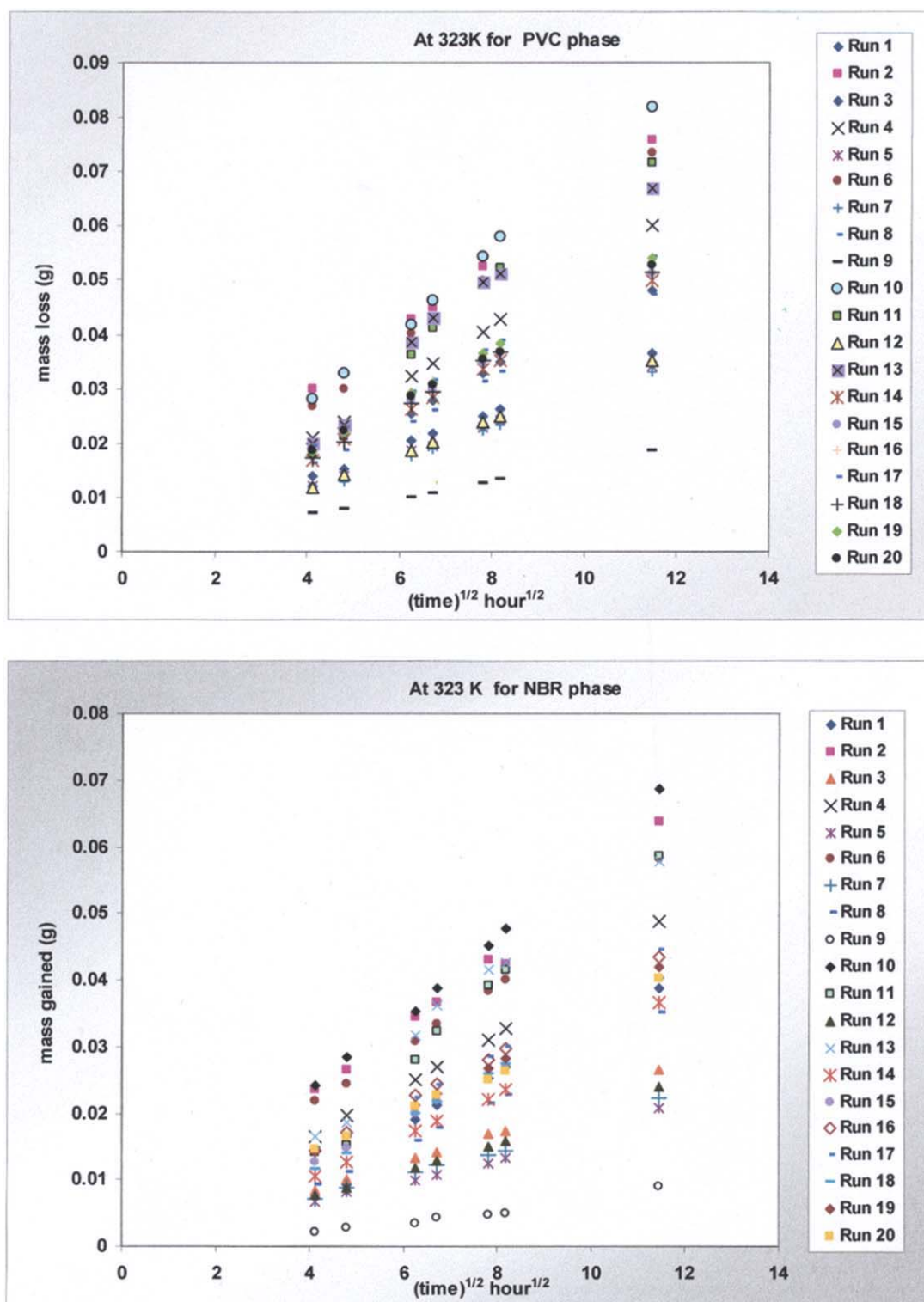
Figure 4 Variation of masses of PVC and NBR specimens at 296 K with square root of time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\Delta m' = \left((\Delta C_0) F \sqrt{\frac{D}{\pi}} \right) \sqrt{t} \qquad (18)$$

where, D is the diffusion coefficient, F is the surface area perpendicular to direction of diffusion, and ΔC_0

is the difference between the initial concentrations of two phases; PVC and NBR. $\Delta m'$ is the increasing in weight of NBR (specimen with low initial concentration) at time t.

Calculated diffusion coefficients for both PVC and NBR phases at temperatures 296 and 323 K are

Figure 5 Variation of masses of PVC and NBR specimens at 323 K with square root of time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

given in the Table VI. Having calculated D for both phases at two temperatures, activation energies for diffusion in PVC and NBR matrices were subsequently evaluated using eq. (19).[21] These values are also given in Table VI.

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \qquad (19)$$

where D is diffusion coefficient, E is activation energy for diffusion, R is gas constant, D_0 is Pre-
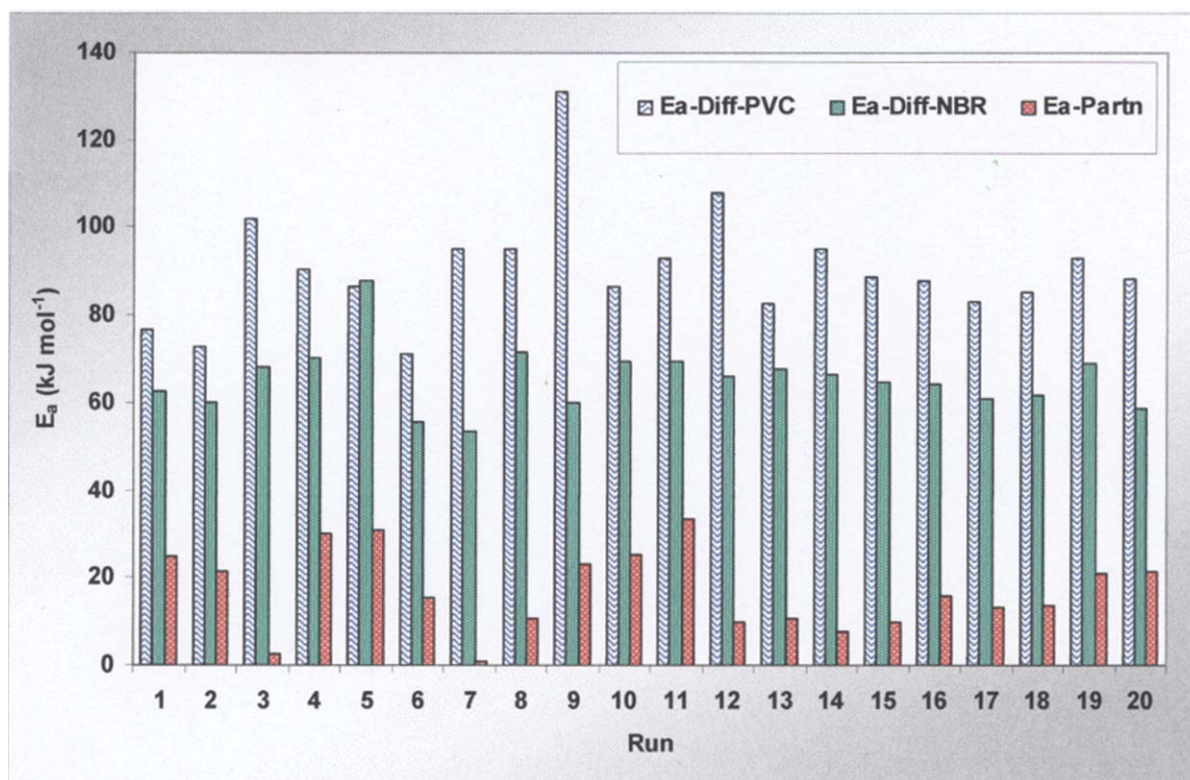
Figure 6 Comparison of activation energies for diffusion and partition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VII
Response Equations Obtained for Parameters Involving Partition and Diffusion

Property	Response equation	Eq. No
Partition Coefficient at 296 K	$K_{D-23} = 0.1320 + 0.0245x - 0.0232y - 0.0069x^2 - 0.0321xy$	(20)
Partition Coefficient at 323 K	$K_{D-50} = 0.4177 - 0.0055y^2 - 0.1204xy + 0.0460xz$	(21)
Over all rate constant at 96 K	$k_{obs-23} = 2.7 \times 10^{-7} - 4.6 \times 10^{-8}x + 4.1 \times 10^{-8}xy$	(22)
Over all rate constant at 323 K	$k_{obs-50} = 4.6 \times 10^{-7} - 8.6 \times 10^{-8}x - 1.3 \times 10^{-7}y + 2.4 \times 10^{-7}xy$	(23)
Activation Energy for over all process of partitioning	$E_{a-T} = 15.92 - 6.46y - 1.95z + 2.7x^2 - 2.68z^2 + 7.0xy - 3.68xz - 2.56yz$	(24)
Enthalpy change of partitioning	$\Delta H = 33.76 - 3.10x + 6.05y + 5.13xz + 4.15yz$	(25)
Forward rate constant at 296 K	$k_{f-23} = 3.1 \times 10^{-8} - 4.4 \times 10^{-9}y$	(26)
Forward rate constant at 326 K	$k_{f-50} = 1.3 \times 10^{-7} - 2.6 \times 10^{-8}y - 2.2 \times 10^{-8}z$	(27)
Activation Energy for forward reaction	$E_{a-F} = 42.99 + 6.03xy$	(28)
Backward Rate constant at 296 K	$k_{b-23} = 2.4 \times 10^{-7} - 4.7 \times 10^{-8}x + 4.5 \times 10^{-8}xy$	(29)
Backward Rate constant at 323 K	$k_{b-50} = 3.2 \times 10^{-7} - 1 \times 10^{-7}y + 2.2 \times 10^{-7}xy$	(30)
Activation Energy for backward reaction	$E_{a-B} = 9.23 + 5.14x - 7.17y + 3.58y^2 + 8.83xy - 4.56xz$	(31)
Diffusion coefficient of PVC at 296 K	$D_{23}(PVC) = 2.1 \times 10^{-9} + 4.7 \times 10^{-10}x - 1.1 \times 10^{-9}y - 6.3 \times 10^{-10}z$	(32)
Diffusion coefficient of PVC at 323 K	$D_{50}(PVC) = 4.2 \times 10^{-8} - 1.0 \times 10^{-8}y - 7.9 \times 10^{-9}z + 2.3 \times 10^{-9}z^2$ $- 4.1 \times 10^{-9}xy + 3.1 \times 10^{-9}xz + 4.2 \times 10^{-9}yz$	(33)
Diffusion coefficient of NBR at 296 K	$D_{23}(NBR) = 2.2 \times 10^{-8} + 4 \times 10^{-9}x - 8.1 \times 10^{-9}y - 6 \times 10^{-9}z$ $- 2.2 \times 10^{-9}x^2 - 4.9 \times 10^{-9}xy + 4.8 \times 10^{-9}yz$	(34)
Diffusion coefficient of NBR at 323 K	$D_{50}(NBR) = 1.9 \times 10^{-7} + 3.5 \times 10^{-8}x - 6.7 \times 10^{-8}y - 5.7 \times 10^{-8}z - 1.8 \times 10^{-8}x^2$ $+ 1.4 \times 10^{-8}z^2 - 1.7 \times 10^{-8}xy + 1.8 \times 10^{-8}xz + 3 \times 10^{-8}yz$	(35)
Activation energy for diffusion in PVC	$E_{a(diff)}(PVC) = 88.06 - 7.75x + 7.42y$	(36)
Activation energy for diffusion in NBR	$E_{a(diff)}(NBR) = 63.18 + 6.86xy - 4.23yz$	(37)

TABLE VIII
Statistical Information Obtained on Each of the Parameters from Design

Property (Eq. No)	F_{EQ}	F_{LF}	Significance of F
Partition Coefficient at 296 K (20)	22.3	2.37	1.8×10^{-5}
Partition Coefficient at 323 K (21)	5.69	1.83	0.006
Over all rate constant at 296 K (22)	*1.67*	9.97	0.2170
Over all rate constant at 323 K (23)	4.81	9.11	0.0110
Activation Energy for over all process of partitioning (24)	11.53	0.32	0.00034
Enthalpy change of partitioning (25)	4.50	0.94	0.0139
Forward rate constant at 296 K (26)	*1.7009*	*15.73*	1.7009
Forward rate constant at 326 K (27)	*1.7538*	*78.8*	0.1969
Activation Energy for forward reaction (28)	*2.4700*	7.0796	2.4791
Backward Rate constant at 296 K (29)	*2.044*	9.4414	0.1403
Backward Rate constant at 323 K (30)	*2.6259*	*15.30*	0.0743
Activation Energy for backward reaction (31)	5.3677	0.7983	0.0074
Diffusion coefficient of PVC at 296 K (32)	4.4973	*38.8*	0.0139
Diffusion coefficient of PVC at 323 K (33)	14.674	2.5543	0.00012
Diffusion coefficient of NBR at 296 K (34)	12.828	8.2441	0.0002
Diffusion coefficient of NBR at 323 K (35)	25.28	7.5869	1×10^{-5}
Activation energy for diffusion in PVC (36)	*2.0398*	*19.06*	0.1410
Activation energy for diffusion in NBR (37)	*1.6462*	4.9917	0.2247

exponential factor, and T is temperature in Kelvin. A comparative illustration of activation energies for diffusion and partition processes is given in Figure 6.

Regression analysis and response equations

A multiple curvilinear regression analysis is an empirical attempt to represent an unknown underlying relationship as a simple polynomial, called response equation.[18] Each power or product appearing in the equation is treated as if it were a separate independent variable in setting up the least-squares equations for the regression coefficients.[18] The general form of response equation obtained for three factor design experiment is given in "Determination of Partition Coefficient" section [eq. (3)]. The Analysis of Variance (ANOVA) table produced by regression analysis on individual set of data gives the coefficients of all terms and their respective probability (P) values.
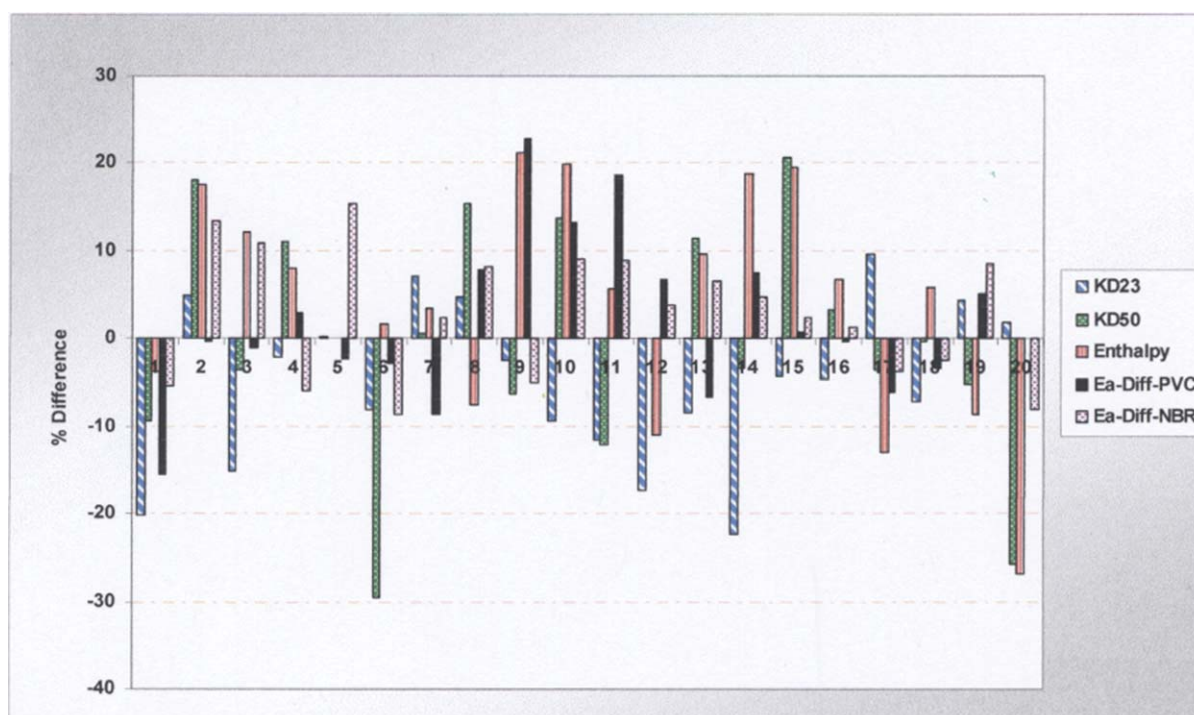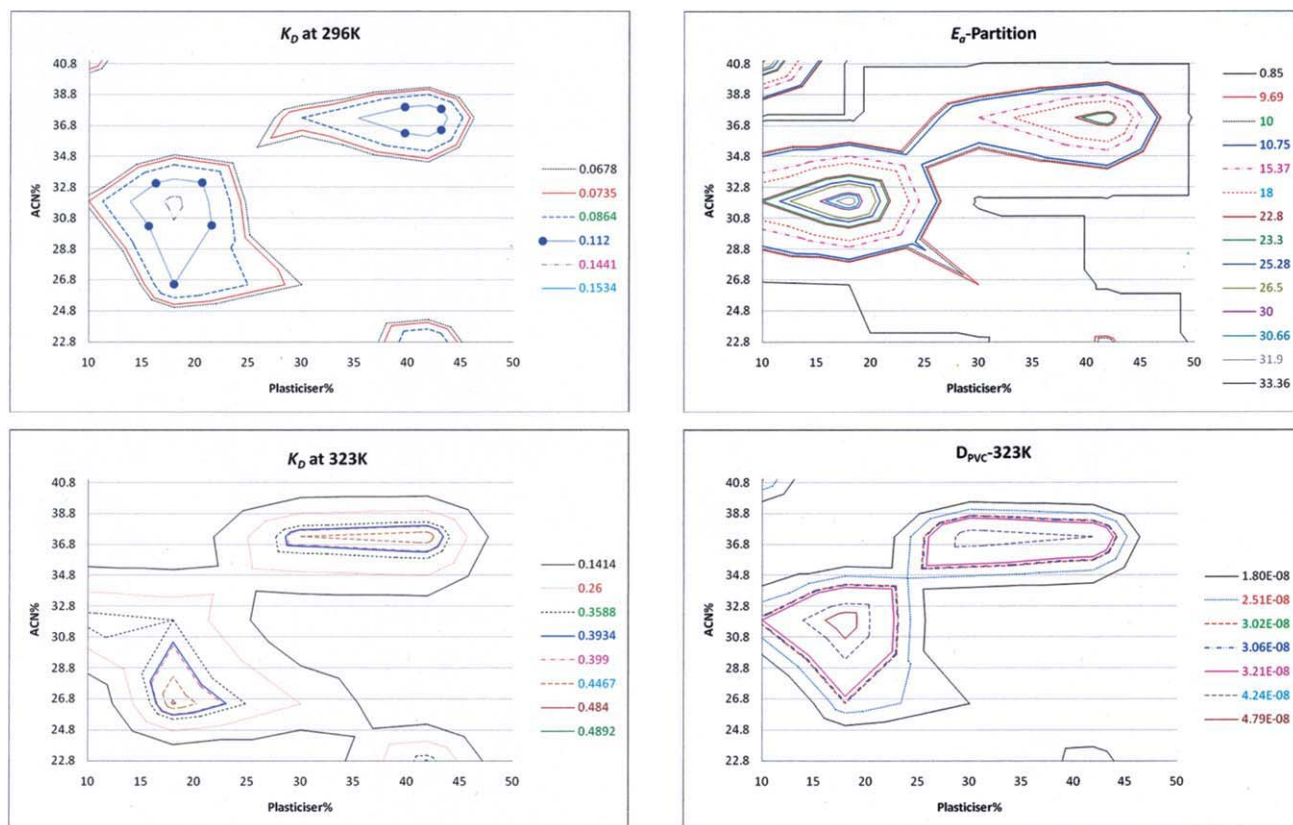

Figure 7 Percentage differences between experimental and calculated values using respective response equations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 Contour diagrams (peroxide levels were kept in the range of 1.75% and 2.3%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Coefficients having P values of 0.1 or higher are not deemed to be statistically significant while those with P values less than 0.01 are highly significant.

Response equations generated for variables obtained in preceding sections, "Partition Coefficients, Kinetics of Partitioning, and Diffusion of Plasticizers," are summarized in Table VII after eliminating statistically insignificant variables. It should be noted that x, y, and z in those equations denote plasticizer% in PVC, nitrile% in NBR, and peroxide% in NBR respectively.

Explanatory power of response equations and adequate representation of data by them were evaluated by respective F ratios, F_{EQ}, and F_{LF}. Equations (4) and (5) were used for this purpose. Values for F_{EQ}, and F_{LF} thus calculated on each of the parameters are delineated in Table VIII. Relevant degrees of freedom and corresponding entries in F distribution table are summarized in Table IX. The criterion for legitimacy of response equations is that, if F_{EQ} obtained is greater than the corresponding entry of F distribution the equation is significant and has explanatory power. On the other hand, if F_{LF} obtained is smaller than the corresponding value in the Table then the response equation is found to fit the results adequately.

Values of F ratio listed in Table VIII shows that the majority of equations obtained are of "good fit"

and have significant explanatory power. Values marked as italics denote poor explanatory power or inadequacy of those response equations. Equations (26), (27), (30), and (36) showed significance level of lack of fit. The first three equations mentioned here are related to rate constants, whereas the latter is for activation energy of diffusing in PVC. It is important to realize that parameters related to response equations that are deemed statistically insignificant cannot be predicted with an acceptable degree of accuracy. Response eqs. (22), (28), (29), and (37) were also found to have lack of explanatory power as smaller values of F_{EQ} were obtained. Yet these response equations should not be rejected because lower values for F_{LF} were generated even at the 1% significance level. The equation representing the diffusion coefficient of PVC at 296 K [eq. (32)] shows some explanatory power ($F_{EQ} = 3.02$) but significant level of lack of fit.

Reliability of recommended models when predicting values for each parameter was tested by evaluating the percentage differences between experimental values and values calculated by appropriate response equations. Figure 7 shows that the percentage differences between experimental values and those predicted from the response equations for the mainstream of samples were between ± 20% for parameters statistically well fitted.

TABLE IX
Relevant Degrees of Freedom

Degrees of Freedom (df)	
Regression Mean Square (RGMS)	9
Residual Mean Square (RSMS)	10
Lack of Fit Mean Square (LFMS)	5
Pure Error Mean Square (PEMS)	5
Entry in F Distribution Table	
F_{EQ} (9,10)	3.0204 (5% level)
	4.9424 (1% level)
F_{LF} (5,5)	5.0503 (5% level)
	10.967 (1% level)

The model suggested for the partition coefficient [eq. (20)] shows direct influence of plasticizer content in PVC (x) and nitrile content in NBR (y), and interactive effects of both variables. It can be seen that K_D is decreasing with increase in ACN% in the NBR phase due to negative coefficients associated with the variable involving y (that is ACN% content). The partition coefficient at 296 K was influenced only by plasticizer content and nitrile content, but at higher temperature interactive effect of plasticizer level and peroxide level on K_D is observed. Therefore extent of migration of the plasticizer (ENO) to NBR phase can be curtailed by increasing the ACN% in NBR. In other words, polarity of the recipient medium plays an important role in plasticizer migration. Migration of ENO will be mitigated by higher polarity in the recipient material. The fact is further confirmed by experimental results showing the lowest K_D for the specimen with the maximum nitrile content of 41% and minimum crosslink density (Run 12).

The response equation obtained for overall rate constants [eqs. (22) and (23)] at both temperatures indicate the dependency on plasticizer level and nitrile content but not on crosslink density. Interactive effect of plasticizer level and nitrile content has an increasing effect on rate constant because of significant positive coefficients for the term "xy" (that is plasticizer/ACN% interaction). Peroxide content used in processing of NBR, which is indirectly related to the crosslink density, shows no influence on rate constants. However, the activation energy related to the partitioning is affected by the crosslink density of the recipient material in addition to the plasticizer level and ACN%. According to eq. (24) lower activation energy is expected with increasing crosslink density since all terms including z produce a negative contribution on E_a. Such a trend is not observed from the results obtained experimentally. It must be emphasized that since the response equation is an empirical model, predictions made are mostly valid within the factorial points. They are $(-1,-1)$, $(-1, 1)$, $(1,-1)$, and $(1, 1)$ and these combinations are represented only up to Run 8. As a result it is probable that outside the region of these factorial points the predictions may become less accurate and precise. In fact, extrapolations beyond the limits of the design are not recommended.[18]

The diffusion coefficient of the PVC phase depends on all three variables, plasticizer level, ACN% and peroxide level. The effect of ACN% in NBR phase has a greater effect on D values because of the large coefficients associated with it. Higher nitrile content in the NBR phase reduces the diffusion coefficient in PVC phase and hence decelerates the diffusion process.

Pictorial representations of the relationships between a response and the independent variables are very useful in design experiments. In view if this, response contours were constructed for some selected parameters; these are shown in Figure 8. It should be noted that the variable, peroxide%, had the least effect on the response equations and, therefore, kept within the range 1.75%–2.2% when constructing the contours.

CONCLUSIONS

Partitioning of ENO as a plasticizer between PVC and NBR follows first order equilibrium kinetics, and the forward reaction is found to be endothermic. The percentage migration of plasticizer at 296 K at equilibrium is well below 25% for majority of samples irrespective of other pertinent factors.

Parameters such as forward, backward, and overall rate constants and their respective activation energies and enthalpy change related to the partitioning phenomenon are influenced to different degrees by plasticizer concentration in PVC, ACN% in NBR and crosslink density of NBR. The influence caused by plasticizer concentration and ACN% was found to be the most significant though the effect of crosslink density cannot be ignored.

The nature of mass transfer in PVC and NBR phases follows Fick's law during the initial stages. Diffusion of plasticizer through PVC matrix is the rate determining step for the overall migration process as the diffusion process of plasticizer was the process identified as having the highest activation energy.

Proposed response equations for most parameters involved in partitioning and diffusion were found to be statistically significant thus indicating that the response equations were considered as having sufficient explanatory power and "good fit" in the statistical sense. The reliability of the response equations was demonstrated further when experimental values were compared with predicted values determined from the response equations; the deviations were within ± 20%.

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