Evaluation of Thermal Migration of Ester-Type Plasticizers in Acrylonitrile-Butadiene Rubbers by Highly Sensitive Automated Thermal Desorption Gas Chromatography

Katsuhiko Yokoe[ab]; Hajime Ohtani[a]; Shin Tsuge[a]

[a] Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya, Japan [b] Tokai Rubber Industries Ltd., Komaki, Aichi Prefecture, Japan

PLEASE SCROLL DOWN FOR ARTICLE

Evaluation of Thermal Migration of Ester-Type Plasticizers in Acrylonitrile–Butadiene Rubbers by Highly Sensitive Automated Thermal Desorption Gas Chromatography

KATSUHIKO YOKOE [†], HAJIME OHTANI and SHIN TSUGE [*]

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

A new method to evaluate thermal migration of plasticizers in acrylonitrile (AN)–butadiene rubbers was developed by use of automated thermal desorption gas chromatography (GC). A small piece of rubber sample weighing ca. 0.5 mg was subjected to thermal desorption at 260°C for 15 min in an automated thermal desorption GC system under a flow of nitrogen carrier gas. The desorbed plasticizer condensed in a trap was then directly stripped at 300°C for 15 min into a wide-bore fused-silica capillary separation column, programmed from 50°C to 280°C at a rate of 7.5°C min^{-1}. Thus rapid and precise determination became possible for various plasticizers, such as di(2-ethylhexyl)-adipate, di(2-ethylhexyl)phthalate and di(2-ethylhexyl)sebacate in samples weighing less than 1 mg taken from given depths of the rubber sheet. This highly sensitive method enabled not only depth profiling of the plasticizers in rubber samples, but also rapid estimation of the diffusion coefficients for the plasticizers in various rubber samples with different AN content at various temperatures.

Keywords: Plasticizer; Acrylonitrile–butadiene rubber; Thermal desorption gas chromatography; Fick's laws

---

* Corresponding author.
[†] Present address: Tokai Rubber Industries Ltd., Komaki, Aichi Prefecture, 485-8550, Japan.

INTRODUCTION

Acrylonitrile–butadiene rubbers (NBR) has been used as oil resistant and/or low-temperature resistant elastomers. These properties of NBR are known to change as a function of copolymerization ratio of acrylonitrile (AN) and butadiene units.[1] Generally, in order to improve its mechanical properties and the low-temperature flexibility, various plasticizers are added to NBR materials. However, liquid plasticizers with relatively low molecular-weight are known to exudate onto the surface of the materials, and/or migrate into other contacted materials.

The determination of the depth profile of the plasticizer concentrations in NBR is necessary to study the migration behavior. Lin[2] studied the distribution of additives such as carbon black, zinc oxide, and sulfur in vulcanized rubber by Auger electron spectroscopy. Curative diffusion at vulcanizing temperatures between dissimilar elastomers has been investigated by light microscopy and attenuated total reflectance infrared (ATR-IR).[3] Furthermore, diffusion of sulfur and vulcanizing accelerators across interfaces between dissimilar rubbers has been measured by microinterferometry based on the difference in the optical path length between the samples containing curing agents and the reference materials,[4] where the relationship between the sulfur content in the materials and the diffusion coefficient of the curative agents was also discussed.

The conventional determination of plasticizers in rubbers is often carried out by solvent extraction followed by gas chromatography (GC). The extraction and the following enrichment procedure, however, are not only time-consuming but also often cause various problems, such as contamination and loss and/or alteration of the components of interest. Furthermore, the solvent extraction requires too much sample size to measure detailed depth profile of the plasticizers in rubbers.

Recently, a fully automated thermal desorption GC system was developed for the analysis of volatile components in solid samples. The dynamic trapping of the thermally desorbed organic components from a given sample and the subsequent stripping for the desired components into the GC column enabled rapid and sensitive determinations of the trace organic components without sample loss and contamination.[5–7]

In this work, a new method to evaluate the thermal migration behavior of typical low-molecular-weight plasticizers, such as di(2-ethylhexyl)adipate (DOA), di(2-ethylhexyl)phthalate (DOP), and di(2-ethylhexyl)sebacate (DOS), between contacted NBR sheets was developed by use of the highly sensitive automated thermal desorption GC. In this approach, less than 1 mg of the rubber section sample can be removed from the desired depth. Thus, observed depth profile of the plasticizer concentration was interpreted in terms of diffusion coefficients of the plasticizers in NBR on the basis of the Fick's laws.

EXPERIMENTAL

Samples

The formulations of the rubber samples are shown in Table I. Four kinds of NBRs with different AN content, 18%, 31%, 42% and 50%, were used as the rubber substrates, and their vulcanization was carried out at 150°C for 20 min. As shown in Figure 1, three sheets of rubber disk (50-mm diameter × 2.0-mm thick) without plasticizers were put symmetrically on both sides of the central disk containing the plasticizers, DOA, DOP and DOS, at 8 wt parts per hundred rubber (phr), respectively.[8]

Thus assembled seven layers of the rubber sheets were heated at a given temperature between 70°C and 150°C for an appropriate period

TABLE I Formulations of rubber samples

Component	Composition[a]
NBR	100
Stearic acid	1
ZnO	5
Carbon black	100
DOA[b]	8 or 0
DOP[c]	8 or 0
DOS[d]	8 or 0
Vulcanizing agents[e]	4.9

[a]Wt parts per hundred rubber.
[b]Di(2-ethylhexyl)adipate.
[c]Di(2-ethylhexyl)phthalate.
[d]Di(2-ethylhexyl)sebacate.
[e]Sulfur and vulcanizing accelerator.

plasticizer-added disk
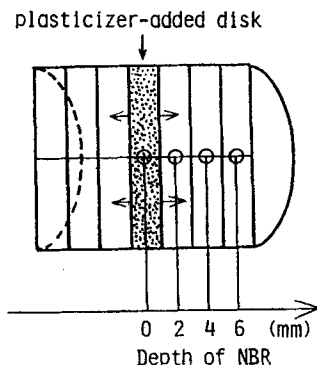

0 2 4 6 (mm)
Depth of NBR

FIGURE 1   Cross section of rubber-sheet assembly for thermal migration of plasticizers. Initially, only the central sheet contains plasticizers.

up to 72 h to promote thermal migration of the plasticizers from the center sheet to the other sheets. After heat-processing, a small piece (ca. 0.5 mg) of rubber was cut off from the center of the respective sheets of one side shown in Figure 1 for the determination of plasticizers by thermal desorption GC. The adopted sample size (0.5 mg) was sufficient to determine plasticizers at less than 0.1% of the initial concentration (8 phr) in the central sheet.

Apparatus

Figure 2 shows a schematic diagram of the automated on-line thermal desorption gas chromatographic system (Yanaco, GTE 10A) used in this work. The quartz tubing (D) is directly attached to the injection port of a gas chromatograph (Yanaco, G-180) with a flame ionization detector (FID) (N) . The quartz tubing (D) consists of three parts: a thermal desorption chamber (E) (14-mm o.d. × 10-mm i.d. × 80-mm long), a trap column (6-mm o.d. × 3-mm i.d. × 9-mm long) packed with sorbents (Tenax-GC, 60-80 mesh) (G), and a connecting tube with a branched line to a venting electromagnetic on–off valve (B) through a protective adsorption column (6-mm o.d. × 3-mm i.d. × 40-mm long copper tube) packed with activated charcoal (J) . These three parts are equipped with individual electric heaters and temperature sensing elements. The trap column is also equipped with a cooling fan (I).
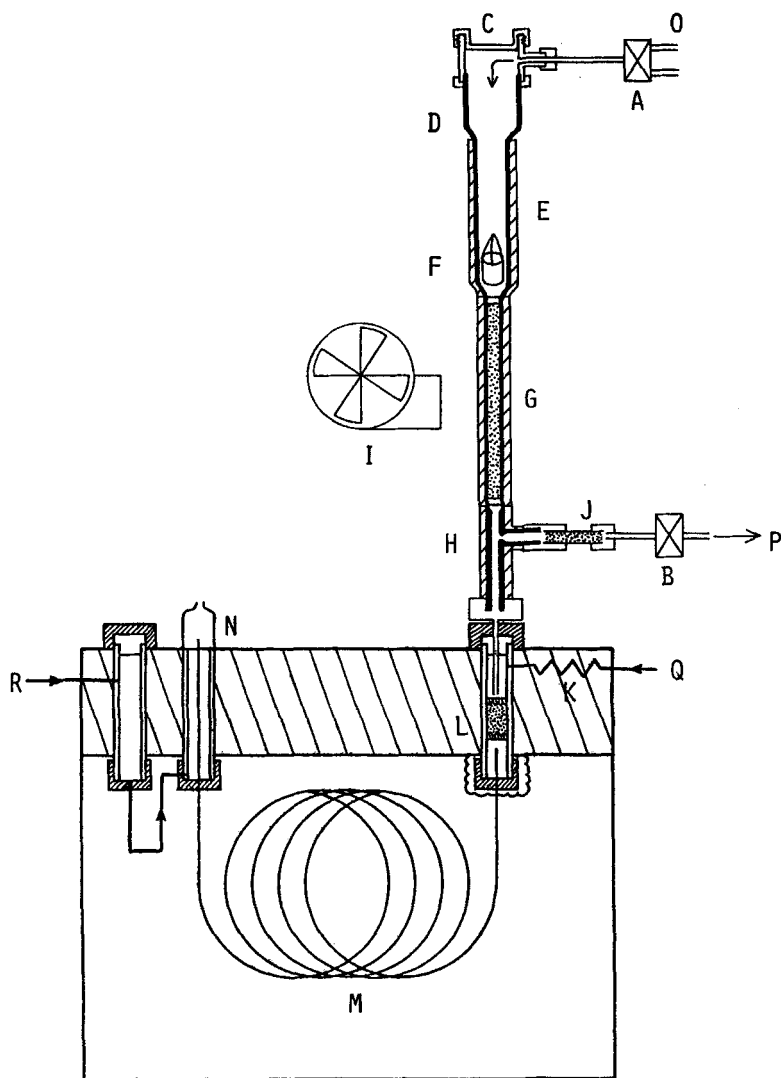
FIGURE 2   Schematic diagram of thermal desorption gas chromatographic system. A, electromagnetic switching valve; B, electromagnetic on–off valve; C, screw-cap; D, quartz tube; E, thermal desorption chamber; F, sample holder; G, trap column; H, connecting tube; I, cooling fan; J, adsorption microcolumn; K, resistance tube; L, glass insert tube; M, fused-silica capillary column; N, flame ionization detector; O, carrier gas inlet (150 mL/min and 6 mL/min); P, vent; Q, carrier gas inlet (1 mL/min); R, scavenger gas inlet (24 mL/min).

A piece of the rubber sample (ca. 0.5 mg) in the sample holder (F) was subjected to thermal desorption at 260°C for 15 min under a flow of nitrogen carrier gas at 150 mL/min. The desorbed plasticizers are then condensed in a trap and directly stripped at 300°C for 15 min at an optimum carrier gas flow of 6 mL/min into the separation column (M) consisting of a wide-bore fused-silica capillary column (0.53-mm i.d. × 30 m) coated with 5 μm thickness of immobilized dimethylsilicone. After stripping, the temperature programming for the GC column (50°C to 280°C at a rate of 7.5°C/min) was started to separate the introduced plasticizers. No further increase in peak intensities of the plasticizers was observed at desorption temperatures higher than 260°C. The repeated thermal desorption for a given sample at 260°C for 15 min gave no plasticizer peaks. These results suggest that the plasticizers in NBR were almost completely recovered under the given thermal desorption conditions.

After the GC analysis, the valve (B) was opened again and the temperature of the trap column was raised to near the maximum usable temperature (330°C) of the sorbent (Tenax-GC) in the trap column to bake out the less volatile components remaining in the trap column into the adsorption microcolumn (J).

The total time for all the analytical steps, including baking-out for the next run, takes about 1 h. Thus rapid and sensitive determinations of the plasticizers in NBR were carried out without performing any preliminary sample treatment.

RESULTS AND DISCUSSION

Figure 3 shows a typical chromatogram of the plasticizers selectively stripped from a piece of an NBR sample weighing ca. 0.5 mg by thermal desorption GC. The relative standard deviation for five repeated runs for the different pieces from the same rubber sheet was about 3% for each plasticizer. This highly sensitive method was used to evaluate the local concentration of the plasticizers in a given rubber sheet by using a minute sample section, weighing less than 1 mg taken from a desired depth.

Thus, observed typical depth profiles of plasticizers, such as DOA, DOP and DOS, in sheets of NBR (31% AN) samples after heat-processing at 70°C for 48 h are shown in Figure 4, where the relative
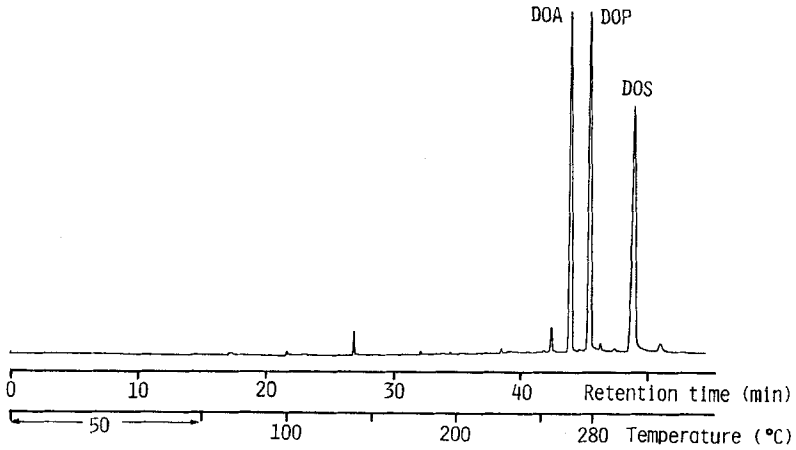
FIGURE 3 Typical gas chromatogram of plasticizers thermally desorbed from NBR sample. Thermal desorption, 260°C for 15 min; AN content, 31%; sample size, 512 μg.
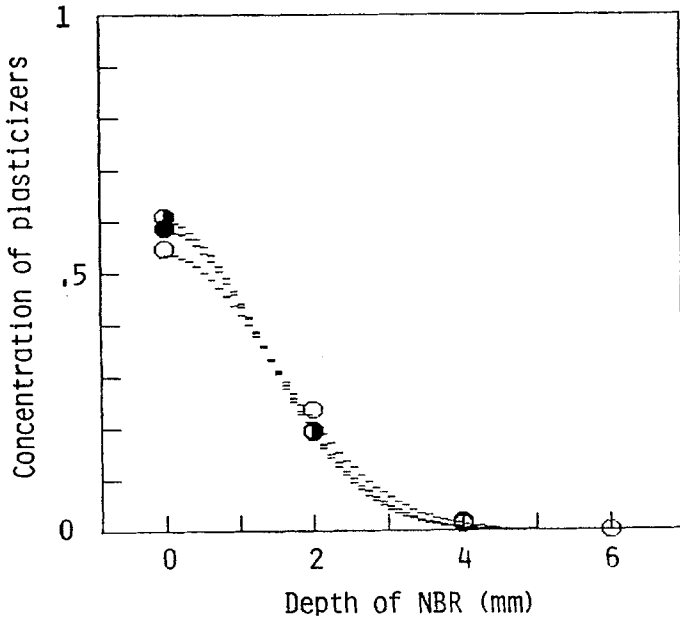
FIGURE 4 Depth profile of plasticizers in NBR (acrylonitrile/butadiene, 31/69) after heating at 70°C for 48 h. Observed concentration of DOA, DOP, and DOS (○, ◑, ●), respectively. Calculated profiles by computer simulation (----). Concentrations are relative to the initial concentration in the central sheet.

concentrations of the plasticizers to the initial concentrations in the central sheet were plotted against the distance from the central sheet (Figure 1). The fact that remaining fraction of DOP on the central sheet is slightly larger than those of the other plasticizers suggests that the aromatic nature of DOP might be associated with a smaller migrative behavior in NBR. However, DOA is most liable to diffuse because of its low molecular-weight. This tendency was commonly observed for the other NBR samples examined in this work.

Figure 5 shows the observed depth profiles of DOP in three NBR samples with different AN contents after heat-processing at 120°C for 24 h. It can be seen that the migration of the plasticizers is strongly influenced by the AN content in the NBR samples.
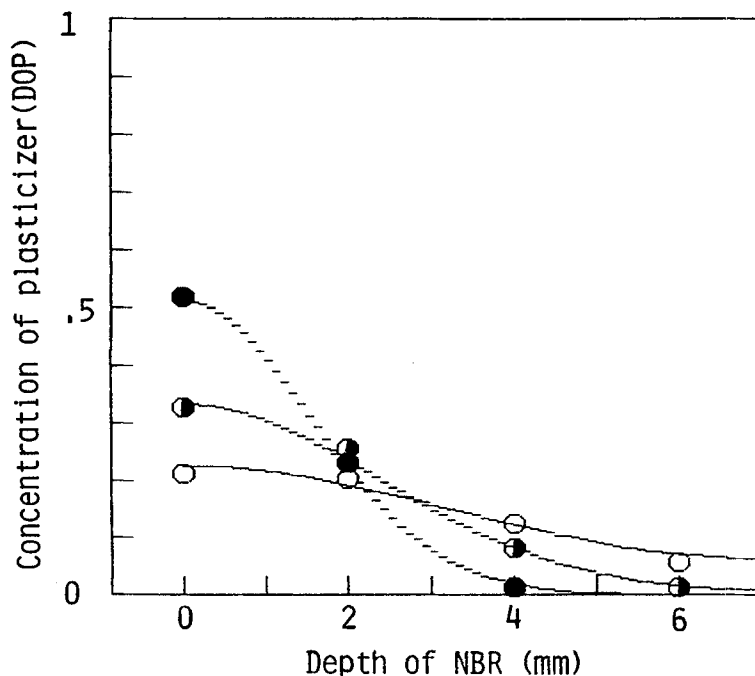
FIGURE 5   Depth profile of DOP in NBR after heating at 120°C for 24 h. Observed concentration in AN 18%, 31%, and 42% (○, ◑, ●), respectively. Calculated profiles by computer simulation (----). Concentrations are relative to the initial one in the central sheet.

In the following discussion, it is assumed that the observed diffusion of the plasticizers in NBR samples obeys Fick's laws:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2},$$
$$c_i = c_{i0}, \quad 0 < x < 1, \ t = 0,$$
$$c_i = 0, \quad 1 < x < 7, \ t = 0,$$
$$\frac{\partial c_i}{\partial x} = 0, \quad x = 7, \ t > 0,$$

(1)

where c_i is the concentration of the plasticizer i, c_{i0} is the initial concentration of the plasticizer in the central sheet, t (s) is heating time, x (mm) is the abscissa diffusion distance measured from the central sheet, and D_i is the diffusion coefficient of the plasticizer. At $t = 0$, the concentration of the plasticizer is c_{i0} in the center sheet, and zero ($c_i = 0$) in the other sheets.

Strictly speaking, D_i value should change as a function of the concentration of the plasticizer in NBR samples.[9] In this case, however, this variation of D_i was regarded as negligibly small. Therefore, the depth profiles of the plasticizer concentration were calculated by means of the finite difference method[10] based on the mean D_i value during the heating time.

In Figure 6, the initial (A), an intermediate (B) and the final (C) depth profiles of a given plasticizer during the heat-processing are given as a function of the distance (x/mm) from the center of the central sheet in which the plasticizer is initially contained, as shown in Figure 1. For the theoretical calculation using the finite difference method, each NBR sheet with 2-mm thickness is considered by dividing it into 20 sections, each with a thickness of Δx (0.1 mm), and the plasticizer concentration at j position after the heat-processing for t ($= k\Delta t$) seconds is described as $c_{j,k}$ where the time increment (Δt) of 30 s was adopted.

Thus, the initial concentrations of the plasticizer at $j = 1-70$ before the processing is as follows:

$$c_{1,0} = c_{2,0} = \cdots = c_{10,0} = 1,$$

(2)

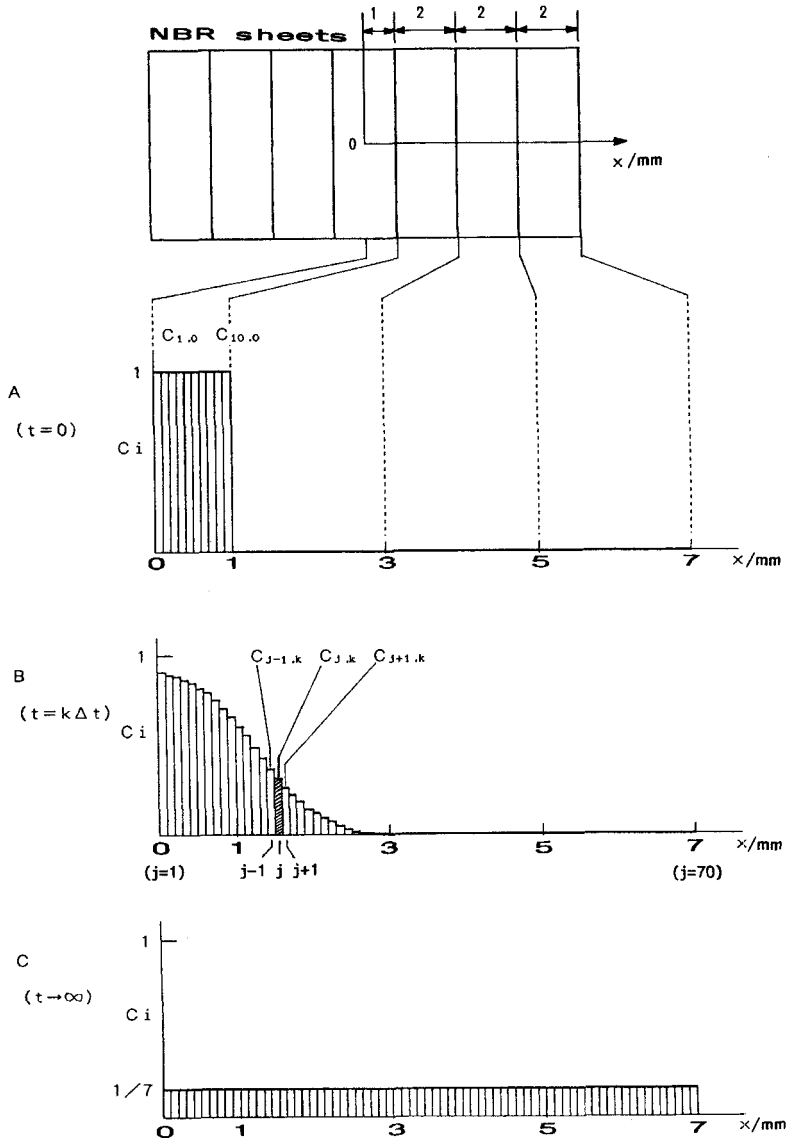$$c_{11,0} = c_{12,0} = \cdots = c_{70,0} = 0.$$

(3)

FIGURE 6   Thermal migration of plasticizers in assembled NBR sheets illustrated for the calculation by the finite difference method: A, before thermal processing; B, after thermal processing for t $(=k\Delta t)$; C, after thermal processing for infinitely long t $(=k\Delta t, k \to \infty)$.

After heat-processing for $t (= k\Delta t)$ seconds, the depth profile of the plasticizer concentration would be like Figure 6B due to the thermal migration of the plasticizer through the sheets. Here, the finite difference method predicts the plasticizer concentration at j position after $(k + 1)\Delta t$ seconds, $c_{j,k+1}$ from the nearest former concentration, $c_{j,k}$ at j position ($j = 2, 3, \ldots, 69$) after $k\Delta t$ seconds heat-processing as follows:

$$c_{j,k+1} = c_{j,k} + \frac{D\Delta t}{(\Delta x)^2}(c_{j-1,k} - c_{j,k}) - \frac{D\Delta t}{(\Delta x)^2}(c_{j,k} - c_{j+1,k}), \quad (4)$$

where D is the diffusion constant of the plasticizer in the rubber matrix at a given temperature. The second and third terms correspond to the in-coming fraction from $j - 1$ to j position, and out-going fraction from j to $j + 1$ position through thermal migration during the heat-processing for $\Delta t (= 30\,\text{s})$, respectively.

Similarly, the plasticizer concentrations at two extreme position ($j = 1$ and 70) after $(k + 1)\Delta t$ seconds treatment can be expressed as follows, respectively:

$$c_{1,k+1} = c_{1,k} - \frac{D\Delta t}{(\Delta x)^2}(c_{1,k} - c_{2,k}), \quad (5)$$

$$c_{70,k+1} = c_{70,k} + \frac{D\Delta t}{(\Delta x)^2}(c_{69,k} - c_{70,k}). \quad (6)$$

After infinitely long thermal processing ($k \to \infty$), the plasticizer concentration in each position should be averaged to one-seventh of the initial concentration in the central sheet:

$$c_{1,\infty} = c_{2,\infty} = \cdots = c_{70,\infty} = \tfrac{1}{7}. \quad (7)$$

The diffusion coefficients of the respective plasticizers for various NBR samples with different AN content at 70°C, 100°C, 120°C, 135°C, and 150°C was estimated by computer simulation of the observed concentrations of the plasticizers (e.g., Figures 4 and 5) to the theoretical Equations (4)–(6) derived by the finite difference method.

TABLE II   Estimated diffusion coefficients of plasticizers in NBRs

Plasticizers	AN content, %	$D\ (\times 10^{-5}\,mm^2/s)$				
		70°C	100°C	120°C	135°C	150°C
DOA	18	2.1[b]	5.4[a]	9.0[a]		
	31	0.54[b]	1.8[a]	3.9[a]	6.2[a]	8.4[a]
	42	0.15[c]	0.73[b]	1.4[a]		
	50	0.036[c]	0.19[c]	0.46[c]		
DOP	18	1.6[b]	4.6[a]	7.0[a]		
	31	0.41[b]	1.4[a]	3.1[a]	5.1[a]	6.9[a]
	42	0.13[c]	0.66[b]	1.2[a]		
	50	0.034[c]	0.20[c]	0.44[c]		
DOS	18	1.8[b]	4.9[a]	7.3[a]		
	31	0.44[b]	1.5[a]	3.7[a]	6.0[a]	7.9[a]
	42	0.12[c]	0.62[b]	1.2[a]		
	50	0.033[c]	0.15[c]	0.44[c]		

Heating time: [a]24, [b]48, and [c]72 h.

Table II summarizes the estimated diffusion coefficients of the plasticizers in four kinds of NBR samples at various temperatures between 70°C and 150°C. The dotted curves in Figures 4 and 5 depict the theoretical distributions of the respective plasticizers corresponding to the diffusion coefficients shown in Table II. Here, it is noted that the diffusion coefficients for the plasticizers generally increase as a function of the processing temperature while they decrease for NBRs with higher AN contents. Thus determined diffusion coefficients (D) are plotted against the reciprocal of the temperature T in Figure 7. It is noted that fairly good linear relationships are observed.

When these relationships are applied to an Arrhenius-type expression,[9]

$$D_i = D_{i0}\exp(-E_{id}/RT),\tag{8}$$

frequency factors (D_{i0}) and the apparent activation energy for diffusion (E_{id}) can be obtained. Table III shows $\ln D_0$ and E_d of each plasticizer for various NBRs with different AN contents.

In Figure 8, typical relationships between E_d values and the AN content in NBR samples is shown for the DOA plasticizer. Thus, the obtained linear relationship can be expressed as follows:

$$E_{id} = 18.7 + 0.770A \quad (\gamma = 0.999),\tag{9}$$

where A (%) is the AN content in NBR samples and γ is a coefficient of correlation. Furthermore, as was anticipated,[11] the observed
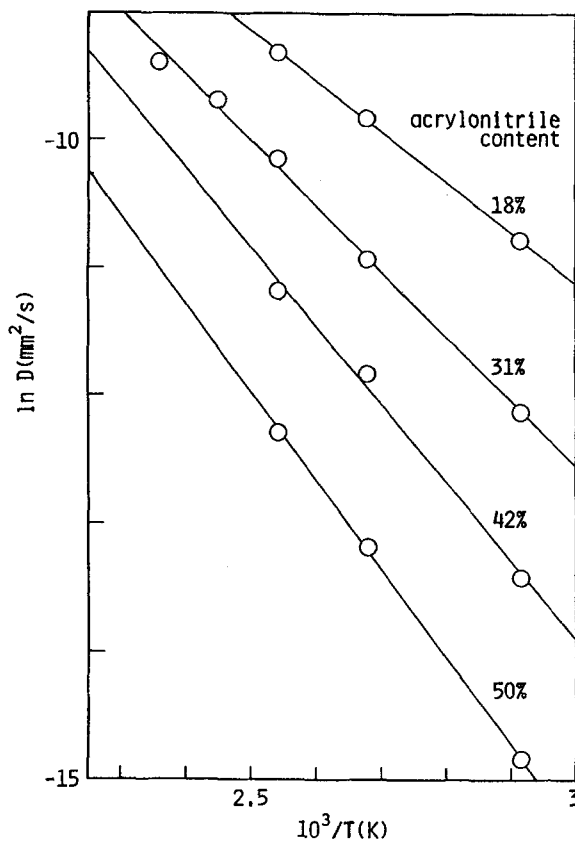
FIGURE 7 Relationships between the logarithm of the diffusion coefficients of DOA in NBRs with various AN content and the reciprocal of processing temperature.

relationship between E_d and $\ln D_0$ for each plasticizer in NBR samples shows fairly good linearity. Figure 9 illustrates the typical relationship for DOA in NBR samples in which the regression line can be expressed as follows:

$$\ln D_{i0} = -5.31 + 0.188 E_{id} \quad (\gamma = 0.955). \tag{10}$$

Combining Equations (8)–(10), we can obtain the following equation among D_i, T, and AN content ($A\%$),

$$\ln D_i = -5.31 + (0.188 - 1/RT)(18.7 + 0.770A). \tag{11}$$

TABLE III   Estimated parameters of the Arrehenius equation for the thermal migration of the plasticizers in NBRs

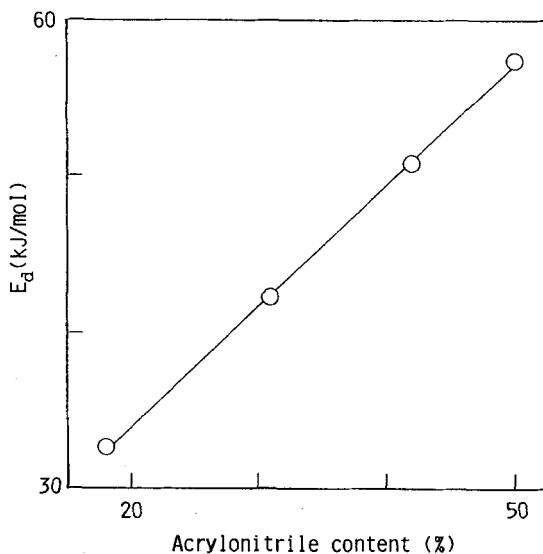| Plasticizers	AN content, %	$\ln D = \ln D_0 - E_d/RT$		
		$\ln D_0$	E_d (kJ/mol)	γ^{a}
DOA	18	0.71	32.7	0.999
	31	2.74	42.3	0.998
	42	4.42	50.8	0.996
	50	5.28	57.4	0.999
DOP	18	0.76	33.6	0.995
	31	2.91	43.6	0.998
	42	4.27	50.7	0.994
	50	5.48	58.0	0.997
DOS	18	0.27	31.9	0.995
	31	3.49	45.1	0.996
	42	4.77	52.4	0.995
	50	5.25	57.6	0.998

[a] Coefficient of correlation.

FIGURE 8   Relationship between the activation energy for diffusion of DOA and AN content of NBRs.

From this empirical equation, the diffusion coefficient of DOA in NBR samples with any AN contents over the range of 18–50% can be estimated by calculation as a function of temperature. The curves shown in Figure 10 indicate the variations of D for DOA, which was
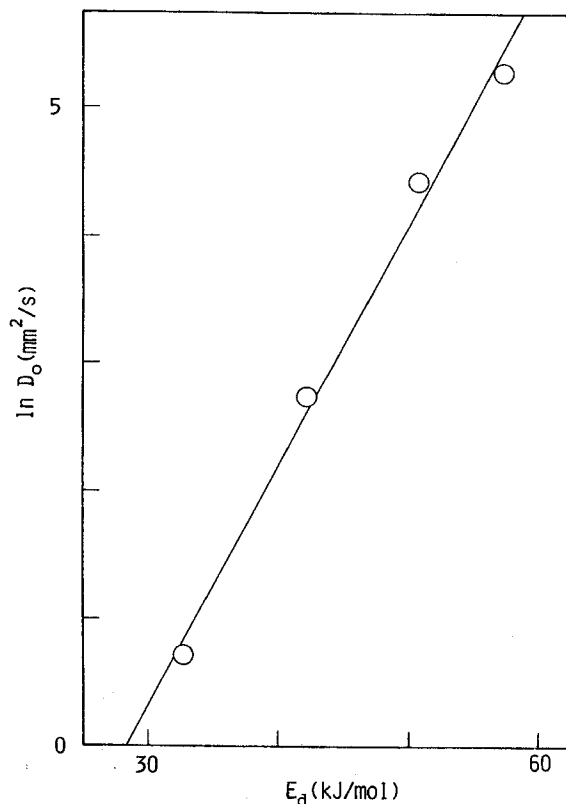
FIGURE 9   Relationship between the logarithm of the frequency factor and activation energy for the diffusion of DOA.

calculated from Equation (11). The plots in the figure indicate the estimated diffusion coefficients at 70°C, 100°C and 120°C by thermal desorption GC. Generally, the diffusion coefficients of the plasticizer decrease as the AN content increases in NBR samples. This phenomenon is associated with the increased E_d values for the corresponding NBR samples (Figure 8). Basically, the same relationships as Equation (11) can be derived for DOP and DOS, and usable for the estimation of their D_i values in NBR samples with any AN content at any diffusion temperature.

   As described above, rapid and sensitive determination of plasticizers in rubbers were able to be made by thermal desorption GC. By this
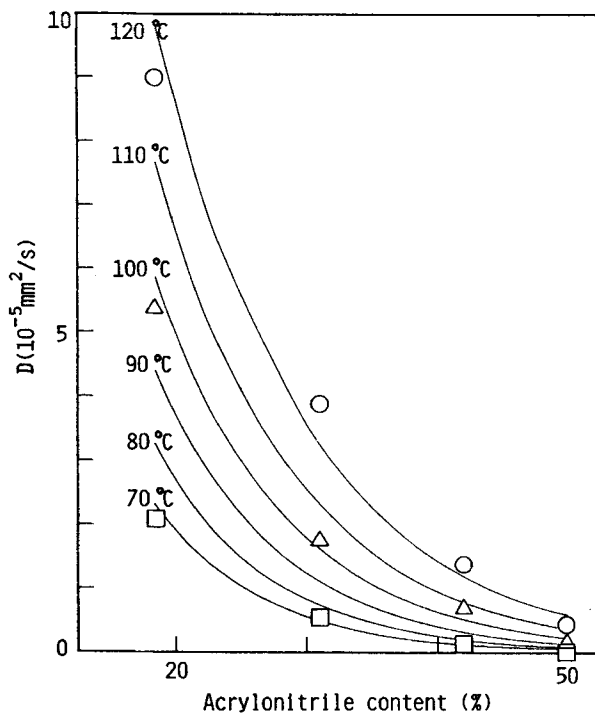
FIGURE 10 Relationships between diffusion coefficients of DOA in NBRs with different AN content at various temperatures between 70°C and 120°C. Observed values for 120°C, 100°C, and 70°C ($\bigcirc$, $\triangle$, $\square$), respectively. Calculated with Equation (11) (—).

highly sensitive method, the thermal migration behavior of the plasticizers in a given NBR sample sheet could be studied in detail by using less than 1 mg sample section taken from a desired depth of the sheet. Further work using this method is now in progress to investigate the type of migration behavior of plasticizers in NBR samples which are contacted with solvents, such as fuels and lubricating oils.

Acknowledgments

"Research for the Future" Program of the Japan Society for the Promotion of Science (JSPS-RFTF, 96R11601).

References

[1] T. Mori and S. Nishibata, *J. Japan Rubber Soc.* **58**, 66 (1985).
[2] S.-S. Lin, *Rubber Chem. Technol.* **58**, 885 (1985).
[3] J.B. Gardiner, *Rubber Chem. Technol.* **41**, 1312 (1968).
[4] J.B. Gardiner, *Rubber Chem. Technol.* **42**, 1058 (1969).
[5] S. Tsuge, Y. Matsushima, N. Watanabe, A. Shintai, K. Nishimura and Y. Hoshika, *Anal. Sci.* **3**, 101 (1987).
[6] S. Tsuge, K. Nishimura, M. Suzuki and H. Hayashi, *Anal. Sci.* **4**, 115 (1988).
[7] S. Tsuge, K. Kuriyama and H. Ohtani, *J. High Res. Chromatogr.* **12**, 727 (1989).
[8] R.-J. Roe, H.E. Bair and C. Gieniewski, *J. Appl. Polym. Sci.* **18**, 843 (1974).
[9] G.J. van Amerongen, *Rubber Chem. Technol.* **37**, 1065 (1964).
[10] J.L. Taverdet and J.L. Vergnaud, *J. Appl. Polym. Sci.* **29**, 3391 (1984).
[11] R.M. Barrer, *Trans. Faraday Soc.* **38**, 322 (1942).