Distribution of Ester Plasticisers between Two Rubber Phases – Estimation of Partition Coefficients and Comparison with Theory

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Partition coefficients have been determined for a range of ester plasticisers distributed between natural rubber and epoxidised natural rubber by placing rubber sheets in contact. Partition coefficient is found to depend on solubility parameters of plasticiser and rubbers, crosslink density in each rubber and overall level of plasticiser. A comparison between experiment and theory was made by using the Flory-Rehner hypothesis and the assumption of equal activity, ln a, of plasticiser in the two rubbers at equilibrium. The correspondence between the resulting estimates of polymer-solvent interaction parameter and expectations from observed values is good, suggesting that the observed K_d values are in accord with theory.

Many factors other than the routine compounding considerations affect the properties of vulcanised rubber blends. These include phase morphology, interfacial adhesion and distribution of filler and crosslinks between the phases. Recent work[1] on high damping blends of natural rubber (NR) and epoxidised natural rubber (ENR) required manipulation of a factor not considered much previously, that is, the distribution of plasticiser. When two rubbers (NR and ENR), which are incompatible, are in contact with each other and a plasticiser which swells both rubbers is added, then the plasticiser should partition itself between the two rubbers in a definite ratio. The numerical value of this ratio is expected to depend on the relative affinity of the plasticiser for each rubber and also the crosslink density of each rubber.

To investigate the distribution of plasticisers between the two rubber phases, a theory developed by Henry-Nernst[2] was used, and the

quantity known as partition or dis- tribution coefficient was employed. If an ENR-50 vulcanisate is swollen by a plasticiser to a low degree of swell, such that crosslink density does not significantly restrain swelling, and is placed in contact with an unswollen NR vulcanisate (which would itself become swollen by the plasticiser), then there would be a movement of plasticiser across the interface between the two rubbers due to the concentration gradient. The rate of transfer of plasticiser will steadily decline, until a state of dynamic equilibrium is reached. At this point the movement of plasticiser across the interface will be equal in both directions.

The equilibrium condition in which the concentration of plasticiser in the NR phase is a function of its concentration in the ENR phase, may be defined thermodynamically as the equality of the chemical potential of the plasticiser in the two rubber phases. Assuming that the plasticiser is dissociated into single

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molecules in both phases, the distribution is described by the Henry-Nernst equation:

$$\text{Partition coefficient, } K_d = \frac{C_{NR}}{C_{ENR}} \quad \dots 1$$

where C_{NR} and C_{ENR} are the concentrations of the plasticisers in the NR and ENR respectively. It is defined more fully in *Appendix 1*.

In accordance with this equation, for a constant temperature, the equilibrium concentration of the plasticiser in the NR phase should increase linearly with the concentration in the ENR phase until one of the phases reaches saturation. The partition coefficient is derived from the difference of the standard chemical potential (μ) of the plasticiser in the two rubber phases, in accordance with the equation:

$$RT\ln(K_d) = \mu_{NR} - \mu_{ENR} = \Delta G \quad \dots 2$$

where ΔG is the free energy of transfer of one mole of plasticiser into the polymers.

This paper describes the determination of partition coefficients between NR and ENR experimentally for a range of ester plasticisers. For three of these plasticisers, the effect of crosslink density in the two rubbers has been investigated. In addition, polymer-solvent interaction parameters have been determined for two of these plasticisers and a comparison of observed partition coefficients with values expected on theoretical grounds *via* the Flory-Rehner relationship has been attempted.

MATERIALS AND EXPERIMENTAL METHODS

NR (SMR L) and ENR having epoxide contents of 50 and 25 mole % (ENR-50 and ENR-25 respectively) were used in the investigation. The plasticisers chosen are non-volatile liquids with physical characteristics listed in *Table 1*.

A standard base formulation was used for each rubber *(Table 2)*, so as to avoid complications associated with variations in the compounding ingredients. For simplicity, as well as on the basis of its suitability for ENR, a semi-EV vulcanisation system was used. When investigating the effect of crosslink levels on the diffusion coefficient of plasticisers in NR and ENR-50, as well as their effect on K_d values, the amounts of sulphur and accelerator incorporated into the rubbers were varied *(Table 3)*. In the investigation of partition coefficients for NR and ENR-25, fixed levels of 1.3 p.h.r. sulphur and 1.3 p.h.r. MBS were used. It should be noted mixes B1 and B7 were unvulcanised.

Base mixes were prepared on a two-roll mill with the rolls set at 30°C and the nip set at 0.12 cm. Sulphur and accelerator were incorporated in required amounts into weighed portions of base mix, also on the mill.

The maximum state of cure for each mix was determined as the time to reach the maximum torque on a Rheometer curve. Vulcanisation to this maximum state was carried out by using a compression mould in a steam-heated press to produce a flat vulcanised sheet of uniform thickness.

Partition coefficients were estimated by following the mass transfer of plasticiser from a sample of ENR-50 vulcanisate containing a specific concentration of plasticiser to a sample of NR vulcanisate without any plasticiser. A pre-weighed sample of ENR was swollen with plasticiser to the desired level, approximately 50 p.h.r. and then allowed to become isotropic over a period of time estimated from diffusion studies[3]. Once isotropic, the swollen ENR sample was placed in intimate contact with a pre-weighed sample of NR vulcanisate of similar size. The plied samples were wrapped in aluminium foil and placed in a sealed

TABLE 1. CHARACTERISTICS OF PLASTICISERS

Plasticisers	Mol. weight	S.G. at 25°C	δ^a (MPa)$^{\frac{1}{2}}$
Dimethyl phthalate (DMP)	194	1.192	21.9
Diethyl phthalate (DEP)	222	1.118	20.5
Dibutyl phthalate (DBP)	278	1.049	19.0
Dioctyl phthalate (DOP)	390	0.978	16.2
Diisodecyl phthalate (DiDP)	446	0.962	14.7
Tributoxyethyl phosphate (TBEP)	344	1.020	19.2
Tricresyl phosphate (TCP)	368	1.158	19.2
Dioctyl sebacate (DOS)	426	0.913	17.6
Diisodecyl adipate (DiDA)	426	0.912	16.8
Reomol[b] *BCD*[d]	436	1.018	18.9
Reomol[b] *MD*[e]	–	0.917	–
Reomol[b] *249*[f]	–	1.059	–
Reofos[b] *65*[g]	–	1.164	–
Diolpate[c] *7017*[h]	–	1.065	–
Diolpate[c] *171*[h]	–	1.075	–

[a]Solubility parameter
[b]Ciba-Geigy Industrial Chemicals
[c]Macpherson Polymers
[d]Di-(butoxyethoxyethyl) adipate
[e]Ester of mixed adipic, glutaric and succinic acids with iso-decanol
[f]A modified phosphate
[g]Isopropylated phenyl phosphate
[h]Polymeric esters

TABLE 2. BASE FORMULATIONS

Reference number	A1	A2	A3
SMR L	100	–	–
ENR-25	–	100	–
ENR-50	–	–	100
Calcium stearate[a]	–	3	3
Zinc oxide	5	5	5
Stearic acid	2	2	2
TMQ[b]	2	2	2
Sulphur	Variable	Variable	Variable
MBS[c]	Variable	Variable	Variable

[a]Stabiliser
[b]Poly-2,2,4-trimethyl,2-dihydroquinoline, *Flectol H,* Monsanto
[c]2-(Morpholinothio) benzothiazole

container at 23°C. Periodically the samples were separated and weighed until constant weights were attained by both samples. K_d was calculated according to *Equation 1*.

RESULTS

The partitioning behaviour of 11 plasticisers *(Table 1)* between NR and ENR-50 was investigated at a single crosslink density for each rubber. The partitioning of 6 of these plasticisers between NR and ENR-25 was also considered, again at a single crosslink density for each rubber.

The partition coefficients observed for the plasticisers investigated are presented in *Table 4*. It is expected that the solubility parameter, δ, of the plasticiser, relative to those of the two rubbers, will be a major factor in determining K_d, the closer the solubility parameters of plasticiser and rubber the higher the interaction. Thus it is anticipated that K_d will reflect higher concentration of plasticiser in the rubber closer in solubility parameter to that of the plasticiser. Whilst a general trend of those plasticisers of lower solubility parameters having the higher K_d values is observed, the detailed ranking of the K_d values does not follow the ranking of solubility parameters of the plasticisers *(Table 5)*. It is possible that specific interactions, such as dipolar interactions between ENR and the plasticiser,

TABLE 3. FORMULATIONS FOR THE INVESTIGATION OF THE EFFECT OF CROSSLINK LEVEL ON PARTITION COEFFICIENT OF PLASTICISERS

Rubber type	A1, Table 2					A3, Table 2				
Mix Number	B1	B2	B4	B5	B6	B7	B8	B10	B11	B12
Base mix	100	109	109	109	109	100	112	112	112	112
Sulphur (p.h.r.)	–	0.6	1.5	2.4	3.5	–	0.6	1.5	2.4	3.5
MBS (p.h.r.)	–	0.6	1.5	2.4	3.5	–	0.6	1.5	2.4	3.5

TABLE 4. PARTITION COEFFICIENT, K_d, OF VARIOUS PLASTICISERS BETWEEN NR AND ENR[a]

Plasticiser	δ (MPa)$^{1/2}$	K_d	
		NR/ENR-50	NR/ENR-25
DBP	19.0	0.224	–
DEP	20.5	0.205	–
TBEP	19.2	0.191	0.224
Reomol BCD	18.9	0.201	0.237
Reomol 249	–	0.261	0.447
Reofos 65	–	0.161	0.215
Diolpate 7017	–	0.187	0.262
Diolpate 171	–	0.101	0.246
DOS	17.6	1.125	–
DOP	16.2	0.638	–
DiDP	14.7	0.706	–

[a]NR vulcanisate B4 [δ = 16.8 (MPa)$^{1/2}$], ENR vulcanisate B10 [δ = 17.4 and 18.2 (MPa)$^{1/2}$ for ENR-25 and ENR-50 respectively]

TABLE 5. K_d RANKING[a]

Plasticiser	NR	ENR-50
DiDP	2	6
DOP	3	5
DOS	1	7
Reomol BCD	6	2
DBP	4	4
TBEP	7	1
DEP	5	3

[a]Plasticisers are listed in increasing order of δ. Numbers indicate K_d ranking (1 = highest, 7 = lowest)

also play a role in determining K_d. As expected given the lower solubility parameter for ENR-25 than ENR-50, K_d for the combination NR/ENR-25 is always higher than for the combination NR/ENR-50 when K_d for the latter is less than unity *(Table 4)*.

K_d *was measured through transfer of liquid* from a sample containing a higher concentration of diffusing liquid to a sample containing a lower concentration. The swelling of the ENR was carried out to 40%, which is much less than the equilibrium stage, so that no significant restraint from crosslinking can occur. The elastic contribution in the swelling of the crosslinked network may be expected therefore to be relatively small.

K_d is related to V_r, the volume fraction of rubber in the swollen vulcanisate, as shown in *Appendix 1*. The Flory-Rehner hypothesis[4] can be used to test experimental values of K_d against theoretical prediction by considering equal activity, ln *a*, of plasticiser in the two rubbers,

$$\ln a = \frac{(\mu_1 - \mu_1^\circ)}{RT}$$
$$= \ln(1 - V_r) + V_r + \chi V_r^2 + \frac{\rho V_o V_r^{1/3}}{M_c} \quad ... 3$$

where R is the gas constant, T is the absolute temperature, V_r is the volume fraction of rubber in the swollen state, χ is the polymer-solvent interaction parameter, V_o is the molar volume of the swelling liquid, ρ is the density of the rubber network and M_c is the average molecular weight between crosslinks. μ_1 is the chemical potential of the solvent in the swollen network and μ_1° is the chemical potential of the solvent in pure solvent at the same temperature and pressure. When swelling a vulcanisate in a solvent, the value of V_r will have reached equilibrium when $\mu_1 = \mu_1^\circ$. When transferring a solvent between two rubbers, equilibrium will be reached when the activity of the solvent in the two rubbers is equal.

Values for χ have been determined[2] for TBEP and *Reomol* BCD with NR and ENR-50 but they are not available in the ranges of V_r prevailing in the estimation of K_d. When these values of χ for both rubbers containing various crosslink levels and swollen to equilibrium in TBEP and *Reomol BCD* are plotted against V_r *(Figure 1)*, the values for NR lie close to the idealisation that the mixing contribution to the chemical potential is zero, *i.e.*,

$$RT\{\ln(1 - V_r) + V_r + \chi V_r^2\} = 0 \quad ... 4$$

or

$$\chi = -\frac{\{\ln(1 - V_r) + V_r\}}{V_r^2} \quad ... 5$$

For ENR-50, the V_r values are much lower and there is a marked departure from the idealisation curve *(Figure 1)*. This is in accord with McKenna *et al.*[5] who also observed departure at low V_r. McKenna explained that for poor solvents in crosslinked rubber, the elastic contribution is small at low degrees of swelling. As the degree of swelling increases, the elastic contribution increases and the observed behaviour deviates from the
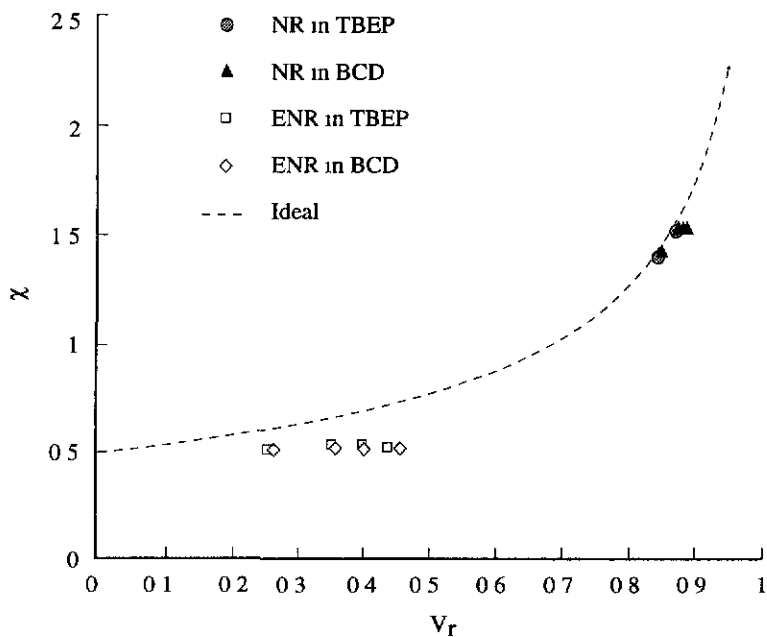
Figure 1. 'Ideal' dependence of χ on V_r from Equation 5 *and values for NR and ENR-50 swollen in TBEP and* Reomol BCD *from* Reference 2
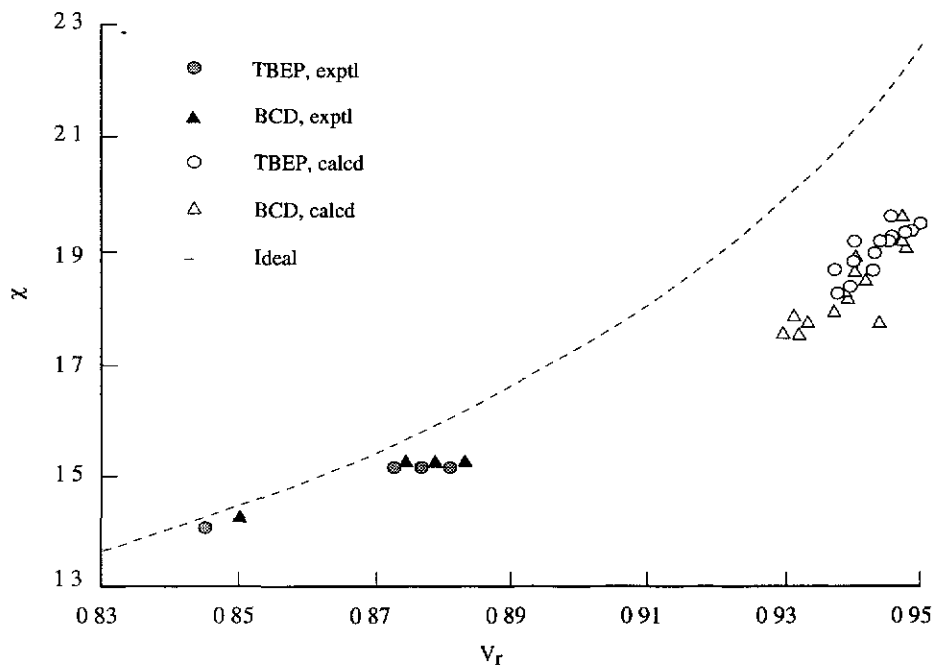

Figure 2 Values of χ from Reference 2 *compared with those calculated from observed values of* K_d.

idealisation curve. The authors also suggest that χ is a function of crosslink density. On the other hand, Gee and others[6] determined χ as a function of V_r for NR swollen by various solvents at 25°C and found that χ increases with V_r but is independent of crosslink density. More recently, Horkay *et al.*[7,8] provide further evidence that χ is dependent on V_r but not on crosslink density.

The dependence of χ on V_r for TBEP and *Reomol BCD* with ENR-50 is very low, and a value of 0.53 may be used for both plasticisers over the V_r range prevailing in the estimation of K_d (0.63–0.72) with some confidence. However, appropriate values of χ for the two plasticisers with NR cannot be fixed over the appropriate V_r range (0.93–0.95) with sufficient certainty. Although it is not possible therefore to calculate values for K_d *via* the Flory-Rehner relationship, an alternative strategy to test the experimentally observed values may be adopted. The activity of the plasticiser in ENR-50 when partition has reached equilibrium may be calculated. Limits may be set on the values of χ which may be shown by the two plasticisers with NR. The upper bound is set by *Equation 5*, whilst the lower bound may be set by a linear extrapolation of the available data for the dependence of χ on V_r since χ is generally a stronger function of V_r than this[5,7]. Appropriate values are 2.0 and 1.6 for upper and lower bounds, respectively, for both plasticisers. For three values of χ (1.6, 1.8 and 2.0), the activity of plasticiser in NR when partition had reached equilibrium was calculated from the observed V_r using *Equation 3*. The calculations were performed for TBEP and *Reomol BCD* and for all of the combinations of NR and ENR-50 vulcanisates considered. Comparison with the activity calculated for the plasticisers in the ENR-50 component of the combination demonstrates that on all occasions the activity

in the NR component will be equivalent when χ lies at some specific value within the prescribed range, as illustrated for *Reomol BCD* in *Table 6*. Furthermore, it is possible to obtain this specific value of χ at equivalence by interpolation. When plotted against V_r, these specific values of χ lie in a region which is a reasonable extrapolation of the data obtained from equilibrium swelling[3] *(Figure 2)*. It is fortuitous that χ values for the two plasticisers are so closely similar.

Since the χ values required for equivalent activities of the plasticisers in the two rubbers are in accord with expectations, this analysis suggests that the observed K_d values are also in accord with theoretical predictions.

The influence of crosslink density in the two rubbers on K_d was investigated for three of the plasticisers, TBEP, *Reomol BCD* and *Diolpate 7017 (Table 7)*, and the results are illustrated best by the three dimensional plots *Figures 3, 4* and *5* respectively. The observed dependences of K_d on crosslink density in the NR component is readily explained in terms of the Flory-Rehner relationship. As crosslink density increases, the elastic contribution to the activity of the plasticiser increases and hence equivalent activities are reached in the two rubbers at a lower plasticiser level in the NR, *i.e.*, a lower K_d. At low to medium crosslink densities in the NR component, a similar argument can be applied to explain the increase in K_d with increasing crosslink density in the ENR; the elastic contribution to the activity of the plasticiser in the latter increases causing equivalent activities to be attained at a higher plasticiser content in the NR component. However, such arguments cannot account for the low K_d values observed when both crosslink densities are high, a phenomenon which is particularly evident for *Diolpate 7017 (Figure 5)*.

TABLE 6. ACTIVITIES OF *REOMOL BCD* IN NR AND ENR VULCANISATES
WHEN PARTITION HAD REACHED EQUILIBRIUM

Vulcanisate[a] combinations: NR/ENR-50	ENR-50 $-\ln a$ when $\chi = 0.53$	NR $-\ln a$ when		
		$\chi = 2.0$	$\chi = 1.8$	$\chi = 1.6$
B2/B8	0.197	0.0965	0.273	0.450
B2/B10	0.209	0.0941	0.271	0.448
B2/B11	0.181	0.0034	0.170	0.344
B2/B12	0.181	0.0044	0.169	0.342
B4/B8	0.200	0.0612	0.238	0.414
B4/B10	0.209	0.0555	0.232	0.408
B4/B11	0.191	0.0017	0.172	0.347
B4/B12	0.181	0.0361	0.137	0.310
B5/B8	0.203	0.0407	0.217	0.393
B5/B10	0.199	0.0226	0.198	0.374
B5/B11	0.195	0.0002	0.175	0.349
B5/B12	0.178	0.0330	0.141	0.314
B6/B8	0.190	0.1080	0.287	0.466
B6/B10	0.205	0.1330	0.313	0.492
B6/B11	0.195	0.0631	0.241	0.418
B6/B12	0.167	0.1280	0.307	0.486

[a]Refer to *Tables 2* and *3* for formulations.

TABLE 7. DEPENDENCE OF K_d ON PHYSICAL CROSSLINK DENSITY OF
NR AND ENR-50 VULCANISATES

| $[X]_{phys} \times 10^2$, molkg^{-1}		K_d		
NR	ENR-50	TBEP	*Reomol BCD*	*Diolpate 7017*
0	0	0.170	0.175	0.127
2.55	1.65	0.177	0.183	0.175
5.45	1.65	0.179	0.193	0.172
8.74	1.65	0.170	0.191	0.167
11.80	1.65	0.163	0.173	0.163
2.55	3.97	0.186	0.194	0.185
5.45	3.97	0.191	0.201	0.187
8.74	3.97	0.172	0.199	0.191
11.8	3.97	0.167	0.192	0.145
2.55	5.78	0.195	0.215	0.210
5.45	5.78	0.203	0.225	0.202
8.74	5.78	0.175	0.189	0.178
11.8	5.78	0.170	0.179	0.135
2.55	8.58	0.210	0.223	0.203
5.45	8.58	0.208	0.229	0.193
8.74	8.58	0.179	0.220	0.102
11.8	8.58	0.164	0.167	0.074
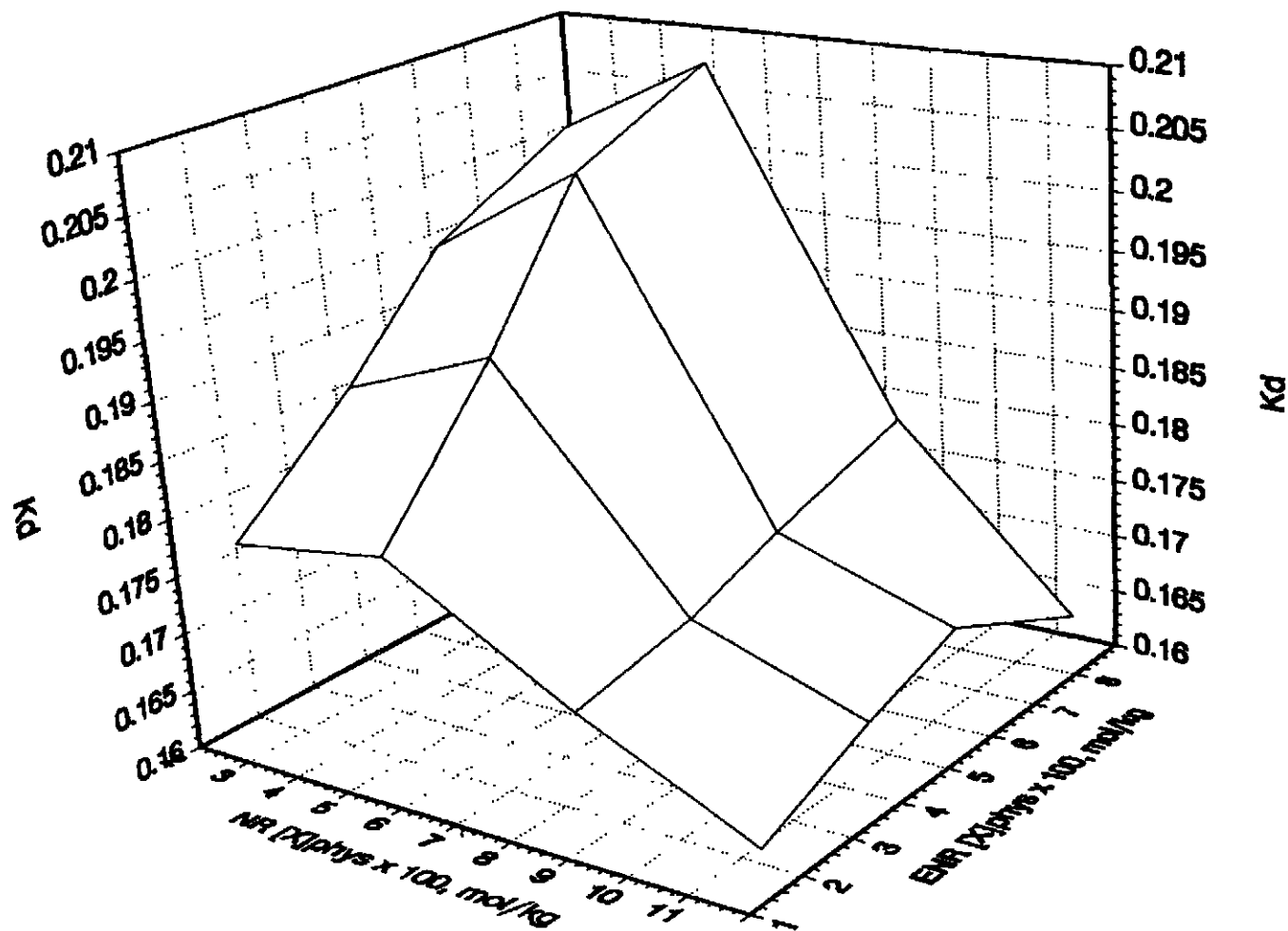
Figure 3. Dependence of K_d for TBEP between NR and ENR-50 on physical crosslink density, $[X]_{phys}$, in the two rubbers. The intersections on the surface grid represent data points.
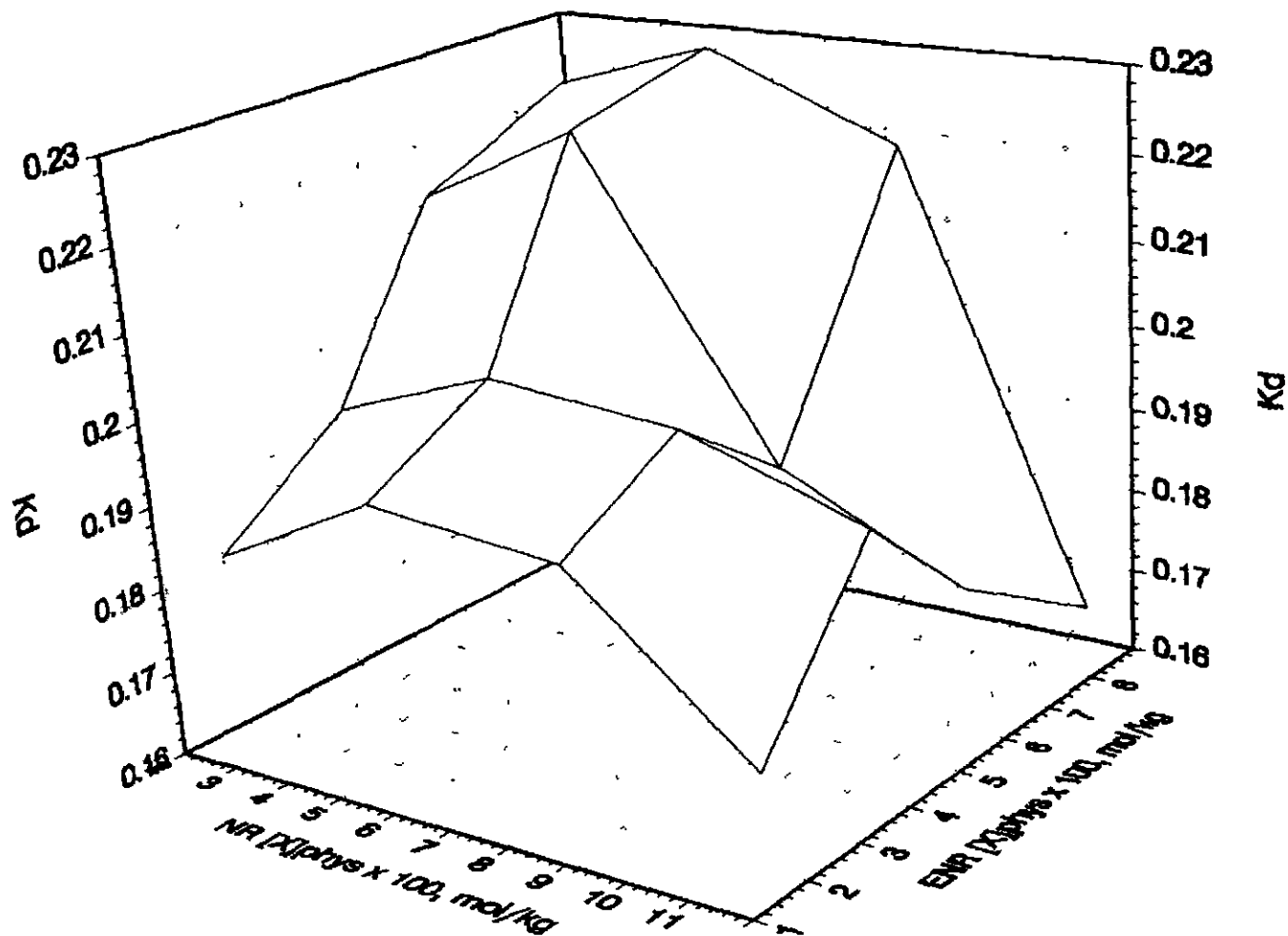
Figure 4. Dependence of K_d for Reomol BCD *between NR and ENR-50 on physical crosslink density, $[X]_{phys}$ in the two rubbers The intersections on the surface grid represent data points*
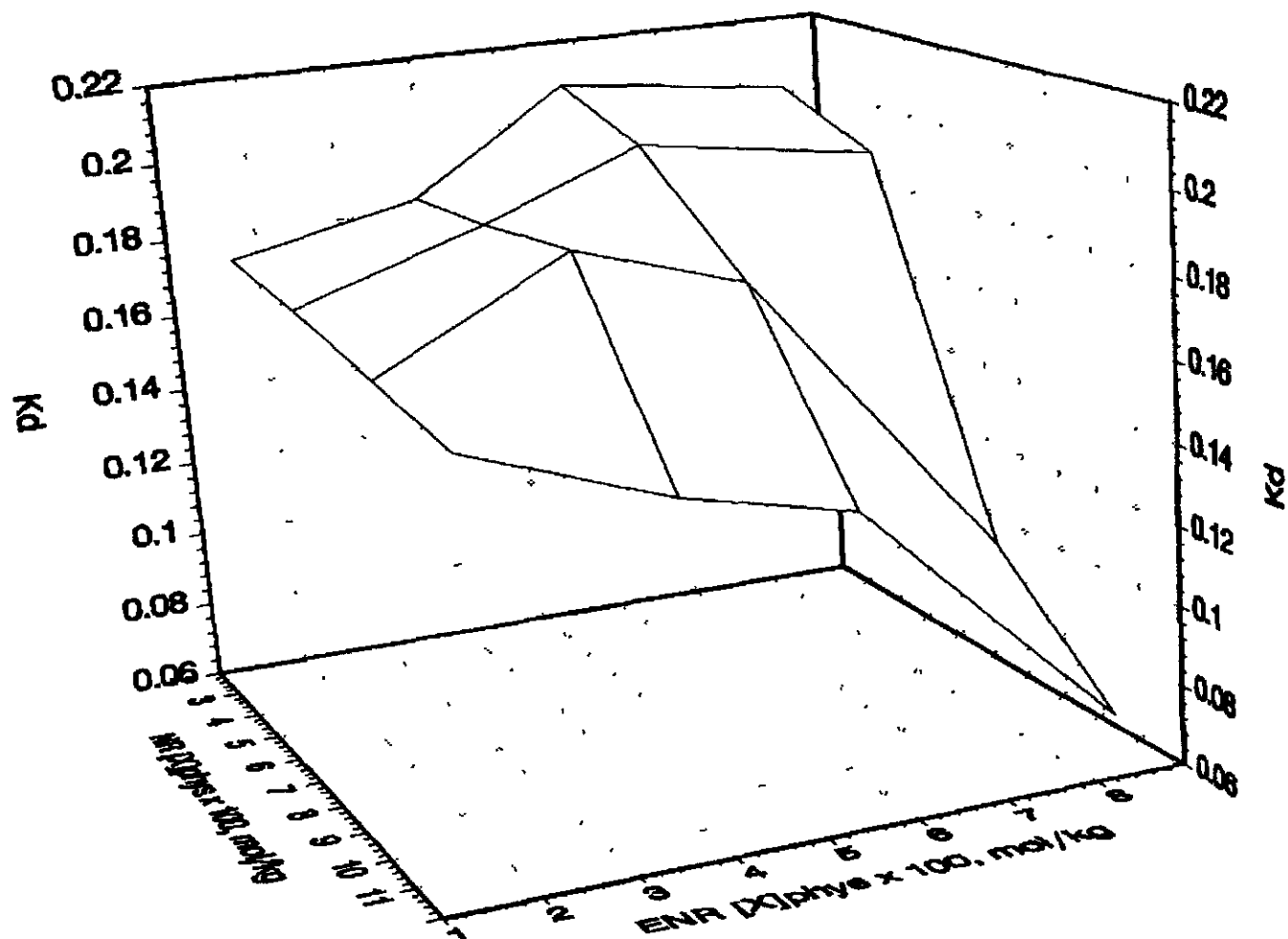
Figure 5 Dependence of K_d for Diolpate 7017 between NR and ENR-50 on physical crosslink density, $[X]_{phys}$, in the two rubbers The intersections on the surface grid represent data points

It is important to note that all of the measurements were performed at approximately the same total level of plasticiser. From the above arguments, it may be anticipated that K_d will also be dependent on the total level of plasticiser in the system. However, given a knowledge of χ in the appropriate range, as is now available from *Figure 2*, it is possible to calculate K_d *via* a numerical iteration.

CONCLUSION

Partition coefficients between NR and ENR for a number of ester plasticisers are found to be dependent on solubility parameters of the rubbers and plasticisers, the crosslink density in each rubber, and the overall level of plasticiser. There is a general trend of the plasticiser partitioning in favour of the rubber which is close in solubility parameter to that of the plasticiser. The partition coefficient tends to increase with decreasing crosslink density in NR (at constant ENR crosslink density) and increasing crosslink density in ENR (at constant NR crosslink density).

The values of partition coefficients evaluated for three of the plasticisers have been shown to be in accord with theoretical expectations based on equal activities of the plasticisers in the two rubbers at equilibrium and the Flory-Rehner relationship.

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APPENDIX 1

The partition coefficient, K_d, of plasticiser between NR and ENR vulcanisates can be related to the volume fractions of rubber, V_r, in the swollen vulcanisates using the following derivations.

K_d is defined as:

$$K_d = \left[\frac{W_p^{NR}}{V_p^{NR} + V^{NR}} \right] \left[\frac{V_p^{ENR} + V^{ENR}}{W_p^{ENR}} \right] \qquad \ldots i$$

where W_p^{NR} and W_p^{ENR} are the weights of plasticiser in the NR and ENR vulcanisates respectively. V_p^{NR} and V_p^{ENR} are volumes of plasticiser in the NR and ENR vulcanisates respectively. V^{NR} and V^{ENR} are volumes of NR and ENR vulcanisates, respectively.

But volume fraction of rubber in the swollen material is given by,

$$V_r = \frac{(W_r / \rho_r)}{(W_r / \rho_r) + (W_p / \rho_p)} \qquad \ldots ii$$

where W_r = weight of rubber

ρ_r = density of rubber

W_p = weight of plasticiser in the swollen vulcanisate

ρ_p = density of plasticiser

i.e.

$$V_r^{NR} = \frac{V^{NR}}{V_p^{NR} + V^{NR}} \quad \text{and} \quad V_r^{ENR} = \frac{V^{ENR}}{V_p^{ENR} + V^{ENR}} \qquad \ldots iia$$

Therefore,

$$1 - V_r^{NR} = \frac{V_p^{NR}}{V_p^{NR} + V^{NR}} \quad \text{and} \quad 1 - V_r^{ENR} = \frac{V_p^{ENR}}{V_p^{ENR} + V^{ENR}}$$

i.e.

$$1 - V_r^{NR} = \left[\frac{W_p^{NR}}{V_p^{NR} + V^{NR}} \right] \frac{1}{\rho_p} \quad \text{and} \quad 1 - V_r^{ENR} = \left[\frac{W^{ENR}}{V_p^{ENR} + V^{ENR}} \right] \frac{1}{\rho_p} \qquad \ldots iii$$

Then,

$$K_d = \left[\frac{W_p^{NR}}{V_p^{NR} + V^{NR}} \right] \left[\frac{V_p^{ENR} + V^{ENR}}{W_p^{ENR}} \right] = \frac{1 - V_r^{NR}}{1 - V_r^{ENR}} \qquad \ldots iv$$