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Studies on the Surface Chemistry of Wool

Part I: The Surface Free Energy of Diiodomethane

by

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PART I: THE SURFACE FREE ENERGY OF DIIODOMETHANE

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ABSTRACT

The liquid diiodomethane has been used extensively for measuring contact angles on solids, and the values obtained are used for the calculation of the surface free energy of the solids. In the literature several values are quoted for the surface tension of diiodomethane. Results obtained experimentally by the author are compared with values obtained by other workers as well as with a value calculated from parachor data.

The interfacial tension of water and diiodomethane is also discussed and the effect of the different surface and interfacial tension values on the calculated polar and dispersion components of the diiodomethane surface tension is examined.

INTRODUCTION

It has been stated that, to render wool shrinkresistant by coating the fibre with polymers, the polymer should spread evenly over the surface of the fibres[1]. The criterion for spreading is that the surface free energy of the polymer must be lower than that of the wool fibre. When the surface free energies of the wool and polymer are known, it is thus possible to establish whether a polymer will spread on a wool fibre. One method to determine the surface free energy of wool or polymers is to measure contact angles of various liquids on these substrates.

Zisman[2] stated that molecules of certain solvents can permeate into films of the solid and this can complicate surface studies. He suggested therefore that a high surface tension liquid consisting of non-linear large molecules should be used for contact angle studies. One such a solvent, diiodomethane, has been used extensively for the examination of the surface free energy of solids[2-10]. Diiodomethane is a solvent with a relatively high surface tension and a high boiling point (180°C). When a drop of diiodomethane is placed on a solid surface it will not evaporate quickly and will exhibit large contact angles with most organic surfaces.

In this report the values reported in the literature for the surface tension of diiodomethane are reviewed and these data compared with the results obtained by the author. Furthermore, the diiodomethane/water interfacial tension values are discussed and the effect of the different surface and interfacial tension values on the calculated polar and dispersion components of the diiodomethane surface tension is examined.

EXPERIMENTAL

Chemicals:

All the solvents, except diiodomethane, were purified by percolation through an alumina column and subsequent distillation under reduced pressure (25 torr). The cyclohexane was of a spectroscopy grade quality and the toluene a "pro-analysi" grade quality. The other solvents (α-bromonaphthalene, benzyl alcohol and ethylene glycol) were of laboratory grade.

The diiodomethane, which had a relative density (d_4^{20}) of 3,316 to 3,319 was treated with sodium thiosulphate solution (1 *per cent* m/v) in a separating funnel. The solution was then washed with water (three times), dried over anhydrous sodium sulphate and subsequently distilled under reduced pressure at 70°C through a 10 cm Vigreaux column. Part of this distillate was retained for surface tension measurements and the rest was fractionally crystallised by freezing and the fraction that melted first was rejected each time. The pure fraction (obtained after six crystallisations) had a light yellow colour, while the unpurified diiodomethane had an orange-brown colour. Another sample was purified by percolation through an alumina column.

Surface tension measurements:

A Du Noüy surface tension apparatus (Cambridge) equipped with a platinum-iridium ring (diameter = 12,7 mm) was used for measuring the surface tensions of the purified solvents. All measurements were carried out at 20 to 21°C, using freshly distilled solvents. The ring was flamed before use and the instrument calibrated with a 0,500 g weight. The correction tables of Harkins and Feldman[11] were used to calculate the surface tension. Initially the surface tensions of toluene, benzyl alcohol, α-bromonaphthalene and ethylene glycol were measured and it was established that these values were 1,0 to 3,8 *per cent* lower than published values.

RESULTS AND DISCUSSION

Surface tension values:

Table I summarises the surface tension values quoted for diiodomethane in the literature. The values obtained ranged from 45 to 52 mN/m (dynes/cm) excepting one of 67 mN/m. Many authors, especially those studying spreading and adhesion, quote a surface tension of 50,8 mN/m for diiodomethane, but several of these authors, in fact, did not determine the surface tension experimentally but used the values quoted by some other authors.

It has been claimed[12, 13] that the maximum bubble pressure method of Sugden gives very accurate surface tension results. The test method is not dependent on the contact angle and, furthermore, the influence of surface active impurities is minimised. Table I shows that Sugden's maximum bubble pressure method, or modifications thereof, gave surface tension values for diiodomethane ranging from 50,8 mN/m to 52,3 mN/m. In one case a value of 67,0 mN/m has been reported.

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TABLE I

**SUMMARY OF DIIODOMETHANE SURFACE TENSION AND DIIODOMETHANE/WATER
INTERFACIAL TENSION VALUES**

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Surface Tension γ_L and temperature	Dispersion component of surface tension γ_L^d	Interfacial tension γ_{12}	Source and Purification	Method of Determination	Ref.
45,0 (22-25°C)	42,1	—	Liquids of highest purity grade used as received	γ_L : Cenco-Du Noüy ring tensiometer and necessary corrections at 22–25°C. γ_L^d : Contact angle on paraffin measured and Owens + Wendt[7] formula applied	5
47,7 (20°C)	43,7	—	Purest commercial grades purified through Florosil if chemical was not of "chromato quality"	γ_L : Du Noüy tensiometer (Platinum ring) γ_L^d : Hansen's solubility parameter and contact angle measurements	9
49,8 (25°C)	—	—	Four different samples : (1) Eastman Kodak sample distilled under reduced pressure. (2) A sample of (1) distilled, repeatedly crystallised at ± 6,1°C. (3) Another sample from Kodak. (4) Sample (3) recrystallised at 6,1°C.	γ_L : Measured equilibrium angles for a mutually saturated two phase fluid system meeting at a common edge. Comment: The value 49,8 mN/m is calculated from the fact that Fox suggested that 2,5 mN/m should be deducted from Carter & Jones' value (52,3). The solubility of diiodomethane in water could effect the γ_L value.	16
50,2 (25°C)	—	—	Best available grades — distilled and percolated through activated silica gel.	γ_L : Du Noüy ring tensiometer and proper corrections	10
50,4 (20°C)	50,4	—	AR Rhône Poulenc grade used as received.	γ_L : Wilhelmy type micro-electro balance (CI Electronics) γ_L^d : —	6
50,5 (22-25°C)	49,3	—	Highest purity grade liquids used as received.	γ_L : Cenco-Du Noüy ring tensiometer and Harkins-Jordan corrections γ_L^d : contact angles measured on paraffin and Fowke's formula used (γ_{12} = 41,6)	25
50,76 (20°C)	—	48,50	Fractionation in high vacuum. Middle fraction used for surface tension measurements. Liquid recrystallised by freezing prior to distillation	γ_L + γ_{12} : Drop-weight method and correction tables of Harkins & Brown.	22,23
50,8 (20°C)	44,1	41,6	Eastman Chemicals, purified by two passages through neutral grade Woelm alumina	γ_L : γ_{12} : not determined — values refer to references 12 and 16. γ_L^d — calculated from Wu's harmonic mean equation and γ^d value of water at 20°C	4
50,8 (20°C)	48,5	—	No details given	Not determined — refers to references 15 and 28	26
50,8 (20°C)	48,5 ± 9	—	No details given	γ_L — γ_L^d derived from contact angle measurements on reference solids	24,27
50,8 (25,5± 1,5°C)	44,1	—	High purity grade (Fisher Scientific Co.) used as received	γ_L and γ_L^d : Not determined — refers to reference 4	3
50,8 (20°C)	49,5	—	—	γ_L : Refers to literature γ_L^d calculated from data for water, i.e. γ^d = 21,8 and γ^p = 51,0 (ref. 24) and γ_{12} = 41,6 (ref. 12, 16, 23) and Owens and Wendt equation.	7
51,2 (20°C)	—	—	No details given	γ_L : Rosano surface tensiometer, Platinum blade	8
50,8 ± 0,3 (20°C)	—	—	B.D.H. purified grade diiodomethane percolated through columns of activated alumina and silica gel and stored in a brown bottle. The pale yellow colour of freshly distilled liquid darkens on standing. This is due to liberation of free iodine which can be removed by shaking with $Na_2S_2O_3$.	γ_L : Sugden's maximum bubble pressure method. The surface tension of freshly purified diiodomethane did not alter significantly over a period of 48 hours despite darkening in colour.	18
52,3 (20°C)	—	40,52	B.D.H. dark brown liquid shaken twice with dilute alkali, washed with water until neutral, dried and de-colourised with lime. Distilled in vacuo (2 mm). Slightly brown distillate frozen (3x) fractionally. Crystalline colourless solid. m.p. 6,05°C d_4^{25} = 3,3079	γ_L : Sugden's modification of the maximum bubble pressure method. γ_{12} : modification of capillary method by Bartell & Miller	12
67,0 (20°C)	—	—	Prepared from Iodoform. Distilled immediately before measurements were made.	One of two methods could have been used: Capillary rise or modification of Sugden's maximum bubble pressure. For liquids that did not appear to wet glass and when an independent check was required, the maximum bubble pressure method was employed.	21

(It is not clear, however, whether the maximum bubble pressure method or the capillary rise method was used in this case.)

It is known[14] that diiodomethane does not spread on bare, flamed platinum and exhibits a contact angle of 11 degrees with the metal substrate. It also does not wet a pyrex glass surface and, therefore, a soda glass capillary was used to measure the interfacial tension of a diiodomethane-water mixture[12] and it was noted that the contact angle in this case was zero. Some of the values obtained by the Wilhelmy plate method and the capillary height method may be suspect because these methods require zero contact angles[15]. Contact angle for the ring tensiometer method need not be zero but must be small[15].

The tensiometer methods, employing a platinum ring gave values of 45,0 50,5 and 50,2 mN/m at 25°C. The platinum blade method gave a value of 51,2 mN/m at 25°C.

A method[16] in which the equilibrium angles were measured for a mutually saturated three-phase system (water-diiodomethane-air) meeting at a common edge yielded a value of 49,8 mN/m at 25°C. However, diiodomethane is not completely immiscible with water (the liquid is soluble in about 70 parts of water[17]), and this could have influenced this result.

In view of the fact that the results quoted in the literature for the surface tension of diiodomethane vary considerably, it was decided to investigate this matter in more detail. Diiodomethane was thoroughly purified and its surface tension was determined with a Du Noüy tensiometer. The results obtained are shown in Figure 1. Since the values obtained with the four liquids mentioned under experimental were lower than those quoted by other authors, the actual value for diiodomethane may possibly be even higher by 0,5 to 1,9 mN/m. It can be seen that a value of 35,6 mN/m was found for freshly distilled diiodomethane. When some further determinations were repeatedly carried out on the same solution, the surface tension increased to 50,5 mN/m after one hour. The platinum ring was flamed at this stage but this had no effect on the surface tension values obtained. When a further portion of the freshly distilled solution was added to the solution used above, the value decreased to 37,0 mN/m. The undistilled diiodomethane, i.e. as received, had a surface tension of 52,5 mN/m. After percolation through an alumina column the value remained at 52,5 mN/m. The surface tension of the sample which was vacuum-distilled followed by crystallisation was also determined and a value of 32,0 mN/m was obtained. Some further determinations were then carried out on the same sample. After 18 measurements taken over a period of more than an hour the value increased to 33,5 mN/m. No explanation can at this stage be offered for this phenomenon. It is known[10, 18] however, that diiodomethane is not stable and that it gradually releases free iodine upon standing. The dark colour which develops upon standing is, in fact, due to the presence of free iodine in the diiodomethane. Nevertheless, it has been claimed[18] that the surface tension of freshly purified diiodomethane does not alter significantly over a period of 48 hours, despite the darkening in colour.

FIGURE 1

The surface tension of diiodomethane measured with the Du Noüy tensiometer (ring) during 27 consecutive measurements
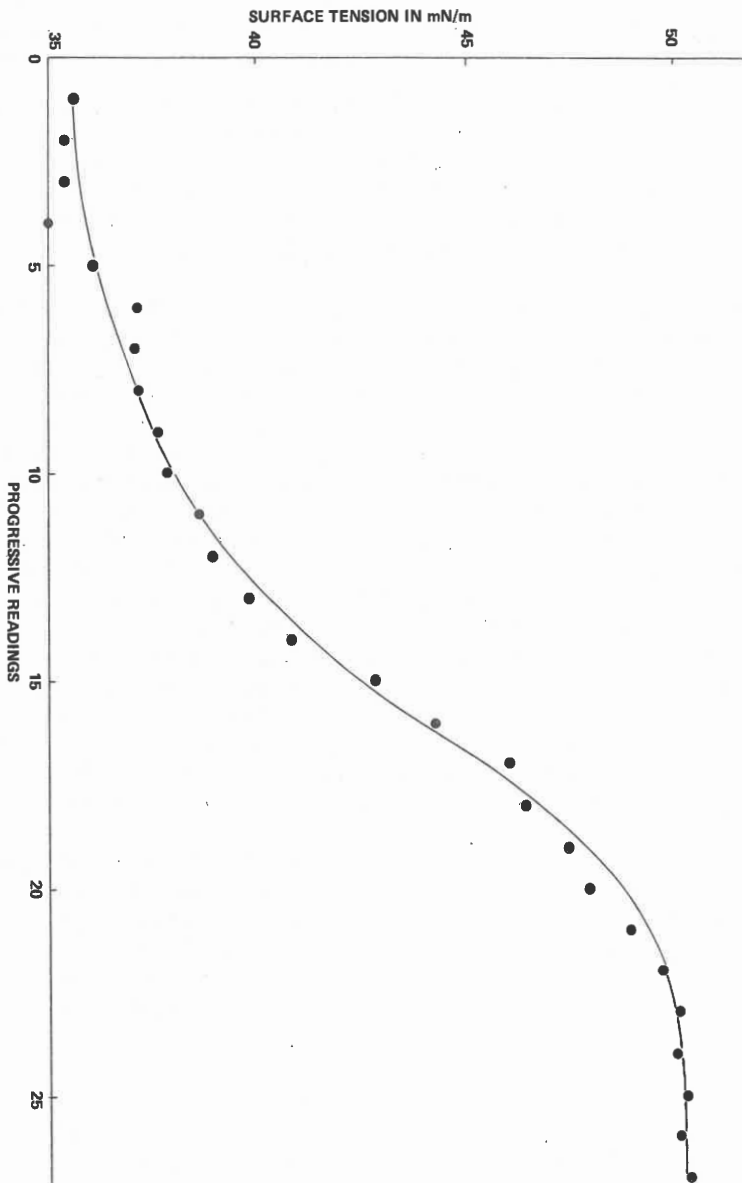
The surface tension of a compound can also be calculated from the following empirical relationship according to Sugden[19]:

$$\gamma = \left[\frac{P.\ (d-d')}{M}\right]^4$$

where γ = surface tension in mN/m
   P = parachor
   d = density in g/cm^3
   d' = density of the vapour (usually negligible when compared to d)
   M = molecular mass.

The parachor is an additive property of atoms or functional groups.

Quayle[20], in a review article on the parachors of organic compounds, pointed out that compounds containing a markedly polar group such as Cl, Br or I exhibit regularity in the -CH$_2$-parachor increment only after the first four or generally five members of a series. Decreases in the parachor seem to be due to interactions between atoms of these and neighbouring groups.

Grzeskowiak et al[21] published values for the parachor, surface tension and densities of a series of polymethylene halides. The difference in parachor (ΔP) between two successive compounds in a homologous series was calculated for the higher members of the series and an average ΔP was obtained. This ΔP value was used to calculate the parachor value of the lower compounds in the series. The surface tension value was calculated using this theoretical parachor value and the calculated values agree reasonably well with the surface tension values found elsewhere for dichloromethane, dichloroethane and dibromoethane (see Table II). The parachor increment in these cases exhibit regularity from the lowest to the highest member in the series. When the same procedure was followed for diiodomethane, a value of 54,98 mN/m was obtained. This is higher than the 50,8 generally assumed to be correct and much lower than the 67,0 mN/m obtained by Grzeskowiak[21]. A comparison between the observed and calculated values could not be made in the case of diiodoethane, as it is a solid with a high melting point.

Ray et al[10] measured the contact angle (θ) of several liquids on films of amylose, amylopectin and polivinyl alcohol. When cosine θ was plotted against the surface tension of the liquids, a straight line was obtained, with the exception of diiodomethane. The authors ascribed this phenomenon to the absorption of free iodine by the polymer film. If, however, one assumes that the surface tension value of 54,98 mN/m, as calculated from the parachor, is correct, the value for diiodomethane would also lie on the straight line obtained by Ray et al.

Diiodomethane-water interfacial tension values:

The interfacial tension values for the diiodomethane-water interface has been reported to be 40,52[12] 41,6[4] and 48,5[22, 23] mN/m. Carter and Jones[12] used a soft soda glass capillary to determine the interfacial tension, because diiodomethane does not spread on pyrex glass. They obtained a contact angle of approximately

TABLE II

PARACHOR AND SURFACE TENSION OF POLYMETHYLENE DIHALIDES

Compound	P (Parachor)		γ (mN m)	
	Literature[a]	Calculated[b]	Literature	Calculated
Dichloromethane	---	146,9	$26,52$[c]	27,72
Dichloroethane	—	188,6	32,2 [c]	$32,93$[d] $30,7$[e]
Dibromomethane	–	172,1	—	37,35
Dibromoethane	217,4	214,35	$38,75$[c]	38,22
Diiodomethane	231,6	219,64	(See Table I)	54,98

(a) Reference 21
(b) Calculated using the average ΔP of compounds with
    $n = 3$ to $n = 9$ in the series $X - (CH_2)_n - X$ for $X = Cl$, Br or I
(c) reference 22
(d) reference 17 ($d^{20} = 1,2569$ g/cm^1)
(e) reference 29 ($d^{20} = 1,2351$ g/cm^3)

TABLE III

THE DISPERSION (γ^d) — AND POLAR (γ^p) SURFACE TENSION COMPONENTS OF DIIODOMETHANE AS CALCULATED USING THE GEOMETRIC MEAN AND HARMONIC MEAN EQUATIONS AND DIFFERENT VALUES FOR SURFACE TENSION (γ_2) AND INTERFACIAL TENSION (γ_{12})*

FORMULA	$\gamma_{12} = 48,5$				$\gamma_{12} = 41,16$			
	$\gamma_2 = 50,8$		$\gamma_2 = 54,98$		$\gamma_2 = 50,8$		$\gamma_2 = 54,98$	
	γ^p	γ^d	γ^p	γ^d	γ^p	γ^d	γ^p	γ^d
Geometric mean equation	0,4	50,4	0,5	54,5	1,3	49,5	1,6	53,4
Harmonic mean equation	4,3	46,5	5,1	49,9	6,7	44,1	7,6	46,4

    * All values in mN/m

18,5 degrees. The higher value of 48,5 mN/m was found using the drop-weight method.

Dispersion component (γ_L^d) and polar component (γ_L^p) of surface tension of diiodomethane:

Fowkes[24] measured the contact angles of liquids on surfaces such as paraffin wax and using a value of 50,8 mN/m for the total surface tension of diiodomethane obtained a value for the dispersion component γ_L^d of 48,5 ± 9 mN/m. He concluded that the contact angle method was not as accurate as the interfacial tension method for measuring γ_L^d. The values in Table I show that γ_L^d varied from 42,1 to 50,4 mN/m.

When the different values quoted in the literature for the diiodomethane-water interfacial tension (41,6 and 48,5 mN/m) are used together with two of the values for the surface tension of diiodomethane [50,8 (literature) and 54,98 mN/m (calculated from parachor, Table II)] to calculate the dispersion and polar components of surface tension according to the geometric mean and harmonic mean equations[4], the results shown in Table III were obtained. It can be seen that a change in the interfacial tension value resulted in a change in the polar fraction of the surface tension. When the geometric mean equation was employed, the value for the polar fraction changed by about 1 to 3 *per cent* and when the harmonic mean equation was used it changed by 9 to 14 *per cent* (absolute). A change in the surface tension, but using the same interfacial tension, only changed the polar component slightly.
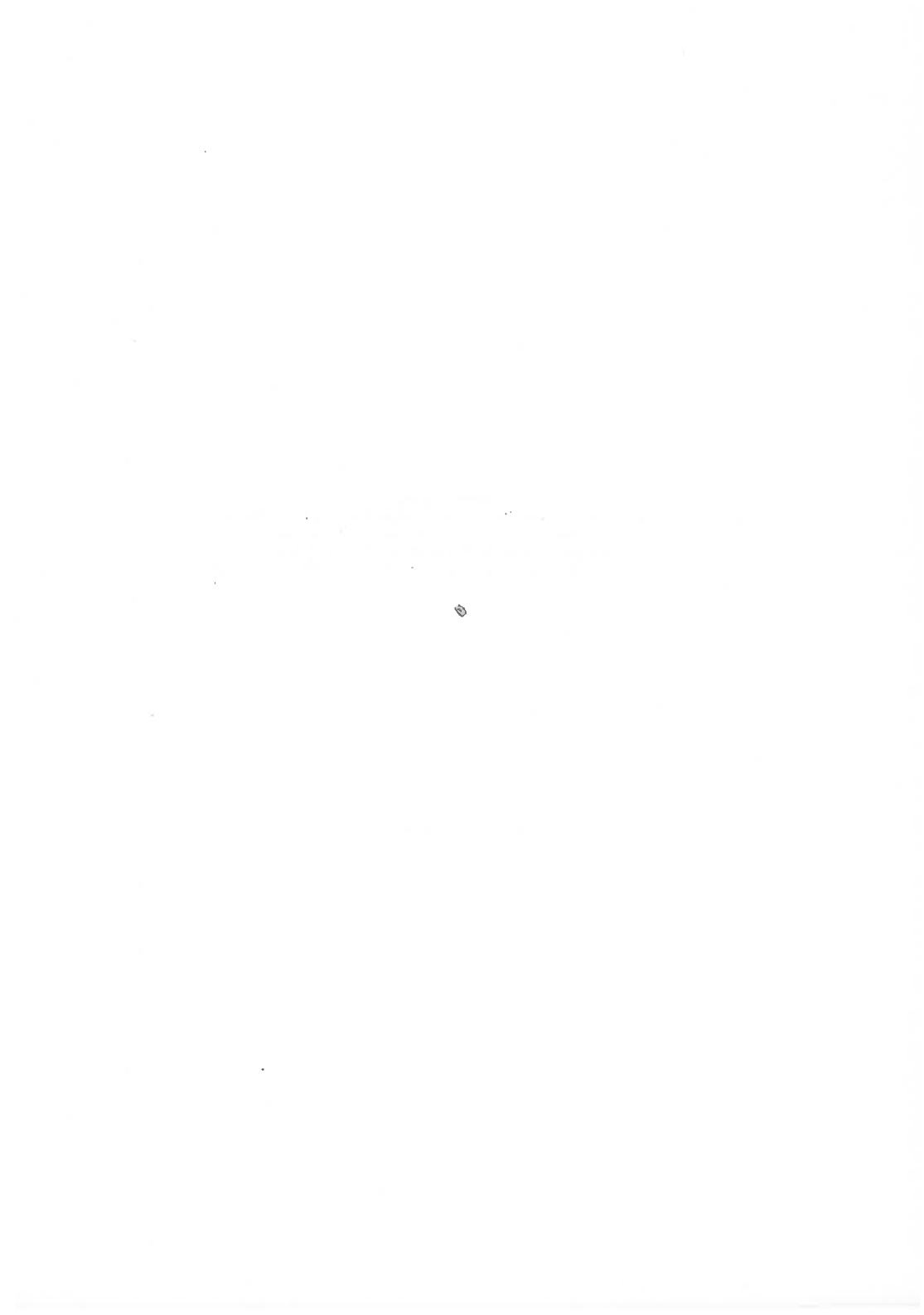
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THE USE OF PROPRIETARY NAMES

The use of proprietary names in this report in no way implies that there are not other products of equal or greater merit.

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