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Dielectric Saturation and Molecular Structure

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Résumé.

La saturation diélectrique positive consiste en l'augmentation de la constante diélectrique d'un liquide sous l'action d'un champ électrique. Cet effet a été trouvé dans le nitrobenzène et reconnu comme effet intermoléculaire. D'autre part, l'effet de saturation positive a été trouvé dans certains liquides dont les molécules présentent la rotation interne de groupes ayant chacun un moment électrique. Dans ce dernier cas, l'effet est intramoléculaire. La théorie de cet effet présentée par les auteurs admet l'existence des structures isomériques *droite* et *gauche*. Cette théorie explique l'existence de l'effet positif de la saturation et conduit à un terme additionnel dans la polarisation diélectrique, terme qui rend compte d'un nouveau mécanisme de cette polarisation consistant dans le fait que le champ électrique extérieur provoque des transitions *droite* $\rightarrow$ *gauche*, de sorte que l'équilibre entre ces deux formes se déplace quelque peu vers la structure *gauche* ayant un moment électrique plus grand que celui de la structure *droite*.

The inverse or positive saturation effect in dielectric liquids consists in an increase $\Delta\epsilon$ in the dielectric permittivity under the influence of an external electric field E [1, 2, 3, 4]. The effect is dependent on the quantity $\frac{\partial}{\partial E} \langle m_E \rangle_E$, where m_E denotes the projection of the electric moment of the molecule on the direction of the field vector E . With the local field F , the mean value of m_E is given by the formula

$$\langle m_E \rangle_E = \frac{\mu^2 F}{3kT} R_p - \frac{\mu^4 F^3}{45k^3 T^3} R_s, \quad (1)$$

provided the polarizability is due only to the orientational effect of the rigid dipoles μ [5]. If this is the case, the quantities R_p and R_s are *correlation factors* for the polarisation and the saturation, respectively. For polar gases, these factors become unity, leading to the normal or negative saturation effect. However, in dense media such as condensed gases and liquids, R_p and R_s are strongly dependent on the intermolecular directional forces. In some cases, as in liquid nitrobenzene, R_s becomes negative

giving rise to the positive saturation effect. The graphs in Fig. 1 show the quantities R_p and R_s plotted *versus* the interaction energy in dimensionless units $Y = \frac{W}{kT}$ of a system of two neighbouring dipoles tending to antiparallel configuration. It is seen from the curve labelled R_s that, for the

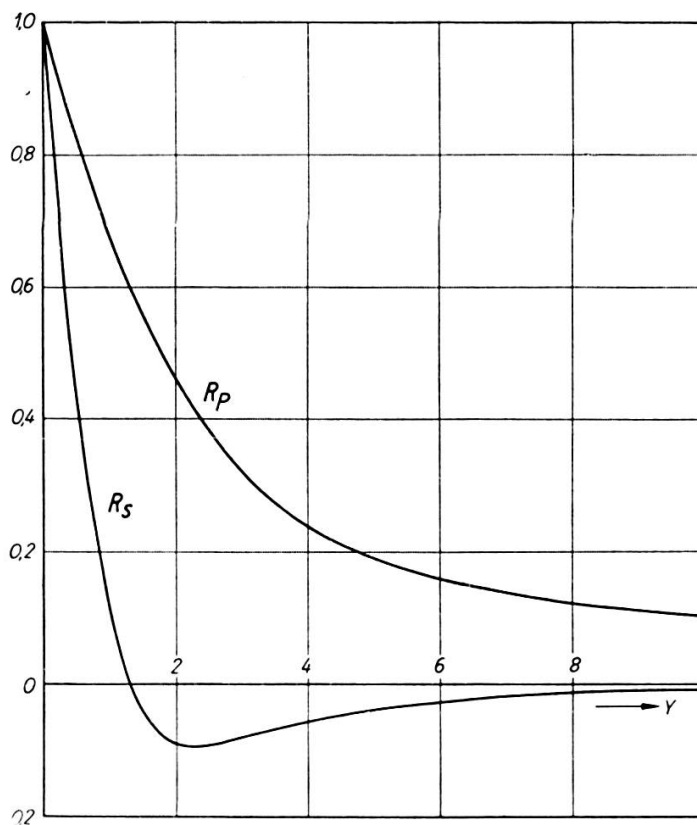


Fig. 1.

Correlation factors R_p , for dielectric polarisation, and R_s , for dielectric saturation as functions of the interaction energy, $Y = \frac{W}{kT}$, expressed in dimensionless units. The case of pair coupling tending to an antiparallel configuration (e.g. nitrobenzene).

weak interaction existing in sufficiently dilute solutions of nitrobenzene in non-polar solvents, the normal saturation effect appears. Thus, the positive saturation effect was first recognized as due to molecular interaction. This point of view has received support from cryoscopic measurements [4, 6].

Now, some liquids present a positive saturation effect of a different kind. These are liquids the molecules of which exhibit internal rotation [2, 3, 7, 8, 9]. In certain liquids belonging to this group, an external field

produces a rise in the dielectric permittivity, $\Delta\epsilon > 0$; this occurs both in the pure liquid and in solutions thereof in non-polar solvents at arbitrary concentrations. The mechanism of this kind of effect is clearly of an intramolecular nature. It is, nevertheless, similar to the mechanism of the intermolecular effect appearing in nitrobenzene. Here, however, the two interacting electric dipole moments are those of two rotating groups within the molecule. In such molecules the *trans* configuration is the privileged one. The external field acts to orient both moments in its direction and thus tends to diminish the angle between them. This results in a minute increase in the effective moment of the molecule and a corresponding increase in the dielectric permittivity. If the potential barrier is sufficiently high, this effect prevails over the normal saturation effect (which consists in a fall in ϵ) and the positive saturation effect appears.

If we follow the assumption made by Mizushima [10] for computing the dielectric polarisation, which is that of a single cosine potential barrier hindering the internal rotation, we again obtain formula (1). In the present case, μ denotes the effective dipole moment of a molecule with two identical rotating groups, provided rotation is entirely free. R_p and R_s are factors reducing the polarisation term and saturation term, respectively, as accounting for hindered rotation. Both *reducing factors* are functions of the interaction energy given in dimensionless units, $Z = \frac{V_0}{kT}$. The amount $2V_0$ is the difference in energy between the *cis* and *trans* positions. Thus, Mizushima's expression for R_p is obtained as follows:

$$R_p = 1 - \frac{I_1(Z)}{I_0(Z)} \quad (2)$$

whereas the reducing factor for dielectric saturation is given by the formula:

$$R_s = \frac{1}{4} - 2 \frac{I_1(Z)}{I_0(Z)} + \frac{5}{2} \left\{ \frac{I_1(Z)}{I_0(Z)} \right\}^2 - \frac{3}{4} \frac{I_2(Z)}{I_0(Z)}, \quad (3)$$

wherein $I_0(Z)$, $I_1(Z)$ and $I_2(Z)$ are Bessel functions. It is easily seen by a survey of Fig. 2 that R_s can change its sign for $Z \geq 0.30$, thus explaining the inverse saturation effect consisting in an increase of the dielectric permittivity in all cases when the potential barrier is sufficiently high.

This, indeed, is the case of the 1,2-dihalogenoethanes experimentally investigated [2, 4, 9]. The measured value of the increase $\Delta\epsilon$ in dielectric permittivity produced by an external field E allows to compute R_s . The theory using the model with single potential barrier yields qualitative

agreement with the experimental results. The degree of quantitative agreement is, however, unsatisfactory.

For this reason we resolved to test a theory assuming the existence of two rotational isomeres, to see whether such a theory would lead to better agreement with the measurements.

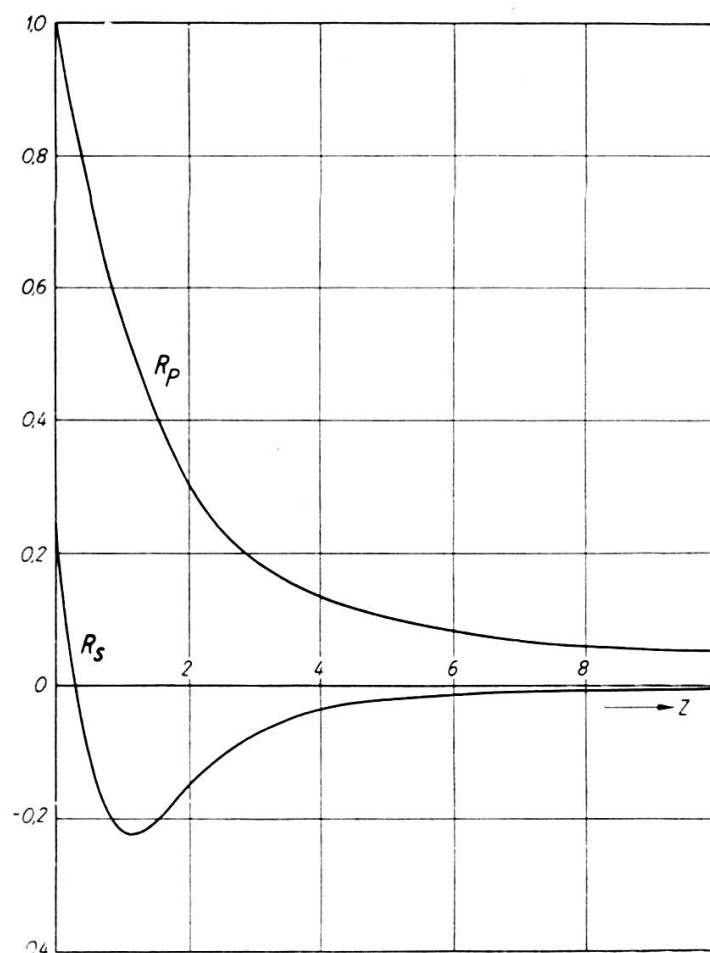


Fig. 2.

Reducing factors R_p and R_s , for dielectric polarisation and saturation, respectively, in 1, 2-dihalogenoethanes in gaseous form, assuming a single potential barrier (of height $2Z$ expressed in kT).

In considering liquid di-halogenated ethanes, let us assume, in agreement with various authors [10, 11, 12], that there is thermal equilibrium between three forms of various stability, the most stable of which is a trans structure, the remaining ones being two equivalent *gauche* structures of lesser stability. Since the dielectric saturation effect in these liquids is a positive one, it seems reasonable to suggest that the electric field can

stimulate transitions from the *trans* to the *gauche* forms, causing an increase in the effective electric moment. Following the procedure of Boltzmann statistics, a general expression for $\langle m_E \rangle_E$ is obtained. For the case that

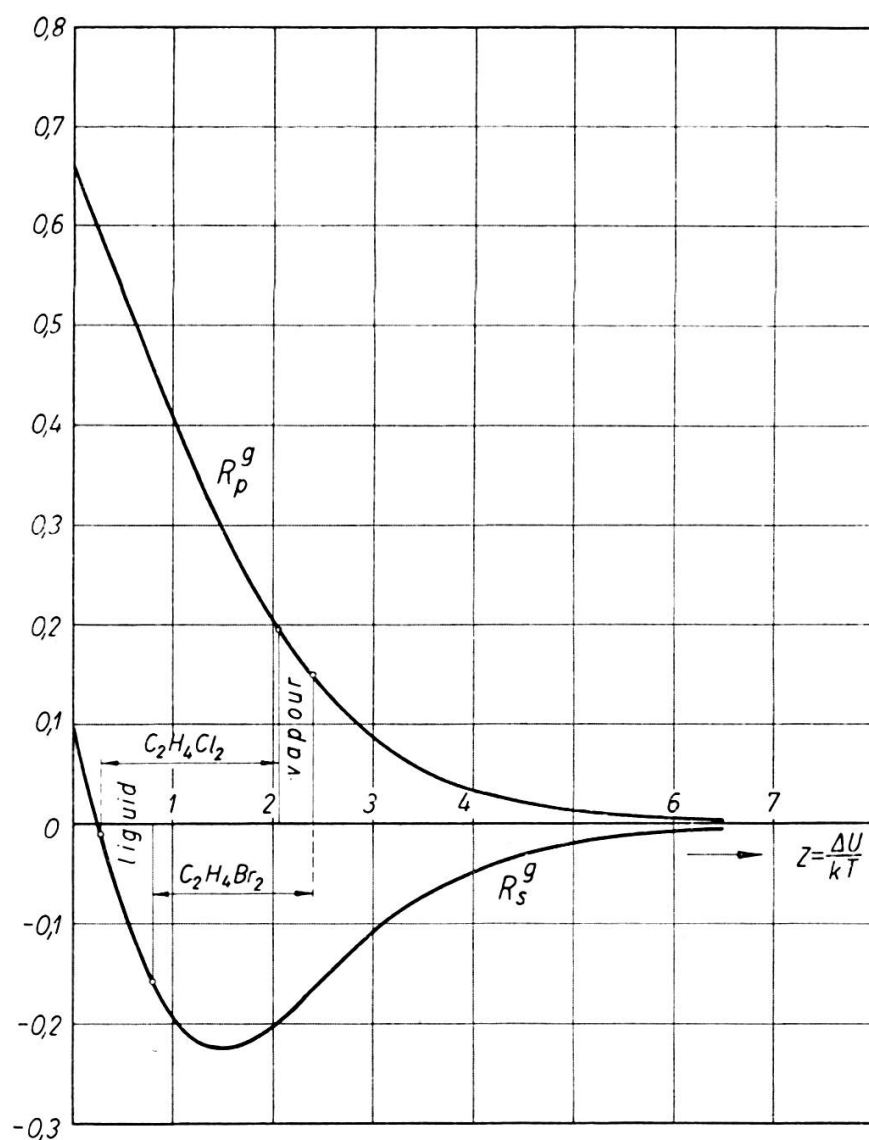


Fig. 3.

Plot of factors R_p^g and R_s^g expressing the contribution of the *gauche* form to the dielectric polarisation and saturation, respectively, vs. the energy difference between the *gauche* and *trans* structures.

the electric moment of the *trans* structure μ_t is zero, the following formula holds:

$$\langle m_E \rangle_E = \frac{\mu_g^2 F}{3kT} R_p^g - \frac{\mu_g^4 F^3}{45k^3 T^3} R_s^g ; \quad (4)$$

here, μ_g denotes the electric moment of the *gauche* structure. R_p^g and R_s^g are factors accounting for dielectric polarisation and dielectric saturation, respectively, and are given by

$$R_p^g = \frac{1}{1 + r_t}, \quad (5)$$

and

$$R_s^g = \frac{1 - \frac{3}{2} r_t}{(1 + r_t)^2}; \quad (6)$$

$r_t = \frac{N_t(0)}{N_g(0)}$ is the ratio of the numbers of molecules of *trans* and *gauche* structure at zero field, and is given by

$$r_t = \frac{1}{\omega} e^{\frac{\Delta U}{kT}}, \quad (7)$$

wherein $\omega = 1,9$ [10], with regard to the presence of two *gauche* forms, and $\Delta U = U_g - U_t$ is the difference between the energy values corresponding to the *gauche* and *trans* forms of the molecule.

The factors R_p^g and R_s^g are plotted *versus* $\frac{\Delta U}{kT}$ in Fig. 3. Throughout the range of small differences in energy ΔU , the factor R_s^g is positive, and we have the normal saturation effect, $\Delta\epsilon < 0$. However, if ΔU exceeds $0,24 kT$, the factor R_s^g becomes negative, yielding the inverse, that is positive effect $\Delta\epsilon > 0$. This is the case of 1,2-dichloro- and 1,2-dibromoethane. For both these liquids, we obtained reasonable values for μ_g and ΔU (for the liquid state), as is shown in the following table:

Compound	Vapour			Liquid	
	ΔU from other investiga- tions [10] (k cal/mole)	μ_g computed according to the present theory from measured dipole moments [10] (D)	μ_g' from bond moments [12, 13] (D)	ΔU computed according to the present theory from measure- ments of $\Delta\epsilon$ [2, 4, 9] and using μ_g (k cal/mole)	ΔU from other investiga- tions [10] (k cal/mole)
$\text{ClH}^2\text{C} - \text{CH}^2\text{Cl}$.	1,2	2,45	2,4	0,16	0
$\text{BrH}^2\text{C} - \text{CH}^2\text{Br}$.	1,4	ca. 2,3	2,3	ca. 0,4	$\geq 0,65$, very disper- sed

The values obtained for μ_g fit well with those computed for μ'_g from the bond moments C — Cl or C — Br and the geometry of the molecule. As to the energy difference $\hat{E}U$ for the liquid state, we consider the value 0 obtained from other experiment (see [10]) is too low, for the reason that it would yield a negative saturation effect which is contrary to experiment.

I think there is just one more point that is worth stressing. If an external electric field is present, then, according to our assumption, in addition to collision-stimulated transitions leading to thermal equilibrium between the *trans* and *gauche* forms, there occur field-stimulated *trans* $\rightarrow$ *gauche* transitions which shift the equilibrium somewhat towards the *gauche* forms possessing an increased electric moment. In this way, rotational isomerism leads to a *new mechanism of (collective) polarizability*, i.e. "field stimulated transition polarizability" due to the appearing of structures possessing a greater electric dipole moment than the vanishing structures they replace. That is why the dielectric saturation effect becomes positive.

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