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Towards a better understanding of the parameter E_i/E in the characterization of polar liquids

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Abstract

In the two previous papers [Stengele, A., Rey, St., Leuenberger, H., 2001. A novel approach to the characterization of polar liquids. Part 1: pure liquids. Int. J. Pharm. 225, 123–134; Stengele, A., Rey, St., Leuenberger, H., 2002. A novel approach to the characterization of polar liquids. Part 2: binary mixtures. Int. J. Pharm. 241, 231–240] it was shown, that the Clausius–Mossotti–Debye equation for the quasi-static dielectric constant (ε) can be extended to liquids if the parameter E_i/E is introduced. E_i corresponds to the local mean field due to close molecule–molecule interactions after the application of an external electric field E. In the present paper, it is demonstrated that the value of E_i/E at room temperature can be (1) related to the density of hydroxy groups and the density of the square of the dipole moment per molar volume for polar liquids and (2) also to the total (δ_t) and partial solubility parameter, for polar (δ_p) and hydrogen bond forming molecules (δ_h).

Keywords: Modification of the Clausius–Mossotti–Debye equation; Hildebrand and Hansen solubility parameters; Dimroth–Reichardt E_T parameter; Polar solvent

1. Introduction

As it was shown in previous papers (Stengele et al., 2001, 2002) pure polar liquids can be characterized by the parameter E_i/E of the Clausius–Mossotti–Debye equation modified according to Leuenberger for the quasi-static dielectric constant (Stengele et al., 2001).

In the present paper the emphasis was put on the study of the nature of the parameter E_i/E and its origin in case of pure polar liquids at room temperature.

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2. Theoretical

2.1. The Clausius–Mossotti–Debye equation modified according to Leuenberger for the quasi-static dielectric constant (Stengele et al., 2001)

The original Clausius–Mossotti–Debye equation is only valid for molecules in the ideal gas phase, i.e. in the case, where the molecules are located far from each other and do not show any interaction:

$$\left(\frac{\varepsilon-1}{\varepsilon+2}\right)\frac{M_r}{\rho}=\frac{N_{\mathrm{A}}}{3\varepsilon_0}\left(\alpha+\frac{\mu_{\mathrm{g}}^2}{3kT}\right) \tag{1}$$

where ε is quasi-static relative dielectric constant; M_{r} is molecular weight; ρ is density; N_{A} is Avogadro number ($6.023 \times 10^{23}\,\mathrm{mol}^{-1}$); ε_0 is electric field constant in the vacuum ($8.854 \times 10^{-12}\,\mathrm{C}^2\,\mathrm{J}^{-1}\,\mathrm{m}^{-1}$); α is polarizability of the molecule ($\mathrm{cm}^2\,\mathrm{V}^{-1}$); μ_{g} is dipole moment in the state of an ideal gas (C m); K is Boltzmann's constant ($1.38 \times 10^{-23}\,\mathrm{J\,K}^{-1}$); T is temperature (K).

The essential point of the original derivation of the Clausius–Mossotti–Debye equation consisted in the fact that the local mean field E_i being the result of short range Van der Waals interactions and of hydrogen bonding of neighboring molecules was neglected. The introduction of the term E_i/E with E is applied external electric field leads to the following modification:

$$\left(\frac{\varepsilon-1}{3(E_i/E)+(\varepsilon+2)}\right)\frac{M_{\mathrm{r}}}{\rho}=\frac{N_{\mathrm{A}}}{3\varepsilon_0}\left(\alpha+\frac{\mu_{\mathrm{g}}^2}{3kT}\right) \tag{2}$$

The classical Clausius–Mossotti–Debye equation (Eq. (1)) is not valid for polar liquids but can be used to estimate quite accurately the dipole moment μ_{g} of water in a highly diluted solution of water in 1,4-dioxane simulating an ideal gas state condition (Hedestrand, 1929).

The Clausius–Mossotti–Debye equation modified according to Leuenberger for the quasi-static dielectric constant (Stengele et al., 2001) (Eq. (2)) can be used to characterize polar liquids. In case of a highly polar liquid such as water the value of E_i/E is -21.0 at room temperature. The parameter E_i/E is temperature dependent and can be modeled as follows:

$$\frac{E_i}{E}=-\,|m|\left(\frac{1}{T}\right)+b \tag{3}$$

where $|m|$ is absolute value for the slope m of $(E_i/E)\ f\,(1/T)$ and b is intercept from the linear regression $(E_i/E)\ f\,(1/T)$.

Interestingly an empirical relationship between $|m|$ and the Hildebrand parameter (δ) could be established (Stengele et al., 2001). This relationship has to be judged with caution as it is often neglected that δ is temperature dependent. The values of δ which are listed in tables such as in the book of Barton (1991) are estimated values valid at room temperature. The slope $|m|$ on the other hand is a temperature-independent parameter. If the temperature T is kept constant, the parameter ($|m|/T$) is a constant, too, and the correlation between the Hildebrand solubility parameter (δ) and ($|m|/T$) is still valid. One can expect that as a consequence the value E_i/E at room temperature may directly yield a good correlation with the total Hildebrand solubility parameter (δ_{t}). Thus, it should be possible to find an empirical relationship between the values of E_i/E and the total Hildebrand solubility parameter (δ_{t}) at room temperature. This evaluation will be part of this paper as well as the study of the correlation of E_i/E value with the partial Hansen solubility parameters for polar and hydrogen bond forming molecules (δ_{p}, δ_{h}).

2.2. Dimroth–Reichardt E_{T} parameter: an empirical solvent polarity parameter

The notion of solvent polarity is often used to choose a solvent or to explain solvent effects. With the exception of some mixtures of two solvents, solvent polarity is not conveniently measured either by the dipole moment or by the dielectric constant. However, very useful correlations were obtained with empirical solvent polarity parameters (Griffiths and Pugh, 1979; Reichardt, 1988) such as the $E_{\mathrm{T}}(30)$ scale of Dimroth–Reichardt (Reichardt, 1994), Z scale of Kosower (Kosower, 1958) or the π^* scale of Kamlet (Kamlet and Taft, 1976).

$E_{\mathrm{T}}(30)$ values (Reichardt, 1994) are defined as the molar electronic transition energies (E_{T}) of the *negatively solvatochromic pyridinium N-phenolate betaine dye* (Fig. 1) in a given solvent measured in kilocalories per mol (kcal/mol) at room temperature (25 °C) and normal pressure (1 bar), according to Eq. (4). The number (30) was added by its originators in order to avoid confusion with E_{T}, often used in photochemistry

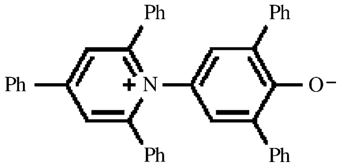

Fig. 1. Negatively solvatochromic pyridinium *N*-phenolate betaine dye.

as abbreviation for triplet energy.

$$E_T(30)\,(\mathrm{kcal\,mol^{-1}}) = hc\bar{\upsilon}_{\max}N_A$$
$$= (2.8591 \times 10^{-3})\bar{\upsilon}_{\max}\,(\mathrm{cm^{-1}}) = \frac{28591}{\lambda_{\max}}(\mathrm{nm}) \quad (4)$$

where $\bar{\upsilon}_{\max}$ is frequency and $\lambda_{\max}$ is wavelength of the maximum of the longest wavelength, intramolecular charge-transfer π–π^* absorption band of the negatively solvatochromic pyridinium *N*-phenolate betaine dye.

In addition, so-called normalized E_T^N values have been introduced (Reichardt, 1994). They are defined according to Eq. (5) as dimensionless figures, using water and tetramethylsilane (TMS) as extreme polar and nonpolar reference solvents, respectively. Hence, the E_T^N scale ranges from 0.000 for TMS, the least polar solvent, to 1.000 for water, the most polar solvent (Reichardt, 1994).

$$E_T^N = \frac{E_T(\mathrm{solvent}) - E_T(\mathrm{TMS})}{E_T(\mathrm{water}) - E_T(\mathrm{TMS})} = \frac{E_T(\mathrm{solvent}) - 30.7}{32.4} \quad (5)$$

A comparison between E_i/E parameter and $E_T(30)$ parameter and also between the E_i/E parameter and the so-called normalized E_T^N values for polar substances will be performed.

3. Materials and methods

3.1. Data analysis

The molar volume of a pure liquid is defined as:

$$V_m\,(\mathrm{cm^3\,mol^{-1}}) = \frac{M_r}{\rho} \quad (6)$$

where M_r is molecular weight (g mol^{-1}) and ρ is density (g cm^{-3}).

Table 1
Physical properties of pure solvents

Substance	OH-groups	E_i/E value[a]	D_{OH} (cm^{-3})	[b]δ_t^2 (MPa)	[b]δ_p^2 (MPa)	[b]δ_h^2 (MPa)	[b]δ_d^2 (MPa)	$(\delta_p^2 + \delta_h^2)^{1/2}$	$D_{\mu\mu}$ (D^2 mol cm^{-3})	[c]$E_T(30)$ (kcal mol^{-1})	[c]E_T^N
Methanol	1	−5.190	0.025	876.160	151.290	497.290	228.010	25.470	0.071	55.400	0.762
Ethanol	1	−2.390	0.017	702.250	77.440	376.360	249.640	21.300	0.049	51.900	0.654
Benzyl alcohol	1	−0.570	0.010	566.440	39.690	187.690	338.560	15.080	0.028	50.400	0.608
2-Methyl-1-butanol	1	−0.550	0.009	470.890	20.250	193.210	256.000	14.610	0.033	48.000	0.534
1-Propanol	1	−0.140	0.013	600.250	46.240	302.760	256.000	18.680	0.032	50.700	0.617
2-Propanol	1	−0.100	0.013	552.250	37.210	268.960	249.640	17.500	0.032	48.400	0.546
2-Methyl-1-propanol	1	−0.170	0.011	515.290	32.490	256.000	228.010	16.980	0.034	48.600	0.552
Water	1.33	−20.620	0.074	2284.840	256.000	1789.290	243.360	45.220	0.190	63.100	1.000
1,2-Ethanediol	2	−8.210	0.036	1082.410	121.000	676.000	289.000	28.230	0.093	56.300	0.790
1,2-Propanediol	2	−4.560	0.027	912.040	88.360	542.890	282.240	25.120	0.066	54.100	0.722
1,2-Butanediol	2	−3.110	0.022	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	52.600	0.676
Glycerol	3	−8.540	0.041	1303.210	146.410	858.490	302.760	31.700	0.092	57.000	0.812

[a] Source: Stengele (2002).
[b] Source: Barton (1991).
[c] Source: Reichardt (1994).

In order to get a parameter, which defines the density of OH-groups per volume (D_{OH}), and the density of the square of the dipole moment per molar volume ($D_{\mu\mu}$), the following variables were defined:

$$D_{\mathrm{OH}}\,(\mathrm{cm}^{-3}) = \frac{(\text{no. of OH-groups per molecule})}{V_{\mathrm{m}}} \qquad (7)$$

$$D_{\mu\mu}\,(\mathrm{D}^2\,\mathrm{mol\,cm}^{-3}) = \frac{\mu^2}{V_{\mathrm{m}}} \qquad (8)$$

The dipole moment μ is given in Debye units (D). The conversion factor to SI units is $1\,\mathrm{D} = 3.33564 \times 10^{-30}\,\mathrm{C\,m}$.

The E_i/E parameter result of the modified Debye equation according to Leuenberger was calculated according to Eq. (2). As the external electric field E varies in a cylinder condensator as a function of the radius r (Frauenfelder and Huber, 1967), it does not make sense to calculate E and to estimate E_i. The values for the polarizability α were calculated using the Lorentz–Lorenz equation (Lorenz, 1880), which gave excellent results compared with literature data (Riddick and Bunger, 1970) both for polar and nonpolar compounds (see Eq. (9)).

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{M_{\mathrm{r}}}{\rho} = \frac{N_{\mathrm{A}}}{3\varepsilon_0}\alpha \qquad (9)$$

For the study of the correlation between the parameter E_i/E and the total and partial solubility parameters and also for the correlation between the parameter E_i/E and D_{OH} the data compiled in Table 1 were analyzed.

The square of the Hansen parameters was taken according to the Hansen equation (see Eq. (10)).

$$\delta_{\mathrm{t}}^2 = \delta_{\mathrm{d}}^2 + \delta_{\mathrm{p}}^2 + \delta_{\mathrm{h}}^2 \qquad (10)$$

For the study of the correlation between the parameter E_i/E and $D_{\mu\mu}$, as well as for the correlation between E_i/E parameter and the $E_{\mathrm{T}}(30)$ parameter and the normalized E_{T}^N values the data also compiled in Table 1 were analyzed.

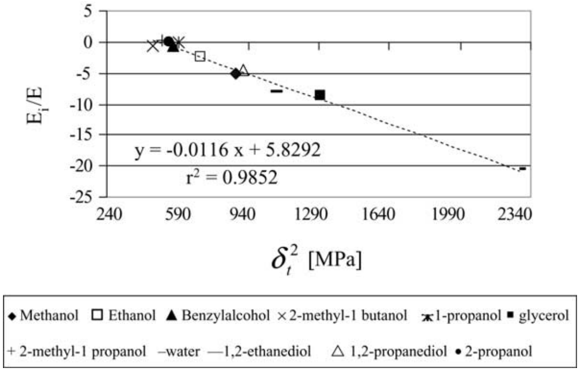

Fig. 2. E_i/E values as a function of the square total Hidelbrand solubility parameter δ_{t} at 298.2 K.

4. Results

4.1. The correlation of E_i/E with the total Hildebrand solubility parameter δ_t and the partial Hansen solubility parameters (δ_p, δ_h) at room temperature

According to Eq. (3) a linear dependence between E_i/E and $1/T$ exists. The slope m of Eq. (3) could be correlated to the Hildebrand solubility parameter (δ), more precisely to the total solubility parameter δ_{t}. A close inspection of the data obtained (see Table 1) so far leads now to the following result. If T is kept constant it is possible to correlate the parameter E_i/E directly to the Hildebrand solubility parameter (δ_{t}) with a mean correlation coefficient $r^2 = 0.99$ (Fig. 2, Eq. (11)):

$$\frac{E_i}{E} = -0.01\delta_{\mathrm{t}}^2 + 5.83, \quad r^2 = 0.99 \qquad (11)$$

Interestingly it is also possible to correlate E_i/E directly with the partial Hansen solubility parameter δ_{h} for molecules being capable to form hydrogen bonds with a $r^2 = 0.98$ (Fig. 3, Eq. (12)).

$$\frac{E_i}{E} = -0.01\delta_{\mathrm{h}}^2 + 2.53, \quad r^2 = 0.98 \qquad (12)$$

A good correlation is also found between the parameter E_i/E and the partial Hansen solubility parameter δ_{p} for polar molecules having a dipole moment ($r^2 = 0.92$, Fig. 4, Eq. (13)).

$$\frac{E_i}{E} = -0.08\delta_{\mathrm{p}}^2 + 3.10, \quad r^2 = 0.92 \qquad (13)$$

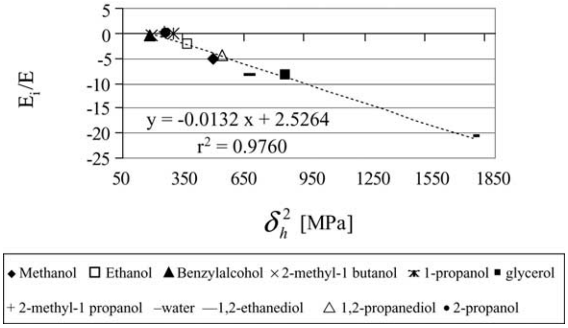

Fig. 3. E_i/E values as a function of the square partial Hanson solubility parameter δ_h at 298.2 K.

E_i/E can also be correlated with the combined partial solubility parameter $\delta_{hp} = (\delta_h^2 + \delta_p^2)^{1/2}$, which leads to a correlation coefficient of $r^2 = 0.96$.

As E_i/E can be determined rather accurately, a good estimate for the total δ_t and partial solubility parameters (δ_p, δ_h) can be obtained. As expected no correlation can be observed with the dispersive partial solubility parameter δ_d ($r^2 < 0.01$).

4.2. The correlation of E_i/E with D_{OH}

Interestingly the following empirical relationship could be obtained, which correlates the D_{OH} with the value of E_i/E in a polar solvent (see Fig. 5). For this relationship the following correlation coefficient was obtained $r^2 = 0.99$ (Eq. (14))

$$\frac{E_i}{E} = -318.91 D_{OH} + 3.43, \quad r^2 = 0.99 \qquad (14)$$

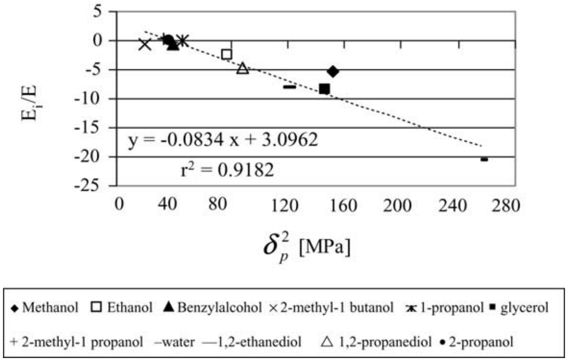

Fig. 4. E_i/E values as a function of the square partial Hanson solubility parameter δ_p at 298.2 K.

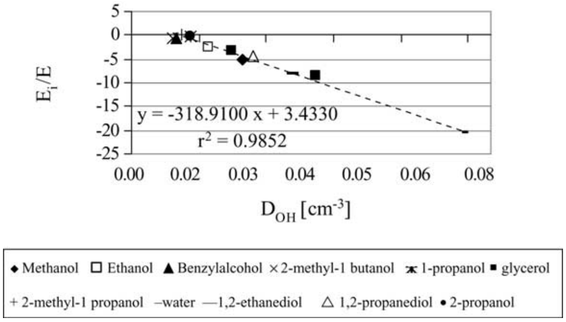

Fig. 5. E_i/E values as a function of D_{OH} at 298.2 K.

It has to be kept in mind that a correlation of E_i/E with the Hildebrand and Hansen solubility parameters exist and that it is possible to estimate theoretically the solubility parameter δ_t and δ_h with the help of a group number concept, i.e. with group cohesion parameters (Barton, 1991). The application of this concept is based on the knowledge of the functional groups of the molecule contributing per unit molar volume a specific value to the solubility parameter. Thus, it is not so surprising that the above empirical correlation between D_{OH} of the solvent was found. As a conclusion it can be postulated that the value of E_i/E can be estimated on the basis of a new group number concept, which can be established on the basis of Eq. (14).

4.3. The correlation of E_i/E with $D_{\mu\mu}$ at room temperature

According to Eq. (15) a linear dependence between E_i/E and $D_{\mu\mu}$ exists (see Fig. 6). However, no

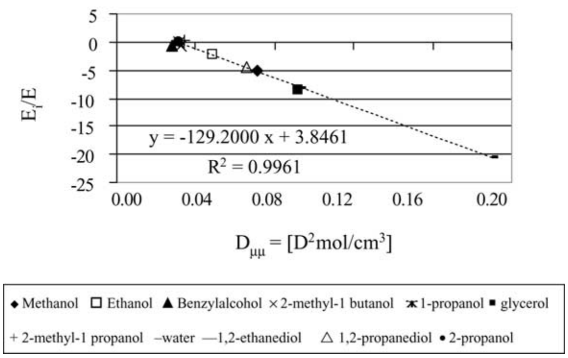

Fig. 6. E_i/E values as a function of $D_{\mu\mu}$ at 298.2 K.

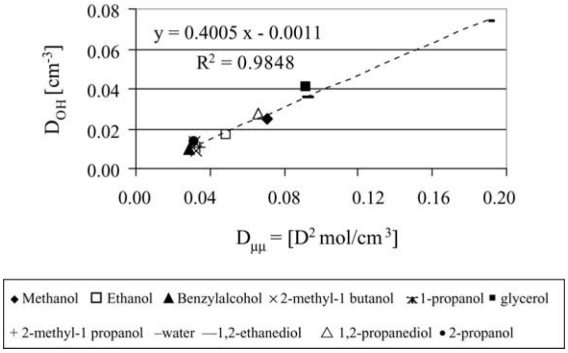

Fig. 7. D_{OH} as a function of $D_{\mu\mu}$ at 298.2 K.

correlation exists between E_i/E and the dipole moment ($r^2 = 0.16$).

$$\frac{E_i}{E} = -129.20 D_{\mu\mu} + 3.85, \quad r^2 = 0.99 \tag{15}$$

The square of the solubility parameter corresponds to the endoergic process of separating the solvent molecules to provide a suitably sized enclosure for the solute and measures the work required to produce a cavity of unit volume in the solvent. This term is related to the tightness or structuredness of solvents as caused by intermolecular solvent/solvent interactions (Barton, 1991). Therefore, the solubility parameter gives us the amount of Van der Waals forces that held the molecules of the liquid together per molar volume. Therefore, it is not surprising that if a good correlation between E_i/E and the solubility parameter is found (see Section 4.1), it is also possible to find an excellent correlation between E_i/E and $D_{\mu\mu}$ ($r^2 = 0.99$ according to Eq. (15)) as can be expected according to modified Clausius–Mossotti–Debye equation by Leuenberger (see Eq. (2)).

4.4. *The correlation between the D_{OH} and $D_{\mu\mu}$ at room temperature*

It could be shown a good correlation ($r^2 = 0.99$) between D_{OH} and $D_{\mu\mu}$ (see Fig. 7, Eq. (16)).

$$D_{\mathrm{OH}} = 0.400 D_{\mu\mu} - 0.001, \quad r^2 = 0.985 \tag{16}$$

It indicates that both parameters are to some extent exchangeable.

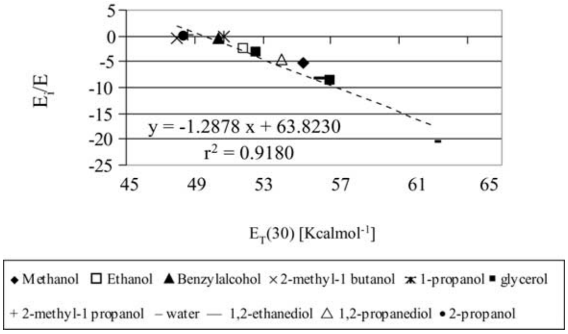

Fig. 8. E_i/E values as a function of $E_{\mathrm{T}}(30)$ at 298.2 K.

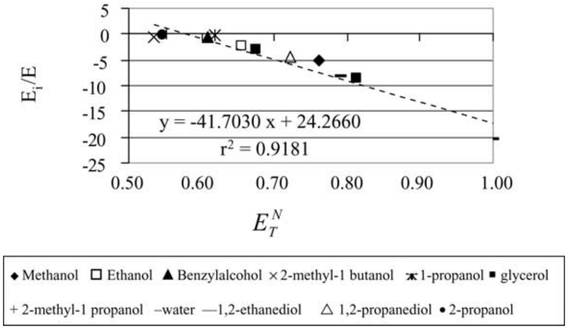

Fig. 9. E_i/E values as a function of E_{T}^{N} at 298.2 K.

4.5. *The correlation of E_i/E with the Dimroth–Reichardt $E_T(30)$ at room temperature*

A good correlation (see Eqs. (17) and (18)) is found between the E_i/E parameter and the empirical solvent polarity parameter $E_{\mathrm{T}}(30)$ at room temperature and also between the E_i/E parameter and the normalized E_{T}^{N} parameter (see Figs. 8 and 9). That confirms the important role of the E_i/E parameter in the characterization of polar liquids.

$$\frac{E_i}{E} = -1.28 E_{\mathrm{T}}(30) + 63.82, \quad r^2 = 0.92 \tag{17}$$

$$\frac{E_i}{E} = -41.70 E_{\mathrm{T}}^{N} + 24.27, \quad r^2 = 0.92 \tag{18}$$

5. Conclusions

An excellent correlation between E_i/E and D_{OH} and $D_{\mu\mu}$ could be found. This confirms that E_i/E describes the close range dipolar and hydrogen bonding interactions.

It could also be shown that due to the possibility of determining rather accurately the E_i/E values of polar liquids in both pure liquid and in binary mixtures of different polarities, it is possible without an enormous experimental effort to get a good estimates for the Hildebrand total (δ_t) and for the Hansen partial solubility parameter for polar molecules capable of forming hydrogen bonds (δ_h).

A good correlation between the E_i/E parameter and the empirical solvent polarity parameter $E_T(30)$ could be established showing that the E_i/E parameter are an easily measurable alternative parameter to describe the polarity of liquids.

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