The Determination of Molecular Quantities from Measurements on Macroscopic Systems

II. The Determination of Electric Dipole Moments

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Some bulk quantities appropriate for the description of dielectric and refractometric measurements on macroscopic systems are defined and their properties are discussed. Based on three molecular models (Lorentz model, Onsager model in spherical approximation, and in ellipsoidal approximation) model molar quantities are introduced, which depend on intrinsic properties of the molecule, i.e. the electric dipole moment and the polarizability. The relations will be applied for the evaluation of the results of dielectric and refractometric measurements on eight aromatic molecules.

1. The General Model for the Evaluation of Permittivity Measurements

Macroscopic systems in stationary states are commonly meeting a few general requirements specified in paper I, Sect. 1, of this series at least approximately [1]. In such cases it is possible to define macroscopic bulk quantities, especially partial molar quantities (PMQ's) without introducing any assumption about the particular molecular structure of a considered phase. To relate a PMQ to molecular quantities a suitable model has to be introduced which allows the definition of corresponding model molar quantities (MMQ's). Some general relations between PMQ's and MMQ's have been presented in paper I. In this paper full details about the determination of electric dipole moments and polarizabilities of isolated molecules from permittivity and refractometric measurements of solutions are given. The method is applied to a few molecules in Sect. 5.

An isotropic phase in a uniform electric field $\boldsymbol{E}_\mathrm{a}$ obtains a dielectric polarization $\boldsymbol{P} = \varepsilon_0 (\varepsilon_{E\mathrm{r}} - 1) \boldsymbol{E}_\mathrm{a}$, where ε_0 is the permittivity of vacuum and $\varepsilon_{E\mathrm{r}}$ is the static relative permittivity. According to (I.150)* the partial molar electric susceptibility Z_{0J} can be introduced, wherewith the limit of $\varepsilon_{E\mathrm{r}} - 1$ for $E_\mathrm{a}^2 \to 0$ can be represented by

$$\lim_{E_\mathrm{a}^2 \to 0} \varepsilon_{E\mathrm{r}} - 1 = \varepsilon_\mathrm{r} - 1 = \sum_{J=1}^{E} \mathsf{Z}_{0J}\, c_{0J} \,. \qquad (1)$$

$c_{0J} = n_{0J}/V$ is the initial concentration and n_{0J} the amount of the substance A_J used to generate the phase by mixing the substances $\mathrm{A}_1, \ldots, \mathrm{A}_E$, V is the volume of the phase. The sum on the right-hand side of (1) has to include all initial substances.

For the solution of a substance A_G in a mixed solvent consisting of the substances $\mathrm{A}_1, \ldots, \mathrm{A}_S$, an average partial molar electric susceptibility $\mathsf{Z}_{0\mathrm{m}}^{(S)}$ of the solvent has been defined by (I.35) ($\Phi_{0L} = \mathsf{Z}_{0L}$). Choosing as concentration variable the mass fraction w_{0G} of the solute, the generalized density, Eq. (I.60), becomes

$$\mathsf{P}_{w\mathsf{Z}} = \frac{\varepsilon_\mathrm{r} - 1}{\varrho} = \frac{\mathsf{Z}_{0\mathrm{m}}^{(S)}}{M_\mathrm{m}^{(S)}} + \left(\frac{\mathsf{Z}_{0G}}{M_G} - \frac{\mathsf{Z}_{0\mathrm{m}}^{(S)}}{M_\mathrm{m}^{(S)}} \right) w_{0G} \,, \qquad (2)$$

where ϱ is the mass density of the solution and $M_\mathrm{m}^{(S)}$ is the average molar mass of the solution defined by (I.35) with $\Phi_{0L} = M_L$. The dependences of the PMQ's on the composition of the solution can be represented by power expansions, or according to Eqs. (I.40) and (I.44) as

$$\mathsf{Z}_{0G} = \mathsf{Z}_{0G}^{*} + \sum_{\alpha_G=1}^{\infty} \Lambda_{w\mathsf{Z}G\alpha_G} w_{0G}^{\alpha_G} \,, \qquad (3)$$

$$\mathsf{Z}_{0\mathrm{m}}^{(S)} = \mathsf{Z}_{0\mathrm{m}}^{(S)*} + \sum_{\alpha_G=2}^{\infty} \Lambda_{w\mathsf{Z}\mathrm{m}\alpha_G} w_{0G}^{\alpha_G} \,. \qquad (4)$$

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* The abbreviation Eq. (I....) signifies equations of paper I of this series [1].

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Starred quantities, as defined by (I.37), are always the limits for the pure solvent ($w_{0G} \to 0$). Because of (I.9) the coefficients $\Lambda_{w\mathsf{Z}G\alpha_G}$ and $\Lambda_{w\mathsf{Z}\mathrm{m}\alpha_G}$ are related as

$$\frac{\Lambda_{w\mathsf{Z}\mathrm{m}\alpha_G}}{M_{\mathrm{m}}^{(S)}} = -\frac{1}{\alpha_G M_G}\left[\Lambda_{w\mathsf{Z}G1} + 2\,\Lambda_{w\mathsf{Z}G2} + \cdots + (\alpha_G - 1)\Lambda_{w\mathsf{Z}G(\alpha_G-1)}\right]. \tag{5}$$

With (3) to (5) it follows from (2)

$$\begin{aligned}\frac{\varepsilon_{\mathrm{r}} - 1}{\varrho} = \frac{\varepsilon_{\mathrm{r}}^* - 1}{\varrho^*} &+ \left(\frac{\mathsf{Z}_{0G}^*}{M_G} - \frac{\varepsilon_{\mathrm{r}}^* - 1}{\varrho^*}\right) w_{0G} \\ &+ \frac{1}{M_G}\sum_{\alpha_G=2}^{\infty}\frac{1}{\alpha_G(\alpha_G - 1)}\left[\Lambda_{w\mathsf{Z}G1} + 2\,\Lambda_{w\mathsf{Z}G2} + \cdots + (\alpha_G - 1)\,\Lambda_{w\mathsf{Z}G(\alpha_G-1)}\right] w_{0G}^{\alpha_G}.\end{aligned} \tag{6}$$

At least in sufficiently dilute solutions only the first few terms of the power expansion are significantly different from zero. A set of available data $\mathrm{D_p} = \{(w_{0G}, \varepsilon_{\mathrm{r}}, \varrho)_{\mathrm{s}}\}$ can be evaluated by multiple regression analysis, according to (6). With suitable tests (F- and t-test, for example), the number of terms significantly different from zero can be determined. Then a corresponding multiple regression leads to estimators for the coefficients and their standard deviations. From the derivatives of (6) one can recognize that a unique determination of the quantities Z_{0G}^*, $\Lambda_{w\mathsf{Z}G1}$, $\Lambda_{w\mathsf{Z}G2}, \ldots$ is possible, if w_{0G}, ε_{r} and ϱ are bulk quantities (Sect. 1 [1]), as is usually the case. For a further evaluation some molecular model has to be introduced.

Molecular models are commonly based on a separate molecular model (SMM) (Sect. 9 [1]), i.e. on the assumption that the dielectric polarization $\boldsymbol{P}$ of the phase can be represented by (I.153), or

$$\boldsymbol{P} = N_{\mathrm{A}}\sum_{J=1}^{K}\overline{\boldsymbol{p}}_{EJ}\,c_{EJ}\,, \tag{7}$$

where N_{A} is the Avogadro constant, $\overline{\boldsymbol{p}}_{EJ}$ is the average electric dipole moment of a molecule and c_{EJ} the concentration of substance A_J in the presence of the applied field and where the sum has to be extended over all substances $\mathrm{A}_1, \ldots, \mathrm{A}_K$ present in the phase. Generally it is $K \geqq E$; for phases where no chemical reaction occurs, the equality commonly holds true. The assumption, introduced in (7), allows the definition of a model molar quantity (MMQ) ζ_J as

$$\zeta_J = \frac{N_{\mathrm{A}}}{\varepsilon_0}\lim_{E_{\mathrm{a}}^2 \to 0}\left(\frac{\partial \tilde{\boldsymbol{E}}_{\mathrm{a}}\overline{\boldsymbol{p}}_{EJ}}{\partial E_{\mathrm{a}}^2}\right)_{n_{0I},\,\vartheta_\iota}. \tag{8}$$

The subscripts of derivatives are explained at (I.6).

With the MMQ's ζ_J the electric susceptibility becomes

$$\varepsilon_{\mathrm{r}} - 1 = \sum_{J=1}^{K}\zeta_J\,c_J\,, \tag{9}$$

where $c_J = n_J/V$ is the concentration and n_J the amount of the substance A_J in absence of an applied field.

For a solution of a substance A_G in a mixed solvent $\mathrm{A}_1, \ldots, \mathrm{A}_S$ the relation between the PMQ Z_{0G} and the MMQ ζ_G is according to (I.78) and (I.80)

$$\begin{aligned}\mathsf{Z}_{0G} = \zeta_G &+ (1 - w_{0G})\,M_G \\ &\cdot\left[\frac{(1 - w_{0G})}{M_{\mathrm{m}}^{(S)}}\left(\frac{\partial \zeta_{\mathrm{m}}^{(S)}}{\partial w_{0G}}\right)_{n_{0L},\,\vartheta_\iota} + \frac{w_{0G}}{M_G}\left(\frac{\partial \zeta_G}{\partial w_{0G}}\right)_{n_{0L},\,\vartheta_\iota}\right],\end{aligned} \tag{10}$$

if any chemical reaction is excluded. $\zeta_{\mathrm{m}}^{(S)}$ is the average MMQ of the solvent defined by (I.80). The dependences of the MMQ's can according to (I.83) also be represented by power expansions, or

$$\zeta_G = \zeta_G^* + \sum_{\alpha_G=1}^{\infty}\lambda_{w\zeta G\alpha_G}\,w_{0G}^{\alpha_G}, \tag{11}$$

$$\zeta_{\mathrm{m}}^{(S)} = \zeta_{\mathrm{m}}^{(S)*} + \sum_{\alpha_G=1}^{\infty}\lambda_{w\zeta\mathrm{m}\alpha_G}\,w_{0G}^{\alpha_G}. \tag{12}$$

Introducing (11) and (12) into (10) and comparing the coefficients with those of (3) leads to

$$\mathsf{Z}_{0G}^* = \zeta_G^* + (M_G/M_{\mathrm{m}}^{(S)})\,\lambda_{w\zeta\mathrm{m}1}\,, \tag{13}$$

$$\begin{aligned}\Lambda_{w\mathsf{Z}G\alpha_G} = (\alpha_G + 1)\,\lambda_{w\zeta G\alpha_G} &- (\alpha_G - 1)\,\lambda_{w\zeta G(\alpha_G-1)} \\ &+ (M_G/M_{\mathrm{m}}^{(S)})\left[(\alpha_G + 1)\,\lambda_{w\zeta\mathrm{m}(\alpha_G+1)}\right. \\ &\left. - 2\,\alpha_G\,\lambda_{w\zeta\mathrm{m}\alpha_G} + (\alpha_G - 1)\,\lambda_{w\zeta\mathrm{m}(\alpha_G-1)}\right].\end{aligned} \tag{14}$$

From (13) and (14) one can recognize that for the determination of the limit ζ_G^* of the MMQ and of the coefficients $\lambda_{w\zeta G\alpha_G}$ the knowledge of the limit Z_{0G}^* of the PMQ and of the coefficients $\Lambda_{wZG\alpha_G}$ is not sufficient; the values of the coefficients $\lambda_{w\zeta\mathrm{m}\alpha_G}$ are also necessary. These values cannot be obtained from experimental data alone, and their determination has to be based on a molecular model. According to Eq. (11) it holds true

$$\lambda_{w\zeta G\alpha_G} = \frac{1}{\alpha_G!}\left(\frac{\partial^{\alpha_G}\zeta_G}{\partial w_{0G}^{\alpha_G}}\right)^*_{n_{0L},\vartheta_\iota}, \tag{15}$$

and a similar relation follows from (12) for the coefficients $\lambda_{w\zeta\mathrm{m}\alpha_G}$. Assuming the MMQ ζ_J ($J = G$ or m) depends on some parameters $\alpha_1, \ldots, \alpha_\varrho$ as has been discussed at (I.73), the derivative of ζ_J with respect to w_{0G} can be represented as

$$\left(\frac{\partial\zeta_J}{\partial w_{0G}}\right)_{n_{0L},\vartheta_\iota} = \sum_{\varkappa=1}^{\varrho}\left(\frac{\partial\zeta_J}{\partial\alpha_\varkappa}\right)_{\alpha_{\varkappa'},\vartheta_\iota}\left(\frac{\partial\alpha_\varkappa}{\partial w_{0G}}\right)_{n_{0L},\vartheta_\iota}, \tag{16}$$

and analogously the derivatives of higher order. If the parameter is a measurable bulk quantity, the derivative $(\partial\alpha_\varkappa/\partial w_{0G})_{n_{0L},\vartheta_\iota}$ can be estimated from experimental data. As an example we consider the case $\alpha_1 = \varepsilon_\mathrm{r}$. The generalized density P_{wV} corresponding to $\Phi = V$ (and choosing the concentration variable w_{0G}, i.e. $\Psi = m_0$) is according to (I.57) equal to ϱ^{-1}, such that from (I.63) follows similar to (6)

$$\begin{aligned}\frac{1}{\varrho} &= \frac{1}{\varrho^*} + \left(\frac{V_{0G}^*}{M_G} - \frac{1}{\varrho^*}\right) w_{0G} \\ &\quad + \frac{1}{M_G}\sum_{\alpha_G=2}^{\infty}\frac{1}{\alpha_G(\alpha_G-1)} \\ &\quad\cdot [\Lambda_{wVG1} + 2\Lambda_{wVG2} + \cdots + (\alpha_G - 1) \\ &\quad\cdot \Lambda_{wVG(\alpha_G-1)}]\, w_{0G}^{\alpha_G}. \end{aligned}\tag{17}$$

V_{0G}^* is the limit of the partial molar volume of A_G for $w_{0G} \to 0$. A set of available data $\mathrm{D_p} = \{(w_{0G}, \varrho)_\mathrm{s}\}$ allows the estimation of V_{0G}^*, the coefficients $\Lambda_{wVG\alpha_G}$ and of their standard deviations, similarly as has been discussed at (6). From (2), (6) and (17) follows

$$\left(\frac{\partial\varepsilon_\mathrm{r}}{\partial w_{0G}}\right)^*_{n_{0L},\vartheta_\iota} = \frac{\varrho^*}{M_G}[\mathsf{Z}_{0G}^* - (\varepsilon_\mathrm{r}^* - 1)\, V_{0G}^*], \tag{18}$$

where all quantities on the right-hand side can be obtained from measurements. Assuming $\zeta_\mathrm{m}^{(S)} = \zeta_\mathrm{m}^{(S)}(\varepsilon_\mathrm{r}, \alpha_2, \ldots, \alpha_\varrho)$ and introducing (15), (16) and (18) into (13) leads to

$$\begin{aligned}\zeta_G^* &= \mathsf{Z}_{0G}^* - \frac{\varrho^*}{M_\mathrm{m}^{(S)}}[\mathsf{Z}_{0G}^* - (\varepsilon_\mathrm{r}^* - 1)\, V_{0G}^*] \\ &\quad\cdot\left(\frac{\partial\zeta_\mathrm{m}^{(S)}}{\partial\varepsilon_\mathrm{r}}\right)^*_{\alpha_{\varkappa'},\vartheta_\iota} - \frac{M_G}{M_\mathrm{m}^{(S)}}\sum_{\varkappa=2}^{\varrho}\left(\frac{\partial\zeta_\mathrm{m}^{(S)}}{\partial\alpha_\varkappa}\right)^*_{\alpha_{\varkappa'},\vartheta_\iota} \\ &\quad\cdot\left(\frac{\partial\alpha_\varkappa}{\partial w_{0G}}\right)^*_{n_{0L},\vartheta_\iota}. \end{aligned}\tag{19}$$

If it is assumed that $\zeta_\mathrm{m}^{(S)}$ depends on just one parameter ε_r, but not on any other bulk quantity at least for fixed values of temperature T and pressure p, then the last term on the right-hand side of (19) vanishes. In such a case every quantity necessary for the determination of ζ_G^* can be obtained from measurements, except the derivative $(\partial\zeta_\mathrm{m}^{(S)}/\partial\varepsilon_\mathrm{r})^*_{\alpha_{\varkappa'},\vartheta_\iota}$. This quantity depends on properties of the solvent only, but not on any property of the solute. Consequently, if it is once determined, the value of the MMQ ζ_G^* of any solute molecule in this solvent can be estimated from experimental data. The further evaluation of the MMQ ζ_G^* leading to the permanent electric dipole moment of the solute A_G has to be based on the same molecular model as is used for the determination of $(\partial\zeta_\mathrm{m}^{(S)}/\partial\varepsilon_\mathrm{r})^*_{\alpha_{\varkappa'},\vartheta_\iota}$.

In the assumed molecular model, any MMQ ζ_J is according to (8) governed by the average electric dipole moment $\bar{\boldsymbol{p}}_{EJ}$ of the molecule A_J and therefore by the orientational distribution of the molecules. In a thermodynamical equilibrium state the orientational distribution is described by the Maxwell-Boltzmann distribution function, and hence (8) becomes

$$\begin{aligned}\zeta_J &= \frac{N_\mathrm{A}}{\varepsilon_0}\lim_{E_\mathrm{a}{}^2\to 0}\left(\frac{\partial}{\partial E_\mathrm{a}^2}\left\{\left[\int\exp\left\{-\frac{W_{EJ}}{kT}\right\}\mathrm{d}\tau\right]^{-1}\right.\right. \\ &\quad\left.\left.\cdot\int\tilde{\boldsymbol{E}}_\mathrm{a}\boldsymbol{p}_{EJ}\exp\left\{-\frac{W_{EJ}}{kT}\right\}\mathrm{d}\tau\right\}\right)_{n_{0I},\vartheta_\iota}. \end{aligned}\tag{20}$$

The integrals in (20) are over all orientations of the molecule. k is the Boltzmann constant and T the temperature. $\boldsymbol{p}_{EJ}$ is the average total electric dipole moment of a molecule A_J in a particular orientation relative to the external applied uniform electric field $\boldsymbol{E}_\mathrm{a}$. Assuming a total electric field $\boldsymbol{E}_{EJ}$ at the location of the molecule A_J, the quantity $\boldsymbol{p}_{EJ}$ can be represented as

$$\boldsymbol{p}_{EJ} = \boldsymbol{\mu}_{\mathrm{g}J} + \boldsymbol{\alpha}_{\mathrm{g}J}\boldsymbol{E}_{EJ}, \tag{21}$$

where $\boldsymbol{\mu}_{\mathrm{g}J}$ is the permanent electric dipole moment and $\boldsymbol{\alpha}_{\mathrm{g}J}$ is the static polarizability of an isolated molecule A_J in its state g. In W_{EJ} only that part of the potential energy of the molecule A_J has to be taken into account, which depends on the external applied field $\boldsymbol{E}_{\mathrm{a}}$. The quantities $\boldsymbol{E}_{EJ}$ and W_{EJ} can be considered as functions of some intensive quantities $\alpha_1, \ldots, \alpha_\varrho$ and these are the parameters of ζ_J, entering into (16) for example. The number and the kind of the parameters $\alpha_\varkappa$ depend on the particularly chosen molecular model; usually one of them is the relative permittivity ε_{r} of the solution, and then (19) relates the PMQ Z^*_{0G} to the MMQ ζ^*_G. In most of the commonly used models it is assumed that $\boldsymbol{E}_{EJ}$ and W_{EJ} and consequently also ζ_J at fixed values of T and p depend only on ε_{r}. This is the case already discussed after (19). In the next section the most common molecular models shall be considered; they differ from each other by different representations of the total local electric field $\boldsymbol{E}_{EJ}$. In all such models the effects due to intermolecular correlations are approximated by some average quantities or ignored altogether [2]

2. Introduction of Particular Molecular Models

2.1. The Langevin-Debye Model

In the Langevin-Debye model [3] the total electric field $\boldsymbol{E}_{EJ}$ at the location of a molecule A_J is assumed to be equal to the external applied field $\boldsymbol{E}_{\mathrm{a}}$, that is

$$(\boldsymbol{E}_{EJ})_{\mathrm{LD}} = \boldsymbol{E}_{\mathrm{a}}. \tag{22}$$

The part W_{EJ} of the potential energy dependent on $\boldsymbol{E}_{\mathrm{a}}$ then becomes

$$(W_{EJ})_{\mathrm{LD}} = -\,\tilde{\boldsymbol{\mu}}_{\mathrm{g}J}\,\boldsymbol{E}_{\mathrm{a}} - \tfrac{1}{2}\,\tilde{\boldsymbol{E}}_{\mathrm{a}}\,\boldsymbol{\alpha}_{\mathrm{g}J}\,\boldsymbol{E}_{\mathrm{a}} \tag{23}$$

and from (7), (8), (20) and (21) follows

$$(\zeta^*_J)_{\mathrm{LD}} = (\zeta_J)_{\mathrm{LD}} = \frac{N_{\mathrm{A}}}{3\,\varepsilon_0}\left[\frac{\mu^2_{\mathrm{g}J}}{k\,T} + \operatorname{tr}\boldsymbol{\alpha}_{\mathrm{g}J}\right]. \tag{24}$$

In this model the MMQ's $(\zeta_J)_{\mathrm{LD}}$ are not dependent on any parameter $\alpha_\varkappa$ but T, and for fixed T follows from (19)

$$(\zeta^*_G)_{\mathrm{LD}} = \mathsf{Z}^*_{0G}. \tag{25}$$

Since all intermolecular interactions are neglected in this model, it can be used only for the evaluation of data of gaseous phases at sufficiently low pressure. For dense phases the model clearly is incomplete.

2.2. The Lorentz Model

In the Lorentz model [3] the total electric field $\boldsymbol{E}_{EJ}$ at the location of a molecule is assumed to be

$$(\boldsymbol{E}_{EJ})_{\mathrm{L}} = \tfrac{1}{3}\,(\varepsilon_{\mathrm{r}} + 2)\,\boldsymbol{E}_{\mathrm{a}}, \tag{26}$$

and then W_{EJ} becomes

$$(W_{EJ})_{\mathrm{L}} = -\,\frac{\varepsilon_{\mathrm{r}} + 2}{3}\,\tilde{\boldsymbol{\mu}}_{\mathrm{g}J}\,\boldsymbol{E}_{\mathrm{a}} - \frac{1}{2}\left(\frac{\varepsilon_{\mathrm{r}} + 2}{3}\right)^2 \cdot \tilde{\boldsymbol{E}}_{\mathrm{a}}\,\boldsymbol{\alpha}_{\mathrm{g}J}\,\boldsymbol{E}_{\mathrm{a}}. \tag{27}$$

Considering the molecular model as an SMM, from (7), (8), (20), and (21) follows

$$(\zeta_J)_{\mathrm{L}} = \frac{(\varepsilon_{\mathrm{r}} + 2)\,N_{\mathrm{A}}}{9\,\varepsilon_0}\left[\frac{\mu^2_{\mathrm{g}J}}{k\,T} + \operatorname{tr}\boldsymbol{\alpha}_{\mathrm{g}J}\right]. \tag{28}$$

In this model the MMQ's $(\zeta_J)_{\mathrm{L}}$ depend only on ε_{r} for fixed T; consequently the last term on the right-hand side of (19) vanishes,

$$\frac{\varrho^*}{M^{(S)}_{\mathrm{m}}}\left(\frac{\partial\zeta^{(S)}_{\mathrm{m}}}{\partial\varepsilon_{\mathrm{r}}}\right)^*_{\alpha_{\varkappa'},\,\vartheta_\iota} = \frac{\varepsilon^*_{\mathrm{r}} - 1}{\varepsilon^*_{\mathrm{r}} + 2} \tag{29}$$

and

$$(\zeta^*_G)_{\mathrm{L}} = \frac{3}{\varepsilon^*_{\mathrm{r}} + 2}\,\mathsf{Z}^*_{0G} + \frac{(\varepsilon^*_{\mathrm{r}} - 1)^2}{\varepsilon^*_{\mathrm{r}} + 2}\,V^*_{0G}. \tag{30}$$

The approximation of the electric field $\boldsymbol{E}_{EJ}$ as given by (26) is not properly founded, as was already recognized by Lorentz himself. Furthermore the intermolecular interactions are not treated adequately, in particular, the effects on the average dipole moments of the solvent molecules caused by the dipole moment of a solute molecule are not taken into account*. In spite of the serious de-

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* According to this point of view one could even assume that the Lorentz model is not based on an SMM but rather on a lumped molecular model (LMM) [1], so that according to (I.90)

$$\zeta^{(S)}_{\mathrm{m}} = \mathsf{Z}^{(S)*}_{0\mathrm{m}} = (\varepsilon^*_{\mathrm{r}} - 1)\,V^{(S)*}_{0\mathrm{m}},$$

i.e. the average MMQ $\zeta^{(S)}_{\mathrm{m}}$ of the solvent is independent of the composition of the phase. In such a model (9) would have to be replaced by

$$\varepsilon_{\mathrm{r}} - 1 = \varepsilon^*_{\mathrm{r}} - 1 + (\zeta_G)_{\mathrm{LL}}\,c_{0G},$$

where

$$(\zeta_G)_{\mathrm{LL}} = (N_{\mathrm{A}}/\varepsilon_0)\lim_{E_{\mathrm{a}}{}^2 \to 0}\,(\partial\tilde{\boldsymbol{E}}_{\mathrm{a}}(\overline{\boldsymbol{p}}_{EG})_{\mathrm{LL}}/\partial E^2_{\mathrm{a}})_{n_{0I},\,\vartheta_\iota}.$$

The quantity $\overline{\boldsymbol{p}}(_{EG})_{\mathrm{LL}}$ represents the average total electric dipole moment of a solute molecule together with all contributions caused by the presence of a solute molecule A_G on the molecules in its environment. The permanent electric dipole moment corresponding to $(\overline{\boldsymbol{p}}_{EG})_{\mathrm{LL}}$, which can be obtained by the evaluation of data based on this LMM, is approximately 20% larger than the permanent electric dipole moment of the isoleted molecule A_G.

ficiencies of the Lorentz model, the data obtained from measurements of solutions in nonpolar solvents and evaluated according to the SMM lead in many cases to a value of the dipole moment of the solute molecule in rather close agreement with the value obtained by evaluating the data on the basis of a more refined model as the Onsager model, for example. This result is accidental, being caused mainly by the fact that for nonpolar solvents the value of the permittivity ($\varepsilon_r \approx 2$) is not too different from the value of the square $(n_G^0)^2$ of the refractive index of many pure solutes A_G*.

2.3. *The Extended Onsager Model*

In the extended Onsager model [3–7] the total electric field $\boldsymbol{E}_{EJ}$ at the location of a molecule A_J is represented by [8]

$$(\boldsymbol{E}_{EJ})_{\mathrm{Os}} = (\mathbf{1} - \mathbf{f}_J \boldsymbol{\alpha}_{gJ})^{-1} (\mathbf{f}_J \boldsymbol{\mu}_{gJ} + \mathbf{f}_{eJ} \boldsymbol{E}_a) + (\boldsymbol{E}_{fJ}). \tag{31}$$

The tensors $\mathbf{f}_{eJ}$ and $\mathbf{f}_J$ have to be calculated on the basis of an appropriate model. Usually it is assumed that the solvent can be represented by a homogeneous and isotropic dielectric where the molecules A_J are localized in cavities with a definite shape and size. In the most simple approximation the shape of the cavities is assumed to be spherical; then the tensor $\mathbf{f}_{eJ}$ is reduced to the scalar f_e,

$$\mathbf{f}_{eJ} = f_e \cdot \mathbf{1} = \frac{3\,\varepsilon_r}{2\,\varepsilon_r + 1} \cdot \mathbf{1}. \tag{32}$$

If furthermore the electric dipole moment of a molecule A_J is approximated either by a point dipole localized at the center of the sphere or by a homogeneous dipole density inside of the sphere, then

$$\mathbf{f}_J = f_J \cdot \mathbf{1} = \frac{2(\varepsilon_r - 1)}{4\pi\varepsilon_0\, a_{wJ}^3 (2\,\varepsilon_r + 1)} \cdot \mathbf{1}, \tag{33}$$

where a_{wJ} is the radius of the sphere (interaction radius). If the shape of the cavities is assumed to be ellipsoidal with axes $2a_{Jx}$, $2a_{Jy}$, and $2a_{Jz}$, then the principal components of the tensors become

$$f_{eJ\lambda} = f_{eJ\lambda}(\varepsilon_r) = \frac{\varepsilon_r}{\varepsilon_r - \varkappa_{J\lambda}(\varepsilon_r - 1)}, \quad \lambda = x, y, z, \tag{34}$$

and

$$f_{J\lambda} = f_{J\lambda}(\varepsilon_r) = \frac{\sigma_{J\lambda}}{a_{Jx} a_{Jy} a_{Jz}}, \tag{35}$$

where

$$\sigma_{J\lambda} = \sigma_{J\lambda}(\varepsilon_r) = \frac{3}{4\pi\varepsilon_0} \frac{\varkappa_{J\lambda}(1 - \varkappa_{J\lambda})(\varepsilon_r - 1)}{\varepsilon_r - \varkappa_{J\lambda}(\varepsilon_r - 1)} \tag{36}$$

and

$$\varkappa_{J\lambda} = \frac{a_{Jx} a_{Jy} a_{Jz}}{2} \int_0^\infty (s - a_{J\lambda}^2)^{-1} \cdot [(s + a_{Jx}^2)(s + a_{Jy}^2)(s + a_{Jz}^2)]^{-1/2}\, \mathrm{d}s. \tag{37}$$

$(\boldsymbol{E}_{fJ})$ represents the fluctuation of the electric field at the location of molecule A_J with the average $\langle \boldsymbol{E}_{fJ} \rangle = 0$, but usually a finite average of its square $\langle \tilde{\boldsymbol{E}}_{fJ} \boldsymbol{E}_{fJ} \rangle \neq 0$ [7].

With the total electric field as given by (31), the total electric dipole moment $\boldsymbol{p}_{EJ}$ of a molecule A_J becomes according to (9)

$$(\boldsymbol{p}_{EJ})_{\mathrm{Oe}} = (\mathbf{1} - \mathbf{f}_J \boldsymbol{\alpha}_{gJ})^{-1} (\boldsymbol{\mu}_{gJ} + \boldsymbol{\alpha}_{gJ} \mathbf{f}_{eJ} \boldsymbol{E}_a) + \boldsymbol{\pi}_J(\boldsymbol{E}_{fJ}), \tag{38}$$

where it has been assumed that the principal axes of the polarizability $\boldsymbol{\alpha}_{gJ}$ coincide with those of the tensors $\mathbf{f}_{eJ}$ and $\mathbf{f}_J$. $\boldsymbol{\pi}_J(\boldsymbol{E}_{fJ})$ represents the contribution to the total dipole moment caused by the fluctuation of the electric field.

In the considered model the part W_{EJ} of the potential energy dependent on $\boldsymbol{E}_a$ becomes [8]

$$(W_{EJ})_{\mathrm{Oe}} = -[\tilde{\boldsymbol{\mu}}_{gJ}(\mathbf{1} - \mathbf{f}_J \boldsymbol{\alpha}_{gJ})^{-1} + \tilde{\boldsymbol{E}}_{fJ}(\mathbf{1} - \mathbf{f}_{fJ} \boldsymbol{\alpha}_{gJ})^{-1} \boldsymbol{\alpha}_{gJ}] \cdot \mathbf{f}_{eJ} \boldsymbol{E}_a + \chi_J(\boldsymbol{E}_{fJ}). \tag{39}$$

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* Introducing the Onsager approximation, (52), and the spherical approximation for $\mathbf{f}'_G$ and $\mathbf{f}'_{eG}$ according to (32) and (33) into eqs. (51) and (47) leads to the well-known Clausius-Mossotti formula

$$[(n_G^0)^2 - 1]/[(n_G^0)^2 + 2] = N_A \operatorname{tr} \boldsymbol{\alpha}_{gG}/9\,\varepsilon_0 V_{0G}^0,$$

where n_G^0 is the refractive index and V_{0G}^0 the molar volume of the pure substance A_G. With the same approximations the total electric field $(\boldsymbol{E}_{EG})_{\mathrm{Os}}$ at the location of a solute molecule A_G represented as in (31) becomes

$$(\boldsymbol{E}_{EG})_{\mathrm{Os}} = (\boldsymbol{E}_{EG})_L\, 3\,\varepsilon_r[(n_G^0)^2 + 2]/[2\,\varepsilon_r + (n_G^0)^2](\varepsilon_r + 2)$$

plus terms independent of $\boldsymbol{E}_a$, where $(\boldsymbol{E}_{EG})_L$ is the total electric field in Lorentz' approximation, Equation (26). Hence for $(n_G^0)^2 = \varepsilon_r$ the part of the total field in Onsager's approximation dependent on $\boldsymbol{E}_a$ is equal to the total field in Lorentz' approximation, which causes the accidental agreement of the values of dipole moments obtained with both methods under that particular condition.

Using (7), (8), (20), (38) and (39) it follows for the MMQ's

$$(\zeta_J)_{0\mathrm{e}} = \frac{N_\mathrm{A}}{3\,\varepsilon_0}\,[(1/k\,T)\,\tilde{\boldsymbol{\mu}}_{\mathrm{g}J}\,\mathbf{f}_{\mathrm{e}J}(\mathbf{1}-\mathbf{f}_J\,\boldsymbol{\alpha}_{\mathrm{g}J})^{-2}\,\boldsymbol{\mu}_{\mathrm{g}J} + \mathrm{tr}\,\{\mathbf{f}_{\mathrm{e}J}(\mathbf{1}-\mathbf{f}_J\,\boldsymbol{\alpha}_{\mathrm{g}J})^{-1}\,\boldsymbol{\alpha}_{\mathrm{g}J}\}] + \eta_J(\boldsymbol{E}_{\mathrm{f}J})\,. \tag{40}$$

The quantities $\chi_J(\boldsymbol{E}_{\mathrm{f}J})$ and $\eta_J(\boldsymbol{E}_{\mathrm{f}J})$ represent the contributions to W_{EJ} and ζ_J, respectively, caused by the fluctuation of the electric field.

In this model the MMQ's $(\zeta_J)_{0\mathrm{e}}$ depend on two parameters $\alpha_\varkappa$, if the value of T is kept fixed, namely on $\alpha_1 = \varepsilon_\mathrm{r}$ and $\alpha_2 = (a_{Jx}a_{Jy}a_{Jz})^{-1}$, and therefore, the sum in the third term of the right-hand side of (19) is reduced to one term

$$(\partial\zeta_\mathrm{m}^{(S)}/\partial\alpha_2)^*_{\varepsilon_\mathrm{r},\,\vartheta_\iota}\cdot(\partial\alpha_2/\partial w_{0G})^*_{\vartheta_\iota}\,.$$

In a hard-core approximation the shape and size of the molecules are assumed fixed, then $(\partial\alpha_2/\partial w_{0G})_{\vartheta_\iota} = 0$ and the third term of (19) vanishes. According to a statistical treatment of the Onsager model [7], the a_{Jx}, a_{Jy} and a_{Jz} can be viewed as averages of the distances of closest approach of two points in the space occupied by two neighboring molecules, namely those points, where the point dipole moments, which are used for the approximate description of intermolecular interactions, have to be localized. Then the derivative $(\partial\alpha_2/\partial w_{0J})_{\vartheta_\iota}$ can be different from zero and the third term of (19) will cause a contribution to ζ_G^*. Usually this contribution is neglected or, more often, not considered at all. Some preliminary experimental investigations have shown that this term usually is small compared to the other ones but not negligible. In spite of that, we will neglect this term also, mainly because we have neither enough experimental data yet nor a good theoretical model for the calculation of $(\partial\alpha_2/\partial w_{0G})_{\vartheta_\iota}$.

The derivative $(\partial\zeta_\mathrm{m}^{(S)}/\partial\varepsilon_\mathrm{r})^*$, which is the only quantity on the right-hand side of (19) in the considered approximation that cannot be obtained from experimental data, can be calculated from (40) if the quantities $\mathbf{f}_{\mathrm{e}J}$, $\mathbf{f}_J$ and $\langle\tilde{\boldsymbol{E}}_{\mathrm{f}J}\,\boldsymbol{E}_{\mathrm{f}J}\rangle$ are represented on the basis of a suitable model [7]. The resulting expression is rather lengthy and not easily applied. For solvents, where not only the permanent dipole moment $\boldsymbol{\mu}_{\mathrm{g}J}$ is zero but also the higher multipole moments are negligibly small, as for aliphatic hydrocarbons for example, follows $\langle\tilde{\boldsymbol{E}}_{\mathrm{f}J}\,\boldsymbol{E}_{\mathrm{f}J}\rangle = 0$, and therefore the equations for ζ_J and $(\partial\zeta_J/\partial\varepsilon_\mathrm{r})_{\vartheta_\iota}$ are considerably simplified. In that case results for a substance A_G in a solvent consisting of only a single substance A_1 from (40)

$$(\zeta_G^*)_{0\mathrm{e}} = \frac{N_\mathrm{A}}{3\,\varepsilon_0}\left[\frac{1}{kT}\,\tilde{\boldsymbol{\mu}}_{\mathrm{g}G}\,\mathbf{f}^*_{\mathrm{e}G}(\mathbf{1}-\mathbf{f}^*_G\,\boldsymbol{\alpha}_{\mathrm{g}G})^{-2}\,\boldsymbol{\mu}_{\mathrm{g}G} + \mathrm{tr}\,\{\mathbf{f}^*_{\mathrm{e}G}(\mathbf{1}-\mathbf{f}^*_G\,\boldsymbol{\alpha}_{\mathrm{g}G})^{-1}\,\boldsymbol{\alpha}_{\mathrm{g}G}\}\right] \tag{41}$$

and

$$\left(\frac{\partial\zeta_1}{\partial\varepsilon_\mathrm{r}}\right)^*_{0\mathrm{e}} = \frac{N_\mathrm{A}}{3\,\varepsilon_0}\left[\mathrm{tr}\left\{(\mathbf{1}-\mathbf{f}^*_1\,\boldsymbol{\alpha}_{\mathrm{g}1})^{-1}\,\boldsymbol{\alpha}_{\mathrm{g}1}\left(\frac{\partial\mathbf{f}_{\mathrm{e}1}}{\partial\varepsilon_\mathrm{r}}\right)^*\right\} + \mathrm{tr}\left\{\mathbf{f}^*_{\mathrm{e}1}(\mathbf{1}-\mathbf{f}^*_1\,\boldsymbol{\alpha}_{\mathrm{g}1})^{-2}\,\boldsymbol{\alpha}^2_{\mathrm{g}1}\left(\frac{\partial\mathbf{f}_1}{\partial\varepsilon_\mathrm{r}}\right)^*\right\}\right]. \tag{42}$$

Assuming spherical cavities for the solvent molecules A_1 with interaction radius $a_{\mathrm{w}1}$, (31) is further simplified to

$$\frac{\varrho^*}{M_1}\left(\frac{\partial\zeta_1}{\partial\varepsilon_\mathrm{r}}\right)^*_{0\mathrm{k}} = \frac{\varepsilon^*_\mathrm{r}-1}{\varepsilon^*_\mathrm{r}(2\,\varepsilon^*_\mathrm{r}+1)} + \frac{3\,N_\mathrm{A}\,\varrho^*\,\varepsilon^*_\mathrm{r}\,\mathrm{tr}\,\{(\mathbf{1}-\mathbf{f}^*_1\,\boldsymbol{\alpha}_{\mathrm{g}1})^{-2}\,\boldsymbol{\alpha}^2_{\mathrm{g}1}\}}{2\,\pi\,\varepsilon_0\,M_1\,a^3_{\mathrm{w}1}(2\,\varepsilon^*_\mathrm{r}+1)^3}\,. \tag{43}$$

To calculate the quantity $(\partial\zeta_1/\partial\varepsilon_\mathrm{r})_{0\mathrm{k}}$ in spherical approximation according to (43) or $(\partial\zeta_1/\partial\varepsilon_\mathrm{r})_{0\mathrm{e}}$ in ellipsoidal approximation according to Eq. (42), the principal components $\alpha_{\mathrm{g}1\lambda}$ ($\lambda = x, y, z$) of the polarizability and the value of $a^3_{\mathrm{w}1}$ or the values of a_{1x}/a_{1z}, a_{1y}/a_{1z} and of $a_{1x}a_{1y}a_{1z}$, respectively, have to be known. These quantities will be estimated for a few solvents in Section 4.

3. The Evaluation of Refractometric Measurements

The relative permittivity depends on the frequency ω_E of the applied electric field, and hence also the MMQ ζ_J. If it is understood that ε_r is the static relative permittivity (for sufficiently small ω_E), then $\boldsymbol{\alpha}_{\mathrm{g}J}$ is the static polarizability in the above equations. The static polarizability can be represented by a sum of two terms

$$\boldsymbol{\alpha}_{\mathrm{g}J} = \mathbf{A}_{\mathrm{g}J} + \mathbf{B}_{\mathrm{g}J}\,, \tag{44}$$

where $\mathbf{A}_{\mathrm{g}J}$ is the electronic polarizability due to the mobility of electrons in the molecule with fixed nuclei, and $\mathbf{B}_{\mathrm{g}J}$ is the nuclear polarizability due to the mobility of the nuclei of the molecule A_J. At frequencies ω_E large compared to those of vibrational frequencies, the nuclei do not move any more and all effects are only due to the mobility of the electrons. At those frequencies (21) has to be replaced by

$$(\boldsymbol{p}_{EJ}) = (\mathbf{A}_{\mathrm{g}J})_\omega (\boldsymbol{E}_{EJ})_\omega \,, \tag{45}$$

and the MMQ $(\zeta_J)_\omega$ becomes similar to (8)

$$(\zeta_J)_\omega = \frac{N_\mathrm{A}}{\varepsilon_0} \lim_{(E_\mathrm{a}{}^2)_\omega \to 0} \left(\frac{\partial (\tilde{\boldsymbol{E}}_\mathrm{a})_\omega (\bar{\boldsymbol{p}}_J)_\omega}{\partial (E_\mathrm{a}^2)_\omega} \right)_{n_{0I},\,\vartheta_\iota} . \tag{46}$$

The relative permittivity in that frequency interval is commonly replaced by the square of the refractive index, $(\varepsilon_\mathrm{r})_\omega = n_\omega^2$, since it is usually determined by refractive measurements. Analogous to (1) and (9) it is

$$n_\omega^2 - 1 = \sum_{J=1}^{E} (\mathsf{Z}_{0J})_\omega c_{0J} = \sum_{J=1}^{K} (\zeta_J)_\omega c_J \,, \tag{47}$$

where $(\mathsf{Z}_{0J})_\omega$ is given by (I.150) with n_ω^2 substituted for ε_r. Furthermore it is usually assumed that $(\boldsymbol{E}_{EJ})_\omega$ can be represented by equations similar to $\boldsymbol{E}_{EJ}$ but ε_r replaced by n_ω^2 and all contributions due to the motions of nuclei vanishing. Since the orientational distribution of molecules is not influenced by $(\boldsymbol{E}_{EJ})_\omega$, at least as long as thermal light sources are used, the MMQ $(\zeta_J)_\omega$ becomes, if the calculation is based on the Onsager model,

$$(\zeta_J)_{\omega 0\mathrm{e}} = \frac{N_\mathrm{A}}{3\,\varepsilon_0} \cdot \mathrm{tr}\,\{(\mathfrak{f}_{\mathrm{e}J})_\omega [\mathbf{1} - (\mathfrak{f}_J)_\omega (\mathbf{A}_{\mathrm{g}J})_\omega]^{-1} (\mathbf{A}_{\mathrm{g}J})_\omega\} \,, \tag{48}$$

where

$$(\mathfrak{f}_{\mathrm{e}J})_\omega = \mathfrak{f}_{\mathrm{e}J}(n_\omega^2) \tag{49}$$

and

$$(\mathfrak{f}_J)_\omega = \mathfrak{f}_J(n_\omega^2) \,. \tag{50}$$

In the frequency interval considered $(\mathbf{A}_{\mathrm{g}J})_\omega$, $(\zeta_J)_\omega$, n_ω^2 and $(\mathsf{Z}_{0J})_\omega$ depend on ω_E. Usually it is assumed that with decreasing ω_E (but still sufficiently large compared to vibrational frequencies) the values of $(\mathbf{A}_{\mathrm{g}J})_\omega$, $(\zeta_J)_\omega$, n_ω^2 and $(\mathsf{Z}_{0J})_\omega$ become constant; these limits shall be denoted $\mathbf{A}_{\mathrm{g}J}$, ζ_J', n^2 and Z_{0J}', respectively. If a few values of n_ω^2 for different ω_E are known, the value of n^2 can be determined using an appropriate extrapolation formula [5]. With a set of available data

$$\mathrm{D_p} = \{(w_{0G}, n^2, \varrho)\}$$

estimators for the limit $Z_{0G}'^{*}$, the coefficient $\Lambda_{w\mathsf{Z}G\alpha_G}$ and their standard deviations can be obtained by multiple regression based on an equation analogous to Eq. (6) with n^2 substituted for ε_r, $\mathsf{Z}_{0G}'^{*}$ for Z_{0G}^{*} and $\Lambda_{w\mathsf{Z}'G\alpha_G}$ for $\Lambda_{w\mathsf{Z}G\alpha_G}$. The PMQ Z_{0G}' is related to the MMQ ζ_G' by an equation similar to Eq. (10) with Z_{0G}' substituted for Z_{0G}, ζ_G' for ζ_G and $\zeta_\mathrm{m}^{(S)\prime}$ for $\zeta_\mathrm{m}^{(S)}$. Their limits $\mathsf{Z}_{0G}'^{*}$ and $\zeta_G'^{*}$ are related by an equation similar to Eq. (19) with the same replacements. The further evaluation can be performed similarly as was described above; one only has to use modified equations, where n^2 is substituted for ε_r, $\mathbf{A}_{\mathrm{g}J}$ for $\boldsymbol{\alpha}_{\mathrm{g}J}$, 0 for $\boldsymbol{\mu}_{\mathrm{g}J}$, $\mathfrak{f}_{\mathrm{e}J}' = \mathfrak{f}_{\mathrm{e}J}(n^2)$ for $\mathfrak{f}_{\mathrm{e}J} = \mathfrak{f}_{\mathrm{e}J}(\varepsilon_\mathrm{r})$ and $\mathfrak{f}_J' = \mathfrak{f}_J(n^2)$ for $\mathfrak{f}_J = \mathfrak{f}_J(\varepsilon_\mathrm{r})$. As an example we consider the limit of ζ_G' based on the Onsager model in ellipsoidal approximation, which becomes according to (41)

$$(\zeta_G'^{*})_{0\mathrm{e}} = \left(\frac{N_\mathrm{A}}{3\,\varepsilon_0} \right) \mathrm{tr}\,\{\mathfrak{f}_{\mathrm{e}G}'^{*} (\mathbf{1} - \mathfrak{f}_G'^{*} \mathbf{A}_{\mathrm{g}G})^{-1} \mathbf{A}_{\mathrm{g}G}\} \,. \tag{51}$$

In the frequency interval at smaller frequencies than vibrational frequencies analogous equations relate $(\zeta_G^{*})_\omega$ to $\mathbf{B}_{\mathrm{g}G}$. But measurements in that range are seldom possible yet. To obtain $\boldsymbol{\alpha}_{\mathrm{g}G}$ from $\mathbf{A}_{\mathrm{g}G}$, one often assumes that $\mathbf{B}_{\mathrm{g}G}$ is of the order 0.05 $\mathbf{A}_{\mathrm{g}G}$ to 0.15 $\mathbf{A}_{\mathrm{g}G}$.

4. The Determination of Interaction Distances and Some Further Quantities

4.1. *Models and Relations*

The model used for the derivation of Eq. (35) usually assumes molecules in cavities with ellipsoidal or spherical shape in a homogeneous and isotropic dielectric without any molecular structure. According to this hardcore model the quantities $2a_{J\lambda}$ $(\lambda = x, y, z)$ are equal to the lengths of the axes of the ellipsoidal cavity or $a_{\mathrm{w}J}$ equal to the radius of the sphere, respectively. Based on this model, $a_{\mathrm{w}J}^3$ has been approximated by Onsager [4]

$$(a_{\mathrm{w}J}^3)_{0\mathrm{k}} = 3\,V_{0J}^{\mathrm{o}}/4\,\pi N_\mathrm{A} \,, \tag{52}$$

where V_{0J}^{o} is the molar volume of the pure substance A_J. A further simple approximation assumes the axes $2a_{J\lambda}$ equal to the corresponding lengths $(2\,a_{J\lambda})_\mathrm{l}$ of the molecule A_J, the estimation of $(2a_{J\lambda})_\mathrm{l}$ being usually based on bond lengths, bond angles and van der Waals radii of the atoms.

Equation (35) can also be derived using statistical methods from a model where all interactions are restricted to dipole-dipole interactions between point dipoles localized at some point inside the molecules

[7]. In this model $a_{J\lambda}$ is some average distance between the location of the point dipole in a molecule A_J and the location of the point dipole of a neighboring molecule A_N in a position at closest approach. According to this model one may assume $a_{J\lambda}$ equal to $(a_{J\lambda})_s$, where

$$(a_{J\lambda})_1 \lesssim (a_{J\lambda})_s \lesssim (a_{J\lambda})_1 + (a_{N\lambda})_1 \,. \tag{53}$$

If the molecule A_N owns a permanent dipole moment, the true value of $a_J = (a_{J\lambda})_s$ should be more likely nearly equal to the upper value of the relation (53), if the dipole moment of A_N is an induced moment, a_J should rather be only somewhat larger than $(a_{J\lambda})_1$.

For pure solvents A_1 the quantities $a_{1x}a_{1y}a_{1z}$ or a_{w1}^3 can be determined in favorable cases. According to the modified (1) and (51) it is for a pure solvent

$$\begin{aligned}&\operatorname{tr}\{\mathbf{f}_{e1}^{\prime *}(\mathbf{1} - \mathbf{f}_1^{\prime *}\mathbf{A}_{g1})^{-1}\mathbf{A}_{g1}\}\\ &= (n^{*2} - 1)\frac{3\,\varepsilon_0 M_1}{N_A\,\varrho^*} = \gamma_1^{\prime *} \,.\end{aligned} \tag{54}$$

For molecules, where all tensors have spheroidal symmetry $(a_{1x} = a_{1y},\ \mathsf{A}_{g1x} = \mathsf{A}_{g1y},\ f'_{e1x} = f'_{e1y},\ f'_{1x} = f'_{1y})$, one obtains from the modified (35) and (54)

$$\begin{aligned}&(a_{1x}^2 a_{1z})^2(\gamma_1^{\prime *} - 2 f_{e1x}^{\prime *}\mathsf{A}_{g1x} - f_{e1z}^{\prime *}\mathsf{A}_{g1z})\\ &+ \gamma_1^{\prime *}\sigma_{1x}^{\prime *}\sigma_{1z}^{\prime *}\mathsf{A}_{g1x}\mathsf{A}_{g1z} - a_{1x}^2 a_{1z}\\ &\cdot[\gamma_1^{\prime *}(\sigma_{1x}^{\prime *}\mathsf{A}_{g1x} + \sigma_{1z}^{\prime *}\mathsf{A}_{g1z})\\ &\quad - (2 f_{e1x}^{\prime *}\sigma_{1z}^{\prime *} + f_{e1z}^{\prime *}\sigma_{1x}^{\prime *})\mathsf{A}_{g1x}\mathsf{A}_{g1z}] = 0 \,.\end{aligned} \tag{55}$$

The values of $\sigma_{1\lambda}^{\prime *}$ and $f_{e1\lambda}^{\prime *}$ can with sufficient accuracy be calculated with estimated values of $(a_{1z})_1/(a_{1x})_1$ and determined values of n^{*2} using (34), (36) and (37). If values of A_{g1x} and A_{g1z} obtained from measurements in gaseous phases are known, (55) can be solved for $a_{1x}^2 a_{1z}$. For molecules, where the cavity is represented by arbitrary ellipsoids with axes $2\,a_{1x} \neq 2\,a_{1y} \neq 2\,a_{1z}$, a similar cubic equation leads to $a_{1x}a_{1y}a_{1z}$ using estimated values of $(a_{1z})_1/(a_{1x})_1$ and $(a_{1y})_1/(a_{1x})_1$ and determined values of n^{*2}.

For molecules, where the tensors $\mathbf{f}_{eG}$ and $\mathbf{f}_G$ have spherical symmetry, (55) is further simplified to

$$a_{1x}^3 = a_{w1}^3 = \frac{(n^{*2} - 1)^2 M_1 \operatorname{tr}\mathbf{A}_{g1}}{(n^{*2} - 1)(2\,n^{*2} + 1)\,6\,\pi\,\varepsilon_0 M_1 - n^{*2}\,6\,\pi N_A\,\varrho^* \operatorname{tr}\mathbf{A}_{g1}} \,. \tag{56}$$

In this case knowledge of $\operatorname{tr}\mathbf{A}_{g1}$, measured in the gaseous phase, and of n^*, measured in the dense phase, allows the determination of a_{1x}^3. A few further methods for the approximation of $a_{1x}a_{1y}a_{1z}$ are described previously [5, 11–15]; some of them are based on other models and cannot be applied to the extended Onsager model.

For the determination of $(\partial\zeta_1/\partial\varepsilon_r)^*$ the static polarizability $\boldsymbol{\alpha}_{g1}$ is needed according to (42). For molecules with spherical symmetric tensors the trace of the tensor $\boldsymbol{\alpha}_{g1}$ can be determined using the equation

$$\operatorname{tr}\boldsymbol{\alpha}_{g1} = \frac{6\,(\varepsilon_r^* - 1)(2\,\varepsilon_r^* + 1)\,\varepsilon_0\,\pi M_1 a_{1x}^3}{6\,\varepsilon_r^*\,\pi\,a_{1x}^3 N_A\,\varrho^* + (\varepsilon_r^* - 1)^2 M_1} \,, \tag{57}$$

which follows from (9) and (40), because for such molecules $\boldsymbol{\mu}_{g1} = 0$.

For the determination of the principal components of $\boldsymbol{\alpha}_{g1}$ of solvent molecules with spheroidal symmetry $(\alpha_{g1x} = \alpha_{g1y})$, one has to have results of further independent measurements or has to introduce some appropriate approximation. Assuming

$$\frac{\alpha_{g1x}}{\mathsf{A}_{g1x}} = \frac{\alpha_{g1z}}{\mathsf{A}_{g1z}} \,, \tag{58}$$

$\boldsymbol{\mu}_{g1} = 0$ and $\langle \tilde{\boldsymbol{E}}_{f1}\,\boldsymbol{E}_{f1}\rangle = 0$, then from (9) and (40) follows

$$\begin{aligned}&\alpha_{g1x}^2\left[\frac{\gamma_1^*\sigma_{1x}^*\sigma_{1z}^*}{a_{1x}^2 a_{1z}} + 2\,f_{e1x}^*\sigma_{1z}^* + f_{e1z}^*\sigma_{1x}^*\right]\\ &\quad\cdot\frac{\mathsf{A}_{g1z}}{a_{1x}^2 a_{1z}\,\mathsf{A}_{g1x}}\\ &\quad - \alpha_{g1x}\left[\left(\sigma_{1x}^* + \sigma_{1z}^*\frac{\mathsf{A}_{g1z}}{\mathsf{A}_{g1x}}\right)\frac{\gamma_1^*}{a_{1x}^2 a_{1z}}\right.\\ &\qquad\left. + 2\,f_{e1x}^* + f_{e1z}^*\frac{\mathsf{A}_{g1z}}{\mathsf{A}_{g1x}}\right] + \gamma_1^* = 0 \,,\end{aligned} \tag{59}$$

where γ_1^* is defined similar to $\gamma_1^{\prime *}$ by (54) but with n^{*2} replaced by ε_r^*. (59) can be solved for α_{g1x}, using (58) again leads to α_{g1z}.

4.2. Evaluation of Data for a Few Solvents

For the solvents benzene (C_6H_6), cyclohexane (C_6H_{12}), carbon disulfide (CS_2) and carbon tetrachloride (CCl_4), which own spheroidal or spherical symmetry, the optical polarizabilities $\mathbf{A}_{g1}$, the relative permittivities ε_r^*, the refractive indices n^* (determined with Na-D line) and the mass densities

Table 1. Determination of interaction distances and some further quantities for a few solvents (A_1).

	Remarks	Eqs. used	A_1				
			C_6H_6	C_6H_{12}	CS_2	CCl_4	
$M_1/\mathrm{kg \cdot mol^{-1}}$			0.078115	0.084163	0.076139	0.153823	
$(a_{1x})_1/10^{-10}\ \mathrm{m}$	1		3.5	3.6	1.6	3.4	
$(a_{1z})_1/10^{-10}\ \mathrm{m}$	1		1.7	2.35	3.15	3.4	
$(\varkappa_{1x})_1$	s	(37)	0.2307	0.2756	0.4132	1/3	
$(\varkappa_{1z})_1$	s	(37)	0.5326	0.4488	0.1736	1/3	
$\mathbf{A}_{g1x}/10^{-40}\ \mathrm{CV^{-1}\ m^2}$	2		13.69	13.00	6.164	11.68	
$\mathbf{A}_{g1z}/10^{-40}\ \mathrm{CV^{-1}\ m^2}$	2		7.065	10.29	16.85	11.68	
$\mathrm{tr}\ \mathbf{A}_{g1}/3 \cdot 10^{-40}\ \mathrm{CV^{-1}\ m^2}$	2		11.48	12.10	9.73	11.68	
T/K			298.15	298.15	293.15	293.15	298.15
$\varepsilon_r{}^*$			2.273	2.015	2.641	2.238	2.228
n^{*2}	3		2.244	2.026	2.642	2.132	2.124
$\varrho^*/\mathrm{kg \cdot m^{-3}}$			873.66	773.90	1263.05	1595.0	1584.2
$a_{1x}^2\, a_{1z}/10^{-30}\ \mathrm{m^3}$	s	(55)	26.31	36.72	21.40		
$a_{w1}^3/10^{-30}\ \mathrm{m^3}$	k	(56)	33.70	39.26	29.16	38.96	38.68
$(a_{1x})_1{}^2\,(a_{1z})_1/10^{-30}\ \mathrm{m^3}$	1		20.8	30.5	8.1	39.3	39.3
$(a_{w1}^3)_{0k}/10^{-30}\ \mathrm{m^3}$		(52)	35.44	43.10	23.9	38.23	38.49
$\boldsymbol{\alpha}_{g1x}/10^{-40}\ \mathrm{CV^{-1}\ m^2}$	s	(59)	13.91	12.90	6.16		
$\boldsymbol{\alpha}_{g1z}/10^{-40}\ \mathrm{CV^{-1}\ m^2}$	s	(58)	7.18	10.21	16.84		
$\mathrm{tr}\ \boldsymbol{\alpha}_{g1}/3 \cdot 10^{-40}\ \mathrm{CV^{-1}\ m^2}$	s	(58), (59)	11.67	12.00	9.72		
$\mathrm{tr}\ \boldsymbol{\alpha}_{g1}/3 \cdot 10^{-40}\ \mathrm{CV^{-1}\ m^2}$	k	(57)	11.67	12.00	9.73	12.46	12.46
$(\partial\zeta_1/\partial\varepsilon_r)_{0e}^*\ \varrho^*/M_1$	s	(42)	0.196	0.177	0.190		
$(\partial\zeta_1/\partial\varepsilon_r)_{0k}^*\ \varrho^*/M_1$	4, k	(43)	0.191	0.174	0.188	0.183	0.183
$(\partial\zeta_1'/\partial n^2)_{0e}^*\ \varrho^*/M_1$	5, s	(42)	0.193	0.178	0.190		
$(\partial\zeta_1'/\partial n^2)_{0k}^*\ \varrho^*/M_1$	4, 5, k	(43)	0.189	0.176	0.188	0.176	0.176

k: spherical approximation, s: spheroidal approximation. (1) According to molecular model. (2) According to [10]. (3) Determined with Na-D line ($\tilde{\nu} = 16.97 \cdot 10^5\ \mathrm{m^{-1}}$). (4) with $\mathrm{tr}\,\{(\mathbf{1} - \mathbf{f}_1\, \boldsymbol{\alpha}_{g1})^{-2}\, \boldsymbol{\alpha}_{g1}^2\} = (1 - \sigma_1{}^*\ \mathrm{tr}\ \boldsymbol{\alpha}_{g1}/3a_{w1}^3)^{-2} (\mathrm{tr}\ \boldsymbol{\alpha}_{g1})^{2/3}$. (5) with substitution of n^2 for ε_r, $\mathbf{f}_{e1}'$ for $\mathbf{f}_{e1}$ and $\mathbf{f}_1{}'$ for $\mathbf{f}_1$.

ϱ^* are known. Their values are listed in Table 1. The optical polarizabilities $\mathbf{A}_{g1}$ are usually determined with light in the visible range (or even with the Na-D line), hence it is assumed that the published values of $\mathbf{A}_{g1}$ correspond to the values of n^* and can consistently be used in Eqs. (55) and (56) for the determination of $a_{1x}^2 a_{1z}$ and $a_{1x}^3 = a_{w1}^3$, respectively. The values used for the ratios of axes $(a_{1z})_1/(a_{1x})_1$ are estimated from bond lengths, bond angles and van der Waals radii of atoms. Small errors in these ratios are unimportant because they are only used for the calculation of the functions $(\varkappa_{1\lambda})_1$, $f_{e1\lambda}'^*$ and $f_{1\lambda}'^*$, and these functions are not too strongly dependent on $(a_{1z})_1/(a_{1x})_1$. All calculations are made twice, first based on spheroidal approximation and second based on spherical approximation, and thus a comparison of different approximations is possible. The results are listed in Table 1, where also the equations used and further information are noted.

For the molecule CCl_4, whose tensors are of spherical symmetry, the values of $(a_{1x})_1^3 = (a_{1x})_1^2\,(a_{1z})_1$, a_{w1}^3 and $(a_{w1}^3)_{0k}$ are nearly equal to each other. For the molecules C_6H_6 and C_6H_{12}, where the tensors are of spheroidal symmetry, the values of $a_{1x}^2 a_{1y}$, determined in spheroidal approximation, are 20 to 30 % larger than the values of $(a_{1x})_1^2\,(a_{1z})_1$, estimated from the molecular structure. The values of a_{w1}^3, determined in spherical approximation, are 30 to 60 % larger than $(a_{1x})_1^2\,(a_{1z})_1$ and 5 to 10 % less than $(a_{w1}^3)_{0k}$ obtained from the molar volume. Much larger are the relative differences for CS_2, where the values of $a_{1x}^2 a_{1z}$, a_{w1}^3 and $(a_{w1}^3)_{0k}$ are 150 to 250 % larger than that of $(a_{1x})_1^2\,(a_{1z})_1$. A possible explanation could be sought in rather strongly excited rotational states of this molecule even in the liquid phase. Assuming the molecule CS_2 as an oblate spheroid, the principal axes are

$$2\,(a_{1x})_1 = 2\,(a_{1y})_1 = 6.3 \cdot 10^{-10}\ \mathrm{m}$$

and $2\,(a_{1z})_1 = 3.2 \cdot 10^{-10}$ m leading to

$$(a_{1x})_1^2\,(a_{1z})_1 = 15.9 \cdot 10^{-30}\ \mathrm{m^3}\,.$$

Assuming the molecule as a sphere with diameter

$2(a_{1x})_{\mathrm{l}} = 6.3 \cdot 10^{-10}\,\mathrm{m}^3$ it becomes $(a_{1x})^3{}_{\mathrm{l}} = 31.3 \cdot 10^{-30}\,\mathrm{m}^3$. The values obtained of $a_{1x}^2 a_{1z}$, $a_{\mathrm{w}1}^3$ and $(a_{\mathrm{w}1}^3)_{0\mathrm{k}}$ are in the range of these values.

The values of tr $\boldsymbol{\alpha}_{\mathrm{g}1}$ determined in spheroidal approximation agree very well with those in spherical approximation. The values of the quantity $(\partial\zeta_1/\partial\varepsilon_{\mathrm{r}})^*_{\vartheta}\,\varrho^*/M_1$, needed for the determination of the MMQ ζ_G^* of a solute molecule from experimental data according to (19), are not much different whether determined in spheroidal or in spherical approximation. An analysis of the evaluation shows that the 95% confidence limit of that quantity is less than 10% of the given values, whereas with previous methods even more than 50% could be expected [6]. A comparison of the values in spheroidal and spherical approximation shows that the latter method, which is much simpler and where only the value of the trace of the optical polarizability, tr $\mathbf{A}_{\mathrm{g}1}$, has to be known, is usually quite sufficient for the determination of $(\partial\zeta_1/\partial\varepsilon_{\mathrm{r}})^*_{\vartheta}\,\varrho^*/M_1$.

5. The Determination of Dipole Moments and Polarizabilities

5.1. The Investigated Systems and the Measuring Devices

Investigated were solutions of 4,4'-(bis-dimethylamino)-benzophenone (Michler's ketone) ($C_{17}H_{20}N_2O$) (I), 2,7-(bis-dimethylamino)-9,9-dimethylanthracene-10-on ($C_{20}H_{24}N_2O$) (II), 2,7-(bis-dimethylamino)-fluorene-9-on ($C_{17}H_{18}N_2O$) (III), 1-dimethylamino-4-nitro-benzene ($C_8H_{10}N_2O_2$) (IV), 1-dimethylamino-2,6-dicyano-4-methyl-benzene ($C_{11}H_{11}N_3$) (V), 4-amino-diphenyl ($C_{12}H_{13}N$) (VI), vanadyl-octaethyl-porphine ($C_{20}H_{12}N_4VO$) (VII) and cobalt(II)-octaethyl-porphin ($C_{20}H_{12}N_4Co$) (VIII). The small solubility of these substances (except VI) in cyclohexane or other aliphatic hydrocarbons prohibits the determination of the necessary data with sufficient accuracy in such solutions. Therefore benzene was chosen as solvent except for VI, where cyclohexane was used. All measurements were made at the temperature $T = (298.15 \pm 0.01)$ K.

The substances and the solvents were purified as usual. The permittivity measurements were performed with a radio-frequency bridge DM 01 (WTW, Weilheim), the refractometric measurements with a Pulfrich refractometer (Bellingham and Stanley, London) using the Na-D line

$$(\tilde{\nu} = 16.97 \cdot 10^5\,\mathrm{m}^{-1})$$

or a differential refractometer [10])

$$(\tilde{\nu} = 18.08 \cdot 10^5\,\mathrm{m}^{-1}),$$

and all density measurements with the device DMA 02 (Paar KG, Graz).

5.2. Evaluation and Results

For solutions of the substances I to V, VII and VIII in benzene and VI in cyclohexane, the mass densities ϱ, the refractive indices n and the relative permittivities ε_{r} have been determined for various values of the mass fraction w_{0G}. Multiple regression analysis of the sets of available data

$$\mathrm{D_p} = \{(w_{0G}, \varrho, n^2, \varepsilon_{\mathrm{r}})\}$$

according to (17) or (6), respectively, has shown that in all cases only the constant term and the term linear in w_{0G} is significantly different from zero. Linear regression leads to estimators for the PMQ's V_{0G}^*, $\mathsf{Z}_{0G}'^*$ and Z_{0G}^*; their values are listed in Table 2. The errors given are always 95% confidence limits based on the Student's *t*-distribution ($\pm t_{1-\alpha} s$, where s is the standard deviation of the mean and $\alpha = 0.025$). Regression including the term square in w_{0G} leads to estimators for the coefficients Λ_{wVG1}, $\Lambda_{w\mathsf{Z}'G1}$, and $\Lambda_{w\mathsf{Z}G1}$, their values in Table 2 show that they are not significantly different from zero.

The determination of the MMQ's $\zeta_G'^*$ and ζ_G^* corresponding to the PMQ's $\mathsf{Z}_{0G}'^*$ and Z_{0G}^* has to be based on some molecular model as has been discussed in Section 1. In the Lorentz model (SMM) the MMQ's $(\zeta_1')_{\mathrm{L}}$ and $(\zeta_1)_{\mathrm{L}}$ depend only on n^2 and ε_{r}, respectively; hence $(\zeta_G'^*)_{\mathrm{L}}$ and $(\zeta_G^*)_{\mathrm{L}}$ follow from (30). In the Onsager model the MMQ's $(\zeta_1')_{0\mathrm{e}}$ and $(\zeta_1)_{0\mathrm{e}}$ can depend furthermore on $\alpha_2 = (a_{1x} a_{1y} a_{1z})^{-1}$. Since a function describing the dependence of α_2 on the composition of the solution is not known yet, this term has to be neglected, but fortunately one may assume that its contribution to $(\zeta_G'^*)_{0\mathrm{e}}$ or $(\zeta_G^*)_{0\mathrm{e}}$ is small. In this approximation (19) leads to $(\zeta_G'^*)_{0\mathrm{e}}$ and $(\zeta_G^*)_{0\mathrm{e}}$, where the values of

$$(\partial\zeta_1'/\partial n^2)^*_{0\mathrm{e}}\,\varrho^*/M_1 \quad \text{and} \quad (\partial\zeta_1/\partial\varepsilon_{\mathrm{r}})^*_{0\mathrm{e}}\,\varrho^*/M_1,$$

as given in Table 1, have to be used.

From the value of $(\zeta_G'^*)_{\mathrm{L}}$ the trace of the polarizability $\mathrm{tr}(\mathbf{A}_{\mathrm{g}G})_{\mathrm{L}}$ in Lorentz' approximation can be obtained with (28) easily, and assuming $(\boldsymbol{\alpha}_{\mathrm{g}G})_{\mathrm{L}} = (\mathbf{A}_{\mathrm{g}G})_{\mathrm{L}}$ from $(\zeta_G^*)_{\mathrm{L}}$ also the magnitude of $(\boldsymbol{\mu}_{\mathrm{g}G})_{\mathrm{L}}$. For the further evaluation based on the Onsager model,

Table 2. Determination of electric dipole moments and polarizabilities from measurements of solutions at $T = 298.15$ K.

	Remarks	Eqs. used	A_G	
			I	II
Solvent	1		B	B
$M_G/\mathrm{kg\cdot mol^{-1}}$			0.26836	0.30843
$w_{0G}/10^{-4}$	2		$4-83$	$3-13$
$V^*_{0G}/10^{-6}\ \mathrm{m^3\,mol^{-1}}$	3	(17)	233.4 ± 5.4	273 ± 15
$(\Lambda_{wVG1}/2M_G)/10^{-2}\ \mathrm{kg^{-1}\,m^3}$	4	(17)	0.5 ± 0.6	7 ± 10
$\mathbf{Z}'^*_{0G}/10^{-4}\ \mathrm{m^3\,mol^{-1}}$	3, 5, 6	(6)	4.81 ± 0.11	5.63 ± 0.31
$(\Lambda_{w\mathbf{Z}'G1}/2M_G)/10^{-2}\ \mathrm{kg^{-1}\,m^3}$	4, 5, 6	(6)	0.8 ± 2	-13 ± 20
$\mathbf{Z}^*_{0G}/10^{-4}\ \mathrm{m^3\,mol^{-1}}$	3	(6)	39.33 ± 0.67	49.2 ± 1.5
$(\Lambda_{w\mathbf{Z}G1}/2M_G)/10^{-2}\ \mathrm{kg^{-1}\,m^3}$	4	(6)	35 ± 80	200 ± 240
$(\zeta'^*_G)_\mathrm{L}/10^{-4}\ \mathrm{m^3\,mol^{-1}}$	5, 6	(30)	4.251 ± 0.080	4.98 ± 0.23
$(\zeta'^*_G)_\mathrm{0e}/10^{-4}\ \mathrm{m^3\,mol^{-1}}$	5, 6, 7	(19)	4.442 ± 0.090	5.20 ± 0.25
$(\zeta^*_G)_\mathrm{L}/10^{-4}\ \mathrm{m^3\,mol^{-1}}$		(30)	28.50 ± 0.47	35.6 ± 1.1
$(\zeta^*_G)_\mathrm{0e}/10^{-4}\ \mathrm{m^3\,mol^{-1}}$	7	(19)	32.20 ± 0.54	40.3 ± 1.2
$[(a_{Gx})_\mathrm{l};\ (a_{Gy})_\mathrm{l};\ (a_{Gz})_\mathrm{l}]/10^{-10}$ m	8		3.0; 8.0; 4.5	2.2; 8.0; 4.5
$[(a_{Gx})_\mathrm{s};\ (a_{Gy})_\mathrm{s};\ (a_{Gz})_\mathrm{s}]/10^{-10}$ m	9		2.3; 8.4; 4.9	2.6; 8.4; 4.9
$(a_{Gx})_\mathrm{s}(a_{Gy})_\mathrm{s}(a_{Gz})_\mathrm{s}/10^{-30}\ \mathrm{m^3}$			94.7	107
$(a^3_{wG})_\mathrm{0k}/10^{-30}\ \mathrm{m^3}$	10	(52)	92.5 ± 2.1	108.2 ± 5.9
$(\varkappa_{Gx})_\mathrm{s};\ (\varkappa_{Gy})_\mathrm{s};\ (\varkappa_{Gz})_\mathrm{s}$		(37)	0.606; 0.129; 0.265	0.574; 0.140; 0.286
$[(\mathbf{A}_{\mathrm{g}Gx})_\mathrm{b};\ (\mathbf{A}_{\mathrm{g}Gy})_\mathrm{b};\ (\mathbf{A}_{\mathrm{g}Gz})_\mathrm{b}]/10^{-40}\ \mathrm{CV^{-1}\,m^2}$	11		33.2; 39.7; 41.1	34.9; 51.6; 45.9
$\mathrm{tr}\,(\mathbf{A}_{\mathrm{g}G})_\mathrm{b}/3\cdot 10^{-40}\ \mathrm{CV^{-1}\,m^2}$	11		38.0	45.3
$\mathrm{tr}\,(\mathbf{A}_{\mathrm{g}G})_\mathrm{L}/3\cdot 10^{-40}\ \mathrm{CV^{-1}\,m^2}$	5, 6	(28)	44.18 ± 0.83	51.8 ± 2.4
$\mathrm{tr}\,(\mathbf{A}_{\mathrm{g}G})_\mathrm{0k}/3\cdot 10^{-40}\ \mathrm{CV^{-1}\,m^2}$	6, k	(51)	43.31 ± 0.88	50.4 ± 2.4
$[(\mathbf{A}_{\mathrm{g}Gx})_\mathrm{0e};\ (\mathbf{A}_{\mathrm{g}Gy})_\mathrm{0e};\ (\mathbf{A}_{\mathrm{g}Gz})_\mathrm{0e}]/10^{-40}\ \mathrm{CV^{-1}\,m^2}$	6, e	(51)	38.5; 46.0; 47.6	40.1; 59.3; 56.9
$\mathrm{tr}\,(\mathbf{A}_{\mathrm{g}G})_\mathrm{0e}/3\cdot 10^{-40}\ \mathrm{CV^{-1}\,m^2}$	6, e	(51)	44.1	52.1
$(\mu_{\mathrm{g}G})_\mathrm{L}/10^{-30}$ Cm	6	(28)	17.57 ± 0.29	19.74 ± 0.61
$(\mu_{\mathrm{g}G})_\mathrm{0k}/10^{-30}$ Cm	6, k	(41)	16.4 ± 1.2	18.3 ± 1.4
$(\mu_{\mathrm{g}G})_\mathrm{0e}/10^{-30}$ Cm	6, e	(41)	17.1 ± 1.5	18.6 ± 1.7

k: spherical approximation, e: ellipsoidal approximation. 1. B = benzene, CH = cyclohexane, $n^{*2}(\mathrm{B}) = 2.255$ and $n^{*2}(\mathrm{CH}) = 2.037$ (at $\tilde{\nu} = 18.08 \cdot 10^5\ \mathrm{m^{-1}}$); the other data for the solvents are given in Table 1. 2. Investigated interval of mass fraction w_{0G}. 3. By linear regression according to given equation (including only the term linear in w_{0G}). 4. By regression including the term square in w_{0G}. 5. Given equation with n^2 substituted for ε_r, zero for $\mu_{\mathrm{g}G}$ and other dashed quantities for the unmarked ones. 6. For substances I to IV, VII and VIII at $\tilde{\nu} = 16.97 \cdot 10^5\ \mathrm{m^{-1}}$, for V and VI at $\tilde{\nu} = 18.08 \cdot 10^5\ \mathrm{m^{-1}}$.

some values for the lengths $a_{G\lambda}$ ($\lambda = x, y, z$) of the axes have to be introduced. The values $(a_{G\lambda})_\mathrm{l}$ listed in Table 1 are estimated from known molecular data (bond length, bond angles and van der Waals radii of atoms), and they are the lengths of the smallest box into which the molecule could be introduced. As was discussed in Sect. 4.1, one may assume that the effective values $(a_{G\lambda})_\mathrm{s}$, which should be used for the calculation of the $\varkappa$'s and the $f_{\mathrm{g}\lambda}$'s are somewhat larger than $(a_{G\lambda})_\mathrm{l}$. With (52) modified by substitution of V^*_{0G} for V°_{0G} values $(a^3_{wG})_\mathrm{0k}$ can be determined as given in Table 2. For the molecules II and IV to VIII these values are not much different from the values of the product $(a_{Gx})_\mathrm{s}(a_{Gy})_\mathrm{s}(a_{Gz})_\mathrm{s}$, where $(a_{G\lambda})_\mathrm{s} = (a_{G\lambda})_\mathrm{l} + 4 \cdot 10^{-11}$ m. For the molecules I and III one can assume that the contribution of solvent molecules at distances smaller than the lengths of the axes (corresponding to the length of the box) is not negligible and hence these lengths should be somewhat reduced. This assumption is particularly justified for the case of molecule I, where the calculation of $(a_{G\lambda})_\mathrm{s}$ is based on the results of electro-optical absorption measurements. It will be shown [16] that one of the benzene rings of molecule I is coplanar to the plane of the CO group, the other one is (nearly) perpendicular to it. Therefore the value $(a_{Gx})_\mathrm{s}$ of molecule I (and III) is chosen equal to the value $(a_{Gx})_\mathrm{s}$ of molecule IV. With such reasonable and rather small adjustments, values of $(a_{G\lambda})_\mathrm{s}$ can be obtained, so that $(a_{Gx})_\mathrm{s}(a_{Gy})_\mathrm{s}(a_{Gz})_\mathrm{s}$ is in rather good agreement with $(a^3_{wG})_\mathrm{0k}$ for all solutes. These values are listed in Table 2, and all further calculations are based upon them. Their relative errors are assumed as 0.3. The

A_G					
III	IV	V	VI	VII	VIII
B	B	B	CH	B	B
0.26635	0.16618	0.18523	0.16923	0.59972	0.59171
2 − 8	8 − 46	2 − 27	7 − 88	0.2 − 1.1	0.1 −0.5
230 ± 11	132.0 ± 5.0	176.8 ± 5.6	161.1 ± 5.1	507 ± 24	452 ± 30
8 ± 12	−2 ± 1.5	0 ± 4	0 ± 2	−2 ± 5	−20 ± 40
5.12 ± 0.80	2.50 ± 0.08	2.356 ± 0.011	2.027 ± 0.014	7.94 ± 0.36	7.2 ± 1.2
60 ± 120	−1.6 ± 2.4	−1 ± 10	0 ± 0.3	−5 ± 30	0 ± 40
66.7 ± 2.1	64.2 ± 1.2	10.48 ± 0.56	5.77 ± 0.34	18.9 ± 1.2	6.3 ± 1.8
300 ± 250	−20 ± 50	60 ± 60	18 ± 20	0 ± 120	0 ± 100
4.46 ± 0.57	2.249 ± 0.059	2.316 ± 0.022	1.935 ± 0.017	7.46 ± 0.27	6.77 ± 0.86
4.68 ± 0.65	2.334 ± 0.066	2.330 ± 0.016	1.964 ± 0.015	7.62 ± 0.30	6.93 ± 0.97
47.7 ± 1.5	45.60 ± 0.85	8.03 ± 0.39	4.72 ± 0.25	15.21 ± 0.85	6.1 ± 1.3
54.2 ± 1.7	51.98 ± 0.96	8.87 ± 0.45	5.04 ± 0.28	16.48 ± 0.97	6.2 ± 1.4
2.0; 7.4; 5.1	1.9; 3.1; 5.6	1.9; 5.0; 4.9	3.1; 3.1; 5.0	7.3; 7.3; 3.0	7.3; 7.3; 2.7
2.3; 7.8; 5.1	2.3; 3.5; 6.0	2.3; 5.4; 5.3	3.4; 3.5; 5.4	7.7; 7.7; 3.4	7.7; 7.7; 3.1
91.5	48.3	65.8	64.3	201.6	183.8
91.3 ± 4.4	52.3 ± 2.0	70.1 ± 2.2	63.9 ± 2.0	201 ± 10	179 ± 12
0.606; 0.143; 0.252	0.514; 0.319; 0.167	0.569; 0.213; 0.218	0.395; 0.382; 0.224	0.219; 0.219; 0.562	0.207; 0.207; 0.586
26.7; 43.9; 42.5	9.9; 16.2; 22.4	19.9; 29.5; 27.2	26.3; 25.7; 34.5	86.4; 86.4; 52.8	86.4; 86.4; 52.8
37.7	16.2	25.5	28.8	75.2	75.2
46.4 ± 5.9	23.37 ± 0.61	24.00 ± 0.23	21.14 ± 0.19	77.5 ± 2.8	70.4 ± 8.9
44.9 ± 6.2	22.63 ± 0.64	23.77 ± 0.16	21.09 ± 0.16	77.1 ± 3.0	70.1 ± 9.8
33.4; 54.9; 53.1	14.5; 23.8; 32.9	19.0; 28.2; 26.0	19.2; 18.8; 25.9	91.7; 91.7; 56.0	83.7; 83.7; 51.2
47.1	23.7	24.4	21.3	79.8	72.9
23.46 ± 0.74	23.50 ± 0.44	8.53 ± 0.41	6.16 ± 0.33	9.91 ± 0.55	0 ± 1.0
21.6 ± 1.7	21.8 ± 1.6	8.36 ± 0.52	6.01 ± 0.37	9.60 ± 0.76	0 ± 2.6
22.4 ± 2.0	24.1 ± 1.9	9.02 ± 0.70	6.29 ± 0.60	9.6 ± 1.0	0 ± 2.6

7. With $\zeta_{\mathrm{m}}^{(S)} = \zeta_1$ and considering ζ_1 dependent only on ε_{r} (for fixed values of T and p), i.e. neglect of the third term on the right-hand side of (19). 8. From bond length, bond angles and van der Waals radii of atoms (maximal length for molecule in a box). 9. Values of length of axes used for further calculations. 10. Equation (52) but V_{0G}^{*} substituted for V_{0G}^{o}. 11. Estimated from group and bond polarizabilities.

lack of a better estimation of $(a_{G\lambda})_{\mathrm{s}}$ causes the essential contribution to the error of the dipole moments $(\mu_{gG})_{0\mathrm{k}}$ and $(\mu_{gG})_{0\mathrm{e}}$ obtained with the Onsager model in spherical and ellipsoidal approximation, respectively.

For the Onsager model in spherical approximation the tensors $\mathbf{f}_{eG}$ and $\mathbf{f}_G$ in (40) are reduced to scalars, which can be calculated according to (32) and (33), respectively, and analogously $\mathbf{f}'_{eG}$ and $\mathbf{f}'_G$. With these values and $(\zeta_G'^{*})_{0\mathrm{e}}$ (51) can be solved for $\mathrm{tr}(\mathbf{A}_{gG})_{0\mathrm{k}}$. Assuming again $\mathrm{tr}(\boldsymbol{\alpha}_{gG})_{0\mathrm{k}} = \mathrm{tr}(\mathbf{A}_{gG})_{0\mathrm{k}}$, (40) with the given value $(\zeta_G^{*})_{0\mathrm{k}}$ leads to $(\mu_{gG})_{0\mathrm{k}}$, if the term dependent $\langle \tilde{\boldsymbol{E}}_{\mathrm{f}G} \boldsymbol{E}_{\mathrm{f}G} \rangle$ is neglected, i.e. if (41) is used.

To evaluate the data in ellipsoidal approximation, one has to assume that the principal axes of the polarizability tensor coincide with those assumed for the cavity, which is at least for Michler's ketone (I) not necessarily the case. Furthermore, the principal components of the polarizability are needed, but usually they are unknown. To surmount this difficulty, the principal components of the polarizability are calculated using known group and bond polarizabilities transformed to the directions of the principal axes. The values of $(\mathsf{A}_{gG\lambda})_{\mathrm{b}}$ estimated with this method are listed in Table 2. Assuming $(\mathsf{A}_{gG\lambda})_{0\mathrm{e}} = u_G (\mathsf{A}_{gG\lambda})_{\mathrm{b}}$ and using the values of $(\varkappa_{G\lambda})_{\mathrm{s}}$ and (34) to (37) and (51), the value of the quantity u_G can be determined from $(\zeta_G'^{*})_{0\mathrm{e}}$ and therefore also the components $(\mathsf{A}_{gG\lambda})_{0\mathrm{e}}$ of the polarizability (Table 2). Assuming as above $(\alpha_{gG\lambda})_{0\mathrm{e}} = (\mathsf{A}_{gG\lambda})_{0\mathrm{e}}$, (41) with the value of $(\zeta_G^{*})_{0\mathrm{e}}$ leads to the magnitude $(\mu_{gG})_{0\mathrm{e}}$ of the permanent electric dipole moment of the isolated molecule in ellipsoidal approximation.

6. Discussion

From the considered molecular models the theoretically best founded one is the extended Onsager model in ellipsoidal approximation. The confidence limit of the values of the permanent dipole moment $(\mu_{gG})_{0e}$ estimated with this model is of the order of 10%. This magnitude is caused mostly by the imperfect knowledge of the interaction axes $a_{G\lambda}$ of the ellipsoidal cavity assumed for the solute molecule. A further improvement of the data necessitates an independent determination of those quantities, which may be possible, for example, from the solvent dependence of electrochromic measurements as has been shown by Kriebel and Labhart [15]. The values of $(\mu_{gG})_{0k}$ obtained with the Onsager model based on spherical cavities, are usually somewhat smaller than $(\mu_{gG})_{0e}$. The values of $(\mu_{gG})_{L}$ obtained with the Lorentz model (SMM) can be larger or smaller than those of $(\mu_{gG})_{0e}$, but both values agree within their limits of error. The limitation of the accuracy is usually not due to inaccurate measurements but due to the imperfection of the molecular models used for the evaluation of the macroscopic quantities and due to the poor knowledge of the lengths $a_{G\lambda}$ of the axes of the interaction ellipsoid.

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[1] W. Liptay, D. Wehning, J. Becker, and T. Rehm, Z. Naturforsch. **37a**, 1369 (1982); paper I.

[2] D. E. Sullivan and J. M. Deutch, J. Chem. Phys. **64**, 3870 (1976).

[3] W. F. Brown, in: Handbuch der Physik, Vol. 17, Ed. S. Flügge, Springer-Verlag, Berlin 1956.

[4] L. Onsager, J. Amer. Chem. Soc. **58**, 1486 (1937).

[5] C. J. F. Böttcher and P. Bordewijk, Theory of Electric Polarization, Elsevier, Amsterdam 1973, p. 1978.

[6] W. Liptay, B. Dumbacher, and H. Weisenberger, Z. Naturforsch. **23a**, 1601 (1968).

[7] W. Liptay and G. Walz, Z. Naturforsch. **26a**, 2007 (1971).

[8] W. Liptay, Ber. Bunsenges. physik. Chem. **80**, 207 (1976).

[9] O. Bodmann, Chem. Ing. Technik **7**, 468 (1957).

[10] H. A. Stuart, Molekülstruktur, Springer, Berlin 1967.

[11] C. J. F. Böttcher, Physica **9**, 945 (1942).

[12] Th. G. Scholte and F. C. DeVos, Rec. Trav. Chim. **72**, 625 (1953).

[13] V. A. Gorodyskii, L. F. Kardashina, and N. G. Bakshiev, Russ. J. Phys. Chem. **49**, 641 (1975).

[14] R. Diguet, P. Bonnet, and J. Barriol, J. Chim. Physique **76**, 15 (1979).

[15] A. Kriebel and H. Labhart, Z. physik. Chem. NF **92**, 247 (1974).

[16] W. Liptay and J. Becker, Z. Naturforsch. **37a**, 1409 (1982); paper III.