

A statistical theory of the Kerr effect in multi-component systems

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By statistical mechanics, the molecular Kerr constant K_m of multi-component systems is obtained in the form

$$K_m = \sum_i x_i K_m^{(i)} + \sum_{ij} x_i x_j K_m^{(ij)} + \sum_{ijk} x_i x_j x_k K_m^{(ijk)} + \dots,$$

where the first term represents the additivity rule, while the subsequent terms account for deviations therefrom. The quantities $K_m^{(ij)}$ and $K_m^{(ijk)}$ responsible for these deviations are expressed by means of the correlation functions $g_{ij}^{(2)}$ and $g_{ijk}^{(3)}$ for pairs and triples of molecules of various species, respectively. The equation as derived for K_m is applied to a two-component system and discussed for some special cases.

1. INTRODUCTION

By the additivity rule, the molecular Kerr constant K_m of the system as a whole coincides with the sum of the molecular Kerr constants for the respective components of the system. For a system of two components, the additivity rule yields

$$K_m = x_1 K_m^{(1)} + x_2 K_m^{(2)}, \quad (1)$$

wherein x_1 and x_2 are the molar fractions of the components, whilst $K_m^{(1)}$ and $K_m^{(2)}$ are the molecular Kerr constants of the solvent and solute, respectively.

In order that K_m of the solution shall be a strictly additive quantity, it is required that the constants $K_m^{(1)}$ and $K_m^{(2)}$ of the components shall not depend on the concentration. The fact is, however, that experimental work by Briegleb [1], Stuart and Volkman [2], Otterbein [3] and others has irrefutably shown that even in dilute solutions the additivity rule (1) is not fulfilled. Particularly large deviations from the rule (1) in the entire concentration range occur for solutions of dipolar liquids in non-dipolar solvents [4, 5], whereas in solutions of non-dipolar liquids alone the deviations are less [6].

Although the classical theory of Kerr's effect as given by Langevin [7] and Born [8] and developed by Buckingham and Pople [9] is conceived for one-component gases, it can be applied formally in accordance with the rule of equation (1) to a mixture of perfect gases and to infinitely dilute solutions.

The earliest theories of the Kerr effect for very concentrated solutions are due to Friedrich [4] and Piekara [10], and are based on the model of dipole coupling proposed by Debye [11] and Fowler [12]; they deal with the case of a solvent consisting of spherical molecules and those of the solute possessing axial

symmetry and a large dipole moment (e.g. nitrobenzene)†. Buckingham applied his statistical-mechanical theory of the Kerr effect [13] to a dilute solution with no interaction between the solute molecules [14]. Le Fevre and Le Fevre [15] investigated a number of dilute solutions and proposed a convenient method of extrapolating the constant $K_m^{(2)}$ to infinite dilution, utilizing the values of $K_{m\infty}^{(2)}$ thus obtained for determining the anisotropy of the molecules of the solutes.

The present investigation is aimed at deriving a statistical-molecular theory of Kerr's effect for multi-component systems. This theory leads to an expression for the molecular Kerr constant K_m of a multi-component system in the form

$$K_m = \sum_i x_i K_m^{(i)} + \sum_{ij} x_i x_j K_m^{(ij)} + \sum_{ijk} x_i x_j x_k K_m^{(ijk)} + \dots \quad (2)$$

The constants $K_m^{(i)}$ contain only the respective molecular parameters determining the electro-optical properties of the isolated molecules of the various components. As the constants $K_m^{(i)}$ depend neither on the concentration nor on the density of the system, the first term in equation (2) expresses additivity of the molecular Kerr constant of the multi-component system. The remaining quantities $K_m^{(ij)}$ and $K_m^{(ijk)}$ are expressed respectively by the correlation functions $g_{ij}^{(2)}$ and $g_{ijk}^{(3)}$ and are non-zero only for a system presenting non-zero interactions between the molecules. In this way, the second, third and higher terms in equation (2) constitute a measure of the deviation from the additivity rule of K_m . The expressions for $K_m^{(i)}$, $K_m^{(ij)}$ and $K_m^{(ijk)}$ derived in the present investigation are valid for molecules of arbitrary symmetry, the quantities $K_m^{(ij)}$ and $K_m^{(ijk)}$ being applicable to all cases irrespective of the nature of the intermolecular forces active in the system, provided these correlations are accessible to treatment by statistical methods.

In particular, equation (2) is applied to the case of a two-component system and discussed for some special examples. Also, the procedure whereby the theory can be easily applied for explaining experimental results is expounded. Moreover, it is proved that certain angular correlation parameters inherent in $K_m^{(ij)}$ appear also in the theories of molecular light scattering, of the Cotton-Mouton effect, and of the molecular polarization of multi-component systems. Clearly this circumstance is of great importance for comparing the results yielded by the theory and those obtained experimentally.

2. MOLECULAR KERR CONSTANT FOR A MULTI-COMPONENT SYSTEM

Let us consider an isotropic medium in the shape of a large spherical sample of refractive index n and dielectric permittivity ϵ . At its centre we shall consider a smaller sphere of macroscopic dimensions and volume V (molar volume). Assuming E to be the field strength of a d.c. homogeneous electric field in the absence of the sample, the mean field strength E_S of the macroscopic electric field existing within the sphere is, by classical electrostatics,

$$E_S = \frac{3}{\epsilon + 2} E. \quad (3)$$

† In Debye's model, the dipolar molecule of the liquid is immersed in the electric field of a great assemblage of neighbouring molecules in almost regular array, resembling that of a crystal. Consequently, the molecule is not free to rotate, but oscillates to a smaller or larger extent about an axis determining the direction of the molecular field. Piekara [10] showed that, in order to interpret satisfactorily the experimental data, it is in some cases not enough to take into account the Debye-Fowler coupling only, but that the coupling between a given dipole and its nearest dipolar neighbour or next dipoles of its nearest neighbourhood has to be distinguished and dealt with specifically.

For the case considered, the molecular Kerr constant K_m is defined thus:

$$K_m = \frac{6n^2}{(n^2+2)^2} \left(\frac{E_S}{E} \right)^2 VK, \quad (4)$$

with

$$K = \frac{n_{\parallel} - n_{\perp}}{n} \frac{1}{E_S^2} \quad (5)$$

being the Kerr constant as determined experimentally; n_{\parallel} and n_{\perp} are the refractive indices for light oscillations parallel and perpendicular to the direction of the electric vector E_S , respectively.

By equations (3) and (4) we have the relation

$$K_m = \frac{54n^2}{(n^2+2)^2(\epsilon+2)^2} VK, \quad (6)$$

whence the molecular Kerr constant can be computed numerically, provided n , ϵ , V and K are known experimentally.

On the other hand, the classical theory of electric birefringence based on electrodynamics and statistical mechanics yields the following equation for the molecular Kerr constant (the method by which it is derived is to be found in references [9, 13, 16]):

$$K_m = \frac{\pi}{45} \epsilon_{\alpha\beta:\gamma\delta} \left\langle \frac{\partial^3 \mathbf{M}_{\alpha}}{\partial \mathcal{E}_{\beta} \partial E_{\gamma} \partial E_{\delta}} - \frac{1}{kT} \left(2 \frac{\partial^2 \mathbf{M}_{\alpha}}{\partial \mathcal{E}_{\beta} \partial E_{\gamma}} \frac{\partial U}{\partial E_{\delta}} + \frac{\partial \mathbf{M}_{\alpha}}{\partial \mathcal{E}_{\beta}} \frac{\partial^2 U}{\partial E_{\gamma} \partial E_{\delta}} \right) + \frac{1}{k^2 T^2} \frac{\partial \mathbf{M}_{\alpha}}{\partial \mathcal{E}_{\beta}} \frac{\partial U}{\partial E_{\gamma}} \frac{\partial U}{\partial E_{\delta}} \right\rangle, \quad (7)$$

with the notation

$$\epsilon_{\alpha\beta:\gamma\delta} = -2\delta_{\alpha\beta}\delta_{\gamma\delta} + 3\delta_{\alpha\gamma}\delta_{\beta\delta} + 3\delta_{\alpha\delta}\delta_{\beta\gamma}; \quad (8)$$

$\delta_{\alpha\beta}$ is the unit tensor; the summation indices α , β , γ , δ take the values 1, 2, 3 corresponding to the components along the axes X_1 , X_2 , X_3 of the reference system.

In equation (7), \mathbf{M}_{α} is the α -component of the oscillating dipole moment induced in the sphere of volume V by the electric field \mathcal{E} of a light wave, in the presence of the d.c. electric field E producing the birefringence of the medium. For the system at configuration τ , we can write $\mathbf{M}_{\alpha} = \mathbf{M}_{\alpha}(\tau, \mathbf{E}, \mathcal{E})$. Also, $U = U(\tau, \mathbf{E})$ is the total potential energy of the system at configuration τ in the electric field E . The brackets $\langle \rangle$ in equation (7) denote statistical averaging at zero external fields ($\mathcal{E} = E = 0$):

$$\langle \Phi \rangle = \frac{\int \Phi(\tau, 0) \exp \left\{ -\frac{U(\tau, 0)}{kT} \right\} d\tau}{\int \exp \left\{ -\frac{U(\tau, 0)}{kT} \right\} d\tau}. \quad (9)$$

As the general equation (7) is valid for an arbitrary isotropic medium, it can be applied to a multi-component system. Assuming $N = \sum_i N_i$ molecules of different species (N_i is the number of molecules of species i) to be present within the sphere of volume V , we can write

$$\mathbf{M}_{\alpha} = \sum_i \sum_{p=1}^{N_i} \mathbf{m}_{\alpha}^{(p, i)}, \quad (10)$$

where $\mathbf{m}_{\alpha}^{(p, i)}$ is the α -component of the oscillating dipole moment induced in the p th molecule of species i by the electric field \mathcal{E} of the light wave, at $E \neq 0$.

Considering the sphere of volume V not as part of the large spherical sample, but *in vacuo*, we can write by analogy to equation (10)

$$\frac{\partial U}{\partial E_\beta} = - \sum_j \sum_{q=1}^{Nj} m_\beta^{(q,j)}; \quad (11)$$

here, $m_\beta^{(q,j)}$ is the β -component of the total electric dipole moment of the q th molecule of species j immersed in the sphere acted upon by the electric field \mathbf{E} .

On substituting (10) and (11) in the general equation (7), we have the following expression for the molecular Kerr constant of a multi-component system :

$$K_m = \frac{\pi}{45} \epsilon_{\alpha\beta:\gamma\delta} \left\langle \sum_i \sum_{p=1}^{Ni} \frac{\partial^3 \mathbf{m}_\alpha^{(p,i)}}{\partial \mathcal{E}_\beta \partial E_\gamma \partial E_\delta} + \frac{1}{kT} \sum_{ij} \sum_{p=1}^{Ni} \sum_{q=1}^{Nj} \left(2 \frac{\partial^2 \mathbf{m}_\alpha^{(p,i)}}{\partial \mathcal{E}_\beta \partial E_\gamma} m_\delta^{(q,j)} \right. \right. \\ \left. \left. + \frac{\partial \mathbf{m}_\alpha^{(p,i)}}{\partial \mathcal{E}_\beta} \frac{\partial m_\gamma^{(q,j)}}{\partial E_\delta} \right) + \frac{1}{k^2 T^2} \sum_{ijk} \sum_{p=1}^{Ni} \sum_{q=1}^{Nj} \sum_{r=1}^{Nk} \frac{\partial \mathbf{m}_\alpha^{(p,i)}}{\partial \mathcal{E}_\beta} m_\gamma^{(q,j)} m^{(r,k)} \right\rangle. \quad (12)$$

3. MOLECULAR KERR CONSTANT EXPRESSED BY MEANS OF THE CORRELATION FUNCTIONS

We assume the molecules contained in the sphere to be dipolar, anisotropically polarizable and hyperpolarizable. Neglecting for simplicity the effect of molecular fields on the optical and electrical properties of the molecules, we can express the dipole moment components $\mathbf{m}_\alpha^{(p,i)}$ and $m_\alpha^{(p,i)}$ as follows :

$$\mathbf{m}_\alpha^{(p,i)} = \{ \alpha_{\alpha\beta}^{(p,i)} + \beta_{\alpha\beta:\gamma}^{(p,i)} E_\gamma + \frac{1}{2} \gamma_{\alpha\beta:\gamma\delta}^{(p,i)} E_\gamma E_\delta + \dots \} \mathcal{E}_\beta, \quad (13)$$

$$m_\alpha^{(p,i)} = \mu_\alpha^{(p,i)} + a_{\alpha\beta}^{(p,i)} E_\beta + \dots, \quad (14)$$

$\mu_\alpha^{(p,i)}$ denoting the α -component of the permanent electric dipole moment of the p th isolated molecule of species i , and $\alpha_{\alpha\beta}^{(p,i)}$, $a_{\alpha\beta}^{(p,i)}$ the components of its optical and electrical polarizability tensors, respectively. The tensors $\beta_{\alpha\beta:\gamma}^{(p,i)}$ and $\gamma_{\alpha\beta:\gamma\delta}^{(p,i)}$ account for the change in the optical polarizability of the molecule due to the external electric field \mathbf{E} , and are termed the hyperpolarizability tensors [9].

By (13) and (14), equation (12) yields K_m as expressed by means of molecular parameters, in the form†

$$K_m = \frac{\pi}{45} \epsilon_{\alpha\beta:\gamma\delta} \left\langle \sum_i \sum_{p=1}^{Ni} \gamma_{\alpha\beta:\gamma\delta}^{(p,i)} + \frac{1}{kT} \sum_{ij} \sum_{p=1}^{Ni} \sum_{q=1}^{Nj} (2\beta_{\alpha\beta:\gamma}^{(p,i)} \mu_\delta^{(q,j)} \right. \\ \left. + \alpha_{\alpha\beta}^{(p,i)} a_{\gamma\delta}^{(q,j)} + \frac{1}{k^2 T^2} \sum_{ijk} \sum_{p=1}^{Ni} \sum_{q=1}^{Nj} \sum_{r=1}^{Nk} \alpha_{\alpha\beta}^{(p,i)} \mu_\gamma^{(q,j)} \mu_\delta^{(r,k)} \right\rangle. \quad (15)$$

By classical statistical mechanics [19], equation (15) can be put in the form of equation (2), wherein the quantities $K_m^{(i)}$, $K_m^{(ij)}$ and $K_m^{(ijk)}$ are given as follows :

$$K_m^{(i)} = \frac{\pi\rho}{45} \int \epsilon_{\alpha\beta:\gamma\delta} \left\{ \gamma_{\alpha\beta:\gamma\delta}^{(p,i)} + \frac{1}{kT} (2\beta_{\alpha\beta:\gamma}^{(p,i)} \mu_\delta^{(p,i)} + \alpha_{\alpha\beta}^{(p,i)} a_{\gamma\delta}^{(p,i)}) \right. \\ \left. + \frac{1}{k^2 T^2} \alpha_{\alpha\beta}^{(p,i)} \mu_\gamma^{(p,i)} \mu_\delta^{(p,i)} \right\} g_i^{(1)}(\tau_p) d\tau_p, \quad (16)$$

† When proceeding from equation (12) to the specialized equation (15), in order to avoid further complicating the already considerably involved problem, we have neglected the long-range dipolar correlations accessible to a 'continuum model' treatment and taken into account *inter alia* by Buckingham and Raab [17] in their computation of K_m for pure polar liquids.

$$\begin{aligned}
 K_m^{(ij)} = \frac{\pi\rho^2}{90kT} \int \int \epsilon_{\alpha\beta:\gamma\delta} & \left\{ 2\beta_{\alpha\beta:\gamma}^{(p,i)} \mu_\delta^{(q,j)} + 2\beta_{\alpha\beta:\gamma}^{(q,j)} \mu_\delta^{(p,i)} + \alpha_{\alpha\beta}^{(p,i)} a_{\gamma\delta}^{(q,j)} \right. \\
 & + \alpha_{\alpha\beta}^{(q,j)} a_{\gamma\delta}^{(p,i)} + \frac{1}{kT} (2\alpha_{\alpha\beta}^{(p,i)} \mu_\gamma^{(p,i)} \mu_\delta^{(q,j)} + 2\alpha_{\alpha\beta}^{(q,j)} \mu_\gamma^{(q,j)} \mu_\delta^{(p,i)} \\
 & \left. + \alpha_{\alpha\beta}^{(p,i)} \mu_\gamma^{(q,j)} \mu_\delta^{(p,i)} + \alpha_{\alpha\beta}^{(q,j)} \mu_\gamma^{(p,i)} \mu_\delta^{(q,j)}) \right\} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (17)
 \end{aligned}$$

$$\begin{aligned}
 K_m^{(ijk)} = \frac{\pi\rho^3}{135k^2T^2} \int \int \int \epsilon_{\alpha\beta:\gamma\delta} & (\alpha_{\alpha\beta}^{(p,i)} \mu_\gamma^{(q,j)} \mu_\delta^{(r,k)} + \alpha_{\alpha\beta}^{(q,j)} \mu_\gamma^{(r,k)} \mu_\delta^{(p,i)} \\
 & + \alpha_{\alpha\beta}^{(r,k)} \mu_\gamma^{(p,i)} \mu_\delta^{(q,j)}) g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r) d\tau_p d\tau_q d\tau_r, \quad (18)
 \end{aligned}$$

where $\rho = N/V$ is the mean number density of the molecules. In the above expressions, $g_i^{(1)}(\tau_p)$ is the ordinary correlation function for the molecules of species i , $g_{ij}^{(2)}(\tau_p, \tau_q)$ the binary correlation function for those of species i and j , $g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r)$ the ternary correlation function for those of species i, j and k , and so forth. The configurational variables τ_p comprise the variables \mathbf{r}_p and ω_p determining the position and orientation of the p th molecule, respectively. Thus, the integral

$$\int d\tau_p = \int_V d\mathbf{r}_p \int_\Omega d\omega_p = V\Omega$$

extends over all possible configurations of the p th molecule.

In particular, if the system presents no interaction between the molecules, the latter assume all possible configurations in volume V with equal probability, i.e. the correlation functions then fulfil the condition

$$\Omega^1 g_i^{(1)}(\tau_p) = \Omega^2 g_{ij}^{(2)}(\tau_p, \tau_q) = \Omega^3 g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r) = \dots = 1. \quad (19)$$

It is readily verified that this condition always implies the vanishing of the quantities $K_m^{(ij)}$ and $K_m^{(ijk)}$ as given by equations (17) and (18), so that equation (2) reduces to

$$K_m = \sum_i x_i K_m^{(i)}, \quad (20)$$

where

$$\begin{aligned}
 K_m^{(i)} = \frac{2\pi N}{45} & \left\{ 3\gamma_{\alpha\beta:\alpha\beta}^{(i)} - \gamma_{\alpha\alpha:\beta\beta}^{(i)} + \frac{2}{kT} (3\beta_{\alpha\beta:\alpha}^{(i)} \mu_\beta^{(i)} - \beta_{\alpha\alpha:\beta}^{(i)} \mu_\beta^{(i)}) \right. \\
 & \left. + \frac{1}{kT} (3\alpha_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(i)}) + \frac{1}{k^2 T^2} (3\alpha_{\alpha\beta}^{(i)} \mu_\alpha^{(i)} \mu_\beta^{(i)} - \alpha_{\alpha\alpha}^{(i)} \mu_\beta^{(i)} \mu_\beta^{(i)}) \right\} \quad (21)
 \end{aligned}$$

is the molecular Kerr constant of the i th component of the ideal mixture. On dropping the index i , equation (21) becomes analogous to the one derived by Born [8] and Buckingham and Pople [9] for a perfect gas.

Hence K_m is seen to be a strictly additive quantity only for the case of a mixture of perfect gases, i.e. if the configuration of a molecule does not statistically depend on the configuration of the remaining molecules of the system. In dense multi-component systems, as a result of correlations between the molecules of a given component or between those of different components of the system, the quantities $K_m^{(ij)}$ and $K_m^{(ijk)}$ are non-zero, and K_m does not fulfil the additivity rule†.

† Were we to take into account in (13) and (14) the effect of the molecular electric field strength F due to the surrounding molecules, as well as the external fields \mathcal{E} and E , additional terms would appear in the expressions (17) and (18), and moreover in equation (2) new terms in higher powers of the molar fractions would arise. We refrain from considering this case here, as it leads to results that contain higher powers of the polarizabilities α and a and are of a highly involved form. This effect is discussed by Mazur and Postma [18] for systems consisting of identical non-polar molecules.

If the system consists of non-dipolar components only, the quantities $K_m^{(ijk)}$ vanish in our approximation of the theory, and $K_m^{(i)}$, $K_m^{(ij)}$ can be expressed as follows:

$$K_m^{(i)} = \frac{2\pi N}{45} \left\{ 3\gamma_{\alpha\beta:\alpha\beta}^{(i)} - \gamma_{\alpha\alpha:\beta\beta}^{(i)} + \frac{1}{kT} \sum_{s,t=1}^3 \alpha_s^{(i)} a_t^{(i)} (3\delta_{st} - 1) \right\}, \quad (22)$$

$$K_m^{(ij)} = \frac{\pi\rho^2}{45kT} \sum_{s,t=1}^3 (\alpha_s^{(i)} a_t^{(j)} + \alpha_s^{(j)} a_t^{(i)}) \iint (3 \cos^2 \theta_{st}^{(pq)} - 1) g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (23)$$

with $\theta_{st}^{(pq)}$ denoting the angle subtended by the s th principle axis of the p th molecule and the t th principal axis of the q th molecule, α_s and a_t being the polarizabilities in the directions of these axes.

If the molecules of all components are in general dipolar, presenting in particular symmetry with respect to the 3-axis, the expressions of equations (17), (18) and (21) reduce to

$$K_m^{(i)} = \frac{4\pi N}{45} \left\{ 5\gamma_i + \frac{6}{kT} \beta_i \kappa_{\beta i} \mu_i + \frac{3}{kT} \alpha_i \kappa_{\alpha i} \left(3a_i \kappa_{\alpha i} + \frac{\mu_i^2}{kT} \right) \right\}, \quad (24)$$

$$K_m^{(ij)} = \frac{4\pi N}{15kT} \left\{ \left[\beta_i \kappa_{\beta i} \mu_j + \beta_j \kappa_{\beta j} \mu_i + \frac{1}{kT} (\alpha_i \kappa_{\alpha i} + \alpha_j \kappa_{\alpha j}) \mu_i \mu_j \right] J_{ij}^I \right. \\ \left. + \frac{1}{2} \left[\alpha_i \kappa_{\alpha i} \left(3a_j \kappa_{\alpha j} + \frac{\mu_j^2}{kT} \right) + \alpha_j \kappa_{\alpha j} \left(3a_i \kappa_{\alpha i} + \frac{\mu_i^2}{kT} \right) \right] J_{ij}^{II} \right\}, \quad (25)$$

$$K_m^{(ijk)} = \frac{4\pi N}{45k^2 T^2} (\alpha_i \kappa_{\alpha i} \mu_j \mu_k + \alpha_j \kappa_{\alpha j} \mu_k \mu_i + \alpha_k \kappa_{\alpha k} \mu_i \mu_j) J_{ijk}^{III}. \quad (26)$$

Here, the following integral parameters have been introduced:

$$J_{ij}^I = \frac{\rho}{V} \iint \cos \theta^{(pq)} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (27)$$

$$J_{ij}^{II} = \frac{\rho}{2V} \iint (3 \cos^2 \theta^{(pq)} - 1) g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (28)$$

$$J_{ijk}^{III} = \frac{\rho^2}{2V} \iint \int (3 \cos \theta^{(pq)} \cos \theta^{(pr)} - \cos \theta^{(qr)}) g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r) d\tau_p d\tau_q d\tau_r, \quad (29)$$

accounting for the angular correlations of the molecules, $\theta^{(pq)}$ being the angle between the axes of symmetry of the p th and q th molecules of the respective components. For a system consisting of non-interacting molecules, the correlation functions are determined by equation (19), and the parameters (27)–(29) obviously vanish.

The quantities

$$\kappa_{\alpha i} = \frac{\alpha_3^{(i)} - \alpha_1^{(i)}}{3\alpha_i}, \quad \kappa_{\alpha i} = \frac{a_3^{(i)} - a_1^{(i)}}{3a_i}, \quad \kappa_{\beta i} = \frac{\beta_{33:3}^{(i)} - \beta_{11:3}^{(i)}}{3\beta_i} \quad (30)$$

determine the anisotropies of the respective polarizabilities and hyperpolarizabilities of the isolated molecule of species i , and

$$\alpha_i = \frac{1}{3}(\alpha_3^{(i)} + 2\alpha_1^{(i)}), \quad a_i = \frac{1}{3}(a_3^{(i)} + 2a_1^{(i)}), \\ \beta_i = \frac{1}{3}(\beta_{33:3}^{(i)} + 2\beta_{11:3}^{(i)}), \quad \gamma_i = \frac{1}{10}(3\gamma_{\alpha\beta:\alpha\beta}^{(i)} - \gamma_{\alpha\alpha:\beta\beta}^{(i)}) \simeq \frac{1}{5}\gamma_{\alpha\alpha\beta\beta}^{(i)} \quad (31)$$

its mean electro-optical properties.

4. APPLICATION TO A TWO-COMPONENT SYSTEM

In the case of a two-component system, equation (2) becomes

$$K_m = x_1 K_m^{(1)} + x_2 K_m^{(2)} + x_1^2 K_m^{(11)} + 2x_1 x_2 K_m^{(12)} + x_2^2 K_m^{(22)} \\ + x_1^3 K_m^{(111)} + 3x_1^2 x_2 K_m^{(112)} + 3x_1 x_2^2 K_m^{(122)} + x_2^3 K_m^{(222)} + \dots \quad (32)$$

Let us consider a mixture of two non-dipolar components, the molecules of component 1 being spherical, and those of component 2 anisotropic. In this case equation (32) assumes the simpler form of

$$K_m = x_1 K_m^{(1)} + x_2 K_m^{(2)} + x_2^2 K_m^{(22)} + \dots, \quad (33)$$

where, by (22) and (23), we have

$$K_m^{(1)} = \frac{4\pi}{9} N \gamma_1, \quad (34)$$

$$K_m^{(2)} = \frac{2\pi N}{45} \left\{ 2\gamma_{\alpha\alpha\beta\beta}^{(2)} + \frac{1}{kT} \sum_{s,t=1}^3 \alpha_s^{(2)} a_t^{(2)} (3\delta_{st} - 1) \right\}, \quad (35)$$

$$K_m^{(22)} = \frac{2\pi\rho^2}{45kT} \sum_{s,t=1}^3 \alpha_s^{(2)} a_t^{(2)} \int \int (3 \cos \theta_{st}^{(pq)} - 1) \delta_{22}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q. \quad (36)$$

If, in particular, the molecules of component 2 possess axial symmetry, the expressions (35) and (36) reduce to

$$K_m^{(2)} = \frac{4\pi N}{45} \left\{ 5\gamma_2 + \frac{9}{kT} \alpha_2 \kappa_{\alpha 2} a_2 \kappa_{\alpha 2} \right\}, \quad (37)$$

$$K_m^{(22)} = \frac{4\pi N}{5kT} \alpha_2 \kappa_{\alpha 2} a_2 \kappa_{\alpha 2} J_{22}^{\text{II}}, \quad (38)$$

wherein the angular correlation parameter J_{22}^{II} is given by equation (28) for $i=j=2$.

Let us now assume that the molecules of component 1 are spherical as before, but that those of component 2 are dipolar and anisotropically polarizable. Equation (2) now reduces to the form

$$K_m = x_1 K_m^{(1)} + x_2 K_m^{(2)} + x_2^2 K_m^{(22)} + x_2^3 K_m^{(222)} + \dots, \quad (39)$$

with $K_m^{(1)}$ determined by (34). The quantities $K_m^{(2)}$, $K_m^{(22)}$, $K_m^{(222)}$ for the dipolar component, in accordance with equations (24), (25) and (26) which hold for axially symmetric molecules, assume the form

$$K_m^{(2)} = \frac{4\pi N}{45} \left\{ 5\gamma_2 + \frac{6}{kT} \beta_2 \kappa_{\beta 2} \mu_2 + \frac{3}{kT} \alpha_2 \kappa_{\alpha 2} \left(3a_2 \kappa_{\alpha 2} + \frac{\mu_2^2}{kT} \right) \right\}, \quad (40)$$

$$K_m^{(22)} = \frac{4\pi N}{15kT} \left\{ 2 \left(\beta_2 \kappa_{\beta 2} \mu_2 + \frac{1}{kT} \alpha_2 \kappa_{\alpha 2} \mu_2^2 \right) J_{22}^{\text{I}} \right. \\ \left. + \alpha_2 \kappa_{\alpha 2} \left(3a_2 \kappa_{\alpha 2} + \frac{\mu_2^2}{kT} \left(J_{22}^{\text{II}} \right) \right) \right\}, \quad (41)$$

$$K_m^{(222)} = \frac{4\pi N}{15k^2 T^2} \alpha_2 \kappa_{\alpha 2} \mu_2^2 J_{222}^{\text{III}}, \quad (42)$$

with the angular correlation parameters J_{22}^{I} , J_{22}^{II} and J_{222}^{III} derived from equations (27)–(29) for $i=j=k=2$.

In the case of a mixture consisting of a non-dipolar component having anisotropic molecules and an arbitrary dipolar component the quantities $K_m^{(111)}$

and $K_m^{(112)}$ in equation (32) vanish. If the molecules of either component possess the axial symmetry, equations (24)–(26) yield

$$K_m^{(1)} = \frac{4\pi N}{45} \left\{ 5\gamma_1 + \frac{9}{kT} \alpha_1 \kappa_{\alpha 1} a_1 \kappa_{\alpha 1} \right\}, \quad (43)$$

$$K_m^{(11)} = \frac{4\pi N}{5kT} \alpha_1 \kappa_{\alpha 1} a_1 \kappa_{\alpha 1} J_{11}^{\text{II}}, \quad (44)$$

$$K_m^{(12)} = \frac{2\pi N}{15kT} \left\{ \alpha_1 \kappa_{\alpha 1} \left(3a_2 \kappa_{\alpha 2} + \frac{\mu_2^2}{kT} \right) + 3\alpha_2 \kappa_{\alpha 2} a_1 \kappa_{\alpha 1} \right\} J_{12}^{\text{II}}, \quad (45)$$

$$K_m^{(122)} = \frac{4\pi N}{45k^2 T^2} \alpha_1 \kappa_{\alpha 1} \mu_2^2 J_{122}^{\text{II}}, \quad (46)$$

with the quantities $K_m^{(2)}$, $K_m^{(22)}$ and $K_m^{(222)}$ determined by equations (40)–(42).

On the other hand, in the case of a mixture of two components, K_m can be expanded in a series in powers of x ($=x_2$, the molar fraction of the solute)

$$K_m = A_0 + A_1 x + A_2 x^2 + A_3 x^3 + \dots = \sum_{n=0}^{\infty} A_n x^n; \quad (47)$$

the coefficients

$$A_n = \frac{1}{n!} \left(\frac{\partial^n K_m}{\partial x^n} \right)_{x=0} \quad (48)$$

of the expansion can be determined directly from the experimental data. The coefficient A_0 accounts for the properties of the solvent only, whereas the others, $A_1, A_2, A_3 \dots$ characterize the properties of the solutions investigated.

Utilizing equation (32), we can express the phenomenological coefficients (48) as follows:

$$\begin{aligned} A_0 &= (f_0)_{x=0}, \\ A_1 &= \left(\frac{\partial f_0}{\partial x} + f_1 \right)_{x=0}, \\ A_2 &= \left(\frac{1}{2} \frac{\partial^2 f_0}{\partial x^2} + \frac{\partial f_1}{\partial x} + f_2 \right)_{x=0}, \\ A_3 &= \left(\frac{1}{6} \frac{\partial^3 f_0}{\partial x^3} + \frac{1}{2} \frac{\partial^2 f_1}{\partial x^2} + \frac{\partial f_2}{\partial x} + f_3 \right)_{x=0}, \dots, \end{aligned} \quad (49)$$

wherein the quantities

$$\begin{aligned} f_0 &= K_m^{(1)} + K_m^{(11)} + K_m^{(111)} + \dots, \\ f_1 &= -K_m^{(1)} + K_m^{(2)} + 2(K_m^{(12)} - K_m^{(11)}) + 3(K_m^{(112)} - K_m^{(111)}) + \dots, \\ f_2 &= K_m^{(11)} - 2K_m^{(12)} + K_m^{(22)} + 3(K_m^{(111)} - 2K_m^{(112)} + K_m^{(122)}) + \dots, \\ f_3 &= -K_m^{(111)} + 3K_m^{(112)} - 3K_m^{(122)} + K_m^{(222)} - \dots, \dots, \end{aligned} \quad (50)$$

are in general functions of the molar fraction x .

If K_m is given by equation (39), the coefficients (49) assume the following simpler form:

$$\begin{aligned} A_0 &= K_m^{(1)}, & A_1 &= K_m^{(2)} - K_m^{(1)}, \\ A_2 &= \{K_m^{(22)}\}_{x=0}, & A_3 &= \left\{ \frac{\partial K_m^{(22)}}{\partial x} + K_m^{(222)} \right\}_{x=0}. \end{aligned} \quad (51)$$

In this special case, A_0 is seen to be expressed directly by the constant $K_m^{(1)}$ given by equation (34) and defining the hyperpolarizability of the isolated molecule

of the solvent only. The coefficient A_1 is expressed by the difference between the constants $K_m^{(2)}$ and $K_m^{(1)}$ determining the optical electrical properties of the isolated molecules of the solute and solvent, respectively. Only beginning with A_2 , A_3 the coefficients are expressed by means of the quantities $K_m^{(22)}$ and $K_m^{(222)}$ which are responsible for the angular correlations of the dipolar molecules of the solute.

From the foregoing it is obvious that the phenomenological coefficients A_0 , A_1 , A_2 , A_3 , . . . can always be expressed by means of the theoretically computed quantities $K_m^{(i)}$, $K_m^{(ij)}$ and $K_m^{(ijk)}$ which, thus, become endowed with a well-defined physical meaning in each case.

5. RELATED PHENOMENA IN MULTI-COMPONENT SYSTEMS

For dense systems, the correlation functions $g_{ij}^{(2)}$ and $g_{ijk}^{(3)}$ have to be known explicitly in each separate case in order that the angular correlation parameters J_{ij}^I , J_{ij}^{II} and J_{ijk}^{III} defined by equations (27)–(29) can be computed numerically†. These difficulties can be circumvented in certain cases by means of additional information derived from the study of other phenomena. Magnetic birefringence is one of them, in considering which the molecular Cotton–Mouton constant can be represented as follows [20]:

$$C_m = \frac{6n^2}{(n^2 + 2)^2} VC = \sum_i x_i C_m^{(i)} + \sum_{ij} x_i x_j C_m^{(ij)} + \dots, \quad (52)$$

wherein

$$C_m^{(i)} = \frac{2\pi N}{45} \left\{ 3\eta_{\alpha\beta:\alpha\beta}^{(i)} - \eta_{\alpha\alpha:\beta\beta}^{(i)} + \frac{1}{kT} (3\alpha_{\alpha\beta}^{(i)}\chi_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)}\chi_{\beta\beta}^{(i)}) \right\} \quad (53)$$

is a constant determining the properties of the isolated i th component of the system, $\chi_{\alpha\beta}^{(i)}$ being the magnetic polarizability tensor of the molecule of species i , and $\eta_{\alpha\beta:\gamma\delta}^{(i)}$ the tensor of its optico-magnetic hyperpolarizability‡.

The quantity $C_m^{(ij)}$ in equation (52) is determined as follows:

$$C_m^{(ij)} = \frac{\pi\rho^2}{45kT} \sum_{s,t=1}^3 (\alpha_s^{(i)}\chi_t^{(j)} + \alpha_s^{(j)}\chi_t^{(i)}) \iint (3 \cos^2 \theta_{st}^{(pq)} - 1) g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q. \quad (54)$$

On inspection, equations (23) and (54) are seen to contain identical integral parameters

$$J_{st}^{(ij)} = \frac{\rho}{2V} \iint (3 \cos^2 \theta_{st}^{(pq)} - 1) g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \quad (55)$$

responsible for the angular molecular interaction in the system.

Another phenomenon whose constants contain the parameters (55) is that of molecular light scattering. Here, the quantity F_{anis} referred to as the molecular constant of anisotropic light scattering, which is related to the measurable quantities D , the degree of depolarization of scattered light and R , the Rayleigh ratio by the formula

$$F_{\text{anis}} = \frac{135\lambda^4 V}{16\pi^4(n^2 + 2)^2} \frac{RD}{1 + D}, \quad (56)$$

† Such computations can be carried out for various molecular models in the case of imperfect gas mixtures, when the quantities $K_m^{(ij)}$ and $K_m^{(ijk)}$ can be expanded in series of virial coefficients according to the method proposed by Buckingham [13] for K_m of imperfect one-component gases.

‡ Equation (52), together with (53) and (54), reduces to the result of Born [8] and Buckingham and Pople [21] in the case of a one-component gas and to Buckingham and Pople's formula [21] in that of pure liquids consisting of axially symmetric molecules.

is expressed as follows [22]:

$$F_{\text{anis}} = \sum_i x_i F_{\text{anis}}^{(i)} + \sum_{ij} x_i x_j F_{\text{anis}}^{(ij)} + \dots, \quad (57)$$

where

$$F_{\text{anis}}^{(i)} = \frac{1}{2} N (3\alpha_{\alpha\beta}^{(i)}\alpha_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)}\alpha_{\beta\beta}^{(i)}) = \frac{1}{2} N \sum_{s,t=1}^3 \alpha_s^{(i)}\alpha_t^{(i)} (3\delta_{st} - 1), \quad (58)$$

$$F_{\text{anis}}^{(ij)} = \frac{1}{2} \rho^2 \sum_{s,t=1}^3 \alpha_s^{(i)}\alpha_t^{(j)} \int \int (3\cos^2 \theta_{st}^{(pq)} - 1) g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q. \quad (59)$$

From equations (23), (54) and (59), the integral parameters (55) can be determined in principle from the experimental data.

In the case of dipolar systems, by equation (25), the quantities $K_m^{(ij)}$ contain the parameter (27) (in addition to the parameter (28), which is a special case of (55) for axially symmetric molecules). The parameter J_{ij}^I appears neither in the theory of the Cotton–Mouton effect nor in that of light scattering; however, it appears in the theory of the electric polarization of dipolar systems. In the approximation of the present investigation, the molecular polarization can be written thus [23]

$$P_m = \frac{\epsilon - 1}{\epsilon + 2} V = \sum_i x_i P_m^{(i)} + \sum_{ij} x_i x_j P_m^{(ij)} + \dots, \quad (60)$$

wherein

$$P_m^{(i)} = \frac{4\pi}{3} N \left(a_i + \frac{\mu_i^2}{3kT} \right), \quad (61)$$

denotes the molecular polarization of the i th component of a perfect dipolar mixture, as resulting from Debye's theory [24], whilst the quantities

$$P_m^{(ij)} = \frac{4\pi\rho^2}{9kT} \mu_i \mu_j \int \int \cos \theta^{(pq)} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q = \frac{4\pi N}{9kT} \mu_i \mu_j J_{ij}^I \quad (62)$$

determine the first deviation from additivity of P_m due to angular correlations of the dipolar molecules in the system†.

All this proves that, with some approximation, the cumbersome work inherent in the numerical evaluation of the angular correlation parameters J_{ij}^I and J_{ij}^{II} of equations (27) and (28) can be avoided in the case of solutions of dipolar substances also, by recurring to other phenomena such as polarization, light scattering, or the Cotton–Mouton effect.

6. CONCLUSIONS

Thus, the present investigation proves the molecular Kerr constant K_m to be a strictly additive quantity only in the case of a mixture of perfect gases. In dense multi-component systems (e.g. real gases or solutions of liquids) presenting correlations of the molecules of different components of the system in addition to correlations of molecules of the same species, the constant K_m fails to fulfil the additivity rule. Consequently, investigation on the deviations of K_m from additivity can provide direct information on the nature of the intermolecular

† It is noteworthy that, on applying (27) (or (62)) to the case of a one-component dipolar liquid, the parameter appearing in Kirkwood's theory of the dielectric permittivity [25] is obtained immediately. Similarly, from (28) in the case of a one-component liquid we can obtain the parameter derived by Anselm [26] within the framework of the theory of Kerr's effect for a non-dipolar liquid and of molecular light scattering in liquids (see also refs. [13, 16, 22, 27]).

forces acting between the molecules of different components, and on the structure of the systems considered. This is all the more feasible as analogous data can be derived from investigations of molecular light scattering, electric polarization, and magnetic birefringence, where the additivity rule is generally not fulfilled either.

An advantage of the theory proposed can be said to consist in the fact that the molecular interactions are described by means of the respective correlation functions, without recurring to the assumption of a special molecular model. Moreover, the theory is relatively simple, at the same time being of a high degree of generality, and with suitable assumptions is applicable to each special case.

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