Orientation Polarization. II. Quadrupolar Systems

by

S. KIELICH

Presented by W. RUBINOWICZ on July 10, 1962

Classical statistical theory leads to an expression for the molecular orientation polarization P_m^0 of a system containing $N = \sum_i N_i$ unlike molecules, of the form [1]:

$$(1) \qquad P_m^0 = \frac{4\pi}{9kT} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} m_\alpha^{(pi)} m_\alpha^{(qj)} \right\rangle.$$

Here, $m_\alpha^{(pi)}$ is the α-component of the total electric dipole moment of the p-th molecule of species i immersed in the medium, and the brackets $\langle \, \rangle$ denote the statistical average.

In this part of our paper Eq. (1) will be discussed for a system consisting of quadrupolar unlike molecules. A problem analogous to the one considered here, albeit for a system of identical quadrupolar molecules, was discussed by Buckingham and Pople [2], Zwanzig [3], and by Jansen [4]. These authors considered only the contribution to P_m^0 arising from the mean square of the dipole moments induced in the molecules by the quadrupoles of neighbouring molecules. We shall take into account the two additional effects resulting from the tensorial quadrupole-quadrupole and anisotropic-dispersional interactions between unlike molecules. Numerical estimations for carbon dioxide show that the two last-mentioned effects contribute to the second polarization virial coefficient so considerably that they cannot be neglected in comparison with the contribution from the quadrupole-induced dipole effect as calculated without considering the tensorial interactions.

Dense quadrupolar systems

We shall consider a system composed of unlike non-dipolar molecules, albeit possessing a permanent electric quadrupole moment defined by the tensor

$$(2) \qquad \Theta_{\alpha\beta}^{(pi)} = \frac{1}{2} \sum e_n^{(pi)} (3r_{pn\alpha} r_{pn\beta} - r_{pn}^2 \delta_{\alpha\beta}),$$

with $e_n^{(pi)}$ denoting the n-th electric charge of the p-th molecule of species i, and r_{pn} — its radius vector; the summation in (2) extends over all the charges of the molecule.

For a quadrupolar anisotropically polarizable molecule $m_\alpha^{(pt)}$ is given by the following equation (the hyperpolarizability and induced quadrupole will be neglected)

(3)
$$m_\alpha^{(pt)} = \alpha_{\alpha\beta}^{(pt)} F_\beta^{(pt)},$$

where $\alpha_{\alpha\beta}^{(pt)}$ is the electric polarizability tensor of the p-th isolated molecule of species i, and

(4)
$$F_\beta^{(pt)} = \frac{1}{3} \sum_k \sum_{r=1}^{N_k} T_{\beta\gamma\delta}^{(pr)} \Theta_{\gamma\delta}^{(rk)}, \quad p \neq r$$

is the electric field at its centre due to the quadrupoles of all the other molecules of the system. The tensor $T_{\alpha\beta\gamma}^{(pr)}$ describing the dipole-quadrupole interactions is of the form

(5)
$$T_{\alpha\beta\gamma}^{(pr)} = 3r_{pr}^{-7} \{5r_{pr\alpha} r_{pr\beta} r_{pr\gamma} - r_{pr}^2 (r_{pr\alpha} \delta_{\beta\gamma} + r_{pr\beta} \delta_{\gamma\alpha} + r_{pr\gamma} \delta_{\alpha\beta})\},$$

where r_{pr} is the distance between the centres of molecules p and r.

On substituting into Eq. (1) the moment of Eq. (3) and the field of Eq. (4), we obtain for a system composed of unlike quadrupolar molecules:

(6)
$$P_m^0 = \frac{4\pi}{81kT} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} \alpha_{\alpha\beta}^{(pt)} \alpha_{\alpha\gamma}^{(qj)} \Theta_{\delta\varepsilon}^{(rk)} \Theta_{\eta\lambda}^{(sl)} T_{\beta\delta\varepsilon}^{(pr)} T_{\gamma\eta\lambda}^{(qs)} \right\rangle.$$

This equation can be put in the form

(7)
$$P_m^0 = \sum_{ij} x_i x_j P_m^{(ij)} + \sum_{ijk} x_i x_j x_k P_m^{(ijk)} + \dots,$$

where x_i is the molar fraction of the i-th component of the system, and

(8)
$$P_m^{(ij)} = \frac{2\pi\varrho^2}{81kT} \int \int \{\alpha_{\alpha\beta}^{(pt)} \alpha_{\alpha\gamma}^{(pt)} \Theta_{\delta\varepsilon}^{(qj)} \Theta_{\eta\lambda}^{(qj)} + 2\alpha_{\alpha\beta}^{(pt)} \alpha_{\alpha\gamma}^{(qj)} \Theta_{\delta\varepsilon}^{(qj)} \Theta_{\eta\lambda}^{(pt)} +$$
$$+ \alpha_{\alpha\beta}^{(qj)} \alpha_{\alpha\gamma}^{(qj)} \Theta_{\delta\varepsilon}^{(pt)} \Theta_{\eta\lambda}^{(pt)}\} T_{\beta\delta\varepsilon}^{(pq)} T_{\gamma\eta\lambda}^{(pq)} g_{ij}^{(2)} (\tau_p, \tau_q) \, d\tau_p \, d\tau_q,$$

(9)
$$P_m^{(ijk)} = \frac{4\pi\varrho^3}{81kT} \int \int \int \{\alpha_{\alpha\beta}^{(pt)} \alpha_{\alpha\gamma}^{(pt)} \Theta_{\delta\varepsilon}^{(qj)} \Theta_{\eta\lambda}^{(rk)} T_{\beta\delta\varepsilon}^{(pq)} T_{\gamma\eta\lambda}^{(pr)} +$$
$$+ \alpha_{\alpha\beta}^{(pt)} \alpha_{\alpha\gamma}^{(qj)} (\Theta_{\delta\varepsilon}^{(rk)} \Theta_{\eta\lambda}^{(pt)} T_{\beta\delta\varepsilon}^{(pr)} T_{\gamma\eta\lambda}^{(pq)} + \Theta_{\delta\varepsilon}^{(qj)} \Theta_{\eta\lambda}^{(rk)} T_{\beta\delta\varepsilon}^{(pq)} T_{\gamma\eta\lambda}^{(qr)}) +$$
$$+ \alpha_{\alpha\beta}^{(pt)} \alpha_{\alpha\gamma}^{(qj)} \Theta_{\delta\varepsilon}^{(rk)} \Theta_{\eta\lambda}^{(rk)} T_{\beta\delta\varepsilon}^{(pr)} T_{\gamma\eta\lambda}^{(qr)}\} g_{ijk}^{(3)} (\tau_p, \tau_q, \tau_r) \, d\tau_p \, d\tau_q \, d\tau_r,$$

where $\varrho = N/V$ is the number density, $g_{ij}^{(2)} (\tau_p, \tau_q)$ and $g_{ijk}^{(3)} (\tau_p, \tau_q, \tau_r)$ are the binary and ternary correlation functions, respectively, and the configuration τ_p of the p-th molecule is described by the positional vector $\mathbf{r}_p$ and the orientational variable ω_p.

In the first approximation, the correlation functions $g_{ij}^{(2)}$ and $g_{ijk}^{(3)}$ are independent of orientation, and we find from (8) and (9), by integration over all orientations of the molecules,

(10) $\qquad P_m^{(ij)} = \dfrac{2\pi\varrho^2}{6075kT}\,(5\alpha_{\alpha\beta}^{(i)}\,\alpha_{\alpha\beta}^{(i)}\,\Theta_{\gamma\delta}^{(j)}\,\Theta_{\gamma\delta}^{(j)} + 6\alpha_{\alpha\beta}^{(i)}\,\Theta_{\alpha\beta}^{(i)}\,\alpha_{\gamma\delta}^{(j)}\,\Theta_{\gamma\delta}^{(j)} +$

$$+ 5\alpha_{\alpha\beta}^{(j)}\,\alpha_{\alpha\beta}^{(j)}\,\Theta_{\gamma\delta}^{(i)}\,\Theta_{\gamma\delta}^{(i)})\int\int T_{\varepsilon\eta\lambda}^{(pq)}\,T_{\varepsilon\eta\lambda}^{(pq)}\,g_{ij}^{(2)}\,(\mathbf{r}_p,\,\mathbf{r}_q)\,d\mathbf{r}_p\,d\mathbf{r}_q,$$

(11) $\qquad P_m^{(ijk)} = \dfrac{4\pi\varrho^3}{3645kT}\,\alpha_{\alpha\alpha}^{(i)}\,\alpha_{\beta\beta}^{(j)}\,\Theta_{\gamma\delta}^{(k)}\,\Theta_{\gamma\delta}^{(k)}\int\int\int T_{\varepsilon\eta\lambda}^{(pr)}\,T_{\varepsilon\eta\lambda}^{(qr)}\,g_{ijk}^{(3)}\,(\mathbf{r}_p,\,\mathbf{r}_q,\,\mathbf{r}_r)\,d\mathbf{r}_p\,d\mathbf{r}_q\,d\mathbf{r}_r.$

By (5), we have

(12) $\qquad T_{\varepsilon\eta\lambda}^{(pr)}\,T_{\varepsilon\eta\lambda}^{(qs)} = 45r_{pr}^{-7}\,r_{qs}^{-7}\,\{5\,(\mathbf{r}_{pr}\cdot\mathbf{r}_{qs})^2 - 3r_{pr}^2\,r_{qs}^2\}\,(\mathbf{r}_{pr}\cdot\mathbf{r}_{qs}),$

and thus we obtain from (10) and (11) for axially symmetric molecules

(13) $\qquad P_m^{(ij)} = \dfrac{2\pi\varrho^2}{15kT}\,\{5\alpha_i^2\,(1 + 2\varkappa_i^2)\,\Theta_j^2 + 12\alpha_i\,\alpha_j\,\varkappa_i\,\varkappa_j\,\Theta_i\,\Theta_j +$

$$+ 5\alpha_j^2\,(1 + 2\varkappa_j^2)\,\Theta_i^2\}\int\int r_{pq}^{-8}\,g_{ij}^{(2)}\,(\mathbf{r}_p,\,\mathbf{r}_q)\,d\mathbf{r}_p\,d\mathbf{r}_q,$$

(14) $\qquad P_m^{(ijk)} = \dfrac{2\pi\varrho^3}{3kT}\,\alpha_i\,\alpha_j\,\Theta_k^2\int\int\int\{5\,(\mathbf{r}_{pr}\cdot\mathbf{r}_{qr})^2 - 3r_{pr}^2\,r_{qr}^2\}\,(\mathbf{r}_{pr}\cdot\mathbf{r}_{qr})\times$

$$\times\,r_{pr}^{-7}\,r_{qr}^{-7}\,g_{ijk}^{(3)}\,(\mathbf{r}_p,\,\mathbf{r}_q,\,\mathbf{r}_r)\,d\mathbf{r}_p\,d\mathbf{r}_q\,d\mathbf{r}_r,$$

where $\alpha_i = (\alpha_{33}^{(i)} + 2\alpha_{11}^{(i)})/3$ and $\varkappa_i = (\alpha_{33}^{(i)} - \alpha_{11}^{(i)})/3\alpha_i$ are the mean polarizability and anisotropy of polarizability of an isolated molecule of species i, and $\Theta_i = \Theta_{33}^{(i)} = -2\Theta_{11}^{(i)} = -2\Theta_{22}^{(i)}$ — its quadrupole moment.

Quadrupolar gas mixture

In the case of a quadrupole imperfect gas mixture, Eq. (8) can be written as follows:

(15) $$P_m^{(ij)} = \varrho\,\{B_P^{(ij)} + O\,(\varrho)\}.$$

Here, $B_P^{(ij)}$ is the second polarization virial coefficient for unlike quadrupolar molecules given by:

(16) $\qquad B_P^{(ij)} = \dfrac{2\pi N}{81kT\Omega^2}\int\int\int\{\alpha_{\alpha\beta}^{(pi)}\,\alpha_{\alpha\gamma}^{(pi)}\,\Theta_{\delta\varepsilon}^{(qj)}\,\Theta_{\eta\lambda}^{(qj)} + 2\alpha_{\alpha\beta}^{(pi)}\,\alpha_{\alpha\gamma}^{(qj)}\,\Theta_{\delta\varepsilon}^{(qj)}\,\Theta_{\eta\lambda}^{(pi)} +$

$$+ \alpha_{\alpha\beta}^{(qj)}\,\alpha_{\alpha\gamma}^{(qj)}\,\Theta_{\delta\varepsilon}^{(pi)}\,\Theta_{\eta\lambda}^{(pi)}\}\,T_{\beta\delta\varepsilon}^{(pq)}\,T_{\gamma\eta\lambda}^{(pq)}\,e^{-\frac{u_{ij}(r_{pq},\,\omega_p,\,\omega_q)}{kT}}\,d\mathbf{r}_{pq}\,d\omega_p\,d\omega_q,$$

with $\Omega = \int d\omega_p = \int d\omega_q$ denoting the integral over the orientations of the molecules.

The total potential energy of the interaction between two quadrupolar molecules of species i and j is of the form [5]

$$(17) \qquad u_{ij}\left(r_{pq}, \omega_p, \omega_q\right) = u_{ij}\left(r_{pq}\right) - \frac{1}{9}\,\Theta_{\alpha\beta}^{(pi)}\,\Theta_{\gamma\delta}^{(qj)}\,T_{\alpha\beta\gamma\delta}^{(pq)} -$$

$$- \frac{h\nu_i\,\nu_j}{4\,(\nu_i+\nu_j)}\left(\alpha_{\alpha\beta}^{(pi)}\,\alpha_{\gamma\delta}^{(qj)} - \alpha_i\,\alpha_j\,\delta_{\alpha\beta}\,\delta_{\gamma\delta}\right) T_{\alpha\gamma}^{(pq)}\,T_{\beta\delta}^{(pq)} - \dots,$$

where $u_{ij}\left(r_{pq}\right)$ is the central force energy. The second term in (17) represents the quadrupole-quadrupole interaction energy and the third — the anisotropic dispersion energy; ν is the electron oscillation frequency and h — the Planck constant.

By (17), we obtain from (16)

$$(18) \qquad B_P^{(ij)} = {}_{q-id}B_P^{(ij)} + {}_{q-q}B_P^{(ij)} + {}_{anis-disp}B_P^{(ij)},$$

where

$$(19) \qquad {}_{q-id}B_P^{(ij)} = \frac{2\pi N}{15kT}\,\{5\alpha_i^2\,(1+2\varkappa_i^2)\,\Theta_j^2 + 12\alpha_i\,\alpha_j\,\varkappa_i\,\varkappa_j\,\Theta_i\,\Theta_j +$$

$$+ 5\alpha_j^2\,(1+2\varkappa_j^2)\,\Theta_i^2\}\,\langle r_{pq}^{-8}\rangle_{ij}$$

describes the quadrupole-induced dipole effect for axially-symmetric molecules, with

$$(20) \qquad \langle r_{pq}^{-n}\rangle_{ij} = \int r_{pq}^{-n}\,e^{-\frac{u_{ij}\,(r_{pq})}{kT}}\,d\mathbf{r}_{pq}.$$

If, in addition to the central forces potential in (17), tensorial quadrupole-quadrupole and anisotropic-dispersional interactions are present, we obtain the two following contributions to $B_P^{(ij)}$, respectively:

$$(21) \qquad {}_{q-q}B_P^{(ij)} = -\frac{8\pi\,\Theta_i\,\Theta_j\,N}{735k^2\,T^2}\,\{42\alpha_i^2\,\varkappa_i\,(2+\varkappa_i)\,\Theta_j^2 +$$

$$+ \alpha_i\,\alpha_j\,\Theta_i\,\Theta_j\,[49 + 14\,(\varkappa_i + \varkappa_j) + 76\,\varkappa_i\,\varkappa_j] + 42\alpha_j^2\,\varkappa_j\,(2+\varkappa_j)\,\Theta_i^2\}\,\langle r_{pq}^{-13}\rangle_{ij} + \dots,$$

$$(22) \qquad {}_{anis-disp}B_P^{(ij)} = \frac{2\pi\alpha_i\,\alpha_j\,N}{1225k^2\,T^2}\left(\frac{h\nu_i\,\nu_j}{\nu_i+\nu_j}\right)\{7\alpha_i^2\,\Theta_j^2\,[20\,\varkappa_j\,(1+2\alpha_i^2) +$$

$$+ (2+\varkappa_i)\,(14+33\,\varkappa_j)\,\varkappa_i^2] + \alpha_i\,\alpha_j\,\Theta_i\,\Theta_j\,[245 + 406\,(\varkappa_i + \varkappa_j) + 470\,\varkappa_i\,\varkappa_j] +$$

$$+ 7\alpha_j^2\,\Theta_i^2\,[20\varkappa_i\,(1+2\,\varkappa_j^2) + (2+\varkappa_j)\,(14+33\,\varkappa_i)\,\varkappa_i^2]\}\,\langle r_{pq}^{-14}\rangle_{ij} - \dots,$$

Application to a one-component gas

For a one-component gas, we can simplify expressions (19), (21) and (22) to (if the well-known Lennard—Jones 6 : 12 potential [6] is used for $u_{ij}\left(r_{pq}\right)$ of Eq. (20))

$$(23) \qquad {}_{q-id}B_P = \frac{\pi^2\,\alpha^2\,qN}{9y^2}\left(1 + \frac{16}{i}\,\varkappa^2\right)H_8(y),$$

(24)
$$_{q-q}B_P = -\frac{\pi^2\,\alpha^2\,q^2\,N}{90}\left(1 + 4\varkappa + \frac{160}{49}\,\varkappa^2\right)H_{13}\,(y),$$

(25)
$$_{anis-disp}B_P = \frac{8\pi^2\,\alpha^2\,\varkappa qN}{315}\left(1 + \frac{91}{40}\,\varkappa + \frac{324}{35}\,\varkappa^2 + \frac{233}{70}\,\varkappa^3\right)H_{14}\,(y),$$

where $H_n\,(y)$ are the functions defined and tabulated by Buckingham and Pople [7], ε and σ the well-known force parameters having the dimensions of an energy and length, respectively, and $y = 2\,(\varepsilon/kT)^{1/2}$, $q = \Theta^2/\varepsilon\sigma^5$.

For the case of very small anisotropy, Eq. (23) becomes identical with the result derived by Buckingham and Pople [2] for isotropically polarizable quadrupole molecules. At the same time, we can see from Eq. (23) that the influence of the anisotropy of the molecule on $_{q-td}B_P$ is here four times larger, amounting to $16/5\,\varkappa^2$, than the value calculated by Jansen [4] (which was $4/5\,\varkappa^2$).

We use the following data for the CO_2-molecule [8] : $\varepsilon/k = 190°K$, $\sigma = 3.996$ Å, $\alpha = 2.92\times10^{-24}$ cm.^{3}, $\varkappa = 0.27$ and $\Theta = 5\times10^{-26}$ e.s.u. By substitution of these parameters into Eqs. (23)—(25), we obtain for $T = 298°K$:

$$_{q-td}B_P = (57 + 13)\times10^{-24}\text{ cm.}^6/\text{mol} = 70\times10^{-24}\text{ cm.}^6/\text{mol.},$$

$$_{q-q}B_P = -(8 + 10)\times10^{-24}\text{ cm.}^6/\text{mol.} = -18\times10^{-24}\text{ cm.}^6/\text{mol.},$$

$$_{anis-disp}B_P = 12\times10^{-24}\text{ cm.}^6/\text{mol.}$$

As can be seen from these evaluations, the contributions to the second polarization virial coefficient of CO_2 from the quadrupole-quadrupole and anisotropic-dispersional interactions constitute 26% and 17%, respectively, of the value of $_{q-td}B_P = 70\times10^{-24}$ cm.^{6}/mol. as obtained for the quadrupole induced dipole effect alone. Eqs. (23) and (24) indicate that the effects of the anisotropy of polarizability are so large that they cannot be neglected in the case of strongly anisotropic molecules such as CO_2, O_2, etc., for which $\varkappa \geqslant 0.2$.

INSTITUTE OF PHYSICS, POZNAŃ BRANCH, POLISH ACADEMY OF SCIENCES
(INSTYTUT FIZYKI, ODDZIAŁ POZNAŃ, PAN)

REFERENCES

[1] S. Kielich, Bull. Acad. Polon. Sci., Sér. math., astr. et phys., **10** (1962), 485 (this issue).
[2] A. D. Buckingham and J. A. Pople, Trans. Faraday Soc., **51** (1955), 1029.
[3] R. W. Zwanzig, J. Chem. Phys., **25** (1956), 211.
[4] L. Jansen, Phys. Rev., **112** (1958), 434.
[5] S. Kielich, Acta Phys. Polon., **22** (1962), 65.
[6] J. E. Lennard-Jones, Proc. Roy. Soc. (London), A **106** (1924), 441.
[7] A. D. Buckingham and J. A. Pople, Trans. Faraday Soc., **51** (1955), 1173.
[8] S. Kielich, Physica, **28** (1962), 511.