Dielectric polarization of the solutions of nitrotoluene and cyclohexane

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Abstract. Dielectric properties of the solutions of nitrotoluene in cyclohexane showing a far pre-critical state are discussed. Dipolar polarization of the solutions was calculated on the lines of the Onsager model of local field, while the energy of interdipolar interactions was calculated with the help of the dipole-dipole coupling model given by Piekara. The character of interdipolar interactions in the solutions studied was found to be analogous to those in critical solutions at the temperatures from 10 to 20 K higher than the critical temperature.

1. Introduction

Molecular motions in a homogeneous liquid medium are observed in general as fluctuations of density and internal field. Both phenomena are particularly strong in solutions of liquids with a critical point. At a critical temperature one can observe strong critical opalescence caused by fluctuations of density and concentration as well as dielectric anomaly being a consequence of fluctuations of the internal field, polarizability and effective dipole moment. After the critical temperature has been reached the solution is separated into two phases coexisting at thermodynamical equilibrium. Temperature investigation of electric permittivity ε of solutions with limited miscibility and critical point revealed the existence of an anomaly of the function $\varepsilon(T)$ near the critical point (Piekara 1932, 1933; Archangielskij and Sementzenko 1961; Zamkow 1962; Debye and Kleboth 1965; Givon et al 1975; Hollecker et al 1975; Thoen et al 1981). Thus, such investigation is useful in the determination of critical binary solutions of o-nitrotoluene in liquid n-alkanes (Śliwińska-Bartkowiak and Hilczer 1974, 1977; Śliwińska-Bartkowiak 1977). These solutions were found to show limited mutual miscibility with a critical point. Also, the critical parameters of these solution were determined. An empirical relation was found between the critical concentrations x_C of the solutions of o-nitrotoluene in n-alkanes and the number of carbon atoms K in a molecule of the n-alkane used as a solvent. The latter value corresponds to the linear dimensions of the solvent molecule. This relation can be presented in the following form (Śliwińska-Bartkowiak 1982):

$$x_C = 0.1543 \, K^{0.54}, \tag{1}$$

where x_C is the molar fraction of o-nitrotoluene in the solution and K is the number of carbon atoms in the solvent molecule. Temperature dependences of ε, density d and

light refractive index n obtained for the above solutions allowed to determine the most important kind of interaction between the molecules of a dipole liquid in these solutions (Śliwińska-Bartkowiak 1978). Applying the model of dipole-dipole coupling given by Piekara (1939) and Piekara and Kielich (1958) the correlation factor of polarization was estimated according to:

$$R_P = 1 \pm L(y), \tag{2}$$

here $L(y)$ is the Langevin function:

$$L(y) = \operatorname{ctg} h\, y - 1/y, \tag{3}$$

$y = W/kT$ is a measure of energy of coupling between a given dipole and the nearest dipole in the environment, k is the Boltzmann constant and T the temperature. The plus sign refers to the interactions as a result of which two neighbouring dipoles tend to be coupled in parallel and the minus refers to the case when the dipoles tend to be coupled in antiparallel. The factor R_P can be found experimentally from:

$$R_P = P^{\mathrm{or}}/P_g^{\mathrm{or}} \tag{4}$$

where P^{or} is the dielectric polarization of a dipole in gaseous phase; P^{or} is the orientational part of the total polarization of P_{12} of solution, which in Onsager approximation of local field is as follows:

$$P^{\mathrm{or}} = [P_{12} - (1 - x_2)g_1 P_1^{\mathrm{def}} - x_2 g_2^{\mathrm{def}}]/x_2 g_2^2. \tag{5}$$

The index "1" refers to the parameters of nonpolar solvent while the index "2" refers to the dipolar liquid;

$$g = [(n^2 + 2)/3][(2\varepsilon_{12} - 1)/(2\varepsilon_{12} + n^2)], \tag{6}$$

where n is the light refractive index of the liquid, ε_{12} the electric permittivity of the solution and x the molar fraction of the liquid in the solution. The deformation polarization is given by the Lorentz-Lorenz relation:

$$P^{\mathrm{def}} = [(n^2 - 1)/(n^2 + 2)](M/d), \tag{7}$$

where d is the density of the liquid and M its molecular mass.

The correlation factor R_P estimated from the above relations for solutions of o-nitrotoluene in n-alkanes was found to take the lowest possible value for the critical concentrations of these systems. This proved the existence of the strongest antiparallel dipole-dipole coupling within these ranges of concentrations observed at temperatures high above the critical one (Śliwińska-Bartkowiak 1978).

The presence of specific intermolecular interactions in the vicinity of critical concentrations in temperatures above T_C was also confirmed by other methods. Investigations of viscosity, light scattering or nonlinear dielectric effect (NDE) i.e. changes in permittivity $\Delta\varepsilon$ in a strong electric field, prove that all these phenomena

show anomalous behaviour at temperatures higher by 20–40 K than T_C (Fechner 1968; Pyżuk and Zboiński 1977; Małecki and Zioło 1978; Zboiński *et al* 1979). Thus, intermolecular interactions leading to phase separation phenomenon can be revealed at temperatures considerably higher than T_C.

This fact enabled the interpretation of anomalous behaviour of NDE typical for critical solutions, which was observed for solutions of *m*-nitrotoluene with *n*-alkanes in spite of the fact that they do not show phase separation phenomenon (Śliwińska-Bartkowiak *et al* 1981; 1983). NDE anomalies typical for critical solutions are found to occur in the solutions under investigation within the concentration ranges that fulfil equation (1). Cooling of the solution leads to an increase in anomalous NDE values in the vicinity of these concentrations till the moment the solutions solidify in a homogeneous phase. Thus, we may conclude the *m*-nitrotoluene solutions with *n*-alkanes are a group of solutions in which a far pre-critical effect is observed. That is intermolecular interactions in these solutions are characteristic for critical solutions and occur at temperatures significantly higher than T_C (Śliwińska-Bartkowiak in press).

A dependence of the critical concentrations and the concentrations at which a far pre-critical effect has been observed in *o*- and *m*-nitrotoluene solutions in *n*-alkanes on the linear dimensions of the solvent molecules suggested the necessity to investigate the solutions of *o*- and *m*-nitrotoluene in cycloalkanes.

Temperature investigation of NDE of these solutions has revealed NDE anomalies characteristic for critical solutions at temperatures considerably higher than T_C (Śliwińska-Bartkowiak 1984). However, the solutions of both *o*- and *m*-nitrotoluene in cycloalkanes did not show the phase separation phenomenon. Their behaviour was analogous to that for the solutions of dipolar liquids: *o*- and *m*-nitrotoluene in *n*-alkanes.

2. Experimental

For the solutions of dipolar liquids: *o*- and *m*-nitrotoluene in cyclohexane the temperature dependence of electric permittivity ε, light refractive index n and density d were measured throughout the whole concentration range. ε was measured by an automatic càpacity bridge (E-315A of "Metronix" Poland) at a frequency of 1 kHz. The measuring condenser was thermostated using a cryostat (MK-70) with an accuracy of 0·1°. The accuracy of the capacity measurements was 10^{-15} F and the maximum error was within 0·5% of the measured value. Light refractive index was determined by a Pulfrich refractometer for sodium line $\lambda = 589·9$ nm. The temperature of the measuring cell was stabilized to within 0.1°. The accuracy of light refractive index was $1·10^{-4}$.

Density was measured by a quartz pycnometer placed in a thermostating vessel connected with a cryostat. The accuracy of the temperature read-out was 0·1°, and the accuracy of density measurement was within 0·1% of the measured value.

The liquid to be studied *o*- and *m*-nitrotoluene (made in Belgium) were distilled twice under increased pressure, then dried over Al_2O_3 and before measurement they were directly centrifuged. The electric conductivity of the purified liquids was about $10^{-10} \Omega,^{-1} m^{-1}$. The conductivity of cyclohexane (made in USSR) which was also distilled twice was about $10^{-15} \Omega^{-1} m^{-1}$.

3. Results and discussion

Electric permittivity ε of o- and m-nitrotoluene solutions in cyclohexane has been studied in the whole concentration range and for temperatures ranging from 283 to 313 K. The concentration x_2 is given in a molar fraction of dipole liquid in cyclohexane. Figures 1a and 1b present ε vs x_2 for both the systems at various temperatures. In the temperature range studied no anomalies in $\varepsilon(T)$ were observed. Below 283 K the solutions solidify.

The relative temperature coefficient of electric permittivity $\eta = (1/\varepsilon)(\Delta\varepsilon/\Delta T)_P$ was determined for each concentration of both systems studied at 294 K, taking $\Delta T = 0\cdot5$ K. Since the maximum error was determined to be about 10% we could only estimate a tendency of behaviour of η as a function of concentration. Figure 2 shows η vs x_2 for both systems studied and a local minimum of this function is observed in both cases at about $x_2 \sim 0\cdot29$. This suggests that in the vicinity of this concentration the destructive influence of the temperature on the ordering effect of the electric field is the weakest, therefore the intermolecular interactions are the strongest. The character of the concentration dependence of the coefficient η is similar as in the case of systems showing limited miscibility with a critical point.

Investigations performed on o-nitrotoluene solutions with some n-alkanes have shown that in the vicinity of the critical concentrations a local minimum in this function occurs, which is also observed as a minimum in the relative temperature coefficient of dipole polarization $(1/P_{or})(\Delta P_{or}/\Delta T)$ vs concentration (Śliwińska-Bartkowiak 1978) again near the critical concentrations of these solutions.

A similar character of the dependence of η on x_2 has also been observed for other critical solutions. For the system nitrobenzene-hexane which has the following critical parameters $T_c = 289\cdot4$ K and $x_c = 0\cdot427$, the temperature coefficient of electric permittivity in the space of (x_2, η, T) is presented in figure 3. A clear minimum in this coefficient is seen in the vicinity of $x_2 = 0\cdot43$, which becomes deeper as T tends to T_C. However, this minimum is also visible at the temperatures higher by about 10 K than T_C. Similar dependences have also been observed in other critical systems.

On the other hand, no minima in η versus concentration, characteristic for critical concentrations, were found for solutions which do not show phase separations in the whole temperature range. Figure 4 presents the dependence of η on x_2 concentration for the solutions of bromobenzene with heptane. As seen in figure 4 there are no concentration ranges within which the function would reach a minimum. Thus we may conclude that the existence of concentration ranges of a particular structure characteristic for critical concentrations is also revealed as an anomaly in η versus concentration and in temperatures relatively far from T_C.

The dependence η vs x_2 observed in the solutions presented in figure 2 which are similar to those obtained for critical solutions, suggests that the intermolecular interactions in the vicinity of $x_2 \sim 0\cdot29$ may be similar to those characteristic for critical solutions in the temperatures higher than T_C.

In order to estimate the character of the interactions the orientation polarization P_{or} as well as the correlation factors of the orientation polarization R_P in these solutions were determined on the lines of the Onsager model of the local field.

The temperature and concentration dependences of orientation polarization P_{or} were obtained from relation (5). Figures 5a and 5b present isotherms of P_{or} vs concentration for o- and m-nitrotoluene solutions in cyclohexane. As seen from
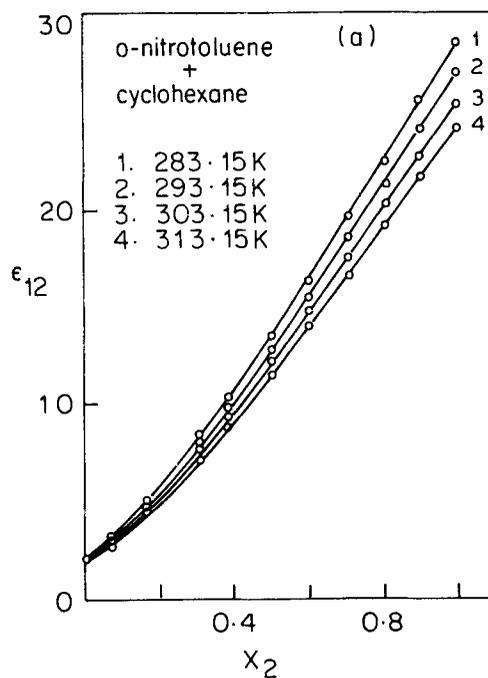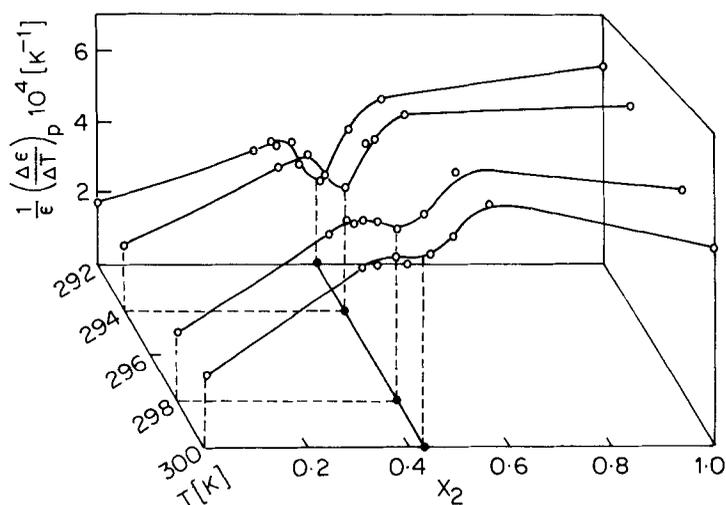
Figure 1a. Electric permittivity vs concentration for the system *o*-nitrotoluene-cyclohexane at various temperatures.
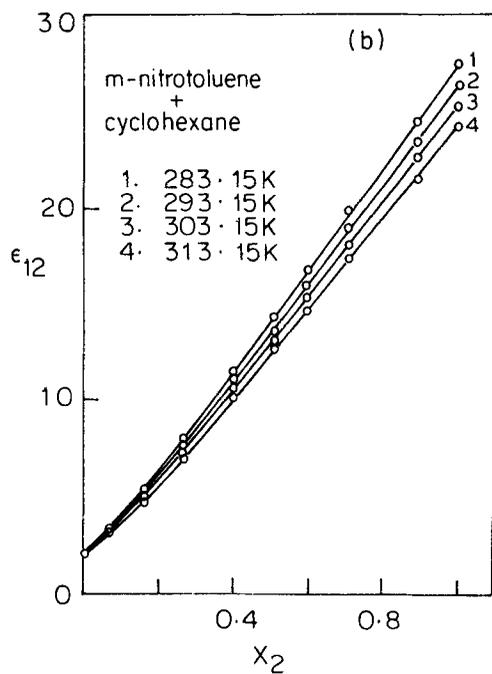
Figure 1b. Electric permittivity vs concentration for the system *m*-nitrotoluene-cyclohexane at various temperatures.
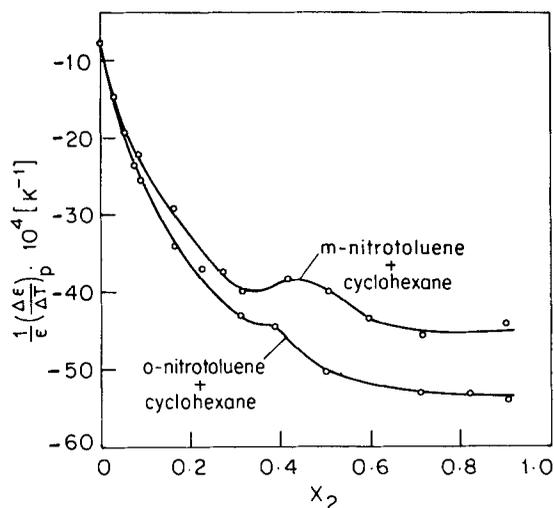
Figure 2. Temperature coefficient of electric permittivity vs concentration for the system o- and m-nitrotoluene in cyclohexane.

Figure 3. Temperature coefficient of electric permittivity vs concentration and temperature for the system nitrobenzene-hexane.

figures 5a, b the character of the dependences is similar for the two systems; P_{or} is inversely proportional to the temperature.

In the vicinity of $x_2 \sim 0.29$ the minima in $P_{or}(x_2)$ appear which point to the existence of the strongest intermolecular interaction between the molecules of the dipolar liquid in this concentration range.

Assuming the model given by Piekara (1939) where only the interaction between the two nearest dipolar molecules is taken into account, R_P values were calculated from equation (4) for both systems studied. Figure 6 presents R_P vs concentration at 298 K determined for o- and m-nitrotoluene solutions in cyclohexane. The fact that the function $R_P(x_2)$ reaches the minimum in the vicinity of $x_2 \sim 0.29$ and
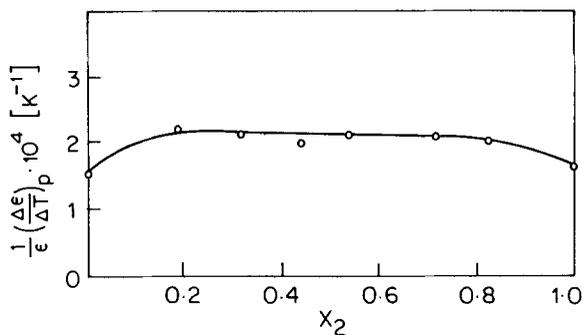
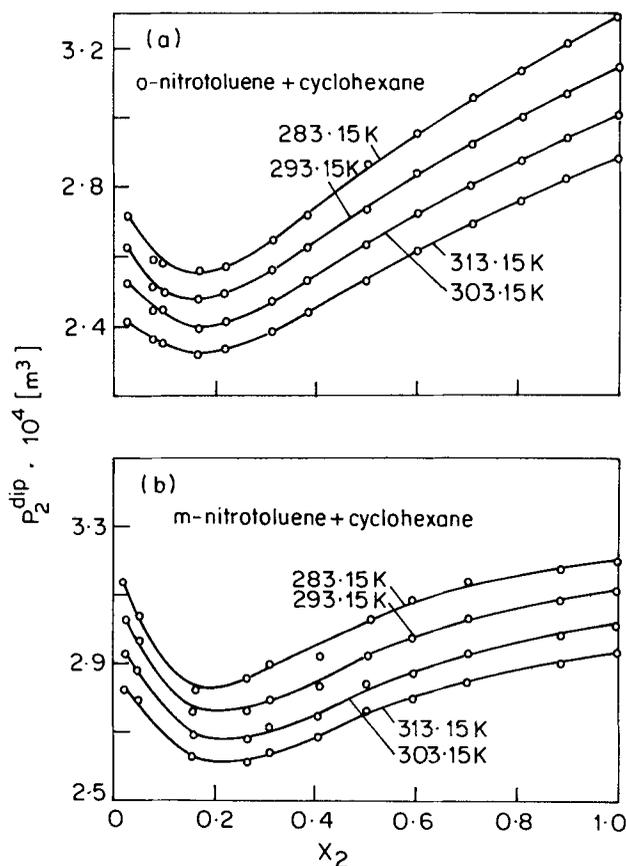**Figure 4.** Temperature coefficient of electric permittivity vs concentration for the system bromobenzene-heptane.

Figure 5. Curve of dependence of orientational polarization P_{or} vs concentration at various temperatures for the system o-nitrotoluene (a) and m-nitrotoluene (b) in cyclohexane.

$R_P < 1$ allows one to conclude that near this concentration the antiparallel dipole-dipole coupling is the strongest. Above this concentration range $R_P(x_2)$ increases which proves the existence of weaker interdipolar couplings. Lower R_P values obtained for m-nitrotoluene solutions with cyclohexane prove that antiparallel dipole-
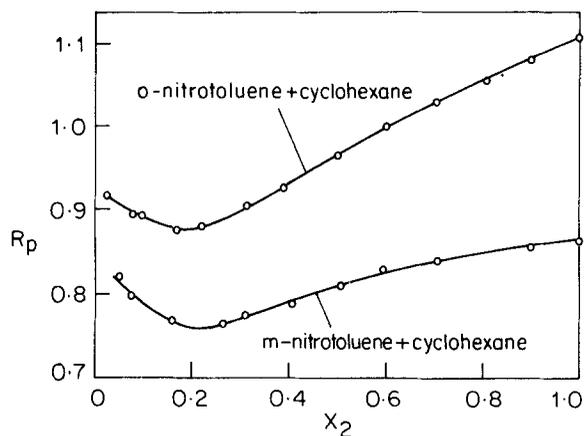
Figure 6. Plot orientational polarization factor R_p vs concentration for the systems o- and m-nitrotoluene in cyclohexane.
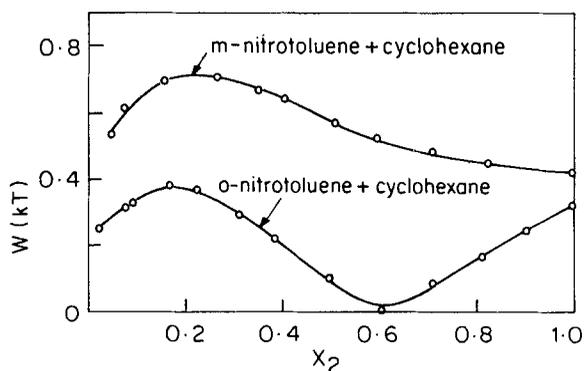

Figure 7. Dipole-dipole coupling energy vs concentration for the systems o- and m-nitrotoluene in cyclohexane.

dipole coupling is much stronger in this system which is a consequence of a greater dipole moment of m-nitrotoluene ($13 \cdot 93 * 10$–30 C/m while $12 \cdot 33 * 10$–30 C/m for o-nitrotoluene).

The interaction energy between two dipoles W is usually expressed in kT and are presented as a function of concentration of both the solutions studied. The energy W calculated from equation (2) with only the first term of Langevin function expansion taken into account, is presented in figure 7 for $T = 298$ K. It is maximum at about $x_2 \sim 0 \cdot 29$ corresponds to the minimum of $R_p(x_2)$ and illustrates the above conclusions. From the analysis performed, the range near $x_2 \sim 0 \cdot 29$ in both systems is a concentration region of particular kind of ordering chai acterized by the highest energy of antiparallel dipole-dipole coupling.

Similar conclusions have been obtained from analogous investigation for critical solutions of o-nitrotoluene in n-alkanes. Also, the minimum in $R_p(x_2)$ observed at temperatures significantly higher than the critical temperature of these solutions was characteristic for the critical concentration (Śliwińska-Bartkowiak 1978).

The concentrations about $x_2 \sim 0.29$ for which we have observed a characteristic behaviour of the parameters studied in solutions of *o*- and *m*-nitrotoluene in cyclohexane, fulfil the modified dependence (equation (1)). Assuming that the critical concentration of *o*-nitrotoluene solutions in *n*-alkanes is dependent on the length of the solvent molecule according to equation (1), we compared linear dimensions of the *chair* form of cyclohexane (this form prevails) with dimensions of *n*-alkane molecules. It is found that the size of cyclohexane molecule is comparable to that of the propane molecule for which $K = 3$ (Tables of Interatomic Distances 1958). With this value of K we obtain from (1) the characteristic concentration of $x_2 = 0.29$. This is the same concentration where we observed the strongest interdipolar interactions in both systems studied (Sliwińska-Bartkowiak 1984).

A formal comparison of dielectric properties of *o*- and *m*-nitrotoluene solutions in cyclohexane with the properties of critical solutions of *o*-nitrotoluene in *n*-alkanes allows us to conclude that in the former ones a far pre-critical region is reached within a certain concentration range. With decreasing temperature of the system dielectric anomalies characteristic of critical solutions appear as T tends to T_C. Phase separation, however, does not occur because the solutions solidify. The critical temperature is lower than their freezing point.

References

Archangielskij K W and Sementzenko W K 1961 *Z. Fiz. Chem.* **35** 454
Debye P and Kleboth K 1965 *J. Chem. Phys.* **42** 3155
Fechner B 1968 *Acta Phys. Polon.* **36** 297
Givon M, Pelach I and Efron U 1975 *Phys. Lett.* **A48** 915
Hollecker M, Goulon J, Thiebaut J M and Rivail J L 1975 *Chem. Phys.* **11** 99
Małecki J and Zioło J 1978 *Chem. Phys.* **35** 187
Piekara A 1933 *Bull. Acad. Polon. Sc. et Lett. Mat.* **A319**
Piekara A 1937 *Acta Phys. Polon.* **6** 130
Piekara A 1939 *Proc. R. Soc. (London)* **A172** 360
Piekara A and Kielich S 1958 *Acta Phys. Polon.* **17** 29
Pyżuk W and Zboiński K 1977 *Phys. Lett.* **52** 577
Śliwińska-Bartkowiak M 1977 *PTPN Fiz. Diel. Rad.* **9** 38
Śliwińska-Bartkowiak M 1978 *PTPN Fiz. Diel. Rad.* **10** 41
Śliwińska-Bartkowiak M 1984 *Chem. Phys. Lett.* **112** 237
Śliwińska-Bartkowiak M and Hilczer T 1974 *Acta Phys. Polon.* **A45** 915
Śliwińska-Bartkowiak M and Hilczer T 1977 *Phys. Lett.* **A64** 101
Śliwińska-Bartkowiak M, Szurkowski B and Hilczer T 1981 *Phys. Lett.* **A81** 411
Śliwińska-Bartkowiak M, Szurkowski B and Hilczer T 1983 *Chem. Phys. Lett* **94** 609
Tables of Interatomic Distances and Configurations in Molecules and Ions 1958 (London: The Chemical Society)
Thoen J, Kindt R and Van Dael W 1981 *Phys. Lett.* **A87** 76
Zamkow V A 1962 *Z. Fiz. Chem.* **36** 1060
Zboiński K, Opiola H and Piekara-Sady L 1979 *Chem. Phys.* **40** 70