experimental determinations of the proton affinities of some key phosphines will be reported in a future publication.[15] The calculations indicate that the conjugation in II does make a significant contribution to the stabilization of the phenylphosphonium ion (calculations were made for $PhPH_3^+$ rather than $PhMe_2PH^+$). The phosphorus orbitals involved are mostly π^*; i.e., the participation of $d\pi$ orbitals is smaller. The role of methyl hyperconjugative stabilization of the $MePH_3^+$ ion is found to be relatively small. The much stronger basicity increasing effect of phenyl for the phosphines relatively to the amines is found to be caused primarily by the basicity decreasing stabilization of the neutral amine base (aniline, conjugation like in structure I). The stabilization of the phenylphosphonium ion by conjugation in II while sizable, is less important.[15]

The basicities of the phosphines in solution (see Table I) decrease with phenyl substitution, i.e., show a behavior opposite to that observed in the gas phase. Obviously, this must be due to adverse solvation effects. The positive charge delocalization onto the phenyl groups and the large size of these groups corresponds to a large effective increase of the phosphonium ion radius. Thus an adverse effect of phenyl on the solvation of these ions is to be expected.

Registry No. Me_3P, 594-09-2; Me_2PhP, 672-66-2; $MePh_2P$, 1486-28-8; Ph_3P, 603-35-0.

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Solution Thermodynamic Studies. 7.[1a] A Thermodynamic Study of Solvent Effects on the Relative Stability of *cis*- and *trans*-Dichloroethylene: Importance of the Quadrupolar and Octupolar Electric Moments in the Reaction Field Model

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Abstract: Calorimetric measurements of heats of solution on the title compounds clearly show a similar solvent effect on both isomers even though the cis isomer is a dipolar molecule and the trans isomer a quadrupolar molecule. Interaction energies of both isomers with various solvents can be described by a reaction field model in which higher moments than the dipole moment are taken into account. The quadrupolar contribution is as important for the trans isomer as for the cis, and even the octupolar contribution to the interaction energy is not negligible in the case of the cis isomer.

It is interesting to note that in organic chemistry a polar molecule is generally considered to be a molecule with a dipole moment. The moments of higher order are generally ignored. In this work we point out that a quantitative or even a semiquantitative description of the so-called "solvent effect" in organic chemistry cannot be developed if the quadrupole moment and, in some cases, the octupole moment of the solute is not explicitly taken into account. The electric component of the interaction energy of a polar solute in various solvents can be estimated by using the reaction field theory. Often, the calculation is limited to a point dipole located at the center of a spherical cavity. As was pointed out many years ago by Böttcher,[2] the application of this model to real dipolar molecules leads to a very crude estimation of intermolecular electrostatic interactions. The interaction energy changes considerably when the dipole is not at the center of the cavity, as was proved by Böttcher[2] in his calculation of the work required to bring a point dipole from an infinite distance to an excentric position inside a spherical cavity surrounded by a homogeneous dielectric. In this case, the energy of interaction is given by an infinite series of terms. It must be noted that this series is reduced to its first, i.e., dipolar term, when the dipole is at the center of the cavity. In 1954, Wada[3] published an evaluation of the energy difference between rotational isomers in various solvents. To improve the estimation of interaction energies, this author introduced two refinements to the original reaction field theory. The shape of the cavity of the solute molecule is taken as an ellipsoid, and the reaction field is evaluated at the two focuses where the two point dipoles are considered to be located.

In 1966, Abraham and his co-workers[4] extended Böttcher's calculation to several point dipoles in a spherical cavity. Wada and Abraham were the first to show the importance of the second term of the series, which can be described as quadrupolar. In a series of works devoted to stereochemical problems, Abraham et al.[4] demonstrated the significance of the quadrupolar term not only for solute molecules without permanent dipoles but also for solute molecules with permanent dipoles.

In 1976, Rivail and co-workers calculated a multipolar expansion of interaction energy. As far as we know, these authors were the first to show that a *n*-polar contribution higher than quadrupolar has to be considered in order to estimate interaction energy. Unfortunately, the expressions they used to calculate them[5] present some typographic errors.

In 1959, Buckingham[6] gave an expression for the reaction field gradient inside a spherical cavity containing a central point quadrupole, the cavity being immersed in a continuum of a given

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electric permittivity. When applied to point dipoles, this approach is equivalent to that proposed by Böttcher and Abraham.

In this context, it is interesting to note that the derivation of the series giving the reaction field of a charge distribution inside a spherical cavity starts from the expression of the electric potential of the charge distribution ϕ_0.[7] ϕ_0 appears in the form of an infinite series of terms, each of which depends on the n-poles ($l = 0, 1, 2, 3, ...$) associated with the charge distribution and with the corresponding spherical harmonics (because the cavity is considered to be spherical). These n-poles are point n-poles located at the center of the cavity. The electric potential ϕ_R inside the cavity[8] that is due to the inhomogeneous polarization of the surrounding solvent and that can be described as a reaction potential is obviously expressed by an infinite series, because ϕ_R is derived from ϕ_0 when the appropriate boundary conditions are taken into account.[2] Each ϕ_0 and corresponding ϕ_R contribution can be associated with a particular n-pole and can therefore be described as the dipole term, the quadrupole term, the octupole term, and so on ...

If ${\phi_R}^i$ values, i.e., the ϕ_R value evaluated at the position of each charge e_i, are known, it is easy to estimate the electrostatic interaction energy of the charge distribution with its surroundings. Obviously, if the charge distribution is described in terms of one or two excentrated point dipoles, the knowledge of reaction field R^i [with $R^i = (-\text{grad } \phi_R)^i$] at their position(s) also leads[9] to the estimation of the interaction energy. Finally, if the charge distribution is described as an infinite sum of point n-poles located at the center of the cavity, the interaction energy can be calculated from the successive derivatives of ϕ_R at this position.[10] This approach is the one that we have used in this work while at the same time extending previous calculations in order to take into account the octupolar term for which, as far as we know, no explicit estimation has been published in the literature.

The advantage of using the centered n-pole model is related to the fact that n-polar moments are experimental values. Obviously, if many dipolar moments have been measured, the situation is not so favorable for quadrupolar moments and is even less so for octupolar moments. The measurement of quadrupolar moments for dipolar molecules was performed in a number of cases, and the problem of the choice of the origin of the coordinates was not trivial.[11,12] Nevertheless, from a theoretical and an experimental point of view, nothing prevents the determination of n-polar moments with $n > 2$. These quantitites can also been calculated, but in this case the number of accurate values of quadrupolar or octupolar moments of organic molecules remains very scarse.

As we will show later, the dipole, quadrupole, and octupole moments for *cis*- and *trans*-1,2-dichloroethylene used in this work are calculated values. These values themselves are based on the estimation of the charge distribution in each isomer. The calculated moment values are certainly inaccurate due to the theoretical difficulty inherent in representing the electronic distribution of a molecule by charges located on each atom of the molecule.[13,14] This limitation is not crucial because our aim during this work was firstly to clarify some problems related to the use of the reaction field theory and secondly to extend the model to the octupolar term and to show by means of a particular example, for which we have experimental thermochemical values, how the theoretical model can be applied. The quality of the theoretical results will certainly depend on the crudeness of our moments values, but this fact does not affect the general conclusions of our work.

Theoretical Model

Several definitions of the quadrupole moment and higher moments are used in the literature. We would like to insist on the importance of being very careful about the self-consistency of the definitions and notations. In this work we have used Buckingham's[15] definitions and tensorial notations.

Briefly the theoretical model is the following: the neutral solute molecule is represented by charges e_i at points x_i, y_i, z_i enclosed in a spherical cavity of radius a. The distance from charge e_i to the center of the cavity is r_i. The field of this charge distribution polarizes the surrounding solvent, which is assimilated to a continuum of permittivity ϵ. The inhomogeneous polarization of the solvent gives rise to an inhomogeneous field—the reaction field. Solute–solvent interaction free energy is described as a sum of two contributions, i.e., the interaction energy of the distribution of charges with its own reaction field (negative contribution) and the polarization energy of the surrounding solvent (positive contribution).

According to this model, the sum of these two contributions can be described by an infinite series of terms

$$\bar{G}_{n\text{-polar int}} = N_A[-(1/2)\mu_\alpha R_\alpha - (1/6)\theta_{\alpha\beta}R_{\alpha\beta}' - (1/30)\Omega_{\alpha\beta\gamma}R_{\alpha\beta\gamma}'' - ...] \quad (1)$$

The first term in relation 1 corresponds to the well-known dipolar interaction term in which μ_α and R_α are the α component of the point dipole and the reaction field at the center of the cavity $\mu_\alpha = \sum_i e_i r_{i\alpha}$ with $r_{i\alpha} = x_i, y_i$, and z_i and

$$R_\alpha = [2(\epsilon - 1)/(1 + 2\epsilon)]a^{-3}\mu_\alpha$$

The second term is the quadrupolar interaction term. $\theta_{\alpha\beta}$, the $\alpha\beta$ component of the quadrupole moment of the distribution (with the center of the cavity taken as origin), is given by

$$\theta_{\alpha\beta} = (1/2)\sum_i e_i[3r_{i\alpha}r_{i\beta} - r_i^2\delta_{\alpha\beta}]$$

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(7) $\phi_0 = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} b_l^{(m)} r^{-l-1} P_l^{(m)}(\cos\theta)e^{jm\zeta}$ where the coefficients $b_l^{(m)}$ can be calculated from the charges and their coordinates; r, θ, ζ is the position where ϕ_0 is calculated, and $P_l^{(m)}(\cos\theta)e^{jm\zeta}$ are the spherical harmonics. Applied to an axial distribution of charges $e_i(z_i)$, it gives

$$\phi_0 = (\sum_i e_i)r^{-1}P_0(\cos\theta) + (\sum_i e_i z_i)r^{-2}P_1(\cos\theta) + (\sum_i e_i z_i^2)r^{-3}P_2(\cos\theta) + ...$$

When ϕ_0 is differentiated by z_i and $e_i\,dz_i = \mu_i$ and $z_i = s_i$, the potential due to the dipoles $\mu_i(s_i)$ is written in terms of Legendre polynomials as follows:

$$\phi_0 = (\sum_i \mu_i)r^{-2}P_1(\cos\theta) + 2(\sum_i \mu_i s_i)r^{-3}P_2(\cos\theta) + ...$$

(8) Expression of ϕ_R at a point $P(z)$ due to the charges $e_i(z_i)$ in spherical cavity of radius a:

$$\phi_R = -[(\epsilon - 1)/\epsilon]\sum_i e_i/a - [2(\epsilon - 1)/(1 + 2\epsilon)][\sum_i e_i z_i/a^3]z - [3(\epsilon - 1)/(2 + 3\epsilon)][\sum_i e_i z_i^2/a^5]z^2 - ...$$

(9) Expression for R at a point $P(z)$ and due to the charges $e_i(z_i)$:

$$R = -\frac{\partial\phi_R}{\partial z} = [2(\epsilon - 1)/(1 + 2\epsilon)][\sum_i e_i z_i/a^3] + [6(\epsilon - 1)/(2 + 3\epsilon)][\sum_i e_i z_i^2/a^5]z + ...$$

Expression for R at a point $P(z)$ and due to the dipoles $\mu_i(s_i)$:

$$R = [2(\epsilon - 1)/(1 + 2\epsilon)][\mu_i/a^3] + [6(\epsilon - 1)/(2 + 3\epsilon)][2\mu_i s_i/a^5]z + ...$$

The interaction free energy, $G = -{}^1/_2\mu R$, for one excentric point dipole directed along the radius vector is given by

$$G = -[(\epsilon - 1)/(1 + 2\epsilon)]\mu^2/a^3 - [6(\epsilon - 1)/(2 + 3\epsilon)]\mu^2 s^2/a^5 - ...$$

and is identical with the relation published by Böttcher.[2]

(10) Successives derivatives of ϕ_R calculated at the center of the cavity in the particular case of an axial charge distribution:

$$R_{z=0} = [2(\epsilon - 1)/(1 + 2\epsilon)][\sum_i e_i z_i/a^3]$$

$$R'_{z=0} = [6(\epsilon - 1)/(2 + 3\epsilon)][\sum_i e_i z_i^2/a^5]$$

This last relation was derived by Buckingham.[6]

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Table I. Heats of Solution (kcal/mol) at Infinite Dilution and at 25 °C

	solvent[a]			
	C_6H_{12}	$(CH_3)_2CO$	CH_3CN	C_6H_6
$\bar{H}_{g\to s}$ cis	−6.4	−8.1	−7.4	−7.6
$\bar{H}_{g\to s}$ trans	−6.4	−7.6	−6.9	−7.0

[a] Permittivity of solvents: C_6H_{12}, 2.015; $(CH_3)_2CO$, 20.70; CH_3CN, 34.58; C_6H_6, 2.274 (at 25 °C).

Table II. Partial Molar Volumes (mL/mol)

	solvent				
	C_6H_{12}	$(CH_3)_2CO$	CH_3CN	C_6H_6	pure liquid
$\bar{V}$ cis	79.0	75.4	75.7	76.2	76.0
$\bar{V}$ trans	80.6	76.8	77.5	78.7	77.8

Table III. Molar Enthalpies of Cavity (kcal/mol)

	solvent			
	C_6H_{12}	$(CH_3)_2CO$	CH_3CN	C_6H_6
$\bar{H}_{cav}$ cis	5.6 (5.3)	7.5 (7.3)	10.1 (10.1)	6.8 (6.8)
$\bar{H}_{cav}$ trans	5.7 (5.4)	7.6 (7.4)	10.3 (10.3)	7.1 (7.0)

Table IV. Heats of Interactions of Solute-Solvent (kcal/mol)

	solvent			
	C_6H_{12}	$(CH_3)_2CO$	CH_3CN	C_6H_6
$\bar{H}_{int}$ cis	−12.0	−15.6	−17.5	−14.4
$\bar{H}_{int}$ trans	−12.1	−15.2	−17.2	−14.1

where $r_{i\alpha}$ and $r_{i\beta} = x_i$, y_i, and z_i. ($\delta_{\alpha\beta}$ is the substitution tensor $= 1$ if $\alpha = \beta$, $= 0$ if $\alpha \neq \beta$). The expression for $R_{\alpha\beta}'$, i.e., $R_{\alpha\beta}' = [6(\epsilon - 1)/(3\epsilon + 2)]a^{-5}\theta_{\alpha\beta}$, of the $\alpha\beta$ component of the reaction field gradient at the center of the cavity has been published by Buckingham.[6]

The third term or octupolar interaction term was derived during our study. According to Buckingham, the $\alpha\beta\gamma$ component of the octupole moment tensor is given by

$$\Omega_{\alpha\beta\gamma} = {}^1\!/_2\sum_i e_i[5r_{i\alpha}r_{i\beta}r_{i\gamma} - r_{i\alpha}r_i^2\delta_{\beta\gamma} - r_{i\beta}r_i^2\delta_{\alpha\gamma} - r_{i\gamma}r_i^2\delta_{\alpha\beta}]$$

for the $\alpha\beta\gamma$ component of the octupole moment. The gradient of the reaction field gradient at the center of the spherical cavity of radius a due to the presence of an octupole moment located at the same position is given by:

$$R_{\alpha\beta\gamma}'' = [24(\epsilon - 1)/(3 + 4\epsilon)]a^{-7}\Omega_{\alpha\beta\gamma}$$

Consequently, the octupolar interaction term is given by relation 2. The corresponding enthalpies of interaction $\bar{H}_{dip}$, $\bar{H}_{quadr}$, and

$$\bar{G}_{oct} = -N_A[4(\epsilon - 1)/5(3 + 4\epsilon)]a^{-7}[\Omega_{xxx}^2 + \Omega_{yyy}^2 + \Omega_{zzz}^2 + 3\Omega_{xxy}^2 + ...] \quad (2)$$

$\bar{H}_{oct}$ can be obtained by application of the Gibbs–Helmholtz relationship.

Results and Discussion

In this study our aim was to obtain a better insight into the factors that govern the relative stability of isomers in solution. Using an experimental approach described previously,[16] we used calorimetry to determine the heat of transfer of the *cis*- and *trans*-1,2-dichloroethylene from the gas phase to different solvents. Strictly speaking, the measurements were performed by using the solutes as pure liquids, but reference to the gas phase can easily be established if the vaporization enthalpy of the solutes are known (as is the case for the two derivatives under study). The molar heats of transfer (gas → solvent), which are obviously equal to the molar heat of dissolution (gas → solvent), are given in Table I. These experimental values are not, per se, a measure of the solute–solvent interactions simply because the heat of dissolution of a gaseous solute is the sum of a solute–solvent term and a solvent–solvent term as was observed more than 40 years ago.[17] It is surprising to observe that this very simple and fundamental concept is not yet generally accepted in the literature. In order to obtain the solute–solvent interaction term we therefore used the approach we developed many years ago.[18] The solvent–solute interaction term is given by the difference between the heat of dissolution and the so-called cavity term.

The calculation of the cavity term requires an estimation of the volume of the cavity occupied by each solute molecule in the solvent. In our previous publication,[19] this volume has always been considered to be the same in all solvents and equal to the molar volume of the pure solute in the liquid state. It can be argued that the molar volume of a solute is not constant from solvent to solvent because it depends on the solute–solvent interaction term. This way of thinking could even be considered to be a limitation of the approach that we have used because it introduces a cross-term between the cavity term and the solute–solvent interaction term. It is obvious that our description of the heat of dissolution as a sum of a solvent–solvent and a solute–solvent term is nothing more than a series limited to the first-order terms. The introduction of second-order terms like the above-mentioned cross-term could, a priori, improve the model. Nevertheless, we are not ready to go in this direction because it is not possible, for the present, to obtain an independent estimation of higher terms. The only "improvement" of the model that we have used in the past and that has been introduced in this study consists of measuring the partial molar volume of the solute in each solvent. We are not even sure that this procedure can be described as a real improvement because the partial molar volume, as indeed all partial molar quantities, is a property of the solution as a whole. It is an oversimplification to consider that in the solvent, each molecule of solute occupies a cavity with a volume equal to the partial molar volume divided by Avogadro's number. Nevertheless, the small difference between the molar volume of each solute and their partial molar volumes in different solvents (Table II) leads to the conclusion that the calculation of the cavity term is not heavily dependent on the previously made assumption that the radius of the cavity is a constant.

The cavity terms given in Table III have been estimated by using, for each solvent, the partial molar volume of the solute determined in this particular solvent. The values indicated in parentheses are given for comparison and have been calculated on the basis of a constant value for the cavity (a volume equal to the molar volume of the pure solute in the liquid state divided by Avogadro's number) for each solvent.

The solute–solvent interaction terms given in Table IV have been obtained by substracting the cavity term (calculated on the basis of a variable cavity volume) from the heat of dissolution ($\bar{H}_{int} = \bar{H}_{diss} - \bar{H}_{cav}$). It appears clearly that the solute–solvent interaction term is not very different for the two diastereoisomers, whatever the solvent. This observation can be explained easily if two factors are taken into account. The first of these is related to the relative importance of London dispersion energy with respect to all the other intermolecular interaction energy terms. Since London's calculations,[20] it has become well-known than even for dipolar molecules, London interaction energy is always strongly dominant and may be ten times higher than the dipole–dipole interaction term (Keesom contribution), which itself strongly dominates the dipole–induced dipole interaction term (Debye

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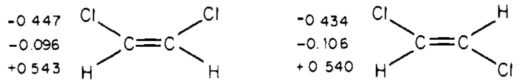

Figure 1. Charge distribution (charges expressed in 10^{-10} esu, $e = 4.803 \times 10^{-10}$ esu).

Table V. Electrostatic Enthalpy of Interaction of *cis*-Dichloroethylene (kcal/mol)

	solvent			
	C_6H_{12}	$(CH_3)_2CO$	CH_3CN	C_6H_6
$\overline{H}_{\text{dip}}$	−0.8 (−0.9)	−1.8 (−2.6)	−1.9 (−2.9)	−0.9 (−1.1)
$\overline{H}_{\text{quad}}$	−0.3	−0.7	−0.8	−0.4
$\overline{H}_{\text{oct}}$	−0.1	−0.3	−0.3	−0.1

Table VI. Electrostatic Enthalpy of Interaction of *trans*-Dichloroethylene (kcal/mol)

	solvent			
	C_6H_{12}	$(CH_3)_2CO$	CH_3CN	C_6H_6
$\overline{H}_{\text{quad}}$	−0.5	−1.3	−1.4	−0.6

contribution). Moreover, for two diastereoisomers, the London energy terms are probably very similar because dispersion energy can be satisfactorily described as an additive contribution property in terms of atom–atom contribution. Therefore, the solute–solvent interaction terms as they appear in Table IV are the sum of a contribution (the London term) that probably accounts for 70–90% and that is more or less equal for the cis and trans isomers. The other terms that can be described as the *n*-polar interaction terms are the only ones that are potentially discriminant with regard to the relative behavior of *cis*- and *trans*-1,2-dichloroethylene.

Obviously, the cis isomer is a dipolar molecule ($\mu = 1.89$ D)[21] whereas the trans isomer is not. However, we have to take the higher moments into account. The trans isomer has a quadrupole moment, its octupole moment is equal to 0 for symmetry reasons, and the cis isomer itself also has moments of order higher than 2. The estimation of the polar contribution to solute–solvent interaction energy therefore requires the calculation of higher terms than the dipolar term, and as we shall see, these contributions are not negligible with respect to the dipolar term. It must be pointed out that the calculation of the quadrupolar and octupolar contributions to the solute–solvent interaction energy requires a knowledge of quadrupolar and octupolar moments. As we said previously, the values that in principle could be determined by using an experimental approach are unknown for the two solutes under study. We were therefore forced to use calculated values even if we knew that such calculated values for molecules of this size are necessarily crude.

In this context, there was no question of calculating the *n*-polar contribution with an accuracy comparable to that which we are able to obtain for the experimental heat of transfer measurements. Indeed, there was little probability of attaining a level of accuracy comparable to that which we were able to obtain in calculating solute–solvent energy from heat of dissolution and cavity term calculation (Table IV).[22] Nevertheless, the values of the dipolar, quadrupolar, and octupolar terms such as they appear in Tables V and VI for cis and trans isomers, respectively, remain very instructive. These values are based on a charge distribution (Figure 1) calculated with a GAUSSIAN-76 program,[23] and each enthalpy contribution itself is evaluated by using the reaction field model for a nonpolarizable dipole, quadrupole, and octupole located at the center of a spherical cavity.

At first view, it may appear unacceptable to neglect the polarizability of the molecule. It is easy to take into account the usual average polarizability α and the reaction field-induced dipole in the expression of dipolar interaction energy,[2] but it is not possible to do the same for the "field gradient quadrupole polarizability" and the "gradient field gradient octupole polarizability" because these are unknown quantities. We therefore decided to compare the various contributions for nonpolarizable solutes (Tables V and VI) and to give in parentheses (in Table V) the dipolar contribution for the cis isomer taken as a polarizable sphere.

The comparison between the values given in Table V clearly shows that the series is not rapidly convergent. The quadrupolar term is far from negligible with respect to the dipolar one, and even the octupolar term is significant. A comparison between the cis and trans isomers (Tables V and VI) leads to the unequivocable conclusion that the quadrupolar contribution of the trans isomer is comparable to the dipolar contribution of the cis isomer (itself not very different from the quadrupolar contribution). This conclusion is far from surprising if we consider some of the results previously reported in the literature by Böttcher[2] and even better by Abraham,[4] for example.

Even so, just as in the case of the solvent–solvent interactions in the dissolution process,[19] it appears necessary to use simple examples to show how the neglect of important contributions can lead to an inaccurate description of the intermolecular interactions in the liquid phase. At a qualitative level, as frequently used by organic chemists in order to describe the so-called solvent effect on the relative stability of isomers, the neglect of interactions implying higher moments than the dipole moment can lead to completely false conclusions. This last comment was also emphasized in Julg's publication[13] where he said: "in these cases (condensed states) it will be necessary to take into account higher order terms of the multipole expansion". The situation is obviously different in the gas phase when the average distance between molecules is larger, with the result that the higher terms become negligible with respect to the first non-zero term.

Experimental Section

cis- and *trans*-dichloroethylene are commercial products (Aldrich). They were further purified by distillation at normal pressures on a Nester-Faust Corp. distillation apparatus. Purity (higher than 99%) was determined by VPC.

Calorimetric Measurements. The heats of solution were measured on an LKB 8700-1 calorimeter. Data treatments were performed as described in Wadsö's original paper.[24]

Partial Molar Volume Determination. The density measurements of the solutions were performed with a digital Precision-Densimeter DMA 10.

Acknowledgment. We thank D. Berckmans for his assistance in obtaining the charge distributions calculated on the basis of a GAUSSIAN-76 program.

Registry No. *cis*-Dichloroethylene, 156-59-2; *trans*-dichloroethylene, 156-60-5.

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