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Mutual Solubilities of Water and Hydrocarbons from an Equation of State: Need for an Unconventional Mixing Rule

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ABSTRACT

For calculating mutual solubilities of water and hydrocarbons with an equation of state, none of the conventional mixing rules are satisfactory for engineering calculations. Based on recent experimental data, an unconventional modification is introduced into the usual quadratic mixing rule for attractive-energy parameter $a$; this modification represents the well-studied hydrophobic effect. For the temperature range 20 to 200°C, quantitative description of mutual solubilities in binary systems is obtained with three binary parameters. Attempts to correlate these parameters with molecular properties were only partially successful.

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Introduction

Aqueous-hydrocarbon systems occur frequently in industrial operations, especially in petroleum-refining, coal-gasification, and similar fossil-fuel processes. For design of process steps, it is important to estimate the compositions of the coexisting equilibrium phases. It is desirable to base these estimates on a molecular-thermodynamic model with parameters which can be calculated from a minimum of experimental data. However, systematic experimental data are required to obtain parameters in the model. While experimental data at normal temperatures have been available for many years, only a few authors have recently reported high-temperature mutual solubilities of hydrocarbons and water (Brady et. al., 1982; Tsonopoulos and Wilson, 1983; Heidman et. al., 1985; Anderson and Prausnitz, 1986; Leet et. al., 1987; Hooper et. al., 1988a). In a recent publication, we reported a hydrocarbon-water mutual-solubility correlation based on UNIFAC (Hooper et. al., 1988b). In this work, we report studies toward correlating mutual-solubility data using an equation of state.

The phase behavior of water-hydrocarbon systems was described by Brady et. al. (1982) and Tsonopoulos and Wilson (1983). The phase diagram indicates that two or three phases may coexist: liquid-liquid equilibria for a hydrocarbon-rich and a water-rich phase, the corresponding vapor-liquid-liquid equilibria along the three-phase curve, and vapor-liquid equilibria with either a water-rich or a hydrocarbon-rich liquid phase. Brady et al (1982) measured mutual solubilities along the three-phase curve for a number of aliphatic and aromatic hydrocarbons with water; some conclusions can be drawn from their extensive and systematic studies. Whereas the solubility of water in the hydrocarbon phase varies only slightly within a class of hydrocarbons, the hydrocarbon solubility in the water phase, which is orders of magnitude lower, is a strong function of molecular weight and molecular structure. The solubilities in both phases are strongly temperature dependent and change by two to three orders of magnitude between room temperature and the three-phase critical end point. It was found that the equilibrium three-phase pressure can often
be estimated as the sum of the pure-component vapor pressures, as reported many years ago by Scheffer (1913,1914).

Gill et al (1975,1976) measured enthalpies of solution for some hydrocarbons in water to study the effect of temperature on hydrocarbon solubility. Since the solubility is very low, the relationship between solubility and enthalpy is given by:

\[
\left( \frac{\partial \ln x_i}{\partial T} \right)_P = \frac{\Delta h_i^\infty}{RT^2} = \frac{\bar{h}_i^\infty - h_i}{RT^2}
\]  

(1)

where \( x_i \) is the mole fraction of hydrocarbon \( i \) in the water-rich phase. The enthalpy of solution at infinite dilution \( \Delta h_i^\infty \) is the difference between the partial molar enthalpy of hydrocarbon \( i \) in solution and the enthalpy of the pure liquid hydrocarbon at the same temperature.

Gill's measurements between 288 and 308 K show that \( \Delta h_i^\infty \) increases linearly with temperature from negative values at low temperatures to positive values at high temperatures. The calorimetric experiments therefore confirm the experimentally observed solubility minimum.

Although phase-equilibrium measurements are essential for the development of a molecular-thermodynamic model, they do not alone reveal the physical nature of water-hydrocarbon interactions, commonly called hydrophobic interactions or the hydrophobic effect. Since the unique behavior of water and aqueous solutions has long been recognized by physical chemists and biochemists, many experimental results are available for these systems in the region 20-50°C. Several properties (e.g. partial heat capacity, activity coefficient) exhibit extrema at dilute hydrocarbon concentrations (Desnoyers, 1982; Mikhailov, 1968) and spectroscopic data indicate solute clustering in dilute aqueous solutions (Shealy and Sandler, 1988). This association is driven by the strong interaction between water molecules which form a
unique three-dimensional structure of hydrogen bonds. But this three-dimensional structure is fragile and changes rapidly as temperature rises, which is evident, for example, in the unusually large heat capacity. This observation is consistent with the large temperature dependence of solubility of hydrocarbons in water.

Detailed structural information can be obtained by computer simulation. Jorgensen (1982) studied the structure of water molecules around an n-butane molecule. He observed that the bonding and energetic characteristics in the first shell around the solute are essentially the same as those in bulk water. Since the coordination number of water molecules in the first shell is lower than that in the bulk, there must be enhanced structuring around the solute molecule. Unfortunately, the temperature dependence of this effect was not studied by computer simulation. An interesting experimental result, however, was found by Shinoda (1968,1977), who observed a linear relation between the logarithm of the solubility and the reciprocal temperature for several n-alkanes in water at high temperatures. He concluded that at high temperatures, structure formation around the solute tends to disappear and that the solution then resembles normal behavior.

Models for aqueous solutions

Along with experimental investigations, various models have been proposed for aqueous solutions. These models were reviewed by Franks (1973) and more recently by Shealy (1985). Unfortunately, applicability of many of these models to engineering calculations is limited because the models are either valid only for a limited concentration range (e.g. the model of Nemethy and Scheraga, 1962) or contain too many adjustable parameters (e.g. the model of Mikhailov, 1968).

Chemical engineers like to use van der Waals-type equations of state and conventional activity coefficient models to calculate phase equilibrium in aqueous systems. Since these simple models cannot easily account for the unique properties of aqueous solutions, the adjustable parameters are essentially empirical with little physical significance.
The solubility of water in the hydrocarbon phase and the composition of the vapor phase can be calculated with simple equations of state using the one-fluid van der Waals mixing rule with one temperature-independent binary parameter for each binary system (Peng and Robinson, 1976; Tsonopoulos and Wilson, 1983). However, to calculate the hydrocarbon solubility in the water phase a different temperature-dependent binary parameter must be used (Peng and Robinson, 1976; Tsonopoulos and Heidman, 1986). This procedure is physically inconsistent. Mutual-solubility data clearly show that the conventional quadratic van der Waals mixing rule for attractive-energy parameter \( a \) is inadequate for water-hydrocarbon systems. The quadratic mixing rule cannot account for the highly specific interactions between water molecules which determine the behavior of the water-rich phase.

Considerable improvement has been obtained in recent years using the mixing rule of Huron and Vidal (1979) and subsequently developed density-dependent mixing rules (For a review see Copeman and Mathias, 1986). For example, Tsonopoulos and Heidman (1986) calculated mutual solubilities in the system water-ethylcyclohexane using the mixing rule of Huron and Vidal. While quantitative agreement was obtained for hydrocarbon solubility over a temperature range of about 50-200°C, representation of the hydrocarbon phase is worse than that obtained with the simple quadratic mixing rule. However, Tsonopoulos and Heidman suggest that significantly better predictions are possible if a temperature dependence is assigned to one of the binary parameters.

Lüdecke and Prausnitz (1985) applied a simple density-dependent mixing rule to vapor-liquid and liquid-liquid equilibria in aqueous solutions. Three binary parameters were necessary to obtain quantitative agreement with experimental data. While it is remarkable that even the minimum in the hydrocarbon solubility can be reproduced with this simple mixing rule, the composition of ternary systems could not be predicted using binary data alone. This failure for multicomponent systems results from the lack of correlation between the model parameters and molecular
Other mixing rules with three binary parameters and a cubic composition dependence were developed by Panagiotopoulos and Reid (1986) and by Mathias and Copeman (1984). The results are similar to those of Lüdecke and Prausnitz.

Cubic mixing rules have also been used by Cotterman and Prausnitz (1986) and by Dimitrelis and Prausnitz (1988) for highly asymmetric mixtures. Whereas Cotterman and Prausnitz calculated aqueous phase equilibria only for light hydrocarbons, the equation of state used by Dimitrelis and Prausnitz has also been applied to aqueous equilibria with heavy hydrocarbons. The solubility in the water phase can be well calculated using a simple temperature dependence for one binary parameter, but a systematic deviation has been observed for the hydrocarbon phase. If the second binary parameter is held constant, calculated solubilities for water in hydrocarbons are systematically too high as shown in Figure 1 for water-cyclohexane.

Chemical theory provides another method for associated mixtures. It has been applied to aqueous solutions by Baumgartner et. al. (1980), Hu et. al. (1984) and Ikonomou and Donohue (1986). Hu et. al. obtained good results for the solubilities of small, nonpolar molecules in water, but found large deviations for molecules like benzene. As in the model of Baumgartner et. al., a slight temperature dependence for the interaction parameter was necessary for quantitative agreement with experimental data. Ikonomou et. al. did not calculate liquid-liquid equilibria for water-heavy hydrocarbon systems.

An approach similar to that of deSantis et al (1974) has recently been used by Lee and Chao (1988). Their model is based on the separation of polar and nonpolar interactions. For the nonpolar part, the BACK equation of state (Chen and Kreglewski, 1977) is used; the polar part was determined empirically for water and extended to other hydrogen-bonding fluids by introducing corresponding states. Remarkable results were obtained for methane and some other light hydrocarbons with only two temperature-independent binary parameters. Unfortunately, no results were given for heavier hydrocarbons which are of primary interest here.
Kabadi and Danner (1985) have proposed a mixing rule which indirectly addresses the change in water structure on adding a nonpolar solute. For the attractive-energy constant they propose

\[ a_M = x_1^2 a_{11} + x_2^2 a_{22} + 2x_1 x_2 (a_{12} + x_1 a_{12}^\prime) \]  
\[ a_{12} = (1-k_{12})(a_{11} a_{22})^{1/2} \]  
\[ a_{12}^{\prime\prime} = G \left( 1 - T_{r1}^{0.8} \right). \]

Here index 1 denotes water, subscript M refers to mixture, \( T_{r1} \) is the system temperature divided by the critical temperature of water, and \( k_{12} \) and \( G \) are binary parameters.

To provide estimates for water-hydrocarbon equilibria when no data are available, Kabadi and Danner developed a procedure for estimating binary parameters \( k_{12} \) and \( G \). Within a homologous series of hydrocarbons, \( k_{12} \) was found to be approximately constant; recommended values are given for seven hydrocarbon classes. A group contribution method was proposed for estimating \( G \), i.e.,

\[ G = \frac{1}{2} \sum_j g_j \]

where the \( g_j \) represent hydrocarbon group parameters. Values of \( g_j \) for fifteen hydrocarbon groups are reported. Figure 2 compares mutual solubilities of water and benzene with estimates based on the correlation of Kabadi and Danner; large deviations are evident, especially for the water-rich phase. However, the correlation of Kabadi and Danner often provides better semi-quantitative estimates for water-hydrocarbon equilibria than some other, generalized correlations (e.g., UNIFAC with the original, temperature-independent parameters).

Figure 3 shows improved results obtained by adjusting \( k_{12} \) and \( G \) to the compositions of the coexisting phases. Large errors remain for the water phase, and the
calculated curvature of the hydrocarbon solubility in water is convex upward instead of concave upward, as observed experimentally. This deficiency of the mixing rule was noted in the original publication. Results for the hydrocarbon phase show systematic deviations at higher temperatures because the proposed mixing rule does not reduce to the expected quadratic mixing rule at high temperatures. Water solubilities in the hydrocarbon phase are appreciable at higher temperatures and thus \( a_{12} \) in Equation 3 contributes to \( a_M \) for the mixture. For comparison, the dashed line in Figure 3 shows the composition of the hydrocarbon phase calculated with the van der Waals mixing rule (i.e. with \( G=0 \)).

Heidman et al (1985) examined the influence of a second binary parameter, which was introduced in the mixing rule for size parameter \( b_M \):

\[
b_M = x_1^2 b_{11} + x_2^2 b_{22} + 2x_1 x_2 b_{12} \tag{7}
\]

\[
b_{12} = \frac{1}{2} (1 + l_{12})(b_{11} + b_{22}) \tag{8}
\]

They found that binary parameter \( l_{12} \) greatly improves the predicted VLE (hydrocarbon-rich phase) at temperatures close to the three-phase critical end point. At lower temperatures (approximately up to 200°C), the results for VLE obtained with one or two parameters are essentially identical. However, the values of \( l_{12} \) required to fit the data for water-hydrocarbon mixtures can be either positive or negative; their physical significance (if any) is obscure.

**An Unconventional Mixing Rule for Water-Hydrocarbon Mixtures**

The ordinary quadratic mixing rule for \( a_M \) seems to be adequate for dilute solutions of water in hydrocarbons but it fails badly for dilute solutions of hydrocarbons in water due to the significant changes in the structure of water in the first coordination shell around the hydrocarbon molecule. As indicated by independent experimental data, the presence of a hydrocarbon molecule in an excess of water
changes the intermolecular forces between water molecules as reflected in the pure-water parameter $a_{11}$. To represent solubility data for both ends of the water-hydrocarbon composition scale, it is therefore necessary to assign a composition dependence not to $a_{12}$ but, instead, to $a_{11}$ with the obvious boundary condition that $a_M \rightarrow a_{11}(\text{pure})$ when $x_1 \rightarrow 1$. For a binary aqueous mixture, therefore, a physically reasonable mixing rule for liquid-liquid equilibria is

$$a_M = x_1^2 a_{11} f(x_2) + x_2^2 a_{22} + 2x_1 x_2 (1-k) (a_{11} a_{22})^{1/2} \quad (9)$$

where the function $f(x_2) \rightarrow 1$ as $x_2 \rightarrow 0$.

In effect, Kabadi and Danner used a mixing rule of this form (Equation 3) but their $f(x_2)$ is not suitable because it is monotonic in $x_2$; their proposal is

$$f(x_2) = 1 + 2 \frac{a_{12}}{a_{11}} x_2 \quad (10)$$

Equation (10) is inconsistent with the experimental data which show that $f(x_2)$ must go through an extremum for small values of $x_2$. For water-hydrocarbon mixtures, we therefore propose

$$f(x_2) = 1 + \beta_{12} x_2 \exp(-\alpha x_2) \quad (11)$$

where $\beta_{12}$ is a temperature-dependent binary parameter and $\alpha$ is a universal positive constant well in excess of unity. Figure 4 shows function $f(x_2)$ for some typical values of $\beta_{12}$ with $\alpha=10$. The position of the maximum in $f$ depends only on $\alpha$ ($x_{2_{\text{max}}} = \frac{1}{\alpha}$). Several thermodynamic properties of hydrocarbons dilute in water exhibit a maximum near 10 mole % solute concentration. Thus, as a reasonable approximation, we set $\alpha=10$ which fixes the maximum position of $f(x_2)$ at $x_2=0.1$. We use Equations 9 and 11 only for liquid-liquid equilibria because the boundary condition for the second virial coefficient at low densities is violated. For a more general form, applicable also to vapor-liquid equilibria, a density dependence must
be included in Equation 11.

Since the simple van der Waals repulsion term (v-b) is known to be incorrect, we prefer to use a van der Waals perturbation of the equation of state of Boublik (1970) and Mansoori et al (1971) for mixtures of hard spheres, as discussed by Dimitrelis and Prausnitz (1987):

\[
A' = A^{BM} - a_M \rho
\]

where \(A'\) is the molar residual Helmholtz energy, \(\rho\) is the molar density and \(A^{BM}\) is given by

\[
\frac{A^{BM}}{RT} = \frac{3DE \xi - E^3}{F^2} + \frac{E^3}{F^2} + \left( \frac{E^3}{F^2} - 1 \right) \ln(1-\xi)
\]

with

\[
\xi = \frac{bp}{4}; \quad b = \frac{2}{3} \pi N_A \sigma^3
\]

\[
F = x_1 \sigma_1^3 + x_2 \sigma_2^3; \quad E = x_1 \sigma_1^2 + x_2 \sigma_2^2; \quad D = x_1 \sigma_1 + x_2 \sigma_2
\]

For a binary mixture, the attractive energy constant \(a_M\) is given by Equations (9) and (11).

When \(x_1\) is very small, the second term in Equation (11) is negligible. Therefore, solubility data for water in hydrocarbons were used to fix binary parameter \(k_{12}\), which varies only slightly from one hydrocarbon to another and which, to a good approximation, is independent of temperature. To fit solubility data for hydrocarbons in water, we find that a good representation can be obtained when \(\alpha\) is set equal to 10 for all hydrocarbons studied over a wide temperature range, and when binary parameter \(\beta_{12}\) is given as a function of temperature according to

\[
\beta_{12} = \tau T^n.
\]

This temperature dependence for \(\beta_{12}\) is empirical, and is too simple to reproduce the
experimentally observed minimum in hydrocarbon solubility at low temperature. However, above this solubility minimum, good agreement with experiment is obtained.

Table 1 gives results for $k_{12}$, $\tau$ and $n$ while Figures 5 to 8 compare calculated and observed mutual solubilities for four representative binary systems. Agreement with experiment is very good but unfortunately, attempts to correlate binary parameters with molecular structure were only partially successful. It was found that at a fixed temperature, $\beta_{12}$ varies linearly with molecular weight for saturated hydrocarbons as shown in Figure 9. Thus, a simple correlation is sufficient for this class of hydrocarbons, although it cannot distinguish between isomers. Unfortunately, no general results were obtained for aromatic hydrocarbons. For aromatic hydrocarbons at least one additional parameter must be included to characterize the interaction between the $\pi$-electrons of the aromatic ring and the water molecules.

Conclusion

Although much progress has been achieved in recent years, an adequate engineering-oriented model for water-hydrocarbon systems is still not available. None of the conventional mixing rules can quantitatively describe the increased ordering of water molecules around a nonpolar solute molecule. However, the unconventional mixing rule (Equations 9 and 11) provides a useful empirical approximation. A truly satisfactory approach must first focus on the equation of state for pure water, clearly separating nonpolar interactions, polar interactions and hydrogen bonding. Some promising progress for hydrogen-bonded fluids has recently been obtained by Chapman et al (1987).

Acknowledgement

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Foundation (West Germany) for the grant of a fellowship.

List of Symbols

\( a \) attractive-force parameter
\( A \) Helmholtz energy
\( b \) van der Waals covolume parameter
\( D, E, F \) defined in Eqn. (13)
\( g \) group contribution parameter
\( G \) defined in Eqn. (5)
\( h \) enthalpy
\( k \) binary interaction parameter (defined in Eqn. (4))
\( l \) binary interaction parameter (defined in Eqn. (8))
\( n \) exponent in Eqn. (11)
\( N_A \) Avogadro's number
\( P \) pressure
\( R \) gas constant
\( T \) temperature
\( x \) mole fraction

Greek letters

\( \alpha \) constant in Eqn. (11)
\( \beta \) binary parameter (defined in Eqn. (11))
\( \rho \) molar density
\( \xi \) reduced density
\( \sigma \) hard-sphere diameter
\( \tau \) constant in Eqn. (11)
Subscripts

i  component i  
M  mixture  
r  reduced property  
1  water  
2  hydrocarbon  

Superscripts

r  residual property  
-  partial property  
∞  infinite dilution  
BM  Boublík-Mansoori
References

Anderson, F.E. and Prausnitz, J.M., 1986. Mutual solubilities and vapor pressures for binary and ternary aqueous systems containing benzene, toluene, m-xylene, thiophene and pyridine in the region 100-200°C. Fluid Phase Equilibria, 32: 63-76


Heidman, J.L., Tsonopoulus, C., Brady, C.J. and Wilson, G.M., 1985. High-temperature mutual solubilities of hydrocarbons and water. Part II:


# TABLE I

Binary parameters for Equations (9) and (11) for Water(1)-Hydrocarbon(2) Systems

<table>
<thead>
<tr>
<th>Component 2</th>
<th>temperature range (K)</th>
<th>$k_{12}$</th>
<th>$\tau$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>313-473</td>
<td>0.237</td>
<td>7.82</td>
<td>-0.306</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>311-550</td>
<td>0.262</td>
<td>37.6</td>
<td>-0.505</td>
</tr>
<tr>
<td>m-diethylbenzene</td>
<td>310-533</td>
<td>0.285</td>
<td>34.4</td>
<td>-0.426</td>
</tr>
<tr>
<td>p-diisopropylbenzene</td>
<td>311-533</td>
<td>0.294</td>
<td>52.9</td>
<td>-0.452</td>
</tr>
<tr>
<td>toluene</td>
<td>372-473</td>
<td>0.273</td>
<td>7.08</td>
<td>-0.240</td>
</tr>
<tr>
<td>m-xylene</td>
<td>373-473</td>
<td>0.303</td>
<td>30.4</td>
<td>-0.443</td>
</tr>
<tr>
<td>1-hexene</td>
<td>310-495</td>
<td>0.355</td>
<td>16.1</td>
<td>-0.332</td>
</tr>
<tr>
<td>1-octene</td>
<td>310-550</td>
<td>0.360</td>
<td>23.9</td>
<td>-0.349</td>
</tr>
<tr>
<td>n-octane</td>
<td>310-540</td>
<td>0.407</td>
<td>26.4</td>
<td>-0.371</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>313-473</td>
<td>0.433</td>
<td>19.0</td>
<td>-0.365</td>
</tr>
<tr>
<td>ethylcyclohexane</td>
<td>311-536</td>
<td>0.422</td>
<td>20.6</td>
<td>-0.328</td>
</tr>
<tr>
<td>n-butylcyclohexane</td>
<td>366-533</td>
<td>0.431</td>
<td>39.9</td>
<td>-0.397</td>
</tr>
</tbody>
</table>
List of Figure Captions

Figure 1: Calculated and observed mutual solubilities for water/cyclohexane. Calculations are based on Dimitrelis' EOS with a cubic mixing rule. Significant deviations arise at higher temperatures.

Figure 2: Calculated and observed mutual solubilities for water/benzene. Calculations are based on EOS, mixing rule and generalized correlation proposed by Kabadi and Danner. Significant deviations are evident.

Figure 3: Calculated and observed mutual solubilities for water/benzene. Calculations are based on EOS and mixing rule proposed by Kabadi and Danner with binary parameters optimized to fit this system. When G=0, the calculated solubility of benzene in water is orders of magnitude too low.

Figure 4: Function $f(x_2)$ for different values of $\beta_{12}$

Figure 5: Calculated and observed mutual solubilities for water/benzene. Calculations based on Equations 9 and 11.

Figure 6: Calculated and observed mutual solubilities for water/m-diethylbenzene. Calculations based on Equations 9 and 11.

Figure 7: Calculated and observed mutual solubilities for water/n-octane. Calculations based on Equations 9 and 11.

Figure 8: Calculated and observed mutual solubilities for water/1-octene. Calculations based on Equations 9 and 11.

Figure 9: Correlation of $\beta_{12}$ with molecular weight and temperature for aqueous mixtures of saturated hydrocarbons.
Figure 1

- Observed (Tsonopoulos and Wilson, 1983)
- Calculated
Figure 2

- $k_{12} = 0.315$
- $G = 3.0207 \times 10^7 \text{ atm cm}^6/\text{mol}$

Observed (Anderson and Prausnitz, 1986)
Calculated

Mole Fraction Water
Mole Fraction Benzene

Temperature (K)
Figure 3

- observed (Anderson and Prausnitz, 1986)

- calculated with $k_{12} = 0.334$ and $G = 2.8482 \times 10^7 \text{ atm cm}^6/\text{mol}$

- calculated with $k_{12} = 0.334$ and $G = 0$
\[ f(x_2) = 1 + \beta_{12} x_2 \exp(-\alpha x_2) \]

\[ \alpha = 10 \]

\[ \beta_{12} = 5 \]

Figure 4
Figure 5
Figure 6

- The graph shows the mole fraction of water and m-diethylbenzene as a function of temperature (K).
- The observed data points are marked with circles and are from Brady et al., 1982.
- The calculated values are represented by a solid line.

Temperature (K):
300 340 380 420 460 500 540

Mole Fraction Water:
10^{-4} \rightarrow 10^{-3} \rightarrow 10^{-2} \rightarrow 10^{-1}

Mole Fraction m-Diethylbenzene:
10^{-6} \rightarrow 10^{-5} \rightarrow 10^{-4} \rightarrow 10^{-3} \rightarrow 10^{-2}
Figure 7
Figure 8

- observed (Brady et al., 1982)
- calculated
Figure 9