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# Internal mixing of the organic aerosol by gas phase diffusion of semivolatile organic compounds

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## Abstract

This paper shows that most of the so far identified constituents of the tropospheric organic particulate matter belong to a semivolatile fraction for which gas phase diffusion in the lower troposphere is sufficiently fast to establish thermodynamic equilibrium between aerosol particles. For the first time analytical expressions for this process are derived. Inspection of vapor pressure data of a series of organic substances reveals that for typical aerosol radii between 0.1 and 1 $\mu$m this mixing process is efficient at 25°C for polar species with molecular weights up to 200 and for non-polar species up to 320. At −10°C, these values are shifted to 150 for polar and to 270 for non-polar substances. Furthermore, this semivolatile fraction is selectively, though not completely, internally mixed with other aerosol constituents, with the extent of mixing governed by equilibrium thermodynamics. The internal mixing leads to a systematic depression of melting and deliquescence points of organic and mixed organic/inorganic aerosols, thus leading to an aerosol population in the lower troposphere which is predominantly liquid.

## 1. Introduction

The tropospheric aerosol is a complex mixture of inorganic and organic components. Depending on location, organic species typically represent 20–50% of the aerosol mass (Dick et al., 2000; Zappoli et al., 1999; Krivácsy et al., 2001). They constitute a very complex mixture covering a wide range of polarity and molecular weights (Rogge et al., 1993). Up to now, the mixing and the physical state of the organic species in the tropospheric aerosol are unclear. Experimental and theoretical thermodynamic considerations indicate that the organic particulate matter remains liquid down to very low relative humidity, if it consists of a high enough number of miscible components. It therefore absorbs/desorbs molecules from/to the gas phase (Marcolli et al., 2004). This assumption is in accordance with smog chamber measurements, which are best



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described by a gas/particle absorptive partitioning model (Odum et al., 1996; Liang et al., 1997). Considering the composition of the so far isolated organic matter (Rogge et al., 1993), which comprises long chain alkanes as well as short chain dicarboxylic acids, at least two liquid phases are expected: a water-soluble and a water-insoluble one. Depending on relative humidity, the water-soluble one will also contain water and inorganic ions.

If a completely internally mixed aerosol is assumed, the partitioning between the gas and the condensed phases can be calculated for a given aerosol composition assuming equilibrium thermodynamics. Such an approach has been described by Pankow (2003). Whether indeed an internal mixture prevails, depends on the efficiency of the mixing processes in the atmosphere. In this work, we estimate the efficiency of mixing by gas phase diffusion for the organic aerosol fraction.

Different processes promote the mixing of the organic aerosol. Sources of primary organic carbon usually emit a multitude of different substances (Seinfeld and Pandis, 1998) with compounds originating from the same source at least partly internally mixed, and coagulation downstream of the source further enhancing internal mixing. Depending on the volatility of the organic compounds, an additional mixing process is gas phase diffusion. This process may establish thermodynamic equilibrium between particles, provided the motion of an air parcel gives the diffusion process enough time.

So far, theoretical studies of transfer processes of volatile species to and from aerosol particles have focused on the equilibration with the gas phase (Wexler and Seinfeld, 1990; Meng and Seinfeld, 1996) without explicitly addressing the coupling between the condensed phases by transport through the gas phase. In this study, particle/particle equilibration is explicitly treated leading to an analytical expression for the time constant of this process. This expression is applied to a broad spectrum of organic aerosol constituents for an estimate of its significance.




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## 2. Analytical solution of internal mixing via the gas phase

As an approximation for the equilibration process of complex aerosol mixtures we consider two monodisperse liquid particle distributions of identical chemical composition except for one species, which is present in different amounts. Gas phase diffusion leads to molecule fluxes between the gas and the liquid phases and between the two particle distributions. In our analysis, the particle distributions and the gas phase form a closed system, which is more general than treating gas/particle phase exchange for each distribution separately. We restrict the analytical solution of the differential equations given below to the case of particle distributions with equal radii. This avoids the algebraic complexity of the unrestricted case, yet provides important insight into the equilibration process. Further, we assess the applicability of this restricted case by comparison with the general case of non-equal radii analyzed by Wienhold et al. (2004)[1].

The molecule number densities of the organic species in the liquid phase, $n^{\ell}_{1,2}$ (taken per unit volume of air), change in time as

$$\frac{dn^{\ell}_{1,2}}{dt} = 4\pi r_{1,2} N_{1,2} D (1+\beta_{1,2})^{-1} \left[ n^{g} - \frac{n^{\ell}_{1,2}}{h_{1,2}} \right], \tag{1}$$

where the indices 1 and 2 refer to particle distributions 1 and 2, respectively, $r_{1,2}$ are the particle radii, $N_{1,2}$ are the particle number densities, $n^{g}$ is the organic molecule number density in the gas phase, $\beta_{1,2}=4D/\alpha r_{1,2}\upsilon$, with $\alpha$ being the accommodation coefficient, $\upsilon$ the mean molecular speed, and $D$ the molecular diffusivity in the gas phase. With the dimensionless Henry's law constant of the corresponding species $H$, defined as the ratio between the liquid phase and the gas phase number density under

[1] Wienhold, F. G., Marcolli, C., Luo, B. P., and Peter, Th.: Analytical treatment of the internal mixing of organic aerosol by gas phase diffusion, Atmos. Environ., to be submitted, 2004.



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thermodynamic equilibrium conditions, $h_{1,2}$ reads

$$h_{1,2} = (4\pi/3) r_{1,2}^3 N_{1,2} H. \tag{2}$$

Mass conservation requires

$$n^{\text{tot}} = n_1^\ell + n_2^\ell + n^g \tag{3}$$

to be constant and couples the differential equations for the liquid phase number densities:

$$\frac{d n_{1,2}^\ell}{dt} = 4\pi r_{1,2} N_{1,2} D (1+\beta_{1,2})^{-1} [n^{\text{tot}} - n_{2,1}^\ell - (1 + \frac{1}{h_{1,2}}) n_{1,2}^\ell]. \tag{4}$$

Assuming now the radii to be equal, $r = r_1 = r_2$ ,

$$\begin{aligned} n_{1,2}^\ell(t) = n_{1,2}^{\ell,\infty} &+ \tfrac{h_{1,2}}{h_1+h_2} \left[ (n_1^{\ell,0} - n_1^{\ell,\infty}) + (n_2^{\ell,0} - n_2^{\ell,\infty}) \right] e^{-t/\tau^g} \\ &\pm \tfrac{1}{h_1+h_2} \left[ h_2 (n_1^{\ell,0} - n_1^{\ell,\infty}) - h_1 (n_2^{\ell,0} - n_2^{\ell,\infty}) \right] e^{-t/\tau^\ell} \end{aligned} \tag{5}$$

solves (Eq. 4) for the initial ($t = 0$) number densities $n_{1,2}^{\ell,0}$ with the equilibrium densities given by $n_{1,2}^{\ell,\infty} = h_{1,2} n^{\text{tot}} \big/ (1 + h_1 + h_2)$. The time evolution of both liquid phases is governed by two distinct time exponentials, while Eqs. (3) and (5) lead to the gas phase solution for the initial number density $n^{g,0}$:

$$n^g(t) = n^{g,\infty} + \left[ n^{g,0} - n^{g,\infty} \right] e^{-t/\tau^g}. \tag{6}$$

Here, $n^{g,\infty} = n^{\text{tot}} \big/ (1 + h_1 + h_2)$ denotes the equilibrium gas phase number density. The time constant

$$\tau^\ell = \frac{H r^2}{3D} (1 + \beta) \tag{7}$$



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describes the equilibration among the liquid particles by diffusion through the gas phase, while the time constant for the equilibration between the gas and the liquid phases is given by

$$\tau^g = \frac{\tau^\ell}{1 + (4\pi/3)Hr^3(N_1 + N_2)}. \tag{8}$$

Interestingly, expression (7) is identical to the time constant for the equilibration between a single droplet and the gas phase in an "open" system, i.e. with the partial pressure held constant. Conversely, the interaction between particles via the gas phase in a "closed" system has not been treated analytically before. The exact shape of Eq. (6) can be traced back to the condition $r_1 = r_2$, resulting in a buffering of the amounts of trace gas shifted between the distributions after the gas phase has come to equilibrium. For $r_1 \neq r_2$, Wienhold et al. (2004)[1] provide a full analytical solution and derive approximations for the limits of (a) non-equal radii with preferred partitioning into the gas phase and (b) near-equal radii or preferred partitioning into the liquid phase without restricting the radii. While (a) reflects the situation of decoupled liquid reservoirs, in (b) the liquid phases are coupled and the time constant for the flux between liquid reservoirs can be approximated by

$$\tau^\ell \cong \frac{H}{3D} \frac{r_1^3 N_1 r_2^3 N_2}{r_1^3 N_1 + r_2^3 N_2} \left( \frac{1+\beta_1}{r_1 N_1} + \frac{1+\beta_2}{r_2 N_2} \right). \tag{9}$$

The relative error of Eq. (9) with respect to the exact analytical solution rises to ~10% for equal partitioning of the species in the gas and liquid phases. Also, $\tau^\ell$ from Eq. (9) is always smaller than or equal to $\tau^\ell$ from Eq. (7) when evaluated at $r = \max(r_1, r_2)$, which makes Eq. (7) a widely applicable formula.

Figure 1 shows examples of the equilibration process starting from the following non-equilibrium situations: the organic species under consideration constitutes 20 wt% of the particles in distribution 1 and 0 wt% in distribution 2, and the gas phase contains half as much of the organic species as distribution 1 in the first case (Figs. 4a and b)




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and nothing in the second case (Figs. 4c and d). The particle number densities are $N_1$=400 cm$^{-3}$ and $N_2$=200 cm$^{-3}$. A molecular weight of 300 is assumed for the organic species. The calculations have been performed for an ambient temperature of 293 K and a dimensionless Henry's law constant of $3\times10^{14}$, corresponding to a vapor pressure of $\sim2\times10^{-10}$ mmHg for the pure substance. The analytical and numerical solutions have been calculated for monodisperse size distributions with particle radii of 0.1 $\mu$m. The numerical solution allows in addition for polydisperse (e.g. initially log-normal) distributions to test the sensitivity on finite size distribution widths, as well as for changes of size due to evaporation/condensation effects. Figure 1 shows that all three cases yield very similar results: the gas phase rapidly reaches equilibrium with a time constant $\tau^g$=7 min. However, the mass transport between the particle distributions is slow: $\tau^\ell\approx$100 h. The very good agreement between the numerical solutions for the monodisperse and polydisperse distributions enables us to apply Eqs. (5) and (6) to particle size distributions under real atmospheric conditions with a high degree of accuracy. Non-monotonous evolutions as displayed in Fig. 1 cannot be described by simpler treatments given in the literature (e.g. the analytical treatment by Meng and Seinfeld, 1996).

## 3. Atmospheric implications

The time constant for the internal mixing of semivolatile components $\tau^\ell$ is proportional to the dimensionless Henry's law constant H. The assessment of $\tau^\ell$ for actual tropospheric conditions requires Henry's law constants of typical organic tropospheric aerosol constituents.

### 3.1. Ideal solutions

The Henry's law constant of a substance depends on both, the volatility of the pure substance and the solubility of a substance in the respective solvent. Mostly, water is



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used as a reference solvent for compilations of Henry's law constants. However, for moderate relative humidities, the water-soluble organic fraction forms a concentrated solution that is not well represented by Henry's law constants for infinitely dilute systems. Moreover, hydrophobic substances such as alkanes do not partition readily into the aqueous phase. Rather, they will partition into the water-insoluble organic fraction consisting of a wide range of hydrophobic substances. Thus, for a representative estimate of the time constants for an organic species dissolving into a predominantly organic solvent, dissolution into an ideal solvent was assumed (Raoult's law). In this case, the Henry's law constants can be estimated based on the vapor pressures of the pure substances, $p^0$, as

$$H \approx \frac{\rho RT}{M p^0}, \tag{10}$$

where $R$ is the universal gas constant, $T$ the absolute temperature, $\rho$ the mass density and $M$ the molar mass of the investigated organic compound. With this approximation, the time constant for equilibration by gas phase diffusion can be expressed as a function of the vapor pressures of the pure substances.

Figure 2 shows vapor pressures of different substance classes at 25°C as a function of molecular weight. For the alkanes (Wilhoit and Zwolinski, 1971), the alkanols (Howard and Meylan, 1997), the alkanoic acids up to ten carbon atoms, small polyols such as glycerol (Howard and Meylan, 1997) and the polycyclic aromatic hydrocarbons (PAH) (Howard and Meylan, 1997; Yaws, 1994), measured values of the liquids and extrapolated values for the supercooled liquids are presented. For the long chain alkanoic acids (Tao and McMurry, 1989), the dicarboxylic acids (Howard and Meylan, 1997; Tao and McMurry, 1989; Chattopadhyay et al., 2001), and the larger polyols such as mannitol, glucose or raffinose (Howard and Meylan, 1997) either estimated or measured values of the solids are given. Figure 2 shows that the vapor pressure is a function of both the molecular weight and the polarity of the substances.

On the right axis in Fig. 2, equilibration time constants are indicated as a function of the vapor pressures of the pure substances for the case of $r$=100 nm particles,



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molecular weights of 100, a diffusion coefficient $D$=0.1 cm$^2$/s, densities of 1.0 g/cm$^3$, a mean molecular speed $\upsilon$=200 m/s, and an accommodation coefficient $\alpha$ = 1. With mixing times longer than 1 week, equilibration by gas phase diffusion for substances with vapor pressures lower than $10^{-10}$ mmHg becomes ineffective. These substances can therefore be considered as non-volatile. Conversely, as a criterion from Eq. (2),

$$(4\pi/3)Hr^3(N_1 + N_2) = 1 \tag{11}$$

must be satisfied for species to partition equally between the condensed and the gas phase. This criterion is approximately fulfilled for the 1 min horizontal line in Fig. 2. Saxena and Hildemann (1996) identified specific organic compounds that are likely to contribute to the water-soluble organic fraction of the aerosol based on the vapor pressure and aqueous solubility of the pure substances. Based on this study, substances with vapor pressures above ~1 mmHg can be assumed to be too volatile to partition effectively into the liquid phase. Thus, substances with vapor pressures in between these two limits, $10^0$–$10^{-10}$ mmHg, are sufficiently non-volatile to be present in the liquid phase and exhibit simultaneously a sufficiently high vapor pressure to establish thermodynamic equilibrium between the aerosol particles on atmospheric timescales (<1 week). Thus, they can be considered as semivolatile. At 25°C, this semivolatile fraction has molecular weights up to 200 for polar, hydrophilic substances and up to 320 for non-polar, hydrophobic substances.

The estimate of the equilibration time constants shown in Fig. 2 depends on several factors, the most important ones being particle size and temperature. Compared to particles with $r$=0.1 $\mu$m used to calculate the equilibration time constants, particles with $r$=1 $\mu$m equilibrate more slowly by a factor of ≈40. Considering that the relevant range in vapor pressure covers about ten orders of magnitude, particle size effects are by far dominated by variations in the Henry's law constants, which depend on temperature and deviations from ideality. Based on either measured or extrapolated values from a compilation by Yaws (1994), it can be concluded that a temperature reduction from 25° to −10°C, leads to a decrease in vapor pressure by one to three orders of magnitude




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depending on the specific substance. Thus, at −10°C equilibration starts to become ineffective for polar substances with molecular weights larger than 150 and for non-polar substances with molecular weights larger than 270.

### 3.2. Non-ideal solutions

For internally mixed liquid aerosol particles, the partial pressure of each individual substance depends on the vapor pressure of the pure substance and its activity in the solution. The time constants for equilibration have been calculated based on the assumption that the substances dissolve into an ideal solvent. In the atmosphere, deviations from ideality may considerably alter the solubility, thus leading to increased or reduced vapor pressures compared with the ideal case. Model calculations of activity coefficients are needed for typical tropospheric aerosol compositions to treat this effect. However, non-ideality will not affect the principal relevance of internal mixing by gas phase diffusion since there is always a range of semivolatile species (hence of $H$ and $M$), for which it will be effective.

### 3.3. Observations

Most of the so far identified constituents of the particulate matter belong to the semivolatile fraction (Rogge et al., 1993). The products from monoterpene oxidation with molecular weights between 130 and 200 have indeed been observed in the gas and in the aerosol phase (Yu et al., 1999). The same is true for PAH and dicarboxylic acids with up to 10 carbon atoms (Fernández et al., 2002; Limbeck et al., 2001; Kavouras and Stephanou, 2002).

For urban samples, Allen et al. (1996) have observed that PAH with molecular weights between 178 and 202 were approximately evenly distributed between the fine and coarse particles. PAH with molecular weights greater than 228 were associated primarily with the fine particle fraction. They proposed slow mass transfer by vaporization and condensation to explain the observed PAH partitioning among particle size




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fractions. This hypothesis is confirmed by our estimates, which predict equilibration times of seconds for PAH with molecular weights below 200 and hours for the ones with molecular weights above 250.

The high degree of internal mixing of the organic aerosol particle fraction has been shown by single particle measurements using on-line mass spectrometry. Based on these measurements, it was concluded that the internal mixture of organic components and sulfate can be regarded as a general characteristic of tropospheric aerosols in the continental region (Lee et al., 2002). Selective mixing is confirmed by the observation that hydrocarbons are rather associated with soot, whereas oxidized organics with sulfate particles (Lee et al., 2003).

Mochida et al. (2003) have studied the size distributions of $C_2$–$C_4$ dicarboxylic acids in aerosols in the marine boundary layer. They found that over the remote ocean these substances were relatively abundant in the supermicron particles whereas over the coastal ocean they were mostly present in submicron particles. Backward trajectory analysis showed that air masses were mostly of continental origin from East Asia, suggesting a shift of the diacids' size distributions from small to larger particles during transport. The $C_2$–$C_4$ dicarboxylic acids exhibit molar Henry's law constants in water in the range from 106–108 M/atm and vapor pressures from $10^{-3}$–$10^{-7}$ mmHg (Saxena and Hildemann, 1996; Howard and Meylan, 1997). Based on both, Henry's law constants and vapor pressures, thermodynamic equilibrium between particles should be established within minutes. Given the decreasing concentration of non-sea-salt sulfate aerosol and assuming a constant level of sea-salt particles, the measurements are indeed in agreement with instantaneous repartitioning of the $C_2$–$C_4$ diacids between the developing inorganic aerosol populations.

### 3.4. Aerosol phase

The internal mixing of the organic aerosol constituents leads to a systematic depression of melting and deliquescence points of organic and mixed organic/inorganic aerosols (Marcolli et al., 2004). Figure 3 shows the abundance of organic substances




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in the water-soluble organic fraction of samples from Tokyo, 1992, in terms of weight percent (Sempéré and Kawamura, 1994). The grey bars give the calculated solubilities assuming ideal behavior (Marcolli et al., 2004). The listed substances will be internally mixed within a second (e.g. pyruvic acid) to an hour (azelaic acid) due to equilibration by gas phase diffusion. The comparison shows that the saturation solubility exceeds the abundance of most substances in the water-soluble organic fraction, thus leading to an aerosol population in the lower troposphere which is predominantly liquid irrespective of the relative humidity conditions.

## 4. Conclusions

The time constants for equilibration between aerosol particles by gas phase diffusion have been calculated analytically under the assumption of monodisperse particle size distributions, and the dependence on this assumption has been demonstrated to be weak. This process contributes considerably to the internal mixing of the organic aerosol particle fraction in the lower troposphere with typical radii between 0.1 and 1 $\mu$m. Inspection of vapor pressure data for a series of organic substances showed that this mixing process is efficient for polar species with molecular weights up to 200 and for non-polar species up to 320 at 25°C, shifting to 150 and 270 at −10°C, respectively. Most of the so far identified constituents of the particulate matter exhibit molecular weights in this range. In order to estimate the overall significance of this mixing process, the whole organic particulate matter has to be characterized better with respect to vapor pressures, or molecular weights and polarities as surrogate properties.

Equilibration by gas phase diffusion leads to a selective – albeit not complete – internal mixture of the organic aerosol. A high degree of internal mixing of the organic fraction with inorganic constituents is experimentally confirmed by an increasing number of single-particle measurements (Murphy and Thomson, 1997; Lee et al., 2002; Lee et al., 2003). Moreover, the internal mixing leads to a systematic depression of




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melting and deliquescence points of organic and mixed organic/inorganic aerosols, thus leading to an aerosol population in the lower troposphere which is predominantly liquid (Marcolli et al., 2004).

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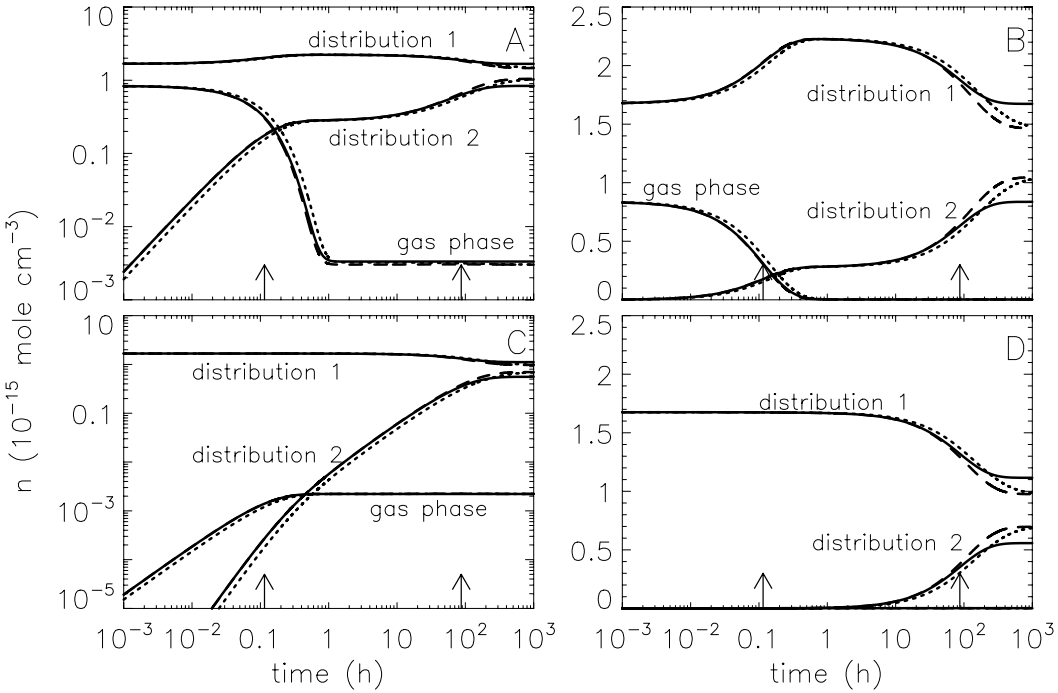


**Fig. 1.** Time evolution of equilibration of an organic species between two particle distributions. Initial conditions: **(a)** and **(b)** distribution 1 contains 2/3 of the organic species of interest (corresponding to 20 wt%), the gas phase the remaining 1/3, distribution 2 is empty; **(c)** and **(d)** the organic species is present only in distribution 1 (again 20 wt%). (a) and (c) show the evolution of the number concentration $n$ in logarithmic, (b) and (d) in linear scales. Solid lines: analytical solutions Eqs. (5–6) neglecting size changes. Dashed lines: numerical simulation for a monodisperse particle size distribution including size changes due to evaporation and condensation of the organic component. Dotted lines: numerical simulation for initially lognormally (mode radius=0.0718 $\mu$m, width $\sigma$=1.6) distributed particle ensembles. Arrows: particle/particle and gas/particle equilibrium time constants, Eqs. (7–8), respectively, which are independent of the initial conditions.



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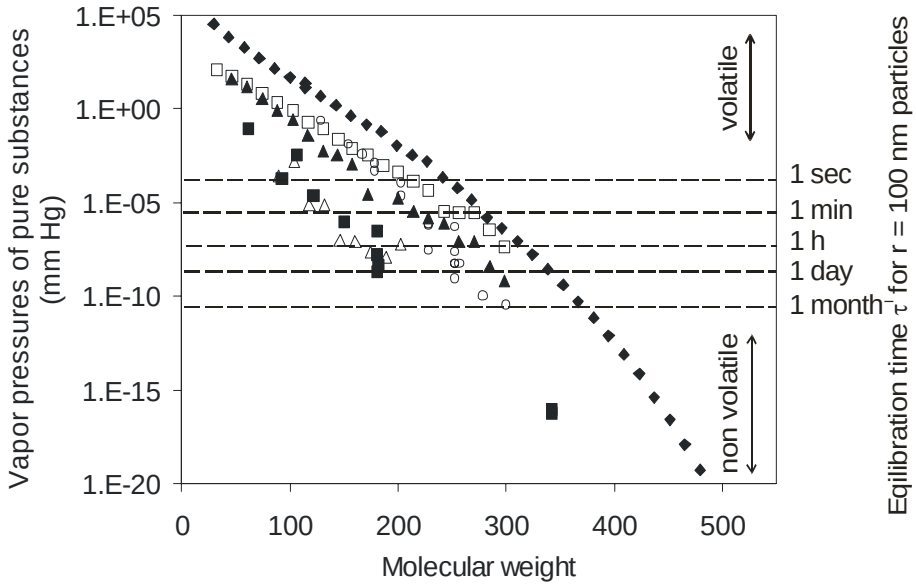


**Fig. 2.** Vapor pressures of pure substances of atmospheric importance at 25°C sorted by molecular weight: alkanes (black ◇), alkanols (□), alkanoic acids (▲), dicarboxylic acids (△), polyols (■), PAH (◯). The right hand axis indicates time constants for equilibration between particles $\tau^{\ell}$ according to Eqs. (7) and (10) for typical atmospheric conditions ($r$=100 nm, $D$= 0.1 cm$^2$/s, $\rho$=1.0 g/cm$^3$, $\upsilon$=200 m/s, $\alpha$=1).



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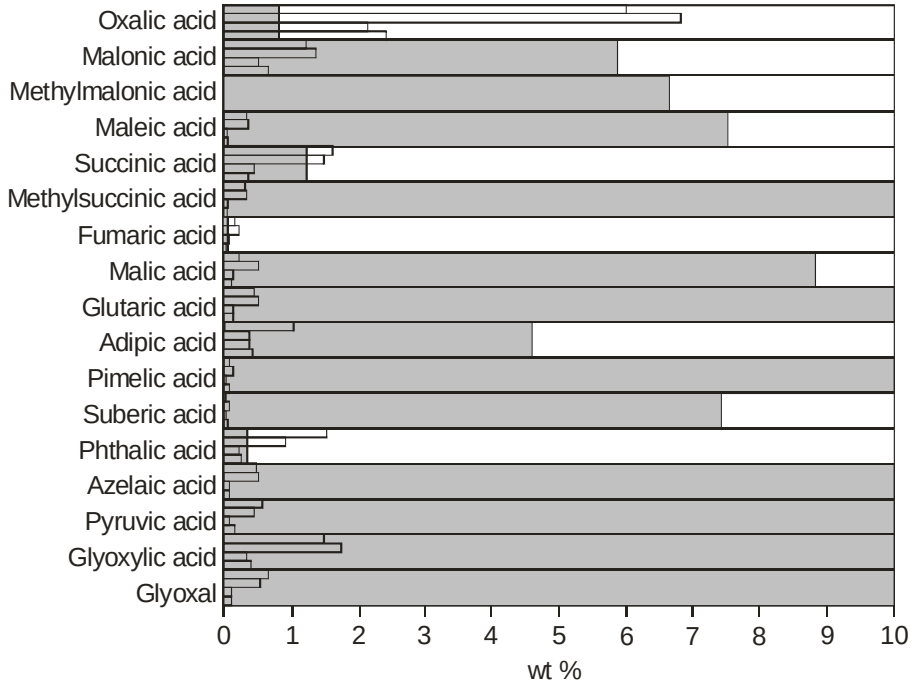


**Fig. 3.** Abundance of organic compounds in the water-soluble organic fraction of four samples from Tokyo, 1992, (transparent bars, four for each compound) (Sempéré and Kawamura, 1994) compared with their solubility in an ideal solvent (grey bars).



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