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Influence of Organics on Structure of Water Adsorbed on Activated Carbons

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Abstract. Influence of organics on the properties of water adsorbed on carbon and silica gel adsorbents was studied by ^{1}H NMR spectroscopy, thermal gravimetry, breakthrough dynamics, and quantum chemistry methods. Te behavior of interfacial water depends strongly on the properties of organic solvents, which can remove a major (nonpolar solvents) or minor (polar solvents) portion of water from narrow pores to larger ones of carbon adsorbents. The opposite effect is observed on the interaction of water/organics with silica gel.

Keywords: activated carbon, silica gel, adsorption, water-organic mixture, ^{1}H NMR, TG, breakthrough

1. Introduction

Carbon adsorbents are used to remove organics from various media with the presence of water. Therefore, it can affect the adsorption of organics (Bansal et al., 1988; Jankowska et al., 1991). The adsorption of water/organic mixtures on carbonaceous or mineral adsorbents is a complex phenomenon because of the nonuniformity of the adsorbent surfaces and specific interaction of polar molecules with polar (e.g. oxygen-containing) surface groups and strong dispersion interaction of aromatics with basal planes of carbons. The kinetics of the adsorption and the displacement of an adsorbate by another one are also of interest because time-dependent efficiency of adsorbents is of importance on their applications. Certain aspects of these effects are unclear (Leboda et al., 2002; Turov et al., 2002; Gun'ko et al., 2003, 2004). Therefore the aim of this work is to elucidate the influence of organics (polar or nonpolar, non-aromatic or aromatic, and soluble or insoluble in water) on the characteristics of water adsorbed on several adsorbents using adsorption, ^{1}H NMR with freezing-out of water, thermal gravimetry, breakthrough dynamics, and quantum chemical methods.

2. Materials and Methods

Commercial carbon Norit R 0.8 Extra (Norit N.V., The Netherlands) (Table 1) was differently treated. Carbons PS1 and PS2 were prepared from plum stones (PSO MASKPOL, Poland). Silica gels Si-40 and Si-100 (Merck) were used in comparative investigations. Suspending in water, drying, freezing by liquid nitrogen, de-ashing, oxidation by H_2O_2, and reduction

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Table 1. Structural characteristics of adsorbents.

Adsorbent	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{mes} (m^2/g)	V_{p} (cm^3/g)	V_{mic} (cm^3/g)
Norit	1553	1101	139	0.80	0.72
PS1	877	800	73	0.45	0.38
PS2	1351	1026	174	0.75	0.59
Si-40	732	296	436	0.54	0.08
Si-100	332	35	297	1.15	0.01

S_{BET}, S_{mic} and S_{mes} are the specific area of all pores, micro-($x < 1$ nm) and mesopores ($1 < x < 25$ nm) respectively; V_{p} and V_{mic} are the total and micropore volume respectively.

Table 2. Free energy of solvation (kJ/mol) of an organic molecule in own solution (E_{o}) or in water (E_{ow}), and a water molecule in organic media (E_{wo}); and relative free energy of solvation E_s, E_{s1}, and E_{s2} (SM5.42/6-31G(d)).

Compound	$-E_o$	$-E_{\mathrm{ow}}$	$-E_{\mathrm{wo}}$	E_{s}	E_{s1}	E_{s2}
C_6H_6	21.9	5.9	2.7	1.62	0.73	0.89
CCl_4	19.5	0.3	0.8	1.96	0.99	0.97
CCl_3H	17.5	2.8	9.8	1.45	0.84	0.61
CH_3CN	10.0	23.1 (0.1)[a]	20.6	−1.11	−1.30	0.19
$(CH_3)_2CO$	23.4	18.5	20.9	0.39	0.21	0.18
$(CH_3)_2SO$	47.8	58.7 (40.0)[a]	25.0	−0.22	−0.23	0.01

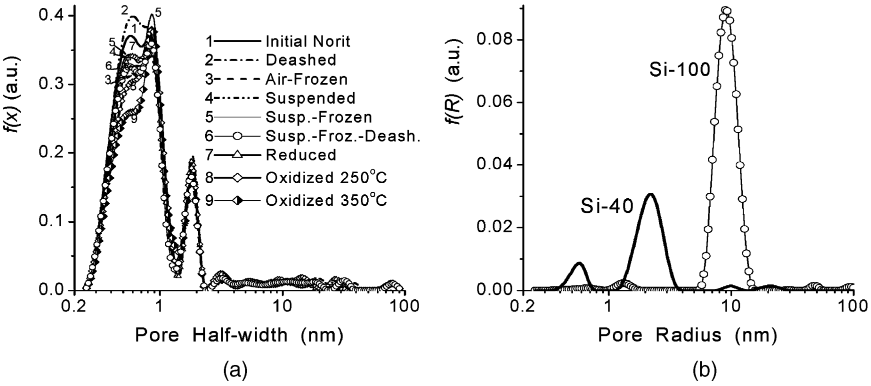
Note: $E_w = -25.4$ kJ/mol; [a]molecule in a slit-like pore. $E_{\mathrm{ow}} = 0.7$ kJ/mol (TBB) and -21.5 kJ/mol (DMMP).

by H_2 applied to carbon Norit affect micropores to a greater extent than mesopores (nitrogen adsorption using a Micromeritics ASAP 2405N analyzer). CD_3CN, $(CD_3)_2CO$, $(CD_3)_2SO$, CCl_4, $CDCl_3$, and C_6D_6 used in the deuterium form to avoid their contribution to the ^1H NMR signal intensity of unfrozen water at $T < 273$ K (WP-100 SY (Bruker) NMR spectrometer) (Turov et al., 2002). These compounds were calculated using quantum chemistry methods with consideration for the solvation effects (Xidos et al., 2002) (Table 2). Thermal gravimetric measurements in quasi-isothermal conditions performed using a Derivatograph C (Paulik, MOM, Budapest) were applied to study desorption of water/organics (tert-butylbenzene (TBB) and metylphosphonic acid dimethyl ester (DMMP)) mixtures.

3. Results and Discussion

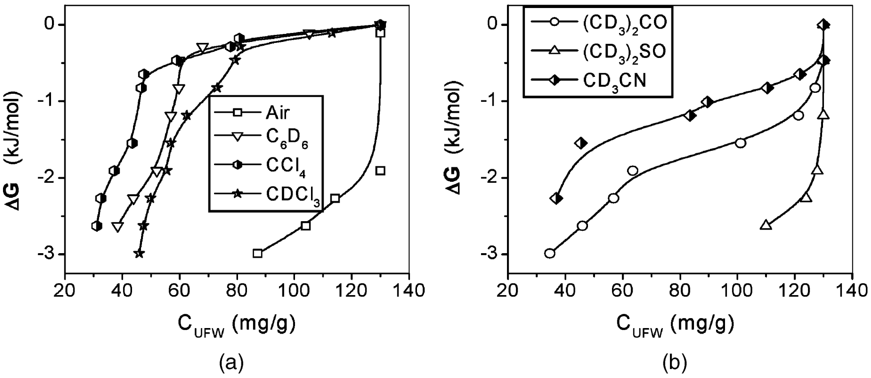
The shape of the pore size distributions (PSD) changes slightly for treated carbon Norit (Fig. 1(a)). The structural characteristics changes in respect to narrow pores. Freezing of the adsorbent (by liquid nitrogen) with adsorbed water (as well as other treatments) gives relatively small structural changes maybe due to appreciable hydrophobic properties of Norit (amount of water adsorbed from air <4 wt.%). A maximal diminution of contribution of the narrowest pores (PSD maximum at $x \approx 0.6$ nm) is caused by oxidation of the carbon Norit, which is also accompanied by enhancement of mesoporosity. A maximal enhancement of the narrow micropores is observed for de-ashed carbon. Silica gels (Fig. 1(b)) are mainly mesoporous. Consequently, one can assume that the structural characteristics determined using the nitrogen adsorption data can be valid on analysis of the ^1H NMR data for water/deuterium organics with freezing-out of adsorbates, as the freezing can be accompanied by relatively small changes in the adsorbent structure (Fig. 1). Therefore, these structural changes can be neglected on the calculations of changes in the Gibbs free energy of adsorbed water (γ_S and differential ΔG_s) determined using calibration function and assuming that ΔG_s of frozen interfacial water is equal to that of ice at the same T (Turov et al., 2002).

Dependences of the ^1H NMR signal intensity of unfrozen adsorbed water and changes in the Gibbs free energy on the amount of unfrozen water (C_{ufw}) (total amount of adsorbed water was constant $C_{H_2O} = 130$ mg per gram of carbon corresponding to 16% of V_p) were studied in the gas phase or with added organics (Fig. 2). The maximal amounts of the used solvents (1000 mg per gram of carbon) correspond to the volume larger than V_p ($\approx$0.8 ccm/g) with the exception of CCl_4 (filling 0.67 cm^3 per gram of carbon at $C_{\mathrm{sol}} = 1000$ mg/g) and CCl_3D (0.63 cm^3 per gram of carbon). However, even for the latter, the total volume of adsorbed water (130 mg/g) and added solvent is close to V_p. Three solvents (CCl_4, $CDCl_3$, C_6D_6) are practically immiscible with water but three others (CD_3CN, $(CD_3)_2CO$, $(CD_3)_2SO$) can form solutions with any concentration of water (in a homogeneous medium). The $\Delta G(C_{\mathrm{ufw}})$ curve for the carbon hydrated in air ($C_{H_2O} = 130$ mg/g) with no addition of organic solvents has a vertical portion. Its appearance is caused by the fact that water becomes frozen in carbon micropores only at a significant lowering of temperature $T \ll 273$ K. This water is strongly bound to the carbon surfaces as $\Delta G < -2$ kJ/mol (which corresponds to the bottom of the vertical portion of $\Delta G(C_{\mathrm{ufw}})$). The $\Delta G(C_{\mathrm{ufw}})$ curve shape changes cardinally in the case of the water/organics if a



(a) (b)

Figure 1. Pore size distributions for (a) treated carbon Norit R 0.8 Extra and (b) silica gels Si-40 and Si-100.



(a) (b)

Figure 2. Changes in Gibbs free energy of interfacial water (total water amount $C_{H_2O} = 130$ mg per gram of carbon) versus the amount of unfrozen water C_{ufw}(a, b) for initial carbon Norit in different media.

solvent is immiscible with water, i.e., its molecules do not form strong hydrogen bonds with water molecules and an absolute magnitude of the free energy of their solvation is relatively small (Table 2). One can see curve portions with small changes in ΔG over a relatively large C_{ufw} range, which can be connected to weakly bound water. Transform of strongly to weakly bound water can be explained by the displacement of a portion (its value dependent on a solvent type) of water molecules (clusters or droplets) by solvent molecules (stronger interacting with nonpolar basal planes than water) from micropores to larger pores. However, a portion of strongly bound water remains in the micropores with the presence of nonpolar solvents. The amount of this water is between 20 and 60 mg per gram of carbon depending on the solvent type. This effect can be caused by the nonuniformity of the carbon surfaces, since different oxygen-containing sites are at the periphery of basal planes (on their edges) at the entrances to narrow pores or in these pores as lattice defects of the planes. Water clusters (Brennan et al., 2001) bonded to such hydrophilic sites correspond to strongly bound water and its displacement by nonpolar organic molecules is difficult, since the interaction energy of nonpolar molecules with hydrophilic sites can be lower than that for water molecules. Additionally, there is the difference in the molecular sizes of water and solvents. Notice that only water and benzene molecules are plain among studied compounds, and this is important, as carbon micropores possess the slit-like shape. That results in different accessibility of narrow pores for adsorbed molecules, and smaller water molecules can remain in these pores inaccessible for larger solvent molecules.

The influence of polar solvents on bound water is significantly weaker than that of nonpolar solvents (Fig. 2), since the vertical portion on the $\Delta G(C_{ufw})$ curves remains (especially for $(CD_3)_2SO$) close to that for water adsorbed in air. The size of this curve

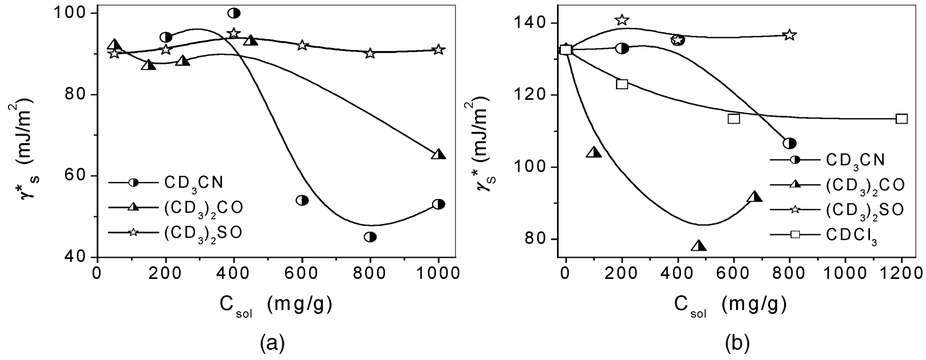


Figure 3. Gibbs free energy of water adsorption on (a) initial carbon Norit and (b) silica gel Si-40 as a function of the concentration of polar organic solvents (C_{sol}) at $C_{\mathrm{H_2O}}$ = (a) 130 mg/g and (b) 175 mg/g (with addition of acetone-d_6), and $C_{\mathrm{H_2O}}$ = 225 mg/g for other organics.

portion decreases in the series $(CD_3)_2SO$ > $(CD_3)_2CO$ > CD_3CN in parallel to diminution of the electron-donor properties of these compounds. The influence of DMSO-d_6 on the γ_S value is very weak (Fig. 3). Consequently, one can assume that this solvent does not remove a marked portion of pre-adsorbed water from narrow pores at $x < 0.7$ nm and its location is akin to that for water adsorbed in air. The molecular size of DMSO-d_6 (as well as acetone-d_6) is larger than that of a water molecule, and a DMSO molecule can be easily placed in a slit-like micropore at the half-width $x \approx 0.5$ nm. Consequently, narrower pores filled by water can be inaccessible or poorly accessible for DMSO. The steric factor can play some role on weak interaction of DMSO-d_6 with water adsorbed in narrow pores ($x < 0.5$ nm). A weaker electron-donor acetone-d_6 does not practically change the γ_S^* value for the interfacial water at the concentration $C_{(CD_3)_2CO} < 400$ mg/g, but with increasing its concentration (>400 mg/g), the water interaction with the carbon surfaces decreases, as γ_S^* drops down. The latter can be caused by two effects such as the water displacement to larger pores and dilution of water in acetone or vice versa. A similar behavior is observed for acetonitrile-d_3, which is a weaker electron-donor than other studied polar solvents. There is tendency towards reduction of the solvent influence on the γ_S^* value with increasing their nucleophilic properties and polarizability, since water molecules are strong competitors for polar but non-aromatic molecules in occupation of polar surface sites of carbon adsorbents. The influence of organics on water adsorbed onto carbon (Fig. 3(a)) and Si-40 (Fig. 3(b)) differs (e.g., curves for CD_3CN and $(CD_3)_2CO$). However, the effect of DMSO is similar.

The relationships between the permittivity (ε), relative free energy of solvation $E_s = E_{s1} + E_{s2}$ (Table 2), where $E_{s1} = (E_{\mathrm{ow}} - E_{\mathrm{o}})/E_{\mathrm{o}}$ and $E_{s2} = (E_{\mathrm{ow}} - E_w)/E_w$; (organic molecule in own solution (E_{o}) or in water (E_{ow}), and for a water molecule in organic (E_{wo}) or aqueous (E_w) media) show that the γ_S^* value increases with increasing ε value and lowering of the free energy of solvation. This corresponds to stabilization of the solvation complexes. The solvation effect is greater for an acetonitrile or DMSO molecule in the aqueous medium than that for a water molecule in the medium of these solvents. Consequently, it is energetically favorably to dissolve some amount of these organic molecules in water located in pores of an appropriate size than to remove water molecules from these pores and to dissolve them in greater amount of organics in larger pores. The absolute magnitude of the free energy of solvation in the aqueous medium decreases for a DMSO or acetonitrile molecule located in a slit-like pore due to a negative effect of hydrophobic pore walls. A similar effect is also observed for water, as for a single molecule in a micropore at $x \approx 0.4$ nm $E_w = 6.4$ kJ/mol, but for a cyclic cluster with six (hydrogen bonded one to another) molecules $E_w = -13$ kJ/mol per a molecule; consequently, water molecules always aspire to form the clusters in carbon micropores. Thus polar solvent molecules can be poorly solvated by water molecules in narrow pores due to the negative influence of the hydrophobic carbon pore walls and the impossibility to form an appropriate solvation shell for these molecules in narrow micropores. Therefore a portion of pre-adsorbed water always remains in narrow micropores independent on the type of the used organic solvents. For nonpolar benzene and carbon tetrachloride or poorly polar trichloromethane,

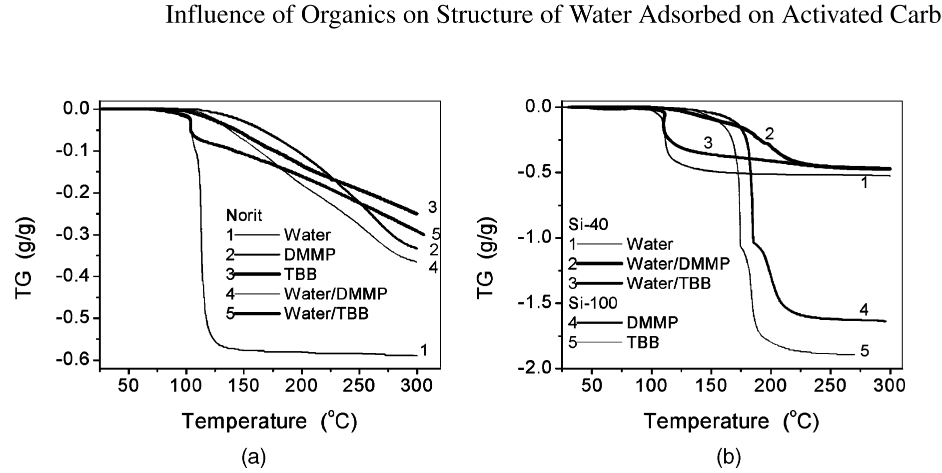
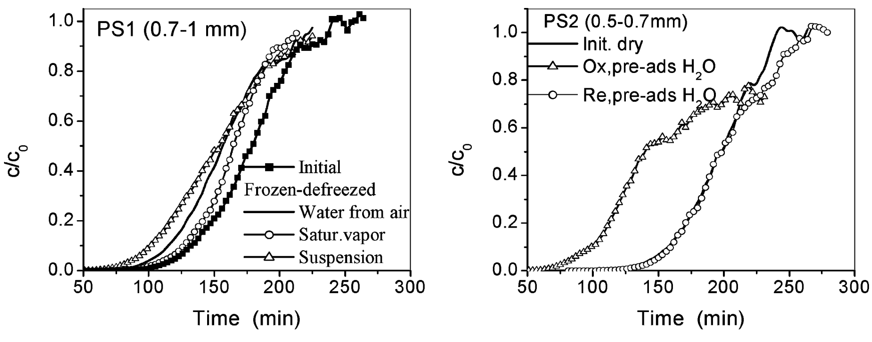


Figure 4. Weight loss on heating of (a) carbon Norit with adsorbed water, TBB, and DMMP; (b) silica gels Si-40 and Si-100 with adsorbed water, TBB, and DMMP (individual or mixture with water and organics).

their dissolution in water or vice versa is energetically unfavorable that causes minimization of the boundary area between pre-adsorbed water and added nonpolar solvents. Since these compounds can more effectively interact with nonpolar hydrophobic basal planes of the pore walls than water which is removed towards larger pores with simultaneous diminution of its interaction with the carbon surfaces, as the γ_S^* value decreases.

Thermodesorption of organics from carbon Norit occurs over a wide temperature range (Fig. 4(a)) because of their strong adsorption in narrow pores. In the case of pre-adsorption of water, a desorption curve for DMMP/water is close to that for organics than that for water. However, for TBB/water, a curve portion at T between 80 and 106°C is close to that for water. A similar picture of desorption is observed for silica gel Si-40 with narrow pores (Fig. 4(b)). The desorption curve of DMMP shifts towards higher temperatures in comparison with TBB because of a stronger bonding of DMMP by the hydrogen bonds $\mathrm{SiO{-}H \cdots O{=}PR}$ or $\mathrm{SiO{-}H \cdots O(CH_3)PR'}$.

Despite polar molecules can form strong hydrogen bonds with water molecules, these molecules can incorporate into water clusters or droplets in carbon micropores with some limitations, as E_{s2} should be lower than E_{s1} and $E_{ow} < E_{wo}$ (Table 2) and the carbon walls in micropores provide the negative effect on embedding of organic molecules into the water clusters. At the same time, nonpolar solvents practically immiscible with water (as $E_w < E_{wo}$ and $E_o < E_{ow}$) can easily remove a major portion of pre-adsorbed water from micropores to reduce the boundary area between different phases. The reasons of observed regularities can be connected to the structure of the interfacial water, which binds to carbon surfaces in the form of compact two-dimension (in narrow micropores) or three-dimension clusters (with n_w water molecules) and embedding of polar solvent molecules (n_{sol}) in such clusters or droplets is energetically favorable only at $n_w \gg n_{sol}$ in pores of an appropriate size. Polar solvent molecules can also interact with boundary water molecules in its droplets in narrow pores or polar oxygen-containing sites at the periphery of basal planes and graphenes without displacement of water from micropores to larger pores if the solvent (e.g. acetone-d_6, acetonitrile-d_3) concentration is less 400 mg/g. On the other hand, nonpolar solvents have relatively great energy of adsorption on basal planes in micropores, e.g. for benzene adsorbed in micropores the adsorption potential $A > 25$ kJ/mol but for water adsorbed in hydrophobic micropores $A < 10$ kJ/mol and the heat of water adsorption (15–30 kJ/mol) is lower than the liquefaction heat. Therefore, similar organic solvents can remove water from hydrophobic micropores to larger pores (e.g. to the entrances of micropores with oxygen-containing sites which can be 'anchors' for water clusters) where water can form larger clusters and droplets (providing smaller contact area between water and nonpolar solvent) weaker disturbed by the carbon surfaces and the γ_S value decreases. Pre-adsorption of water leads to reduction of the TBB adsorption by activated carbons (Fig. 5). This effect depends on the state of the carbon surface, since its oxidation enhances the negative effect of the adsorbed water (Palijczuk et al., 2002).



(a) (b)

Figure 5. Relative TBB breakthrough concentration for dry or wetted carbon beds with initial and treated (a) PS1 and (b) PS2; Ox denotes carbons oxidized by H_2O_2 at 250°C; Re denotes carbons reduced by H_2 at 800°C; pre-ads H_2O denotes pre-wetted carbon beds by air with RH = 80%.

4. Conclusion

Suspending drying, freezing by liquid nitrogen, deahsing, oxidation by H_2O_2, and reduction by H_2 of activated carbon Norit R 0.8 Extra change pores at half-width $x < 0.7 - 0.9$ nm. Interaction of water with carbon Norit and silica gels with the presence of organic solvents depends on their molecular size, polarity, polarizability, solubility in water and vice versa, and their concentrations. Nonpolar solvents (immiscible with water) remove water from micropores more effectively than polar ones (soluble in bulk water) due to different nature of forces giving the main contribution to the interaction energy of solvents with polar (e.g. oxygen-containing) surface sites, nonpolar basal carbon planes and adsorbed water molecules forming clusters and droplets. The hydrophilic nature of the silica surface changes the interaction of water with both polar and nonpolar organics in comparison with more hydrophobic carbon.

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References

Bansal, R.C., et al., *Active Carbon*, Dekker, New York, 1988.
Brennan, J.K., et al., *Colloids Surf. A*, **187/188**, 539–568 (2001).
Gun'ko, V.M., et al., *Appl. Surf. Sci.*, **214**, 178–189 (2003).
Gun'ko, V.M., et al., *Colloids Surf. A*, **235**, 101–111 (2004).
Jankowska, H., et al., *Active Carbon*, Ellis Horwood, New York, 1991.
Leboda, R., et al., *Carbon*, **40**, 389–396 (2002).
Palijczuk, D., et al., *J. Colloid Interface Sci.*, **250**, 5–17 (2002).
Turov, V.V., et al., *J. Colloid Interface Sci.*, **253**, 23–34 (2002).
Xidos, J.D., et al., *GAMESOL–version 3.1*, University of Minnesota, Minneapolis, 2002.