SURFACE ENERGY OF EXTRACTED AND NON-EXTRACTED NORWAY SPRUCE WOOD PARTICLES STUDIED BY INVERSE GAS CHROMATOGRAPHY (IGC)

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(Received November 1999)

ABSTRACT

The surface energy of extracted and nonextracted Norway spruce wood particles was studied by means of inverse gas chromatography (IGC). The measurements were performed at infinite-dilution, using a series of dispersive *n*-alkanes and Lewis acid-base probes. Results from the *n*-alkane series indicate that the removal of extractives from the spruce wood particles increases their Lifshitz-van der Waals (dispersive) surface free energy component. The interaction process between the acid-base probes and the wood particles is complex and complicates the IGC analysis. The acid-base characteristics are interpreted by comparing the specific interaction between the acid-base probes and the different wood particles at one single temperature. This analysis indicates that the extraction of the spruce wood particles results primarily in increased interaction with predominantly Lewis base probes. In contrast, the extraction results primarily in decreased interaction with predominantly Lewis acid probes. Hence, it is indicated that the wood substance without extractives exhibits greater acidic (electron-accepting) character and less basic (electron-donating) character, than wood substance containing extractives.

Keywords: Wood particles, inverse gas chromatography (IGC), surface free energy, Lewis acid-base properties, Lifshitz-van der Waals.

INTRODUCTION

To obtain the most desirable behavior of certain wood or wood-based products, combinations between wood and other natural or synthetic polymers are often necessary. In this situation, the processing, in-service performance, and durability of these combined products are strongly dependent on intermolecular forces and binding energies between the constituents. Such interactions between different materials may be characterized by using thermodynamic wetting parameters. Examples of such parameters are contact angles, surface and interfacial free energy, work of adhesion, and Lewis acid-base parameters (Berg 1993).

Contact angle analysis is a widely used method when determining wetting parameters of rigid solid materials with homogeneous and smooth surfaces. In contrast to such materials, wood is highly heterogeneous, both considering its macro- and microscopic structure. Macroscopically, wood may be considered as composed of early- and latewood, and as non-

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Wood and Fiber Science, 32(4), 2000, pp. 478–488 © 2000 by the Society of Wood Science and Technology

smooth with high surface roughness. Microscopically, wood is composed of cellular elements, i.e., a porous and varying structure. Thus, because of capillary forces, liquids will easily penetrate from the exterior wood surface into the porous structure. In addition, on the molecular level, wood is composed mainly of cellulose, hemicelluloses, lignin, and extractives. The extractive constituents in softwoods are generally hydrophobic in nature and play a central role when analyzing the surface energy of wood.

Moreover, wood is a hygroscopic material; it has a high affinity for sorption of especially water and other polar liquids in the cell-wall material: When these processes occur, the cellwall substance will change its dimensions, i.e., shrink or swell. Many other wood properties are also strongly related to the water sorption processes and the actual moisture content in wood.

In summary, because of the heterogeneous and complex nature of wood, precise direct optical measurement of contact angles to determine the surface energy is inherently difficult.

Inverse gas chromatography (IGC) is a useful technique for determining surface energy of particle surfaces (Lloyd et al. 1989). By using appropriate gas probes, IGC can provide information on the surface thermodynamic characteristics of particles including surface free energy, acid-base interactions, enthalpy, and entropy. IGC has been applied to many materials, for example various polymers (Lloyd et al. 1989), suberin (Cordeiro et al. 1997), wood pulp fibers, cellulose or lignin (Dorris and Gray 1980; Kamdem and Riedl 1992; Felix and Gatenholm 1993; Jacob and Berg 1994; Garnier and Glasser 1996; Belgacem et al. 1996; Chtourou et al. 1995; Börås et al. 1997; Czeremuszkin et al. 1997; Kazayawoko et al. 1997; Lundqvist and Ödberg 1997; Shi et al. 1997; Gauthier et al. 1998; Shen et al. 1998; Matuana et al. 1999), and wood particles (Kamdem et al. 1993; Tshabalala 1997; Gardner et al. 1999).

The operation of IGC is like regular gas

chromatography where gases are injected into an inert gas stream passing through a packed column held in an environmentally controlled oven. As the gases pass through the end of the column, they are detected using a flame ionization detector. The gases are separated according to their particular affinity to the column packing material. In normal gas chromatography, the columns are chosen for their ability to separate gases adequately, whereas in IGC, known gas probes are chosen for their ability to interact with an unknown packing material. The time it takes a known gas to pass through the IGC column relative to a reference gas is the parameter used in determining thermodynamic parameters. In normal IGC, the measurements are performed at infinite-dilution, which means that only an extremely small concentration of the probe is injected into the columns. For energetically heterogeneous surfaces, this means that such analysis assesses adsorption only on the high-energy sites (Jacob and Berg 1994). In contrast to this, e.g. advancing contact angle measurements using the Wilhelmy or the drop method assess mainly the lower energy regions of the surface (Good 1993).

The total molecular interaction in condensed phases, or across their interfaces, may be recognized as the sum of physical and chemical interactions (Berg 1993). Recently, it has been shown that the physical interactions can be described as Lifshitz-van der Waals (LW) interactions (van Oss et al. 1987; Berg 1993). These interactions are also approximately equal to, so-called, dispersive or nonpolar interactions. Fowkes and Mostafa (1978) suggested that, in wetting-related phenomena, the chemical interactions might be recognized mainly as Lewis acid-base (AB) interactions, also referred to as polar or specific interactions. In such AB-interactions, an electron pair is donated by the base (electron-donor) and is shared with the acid (electron-acceptor), together forming an "adduct." For example, hydrogen bonding is a type of AB-interaction. Hence, the sum of the physical and the chemical interactions in wetting-related phenomena may therefore be expressed as the sum of the Lifshitz-van der Waals (LW) and the Lewis acid-base (AB) interactions. To characterize the interaction of molecular forces at an interface, it is therefore desirable not to only determine the total interaction, but also to distinguish between the LW and AB contribution.

The objective of this work is to characterize the surface energy of extracted and non-extracted spruce wood particles by means of inverse gas chromatography (IGC). This includes analysis of the Lifshitz-van der Waals (LW) interactions and the Lewis acid-base (AB) interactions. The latter may be obtained by IGC runs at two or more temperatures combined with the Gutmann's donor-acceptor approach, using so-called K_A (acidic) and K_B (basic) constants (Saint Flour and Papirer 1982; Kamdem et al. 1993; Tshabalala 1997; Liu et al. 1998; Gardner et al. 1999; Matuana et al. 1999). An alternative method is to analyze the specific interaction between the acid-base probes and the different wood particle samples at one single temperature (Lundqvist and Ödberg 1997; Shen et al. 1998).

Analysis of the surface energy properties of wood particles and the effect of extractive removal should add valuable information to the understanding of the surface and adhesion properties of wood used in composite products, and also of gluability and coatability of solid wood products. The specific acid-base interactions between lignocellulosics and certain polar probes (see e.g., Jacob and Berg 1994; Lunqvist and Ödberg 1997; Gardner et al. 1999) indicate that it might be possible to improve molecular acid-base interactions between e.g. wood and adhesives. From a practical standpoint, new advanced glues and coatings could then be 'tailored' in order to improve e.g., durability and in-service properties of various wood and wood-based products, especially for exposure in demanding outdoor environments.

EXPERIMENTAL PROCEDURE Materials

Samples with dimensions of approximately $100 \times 20 \times 6$ mm³ of clear heart- and sap-

wood of Norway spruce (Picea abies Karst.) were prepared. To minimize the effects of variation and heterogeneity within and between the samples, each sample was chosen from the same annual rings and same part of the tree stem. Half of the samples were extracted (see below). Thereafter, all samples were conditioned to a moisture content of about 7-8% (based on oven-dry weight), and then cut into thin veneers, ground in a Wiley mill, and sifted through a 60-mesh screen. After the grinding process, it was evident that, even for extracted wood, considerable amounts of volatile extractives were released from the wood powder. These gases may strongly affect the IGC analyses and, therefore, the powder was conditioned at 70°C for 24 h in a convection oven. By this process, the moisture content dropped to about 4-5%.

The wood particles were packed into Teflon columns of about 600-mm length using an electric vibrator. The column packing density was determined and controlled by weighing the columns before and after the packing procedure. In summary, this resulted in four different spruce samples for analysis: 1) sapwood. 2) extracted sapwood, 3) heartwood, and 4) extracted heartwood.

Extraction procedure

The presence of extractives strongly influences the wettability of wood. It is also likely that these extractives will affect and cause difficulties in the IGC analyses (Gardner et al. 1999). From pretesting experience, we found that extraction of thin veneers will leave extractive residuals on their exterior surfaces. This means that even if most of the extractives are removed through extraction, some of the remaining residuals will gather on the exterior surfaces. To avoid this, larger pieces of wood were extracted and then cut into thin veneers and ground in a Wiley mill. A high efficiency of this new extraction procedure was demonstrated by Wålinder (2000). With this procedure, compared with extraction of thin veneers or wood powder, it takes a considerably longer

Probes	(Å ²]	γ_L^{LW} [mJ/m ²]	DN [kcal/mol]	AN* [kcal/mol]	DN/AN*
Alkane probes		_			
<i>n</i> -hexane	51.5	18.4		_	
<i>n</i> -heptane	57.0	20.3			—
<i>n</i> -octane	63.0	21.3	—	—	
<i>n</i> -nonane	69.0	22.7	—	_	_
Acid-base probes					
Methylene chloride	31.5	27.6	_	3.9	0.0
Chloroform	44.0	25.9	0	5.4	0.0
Benzene	46.0	26.7	0.1	0.17	0.6
Acetone	42.5	16.5	17.0	2.5	6.8
Ethyl acetate	48.0	16.5	17.1	1.5	11.4
Diethyl ether	47.0	15.0	19.2	1.4	13.7
Tetrahydrofuran	45.0	22.5	20.1	0.5	40.2

TABLE 1. Properties of the probes used in the IGC analysis.

a = area covered by one adsorbed probe molecule.

 γ_L^{LW} = Lifshitz-van der Waals (LW) component of the liquid (L) surface free energy

 \overline{DN} = Donor number, AN^* = Acceptor number.

Sources: CRC Handbook of Chemistry and Physics. 77th ed. CRC press; Riddle and Fowkes (1990).

extraction time to remove a similar amount of extractives.

The extraction procedure was performed using Soxhlet solvent extraction and is described as follows: 1) Vacuum pressure impregnation of wood samples with deionized water to obtain fully saturated samples. 2) Soxhlet extraction for 2 days each with (in order) ethanol, acetone, petroleum ether, and once again ethanol. 3) Leaching in deionized water with stirring for 2 days. Between each step in the procedure, i.e., when changing between solvents, no drying was allowed in order to keep a continuous liquid phase in the samples.

Apparatus and measurements

The IGC analysis was performed on an HP (Model 5890A) gas chromatograph (GC) equipped with a flame ionization detector. The injector and detector were maintained at 220°C. Purified helium was used as the inert carrier gas and the flow rate was adjusted to 15 cm³/min, measured with a soap-bubble flow meter. In addition to the preconditioning of the wood samples in a convection oven, as described above, the columns were further conditioned in the GC at 70°C in a stream of helium until the baseline signal from the flame

ionization detector was approximately constant.

The IGC probes used are listed in Table 1 along with some of their physicochemical properties. All probes were of chromatographic grade, purchased from Aldrich. The probes were either inert, acidic, basic, or amphoteric (bifunctional). A small amount of the liquid probe was stored in a standard sealed chromatography vial, and a small volume of vapor was then extracted from above the liquid and injected by a chromatography syringe into the columns using an automatic injector. By injecting less than 0.1 µl gas vapor of the probe into the column, it is assumed that the measurements are performed at infinite-dilution, where interactions between adsorbed molecules are negligible. This is an important assumption when calculating some thermodynamic parameters from the IGC measurements. An HP 5880A integrator was used to determine the retention time of the various probe chromatograms relative to that of propane, which was used as a reference gas probe. At least two injections were performed for each condition. The repeatability in calculated retention times between two injections was greater than 1%. Two replicates were tested for each wood particle sample. If the deviation of the value of the dispersive energy for two replicates was higher than 1%, this was attributed to variations of e.g. the packing density of the columns, and subsequently an additional replicate was tested. A low deviation (not more than about 1% for all replicates) indicates that the reproducibility of these measurements is satisfactory. The experiments were performed with oven temperatures held at 60, 45, and 30°C. It was assumed that the column and oven temperatures are approximately equal since the Teflon columns and wood particles should not conduct any greater amount of heat from the injector or the detector.

Data analyses

The data analyses in this study mainly followed methodologies, described in detail elsewhere (Lloyd et al. 1989). The net retention volume V_N , the fundamental parameter in IGC measurements, is defined as the volume of carrier gas required to elute a given amount of the adsorbate (probe) from the adsorbent (in this case the wood powder) in the column. For IGC measurements carried out at infinite-dilution (zero surface coverage), the Henry's law region is reached, which means that the adsorption isotherm is linear and that the retention mechanism is due only to surface adsorption. From the retention time measured by IGC for a given probe, V_N (m³) is then given by the following equations (Conder and Young 1979; Chtourou et al. 1995):

$$V_N = K_S A = Q(t_r - t_p)$$
 (1)

where K_s (m) is the surface partition coefficient for solute (Henry's law constant), A (m²) is the total surface area of the adsorbent in the column, Q (m³/s) is the flow rate of the carrier gas corrected for pressure drop caused by gasphase compressibility, and t_r and t_p are the retention times in seconds of the probe and propane, respectively.

For IGC measurements carried out at infinite-dilution, it is assumed that interactions between the adsorbed molecules are negligible, and that the ideal gas law applies. V_N is then related to the molar free energy change of adsorption, ΔG_A (J/mol), by

$$\Delta G_A = -RT \ln V_N + C \qquad (2)$$

where R is the gas constant, T is the absolute temperature, and C is a constant depending on the weight and specific surface area of the packed material in the column and the chosen reference states of the probes in the gaseous and the adsorbed states.

Dorris and Gray (1980) suggested a relationship between ΔG_A and the work of adhesion across a solid-liquid interface, W_a (J/m²) given by

$$-\Delta G_A = aNW_a \tag{3}$$

where a (m²) is the area covered by one adsorbed probe molecule and N is the Avogadro's number. In addition, W_a across a solidliquid interface may be written as the sum of the Lifshitz-van der Waals (LW) and the acidbase (AB) interactions (Fowkes and Mostafa 1978; van Oss et al. 1987):

$$W_a = W_a^{LW} + W_a^{AB} \tag{4}$$

For nonpolar interactions, the work of adhesion due to LW-interactions, W_a^{LW} , is given by the geometric mean combining rule (Good and Girifalco 1960; Fowkes 1963):

$$W_a^{\ LW} = 2(\gamma_s^{\ LW} \ \gamma_L^{\ LW})^{1/2}$$
(5)

where γ^{LW} (J/m²) is the LW-component of the solid (S) and liquid (L) surface free energy. Combining Eqs (2), (3), and (5) for adsorption of a series of *n*-alkanes leads to the expression:

$$RT \ln V_N^{alkane} = 2N(\gamma_S^{LW})^{1/2} \alpha(\gamma_L^{LW})^{1/2} + C$$
(6)

Thus, a plot of *RT* ln V_N versus $a(\gamma_L^{LW})^{1/2}$ for a series of nonpolar probes, such as *n*-alkanes, should be linear, and the γ_S^{LW} component of the solid can thus be determined from the slope of this function.

Because of the additivity of the intermolecular interactions, as described in Eq. (4), the molar free energy change due to Lewis acidbase (AB) interactions, $\Delta G_A{}^{AB}$, can be quantified by comparing the retention behavior between adsorption of nonpolar and polar probes. This may be expressed as (Schultz et al. 1987):

$$\Delta G_A{}^{AB} = -RT \ln \left(\frac{V_N}{V_N{}^{ref}} \right) \tag{7}$$

where V_N and V_N^{ref} are the net retention volumes of an acid-base and alkane probe, respectively, at the same value of $(\gamma_L^{LW})^{1/2}$. ΔG_A^{AB} is also referred to as the specific interaction.

Additionally, the molar enthalpy of adsorption due to AB-interactions, $\Delta H_A{}^{AB}$, can be determined using the thermodynamic relation:

$$\Delta G_A{}^{AB} = \Delta H_A{}^{AB} - T \Delta S_A{}^{AB} \tag{8}$$

where $\Delta S_A{}^{AB}$ is the molar entropy of adsorption due to AB-interactions. Thus, the intercept of a plot of $\Delta G_A{}^{AB}$ versus temperature corresponds to the $\Delta H_A{}^{AB}$. In other words, IGC measurements of a series at different temperatures enable the determination of $\Delta H_A{}^{AB}$.

Furthermore, the Lewis acid-base interactions between the probes and the solid can be characterized by using Gutmann's approach (Gutmann 1978) where the acid-base properties of solids and liquids are characterized by their acceptor (AN) and donor (DN) number, representing their electron acceptor (acidic) or donor (basic) ability, respectively. Additionally, Riddle and Fowkes (1990) redefined a new acceptor number (AN^*) on the same scale and same unit (kcal/mol) as the donor number. The donor-acceptor values (DN and AN^*) of the acid-base probes used in this study are presented in Table 1.

The acceptor and donor number may then be related to $\Delta H_A{}^{AB}$, by the expression (Saint Flour and Papirer 1982; Schultz et al. 1987)

$$-\Delta H_A^{AB} = K_A DN + K_B AN^* \qquad (9)$$

where K_A and K_B are dimensionless acceptor and donor constants of the investigated material, respectively. The plot of $-\Delta H_A{}^{AB}/AN^*$ versus DN/AN^* for different probes should thus be linear and K_A and K_B can be determined from the slope and the intercept, respectively, of this linear function.

RESULTS AND DISCUSSION

Figure 1 shows an example plot of RT In V_N versus $(\gamma_L^{LW})^{1/2}$ for adsorption of a series of nonpolar alkane probes, represented by the reference line, combined with the corresponding plot for the acid-base probes, represented as single points. According to Eqs. (6) and (7) this type of plot enables determination of the Lifshitz-van der Waals component of the solid surface free energy, γ_S^{LW} , and the specific interaction, ΔG_A^{AB} , i.e., interactions between the probes and the solid other than the LW-interactions.

Lifshitz-van der Waals interactions

The γ_s^{LW} increases linearly with a decrease in temperature, and therefore γ_S^{LW} values obtained from IGC measurements at 60, 45, and 30°C can be extrapolated to room temperature. Table 2 presents the obtained γ_{S}^{LW} at 20°C for the different wood samples. As indicated in this table, the removal of extractives results in increased γ_{S}^{LW} for both sapwood and heartwood. This phenomenon has also been observed in other IGC analyses of extracted and non-extracted wood (Tshabalala 1997; Liu et al. 1998), and kraft pulp fibers (Shen et al. 1998). In addition, the $\gamma_{\rm S}^{LW}$ for heartwood and extracted heartwood are in both cases lower than for the corresponding values of sapwood, which may indicate that the former, intrinsically, contains more low-energy extractives. In addition, more extractive residuals may be left in the heartwood samples after the extraction procedure compared to the sapwood samples. The ranges of the absolute values of the obtained γ_{s}^{LW} are in good agreement with results from other investigations of lignocellulosic materials (Kamdem et al. 1993; Shi et al. 1997; Gardner et al. 1999; Shen et al. 1998; Simonsen et al. 1997; Tshabalala 1997; Liu et al. 1998).

Acid-base interactions

An example of the specific interaction, $\Delta G_A{}^{AB}$, between a sample of spruce particles and chloroform is shown in Fig. 1. Table 3



FIG. 1. Example plot of RT In V_N versus $\alpha(\gamma_L^{LW})^{1/2}$ at a given temperature for the adsorption of a series of nonpolar *n*-alkane probes (ref. line), and also of various acid-base probes (single points) on the wood particles.

summarizes the values of $-\Delta G_A{}^{AB}$ at 60, 45, and 30°C and corresponding values of $-\Delta H_A{}^{AB}$ for the different wood samples. In contrast to the $\gamma_s{}^{LW}$, as discussed above, the $-\Delta G_A{}^{AB}$ generally decreases with a decrease in temperature (see for example most values of the extracted heartwood sample). In most cases, this results in a negative $-\Delta H_A{}^{AB}$ value, as shown in Table 3. Negative enthalpies of adsorption due to acid-base interactions have also been observed for wood or wood fibers by Kamdem et al. (1993), Shi et al. (1997), Gardner et al. (1999), Tshabalala (1997), and Czeremuszkin et al. (1997). Wood is a hygroscopic material and will change its adsorption properties and moisture content with temperature and relative humidity. In the IGC measurements, the wood meal contains a certain amount of water. The moisture content of the wood powder after the IGC measurements was difficult to determine, but was at a rough estimate in the range of 2– 4%. The water adsorption properties of the wood substance will depend on the column temperature. In other words, the temperature change during a normal IGC run may affect the adsorption properties of the hygroscopic wood material, which may result in an apparent negative $-\Delta H_A^{AB}$ value for some of the probes.

Gardner et al. (1999) also pointed out that

TABLE 2. Lifshitz-van der Waals (dispersive) component of the surface free energy, γ_5^{LW} (mJ/m²) of non-extracted and extracted spruce wood particles at 20°C determined from IGC analysis.

. <u> </u>	(Non-extracted)	Extracted	(Non-extracted)	Extracted
	sapwood	sapwood	heartwood	heartwood
γ_{S}^{LW}	42.3	44.9	41.9	42.7

TABLE 3. Results of the IGC analysis of the different wood samples presented as molar free energy change of adsorption due to acid-base interactions. ΔG_A^{AB} , at different temperatures; and the corresponding enthalpy of adsorption, ΔH_A^{AB}

	$-\Delta G_A{}^{AB}$ [kJ/mol]			A 77 AB
	60°C	45°C	30°C	$-\Delta H_A^{AB}$ [kJ/mol]
Sapwood				
Methylene chloride	4.8	4.9	4.9	6.0
Chloroform	2.5	2.7	2.6	3.8
Benzene	1.8	1.7	1.6	-1.1
Acetone	4.2	4.3	4.1	2.6
Ethyl acetate	4.0	4.2	4.1	4.7
Diethyl ether	1.0	1.2	1.2	3.7
Tetrahydrofuran	3.4	3.5	3.4	2.9
Extracted sapwood				
Methylene chloride	5.8	5.0	4.8	-6.0
Chloroform	1.9	1.8	1.7	-0.9
Benzene	0.9	0.6	0.4	-4.7
Acetone	6.5	5.8	5.7	-2.0
Ethyl acetate	5.6	5.6	5.9	8.6
Diethyl ether	2.1	2.1	2.3	5.0
Tetrahydrofuran	3.6	3.4	3.4	1.5
Heartwood				
Methylene chloride	4.6	4.4	4.3	0.5
Chloroform	2.1	2.0	1.9	0.6
Benzene	1.3	1.1	0.9	-3.2
Acetone	3.9	3.8	3.5	-0.6
Ethyl acetate	3.7	3.6	3.6	3.2
Diethyl ether	0.9	0.9	0.8	-0.1
Tetrahydrofuran	3.1	2.9	2.8	-0.5
Extracted heartwood				
Methylene chloride	5.0	4.4	4.1	-5.0
Chloroform	1.6	1.4	i.2	-2.7
Benzene	0.8	0.5	0.2	-5.5
Acetone	5.4	4.8	4.5	-4.7
Ethyl acetate	4.5	4.4	4.5	4.5
Diethyl ether	1.2	1.3	1.4	2.6
Tetrahydrofuran	3.0	2.7	2.6	-0.7

some of the probes, e.g., benzene and acetone, may also act as extractive solvents that will remove extractives during the IGC measurements; and thus the adsorption measurements may be affected, also resulting in negative enthalpies. Furthermore, the attainment of Henry's law region, which is the presumption for the determination of the thermodynamic parameters, should be indicated by the symmetry of the elution curves. However, the elution curves for some of the acid-base probes show a tendency of tailing, i.e., an asymmetric curve. The presence of large peak tailing is normally attributed to bulk diffusion of the probes (Hattam et al. 1989). In an IGC analysis of wood fibers, Czeremuszkin et al. (1997) observed that some acid-base probes were preferentially adsorbed on the cellulose, and were removed by injecting water onto the column. In other words, this indicates that the elution of these probes was incomplete and therefore delayed. However, they also showed that bulk diffusion unlikely occurs under normal IGC conditions, and instead the delayed elution was attributed to non-equilibrium sorption processes of the probes. Hence, a possible explanation for the negative enthalpies obtained in the present study may therefore be attributed to a preferential adsorption of the acid-base probes on some specific high energy sites of the wood particles.

Because of the negative enthalpies obtained, the analysis of the acid-base interactions using the relation in Eq. (9) and the K_A and K_B constants, is not meaningful. Lundqvist and Ödberg (1997) and Shen et al. (1998), showed, however, that a change in the acid-base properties of different treated wood fibers can be correctly determined in IGC measurements by analyzing specific interactions at one single temperature. The specific interaction, $-\Delta G_A^{AB}$, was therefore analyzed at one single temperature for adsorption of the acid-base defined probes on the extracted and non-extracted wood particles. Figure 2 shows the obtained $-\Delta G_A^{AB}$ values for the different wood samples at 45°C. As can be seen in this figure, extraction of the wood material results in a distinct change in the interaction with most of the probes. The interaction decreases for chloroform and benzene. In contrast, an increase is observed for acetone, ethyl acetate, and diethyl ether. According to Gutmann's approach, and the definition of donor and acceptor numbers, as shown in Table 1, the former probes are predominantly Lewis acid (low DN/AN* value) and the latter amphoteric or predominantly Lewis basic (high DN/AN* value). The decreased interaction between the acidic probes and the extracted wood particles, com-



FIG. 2. Diagram showing acid-base interactions, $\Delta G_A{}^{AB}$, at 45°C between the acid-base probes and the non-extracted and the extracted spruce wood particles. MeC12 = Methylene chloride, DEE = Diethyl ether, and THF = Tetrahydro-furan.

pared to the non-extracted ones, indicates that extraction decreases the basic character of wood. In contrast, extraction of the wood particles results in increased interaction with the amphoteric or basic probes, indicating that extraction increases the acidic character of wood. Similar results were obtained by Liu et al. (1998) and Tshabalala (1997). A strong electron-accepting ability or acidic character of the extracted wood substance also agrees with acid-base analyses of cellulose and wood fibers by IGC (Shen et al. 1998; Felix and Gatenholm 1993; Lee and Luner 1989; Jacob and Berg 1994; Garnier and Glasser 1996; Lundqvist and Ödberg 1997; Matuana et al. 1999), which indicates that cellulose has strong electron-accepting ability or acidity.

Some contradictions to these conclusions about the differences in acid-base properties for the extracted and non-extracted wood samples may, however, be observed for the adsorption of methylene chloride and tetrahydrofuran, i.e., probes with strong electron acceptor and donor ability, respectively. These probes do not show the same tendency as the other probes regarding the acid-base interactions with the different wood samples. Jacob and Berg (1994) pointed out that one drawback with the Gutmann approach, with defined acceptor and donor numbers, is that it does not distinguish differences in the "hardness" and "softness" nature of Lewis acids and bases. For example methylene chloride $(DN/AN^* =$ 0) is a much harder acid than chloroform (DN/ $AN^* = 0$) which may lead to a stronger interaction with a soft base. Hence, this may explain the deviating acid-base interactions for these probes.

CONCLUSIONS

Inverse gas chromatography (IGC) is a useful technique for determining surface energy of wood particles. Results from the IGC analysis using an *n*-alkane series indicate that extraction of the spruce wood particles increases their Lifshitz-van der Waals (dispersive) surface free energy component. The Lewis acidbase characterization of the wood particles using K_A and K_B constants is not meaningful because of obtained negative values of the enthalpies of adsorption $(-\Delta H_A^{AB})$. However, the Lewis acid-base characteristics of extracted and non-extracted wood substance may be compared and interpreted by analysis of the specific interaction at one single temperature between the acid-base probes and the different wood particle samples. This analysis shows that extraction of spruce wood substance primarily results in increased interaction with basic probes, i.e., probes with considerably higher donor (DN) than acceptor number (AN^*) . In contrast, extraction primarily results in decreased interaction with acidic probes, i.e., probes with considerably higher acceptor (AN^*) than donor number (DN). Hence, wood substance without extractives has more acidic (electron-accepting) character and less basic (electron-donating) character, than wood substance containing extractives.

By better understanding of the thermodynamic properties of wood surfaces, valuable technical information about the capacity of wood to interact with adhesives and coatings may be generated.

ACKNOWLEDGMENTS

The authors thank Professor Ingvar Johansson and Dr. Göran Ström for helpful comments during the preparation of the manuscript.

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