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Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Contribution enthalpic in the interaction of activated carbon with polar and apolar solvents

Y.S. Murillo^a, L. Giraldo^a, J.C. Moreno-Piraján^{b,*}

^a Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Colombia

^b Grupo de Investigación en Sólidos Porosos y Calorimetría, Departamento de Química, Facultad de Ciencias, Universidad de los Andes, Colombia

Received 30 June 2011; accepted 7 July 2012

Available online 16 July 2012

KEYWORDS

Immersion enthalpy;
Activated carbon;
Water;
Differential enthalpies;
Partial relative enthalpies

Abstract A method is presented for calculating the contribution that enthalpies make for every component of mixtures of activated carbon–water and activated carbon–hexane to the immersion enthalpy using the concepts that are used in the solution enthalpies. The immersion enthalpies of microporous activated carbon in water and in hexane have values from -18.97 to -27.21 and -25.23 to -47.89 J g⁻¹, respectively. From the immersion enthalpies and mass relation of the activated carbon in each of the solvents, the differential enthalpies are calculated for the activated carbon in water, $H_{W,DIFac}$, with values between -15.95 and -26.81 J g⁻¹, as are the differential enthalpies for the activated carbon in hexane, $\Delta H_{h,DIFac}$, with values between -6.86 and -46.97 J g⁻¹. For a low mass relation of the mixture components the contributions to the immersion enthalpy of the activated carbon and water differ by 3.20 J g⁻¹, while the difference between the contributions of the activated carbon and hexane is 19.41 J g⁻¹.

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1. Introduction

When a solid and a liquid are contacted a certain amount of heat is generated by the surface and chemical reactions, and this can be determined by means of suitable calorimetric techniques, which leads to the determination of the immersion enthalpy as a characteristic thermodynamic parameter for a specific system (Silvestre-Albero et al., 2001; Stoeckli and Centeno, 2005). If one thinks that the system is formed by the solid and the liquid one can suppose that the immersion enthalpy is due to the contribution of each one of these, as it happens with the thermodynamic partial molar properties in the case of multicomponent solutions (Tripathi, 2010).

In a closed system with two components and conditions of temperature T and pressure P , the variation of a considered property thermodynamic X can be expressed as:

* Corresponding author. Tel.: +57 3394949x2786.
E-mail address: jumoreno@uniandes.edu.co (J.C. Moreno-Piraján).

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Peer review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2012.07.003



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$$dX = \left(\frac{\partial X}{\partial T} \right)_{P,n_i} dT + \left(\frac{\partial X}{\partial P} \right)_{T,n_i} dP + \left(\frac{\partial X}{\partial n_1} \right)_{T,P,n_2} dn_1 + \left(\frac{\partial X}{\partial n_2} \right)_{T,P,n_1} dn_2 \quad (1)$$

where,

$$\left(\frac{\partial X}{\partial n_1} \right)_{T,P,n_2} \text{ and } \left(\frac{\partial X}{\partial n_2} \right)_{T,P,n_1} \quad (2)$$

are the molar properties of components 1 and 2, respectively (Atkins, 2002).

The mixing enthalpy corresponds to the change of enthalpy that presents to mix the components at given conditions of temperature and pressure and is expressed as the change in the experimental enthalpy, ΔH_{exp} . When the experimental enthalpy is expressed for the mole of each of the components, the integral enthalpy can be obtained; for example the integral enthalpy for component 2 is:

$$\Delta H_{\text{INT2}} = \frac{\Delta H_{\text{exp}}}{n_2} \quad (3)$$

It expresses the total quantity of moles obtained for the change in the excess molar enthalpy, ΔH^E (Kimura et al., 2006; Duce et al., 2008).

The solution of differential enthalpies, ΔH_{DIF2} and ΔH_{DIF1} , corresponds to the enthalpy variation that is a result of when 1 mol of one component mixes with a large quantity of solution in such a way that the addition of the above mentioned component does not change the composition of the solution. The differential enthalpy of component 2 will therefore be:

$$\Delta H_{\text{DIF2}} = \left(\frac{\partial \Delta H_{\text{exp}}}{\partial n_2} \right)_{T,P,n_1} = \left(\frac{\partial \Delta H_{\text{sol}}}{\partial n_2} \right)_{T,P,n_1} - H_2^* = (\overline{H}_2 - H_2^*) \quad (4)$$

where ΔH_{sol} is the change in the solution enthalpy, H_2^* is the enthalpy of the pure component 2 and \overline{H}_2 is the molar partial enthalpy of component 2. It is not possible to determine values of absolute enthalpy, but the difference between the enthalpic content of the solution and the pure components can be determined.

The change in enthalpy when the quantity of component 2 is very small is defined as the enthalpy at infinite dilution and is symbolized by ΔH_2° (Li et al., 2007).

Another way of expressing the enthalpy change is to choose as a reference condition the diluted mixture, and thus an expression is obtained for the change between the enthalpy of the mixture at a given composition and the enthalpy for the mixture at infinite dilution; as shown in the following expression for component 2 (Klotz and Rosenberg, 2008):

$$\overline{L}_2 = (\overline{H}_2 - \overline{H}_2^\circ) = \left(\frac{\partial H_{\text{exp}}}{\partial n_2} \right)_{T,P,n_1} - \left(\frac{\partial \Delta H_{\text{exp}}}{\partial n_2} \right)_{T,P,n_1}^\circ \quad (5)$$

For the mixture of a solid macromolecule, such as activated carbon, with a polar solvent, such as water, and an apolar solvent, such as hexane, it is important to calculate the enthalpic contribution of each component because in the case of hexane the physical interactions of the solvent with the solid surface are revealed (Rodríguez Reinoso et al., 1997), while in the case of the immersion of the activated carbon in water the interac-

tions that are present are with the chemical groups' surface, which shows that the enthalpic contributions are different.

In this work, from the experimental enthalpies obtained when carbon is activated with solvent mixes, it is possible to calculate the enthalpic contributions that present the activated carbon and water or hexane at the immersion enthalpy of the solid in the liquid; the calculation is made possible by the similarity with the partial molar enthalpies in the solutions. Nevertheless in the case of the mixture, as described in this work, the change in the experimental enthalpy is determined for the mixture of activated carbon and solvent, therefore the contribution cannot be calculated for the mole but for the gram of each of the components of the binary system.

2. Experimental

2.1. Textural and chemical characterization of activated carbon

The carbonaceous samples measuring about 0.100 g are degassed at 250 °C for a period of 3 h in an Autosorb 3B, Quantachrome Co. The corresponding adsorption nitrogen isotherms are obtained with this equipment at 77 K. The surface area is determined by the B.E.T method and the micropore volume is determined by Dubinin–Radushkevich method.

Total acidity and basicity of the activated carbon are determined by means of the Boehm method (Boehm, 2002).

2.2. Experimental immersion enthalpy determination

In the present work, experimental immersion enthalpies of the activated carbon in water as a function of its mass are determined for the estimation of the energetic interactions when the solid is in contact with water. A heat conduction microcalorimeter equipped with a calorimetric cell made of stainless steel is used for the determination of the experimental immersion enthalpies (Giraldo and Moreno, 2007). Inside the cell, approximately 8 mL of water is set out (previously kept at 298 K in a thermostat). Samples between 50 and 800 mg of the activated carbon are put in a glass bulb point inside the calorimetric cell and the microcalorimeter is assembled. When the device reaches a temperature of 298 K, it starts to record the output potential for approximately 15 min, taking data of potential every 20 s. After that, the glass bulb breakage takes place and the generated thermal effect is recorded while the potential readings continue for 15 more minutes. Finally, the device gets calibrated electrically.

3. Results and discussion

The activated carbon that is used in this work, in order to find the enthalpic characterization when it is put in contact with water, is obtained from a lignocellulosic material which is physically activated and has been used in the adsorption of organic compounds in other works (Blanco et al., 2009). The textural and chemical characteristics of this activated carbon are shown in Table 1.

The values of the surface area and the acidic and basic sites' contents of the activated carbon allow for the analysis of the immersion enthalpy, in water and in hexane, as a function of the mass, and differences in heat production in the process of wetting can be observed due to changes in the solid mass.

Table 1 Textural and chemical characteristics of activated carbon.

Surface area B.E.T./m ² g ⁻¹	1140
Micropore volume/cm ³ g ⁻¹	0.51
Mesopore volume/cm ³ g ⁻¹	0.12
Total acidity/mmol g ⁻¹	0.30
Total basicity/mmol g ⁻¹	0.60

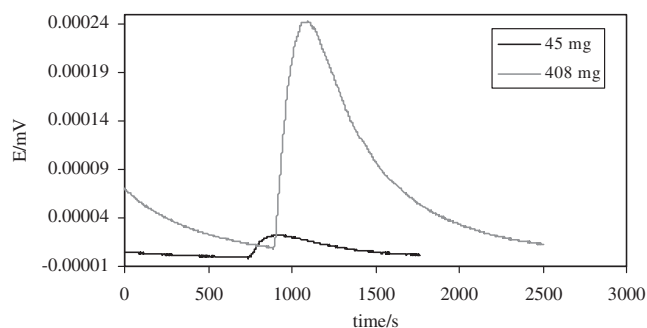
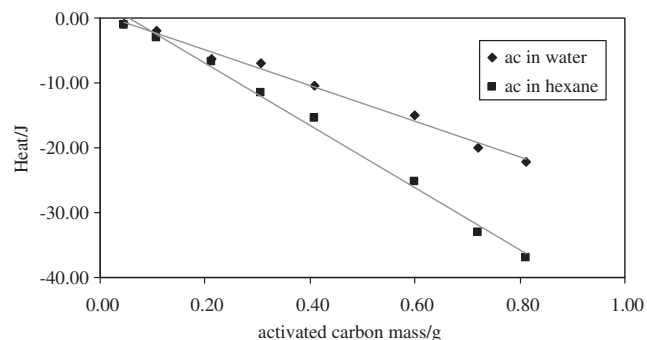
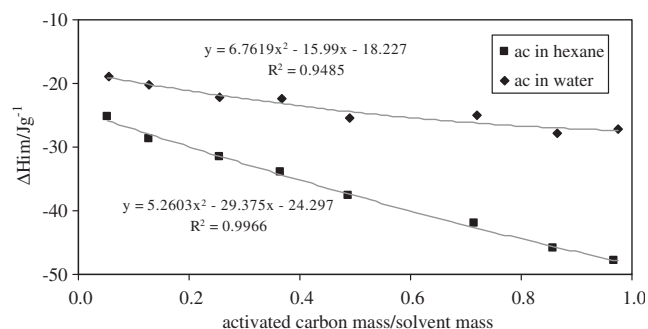
**Figure 1** Calorimetric curves of activated carbon immersion in water.

Fig. 1 shows the typical curves of the calorimetric signal for the immersion of 45 and 408 mg of the activated carbon in water in quantities of about 8.0 g. An increase is observed in the electrical potential signal that indicates that the effect is exothermic and that the heat that takes place due to the immersion of the solid in the liquid is proportional to the area of the curve of the electrical potential signal as a function of time.

Fig. 2 displays the results obtained for the heat generated following the immersion of different quantities of the activated carbon in a constant quantity of the immersion solvent, water in one case and hexane in the other. As the quantity of the solid increases the quantity of heat generated when the activated carbon and the solvent are contacted also increases. Higher values of heat are observed when the activated carbon is submerged in hexane, with maximum values of -22.09 and -37.02 J for water and hexane, respectively. Similar values of heat for the immersion of an activated carbon named PLW were obtained by Stoeckli et al., 2001, and the values of heat obtained from this experiment are proportional to the textural characteristics of the activated carbon; with regard

**Figure 2** Heat generated by the immersion of different amounts of activated carbon in water and hexane.**Figure 3** Immersion enthalpy as a function of relationship between the activated carbon mass and the solvent mass.

to the immersion enthalpy values in water they find comparable values in a recent work in which the activated carbon is prepared with a different burn-off (Vargas et al., 2010).

To find the contribution of the activated carbon and of the solvent to the immersion enthalpy, bearing in mind that each of these will provide a contribution to the final value of the immersion enthalpy and that the activated carbon quantity cannot be expressed as number of moles due to its structural changes in agreement to the preparation method, the quantity is expressed in grams of every component and the immersion enthalpy in Joules for gram of the activated carbon. From this expression it is possible to obtain the behavior between the immersion enthalpy and the relationship between the activated carbon mass, acm , and the solvent mass, sm , for the mass of water or the mass of hexane, that is shown in Fig. 3.

Since the immersion enthalpy is of exothermic character a decrease in the value of heat is observed as the relationship acm/sm increases, and the curve adjusts to equations of the second order, which reflect the fact of the increase of the mixture enthalpies up to a certain value of concentration (Wang and Lu, 2004).

From the equations it is possible to obtain the values of the immersion enthalpy when the quantity of the activated carbon tends to zero, ΔH_{im}° , which provide values of -18.23 and -24.30 J g⁻¹ for water and hexane, respectively. These are similar to the enthalpy at infinite dilution, ΔH_2° , in the description of the partial molar solution enthalpies.

From the graphs between the immersion enthalpy as a function of the relationship between the mass of the activated carbon and the solvents, the differential enthalpies can be obtained for each of the components of the activated carbon–water and activated carbon–hexane mixtures, from which ΔH_{DIFac} , ΔH_{DIFw} and ΔH_{DIFh} are obtained which correspond to the differential enthalpy of the activated carbon, water and hexane. The differential enthalpies of each component are:

$$\Delta H_{DIFac} = \Delta H_{im} - x_m \left(\frac{\partial H_{im}}{\partial x_m} \right) \quad (6)$$

$$\Delta H_{DIFs} = \frac{\Delta H_{im} - (1 - x_m) \Delta H_{DIFac}}{x_m} \quad (7)$$

where x_m corresponds to the relation of solvent mass and activated carbon mass in each mixture.

Fig. 4 presents the values obtained for the differential enthalpy of the activated carbon, ΔH_{DIFac} , whose range is between -15.95 and -26.81 J g⁻¹ and of water, ΔH_{DIFw} , which

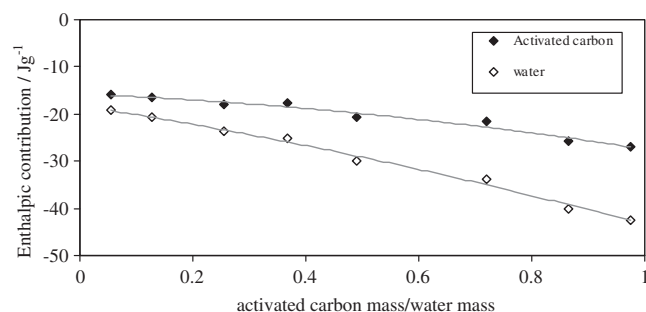


Figure 4 Contribution of the activated carbon and water at immersion enthalpy.

ranges between -19.14 and -42.45 J g^{-1} . The differential enthalpies are of exothermic character and the contribution of water at the immersion enthalpy is greater provided that the water mass was more than that of the activated carbon mass for all the mixtures that were realized and because the solvent has the capacity to interact with solids of different forms.

Fig. 4 provides an interesting result since it shows that the contribution of each one of the components is different for different relations of masses, similar to the description that is made for the partial molar enthalpies, such as Zielenkiewicz (2007) in whose study of mixtures of aqueous solutions of human serum albumen with NaCl the albumen presented a matrix with a high carbon content.

Fig. 5 shows the graphs obtained for the enthalpic contribution of the activated carbon in water as in hexane and it can be observed that the differential enthalpy of the activated carbon, ΔH_{DIFac} , is more when the activated carbon mixes with hexane than when mixes with water, which can be explained because the apolar solvent interacts with the surface of the solid and the enthalpy is proportional to the physical contact between both components of the mixture. While water besides the interaction with the surface of the solid presents interactions with the chemical groups of the surface, generally composed of oxygen (Moreno-Castilla, 2004) and with the π electrons of the graphene layers of the activated carbon, it means that the effect is superposed and the total enthalpic contribution is minor.

Table 2 presents the results obtained for the partial relative enthalpy of the activated carbon, \overline{L}_{ac} , as much in water as in hexane in that it is observed that the difference happens in both immersion processes and water being a polar solvent presents a variety in the interactions with the activated carbon.

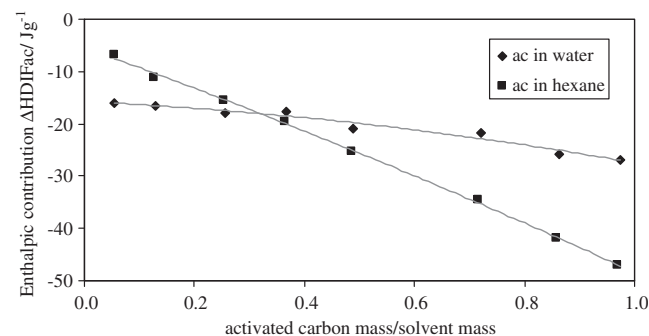


Figure 5 Contribution of the activated carbon in water and hexane at immersion enthalpy.

Table 2 Partial relative enthalpy of activated carbon.

Activated carbon mass/solvent mass	\overline{L}_{ac} in water/ J g^{-1}	\overline{L}_{ac} in hexane/ J g^{-1}
0.05	2.28	-31.15
0.012	1.72	-35.34
0.25	0.41	-39.81
0.36	0.46	-43.89
0.49	-2.57	-49.69
0.72	-3.41	-58.77
0.86	-7.56	-66.22
0.97	-8.57	-71.26

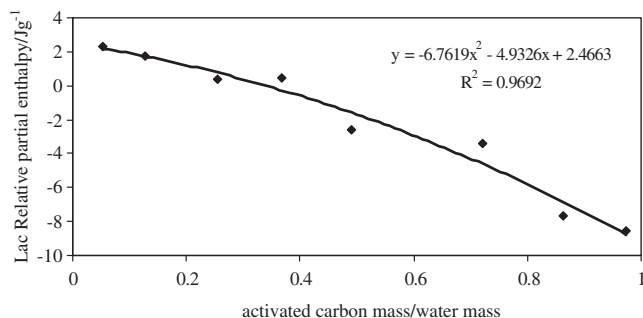


Figure 6 Relative partial enthalpy for the immersion of the activated carbon in water.

Finally, Fig. 6 shows the behavior obtained for the partial relative enthalpy for the activated carbon, \overline{L}_{ac} , as a function of the mass relation of the activated carbon and water, with values for the mass relations established between 2.28 and -8.58 J g^{-1} . In the graph it appears that for mass relations of the components between 0.05 and 0.30, the values of the partial relative enthalpies are endothermic and from the previously mentioned relation they are exothermic, which indicates the effect of the select condition of reference that was the mixture with a quantity of the activated carbon tending to zero. So, for low mass relations the contributions to the immersion enthalpy of the activated carbon and to water differ by 3.20 J g^{-1} .

4. Conclusions

The immersion enthalpies of a microporous activated carbon, with a BET surface area of $1140 \text{ m}^2 \text{ g}^{-1}$ and basic character, in water and in hexane produce values from -18.97 to -27.21 and -25.23 to -47.89 J g^{-1} , respectively. The enthalpic contributions to the immersion enthalpy of the activated carbon and the solvents when mixed are calculated by following the concepts of the theory of partial enthalpies. For these particular cases of mixtures of activated carbon–water and activated carbon–hexane, the quantities cannot be expressed in mass for both components, for which it is necessary to resort to the interpretation by means of mass relations. The results show that the immersion enthalpies are of exothermic character as the contributions of each one of the components, this way there is evidence that for the activated carbon the differential enthalpy, ΔH_{DIFac} , presents values between -15.95 and -26.81 J g^{-1} for the immersion in water and between -6.86 and -46.97 J g^{-1} for the immersion in hexane. The value of the enthalpy when the quantity of the activated carbon tends

to zero, ΔH_{ac}° , is of -18.23 and -24.30 J g^{-1} for water and hexane, respectively, and the partial relative enthalpy with regard to the solid, \overline{L}_{ac} , is more for the immersion of the activated carbon in hexane, which reflects the interactions in the process of physical contact.

Acknowledgments

The authors wish to thank the Master Agreement established between the Universidad de los Andes and the Universidad Nacional de Colombia and the project No. 1141 DIB Universidad Nacional de Colombia.

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