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Determination of partial immersion enthalpy in the interaction of water and activated carbon

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Abstract A way to calculate the enthalpic contributions of each component of the mixture of activated carbon and water to the immersion enthalpy using the concepts of the solution enthalpies is presented. By determining the immersion enthalpies of a microporous activated carbon in water, with values that are between –18.97 and -27.21 Jg^{-1}, from these and the mass ratio of activated carbon and water, differential enthalpies for the activated carbon, $\Delta H_{\mathrm{DIF}_{\mathrm{ac}}}$ and water, $\Delta H_{\mathrm{DIF}_{\mathrm{w}}}$ are calculated, and values between –15.95 and –26.81 Jg^{-1} and between –19.14 and –42.45 Jg^{-1}, respectively are obtained. For low ratios of the mixture, the components' contributions to the immersion enthalpy of activated carbon and water differ by 3.20 Jg^{-1}.

Keywords Enthalpy of immersion · Activated carbon · Water · Enthalpy differential relative partial enthalpies

Introduction

When they make contact, a solid and liquid generate a certain amount of heat which is produced by the surface and chemical interactions that occur between them and can be determined through appropriate calorimetric techniques, leading to the determination of the immersion enthalpy as a thermodynamic parameter characterization for a specific system [1, 2].

Assuming that the system is composed of solid and liquid, it can be assumed that the immersion enthalpy of is due to the contribution of each of these, as with the partial molar thermodynamic properties for multicomponent solutions [3].

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

$$\mathrm{d}X = \left(\frac{\partial X}{\partial T}\right)_{\mathrm{P,n_i}} \mathrm{d}T + \left(\frac{\partial X}{\partial P}\right)_{\mathrm{T,n_i}} \mathrm{d}P + \left(\frac{\partial X}{\partial \mathrm{n}_1}\right)_{\mathrm{T,P,n_2}} \mathrm{dn}_1 + \left(\frac{\partial X}{\partial \mathrm{n}_2}\right)_{\mathrm{T,P,n_1}} \mathrm{dn}_2 \quad (1)$$

where:

$$\left(\frac{\partial X}{\partial \mathrm{n}_1}\right)_{\mathrm{T,P,n_2}} \mathrm{y} \left(\frac{\partial X}{\partial \mathrm{n}_1}\right)_{\mathrm{T,P,n_1}} \quad (2)$$

are the molar properties for the components 1 and 2, respectively [4].

The enthalpy of mixing corresponds to the change in enthalpy that occurs when components are attached to conditions of temperature and pressure and can be expressed as the change in enthalpy experimental ΔH_{exp}. Expressing the experimental enthalpy per mole of each component gives the integral enthalpy; for example, for the integral enthalpy for component 2 the authors have:

$$\Delta H_{\mathrm{INT2}} = \frac{\Delta H_{\mathrm{exp}}}{\mathrm{n}_2} \quad (3)$$

and if expressed as the total number of moles this gives the change in the excess molar enthalpy, ΔH^{E} [5, 6].

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The differential enthalpies of a solution, ΔH_{DIF2} and ΔH_{DIF1}, correspond to the enthalpy change that results when 1 mol of a component is mixed with a large amount of solution so that the addition of that component does not change the composition of the solution. The differential enthalpy of component 2 is:

$$\Delta H_{\mathrm{DIF2}} = \left(\frac{\partial \Delta H_{\mathrm{exp}}}{\partial \mathrm{n}_2}\right)_{\mathrm{T,P,n_1}} = \left(\frac{\partial \Delta H_{\mathrm{sol}}}{\partial \mathrm{n}_2}\right)_{\mathrm{T,P,n_1}} - H_2^{\bullet} = \left(\overline{H_2} - H_2^{\bullet}\right) \qquad (4)$$

Where ΔHsol is the change in enthalpy of solution, $H_2^{\bullet}$ is the enthalpy of pure component 2 and $\overline{H_2}$ is the partial molar enthalpy of component 2. It is noted that one can not determine the absolute values of enthalpy but the difference between the enthalpic content of the solution and the pure component.

The change in enthalpy when the amount of component 2 is very small is defined as the enthalpy at infinite dilution and is symbolized as $\Delta H_2^{\bullet}$ [7].

Another way to express the enthalpy change is to choose as reference state the dilute mixture so obtained from the enthalpy change for the mixture to a given composition and the mixing enthalpy at infinite dilution, as shown in the following relations for component 2 [8]:

$$\overline{L}_2 = \left(\overline{H_2} - \overline{H_2^{\bullet}}\right) = \left(\frac{\partial H_{\mathrm{exp}}}{\partial \mathrm{n}_2}\right)_{\mathrm{T,P,n_1}} - \left(\frac{\partial \Delta H_{\mathrm{exp}}}{\partial \mathrm{n}_2}\right)^{\bullet}_{\mathrm{T,P,n_1}} \qquad (5)$$

In the case of partial molar enthalpies of solutions, the authors consider the contribution to the property of each component per mole in the mix; however, in the case of the mixture, as described in this article, in which the experimental enthalpy change in the mixture of activated carbon and water is determined, the contribution can not be calculated per mole but per gram for each of the components of the binary system. In this article the authors made this approximation, calculated the enthalpy changes listed above, and studied the behaviour of the mixture in relation to the mass of activated carbon.

Experimental

Textural and chemical characterization of activated carbon

The carbonaceous samples measuring about 0.100 g are degasified 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 activated carbon are determined by means of the Boehm method [9].

Experimental immersion enthalpy determination

In this study, experimental immersion enthalpies of the activated carbon in water in function of its mass are determined for the estimation of the energetic interactions when the solid is in contact with the water. A heat conduction microcalorimeter equipped with a calorimetric cell made of stainless steel is used for the determination of the experimental immersion enthalpies [10]. 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 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 min more. Finally, the device gets calibrated electrically.

Results and discussion

The activated carbon that is used in this study, in order to find its enthalpic characterization when placed in contact with water is obtained from a lignocellulosic material activated physically and has been used in adsorption of organic compounds in other studies [11]. The textural and chemical characteristics of the activated carbon are shown in Table 1.

The surface area value and content of acidic and basic sites of activated carbon allow that the immersion enthalpy of this in water can be observed in function of mass and is sensitive to differences in heat produced in the wet process, due to the change in mass of the solid.

Figure 1 shows typical curves of the calorimetric signal for the immersion of 45 and 408 mg of activated carbon in amounts of water of about 8.0 g. It is noted that the effect is exothermic and the heat produced by the solid immersion in the liquid is proportional to the area under the curve of electric potential signal as a function of time.

Table 1 Textural and chemical characteristics of activated carbon

Surface area B.E.T./$\mathrm{m^2g^{-1}}$	1,140
Micropore volume/$\mathrm{cm^3g^{-1}}$	0.51
Mesopore volume/$\mathrm{cm^3g^{-1}}$	0.12
Total acidity/$\mathrm{mmolg^{-1}}$	0.30
Total basicity/$\mathrm{mmolg^{-1}}$	0.60

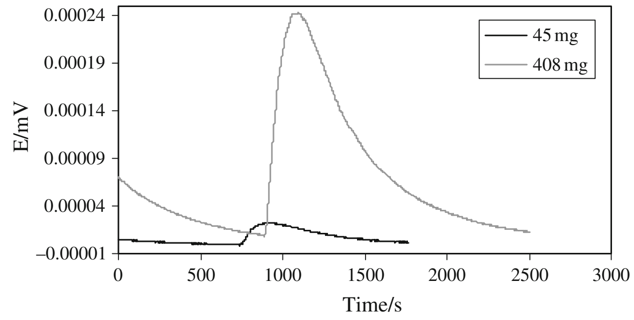

Fig. 1 Calorimetric curves of activated carbon immersion in water

Figure 2 shows the results for the heat generated by the immersion of different amounts of activated carbon in a constant amount of water; increasing the amount of the solid increases the amount of heat generated when the activated carbon and water are placed in contact. Similar results for the immersion heats of an activated carbon PLW were obtained by Stoeckli et al. [12] and these heats are proportional to the textural characteristics of activated carbon, with respect to the values of immersion enthalpy in water these are comparable to values obtained in a recent article in which activated carbons with different burn-offs are prepared [13].

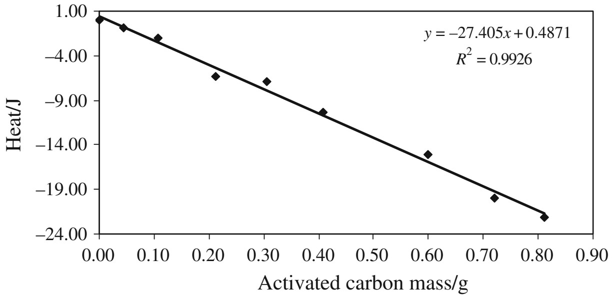

Fig. 2 Heat generated by the immersion of different amounts of activated carbon in water

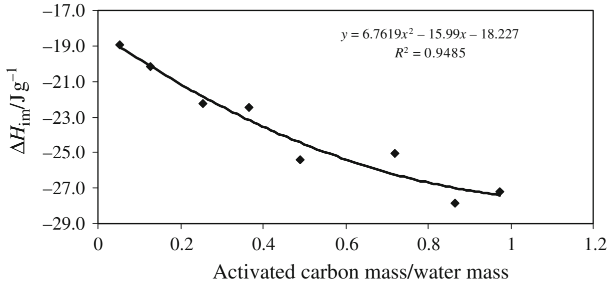

Fig. 3 Enthalpy of immersion in terms of mass ratio of activated charcoal in water

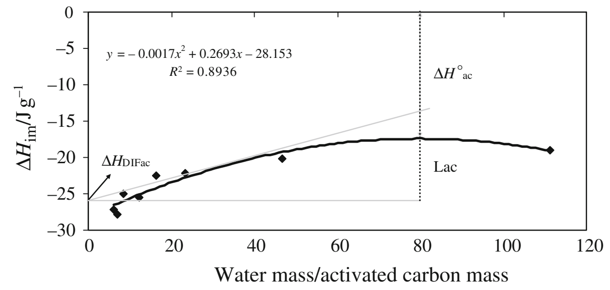

Fig. 4 Immersion enthalpy in function to the ratio of water mass and the mass of activated carbon

As the aim is to find the contributions of activated carbon and water to immersion enthalpies, given that each of these will make a contribution to the final value of the immersion enthalpy and the amount of activated carbon cannot be expressed as the number of moles because its structure changes according to the method of preparation, the amount is expressed in grams of each component and the immersion enthalpy in Joules per gram of activated carbon. In this way the authors find the behaviour that occurs between the immersion enthalpy and the relationship between the mass of activated carbon, acm, and the mass of water, wm, which corresponds to Fig. 3, as the immersion enthalpy is of exothermic character, exhibiting a decline in value with increases in the ratio acm/wm, which follows a second order equation with a correlation coefficient of 0.9485, and the equation gives the value of the immersion enthalpy when the amount of activated carbon tends to zero, $\Delta H^0_{\mathrm{im_{ac}}}$, with a value of –18.23 $\mathrm{Jg^{-1}}$, similar to the enthalpy at infinite dilution, ΔH^0_2, in the description of the partial molar enthalpies of solution.

The authors represent the immersion enthalpy in terms of the mass ratio, wm/acm, as shown in Fig. 4. The representation of the experimental results in this way again follows a second order function with a correlation coefficient of 0.8936, and allow to find by mean of the slopes at each point the differential enthalpy for both activated carbon and for the water, ΔH_{DIF}, which in the case of activated carbon is shown in the cut of a tangential line at a given point of the curve. The enthalpy when the amount of activated carbon tends to zero, ΔH^0_{ac}, which can be established as the value between x-axis and the maximum point in the curve, shown in Fig. 4 with a double arrow in grey, and the partial relative enthalpy of activated carbon, $\overline{L_{\mathrm{ac}}}$, which is indicated in figure with the dotted line [8, 14].

Figure 5 shows the values obtained for the enthalpy differential for activated carbon, $\Delta H_{\mathrm{DIF_{ac}}}$ whose range is between –15.95 and –26.81 $\mathrm{Jg^{-1}}$ and for water, $\Delta H_{\mathrm{DIF_w}}$, between –19.14 and –42.45 $\mathrm{Jg^{-1}}$. The differential enthalpies are of exothermic character and the contribution of water to immersion enthalpy is greater because the mass of water was greater than that of activated carbon for all the mixes that were made.

Figure 5 is an interesting result because it allows us to observe that the contribution of each component is

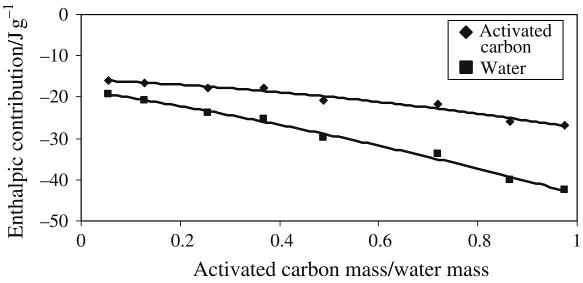

Fig. 5 Contribution of activated carbon and water immersion enthalpies

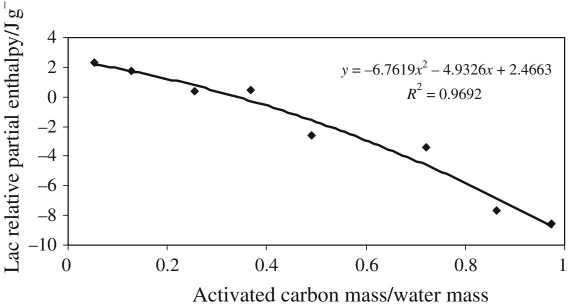

Fig. 6 Relative partial enthalpy for the immersion of activated carbon in water

different for different mass ratios of these, similarly to the description given for the partial molar enthalpies in the case of solutions as shown by Zielenkiewicz [15] in his study of mixing aqueous solutions of human serum albumin with aqueous solutions of NaCl; in this the mixture of albumin represents a matrix with a high carbon content.

Finally, in Fig. 6 the behaviour for the partial relative enthalpy for the activated carbon is obtained. Depending on the ratio of activated carbon mass and mass of water, with values for the mass ratios between 2.28 and –8.58 in Jg^{-1}, the graph shows that for mass ratios of the components between 0.05 and 0.30, values concerning the partial relative enthalpies are endothermic and from this relationship are exothermic, indicating the effect of the reference state that was chosen for the mixture with the amount activated carbon tending to zero. Thus for low mass ratios, contributions to the immersion enthalpy of activated carbon and water differ by 3.20 Jg^{-1}.

Conclusions

The enthalpies of immersion of a microporous activated carbon with a BET surface area value of 1140 m^2 g^{-1} and basic character in water were determined, and values between –18.97 and 27.21 Jg^{-1} were obtained.

The enthalpic contributions to the immersion enthalpy of activated carbon and water, when these are mixed, are determined, which follow the concepts of partial enthalpies of the theory of solutions. For the case of the activated carbon–water mixture the amounts cannot be expressed in the number of moles of the two components for which are used for the interpretations relations in mass.

The results show that the immersion enthalpies are of exothermic character as well as the contributions of each component, and it is determined that the activated carbon differential enthalpy, $\Delta H_{\mathrm{DIF}_{\mathrm{ac}}}$, presents values between –15.95 and –26.81 Jg^{-1}.

The enthalpy value when the amount of activated carbon tends to zero, $\Delta H^0_{\mathrm{im}_{\mathrm{ac}}}$, is –18.23 Jg^{-1} and the relative partial enthalpy with respect to solid, $\overline{L_{\mathrm{ac}}}$, is between 2.28 and –8.58 Jg^{-1}, which indicates the influence of the chosen reference for the calculation.

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