# Evaluation of Excess Molar Enthalpies for a Quaternary Mixture System of Acetic Anhydride, Ethanol, Acetic Acid, and Ethyl Acetate

Laurent Balland,* Imed Ben Talouba, Nordine Mouhab, and Ahmed Abdelghani-Idrissi

Laboratoire de Sécurité des Procédés Chimiques (LSPC), Université de Rouen/INSA, rue Lavoisier, F-76821 Mont Saint Aignan Cedex, France

ABSTRACT: Excess molar enthalpies were measured using a Mettler-Toledo RC1 calorimetric reactor at 298 K and 0.1 MPa for the quaternary system which may occur during the hydrolysis of acetic anhydride with ethanol (production of acetic acid and ethyl acetate). A novel formula for the excess molar enthalpies of the quaternary system as a function of the molar composition has been developed. It is mainly based on a Margules-type equation which illustrates the quaternary excess enthalpies by taking into consideration the contributions from the corresponding binary and ternary systems. With no solvent present in the reaction system, the thermal behavior may significantly vary with the extent of the reaction taking place. The evolutions of the partial excess enthalpy on the calculation of both the heat of mixing during reaction and the reaction enthalpy were tabulated for various extents of the chemical reaction.
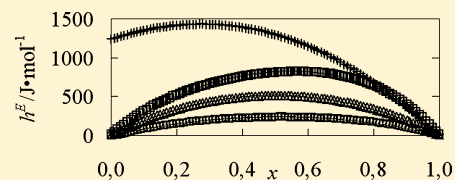
INTRODUCTION

Process productivity can easily be improved by the reduction of the quantities of solvent used. The reduction, or even the total elimination of solvent use, has the ability to identify physical, chemical, and thermal phenomena that can be related to the solvation of the reagents and mixing heats generated within the reaction system. For a solvent-free reaction mixture, the thermal behavior may significantly change between the beginning of the reaction when only reagents are present in the mixture and the end when the reaction mixture contains only the products, in the case of the total equimolar reaction.[1,2] This evolution is linked to the partial molar excess enthalpies of the chemical species present in the reaction system[3] and depends on the molar composition of the reaction mixture. Their progress is usually concealed in the presence of a solvent in the system.

In this work, the excess molar enthalpies were investigated in the case of the hydrolysis of acetic anhydride by ethanol, catalyzed by sulfuric acid without solvent. The overall equation of the reaction is given below:

$$\tag{1}$$
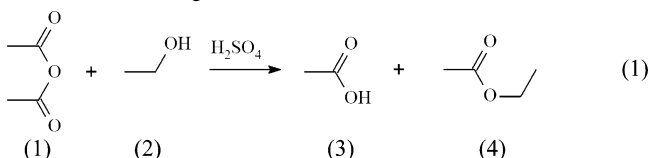
At the beginning, the reaction system contains only ethanol (2), then successive additions of acetic anhydride (1) are carried out, and the reaction produces acetic acid (3) and ethyl acetate (4). Only the excess enthalpy of the ethanol (2)/ethyl acetate (4) binary system has been studied and reported in the published literature.[4−6]

Excess molar enthalpies are usually difficult to calculate from liquid−vapor equilibrium data for multicomponent systems.[7] In this work, an experimental method based on calorimetric measures has been used to determine the excess molar enthalpy of the quaternary mixture derived from the one corresponding to the binary and ternary systems. The thermal power generated during the mixing process was measured using a Mettler-Toledo RC1 calorimetric reactor for each system. The excess molar enthalpy of the mixture was then quantified by calculating the area of the generated thermal power divided by the corresponding molar composition of the reaction mixture (eq 5). In this work the excess molar enthalpies of the binary, ternary, and quaternary systems have been expressed according to a Margules-type polynomial equation.

MATERIALS AND METHODS

Apparatus. The Mettler-Toledo RC1 glass made calorimetric reactor used by Balland et al.[8] worked at atmospheric pressure. It was composed of a jacketed reactor (2 L capacity) with tangential input for the heat transfer fluid. It was equipped with a Pt100 temperature probe, an electrical calibration heating, a stirring system (anchor, diameter = 0.104 m), and an introduction system (dosing pump and balance, with the measurement of the temperature at introduction). Every measure was carried out at atmospheric pressure, a temperature of 298 K, and a stirring speed of 150 rpm (turbulent flow: Reynold's number $Re > 2 \cdot 10^4$). The heating−cooling system, which uses a single heat transfer fluid (silicone oil 47 V20 Rhodorsil), works within a temperature range from (258 to 473) K. The uncertainty of the initial and dosed masses is ± 0.1 g. Considering several hundreds of grams for both masses, this involves an uncertainty in the mole fraction less than 10^{-3}. In all experiments carried out in isothermal mode, the temperature deviation due to endothermic phenomenon was less than 1 K.

Experimental values of the thermal power released by the mixture are given by the exploitation software. This balance is
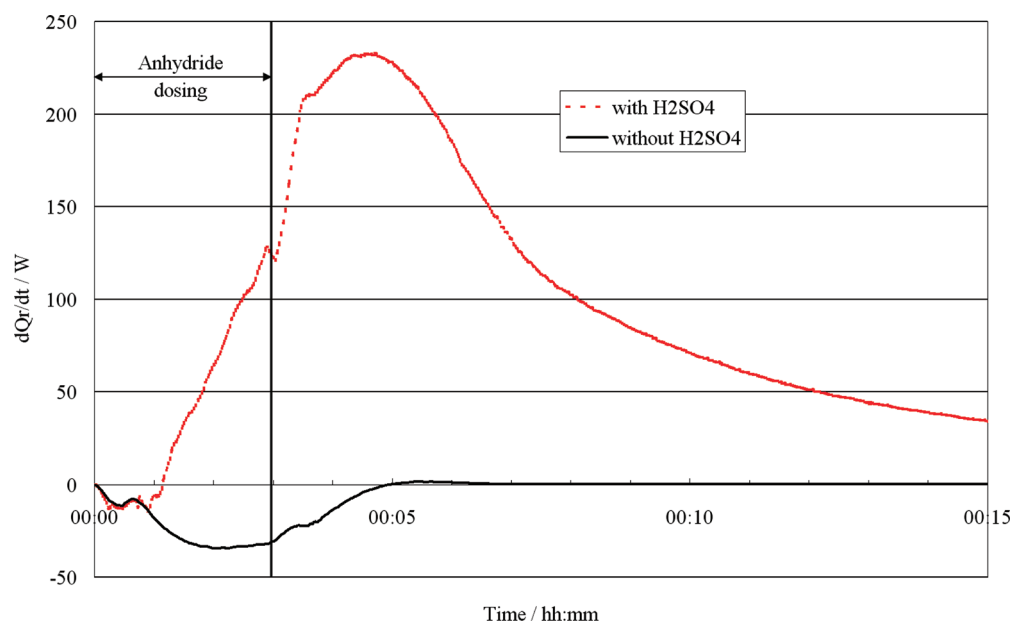
Figure 1. Power profile during dosing of acetic anhydride in ethanol, with and without H_2SO_4 in the initial mixture.

established with the hypotheses that agitation is perfect and that temperature T_f is homogeneous throughout the jacket:

$$\frac{dQ_{acc}}{dt} = \frac{dQ_f}{dt} + \frac{dQ_{cov}}{dt} + \frac{dQ_{dos}}{dt} + \frac{dQ_R}{dt} \qquad (2)$$

where the different terms are explained in a previous article:[8] (dQ_{acc}/dt) the thermal power accumulated by the system and the inserts, (dQ_f/dt) the power exchanged with the heat transfer fluid of the jacket, (dQ_{cov}/dt) the power exchanged by natural convection and radiation with ambient air, and (dQ_{dos}/dt) the power absorbed or given by the constituents introduced during the dosing. The last term (dQ_R/dt) is given by the energetic balance in eq 2 every two seconds, which corresponds to the power released by the physical and chemical transformations according to the equation:

$$\frac{dQ_R}{dt} = \frac{dQ_{PP}}{dt} - V \cdot r \cdot \Delta H_R \qquad (3)$$

In this work, the first term (dQ_{PP}/dt) of eq 3, power released by the physical transformations, only represents the mixing power due to the nonideality of the solutions. Power released by the chemical transformations depends upon the reaction enthalpy ΔH_R, the rate of chemical reaction r, and the volume of the system V.

Chemicals. Acetic anhydride (mass fraction purity >0.99, compound (1)) and acetic acid (mass fraction purity >0.998, compound (3)) were supplied by Aldrich. Ethanol (mass fraction purity >0.9999, compound (2)) was supplied by Carlo Erba. Ethyl acetate (mass fraction purity >0.995, compound (4)) was supplied by Acros. All liquids were used without further purification.

Experiments. To demonstrate that the chemical reaction is too slow without an acid catalyst, thermal information (power profile absorbed or released, eq 3) was used. Two experiments were carried out with the reactor filled with ethanol: during the first experiment 1 g of H_2SO_4 as a catalyst was added in the initial mixture and nothing during second experiment; then acetic anhydride was dosed. Figure 1 shows both power profiles. The difference between both profiles can be explained by

the chemical reaction (eq 1) occurring in the first experience. In the second experiment, only the endothermic heat of mixing was measured. In the following study, the chemical reaction of eq 1 was then considered to be too slow without catalyst (H_2SO_4), and therefore the last term of eq 3 was neglected.

To evaluate the excess molar enthalpies of the quaternary system we need first to determine the excess molar enthalpies of the corresponding binary and ternary systems. The latter were experimentally determined from the thermal power measurements of mixing heats for each multicomponent system. In the case of a binary system, the range of compositions is represented by a line segment, and it is then possible to experimentally scan every composition. In the case of a ternary and a quaternary system, the range of compositions is represented by the surface of a triangle and the volume of a tetrahedron, respectively, and hence experimental scanning of all compositions is not applicable.
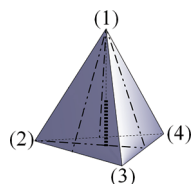
For the calorimetric study of each of the six binaries, the calorimetric reactor was loaded with a minimum volume of a given component (800 mL imposed by the sensors position). Then the second component was dosed at a constant rate of 30 g·min⁻¹ up to the maximum capacity of reactor (2 L). A second experiment was carried out again with the permutation of the component which was initially present in the reactor and the one dosed.

For the calorimetric study of the ternary systems, it is not possible to use all of the compositions, and hence some selected compositions were chosen among those encountered during the hydrolysis reaction of acetic anhydride by ethanol. In the case of acetic anhydride (1)/acetic acid (3)/ethyl acetate (4) ternary system, the experiment consisted of dosing acetic anhydride in a 50:50 mol % acid−ester mixture. During the second experiment, a 50:50 mol % acid−ester mixture was dosed in acetic anhydride. The acid−ester molar proportion is dictated by the stoichiometry given in eq 1. A similar strategy was taken with the study of the three other ternary systems. The molar compositions of the initial mixture and of the dosing are given in Table 1.

Table 1. Initial Compositions and Additions to Study Ternary Systems

ternary system	experiment 1		experiment 2	
	initial mixture	addition	initial mixture	addition
(1)/(3)/(4)	$x_3 = x_4 = 0.500$	(1)	(1)	$x_3 = x_4 = 0.500$
(2)/(3)/(4)	$x_3 = x_4 = 0.500$	(2)	(2)	$x_3 = x_4 = 0.500$
(1)/(2)/(3)	$x_2 = x_3 = 0.500$	(1)	(1)	$x_2 = x_3 = 0.500$
(1)/(2)/(4)	$x_2 = x_4 = 0.500$	(1)	(1)	$x_2 = x_4 = 0.500$

For the calorimetric study of the quaternary system, an initial mixture with a molar composition of one-third of ethanol, acetic acid, and ethyl acetate, was loaded in the reactor. Acetic anhydride was dosed in the reactor up to the maximum capacity of the reactor. The mole fraction range for anhydride was limited between 0 and 0.43. The anhydride mole fraction is always less than 0.5 according to the stoichiometry of the hydrolysis reaction shown in eq 1. Figure 2 represents the

Figure 2. Studied compositions for the quaternary system.

molar compositions used for the calorimetric study: each edge for the binaries, each bisection on faces with dotted lines for the ternaries, and a segment altitude of the tetrahedron with a heavy dotted line for the quaternary.

Experimental Excess Enthalpy. To determine the excess molar enthalpy from the experiments, the instantaneous molar compositions x_j are determined from the initial composition and the dosed mass at time t. Partial integral of the power from initial to time t is divided by the total mole number $\sum_j n_j(t)$ at this time and gives $h_\phi^{E,exp}$, the measured excess molar enthalpy.

$$h_\phi^{E,exp}(x_j, t) = \frac{-1}{\sum_j n_j(t)} \int_0^t \frac{dQ_R}{dt} \cdot dt \tag{4}$$

To get the total excess molar enthalpy of the mixture, it is necessary to add the molar excess enthalpy of the initial mixture, which is zero for pure constituent and is calculated from previous experiments in other cases (eq 5).

$$h^{E,exp}(x_j, t) = \frac{n_{0T}}{\sum_j n_j(t)} \cdot h_{(t=0)}^{E,calc} + h_\phi^{E,exp}(x_j, t) \tag{5}$$

where n_{0T} is the initial number of moles:

$$n_{0T} = \sum_j n_j(t = 0) \tag{6}$$

The uncertainty in excess molar enthalpy measurements is estimated to be better than 5 %.

Excess Enthalpy Formulation. The excess molar enthalpy for the quaternary system is made of the sum of the excess enthalpies of the corresponding binary systems $h_{j,k}^E$, plus the sum of contributions of the corresponding ternary systems

$h_{j,k,l}^{E,cont}$, plus a specific contribution of the quaternary system $h_{1,2,3,4}^{E,cont}$.

$$h^E = \sum_{j \neq k} h_{j,k}^E + \sum_{j \neq k \neq l} h_{j,k,l}^{E,cont} + h_{1,2,3,4}^{E,cont} \tag{7}$$

The excess molar enthalpies expressions according to the molar composition must be kept simple to be included in the thermal behavior model of the reaction mixture. A Margules-type polynomial equation was chosen to represent each term of eq 7. For binaries it is given by:

$$h_{j,k}^E = x_j x_k (a_{jk} x_j + a_{kj} x_k) \tag{8}$$

Contributions for ternary (eq 9) and quaternary (eq 10) systems are given by:

$$h_{j,k,l}^{E,cont} = x_j x_k x_l (a_{jkl} x_j + a_{kjl} x_k + a_{ljk} x_l) \tag{9}$$

$$h_{1,2,3,4}^{E,cont} = x_1 x_2 x_3 x_4 (a_{1234} x_1 + a_{2134} x_2 + a_{3124} x_3 + a_{4123} x_4) \tag{10}$$

The values of Margules coefficient a were estimated by using a quasi-Newton-fit method (BFGS method[9]).

RESULTS AND DISCUSSION

Experimental Results. Among the six corresponding binary systems for the quaternary system studied, the calorimetric study has shown that only ethanol (2)/ethyl acetate (4), ethanol (2)/acetic anhydride (1), and acetic anhydride (1)/acetic acid (3) binary systems had significant thermal power. The thermal power released for the three other binary systems (acetic acid (3)/ethyl acetate (4), acetic anhydride (1)/ethyl acetate (4), and ethanol (2)/acetic acid (3)) was less than the sensibility of the calorimetric reactor (2 W) used.

For the ethanol (2)/ethyl acetate (4) binary system, the experiments followed the procedure described above. As the reaction calorimeter gave data every two seconds, more than 1000 experimental points were collected. All data could not be reported in this paper. A selection of excess enthalpies obtained in this work for the binary mixtures are listed in Table 2.

Figure 2 shows the excess molar enthalpy versus the mole fraction of ethanol x_2. This experimental curve can be fitted to a Margules-type polynomial equation as follows:

$$h_{2,4}^E = x_2 x_4 (4078 x_2 + 5827 x_4) \tag{11}$$

The normalized root-mean-square deviation (NRMSD, eq 12) between the experimental and the calculated excess molar enthalpies values was 2.2 %.

$$NRMSD = \frac{1}{h_{max}^{E,exp}} \sqrt{\frac{\sum_{i=1}^N (h_i^{E,exp} - h_i^{E,calc})^2}{N}} \tag{12}$$

where N is the number of measured values. The results are similar to those obtained by Grolier and Viallard,[4] Nagata et al.,[5] and Zhang et al.[6] as shown in Figure 3. The maximum deviation is about 5 % with Grolier or Nagata's values and 8 % with Zhang's values which were determined at 10.0 MPa. Larger differences with Zhang's values may be explained by different pressure conditions.

The two other binary systems were similarly studied, and some values are listed in Table 2. Results are plotted in Figure 3

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Table 2. Experimental Excess Molar Enthalpy for the Ethanol (2)/Ethyl Acetate (4), Acetic Anhydride (1)/Ethanol (2), and Acetic Anhydride (1)/Acetic Acid (3) Binary Systems

| x_2	$h_{2,4}^{E,exp}$ J·mol^{-1}	$h_{1,2}^{E,exp}$ J·mol^{-1}	x_1	$h_{1,3}^{E,exp}$ J·mol^{-1}
0.050	298	344	0.050	45
0.100	564	643	0.100	89
0.150	775	895	0.150	134
0.200	930	1111	0.200	177
0.250	1048	1282	0.250	217
0.300	1131	1418	0.300	254
0.350	1185	1521	0.350	288
0.400	1216	1600	0.400	317
0.450	1224	1657	0.450	340
0.500	1211	1693	0.500	356
0.550	1189		0.550	366
0.600	1153	1604	0.600	368
0.650	1095	1518	0.650	361
0.700	977	1411	0.700	344
0.750	859	1280	0.750	317
0.800	728	1122	0.800	280
0.850	577	926	0.850	230
0.900	420	687	0.900	168
0.950	232	393	0.950	92
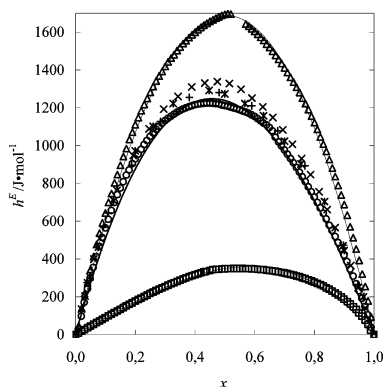
Figure 3. Excess molar enthalpy for binary systems. Experimental values of: {x ethanol + $(1 - x)$ ethyl acetate}, ∗, from Grolier ref 4; +, from Nagata ref 5; ×, Zhang ref 6; ○, from this work; △, {x acetic anhydride + $(1 - x)$ ethanol} from this work; □, {x acetic anhydride + $(1 - x)$ acetic acid} from this work; −, fitting curves from eqs 11, 13, and 14.

for acetic anhydride (1)/ethanol (2) and acetic anhydride (1)/acetic acid (3) binary systems. Equations 13 and 14 illustrate the best fit of the experimental excess molar enthalpies, with respective NRMSD's of 1.8 % and 3.1 %:

$$h_{1,2}^{E} = x_1 x_2 (6660 x_1 + 6845 x_2) \qquad (13)$$

$$h_{1,3}^{E} = x_1 x_3 (1908 x_1 + 888 x_3) \qquad (14)$$

For the acetic anhydride (1)/acetic acid (3)/ethyl acetate (4) ternary system, the mole fraction x_3 is kept equal to x_4. The same applies to the ethanol (2)/acetic acid (3)/ethyl acetate (4) ternary system. As $h_{3,4}^{E}$ is neglected, then $h_{1,3,4}^{E,exp} = h_{\phi,1,3,4}^{E,exp}$ and $h_{2,3,4}^{E,exp} = h_{\phi,2,3,4}^{E,exp}$ for these measurements. The excess enthalpies for these ternary systems are plotted in Figure 4. The experimental results appear in Table 3. The results obtained fit best
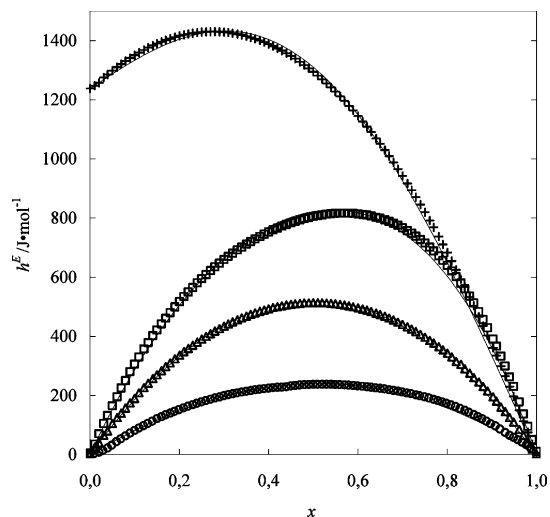

Figure 4. Excess molar enthalpy of ternary systems. Experimental values of: ○, {x acetic anhydride + $(1 - x)(0.5$ acetic acid + 0.5 ethyl acetate)}; △, {x ethanol + $(1 - x)(0.5$ acetic acid + 0.5 ethyl acetate)}; □, {x acetic anhydride + $(1 - x)(0.5$ ethanol + 0.5 acetic acid)}; +, x acetic anhydride + $(1 - x)(0.5$ ethanol + 0.5 ethyl acetate)}; −, fitting curves from eqs 15, 16, 18, and 19.

Table 3. Experimental Excess Molar Enthalpy for the Acetic Anhydride (1)/Acetic Acid (3)/Ethyl Acetate (4) and Ethanol (2)/Acetic Acid (3)/Ethyl Acetate (4) Ternary Systems

x_1	$x_3 = x_4$	$h_{1,3,4}^{E,exp}$ J·mol^{-1}	x_2	$x_3 = x_4$	$h_{2,3,4}^{E,exp}$ J·mol^{-1}
0.000	0.500	0	0.000	0.500	0
0.050	0.475	32	0.050	0.475	105
0.100	0.450	81	0.100	0.450	190
0.150	0.425	121	0.150	0.425	270
0.200	0.400	152	0.200	0.400	336
0.250	0.375	178	0.250	0.375	390
0.300	0.350	199	0.300	0.350	435
0.350	0.325	214	0.350	0.325	469
0.400	0.300	225	0.400	0.300	493
0.450	0.275	232	0.450	0.275	508
0.500	0.250	237	0.500	0.250	513
0.550	0.225	237	0.550	0.225	510
0.600	0.200	232	0.600	0.200	496
0.650	0.175	224	0.650	0.175	474
0.700	0.150	212	0.700	0.150	441
0.750	0.125	195	0.750	0.125	397
0.800	0.100	173	0.800	0.100	343
0.850	0.075	143	0.850	0.075	275
0.900	0.050	104	0.900	0.050	195
0.950	0.025	58	0.950	0.025	110
1.000	0.000	0	1.000	0.000	0

the following overall equations (corresponding to the binary systems and ternary contribution):

$$h_{1,3,4}^{E} = x_1 x_3 (1908 x_1 + 888 x_3) + x_1 x_3 x_4 (2575 + 883 x_1) \qquad (15)$$

$$h_{2,3,4}^{E} = x_2 x_4 (4078 x_2 + 5827 x_4) + x_2 x_3 x_4 (2407 + 451 x_2) \qquad (16)$$

The corresponding NRMSD's are 1.4 % and 2.8 %.

For the two other ternary systems, acetic anhydride (1)/ethanol (2)/acetic acid (3) and acetic anhydride (1)/ethanol (2)/ethyl acetate (4), the mole fraction x_2 is kept equal to x_3 and x_4, respectively. As $h_{2,3}^E$ is neglected, then $h_{1,2,3}^{E,exp} = h_{\phi,1,2,3}^{E,exp}$ for these measurements. However, initial $h_{2,4}^E$ must be included in $h_{1,2,4}^{E,exp}$:

$$h_{1,2,4}^{E,exp}(x_j, t) = (x_2 + x_4) \cdot h_{0,2,4}^{E,calc} + h_{\phi,1,2,4}^{E,exp}(x_j, t) \quad (17)$$

The excess enthalpies for these ternary systems are shown in Figure 4. The experimental results appear in Table 4.

Table 4. Experimental Excess Molar Enthalpy for the Acetic Anhydride (1)/Ethanol (2)/Acetic Acid (3) and Acetic Anhydride (1)/Ethanol (2)/Ethyl Acetate (4) Ternary Systems

		$h_{1,2,3}^{E,exp}$			$h_{\phi,1,2,4}^{E,exp}$	$h_{1,2,4}^{E,exp}$
x_1	$x_2 = x_3$	J·mol^{-1}	x_1	$x_2 = x_4$	J·mol^{-1}	J·mol^{-1}
0.000	0.500	0	0.000	0.500	0	1238
0.050	0.475	165	0.050	0.475	122	1298
0.100	0.450	306	0.100	0.450	236	1351
0.150	0.425	421	0.150	0.425	337	1390
0.200	0.400	517	0.200	0.400	426	1416
0.250	0.375	595	0.250	0.375	501	1429
0.300	0.350	659	0.300	0.350	563	1429
0.350	0.325	711	0.350	0.325	611	1415
0.400	0.300	753	0.400	0.300	645	1388
0.450	0.275	784	0.450	0.275	667	1348
0.500	0.250	805	0.500	0.250	675	1295
0.550	0.225	816	0.550	0.225	670	1227
0.600	0.200	814	0.600	0.200	650	1145
0.650	0.175	799	0.650	0.175	618	1051
0.700	0.150	767	0.700	0.150	571	942
0.750	0.125	715	0.750	0.125	510	819
0.800	0.100	640	0.800	0.100	435	683
0.850	0.075	535	0.850	0.075	347	532
0.900	0.050	391	0.900	0.050	240	361
0.950	0.025	230	0.950	0.025	133	197
1.000	0.000	0	1.000	0.000	0	0

The results show that they fit best the overall equations corresponding to the binary systems and ternary contributions as follows:

$$h_{1,2,3}^E = x_1 x_2 (6660 x_1 + 6845 x_2) + x_1 x_3 (1908 x_1 + 888 x_3)$$
$$+ x_1 x_2 x_3 (5316 - 7767 x_1) \quad (18)$$

$$h_{1,2,4}^E = x_1 x_2 (6660 x_1 + 6845 x_2) + x_2 x_4 (4078 x_2$$
$$+ 5827 x_4) + x_1 x_2 x_4 (11986 + 9650 x_1) \quad (19)$$

The corresponding NRMSD's are 2.5 % and 1.4 %.

For the quaternary system, the mole fractions x_2, x_3 and x_4 are kept equal. The experimental results appear in Table 5. Initial $h_{2,4}^E$ and $h_{2,3,4}^E$ must be included in $h_{1,2,3,4}^{E,exp}$ for this experiment:

$$h_{1,2,3,4}^{E,exp}(x_j, t) = (x_2 + x_4) \cdot h_{0,2,4}^{E,calc} + (x_2 + x_3 + x_4) \cdot h_{0,2,3,4}^{E,calc}$$
$$+ h_{\phi,1,2,3,4}^{E,exp}(x_j, t) \quad (20)$$

Table 5. Experimental Excess Molar Enthalpy for the Acetic Anhydride (1)/Ethanol (2)/Acetic Acid (3)/Ethyl Acetate (4) Quaternary System

		$h_{\phi,1,2,3,4}^{E,exp}$	$h_{1,2,3,4}^{E,exp}$
x_1	$x_2 = x_3 = x_4$	J·mol^{-1}	J·mol^{-1}
0.000	0.333	0	462
0.020	0.327	42	492
0.040	0.320	88	531
0.060	0.313	138	572
0.080	0.307	188	613
0.100	0.300	233	648
0.120	0.293	274	680
0.140	0.287	313	709
0.160	0.280	350	736
0.180	0.273	384	762
0.200	0.267	415	785
0.220	0.260	445	804
0.240	0.253	472	823
0.260	0.247	497	838
0.280	0.240	519	851
0.300	0.233	539	862
0.320	0.227	558	872
0.340	0.220	575	879
0.360	0.213	587	882
0.380	0.207	598	885
0.400	0.200	608	885
0.420	0.193	616	884
0.430	0.190	621	884

The results shown in Figure 5 illustrate the contribution of the quaternary system. The overall expression of the excess

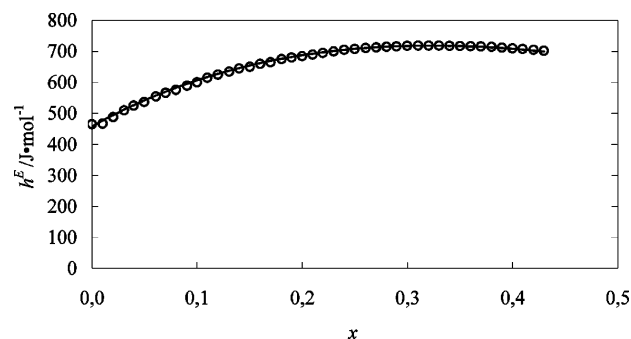**Figure 5.** Excess molar enthalpy of the quaternary system. Experimental values of ○, {x acetic anhydride + $(1 - x)$(0.333 ethanol + 0.333 acetic acid + 0.333 ethyl acetate)}; −, fitting curve from eq 21.

molar enthalpy of acetic anhydride (1)/ethanol (2)/acetic acid (3)/ethyl acetate (4) quaternary system, at 298 K under atmospheric pressure is given by:

$$h^E = x_2 x_4 (4078 x_2 + 5827 x_4) + x_1 x_2 (6660 x_1 + 6845 x_2)$$
$$+ x_1 x_3 (1908 x_1 + 888 x_3) + x_2 x_3 x_4 (2407 + 451 x_2)$$
$$+ x_1 x_3 x_4 (2575 + 883 x_1) + x_1 x_2 x_3 (5316 - 7767 x_1)$$
$$+ x_1 x_2 x_4 (11986 + 9650 x_1) + x_1 x_2 x_3 x_4 (12146$$
$$+ 12505 x_1) \quad (21)$$

The NRMSD is 0.3 %.

Applications. In this section, the influence of excess enthalpies on the thermal behavior of the chemical reaction (eq 1) was modeled for several extents of the reaction. Both power terms in eq 3 (mixing heat and reaction heat) were linked to the partial excess enthalpies defined by the following expression:[3]

$$h_j^E = h^E + \frac{\partial h^E}{\partial x_j} - \sum_k x_k \frac{\partial h^E}{\partial x_k} \tag{22}$$

The thermal power term due to mixing heat during the dosing of acetic anhydride (1) with (dn_1^{In}/dt) flow rate is:

$$\frac{dQ_{PP}}{dt} = -\frac{dn_1^{In}}{dt} h_1^E \tag{23}$$

with h_1^E being the partial molar excess enthalpy of acetic anhydride.

The chemical reaction enthalpy ΔH_R is the sum of $\Delta H°$ (function of the formation enthalpies of the reagents and the products) and a contribution due to the partial molar excess enthalpies of the species involved and is given by:

$$\Delta H_R = \Delta H° + \sum_j \nu_j h_j^E = \Delta H° - h_1^E - h_2^E + h_3^E + h_4^E \tag{24}$$

The partial molar excess enthalpies of the four species h_j^E were calculated at three different molar compositions values of x_j. Each set of values simulated an extent of the hydrolysis reaction (eq 1). The first one represented the initial stage of the reaction mixture which contained only ethanol. The second and third sets represented the dosing and reaction extents as indicated in Table 6. Z_1 (0.50 and 1.00, respectively) was the ratio of dosed

Table 6. Partial Molar Excess Enthalpies

stage	initial		$Z_1 = 0.50;$ $\chi = 0.44$		$Z_1 = 1.00; \chi = 0.87$	
		h_j^E		h_j^E		h_j^E
constituent	x_j	$J \cdot mol^{-1}$	x_j	$J \cdot mol^{-1}$	x_j	$J \cdot mol^{-1}$
(1) anhydride	0.00	6845	0.01	4945	0.02	3580
(2) ethanol	1.00	0	0.83	−270	0.69	−280
(3) acid	0.00	0	0.08	−775	0.145	−1200
(4) ester	0.00	4080	0.08	2860	0.145	2000
$\sum_j \nu_j h_j^E$		−2770		−2590		−2500

anhydride, compared to the total of 4 mol added. χ (0.44 and 0.87, respectively) was the reaction extent arbitrarily determined, compared to the consumption of these 4 mol by the chemical reaction.

These calculations show that the mixing heat h_1^E was reduced by more than 40 % during the reaction. The contribution of the excess enthalpy to the reaction enthalpy $\sum_j \nu_j h_j^E$ cannot be neglected: with a mean value, measured in the calorimetric reactor, of 50 kJ·mol^{-1} for ΔH_R^1 this correction represents (3 to 5) %.

■ CONCLUSIONS

The excess molar enthalpy was measured using a Mettler-Toledo RC1 calorimetric reactor for the quaternary system: acetic anhydride, ethanol, acetic acid, and ethyl acetate. The excess molar enthalpies of the corresponding binary and ternary systems were first evaluated. Not all binary systems had sufficient

excess heat to be measured, and hence the following have not been taken into consideration: acetic acid/ethyl acetate, acetic anhydride/ethyl acetate, and ethanol/acetic acid. The excess molar enthalpies for the corresponding ternary systems and the quaternary system were only determined for molar compositions corresponding to the stoichiometry of acetic anhydride hydrolysis by ethanol. The excess molar enthalpy of the quaternary system was quantified as being the sum of the excess molar enthalpies of the corresponding binary systems, plus the contributions of the corresponding ternary systems and the contribution of the quaternary system. The results were best fitted to a Margules-type polynomial equation.

The partial molar excess enthalpies of each species were derived from the overall expression of the excess molar enthalpy. The evolution of these partial enthalpies during the chemical reaction have a significant effect on the thermal behavior of the reaction mixture, particularly on the mixing heat of dosed acetic anhydride and on the reaction enthalpy.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: laurent.balland@univ-rouen.fr.

Notes

The authors declare no competing financial interest.

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