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Excess Enthalpy of the System Butyl Acetate + Butan-1-ol + Acetic Acid + Water at 313 K and Ambient Pressure

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Abstract

Experimental data of molar excess enthalpies h^E of the quaternary system (butyl acetate + butan-1-ol + acetic acid + water) are presented which have been determined at 313 K and ambient pressure using an isothermal flow calorimeter. The data include the six constituting binaries of the quaternary system. NRTL parameters fitted to the binary data are used to predict excess enthalpies for quaternary mixtures in sufficient agreement with experimental results. The temperature dependence of the activity coefficients of the four components in the quaternary mixture can be predicted using the NRTL-parameters. Calorimetric measurements have been carried out in absence of any catalyst in order to avoid chemical reaction.

INTRODUCTION

The studies reported in this paper are motivated by a problem arising in industrial chemistry. The chemical yield of the esterification reaction

$$CH_3COOH + C_4H_9OH \rightleftharpoons CH_3COOC_4H_9 + H_2O \qquad (1)$$

can be improved if the water produced by the reaction is removed continuously from the reacting mixture. For this purpose non-porous, hydrophilic membranes like the polyvinylalcohol(PVA)-membrane can be used. Separation of liquid mixtures by non-porous membranes is called pervaporation. Model calculations of the pervaporation process can be carried out using the solution-diffusion model [1, 2]. In order to perform such calculations the thermodynamic activities of the components in the liquid mixture have to be known. Activities a_i and activity coefficients γ_i can be determined by vapor pressure measurements. The dependence of the thermodynamic activities on temperature is given by the relation:

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$$\left(\frac{\partial \ln a_i}{\partial T}\right)_{p,n_i} = \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{p,n_i} = -\frac{1}{R\cdot T^2}\cdot\left(\frac{\partial H^E}{\partial n_i}\right)_{T,p,n_j\neq n_i} = -\frac{1}{R\cdot T^2}\cdot h_i^E \tag{2}$$

If the activities at a temperature T_0 are given, activities at any other temperature can be calculated, provided partial molar excess enthalpies $h^E{}_i$ are known, i. e. the derivatives of the excess enthalpy H^E with respect to the mole numbers n_i. In this paper, experimental h^E-measurements of the quaternary system and its constituting binaries are presented for 313 K and 0.1 MPa. The NRTL-model is used for the description of binary and the prediction of quaternary data. The dependence of activity coefficients on temperature is also predicted on the basis of the NRTL-model using eq. (2).

Principally, chemical reaction can occur in the mixtures during the measurements falsifying the calorimetric results. In order to estimate the reaction rate an approximately equimolar mixture of butan-1-ol and acetic acid was analyzed by means of gas liquid chromatography. Signals were observed indicating ≈0.05 and ≈0.15 weight-% butyl acetate 20 and 60 minutes after mixing the two components respectively. During the h^E measurements, the mixtures stay inside the calorimetric cell less than three minutes. This indicates that the reaction rate of the esterification is very slow in absence of a catalyst and therefore the influence of reaction enthalpies on the calorimetric measurements can be neglected.

EXPERIMENTAL

A modified TRONAC 1250 calorimeter has been used for the measurements. The apparatus is operated as an isothermal flow calorimeter. Details of the procedure have been described previously [3]. Two precision syringe pumps (ISCO LC-2600) have been used delivering continously the two liquids at constant volume fluxes into the calorimetric cell where the components are mixed and the heat of mixing per second is measured. Endothermic as well as exothermic processes can be studied. Using different ratios of volume fluxes a wide range of liquid compositions can be investigated experimentally. In order to obtain h^E of binary mixtures the two pumps are filled with the pure components. h^E of ternary and quaternary mixtures can easily be investigated if binary mixtures of known compositions and known binary h^E are delivered by the pumps instead of pure liquids. The molar excess enthalpy of quaternary mixtures is evaluated by the equation

$$h^E{}_{ABCD} = \frac{\dot{Q} + (\dot{n}_A + \dot{n}_B)\cdot h^E{}_{AB} + (\dot{n}_C + \dot{n}_D)\cdot h^E{}_{CD}}{\dot{n}_A + \dot{n}_B + \dot{n}_C + \dot{n}_D}\quad, \tag{3}$$

where $\dot{Q}$ is the measured heat effect per time. $\dot{n}_i$ are the molar fluxes of the components (i=A, B, C, D) and $h^E{}_{AB}$ and $h^E{}_{CD}$ are the molar excess enthalpies of the two binary mixtures (A+B) and (C+D) delivered by the pumps. The results obtained by this method can be considered as data of pseudo-binary systems and represented in $h^E(x)$-plots as functions of the sums (x_A+x_B) or (x_C+x_D).

The experimental error of the h^E data obtained is about ±2% of the maximum of the $h^E(x)$-curve considered.

The organic chemicals used for the measurements were supplied by MERCK and Riedel-de-Haën with purities better than 99.5%. They were used without further purification. Water was purified by reverse osmosis (System Millipore). The liquids were degassed before filling them into the pumps.

RESULTS

A. Binary mixtures

Binary results are given in Table 1. The systems (butan-1-ol + water) and (butyl acetate + water) show liquid/liquid separation at 313 K. The regions of immiscibility are $0.017 < x_{(\text{butan-1-ol})} < 0.474$ and $0.001 < x_{(\text{butyl acetate})} < \approx 0.85$ respectively [4]. Experimental data listed in Table 1 refer to total mole fractions in the two phase region and are indicated with an asterisk. Binary data can be represented using eq. (4).

$$h^E_{AB}\ [\mathrm{J \cdot mol^{-1}}] = x_A \cdot (1-x_A) \cdot \sum_{k=0}^{m-1} A_k \cdot (2 \cdot x_A - 1)^k / (1 + b \cdot (2 \cdot x_A - 1)) \, , \qquad (4)$$

where x_A is the mole fraction of component A in the binary mixture. The coefficients A_k and b for five of the six binaries are given in Table 2. For the (butyl acetate + water) system only two experimental data points are located outside the two-phase region. Therefore coefficients for this system cannot be evaluated according to eq. (4).

The binary experimental data are presented graphically in Figs. 1-3 and discussed together with the results of the NRTL-model calculations.

B. The quaternary mixture

The esterification reaction (1) yields the products butyl acetate and water in equimolar quantities. Therefore experimental h^E-data are of particular interest where stoichiometric mixtures are obtained, i. e. mixtures where the value of the ratios $x_{(\text{butyl acetate})}/x_{(\text{water})}$ and $x_{(\text{butan-1-ol})}/x_{(\text{acetic acid})}$ is one. The composition of a quaternary mixture can be represented by a point inside the space of an equilateral tetrahedron (see Fig. 4). The six edges of the tetrahedron correspond to the constituting binary systems, the four apexes to the pure components of the system. Quaternary compositions obtained by mixing two binary mixtures with different mixing ratios are located on straight

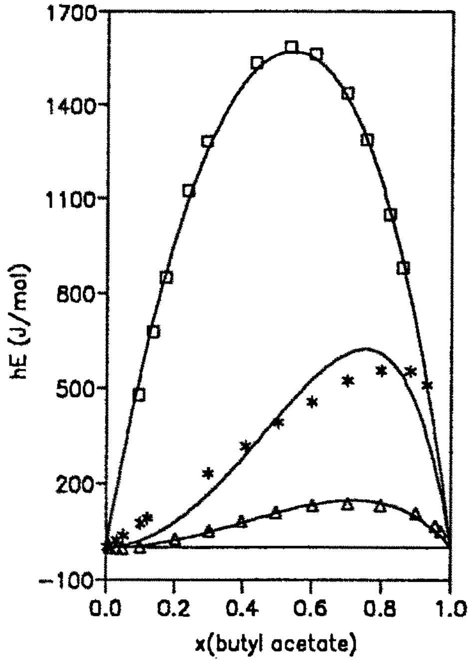

Fig. 1. Concentration dependence of the molar excess enthalpy at 313 K and ambient pressure of the binary systems. Experimental results: butyl acetate + butan-1-ol (□), butyl acetate + water (*), and butyl acetate + acetic acid (Δ); ——— : NRTL model calculations.

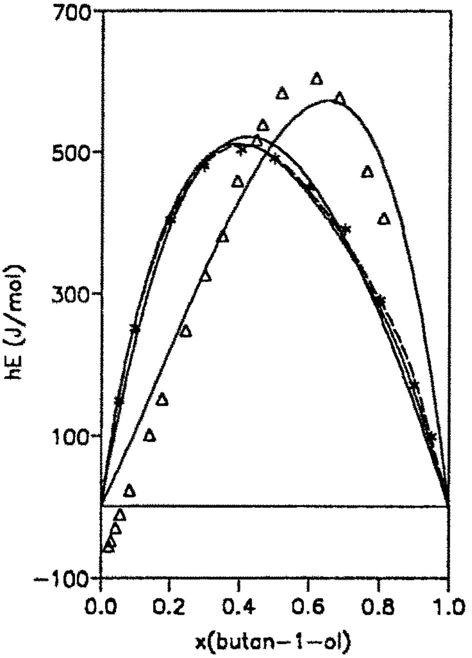

Fig. 2. Concentration dependence of the molar excess enthalpy at 313 K and ambient pressure of the binary systems. Experimental results: butan-1-ol + water (Δ) and butan-1-ol + acetic acid (*); ——— : NRTL model calculations. — — —, ... : experimental results given in /6/ for 298 K and 318 K.

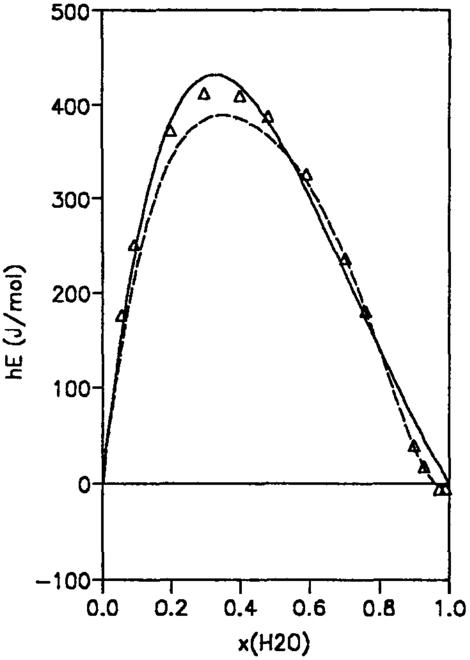

Fig. 3. Concentration dependence of the molar excess enthalpy at 313 K and ambient pressure of the binary systems. Experimental results: acetic acid + water (Δ); ——— : NRTL model calculations. — — — : experimental results given in /7/ for T=313 K.

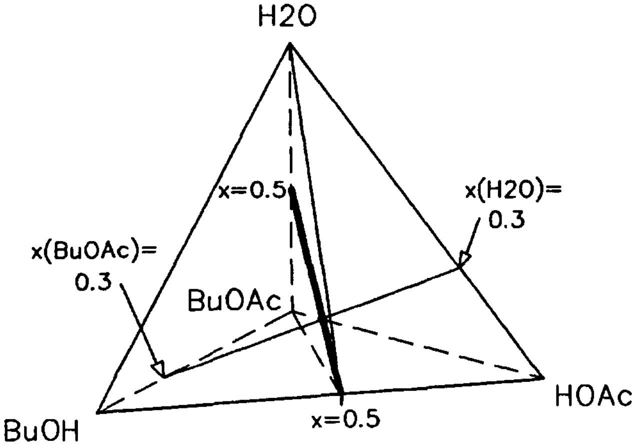

Fig. 4. The composition of a quaternary mixture can be represented by a point inside the space of an equilateral tetrahedron. The tetrahedron is shown for the butyl acetate (BuOAc) + butan -1-ol (BuOH) + acetic acid (HOAc) + water system. ——— : Stoichiometric compositions. Detailed explanation is given in the text.

Table 1. Excess molar enthalpy for the six constituting binaries of the (butyl acetate + butan-1-ol + acetic acid + water) system at 298 K and 0.1 MPa.

x	h^E	x	h^E	x	h^E
-	$J\cdot mol^{-1}$	-	$J\cdot mol^{-1}$	-	$J\cdot mol^{-1}$
		x ($CH_3COOC_4H_9$) + (1-x) (C_4H_9OH)			
0.072	351	0.293	1282	0.698	1437
0.094	476	0.435	1535	0.755	1288
0.135	675	0.536	1585	0.822	1048
0.172	848	0.606	1564	0.860	879
0.237	1126				
		x ($CH_3COOC_4H_9$) + (1-x) (CH_3COOH)			
0.010	-2.4	0.301	50	0.799	129
0.030	-3.5	0.398	81	0.901	103
0.047	-3.5	0.499	106	0.955	66
0.098	-0.6	0.603	129	0.971	49
0.201	24	0.705	134		
		x ($CH_3COOC_4CH_9$) + (1-x) (H_2O)			
0.002	-0.4	0.120*	89	0.703*	523
0.010*	5.3	0.299*	230	0.800	554
0.030*	20	0.409*	315	0.883	552
0.049*	34	0.504*	390	0.931	509
0.099*	73	0.600*	455		
		x (C_4H_9OH) + (1-x) (CH_3COOH)			
0.050	149	0.403	503	0.803	291
0.097	251	0.500	491	0.900	171
0.199	403	0.599	449	0.950	99
0.297	480	0.702	390		
		x (C_4H_9OH) + (1-x) (H_2O)			
0.021*	-56	0.178*	151	0.464*	539
0.028*	-48	0.245*	247	0.520	584
0.042*	-30	0.302*	326	0.619	605
0.055*	-11	0.351*	380	0.684	578
0.081*	22	0.394*	459	0.765	474
0.140*	102	0.448*	517	0.812	406
		x (CH_3COOH) + (1-x) (H_2O)			
0.010	-5.1	0.299	236	0.704	412
0.030	-6.1	0.408	325	0.802	373
0.073	17	0.519	388	0.907	251
0.100	39	0.601	410	0.945	176
0.240	180				

* Two-phase region

lines penetrating the tetrahedron. These lines connect the two points on opposite edges of the tetrahedron that correspond to the compositions of binary mixtures. Particularly stoichiometric mixtures are located on a line that connects the central points ($x=0.5$) of the two edges corresponding to the (butan-1-ol + acetic acid) and the (butyl acetate + water) binaries.

Due to the immiscibility of butyl acetate and water, stoichiometric mixtures cannot be prepared directly by mixing equimolar (buyl acetate + water) and (butan-1-ol + acetic acid) mixtures. Stoichiometric mixtures also can be prepared from binary mixtures containing butyl acetate and butan-1-ol and those containig acetic acid and water if the mole fraction of butyl acetate in the (butyl acetate + butan-1-ol) mixture is equal to the mole fraction of water in the (acetic acid + water) mixture (see Fig. 4). Most of the quaternary data reported here were obtained using this way of operation. In the upper part of Fig. 5 straight lines indicate compositions for which h^E data were obtained. If the lines drawn through the tetrahedron in Fig. 5 are projected on a common plane and h^E-data are plotted perpendicular to this plane the lower part of Fig. 5 is obtained. The h^E_{AB} and h^E_{CD}-values belonging to the binaries are connected by straight lines. The distances between these straight lines and the data points correspond to the heat effects measured by mixing the two binary mixtures with $x_{\text{(butyl acetate)}} = x_{\text{(water)}}$. It has to be pointed out that this heat effect changes its sign twice if it is regarded as a function of the water and butyl acetate mole fractions. The linear behaviour of the pseudobinary h^E-curve at $x_{\text{(butyl acetate)}} = x_{\text{(water)}} = 0.9$ covering a wide range of the pseudo-binary composition indicates a miscibility gap.

Table 2. Coefficients for eq. (4) for five of the six constituting binaries of the (butyl acetate + butan-1-ol + acetic acid + water) systems at 298 K and 0.1 MPa.1)

System	A_0	A_1	A_2	A_3	A_4	b	σ
			J/mol			-	J/mol
$CH_3COOC_4H_9$(A)+C_4H_9OH	6320	627	1594	694	-2237	-	7
$CH_3COOC_4H_9$(A)+CH_3COOH	433	99	-367	205	-	-0.834	2
C_4H_9OH(A)+CH_3COOH	1959	-568	675	-	-	-	4
C_4H_9OH(A)+H_2O 2)	2297	1508	-1522	-	-	-	7
CH_3COOH+H_2O	1512	845	249	1166	-	-	4

1) Coefficients for eq. (4) cannot be obtained for the (butyl acetate + water) system since the two phase region covers nearly the whole range of concentration.

2) Equation (4) does not fit data for $0.017 < x_{(BuOH)} < 0.474$ (two-phase region).

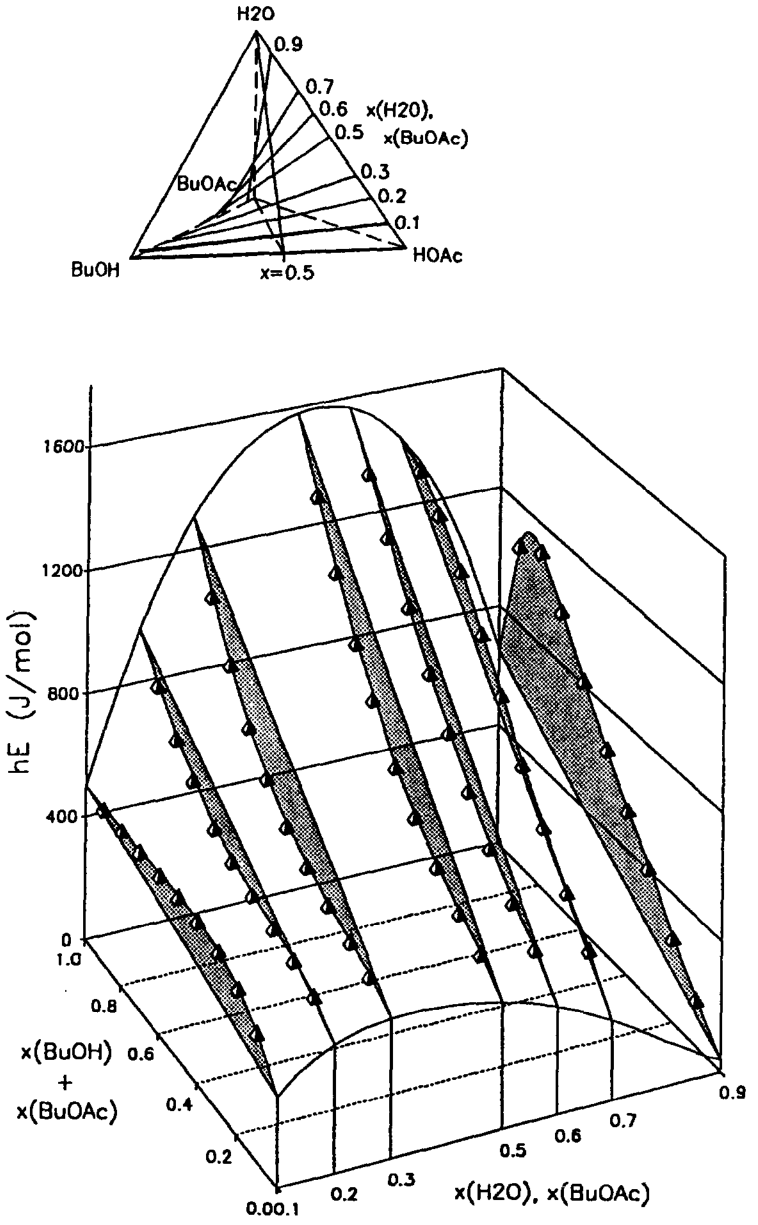

Fig. 5. Concentration dependence of the molar excess enthalpy of the quaternary system butyl acetate (BuOAc) + butan-1-ol (BuOH) + acetic acid (HOAc) + water at 313 K and ambient pressure. Detailed explanation is given in the text.

In addition to the results shown in Fig. 5 h^E-values have also been measured for three other pseudo-binary systems in order to obtain data for two quaternary compositions defined as standards. The standard compositions are:

Standard I :

$0.340(CH_3COOC_4H_9) + 0.340(H_2O) + 0.164(C_4H_9OH) + 0.156(CH_3COOH)$

Standard II :

$0.753(CH_3COOC_4H_9) + 0.083(H_2O) + 0.081(C_4H_9OH) + 0.083(CH_3COOH)$

These standard compositions are of particular interest in the technical application of pervaporation for extracting water from the reactive mixture according to eq. (1). There are principally three ways to prepare a certain quaternary mixture by mixing binary mixtures. Only three from six possible combinations of binary mixtures could be used to prepare the standard mixtures due to the partial immiscibility of (butan-1-ol + water) and (butyl acetate + water). The standard mixture compositions lie on the lines inside the tetrahedron shown in the upper parts of Figs. 6 and 7 and are marked by points. h^E-data are obtained along these lines and the results are plotted in the lower parts of Figs. 6 and 7 as function of the sum of (butyl acetate + butan-1-ol) mole fraction and (butyl acetate + acetic acid) mole fraction respectively. Regions of immiscibility are indicated at the corresponding edges of the tetrahedrons.

The h^E-value for standard II was measured as constituent of two pseudo-binary $h^E(x)$-curves, i. e. the two lines through the tetrahedron corresponding to these two pseudo-binaries intersect at the point indicating the composition of standard II. The $h^E(x)$-curves belonging to the two pseudobinaries are plottted in Fig. 6 (lower curve) and Fig. 7 respectively. The dashed line through the terahedron in Fig. 7 corresponds to the lower curve of Fig. 6 and is shown to indicate the intersection of the lines at the standard II composition. The h^E-data point corresponding to the lower curve in Fig. 6 is also shown in the lower part of Fig. 7 as a test for consistency of the measurements.

All experimental data obtained for quaternary compositions are listed in Table 3. Only the pseudo-binary mole fraction x^p is given in the table. In order to calculate the quaternary mole fractions of the four components, x^p or $(1-x^p)$ respectively has to be multiplied with the corresponding binary mole fractions given in cranked paranthesis in the headings of Table 3. For example the quaternary mole fraction of butyl acetate of the first (x, h^E) pair given in Table 3 ($x=0.099$, $h^E=383$ J·mol^{-1}) is $0.099 \cdot 0.100 = 0.010$.

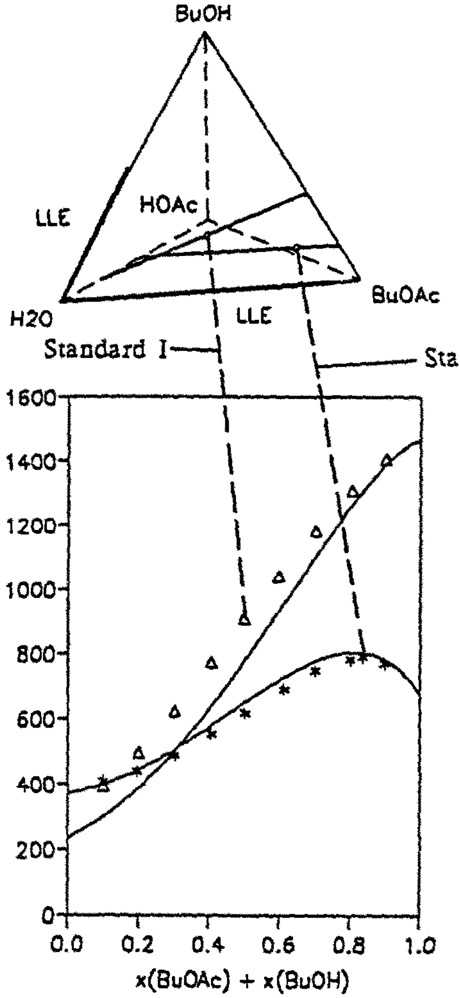

Fig. 6. Concentration dependence of the molar excess enthalpy at 313 K and ambient pressure of two pseudobinaries selected in order to obtain data for standard I (Δ) and standard II (*); —— : NRTL model predictions. Detailed explanation is given in the text.

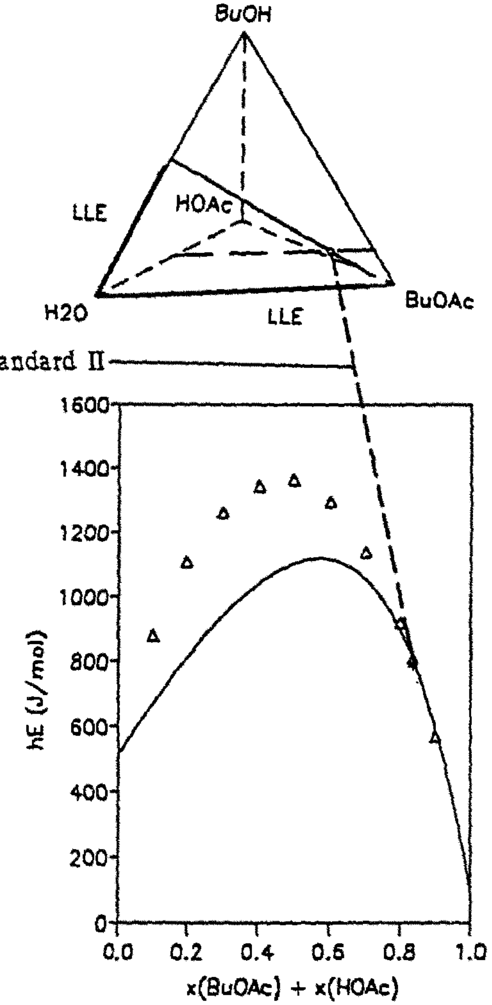

Fig. 7. Concentration dependence of the molar excess enthalpy at 313 K and ambient pressure of a pseudobinary selected in order to obtain data for standard II (Δ). The single data point indicated by (*) was obtained as a constituent of another pseudobinary $h^E(x)$-curve (indicated by (*) in Fig. 6) and is plotted to test the consistency of the experimental data; ——— : NRTL model predictions. Detailed explanation is given in the text.

Table 3. Molar excess enthalpy h^E of the (butyl acetate + butan-1-ol + acetic acid + water) systems at 298 K and 0.1 MPa.

x^p –	h^E $J\cdot mol^{-1}$	x^p –	h^E $J\cdot mol^{-1}$	x^p –	h^E $J\cdot mol^{-1}$
$x^p\{0.100\,(CH_3COOC_4H_9) + 0.900\,(C_4H_9OH)\}$ + $(1-x^p)\{0.900\,(CH_3COOH) + 0.100\,(H_2O)\}$					
0.099	383	0.399	498	0.700	499
0.191	447	0.501	501	0.798	499
0.294	484	0.596	500	0.899	499
$x^p\{0.200\,(CH_3COOC_4H_9) + 0.800\,(C_4H_9OH)\}$ + $(1-x^p)\{0.800\,(CH_3COOH) + 0.200\,(H_2O)\}$					
0.100	451	0.401	538	0.710	685
0.195	488	0.504	569	0.799	758
0.296	512	0.597	611	0.900	860
$x^p\{0.300\,(CH_3COOC_4H_9) + 0.700\,(C_4H_9OH)\}$ + $(1-x^p)\{0.700\,(CH_3COOH) + 0.300\,(H_2O)\}$					
0.100	469	0.403	584	0.698	827
0.192	505	0.504	643	0.800	959
0.299	540	0.606	725	0.899	1115
$x^p\{0.500\,(CH_3COOC_4H_9) + 0.500\,(C_4H_9OH)\}$ + $(1-x^p)\{0.500\,(CH_3COOH) + 0.500\,(H_2O)\}$					
0.100	455	0.406	662	0.698	1022
0.196	509	0.500	758	0.800	1188
0.302	578	0.612	896	0.900	1373
$x^p\{0.600\,(CH_3COOC_4H_9) + 0.400\,(C_4H_9OH)\}$ + $(1-x^p)\{0.400\,(CH_3COOH) + 0.600\,(H_2O)\}$					
0.100	427	0.405	707	0.696	1105
0.199	500	0.500	831	0.803	1266
0.305	595	0.593	958	0.901	1414
$x^p\{0.700\,(CH_3COOC_4H_9) + 0.300\,(C_4H_9OH)\}$ + $+ (1-x^p)\{0.300\,(CH_3COOH) + 0.700\,(H_2O)\}$					
0.100	385	0.403	754	0.698	1185
0.200	491	0.504	908	0.804	1304
0.306	624	0.594	1047	0.901	1390

Table 3. Continued

x^P -	h^E $J\cdot mol^{-1}$	x^P -	h^E $J\cdot mol^{-1}$	x^P -	h^E $J\cdot mol^{-1}$
$x^P\{0.900\ (CH_3COOC_4H_9) + 0.100\ (C_4H_9OH)\} + (1-x^P)\{0.100\ (CH_3COOH) + 0.900\ (H_2O)\}$					
0.103	148	0.398*	534	0.703*	977
0.202*	266	0.491*	668	0.799	1116
0.309*	412	0.597*	818	0.903	1068
$x^P\{0.675\ (CH_3COOC_4H_9) + 0.325\ (C_4H_9OH)\} + + (1-x^P)\{0.315\ (CH_3COOH) + 0.685\ (H_2O)\}$					
0.101	394	0.407	776	0.701	1184
0.200	496	0.501**	909	0.805	1308
0.302	622	0.598	1041	0.902	1406
$x^P\{0.903\ (CH_3COOC_4H_9) + 0.097\ (C_4H_9OH)\} + (1-x^P)\{0.500\ (CH_3COOH) + 0.500\ (H_2O)\}$					
0.101	408	0.503	617	0.801	783
0.197	438	0.612	691	0.836***	790
0.302	487	0.701	748	0.899	770
0.408	552				
$x^P\{0.494\ (C_4H_9OH) + 0.506\ (H_2O)\} + (1-x^P)\{0.901\ (CH_3COOC_4H_9) + 0.099\ (CH_3COOH)\}$					
0.097	567	0.397	1295	0.700	1264
0.164***	808	0.500	1365	0.802	1109
0.199	918	0.597	1346	0.900	879
0.290	1138				

* Two-phase region.

** Composition corresponds approximately to standard I.

*** Composition corresponds approximately to standard II.

NRTL-MODEL-CALCULATIONS

From the equations for the molar excess gibbs energy g^E and the activity coefficients γ_i given in [5] expressions for the molar excess enthalpy h^E and the partial molar excess enthalpies $h^E{}_i$ were derived:

molar excess enthalpy:

$$h^E/R\cdot T \;=\; -\sum_{i=1}^{m} x_i\cdot\eta_i \qquad (5)$$

x_i is the mole fraction of component i. η_i is given by:

$$\eta_i \;=\; \frac{\sum_{k=1}^{m} x_k\cdot\tau_{ki}\cdot G_{ki}\cdot\left\{\alpha\cdot\left[\tau_{ki}-\frac{\sum_{n=1}^{m} x_n\cdot\tau_{ni}\cdot G_{ni}}{\sum_{l=1}^{m} x_l\cdot G_{li}}\right]-1\right\}}{\sum_{l=1}^{m} x_l\cdot G_{li}}$$

with

$$G_{ji} \;=\; \exp\left\{-\alpha\cdot\tau_{ji}\right\} \quad \text{and} \quad \tau_{ji} \;=\; \frac{g_{ji}-g_{ii}}{R\cdot T} \qquad (\, j = k,\, n,\, l)$$

partial molar excess enthalpy:

$$h_i^E/R\cdot T \;= \qquad (6)$$

$$-\eta_i \;-\; \sum_{r=1}^{m} \frac{x_r\cdot G_{ir}}{\sum_{l=1}^{m} x_l\cdot G_{lr}}\cdot\left\{\alpha\cdot\left[\tau_{ir}-\frac{\sum_{n=1}^{m} x_n\cdot\tau_{nr}\cdot G_{nr}}{\sum_{l=1}^{m} x_l\cdot G_{lr}}\right]^2-\tau_{ir}-\eta_r\right\}$$

m is the number of components in the mixture. For a binary system two parameters τ_{ji} and τ_{ij} have to be adjusted to experimental h^E data (i, j = 1, 2, 3, 4). The third parameter α can also be adjusted. Good description of binary and multinary data can be attained with a single value for α. For the calculations reported here α was chosen to be 0.2 for all six binary systems and also for the quaternary system. values of $(g_{ji} - g_{ii})$ obtained by fitting eq. (5) to the binary results are listed in Table 4.

Table 4. Parameters $(g_{ji} - g_{ii})$ in $J\cdot mol^{-1}$ to be used in eq. (5) for the description of h^E-data of the (butyl acetate(1) + butan-1-ol(2) + acetic acid(3) + water(4)) system at 313 K and 0.1 MPa (α=0.2).

	i = 1	i = 2	i = 3	i = 4
j = 1	-	6319	4036	8419
j = 2	4243	-	-387	5296
j = 3	-2058	3223	-	5163
j = 4	-1539	-1052	-1509	-

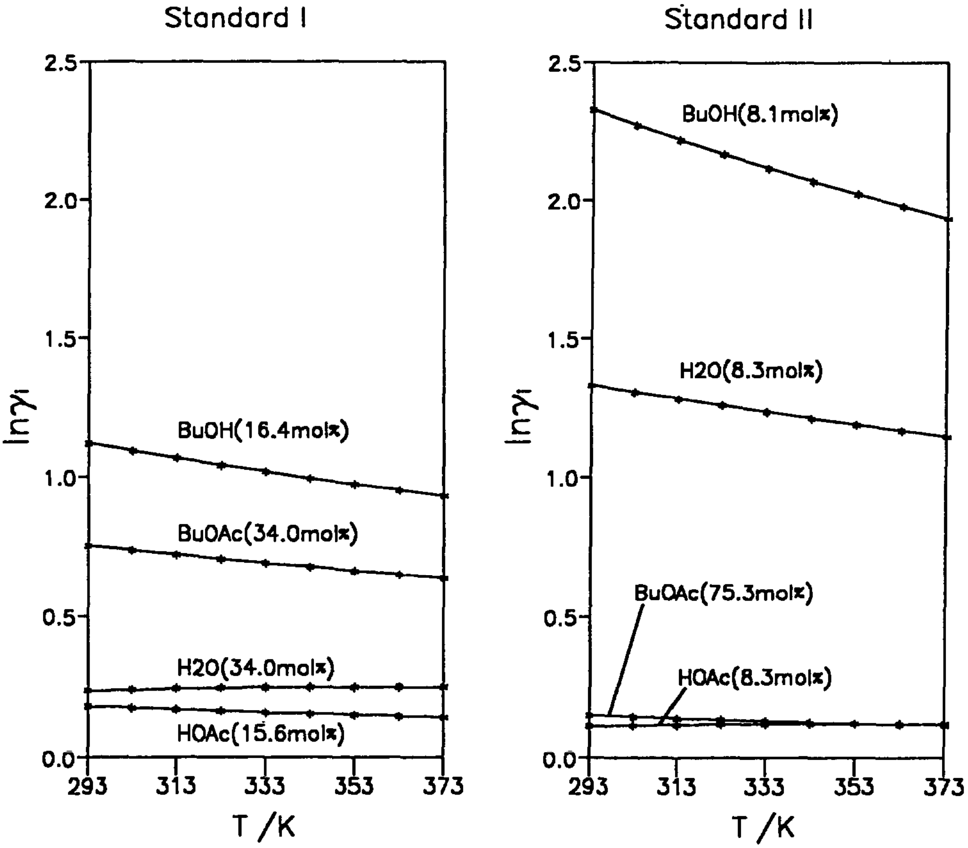

Fig. 8. Dependence on temperature of activity coefficients in standard I and standard II predicted using the NRTL model. The scale on the ordinate is arbitrary. Detailed explanation is given in the text.

Results of the calculations are compared to binary experimental data in Figs. 1-3. The calculated curves describe the experimental results with exception of the (butyl acetate + water) system in Fig. 1 which exhibits a miscibility gap between $0.001 < x_{(\text{butyl acetate})} < \approx 0.85$. The same holds for the partially immiscible (butan-1-ol + water) system shown in Fig. 2. The dashed and dotted lines in Fig. 3 represent experimental data for the (butan-1-ol + acetic acid) system at 298 K and 318 K measured by Haase et al. [6]. The dependence of h^E on temperature is very small for this system, i. e. the molar excess heat capacity c_p^E is small. The data obtained in this work confirm this result. The dashed line in Fig. 3 represents experimental h^E-data for (acetic acid + water) at 313 K given in [7]. The agreement with our data is acceptable even though systematic deviations are observed at mole fractions of H_2O lower than 0.6.

h^E-curves predicted by eq. (5) are plotted in Figs. 6 and 7. The description of the experimental data is satisfying with respect to the fact that the quaternary data are predicted from parameters which were obtained by adjustment to binary data only.

Using the formalism of the NRTL-model predictive calculations of the temperature dependence of the activity coefficients can be carried out. Activity coefficients of the two standards are obtained by integrating eq. (2) using eq. (6) with $(g_{ji} - g_{ii})$-values taken from Table 4:

$$\ln\gamma_i(T) = \text{Constant} + \qquad (7)$$

$$\frac{\sum_{j=1}^{m} x_j\cdot\tau_{ji}\cdot G_{ji}}{\sum_{l=1}^{m} x_l\cdot G_{li}} + \sum_{j=1}^{m}\frac{x_j\cdot G_{ij}}{\sum_{l=1}^{m} x_l\cdot G_{li}}\cdot\left[\tau_{ij} - \frac{\sum_{n=1}^{m} x_n\cdot\tau_{nj}\cdot G_{nj}}{\sum_{l=1}^{m} x_l\cdot G_{li}}\right]$$

Symbols in eq. (7) are identical with those appearing in eqs. (5)-(6). The constant in eq. (7) is fixed if absolute values of $\ln\gamma_i$ at a given temperature are known. Calculated activity coefficients are shown in Fig. 8. Due to the lack of experimental data of activity coefficients absolute values on the scale of the ordinate in Fig. 8 have been arbitrarily chosen by the condition that Constant=0 in eq. (7). It follows from these results that the temperature dependence of activity coefficients obtained from VLE-data at a given temperature can be evaluated from calorimetric measurements according to the general thermodynamic relation given in eq. (2).

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