

# Excess molar enthalpies for ternary mixtures of (methanol or ethanol + water + tributyl phosphate) at $T = 298.15$ K

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**Abstract** Excess molar enthalpies for two ternary mixtures of  $\{x_1$  tributylphosphate (TBP) +  $x_2$  water +  $x_3$  methanol/ethanol $\}$  were measured at  $T = 298.15$  K and atmospheric pressure using a TAM Air isothermal calorimeter, by mixing methanol or ethanol with binary mixtures of (water + TBP). Excess enthalpies for initial binary mixtures of (water + TBP) were also measured under the same conditions, which showed phase separation at low molar fraction of TBP. Experimental results of the ternary mixtures were expressed with constant excess molar enthalpy contours on Roozeboom diagrams.

**Keywords** Excess enthalpies · TBP · Water · Ternary systems · Roozeboom diagrams

## Introduction

Since tributylphosphate (TBP) plays an important role in the extraction of rare earth and heavy metals [1–7], and the alcohols have the significant effect in extractive process [8–12], it is very interesting for us to investigate the thermodynamic properties of related systems, which is important for understanding the mechanism of extraction, synergistic extraction, and the co-solvent effects in extraction process. Excess molar enthalpies at 298.15 K for binary mixtures of (TBP + methanol/ethanol) have been reported previously [13] to understand the molecular interactions existing in liquid mixtures. As a part of the systematic study, excess molar enthalpies for ternary

mixtures of (TBP + water + methanol/ethanol) have been measured at 298.15 K in this article. Binary excess molar enthalpies for (TBP + water) at 298.15 K, which making up the two ternary systems of our present interest also have been measured.

## Experiments and methods

### Materials and apparatus

Materials of TBP, methanol, ethanol were purchased from Aldrich and used after drying over 0.4 nm molecular sieves, treated with same way as the earlier investigations [13, 14]. Care was taken to protect the samples from contamination by atmospheric moisture. Water contents of TBP, methanol, ethanol were 0.0311, 0.0723, and 0.1002 mol kg<sup>-1</sup>, respectively, which were determined by a Karl–Fischer method (Kyoto Electronics, E-511). Water was double distilled. All materials in experiments were quantified by weighing.

The measurements of excess enthalpies were performed using a TAM Air isothermal calorimeter (Thermometric 3114/3236, Sweden) at  $(298.15 \pm 0.02)$  K and ambient. The accuracy of the calorimeter was checked as same way as described previously [13, 14]. The errors in the excess molar enthalpy were estimated to be less than  $\pm 0.5\%$ .

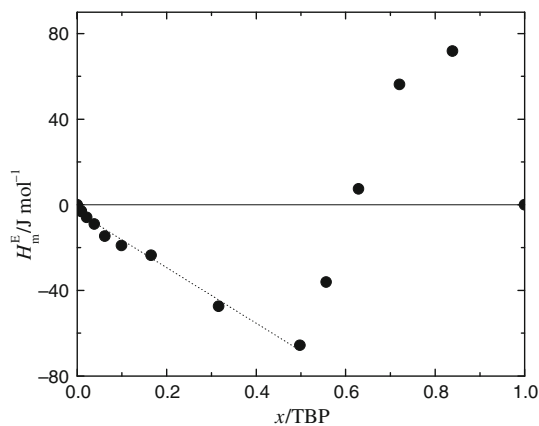
### Methods

Excess enthalpies for binary mixtures of  $\{x_1'$  TBP +  $(1 - x_1')$  water $\}$  were measured firstly, where  $x_1'$  was the molar fraction of TBP in this initial binary mixture. A ternary mixture can be considered as a pseudobinary mixture formed by mixing of methanol or ethanol with the initial

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**Table 1** Excess enthalpies  $H_{m,12}^E$  for binary mixtures of  $\{x_1'$  TBP +  $(1-x_1')$  water} at 298.15 K

$x$	$H_{m,12}^E / \text{J mol}^{-1}$	$x$	$H_{m,12}^E / \text{J mol}^{-1}$	$x$	$H_{m,12}^E / \text{J mol}^{-1}$
0.1610	71.83	0.6840	-47.42	0.9785	-5.881
0.2799	56.22	0.8348	-23.60	0.9907	-3.170
0.3711	7.460	0.9008	-19.07	0.9907	-2.953
0.4437	-36.11	0.9382	-14.64	0.9992	-0.8200
0.5024	-65.58	0.9619	-8.970		

**Fig. 1** Excess enthalpies  $H_{m,12}^E$  for binary mixtures of  $\{x_1'$  TBP +  $(1-x_1')$  water} at 298.15 K: filled circle, Experimental results; dotted line, linear fit of excess enthalpies

binary mixture includes TBP and water. Three experimental runs were performed by mixing methanol or ethanol with the initial binary mixtures  $\{x_1'$  TBP +  $(1-x_1')$  water} whose three specified compositions were  $x' = 0.8390, 0.6777, 0.5736$  in mole fraction of TBP. The excess molar enthalpies  $H_{m,123}^E$  of ternary mixture [15] can be expressed as:

$$H_{m,123}^E = H_{m,12+3}^E + (1-x_3)H_{m,12}^E \quad (1)$$

where  $H_{m,12+3}^E$  is the measured excess molar enthalpy for the pseudobinary mixtures,  $H_{m,12}^E$  is the excess molar enthalpies of the initial binary mixtures  $\{x_1'$  TBP +  $(1-x_1')$  water}, and  $x_3$  is the mole fraction of methanol or ethanol.

## Results and discussion

The experimental results for binary mixtures of  $\{x_1'$  TBP +  $(1-x_1')$  water} were given in Table 1 and shown in Fig. 1. Since the solubility of water in TBP and TBP in water was 1% and 7%, respectively [16], the appearance of phase separation must be found at the molar fraction in range of  $0.0001 < x < 0.4731$  theoretically. According to the experimental results, excess enthalpy  $H_{m,12}^E$  of the binary mixtures was dependent on composition, and in most instances, was linear with respect to molar fraction in range around 0–0.50 as shown in Fig. 1. Experimental molar fraction with linear correlation agree well with that of solubility in rang of  $0.0001 < x < 0.4731$ .

Excess molar enthalpies  $H_{m,ij}^E (i < j)$  for other four of the constituent binary systems of this study have been reported: {TBP(1) + methanol(3)} [13], {water(2) + methanol(3)} [17], {TBP(1) + ethanol(3)} [13], {water(2) + ethanol(3)} [18]. Five sets of the constituent-binary results have been correlated with the following polynomial:

$$H_{m,ij}^E = x_i(1-x_j) \sum_{k=1}^p A_n \cdot (1-2x_i)^{k-1} \quad (2)$$

where  $x$  is the mole fraction of the TBP,  $n$  is the number of parameters. The standard deviations  $S_f = [\sum \{H_m^E(\text{expt.}) - H_m^E(\text{calc.})\}^2 / (k-n)]^{0.5}$ , where  $k$  is the number of experimental data points, for methanol  $k = 15$  and ethanol

**Table 2** Coefficients  $A_{1-n}$  in Eq. 2 for the molar excess enthalpies and standard deviations  $S_f$  for the binary mixtures

Component		$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$S_f / \text{J mol}^{-1}$
$i$	$j$						
TBP <sup>a</sup>	CH <sub>3</sub> OH	-1160.6	-396.5	695.5	-403.9	-869.1	6.80
TBP <sup>a</sup>	C <sub>2</sub> H <sub>5</sub> OH	336.97	-840.45	618.31	635.30	-1027	5.00
CH <sub>3</sub> OH <sup>b</sup>	H <sub>2</sub> O	-3213.2	1528.60	-2254.4	821.53		0.18
C <sub>2</sub> H <sub>5</sub> OH <sup>c</sup>	H <sub>2</sub> O	-1625.0	1797.30	-3183.4	3054.1	-2263.6	10
TBP <sup>d</sup>	H <sub>2</sub> O	-237.02	-604.26	1702.30	231.97	-1637.0	3.5

<sup>a</sup> Peng et al. [15]<sup>b</sup> Feng [16]<sup>c</sup> Simonsen et al. [17]<sup>d</sup> This study

**Table 3** Experimental molar excess enthalpies  $H_{m,12+3}^E$  and  $H_{m,123}^E$  at  $J\ mol^{-1}$  for  $\{x_1TBP + x_2H_2O + x_3CH_3OH\}^a$  at  $T = 298.15\ K$

$x_1$	$x_2$	$H_{m,12+3}^E$	$H_{m,123}^E$	$x_1$	$x_2$	$H_{m,12+3}^E$	$H_{m,123}^E$	$x_1$	$x_2$	$H_{m,12+3}^E$	$H_{m,123}^E$
$x_1' = 0.5736, H_{m,12}^E = -70.71\ J\ mol^{-1}$											
0.0195	0.0145	-64.0	-66.4	0.1670	0.1242	-349.4	-361.0	0.3629	0.2700	-389.8	-434.6
0.0435	0.0323	-138.9	-144.3	0.2090	0.1558	-382.1	-407.9	0.4128	0.3072	-346.6	-397.5
0.0738	0.0549	-215.5	-224.6	0.2438	0.1812	-410.6	-440.7	0.4725	0.3516	-256.0	-314.3
0.1135	0.0844	-271.7	-285.7	0.2962	0.2204	-434.9	-471.4	0.5193	0.3864	-168.7	-232.8
$x_1' = 0.6777, H_{m,12}^E = -55.12\ J\ mol^{-1}$											
0.0199	0.0095	-44.8	-46.4	0.1771	0.0842	-298.5	-312.9	0.4451	0.2116	-383.9	-420.1
0.0448	0.0213	-106.3	-109.9	0.2157	0.1026	-332.3	-349.9	0.5157	0.245	-320.3	-362.2
0.0765	0.0364	-162.1	-168.3	0.2746	0.1306	-404.2	-426.5	0.5726	0.2723	-253.3	-299.9
0.1186	0.0564	-197.5	-207.1	0.3388	0.1611	-435.3	-462.9	0.6400	0.3041	-125.3	-177.3
0.1288	0.0612	-210.3	-220.8	0.4050	0.1926	-411.2	-444.2				
$x_1' = 0.8390, H_{m,12}^E = -18.61\ J\ mol^{-1}$											
0.0461	0.0089	-64.9	-65.9	0.2885	0.0554	-302.6	-309.0	0.6072	0.1165	-341.5	-355.0
0.1247	0.0239	-121.7	-124.5	0.3615	0.0694	-347.4	-355.4	0.6859	0.1316	-270.6	-285.8
0.1892	0.0363	-195.7	-199.9	0.4614	0.0886	-379.4	-389.6	0.7316	0.1404	-213.9	-230.1
0.2328	0.0447	-248.6	-253.8	0.5125	0.0984	-378.6	-381.0	0.7823	0.1501	-144.5	-161.9

<sup>a</sup> Ternary mixtures were prepared by mixing dried methanol with  $\{x_1' TBP + (1-x_1')$  water}

**Table 4** Experimental molar excess enthalpies  $H_{m,12+3}^E$  and  $H_{m,123}^E$  at  $J\ mol^{-1}$  for  $\{x_1TBP + x_2H_2O + x_3C_2H_5OH\}^a$  at  $T = 298.15\ K$

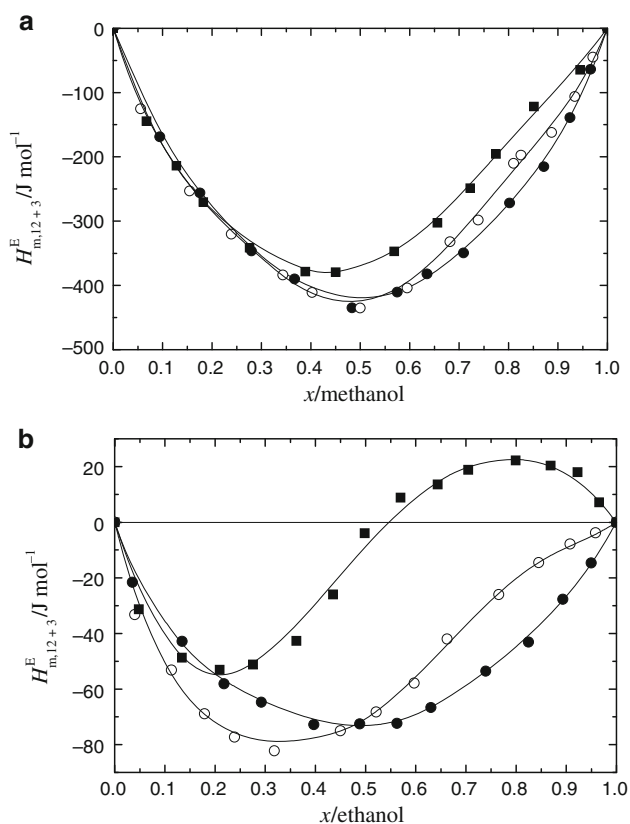
$x_1$	$x_2$	$H_{m,12+3}^E$	$H_{m,123}^E$	$x_1$	$x_2$	$H_{m,12+3}^E$	$H_{m,123}^E$	$x_1$	$x_2$	$H_{m,12+3}^E$	$H_{m,123}^E$
$x_1' = 0.5736, H_{m,12}^E = -70.71\ J\ mol^{-1}$											
0.0288	0.0214	-14.7	-18.3	0.2124	0.1576	-66.7	-92.9	0.4062	0.3013	-64.7	-114.7
0.0611	0.0455	-27.7	-35.2	0.2511	0.1863	-72.4	-103.3	0.4491	0.3332	-58.1	-113.4
0.1007	0.0748	-43.1	-55.5	0.2935	0.2178	-72.5	-108.7	0.4969	0.3686	-42.9	-104.1
0.1494	0.1109	-53.6	-72.0	0.3460	0.2570	-72.8	-115.4	0.5537	0.4111	-21.6	-89.83
$x_1' = 0.6777, H_{m,12}^E = -55.12\ J\ mol^{-1}$											
0.0283	0.0135	-3.8	-6.1	0.2730	0.1298	-57.9	-80.1	0.5564	0.2646	-68.9	-114.2
0.0627	0.0298	-7.8	-12.9	0.3244	0.1542	-68.3	-94.7	0.6012	0.2858	-53.2	-102.1
0.1049	0.0499	-14.5	-23.0	0.3729	0.1773	-75.0	-105.3	0.6508	0.3094	-33.2	-86.1
0.1588	0.0755	-26.0	-38.9	0.4619	0.2196	-82.2	-119.8				
0.2288	0.1088	-42.0	-60.6	0.5160	0.2453	-77.3	-119.3				
$x_1' = 0.8390, H_{m,12}^E = -18.61\ J\ mol^{-1}$											
0.0290	0.0056	7.1	6.5	0.2990	0.0573	13.6	7.0	0.6075	0.1166	-51.2	-64.7
0.0649	0.0125	18.0	16.6	0.3608	0.0692	8.8	0.8	0.6633	0.1273	-53.1	-67.8
0.1098	0.0211	20.4	18.0	0.4208	0.0808	-4.0	-13.3	0.7265	0.1394	-48.7	-64.8
0.1686	0.0324	22.2	18.5	0.4737	0.0909	-26.0	-36.5	0.7988	0.1533	-31.3	-49.0
0.2477	0.0475	18.8	13.3	0.5353	0.1027	-42.7	-54.6				

<sup>a</sup> Ternary mixtures were prepared by mixing dried ethanol with  $\{x_1' TBP + (1-x_1')$  water}

$k = 22$ . The coefficients  $A_1-A_n$  are listed for all the binary systems in Table 2 along with the standard deviation  $S_f$

The experimental results  $H_{m,12+3}^E$  for the pseudobinary mixtures of  $\{(x_1TBP + x_2water) + x_3methanol\}$  and  $\{(x_1TBP + x_2water) + x_3 ethanol\}$  systems at 298.15 K

are listed in Tables 3 and 4, respectively, and together with the ternary experimental  $H_{m,123}^E$  calculated from Eq. 1. The results for  $H_{m,12+3}^E$  in Tables 3 and 4 are plotted in Fig. 2a and b, respectively. Mixing processes for pseudobinary systems of  $\{(x_1TBP + x_2water) + x_3methanol\}$  showed



**Fig. 2** Excess enthalpies  $H_{m,12+3}^E$  of pseudobinary mixtures for: **a**  $\{(x_1' \text{ TBP} + (1-x_1' \text{ water}) + \text{methanol})\}$ ; **b**  $\{(x_1' \text{ TBP} + (1-x_1' \text{ water}) + x_3 \text{ ethanol})\}$  systems at 298.15 K, where: (filled circle)  $x_1' = 0.5736$ ; (open circle)  $x_1' = 0.6777$ ; (filled square)  $x_1' = 0.8390$

exothermic peaks for all three runs of experiments at  $x' = 0.5736, 0.6777$ , and  $0.8390$ , the maximum values of  $H_{m,12+3}^E$  occur near  $x_{(\text{methanol})} = 0.45\text{--}0.55$ . While mixtures of  $\{(x_1 \text{ TBP} + x_2 \text{ water}) + x_3 \text{ ethanol}\}$  showed exothermic effect at the whole molar fraction of ethanol when  $x' = 0.5736$  and  $0.6777$ , and the measured excess enthalpies  $H_{m,12+3}^E$  at  $x' = 0.8390$  shown negative value at lower molar fraction but positive at higher molar fraction.

The measured values of the ternary mixtures were correlated using the following equation [19]:

$$H_{m,12+3}^E = \left( \frac{x_1}{1-x_3} \right) H_{m,13}^E + \left( \frac{x_2}{1-x_3} \right) H_{m,23}^E + H_T^E \quad (3)$$

where  $H_{m,13}^E, H_{m,23}^E$  are the excess molar enthalpies for the binary systems (TBP + methanol/ethanol) and (water + methanol/ethanol), respectively, and were fit to Eq. 2 using the coefficients in Table 1. The ternary contribution term  $H_T^E$  is expressed by the following equation:

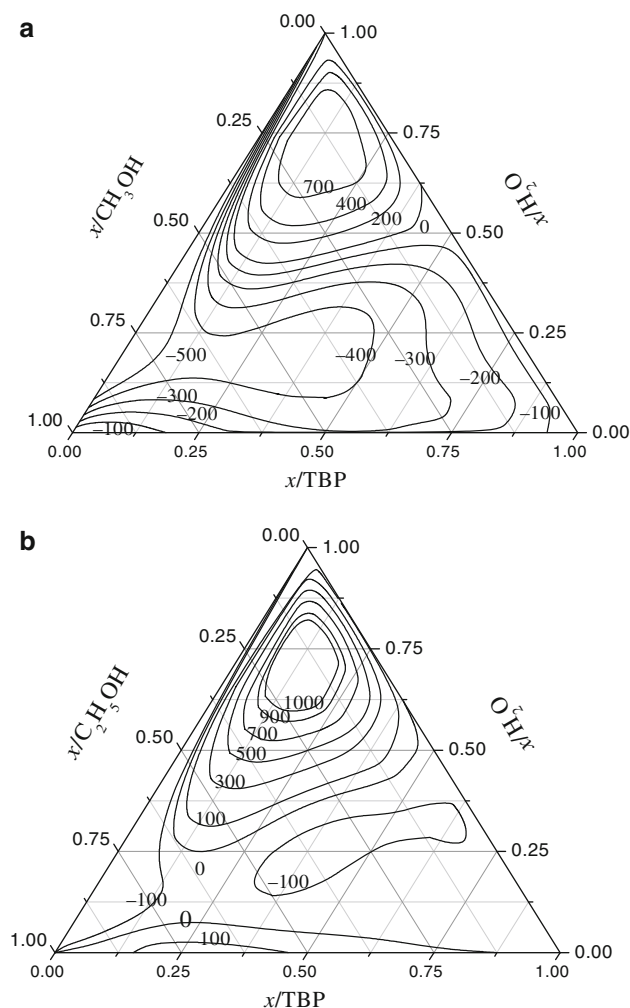
$$H_T^E = x_1 x_2 x_3 \cdot RT \cdot (C_0 + C_1 x_1 + C_2 x_2 + C_3 x_1 x_2 + C_4 x_1^2 + C_5 x_2^2 + C_6 x_1^3 + C_7 x_2^3 + C_8 x_1^2 x_2) \quad (4)$$

which is similar to the form used by Nagata et al. [20]. The values of coefficients  $C_j$  were adjusted by least-squares analyses, and are given in Table 5 along with the absolute arithmetic mean deviations:  $\langle |\delta H_m^E| \rangle = \sum_{i=1}^k |H_{\text{expt.}}^E - H_{\text{cal.}}^E| / k$  and the standard deviations  $S_f$ .

Excess enthalpies  $H_{m,123}^E$  for ternaries of  $(x_1 \text{ TBP} + x_2 \text{ water} + x_3 \text{ methanol})$  and  $(x_1 \text{ TBP} + x_2 \text{ water} + x_3 \text{ ethanol})$  are calculated from Eqs. 1–4, constant contours are illustrated on the Roozeboom diagram in Fig. 3a and b, respectively. The two ternaries showed significant positive, zero, and negative excess enthalpies. Similarly the maximum positive excess enthalpies for both ternaries of  $(x_1 \text{ TBP} + x_2 \text{ water} + x_3 \text{ methanol})$  and  $(x_1 \text{ TBP} + x_2 \text{ water} + x_3 \text{ ethanol})$  are exist in the mixing of low methanol/ethanol containing and high composition of water and TBP, especially in the area of  $x' \geq 0.5736$ , in which TBP and water are mutually soluble. With the increasing of methanol/ethanol, excess enthalpies for ternary systems changed quickly from positive to negative, the significant intermolecular interaction was deeply modified. Another maximum negative excess enthalpy value was found for mixtures of  $(x_1 \text{ TBP} + x_2 \text{ water} + x_3 \text{ ethanol})$ . Few of references were found for co-exists of maximum positive and negative excess enthalpies

**Table 5** Parameters  $C_j$  of Eq. 4, the absolute arithmetic-mean deviations  $\langle |\delta H_m^E| \rangle$  and the standard deviations  $S_f$  in  $\text{J mol}^{-1}$

$(x_1 \text{ TBP} + x_2 \text{ water} + x_3 \text{ methanol})$				$(x_1 \text{ TBP} + x_2 \text{ water} + x_3 \text{ ethanol})$			
$\langle  \delta H_m^E  \rangle = 11.58$		$S_f = 14.30$		$\langle  \delta H_m^E  \rangle = 18.60$		$S_f = 25.50$	
$C_0$	−6.11	$C_5$	−190.57	$C_0$	17.22	$C_5$	−174.69
$C_1$	−2.26	$C_6$	−25.85	$C_1$	−123.00	$C_6$	−157.00
$C_2$	87.18	$C_7$	257.22	$C_2$	35.30	$C_7$	262.00
$C_3$	−136.17	$C_8$	132.61	$C_3$	32.20	$C_8$	−61.93
$C_4$	27.32			$C_4$	250.00		



**Fig. 3** Contours for constant values of  $H_{m,123}^E$  ( $\text{J mol}^{-1}$ ) at 298.15 K for: **a** ( $x_1\text{TBP} + x_2\text{H}_2\text{O} + x_3\text{CH}_3\text{OH}$ ); **b** ( $x_1\text{TBP} + x_2\text{H}_2\text{O} + x_3\text{C}_2\text{H}_5\text{OH}$ )

in a ternary mixture. The possible reason was that the low solubility of TBP in water.

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