

EXCESS MOLAR ENTHALPIES OF BINARY MIXTURES FOR (TRIBUTYL PHOSPHATE+METHANOL/ETHANOL) AT 298.15 K

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Excess molar enthalpies of binary mixtures for tributyl phosphate (TBP)+methanol/ethanol were measured with a TAM air Isothermal calorimeter at 298.15 K and ambient. The results for $x\text{TBP}+(1-x)\text{CH}_3\text{OH}$ are negative in the whole range of composition, while the values for $x\text{TBP}+(1-x)\text{C}_2\text{H}_5\text{OH}$ change from positive values at low x to small negative values at high x . The experimental results have been correlated with the Redlich–Kister polynomial. IR spectra of the mixtures were measured to investigate the effect of hydrogen bonding in the mixture.

Keywords: ethanol, excess molar enthalpies, methanol, tributyl phosphate (TBP)

Introduction

Tributyl phosphate (TBP) is a polar molecule (showed in Fig. 1) and has extensive uses in the field of extraction of metals, not only as a primary extractant, but also as a synergist and phase modifier [1–6]. Especially as a solvent in nuclear fuel reprocessing, it extracts uranium and plutonium from other aqueous fission products [7].

The study of the supercritical fluid extraction (SFE) of metals has become an interesting subject [8, 9]. TBP is also an alternative extractant in SEF for the extraction of rare earth and heavy metals [10–12]. The application of a cosolvent in SFE is a powerful method to modify the solvent properties of the supercritical fluids [13]. Such cosolvent effects are useful and frequently adopted to increase the solubility of solutes, to change the reaction equilibrium constants, to vary the reaction rate constants, etc. Methanol or ethanol is effective used as such cosolvent especially in supercritical carbon dioxide [14–16].

The thermodynamic studies for the interaction of TBP with cosolvent are significant for understanding the mechanism of SFE by adding cosolvent. The investigation on the interaction between unlike molecules in the system of interest can be carried out by measurement of the excess molar enthalpies. There is no report on the measurement of excess molar enthalpies for the mixing of TBP with methanol or ethanol. In present paper, excess molar enthalpies of (TBP +methanol/ethanol) were measured at 298.15 K and ambient. IR spectra of the mixtures were measured to investigate the effect of hydrogen bonding in the mixture [17, 18].

Experimental

Materials

TBP (Aldrich, mole fraction >0.99), methanol (guaranteed reagent, mole fraction >0.995), ethanol (guaranteed reagent, mole fraction >0.995) were used without further purification. The water contents of these materials were determined by a Karl-Fischer Moisture Titrator (Kyoto Electronics, E-511), the results for TBP, methanol and ethanol are 0.0311, 0.0723 and 0.100 mol kg⁻¹, respectively. The methanol and ethanol were stored over 0.4 nm molecular sieves to remove water. Care was taken to protect the samples from contamination by atmospheric moisture. Water was carefully purified by double-distillation. All the materials in experiment were quantified by mass.

Apparatus and measurements

The measurements of heat of mixing were performed using a TAM Air Isothermal calorimeter (Thermometric 3114/3236, Sweden) at 298.15 K and ambient. A steady-state electrical calibration was performed to obtain a calibration constant, the calibration constant was then entered into the software as a factor to cor-

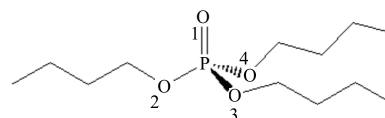


Fig. 1 Scheme of the structure of tributyl phosphate

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rect the experimental result. IR spectra of the mixture were measured with an AVATAR-360 (SMART) IR spectrophotometer in the range of the wave number from 2000 to 4000 cm^{-1} .

The enthalpies for the reaction of $\text{HCl}(aq)$ ($3.096 \cdot 10^{-4}$ mol) with $\text{NaOH}(aq)$ ($6.215 \cdot 10^{-4}$ mol) were measured at the same condition to check the accuracy of the calorimeter. The average heat of the three experimental results was $-(17.534 \pm 0.074)$ J. Combining this with the enthalpies of dilution of $\text{NaOH}(aq)$ [19], $\text{HCl}(aq)$ [20] and $\text{NaCl}(aq)$ [21], leads to the standard molar enthalpy of reaction: $\Delta_r H_m^0(298.15 \text{ K}) = -56.098 \text{ kJ mol}^{-1}$. Result is in good agreement with the value $-55.815 \text{ kJ mol}^{-1}$ from the literature [22]. The excess molar enthalpies of (water+ethanol) at 298.15 K and ambient were also measured to check the reliability of the apparatus used in this study. Experimental results of six runs at different molar fraction are in good agreement with the literature data [23], which are presented in Fig. 2. The accuracy of the calorimeter was therefore considered reliable.

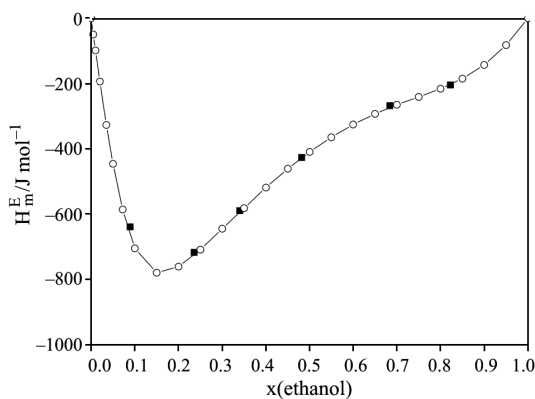


Fig. 2 Excess molar enthalpies H_m^E vs. mole fraction x at 298.15 K for $(1-x)\text{H}_2\text{O}+x\text{C}_2\text{H}_5\text{OH}$: \circ – [23]; \blacksquare – this work

Table 1 Experimental molar excess enthalpies H_m^E at 298.15 K and ambient for $x\text{TBP}+(1-x)\text{CH}_3\text{OH}$ and $\{x\text{TBP}+(1-x)\text{C}_2\text{H}_5\text{OH}\}$

x	$H_m^E/\text{J mol}^{-1}$	x	$H_m^E/\text{J mol}^{-1}$	x	$H_m^E/\text{J mol}^{-1}$
$x\text{TBP}+(1-x)\text{CH}_3\text{OH}$					
0.0472	-25.33	0.2825	-181.07	0.6478	-278.68
0.1316	-62.16	0.3736	-238.11	0.7388	-256.05
0.1540	-81.86	0.457	-268.64	0.7924	-207.49
0.1826	-100.85	0.5719	-296.17	0.8533	-177.20
0.2168	-120.05	0.6476	-289.70	0.9216	-130.29
$x\text{TBP}+(1-x)\text{C}_2\text{H}_5\text{OH}$					
0.0174	10.08	0.2817	144.86	0.5461	65.37
0.0671	37.08	0.2833	145.05	0.5460	65.84
0.1231	63.02	0.3320	144.70	0.5965	50.36
0.1753	120.82	0.3313	147.16	0.7236	16.75
0.2147	141.62	0.3892	128.51	0.8448	7.35
0.2419	143.33	0.3921	126.11	0.8921	-4.30
0.2413	144.29	0.4593	104.29	0.9437	-6.30
0.2827	142.96				

Results and discussion

The values of excess molar enthalpies H_m^E obtained for (tributyl phosphate+methanol/ethanol) at 298.15 K are given in Table 1, and plotted in Fig. 3 together with the curves calculated using the Redlich–Kister polynomial equation [24]:

$$H_m^E (\text{J mol}^{-1}) = x(1-x) \sum_{n=1}^k A_n (2x-1)^{n-1} \quad (1)$$

where x is the mole fraction of the TBP, m is the number of experimental data points and n is the number of parameters. The coefficients A_n in Eq. (1) and the standard deviations of the fits

$$sf. = \sqrt{\Sigma [H_m^E(\text{expt}) - H_m^E(\text{calc})]^2 / (m-n)}$$

are listed in Table 2.

IR spectra of the mixtures are showed in Fig. 4.

In general, the excess molar enthalpies are negative when the interactions between unlike molecules are stronger than the interaction between like mole-

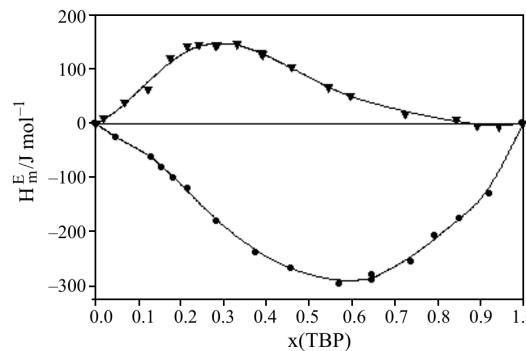
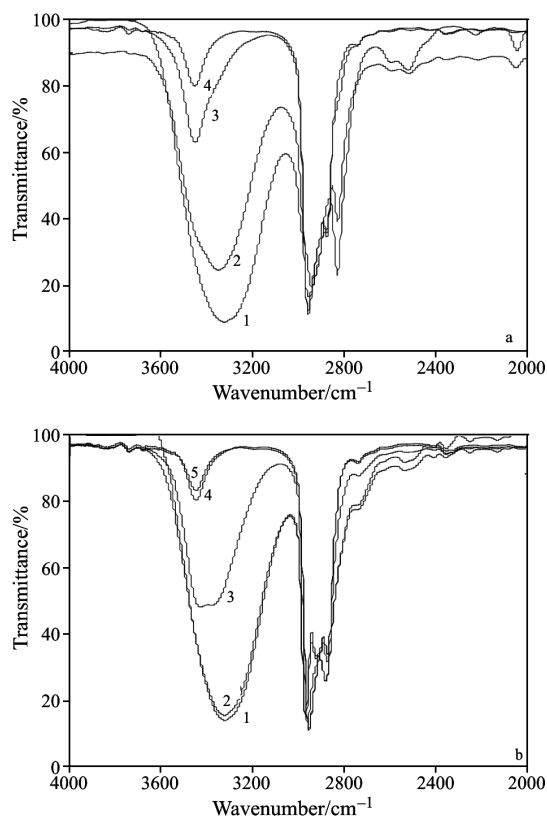


Fig. 3 Experimental excess molar enthalpies H_m^E at 298.15 K for $\blacktriangledown -x\text{TBP}+(1-x)\text{CH}_3\text{OH}$ and $\bullet -x\text{TBP}+(1-x)\text{C}_2\text{H}_5\text{OH}$. Solid lines are calculated by polynomial equation

Table 2 Coefficients in Eq. (1) for the molar excess enthalpies and standard deviations sf

Mixture	A_1	A_2	A_3	A_4	A_5	A_6	A_7	$sf/J \text{ mol}^{-1}$
$x\text{TBP}+(1-x)\text{CH}_3\text{OH}$	-608.44	-255.9	-169.04	197.95	1678.1	-636.54	-2046.8	0.23
$x\text{TBP}+(1-x)\text{C}_2\text{H}_5\text{OH}$	337.16	-836.71	614.11	604.8	-1016.7	40.79	-6.814	0.52


Fig. 4 IR spectra of the mixture. a – $(1-x)$ methanol+ x TBP, x : 1 – 0, 2 – 0.13, 3 – 0.57, 4 – 0.85; b – $(1-x)$ ethanol+ x TBP, x : 1 – 0, 2 – 0.02, 3 – 0.33, 4 – 0.84, 5 – 0.89

cules, while positive enthalpies are shown when the interactions between the unlike molecules are weaker [25]. The experimental results of the excess molar enthalpies indicate that in the mixture, the interaction between TBP and methanol is stronger than the total interactions of TBP–TBP and methanol–methanol, while the interaction between TBP and ethanol is weaker than the total interactions of TBP–TBP and ethanol–ethanol.

The enthalpy of mixing H_m^E could be considered as being due to three effects: the dissociation of alcohol, which is an endothermic effect; the dissociation of TBP, also the endothermic effect; and the cross interaction of alcohol and TBP, which is an exothermic effect. It is well known that alcohol is association by H-bonding in pure state, in inert solvent, and in solvating solvent [17, 18]. TBP (dipole moment, 2.36 Debye) should associate by dipole–dipole interaction. The cross interaction of alcohol and TBP in the mixture are probable both of H-bonding and dipole–dipole interaction.

IR spectra of OH-group in methanol and ethanol can show the H-bonding [17, 18]. The OH-group without H-bonding has absorption at about 3660 cm^{-1} [18]. The absorption is shifted towards lower wave numbers when H-bonding occurs. IR spectra of the binary mixtures of TBP with methanol and ethanol are showed in Fig. 4. The pure methanol and ethanol have absorption at about 3320 cm^{-1} because association by H-bonding. The absorption is shifted towards higher wave numbers with increasing TBP concentration. This shift shows the dissociation of alcohol. However, the absorption of OH-group in higher TBP concentration is almost same occurred at about 3450 cm^{-1} with increasing TBP concentration. This should indicate the H-bonding between alcohol and TBP.

It should be pointed out that in general methanol and ethanol have the same thermodynamic behavior (i.e. the excess molar enthalpies are both negative or both positive or both S shaped) in the binary mixture of alcohol with other component, such as water [23, 26], N,N-dimethylamide [27], benzene [26], chlorobenzene [28], toluene [29, 30], 1, 4-dimethylbenzene [31], tetrachloromethane [32, 33], hexane [34, 35], propylene carbonate [36]. Only a little literature reported the difference between the thermodynamic behavior of methanol and ethanol [37]. The present experiment results show the interaction of methanol with TBP is quite stronger than that of ethanol with TBP especially at lower TBP concentration.

The probable explain is the steric hindrance. When associated alcohol (dimer or oligomer [18]) interacting with big associated TBP molecule, the steric hindrance must be conquered not only by H-bonding but also by dipole–dipole interaction. The smaller the alcohol molecule is, the easier it will be to associate with the TBP molecule. Methanol is the smallest one in alcohols, so it is quite favorable to associate with TBP, which resulting the negative excess molar enthalpies. From this, it can be predicated that the excess molar enthalpy of binary mixture of TBP with other aliphatic alcohols should be endothermic.

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