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Short communication

Excess molar enthalpies for binary mixtures of trimethyl phosphate with alkanols $\{CH_3(CH_2)_nOH, n = 0–3\}$ at 298.15 K

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ABSTRACT

The excess molar enthalpies (H_m^E) for the binary mixtures of trimethyl phosphate (TMP) with alkanols $\{CH_3(CH_2)_nOH, n = 0–3\}$ have been measured with an isothermal calorimeter at 298.15 K and atmospheric pressure. The H_m^E values are positive for all the mixtures over the whole composition range. The values increase in the order methanol < ethanol < 1-propanol < 1-butanol. The experimental results have been correlated with the Redlich–Kister equation.

1. Introduction

The study of hydrogen bonded systems involving organic phosphates is of considerable significance for a variety of reasons. Organic phosphates–water systems serve as model systems for understanding biological processes [1–3]. Organic phosphates also have widely industrial applications, as extractant used together with diluent in a number of solvent extraction processes [4–6], as flame-retardant to reduce the electrolyte flammability in lithium ion cells [7,8]. Because of its importance in influencing a variety of chemical and biochemical processes, a number of studies on the hydrogen bonded interactions of organic phosphates, such as trimethyl phosphate (TMP) and tributyle phosphate (TBP), with the proton donors, such as water and alcohols, have been reported [9–14]. These studies are mainly performed using IR, NMR, and computation.

The thermodynamic properties, especially the excess molar enthalpy for hydrogen bonded systems, are important and useful for understanding the formation of hydrogen bonded complex. The thermodynamic properties for a few mixtures involving TMP or TBP have been studied [15–19], but the excess molar enthalpy H_m^E of TMP with alkanols over the whole composition range has not been reported. Continuing our interesting in the H_m^E of TBP with alkanols [18], the excess molar enthalpies for the mixtures of (trimethyl phosphate + methanol/ethanol/1-propanol/1-butanol) at 298.15 K and atmospheric pressure are reported in the present paper.

2. Experimental

2.1. Materials

Trimethyl phosphate (AR, mole fraction >0.99, Alfa), methanol (GR, mole fraction >0.995, Sinopharm Group Chemical Reagent Co., Ltd.), ethanol (GR, mole fraction >0.995, Sinopharm Group Chemical Reagent Co., Ltd.), 1-propanol (AR, mole fraction >0.998, Tianjin Bodi Chemical Co., Ltd.), 1-butanol (AR, mole fraction >0.998, Tianjin Bodi Chemical Co., Ltd.) were used without further purification other than drying with 3A (Ø 3–5 mm, spherical) molecular sieves. Care was taken to protect the samples from contamination by atmospheric moisture. All the materials in experiment were quantified by weight within ±0.0001 g.

2.2. Apparatus and measurements

The measurements of heat of mixing were performed using a TAM Air Isothermal calorimeter (Thermometric 3114/3236, Sweden) at 298.15 ± 0.02 K and atmospheric pressure. Before mixing, one liquid was maintained in the cell and another liquid was maintained in the syringe, both the cell and syringe are kept in a calorimetric chamber. When baseline was steady, the quantified amount of pure reagent in cell was mixed with that in a syringe by batch injecting. For a test of the calorimeter, our H_m^E results

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Table 1
Values of the fitting parameters, A_n in Eq. (1) and the standard deviation, σ, for TMP + alkanols at 298.15 K

Mixture	A_1	A_2	A_3	A_4	A_5	σ (J mol^{-1})
xTMP + (1 − x)CH_3OH	623.06	−879.60	284.89	366.73	−321.28	10
xTMP + (1 − x)C_2H_5OH	3330.17	−1333.36	−641.40	46.88	1912.29	15
xTMP + (1 − x)C_3H_7OH	4810.12	−1324.56	−278.38	−536.61	1712.09	14
xTMP + (1 − x)C_4H_9OH	5785.46	−1516.46	2005.01	−669.75	−1104.76	8

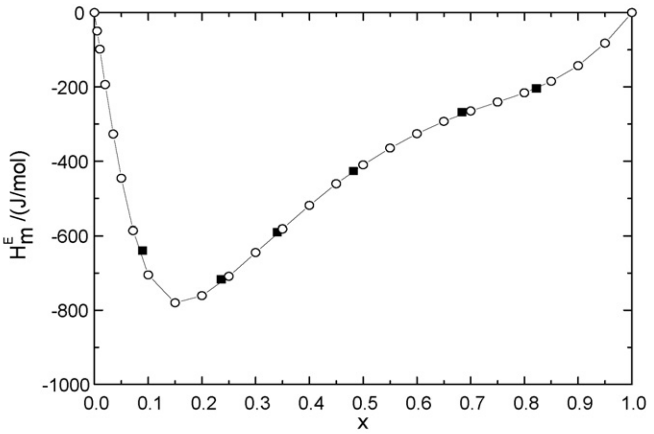

Fig. 1. Excess molar enthalpies H_m^E against mole fraction x at 298.15 K for {(1 − x)H_2O + $x$$C_2H_5OH$}: ○, Ref. [20]; ■, this work.

measured for the (ethanol + water) mixture were in reasonable agreement with the literature values [20], which are showed in Fig. 1.The experimental errors of H_m^E were estimated to be better than ± 0.5%.

3. Results and discussion

The experimental values of H_m^E are listed in supplement and shown in Fig. 2. The experimental data were regressed with all points weighted equally by the Redlich–Kister equation:

$$H_m^E\,(\mathrm{J\,mol^{-1}}) = x(1-x)\sum_{n=1} A_n(2x-1)^{n-1} \qquad (1)$$

where x is the mole fraction of TMP, A_n are fitting parameter, and n is the number of fitting parameters. These parameters are listed in Table 1 together with the standard deviation.

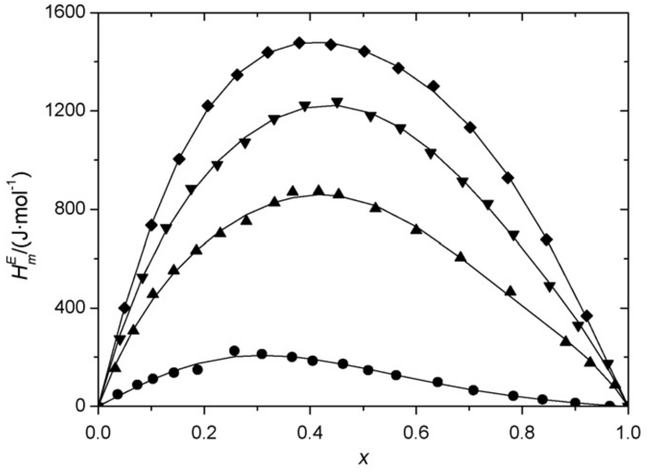

Fig. 2. Excess molar enthalpies H_m^E at 298.15 K for {xTMP + (1 − x)CH_3OH}: ●, {xTMP + (1 − x)C_2H_5OH}: ▲, {xTMP + (1 − x)C_3H_7OH}: ▼, and {xTMP + (1 − x)C_4H_9OH}: □. Solid lines are calculated by Eq. (1).

All systems (TMP + alkanols) showed endothermic and same behaviour over the whole range of composition, which differs from that of systems (tributyl phosphate + alkanols) [18]. As the carbon number of alkanols increases, the excess molar enthalpy for the mixtures of TMP + alkanols also increases in the order 1-butanol > 1-propanol > ethanol > methanol. H_m^E for the {xTMP + (1 − x)methanol} mixture in $x \geq 0.8946$ has been reported [19]. Our results are in reasonable agreement with this literature values [19], for example, when $x = 0.9190$, literature result is 11.2 J mol^{-1}, our calculated result is 10.7 J mol^{-1}.

TMP exists in two conformers in the liquid phase or solution, a more stable and polar (dipole moment 16.7 × 10^{-30} C m) C_1 symmetry conformer and a less polar (dipole moment 3.3 × 10^{-30} C m) C_3 symmetry conformer [10]. Because of high polarity, TMP is self-associated in the pure state. Alkanols are also polar and are self-associated by hydrogen bonding. When mixing with the proton donors, such as alkanols, TMP can offer two sites to form hydrogen bonds, the phosphoryl and alkoxy oxygen [14]. The intermolecular hydrogen bonding between TMP and alkanols has been shown by the IR, ^{13}C and ^{31}P NMR, and computation [11–14]. The strength of the hydrogen bonds between TMP and alkanols are due not only to contributions from the acidity of the OH proton but also to steric effects [13]. It is therefore expected that the strength of interaction between TMP and alkanols varied in the order 1-butanol < 1-propanol < ethanol < methanol.

The positive excess molar enthalpies for the present mixtures are attributed to the fact that the positive contribution due to the breaking of alkanols-to-alkanol hydrogen bonds and TMP-to-TMP dipolar–dipolar interactions is greater than the negative contribution due to the formation of hydrogen bonds between TMP and alkanols. Because the enthalpies of depolymerization are about the same, (25 ± 2) kJ mol^{-1}, for several low molar mass alkanols [21], the difference in H_m^E for the present mixtures is mainly attributed to the different strength of interaction between TMP and alkanols.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.02.015.

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