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Enthalpies of Mixing of Tributylphosphate with Hydrogen-Bonding Solvents[†]

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Excess enthalpies of mixing of tri-n-butyl phosphate with tert-butyl alcohol (303.15 K) are endothermic, but with chloroform (298.15 K) are exothermic, in spite of the fact that both solvents form hydrogen bonds with the proton acceptor phosphoryl oxygen of the ester. The results are discussed in terms of the apparent endothermic contribution of breaking the bonds in the self-associated solvents, and the apparent exothermic contribution from the newly formed hydrogen bonds between the ester and the solvent molecules.

Apart from the intrinsic interest in the thermodynamic functions of mixing of associated polar nonelectrolyte liquids, the information obtained here is relevant to the fundamental chemistry of solvent extraction processes. Namely, tributyl phosphate is one of the most powerful and most widely used extractants for inorganic compounds from aqueous solutions. Chloroform and water-immiscible alcohols are employed as diluent for the extractant, and the nature of the interaction between the extractant and its diluent—which together constitute the organic phase—has been studied by a variety of techniques in the past (7). Though much of that information is qualitative in nature, it clearly demonstrates that there is a reasonably strong H bonding between diluents containing a hydrogen atom capable of forming a hydrogen bridge and the phosphoryl oxygen of the ester.

Tri-n-butyl phosphate, $(C_4H_9O)_3PO$, has a dielectric constant of 8.05 and a dipole moment of about 3.1 D at room temperature (10). There is a variety of physicochemical evidence (7) to indicate that the ester is self-associated through a system of dipole–dipole bonds, when the predominating aggregate is the dimer. From infrared, vapor pressure, and dielectric measurements, the dimerization constant of the ester has been found to vary at 25 °C between k_2 = 1.2 and 2.9 dm^3 mol^{-1}, depending on the solvent used and the experimental method employed (7, 10). The energy of the bond was estimated (7) to be about 10 kJ mol^{-1}.

Chloroform, dipole moment ∼1.2 D, is only slightly dimerized. A dimerization constant of k_2 = 0.013 dm^3 mol^{-1} in dilute solutions of cyclohexane at room temperature has been calculated from spectral data (6). In the neat liquid, which is about 12 M, the fraction of dimers is likely to be higher than that calculated from this dimerization constant.

Literature data on the self-association of tert-butyl alcohol, dipole moment ∼1.7 D, do not present a uniform picture. Re-evaluation (14) of most of the existing spectral data shows that the importance of dimers in the self-association of the alcohol has been overestimated, and that other oligomers, trimers, tetramers, and perhaps even higher n-mers coexist in equilibrium. The major problem is frequently what oligomer can be identified and included in the set of mass-action law equilibria describing the process of polymerization of tert-butyl alcohol. Since this is a crucial factor affecting the calculation of equilibrium constants, it is not surprising that the reported numerical data are in poor agreement. The dimerization constant of tert-butyl alcohol in dilute solutions of cyclohexane or carbon tetrachloride at room temperature has been estimated to have a value ranging between k_2 = 0.6 and 1.0 dm^3 mol^{-1} (11). The enthalpy of formation of a single hydrogen bond has been calculated to be about 10 ± 2 kJ mol^{-1} (2, 11, 14).

Experimental Section

Materials. Tri-n-butyl phosphate (Koch-Light) was dried, purified, and analyzed as described before (13). Its purity was better than 99.5 mole %. 2-Methyl-2-propanol, tert-butyl alcohol (BDH), melting point 25.8 °C, and chloroform (Schuchardt), both of the highest purity commercially available, were dried over Perlform molecular sieve for several days prior to fractional distillation. The middle fractions retained, and kept in dark over molecular sieve, gave a single peak in GLC analysis, indicating a purity of better than 99.6 and 99.9%, respectively. Densities of the liquids: tributyl phosphate, d_{30} = 0.9687; tert-butyl alcohol, d_{30} = 0.7770; and chloroform, d_{25} = 1.4785. The water content of all liquids was determined by Karl Fischer titration, and found to be less than 0.01 mole %.

Calorimeter. Heats of mixing were determined using a Tronac Model 1000A continuous titration calorimeter. The original commercial calorimeter was modified to operate as a dual-bath

Table I. Excess Enthalpies of Mixing of Tri-n-butyl Phosphate (x_1) with Chloroform and tert-Butyl Alcohol

Tributyl phosphate–chloroform 298.15 K		Tributyl phosphate–t-butyl alcohol 303.15 K	
x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0370	−514.1	0.0329	10.01
0.0623	−1087	0.0422	14.56
0.0831	−1505	0.0711	29.60
0.1146	−2090	0.0770	34.12
0.1686	−2822	0.1060	65.09
0.2320	−2968	0.1440	111.2
0.2749	−3244	0.1820	159.1
0.3156	−3428	0.2254	196.4
0.3647	−3469	0.2536	210.6
0.4383	−3277	0.2777	222.4
0.5335	−2989	0.2975	230.9
0.5975	−2424	0.3292	244.8
0.6833	−2006	0.3638	252.4
0.7625	−1496	0.4103	256.5
0.8730	−773.3	0.4568	250.5
		0.6200	196.7
		0.7000	168.3
		0.7900	136.1

equipment. The added constant temperature bath, constructed in this laboratory of the same volume and equipped with separate but identical temperature control systems (±0.001 °C) had the performance of the original one. A Tronac-type immersed glass buret of about 6-mL capacity, with a programmed synchronous motor-driven piston in contact with mercury, was connected to a standard reaction vessel assembly of an LKB 8700 calorimeter consisting of the stainless-steel jacket and standard 100-mL glass reaction vessel and the motor stirrer.

Routine electrical calibrations were performed on the whole assembly, and in order to verify the performance of the modified equipment, excess enthalpies of mixing of the standard n-hexane–cyclohexane system at 25 °C were measured at eight compositions in the intermediate concentration range of 0.2 < x < 0.8. The results, with a standard deviation of 0.9 J mol^{-1}, agreed to better than ±1% of the reported and critically evaluated enthalpy values (3).

The general experimental procedure, as well as the precision of the heats of mixing results, was identical with those described earlier (4).

Results and Discussion

The experimentally measured excess enthalpies of mixing, H^E, for tri-n-butyl phosphate (component 1) and chloroform at 298.15 K, and tert-butyl alcohol at 303.15 K are compiled in Table I as functions of the mole fraction of the ester, x_1. The corresponding smoothing equations calculated by a least-squares computer program and the standard deviations (in J mol^{-1}) are:

tributyl phosphate + chloroform, 298.15 K

$$H^E = x_1 x_2 [-12\,500 + 7570](x_1 - x_2), \sigma = 16 \text{ J mol}^{-1}$$

tributyl phosphate + tert-butyl alcohol, 303.15 K

$$H^E = x_1 x_2 [958.6 - 708.6(x_1 - x_2) - 44.2(x_1 - x_2)^2$$
$$+ 1616(x_1 - x_2)^3], \sigma = 8 \text{ J mol}^{-1}$$

Two types of enthalpy changes contribute to the properties of the mixtures under consideration: an endothermic contribution due to disruption of the self-associated liquids, and an exothermic one arising from newly formed hydrogen bonds between the components. Obviously, in the ester–chloroform system where

H^E (mix) is exothermic throughout the whole composition range, the interaction between two different molecules overcompensates for the breaking of the bonds in the ester and the slightly dimerized chloroform. Indeed, independent spectral data (9) have shown that an equimolar adduct of considerable stability is formed between the ester and chloroform. The H^E vs. mole fraction curve is asymmetric, the maximum appearing around $x_1 = 0.34$. The more negative H^E values on the chloroform-rich side suggest that the endothermic contribution from breaking the dimerized chloroform is not significant, in line with its low value of the dimerization constant. The markedly less negative, by a factor of two, H^E values on the ester-rich side of the mixture are again in agreement with the corresponding dimerization constants: k_2 for the ester is by more than two orders of magnitude larger than that for chloroform.

In the ester–alcohol system the balance between the two enthalpy changes is reversed. The exothermic contribution from newly formed bonds is smaller than the endothermic one from the disruption of the relatively strong hydrogen bonds in the self-associated alcohol. Formation of equimolar adducts between the ester and the first three members of the alcohol homologues has been proposed from dielectric constant and NMR measurements (5). The stability constants of these adducts are comparable to that formed between chloroform and the ester (9), about 3–5 dm^3 mol^{-1}, at room temperature. One can assume that tert-butyl alcohol forms a similar adduct with tributyl phosphate with a stability constant not much different. Accordingly, the opposite sign of enthalpies of mixing in the two systems must be entirely due to the difference in the extent of self-association of chloroform and tert-butyl alcohol.

Finally, mention should be made of the heat of mixing data in the ester–chloroform system existing in the literature. In what appears to be a short screening study, Kosolapoff and McCullough (8) report H^E (max) = −4690 J mol^{-1} appearing at $x_1 = 0.385$ at an unspecified temperature, but which might have been 3 °C. The position of the maximum is in reasonable agreement with that found here, but the enthalpy value is higher by as much as 35%. If their data refer to 3 °C, as we think they do, the temperature coefficient $\partial H/\partial T$ at values of x_1 near at which H^E has its maximum, should be −55 J K^{-1} mol^{-1}, which seems unreasonably high.

Afanasiev et al. (1) have also measured the enthalpies of mixing in the tributyl phosphate–chloroform system at the same temperature under apparently identical conditions. They report 15 points in the concentration range 0.017 < x_1 < 0.942 with H^E (max) = −5460 J mol^{-1} at $x_1 = 0.384$. Their H^E (max) value is over 60% higher than the one reported here. The authors (1) have investigated at 298.15 K the heat of mixing of six binary systems of tributyl phosphate, with n-heptane, n-nonane, n-decane, di-n-butyl ether, carbon tetrachloride, and chloroform, the last two being exothermic. Since we have found previously that their endothermic heats of mixing in the ester–n-alkane systems were in reasonable agreement with those reported from this laboratory (13), no immediate explanation for the present discrepancies is at hand. It might be informative to note, however, that there is some circumstantial evidence that their data in both exothermic systems might be substantially off. The H^E values reported by Afanasiev for the tri-n-butyl phosphate–CCl$_4$ system are higher by about 50% than those found by Schwabe and Wiesener (12) for the triisobutyl phosphate–CCl$_4$ system under otherwise identical conditions. On the other hand, a comparison of the heats of mixing data of the two isomers with n-hexane (13) indicates that those for the isoester system are lower by about 15% throughout the whole concentration range. This comparative reasoning suggests thus that Afanasiev's data for the carbon tetrachloride system equally are likely to be inaccurate to roughly the same extent and in the same direction as those for the chloroform system. That in turn implies a systematic error in their exothermic heats of mixing data.

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Determination of Density, Viscosity, and Surface Tension for the System Isobutene–Sulfuric Acid–*tert*-Butyl Alcohol–Water

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The density, viscosity, and surface tension of the system isobutene–sulfuric acid–*tert*-butyl alcohol–water were measured in the range of concentrations including those of industrial significance. For each property, regression functions depending on c_{A_0} and c_t are presented. The data can be valuable for the design of isobutene absorbers.

The separation of isobutene from a gaseous mixture of C_4-hydrocarbons is an important industrial process. It is based on the high chemical reactivity of isobutene to form *tert*-butyl alcohol when selectively absorbed in sulfuric acid solutions up to 45 wt % (*7*).

A lot of experimental studies have been published referring to the kinetics of the reaction (*2*), to the effect of *tert*-butyl alcohol on the solubility of isobutene (*1*), and on the absorption rate in a bubble column (*8*). Yet it is necessary to get a detailed knowledge of the physical parameters of the system like density, viscosity, and surface tension, because these variables directly influence the values of gas holdup and the product of mass transfer coefficient and specific interfacial area in bubble columns (*3–5*).

It is the aim of this paper to present measured data of density, viscosity, and surface tension as a function of the sulfuric acid and *tert*-butyl alcohol concentration. The dependences are investigated under conditions similar to those found in the bubble column reactor. The data may be valuable for designing isobutene absorbers.

Experimental Section

The absorption–reaction that occurs is:
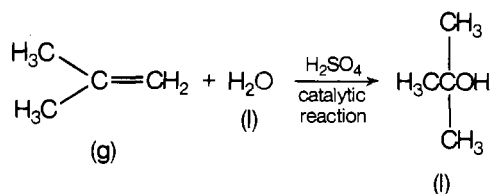
Because of 1 to 1 correspondence between water and *tert*-butyl alcohol and of a large difference in the molecular weights, the molar volume increases by 78.3 ml at 30.0 °C, the density of

tert-butyl alcohol being 0.77 g cm^{-3}. Thus the initial acid is diluted as well as the alcohol. To simulate the course of the reaction in the bubble column, an experimental design was proposed with the variables: initial acid concentration varying from 3 to 10 g-mol l.$^{-1}$ and number of moles of isobutene n_i reacted lying between 0 and 10 mol.

The actual concentration of acid c_A and the number of moles of *tert*-butyl alcohol n_t can be calculated by the equations

$$c_A = c_{A_0} \frac{1000}{1000 + n_i 78.3} \tag{1}$$

$$n_t = n_i \frac{1000}{1000 + n_i 78.3} \tag{2}$$

The volume contraction, occurring when highly concentrated acid solutions are used, and the heat released during the dilution of sulfuric acid solutions with water were taken into account during the preparation of the solutions. The density of the sulfuric acid–*tert*-butyl alcohol–water mixture was measured at 30.0 °C with the digital densimeter DMA 50 (manufactured by Anton Paar K.G., sold by Heraeus, Germany). The solution was filled into a U-shaped Duran 20 glass tube, representing a mechanical oscillator. The method assumes a quadratic relation

$$\rho = AT^2 + B \tag{3}$$

between the density of the fluid and the period of the oscillator, where A and B are empirical constants to be determined with the help of two liquids with known densities.

The kinematic viscosity ν was measured with the Ubbelohde viscosimeter (Schott) at 30.0 °C. Considering the Hagenbach correction term, ν is given by

$$\nu = kt - \frac{2.5}{t} \tag{4}$$

where k is a capillary constant and t means the flow time between two calibration marks. The dynamic viscosity η is then $\eta = \nu\rho$.

The surface tension σ of the solution against air and isobutene was measured at 30.0 °C with a tensiometer (MGW Lauda, Germany), that allowed σ to be recorded automatically as a function of time. For the measurement of σ against isobutene