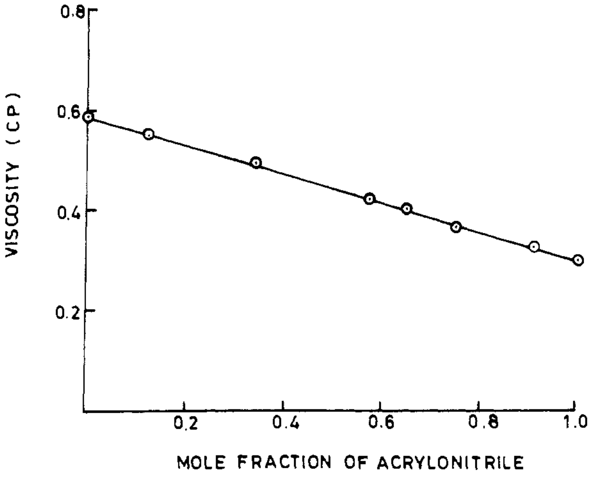

Figure 4. Variation of viscosity at 307.4 K with mole fraction of acrylonitrile in acrylonitrile-mesitylene mixture.

used as nonpolar components in the mixture.

It seems that in the case of acrylonitrile + cyclohexane binary liquid mixtures, the forces between unlike molecules are far less as compared to the forces between like molecules and that is why the mixture is more fluid, i.e., less viscous. This is quite likely in view of the known associating tendency of acrylonitrile. However, acrylonitrile + aromatic solvent mixtures of a certain composition become less fluid, i.e., more viscous, due to enhanced intermolecular forces between unlike molecules. This enhancement could be due to dipole-induced dipole interaction which is proportional to the polarizability of the aromatic molecule. The values of the polarizability of *p*-xylene and mesitylene are higher than that for benzene; the greater interaction of acrylonitrile with the former two aromatic solvents results in a higher viscosity as compared to benzene. Apparent linear dependence of mixture viscosity on molar proportion in the case of *p*-xylene and mesitylene could be fortuitous.

A perusal of Tables I-IV shows that the values of the parameter d are large and negative with cyclohexane, small and negative with benzene, and positive with *p*-xylene and mesitylene. Large negative values of d for the binary mixture with cyclohexane indicate the existence of weak interaction mainly due to dispersion forces. Increased (less negative) d values for the mixture with benzene indicate stronger interaction due to dipole-induced dipole interaction. Positive d values for the mixtures with *p*-xylene and mesitylene seem to be due to enhanced dipole-induced dipole interaction on account of higher polarizability of the methyl-substituted benzenes.

The values of W_{visc} have the following trend; highly positive with cyclohexane, less positive with benzene, negative with *p*-xylene, and more negative with mesitylene. This also supports the same contention as derived from d values.

Registry No. acrylonitrile, 107-13-1; cyclohexane, 110-82-7; benzene, 71-43-2; *p*-xylene, 106-42-3; mesitylene, 108-67-8.

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Solubility of Trialkyl Phosphate Adducts of Thorium Nitrate in Trialkyl Phosphate-Alkane Mixtures[†]

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Phase diagrams have been determined at 25 °C for several systems of the type $Th(NO_3)_4 \cdot x$TAP-TAP-alkane (where TAP ≡ trialkyl phosphate and $Th(NO_3)_4 \cdot x$TAP is a solid adduct). The trimethyl phosphate (TMP) adduct has an extremely limited solubility in TMP solutions containing hexane. For the system $Th(NO_3)_4 \cdot 2.8$TPP-TPP-*n*-dodecane (TPP = tri-*n*-propyl phosphate), a substantial region of liquid-liquid immiscibility exists as well as an extensive invariant region. For the corresponding triisobutyl phosphate system, no region of liquid-liquid immiscibility was found. For the TPP system, the size of the region of immiscibility was found to be significantly smaller when *n*-octane or 2,2,4-trimethylpentane was used instead of *n*-dodecane. No solid thorium nitrate adducts of triethyl phosphate or tri-*n*-butyl phosphate (TBP) could be prepared, but phase separation was found in systems containing *n*-dodecane and anhydrous liquids with a TBP:$Th(NO_3)_4$ ratio close to 3.0:1.

Introduction

There is a large body of data in the chemical literature concerning the extraction of actinides from aqueous solutions using trialkyl phosphates (*1-3*). Most of these data are from experiments in which a nitrate salt was partitioned between organic and aqueous phases—often with a fixed composition mixture as the organic phase (e.g., 30% tri-*n*-butyl phosphate (TBP) in kerosene). The formation of a third liquid phase (i.e., phase separation of the predominantly organic liquid) has been reported in many cases, most notably in thorium nitrate-TBP-alkane diluent-water-nitric acid systems (*4*, *5*). The third liquid phase can cause substantial difficulties in extraction procedures during the reprocessing of thorium fuel for nuclear reactors.

There has been little systematic study of phase relationships in this five-component system, at least in part because no solid adducts of $Th(NO_3)_4$ with TBP have been reported. However, solid anhydrous adducts of $Th(NO_3)_4$ with other trialkyl phosphates have been synthesized (*6*, *7*). Thus, we decided to carry out a detailed study of phase relationships in simple anhydrous subsystems each containing only $Th(NO_3)_4$, a trialkyl phosphate (TAP) capable of forming a solid adduct with $Th(NO_3)_4$, and an alkane diluent. The work was then extended

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to the corresponding TBP system, with particular attention to conditions for liquid–liquid phase separation. The separation of these anhydrous solutions into two liquid phases represents the limiting case of formation of the third liquid phase in the five-component system.

Experimental Section

Materials and Synthesis of the Adducts. Trimethyl phosphate (TMP) and triethyl phosphate (TEP) (Aldrich) were used without purification for the syntheses. For the phase diagram studies the TMP used was distilled from Na_2CO_3 under vacuum (discarding the first and last tenths of the distillate), and stored in a drybox over molecular sieve (4A, 8–12 mesh). Tri-*n*-propyl phosphate (TPP) (Columbia Organic Chemicals) was treated similarly. TBP (Fisher purified) was further purified as described by Irving and Edgington (*8*). Triisobutyl phosphate (T*i*BP) was prepared from phosphoryl chloride and sodium isobutoxide by the method of Evans et al. (*9*), and purified by vacuum distillation. Alkane solvents (Fisher purified or spectral grade) were dried over molecular seive before use.

We prepared a solid TMP adduct of $Th(NO_3)_4$ from hydrated $Th(NO_3)_4$ and TMP using the method described by Legin et al. (*6*) for the synthesis of $Th(NO_3)_4 \cdot 3TMP$. Attempts to prepare a solid adduct of $Th(NO_3)_4$ with TEP by this method were unsuccessful. Analyses of the freshly prepared TMP adduct (24.6 ± 0.3 wt % Th) indicated a thorium content slightly lower than required for a 1:3 adduct (25.8 wt % Th), but considerably higher than expected for a 1:4 adduct (22.3 wt % Th). The adduct melted with decomposition at temperatures above 85 °C. As reported by Legin et al. (*6*), the adduct gradually decomposes at room temperature when left over P_2O_5 under vacuum. However, we found the decomposition occurred even when the solid was stored under nitrogen at atmospheric pressure. The partially decomposed compound has a higher thorium content than the freshly prepared material and is less readily soluble in water.

A solid T*i*BP adduct of $Th(NO_3)_4$ was prepared by extraction from aqueous thorium nitrate solutions using the method of Horx and Rost (*7*), although the melting point found for the solid, recrystallized from CCl_4, CS_2, or petroleum ether, was 87 ± 2 °C—considerably lower than the previously reported 96–98 °C. A solid adduct of $Th(NO_3)_4$ with TPP was prepared by a similar method. Maximum yields of the TPP adduct were obtained when the TPP:Th ratio in the reaction mixtures was 2.6:1; however, yields were also generally lower than those for the T*i*BP adduct. The TPP adduct was recrystallized from CS_2 or CCl_4. Thorium analyses indicated the solid (mp 72–73 °C) was 20.9 ± 0.2% Th; the calculated amount of thorium in $Th(NO_3)_4 \cdot 3TPP$ is 20.1%.

In an attempt to determine if the TPP adduct prepared by this method contained a significant amount of water, a sample was prepared by using solutions in which approximately 25% of the water was D_2O. Comparison of the infrared spectrum of the solid from this synthesis with spectra of solids prepared either normally by the Horx and Rost method (using no D_2O) or from ethyl acetate–acetonitrile solutions (see below) showed essentially no differences, even in the O–D stretching region. Thus, there was very little, if any, water in the recrystallized TPP adduct. No solid TEP or TBP adducts could be isolated by this method, although the TAP:Th ratios in the reaction mixture were systematically varied from 1.8:1 to 3.2:1.

Anhydrous thorium nitrate was prepared by the methods of Ferraro et al. (*10*) and Ferraro and Walker (*11*). Addition of the anhydrous salt to TBP (pure or in alkane solution, TBP:Th $\leq$3.0:1) gave visible decomposition (evolution of NO_2), even from solutions cooled in dry ice. TPP solutions appeared to give less decomposition, and an adduct, similar to that from the extraction synthesis discussed above, was isolated after filtration and addition of excess *n*-dodecane.

A metathetical synthesis was also used in an attempt to obtain TBP and TEP adducts of $Th(NO_3)_4$. Nominally anhydrous $ThCl_4$ (Pfaltz and Bauer) was dissolved in refluxing dry ethyl acetate using a Soxhlet extraction system. Any water was removed by azeotropic distillation (*12*), and the solution was cooled, filtered, and analyzed for thorium. A weighed amount of TAP was added to give a solution with the desired TAP:Th ratio (generally between 2.1:1 and 3.2:1). Silver nitrate (4 mol per mole of thorium in the ethyl acetate solution) was dissolved in dry acetonitrile, and then added, with stirring, to the $ThCl_4$–TAP solution. After 2 h, the precipitated AgCl was filtered off, and the ethyl acetate and acetonitrile were removed from the filtrate by using a rotary evaporator.

For TEP and TBP liquids with TAP:Th ratios of 3.0:1, cooling caused the formation of glassy solids with melting points below −40 °C. Proton nuclear magnetic resonance (^1H NMR) spectra showed the presence of only trace quantities of ethyl acetate or acetonitrile. Therefore, these solutions did not contain significant quantities of thorium nitrate adducts other than those with the trialkyl phosphates. The 3.0:1 TPP adduct prepared by this method solidified and was found to have the same melting point, solubility behavior, and infrared spectrum as the TPP adduct prepared by the extraction method (*7*). A solid compound was also obtained from a mixture with a TPP:Th ratio of 2.6. Karl Fisher analyses of the liquids and solid adducts indicated <0.1 mol H_2O per mole Th.

Solutions with a TBP:Th ratio of 2.5:1 were obtained by extraction of $Th(NO_3)_4$ into TBP from a saturated aqueous solution of $Th(NO_3)_4$ over solid $Th(NO_3)_4 \cdot xH_2O$. Karl Fisher analyses of these TBP solutions indicated approximately 0.3 mol H_2O per mole Th.

Methods. Thorium analyses were done by titration of aqueous solutions of samples using standardized EDTA solutions. Time was allowed during the titrations to extract (into the water) any thorium present in an insoluble organic phase.

Phase diagram experiments using *n*-dodecane or octane solutions were done in closed weighing bottles or scintillation vials thermostated in a bath at 25.0 ± 0.2°C. Analyzed samples of a solid adduct were added in small portions to TAP/alkane mixtures over a period of several days until liquid–liquid phase separation or saturation with the solid occurred. Solutions containing high concentrations of thorium came to solid–liquid equilibrium slowly, sometimes requiring more than 2 weeks. Solutions containing two liquid phases but no solid were assumed to reach equilibrium if stirred at 25 °C for 24 h. Vials were weighed after equilibration to verify that no significant quantities of the slightly volatile alkanes had been lost during the experiments.

For systems in which no solid adduct could be isolated, solutions having a high thorium content were successively titrated with pure alkane and TAP at 25.0 ± 0.5°C. Thus, compositions at which liquid-phase separation occurs could be determined. This procedure was also used to obtain some boundary compositions in the $Th(NO_3)_4$–TPP–dodecane system.

In the $Th(NO_3)_4$–TPP–dodecane system the positions of several tie lines in the phase diagram were determined, as was the position of one tie line in the $Th(NO_3)_4$–TBP–dodecane system. Solutions with a total composition in the two-liquid-phase region were prepared and allowed to come to equilibrium at 25 °C. Portions of both layers were then analyzed for thorium.

The uncertainties in the phase boundary compositions are generally <0.01 in weight fraction thorium adduct and <0.005 weight fraction for the other two components. However, the actual uncertainties depend strongly on the specific compositions. Because of variability in the stoichiometry of the adducts (from batch-to-batch), compositions prepared from the solids,

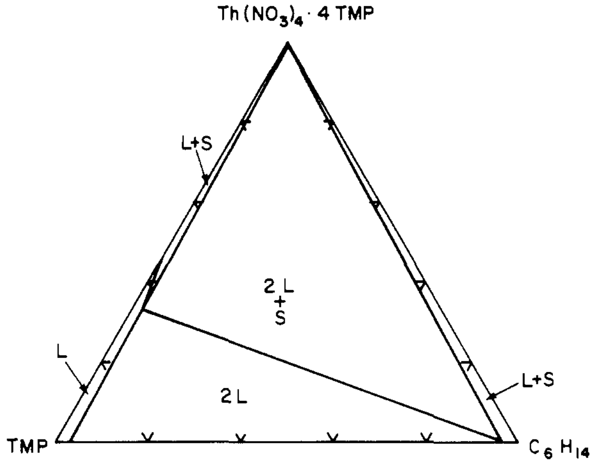

Figure 1. $Th(NO_3)_4$·4TMP–TMP–*n*-hexane phase diagram (wt %) at 25 °C. A single-liquid region exists at compositions near pure *n*-hexane, but this region is too small to be shown.

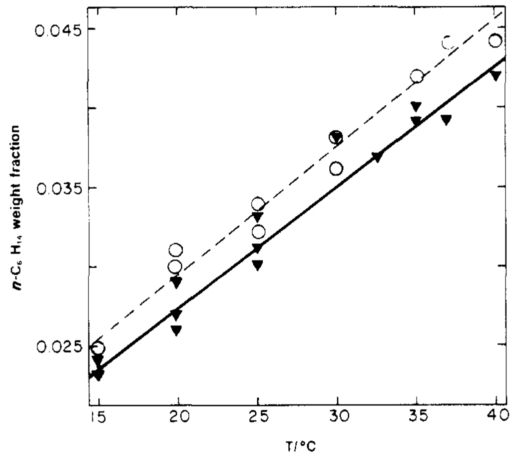

Figure 2. Solubility of *n*-hexane in TMP (- -O- -) and in TMP containing 0.015 weight fraction $Th(NO_3)_4$ (–▼–).

and having a high weight fraction thorium, have the potential for slightly larger errors in the TAP and adduct weight fractions (<0.03). Uncertainties in the positions of the tie lines are also slightly larger because there are contributions of ~1% from the thorium analysis of each layer as well as those from the uncertainties in the location of the liquid–liquid boundary.

Phase diagram and solubility experiments involving *n*-hexane–TMP solutions were done using sealed glass ampules in a thermostated bath. The solubility of *n*-hexane at a particular $Th(NO_3)_4$:TMP ratio was determined by using a series of ampules containing identical quantities of TMP and $Th(NO_3)_4$ and different amounts of *n*-hexane. This procedure allowed the coalescence composition to be determined within about 0.002 in weight fraction *n*-hexane.

Results and Discussion

***Th*(*NO*$_3$)$_4$–*TMP*–*n*-*Hexane*.** The mutual solubility of each pair of components in the $Th(NO_3)_4$–TMP–*n*-hexane system is limited. The phase diagram shown in Figure 1 is based on the stable solid being $Th(NO_3)_4$·4TMP. A solid of approximately that composition (based on thorium analyses) is found when freshly prepared adduct (~1:3) is allowed to equilibrate with TMP–*n*-hexane mixtures for several days.

The solubility of *n*-hexane in TMP and in the $Th(NO_3)_4$–TMP solutions increases with increasing temperature (see Figure 2). TMP is even less soluble in *n*-dodecane than in *n*-hexane and, thus, no ternary system measurements were done using *n*-dodecane.

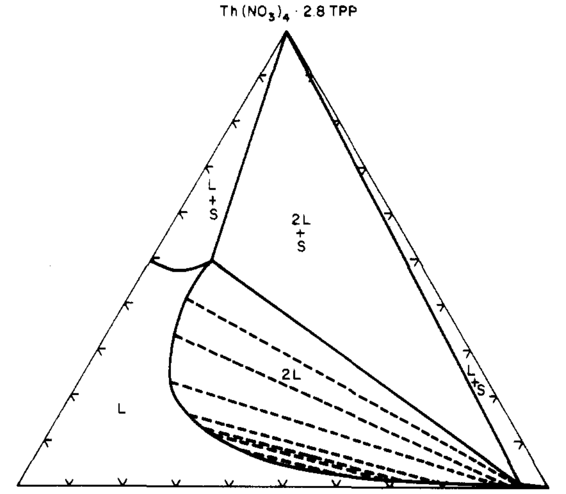

Figure 3. $Th(NO_3)_4$·2.8TPP–TPP–*n*-dodecane phase diagram (mol %) at 25 °C. Tie lines (- - -) are shown.

As was noted in the Experimental Section, the solid adduct seems to decompose gradually, even in an atmosphere of dry nitrogen. This "aged" solid is markedly less soluble than the freshly prepared adduct in TMP-rich mixtures. It was also found that, over a period of months, TMP adduct in contact with TMP and *n*-hexane was slowly converted to another solid. This (probably polymeric) material is much less soluble than $Th(NO_3)_4$·4TMP in TMP or in water. The positions of the solid–liquid and solid–liquid–liquid boundaries in the phase diagram (Figure 1) are only approximate, and refer to a system in which the metastable $Th(NO_3)_4$·4TMP is the only solid adduct (as was found experimentally for times ranging from days to weeks).

***Th*(*NO*$_3$)$_4$–*TEP*–*n*-*Dodecane*.** The TEP–*n*-dodecane binary system has a somewhat smaller region of liquid–liquid immiscibility than found in the corresponding TMP–*n*-dodecane system. However, the size of the two-phase region is still substantial (0.15 mole fraction to 0.82 mole fraction *n*-dodecane). For this reason, and because no solid TEP adduct of $Th(NO_3)_4$ could be prepared, the $Th(NO_3)_4$–TEP–*n*-dodecane system was not studied in detail.

***Th*(*NO*$_3$)$_4$·*2.8TPP*–*TPP*–*Alkane*.** The TPP adduct of thorium nitrate is quite soluble in a large number of nonpolar and polar solvents such as $CHCl_3$, CCl_4, CS_2, acetone, and TPP itself. However, the adduct is not particularly soluble in higher *n*-alkanes. The phase diagram for the adduct with TPP and *n*-dodecane is shown in Figure 3. The experimental phase boundary and tie line composition data for the TPP systems have been deposited as supplementary material (see paragraph at end of text regarding supplementary material).

Although TPP and *n*-dodecane are miscible in all proportions, addition of the adduct gives rise to a large region of liquid–liquid immiscibility and, at high adduct mole fractions, a substantial invariant region. The solid at equilibrium in the invariant region has a TPP:Th ratio of (2.83 ± 0.05):1, and this ratio was found to be independent of the initial TPP:Th ratio in the adduct as prepared by the metathetical synthesis (2.6:1–3.0:1). No significant differences could be seen in the powder X-ray patterns of the solids with different TPP:Th ratios. The positions of the tie lines are based only on thorium analyses of the two phases formed from solutions of known initial compositions.

The regions of liquid–liquid immiscibility in $Th(NO_3)_4$·2.8TPP–TPP–octane systems at 25 °C are considerably smaller than the region in the corresponding system with *n*-dodecane (see Figure 4). The branched isooctane (2,2,4-trimethylpentane) tends to suppress the phase separation to a slightly greater extent than does *n*-octane. On a mole fraction basis, the solid is soluble to a similar extent in the three TPP–alkane mixtures,

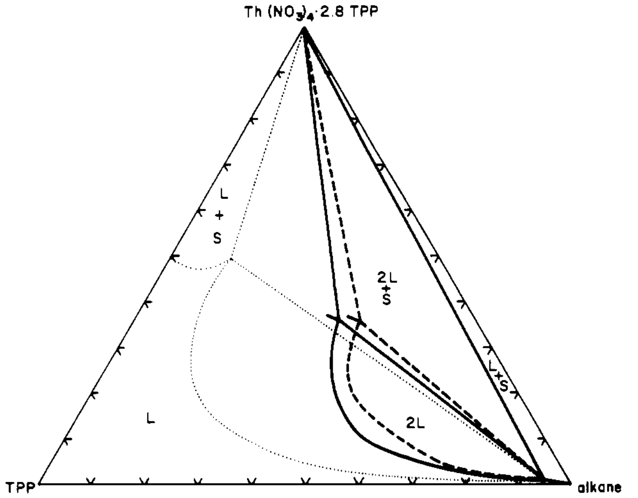

Figure 4. Phase diagrams for the $Th(NO_3)_4 \cdot 2.8TPP$–TPP–alkane systems at 25 °C: isooctane (- - -), *n*-octane (—), and *n*-dodecane (···).

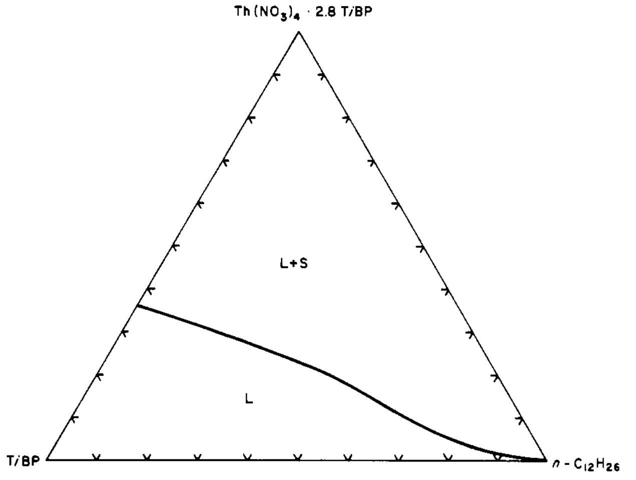

Figure 5. $Th(NO_3)_4 \cdot 2.8T/BP$–T/BP–*n*-dodecane phase diagram (mol %) at 25 °C.

and the solubility of the adduct in the pure alkanes is ≤0.0006.

***Th*(*NO*$_3$)$_4$·*2.8TIBP*-TIBP-*n*-*Dodecane*.** In comparison with the TPP system, this system is very simple (see Figure 5). No liquid–liquid phase separation was found, and the solubility of the adduct decreases almost linearly with increasing *n*-dodecane content of the mixtures. The adduct is less soluble in T/BP than is the TPP adduct in TPP. In *n*-dodecane, the T/BP adduct is slightly more soluble than the TPP adduct. The 2.8:1.0 (T/BP:Th) stoichiometry of the adduct was established by thorium analyses of samples recovered after long periods of contact with T/BP-rich and T/BP-poor solutions. Freshly recrystallized material was found to have a stoichiometry closer to 3.0:1, but powder X-ray patterns of these solids showed no substantive differences. The experimental phase boundary data for this system have been deposited as supplementary material.

***Th*(*NO*$_3$)$_4$–*TBP*-*n*-*Dodecane*.** Although many procedures were tried, no solid TBP adduct of thorium nitrate was obtained. Liquid solutions were prepared with TBP:$Th(NO_3)_4$ ratios of 2.1:1 to 3.2:1 by using the metathetical synthesis. Analysis of the liquids for thorium gave results that were systematically 1–5% lower than values calculated from the quantities of $Th(NO_3)_4$ originally dissolved in ethyl acetate and the known weights of added TBP. Proton NMR spectra indicated that the liquid "adducts" contained insufficient quantities of residual ethyl acetate, or acetonitrile, to account for the low thorium analyses. Samples of the liquid $Th(NO_3)_4$–TBP solutions were titrated successively with *n*-dodecane and with TBP to establish regions of immiscibility. The experimental points shown in Figure 6 (●) represent data from experiments using solutions from three different syntheses, all with TBP:Th ratios ≥3.0:1. The dashed tie line is almost parallel to a line drawn from addition of pure *n*-dodecane to a solution with a TBP:$Th(NO_3)_4$ ratio of 3:1. No phase separation was observed on titration of these $Th(NO_3)_4$–TBP solutions (TBP:Th ≥ 3.0) with isooctane or *n*-decane.

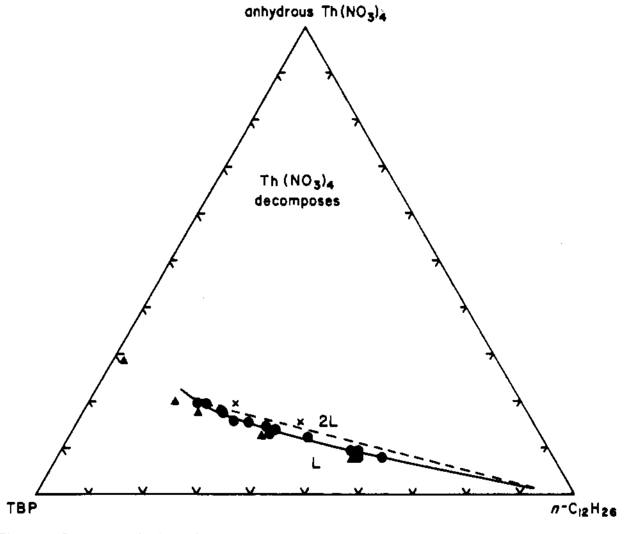

Figure 6. Liquid–liquid immiscibility in the $Th(NO_3)_4$–TBP–*n*-dodecane system (mol %, 25 °C) using "anhydrous" solutions TBP:Th ≥ 3.0:1 (●), TBP:Th = 2.7:1 (X), and slightly aqueous solutions from extraction (▲). One tie line is shown (- - -).

Although no significant differences could be seen in the proton NMR spectra, solutions prepared with TBP:Th ratios significantly less than 3.0 showed different solubility behavior. A solution with a ratio of 2.7:1 (X in Figure 6) dissolved more *n*-dodecane than would have been expected from the experiments using solutions with TBP:Th ≥ 3.0:1. A solution with TBP:Th = 2.1:1 gradually decomposed at room temperature over a period of weeks, with precipitation of a white solid. A few preliminary experiments indicated that the phase separation behavior of slightly aqueous solutions of $Th(NO_3)_4$ in TBP (prepared by extraction and addition of extra TBP, H_2O:Th = 0.3:1) with *n*-dodecane (▲ in Figure 6) differs only marginally from that of the nominally anhydrous liquid adducts with TBP:Th ≥ 3.0:1. The region of liquid–liquid immiscibility appears slightly larger in the presence of the small amount of water.

***General*.** The phase diagrams indicate that separation of the liquid solutions into TAP-rich and alkane-rich phases is a general phenomenon, particularly in alkane–TAP mixtures containing greater than 0.6 mole fraction alkane. The degree of phase separation decreases as the alkyl chain on the TAP becomes longer.

The TMP–*n*-dodecane and TEP–*n*-dodecane binary systems need no added thorium nitrate to exhibit a region of liquid–liquid immiscibility, and the region of liquid–liquid immiscibility is much larger for TPP solutions than for TBP solutions. Liquid–liquid miscibility in the $Th(NO_3)_4$–TAP–alkane systems increases with decreasing alkane molecular weight, and probably with increased branching of the alkane.

T/BP and TBP have similar capabilities as extractants for actinide(IV) nitrates (*7*, *13*). However, if *n*-dodecane is used as the diluent, the maximum concentration for thorium nitrate in an anhydrous T/BP phase is limited by the formation of solid adduct. In corresponding TBP–*n*-dodecane solutions, much higher concentrations of thorium nitrate can be dissolved because solid TBP adducts do not form readily, if at all. However, the *n*-dodecane–T/BP solutions show no phase separation at much higher thorium concentrations than those that cause phase separation in *n*-dodecane–TPP mixtures.

The TPP systems are more experimentally accessible than the corresponding TBP systems. Hence, the TPP systems (with large two-liquid-phase regions) may be useful model systems in examining additives that might suppress phase separation in $Th(NO_3)_4$–TAP–alkane systems.

Acknowledgment

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Registry No. TMP, 512-56-1; TPP, 513-08-6; TEP, 78-40-0; TiBP, 126-71-6; TBP, 126-73-8; $Th(NO_3)_4$, 13823-29-5; $Th(NO_3)_4 \cdot 4TMP$, 105183-08-2; $Th(NO_3)_4 \cdot 3TPP$, 105205-29-6; $Th(NO_3)_4 \cdot 3TiBP$, 19651-57-1; hexane, 110-54-3; dodecane, 112-40-3; octane, 111-65-9; 2,2,4-trimethylpentane, 540-84-1.

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Supplementary Material Available: Experimental phase boundary and tie-line composition data for the TPP and T*i*BP systems (3 pages). Ordering information is given on any current masthead page.

Solubility of Pyrene in Binary Solvent Mixtures Containing Cyclohexane

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Solubilities are reported for pyrene at 26.0 °C in binary mixtures of cyclohexane with *n*-hexane, *n*-heptane, *n*-octane, isooctane, and cyclooctane. The results of these measurements are compared to the predictions of equations developed previously for solubility in systems of nonspecific interactions. The nearly ideal binary solvent (NIBS) model predicts these solubilities with a maximum deviation of 4.6%, using as input data the solubility of pyrene in each pure solvent. The NIBS model correctly predicts a small maxima for the mole fraction solubility of pyrene in cyclohexane + *n*-heptane mixtures.

Introduction

The use of binary solvents for influencing solubility and multiphase partitioning has many potential applications in the chemical industry. Maximum realization of these applications depends on the development of equations that enable a priori prediction of solution behavior in mixed solvents from a minimum number of experimental observations. The nearly ideal binary solvent (NIBS) approach developed previously (*1*–*5*) provides a relatively simple method for estimating the excess partial molar properties of a solute, $(\Delta \bar{Z}_3^{ex})^*$ at infinite dilution in a binary solvent (components 1 and 2)

$$(\Delta \bar{Z}_3^{ex})^* = f_1^0(\Delta \bar{Z}_3^{ex})_1^* + f_2^0(\Delta \bar{Z}_3^{ex})_2^* - \Gamma_3(X_1^0\Gamma_1 + X_2^0\Gamma_2)^{-1}\Delta \bar{Z}_{12}^{ex} \tag{1}$$

$$f_1^0 = 1 - f_2^0 = X_1^0\,\Gamma_1/(X_1^0\Gamma_1 + X_2^0\Gamma_2)$$

in terms of a weighted mole fraction average of the properties of the solute in the two pure solvents $(\Delta \bar{Z}_3^{ex})_1^*$ and $(\Delta \bar{Z}_3^{ex})_2^*$ and a contribution due to the unmixing of the solvent pair by the presence of the solute. Equation 1 leads to accurate predictions of enthalpies of solution (*1*), gas–liquid partition coefficients (*3*), and solubilities (*2*, *4*–*11*) in systems of nonspecific interactions when the weighting factors (Γ_i) are approximated with molar volumes.

The success of the NIBS in predicting solubility in noncomplexing solvent mixtures suggested the possibility that this solution model may provide a foundation for approximations of the physical interactions even in a system known to contain chemical interactions. To pursue this idea further, Acree et al. (*12*) extended the basic NIBS model to systems containing association between the solute (component A) and a complexing cosolvent (component c)

$$A_1 + C_1 \rightleftharpoons AC$$

$$K_{AC} = \phi_{AC}/\phi_{A_1}\phi_{C_1}$$

Postulating the formation of a 1:1 anthracene–benzene complex, the authors demonstrated that the solubility of anthracene in benzene + *n*-heptane and benzene + isooctane could be described to within a maximum deviation of 4% using a single equilibrium constant. More importantly, it was noted that the determination of solute–solvent equilibrium constants from solubility measurements does depend on the manner in which nonspecific interactions are incorporated into the model.

Continued development of solution models for predicting the properties of a solute in binary solvent systems requires that a large data base be available for assessing the applications and limitations of derived predictive expressions. Currently, only a limited data base exists for crystalline nonelectrolyte solubility in binary solvent systems. For these reasons, we report the solubility of pyrene in mixtures containing cyclohexane with