# Viscosity and Density of Tri-*n*-butyl Phosphate + Benzene + Toluene from 30 °C to 45 °C

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Viscosities and densities of the ternary liquid mixtures of tri-*n*-butyl phosphate + benzene + toluene were measured at (30, 35, 40, and 45) °C. The deviations in the viscosity from a mole fraction average were fitted in a Redlich−Kister type equation, which includes the contribution of each constituent binary system along with a ternary contribution term. The viscosity deviations were negative in most of the cases.

## Introduction

Measurement of some of the bulk properties such as viscosity and density of liquids provides insight into the intermolecular arrangement in liquids and helps one to understand the thermodynamic properties of liquid mixtures. Tri-*n*-butyl phosphate (TBP) is chosen as one of the components in ternary liquid mixtures as it is effective as an extractant for lanthanides and actinides. This extractant dominates the chemical reprocessing of nuclear fuels in the atomic energy industry. The extraction efficiency of the extractant improves with the addition of suitable organic diluents and modifiers (Fort and Moore, 1965; Prasad et al., 1976; De et al.,1970; Rout et al., 1993, 1996; Swain and Chakravortty, 1996). To study the solvent extraction of actinides using binary mixtures as diluents, it is necessary to have the appropriate density and viscosity data. In a continuation of our earlier work (Swain and Chakravortty, 1996; Swain et al., 1997) on viscosities and densities of liquid mixtures, the present paper reports the viscosities and densities for ternary mixtures of tri-*n*-butyl phosphate + benzene + toluene in the temperature range (30−45) °C.

## Experimental Section

***Materials.*** The chemicals used were of analytical grade. Tri-*n*-butyl phosphate (TBP) with purity greater than 98 mol % was obtained from S.D. Fine Chemicals, India. Benzene (BDH) and toluene (BDH) were obtained with maximum purity greater than 98 mol %. Benzene and toluene were purified by the method of fractional distillation (Weissberger, 1959). Tri-*n*-butyl phosphate was purified by the method of Alcock and co-workers (Alcock et al., 1956). The purity of the sample was checked by comparing the viscosity and density with those reported in the literature (Dean, 1979; McCabe and Smith, 1970; Rout et al., 1994). The densities and viscosities of pure components at different temperatures are presented in Table 1.

**Table 1. Pure Component Properties**

| pure component | $t$/°C | $10^{-3}\rho$/kg m$^{-3}$ | $\eta$/mPa·s |
|---|---|---|---|
| TBP | 25 | 0.975 | 3.388 |
| | | (0.976)[a] | (3.390)[a] |
| | 30 | 0.968 | 2.970 |
| | 35 | 0.963 | 2.680 |
| | 40 | 0.961 | 2.430 |
| | 45 | 0.954 | 2.210 |
| benzene | 25 | 0.876 | 0.647 |
| | | (0.874)[a] | (0.645)[b] |
| | | (0.874)[c] | (0.643)[c] |
| | 30 | 0.866 | 0.630 |
| | 35 | 0.862 | 0.604 |
| | 40 | 0.859 | 0.598 |
| | 45 | 0.856 | 0.553 |
| toluene | 25 | 0.863 | 0.554 |
| | | (0.862)[a] | (0.552)[a] |
| | 30 | 0.857 | 0.523 |
| | 35 | 0.854 | 0.499 |
| | 40 | 0.851 | 0.478 |
| | 45 | 0.848 | 0.458 |

[a] Dean, 1979. [b] McCabe and Smith, 1970. [c] Rout et al., 1994.

***Experimental Measurements.*** Ternary mixtures of TBP, benzene, and toluene were prepared by volume. Sixteen mixtures were prepared. Densities and viscosities of the solutions were measured at four different temperatures, (30, 35, 40, and 45) °C. The increment in temperature level was kept regular at 5 °C with a view to ensure measurable effects of temperature change on experimental observations. The highest temperature was (45 ± 0.1) °C in order to avoid errors due to evaporation losses during the measurements (Swain et al., 1997; Singh et al., 1990). The densities of all the components were measured by a bicapillary pycnometer calibrated with deionized double-distilled water with $0.996 \times 10^3$ kg m$^{-3}$ as its density at 30 °C. The accuracy of density measurements was within ±0.7%. Viscosities of the solutions were measured by a thoroughly cleaned, dried, and calibrated Ostwald viscometer (Das et al., 1996). The viscometer was kept in a

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**Table 2. Experimental Densities $\rho$, Viscosities $\eta$, and $\Delta\eta$ for the Ternary Mixtures TBP (1) + Benzene (2) + Toluene (3) at Different Temperatures**

| $x_1$ | $x_2$ | $x_3$ | $t$/°C | $10^{-3}\rho$/kg m$^{-3}$ | $\eta$/mPa·s | $\Delta\eta$/mPa·s |
|---|---|---|---|---|---|---|
| 0.037 | 0.524 | 0.440 | 30 | 0.872 | 0.590 | -0.080 |
| | | | 35 | 0.868 | 0.556 | -0.079 |
| | | | 40 | 0.864 | 0.526 | -0.087 |
| | | | 45 | 0.861 | 0.500 | -0.074 |
| 0.084 | 0.497 | 0.419 | 30 | 0.883 | 0.675 | −0.106 |
| | | | 35 | 0.879 | 0.635 | −0.099 |
| | | | 40 | 0.875 | 0.600 | -0.101 |
| | | | 45 | 0.872 | 0.571 | -0.080 |
| 0.105 | 0.488 | 0.406 | 30 | 0.889 | 0.713 | −0.118 |
| | | | 35 | 0.885 | 0.670 | -0.109 |
| | | | 40 | 0.881 | 0.639 | -0.102 |
| | | | 45 | 0.878 | 0.560 | -0.128 |
| 0.133 | 0.473 | 0.394 | 30 | 0.894 | 0.746 | −0.153 |
| | | | 35 | 0.890 | 0.703 | -0.136 |
| | | | 40 | 0.887 | 0.667 | -0.127 |
| | | | 45 | 0.884 | 0.627 | -0.109 |
| 0.158 | 0.456 | 0.386 | 30 | 0.899 | 0.813 | −0.145 |
| | | | 35 | 0.896 | 0.763 | −0.128 |
| | | | 40 | 0.892 | 0.721 | −0.120 |
| | | | 45 | 0.888 | 0.672 | −0.107 |
| 0.191 | 0.441 | 0.368 | 30 | 0.903 | 0.884 | −0.153 |
| | | | 35 | 0.901 | 0.830 | -0.132 |
| | | | 40 | 0.897 | 0.769 | -0.134 |
| | | | 45 | 0.895 | 0.722 | -0.113 |
| 0.228 | 0.421 | 0.352 | 30 | 0.909 | 0.956 | −0.170 |
| | | | 35 | 0.905 | 0.890 | −0.151 |
| | | | 40 | 0.902 | 0.831 | −0.143 |
| | | | 45 | 0.898 | 0.780 | −0.118 |
| 0.259 | 0.403 | 0.338 | 30 | 0.915 | 1.023 | −0.177 |
| | | | 35 | 0.912 | 0.954 | −0.152 |
| | | | 40 | 0.909 | 0.890 | −0.142 |
| | | | 45 | 0.905 | 0.832 | −0.198 |
| 0.303 | 0.378 | 0.318 | 30 | 0.921 | 1.135 | −0.169 |
| | | | 35 | 0.918 | 1.050 | −0.149 |
| | | | 40 | 0.915 | 0.990 | −0.124 |
| | | | 45 | 0.911 | 0.921 | −0.104 |
| 0.349 | 0.357 | 0.294 | 30 | 0.926 | 1.241 | −0.175 |
| | | | 35 | 0.922 | 1.142 | −0.156 |
| | | | 40 | 0.919 | 1.093 | −0.109 |
| | | | 45 | 0.917 | 1.016 | −0.086 |
| 0.400 | 0.325 | 0.275 | 30 | 0.936 | 1.473 | −0.064 |
| | | | 35 | 0.932 | 1.346 | −0.059 |
| | | | 40 | 0.929 | 1.265 | −0.032 |
| | | | 45 | 0.925 | 1.180 | −0.010 |
| 0.455 | 0.295 | 0.250 | 30 | 0.944 | 1.701 | −0.033 |
| | | | 35 | 0.941 | 1.556 | 0.034 |
| | | | 40 | 0.938 | 1.443 | 0.042 |
| | | | 45 | 0.934 | 1.336 | 0.437 |
| 0.519 | 0.264 | 0.219 | 30 | 0.949 | 1.859 | 0.038 |
| | | | 35 | 0.945 | 1.694 | 0.035 |
| | | | 40 | 0.941 | 1.553 | 0.029 |
| | | | 45 | 0.938 | 1.465 | 0.072 |
| 0.586 | 0.222 | 0.192 | 30 | 0.953 | 2.012 | −0.032 |
| | | | 35 | 0.949 | 1.828 | 0.028 |
| | | | 40 | 0.946 | 1.667 | 0.018 |
| | | | 45 | 0.942 | 1.585 | 0.079 |
| 0.667 | 0.183 | 0.150 | 30 | 0.956 | 2.221 | 0.047 |
| | | | 35 | 0.952 | 2.030 | 0.056 |
| | | | 40 | 0.948 | 1.825 | 0.024 |
| | | | 45 | 0.945 | 1.700 | 0.056 |
| 0.776 | 0.129 | 0.094 | 30 | 0.960 | 2.427 | −0.008 |
| | | | 35 | 0.957 | 2.238 | 0.033 |
| | | | 40 | 0.954 | 1.978 | −0.030 |
| | | | 45 | 0.951 | 1.822 | −0.007 |

thermostatic water bath, and the temperature variation was maintained within ±0.1 °C. The time of flow was determined after equilibrating the viscometer with the bath temperature. The accuracy of the viscosity measurements was within ±0.1%. The same procedure was followed for the measurement of viscosities of constituent binary mixtures TBP (1) + benzene (2), TBP (1) + toluene (3), and benzene (2) + toluene (3). The binary results of TBP (1) + benzene (2) are in good agreement with the available experimental work (Rout et al., 1994).

**Table 3. Experimental Viscosities $\eta$ for the Constituent Binary Mixtures TBP (1) + Benzene (2), TBP (1) + Toluene (3), and Benzene (2) + Toluene (3) at Different Temperatures**

| | | $\eta$/mPa.s | | | |
|---|---|---|---|---|---|
| | | 30 °C | 35 °C | 40 °C | 45 °C |
| TBP (1) + Benzene (2) | | | | | |
| $x_1$ | $x_2$ | | | | |
| 0.000 | 1.000 | 0.630 | 0.604 | 0.598 | 0.553 |
| 0.106 | 0.893 | 0.794 | 0.748 | 0.720 | 0.681 |
| 0.200 | 0.800 | 0.984 | 0.910 | 0.865 | 0.816 |
| 0.403 | 0.596 | 1.385 | 1.263 | 1.172 | 1.118 |
| 0.609 | 0.390 | 1.883 | 1.712 | 1.575 | 1.472 |
| 0.805 | 0.195 | 2.341 | 2.108 | 1.927 | 1.792 |
| 0.904 | 0.096 | 2.582 | 2.324 | 2.095 | 1.963 |
| 1.000 | 0.000 | 2.970 | 2.680 | 2.430 | 2.210 |
| TBP (1) + Toluene (3) | | | | | |
| $x_1$ | $x_3$ | | | | |
| 0.000 | 1.000 | 0.523 | 0.499 | 0.478 | 0.458 |
| 0.103 | 0.897 | 0.690 | 0.655 | 0.620 | 0.590 |
| 0.200 | 0.800 | 0.854 | 0.805 | 0.750 | 0.709 |
| 0.400 | 0.600 | 1.366 | 1.250 | 1.160 | 1.075 |
| 0.600 | 0.400 | 1.870 | 1.670 | 1.563 | 1.440 |
| 0.800 | 0.200 | 2.323 | 2.095 | 1.915 | 1.740 |
| 0.900 | 0.100 | 2.575 | 2.322 | 2.110 | 1.918 |
| 1.000 | 0.000 | 2.970 | 2.680 | 2.430 | 2.210 |
| Benzene (2) + Toluene (3) | | | | | |
| $x_2$ | $x_3$ | | | | |
| 0.000 | 1.000 | 0.523 | 0.499 | 0.478 | 0.458 |
| 0.101 | 0.899 | 0.530 | 0.507 | 0.483 | 0.464 |
| 0.200 | 0.800 | 0.539 | 0.518 | 0.491 | 0.471 |
| 0.400 | 0.600 | 0.551 | 0.532 | 0.505 | 0.484 |
| 0.601 | 0.402 | 0.563 | 0.541 | 0.517 | 0.500 |
| 0.800 | 0.200 | 0.576 | 0.556 | 0.529 | 0.517 |
| 0.900 | 0.100 | 0.587 | 0.564 | 0.550 | 0.531 |
| 1.000 | 0.000 | 0.630 | 0.604 | 0.598 | 0.553 |

## Results and Discussion

The viscosity and density data for the ternary mixtures TBP (1) + benzene (2) + toluene (3) at (30, 35, 40, and 45) °C are presented in Table 2. Table 3 shows the viscosity data for the constituent binary mixtures TBP (1) + benzene (2), TBP (1) + toluene (3), and benzene (2) + toluene (3).

The molecules of TBP, one of the components forming the ternaries, are polar and show nonideal behaviors in mixtures. The excess viscosities have been calculated using eq 1 (Singh et al., 1989, 1990) from the viscosity data for the ternary mixtures of TBP (1) + benzene (2) + toluene (3).

$$\Delta\eta = \eta - \sum x_i\eta_i \qquad (1)$$

where $\eta$ is the mixture viscosity, $x_i$ is the mole fraction of component $i$, and $\eta_i$ is the viscosity of pure $i$. Negative values of $\Delta\eta$ in most of the cases are a consequence of the lower viscosity contribution of nonspecific interactions in nonideal mixtures. In the present system $\Delta\eta$ values are mostly negative and positive in a few cases depending on the contribution of component mole fraction. The ternary results were fitted in eq 2, which includes the contribution of each constituent binary as calculated by a three-parameter Redlich−Kister type equation (Redlich and Kister, 1948) along with a ternary contribution term.

$$\eta = \sum_{i}^{3} x_i\eta_i + \sum_{i\neq j}^{3} x_i x_j[A_{ij} + B_{ij}(x_j - x_i) + C_{ij}(x_j - x_i)^2] + x_i x_j x_k A_{ijk}^{*} \qquad (2)$$

**Table 4. Values of Binary Polynomial Constants[a] $A_{ij}$, $B_{Ij}$, and $C_{ij}$ and Additional Ternary Constant $A_{ijk}$* Used in Eq 2 and Root-Mean-Square (rms) Deviations at Different Temperatures**

| system | parameter | 30 °C | 35 °C | 40 °C | 45 °C |
|---|---|---|---|---|---|
| TBP (1) + benzene (2) | $A_{12}$ | −0.3481 | −0.3227 | −0.2868 | −0.1860 |
| | $B_{12}$ | 0.1644 | 0.1604 | 0.1471 | 0.0782 |
| | $C_{12}$ | −0.4011 | -0.4012 | -0.4099 | −0.2461 |
| rms deviation[b] | | 0.0107 | 0.0122 | 0.0149 | 0.0075 |
| TBP (1) + toluene (3) | $A_{13}$ | −0.2435 | −0.2495 | −0.1727 | −0.1408 |
| | $B_{13}$ | 0.0613 | 0.1172 | 0.0727 | 0.0939 |
| | $C_{13}$ | −0.6627 | −0.5126 | −0.5473 | −0.5244 |
| rms deviation[b] | | 0.0167 | 0.0129 | 0.0173 | 0.0177 |
| benzene (2) + toluene (3) | $A_{23}$ | −0.0376 | −0.0281 | −0.0534 | −0.0285 |
| | $B_{23}$ | 0.0777 | 0.0746 | 0.0896 | 0.0286 |
| | $C_{23}$ | −0.0796 | −0.0722 | −0.0993 | −0.0231 |
| rms deviation[b] | | 0.0043 | 0.0046 | 0.0025 | 0.0008 |
| TBP (1) + benzene (2) + toluene (3) | $A_{123}$* | 1.4040 | 1.5882 | 1.3630 | 0.9180 |
| rms deviation[b] | | 0.0951 | 0.0998 | 0.0925 | 0.1036 |

[a] If the constituents of the binary systems are interchanged [e.g., the binary TBP (1) + benzene (2) is changed to benzene (1) + TBP (2)], then the values of $A_{ij}$ and $C_{ij}$ will remain the same. The value of $B_{ij}$ will also remain the same, but its sign will change. [b] rms deviation $= [\sum d_i^2/n]^{1/2}$, where $n$ is the number of observations and $d = [(\eta_{\text{exptl}} - \eta_{\text{calcd}})/\eta_{\text{exptl}}]$.

The constants $A_{ij}$, $B_{ij}$, and $C_{ij}$ were determined by the least-squares method for the constituent binary using the binary results.

The constants $A_{ij}$, $B_{ij}$, $C_{ij}$, and $A_{ijk}$* of eq 2 were determined by the least-squares method for each temperature, and the values are listed in Table 4. The parameters were used as input in eq 2 for calculating root-mean-square deviations as listed in Table 4.

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