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## Abstract

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# INTERACTION OF TRIBUTYL PHOSPHATE (TBP) AND A TBP SOLVATE WITH DILUENTS

*(Presented by Academician A. N. Frumkin, 17 VII 1963)*

The aim of the present work is to investigate the interactions of TBP and a TBP solvate with diluents by studying the activity coefficients of binary systems.

The vapor pressure of the volatile diluent and its activity coefficient were determined as
$\gamma_1 = P_1/P_{1\ \mathrm{id}} = P_1/P_1^0 N_1$, where $P_1^0$ and $N_1$ are the vapor pressure of the pure diluent and its mole fraction. The activity coefficient of the nonvolatile component, TBP ($\gamma_2$) or the TBP solvate of uranyl nitrate ($\gamma_3$), was calculated from the Gibbs–Duhem equation. Vapor pressures were measured by the isoteniscope method ([1]) at temperatures of 25, 37.5, and 50°. The values found for the activity coefficients are shown in Fig. 1. It turned out that systems with hexane exhibit positive nonideality, while all the others exhibit negative nonideality (especially strong in the TBP–chloroform system). These results agree with the conclusions of ([2,3]); however, it turned out that the solutions are not regular: the quantities $a = \ln\gamma_1/N_2^2$ and $b = \ln\gamma_1/\varphi_2^2$ (where $\varphi$ is the volume fraction) depend on concentration* (approximately linearly), i.e.
$\ln\gamma_1 = N_2^2(a_1 - a_2N_2)$;
$\ln\gamma_2 = N_1^2[(a_1 - 3a_2/2) + a_2N_1]$, or
$\ln\gamma_1 = \varphi_2^2(b_1 - b_2\varphi_2)$;
$\ln\gamma_2 = \varphi_1^2[(b_1 - 3b_2/2) + b_2\varphi_1] \cdot V_2/V_4$.
The values found for the constants are given in Table 1.

One of the causes of the nonregularity of the solutions, and partly a cause of the negative nonideality, may be an athermal effect—the increase in the entropy of the solution due to the substantial difference in the sizes of the molecules (molar volumes $V$) of the components (see Table 1). Taking this effect into account, the equation of the regular solution will be

$$\ln\gamma_1 = \ln\gamma_{1\ \mathrm{atherm}} + b'\varphi_2^2, \tag{1}$$

where $\gamma_{1\text{atherm}}$ is the athermal activity coefficient:

$$\gamma_{1\text{atherm}} = \frac{[(N_1 + N_2 r)/(N_1 + N_2 q)]^{z/2}}{N_1 + N_2 r};$$

$r \approx V_2/V_1$; $z$ is the coordination number of the lattice; $q = r - 2(r-1)z$ (6). At $z = \infty$

$$\ln \gamma_{1\text{atherm}} = \ln \varphi_1/N_1 + \varphi_2(1 - 1/r).$$

A comparison of $\gamma_{\text{atherm}}$ at $z = 6$ and $z = \infty$ (according to Flory) with the experimental data (Fig. 1) shows that the athermal effect is the principal cause of the negative nonideality of all the systems studied*, with the exception of the TBP—chloroform system, where there is a comparatively strong chemical interaction. In addition, when differences in molecular sizes are taken into account, the solutions are closer to regular ones.

**Table 1**

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* This fact does not introduce any qualitative changes into the theory (3), which explains the action of diluents, but it leads to a complication of the equations for the complex $\gamma_T^2/\gamma_c = \gamma_2^2/\gamma_3 = \alpha/\alpha_{\text{id}}$. However, expression (3.10) in (3), which characterizes the deviation of the distribution from ideal at high dilution, $N_2 = N_3 \to 0$ (indices 2 and 3 denote TBP and the solvate), practically does not change. We obtain $\ln \alpha/\alpha_{\text{id}} = \ln \gamma_2^2(0)/\gamma_3(0) = 2A_{21} - A_{31} + A_{32} = 2B_{21} - B_{31} + B_{32}$, where $A_{21}, A_{31} = a_1 - a_2/2$, $B_{21} = (b_1 - b_2/2)V_2/V_1$. According to Table 1, the numerical values $\gamma_2^2(0)/\gamma_3(0) \sim \alpha/\alpha_{\text{id}}$ for the systems with $CCl_4$, hexane, $C_6H_6$, and $CHCl_3$ are 0.99, 1.55, 2.42, and 0.017, respectively, which correctly characterizes the influence of diluents on extraction. (The effective extraction constants $\overline{K}_C = K_C\gamma_2^2/\gamma_3$ for macroquantities of uranium in 10% TBP at $x_U \to 0$ and dilutions with $CCl_4$, $C_6H_{14}$, $C_6H_6$, and $CHCl_3$, respectively, are 55, 113, 120, and 0.9; and when referred to mole fractions, $\overline{K} = \overline{K}_N = \overline{K}_C \sum n = 525, 820, 1240$, and 10.3, whence $\overline{K}/K_{CCl_4} = \alpha/\alpha_{CCl_4}$ equals 1.55, 2.35, and 0.02. Similarly, from the data of (3) on extraction of microquantities, we find $\alpha/\alpha_{CCl_4} = 2.0; 2.4$; and 0.025.) The conclusion of (3) is confirmed: the increase (in comparison with $CCl_4$) in extraction when hexane is used is due to the positive nonideality of the TBP—hexane solution ($\gamma_T^2 > \gamma_c$), while when benzene is used it is due to a comparatively strong solvate—benzene interaction, as a result of which $\gamma_c < \gamma_T^2$.

| No. | System | $a_1$ | $a_2$ | $b_1$ | $b_2$ | $\gamma_1(0)$ | $\gamma_2(0)^*$ | $b'$, $z = 6$ | $b'$, $z = \infty$ | $V_2/V_1^{***}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Hexane – TBP | – | – | 0.90 | 0.40 | 1.65 | 4.36 | 0.69 | $0.78^{**}$ | 2.1 |
| 2 | $CCl_4$ – TBP | −1.45 | −0.99 | 0.0 | 0.53 | 0.63 | 0.38 | −0.20 | −0.13 | 2.83 |
| 3 | $C_6H_6$ – TBP | −1.46 | −1.02 | −0.12 | 0.38 | 0.65 | 0.38 | −0.16 | −0.05 | 3.06 |
| 4 | $CHCl_3$ – TBP | −7.80 | −5.60 | −0.04 | 2.56 | 0.08 | 0.010 | | | 3.4 |
| 5 | Hexane – solvate | – | – | 0.675 | 0.275 | 1.49 | 12.3 | 1.0 | 1.15 | 4.65 |
| 6 | $CCl_4$ – solvate | −3.00 | −2.20 | – | – | 0.45 | 0.15 | −0.076 | – | 6.26 |
| 7 | $C_6H_6$ – solvate | −4.40 | −3.20 | – | – | 0.30 | 0.060 | −0.35 | −0.20 | 6.78 |
| 8 | $CHCl_3$ – solvate | – | – | 0.00 | 1.29 | 0.28 | 0.006 | −0.39 | −0.24 | 7.5 |

* The accuracy of the data worsens as the concentration of diluent decreases, which leads to inaccuracy in the calculation of $\gamma_2$ at $N_2 \to 0$. To check the method ($^3$), we calculated $\gamma_{\text{TBP}}$ from data on its solubility in water ($^4$). For the system with $C_6H_6$, $\gamma_2(0) = 0.55$ was found; for the system with hexane $\gamma_2(0) = 4 \div 4.2$. The calculation no longer gives the data 0.38 and 4.36, which is satisfactory. The accuracy of determining $\gamma_1(0)$ and $\gamma_2(0)$ for solvates is considerably lower.
** The corresponding values of the solubility parameter are $\delta_{\text{TBP}} = 9.2$ and $\delta_{\text{solv}} = 9.75$.
*** $V_{\text{TBP}} = 274$ cm$^3$/mol; $V_{\text{solv}} = 606$ cm$^3$/mol.

However, along with the athermal effect, in systems No. 2–4 and No. 6–8 a “true” negative nonideality is observed: the values of $b'$ are negative (Table 1), the residual activity coefficients $\gamma' = \gamma_{\text{exp}}/\gamma_{\text{atherm}}$ are less than unity, and the heat effect found experimentally ($^3$) and calculated approximately (to an accuracy of ±30%) from the present data is negative (Fig. 2). Consequently, molecules of both TBP and the solvate interact more strongly with $C_6H_6$, $CCl_4$, and $CHCl_3$ than with one another, whereas in the presence of only van der Waals forces the relation of interactions is the reverse (at least for spherical molecules), and positive nonideality is observed, as in systems with hexane.

The comparatively strong TBP—$CHCl_3$ interaction (interaction constant $A = aRT = 2.8 \div 4$ kcal; from the heat effect $A = 4h^E_{\text{max}} = 3$ kcal ($^3$) $\div$ 4 kcal (Fig. 2)) leaves no doubt as to the presence of a hydrogen bond ($^3$,$^5$ ), which agrees with the notion of the properties of $CHCl_3$. The disappearance of the strong interaction when TBP is replaced by the solvate, i.e., when the phosphoryl oxygen is blocked by the metal, indicates that the hydrogen bond with chloroform is formed through the phosphoryl oxygen of TBP. It is much more difficult to explain the interaction with such nonpolar molecules as $C_6H_6$ and $CCl_4$. It is possible that there is an interaction of the $\pi$-electrons of benzene with the oxygen in PO or COP, analogous to the interaction of benzene with iodine and chlorine ($^8$). The bonding of TBP with $CCl_4$ may be explained by the interaction of the phosphoryl oxygen with the vacant $3d$-orbital of chlorine ($^9$). The increase in negative nonideality when TBP is replaced by the solvate may be explained by interaction with the oxygen of the uranyl group or with the ether oxygen.

* Closest to an athermal solution is benzene—TBP, for which the smallest heat effect is observed, $h^E \approx 160N_1N_2$ cal.

Negative nonideality can also be described as the formation of compounds. The corresponding constants $K$ can be found from data on activity coefficients: in the chemical treatment, in the absence of association, the latter are equal to the fraction of monomer (7); $\gamma_A = N_{A1}/N_A$ ($N_{A1}$ is the concentration of monomer, $N_A$ is the analytical concentration of the component, $n_{A1}$ and $n_A$ are the same in mol/l). On the other hand, $N_{A1}$ can be expressed, by means of the law of mass action, through the constant $K$.

The calculation procedure will be set out for the case in which several compounds are formed: $A_1B$, $A_2B, \dots, A_iB$, with equilibrium constants $K_1, K_2, \dots, K_i$ (so that the mole fraction of the corresponding compounds will be $N_{ci} = K_iN^i_{A1}N_{B1}$). Let us denote the effective fractions of the compounds by
$\psi_i = in_{ci}/(n_A + n_B)$; $\psi = \psi_1 + \psi_2 + \cdots + \psi_i$,
$\underline{\psi} = \psi_1 + \psi_2/2 + \psi_3/3 + \cdots$. Since

Figure 1 and Figure 2 graphs: Activity coefficients and excess thermodynamic functions.

**Fig. 1.** Activity coefficients in the systems TBP—diluent (A) and solvate—diluent (B) at 25°. Curves with points—$\gamma$ of the diluent; without points—$\gamma_2$; $a$

$-\gamma$ of an athermal solution ($z = 6$; for $z = \infty$, for systems 2, 3, 6, 8, $\gamma_{\text{atherm}}$ is close to $\gamma_{\text{expt}}$); $b$–$\gamma_2$ at high dilution (scale at right). The number at the curve corresponds to the system in Table 1. Diluents: –hexane, –$CCl_4$, –$C_6H_6$, –$CHCl_3$.

**Fig. 2.** Excess thermodynamic functions of several systems: free energy (A), enthalpy (B), and entropy (C). For notation see Fig. 1.

$$n_{A1} = n_A - \sum i n_{ci}, \qquad n_{B1} = n_B - \sum n_{ci}, \qquad \sum n = (n_A + n_B)(1 - \psi),$$

the mole fractions of the monomers and compounds are

$$N_{A1} = \frac{n_{A1}}{\sum n} = \frac{N_A - \psi}{1 - \psi}; \qquad N_{B1} = \frac{N_B - \bar{\psi}}{1 - \psi}; \qquad N_{ci} = \frac{\psi_i}{i(1 - \psi)}. \tag{2}$$

Taking into account that $\sum N_{ci} = N_{B1} N_{A1} \sum K_i N_{A1}^{i-1}$, and, according to (2), $\sum N_{ci} = \bar{\psi}/(1 - \psi)$, we obtain the equation for calculating the constants

$$K_1 + K_2 N_{A1} + K_3 N_{A1}^2 + \cdots = \bar{\psi}(1 - \psi)/(N_A - \psi)(N_B - \bar{\psi}) = f, \tag{3}$$

where $N_{A1} = N_A \gamma_A$, while the quantities $\psi$, $\bar{\psi}$, and $f$ are determined from the values of the coefficien-

activities:

$$\psi = \frac{N_A(1 - \gamma_A)}{1 - N_A \gamma_A}; \qquad \bar{\psi} = N_B[1 - \gamma_B(1 - \psi)]; \qquad f = \frac{1 - (N_A \gamma_A + N_B \gamma_B)}{N_A N_B \gamma_A \gamma_B}. \tag{4}$$

The determination of $K_i$ from $f(N_{A1})$ can be carried out by the usual methods for calculating complex-formation constants ($K_1 = f(0)$, etc.). If any one compound $A_i B$ is formed, then $f/N_{A1}^{i-1}$ must be constant. In particular, if $f = \text{const}$, then only the compound AB is formed. In this case it must be that $\psi = \bar{\psi} = \psi_1$; calculation of $\psi$ from the values of $\gamma_A$ and $\gamma_B$ must give coincident results: $\psi_A = \psi_B$, and $f(N) = f(0)$, so that

$$K_1 = f = (1 - \gamma_A)/\gamma_A(1 - 2N_A + N_A^2 \gamma_A) = f(0) = [1 - \gamma_A(0)]/\gamma_A(0), \tag{5}$$

where $\gamma_A(0)$ is the value of $\gamma_A$ at $N_A = 0$. The last of relations (5) is also valid when several compounds are formed, but in the case of formation of only AB it must be valid for both components; consequently, $K_1 = [1 - \gamma_B(0)]/\gamma_B(0)$ and $\gamma_A(0) = \gamma_B(0)$, i.e., the solution must be symmetrical. For this reason, the equations for regular solutions with moderate negative nonideality are practically equivalent to the chemical equilibrium equations describing the formation of the compound AB (³). The relation between the nonideality constant $A_{12}$ and the equilibrium constant in this case is as follows: since $\ln\gamma_A(0) = \ln\gamma_B(0) = A_{12}/RT$, then, taking (5) into account,

$$\gamma(0) = 1/(1+K); \qquad A = RT\ln(1+K); \qquad K = \exp(-A/RT) - 1. \tag{6}$$

An approximate* calculation of the formation constants of compounds in the systems studied was carried out from equations (3)–(4). In order to exclude the influence of the athermal effect, the values of $f$ were calculated not from the experimental values of $\gamma$, but from the residual activity coefficients $\gamma' = \gamma_{\text{exp}}/\gamma_{\text{atherm}}$. In most cases $\gamma'_A(0)$ and $\gamma'_B(0)$, $\psi_A$ and $\psi_B$ did not coincide; $f$ depended on concentration (see Table 2), which corresponded to the formation, along with AB, of the compound $A_2B$ (A is the diluent).

Table 2

| System No. | $f(0)$ | $f(1)$ | $K_1$ | $K_2$ | Max. yield of compounds, $\psi_{\max}$ | Min. fraction of monomer, $N'_{A1}/N_A = \gamma'_A(0)$ |
|---:|---:|---:|---:|---:|---:|---:|
| 2 | 0.1 | 0.26 | 0.1 | 0.16 | 0.0422 | 0.9 |
| 3 | 0.05 | 0.24 | 0.05 | 0.19 | 0.0655 | 0.97 |
| 4 | 6 | 22 | 6 | 16 | 0.375 | 0.117 |
| 6 | 0.0 | 0.4 | 0.0 | 0.4 | 0.05 | 0.95 |
| 7 | 0.91 | – | 0.91 | – | 0.137 | 0.523 |
| 8 | 0.5 | 6.0 | 0.5 | 1.0 | 0.187 | 0.706 |

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* The possibility of association of TBP, nonideality of the solution of monomers —compounds, etc., was not taken into account.

*Note: Figure translations are in progress. See original paper for figures.*