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THERMODYNAMICS OF EXTRACTION OF NITRIC ACID BY TRI-n-BUTYL PHOSPHATE--HYDROCARBON DILUENT SOLUTIONS

3. Comparison of Literature Data

Wallace Davis, Jr.

ABSTRACT

Some of the published data on the extraction of nitric acid from aqueous solutions, containing ≤ 5 M acid, by tributyl phosphate-hydrocarbon diluent solutions were tested for their agreement with a mathematical description presented in Part 1. In all cases the agreement of the literature data with this description ranged from adequate to very good, thereby adding support to the interpretation of the parameters of the equation in terms of the equilibrium constant, K_1^c, for the extraction reaction and the two activity coefficients y_T' and y_{TN}'. The form of the mathematics suggests that TBP and TBP·H_2O are indistinguishable in their reaction with HNO_3 and that y_T' is an approximate mean molar activity coefficient of these two in the water-saturated system; similarly, y_{TN}' is an approximate mean molar activity coefficient of the two species TBP·HNO_3 and TBP·HNO_3·H_2O. The quantity $K_1^c y_T'$ has a value of ~1.5 in molar units for diluent-free TBP; its extrapolated value in the pure diluent Amsco 125-82, or odorless kerosene, is ~0.23, while its value in n-hexane is ~0.27.

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INTRODUCTION

The purpose of this report is to summarize literature data on the extraction of nitric acid from aqueous solutions by tributyl phosphate-hydrocarbon diluent solutions in terms of equations similar to those previously developed. In the first paper (1) of this series data were presented for the extraction of aqueous nitric acid, in the 0-5 M concentration range, by tributyl phosphate-Amsco 125-82 solutions and a representation of these data by eqs. 1 and 2, the first of which applies for a constant ratio (diluent)/(TBP), the second of which is completely general:

$$\log \frac{(HNO_3)^m_{org}}{\left[HNO_3\right]^m_{aq} \left\{3.75493-(HNO_3)^m_{org}\right\}} = A + B\,(HNO_3)^m_{org} \qquad (1)$$

$$\log \frac{(HNO_3)^m_{org}}{\left[HNO_3\right]^m_{aq} \left\{3.75493-(HNO_3)^m_{org}\right\}} = \log \left\{0.2282 + 1.2397\,(Y^o_{H_2O} + Y^o_{TBP})\right\}$$

$$-0.4393\,(HNO_3)^m_{org} \left(Y^o_{H_2O} + Y^o_{TBP}\right)^{1/2} \qquad (2)$$

In these and subsequent equations square brackets refer to activities, parentheses to concentrations, aq and org to aqueous and organic phases, and the superscripts m and c to molal and molar scales, respectively; Y^o_{TBP} and $Y^o_{H_2O}$ are the mole fractions of TBP and H_2O in water-saturated TBP-Amsco 125-82 solutions.

As in the previous report (1), the scope of this work is limited to aqueous solutions containing less than about 5 M HNO_3. Literature data analyzed are those of Codding, Haas, and Heumann (2), Geary (3), Healy and Brown (4), Olander, Donadieu, and Benedict (5), Savolainen (6), and Damiani and Fattore (7). The diluent used in references 2, 3, and 4 was of the odorless mineral spirits type; that of references 5 and 6, n-hexane. Damiani and Fattore used diluent-free TBP.

DATA ANALYSIS

Literature data cannot generally be analyzed in terms of the molal eqs. 1 and 2 because of lack of density and water content of the organic phase. However, they can be analyzed in terms of the approximate molar eqs. 3 and 4 if the simplifying assumption is made that the molar volume of nitric acid in the organic phase is constant, at 42.5 ml/mole in the present calculations, and that dissolved water in the organic phase has a molar volume of zero.

$$\log \frac{(HNO_3)^c_{org}}{[HNO]^c_{aq}\left\{C' - (HNO_3)^c_{org}\right\}} = A + B\,\frac{(HNO_3)^c_{org}}{C'} \tag{3}$$

$$= \log\left\{B_1 + B_2\left(Y^o_{H_2O} + Y^o_{TBP}\right)\right\} + B_3\left(Y^o_{H_2O} + Y^o_{TBP}\right)^{1/2}\frac{(HNO_3)^c_{org}}{C'} \tag{4}$$

The simplifying assumptions concerning calculation of the approximate stoichiometric concentration, C', of TBP in the organic phase corresponds to

$$C' = (TBP_s)^c_{dry} \left\{1-0.0425\,(HNO_3)^c_{org}\right\} \approx \frac{(TBP_s)^c_{dry}}{1 + 0.0425\,(HNO_3)^c_{org}} \tag{5}$$

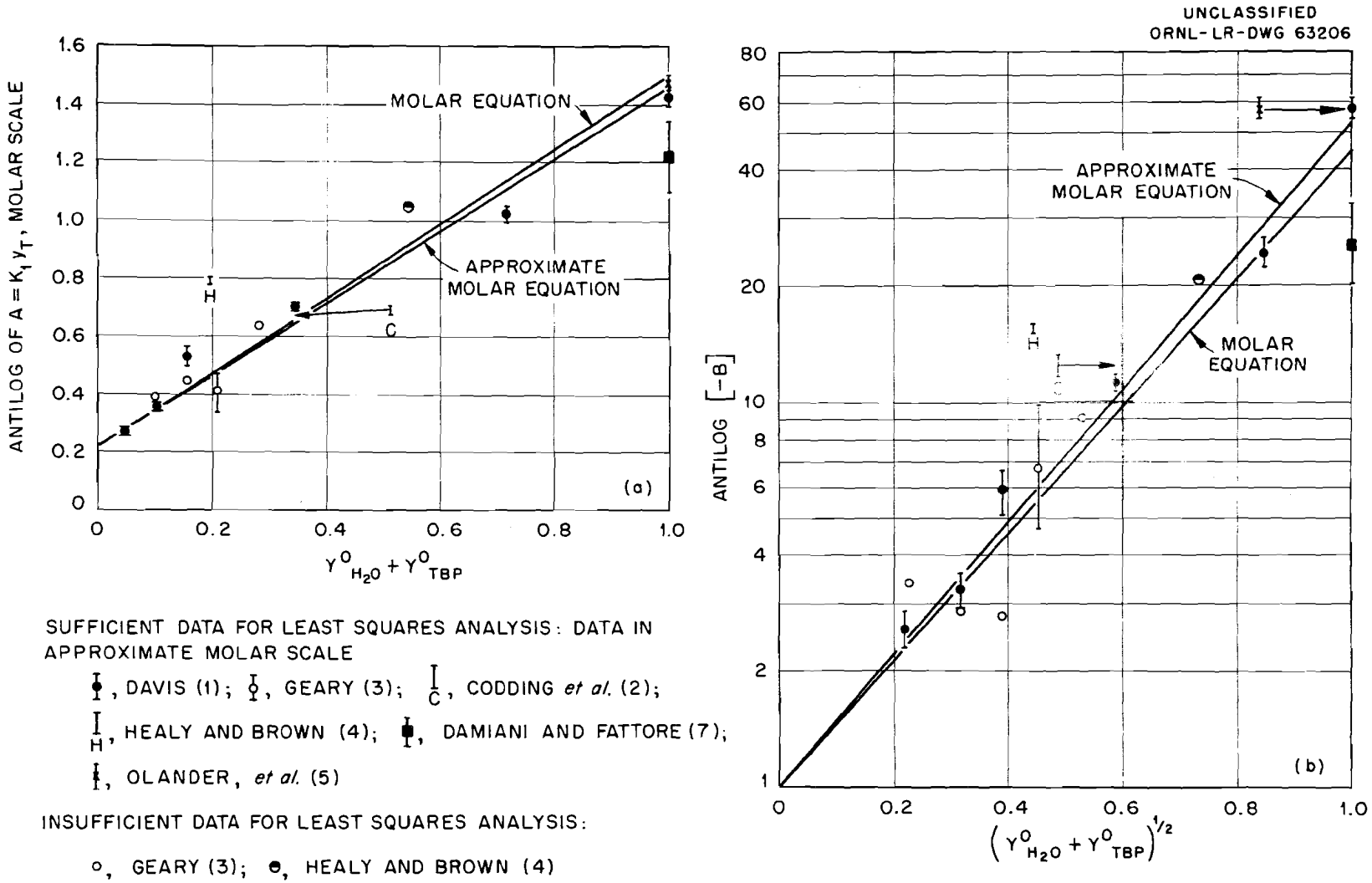
where $(TBP_s)^c_{dry}$ is the stoichiometric molar concentration of TBP in dry, acid-free diluent solutions.

To determine the magnitude of errors introduced by the above assumptions, previous data (1) were fitted to eqs. 4 and 5 and also to the accurate molar eq. 6,

$$\log \frac{(HNO_3)^c_{org}}{\left[HNO_3\right]^c_{org}\left\{(TBP_s)_{org} - (HNO_3)^c_{org}\right\}} = \log\left\{B_1 + B_2\left(Y^o_{H_2O} + Y^o_{TBP}\right)\right\}$$

$$+ B_3\left(Y^o_{H_2O} + Y^o_{TBP}\right)^{1/2} \frac{(HNO_3)^c_{org}}{(TBP_s)} \tag{6}$$

where (TBP_s) is the stoichiometric concentration of TBP in the organic phase calculated from density, water, and acid contents and the measured weight ratio W_{Dil}/W_{TBP}. Although different values of constants B_1, B_2, and B_3 are obtained for eqs. 4 and 6 (Table 1), the differences are small and the standard ranges overlap. Figure 1 summarizes the data of reference 1 as well as some of the literature data, discussed below, in terms of eqs. 4 and 6.



SUFFICIENT DATA FOR LEAST SQUARES ANALYSIS: DATA IN APPROXIMATE MOLAR SCALE

DAVIS (1); GEARY (3); C, CODDING *et al.* (2);

H, HEALY AND BROWN (4); DAMIANI AND FATTORE (7);

OLANDER, *et al.* (5)

INSUFFICIENT DATA FOR LEAST SQUARES ANALYSIS:

GEARY (3); HEALY AND BROWN (4)

Fig. 1. Correlation of Antilog of (a) Parameter A, eq. 3, with the Sum of the mole Fractions of H_2O and TBP in H_2O-Saturated TBP-Diluent Phase; (b) Parameter B, eq. 3, with the Square Root of the Sum of the mole Fractions of H_2O and TBP in the H_2O-Saturated Acid-Free TBP-Diluent Phase. Lines for Molar eq. 6 and Approximate Molar eq. 4 Represent Fit of the Data of Davis to These Equations.

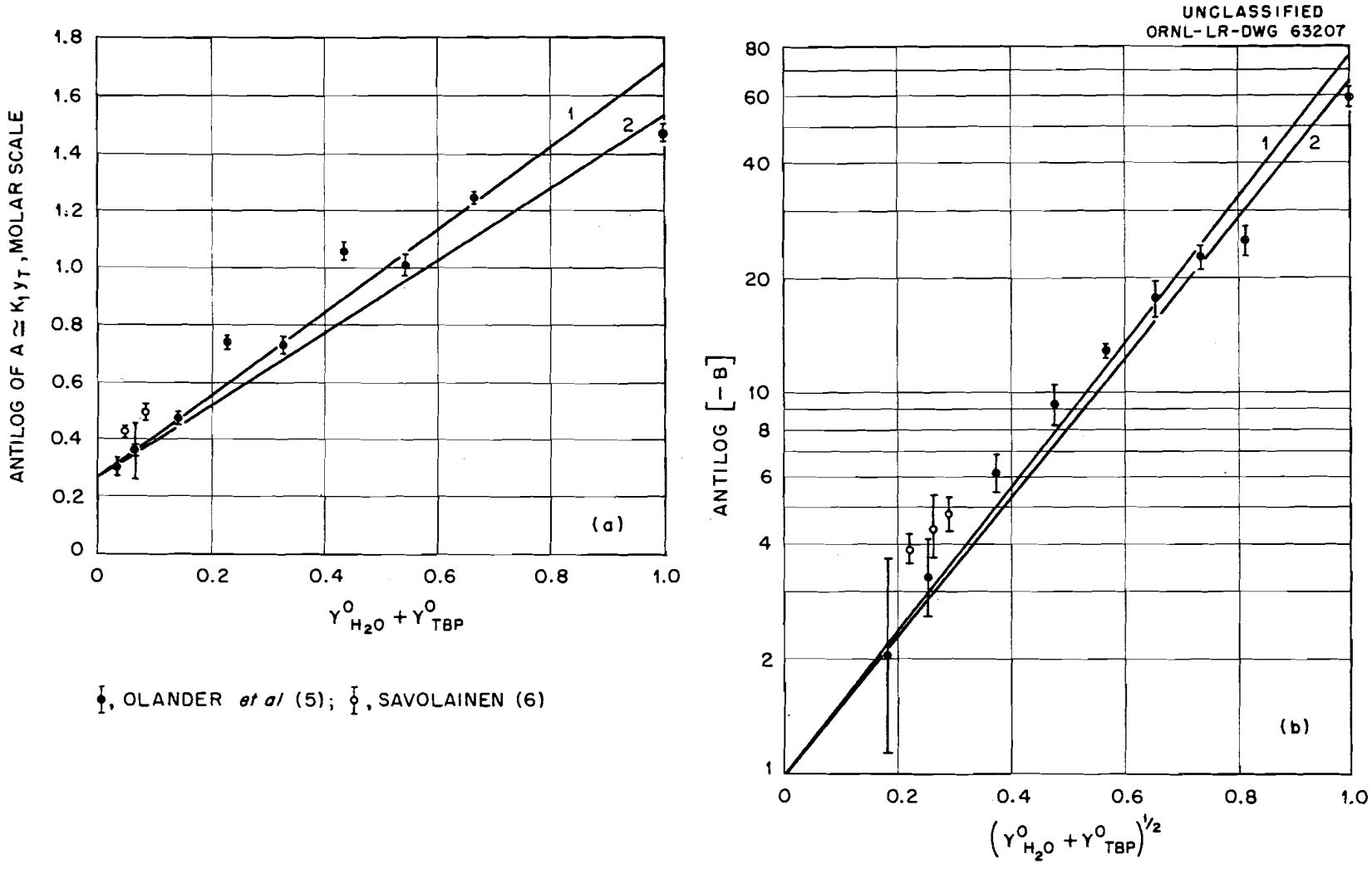
Table 1. Parameters of Equations 4 and 6

Reference	Diluent	B_1	σ_{B_1}	B_2	σ_{B_2}	B_3	σ_{B_3}	$\sigma_{\log G1}$
(1), eq. 6	Amsco 125-82	0.2295	0.0076	1.2470	0.0405	-1.6497	0.0370	0.0558
(1), eq. 4	Amsco 125-82	0.2396	0.0078	1.1920	0.0401	-1.7189	0.0385	0.0558
(5), eq. 4	n-Hexane	0.2767	0.0125	1.4544	0.0550	-1.8788	0.0468	0.0549
(5), eq. 4*	n-Hexane	0.2717	0.0082	1.2703	0.0410	-1.8164	0.0348	0.0368

*Data for 30, 50, and 70 vol % TBP omitted in this fit.

Only one other extensive set of data is available for checking the validity of eq. 4 over the full range of TBP concentration in a hydrocarbon diluent, namely that of Olander, Donadieu, and Benedict (5) in which the diluent was n-hexane. Values of antilogs of A and -B, and their standard deviations, obtained by fitting the data of these authors to eq. 3 are shown in Fig. 2, which also contains the straight lines corresponding to fitting these data to eq. 4. Values of the constants B_1, B_2, and B_3 (Table 1) applying to these data are only slightly different from corresponding constants for the data of Davis (1). The degree of disagreement may be seen from the sum $B_1 + B_2$, which corresponds to extraction by diluent-free TBP. This sum is 1.54-1.73 for the data of Olander, Donadieu, and Benedict (5) and 1.43 for the data of Davis (1). The corresponding quantity, i.e., antilog A of eq. 3, obtained from the data of Damiani and Fattore (7) on the TBP extraction of nitric acid is 1.23 (Fig. 1). Each value was obtained by using, in eq. 5, $(TBP_s)^o_{dry} = 3.652$ moles/liter, which was calculated from a dry TBP density of 0.9725 g/ml at 25°C obtained in this laboratory (9) with purified, molecularly distilled TBP.

Beyond the data of references 1 and 5, there are no studies of extraction of nitric acid by TBP-hydrocarbon diluent solutions over a wide range of TBP/diluent ratios. Thus, although they can be analyzed in terms of the approximate eqs. 3 and 5, they cannot be used to obtain, independently, the three parameters of eq. 4 or 6. In addition the solubility of water in the acid-free TBP-diluent solution is frequently unavailable. To extend the potential utility of eq. 4, the available water solubility data were correlated (9) in terms of the variable $Y^o_{H_2O} + Y^o_{TBP}$ (Fig. 3). From the curve drawn through the data of Olander, Donadieu, and Benedict (5) for n-hexane, values



⊥, OLANDER *et al* (5); ⊥, SAVOLAINEN (6)

Fig. 2. Correlation of Antilog of (a) Parameter A, eq. 3, With the Sum of the mole Fractions of H_2O and TBP in the H_2O-Saturated TBP-*n*-Hexane Organic Phase; (b) Parameter B, eq. 3, With the Square Root of the Sum of the mole Fractions of H_2O and TBP in the H_2O-Saturated Acid-Free TBP-*n*-Hexane Phase. Lines Represent Fit of the Data of Olander *et al* to eq. 4; Line 1, All Data; Line 2, Data at 30, 50, and 70 % Omitted.

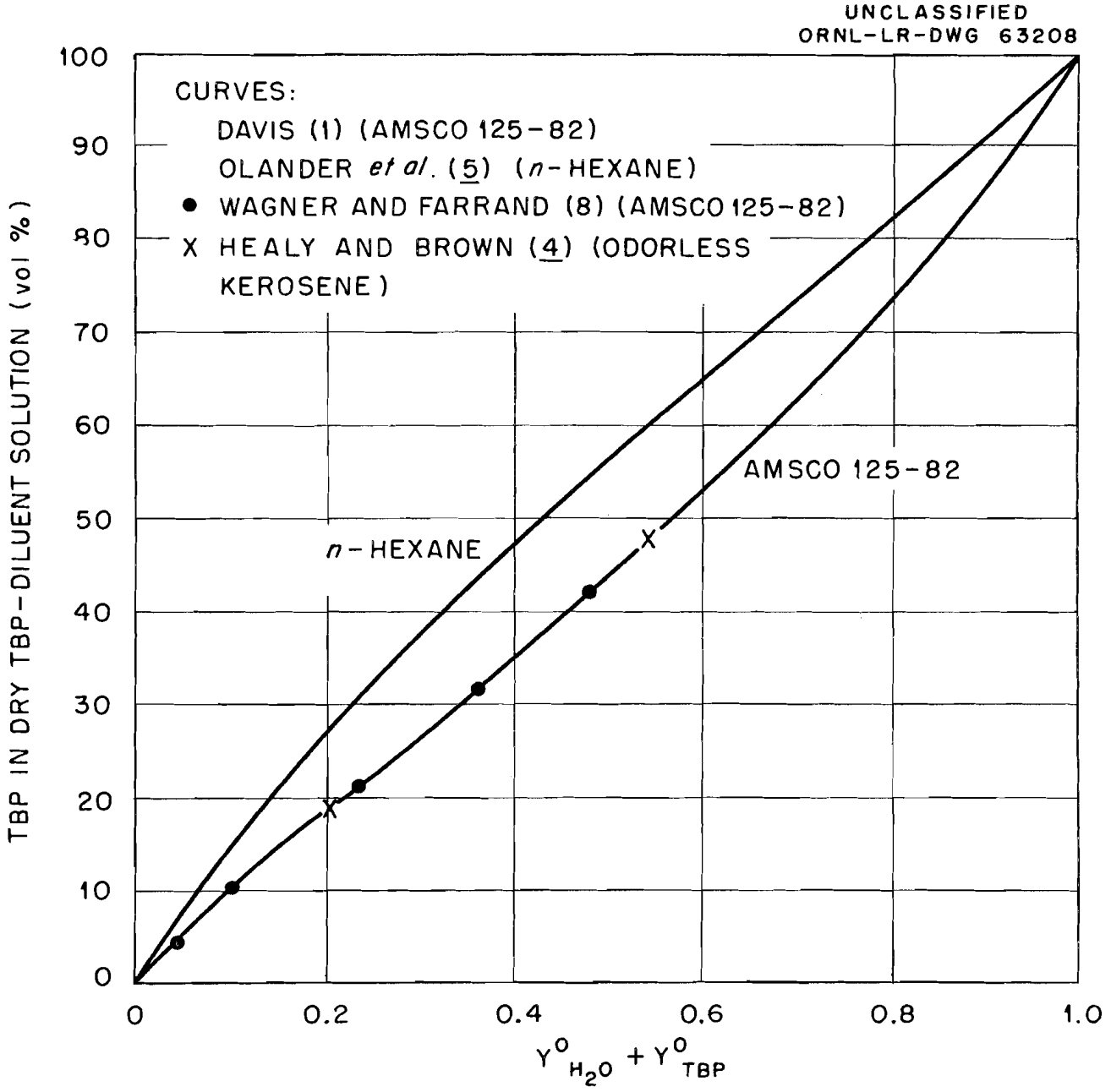


Fig. 3. Correlation of mole Fractions of H_2O and TBP in H_2O-Saturated Organic Phase with Concentration of TBP in Dry TBP-Diluent Solution. Amsco 125-82 and Odorless Kerosene Assumed to Have Molecular Weight of 185.0.

of the parameter $Y^o_{H_2O} + Y^o_{TBP}$ for use with data of Savolainen (6) were obtained and from the curve drawn through the data of Davis (1) for Amsco 125-82 values of this parameter for use with odorless kerosene diluents were obtained. Water solubility data of Healy and Brown (4) agree very closely with those of Davis (1) and of Wagner and Farrand (8), who also used Amsco 125-82, indicating the similarity of Amsco 125-82 and the odorless kerosene used in England. Plots of the antilogarithms of A and -B, including standard deviations, against the values $Y^o_{H_2O} + Y^o_{TBP}$ obtained from Fig. 2 are summarized in Figs. 1 and 2.

DISCUSSION

On the basis of normal experimental errors and occasional, unexpected analytical biases, eqs. 3-5 well describe a majority of the literature data on the extraction of nitric acid by TBP-hydrocarbon diluent solutions provided the aqueous nitric acidity is equal to or less than ~5 M. The variables of these equations include the generally unmeasured quantity $(H_2O)_{org}$ or $Y^o_{H_2O}$, in addition to the usually measured variables $(HNO_3)_{aq}$ and $(HNO_3)_{org}$. One interpretation of these results is that HNO_3 reacts with both TBP and TBP·H_2O to form TBP·HNO_3 and TBP·HNO_3·H_2O. Depending on the concentration of TBP in the diluent, the water content of the organic phase may decrease, remain constant, or increase (1). Since the water concentration does not appear as a variable except in calculation of the TBP concentration, the presence of water in the organic phase does not appear to affect the reaction of HNO_3 with TBP or TBP·H_2O. Thus, at the lower acidities, the extraction process is equivalent to the reaction

$$\left.\begin{array}{l} TBP_{org} \\ + \\ TBP{\cdot}H_2O_{org} \end{array}\right\} + HNO_{3_{aq}} \longrightarrow \left\{\begin{array}{l} TBP{\cdot}HNO_{3_{org}} \\ + \\ TBP{\cdot}HNO_3{\cdot}H_2O_{org} \end{array}\right. \tag{7}$$

while in the region 2-5 M HNO_3 the reaction

$$TBP{\cdot}H_2O_{org} + 2HNO_{3_{aq}} \longrightarrow TBP{\cdot}2HNO_{3_{org}} + H_2O_{aq} \tag{8}$$

becomes important.

By analogy with a previous suggestion (1), the quantity A of eq. 3 can be interpreted as

$$K_1^c y_T' = \text{antilog } A = B_1 + B_2 \left(Y^o_{H_2O} + Y^o_{TBP} \right) \tag{9}$$

while the quantity B can be interpreted as

$$\log y_{TN}' = B \frac{(HNO_3)^c_{org}}{C'} = B_3 \left(Y^o_{H_2O} + Y^o_{TBP} \right)^{1/2} \frac{(HNO_3)^c_{org}}{C'} \tag{10}$$

In these equations y_T' is an approximate mean molar activity coefficient of the species TBP and TBP·H_2O, y_{TN}' is approximate mean molar activity coefficient of the species TBP·HNO_3 and TBP·HNO_3·H_2O; the constants B_i are given in Table 1. The standard states correspond to $y_T' = 1$ for anhydrous, acid-free TBP and $y_{TN}' = 1$ for the nitric acid complexes of TBP and TBP·H_2O infinitely dilute in the hydrocarbon diluent. Therefore the sum $B_1 + B_2$ is independent of diluent, and has a value of ~1.5 (moles

HNO_3 org/mole "TBP")/(mole HNO_{3aq}/liter)^2. The quantity B_3 has about the same value for n-hexane and for hydrocarbon fractions of the Amsco 125-82 type. The effect of diluent is more associated with the solubility of water in the TBP-diluent solution (Fig. 3).

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