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The Aggregation and Interactions of Tributyl Phosphate and Tricaprylmethylammonium Nitrate in Hexane by Osmometry

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Abstract

The dimerization constant of tributyl phosphate in hexane has been determined by vapor pressure osmometry and was found to be in agreement with the values in the literature obtained by infrared spectroscopy. The tributyl phosphate–tricaprylmethylammonium nitrate extractants strongly associate with each other. The addition of varying concentrations of tricaprylmethylammonium nitrate to a constant concentration of tributyl phosphate results in a linear relationship of the average degree of aggregation of the mixture with the initial concentration of tricaprylmethylammonium nitrate. Varying the tributyl phosphate concentration results in a series of straight lines intersecting at one point. Extrapolation of the tributyl phosphate concentration to zero allows estimation of aggregation constants of tricaprylmethylammonium nitrate in hexane by the linear regression technique.

INTRODUCTION

In liquid–liquid extraction chemistry, an understanding of the interactions between the components of the extraction system is important in clarifying the processes which take place in solution and in correctly interpreting the phenomena observed. This is especially true in a synergic liquid–liquid extraction system.

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Liquid–liquid extraction of tributyl phosphate (TBP) and some quaternary amine synergic systems have been reported in the literature (*1–4*). The TBP–Aliquat 336 synergic system has been used in the separation of Sm and Gd (*1*). In this paper is reported new experimental data on the interactions of TBP and tricaprylmethylammonium nitrate (TCMAN). A method to calculate the dimerization constant of TBP using data from osmometry measurements is also discussed. The results obtained by this method are in good agreement with data from infrared spectroscopy (*5, 6*).

The aggregation equilibrium constants of TCMAN in hexane have not been reported in the literature because of its very low solubility. Their aggregation equilibrium constants are reported in this work by treating the data from the study of the various degrees of aggregation of the TBP-TCMAN system.

EXPERIMENTAL

Osmometry is based on the measurement of the difference in electrical resistance, ΔR, generated by difference in temperature when one drop of solution and one drop of reference-solvent are exposed to saturated solvent vapor and measured by a two-matched thermistor. For an ideal situation, the temperature rise, ΔT, is predicted by the Clausius-Clapeyron equation:

$$\Delta T = \frac{RT^2}{\lambda 1000} \cdot CN \tag{1}$$

where λ is the heat of vaporization, R is the ideal gas constant, and CN is the apparent molarity of the solution measured by osmometry. Since the temperature shift is a colligative effect, the value of CN depends solely upon the number of molecules of all species and is independent of their chemical characteristics. A 0.2 M TBP solution when measured by osmometry gives an apparent molarity of only 0.160 M. This is due to the aggregation of TBP, the monomeric TBP concentration being 0.120 M and the dimeric TBP concentration being 0.04 M.

In order to obtain greater sensitivity, hexane was used as a model compound for the alkanes. A Hewlett-Packard vapor pressure osmometer model 301 was used in this work. Squalane, n-$C_{30}H_{62}$, was used as the standard material for the calibration curve since it does not aggregate in hexane and has a high solubility. ΔR, measured by osmometry, was plotted against the concentration of the standard squalane solution. The straight line obtained was used as the calibration curve and is shown in Fig. 1.

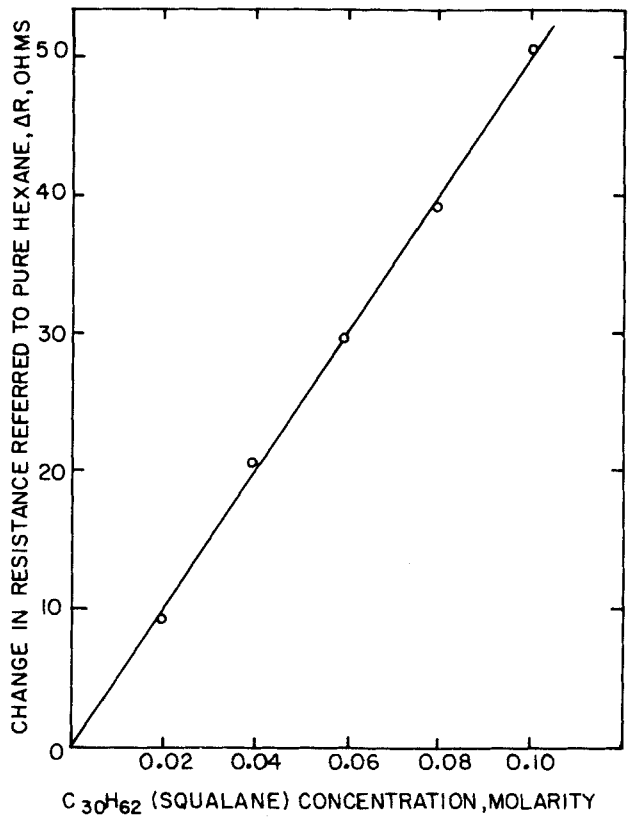

FIG. 1. The relationship of ΔR vs molarity of $C_{30}H_{62}$ (squalane) in hexane.

Tricaprylmethylammonium chloride (molecular weight 404.17) was obtained from Aldrich Chemical Company Inc. It has a density of 0.884 g/mL. Tricaprylmethylammonium chloride was converted into nitrate by contacting it with 2.0 M NH_4NO_3 five or six times. The solution was washed with distilled water in order to remove the excess NH_4NO_3. Water was removed from the solution under vacuum.

Tributyl phosphate was obtained from Aldrich Chemical Company Inc. Squalane, n-$C_{30}H_{62}$, was obtained from Pfaltz and Bauer Inc. Both were treated under vacuum to remove water. Hexane was also obtained from Aldrich Chemical Company and used as received. The same batch of hexane was used in all the experiments.

RESULTS AND DISCUSSION

Dimerization Constant of TBP

The apparent molarity of TBP measured by osmometry was found to be always smaller than the true molarity and the data indicate the presence of the dimer species. Therefore the aggregation of TBP in hexane can be represented by the reaction:

$$2\text{TBP} \rightleftarrows (\text{TBP})_2 \tag{2}$$

Hence, for each experiment the following three equations can be written:

$$\beta = [(\text{TBP})_2]/[\text{TBP}]^2 \tag{3}$$

$$M = [\text{TBP}] + 2[(\text{TBP})_2] \tag{4}$$

$$CN = [\text{TBP}] + [(\text{TBP})_2] \tag{5}$$

where β is the equilibrium dimerization constant of TBP, M is the total molar concentration of TBP, CN is the total apparent molar concentration of the different TBP species as measured by osmometry, and $[(\text{TBP})_2]$ is the molar concentration of dimeric TBP. M and CN can be measured experimentally. The three unknowns, [TBP], $[(\text{TBP})_2]$, and β, can be calculated from Eqs. (3), (4), and (5). The results for the dimerization constant β remain constant over a large concentration range and are given in Table 1. The average value

TABLE 1
The Dimerization Constant of TBP in Hexane at 298 K

TBP initial molarity	Apparent molarity of all TBP species, CN	Dimerization constant β
0.0200	0.0190	2.80
0.0400	0.0370	2.60
0.0600	0.0538	2.74
0.0800	0.0706	2.51
0.1000	0.0862	2.63
0.1500	0.1255	2.40
0.2000	0.1616	2.54
0.2400	0.1860	3.01
		Average $\beta = 2.76 \pm 0.30$

of β obtained in this work is 2.76, which is in very good agreement with those obtained by infrared spectroscopy given in Table 2.

Interactions between TBP and TCMAN

The solubility of tricaprylmethylammonium nitrate in hexane is very small, although its chloride form readily dissolves in alkane. The solubility of tricaprylmethylammonium nitrate in hexane was found to increase with the addition of TBP as shown in Fig. 2.

The aggregations were examined at three different TBP concentrations, 0.240, 0.270, and 0.300 *M*, and varying amounts of tricaprylmethylammonium nitrate. The results are given in Table 3 and shown in Fig. 3. At constant TBP concentrations, addition of increasing concentrations of tricaprylmethylammonium nitrate resulted in smaller total concentrations of all species as measured by osmometry. When 0.1180 *M* of tricaprylmethylammonium nitrate was added to 0.3001 *M* TBP, the apparent molar concentration of all the species measured by osmometry was 0.2045. When 0.4676 *M* tricaprylmethylammonium nitrate was added to 0.3001 *M* TBP, the apparent molar concentration of all the species measured by osmometry was only 0.1860. In both cases the total apparent molar concentrations measured were smaller than the true molar concentration of 0.3001 *M*. It is also smaller than the 0.226 *M* apparent molarity of the initial total concentration of the monomer and the dimer species in 0.3001 *M* TBP. This indicates that both the monomeric and dimeric TBP are strongly associated with different tricaprylmethylammonium nitrate species. Moreover, the association constant between the dimeric TBP and TCMAN is much larger than the monomeric TBP and TCMAN association. The dimerization equilibrium reaction will move toward the formation of more dimers when most of the TBP dimer is associated with the quaternary amine. This then decreases the total number of molecules in the system to less than

TABLE 2
A Comparison of the Reported Dimerization Constants of TBP

Dimerization constant	Solvent	Reference	Method
2.9	*n*-Hexane	5	IR
2.6	*n*-Dedecane	6	IR
2.5	Cyclohexane	6	IR
2.76	*n*-Hexane	This work	Osmometry

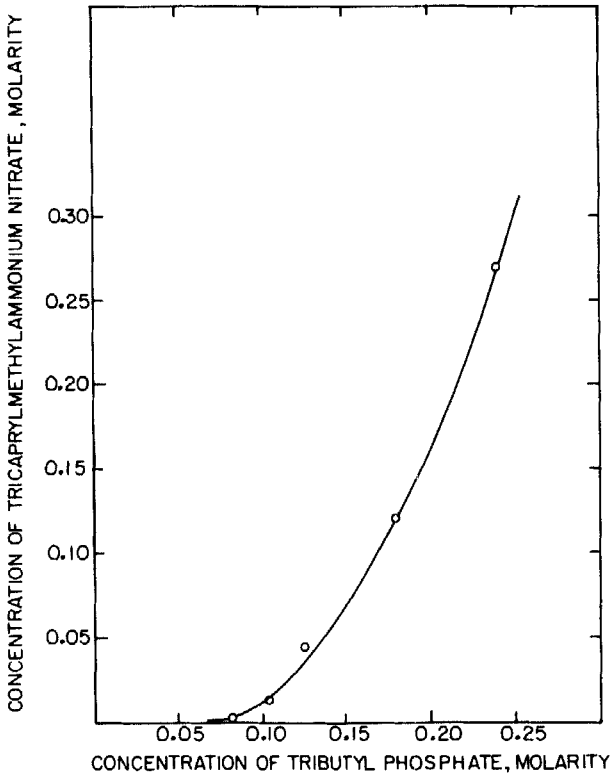

FIG. 2. The solubility of tricaprylmethylammonium nitrate as a function of the concentration of tributyl phosphate in hexane.

the original number. In this synergic extraction system the maximum value of the distribution ratio was found at a TBP concentration of 0.4 *M* and TCMAN concentration of 0.2 *M*. This strongly supports the idea that $(TBP)_2TCMAN$ is the predominant associated molecule in this system. (See Fig. 4.)

TBP has been reported to dimerize (*5, 6*), and quaternary amine has been reported to polymerize in solution (*7, 8*). The polymerization equilibrium of TCMAN can be expressed as

$$nA \overset{K_n}{\rightleftarrows} A_n \qquad [A_n] = K_n[A]^n \tag{6}$$

where A is the monomeric TCMAN and n is an integer. The possible

TABLE 3
The Interaction between Tributyl Phosphate and Tricaprylmethylammonium Nitrate as Represented by the Average Degree of Aggregation

TBP initial molarity	TCMAN initial molarity	Apparent molarity of all species, CN	Average degree of aggregation, $\bar{n}$
0.2400	0.02944	0.1817	1.483
	0.06021	0.1775	1.691
	0.1453	0.1705	2.260
	0.2698	0.1620	3.147
0.2700	0.0377	0.1965	1.566
	0.1283	0.1870	2.130
	0.2250	0.1800	2.750
	0.3065	0.1737	3.319
	0.3483	0.1721	3.593
0.3001	0.0262	0.2180	1.497
	0.1186	0.2045	2.052
	0.2170	0.1977	2.616
	0.2917	0.1952	3.032
	0.3492	0.1925	3.373
	0.4676	0.1865	4.116

interaction reactions between TBP (denoted as T) and TCMAN (denoted as A) are:

$$T + A \rightleftarrows TA \tag{7}$$

$$T + A_2 \rightleftarrows TA_2 \tag{8}$$

$$\cdots\cdots\cdots\cdots$$

$$T + A_n \rightleftarrows TA_n \tag{9}$$

and

$$T_2 + A \rightleftarrows T_2A \tag{10}$$

$$T_2 + A_2 \rightleftarrows T_2A_2 \tag{11}$$

$$\cdots\cdots\cdots\cdots$$

$$T_2 + A_n \rightleftarrows T_2A_n \tag{12}$$

A material balance gives the following equations:

$$M_A = [A]_i + 2[A_2]_i + \cdots + n[A_n]_i + [TA]_i + 2[TA_2]_i + \cdots + n[TA_n]_i + [T_2A]_i + 2[T_2A_2]_i + \cdots + n[T_2A_n]_i \tag{13}$$

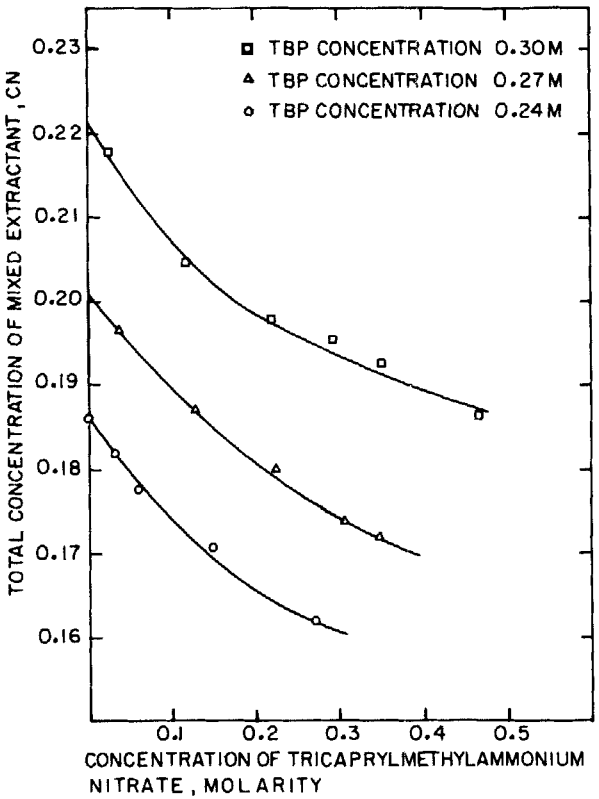

FIG. 3. The interaction between tributyl phosphate and tricaprylmethylammonium nitrate.

$$M_T = [T]_i + 2[T_2]_i + [TA]_i + [TA_2]_i + \cdots + [TA_n]_i + 2[T_2A]_i + 2[T_2A_2]_i + 2[T_2A_n]_i \quad (14)$$

$$CN = [T]_i + [T_2]_i + [A]_i + [A_2]_i + \cdots + [A_n]_i + [TA]_i + [TA_2]_i + \cdots + [TA_n]_i + [T_2A]_i + [T_2A_2]_i + \cdots + [T_2A_n]_i \quad (15)$$

where M_A is the initial molarity of the quaternary amine, M_T is the initial molarity of TBP, and CN is the total apparent molar concentration of all the species measured by osmometry. The average degree of aggregation, $\bar{n}$, is defined by the equation

$$\bar{n} = \frac{M_A + M_T}{CN} \quad (16)$$

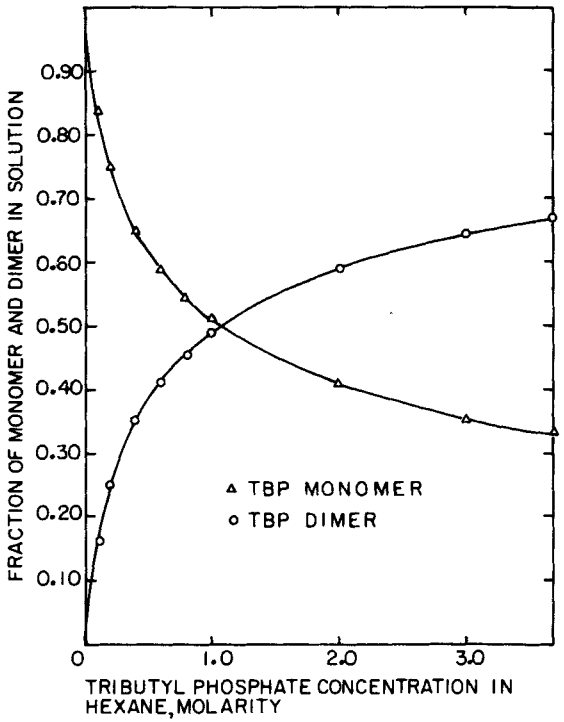

FIG. 4. The relationship between tributyl phosphate molarity and its monomer and dimer mole fraction in hexane.

For a given initial concentration of TBP, a plot of T_i versus M_A gives a straight line. Different values of the initial TBP concentration also give straight lines with different slopes, all lines passing at one point (x_1, y_1) as shown in Fig. 5. The value of y_1 equals the average degree of aggregation of pure TBP. For example, the molar concentration of pure TBP is 3.64 M. The apparent molarity of pure TBP is 2.18 M where the monomeric TBP and dimeric TBP are 0.726 and 1.456 M, respectively. Therefore, the average degree of aggregation of pure TBP, $\bar{n}_{\text{TBP(pure)}}$, is given by

$$y_1 = \bar{n}_{\text{TBP(pure)}} = \frac{\text{true molar concentration of pure TBP}}{\text{total apparent molar concentration of pure TBP}}$$

$$= \frac{3.64}{0.726 + 1.456} = 1.668\ M \tag{17}$$

The value of x_1 depends on both the quaternary amine and the solvent. It decreases with an increase in the degree of aggregation of the amine. In the present system $x_1 = m_{TCMAN} = 0.0565$. The intercepts of these lines depend on the TBP concentration. The calculated values of TBP, $(TBP)_2$, and the average degree of aggregation, $\bar{n}_{TBP(mix)}$ for each given concentration of TBP in hexane solution are given in Table 4. Each $\bar{n}_{TBP(mix)}$ is the intercept of each straight line which shows the relationship between average degree of aggregation and the initial molarity of the quaternary amine. The set of straight lines can be represented by

$$y = \frac{\bar{n}_{TBP(pure)} - \bar{n}_{TBP(mix)}}{m_{TCMAN}} x + \bar{n}_{TBP(mix)} \tag{18}$$

The different lines intersect at a point $(\bar{n}_{TBP(pure)}, m_{TCMAN})$ and encompass the area included by the angle θ. The change in the average degree of aggregation with the molar concentration of TCMAN at a known initial molar concentration of TBP can be readily estimated using Eq. (18). (See Table 5.)

The Aggregation of TCMAN in Hexane

Figure 5 shows that the line with the larger slope represents lower TBP initial concentration. In the special case where the quaternary amine

TABLE 4
The Mole Fractions of Monomeric and Dimeric TBP under Different TBP Concentrations in Hexane

TBP initial molarity	Concentration (M)		Average degree of aggregations $\bar{n}_{TBP(mix)}$	Mole Fractions	
	Monomeric [TBP]	Dimeric $[(TBP)_2]$		[TBP] / [TBP] + $[(TBP)_2]$	$[(TBP)_2]$ / [TBP] + $[(TBP)_2]$
0.200	0.120	0.040	1.250	0.750	0.250
0.400	0.195	0.104	1.347	0.650	0.350
0.600	0.251	0.175	1.408	0.589	0.411
0.800	0.301	0.250	1.452	0.546	0.454
1.00	0.345	0.328	1.486	0.513	0.487
2.00	0.518	0.741	1.589	0.411	0.589
3.00	0.652	1.174	1.643	0.357	0.643
3.64	0.727	1.456	1.668	0.333	0.667

TABLE 5
The Calculated Parameters in Eq. (18)

TBP molarity	$\bar{n}_{TBP(pure)}$	m_{TCMAN}	Intercepts $\bar{n}_{TBP(mix)}$	Slope $[\bar{n}_{TBP(pure)} - \bar{n}_{TBP(mix)}/m_{TCMAN}]$
0.3001	1.668	0.0565	1.306	6.411
0.2700	1.668	0.0565	1.291	6.678
0.2400	1.668	0.0565	1.274	6.979

concentration added to TBP–hexane solution approaches zero as a limit, the average degree of aggregation of TBP in hexane, $\bar{n}_{TBP(mix)}$, then approaches 1. This means that there is no dimer when TBP is in an indefinitely dilute hexane solution. In this case, Eq. (18) can be simplified to

$$y = \frac{\bar{n}_{TBP(pure)} - 1}{m_{TCMAN}} x + 1 \tag{19}$$

or

$$y = 11.823x + 1 \tag{20}$$

where y is the average degree of aggregation of TCMAN and x is the initial molarity of TCMAN. In the general case,

$$y = \frac{[A] + 2[A_2] + 3[A_3] + \cdots + n[A_n]}{[A] + [A_2] + [A_3] + \cdots + [A_n]} \tag{21}$$

and

$$x = [A] + 2[A_2] + 3[A_3] + \cdots + n[A_n] \tag{22}$$

Substituting Eqs. (6), (21), and (22) into (20) gives the following identical equation for [A]:

$$\frac{[A] + 2K_2[A]^2 + 3K_3[A]^3 + \cdots + nK_n[A]^n}{[A] + K_2[A]^2 + K_3[A]^3 + \cdots + K_n[A]^n} = 11.823\{[A] + 2K_2[A]^2 + 3K_3[A]^3 + \cdots + nK_n[A]^n\} + 1 \tag{23}$$

where [A] is the monomer concentration of amine in the equilibrium system and $K_2, K_3, \ldots, K_n$ are the cumulative aggregation equilibrium constants of

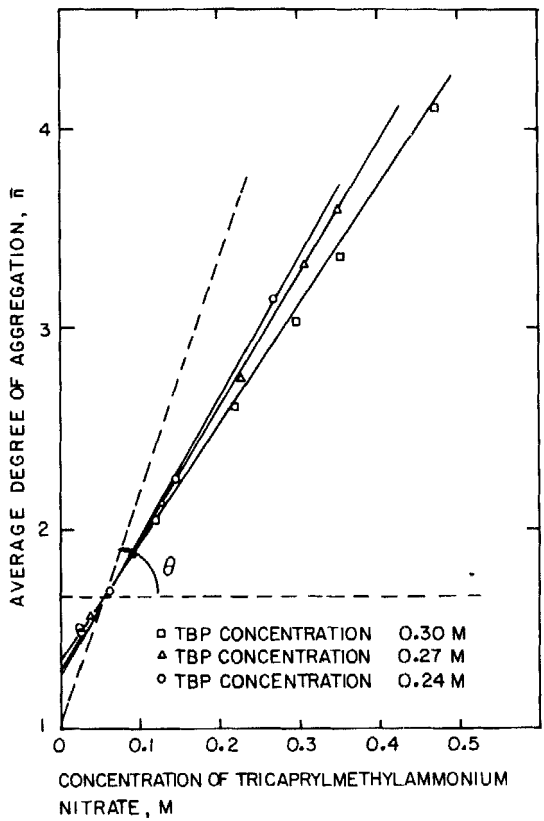

FIG. 5. The relationship between the concentration of tricaprylmethylammonium nitrate and the average degree of aggregation under certain concentrations of tributyl phosphate in hexane.

the species A_2, A_3, . . . , A_n, respectively. Since [A] is a positive number continuously changing in a certain range, the method of linear regression (*9*) was used to obtain $n - 1$ equations containing $n - 1$ unknowns ($K_2, K_3, \ldots, K_n$). The calculated values of the cumulative aggregation equilibrium constants, K's, were then changed into stepwise aggregation equilibrium constants β using the following equations:

$$A_{n-1} + A \rightleftarrows A_n \tag{24}$$

$$\beta_n = \frac{[A_n]}{[A_{n-1}][A]} = \frac{K_n}{\beta_2 \cdot \beta_3 \cdots \beta_{n-1}} \tag{25}$$

The cumulative and stepwise aggregation equilibrium constants corresponding to each species are given in Table 6. These results show the complexity of the aggregation of TCMAN in hexane. For example, when the initial molarity of TCMAN is equal to 0.01, Eq. (22) gives

$$\begin{aligned} 0.01 &= [A] + 2[A] + 3[A_3] + \cdots + n[A_n] \\ &= [A] + 2K_2[A]_2 + 3K_3[A]^3 + \cdots + nK_n[A]^n \\ &= [A] + (2)(1.182)(10)[A]^2 + (3)(2.097)(10)^2[A]^3 + \cdots \end{aligned} \quad (26)$$

TABLE 6
The Aggregation Constants of Tricaprylmethylammonium Nitrate in Hexane

Species	Cumulative aggregation equilibrium constants, K_n $NA \overset{K_n}{\rightleftarrows} A_n$	Mole percent of aggregation species at different initial concentrations of TCMAN				
		0.01 *M*	0.03 *M*	0.05 *M*	0.07 *M*	0.09 *M*
A		80.47	56.84	43.36	34.81	28.99
A_2	1.182×10	15.31	22.91	22.22	20.06	17.88
A_3	2.097×10^2	3.28	10.40	12.82	13.01	12.42
A_4	4.407×10^3	0.74	4.97	7.78	8.88	9.08
A_5	1.018×10^5	0.17	2.45	4.88	6.25	6.84
A_6	2.495×10^6	0.04	1.23	3.11	4.48	5.25
A_7	6.376×10^7		0.62	2.01	3.25	4.08
A_8	1.680×10^9		0.32	1.31	2.39	3.21
A_9	4.529×10^{10}		0.17	0.86	1.77	2.54
A_{10}	1.244×10^{12}		0.09	0.57	1.31	2.02
A_{11}	3.468×10^{13}		0.04	0.37	0.98	1.62
A_{12}	9.787×10^{14}			0.25	0.74	1.30
A_{13}	2.791×10^{16}			0.17	0.55	1.05
A_{14}	8.030×10^{17}			0.11	0.41	0.85
A_{15}	2.328×10^{19}			0.08	0.31	0.69
A_{16}	6.794×10^{20}			0.05	0.24	0.56
A_{17}	1.994×10^{22}				0.18	0.45
A_{18}	5.884×10^{23}				0.13	0.37
A_{19}	1.744×10^{25}				0.11	0.30
A_{20}	5.191×10^{26}				0.08	0.25
A_{21}	1.551×10^{28}				0.06	0.20
Average degrees of aggregation		1.12	1.35	1.59	1.83	2.06

Solving Eq. [26] for [A] gives

$$[A] = (8.0469)(10^{-1})$$

$$[A_2] = K_2[A]^2 = (1.82)(10)[(8.0469)(10^{-1})]^2 = 0.15307$$

$$[A_3] = K_3[A]^3 = (2.097)(10^2)[(8.0469)(10^{-1})]^3 = 0.03278$$

$$[A_4] = K_4[A]^4 = (4.407)(10^3)[(8.0469)(10^{-1})]^4 = 0.00739$$

Their percentages of the different species present are given in Table 6 for different TCMAN initial concentrations. The molecules with degrees of aggregation greater than 5 are negligible for an initial TCMAN concentration of 0.01 *M*. When the initial TCMAN molarity of TCMAN is about 0.1, there are more than 20 species which must be accounted for. In a dilute solution of TCMAN, the monomer can be considered as the predominant species. These calculations support the assumptions made that $(TBP)_2(TCMAN)$ is the predominant associated molecule present in the TBP-TCMAN-hexane system.

CONCLUSIONS

The dimerization constant of TBP in hexane was found to be 2.76, which is in agreement with the values in the literature obtained by infrared spectroscopy.

TBP and TCMAN associate strongly with each other in hexane, the predominant associated molecule being $(TBP)_2TCMAN$.

The aggregation equilibrium constants of TCMAN in hexane were obtained by treatment of the data obtained from a study of the aggregation of the TBP-TCMAN system by osmometry. The results showed that the higher the degrees of aggregation of the molecules, the fewer the number of molecules present in a dilute solution of TCMAN.

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