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Thermodynamics of Dissolution for Bis(triazine)−Bipyridine-Class Ligands in Different Diluents and Its Reflection on Extraction

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Hydrochemical separation processes are one of the methods used for the treatment of spent nuclear fuel. Solvent extraction is also used in many other non-nuclear applications like the mining industry. In the nuclear case, hydrochemical separation processes are already employed in the world today for the recovery of uranium and plutonium. The method is however also considered for future separation systems for use in combination with the transmutation of the minor actinides. In a hydrochemical separation process the two phases are the pregnant (usually) aqueous feed and the organic phase comprising a diluent together with one or more extractants. One such class of extractants developed for partitioning and transmutation purposes is the bis(triazine)−bipyridine-type (BTBP) molecules. When assessing the feasibility and loading properties of such an extraction system, the solubility of the ligands is of the outmost importance. The understanding of whether the dissolution is enthalpically or entropically driven will also help the understanding of the differences in extraction observed between various diluents and temperatures. In this paper the enthalpy and entropy of dissolution of the BTBP-class ligands have been determined for different diluents. It has also been shown that it is possible to predict the extraction behavior of these molecules in the selected diluent once the solubility is known.

Introduction

Separation for transmutation of nuclear waste by the means of solvent extraction has become more and more focused in the past decade. The development of new extraction ligands has been fast, and the results obtained presently by far supersede what was possible only ten years ago.

In Europe the so-called bis(triazine)−pyridine (BTP)[1] and bis(triazine)−bipyridine (BTBP)[2] class ligands, as in Figure 1, have been dominating the separation for transmutation purposes throughout two consecutive European framework programmes, EUROPART[3] and ACSEPT.[4] By using these chelating ligands in solvent extraction, it is now possible to obtain almost complete separation between the very similar trivalent actinides and lanthanides, and tests have successfully been carried out using BTBP and genuine spent nuclear fuel.[5]

As can be seen in Figure 1, both the BTP and the BTBP ligands contain a so-called core molecule upon which several side chains have been attached, and other modifications have been made over the years to optimize their abilities.[6] The different BTBPs used in this study [C2-BTBP (6,6′-bis(5,6-diethyl-[1,2,4]triazin-3-yl)-[2,2′]bipyridinyl), CyMe$_4$-BTBP (6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]triazin-3-yl)-[2,2′]bipyridine), C5-BTBP (6,6′-bis(5,6-dipentyl-[1,2,4]-triazin-3-yl)-[2,2′]bipyridinyl), MF1-BTBP (4-*tert*-butyl-6,6′-bis(5,6-diethyl-[1,2,4]triazin-3-yl)-[2,2′]bipyridinyl), and MF2-BTBP (4-tert-butyl-6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]triazin-3-yl)-[2,2′]bipyridine)] can be seen in Figure 2. Changing the side groups will affect many different chemical properties like the sensitivity toward hydrolysis and radiolysis, extraction efficiency (higher or lower distribution ratio), separation factor, and so forth.[7−10] Another factor that also is influenced by the change of side groups is the solubility of the extractant in different diluents. The present study aims at investigating how the different thermodynamic entities, that is, enthalpy and entropy, govern the dissolution of the different BTBP-type molecules displayed in Figure 2. The solubility of the BTBP-type molecules will also be correlated to their respective extraction efficiency.

It can be clearly seen in Figure 2 that all molecules have the same core molecule, but the side group varies between the CyMe$_4$-, C5-, and C2-BTBP, respectively. In addition, the effect of an asymmetric addition to the CyMe$_4$-BTBP and C2-BTBP was studied using the MF1-BTBP and MF2-BTBP molecules where a *tert*-butyl group was added on one of the pyridine rings.

Theory

The dissolving process of a solid phase in reaction 1 can be described by the solubility constant K_s in eq 2.

$$\mathrm{BTBP(s)} \rightarrow \mathrm{BTBP(l)} \qquad (1)$$

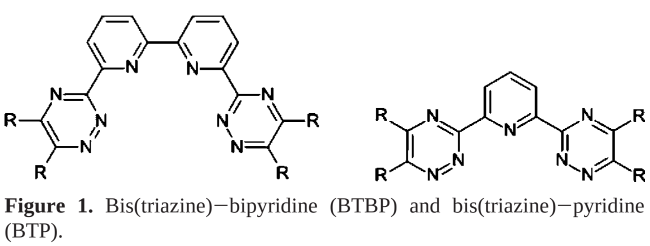

Figure 1. Bis(triazine)−bipyridine (BTBP) and bis(triazine)−pyridine (BTP).

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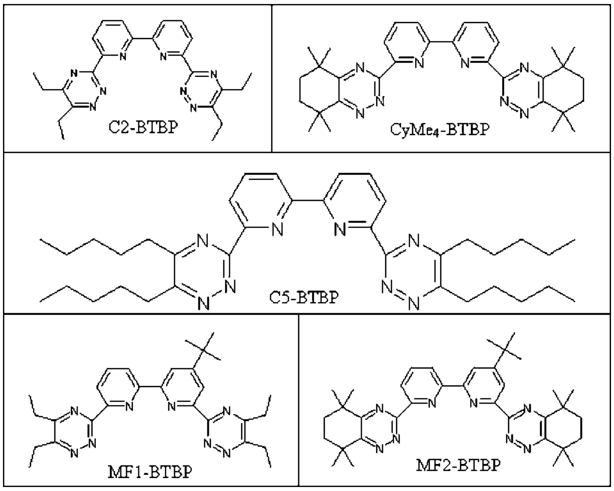

Figure 2. Structures of studied molecules: C2-BTBP (6,6′-bis(5,6-diethyl-[1,2,4]triazin-3-yl)-[2,2′]bipyridinyl), CyMe$_4$-BTBP (6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]triazin-3-yl)-[2,2′]bipyridine), C5-BTBP (6,6′-bis(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2′]bipyridinyl), MF1-BTBP (4-*tert*-butyl-6,6′-bis(5,6-diethyl-[1,2,4]triazin-3-yl)-[2,2′]bipyridinyl), and MF2-BTBP (4-tert-butyl-6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]triazin-3-yl)-[2,2′]bipyridine).

$$K_s = \frac{\{\mathrm{BTBP(l)}\}}{\{\mathrm{BTBP(s)}\}} = \frac{[\mathrm{BTBP(l)}]\cdot\gamma_{\mathrm{BTBP(l)}}}{\{\mathrm{BTBP(s)}\}} \qquad (2)$$

where {BTBP(l)} and {BTBP(s)} are the chemical activities of the molecule dissolved in a diluent and solid phase, and [BTBP(l)] and $\gamma_{\mathrm{BTBP(l)}}$ are the concentration and the activity coefficient of the dissolved molecule in diluent, respectively. The activity of the solid phase equals 1, and the activity coefficient of the dissolved molecule $\gamma_{\mathrm{BTBP(l)}}$ is assumed to be equal to 1. This can be done since the molecule in solution is not charged and the activity coefficient $\gamma_{\mathrm{BTBP(l)}}$ strongly depends on charged species in the solution. Thus, the solubility constant equals the concentration of the dissolved molecule in the diluent.

The Gibbs energy change (ΔG^0) during the dissolution can be calculated by using either the solubility constant (eq 3) or the change in enthalpy and entropy (eq 4). Measuring the solubility constants over a limited temperature interval enables the determination of the values of enthalpy (ΔH^0) and entropy (ΔS^0) at a standard state (eq 5), assuming that the enthalpy and entropy are temperature-independent in the studied temperature range.

$$\Delta G^0 = -RT \ln K_s \qquad (3)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (4)$$

$$\ln K_s = -\frac{\Delta H^0}{R}\cdot\frac{1}{T} + \frac{\Delta S^0}{R} \qquad (5)$$

where R is the molar gas constant, T is the absolute temperature, ΔH^0 is the enthalpy change for the dissolution, and ΔS^0 is the entropy change for the dissolution. Here it is assumed that the solubility is sufficiently low to make ligand−ligand interaction negligible compared to ligand−diluent interactions. As shown below, this assumption may be dubious in the case of MF2-BTBP since a high concentration of the ligand was achieved. The linearity of eq 5 was however maintained, and it may therefore be assumed that the ligand−ligand interactions are sufficiently weak. The enthalpy and entropy of dilution are also neglected compared to those for dissolution. The values of entropy and enthalpy can then be determined from a linear regression of the natural logarithm of the solubility (in M) versus $1/T$.

Experimental Section

Determinations of the concentration of BTBP molecules utilize the fact that they form a blue complex with Fe^{2+} ions in solution. For measuring the molecule concentrations a fresh saturated stock of iron(II) solution was prepared prior to each concentration determination. This stock solution was made using an excess of solid $FeSO_4\cdot 7H_2O$ (Fluka, purum p.a.) and then adding equal amounts of 95 % ethanol and Milli-Q water (Millipore, > 18 MΩ) in that order. This solution is sensitive toward aging, that is, oxidation of the Fe(II) to Fe(III), and therefore had to be freshly prepared for each sampling. A calibration curve was constructed for each BTBP using solutions with known concentrations. The absorbance was measured with a spectrophotometer (either Perkin-Elmer Lambda 19 or Ocean Optics Inc. LS-1 tungsten halogen lamp) for three samples containing 10 mL of 95 % ethanol, 0.5 mL of iron(II) solution, and 0.4 mL of solution of known BTBP concentration. The iron(II) solution was prepared in the same way as described earlier. It was shown that the shape of the calibration curve does not depend on the type of diluent, and thus the calibration curve for each BTBP molecule was constructed using cyclohexanone as diluent. Naturally the background for each case was the same as the sample but without BTBP. Thus, the dependence of the diluent was canceled out.

The first experiments were performed at low temperatures, (283 to 287) K. The diluents, cyclohexanone, octanol, hexanol, and nitrobenzene, were cooled down in a fridge, and a few milliliters of the diluents were put in glass vials containing an excess of solid phase (BTBP).

The glass vials were shaken at the desired temperature for approximately two days and were then left for (2 to 3) days in a water bath of the same temperature to allow settling. Samples of the liquid phases were then removed and analyzed with the spectrophotometer. This procedure was repeated 2 to 4 times each for the three different temperatures: (283, 293, and 303) K.

To determine the solubility at a certain temperature a volume equal to or less than 0.3 mL of liquid phase was added to 10 mL of 95 % ethanol with 0.5 mL of stock iron(II) solution. Pure diluent was added to make up a total volume of 0.4 mL of added liquid phase. The zero sample was prepared from 10 mL of 95 % ethanol, 0.5 mL of stock iron(II) solution, and 0.4 mL of pure diluent. The absorption peak for the Fe-BTBP complex was measured at a 598.27 nm wavelength for MF2-, C5-, and CyMe$_4$-BTBP and at a 608.12 nm wavelength for MF1- and C2-BTBP.

Results and Discussion

A comparison of the solubility of all ligands in cyclohexanone at 293 K can be seen in Figure 3. The choice of using cyclohexanone as the base case is due to the amount of results previously published using this diluent together with the BTP and BTBP class ligands for extraction studies and for its excellent performance regarding both solubility and kinetics of extraction.[7−9,11,13,14] It is obvious that MF2-BTBP is the most soluble ligand in this series with a maximum concentration of (303 ± 35) mM followed by C5-BTBP with a value of (83 ±

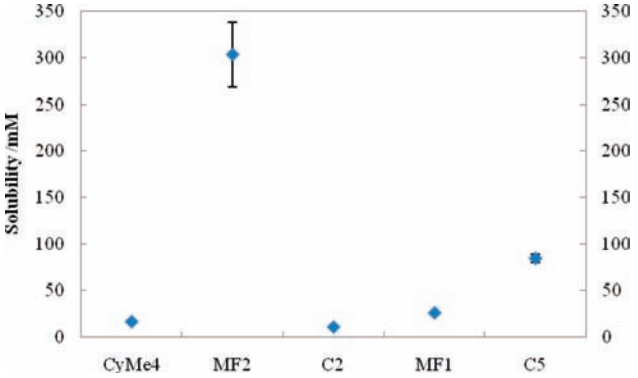

Figure 3. Solubility of different BTBP-type molecules in cyclohexanone at 293 K.

Table 1. Solubility of BTBP Molecules in Different Diluents at Three Temperatures, (283, 293, and 303) K

system	solubility/mM		
ligand/diluent	283 K	293 K	303 K
$CyMe_4$-BTBP			
cyclohexanone	8.7 ± 1.4	16.8 ± 1.6	25.2 ± 1.6
octanol	4.3 ± 1.1	8.2 ± 0.8	13.1 ± 1.0
hexanol	6.4 ± 1.4	10.0 ± 2.1	11.4 ± 1.2
nitrobenzene	40.9 ± 5.8[a]	51.3 ± 4.6	64.6 ± 6.1
C5-BTBP			
cyclohexanone	38.6 ± 2.0	84.3 ± 4.2	249.7 ± 15.2
octanol	11.1 ± 1.2	23.9 ± 1.5	45.9 ± 2.4
hexanol	15.3 ± 1.8	26.6 ± 2.2	50.1 ± 1.9
nitrobenzene	48.7 ± 4.8[a]	58.6 ± 3.5	105.5 ± 5.5
C2-BTBP			
cyclohexanone	9.2 ± 0.06	11.1 ± 0.06	16.0 ± 0.05
MF1-BTBP			
cyclohexanone	17.0 ± 0.5	26.3 ± 0.6	52.4 ± 0.8
octanol	6.1 ± 0.2	9.9 ± 0.2	17.4 ± 0.2
MF2-BTBP			
cyclohexanone	33.8 ± 5.3	303.5 ± 34.9	1106 ± 151

[a] $T = 287$ K.

4) mM. The least soluble ligand is C2-BTBP with a maximum concentration of (11.1 ± 0.1) mM. The uncertainties given throughout the paper are derived using the χ^2 method outlined by Meinrath et al.[15]

All measured values of solubilities at the three different temperatures can be seen in Table 1. To show the actual linearity, Figures 4 and 5 display the values presented in Table 1 for C5- and $CyMe_4$-BTBP. The values are plotted as the natural logarithm of the solubility versus $1/T$ with the uncertainties visualized according to the method described by Allard and Ekberg.[16]

From the slopes and intercepts of these curves the values of standard enthalpies and entropies of dissolution can be calculated using eq 5. The values are shown in Table 2, together with corresponding r^2 values. In general, r^2 values less than 0.95 are not to be regarded as linear, but since all $r^2 > 0.95$ it is reasonable to assume that we have a linear dependence in the narrow temperature range investigated here.

The changes in enthalpies of all systems are positive, which means that the dissolution is an endothermic process requiring energy from the outer environment. The lower values of the change in enthalpy for some diluents probably indicate that the bonds between the BTBP molecules, and these diluents are stronger. Therefore, if two systems have close values of ΔS^0, the system with the lower value of enthalpy will be more soluble. This explanation could be applied to the systems with $CyMe_4$-BTBP dissolved in cyclohexanone and octanol. The values of entropies are very similar [(98.0 and 98.1) $J \cdot mol^{-1} \cdot K^{-1}$, respectively], but the system with cyclohexanone has a lower enthalpy. This enthalpy difference suggests that $CyMe_4$-BTBP is more soluble in cyclohexanone than in octanol, a behavior that is supported by practical experience. In the case of C5-BTBP, the dissolution entropies for the different diluents are however too different to be able to draw any conclusion between enthalpy and solubility.

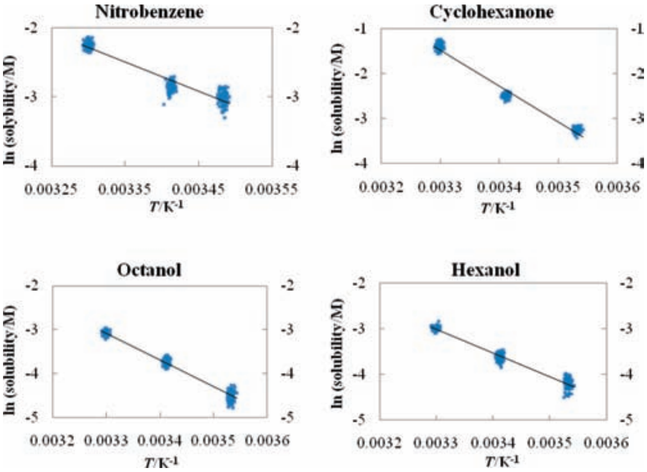

Figure 4. Dependences of the natural logarithm of solubility of C5-BTBP vs $1/T$ in different diluents (nitrobenzene, cyclohexanone, octanol, and hexanol).

There are several factors that can explain the solubility of a substance in a diluent. This can be steric effects but also different interactions both between the solute and the diluent as well as between the diluent molecules themselves, like hydrogen bonding, dipole−dipole, and van der Waals interactions.[17] Some of these effects can be described by the dielectric constant of the diluents. The dielectric constants for the diluents used are shown in Table 3.[18]

If the solubility of both C5-BTBP and CyMe4-BTBP in the aliphatic diluents is compared to the dielectric constant (ε) of the same, it is evident that a higher ε gives a higher solubility.

When comparing the cyclohexanone systems containing $CyMe_4$-BTBP and C2-BTBP with MF2-BTBP and MF1-BTBP, respectively, some steric trends can be found. By adding a *tert*-butyl group to the structure of the BTBP molecules, the values of entropies increase around three times, that is, the level of disorder in the solution is much higher for the molecules containing a *tert*-butyl group. At the same time the values of enthalpies are approximately doubled, which can indicate that the bonds between the diluent and the molecules weaken when increasing the disorder in the solution. As a consequence of this, the solubility is also increased when the disorder increases.

The entropy is also found to be consequently higher for C5-BTBP than for $CyMe_4$-BTBP in the same diluents, and hence also the solubility of C5 is higher. This is most likely due to steric effects from the long side chains. This reasoning is also valid when comparing C5- and $CyMe_4$-BTBP to C2-BTBP in cyclohexanone.

The distribution of a solute (in this case americium) between an aqueous and an organic phase for the BTBP systems investigated can be expressed according to eq 6.

$$D_{\mathrm{Am}} = \frac{\beta_2[\mathrm{Am(NO_3)_3}][\mathrm{BTBP}]^2}{[\mathrm{Am}^{3+}] + [\mathrm{AmNO_3}^{2+}] + [\mathrm{Am(NO_3)_2}^{+}] + [\mathrm{Am(NO_3)_3}]} \qquad (6)$$

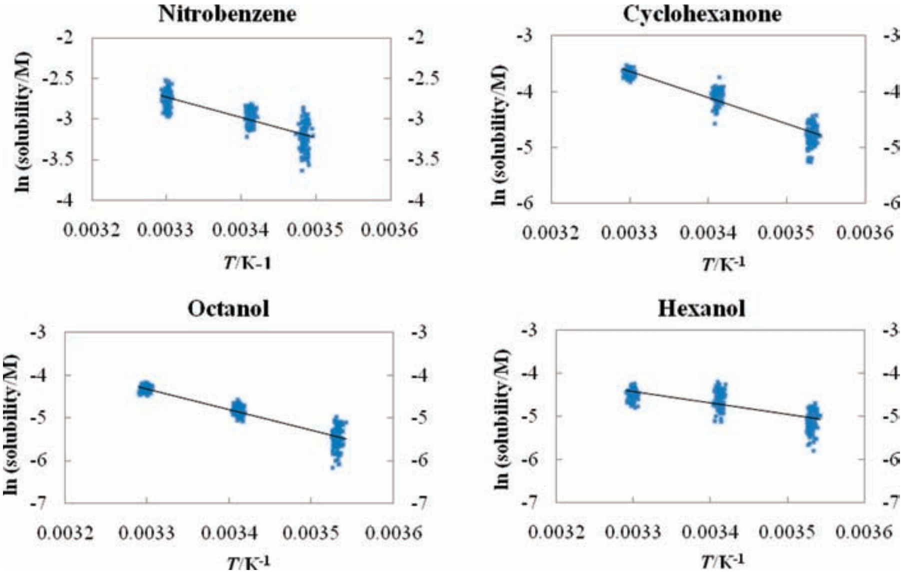

Figure 5. Dependences of the natural logarithm of solubility of CyMe$_4$-BTBP vs 1/*T* in different diluents (nitrobenzene, cyclohexanone, octanol, and hexanol).

Table 2. Standard Enthalpies and Entropies of Dissolution of the Systems Containing BTBP Molecules Dissolved in Different Diluents: The Uncertainties Present One Standard Deviation

ligand/diluent	ΔH kJ·mol^{-1}	ΔS J·mol^{-1}·K^{-1}
CyMe$_4$-BTBP		
cyclohexanone	38.9 ± 0.7	98.0 ± 2.5
octanol	40.6 ± 0.8	98.1 ± 2.8
hexanol	21.6 ± 1.0	34.6 ± 3.5
nitrobenzene	20.7 ± 0.8	45.7 ± 2.6
C5-BTBP		
cyclohexanone	66.3 ± 0.5	206.6 ± 1.9
octanol	50.9 ± 0.4	142.3 ± 1.5
hexanol	42.8 ± 0.4	116.0 ± 1.5
nitrobenzene	35.5 ± 0.6	98.3 ± 2.0
C2-BTBP		
cyclohexanone	19.4 ± 0.2	29.5 ± 0.8
MF1-BTBP		
cyclohexanone	39.7 ± 0.4	106.0 ± 1.3
octanol	37.5 ± 0.2	89.9 ± 0.6
MF2-BTBP		
cyclohexanone	123.9 ± 1.1	410.6 ± 3.9

Table 3. Values of the Dielectric Effect (ε) for Some Diluents

diluent	ε
cyclohexanone	15.5
octanol	10.34
hexanol	13.3
nitrobenzene	34.78

where β_2 is the stability constant for the formation of the complex: Am(NO$_3$)$_3$BTBP$_2$. Here it is assumed that no complexation between the BTBP and the metal occurs in the aqueous phase and that the concentration of the (1:1) BTBP complex is negligible compared to the concentration of the (1:2) complex.[19] The latter is clear from slope analysis of the extraction of the Am versus the BTBP concentration.[12,20,21] If the nitrate concentration is also held constant, then eq 6 can be simplified to eq 7.

$$D_{\mathrm{Am}} = K \cdot [\mathrm{BTBP}]^2 \tag{7}$$

As seen from eqs 6 and 7, there is a quadratic dependence of the *D* versus the BTBP concentration.

Table 4. D_{Am} from 0.01 M HNO$_3$ + 0.99 M NaNO$_3$ for CyMe$_4$-BTBP and C5-BTBP at 293 K in Different Diluents

ligand/diluent	*D*	reference for *D*
CyMe$_4$-BTBP		
cyclohexanone	20	mean of 11, 20, and 22
octanol	0.35	11
hexanol	2.2	11
nitrobenzene	450	mean of 11 and 14
C5-BTBP		
cyclohexanone	160	23
octanol	5.9	*a*
hexanol	16	23
nitrobenzene	100	*a*

[a] Experimentally determined according to a standard protocol described by Aneheim et al.[22]

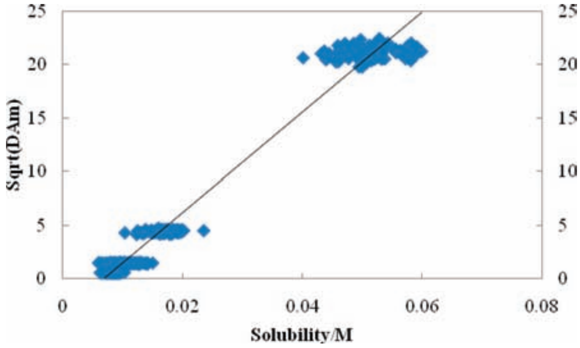

Figure 6. Square root of D_{Am} for CyMe$_4$-BTBP (0.01 M) vs the solubility in different diluents (hexanol, octanol, cyclohexanone, and nitrobenzene).

The distribution ratio of americium (D_{Am}) for 0.01 M CyMe$_4$-BTBP and C5-BTBP in the different diluents are given in Table 4.

If the distribution is governed by the solvation of the BTBP molecule, it should be possible to find a linear relation between the square root of *D* and the BTBP solubility. Such a relation is shown in Figures 6 and 7 for CyMe$_4$-BTBP and C5-BTBP, respectively. Since uncertainties were not given for all distribution ratios taken from the literature, an uncertainty of 5 % has been applied for all of these data.

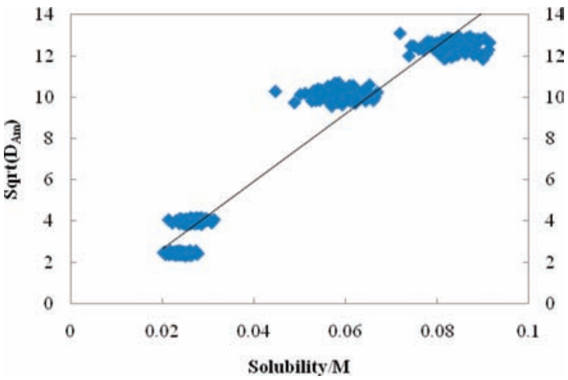

Figure 7. Square root of D_{Am} for C5-BTBP (0.01 M) vs the solubility in different diluents (octanol, hexanol, cyclohexanone, and nitrobenzene).

Conclusion

The maximum solubility of a number of different BTBP-type molecules was determined in several different diluents at three different temperatures. MF2-BTBP showed a very high solubility in cyclohexanone, reaching a concentration of (1.11 ± 0.07) M at 303 K. From the dependencies of the natural logarithm of solubility on $1/T$ the values of standard enthalpies and entropies of the dissolution were calculated using the van't Hoff equation. The dissolution seems to be highly dependent on the dielectric effect of the diluent as well as on steric effects. This is evident since the attachment of a *tert*-butyl group to the BTBP core molecule, making it asymmetrical, gives a significant increase in the entropy of dissolution and hence also in the solubility. By comparing the solubility of the ligand and the distribution ratio for americium, it can be shown that the solubilities of the extractant and the distribution ratio are strongly correlated. This correlation indicates that solvation of the extractant in a specific diluent has a large impact on the distribution ratio of the solute.

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