

# Diluent paraffin nature and plutonium(IV) organic solution lamination: new results and new approach

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## Abstract

The knowledge of the relation between the diluent composition and structure and the critical (maximum achievable) concentration ( $CC(\text{Me})$ ) of metals, including plutonium(IV), in the organic phase is an actual goal of a radiochemical extraction technology (PUREX process).

Using  $\gamma$ -spectrometry analysis with high accuracy, the parameter  $CC(\text{Pu})$  has been determined in application to Pu(IV) nitrate solution in 30% (vol.) TBP diluent solutions. n-Paraffins  $C_{10}C_{16}$ , iso-paraffins (mono- and dimethyl derivatives), iso-paraffins with C-quaternary atoms (hydrogenated mixtures of tetra- and pentapropylene isomers) have been used as diluents. Regular correlations between  $CC(\text{Pu})$  parameters and some individual (and mixture) diluent structure characteristics, including practically linear inversely proportional decrease of  $CC(\text{Pu})$  with C-atom number increase (in molecules of  $n-C_nH_{2n+2}$ ), symbatically development of this relation to both the paraffin types (n- and iso-) have been found.

The general straight proportional relation between  $CC(\text{Pu})$ -parameter and fluidity ( $F=1/\eta$ , where  $\eta$ -dynamic viscosity at given temperature) has been discovered for all paraffins investigated – both individual and mixtures – at different temperatures.

## 1. Introduction

The use of n-paraffin hydrocarbons as diluents of extractants (alkylphosphates) in the extraction processes of management, with NPP spent nuclear fuel solutions, causes a segregation (lamination) metal-containing extractant at reaching a certain (critical) concentration of metal (thorium, plutonium, strontium, etc.) that deteriorates the extraction process realization (violations in hydrodynamics and nuclear safety). Among various ways for increasing extractant capacity (by metals) are temperature increase, introduction of aromatic compound, alcohols and isoparaffins [1]. The known advantages of the following properties can be related: low temperature of freezing, increased solubility in water of the nitration products.

We have shown recently [2] that in accordance with the main requirements imposed for extractant diluent in radiochemical practice (density, flash and freezing temperature, viscosity, chemical and radiation stability, economical efficiency), the synthetic isoparaffins  $C_{10}C_{16}$  with tertiary carbon (that is mono- and dimethyl-derivative paraffins) that we have obtained, are applicable in line with n-paraffins. Being slightly unfavourably compared with the latter in flash and resistance to nitration, isoparaffins have superiority compared with

ones in freeze resistance and with considerable increase of extractant capacity (trialkylphosphate) by thorium(IV) and plutonium(IV) [3].

## 2. Isoparaffin production

With the help of catalytical hydroisomerization of n-paraffin diluent of extractants  $C_{10}C_{16}$  (RED-1) in reactor with bifunctional aluminoplatinum catalyst AP-64 (IPChS), a 45–90% isomerization of n-paraffins was achieved [4]. As a result of light (benzene) fraction distillation (140–190 °C), dearomatization (Cattwinkel sulfonation), n-paraffin removal and starting up at rectification column (more than 150 theoretical steps, flegma number 15–20), narrow fraction of isoparaffin hydrocarbons  $C_{10}C_{16}$  were obtained. De-n-paraffinization made it possible to reduce n-paraffin content to 1%. Cycle structure products (CSP) being formed at hydroisomerization – aromatics and naphthenics – in a quantity of up to 20%, could be removed almost completely (less than 0.6%). For example, in isoparaffins  $C_{13}$ -fraction, at benzene sensitivity of 0.1%, aromatic compounds were not found by PMR method, or with holding of predicted CSP concentration, depending upon the regime of sulfonation. Products of primary

hydroisomerization (mixture of n-paraffins, iso-paraffins and CSP) as well as narrow fractions containing 96–100% of isoparaffins with constant molecular mass from C<sub>11</sub> to C<sub>16</sub> are used in the investigation. To purify the sulfuric acid treatment from resinification products as well as purification with use of commercial adsorbant AS-230SH, turned out to be effective. The hydrogenated tetra- and penta-propylenes with tert-C-atoms were produced by means of iso-propylene oligomerisation, partitioning distillation and hydrogenization (V.I. Smetanjuk, Topchijevs IPChS Moscow, Russia, B.A. Grigorovich, 'NIZHNEKAMSKNEPHTTECHIM' Production Unit, Nizhnekamsk, Russian Federation.

### 3. Results

Gas-liquid chromatography gave information on the presence of n-paraffins and isoparaffins with mono-methyl and dimethyl structure in branching (Figs. 1 and 2). To disclose the structure of mono- and dimethyl-isoparaffin diluents (IPD) obtained, NMR <sup>13</sup>C{<sup>1</sup>H} spectra were studied at room temperature; <sup>13</sup>C spectra with proton decoupling at NMR spectrometer BRUCKER AM-400 (working frequency for <sup>13</sup>C, 100 MHz) and

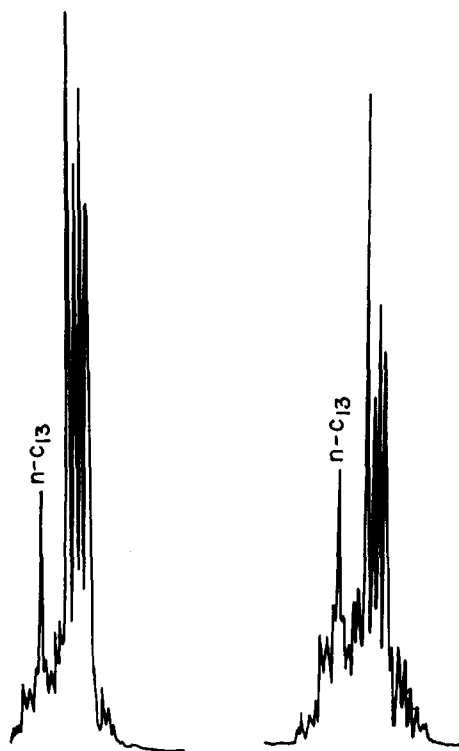


Fig. 1. Hydrocarbons diluent: 5.66% -n.-C<sub>13</sub>H<sub>28</sub>; 3.19% -iso-C<sub>13</sub>H<sub>28</sub> (dimethyl); 86.99% -iso-C<sub>13</sub>H<sub>28</sub> (monomethyl); 4.26% -iso-C<sub>14</sub>H<sub>30</sub> (dimethyl); T<sub>b</sub> = 223–225 °C. Hydrocarbon diluent: 7.80% -n.-C<sub>13</sub>H<sub>28</sub>; 8.02% -iso-C<sub>13</sub>H<sub>28</sub> (dimethyl); 72.19% -iso-C<sub>13</sub>H<sub>28</sub> (monomethyl); 11.99% -iso-C<sub>14</sub>H<sub>30</sub> (dimethyl); T<sub>b</sub> = 228.5–230 °C.

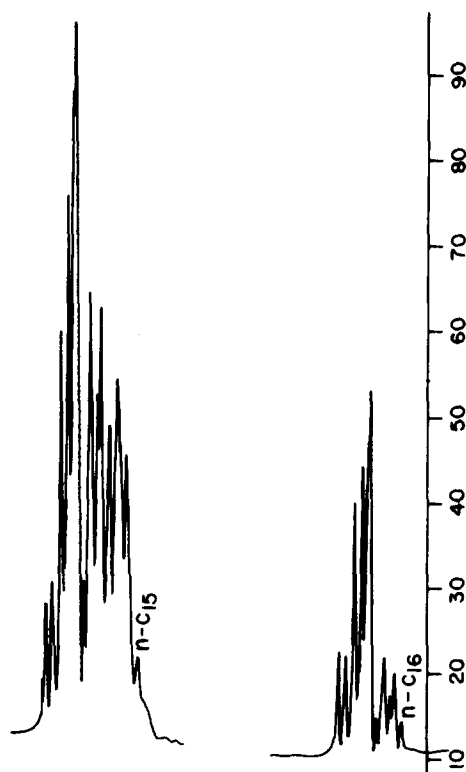


Fig. 2. Hydrocarbon diluent: 2.02% n.-C<sub>15</sub>H<sub>32</sub>; 55.04% iso-C<sub>16</sub>H<sub>34</sub> (dimethyl); 42.94% iso-C<sub>16</sub>H<sub>34</sub> (monomethyl); T<sub>b</sub> = 276–283 °C. Hydrocarbon diluent: 18.93% iso-C<sub>16</sub>H<sub>34</sub> (dimethyl); 81.07% iso-C<sub>16</sub>H<sub>34</sub> (monomethyl); T<sub>b</sub> = 283–287 °C.

for deuterium stabilization of spectrometer about 30 vol.% d-acetone were introduced into IPD specimens (V.A. Glebov, ARSRIM, A.D. Pershin, IChPh RAS). NMR spectra analysis was carried out with the use of Lindeman-Adams equation (I.P. Lindeman, T.A. Adams, *Anal. Chem.*, v43, N. 10, 1971, p. 1245–1252), based on additiveness of substituent effects on <sup>13</sup>C chemical shifts in the NMR spectrum.

Isomerization of n-paraffin diluents (NPD) was found to go with the formation of isoparaffins with tertiary carbon, and CH<sub>3</sub>-group in monomethyl derivatives of IPD is located mainly in the carbon chain centre, and in the case of IPD dimethyl derivatives, closer to the ends of the carbon chain. Quaternary atoms of carbon were not found. For example, for C<sub>13</sub>H<sub>28</sub> IPD fraction (composition 63.5% monomethyl-IPD, 33.7% dimethyl-IPD and 2.4% n-paraffin) monomethyl-IPD consist of 4-methyl-, 5-methyl- and 6-methyl-dodecanes, and dimethyl-IPD consist of 3,6-dimethyl-, 3,9-dimethyl- and 3,8-dimethyl-(dominate)-undecanes.

Values of density and viscosity for individual IPD groups from iso-decane to iso-hexadecanes in 25–60 °C temperature range (Table 1) are calculated with the measurement of results of IPD fraction density and viscosity dependence on temperature, using the principle of physical properties additivity, in particular, Porter

TABLE 1. Density and dynamic viscosity of normal and isoparaffins (mono- and dimethyl-derivatives) C<sub>10</sub>–C<sub>16</sub> at 25–60 °C. Density = C + DT, g cm<sup>-3</sup>. Viscosity = A exp(B/T), cP

Paraffins	A × 10 <sup>3</sup>	B	C	D × 10 <sup>3</sup>	
C <sub>10</sub>	normal*	9.307	1344	0.9438	-0.7299
	monomethyl	9.982	1294	0.9515	-0.7500
	dimethyl	8.465	1358	0.9758	-0.7275
C <sub>11</sub>	normal*	9.968	1393	0.9557	-0.7350
	monomethyl	15.28	1244	0.8897	-0.5041
	dimethyl	10.89	1336	0.9155	-0.5419
C <sub>12</sub>	normal*	8.421	1515	0.9631	-0.7291
	monomethyl	11.42	1413	0.9181	-0.5611
	dimethyl	8.523	1474	0.9123	-0.5240
C <sub>13</sub>	normal*	7.658	1608	0.9605	-0.6976
	monomethyl	7.198	1618	0.9065	-0.4957
	dimethyl	7.955	1563	0.9194	-0.5249
C <sub>14</sub>	normal*	7.727	1669	0.9588	-0.6696
	monomethyl	0.661	1976	0.9438	-0.5849
	dimethyl	21.80	1331	0.8800	-0.3806
C <sub>15</sub>	normal*	7.147	1749	0.9672	-0.6777
	monomethyl	11.07	1656	0.8094	-0.3809
	dimethyl	1.513	2179	0.9203	-0.5040
C <sub>16</sub>	normal*	6.133	1850	0.9720	-0.6786
	monomethyl	5.258	1882	0.9134	-0.4643
	dimethyl	3.496	2012	0.9372	-0.5343

\*Produced using most of data to be published (20–70 °C).

TABLE 2. Some parameters of "TBP – individual n-paraffin diluent, Pu(IV), 3.5 M nitric acid" system (25 °C)

Diluent	Diluent dynamic viscosity (η), cP	Critical plutonium concentration, g l <sup>-1</sup> (30% TBP-diluent)	Diluent fluidity (F = 1/η)
C-10	0.846	100.0	1.18
C-11	1.068	78.6	0.94
C-12	1.359	57.6	0.74
C-13	1.689	42.6	0.59
C-14	2.091	24.9	0.48
C-15	2.530	13.5	0.40
C-16	3.046	4.5	0.33

equation for solvent fluidity additivity, and assuming density and viscosity value constancy for all mono-(or all di-)isomers of the given isoparaffin.

Investigations of critical concentration metals (IV) (CC–Me) [2] in of 30% TBP solution systems in IPD of various composition and 3 M nitric acid in equilibrium aqueous phase have shown CC–Me increase for thorium and plutonium, with growth of IPD concentration in diluent and reduction of IPD chain length; the latter dependence being faster for plutonium than for thorium.

Critical concentration plutonium(IV) (CC–Pu) (in 30 vol.% TBP solutions) was investigated with high accuracy at 10–49 °C and equilibrium nitric acid concentration

TABLE 3. Some parameters of "TBP – n-paraffin diluent, mixtures, Pu(IV), 3.5 M nitric acid" system (25 °C)

Mixture number	Diluent composition (mole fraction)	Diluent dynamic viscosity (η), cP	Critical plutonium concentration, g l <sup>-1</sup> (30% TBP-diluent)	Diluent fluidity (F = 1/η)
1	C-11(0.83) C-15(0.17)	1.32	58.6	0.76
2	C-11(0.57) C-15(0.43)	1.70	41.6	0.59
3	C-11(0.31) C-15(0.69)	2.08	29.2	0.48
4	C-12(0.11) C-13(0.31) C-14(0.19) C-15(0.19)	1.91	27.1	0.52

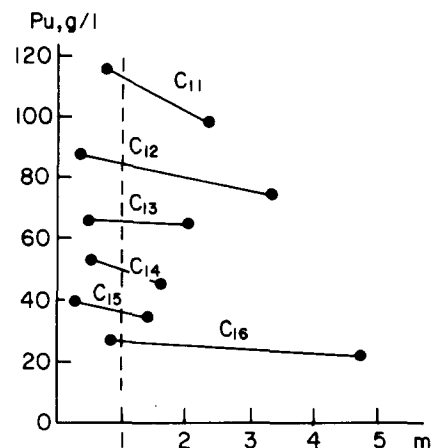


Fig. 3. Effect of iso-paraffins diluent structure (*m*-parameter) on the value of Pu(IV) critical concentration in 30% TBP solution, 25 °C, aqueous HNO<sub>3</sub> concentration 3.5 mol l<sup>-1</sup>. *m* = ratio between mono- and dimethyl-derivative iso-paraffins in diluent used.

in aqueous phase 3.5 mol l<sup>-1</sup> (Tables 2–5) in the diluents indicated, using both the narrow IPD fractions and their mixtures obtained.

It follows from the CC–Me dependence on mono- and dimethyl- derivatives for the given isoparaffins with a constant molecular mass (Fig. 3) and CC–Me dependence on a C atom number in an isoparaffin molecule (for a formal IPD composition calculated by Fig. 3, with mono- and dimethyl- derivatives (*m*) ratio equal to 1). For the sake of comparison, n-paraffin (Fig. 4), the CC–Me value for Pu(IV) goes up:

– with the reduction of the C atom number in an n-paraffin molecule as well as in isoparaffin molecules with a factor of 16.5 g l<sup>-1</sup> for a C atom with clearly pronounced analogy for both the paraffin classes;

– with transfer from mono- and dimethyl- derivatives of isoparaffins; the dependence is not very fast, but clearly pronounced for all the investigated IPD

TABLE 4. Temperature dependence of some parameters of "TBP – n-paraffin diluent, Pu(IV), 3.5 M nitric acid" system

Diluent	Temperature, °C	Diluent dynamic viscosity ( $\eta$ ), cP	Critical plutonium concentration, $\text{g l}^{-1}$ (30% TBP-diluent)	Diluent fluidity ( $F=1/\eta$ )
n.-C12	10	1.78	33.0	0.56
	15	1.62	40.0	0.62
	20	1.48	46.0	0.68
	31	1.23	65.0	0.81
	35	1.15	72.0	0.87
	38	1.10	80.0	0.91
Mixture no 4 (see Table 3)	28.5	1.80	35.1	0.56
	32.5	1.67	45.7	0.60
	42	1.42	51.0	0.70
	49	1.27	58.1	0.79

TABLE 5. Some parameters of "TBP – individual iso-paraffin diluent, Pu(IV), 3.5 M nitric acid" system (25 °C)

Iso-paraffin content (% mass)	Structure characteristics of tret- iso- paraffins		Diluent dynamic viscosity ( $\eta$ ), cP	Critical plutonium concentration, $\text{g l}^{-1}$ (30% TBP-diluent)	Diluent fluidity ( $F=1/\eta$ )
	Mono-	Di-			
-methyl-derivatives					
C-11(93)	0.43	0.57	0.976	113	1.03
C-11(96)	0.69	0.31	0.984	98.2	1.02
C-12(94)	0.24	0.76	1.225	87.4	0.82
C-12(96)	0.46	0.54	1.282	74.0	0.78
C-13(94)	0.32	0.68	1.550	65.9	0.65
C-13(98)	0.66	0.34	1.595	63.4	0.63
C-14(95)	0.35	0.65	1.940	53.0	0.52
C-14(95)	0.60	0.40	1.969	45.6	0.51
C-15(91)	0.21	0.79	2.389	38.4	0.42
C-15(96)	0.57	0.43	2.605	34.8	0.38
C-16(98)	0.44	0.56	2.954	25.3	0.34
C-16(100)	0.81	0.19	2.923	21.8	0.34

from C<sub>11</sub> to C<sub>16</sub>, namely  $4.8 \pm 3 \text{ g l}^{-1}$  per unit of  $m$ -parameter;

– with transfer from n-paraffin to isoparaffin with the same number of C atoms, by  $25 \pm 2 \text{ g l}^{-1}$ .

Temperature dependence CC–Me for IPD is as fast as for n-paraffins (system with 30 vol.% TBP in diluent, equilibrium aqueous phase acidity is near  $3.4 \text{ mol l}^{-1}$ ) (Fig. 5); CC–Me values for hydrogenated tetrapropylene (fraction 205–225 °C) (Table 4) are also given. It can be seen that this synthetic diluent maintains a greater plutonium capacity in TBP. Taking into account a preferable economical efficiency of production of IPD with C tertiary atom (that is by hydroisomerization of practically any natural paraffin a material), even a 1.5–2-fold effect of IPD in extractant capacity increase by multicharge metals, should be considered as a noticeable improvement of hydrocarbon diluents in radiochemical practice.

It can also be seen in Fig. 5 that a temperature of more than 50–60 °C IPD provides safe homogeneity of plutonium-containing extractant (it is known that exactly high temperature patterns of FBR fuel solution extraction – the so called IMPUREX process – can provide one-cycle technology for fuel regeneration in a plutonium stream (Ref. 5)).

#### 4. Conclusions

The magnitude of CC(Pu) (without account for organic phase swelling) was found to be inversely proportional to dynamic viscosity of a diluent. This is true for both pure n-paraffins and their mixtures; it follows from Fig. 6 that CC(Pu) magnitudes increase linearly with  $F=1/\eta$ -parameter (i.e. fluidity of diluent).

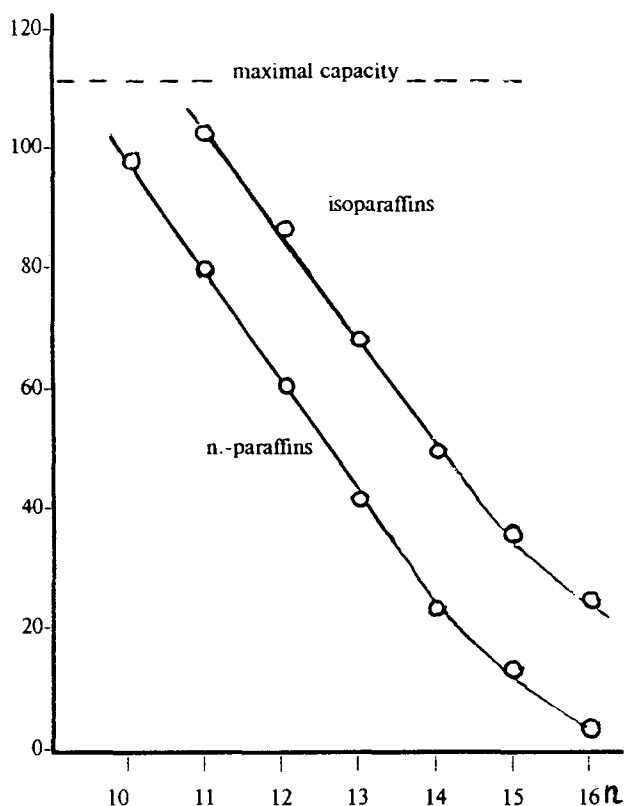


Fig. 4. Diluents molecule carbon atom number dependence of plutonium(IV) critical concentration in solution, 25 °C, aqueous  $\text{HNO}_3$  concentration  $3.5 \text{ mol l}^{-1}$ .  $n$ , diluent C-atom number in  $\text{C}_n\text{H}_{2n+2}$ . (Note: values  $\text{CC}(\text{Pu})$  for 1:1 molecular ratio of mono and di-methyl-derivative iso-paraffin diluents are presented.)

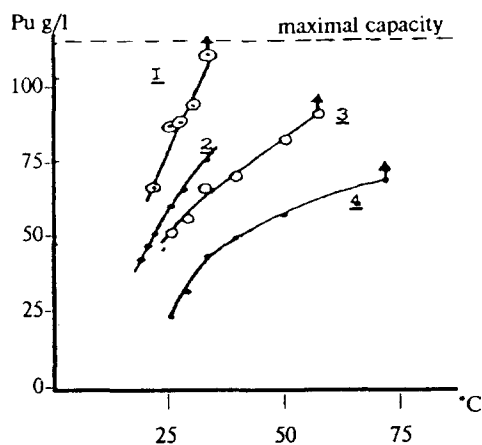


Fig. 5. Temperature dependence of plutonium(IV) critical concentration for 30% TBP solutions. 1, hydrogenated tetrapropylene; 2, iso-dodecane mixture; 3, paraffins mixture (46% iso-paraffin (mono- and dimethyl-derivatives) + 53% n-paraffin); 4, RED-1 (100% n-paraffins C10–C15),  $\uparrow$ , a lamination is absent.

Points derived for different temperatures of particular diluents fall on the same straight line. For mixtures, the dynamic viscosity was calculated using the derived empirical formula tabulated in Table 1, and taking account of the additivity of the physical properties of

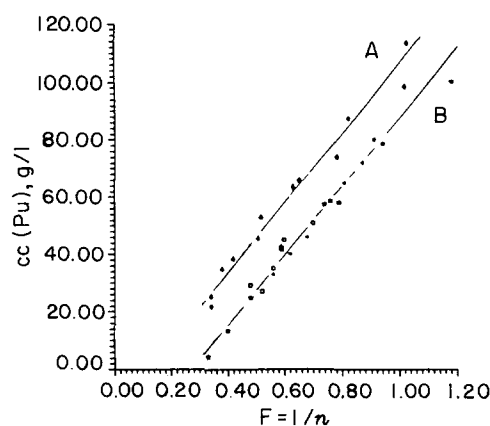


Fig. 6. The correlation between a Pu(IV) critical concentration parameter and a diluent fluidity in application to both individual and mixtures of diluents (the point – from Tables 2(\*), 3( $\square$ ), 4(\*,  $\circ$ ), 5( $\diamond$ ), A, iso-paraffins; B, n.-paraffins).

a diluent using the known mole fraction of each component in the mixture. The linear “F–CC(Pu)” relationship is expressed by the formula of the type:

$$\text{CC}(\text{Pu}) = a + bF$$

where  $a = -30 \pm 1.5$ ,  $b = 115 \pm 5$ ,  $F$  is diluent fluidity at a particular temperature. When going to iso-paraffins with sec- and tert- atoms C, the linear dependence of the same type, but with somewhat different  $a$  and  $b$  values is retained:

$$a = -12 \pm 1.3$$

$$b = 118 \pm 6.0$$

A more detailed study of strong linear correlation, discovered by us, between viscosity, hence, composition and structure of aliphatic hydrocarbons will allow a predictable selection of diluents both individual and commercial mixtures to be used in extraction processing the solution containing multivalent metals for their extraction in trialkylphosphates.

Processing from an increase of the solubilizing ability of paraffin diluents with the rising of isomerization depth (sec-C  $\rightarrow$  tert-C  $\rightarrow$  tert-C), one can conclude that firstly it is the steric differences between diluent molecules, that solvate metal salts and define organic phase macrostructure (geometrical) ordering (molecules packing) extent, that dictate the actual capacity of diluent in relation to solvates.

One can hope that the study of distant coordination, i.e. of the external solvating layers, (consisting of the diluents molecules) can help with the understanding of “third phase” phenomenon. The work is in progress.

The correlation of fine structure and isoparaffin diluents composition and their solubilization effect as far as metal solvates are concerned, will make it possible to search purposefully for new diluents and their syntheses.

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