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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Mutual Solubility of Components in the Systems $(R_4N)_2[Nd(NO_3)_5]$–Decane–*n*-Octanol (*n*-Butanol, *n*-Decanol, Cyclohexanol) at Different Temperatures

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Abstract—The influence of the reactant ratio on the specific surface area, total pore volume, and mean pore diameter of mesoporous silicon dioxide prepared by the sol–gel method was examined. The optimal reactant ratio for preparing the material with a high specific surface area was determimed.

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Salts of quaternary ammonium bases (QABs) with mineral acids (nitrates, chlorides), and also binary extractive agents, salts of QABs with organic acids, are used or have been suggested for use in separation and purification of rare-earth metals and other elements [1–5]. As a rule, QAB salts are used as 10–40% solutions in organic solvents. The choice of a solvent and concentration of an extractive agent are of fundamental importance when performing technological processes. Toluene is the most frequently used in laboratory studies of physicochemical parameters of extraction processes (extraction isotherms, distribution coefficients, and element separation factors) as a solvent in systems with QABs [4, 5]. However, use of toluene in technological practice is complicated by its low boiling and flash points.

It is difficult to use hydrocarbon solvents (kerosene, synthine, etc.) when working with QAB salts because of the mutual solubility of the forming solvates in the organic phase and hydrocarbon solvents. This leads to stratification of the organic phase and formation of a "third phase" in extraction systems. The organic phase can be stabilized by choosing an appropriate modifier and its concentration, e.g., by introduction of long-chain aliphatic alcohols into the extraction system [1]. At the same time, there is no published evidence about phase diagrams of ternary liquid systems constituted by a rare-earth metal(III) solvate, hydrocarbon solvent, and aliphatic alcohol in the range of homogeneous and heterogeneous solutions at different temperatures, which gives no way of evaluating the possible stratification of the organic system and developing recommendations for use of modifiers for practical purposes.

In this study, we examined phase diagrams of ternary liquid systems $(R_4N)_2[Nd(NO_3)_5]$–$C_{10}H_{22}$–*n*-octanol (*n*-butanol, *n*-decanol, cyclohexanol) (where R_4N is trialkylbenzylammonium), which are of theoretical and practical interest for the technology of rare-earth metals, at temperatures of 298.15–333.15 K.

We used trialkylbenzylammonium chloride $(C_6H_5CH_2)(C_7H_{15}–C_9H_{19})_3NCl$. QAB nitrate was produced by triple or quadruple contact of QAB chloride with a 6–8 M solution of ammonium nitrate. $(R_4N)_2[Nd(NO_3)_5]$ solvate was prepared by triple or quadruple shaking of concentrated aqueous solutions of neodymium nitrate (special purity grade) with a QAB nitrate solution (100%). The concentration of $(R_4N)_2[Nd(NO_3)_5]$ solvate in the extract obtained was 0.724 ± 0.005 M, $\rho_{298.15}$ = 0.9710 ± 0.015 g cm^{-3}. The following solvents were used: decane ($\rho_{298.15}$ = 0.7263 g cm^{-3}), *n*-butane ($\rho_{298.15}$ = 0.8075 g cm^{-3}), *n*-octanol ($\rho_{298.15}$ = 0.8221 g cm^{-3}), *n*-decanol ($\rho_{298.15}$ = 0.8300 g cm^{-3}), and cyclohexanol ($\rho_{298.15}$ = 0.9684 g cm^{-3}), all of chemically pure grade. The optical density of the aqueous solutions was measured with an SF-16 spectrophotometer.

Binodal curves of the binary and ternary systems were obtained using the visual-polythermic method [6–8]. The formation conditions of heterogeneous solutions were additionally monitored by the nephelometric technique with a Kernco 966 R turbidimeter and a light filter (λ = 850 nm). Consistent data were obtained in titration of stratifying-phase binary systems with a third component until homogeneous solutions were formed and in titration

Table 1. Mutual solubility of components in the systems $(R_4N)_2[Nd(NO_3)_5]$–decane–*n*-butanol (*n*-decanol, cyclohexanol, *n*-octanol) (mass fraction of the components) at different temperatures

Content, mass fraction			
$(R_4N)_2[Nd(NO_3)_5]$	decane	alcohol	water
n-Butanol			
T = 298.15 K			
0.886	0.114	0	0
0.417	0.369	0.214	1
0.479	0.326	0.195	2
0.664	0.230	0.106	3
0.810	0.157	0.033	4
0.041	0.900	0.059	4
0.029	0.930	0.041	3
0.011	0.974	0.015	2
0.005	0.992	0.003	1
<0.003	1	0	0
T = 313.15 K			
0.862	0.138	0	0
0.342	0.447	0.211	1
0.512	0.324	0.164	2
0.695	0.229	0.076	3
0.732	0.215	0.053	4
0.060	0.863	0.077	4
0.019	0.954	0.027	3
0.004	0.985	0.011	2
0.009	0.982	0.009	1
<0.003	1	0	0
T = 333.15 K			
0.817	0.183	0	0
0.283	0.510	0.207	1
0.471	0.364	0.165	2
0.638	0.277	0.085	3
0.726	0.239	0.035	4
0.079	0.823	0.098	4
0.023	0.942	0.035	3
0.012	0.975	0.013	2
0.005	0.990	0.005	1
<0.003	1	0	0
n-Decanol			
T = 298.15 K			
0.886	0.114	0	0
0.480	0.366	0.154	1
0.626	0.266	0.108	2
0.692	0.229	0.079	3
0.791	0.170	0.039	4
0.049	0.910	0.041	4
0.018	0.964	0.018	3
0.021	0.963	0.016	2
0.007	0.989	0.004	1
<0.003	1	0	0
n-Decanol			
T = 313.15 K			
0.862	0.138	0	0
0.477	0.375	0.148	1
0.624	0.278	0.098	2
0.700	0.226	0.074	3
0.752	0.202	0.046	4
0.036	0.926	0.038	4
0.020	0.962	0.018	3
0.005	0.982	0.013	2
0.001	0.993	0.006	1
<0.003	1	0	0
T = 333.15 K			
0.817	0.183	0	0
0.452	0.404	0.144	1
0.561	0.331	0.108	2
0.676	0.258	0.066	3
0.755	0.218	0.027	4
0.037	0.928	0.035	4
0.023	0.954	0.023	3
0.010	0.980	0.010	2
0.002	0.995	0.003	1
<0.003	1	0	0
Cyclohexanol			
T = 298.15 K			
0.886	0.114	0	0
0.497	0.282	0.221	1
0.605	0.236	0.159	2
0.675	0.213	0.112	3
0.775	0.172	0.053	4
0.033	0.913	0.054	4
0.015	0.956	0.029	3
0.010	0.973	0.017	2
0.007	0.982	0.011	1
<0.003	1	0	0
T = 313.15 K			
0.862	0.138	0	0
0.447	0.326	0.227	1
0.566	0.271	0.163	2
0.673	0.227	0.100	3
0.732	0.203	0.065	4
0.031	0.906	0.063	4
0.025	0.941	0.034	3
0.010	0.973	0.017	2
0.004	0.988	0.008	1
<0.003	1	0	0

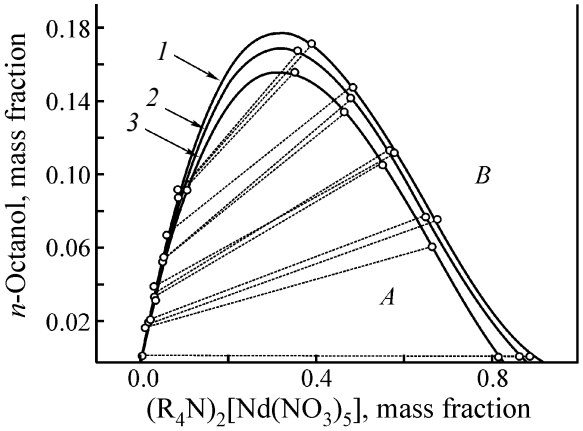
Table 1. (Contd.)

Content, mass fraction			
$(R_4N)_2[Nd(NO_3)_5]$	decane	alcohol	water
Cyclohexanol			
T = 333.15 K			
0.817	0.183	0	0
0.399	0.376	0.225	1
0.524	0.305	0.171	2
0.66	0.251	0.089	3
0.763	0.201	0.036	4
0.046	0.885	0.069	4
0.019	0.945	0.036	3
0.010	0.973	0.017	2
0.005	0.990	0.005	1
<0.003	1	0	0
n-Octanol			
T = 298.15 K			
0.886	0.114	0	0
0.393	0.436	0.171	1
0.491	0.362	0.147	2
0.581	0.308	0.111	3
0.682	0.243	0.075	4
0.085	0.824	0.091	4
0.056	0.878	0.066	3
0.025	0.937	0.038	2
0.015	0.966	0.019	1
<0.003	1	0	0
T = 313.15 K			
0.862	0.138	0	0
0.361	0.473	0.166	1
0.483	0.376	0.141	2
0.575	0.313	0.112	3
0.657	0.267	0.076	4
0.081	0.833	0.086	4
0.047	0.901	0.052	3
0.030	0.938	0.032	2
0.016	0.964	0.02	1
<0.003	1	0	0
T = 333.15 K			
0.817	0.183	0	0
0.669	0.060	0.271	1
0.557	0.105	0.338	2
0.358	0.155	0.487	3
0.470	0.135	0.395	4
0.102	0.091	0.807	4
0.053	0.054	0.893	3
0.029	0.033	0.938	2
0.006	0.016	0.978	1
<0.003	1	0	0

of homogeneous binary systems with a third component until a second phase appeared. The binodal curves were approximated with third- or fourth-order polynomials.

Solutions containing a mixture of decane, alcohol, and $(R_4N)_2[Nd(NO_3)_5]$ solvate (in coexisting phases upon stratification of the systems) were analyzed using the procedure described in [6–8]. It was found in preliminary experiments that the change in volume upon mixing of solutions of $(R_4N)_2[Nd(NO_3)_5]$ solvate, decane, and alcohols does not exceed 0.3%. To measure the $(R_4N)_2[Nd(NO_3)_5]$ concentration in the organic phase, we trice re-extracted neodymium with water, combined the re-extracts, and spectrophotometrically determined the metal by the method described in [9]. The compositions of the coexisting phases (nodes) (vol %) were recalculated to mass fractions with account of the solution densities (Table 1).

All the results for the phase diagrams of the ternary system in constant-temperature cuts (see figure) are presented in the orthogonal coordinates for two components of ternary liquid systems, with indication of the mass fractions (for the third component, $\omega_3 = 1 - \omega_1 - \omega_2$). To find points corresponding to the critical composition of the ternary systems, we used various methods: passed tangents to the binodal curves from points of node intersections, plotted dependences of the distribution coefficients of the components of the system among phases I and II on the composition of one of the phases, and extrapolated the data to a composition for which $D \Rightarrow 0$ (third-order polynomial). We also used the method in which a line connecting the midpoints of



Effect of temperature on the stratification of the system $(R_4N)_2[Nd(NO_3)_5]$–$C_{10}H_{22}$–*n*-octanol. (*A*) Field of stratification into two liquid phases and (*B*) field of homogeneous solutions. Solid lines, binodals; dashed lines, nodes; arrows, critical points. T(K): (*1*) 298.15, (*2*) 313.15, (*3*) 333.15.

the nodes were drawn and the intersection point of the extensions of these lines with the binodal curves was found [8]. All the calculations were made using Origin v. 6.0 graphical editor software. The errors in determining the compositions at the critical points were ±0.01–0.02 mass fraction.

The binary systems constituted by decane and n-octanol (*n*-butanol, *n*-decanol, cyclohexanol) are liquid single-phase systems in the whole range of temperatures studied. The binary system $(R_4N)_2[Nd(NO_3)_5]$–decane is a liquid two-phase system in the range $T \le 333.15$ K. In one of the phases (I), the content of $(R_4N)_2[Nd(NO_3)_5]$ is less than 0.003 mass fraction, and the other phase (II) is enriched in $(R_4N)_2[Nd(NO_3)_5]$, with the decane content of 0.11 to 0.18 mass fraction, depending on temperature (see figure, Table 1). It is impossible to determine the upper critical point for the systems $(R_4N)_2[Nd(NO_3)_5]$–decane because even raising the temperature to 400 K does not lead to phase stratification, with evaporation of the hydrocarbon solvent from the systems observed instead. Similar systems have been characterized in the literature [10] as systems with "single sided" solubility, e.g., liquid polymers, which are not dissolved themselves in various solvents, but dissolve a number of liquids. In the given case, the state of the $(R_4N)_2[Nd(NO_3)_5]$ solvate can be characterized as the state of a liquid polymer because of the pronounced dipole-dipole interactions between asymmetric coordination compounds.

The systems $(R_4N)_2[Nd(NO_3)_5]$–decane–*n*-octanol (*n*-butanol, *n*-decanol, cyclohexanol) have, at different temperatures, a region of homogeneous liquid solutions (*B*) and a two-phase region (*A*) delimited by the binodal curves (see figure, Table 1). The region of stratification into two phases (*A*) becomes somewhat narrower as temperature increases. Analysis of the nodes of the systems at different temperatures shows that, in the heterogeneous regions, one of the phases formed is enriched in $(R_4N)_2[Nd(NO_3)_5]$ and n-octanol (*n*-butanol, *n*-decanol, cyclohexanol), and the other, in decane. The stratification regions become somewhat narrower as temperature increases. The critical composition points at fixed temperatures depend on the nature of an alcohol. Table 2 lists compositions at the critical points at T = 298.15 K, whence follows that the content of $(R_4N)_2[Nd(NO_3)_5]$ and alcohols at the critical points are rather close and substantially lower than that of decane. The content of an alcohol at the critical composition point at fixed temperatures decreases in the order cyclohexanol > *n*-butanol > *n*-octanol > *n*-decanol.

Table 2. Critical composition points of ternary liquid systems $(R_4N)_2[Nd(NO_3)_5]$–decane–alcohols (R_4N is trialkylbenzylammonium) at T = 3298.15 K

Component	Content, mass fraction		
	$(R_4N)_2[Nd(NO_3)_5]$	alcohol	$C_{10}H_{22}$
n-Butanol	0.169	0.181	0.650
n-Octanol	0.175	0.150	0.675
n-Decanol	0.185	0.130	0.685
Cyclohexanol	0.167	0.218	0.615

The results of our study indicate that the main reason for stratification of the organic phase and formation of a third phase in extraction systems based on a nitrate of a quaternary ammonium base, hydrocarbon solvent, and rare-earth metal nitrates are limitation imposed by the mutual solubility of the forming solvates, e.g., $(R_4N)_2[Nd(NO_3)_5]$ and $C_{10}H_{22}$. This phenomenon occurs as the organic phase containing trialkylbenzylammonium nitrate and a hydrocarbon solvent is saturated with metal nitrates to a noticeable extent. The phase stratification effect cannot be eliminated by raising the temperature in the systems, which is frequently used in technological practice. The role of modifier alcohols consists in that they are predominantly distributed into a phase enriched in $(R_4N)_2[Nd(NO_3)_5]$, solvate the coordination compound, and raise its solubility in hydrocarbon solvents, and thereby homogenize the systems at critical composition points.

To enable practical use of extraction systems based on nitrates of quaternary ammonium bases and decane under conditions of complete saturation of the organic phase with neodymium(III) nitrate to obtain $(R_4N)_2[Nd(NO_3)_5]$ without stratification of the organic phase at any of the temperatures studied, it is necessary to replace decane with *n*-octanol or *n*-decanol to 0.18 mass fraction (~20 vol %). Use of n-butanol and cyclohexanol as modifiers of the organic phase is less advisable.

CONCLUSIONS

(1) The system $(R_4N)_2[Nd(NO_3)_5]$–decane forms two stratifying liquid phases. One of the phases contains less than 0.001 mass fraction of $(R_4N)_2[Nd(NO_3)_5]$, and the other is enriched in $(R_4N)_2[Nd(NO_3)_5]$ and contains 0.11 to 0.18 mass fraction of $C_{10}H_{22}$, depending on temperature.

(2) In ternary liquid systems $(R_4N)_2[Nd(NO_3)_5]$]–decane–*n*-octanol (cyclohexanol, *n*-butanol, *n*-decanol), two stratifying liquid phases are formed. The first phase is enriched in $(R_4N)_2[Nd(NO_3)_5]$ solvate and alcohols, and the second, in decane. The region of stratification into two phases becomes somewhat narrower as temperature increases, and the content of alcohols at the critical points at fixed temperatures decreases in the order cyclohexanol > *n*-butanol > *n*-octanol > *n*-decanol.

(3) To enable practical use of extractive systems based on nitrates of quaternary ammonium bases and decane without stratification of the organic phase, it is necessary to replace decane with n-octanol or *n*-decanol to 0.128 mass fraction (~20 vol %). Use of *n*-butanol and cyclohexanol as modifiers of the organic phase is less advisable.

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