Journal of chemical & engineering data

Cite This: *J. Chem. Eng. Data* XXXX, XXX, XXX−XXX

Article

pubs.acs.org/jced

Volumetric Properties of the D2EHPA−*o*-Xylene−Neodymium (Samarium, Europium, Gadolinium, Terbium, Dysprosium) Di(2-ethylhexyl)phosphate Systems at 298.15 K

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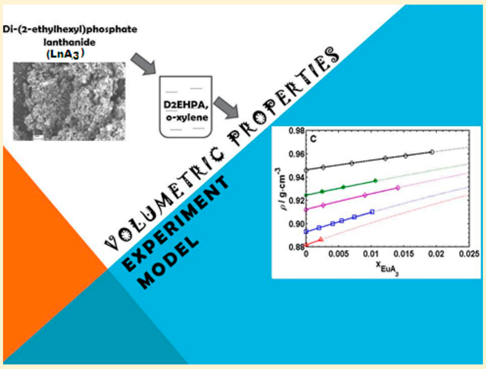
Supporting Information

ABSTRACT: Densities of ternary solutions in the lanthanide di(2-ethylhexyl)phosphate (LnA_3, Ln = Nd, Sm, Eu, Gd, Tb, Dy)−D2EHPA−*o*-xylene systems were measured by the vibrating tube densimeter at 298.15 K and atmospheric pressure. For the preparation of liquid mixtures under investigation, LnA_3 (Ln = Nd, Sm, Eu, Gd, Tb, Dy) were synthesized and characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), and chemical elemental analysis. Excess volumes of solutions were correlated by the Redlich−Kister equation. The maximum absolute deviation between experimental and calculated values of densities was found for the D2EHPA−*o*-xylene−TbA_3 system, and it was 6.3×10^{-4} g·cm^{-3}. Densities of virtual liquid lanthanide di(2-ethylhexyl)phosphates were estimated as adjustable parameters. The impact of the impurities on the densities and excess volumes of solutions was investigated. The results obtained in this work may be of interest for extraction experiments where D2EHPA of different purity is usually used.



1. INTRODUCTION

Di(2-ethylhexyl)phosphoric acid (D2EHPA, $C_{16}H_{35}PO_4$, HA) is widely used as an extractant for separation and purification of rare earth elements (REE) during liquid−liquid phase extraction. Since D2EHPA has a high viscosity, different diluents are applied for its viscosity decrease and rheological property improvement. To optimize the conditions of the extraction process, a physicochemical model should be known, i.e., the Gibbs energy of system as a function of temperature (T), pressure (p), and composition (n). The derivative $(\partial G/\partial p)_{T,n} = V$, thus $G(p)$ dependence, may be restored if volumetric properties of the aqueous and organic phases are measured. Volumetric properties of REE extraction systems included in the aqueous phases are well studied,[1−6] whereas organic subsystems received less attention.

During extraction by D2EHPA, rare earth elements are recovered from the aqueous to the organic phase as a complex di(2-ethylhexyl)phosphate, and this complex may be regarded as a quasi-component of the organic phase in the investigated extraction subsystems. According to Harada et al. the formula of this complex can be shown in a simple form as LnA_3 (Ln: lanthanide, A: the acid group of D2EHPA).[7] Several methods of synthesis of solid LnA_3 were reported.[8,9] The identification of these compounds was done by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA),[10] IR spectroscopy,[8,11−13] and powder X-ray diffraction analysis (PXRD).[8,9,11]

Experimental data oof binary LnA_3−D2EHPA systems were not found in the literature. More attention was given to binary D2EHPA−diluent systems. Thus, the density and viscosity of mixtures in the D2EHPA−kerosene system in a wide range of temperatures were given in refs 14 and 15, and thermodynamic (activity coefficients) and volumetric properties of the D2EHPA−toluene system were also studied.[16,17] The density and viscosity of binary mixtures of D2EHPA with benzene, carbon tetrachloride and *n*-pentane,[18] 1-alkanols (C1−C4, C8),[19] and monosubstituted benzenes were obtained by Dalai et al.[17] All of the volumetric data were measured at the temperature not less than 303 K, while the extraction is usually performed at 298 K. Previously, we studied thermodynamic (including volumetric) properties of the D2EHPA−*o*-xylene system from 298.15 to 308.15 K.[20]

Data for the volumetric properties of ternary LnA_3−D2EHPA diluent systems were not found in the literature. In the present work densities of the lanthanide di(2-ethylhexyl)-phosphate (LnA_3, Ln = Nd, Sm, Eu, Gd, Tb, Dy)−D2EHPA and lanthanide di(2-ethylhexyl)phosphate−*o*-xylene systems are measured at 298.15 K.

Received: June 13, 2018
Accepted: September 7, 2018

DOI: 10.1021/acs.jced.8b00487
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Table 1. Purities and Sources of Chemicals

chemical name	CAS number	source	initial weight purity	purification method	final weight fraction purity	analysis method[a]
Nd_2O_3, neodymium oxide	1313-97-9	Ganzhou Jin Chengyuan New Material Co., Ltd. (China)	0.9995	none	-	PXRD, EDX
Sm_2O_3, samarium oxide	12060-58-1		0.9995	none	-	PXRD, EDX
Eu_2O_3, europium oxide	1308-96-9		0.9999	none	-	PXRD, EDX
Gd_2O_3, gadolinium oxide	12064-62-9		0.9999	none	-	PXRD, EDX
Tb_2O_3, terbium oxide	12037-01-3		0.9999	none	-	PXRD, EDX
Dy_2O_3, dysprosium oxide	1308-87-8		0.9995	none	-	PXRD, EDX
o-C_8H_{10}, *o*-xylene	95-47-6	Chimmed (Russia)	0.9980	none	-	GC
$C_{16}H_{35}PO_4$ (D2EHPA, di(2-ethylhexyl)-phosphoric acid, HA)[b]	298-07-7	Sigma-Aldrich (USA)	0.9790	as described in ref 9	0.99	^1H and ^{31}P NMR
$NdC_{48}H_{102}O_{12}P_3$ (NdA_3, neodymium di(2-ethylhexyl)phosphate)	-	synthesis	0.99	none	-	PXRD, EDX, TGA, EA
$SmC_{48}H_{102}O_{12}P_3$ (SmA_3, samarium di(2-ethylhexyl)phosphate)	-	synthesis	0.99	none	-	PXRD, EDX, TGA, EA
$EuC_{48}H_{102}O_{12}P_3$ (EuA_3, europium di(2-ethylhexyl)phosphate)	-	synthesis	0.99	none	-	PXRD, EDX, TGA, EA
$GdC_{48}H_{102}O_{12}P_3$ (GdA_3, gadolinium di(2-ethylhexyl)phosphate)	-	synthesis	0.99	none	-	PXRD, EDX, TGA, EA
$TbC_{48}H_{102}O_{12}P_3$ (TbA_3, terbium di(2-ethylhexyl)phosphate)	-	synthesis	0.99	none	-	PXRD, EDX, TGA, EA
$DyC_{48}H_{102}O_{12}P_3$ (DyA_3, dysprosium di(2-ethylhexyl)phosphate)	-	synthesis	0.99	none	-	PXRD, EDX, TGA, EA

[a] PXRD, powder X-ray diffraction analysis; EDX, energy-dispersive X-ray spectroscopy; NMR, nuclear magnetic resonance; GC, gas chromatography; EA, elemental analysis (text in the Supporting Information). [b] Purified reagent and D2EHPA without purification were used.

2. EXPERIMENTAL SECTION

Reagents. Purities and sources of reagents, used in this work, are shown in Table 1.

Synthesis of Lanthanide Di(2-ethylhexyl)phosphate. Solid complexes of lanthanide di(2-ethylhexyl)phosphates (NdA_3, SmA_3, EuA_3, GdA_3, TbA_3, DyA_3) were obtained according to the reaction of REE nitrates (they were synthesized from oxides) with sodium salt of D2EHPA (NaA) in acetone.[9,10] Sodium salt NaA was synthesized by neutralization of D2EHPA with an equivalent amount of NaOH. Lanthanide nitrate dissolved in acetone was added to NaA in the molar ratio NaA:Ln^{3+} = 1:3. The mixture was stirred with a magnetic stirrer for 1 h at room temperature. Then, water was added to the organic solution (volumes of aqueous and organic phases were equal to each other), and the mixture was allowed to stand for 2 days. Precipitated lanthanide di(2-ethylhexyl)phosphate was separated from solution by vacuum filtration, washed by distilled water and acetone, and dried under vacuum.

Obtained powder was characterized by powder X-ray diffraction (PXRD) (Figure S1 and Table S1 in the Supporting Information), scanning electron microscopy (SEM) (Figure S2 in the Supporting Information), Fourier transform infrared spectroscopy (FTIR) (Figure S3 in the Supporting Information), thermal gravimetric analysis (TGA) (Figures S4−S5 in the Supporting Information), and chemical elemental analysis (text in the Supporting Information).

On the basis of comprehensive investigations, the synthesized samples are anhydrous complexes $LnC_{48}H_{102}O_{12}P_3$ (LnA_3, Ln = Nd, Sm, Eu, Gd, Tb, Dy).

Density Measurements. A VIP-2MP vibrating tube densimeter (Termex) was used to measure densities of solutions at temperature 298.15 ± 0.05 K. The measuring technique was similar to the one described previously.[20] The work of the densimeter is based on measurement of the period of fluctuations of the hollow U-shaped tube filled with the studied liquid. The density was calculated from the results of measurements of the resonant vibration period of a cell according to the relation

$$\rho = A\tau^2 + B \tag{1}$$

where ρ is the density of the solution; τ is the oscillation period of the measuring cell; and A and B are coefficients determined during calibration of the densimeter. The validity of eq 1 for the densimeter used was verified by measuring the dry air, distilled water, and standard samples listed in Table 2.

Table 2. Density (ρ) of VNIIM Standard Materials at 298.15 K[a]

tested sample	ρ/g·cm^{-3}	tested sample	ρ/g·cm^{-3}
REP-2	0.72657	REP-7	1.31556
REP-5	0.99704	REP-12	1.09032

[a] The combined expanded uncertainty is $U_c(\rho) = 5 \times 10^{-5}$ g·cm^{-3} ($k = 2$, with 95% confidence level), specified by the manufacturer.

However, to calibrate the device before measuring the density of the solutions under study, usually three standard samples (dry air, distilled water, and REP-2) were used. The use of three standards instead of two to determine the linear calibration dependence by the least-squares method made it possible to reduce random error in the determination of the parameters A and B in eq 1.

If eq 1 was considered, the combined expanded ($k = 2$) uncertainty of the density may be evaluated using the following expression

$$U(\rho) = 2((\tau^2)^2u^2(A) + (2A\tau)^2u^2(\tau) + u^2(B))^{1/2} \tag{2}$$

The standard uncertainties $u(A)$ and $u(B)$ were calculated after linear regression of the density of standard samples and the oscillation period of the measuring cell. The standard uncertainty in the period of oscillation was specified by the

DOI: 10.1021/acs.jced.8b00487
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manufacturer. According to eq 2, $U(\rho)$ was estimated as 3×10^{-4} g·cm^{-3}, but taking into account the fact that density measurements provided by vibrating-tube technique are affected by sample viscosity,[21,22] and the viscosity of D2EHPA is about 20 mPa·s,[19] the value of the combined standard (95% confidence level, $k = 2$) uncertainty $U(\rho)$ was rounded up to 5×10^{-4} g·cm^{-3}.

Liquid mixtures were prepared by dissolution of solid complex LnA_3 in pure D2EHPA or a mixture {D2EHPA + *o*-xylene} of known composition. The amount of components in the solution was determined by their weighing on the balance ($\pm 5 \times 10^{-5}$ g) before mixing. Obtained mixtures were stirred on a shaker at 298.15 ± 0.5 K in an air thermostat until complete dissolution. Then the densities of these solutions were measured at 298.15 ± 0.05 K.

3. RESULTS AND DISCUSSION

Experimental Data. Measured densities of pure solvents (D2EHPA and *o*-xylene), the binary solutions D2EHPA + LnA_3, and the ternary D2EHPA + *o*-xylene + LnA_3 (Ln = Nd, Sm, Eu, Gd, Tb, Dy) solutions are presented in Tables 3, 4, and 5, respectively. For all the values of mole fraction x, we give an additional digit after the decimal point in order to reduce the error of further calculation of excess volumes of solutions.

Table 3. Experimental and Estimated Density (ρ) of Liquid D2EHPA, *o*-Xylene, and LnA_3 (Ln = Nd, Sm, Eu, Gd, Tb, Dy) at Temperature T = 298.15 K and Pressure p = 0.101 MPa[a]

component	ρ/g·cm^{-3}	component	ρ/g·cm^{-3}
D2EHPA[b]	0.9710[e]	NdA_3	1.1403 ± 0.0005[f]
D2EHPA[c]	0.9705[e]	SmA_3	1.1418 ± 0.0008[f]
D2EHPA[d]	0.9691[e]	EuA_3	1.1406 ± 0.001[f]
o-xylene	0.8756[e]	GdA_3	1.1455 ± 0.001[f]
		TbA_3	1.1512 ± 0.001[f]
		DyA_3	1.1550 ± 0.0007[f]

[a] Standard uncertainties are $u(T)$ = 0.05 K, $u(p)$ = 0.01 MPa. Expanded uncertainty for the density $U(\rho)$ = 0.0005 g·cm^{-3} (0.95 level of confidence, the purity of the samples was not taken into account). [b] D2EHPA from the bottle N1 without purification. [c] D2EHPA from the bottle N2 without purification. [d] D2EHPA from the bottle N1 after purification. [e] Experimental data. [f] Estimated values with 95% confidence level.

When performing the measurements we faced the problem of density determination of pure D2EHPA due to the impossibility to obtain the high purity grade D2EHPA. It should be noted that the presence of impurities strongly affects the value of measured property.

Density values of D2EHPA from different bottles (N1 and N2) which were supplied by the same manufacturer are presented in Table 3. As can be seen the difference between measured densities was 0.0005 g·cm^{-3} which is quite significant. It is well-known that impurities in solutions affect the excess volume considerably less than density. Thus, for excess volume calculation of each solution we used the value of density of that of pure D2EHPA from which the mixture under investigation was prepared. To test the quantitative influence of impurities, three series of measurements were performed with solutions of the D2EHPA−NdA_3 system (Table 4); in each series we used different D2EHPA samples produced by Sigma-Aldrich (USA): (1) D2EHPA without purification from the bottle N1, (2) D2EHPA without purification from the bottle N2, and (3) purified D2EHPA from the bottle N1. The difference between densities of purified (99 wt %) and unpurified (97.9 wt %) D2EHPA is about 0.002 g·cm^{-3} (see Table 3).

Table 4. Experimental Values of Density (ρ) of the Binary {D2EHPA(1) + LnA_3(2)} (Ln = Nd, Sm, Eu, Gd, Tb, Dy) Solutions As a Function of LnA_3 Mole Fraction x_2 at Temperature T = 298.15 K and Pressure p = 0.101 MPa[a]

x_2	ρ/g·cm^{-3}	x_2	ρ/g·cm^{-3}	x_2	ρ/g·cm^{-3}
D2EHPA + NdA_3		D2EHPA + SmA_3		D2EHPA + EuA_3	
I run		I run			
0.00000	0.9710	0.00000	0.9710	0.00000	0.9705
0.01187	0.9768	0.00583	0.9740	0.01457	0.9775
0.02653	0.9836	0.01616	0.9789	0.04158	0.9899
0.04214	0.9904	0.03185	0.9862	0.03221	0.9856
0.05317	0.9949	0.05017	0.9939	0.05518	0.9956
0.08370	1.0066	0.06022	0.9982	0.07111	1.0017
II run		II run		D2EHPA + GdA_3	
0.00000	0.9705	0.00000	0.9705	0.00000	0.9705
0.01427	0.9773	0.01288	0.9769	0.01568	0.9784
0.03921	0.9886	0.02646	0.9831	0.03490	0.9874
0.02822	0.9838	0.03372	0.9864	0.04335	0.9912
0.04708	0.9921	0.05958	0.9972	0.05925	0.9978
0.07290	1.0023	0.07053	1.0018	D2EHPA + TbA_3	
0.04446	0.9910			0.00000	0.9705
0.07322	1.0025			0.00621	0.9737
III run				0.01030	0.9758
0.00000	0.9691			0.01167	0.9766
0.01364	0.9757			0.01875	0.9800
0.04020	0.9876			0.02771	0.9844
0.02626	0.9817			0.04671	0.9933
0.04955	0.9916			D2EHPA + DyA_3	
0.07707	1.0026			0.00000	0.9710
				0.00390	0.9731
				0.00883	0.9757
				0.02055	0.9816
				0.03494	0.9887
				0.04879	0.9951

[a] Standard uncertainties are $u(x) = 1 \times 10^{-4}$ (the purity of the samples was not taken into account), $u(T)$ = 0.05 K (according to the manufacturer), $u(p)$ = 0.01 MPa. Expanded uncertainty for the density $U(\rho)$ = 0.0005 g·cm^{-3} (0.95 level of confidence, the purity of the samples was not taken into account).

Density Correlations. Density (ρ) of the multicomponent liquid may be calculated by means of the following equation

$$\rho = \frac{\sum_i^N M_i \cdot x_i}{\sum_i^N \frac{M_i \cdot x_i}{\rho_i^0} + V^E} \tag{3}$$

where M_i and ρ_i^0 are molar mass and density of the pure component i, respectively; N is the number of components; x_i is the mole fraction of the i^{th} component; and V^E is the molar excess volume of the solution. Excess volumes of solutions are frequently approximated by the Redlich−Kister equation, which in the case of a multicomponent system can be represented in the form of eq 4.

Table 5. Experimental Values of Density (ρ) of the Ternary {D2EHPA (1) + *o*-Xylene (2) + LnA_3 (3)} (Ln = Nd, Sm, Eu, Gd, Tb, Dy) Solutions As a Function of Mole Fraction of Components (x) at Temperature T = 298.15 K and Pressure p = 0.101 MPa[a,b]

x_2	x_3	$\rho/g \cdot cm^{-3}$	x_2	x_3	$\rho/g \cdot cm^{-3}$
D2EHPA + *o*-xylene + NdA_3			D2EHPA + *o*-xylene + GdA_3		
0.97603	0.00000	0.8820	0.94065	0.00000	0.8900
0.97581	0.00023	0.8865	0.93899	0.00176	0.8934
0.92752	0.00000	0.8929	0.93706	0.00379	0.8972
0.92722	0.00029	0.8979	0.81950	0.00000	0.9124
0.92713	0.00042	0.9002	0.81773	0.00211	0.9155
0.73128	0.00000	0.9244	0.81585	0.00439	0.9189
0.73110	0.00032	0.9282	0.81148	0.00975	0.9263
0.73067	0.00085	0.9342	0.51983	0.00000	0.9447
0.73043	0.00122	0.9383	0.51762	0.00419	0.9485
0.73002	0.00176	0.9437	0.51561	0.00790	0.9518
0.50024	0.00000	0.9462	0.51231	0.01424	0.9570
0.49988	0.00084	0.9530	0.50339	0.03146	0.9701
0.49905	0.00249	0.9651			
0.49821	0.00402	0.9752			
D2EHPA + *o*-xylene + EuA_3			D2EHPA + *o*-xylene + TbA_3		
0.97603	0.00000	0.8820	0.97589	0.00000	0.8820
0.97381	0.00226	0.8865	0.97475	0.00116	0.8847
0.92747	0.00000	0.8932	0.94065	0.00000	0.8903
0.92559	0.00203	0.8966	0.93889	0.00187	0.8939
0.92363	0.00413	0.9001	0.93730	0.00355	0.8972
0.92241	0.00546	0.9024	0.81950	0.00000	0.9126
0.92059	0.00742	0.9056	0.81755	0.00246	0.9163
0.91806	0.01015	0.9101	0.81588	0.00449	0.9193
0.82036	0.00000	0.9122	0.80891	0.01296	0.9309
0.81812	0.00267	0.9160	0.52008	0.00000	0.9446
0.81294	0.00904	0.9245	0.51790	0.00409	0.9483
0.80881	0.01409	0.9310	0.51673	0.00632	0.9503
0.73128	0.00000	0.9244	0.51216	0.01523	0.9579

x_2	x_3	$\rho/g \cdot cm^{-3}$	x_2	x_3	$\rho/g \cdot cm^{-3}$
D2EHPA + *o*-xylene + EuA_3			D2EHPA + *o*-xylene + DyA_3		
0.72942	0.00252	0.9277	0.97603	0.00000	0.8819
0.72712	0.00575	0.9315	0.97520	0.00083	0.8837
0.72351	0.01066	0.9370	0.97465	0.00139	0.8849
0.50024	0.00000	0.9461	0.94061	0.00000	0.8901
0.49891	0.00266	0.9485	0.93886	0.00189	0.8938
0.49671	0.00699	0.9521	0.93715	0.00369	0.8973
0.49420	0.01215	0.9560	0.93580	0.00515	0.9000
0.49264	0.01526	0.9584	0.81974	0.00000	0.9125
0.49055	0.01932	0.9615	0.81763	0.00252	0.9164
D2EHPA + *o*-xylene + SmA_3			0.81588	0.00469	0.9196
0.97602	0.00000	0.8818	0.81221	0.00917	0.9258
0.97544	0.00059	0.8831	0.52008	0.00000	0.9446
0.92752	0.00000	0.8929	0.51752	0.00481	0.9493
0.92528	0.00242	0.8973	0.51622	0.00737	0.9515
0.92387	0.00393	0.9000	0.51090	0.01773	0.9604
0.92261	0.00529	0.9023	0.50535	0.02835	0.9691
0.91982	0.00830	0.9067			
0.82034	0.00000	0.9124			
0.81421	0.00747	0.9228			
0.80621	0.01722	0.9352			
0.50024	0.00000	0.9462			
0.49506	0.01035	0.9549			
0.49251	0.01544	0.9589			
0.48811	0.02425	0.9655			

[a] Standard uncertainties are $u(x) = 1 \times 10^{-4}$ (the purity of the samples was not taken into account), $u(T)$ = 0.05 K (according to the manufacturer), $u(p)$ = 0.01 MPa. Expanded uncertainty for the density $U(\rho) = 0.0005$ g·cm^{-3} (0.95 level of confidence, the purity of the samples was not taken into account). [b] Density of pure D2EHPA is 0.9710 g·cm^{-3} for these measurements.

$$V^{E} = \sum_{i=1}^{N} \sum_{j>i}^{N} \left(x_i x_j \sum_{\nu=0} (x_i - x_j)^{\nu} l_{ij}^{\nu} \right) \tag{4}$$

where N is the number of the components in the solution, and l_{ij}^{ν} is the binary parameter. If necessary, ternary parameters or higher-order parameters can be introduced in eq 4.

In the present work excess volumes of the ternary solutions {D2EHPA (1) + *o*-xylene (2) + LnA_3 (3)} were approximated by the Redlich–Kister equation, and three binary parameters were used: l_{12}^{0}, l_{12}^{1}, and l_{23}^{0}. As a result, eq 4 was reduced to eq 5

$$V^{E} = x_1 x_2 (l_{12}^{0} + l_{12}^{1}(x_1 - x_2)) + x_2 x_3 l_{23}^{0} \tag{5}$$

Binary parameters for the {D2EHPA (1) + *o*-xylene (2)} subsystem ($l_{12}^{0} = -0.813$ and $l_{12}^{1} = -0.488$) were determined earlier.[20] Other parameters were evaluated in the present work by the least-squares fitting of experimental data. In addition to parameters their 95% confidence intervals were calculated. Binary parameters for the {D2EHPA (1) + LnA_3 (3)} subsystem were set to zero (i.e., $V^{E} = 0$ for this binary system). Since the densities of pure liquid complexes LnA_3 are unknown, ρ_3^0 in eq 3 was also determined as an adjustable parameter. Pure liquid LnA_3 density ρ_3^0 parameters (Table 3) were evaluated from experimental data for the {D2EHPA (1) + LnA_3 (3)} system. Deviations between experimental and calculated data for the {D2EHPA (1) + LnA_3 (3)} subsystem are presented in Figure 1. Due to low solubility of LnA_3 in *o*-xylene this binary system was not experimentally studied. Consequently binary parameters l_{23}^{0} were determined only during the evaluation of the ternary solution densities.

Binary systems parameters (l_{12}^{0} and l_{12}^{1}) and density of pure liquid LnA_3 (ρ_3^0) obtained during the evaluation of the D2EHPA–*o*-xylene and D2EHPA–LnA_3 subsystems were used for the prediction of densities for the D2EHPA (1)–*o*-xylene (2)–LnA_3 (3) ternary systems. At the first stage l_{23}^{0} parameters were assumed to be equal to zero. Predicted values of density were in satisfactory agreement with experimental data, as shown in Table 5. The maximum deviation was found for the D2EHPA–*o*-xylene–TbA_3 system, and it was 6.3×10^{-4} g·cm^{-3} (see Table 6). Meanwhile, it was also decided to clarify the model taking into account the experimental data for the ternary systems; additionally, l_{23}^{0} parameters were determined. The results are presented in Table 6. The use of nonzero l_{23}^{0} parameters allowed us to slightly improve the correlation. According to the results presented in this work and our previous paper[20] the excess molar volumes of liquid in the D2EHPA–LnA_3 system are equal to zero, and the excess molar volumes in the D2EHPA–*o*-xylene, *o*-xylene–LnA_3, and D2EHPA–*o*-xylene–LnA_3 systems take negative values. Calculated and experimental densities for the D2EHPA–*o*-xylene–LnA_3 ternary solutions are shown in Figures 2–7.

The dependence of the estimated density (ρ) of liquid LnA_3 on the REE ionic radii[23] for coordination number 6 is

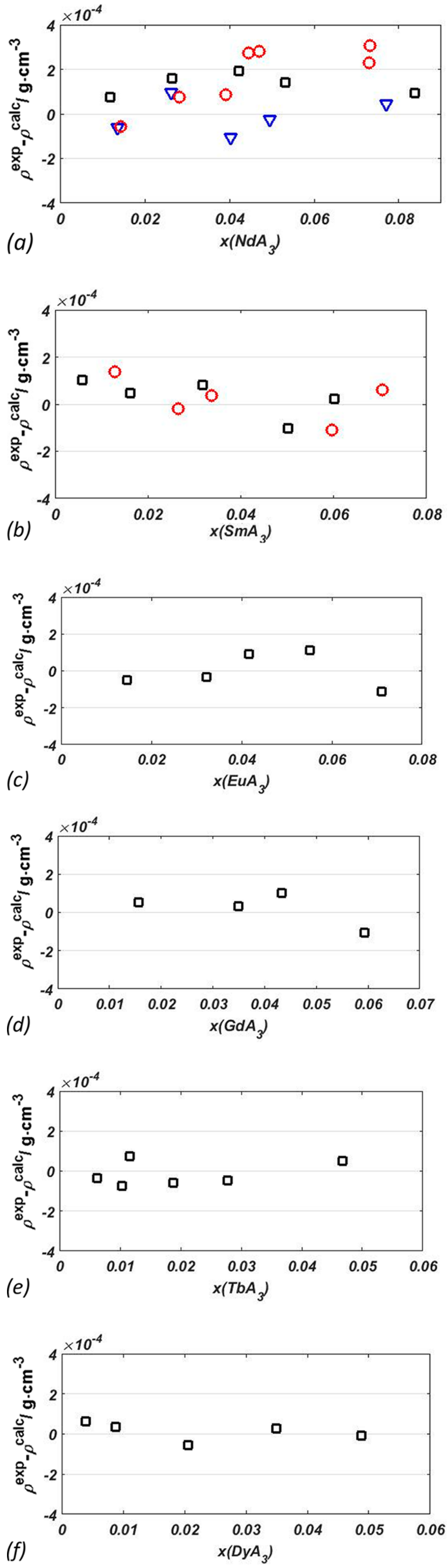

Figure 1. Absolute deviations $\Delta\rho = \rho^{\mathrm{exp}} - \rho^{\mathrm{calc}}$ between experimental (ρ^{exp}) and calculated (ρ^{calc}) values of densities for binary systems: (a) D2EHPA + NdA_3, (b) D2EHPA + SmA_3, (c) D2EHPA + EuA_3, (d) D2EHPA + GdA_3, (e) D2EHPA + TbA_3, and (f) D2EHPA + DyA_3. □, I run, ○, II run, ▽, III run (see Table 4).

Table 6. Absolute Average Deviation (AAD), Maximum Deviation (MD), and Estimated Parameters with 95% Confidence Level for Calculated Densities of the Ternary {D2EHPA (1) + *o*-Xylene (2) + LnA_3 (3)} (Ln = Nd, Sm, Eu, Gd, Tb, Dy) Solutions[a]

system	l_{23}^{0}	AAD/%[b]	$MD\cdot10^4$/ $g\cdot cm^{-3}$[c]
D2EHPA + o-xylene + NdA_3	0	0.013	2.8
	−2.6 ± 1.4	0.010	1.3
D2EHPA + o-xylene + SmA_3	0	0.021	6.0
	−7.3 ± 1.1	0.005	1.4
D2EHPA + o-xylene + EuA_3	0	0.014	4.1
	−2.1 ± 2.5	0.013	3.3
D2EHPA + o-xylene + GdA_3	0	0.017	5.6
	−5.1 ± 3.0	0.011	3.5
D2EHPA + o-xylene + TbA_3	0	0.031	6.3
	−7.6 ± 7.0	0.026	3.3
D2EHPA + o-xylene + DyA_3	0	0.020	4.5
	−7.6 ± 2.6	0.010	2.5

[a] l_{12}^{0} and l_{12}^{1} parameters were taken from our previously published work;[20] other l_{ij} parameters not presented in the table were assumed to be equal to zero. [b] Absolute average deviation AAD = $1/N\cdot\Sigma|\rho^{\mathrm{exp}} - \rho^{\mathrm{calc}}|/\rho^{\mathrm{exp}}\cdot100\%$, where ρ^{exp} and ρ^{calc} are experimental and calculated values of density, and N is the number of experimental points. [c] Maximum deviation MD = $\max(|\rho^{\mathrm{exp}} - \rho^{\mathrm{calc}}|)$.

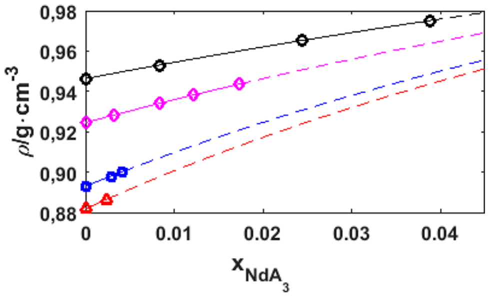

Figure 2. Experimental (symbols) and calculated (lines, see eq 3) values of density for the D2EHPA (1)−*o*-xylene (2)−NdA_3 (3) system. ○, $x_1/x_2 = 0.9991$, ◇, $x_1/x_2 = 0.3674$, □, $x_1/x_2 = 0.0781$, △, $x_1/x_2 = 0.0246$; — — — extrapolation.

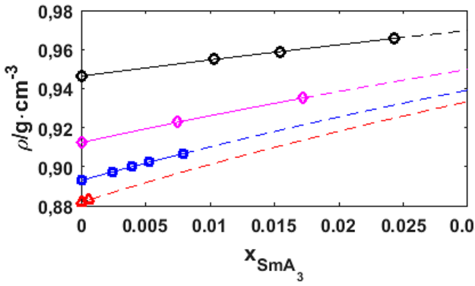

Figure 3. Experimental (symbols) and calculated (lines, see eq 3) values of density for the D2EHPA (1)−*o*-xylene (2)−SmA_3 (3) system. ○, $x_1/x_2 = 0.9991$, ◇, $x_1/x_2 = 0.2190$, □, $x_1/x_2 = 0.0781$, △, $x_1/x_2 = 0.0246$; — — — extrapolation.

presented in Figure 8. The density of the liquid EuA_3 is different on the total dependence. "Special" electron configuration of the europium can be a reason for this phenomenon. The obtained correlation can be used to define the density of liquid LnA_3 not represented in this work.

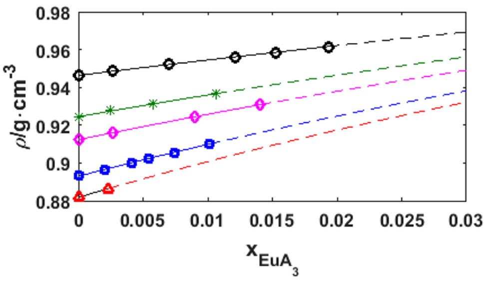

Figure 4. Experimental (symbols) and calculated (lines, see eq 3) values of density for the D2EHPA (1)−*o*-xylene (2)−EuA$_3$ (3) system. ○, x_1/x_2 = 0.9991, ∗, x_1/x_2 = 0.3674, ◇, x_1/x_2 = 0.2190, □, x_1/x_2 = 0.0782, △, x_1/x_2 = 0.0246; — — — extrapolation.

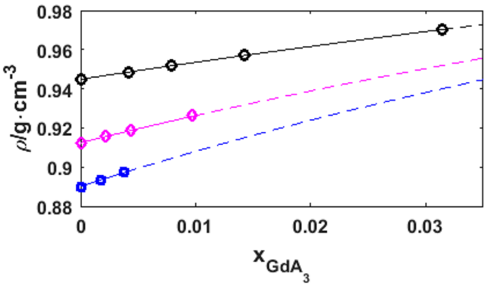

Figure 5. Experimental (symbols) and calculated (lines, see eq 3) values of density for the D2EHPA (1)−*o*-xylene (2)−GdA$_3$ (3) system. ○, x_1/x_2 = 0.9243, ◇, x_1/x_2 = 0.2206, □, x_1/x_2 = 0.0634; — — — extrapolation.

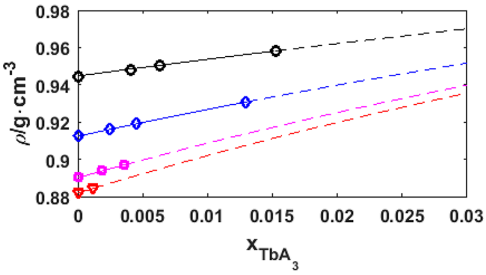

Figure 6. Experimental (symbols) and calculated (lines, see eq 3) values of density for the D2EHPA (1)−*o*-xylene (2)−TbA$_3$ (3) system. ○, x_1/x_2 = 0.9228, ◇, x_1/x_2 = 0.2203, □, x_1/x_2 = 0.0631, △, x_1/x_2 = 0.0247; — — — extrapolation.

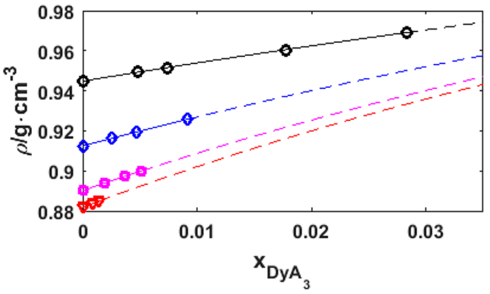

Figure 7. Experimental (symbols) and calculated (lines, see eq 3) values of density for the D2EHPA (1)−*o*-xylene (2)−DyA$_3$ (3) system. ○, x_1/x_2 = 0.9228, ◇, x_1/x_2 = 0.2199, □, x_1/x_2 = 0.0631, △, x_1/x_2 = 0.0246; — — — extrapolation.

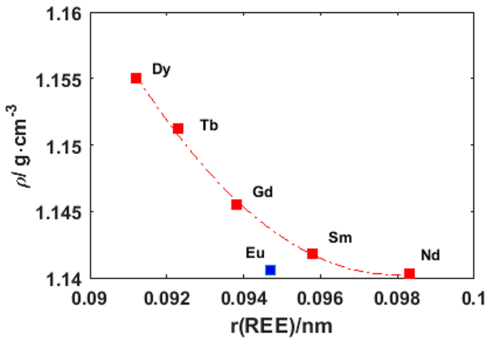

Figure 8. Dependence of the estimated density (ρ) of liquid LnA$_3$ on the REE ionic radii for coordination number Z = 6. The uncertainties of density values do not exceed the symbol size.

Impact of Impurities. In the present work we investigated solutions that were prepared from chemicals of different purity. The main problem was related to D2EHPA, which was used as a purified (99 wt %) and unpurified (97.9 wt %) sample. A rough estimate of the contribution of sample impurity to the uncertainty for densities allows us to conclude that each 1 wt % of the impurity can lead to an error in measurements corresponding to 0.002 g·cm^{-3}. This value considerably exceeds the indicated uncertainty of density measurements (Table 3). On the one hand, this makes senseless high-precision measurements of the density of these samples. However, on the other hand, the impurities in D2EHPA are insignificant for excess volumes and estimated density of pure liquid LnA$_3$. This assumption is confirmed by the fact that fitting results are in agreement with experimental densities (the NdA$_3$−D2EHPA system) even for runs with two types of D2EHPA with different purity (see Figure 1). Thus, the most important results of this work are not the densities of solutions but their excess volumes, which one can calculate using the given model parameters. Information on excess volumes makes it possible to estimate the density of solutions with D2EHPA of different purity if its density is known. The results obtained in this work may be used for extraction experiments where D2EHPA of different purity is usually used. Taking into account the foregoing, as well as the fact that purification of D2EHPA is a time-consuming process, most of the experiments in this work were carried out with unpurified (97.9 wt %) D2EHPA.

4. CONCLUSIONS

Densities for the solutions of lanthanide di(2-ethylhexyl)-phosphate (LnA$_3$, Ln = Nd, Sm, Eu, Gd, Tb, Dy) with D2EHPA and mixed D2EHPA + *o*-xylene solvent in the wide concentration range at 298.15 K and atmospheric pressure were measured. Besides *o*-xylene and D2EHPA, lanthanide di(2-ethylhexyl)phosphate was used for the mixture preparation. Synthesized LnA$_3$ were characterized by powder X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, thermal gravimetric analysis, and chemical elemental analysis.

The Redlich−Kister expression was used for data correlation. Densities of virtual liquid lanthanide di(2-ethylhexyl)phosphates were estimated as adjustable parameters. The correlation density vs radii of REE (Z = 6) allows us to predict the density of liquid LnA$_3$ not represented in this work. It was shown that D2EHPA impurities contributed insignificantly to the excess volumes of solutions, in contrast to the densities.

DOI: 10.1021/acs.jced.8b00487
J. Chem. Eng. Data XXXX, XXX, XXX−XXX

The volumetric properties obtained may be useful for modeling of REE extraction processes where the complexing agent is D2EHPA.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.8b00487.

> Additional text, figures, and table (Figures S1−S5, Table S1, and text) as described in the text, including diffraction patterns of NdA_3, relative peak intensity (I/I_0), and lattice spacing (d-value) of LnA_3 (Ln = Nd, Sm, Eu, Gd, Tb, Dy), SEM images, and chemical elemental analysis of LnA_3, TGA of LnA_3 (Ln = Nd, Sm, Eu, Gd, Tb, Dy), and IR spectrum of LnA_3 (Ln = Nd, Sm, Eu, Gd, Tb, Dy) (PDF)

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Funding

The investigations were financially supported by the URALCHEM OJSC.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work is performed at User Facilities Center under support from M.V. Lomonosov Moscow State University Program of Development.

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