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Liquid-liquid equilibrium of water + 2,3-butanediol + n-alcohols (1-heptanol, 1-octanol, 1-nonanol, 1-decanol) and water + acetoin + n-alcohols ternary systems at 298.2 K

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ABSTRACT

Liquid-liquid equilibrium (LLE) data were experimentally determined for ternary systems containing 2,3-butanediol (2,3-bdo) or acetoin as solutes, water and 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol as solvents, at 298.2 K and atmospheric pressure. Distribution coefficients increased with decreasing carbon-chain length of the solvents, ranging from 0.2610 (1-decanol) to 0.3827 (1-heptanol) for 2,3-bdo and from 0.2817 (1-decanol) to 0.4252 (1-heptanol) for acetoin. Acetoin exhibited higher maximum distribution coefficients (0.4252 in 1-heptanol) and selectivities (7.9429 in 1-decanol) compared to 2,3-bdo (0.3827 in 1-heptanol and 4.5745 in 1-heptanol, respectively). Trends are consistent with solute functionality and solvent polarity. Experimental LLE data were correlated using the NRTL activity coefficient model, and the binary interaction parameters were successfully regressed. A topological analysis confirmed the consistency of the model correlations at 298.2 K.

1. Introduction

2,3-bdo and acetoin are biotechnologically derived platform chemicals with significant industrial potential as chemical feedstocks, precursors for renewable fuel, and valuable flavoring additives [1,2]. Both compounds can be sustainably produced through microbial fermentation processes involving various yeast and bacterial strains, particularly those belonging to the *genera Klebsiella, Bacillus, Serratia, Pseudomonas,* and *Enterobacter* [3]. Purification and separation of these compounds is challenging because these molecules are produced in aqueous media, coexist with many by-products, and boil far above water (147,8 °C for acetoin and 180 °C for 2,3-bdo at 101.3 kPa) [4]. Direct distillation is therefore energy-intensive. Acetoin further complicates matters by forming an azeotrope with water [2,5]. Liquid–liquid extraction has been discussed as a promising more energy-efficient alternative for recovering 2,3-bdo and acetoin [6]. Previous research efforts have explored the extraction of 2,3-bdo from water using various organic solvents, including oleyl alcohol [7] short-chain alcohols such as 1-butanol [1,2], 1-pentanol [8], 1-hexanol [4] and others. In contrast, acetoin extraction has not been sufficiently investigated and suitable solvents have not yet been identified [2].

To address this gap, the presented work reports experimental LLE data for the ternary systems water+2,3-bdo+*n*-alcohol (1-heptanol, 1-octanol, 1-nonanol, 1-decanol) and water+acetoin+*n*-alcohol (1-heptanol, 1-octanol, 1-nonanol, 1-decanol) at 298.2 K and atmospheric pressure. While the full miscibility gap was not charted, the measured subregion captures the range that governs distribution and selectivity for relevant solute concentrations (0 wt % to 15 wt %) and, thus, the key trade-offs required for future works. Additionally, the measured tie-lines are correlated using the Non-Random Two-Liquid (NRTL) activity coefficient model. The accuracy of the correlations is compared to experimental results. The topological analysis of the Gibbs energy of mixing was used to evaluate the consistency of the binary interaction parameters [9,10].

2. Experimental

The chemicals used, the experimental procedure, and the description of the NRTL correlation are explained in more detail below.

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Table 1
Compounds, supplier (origin), reported purity (%) of used chemicals.

Compound	CAS number	Supplier (Origin)	Reported Purity
Water	7732–18–5	In-house produced	Conductivity < 0.7 μS cm^{-1}
2,3-butanediol (D-, L-, *meso* isomers)	24,347–58–8	VWR Chemicals (Germany)	≥ 98 % (mass) isomer ratio: (DL : *meso*) = (6.7 : 93.3)
3-hydroxy-2-butanone	513–86–0	VWR Chemicals (Germany)	≥ 96 % (mass)
1-heptanol	111–70–6	Sigma-Aldrich (USA)	MQ2000.
1-octanol	111–87–5	Sigma-Aldrich (USA)	MQ2000.
1-nonanol	143–08–8	Sigma-Aldrich (USA)	MQ2000.
1-decanol	112–30–1	Sigma-Aldrich (USA)	MQ2000.
Acetonitrile	75–05–8	VWR Chemicals (Germany)	≥ 99.9 % (volume)

2.1. Chemicals

All chemicals listed in Table 1 were purchased from commercial sources and used without further purification. Acetoin was supplied in crystalline dimer form. As investigated by Wu et al. 2011, the crystalline dimer can be converted into its liquid monomerized form by heating it to 333.15 K for 8 h. 72 h after monomerization at 293.15 K, no dimerization of acetoin could be detected [2]. All experiments involving acetoin in this study were carried out within 36 h after the liquid acetoin was obtained to guarantee that acetoin has not dimerized. Deionized water was distilled once before use.

2.2. Experimental procedure

To study the LLE of the water+2,3-bdo+*n*-alcohol and water+acetoin+*n*-alcohol ternary systems, tie-lines were determined at 298.2 K and atmospheric pressure (99.3 kPa). A total of seven tie-lines were measured for each ternary system. Relevant solute concentrations in the aqueous phase ranging from 0 wt % to 15 wt % were selected based on the literature [3]. Mapping of the entire ternary LLE (including composition extremes near the solvent- or solute-rich corners) was not pursued, because these regions are compositionally inaccessible under realistic fermentation titers [11]. Samples for each tie-line were independently prepared and analyzed in triplicate. The compositions comprised water and solvent with a mass ratio of 1:1. The LLE experiments were conducted in 20 mL screw cap glass vials in a HLC Heating-ThermoMixer MHR 23 from DITABIS (Germany). Samples were shaken at 500 rpm for 24 h in a temperature-controlled shaker to ensure that the LLE was attained. The equilibration time of 24 h was chosen in accordance with typical procedures reported for LLE measurements in comparable aqueous organic systems, where contact and settling times between several hours and 24 h are commonly employed to guarantee phase equilibrium. In these studies, no further systematic changes in phase compositions were observed beyond such equilibration periods [11,12]. A contact time of 24 h can thus be regarded as a conservative choice to ensure equilibrium for the systems investigated here. Subsequently, the mixtures were allowed to settle undisturbed for 4 h at 298.2 K to facilitate complete phase separation. Each phase was withdrawn using a syringe equipped with a cannula. The aqueous phase was taken from very far down and the organic phase from very far up to counteract the major source of error caused by foreign phase mixing. Sample compositions were determined via peak integration in nuclear resonance spectroscopy (NMR) using a Magitek (Germany) Spinsolve 60 Ultra equipped with a Spinsolve autosampler. No deuterated solvent was used, instead 500 μl of pure liquid phase was filled into a 5 mm NMR tube. Spectra were analyzed using PEAXACT software (S-PACT, DE). Further information about NMR analysis can be found in Supplementary Information (SI).

The combined uncertainties of mass fractions u are reported. The

Table 2
The experimental ternary LLE weight fractions for the ternary systems consisting of water, 2,3-bdo, and n-alcohol (1-heptanol, 1-octanol, 1-nonanol, 1-decanol) at 298.2 K and atmospheric pressure (99.3 kPa). Here, w denotes the mass fraction; the superscripts "org" and "aq" refer to the organic and aqueous equilibrium phase, respectively. The uncertainty in temperature is $u(T) = 0.1$ K while uncertainty in pressure is $u(p) = 0.74$ kPa. The uncertainties of the weight fractions is calculated as mentioned previously and can be found in the SI.

System	w^{org}_{water}	$w^{org}_{2,3-bdo}$	$w^{org}_{n-alcohol}$	w^{aq}_{water}	$w^{aq}_{2,3-bdo}$	$w^{aq}_{n-alcohol}$
1-heptanol	0.0566	0.0000	0.9434	0.9970	0.0000	0.0030
	0.0588	0.0108	0.9304	0.9573	0.0407	0.0020
	0.0611	0.0233	0.9156	0.9199	0.0770	0.0031
	0.0638	0.0376	0.8986	0.8829	0.1139	0.0032
	0.0661	0.0488	0.8851	0.8458	0.1500	0.0042
	0.0695	0.0645	0.8660	0.8120	0.1834	0.0046
	0.0733	0.0821	0.8446	0.7799	0.2147	0.0054
1-octanol	0.0492	0.0000	0.9508	0.9998	0.0000	0.0002
	0.0534	0.0060	0.9406	0.9508	0.0458	0.0034
	0.0551	0.0148	0.9301	0.9167	0.0798	0.0035
	0.0576	0.0268	0.9156	0.8786	0.1169	0.0045
	0.0602	0.0406	0.8992	0.8426	0.1523	0.0051
	0.0636	0.0546	0.8818	0.8072	0.1860	0.0068
	0.0673	0.0705	0.8622	0.7739	0.2176	0.0085
1-nonanol	0.0434	0.0000	0.9566	0.9998	0.0000	0.0002
	0.0455	0.0061	0.9484	0.9574	0.0417	0.0009
	0.0468	0.0166	0.9366	0.9159	0.0823	0.0018
	0.0484	0.0270	0.9246	0.8782	0.1187	0.0031
	0.0506	0.0388	0.9106	0.8404	0.1560	0.0036
	0.0533	0.0510	0.8957	0.8053	0.1906	0.0041
	0.0565	0.0661	0.8774	0.7712	0.2240	0.0048
1-decanol	0.0382	0.0000	0.9618	0.9988	0.0000	0.0012
	0.0398	0.0064	0.9538	0.9570	0.0402	0.0028
	0.0406	0.0148	0.9446	0.9153	0.0822	0.0025
	0.0420	0.0258	0.9322	0.8745	0.1228	0.0027
	0.0436	0.0373	0.9191	0.8361	0.1606	0.0033
	0.0462	0.0470	0.9068	0.8033	0.1930	0.0037
	0.0487	0.0591	0.8922	0.7689	0.2264	0.0047

Table 3
The experimental ternary LLE weight fractions for the ternary systems consisting of water, acetoin, and n-alcohol (1-heptanol, 1-octanol, 1-nonanol, 1-decanol) at 298.2 K and atmospheric pressure (99.3 kPa). The uncertainty in temperature is $u(T) = 0.1$ K while uncertainty in pressure is $u(p) = 0.74$ kPa. The uncertainties of the weight fractions is calculated as mentioned previously and can be found in the SI.

System	w^{org}_{water}	$w^{org}_{acetoin}$	$w^{org}_{n-alcohol}$	w^{aq}_{water}	$w^{aq}_{acetoin}$	$w^{aq}_{n-alcohol}$
1-heptanol	0.0565	0.0000	0.9435	0.9992	0.0000	0.0008
	0.0550	0.0141	0.9309	0.9623	0.0360	0.0017
	0.0579	0.0264	0.9157	0.9272	0.0704	0.0024
	0.0604	0.0394	0.9002	0.8935	0.1033	0.0032
	0.0632	0.0527	0.8841	0.8612	0.1349	0.0039
	0.0660	0.0673	0.8667	0.8300	0.1651	0.0049
	0.0692	0.0825	0.8483	0.8000	0.1941	0.0059
1-octanol	0.0499	0.0000	0.9501	0.9995	0.0000	0.0005
	0.0485	0.0138	0.9377	0.9617	0.0369	0.0014
	0.0505	0.0252	0.9243	0.9251	0.0726	0.0023
	0.0529	0.0372	0.9098	0.8899	0.1070	0.0031
	0.0551	0.0499	0.8950	0.8559	0.1401	0.0040
	0.0572	0.0635	0.8793	0.8246	0.1705	0.0049
	0.0601	0.0784	0.8615	0.7942	0.1999	0.0059
1-nonanol	0.0429	0.0000	0.9571	0.9997	0.0000	0.0003
	0.0411	0.0125	0.9464	0.9606	0.0383	0.0011
	0.0426	0.0224	0.9351	0.9229	0.0752	0.0019
	0.0444	0.0331	0.9225	0.8872	0.1102	0.0026
	0.0461	0.0443	0.9096	0.8531	0.1436	0.0033
	0.0481	0.0559	0.8960	0.8222	0.1737	0.0041
	0.0501	0.0693	0.8806	0.7890	0.2059	0.0051
1-decanol	0.0389	0.0000	0.9611	1.0000	0.0000	0.0000
	0.0365	0.0119	0.9516	0.9597	0.0396	0.0007
	0.0381	0.0209	0.9410	0.9220	0.0764	0.0016
	0.0398	0.0304	0.9299	0.8848	0.1128	0.0024
	0.0411	0.0402	0.9186	0.8501	0.1467	0.0032
	0.0428	0.0505	0.9067	0.8164	0.1795	0.0041
	0.0448	0.0608	0.8944	0.7846	0.2105	0.0049

uncertainties were calculated by the equation:

$$u = \sqrt{\left[(u_i^2) + (u_j^2)\right]} \tag{1}$$

wherein A-type uncertainty u_i and B-type uncertainty u_j. u_i is calculated by the following equation:

$$x_i = \frac{1}{n}\sum_{k=1}^{n} X_{i,k} \tag{2}$$

$$u_i = \left[\frac{1}{n(n-1)}\sum_{k=1}^{n}\left(X_{i,k} - x_i\right)^2\right]^{\frac{1}{2}} \tag{3}$$

where $X_{i,k}$, denotes the measured value of component i in replicate k ($k = 1, 2, 3$) obtained under identical initial concentrations and experimental conditions. The arithmetic average of the triplicate measurements, x_i is taken as the equilibrium value for component i. The index k labels the individual experiments, while n specifies the total number of replicates.u_j is calculated by the following equations:

$$a = \frac{(a_+ + a_-)}{2} \tag{4}$$

$$u_j = \frac{a}{\sqrt{3}} \tag{5}$$

where a_+ are upper limits and a_- are the lower limits of the measured value [8].

The deviation between the weighed-in and calculated mass of the solute serves as a quality indicator of the tie-line data. To this end, the mass balances of the three components and the total mass balance of the ternary system are set up

$$m_i = m^{aq}\, w_i^{aq} + m^{org}\, w_i^{org} \tag{6}$$

$$m_{ges} = m^{org} + m^{aq} \tag{7}$$

where m_i is taken from the weighed-in amounts of the feed and w_i^{org} and w_i^{aq} from the analysis of the phases by NMR, respectively. In a first step, the unknown masses of the phases in equilibrium (m^{org}, m^{aq}) are determined by solving the mass balance of the water m_1 and the solvent m_2. Once m^{aq} is known, m^{org} follows from the overall mass balance, and vice versa. With the two masses of the phases, the mass of the solute m_2 can be calculated. Next, the deviation of the calculated solute mass from the weighed-in mass is determined. The quality metric $ER_i^{org,\ aq}$ is the relative error between the calculated and the weighed-in solute mass:

$$ER_i^{org/aq} = \frac{\left(m_i^{\text{weight}} - m_i^{\text{NMR}}\right)}{m_i^{\text{weight}}} \tag{8}$$

where m_i^{weight} is the weighed quantity of the solute and m_i^{NMR} is the calculated quantity of the solute based on the NMR data. $ER_i^{org/\ aq}$ indicates whether the organic phase (ER_i^{org}) or aqueous phase (ER_i^{aq}) was calculated using the component balances.

The distribution coefficient D_i of component i and selectivity S are used to describe the LLE. The distribution coefficient and the selectivity compared to water are defined as

$$D_i = \frac{w_i^{org}}{w_i^{aq}} \tag{9}$$

$$S = \frac{\frac{w_2^{org}}{w_2^{aq}}}{\frac{w_1^{org}}{w_1^{aq}}} = \frac{D_2}{D_1} \tag{10}$$

where w_1^{org} and w_2^{org} are the mass fractions of water (1) and solute (2) in the solvent-rich phase and w_1^{aq} and $w_2^{aq}$are the mass fractions of water (1) and solute (2) in the water-rich phase, respectively [11].

2.3. Correlation

The experimental data for the systems studied were used to regress binary parameters for the NRTL activity coefficients model using the software Aspen Plus V14 (Aspen Technology Inc.) [13]. The activity coefficients and mass balance equations for the aqueous- and solvent-rich phase at equilibrium are defined as:

$$\ln\gamma_i = \frac{\sum_j x_j\tau_{ji}G_{ji}}{\sum_k x_k G_{kj}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}}\left(\tau_{ij} - \frac{\sum_m x_m\tau_{mj}G_{mj}}{\sum_k x_k G_{kj}}\right) \tag{11}$$

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \tag{12}$$

$$\tau_{ij} = a_{ij};\ (\tau_{ii} = 0 \tag{13}$$

$$\alpha_{ij} = 0.3;\ \left(\alpha_{ij} = \alpha_{ji}\right);\ (\alpha_{ii} = 1) \tag{14}$$

To model the isothermal ternary LLE data, binary interaction parameters were regressed by adjusting a_{ij} using the Maximum-likelihood objective function. In the NRTL model, the non-randomness parameter α_{ij} was fiexted to 0.3 for all binary pairs. This value lies within the classical range of 0.2 to 0.3 that is widely recommended for moderately non-ideal aqueous/organic systems and for which the NRTL model is known to show a weak sensitivity of the objective function toward α_{ij}[14]. Moreover, $\alpha_{ij} = 0.3$ has been successfully employed for phase equilibrium correlations of aqueous 2,3-bdo systems with higher boiling organic solvents and for numerous systems involving water, carboxylic acids, and higher alcohols or esters[11]. In line with these studies, α_{ij} was not treated as an adjustable parameter in this work to avoid over-parameterization. All non-ideality is captured via the binary interaction parameters [7,8,15].

Root-mean-square deviation (RMSD) was calculated to evaluate the

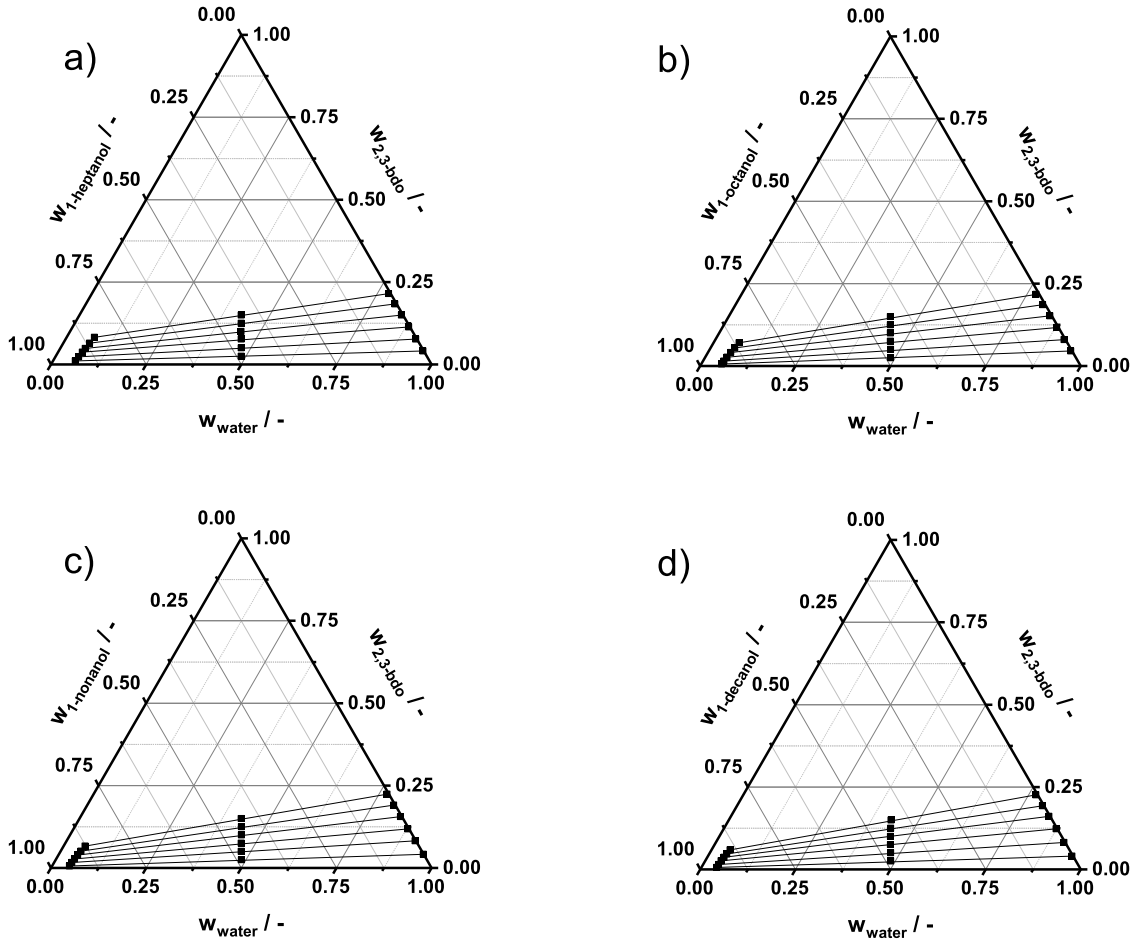

Fig. 1. Ternary diagrams of the mass fraction of the extraction systems consisting of water, 2,3-bdo, and 1-heptanol (a), 1-octanol (b), 1-nonanol (c) and 1-decanol (d) at 298.2 K and atmospheric pressure (99.3 kPa). The uncertainty in temperature is $u(T) = 0.1$ K while uncertainty in pressure is $u(p) = 0.74$ kPa. Black squares indicate experimental tie-line data and the mixing point.

deviation between NRTL correlation and the measured LLE data. RMSD is calculated by

$$RMSD = \left[\frac{\sum_n^N \sum_j^J \sum_k^K \left(x_{njk}{}^{\exp} - x_{njk}{}^{\mathrm{NRTL}}\right)^2}{6N}\right]^{\frac{1}{2}} \quad (15)$$

where $x_{njk}{}^{exp}$ denotes the experimentally determined mole fraction of component j in phase k on tie line n, while $x_{njk}{}^{NRTL}$ is the corresponding value calculated with the NRTL model. The full data set comprises $6N$ composition values that enter the RMSD calculation [8].

3. Results and discussion

The experimentally derived mass fractions in the organic (org) and aqueous (aq) phase of the ternary systems are given in Table 2 for 2,3-bdo and Table 3 for acetoin. The uncertainties of the experimental mass fractions can be found in Tables S5 and S6 in the SI, respectively. Figs. 1 and 2 show the triangular phase diagrams for the water+2,3-bdo+*n*-alcohol and water+acetoin+*n*-alcohol systems.

The deviations between the weighed-in and calculated 2,3-bdo and acetoin mass based on the NMR results can be found in Table 4 and Table 5, respectively.

The corresponding binary interaction parameters in NRTL and the RMSD of the compositions for the different solvents are listed in Table 6 for the 2,3-bdo systems and in Table 7 for the acetoin systems, respectively.

A comparison of the RMSD values with those of comparable systems and models (NRTL and UNIQUAC) from the literature (compare [2,4,8]) shows that the correlated parameters correspond very well with the experimental data.

A topological examination of the dimensionless Gibbs energy of mixing $\left(G^M/RT\right)$ has proven valuable for evaluating binary interaction parameters [9,16]. For all the ternary mixtures in this study the computed G^M/RT surface together with the experimental tie-lines are presented in Figures S12 to S23 in the SI. All Figures reveal common tangents between the conjugate liquid phases, indicating agreement between the experimental tie-lines and the G^M/RT surface derived from the regressed parameters. The regressed τ_{ij} for the binary subsystems demonstrated that only one subsystem (water+solvent) is in the heterogeneous region, which verifies that the parameters are consistent with the behavior in the ternary phase diagram. The ternary diagrams including the tie-lines of the regressed NRTL parameters and the experimental tie-lines can be found in Figures S24 and S25 in the SI. The tie-lines from the NRTL model show good agreement with those measured experimentally.

The distribution coefficient and selectivities for the 2,3-bdo ternary systems are presented in Fig. 3 and documented in Table 8. Data for other solvents from the literature, including 1-butanol [1], 1-pentanol [8] and 1-hexanol [4], are also provided. The distribution coefficient and selectivities for the acetoin ternary systems are presented in Fig. 4 and documented in Table 9. Data of 1-butanol from the literature [2] is also provided.

Across all solvents (C7 to C10) distribution coefficients decrease with increasing carbon-chain length for both solutes when compared at

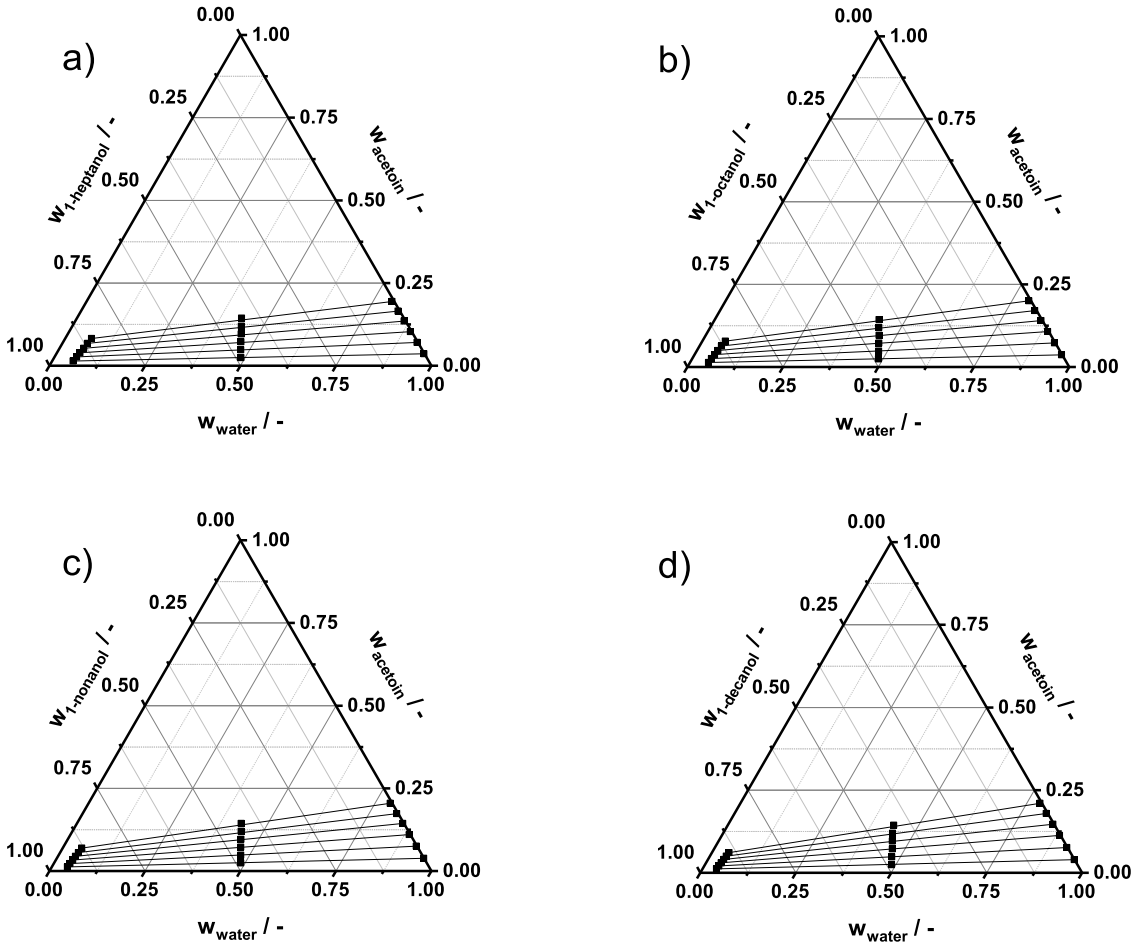

Fig. 2. Ternary diagrams of the mass fraction of the extraction systems consisting of water, acetoin, and 1-heptanol (a), 1-octanol (b), 1-nonanol (c) and 1-decanol (d) at 298.2 K and 99.3 kPa. Black squares indicate experimental tie-line data and the mixing point.

Table 4
Deviation of the weighed 2,3-bdo mass from the calculated 2,3-bdo mass based on the concentrations of the NMR at 298.2 K and atmospheric pressure (99.3 kPa) calculated as described previously. The uncertainty in temperature is $u(T)$ = 0.1 K while uncertainty in pressure is $u(p)$ = 0.74 kPa.

1-heptanol			1-octanol		
$\mathbf{w}_{2,3-\mathbf{bdo}}^{\mathbf{aq,eq}}$	$ER_{2,3-bdo}^{org,}$	$ER_{2,3-bdo}^{aq}$	$\mathbf{w}_{2,3-\mathbf{bdo}}^{\mathbf{aq,eq}}$	$ER_{2,3-bdo}^{org,}$	$ER_{2,3-bdo}^{aq}$
0.0407	0.0036	0.0037	0.0458	−0.0106	−0.0110
0.0770	0.0182	0.0193	0.0798	0.0722	0.0772
0.1139	0.0245	0.0266	0.1169	0.0483	0.0533
0.1500	0.0150	0.0168	0.1523	0.0324	0.0366
0.1834	0.0104	0.0119	0.1860	0.0287	0.0333
0.2147	0.0103	0.0120	0.2176	0.0272	0.0323
1-nonanol			1-decanol		
$\mathbf{w}_{2,3-\mathbf{bdo}}^{\mathbf{aq,eq}}$	$ER_{2,3-bdo}^{org,}$	$ER_{2,3-bdo}^{aq}$	$\mathbf{w}_{2,3-\mathbf{bdo}}^{\mathbf{aq,eq}}$	$ER_{2,3-bdo}^{org,}$	$ER_{2,3-bdo}^{aq}$
0.0417	0.0639	0.0663	0.0402	0.0973	0.1008
0.0823	0.0250	0.0267	0.0822	0.0336	0.0360
0.1187	0.0275	0.0303	0.1228	0.0048	0.0054
0.1560	0.0174	0.0199	0.1606	−0.0048	−0.0055
0.1906	0.0176	0.0207	0.1930	0.0150	0.0177
0.2240	0.0128	0.0154	0.2264	0.0164	0.0199

Table 5
Deviation of the weighed acetoin mass from the calculated acetoin mass based on the concentrations of the NMR at 298.2 K and atmospheric pressure (99.3 kPa) calculated as described previously. The uncertainty in temperature is $u(T)$ = 0.1 K while uncertainty in pressure is $u(p)$ = 0.74 kPa.

1-heptanol			1-octanol		
$\mathbf{w}_{\mathbf{acetoin}}^{\mathbf{aq,eq}}$	$ER_{acetoin}^{org,}$	$ER_{acetoin}^{aq}$	$\mathbf{w}_{\mathbf{acetoin}}^{\mathbf{aq,eq}}$	$ER_{acetoin}^{org,}$	$ER_{acetoin}^{aq}$
0.0360	−0.0152	−0.0155	0.0369	−0.0332	−0.0337
0.0704	0.0073	0.0077	0.0726	−0.0074	−0.0073
0.1033	0.0192	0.0206	0.1070	0.0037	0.0049
0.1349	0.0276	0.0302	0.1401	0.0093	0.0115
0.1651	0.0324	0.0362	0.1705	0.0151	0.0187
0.1941	0.0370	0.0421	0.1999	0.0188	0.0236
1-nonanol			1-decanol		
$\mathbf{w}_{\mathbf{acetoin}}^{\mathbf{aq,eq}}$	$ER_{acetoin}^{org,}$	$ER_{acetoin}^{aq}$	$\mathbf{w}_{\mathbf{acetoin}}^{\mathbf{aq,eq}}$	$ER_{acetoin}^{org,}$	$ER_{acetoin}^{aq}$
0.0383	−0.0263	−0.0268	0.0396	−0.0542	−0.0555
0.0752	−0.0065	−0.0063	0.0764	−0.0120	−0.0123
0.1102	0.0068	0.0081	0.1128	0.0007	0.0014
0.1436	0.0140	0.0167	0.1467	0.0091	0.0111
0.1737	0.0293	0.0348	0.1795	0.0140	0.0173
0.2059	0.0242	0.0300	0.2105	0.0223	0.0279

similar equilibrium loadings. At the highest solute loading, D for 2,3-bdo follows 1-heptanol (0.383) > 1-octanol (0.324) > 1-nonanol (0.295) > 1-decanol (0.261), and acetoin shows the same ordering 0.425 > 0.394 > 0.337 > 0.290. Over the investigated solute composition window, values span roughly 0.13–0.38 for 2,3-bdo and 0.27–0.43 for acetoin. Acetoin consistently exceeding 2,3-bdo in any given solvent and composition. Selectivities mirror the balance between solute transfer and water co-extraction. At the highest solute concentration S for 2,3-bdo is about 4.07 (1-heptanol), 3.72 (1-octanol), 4.03 (1-nonaol), 4.12 (1-decanol), while acetoin gives 4.92, 5.19, 5.30, 5.06 respectively. At

Table 6
RMSD and NRTL parameters for correlation of ternary system water (1), 2,3-bdo (2), and n-alcohol (3) (1-heptanol, 1-octanol, 1-nonanol, 1-decanol).

System	τ_{12}	τ_{21}	τ_{23}	τ_{32}	τ_{13}	τ_{31}	RMSD
1-heptanol	−2.9240	−1.2165	2.2491	−5.192	7.0000	1.1985	0.0012
1-octanol	−2.9240	−1.2165	1.7267	−4.785	7.1150	1.2125	0.0031
1-nonanol	−2.9240	−1.2165	3.4161	−5.2174	7.1547	1.2929	0.0025
1-decanol	−2.9240	−1.2165	2.4901	−5.008	7.4939	1.5087	0.0054

Table 7
RMSD and NRTL parameters for correlation of ternary system water (1), acetoin (2), and n-alcohol (3) (1-heptanol, 1-octanol, 1-nonanol, 1-decanol).

System	τ_{12}	τ_{21}	τ_{23}	τ_{32}	τ_{13}	τ_{31}	RMSD
1-heptanol	−3.5153	−0.2946	1.9092	−5.1809	7.0000	1.1985	0.0054
1-octanol	−3.5153	−0.2946	2.1568	−5.1964	7.1150	1.2125	0.0059
1-nonanol	−3.5153	−0.2946	3.0285	−5.3116	7.1547	1.2929	0.0056
1-decanol	−3.5153	−0.2946	2.5295	−5.1974	7.4939	1.5087	0.0038

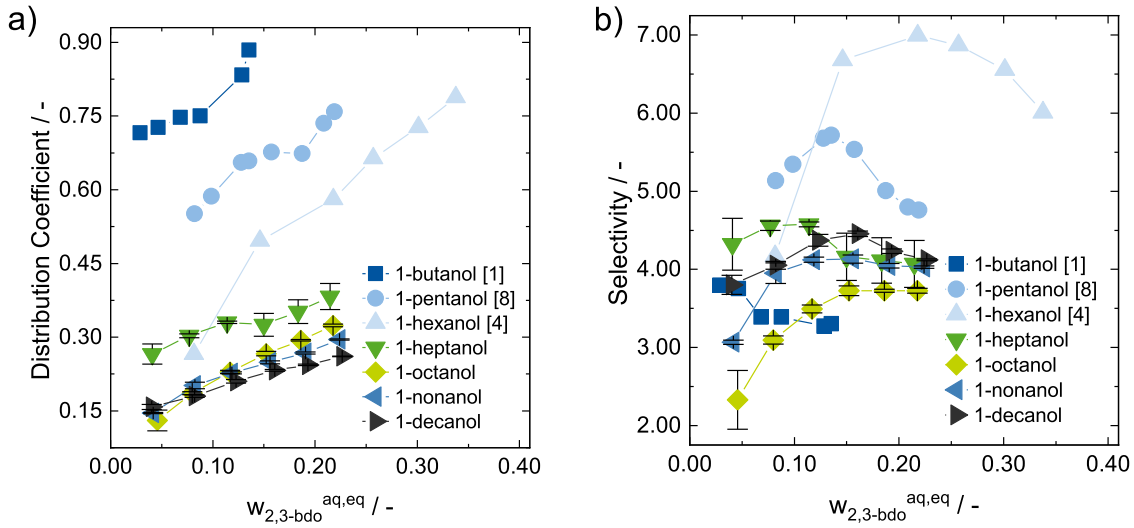

Fig. 3. Distribution coefficients (a) and selectivities (b) in the ternary system water, 2,3-bdo, and n-alcohol (1-butanol [1], 1-pentanol [8], 1-hexanol [4], 1-heptanol, 1-octanol, 1-nonanol, 1-decanol) as a function of the equilibrium weight fraction of 2,3-bdo in the aqueous phase $w_{2,3-bdo}^{aq,eq}$.

lower solute loadings, selectivity increases and reaches the highest values in the longer n-alcohols (7.94 for acetoin in 1-decanol). Acetoin exhibits higher maximum distribution coefficients and selectivities than 2,3-bdo in the same solvent. Water distribution is similar in experiments conducted for both solutes resulting in larger D_{solute} translates into larger S.

The observed ordering is consistent with solvent polarity along the n-alcohol series with the distinct intermolecular interactions of the two solutes. 2,3-bdo, a vicinal diol with two strong hydrogen bond-donor and acceptor sites is strongly hydrated and engages in extensive hydrogen bonds in water. These hydrogen bonds lower the driving force of 2,3-bdo to transfer into the solvent phase. Acetoin, an α-hydroxyketone, has a carbonyl group that acts as a strong hydrogen bond acceptor and a single hydroxyl group. This combination forms interaction with the hydroxy group of the solvent while being less hydrated than the diol, leading to larger D. With sdonor strength of the solvent decrease. This decrease leads to reduced solvent interactions and reduced water co-extraction. These trends are in line with the octanol/water distribution coefficients ($\log(P) = -0.36$ for acetoin and $\log(P) = -0.9$ for 2,3-bdo [17,18].). The calculated distribution coefficients and selectivities from the NRTL correlation reproduce the experimental ordering and composition dependence (cf. Figures S26–S27 Tables S7-S8).

Beyond the linear C7 to C10 n-alcohols investigated in this work, recent studies on 2,3-bdo downstream processing highlight additional solvent families that are relevant for future solvent screening [11,19]. A particular promising group are terpenoid-based solvents. Westarp et al. reported ternary LLE and binary VLE data for water + 2,3-bdo + menthol, thymol and carvacrol. Thymol and Carvacrol were classified as solvent with higher distribution coefficients than reported in this work (D = 0.55–0.66) and selectivities (S = 8–12) [11]. These bio-based terpenoids thus constitute a promising class of green, high boiling solvents that should be considered alongside the n-alcohols studied here.

4. Conclusion

Isothermal LLE data is reported for the ternary systems water+2,3-bdo+*n*-alcohol and water+acetoin+*n*-alcohol (1-heptanol to 1-decanol) at 298.2 K. From these data, distribution coefficients D and selectivity S were determined across multiple tie-lines to compare solvents and solutes. Acetoin exhibits systematically higher D and S than 2,3-bdo in each solvent and composition. (D up to 0.4252 and S up to 7.94 for acetoin, versus D up to 0.3827 and S up to 4.57 for 2,3-bdo). Along with the n-alcohol series, D decreases with increasing alkyl-chain length for both solutes, while S tends to increase toward the longer n-alcohols due to reduced water co-extraction.

The trends are consistent with the solvent polarity and with distinct intermolecular interactions of the solutes. The vicinal diol 2,3-bdo has two strong hydrogen-bond donor/acceptor sites. Because of this, 2,3-bdo is strongly hydrated and therefore less prone to transfer into the

Table 8
The experimental distribution coefficients and selectivities and their uncertainties for the extraction of 2,3-bdo at 298.2 K and atmospheric pressure (99.3 kPa). The uncertainty in temperature is $u(T) = 0.1$ K while uncertainty in pressure is $u(p) = 0.74$ kPa.

System	$w^{aq,eq}_{2,3-bdo}$	$D_{2,3-bdo}$	$u_{D,\ 2,3-bdo}$	$S_{2,3-bdo}$	$u_{S,\ 2,3-bdo}$
1-heptanol	0.0407	0.2656	0.0203	4.3221	0.3307
	0.0770	0.3029	0.0040	4.5590	0.0606
	0.1139	0.3303	0.0022	4.5745	0.0308
	0.1500	0.3251	0.0233	4.1611	0.3033
	0.1834	0.3520	0.0239	4.1133	0.2902
	0.2147	0.3827	0.0265	4.0698	0.3017
1-octanol	0.0458	0.1307	0.0211	2.3284	0.3758
	0.0798	0.1861	0.0032	3.0945	0.0531
	0.1169	0.2290	0.0033	3.4920	0.0508
	0.1523	0.2664	0.0044	3.7264	0.0621
	0.1860	0.2937	0.0014	3.7258	0.0203
	0.2176	0.3239	0.0026	3.7244	0.0304
1-nonanol	0.0417	0.1456	0.0012	3.0662	0.0257
	0.0823	0.2018	0.0068	3.9505	0.1326
	0.1187	0.2273	0.0019	4.1233	0.0343
	0.1560	0.2487	0.0032	4.1315	0.0527
	0.1906	0.2679	0.0019	4.0460	0.0293
	0.2240	0.2950	0.0012	4.0271	0.0160
1-decanol	0.0402	0.1581	0.0051	3.8006	0.1221
	0.0822	0.1800	0.0022	4.0527	0.0502
	0.1228	0.2101	0.0036	4.3713	0.0760
	0.1606	0.2325	0.0018	4.4556	0.0347
	0.1930	0.2436	0.0016	4.2321	0.0279
	0.2264	0.2610	0.0008	4.1215	0.0132

solvent. Acetoin (an α-hydroxyketone) benefits from favorable OH—*O* = *C* interactions in the solvents combined with a less structured hydration shell leading to larger *D*. Since water co-extraction is approximately similar for both solutes, acetoin exhibits larger *S*. The NRTL correlation reproduces the experimental tie-lines and their compositions dependence and captures the solvent ordering observed across the series. According to the topological analysis of Gibbs energy of mixing, the parameters were consistent with the experimental findings. Taken together, the results provide a coherent thermodynamic picture of how solute functionality and solvent polarity govern *D* and *S* in aqueous/alkanol systems for 2,3-bdo and acetoin as solutes, offering a solid basis for model evaluation and comparative studies.

CRediT authorship contribution statement

Peter Förster: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **William Graf von Westarp:** Writing – review & editing, Conceptualization. **Janik Hense:** Writing – review & editing, Conceptualization. **Johannes von Campenhausen:** Writing – review & editing, Methodology. **Andreas Jupke:** Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors have no conflicts of interest to declare that are relevant to this article.

Table 9
The experimental distribution coefficients and selectivities and their uncertainties for the extraction of acetoin at 298.2 K and atmospheric pressure (99.3 kPa). The uncertainty in temperature is $u(T) = 0.1$ K while uncertainty in pressure is $u(p) = 0.74$ kPa.

System	$w^{aq,eq}_{acetoin}$	$D_{acetoin}$	$u_{D,acetoin}$	$S_{acetoin}$	$u_{S,acetoin}$
1-heptanol	0.0360	0.3914	0.0032	6.8487	0.0575
	0.0704	0.3754	0.0016	6.0168	0.0338
	0.1033	0.3811	0.0009	5.6353	0.0161
	0.1349	0.3911	0.0012	5.3325	0.0167
	0.1651	0.4076	0.0005	5.1266	0.0090
	0.1941	0.4252	0.0006	4.9175	0.0122
1-octanol	0.0369	0.3738	0.0014	7.4097	0.0384
	0.0726	0.3468	0.0022	6.3427	0.0425
	0.1070	0.3489	0.0010	5.8617	0.0201
	0.1401	0.3570	0.0007	5.5409	0.0138
	0.1705	0.3735	0.0009	5.3632	0.0130
	0.1999	0.3938	0.0004	5.1862	0.0102
1-nonanol	0.0383	0.3268	0.0028	7.6357	0.0898
	0.0752	0.2977	0.0007	6.4481	0.0155
	0.1102	0.3001	0.0010	5.9805	0.0248
	0.1436	0.3090	0.0004	5.7001	0.0093
	0.1737	0.3221	0.0051	5.4939	0.0894
	0.2059	0.3373	0.0003	5.3029	0.0073
1-decanol	0.0396	0.3017	0.0012	7.9429	0.0319
	0.0764	0.2737	0.0013	6.6276	0.0321
	0.1128	0.2694	0.0006	5.9950	0.0234
	0.1467	0.2745	0.0003	5.6588	0.0133
	0.1795	0.2817	0.0004	5.3561	0.0185
	0.2105	0.2895	0.0013	5.0557	0.0257

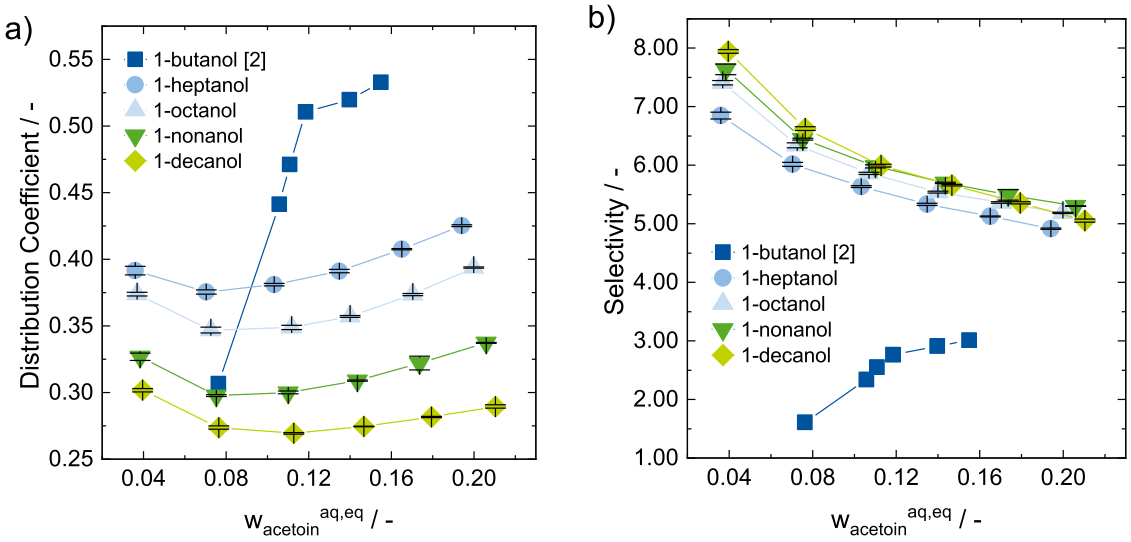

Fig. 4. Distribution coefficients (a) and selectivities (b) in the ternary system water, acetoin, and n-alcohol (1-butanol [2], 1-heptanol, 1-octanol, 1-nonanol, 1-decanol) as a function of the equilibrium weight fraction of acetoin in the aqueous phase $w_{acetoin}^{aq,eq}$.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2025.114657.

Data availability

Data will be made available on request.

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