Measurement and Thermodynamic Modeling of LLE Data of Ternary System (Water + Caproic Acid + Undecan-1-ol) at 298.2 K

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In the present study, undecan-1-ol was used as an extractant to remove caproic acid from aqueous phase. Experimental tie-line data of the ternary system (water + caproic acid + undecan-1-ol) were measured at T = 298.2 K and atmospheric pressure. Acid-base and Karl Fisher titrations were used to determine the mass fractions of the acid and water, respectively. Solvent compositions were computed using mass balance equation. The obtained tie-line data were then correlated with UNQUAC and NRTL thermodynamic models. The values of root mean square deviations (up to 0.4%) proved that the correlated results of both the models were in great agreement with experimental points. Distribution coefficients of caproic acid (23.2 to 49.4) and separation factors (678 to 904) were calculated over the biphasic region. Both partition factors had high values and confirmed the high ability of undecan-1-ol for purification of caproic acid. The efficiency of extraction was also calculated for each tie-line and the results were better than 96%.

INTRODUCTION

Caproic Acid (hexanoic acid, CA) is the first member of medium-chain fatty acids (MCFAs), which are widely produced through fermentation processes. MCFAs have a variety of applications in the production of industrial chemicals and food industries [1]. Liquid-liquid extraction (LLE) is an economic and applicable method for purification of MCFAs from fermentation broth. Many solvents with different functional groups have been tested for extraction of short-chain fatty acids (SCFAs) and MCFAs from aqueous phase [2-14].

Furfural [15], tributylphosphate [16,17], trialkyl-phosphine cxide [18], 1-octanol [19] and four acetate esters (n-propyl, isopropyl, n-amyl, and n-hexyl acetates) [20] were the only solvents that have been used for investigation of ternary liquid-liquid equilibria of caproic acid aqueous mixtures. Unlike the SCFAs, MCF As (including caproic

acid) have not been investigated widely by researchers. For instance, only the reactive extraction of CA was investigated by Wasewar *et al.* in 2011 [21-22].

In current research, the ability of undecan-1-ol (U1OH) for solvent extraction of CA from aqueous solution was investigated. The selected solvent has suitable functional group. Its water solubility is very slight and it boils at 516 K which is far from the boiling point of water. It has a high flashpoint (381 K) and its density is 0.83 g ml^{-1} which is much lower than the density of water. The mentioned characteristics make U1OH a good candidate for removing CA from water. Low toxicity of U1OH is another important property which makes it suitable for use in food and the pharmaceutical industry. Undecan-1-ol was previously applied as solvent in ternary aqueous mixtures for extraction of C1-C5 linear SCFAs, 2-propanol, and phosphoric acid [23-25].

In this study, Phase diagram was determined at 298.2 K using tie-line data measurements. Distribution coefficients of caproic acid (D_a), water (D_w), separation factors (S) and

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efficiency of extraction (E) were computed to assess the ability of U1OH for separation of caproic acid from aqueous phase. Tow thermodynamic models including UNIQUAC and NRTL equations [26] were employed to correlate the measured tie-line data. Binary interaction parameters were deduced through the modeling process and root mean square deviation (rmsd) values were calculated for assessment of correlation results. The possibility of azeotrope formation between CA and U1OH was also investigated by UNIFAC [27] model.

EXPERIMENTAL

Chemicals

Undecan-1-ol and caproic acid were prepared from Sigma. Gas chromatography validated the purity of chemicals and they were applied without any purification. The mass fraction purities of both purchased chemicals were larger than 0.98. Because of water impurity, both of the chemicals were dried and stored in molecular sieves before use. Purified water with conductivity lower than 1.5 $\mu S.cm^{-1}$ and filtered using a 0.22 μm pore size non-sterile Millex filter was applied throughout all data measurements.

Instruments and Analysis

Temperature of water circulation was kept constant with an accuracy of ±0.1 K. A digital thermometer (Testo-735) was used to check the temperature fluctuations. An electronic analytical balance (Precisa, model LS120A) with an accuracy of ±0.0002 g was used to prepare feed mixtures. Karl Fischer titrations were performed using MKV-710D KF titrator.

Determination of tie-line data for the ternary system (water + caproic acid + undecan-1-ol) was performed at $T = 298.2$ K. Ternary mixtures containing certain amounts of water, CA, and U1OH were prepared in equilibrium glass cells with volumes of 20 ml. The mixtures were stirred by a magnetic stirrer for 4 h, and then settled for 4 h until the two clear and transparent phases were formed. After 4 h of relaxing, concentration of CA in both phases were constant. Different situations between 1 to 5 h were tested for the time of mixing and relaxing; after 4 h, no changes were observed in the content. When the equilibrium was reached, two glass

syringes were used for removing samples from upper (alcoholic) and lower (aqueous) phases.

All analysis resulted in mass fractions for tie-line endpoints. Caproic acid content in organic and aqueous layers (w_{21} for aqueous phase and w_{23} for organic phase) was determined by acid-base titration using a strong base (NaOH). Water content of aqueous (w_{11}) and organic (w_{13}) layers were measured by Karl Fisher titration [28]. The mass fractions of undecan-1-ol in each layer (w_{31} means content of alcohol in aqueous layer and w_{33} indicates solvent mass fraction in solvent layer) were exploited using the mass balance equation ($\sum w_i = 1$). Using Eq. (1) [29], the standard uncertainty was estimated for all of the measured mass fractions and the value was better than ± 0.005:

$$u(x) = \frac{\sqrt{\frac{\sum_{i=1}^{n}(w_i - \overline{w})^2}{n-1}}}{\sqrt{n}}$$

$$(1)$$

Here, w_i, $\overline{w}$, and n represent mass fraction, average of measurement, and total number of measurements.

RESULTS AND DISCUSSION

UNIFAC Predictions

Since U1OH is the extracting solvent in this research, the possibility of azeotrope formation between caproic acid and unecan-1-ol must be investigated. Here, UNIFAC predictive method [27] was used to estimate the boiling points of the binary mixtures of CA+U1OH. After liquid extraction process, the extract such as caproic acid moves to solvent phase and the extract must be separated from solvent. In this step, distillation is a routine method and formation of azeotrope limits the distillation process. For this reason, investigation of azeotrope formation between solvent and extract is necessary before choosing a solvent for liquid extraction experiments.

To plot Fig. 1, 41 points were predicted for binary solutions of CA+U1OH. As could be seen from this figure, blue squares and green circles do not meet each other in any point and this proves that the binary mixtures containing CA+U1OH do not form azeotrope in any mole fraction from theoretical point of view.
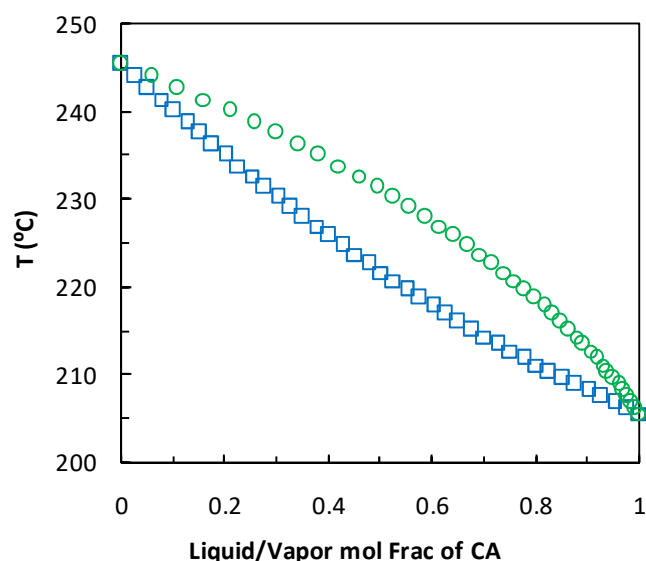
Fig. 1. UNIFAC predicted boiling points for the binary system caproic acid + undecan-1-ol. Mole fractions of CA in (○) vapor and (□) liquid phases.
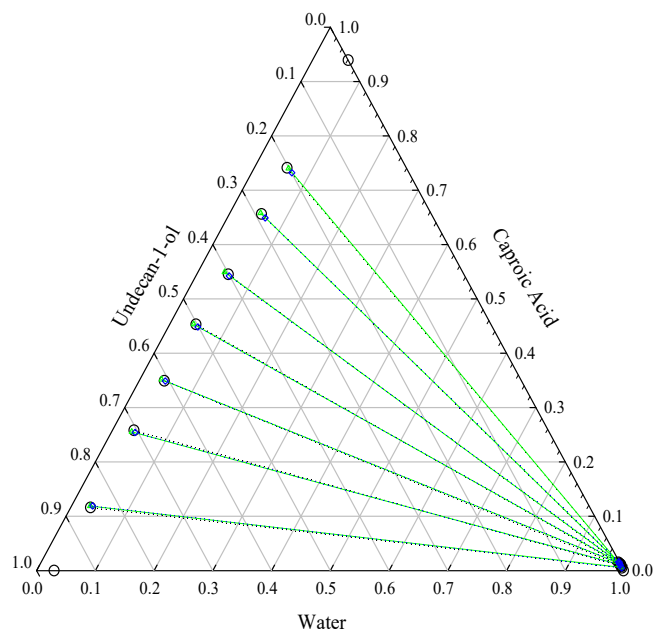

Fig. 2. Ternary phase diagram for LLE of [water + caproic acid + undecan-1-ol] at $T = 298.2$ K; (○) experimental tie-line data, (Δ) NRTL correlated points ($\alpha = 0.3$). (◊) UNIQUAC correlated points.

Tie-Line Data Measurements

The experimental tie-line data of the ternary system (water + caproic acid + undecan-1-ol) were measured at $T = 298.2$ K and barometric pressure (1012 hPa). The equilibrated tie-line data of the studied ternary mixtures in mentioned conditions are inserted in Table 1. The obtained tie-line data were shown in triangle diagram (Fig. 2) to present biphasic region and the power of solvent for extraction process. Type-II LLE behavior can be seen in Fig. 2. In the studied system, there are two pairs with partial

Table 1. Experimental Tie-line Points in Mass Fraction, Separation Factors (S) and Distribution Coefficients of CA (D_a) and Water (D_w) for (Water + Caproic Acid + Undecan-1-ol) at $T = 298.2$ K[a]

w_{11}	w_{21}	w_{31}	w_{13}	w_{23}	w_{33}	D_w	D_a	% E	S
Aqueous phase			Organic phase						
0.999[b]	0.000	0.001[b]	0.030[b]	0.000	0.970[b]				
0.989[b]	0.011[b]	0.000	0.061[b]	0.939[b]	0.000				
0.994	0.005	0.001	0.034	0.116	0.85	23.20	0.03	96	678
0.991	0.008	0.001	0.037	0.258	0.705	32.25	0.04	97	864
0.99	0.009	0.001	0.043	0.349	0.608	38.78	0.04	97	893
0.988	0.011	0.001	0.045	0.453	0.502	41.18	0.05	98	904
0.987	0.012	0.001	0.054	0.545	0.401	45.42	0.05	98	830
0.985	0.013	0.002	0.055	0.656	0.289	50.46	0.06	98	904
0.983	0.015	0.002	0.056	0.741	0.203	49.40	0.06	98	867

[a]Standard uncertainties u are u(T) = 0.1 K, u(P) = 5 hPa, u(w) = 0.005. [b]Mutual solubilities of immiscible pairs.
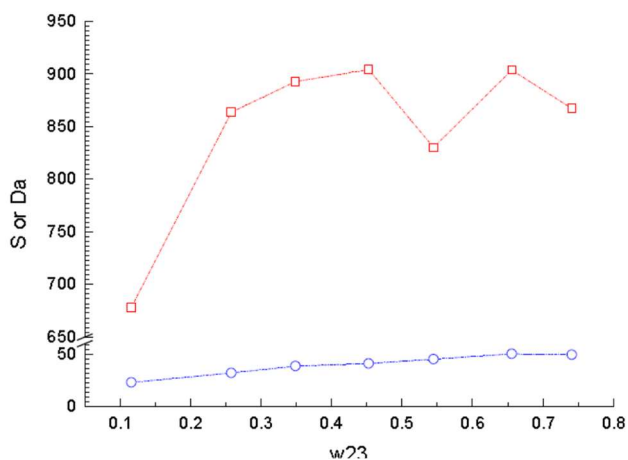
Fig. 3. Plot of the partition factors (S and D_a) against w_{23}; ($\square$) Separation factor and ($\circ$) Distribution coefficient of CA.

miscibility (water-U1OH and water-CA) and the only miscible pair belongs to the CA-U1OH mixtures. The biphasic area is extremely wide and it is more than 90% of whole triangular area. This is an important finding showing the applicability of U1OH for extraction of caproic acid from water.

The ability of U1OH for removing the CA was judged by calculating two partition factors; distribution coefficients of extract (here means CA) defined as $D_a = \frac{w_{23}}{w_{21}}$ and separation factors ($S = \frac{D_a}{D_w}$, where D_w is distribution coefficient of water defined as $D_w = \frac{w_{13}}{w_{11}}$). All partition factors were calculated by measured tie-line data and are shown in Table 1. Separation factor must be larger than unity. In this study, separation factors were much larger than 1 and this proves the strong tendency of CA to transfer to alcohol phase. Distribution coefficients of CA could be any value, but larger values indicate that little amount of solvent is needed for the extraction process. The values for D_a were very suitable in this ternary system. The efficiency of extraction can be calculated using measured mass fractions of the extract component ($\% E = 100 \times \frac{w_{23}}{w_{23}+w_{21}}$). As it is clear from Table 1, the extraction efficiency was greater than 96% in all investigated mixtures.

For better understanding of the solvent capacity, Fig. 3 was plotted in which both partition factors (S and D_a) were plotted against w_{23} (mass fraction of CA in alcohol phase).
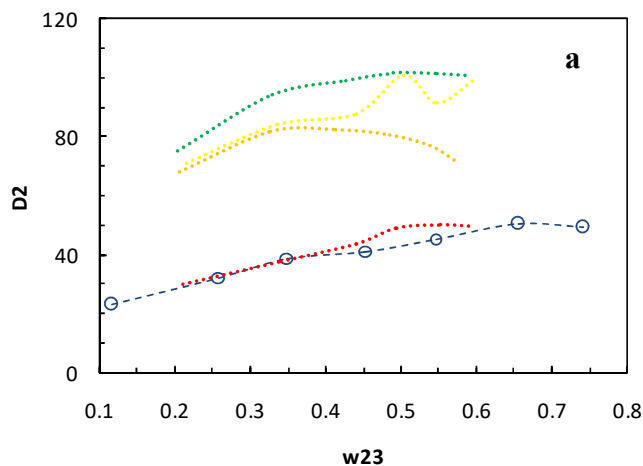

Fig. 4a. Plot of the distribution coefficients of (water + CA + Solvent) at 298.2 K against w_{23}; (-$\circ$-) undecan-1-ol, (...) n-propyl acetate, (...) isopropyl acetate, (...) n-amyl acetate and (...) n-hexyl acetate.

Fig. 4b. Plot of the separation factors of (water + CA + Solvent) at 298.2 K against w_{23}; (-$\circ$-) undecan-1-ol, (...) n-propyl acetate, (...) isopropyl acetate, (...) n-amyl acetate and (...) n-hexyl acetate.
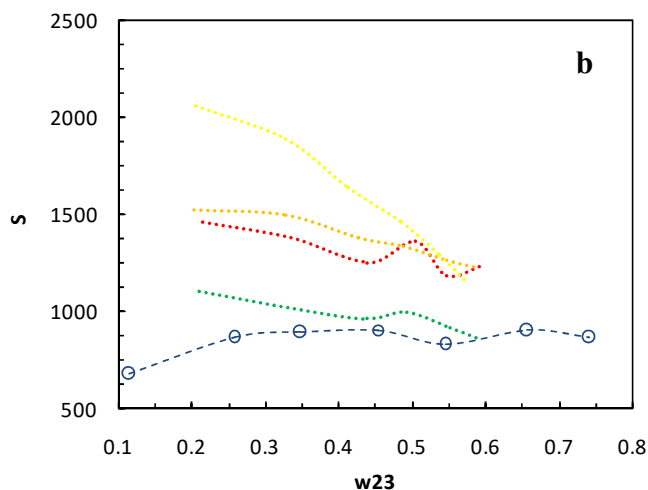
This figure evidently shows that the values of the separation factor fluctuated around 850; however, distribution coefficients increased with an increase in acid content in organic phase.

To compare the results of the present study to the previous works, Figs. 4 and 5 were plotted. In these figures,

distribution coefficients and separation factors of (water + CA + UOH) ternary system and 4 esteric solvents (n-propyl acetate, isopropyl acetate, n-amyl acetate and n-hexyl acetate) [20] were plotted against mass fraction of caproic acid in the organic phase. As it is clear from the figures, LLE results of undecan-1-ol ternary system are in close agreement with the results of n-hexyl acetate ternary system. Undecan-1-ol has 11 carbon atoms and 1 polar oxygen atom and n-hexyl acetate has 8 carbon atoms and 2 oxygen atoms with one polar oxygen atom.

Thermodynamic Modeling

Correlation of tie-line data were performed by UNIQUAC and NRTL models [26]. Results of correlations are shown in Table 2. The table contains correlated tie-lines obtained by thermodynamic models and the UNIQUAC structural parameters r and q. Correlated tie-line data of both models are shown in Fig. 1. The figure obviously reveals that the correlated and experimental tie-lines are in good agreement. The values of r and q were determined using the

Bondi method [26]. For NRTL modeling, the value of non-randomness (α) must be optimized. The value 0.3 showed the best results among the values 0.1, 0.2 and 0.3.

Considering fixed values for r, q and α, there are 6 adjustable parameters for each mentioned model. To optimize the models and obtaining binary interaction parameters, an objective function (OF) is needed [30-32]. After performing the correlation process, the nearness of correlated and measured data was investigated using the root-mean square deviation (rmsd) as follows:

$$rmsd = \sqrt{\frac{\sum_{i=1}^{n}\left(w_i^{Exp.} - w_i^{Corr.}\right)^2}{n}} \qquad (2)$$

Here, n is the number of data and $w_i^{Exp.}$ and $w_i^{Corr.}$ stand for the measured and modeled mass fractions. Optimization strategy and thermodynamic equations applied in the present study have been taken from N. Lami *et al.* [33].

Binary interaction parameters and the rmsd values of UNIQUAC and NRTL models are listed in Table 3. The rmsd

Table 2. The UNIQUAC Structural Parameters (r and q) for Pure Components and Calculated UNIQUAC and NRTL ($\alpha = 0.3$) Tie-line Data in Mass Fraction for (Water + Caproic Acid + Undecan-1-ol) at $T = 298.2$ K[a]

$w_{11}^{UNIQ.}$	w_{11}^{NRTL}	$w_{21}^{UNIQ.}$	w_{21}^{NRTL}	$w_{13}^{UNIQ.}$	w_{13}^{NRTL}	$w_{23}^{UNIQ.}$	w_{23}^{NRTL}
0.994	0.9924	0.005	0.0060	0.036	0.0320	0.119	0.1188
0.989	0.9876	0.010	0.0110	0.041	0.0344	0.254	0.2555
0.986	0.9856	0.013	0.0131	0.045	0.0371	0.349	0.3517
0.984	0.9845	0.015	0.0142	0.050	0.0408	0.448	0.4533
0.983	0.9844	0.016	0.0143	0.057	0.0455	0.542	0.5492
0.983	0.9849	0.016	0.0138	0.065	0.0524	0.649	0.6580
0.984	0.9853	0.014	0.0131	0.069	0.0589	0.732	0.7400

[a]The number of segments per molecules (r) and the relative surface area per molecules (q) of water: 0.920, 1.400, caproic acid: 4.900, 4.232 and undecan-1-ol: 8.645, 7.448.

Table 3. Binary Interaction Parameters of the UNIQUAC (a_{ij} and a_{ji}) and NRTL (b_{ij} and b_{ji}) Models and the Corresponding rmsd Values for the Ternary System [Water (1) + Caproic Acid (2) + Undecan-1-ol (3)] at 298.2 K

Components i-j	a_{ij}^{a}/K	a_{ji}/K	*rmsd* %	b_{ij}^{b}/K	b_{ji}/K	*rmsd* %
1-2	-149.51	-341.67		1675.19	156.75	
1-3	-94.74	-327.86	0.4	2233.99	466.69	0.3
2-3	-2480.30	212.35		1203.69	-31.08	

[a] $a_{ij} = \frac{(u_{ij} - u_{jj})}{R}$ for UNIQUAC model. [b] $b_{ij} = \frac{(g_{ij} - g_{jj})}{R}$ for NRTL model $\alpha = 0.3$.
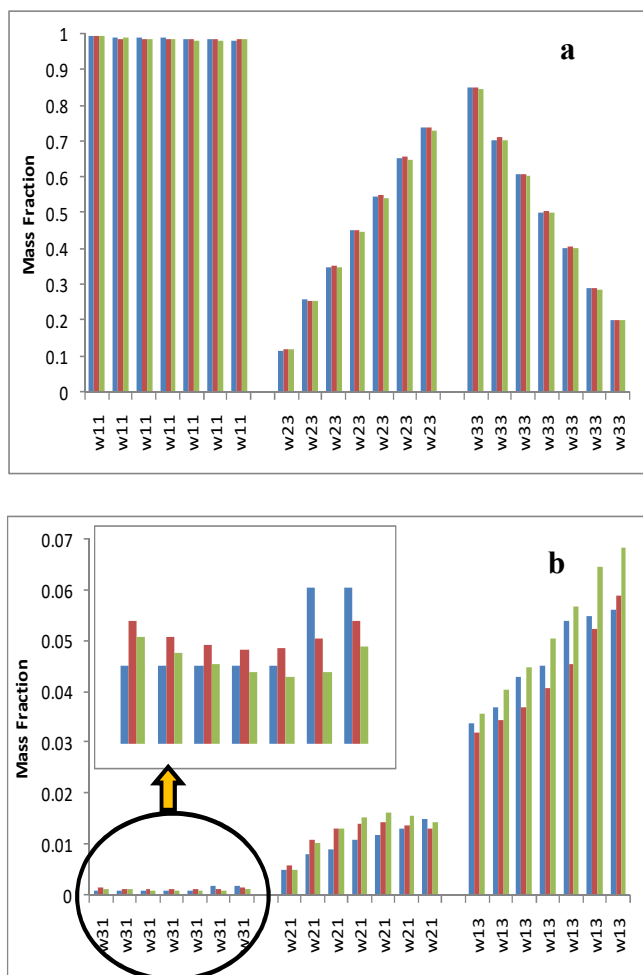
Fig. 5. Plot of experimental data and correlation results: (blue columns) experimental, (red columns) NRTL and (green columns) UNIQUAC data. (a) w_{11}, w_{23}, w_{33} and (b) w_{31}, w_{21}, w_{13}.

Fig. 6. Plot of absolute difference of experimental and model data: (blue columns) $\left|w_{exp.} - w_{NRTL}\right|$ and (red columns) $\left|w_{exp.} - w_{UNIQUAC}\right|$.

CONCLUSIONS

Tie-line data of the ternary system (water + CA + U1OH) were obtained using Karl Fischer and acid-base titration at 298.2 K and 1012 hPa. Type II LLE behavior was observed for the ternary system. Two applied thermodynamic models of NRTL and UNIQUAC correlated well with experimental data and the calculated rmsd values were used to prove the quality of correlation. UNIFAC predictions showed that there was no azeotrope point in the CA-U1OH binary system. The results of distribution coefficients, separation factors and efficiency of extraction revealed the extreme power of undecan-1-ol for removing the caproic acid from aqueous phase.

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values prove that the correlation processes had excellent results and trustable binary interaction parameters, which could produce accurate tie-line data in close agreement with experimental results. Figures 5a and 5b were also prepared to show the agreement of UNIQUAC and NRTL modeling data to experimental points. The figures obviously demonstrate the accuracy of modeling. Figure 6 also shows the deviations of modeling data from experimental points. It shows that aqueous phase mass fractions were correlated better than organic phase ones. Highest deviations were observed in water content of organic phase, while least deviations were related to the CA content in aqueous layer.
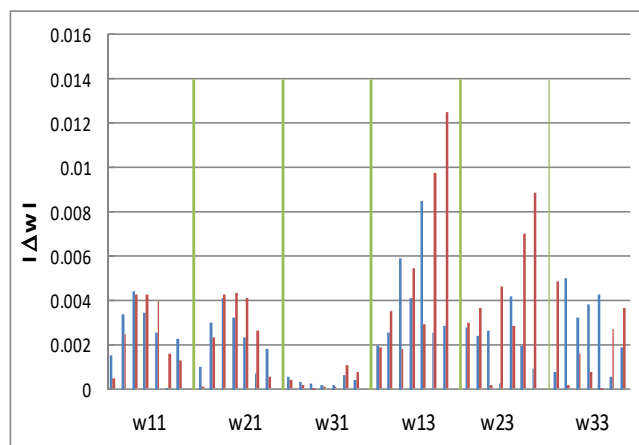
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