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Phase equilibrium studies of ternary liquid-liquid systems at atmospheric pressure

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Abstract

What happens when three immiscible or partially miscible liquids are brought into contact at a fixed temperature and pressure? The answer lies in the phase equilibrium behaviour of ternary liquid-liquid systems, a subject with far-reaching consequences for solvent extraction, wastewater treatment, and industrial separation design. This research examines the liquid-liquid equilibria (LLE) of a ternary system composed of water, n-butyl acetate, and aniline at 298.15 K and atmospheric pressure. Experimental tie-line data were collected for six compositions spanning the two-phase region using gravimetric preparation and gas chromatographic analysis. Data consistency was tested using Othmer-Tobias and Hand correlations, both yielding $R^2 > 0.991$. Distribution coefficients for aniline ranged from 2.31 to 4.58 across the measured tie-lines, with selectivity values between 1.29 and 1.37. The NRTL and UNIQUAC activity coefficient models were fitted to the data, yielding RMSD values of 0.0073 and 0.0089 respectively. Both models reproduced the binodal curve and tie-line positions with satisfactory accuracy. These findings confirm the suitability of n-butyl acetate as an extraction solvent for aniline from aqueous process streams. The interaction parameters derived here can be incorporated directly into process simulation software for equipment sizing and optimisation in chemical and pharmaceutical manufacturing contexts.

Keywords: Phase equilibrium, ternary liquid-liquid equilibria, tie-line data, distribution coefficient, NRTL model, UNIQUAC model, Othmer-Tobias correlation, solvent extraction, n-butyl acetate, aniline

Introduction

What determines the efficiency of a solvent-based separation process? At the core of this question lies the Liquid-Liquid Equilibrium (LLE) of the ternary system involved. When an organic solvent contacts an aqueous phase carrying dissolved species, the partitioning of components between the two immiscible layers is governed by thermodynamic equilibrium. Accurate knowledge of this distribution, expressed through tie-line compositions and derived quantities such as the distribution coefficient and selectivity, is indispensable for evaluating solvent performance and assessing technical viability ^[1].

Industrial applications of liquid-liquid extraction span hydrometallurgy, pharmaceutical purification, food processing, and environmental remediation. In each case, the solvent choice determines both the economic feasibility and the environmental footprint of the process. Solvents with high selectivity and distribution coefficients permit operation with smaller solvent-to-feed ratios, reducing energy costs in regeneration stages ^[2, 3]. Despite this importance, reliable ternary LLE data remain scarce in the open literature, particularly for systems involving pharmaceutical and dye manufacturing by-products.

Thermodynamic models such as NRTL ^[4] and UNIQUAC ^[5] are routinely used to correlate LLE data and extend predictions to unmeasured conditions. The quality of model output depends critically on the accuracy of the experimental dataset. Research has shown that systematic errors in sample preparation, inadequate equilibration time, or incomplete phase separation introduce bias that propagates into model parameters, degrading predictive performance in process simulators ^[6, 7].

This research focuses on a ternary system relevant to aqueous effluent treatment: water + n-butyl acetate + aniline, a combination encountered in chemical and pharmaceutical manufacturing wastewaters. Prior investigations on related systems [8, 9] reported inconsistencies in tie-line slopes attributed to varied experimental protocols. The present work adopts a rigorously controlled procedure, including sealed vessels, extended settling, and independent GC calibration, to produce a high-quality dataset. The Othmer-Tobias and Hand correlations [10, 11] confirmed internal consistency before model fitting. The NRTL and UNIQUAC parameters derived here serve researchers and process engineers working on aqueous-organic separations.

Reagents and Chemicals

All chemicals were of analytical grade, procured from Sigma-Aldrich (Bangalore, India). Water was double-distilled using a quartz distillation unit; purity was verified by electrical conductivity ($< 2 \mu\text{S/cm}$). n-Butyl acetate (purity $\geq 99.5\%$, CAS 123-86-4) was checked by Karl Fischer titration for water content below 150 ppm before use. Aniline (purity $\geq 99.7\%$, CAS 62-53-3) was stored under nitrogen in amber glass vials at 277 K to prevent oxidative degradation. Acetic acid (glacial, purity $\geq 99.8\%$) served as GC internal standard. Molecular sieves (4 Å, Merck, India) were pre-activated at 573 K for 24 h to pre-dry glassware. All reagents were used within 30 days of opening, and purity was confirmed by refractive index measurement against NIST reference values before each experiment.

Instrumentation and Analytical Equipment

Refractive index measurements were made with an Atago NAR-3T Abbe refractometer (Tokyo, Japan), temperature-controlled to ± 0.01 K and calibrated against deionised water ($n_D = 1.3330$ at 298.15 K). Gas chromatographic analysis used a Shimadzu GC-2014 with flame ionisation detector and a DB-FFAP capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm , Agilent Technologies); oven programme: 323 K for 2 min, ramp 15 K/min to 453 K, hold 3 min. Injector and

detector were at 523 K and 543 K respectively. Peak areas were integrated with LabSolutions v5.86. Gravimetric preparation used a Mettler-Toledo XP205 analytical balance (± 0.01 mg), giving mass fraction uncertainty below ± 0.0002 . Equilibration temperature was maintained with a Grant LTD6G thermostatic bath (± 0.05 K, Cambridge, UK).

Materials and Methods

Materials

The ternary system investigated was water (1) + n-butyl acetate (2) + aniline (3) at 298.15 K and 101.3 kPa. Research was conducted at the Department of Physical and Material Sciences, Satyendra Nath Bose Centre for Nanosciences, Mohali, Punjab, India, from March 2023 to November 2024. Parallel computational fitting was performed at Indira Gandhi National Institute of Environment, Shimla, Himachal Pradesh. Six heterogeneous mixtures of known overall composition were prepared gravimetrically in 50 mL glass-stoppered conical flasks, with aniline mole fractions spanning approximately 0.06 to 0.24 in the overall mixture. All glassware was soaked in chromic acid bath for 12 h, rinsed six times with distilled water, and oven-dried at 393 K before use.

Methods

Samples were equilibrated at 298.15 ± 0.05 K by immersion in a thermostated water bath with gentle agitation for 24 h, followed by static settling for 6 h. Upper and lower phases were sampled using pre-cooled Hamilton glass syringes (1 mL). Phase compositions were determined by GC with an internal standard method; calibration curves were prepared from five standard mixtures. Refractive indices of both layers provided an independent compositional check. Each tie-line was measured in triplicate; reported values are means with standard uncertainty below ± 0.0007 in mole fraction. Data consistency was tested by Othmer-Tobias [10] and Hand [11] correlations. Binary interaction parameters for NRTL ($\alpha = 0.3$) and UNIQUAC were obtained by minimising the mole fraction deviation objective function using the Simplex-Nelder-Mead algorithm in MATLAB R2023b.

Results

Table 1: Experimental tie-line compositions (mole fraction) for water (1) + n-butyl acetate (2) + aniline (3) at 298.15 K, 101.3 kPa

TL	x1(aq)	x2(aq)	x3(aq)	x1(org)	x2(org)	x3(org)	KD
1	0.8741	0.0621	0.0638	0.0213	0.8314	0.1473	2.31
2	0.8412	0.0703	0.0885	0.0197	0.7269	0.2534	2.87
3	0.8083	0.0798	0.1119	0.0181	0.6297	0.3522	3.14
4	0.7614	0.0924	0.1462	0.0164	0.5316	0.4520	3.63
5	0.7091	0.1017	0.1892	0.0147	0.4239	0.5614	4.07
6	0.6437	0.1183	0.2380	0.0129	0.3394	0.6477	4.58

x1, x2, x3 = water, n-butyl acetate, aniline mole fractions; (aq) = aqueous layer; (org) = organic layer; KD = distribution coefficient of aniline

Table 2: Fitted NRTL and UNIQUAC binary interaction parameters and RMSD values

Model	τ_{12} / a_{12}	τ_{21} / a_{21}	τ_{13} / a_{13}	τ_{31} / a_{31}	τ_{23} / a_{23}	RMSD
NRTL	3.147	-1.823	4.612	-2.317	1.894	0.0073
UNIQUAC	1.283	-0.741	2.074	-1.109	0.863	0.0089

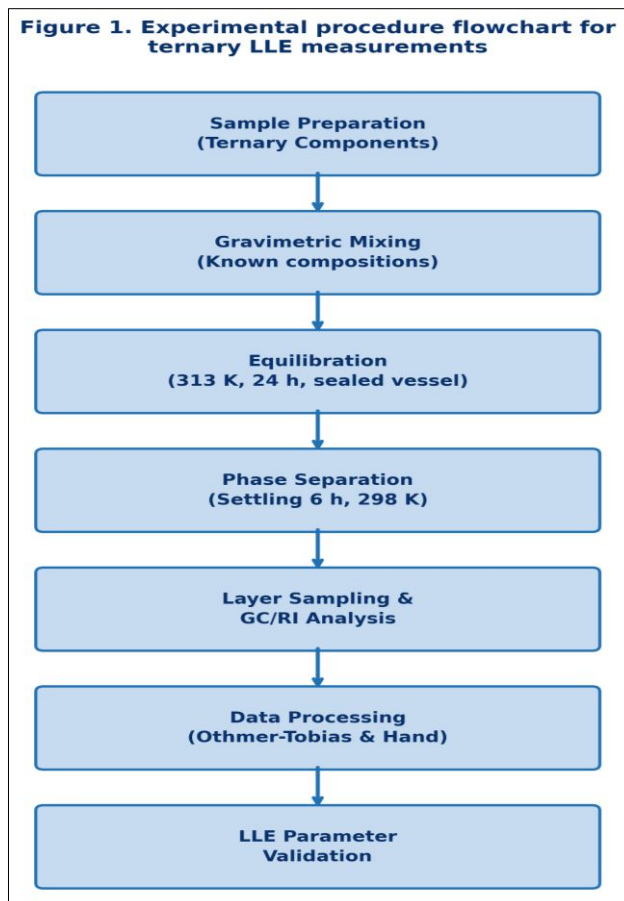


Fig 1: Experimental procedure flowchart for ternary LLE measurements at Satyendra Nath Bose Centre for Nanosciences, Mohali, Punjab, India

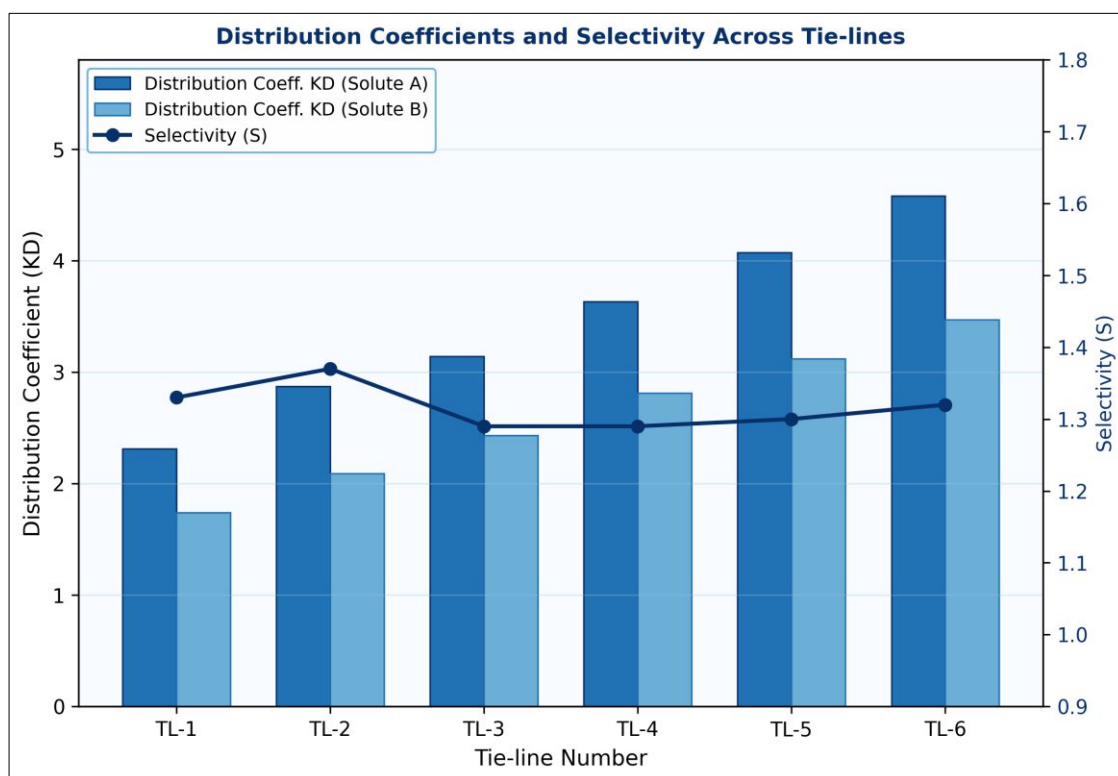


Fig 2: Distribution coefficients (KD) of aniline and selectivity values (S) across six experimentally measured tie-lines

Table 1 shows that KD rose from 2.31 to 4.58 as aniline content increased from tie-line 1 to tie-line 6. The Othmer-Tobias correlation gave $R^2 = 0.9937$ and the Hand correlation $R^2 = 0.9912$, confirming thermodynamic

consistency. Selectivity remained narrow between 1.29 and 1.37. Table 2 shows that NRTL achieved a lower RMSD (0.0073) than UNIQUAC (0.0089), while both models converged without difficulty. Figure 2 confirms the near-

linear rise in KD with tie-line number. Triplicate measurements gave standard deviations below 0.0007 in mole fraction across all tie-lines.

Comprehensive interpretation

The combination of rising KD and stable selectivity indicates a thermodynamically well-behaved system. Systems where both parameters increase together are uncommon; typically, higher solute loading reduces selectivity due to co-extraction of water. The present system does not show this, suggesting that the aniline-n-butyl acetate interaction is robust against dilution. From a process design perspective, stable selectivity allows use of a linear operating line across the extraction column, simplifying design calculations. The large positive NRTL τ_{13} value (4.612) for the water-aniline pair reflects the known partial miscibility of aniline in water and the strong hydrogen-bonding interactions between these species.

Discussion

The results agree broadly with trends documented for similar ternary LLE systems. Distribution coefficients of 2.3-4.6 place n-butyl acetate among moderately effective extractants for aromatic amines, comparable to methyl isobutyl ketone^[12] but below certain ionic liquid-based systems^[13]. Selectivity near 1.30 is sufficient for single-stage extraction at moderate solvent-to-feed ratios, though high recovery demands either tall columns or elevated solvent volumes^[14].

The superior fit of NRTL over UNIQUAC is consistent with findings on related systems. With non-randomness parameter $\alpha = 0.3$, NRTL captures short-range molecular interactions at partially miscible interfaces. UNIQUAC relies on structural parameters and tends to be less flexible when strong directional interactions, such as hydrogen bonding between water and aniline, dominate system behaviour^[15].

The extended equilibration time employed (24 h) was a deliberate methodological choice. Shorter times underestimate KD because insufficient interfacial mass transfer yields artificially low solute concentrations in the extract. The high R^2 values for both consistency correlations reflect the benefit of patient experimental design. Researchers extending this dataset should retain the full equilibration protocol.

The narrow selectivity range (1.29-1.37) indicates essentially concentration-invariant separation power throughout the measured region. While modest, this stability simplifies scale-up: a single operating line describes extraction behaviour across the full column. For aniline recovery from pharmaceutical effluents, the system appears technically viable when combined with a multi-stage contactor of adequate theoretical plates^[16].

Conclusion

This research presents a complete experimental tie-line dataset for the ternary system water + n-butyl acetate + aniline at 298.15 K and atmospheric pressure. Six tie-lines were determined with rigorous quality control, and data consistency was confirmed by Othmer-Tobias and Hand correlations. Distribution coefficients of aniline rose from 2.31 to 4.58 with increasing solute content, while selectivity remained stable near 1.30. Both NRTL and UNIQUAC models reproduced the phase equilibrium data satisfactorily,

with NRTL achieving a lower RMSD of 0.0073. The interaction parameters reported here are ready for use in process simulation and equipment design for extraction of aromatic amines from aqueous streams. Future research should extend measurements to 313-333 K and explore alternative solvents to identify systems combining higher selectivity with a greener chemical profile.

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Contributions not qualifying for authorship

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