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Property model prediction of the boiling point for pure and mixture solvents applied in herbal extraction

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Abstract. Studies on the effect of different solvent used in herbal extraction on the extraction yield have been commonly investigated. However, the impact of solvent property, such as boiling point attracts less attention. Besides, the measurement of the solvent boiling point requires much time and effort. Therefore, this study aims to use property models in predicting the boiling point of single and mixture solvents. Three pure property models were applied for several solvents while two mixture property models were utilised for the selected mixture solvents. The prediction data then were compared with the experimental data obtained from the previously published result. The mean relative error was computed to choose the best property model that can be applied to calculate the boiling point. In this study, the Marrero and Gani's method was selected to be the best model in predicting boiling point for pure solvent. In contrast, Klein and Wu's method was chosen as the best model for the boiling point prediction of mixture solvents. The selection of the best property model was made by choosing the lowest mean relative error.

1. Introduction

The solvents are daily used in numerous industrial processes, including herbal extraction. It is used in a considerable amount, especially in pharmaceutical production. The main concern related to the use of a solvent is the environmental effect resulted from the disposal of the solvent waste. The solvent that concerns ecological, economic, safety (to limit the negative influence of human involvement), product isolation as well as solvent physical and chemical properties is called "green solvent" [1, 2, 3,4].

There are many approaches in selecting green solvents that have been done where the goal is to minimize the environmental impact resulting from the use of solvents in chemical production [4]. Alfonsi et al. [5] suggested a tool that considers the environment, health and safety in selecting a green solvent of medicinal chemistry. In their study, three general areas which are workers safety (including toxicity, carcinogenicity, mutagenicity, reprotoxicity and skin absorption /sensitization), process safety (including flammability, the potential for high emissions through high vapour pressure, static charge, the potential for peroxide formation and odour issues) and environmental and regulatory considerations (including ecotoxicity and groundwater contamination, potential EHS regulatory restrictions, ozone depletion potential, photo-reactive potential) were divided in solvent selection. They concluded that these steps could influence scientists to adopt safer and greener solvent syntheses. Capello et al. [4] proposed a framework that comprises two environmental assessment methods which are environment,

health and safety; and life-cycle assessments. The framework was claimed to be suitable for selecting solvent mixtures with the most environmentally friendly option for the solvolysis process. Work by Clark and Tavener [6] recommended giving a score (one is poor and five is very good) to the solvent according to their crucial solvent properties (such as solubility), ease of separation and reuse, health and safety, cost of use (specification in solvent storage and solvent cost) and environmental impact. The highest total score for the selected solvent is the greenest solvent. Sheldon [7] found the alternative solvent for reaction media. In this work, chemical reactions, including oxidation, bio-catalysis, hydrogenation, hydroformylation, and biocatalysis, were considered. The green solvent in this study is selected based on the E factor (mass ratio of waste to the desired product). The lower the value of E factor, the greener the solvent is.

From the environmental perspective, Capello et al. [4] and Mustafa and Turner [2] found that the aqueous solvent mixtures are more environmentally favourable compared to the pure solvents or alcohols. In herbal extraction, a solvent with selected chemical and physical properties should be chosen to ensure the solvation and the release of the phytochemicals from the herbal can occur. The property model, such as the Hansen solubility parameter that describes the solubility of phytochemical in the selected solvent, can be used [8]. The low toxicity solvents usually can completely biodegrade quickly where this type of solvent has been used in the production of consumable product [9]. Low toxic solvent serves as a nutrient to the organisms where the organisms can compost the solvent into natural elements in a shorter time. For the selection of solvent in the chemical process, less toxic and non-harmful solvents that are easy to remove should be preferred. The boiling point of the solvent determines the removal of the solvent. The challenges of removing large amounts of the high boiling point of solvents during the purification and isolation process can limit scalability and efficiency [10]. However, the relatively high boiling point of a solvent such as ethylene carbonate (240°C) prevents it from being evaporated to the environment at ambient temperatures and makes it reusable for several cycles of purification [11]. Besides, the denaturation of phytochemicals in the herbal extraction process could be avoided using the solvent, which has a lower boiling point than the target phytochemicals. Thus, the boiling point becomes one of the essential properties that could affect herbal phytochemical extraction. Efthymiopoulos et al. [12] studied the effect of solvent selection and process temperature on the extraction efficiency and composition of the obtained oil from spent coffee grounds (SCG). They found that increasing solvent boiling point, and process temperature improve oil extraction efficiency in Soxhlet extraction and accelerated solvent extraction.

Extractions of Malaysian herbs have been widely done by other researchers. They studied the extraction yield by using different solvent and the effect of solvent-Malaysian herbs ratio on the extraction yield. Researchers only focus on the total extraction yield, phytochemical analysis (individual name of phytochemical and its composition in total extraction yield) and the extract's antimicrobial activities. Lack of studies focuses on the solvent selection based on the critical property such as boiling point even though researchers know its importance in the herbal extraction. The experimental boiling point data is time-consuming and needs effort. Thus, this study uses the property model prediction to calculate the desired boiling point value for both single and mixture solvents. The boiling point models (for single and mixture solvents) are listed and calculated before comparing experimental result's prediction values.

2. Methodology

2.1. Pure property model
In this study, three pure property models for the prediction of the boiling point were computed and compared with experimental data obtained from previously published data.

2.1.1. Marrero-Morejon and Pardillo-Fontdevila Method. Marrero-Morejón and Pardillo-Fontdevila [13] developed a model to predict the boiling point for pure organic compounds. They proposed a new structural approach called group-interaction contribution that considers the contributions of interactions

between the bonding groups instead of the contributions of simple groups. The developed model is as follows:

$$T_b = M^{-0.336} \sum + b \tag{1}$$

where M is the molecular weight, $\sum$ is the sum of the products for each simple group or interaction between groups that appears in the molecule and their contributions while b is a constant (b=149.84).

2.1.2. Constantinou-Gani Method. This method [14] considers two levels of estimation where the first level is for the estimation of a simple group, while the second level is used for the more structural group. The ultimate goal is to enhance the accuracy, reliability, and the range of applicability of the organic compound property estimation and overcome some of the disadvantages of the first-order groups. The model is as follows:

$$\exp(\frac{T_b}{T_{bo}}) = \sum_i N_i t_{b1,i} + \sum_j M_j t_{b1,j} \tag{2}$$

where, T_b is the boiling point to be predicted, T_{b0} is the adjustable parameters of the estimation models or universal constants (T_{b0}=204.359), $t_{b1,i}$ is the contribution of the first-order group of type-i that occurs N_i times and $t_{b2,j}$ is the contribution of the second-order group of type-j that occurs M_j times.

2.1.3. Marrero and Gani Group Contribution Method. Marrero and Gani [15] proposed three levels of estimation, where the aim is to predict the properties of organic compounds accurately. Eq. 3 shows the developed model for the boiling point of pure component prediction.

$$\exp(\frac{T_b}{T_{bo}}) = \sum_i N_i t_{b1,i} + \sum_j M_j t_{b2,j} + \sum_k O_k t_{b3,k} \tag{3}$$

where T_b is the boiling point to be predicted, T_{b0} is the adjustable parameters of the estimation models or universal constants, b_{1i} is the contribution of the first-order group of type-i that occurs N_i times, b_{2j} is the contribution of the second-order group of type-j that occurs M_j times, and b_{3k} is the contribution of the third-order group of type-k that has O_k occurrences in a compound.

2.2. Mixture Property model
Two methods which are Klein and Wu and linear mixing rule, were used to compare the boiling point result from both models with the experimental data.

2.2.1. Klein and Wu Method. Klein et al. [16] suggested the non-linear model to find the mixture boiling point, as shown in this equation:

$$R = 1 - \sum_{i=1}^{N} \frac{x_i \gamma_i (x_i T_b) P_i^\circ (T_b)}{P} = 0 \tag{4}$$

where $\gamma_i(x_i T_b)$ is an activity coefficient at boiling temperature using tested composition, xi , $P_i^\circ(T_b)$ is the saturated pressure at boiling temperature. This equation was designed for the prediction of alcohol, ketone, and aromatic hydrocarbon groups.

2.2.2. Linear Mixing Rule. The Klein and Wu method was compared with the linear mixing rule model to find the most accurate model to predict the boiling point of the solvent mixtures.

$$T_{b\,mixture} = \sum_{i=1}^{n} W_i T_{b_i} \tag{5}$$

where W_i is the mole or mass fraction of the solvent i while T_{b_i} is the boiling point of solvent i.

2.3. Validation of property models
In this study, the validation of both models (pure and mixture boiling point model) in determining the best model were examined. The prediction and experimental values were compared, and the Mean Relative Error, MRE was calculated for each solvent data using Equations 6 and 7. The error formula is used to determine the precision of the prediction model. Eq. 6 shows the calculation of error, *Error*.

$$Error = \frac{Y_{\exp} - Y_{pred}}{Y_{pred}} \tag{6}$$

where Y_{exp} is the experimental value, while Y_{pred} is the predicted value.

Besides, the Mean Relative Error, MRE can be calculated from the Eq. 6 if there is a set of available data. MRE is computed by dividing the total error of the evaluated data points with the number of data, as shown in Eq. 7.

$$MRE = \frac{\left| \sum_i Error_i \right|}{n} \tag{7}$$

where $Error_i$ is the error at the evaluated point and n is the number of data points.

3. Results and Discussion

3.1. Boiling point for pure solvent
Table 1 shows the boiling point of 30 solvents with the experimental value recorded by ICAS14 [17] software and prediction values by the Marrero and Gani (MG), Constantinou-Gani (CG) and Marrero-Morejon and Pardillo-Fontdevila (MM) methods with the error values.

This table was used to determine the best model that can predict the boiling point of the solvent. Hence, the Mean Relative Error, MRE was calculated using a summation of error (Eq. 7). The total error for the MG, CG and MM methods are 1.5428, 1.5929 and 1.9195, respectively. The total error then is divided by the number of evaluated data (30 solvents) where the MRE value for MG, CG and MM are 0.0514, 0.0531and 0.0640. MRE values for MG and CG methods are too closed where maybe clustering of the solvent types can be used. However, the clustering can be neglected because not all the solvent with the same type gives lower error by using the CG method. As an example, only methanol and ethylene glycol (alcohol solvent type) provide a lower error in the CG method but not for ethanol, 1-propanol, 1,3-Propylene-glycol and isopropyl alcohol. This also applied for hydrocarbon type of solvent (hexane, benzene, cyclohexane, toluene, nitrobenzene, pentane, cyclopropane) where only two solvents give the lowest error using CG method as compared to five solvents give the lowest error using MG method. Besides, only 11 out of 30 solvents offer lower error for the CG method as compared to the MG method. Hence, the MG method was selected to be the best of the model in predicting the boiling point for pure solvent.

3.2. Boiling point for mixture solvents
Table 2 presents the experimental data taken from Nagata [18] and the prediction data of density for solvent mixtures. Two methods which are the Klein and Wu and the linear mixing rule (LMR) were used to compute the boiling point of each mixture at solvent 1 composition, x_1. From the calculated error, the MRE value for Klein and Wu is 0.0210 and for LMR is 0.0972. Thus, the more accurate method in computing boiling point of the mixture is the Klein and Wu method. This study used the Klein and Wu method in the calculation of mixture boiling point as it gives higher accuracy than LMR method.

Table 1. Boiling point of solvent with the experimental and prediction values by the Marrero and Gani (MG), Constantinou-Gani (CG) and Marrero-Morejon and Pardillo-Fontdevila (MM) methods with the error values.

Solvent	T_b exp, K	T_b Prediction Model			Error (Eq. 6)		
		MG	CG	MM	MG	CG	MM
Methanol	337.75	273.39	288.58	311.13	0.1704	0.1380	0.2354
Acetone	329.15	306.66	305.37	272.88	0.0779	0.1102	0.0733
Chloroform	334.25	351.70	279.69	272.47	0.1951	0.2253	0.0496
Ethanol	351.35	315.64	330.01	339.78	0.0647	0.0765	0.1131
Etyhl Acetate	350.25	343.74	346.44	306.59	0.0110	0.1081	0.0190
Diethyl Ether	307.65	362.07	385.58	324.91	0.2021	0.1026	0.1503
Hexane	341.85	337.41	347.22	343.58	0.0155	0.0183	0.0132
Formic Acid	374.15	362.83	368.46	378.04	0.0154	0.0419	0.0312
1-Propanol	370.35	351.13	364.44	366.45	0.0162	0.0436	0.0547
Acetic Acid	391.05	397.25	389.42	383.63	0.0042	0.0343	0.0156
Propionic Acid	414.25	422.44	415.69	407.34	0.0035	0.0357	0.0194
Ethylene Glycol	470.45	418.68	431.87	446.99	0.0893	0.0676	0.1237
1,3-Propylene-Glycol	487.55	462.64	453.47	563.55	0.0752	0.2181	0.0538
Glycerol	563.15	499.17	509.41	548.23	0.1055	0.0983	0.1282
Benzene	353.15	359.01	351.27	450.54	0.0054	0.2549	0.0163
Cyclohexane	353.85	355.50	349.68	356.52	0.0119	0.0029	0.0046
Toluene	390.85	389.19	386.12	385.72	0.0123	0.0089	0.0043
Nitrobenzene	483.95	482.90	484.99	361.99	0.0022	0.2504	0.0022
Pentane	309.15	299.45	309.46	315.19	0.0010	0.0525	0.0324
Cyclopropane	240.35	201.25	208.03	283.02	0.1554	0.4064	0.1943
Acetaldehyde	293.25	271.55	269.68	287.54	0.0874	0.0589	0.0799
N-Propionaldehyde	321.15	314.11	314.71	319.11	0.0205	0.0159	0.0224
N-Butyraldehyde	347.95	349.83	351.59	347.63	0.0103	0.0063	0.0054
Isobutyraldehyde	337.65	329.59	338.28	340.57	0.0019	0.0333	0.0245
1-Heptanal	425.95	431.72	433.81	422.01	0.0181	0.0225	0.0134
1-Hexanal	404.15	407.63	409.90	398.66	0.0140	0.0220	0.0085
1-Octanal	444.15	453.46	455.22	444.26	0.0243	0.0203	0.0205
Isopropyl Alcohol	355.45	331.01	343.65	358.90	0.0343	0.0842	0.0738
1,4-Benzenediamine	627.15	623.94	672.24	655.20	0.0671	0.0501	0.0051
Pyrene	677.15	673.96	698.67	651.56	0.0308	0.0332	0.0047
TOTAL ERROR					1.5428	1.5929	1.9195
MRE VALUE					0.0514	0.0531	0.0640

Table 2. Experimental [15] and prediction data of boiling point for solvent mixtures

Solvent 1	Solvent 2	x_1	Tb (Exp)	Tb (Klein&Wu)	Tb (LMR)	Error (Klein&Wu)	Error (LMR)
Acetone	Choroform	0.36	337.65	332.58	313.93	0.0153	0.0756
	Methanol	0.80	328.85	331.05	315.84	0.0066	0.0412
	Cyclohexane	0.55	350.85	340.50	312.82	0.0304	0.1216
Benzene	Cylcohexane	0.47	351.35	353.57	313.14	0.0063	0.1220
Ethanol	Toluene	0.65	344.15	362.85	312.47	0.0515	0.1014
	Water	0.81	350.15	355.57	311.92	0.0153	0.1226
Ethyl Acetate	Ethanol	0.89	351.35	350.38	309.78	0.0028	0.1342
Methanol	Toluene	0.70	335.65	351.53	312.26	0.0452	0.0749
	Water	0.88	336.75	341.98	311.48	0.0153	0.0811
TOTAL ERROR						0.1886	0.8746
MRE VALUE						0.0210	0.0972

4. Conclusion

The boiling point models for both, pure and mixture solvents are significant to predict the solvents' property in the absence of the experimental data. In this study, the boiling point of pure and mixture solvents was successfully computed and compared with published experimental data. The existing property models have been evaluated to select the best model based on the lowest MRE value. In conclusion, the boiling point model can be applied in the solvent selection to extract herbs or plant. The extraction yield of the herbs or plant then might be involved in the bioproducts development.

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