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A new structure-based model for estimation of true critical volume of multi-component mixtures

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ABSTRACT

In this study, a new quantitative structure–property relationship (QSPR) has been proposed to estimate true vapor–liquid critical volume of multi-component mixtures. In developing this model, 598 experimental data on true critical volume for 110 different binary mixtures were applied. The mixture molecular descriptors were computed according to the molecular descriptors of pure components involved in the mixture and their molar fractions. Enhanced replacement method (ERM), as an effective tool for subset variable selection, was utilized. The proposed model is simple multivariate linear equations with six variables. The prediction capability of the proposed model for different families of compounds was critically analyzed. Besides, the capability of the proposed model has been tested by predicting true critical volume of 7 different multi-component mixtures containing 40 experimental data points. The average absolute relative deviation of the proposed QSPR model over all experimental data is 9.7% and 8.7% for binary mixtures and multi-component mixtures, respectively.

1. Introduction

Accurate estimation of critical properties of mixtures is important in studying the overall phase behavior [1–3]. Several practical applications such as designing super critical-fluid extraction processes, compression and refrigeration units and evaluation of the probability of retrograde condensation or evaporation are dependent on the understanding the critical behavior of multi-component mixtures [4,5]. The best method to determine the critical properties of a multi-component mixture is experimental measurement. However, these measurements are often expensive and laborious, thus, prediction methods, including theoretical and empirical models become valuable.

Different approaches, including fast estimation methods and rigorous methods have been followed for prediction of true critical properties for multi-component mixtures [6]. We have recently conducted a critical review on the applicability of the fast estimation methods [7,8]. Besides, different methods for estimation of true vapor–liquid critical properties of mixtures were evaluated and compared in details, elsewhere [1,2,9,10]. Rigorous methods have several advantages such as their basis in thermodynamics, their capability in predicting global critical behavior and also building complex phase envelops.

However, as it has been mentioned by Najafi et al. [6], these methods suffer from some disadvantages such as inaccuracies related to the mixing rules or binary interaction coefficients of the equations of state. Besides, the largest deviations are observed for the prediction of critical volume in comparison with the other critical properties [11].

Fast estimation methods have advantages such as low computational cost, and simplicity of application. However, as the fast estimation methods are empirical techniques based on binary interaction parameters, their prediction accuracy is mainly dependent on the availability of experimental data [12,13] and these methods are not applicable to the mixtures containing new designed compounds for which no experimental data or fitted interaction parameters are available. Moreover, vapor–liquid critical volume measurement for a mixture is usually an expensive and difficult task, and so the available data in the literature is rare and hard to find.

Quantitative structure–property relationship (QSPR) is another approach for prediction of different physical properties [14–20]. In this approach, the considered physical property is correlated in term of parameters relating to the molecular structure. These molecular-based parameters are called molecular descriptors. Certain mathematical algorithms have been applied in order to calculate molecular descriptors from the chemical structure of the components. The developed model can be applied to predict the property of new designed compounds solely from their molecular structure. Katritizky et al. [14] reviewed the QSPR models proposed for prediction of critical properties of pure compounds. Despite the availability of a large number of proposed QSPR models for prediction of physical properties of pure compounds, a few QSPR models for mixtures have been developed. Following to the introduction of QSPR methodology to the mixtures by Ajmani et al. [21], a few works have been carried out in the development of QSPR models for the prediction of different physical properties of

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Table 1
The main specifications of the data set on true critical volume of binary mixtures.

No.	Component A	Component B	n	x_{Bmin}	x_{Bmax}	Ref.
1	Butan-1-ol	Benzene	6	0.112	0.899	[25]
2	2,2-Dimethylpropane	Propane	5	0.158	0.934	[25]
3	Dodecafluorocyclohexane	1,2,3,4,5,6-Hexafluorobenzene	4	0.203	0.803	[25]
4	Ethanol	Benzene	7	0.014	0.875	[25]
5	Ethylene	Carbon dioxide	5	0.132	0.744	[25]
6	Ethylene	methylamine	11	0.141	0.923	[25]
7	n-Heptane	n-Butane	5	0.159	0.940	[25]
8	Methanol	Benzene	9	0.044	0.889	[25]
9	Methanol	n-Hexane	3	0.416	0.845	[25]
10	n-Pentane	Methane	10	0.295	0.824	[1,25]
11	1-Pentene	n-Pentane	3	0.249	0.790	[25]
12	Perfluorobutane	Trifluoroacetic acid	4	0.178	0.793	[25]
13	Perfluorocyclobutane	Monochlorotetrafluoroethane	1	0.770	0.770	[25]
14	Propane	Perfluorocyclobutane	7	0.075	0.752	[25]
15	1-Propanol	Benzene	7	0.015	0.899	[25]
16	Methane	Propane	13	0.254	0.900	[1]
17	Methane	n-Heptane	4	0.150	0.200	[1]
18	Methane	n-Octane	2	0.202	0.213	[1]
19	Methane	n-Nonane	4	0.115	0.140	[1]
20	Methane	n-Decane	12	0.095	0.261	[1]
21	Methane	n-Butane	7	0.229	0.640	[1]
22	Methane	n-Hexane	1	0.253	0.253	[1]
23	Ethane	n-Heptane	5	0.032	0.735	[1]
24	Ethane	n-Decane	8	0.005	0.302	[1]
25	Propane	n-Butane	11	0.074	0.853	[1]
26	Ethane	n-Butane	5	0.053	0.825	[1]
27	Propane	n-Pentane	9	0.122	0.853	[1]
28	Propane	n-Hexane	11	0.078	0.857	[1]
29	Propane	n-Octane	7	0.041	0.786	[1]
30	Propane	n-Decane	5	0.013	0.288	[1]
31	n-Butane	n-Decane	3	0.044	0.261	[1]
32	Methane	Cyclohexane	6	0.235	0.392	[1]
33	Ethane	Cyclohexane	6	0.138	0.862	[1]
34	Methane	2,2-Dimethylpropane	1	0.155	0.155	[1]
35	Ethane	Propene	9	0.050	0.948	[1]
36	Ethane	Benzene	6	0.124	0.935	[1]
37	Propane	2-Methylbutane	5	0.101	0.899	[1]
38	Propane	2,2-Dimethylbutane	5	0.081	0.847	[1]
39	Propane	2,3-Dimethylbutane	5	0.085	0.848	[1]
40	Propane	2-Methylpentane	5	0.081	0.850	[1]
41	Propane	3-Methylpentane	5	0.115	0.855	[1]
42	n-Hexane	Acetylene	4	0.375	0.665	[1]
43	n-Hexane	Toluene	3	0.300	0.634	[1]
44	Ethylene	Propene	7	0.086	0.883	[1]
45	Benzene	Ethylene	14	0.100	0.940	[1,26]
46	Benzene	Naphthalene	11	0.099	0.682	[1]
47	Naphthalene	Cyclohexane	5	0.460	0.785	[1]
48	Benzene	Phenanthrene	5	0.106	0.291	[1]
49	Benzene	Anthracene	4	0.048	0.103	[1]
50	Nitrogen	Carbon dioxide	3	0.707	0.982	[1,27]
51	Oxygen	Carbon dioxide	1	0.688	0.688	[1]
52	n-Perfluoroheptane	Ethane	5	0.103	0.891	[1]
53	n-Perfluoroheptane	Propane	5	0.094	0.809	[1]
54	n-Perfluoroheptane	n-Butane	5	0.130	0.916	[1]
55	n-Perfluoroheptane	n-Pentane	5	0.291	0.913	[1]
56	n-Perfluoroheptane	n-Hexane	7	0.130	0.904	[1]
57	n-Perfluoroheptane	n-Heptane	7	0.100	0.904	[1]
58	n-Perfluoroheptane	n-Octane	3	0.054	0.475	[1]
59	n-Perfluoroheptane	n-Nonane	5	0.132	0.843	[1]
60	Methane	Hydrogen sulfide	3	0.450	0.791	[1]
61	Ethane	Hydrogen sulfide	6	0.110	0.890	[1]
62	Ethane	Carbon dioxide	2	0.573	0.579	[1]
63	Propane	Hydrogen sulfide	7	0.163	0.898	[1]
64	Propane	Carbon dioxide	3	0.407	0.795	[1]
65	n-Butane	Carbon dioxide	8	0.173	0.875	[1,28]
66	n-Pentane	Hydrogen sulfide	12	0.100	0.966	[1]
67	n-Decane	Hydrogen sulfide	3	0.900	0.994	[1]
68	n-Decane	Carbon dioxide	9	0.728	0.995	[1,29]
69	Ethylene	Ethanol	5	0.425	0.825	[1]
70	Methanol	Butan-1-ol	4	0.167	0.762	[1]
71	Butan-1-ol	Butan-2-ol	3	0.236	0.779	[1]
72	Butan-1-ol	Diethyl ether	4	0.131	0.744	[1]
73	Sulfur dioxide	Dimethyl ether	4	0.401	0.777	[1]
74	Sulfur dioxide	Methyl ethyl ether	5	0.272	0.785	[1]
75	Propane	Sulfur hexafluoride	6	0.163	0.877	[1]