

A Predictive Vapor Pressure Correlation for Organic Liquids

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Abstract

A new vapor pressure correlation has been developed to represent vapor pressures of organic liquids accurately between the melting and the critical temperatures. The model was originally developed for aromatic liquids, but has been applied to other organic liquids as well. It is based on Pitzer's 3-parameter corresponding states equation with two major features, (i) benzene is used as the reference fluid instead of an atomic fluid or noble gas and (ii) Wagner's equation is used to correlate vapor pressure of reference fluid and the perturbation term. The perturbation term is characterized by a parameter Φ . Regressed compound specific values of Φ are tabulated. Also, a correlation of Φ in terms of shape factor Ψ has been developed. Ψ is defined as the ratio of surface area per unit volume of the compound molecule to surface area per unit volume of benzene, or, $(\Psi - 1)$ represents the deviation in shape of the compound molecule from that of benzene molecule. A group contribution method has been developed to predict Ψ 's from volume (R) and surface area (Q) parameters of individual functional groups. In most cases, same R and Q are used as in UNIFAC. Adjustment of Q necessary for some groups is justified based on the polarity of the groups. It is also shown that Ψ is a good correlating parameter for acentric factor ω . In all, a range of vapor pressure correlations are presented from the compound specific regressed Wagner's equation to the predictive model using the group contribution method for Ψ and a correlation for Φ in terms of Ψ . In general, these correlations provide the best accuracy between the melting and the critical temperatures of all correlations available in the literature.

Introduction

A variety of equations for estimating vapor pressures of organic liquids are available in the literature. Most of the methods involve an extension of the Clausius-Clapeyron equation combined with Pitzer's three-parameter corresponding states approach [1]. The Lee-Kesler equation [2] is the most commonly used equation for engineering applications and generally predicts vapor pressure to within 1% error between the boiling point and the critical temperature. This error, however, increases rapidly at lower reduced temperatures approaching the melting point. An accurate and generalized vapor pressure correlation for organic liquids valid from the melting to the critical temperature is currently not available. Such a correlation is crucial in the development of accurate liquid state and vapor state equations of state where the knowledge of the coexistence boundary between the two phases is essential.

The three parameter corresponding states methods for vapor pressure involve two significant aspects. The first one is the functional form used to represent vapor pressure of a specific compound, and the second one is the choice of the reference fluid and the third parameter that characterizes

the perturbation term. In other words, the general representation has the form

$$\ln P_r = f^{(0)}(T_r) + \Phi f^{(1)}(T_r) \quad (1)$$

In Lee-Kesler equation Φ is the acentric factor. Although Lee-Kesler equation has been extensively used for engineering applications, recent literature indicates that improvement of this correlation in terms of better functional forms for $f^{(0)}$ and $f^{(1)}$ and better formulation of the perturbation term are possible and this is the objective of this work.

Exhaustive studies of functional forms to represent vapor pressure of organic liquids are available in the literature [3-6]. Based on equations proposed by many others, Wagner [6] started with an equation with an excess of twenty-five temperature dependent terms and using sophisticated regression methods determined the statistically most significant of these terms. The final equation (referred to as Wagner's equation) has the form

$$f(T_r) = \frac{1}{T_r} (aX + bX^{1.5} + cX^3 + dX^6) \quad (2)$$

$$\text{where } X = (1 - T_r)$$

It has been generally concluded by a number of researchers that this is one of the most accurate forms to represent va-

por pressure data [3,5,7], and may provide the best method for vapor pressure computation with tabulated values of specific constants a , b , c , and d for various compounds.

For generalization of the correlation, the reference fluid (corresponding to term $f^{(o)}$ in equation 1) and the parameter Φ need to be defined. In Lee-Kesler equation, $f^{(o)}$ is obtained from noble gas vapor pressure and Φ is the acentric factor. In other variations available in the literature is the method of Teja et al. [8] that uses two nonspherical reference fluids while still keeping acentric factor as the third parameter. More recently Twu et al. [9] have developed a vapor pressure equation for heavy hydrocarbons using the Wagner equation and defining the third parameter as the modified acentric factor at $T_r = 0.5$ instead of $T_r = 0.7$. They report this method to work very well at low reduced temperatures. Simultaneously, Morgan and Kobayashi [10] reported a new correlation "Pert 2" which uses an additional perturbation term quadratic in acentric factor. $f^{(o)}$, $f^{(1)}$, and $f^{(2)}$ are given by Wagner equation with parameters regressed from experimental data.

In all the above methods, parameter Φ either as the acentric factor or the modified acentric factor needs a vapor pressure data point, and no accurate method for estimating these parameters from molecular properties have been successfully developed. In this work, our objective is to develop a vapor pressure correlation similar to that of Twu et al. [9] that is applicable to most organic liquids and make attempts to generalize the regressed parameters Φ in terms of molecular parameters. We have used benzene as the reference fluid and Van der Waals volumes and surface areas are the molecular parameters explored. In all, six methods are presented ranging from specific to most general. The generalized method allows computation of Φ by a group contribution method that defines molecules in terms of functional groups similar to the UNIFAC groups [11] and uses UNIFAC R and UNIFAC Q (modified for some groups) as the group parameters. These six methods outlined here represent the most versatile procedures for vapor pressure computation and allow computations from the melting to the critical temperatures with fair accuracy. The vapor pressure methods and results are discussed in the following sections.

Development of Vapor Pressure Methods

A vapor pressure databank of 127 organic compounds with a total of 2971 data points was compiled for the development. Most of the data were obtained from three sources [12, 13, 14] although for a few compounds data were extracted from original articles. The compounds may be classified as alkanes (43 compounds, 906), alcohols (10 compounds, 185 points), alkylbenzenes (22 compounds, 706 points), phenols (7 compounds, 218 points), hydroaromatics (9 compounds, 174 points), two-ring aromatics (13 compounds, 298 points), three and four ring aromatics (8 compounds, 173 points), and other ring compounds (15 compounds, 311 points). Other ring compounds include some pyridines, anilines, thiophenes and furans. The databank is somewhat biased towards aromatic compounds, as initially the method was intended for application to coal liquid model compounds; other compounds were included later when it became clear that the approach was ap-

plicable to all organic liquids. Alkenes and acetylenes were, however, not included in the databank, but extension to these compounds is easily possible.

Using the databank, Wagner constants a , b , c , and d for the 127 compounds were regressed using "UNLSF" nonlinear regression subroutine of the IMSL library [15]. Excellent regression fits were obtained. The constants are listed in Table 1 and we denote the method using Wagner's equation with these specific constants as Method 1.

Benzene was chosen as the reference fluid. Thus $f^{(o)}$ in equation 1 was obtained from Wagner's equation with a , b , c , and d of benzene from Table 1. $f^{(1)}$ was also expressed as Wagner's equation and constants a , b , c , and d for $f^{(1)}$ together with 127 Φ 's corresponding to various compounds were regressed simultaneously from the vapor pressure data. Regressed values of a , b , c , and d for $f^{(1)}$ are: $a = -1.273103$, $b = -0.219368$, $c = -0.263757$, and $d = -4.487833$. Regressed values of Φ are denoted as Φ_1 and tabulated in Table 1. The method using benzene as the reference fluid, with $f^{(1)}$ represented as above and with Φ_1 from Table 1 is denoted as Method 2.

Analogous to the definition of acentric factor, a third method was devised that uses same $f^{(o)}$ and $f^{(1)}$ as in Method 2, but Φ 's are re-defined to obtain an exact fit with experimental data at $T_r = 0.6$. Choice of $T_r = 0.6$ was considered optimum for maximum accuracy from melting to critical temperature for most compounds. Thus,

$$\Phi_2 = \left[\frac{\ln(P_r) - f^{(o)}(T_r)}{f^{(1)}(T_r)} \right]_{T_r=0.6} \quad (3)$$

These values of Φ denoted as Φ_2 are also given in Table 1 and this method we call Method 3.

The three methods developed so far are compound specific, in that, either a vapor pressure data point, or compound specific parameters are necessary or none of these methods can be applied to compounds for which no data are available. We, therefore, undertook the development of a fourth and generalized method that involves a group contribution method for Φ using basic and known molecular properties as parameters. This method is discussed below.

Group Contribution Method for Φ

Some methods are available in the literature for estimation of acentric factors [3]. However, they use boiling points or other properties that need to be estimated separately. Even so, accuracy of these methods is limited. The approach followed here uses a group contribution method with Van der Waals volumes and surface areas [16] as group parameters. In particular, we define the shape factor Ψ for a molecule that characterizes the difference in shape of the molecule from that of the reference fluid benzene and is expressed as

$$\Psi = \frac{\frac{S}{V^{\frac{2}{3}}}}{\frac{S_b}{V_b^{\frac{2}{3}}}} \quad (4)$$

Table 1: Compound by Compound Listing of Vapor Pressure Model Parameters

Regressed Parameters of Wagner's Equation									
Compound	No. Pts.	a	b	c	d	F1	F2	Y	F3
ethane	23	-5.59565	-1.0945	2.78646	-9.3164	-0.4866	-0.4385	0.8703	-0.45963
propane	19	-6.54611	0.92229	-1.70431	-1.8152	-0.231	-0.2274	0.92829	-0.2791
n-butane	31	-6.734	0.75885	-1.4742	-3.4469	-0.104	-0.0466	0.98152	-0.07701
isobutane	31	-6.53199	0.36853	-0.48984	-5.23761	-0.1605	-0.1095	0.95096	-0.19687
n-pentane	32	-7.30208	1.45347	-2.24214	-4.03716	0.1188	0.1443	1.03025	0.13266
isopentane	30	-6.91052	0.9857	-1.86811	-4.62577	0.0151	0.0255	1.0034	0.01451
n-hexane	34	-7.28328	0.87839	-1.91476	-6.36663	0.335	0.3361	1.07512	0.34209
2-2-di-methylbutane	11	-7.10888	1.32372	-2.55661	-2.82332	0.0797	0.0763	1.00409	0.01746
2-3-di-methylbutane	13	-7.24076	1.48146	-2.9798	-1.68744	0.1367	0.1351	1.02691	0.11762
2-methylpentane	14	-7.45418	1.67489	-3.66965	0.00269	0.2581	0.2579	1.05102	0.22788
3-methylpentane	14	-7.45965	1.72423	-3.55217	-0.44062	0.2322	0.2312	1.05102	0.22788
n-heptane	36	-7.64773	1.15691	-2.59755	-6.70798	0.5506	0.5368	1.11672	0.54676
2-2-3-trimethylbutane	19	-7.13165	1.20143	-2.58446	-2.73257	0.1432	0.1454	1.03003	0.13165
2-2-di-methylpentane	18	-7.31069	1.21186	-2.86826	-3.19086	0.293	0.2938	1.052	0.23247
2-3-di-methylpentane	20	-7.44785	1.42192	-3.21231	-2.31023	0.3259	0.3273	1.07279	0.33089
2-4-di-methylpentane	19	-7.3044	1.01587	-2.69603	-3.8256	0.3572	0.3582	1.07279	0.33089
2-methylhexane	20	-7.82998	1.98653	-4.42607	-0.1946	0.4577	0.4591	1.09476	0.43766
3-3-di-methylpentane	19	-7.25164	1.25263	-2.67538	-2.76706	0.2112	0.2138	1.052	0.23247
3-ethyl-pentane	18	-7.49901	1.40655	-3.39867	-2.34554	0.3871	0.3881	1.08449	0.38744
3-methylhexane	20	-7.8771	2.15721	-4.55298	-0.06726	0.4301	0.4312	1.09476	0.43766
n-octane	35	-7.90361	1.34158	-3.4899	-5.96962	0.7385	0.7196	1.15555	0.74408
2-2-4-tri-methylpentane	20	-7.36222	1.11796	-2.70643	-3.984	0.3551	0.3559	1.07566	0.3447
2-3-4-tri-methylpentane	20	7.53354	1.40208	-3.2857	-2.6141	0.4016	0.4027	1.09482	0.43799
2-methylheptane	20	-8.04601	1.96651	-4.78937	-0.66482	0.65	0.6535	1.13531	0.64065
3-methylheptane	20	-8.06158	2.08511	-4.92889	-0.15956	0.6223	0.6253	1.13531	0.64065
n-nonane	27	-7.89929	0.82183	-3.02933	-8.37942	0.9386	0.9032	1.19201	0.9325
2-2-3-3-tetra-methylpentane	20	-7.681	1.89836	-3.97106	-1.08065	0.3535	0.3544	1.08108	0.37089
2-2-3-4-tetra-methylpentane	20	-7.75707	2.00052	-4.35161	-0.01914	0.3941	0.3954	1.0989	0.45807
2-2-4-4-tetra-methylpentane	20	-7.83728	2.16374	-4.45979	0.03498	0.3902	0.312	1.08108	0.37089
2-2-5-tri-methylhexane	18	-7.64442	1.28515	-3.84325	-2.48831	0.5799	0.5846	1.11773	0.55183
2-3-3-4-tetra-methylpentane	18	-7.82858	2.14703	-4.48897	0.54966	0.3904	0.3921	1.0989	0.45807
3-3-di-ethylpentane	19	-7.85395	1.84927	-3.79489	-1.11196	0.4708	0.4719	1.10136	0.47025
n-decane	28	-7.81158	0.23995	-2.6346	-10.49723	1.1185	1.0625	1.22642	1.11119
n-undecane	25	-7.77993	-0.2868	-2.22837	-12.84721	1.3132	1.2362	1.25903	1.27968
n-dodecane	27	-8.11846	-0.00634	-2.83113	-13.73006	1.4876	1.4139	1.29007	1.4378
n-tridecane	19	-8.62118	0.68739	-4.13904	-11.97139	1.609	1.5841	1.3197	1.58553
n-tetradecane	16	-8.45923	0.0005	-3.3294	-16.35672	1.6839	1.7093	1.34807	1.72295
n-pentadecane	16	-9.1593	1.31754	-6.11528	-9.61501	1.8254	1.8718	1.3753	1.85024
n-hexadecane	10	-9.12882	0.61091	-4.85544	-1.52794	1.8879	2.0964	1.40151	1.9676
n-heptadecane	17	-9.97306	2.26434	-7.83738	-11.89699	2.1494	2.2144	1.42678	2.07524
n-octadecane	16	-10.72341	3.7376	-11.04394	0.17809	2.2738	2.3531	1.45119	2.17342
n-nonadecane	17	-10.90346	3.79466	-11.71575	0.40109	2.4203	2.5192	1.47481	2.26238
n-eicosane	17	-8.5664	-1.82602	-1.60768	-41.44102	2.3889	2.5385	1.4977	2.34238
methanol	20	-8.53079	0.68536	-2.81112	0.22383	1.2365	1.2998	1.29642	1.4698
ethanol	25	-8.35306	-0.12418	-4.70599	4.60894	1.6788	1.6948	1.27728	1.37298
1-propanol	19	-8.09833	0.15845	-7.94358	10.03245	1.6093	1.7141	1.28086	1.39118
1-butanol	16	-7.88499	0.22139	-8.75789	4.82301	1.4887	1.6678	1.29449	1.4601
2-butanol	16	-7.76006	0.26168	-9.36987	1.85645	1.4358	1.653	1.29345	1.45484
1-pentanol	19	-7.98753	0.54258	-8.66317	-3.32416	1.5312	1.6462	1.31302	1.55256
1-hexanol	13	-8.57561	0.61328	-5.86025	-15.2799	1.8374	1.7911	1.33399	1.65531
1-heptanol	13	-7.48636	-0.6308	-5.62355	-21.5866	1.6829	1.6073	1.35615	1.76125
1-octanol	18	-9.65249	4.11604	-12.77675	-4.75792	1.5928	1.6981	1.37881	1.86625
1-decanol	26	-8.62059	1.38726	-8.2356	-19.25497	1.6903	1.7753	1.42419	2.0645
benzene	115	-6.95798	1.27757	-2.56466	-3.40352	0	0	1	0
toluene	112	-7.39804	1.64984	-3.06826	-2.53253	0.1653	0.1842	1.03777	0.16678
ethylbenzene	26	-7.3154	0.91993	-1.99607	-5.94949	0.3359	0.3458	1.07612	0.34691
n-propyl-benzene	19	-8.07079	2.32368	-4.81737	-0.0903	0.5176	0.5185	1.11233	0.52481

n-butyl-benzene	26	-7.61102	0.61289	-2.16887	-7.71802	0.7105	0.7029	1.14659	0.69815
iso-butyl-benzene	20	-8.66956	2.95178	-4.54902	-2.53335	0.6638	0.6609	1.14116	0.67044
sec-butyl-benzene	20	-6.68538	0.35064	-4.01077	0.81494	0.3361	0.3346	1.13156	0.62164
iso-propyl-benzene	26	-7.45775	1.06834	-2.71781	-5.74456	0.4671	0.4537	1.09605	0.44405
1-4-diethyl-benzene	20	-8.00395	1.5275	-4.05704	-2.44118	0.7418	0.7446	1.15522	0.74241
o-xylene	43	-7.56459	1.41311	-2.72987	-4.59685	0.3586	0.373	1.07436	0.33843
m-xylene	47	-7.59129	1.30824	-2.56743	-5.05894	0.4037	0.4209	1.08027	0.36697
p-xylene	36	-7.75577	1.77479	-3.37221	-2.91407	0.3976	0.405	1.08027	0.36697
1-methyl-4-ethylbenzene	19	-7.28408	0.97666	-4.12247	0.02666	0.4851	0.487	1.11623	0.54433
1-methyl-3-ethylbenzene	20	-7.06611	0.62742	-4.39562	2.12164	0.4988	0.5038	1.11623	0.54433
1-methyl-2-ethylbenzene	20	-7.00373	0.87653	-4.85234	3.08004	0.3989	0.3994	1.1091	0.50871
1-3-5-tri-methylbenzene	19	-7.77784	0.95226	-2.78975	-4.3688	0.7132	0.7143	1.12004	0.56347
1-2-4-tri-methylbenzene	20	-7.83751	1.40376	-3.53583	-2.18288	0.6268	0.6284	1.11474	0.53685
1-2-3-tri-methylbenzene	20	-8.09552	2.1062	-4.41847	-0.44484	0.585	0.5865	1.1201	0.56377
o-cymene	15	-6.75929	-0.75157	-1.85524	-0.06929	0.5797	0.6247	1.12718	0.59945
m-cymene	15	-6.56127	-0.78001	-2.51237	-0.0455	0.5651	0.5746	1.13534	0.64081
p-cymene	28	-7.11186	-0.20253	-1.40842	-7.24285	0.6275	0.6295	1.13534	0.64081
phenol	74	-9.68802	5.08371	-9.02709	-0.91117	0.9449	0.8875	1.20998	1.02586
o-cresol	25	-7.7902	0.45727	-1.59521	-13.91698	0.9199	0.8691	1.2151	1.05242
m-cresol	25	-8.03008	1.18752	-4.39333	-9.61539	1.078	0.9902	1.22475	1.10252
p-cresol	26	-10.22684	5.17427	-7.86589	-7.98705	1.2237	1.133	1.22475	1.10252
2-4-xylenol	26	-8.30519	0.90277	-3.31262	-8.22828	1.1924	1.1689	1.24063	1.18481
2-5-xylenol	21	-8.44273	0.1392	-0.0099	-16.83746	1.2903	1.289	1.24063	1.18481
3-5-xylenol	21	-8.25477	1.55988	-6.24146	-8.12596	1.2298	1.1699	1.24931	1.22965
cyclohexane	12	-7.18238	1.86726	-3.68252	-0.62253	0.0011	0.0012	1.00031	0.00131
1-1dimethyl-cyclohexane	20	-6.87074	0.90897	-2.9341	-1.88465	0.1275	0.1263	1.02909	0.12744
1-2-dimethyl-cyclohexane	20	-6.76614	0.77502	-3.31713	-0.8051	0.1497	0.1465	1.02557	0.11165
n-propyl-cyclohexane	20	-6.6203	0.35418	-3.79283	0.27771	0.2723	0.2701	1.06738	0.30503
iso-propyl-cyclohexane	20	-6.6906	0.80886	-4.46909	1.74809	0.193	0.1873	1.05246	0.23462
n-butyl-cyclohexane	20	-10.19568	6.94164	-10.52176	5.58311	0.5662	0.5577	1.10535	0.49003
iso-butyl-cyclohexane	20	-7.90431	2.28039	-4.66688	-0.86496	0.4153	0.415	1.10035	0.46527
tert-butyl-cyclohexane	20	-6.72956	0.6981	-4.32554	1.44896	0.2485	0.2468	1.06028	0.27135
cyclohexene	22	-6.6073	0.42158	-1.22426	-5.35363	0.0095	0.0025	0.8809	-0.43009
aniline	32	-6.81477	-0.8711	-0.93187	-7.39148	0.6602	0.6636	1.15535	0.74307
2-methyl-aniline	33	-9.02981	3.26242	-5.54458	-6.06555	0.9206	0.8804	1.17049	0.82107
3-methyl-aniline	33	-7.10117	-0.62492	-0.95586	-12.46182	0.8514	0.7879	1.17785	0.85909
diemthyl-aniline	15	-6.62482	-2.21802	3.2409	-22.52547	0.7751	0.7631	1.16159	0.77515
bromobenzene	12	-7.25464	1.51101	-3.14369	-1.34609	0.1488	0.1471	1.03382	0.1488
chlorobenzene	26	-8.70484	4.8664	-7.75994	5.62787	0.1124	0.1439	1.02576	0.11249
benzoic acid	7	-7.73299	-0.95846	-4.52363	-6.21157	1.6395	1.6876	1.33073	1.6395
anisole	6	-8.02577	2.18608	-4.70797	-0.05723	0.5335	0.5346	1.1142	0.53413
phenetole	6	-8.3503	2.17465	-5.11306	-1.08888	0.8123	0.8112	1.16879	0.81226
styrene	16	-6.73453	0.84102	-3.90241	-0.10466	0.1773	0.1553	1.04019	0.17786
pyridine	47	-6.98929	1.07795	-2.78209	-2.54204	0.1187	0.1224	1.0296	0.1297
2-methyl-pyridine	15	-7.76788	2.15492	-4.36708	0.02985	0.3384	0.3388	1.06215	0.28017
4-methyl-pyridine	21	-7.19372	1.0526	-3.05789	-2.58571	0.2985	0.299	1.06215	0.28017
furan	13	-6.8137	1.09426	-2.72694	-2.3388	-0.0103	-0.0088	0.99243	-0.03193
thiophene	29	-6.81896	1.08263	-2.02187	-4.49968	-0.0589	-0.0609	0.98592	-0.059
naphthalene	10	-7.86714	2.37544	-4.65037	0.58026	0.3321	0.3385	1.08227	0.37664
1-methyl-naphthalene	42	-8.06523	1.77448	-3.40615	-2.71664	0.5677	0.6137	1.11727	0.54955
2-methyl-naphthalene	37	-9.34223	4.79077	-7.28657	0.59456	0.5787	0.5846	1.11727	0.54955
tetralin	31	-5.32759	-3.06718	1.25547	-8.67456	0.3991	0.3735	1.11583	0.54231
quinoline	29	-7.10013	0.02499	-0.56556	-9.91599	0.4648	0.4541	1.10177	0.47229
isoquinoline	27	-6.49217	-0.67718	-0.56918	-5.76787	0.2932	0.317	0.87413	-0.44916
benzofuran	14	-6.73664	-0.91101	1.28075	-13.91238	0.4311	0.4368	1.06442	0.29094
indan	29	-7.57201	1.52604	-3.12867	-3.13642	0.3394	0.3629	1.07376	0.33558
indene	21	-6.7121	0.03756	-1.4663	-8.08464	0.3317	0.2737	0.97021	-0.12252
indole	24	-7.75449	1.38708	-4.78508	0.07885	0.6967	0.6979	1.05901	0.26536
4-indanol	12	-3.24277	-10.05979	8.10013	-11.45164	1.1614	1.2208	1.23908	1.17681

biphenyl	13	-6.0338	-2.46451	2.47775	-14.43551	0.4938	0.4991	1.1346	0.63705
diphenyl-methane	9	-8.16299	1.22571	-1.56002	-37.20504	0.8686	0.9488	1.1726	0.83195
anthracene	32	-13.5676	11.19201	-15.889	22.81225	1.22	1.4684	1.1855	0.89873
pyrene	36	-19.34349	27.2188	-40.83796	53.28185	1.0064	1.0147	1.18126	0.87676
triphenylene	15	-8.40185	1.69384	-4.409	12.46838	0.8603	0.8755	1.22665	1.11238
phenanthrene	17	-12.22745	9.09521	-10.97417	4.85026	1.0264	1.0574	1.18559	0.89922
dibenzofuran	21	-5.5094	-5.7766	12.38893	-32.23669	0.6187	0.6104	1.14874	0.70917
fluorene	26	-7.08452	0.00806	-5.27437	7.87133	0.8136	0.8317	1.15599	0.74636
carbazole	11	-12.43274	11.65961	-23.09508	57.52573	1.043	1.0464	1.22592	1.1086
acridine	15	-7.56196	0.07095	-2.134	-0.27849	0.748	0.8442	1.13212	0.62444

where S and V are molecular surface area and volume of the compound and S_b and V_b are the same for benzene. Furthermore, the molecular surface area and volume parameters are obtained as summations over surface areas and volumes of groups constituting the molecule. UNIFAC R and Q [11] are used as the group volume and area parameters, so that

$$V = \sum_{g=1}^N n_g R_g \quad (5)$$

$$S = \sum_{g=1}^N n_g Q_g \quad (6)$$

where n_g is the number of groups of type g and N is the number of group types in the molecule.

For all groups same R values are used as in UNIFAC. For non-polar groups the UNIFAC Q's were used unchanged and rendered excellent results. However for polar groups such as alcohol, amine, halides, carboxylic acid, ether, sulfide etc., instead of defining more parameters the UNIFAC Q was adjusted for better accuracy as is discussed below. Some additional modifications of Q were also necessary to account for some composite molecular structures.

First, Ψ 's for all compounds were calculated from equations 4, 5 and 6 using UNIFAC R's and Q's. A plot was prepared of Φ versus Ψ . A curve was fitted through the n-alkane data points that followed an excellent trend. Compounds that showed significant deviations from this curve were identified and it was quickly recognized that these compounds either contained polar groups or certain composite molecular structures. Q's for polar groups were next regressed for best fit of Ψ 's of these compounds with the n-alkane curve. Differences between these regressed Q's and original UNIFAC Q's may be seen from Table 2. A simply additive function such as equation 6 does not characterize the shape of the molecule completely. Consequently, some additional contributions to surface area were defined to represent multiple ring structures, alkyl branches and isomeric compounds resulting from ortho, meta or para attachments to rings. It was observed that hydroaromatic and aromatic compounds showed systematic deviations from the n-alkane curve which could be minimized by assigning contributions to S because of composite ring structures, which are listed in Table 3. Modifications were also devised to account for other molecular structures, and as a result equation 6 was reformulated as follows

Id	Group Symbol	Rg	Qg	Q (UNIFAC)	Example
g1	CH3	0.9011	0.848	0.848	2,2,4- tri-methylpentane
g2	CH2	0.6744	0.54	0.54	5 CH3, 1 CH2, 1 CH, 1C
g3	CH	0.4469	0.228	0.228	
g4	C	0.2195	0.0000	0.0000	
g5	OH	1.0000	1.7700	1.2000	Ethanol 1 CH3, 1 CH2, 1 OH
g6	ACH*	0.5313	0.4000	0.4000	Iso-butylbenzene
g7	AC	0.3652	0.1200	0.1200	5 ACH, 1AC, 2CH3, 1CH2 1CH
g8	ACOH	0.8952	1.2562	0.6800	Phenol 5 ACH, 1 ACOH
g9	ACNH2	1.0600	1.1975	0.8160	Aniline 5 ACH, 1 ACNH2
g10	CAN	0.8978	0.5332	-----	Dimethylaniline 5 ACH, 1 ACN, 2 CH3
g11	ACCl	1.1562	0.8440	0.8440	Chlorobenzene 5 ACH, 1ACCl
g12	ACBr	1.3144	0.9611	0.9520	Bromobenzene 5ACH, 1ACBr
g13	ACCOOH	1.6665	2.1967	1.3440	Benzoic acid 5 ACH, 1AC-COOH
g14	ACOCCH3	1.5102	1.3462	1.2080	Anisole 5 ACH, 1 ACOCH3
g15	ACOCCH2	1.2835	1.1031	0.9000	Phenetole 5 ACH, 1 AC-OCH2, 1 CH3
g16	ACCH=CH2	1.7106	1.2068	1.2960	Styrene 5 ACH, 1ACCH=CH2
g17	AN	0.3428	0.3675	0.1130	Pyridine 5 ACH, 1 AN
g18	ANH	0.5326	0.7742	-----	Carbazole 8 ACH, 4AC, 1 ANH
g19	AO	0.2439	0.2706	-----	Furan 4 ACH, 1 AO
g20	AS	0.9188	0.6747	-----	Thiophene 4 ACH, 1AS

*: All groups starting with "A" are aromatic groups

Table 2: Volume (Rg) and Surface area (Qg) Contributions of various groups (equation 7)

Id.	Structure	Qr
r1	One aromatic-ring	0.45023
r2	Two aromatic-ring	0.71355
r3	Three aromatic-ring	1.10481
r4	Four aromatic-ring	1.238
r5	One aromatic-one naphthalene (fused)	0.60446
r6	Two aromatic-one naphthalene (fused)	1.01571
r7	Cyclohexane (without attachment)	0.102451
r8	Cyclohexane (with attachment)	-0.118173
r9	Isoquinoline	-0.13794

Table 3: Contributions to Surface Area (Qr) of Various Ring Structures (Equation 7)

$$S = \sum_{g=1}^N n_g Q_g + \sum_{r=1}^M n_r Q_r + \sum_{s=1}^L n_s Q_s + \sum_{p=1}^K \left(\sum_{g=1}^N n_{gp} Q_g \right) \Theta_p \quad (7)$$

The first summation in equation 7 is over all the groups in the molecule and is identical to the UNIFAC group contribution method except that a few Q's have been modified to account for polarity. The second summation gives the additional contribution to surface area because of composite ring structures. nr represents number of ring structures of type r and Qr the corresponding contribution from Table 3. The third summation is over other selected molecular structures. From the vapor pressure data, two such structures were identified that affect the model results; they are (1) alkyl branches and (2) alkyl groups in the longest straight chain attached to a ring. ns is a characteristic integer and Qs represents contributions listed in Table 4. s=1 and 2 correspond to methyl and ethyl branches. For these ns is defined in the following manner

$$n_s = \sum_{j=1}^{B_s} (n_j^*) \quad (8)$$

For alkyl branches (s=1 or 2), ns is calculated in the following manner. Bs represents total number of branches of type s. For each of these a characteristic integer nj* is defined. nj* is unity for all branches, with two exceptions; when there are two alkyl branches attached to the same carbon atom, nj*=2 for each branch, and for an alkyl branch attached to a carbon atom in β position corresponding to an aromatic ring nj*=0.5. For s=3, ns represents number of carbon atoms in the longest straight chain attached to a ring.

The last summation in equation 7 corrects for some group contributions because of their position in the molecule. These

Id.	Structure	Qs	Qp
s1	Branch	-0.08289	----
s2	Branch	-0.1233	----
s3	An alkyl group in the longest chain attached to a ring	-0.02157	----
P1	Attachment to an aromatic ring in ortho position	----	-0.0128
P2	Two attachments to a carbon in a hydro-aromatic ring	----	-0.0539

Table 4: Contributions to Surface Area (Qs) and Positional factors (Qp) for Some Molecular Structures (Equation 7)

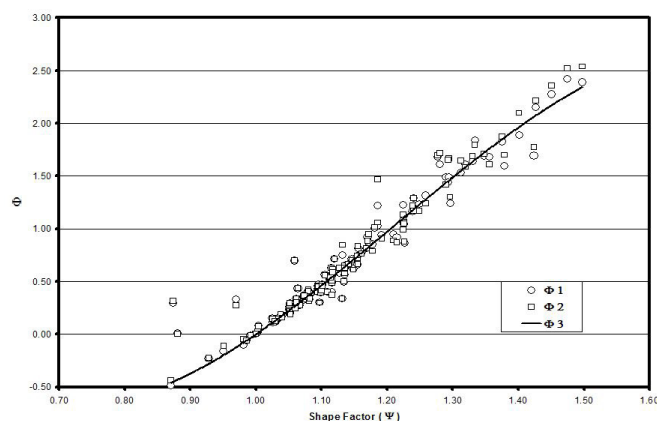


Figure 1: Experimental Φ 's and Φ 's calculated from equation 9 are plotted versus shape factor Ψ .

groups were already included in the summation given by the first term. Hence Θ_p represents a small factor that corrects for contributions of groups found in position characterized by p. Only two positional parameters are defined, p=1 corresponds to the attachments to aromatic rings in ortho positions and p=2 corresponds to double attachment to a carbon atom in a hydroaromatic ring. n_{gp} , therefore, represents number of groups to type g in position corresponding to p. Θ_p for p=1 and 2 are listed in Table 4. Although only a few structural and positional parameters are defined, these developments can be extended to various other structures if more extensive vapor pressure data on compounds with these structures are included. However, it should be noted that the dominant contribution to S in equation 7 comes from the first two summations, and the other two terms serve as minor correction terms for better accuracy. In other words, although it is possible to improve the accuracy of the method by including more molecular structures, equation 7 gives Ψ for most molecular types that correlate very well with Φ and provides a very useful development towards a generalized and predictive vapor pressure correlation.

A few of examples of calculation of Ψ using equations 4-8 are included in the Appendix. Also a plot of Φ versus Ψ for the 127 compounds in our databank is shown in Figure 1. An excellent correlation is observed. The following expression was fitted through these points

$$\Phi = -4.25456 (1 - \Psi) + 4.53448 (1 - \Psi)^2 + 7.28665 (1 - \Psi)^3 \quad (9)$$

For the 127 compounds in our databank, Φ 's calculated from equation 9 (called Φ_3) are shown in Table 1.

Method 4 thus involves calculation of Ψ by the group contribution method described above, then using equation 9 to calculate Φ for the compound and finally calculating the vapor pressure from equation 1 with benzene as the reference fluid and using the Wagner parameters listed before.

Two additional and predictive vapor pressure methods

The four methods outlined above all use experimental values

for Tc and Pc. Although method 4 uses a group contribution method for parameter Φ it is not entirely predictive and cannot be applied to compounds for which experimental critical properties are not available. To investigate the accuracy of a completely predictive vapor pressure correlation, two additional methods were formulated and are described below. Both the methods are identical to method 4, except that predicted critical properties are used instead of experimental values. In both the methods, Joback's group contribution procedure [3] is used to estimate Pc. For the 127 compounds in our databank, this method predicted Pc with an average error of 5%. Joback's group contribution method for Tc requires the knowledge of normal boiling point Tb of the compound. Joback has also developed a group contribution method for Tb [3]. An additional method considered for the prediction of Tc is the group contribution method of Fedors [3]. This method does not require only the group composition of the molecules. For the 127 compounds in our databank, the method of Joback with experimental boiling points was found to be superior to Fedors method, the average errors in the prediction of Tc for the two methods being 0.76% and 2.04% respectively. Our method 5 for vapor pressure calculation is identical with method 4, except the Tc and Pc are estimated using Joback's group contribution method with experimental values of the normal boiling points.

Method 6 was designed to be completely predictive, such that vapor pressure would be calculated from the knowledge of the group composition of the molecule without need for any experimental data. Two possibilities were considered for the prediction of Tc, Fedors group contribution method and Joback's method with predicted values of Tb. For comparison of the two, compounds were divided into 74 ring compounds, and 53 non-ring alkanes and alcohols. For non-ring compounds, Joback's group contribution method gave an average error of 3.36% in predicting Tb which resulted in an average error of 3.64% in estimation of Tc. Compared to these, average error in Tc predicted by Fedors method was only 1.07%. We, therefore, chose Fedors method for Tc of non-ring compounds. For the 74 ring compounds, Fedors method was found to be not quite so accurate, and gave an average error of 2.73%. Joback's method was found to be more accurate for these compounds and gave an average error of 1.79% in prediction of Tb. In analyzing the results obtained from Joback's group contribution method for Tb, it was observed that the errors were especially large for certain compounds containing multiple fused rings, ring oxygen like in furan, and ring -NH- group like in indole. For better accuracy, Joback's group contributions were modified as follows:

1. Add 10 K to the final Tb if the compound contains two fused rings
2. Add 15 K to the final Tb if the compound contains three or more fused rings.
3. For "— O —" ring group, Joback's value was modified from 31.22 to 11.22.
4. For "— NH —" ring group, Joback's value was modified from 52.82 to 82.82.

The above modifications resulted in the overall error for Tb

reducing from 1.79% to 1.40%. With the modified method for Tb, the average error in predicting Tc of ring compounds from Joback's method was found to be 1.66% compared to 2.73% for the Fedors method. Our method 6 for vapor pressure calculation was formulated to be exactly like method 5, except for the method to estimate Tc, which was estimated from Fedors group contribution method for non-ring compounds, and for ring compounds from the Joback's group contribution method using Tb estimated from the modified Joback's procedure as described above.

Comparison with Experimental Data

Compound by compound errors were obtained for vapor pressures computed from the six methods described in the previous sections. Errors were also generated for four literature correlations, the Lee-Kesler (L-K) method [2], two methods of Twu et al. [9], one using acentric factor ω (Twu- ω), and the other using modified acentric factor Ω calculated from vapor pressure data at $T_r=0.5$ (Twu- Ω), and the Pert2 correlation of Morgan and Kobayashi [10] which uses an additional perturbation term quadratic in ω . The compounds were aggregated into eight different classes, and the vapor pressure data were divided into three different reduced temperature ranges (0.3 to 0.5, 0.5 to 0.7, 0.7 to 1.0) and errors for each class and each temperature range are listed in Table 5. All the errors here and elsewhere in this paper are computed as absolute percentage values normalized by the experimental value as

$$Error(\%) = \frac{1}{N} \sum_{i=1}^N \left| \frac{P_i^{\text{exp}} - P_i^{\text{calc}}}{P_i^{\text{exp}}} \right| * 100$$

The results further confirm that Wagner's equation provides an excellent mathematical expression for vapor pressure as indicated by extremely low errors of Method 1. Methods 2 and 3 are equivalent to the four literature methods, i.e., L-K, Twu- ω , Twu- Ω , and Pert2 methods. All these methods require a single parameter for each compound, Φ_1 and Φ_2 for methods 2 and 3, ω for the L-K, Twu- ω , and Pert2, and Ω for Twu- Ω . Our method 3 and the literature methods are particularly similar in that the parameters Φ_2 , ω and Ω use a single vapor pressure data point. Errors for method 2 are understandably lower than the other two as it uses regressed values of Φ . Direct comparison of our method 3 with the literature correlations shows that method 3 is more accurate (average error of 3.44%) than any of the literature methods. Average errors of the literature correlations are around 5%. A detailed comparison of all these correlations must include a study of the effect of two major features of the models.

- (1) Choice of temperature for the vapor pressure data point: In all five of these correlations, Φ is calculated from a vapor pressure data point. In the L-K, Twu- ω , and Pert2 methods Φ is equivalent to the acentric factor ω which is calculated from vapor pressure at $T_r=0.7$. In the Twu- Ω method, Φ is equivalent to the modified acentric factor Ω which is calculated from the vapor pressure at $T_r=0.5$. In our method 3, Φ_3 is calculated from the vapor pressure at $T_r=0.6$. It would therefore be expected that the L-K, Twu- ω , and Pert2 models will be most accurate around $T_r=0.7$, Twu- Ω model should be most accurate around $T_r=0.5$, and our model 3 should be most

Table 5: Comparison of errors in vapor pressures computed from different models

Absolute percent errors for 10 models															
Compound types	T_r Range	Pts.	Meth-od 1	Meth-od 2	Meth-od 3	Meth-od 4	L-K	Twu- ω	Pert2	Meth-od 5		Meth-od 6		Twu- ω	
										Pts.	Error	Pts.	Error	Pts.	Error
Alkanes	0.3-0.5	76	1.26	4.85	13.32	8.41	8.73	4.9	6.46	76	10.19	75	12.92	76	8.52
	0.5-0.7	599	0.1	1.34	1.2	2.71	2.99	1.91	1.6	593	4.79	576	12.29	128	1.74
	0.7-1.0	231	0.3	2.62	2.79	2.23	1.79	1.78	1.77	237	3.85	255	9.26	155	0.96
	Total	906	0.25	1.96	2.62	3.07	3.17	2.13	2.05	906	5	906	11.49	359	2.84
Alcohols	0.5-0.7	154	0.09	5.15	7.33	16.41	10.72	11.16	11.17	139	32.22	149	36.05	0	---
	0.7-1.0	31	0.05	8.72	14.06	15.74	1.92	2.05	1.99	46	21.18	36	59.8	0	---
	Total	185	0.08	5.75	8.46	16.3	9.24	9.63	9.63	185	29.48	185	40.67	0	---
Alkyl-benzenes	0.3-0.5	9.4	0.76	1.39	3.93	10.05	8.43	7.08	5.36	94	10.65	98	20.57	94	4.31
	0.5-0.7	421	0.21	1.18	0.97	4.27	3.83	3.18	3.03	423	4.63	419	14.31	204	2.04
	0.7-1.0	191	0.18	0.87	0.64	0.67	0.64	0.57	0.59	189	3.06	189	8.88	191	1.26
	Total	706	0.28	1.12	1.27	4.06	3.58	2.99	2.68	706	5.01	706	13.73	489	2.17
Phenols	0.3-0.5	29	6.36	12.08	24.17	13.12	17.25	17.56	19.26	31	10.57	23	53.73	29	10.35
	0.5-0.7	117	0.52	3.11	6.4	7.67	3.08	3.36	4.1	115	10.38	121	43.61	117	3.56
	0.7-1.0	72	1.37	3.39	2.87	4.6	2.3	2.25	2.3	72	5.65	74	12.19	72	3.44
	Total	218	1.58	4.4	7.6	7.38	4.71	4.88	5.52	218	8.85	218	34.01	218	4.42
Hydro-aromatics	0.3-0.5	7	0.15	0.73	2.05	16.85	8	9.53	13.59	7	16.26	8	5.14	7	9.03
	0.5-0.7	151	0.14	1.47	1.56	5.05	4.3	5.07	5.35	151	10.13	146	17.31	11	0.66
	0.7-1.0	16	0.3	0.18	0.09	1.08	0.19	0.27	0.4	16	1.37	20	14.72	4	0.4
	Total	174	0.16	1.32	1.45	5.16	4.07	4.81	5.22	174	9.57	174	16.46	22	3.28
Two-ring aromatics	0.3-0.5	73	1.26	4.59	9.96	9.56	28	26.69	29.57	70	20.09	69	25.36	73	6.6
	0.5-0.7	130	0.44	2.39	1.58	4.24	13.43	13.67	13.81	134	13.04	136	24.03	124	5.66
	0.7-1.0	95	0.79	2.92	2.82	3.25	3.87	3.87	3.87	94	7.88	93	13.39	92	3.65
	Total	298	0.75	3.1	4.03	5.23	13.95	13.74	14.5	298	13.07	298	21.03	289	5.26
3,4-ring aromatics	0.3-0.5	13	2.07	12.38	20.18	18.69	37.78	39.03	38.81	14	24.93	16	29.24	13	14.84
	0.5-0.7	128	7.28	5.8	8.83	16.48	18.1	17.83	17.88	136	25.13	132	26.06	68	31.89
	0.7-1.0	32	4.46	8.95	7.39	12.9	8.76	8.65	8.66	23	24.54	25	16.47	13	28.65
	Total	173	6.37	6.88	9.42	15.99	17.85	17.72	17.75	173	25.03	173	24.97	94	29.08
Other ring compounds	0.3-0.5	53	0.64	3.3	7.01	12.42	6.19	7.03	7.75	55	12.28	49	51.98	51	6.52
	0.5-0.7	194	0.26	1.48	0.92	5.66	2.84	1.9	1.83	193	10.3	197	27.59	104	1.69
	0.7-1.0	64	0.53	1.92	1.66	3.07	1.62	1.63	1.67	63	4.41	65	17.52	60	1.81
	Total	311	0.38	1.88	2.11	6.28	3.16	2.72	2.81	311	9.46	311	29.33	215	2.87
All compounds	0.3-0.5	345	1.47	4.42	10.02	10.67	14.13	12.88	13.69	347	13.39	338	26.71	343	7.07
	0.5-0.7	1894	0.68	2.12	2.51	6	5.64	5.17	5.11	1884	10.17	1876	20.46	756	5.43
	0.7-1.0	732	0.63	2.7	2.76	3.28	2.07	2.05	2.06	740	6.05	757	13.45	587	2.48
	Total	2971	0.76	2.53	3.44	5.87	5.74	5.29	5.35	2971	9.52	2971	19.39	1686	4.74

accurate around $T_r = 0.6$. The errors for the homologous series of compounds, as well as the cumulative errors listed in Table 5, indeed exhibit this behavior, with the ω methods giving the best results in the T_r range of 0.7 to 1.0, Twu- Ω being most accurate in the T_r range of 0.3 to 0.5, and our model 3 giving the best results in the T_r range of 0.5 to 0.7. It is very clear from these results that the choice of a correlation from this class of methods must depend on the reduced temperature range of the desired application. However, if a single method is needed

that will give the best overall accuracy over the entire temperature range from the triple point to the critical temperature, $T_r = 0.6$ provides a better choice for the experimental vapor pressure data point as indicated by the lower overall errors for our method 3.

(2) Choice of the reference fluid: The choice of ω as the perturbation parameter implies that the reference fluid is a noble gas, although the coefficients in the expression for the term $f^{(0)}$

are not generally obtained by regressing vapor pressure data for noble gases, but are obtained simultaneously with the corresponding coefficients for $f^{(1)}$ by fitting experimental vapor pressure data for real liquids of interest.

To further show the accuracy of various vapor pressure methods we computed average errors in two narrow temperature ranges around the melting points and the boiling points of the compounds. These are shown in Table 6. For the second temperature range a single point closest to the boiling point was selected for each compound. Lee-Kesler method performs very well near the boiling point, but gives large errors near the melting point. The generalized vapor pressure method (Method 4) performs quite adequately in both the temperature ranges. Results for Method 1 are not shown in this table as these errors are significantly lower.

Temperature Range	No. Pts	Method 2	Method 3	Method 4	Lee-Kesler
$T_m \leq T \leq (T_m + 30^\circ\text{K})$	100	8.06%	15.65%	13.70%	20.29%
T nearest to T_b	127	3.15%	2.92%	5.01%	2.54%

Table 6: Comparison between our methods and Lee-Kesler Method in Temperature ranges around melting and boiling points.

Conclusions

A series of methods are presented for the calculation of vapor pressures of organic liquids. These methods use the Wagner's equation as the functional form and benzene as the reference fluid. The most significant of the methods is a generalized correlation (method 4) that allows computation of Φ in terms of a shape factor Ψ which in turn is evaluated by a group contribution method from the detailed information on functional groups that make up the molecule. Comparisons with experimental data show that this correlation represents the most accurate generalized vapor pressure method in the literature and gives similar accuracy as some of the more specific vapor pressure correlations. Furthermore, the correlation is applicable in the entire temperature range from the melting point to the critical temperature. That Ψ provides a good correlating parameter for vapor pressure is further confirmed by plotting acentric factor ω versus Ψ in Figure 2. Again an excellent correlation is observed and least squares fit through these points resulted in the following expression

$$\omega = -0.54388 + 0.44247\Psi + 0.32051\Psi^2 \quad (11)$$

ω calculated from the above expression were found to give an average error of 5.82% when compared with experimental values for the 127 compounds in our databank. Equation 11 thus serves as a good estimation procedure for $\hat{e}$ if experimental value is not available.

The current work did not consider unsaturated hydrocarbons such as alkenes and acetylenes. Also, group contributions are listed for only a subset of the original UNIFAC groups (Table 2). However, the correlation can be easily extended to these and other compounds by compiling data and generating Φ 's

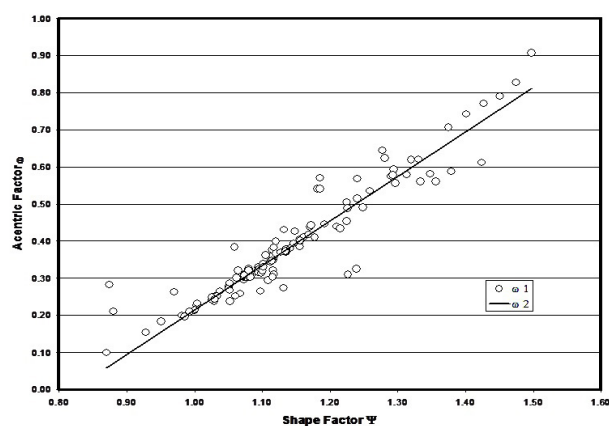


Figure 2: Experimental ω 's and ω 's calculated from equation 11 are plotted versus shape factor Ψ .

by the same procedure as discussed above. Method 4 may be applied for vapor pressures of compounds containing groups not defined in Table 2, as it allows for calculation of Ψ of these compounds using UNIFAC R and Q values [11]. For nonpolar groups, this procedure should give better results than for polar groups. In any case it would be interesting to investigate the accuracy of the vapor pressures of these compounds calculated in this manner and this can serve as another test for the shape factor Ψ as the correlating parameter for Φ .

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Appendix

Examples of calculation of Ψ and Φ by the group contribution method:

1. Benzene (C_6H_6)

Group Composition:

$$\text{Id} = \text{g6} \quad \text{ng} = 6 \quad \text{Id} = \text{r1} \quad \text{nr} = 1$$

Volume (V): From eq. 5 and Table 2, $V = 6(0.5313) = 3.1878$

Surface area (S):

$$\begin{aligned} &\text{From eq. 7 and Tables 2 and 3,} \\ &S = 6(0.4) + 0.45023 = 2.85023 \end{aligned}$$

Ψ : From eq. 4, $\Psi = 1$

Φ : From eq. 9, $\Phi = 0$

2. 2,2,3,4 - tetramethylpentane (C_9H_{20})

Group composition:

$$\text{Id} = \text{g1} \quad \text{ng} = 6, \quad \text{Id} = \text{g2} \quad \text{ng} = 1, \quad \text{Id} = \text{g4} \quad \text{ng} = 2$$

$$\text{Id} = \text{s1} \quad \text{ns} = 8 \quad (\text{equation 8})$$

Volume (V): From eq. 5 and Table 2,

$$V = 6(0.9011) + 1(0.6744) + 2(0.2195) = 6.5200$$

Surface area (S): From eq. 7 and Tables 2 and 4,

$$S = 6(0.848) + 1(0.5400) + 1(0.00) + 8(-0.08289) = + 2(0.000) = 4.9649$$

$$\Psi: \text{From eq. 4, } \Psi = [4.9649/6.5200]^{2/3} [(2.85023/(3.1878)^{2/3})] = 1.0811$$

$$\Phi: \text{From eq. 9, } \Phi = -4.25456(-0.0811) + 4.53448(-0.0811)^2 + 7.28665(-0.0811)^3 = 0.3709$$

From vapor pressure data, regressed $\Phi = 0.3535$

3. iso-butylbenzene ($C_{10}H_{14}$)

Group Composition: $I_d = g1$ $ng = 2$, $I_d = g2$ $ng = 1$, $I_d = g3$ $ng = 1$, $I_d = g6$ $ng = 5$, $I_d = g7$ $ng = 1$

$$I_d = r1 \quad nr = 1$$

$$I_d = s1 \quad ns = 0.5 \text{ (equation 8), } I_d = s3, \quad ns = 3$$

Volume (V): From eq. 5 and Table 2,

$$V = 2(0.9011) + 1(0.6744) + 1(0.4469) + 5(0.5313) + 1(0.3652) = 5.9452$$

Surface area (S): From eq. 7 and Tables 2, 3 and 4,

$$S = 2(0.848) + 1(0.540) + 1(0.2280) + 5(0.400) + 1(0.120) + 1(0.45023) + 0.5(-0.08289) + 3(-0.02157) = 4.9281$$

$$\Psi: \text{From eq. 4, } \Psi = [4.9281/(5.9452)^{2/3}] / [(2.85023/(3.1878)^{2/3})] = 1.1412$$

$$\Phi: \text{From eq. 9, } \Phi = -4.25456(-0.1412) + 4.53448(-0.1412)^2 + 7.28665(-0.1412)^3 = 0.6705$$

From vapor pressure data, regressed $\Phi = 0.6638$

4. O-cymene

Group Composition: $I_d = g6$ $ng = 4$, $I_d = g7$ $ng = 2$, $I_d = g3$ $ng = 1$, $I_d = g1$ $ng = 3$

$$I_d = r1 \quad nr = 1, \quad I_d = s1 \quad ns = 1, \quad I_d = s3 \quad ns = 2, \quad I_d = P1 \quad np = 1$$

Volume (V): From equation 5 and table 2,

$$V = 4(0.5313) + 2(0.3652) + 1(0.4469) + 3(0.9011) = 6.0058$$

Surface Area (S): From equation 7 and Tables 2,3 and 4

$$S = 4(0.4) + 2(0.12) + 0.2280 + 3(0.848) + 0.45023 - 0.08289 - 2(0.02157) - 0.0128[3(0.848) + 0.2280] = 4.9007184$$

$$\Psi: \text{From eq. 4, } \Psi = [4.9007184/(6.0058)^{2/3}] / [(2.85023/(3.1878)^{2/3})] = 1.1272$$

$$\Phi: \text{From eq. 9, } \Phi = -4.25456(1-1.1272) + 4.53448(1-1.1272)^2 + 7.28665(1-1.1272)^3 = 0.59945$$

From vapor pressure data, regressed $\Phi = 0.5797$

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