A Method To Estimate the Patel−Teja Equation of State Constants

Luis A. Forero and Jorge A. Velásquez*

Facultad de Ingeniería Química, Universidad Pontificia Bolivariana, A.A. 56006, Medellín, Colombia

A method to determine the Patel−Teja equation of state (EoS) constants F and ζ_c is presented. The method uses Wagner and Rackett equations to generate vapor pressure and liquid volume data. Constants were estimated for 498 pure substances. For 19 substances the new constants were used to predict some thermodynamical properties like vapor pressure, liquid molar volume, vapor molar volume, and enthalpy of vaporization. An extension to mixtures was done by using the Panagiotopoulous−Reid mixing rule. New constants are comparable to the original ones reported in the Patel−Teja work, and they preserve the good features of the equation of state.

Introduction

Equations of state (EoSs) are fundamental to calculate thermodynamical properties for pure substances and mixtures. Using an EoS, phase equilibria calculations and material and energy balances can be solved to design, evaluate, and optimize chemical processes. Engineers choose cubic equations of state to solve practical problems rapidly and efficiently because cubic EoSs are simple and easy to handle.[1] The Patel−Teja cubic equation of state (PT)[2] has some advantages over other classic EoSs like the van der Waals,[3] the Soave−Redlich−Kwong,[4] and the Peng−Robinson[5] equations. The PT equation can predict thermodynamical properties for polar and nonpolar substances in liquid and vapor phases. In a recent study a comparison of the prediction power of 23 generalized equations of state is made,[6,7] and the PT EoS is a member of the group which provides the most accurate predictions for 102 pure substances.

Despite the good features of the PT EoS, it is not widely used in chemical process simulation because it has two substance-dependent constants (F and ζ_c). These constants were generalized in terms of the acentric factor for nonpolar compounds, but for polar substances there are few F and ζ_c values reported in the literature.[2] To solve this problem, this paper proposes a technique based in the EoS error minimization to predict vapor pressures and saturated liquid volumes. The objectives of this work are present and validate a method that can be used for any substance. Validation was made by predictions and comparisons with experimental data for the thermodynamical properties of some pure substances and mixtures.

Patel−Teja Equation of State

The PT EoS is a three-parameter (a, b, c) van der Waals type EoS.[2] One of these parameters (a) is temperature-dependent, and it has the Soave functionality.[4,8] To use the PT EoS, critical temperature (T_c), critical pressure (P_c), and two substance-dependent parameters, F and ζ_c, are needed. F is the optimal value that minimizes the quadratic error in vapor pressure calculations; on the other hand, ζ_c is the optimal value that adjusts saturated liquid volume predictions to experimental data. T_c and P_c values are reported in the Reid et al. property data bank.[9] F and ζ_c values for nonpolar compounds can be calculated using the acentric factor (ω) according to:

$$F = 0.452413 + 1.30982\omega - 0.295937\omega^2 \quad (1)$$

$$\zeta_c = 0.329032 - 0.076799\omega + 0.0211947\omega^2 \quad (2)$$

The acentric factor is also available in the Reid et al. property data bank. Equations 1 and 2 cannot be used to polar substances, and they predict only an approximation to the optimal values for nonpolar compounds. F and ζ_c values for some polar substances like water, ammonia, and some alcohols were reported in the original Patel−Teja work.[2]

Table 1. Average Absolute Deviations in Vapor Pressure and Liquid Saturated Volume Using the Wagner and the Rackett Equations, Respectively[a]

compound	AAD P^{sat}	AAD^{VL}	no data
ethanol	0.294 %	1.980 %	16
argon	0.458 %	0.322 %	13
acetylene	0.931 %	0.750 %	14
ammonia	0.657 %	0.362 %	22
butane	0.344 %	0.225 %	24
carbon dioxide	0.179 %	0.154 %	15
ethane	0.627 %	0.156 %	19
ethene	0.269 %	0.145 %	20
heptane	0.135 %	0.204 %	13
isobutane	2.210 %	0.495 %	21
methane	0.733 %	0.684 %	21
methanol	0.226 %	0.268 %	20
nitrogen	0.238 %	0.362 %	15
octane	1.222 %	0.480 %	17
oxygen	0.548 %	0.667 %	22
propane	1.161 %	0.202 %	23
carbon tetrachloride	0.194 %	0.436 %	27
toluene	0.464 %	0.255 %	22
average	0.605 %	0.453 %	

[a] $$Y(\mathrm{AAD}) = \frac{1}{N}\sum_{1}^{N}\frac{|Y_i^{exp} - Y_i^{PT}|}{Y_i^{exp}}$$ where $Y = P^{sat}, V^l$

* Corresponding author. E-mail: jorge.velasquezj@upb.edu.co.

10.1021/je100656d
Published on Web 09/01/2010

Table 2. F and ζ_c Values for Hydrocarbons

no.	molecular formula	IUPAC name	*F*	ζ_c	no.	molecular formula	IUPAC name	*F*	ζ_c
1	CH_4	methane	0.468132	0.326	97	C_8H_{16}	propan-2-ylcyclopentane	0.737875	0.304
2	C_2H_2	acethylene	0.687807	0.31	98	C_8H_{16}	cyclooctane	0.788865	0.314
3	C_2H_4	ethene	0.578164	0.323	99	C_8H_{16}	oct-1-ene	0.918808	0.303
4	C_2H_6	ethane	0.588274	0.323	100	C_8H_{16}	(*E*)-oct-2-ene	0.890006	0.311
5	C_3H_4	propadiene	0.875291	0.265	101	C_8H_{18}	octane	0.928158	0.301
6	C_3H_4	propyne	0.728151	0.313	102	C_8H_{18}	2-methylheptane	0.90866	0.302
7	C_3H_6	cyclopropane	0.595368	0.312	103	C_8H_{18}	3-methylheptane	0.909084	0.304
8	C_3H_6	prop-1-ene	0.650733	0.319	104	C_8H_{18}	4-methylheptane	0.89852	0.302
9	C_3H_8	propane	0.657228	0.319	105	C_8H_{18}	2,2-dimethylhexane	0.88566	0.309
10	C_4H_4	but-1-en-3-yne	0.617392	0.307	106	C_8H_{18}	2,3-dimethylhexane	0.89281	0.308
11	C_4H_6	buta-1,2-diene	0.761961	0.309	107	C_8H_{18}	2,4-dimethylhexane	0.897673	0.31
12	C_4H_6	buta-1,3-diene	0.696499	0.314	108	C_8H_{18}	2,5-dimethylhexane	0.89854	0.306
13	C_4H_8	but-1-ene	0.705583	0.316	109	C_8H_{18}	3,3-dimethylhexane	0.858749	0.308
14	C_4H_8	(*Z*)-but-2-ene	0.710377	0.313	110	C_8H_{18}	3,4-dimethylhexane	0.900965	0.313
15	C_4H_8	(*E*)-but-2-ene	0.694393	0.309	111	C_8H_{18}	3-ethylhexane	0.919538	0.31
16	C_4H_8	cyclobutane	0.684894	0.316	112	C_8H_{18}	2,2,3-trimethylpentane	0.85659	0.315
17	C_4H_8	2-methylprop-1-ene	0.710284	0.315	113	C_8H_{18}	2,2,4-trimethylpentane	0.850607	0.313
18	C_4H_{10}	butane	0.717615	0.316	114	C_8H_{18}	2,3,3-trimethylpentane	0.846002	0.317
19	C_4H_{10}	2-methylpropane	0.706253	0.319	115	C_8H_{18}	2,3,4-trimethylpentane	0.881952	0.316
20	C_5H_8	cyclopentene	0.727326	0.319	116	C_8H_{18}	2-methyl-3-ethylpentane	0.891813	0.313
21	C_5H_8	penta-1,2-diene	0.659958	0.309	117	C_8H_{18}	3-methyl-3-ethylpentane	0.853109	0.314
22	C_5H_8	(3*E*)-penta-1,3-diene	0.680792	0.311	118	C_8H_{18}	2,2,3,3-tetramethylbutane	0.962612	0.326
23	C_5H_8	penta-1,4-diene	0.588397	0.311	119	C_9H_{10}	2,3-dihydro-1*H*-indene	0.821496	0.306
24	C_5H_8	pent-1-yne	0.723201	0.318	120	C_9H_{10}	prop-1-en-2-ylbenzene	0.858494	0.295
25	C_5H_8	2-methylbuta-1,3-diene	0.63117	0.304	121	C_9H_{12}	propylbenzene	0.862733	0.303
26	C_5H_8	3-methylbuta-1,2-diene	0.685666	0.316	122	C_9H_{12}	propan-2-ylbenzene	0.854576	0.306
27	C_5H_{10}	cyclopentane	0.689206	0.311	123	C_9H_{12}	1-ethyl-2-methylbenzene	0.751219	0.29
28	C_5H_{10}	pent-1-ene	0.745753	0.311	124	C_9H_{12}	1-ethyl-3-methylbenzene	0.773595	0.287
29	C_5H_{10}	(*Z*)-pent-2-ene	0.757607	0.313	125	C_9H_{12}	1-ethyl-4-methylbenzene	0.788375	0.291
30	C_5H_{10}	(*E*)-pent-2-ene	0.766074	0.313	126	C_9H_{12}	1,2,3-trimethylbenzene	0.915502	0.308
31	C_5H_{10}	2-methylbut-1-ene	0.709394	0.303	127	C_9H_{12}	1,2,4-trimethylbenzene	0.897506	0.302
32	C_5H_{10}	2-methylbut-2-ene	0.770215	0.299	128	C_9H_{12}	1,3,5-trimethylbenzene	0.928429	0.301
33	C_5H_{10}	3-methylbut-1-ene	0.769217	0.315	129	C_9H_{18}	propylcyclohexane	0.751292	0.299
34	C_5H_{12}	pentane	0.770322	0.311	130	C_9H_{18}	propan-2-ylcyclohexane	0.721097	0.299
35	C_5H_{12}	2-methylbutane	0.757796	0.316	131	C_9H_{18}	non-1-ene	0.960206	0.299
36	C_5H_{12}	2,2-dimethylpropane	0.721653	0.317	132	C_9H_{20}	nonane	0.98519	0.3
37	C_6H_6	benzene	0.719798	0.312	133	C_9H_{20}	2-methyloctane	0.968777	0.304
38	C_6H_{10}	hexa-1,5-diene	0.769059	0.311	134	C_9H_{20}	2,2-dimethylheptane	0.944471	0.307
39	C_6H_{10}	cyclohexene	0.722663	0.313	135	C_9H_{20}	2,2,3-trimethylhexane	0.894731	0.312
40	C_6H_{12}	cyclohexane	0.73283	0.315	136	C_9H_{20}	2,2,4-trimethylhexane	0.900306	0.309
41	C_6H_{12}	methyl cyclopentane	0.755134	0.314	137	C_9H_{20}	2,2,5-trimethylhexane	0.900054	0.307
42	C_6H_{12}	hex-1-ene	0.814038	0.309	138	C_9H_{20}	3,3-diethylpentane	0.884503	0.309
43	C_6H_{12}	(*Z*)-hex-2-ene	0.76752	0.308	139	C_9H_{20}	2,2,3,3-tetramethylpentane	0.850377	0.313
44	C_6H_{12}	(*E*)-hex-2-ene	0.76873	0.309	140	C_9H_{20}	2,2,3,4-tetramethylpentane	0.864087	0.312
45	C_6H_{12}	(*Z*)-hex-3-ene	0.754632	0.311	141	C_9H_{20}	2,2,4,4-tetramethylpentane	0.720711	0.312
46	C_6H_{12}	(*E*)-hex-3-ene	0.735442	0.31	142	C_9H_{20}	2,3,3,4-tetramethylpentane	0.874356	0.315
47	C_6H_{12}	2-methylpent-2-ene	0.752651	0.308	143	$C_{10}H_8$	naphtalene	0.819944	0.306
48	C_6H_{12}	(*Z*)-3-methylpent-2-ene	0.742923	0.306	144	$C_{10}H_{12}$	1,2,3,4-tetrahydronaphtalene	0.855635	0.302
49	C_6H_{12}	(*E*)-3-methylpent-2-ene	0.752508	0.305	145	$C_{10}H_{14}$	butylbenzene	0.920094	0.302
50	C_6H_{12}	(*Z*)-4-methylpent-2-ene	0.802189	0.305	146	$C_{10}H_{14}$	2-methylpropylbenzene	0.990567	0.316
51	C_6H_{12}	(*E*)-4-methylpent-2-ene	0.805989	0.304	147	$C_{10}H_{14}$	butan-2-ylbenzene	0.791515	0.303
52	C_6H_{12}	2,3-dimethylbut-1-ene	0.744353	0.311	148	$C_{10}H_{14}$	*tert*-butylbenzene	0.766971	0.301
53	C_6H_{12}	2,3-dimethylbut-2-ene	0.765665	0.306	149	$C_{10}H_{14}$	1,4-diethylbenzene	0.902394	0.295
54	C_6H_{12}	3,3-dimethylbut-1-ene	0.662914	0.32	150	$C_{10}H_{14}$	1,2,3,5-tetramethylbenzene	0.892761	0.291
55	C_6H_{14}	hexane	0.81935	0.306	151	$C_{10}H_{14}$	1,2,4,5-tetramethylbenzene	0.970185	0.297
56	C_6H_{14}	2-methylpentane	0.807181	0.311	152	$C_{10}H_{18}$	*cis*-1,2,3,4,4a,5,6,7,8,8a-decahydronaphtalene	0.803248	0.307
57	C_6H_{14}	3-methylpentane	0.805551	0.313	153	$C_{10}H_{18}$	*trans*-1,2,3,4,4a,5,6,7,8,8a-decahydronaphtalene	0.830925	0.311
58	C_6H_{14}	2,2-dimethylbutane	0.776344	0.319	154	$C_{10}H_{20}$	2-methylpropylcyclohexane	0.970598	0.336
59	C_6H_{14}	2,3-dimethylbutane	0.777339	0.314	155	$C_{10}H_{20}$	butan-2-ylcyclohexane	0.789108	0.301
60	C_7H_8	methylbenzene	0.767388	0.306	156	$C_{10}H_{20}$	*tert*-butyl cyclohexane	0.772741	0.303
61	C_7H_{14}	cycloheptane	0.767179	0.314	157	$C_{10}H_{20}$	dec-1-ene	1.040527	0.3
62	C_7H_{14}	1,1-dimethylcyclopentane	0.858514	0.324	158	$C_{10}H_{22}$	decane	1.027688	0.297
63	C_7H_{14}	(1*S*,2*R*)-1,2-dimethylcyclopentane	0.804373	0.314	159	$C_{10}H_{22}$	3,3,5-trimethylheptane	0.943788	0.31
64	C_7H_{14}	(1*R*,2*R*)-1,2-dimethylcyclopentane	0.849225	0.323	160	$C_{10}H_{22}$	2,2,3,3-tetramethylhexane	0.934524	0.317
65	C_7H_{14}	ethylcyclopentane	0.805958	0.311	161	$C_{10}H_{22}$	2,2,5,5-tetramethyl-hexane	0.961521	0.313
66	C_7H_{14}	methylcyclohexane	0.761558	0.314	162	$C_{11}H_{10}$	1-methylnaphtalene	0.846398	0.3
67	C_7H_{14}	hept-1-ene	0.886822	0.304	163	$C_{11}H_{10}$	2-methylnaphtalene	0.876791	0.3
68	C_7H_{14}	2,3,3-trimethylbut-1-ene	0.686453	0.303	164	$C_{11}H_{16}$	1,2,3,4,5-pentamethylbenzene	0.852346	0.275
69	C_7H_{16}	heptane	0.878022	0.304	165	$C_{11}H_{22}$	hexylcyclopentane	0.955392	0.286
70	C_7H_{16}	2-methyl hexane	0.864132	0.307	166	$C_{11}H_{22}$	undec-1-ene	1.032691	0.292
71	C_7H_{16}	3-methyl hexane	0.860126	0.308	167	$C_{11}H_{24}$	undecane	1.057994	0.292
72	C_7H_{16}	2,2-dimethyl pentane	0.82561	0.311	168	$C_{12}H_{10}$	phenylbenzene	0.990824	0.325
73	C_7H_{16}	2,3-dimethyl pentane	0.838966	0.312	169	$C_{12}H_{18}$	1,2,3,4,5,6-hexamethylbenzene	1.043554	0.298
74	C_7H_{16}	2,4-dimethyl pentane	0.847426	0.311	170	$C_{12}H_{24}$	dodec-1-ene	1.064349	0.288
75	C_7H_{16}	3,3-dimethyl pentane	0.813495	0.316	171	$C_{12}H_{26}$	dodecane	1.104696	0.291
76	C_7H_{16}	3-ethyl pentane	0.850693	0.31	172	$C_{13}H_{12}$	phenylmethylbenzene	0.946653	0.293
77	C_7H_{16}	2,2,3-trimethyl butane	0.789975	0.316	173	$C_{13}H_{26}$	tridec-1-ene	1.084449	0.282
78	C_8H_8	etenylbenzene	0.758211	0.307	174	$C_{13}H_{28}$	tridecane	1.142303	0.288
79	C_8H_{10}	1,2-dimethylbenzene	0.82795	0.305	175	$C_{14}H_{10}$	antracene	0.913651	0.275
80	C_8H_{10}	1,3-dimethylbenzene	0.83111	0.302	176	$C_{14}H_{10}$	fenantrene	0.742364	0.255
81	C_8H_{10}	1,4-dimethylbenzene	0.822511	0.301	177	$C_{14}H_{28}$	tetradec-1-ene	1.108198	0.277
82	C_8H_{10}	ethylbenzene	0.802313	0.304	178	$C_{14}H_{30}$	tetradecane	1.014274	0.269
83	C_8H_{16}	1,1-dimethylcyclohexane	0.720328	0.302	179	$C_{15}H_{30}$	pentadec-1-ene	1.125744	0.272
84	C_8H_{16}	(1*S*,2*R*)-1,2-dimethylcyclohexane	0.695125	0.295	180	$C_{15}H_{32}$	pentadecane	1.222559	0.284
85	C_8H_{16}	(1*S*,2*S*)-1,2-dimethylcyclohexane	0.704645	0.299	181	$C_{16}H_{32}$	decylcyclohexane	0.968357	0.251
86	C_8H_{16}	(1*R*,3*S*)-1,3-dimethylcyclohexane	0.749446	0.306	182	$C_{16}H_{32}$	hexadec-1-ene	1.129536	0.265
87	C_8H_{16}	(1*R*,3*R*)-1,3-dimethylcyclohexane	0.707786	0.301	183	$C_{16}H_{34}$	hexadecane	1.218855	0.276
88	C_8H_{16}	*cis*-1,4-dimethylcyclohexane	0.70526	0.299	184	$C_{17}H_{36}$	heptadecane	1.239361	0.273
89	C_8H_{16}	*trans*-1,4-dimethyl cyclohexane	0.778624	0.307	185	$C_{18}H_{14}$	1,2-di(phenyl)benzene	1.21365	0.338
90	C_8H_{16}	ethylcyclohexane	0.724804	0.298	186	$C_{18}H_{14}$	1,3-di(phenyl)benzene	1.288713	0.338
91	C_8H_{16}	1,1,2-trimethylcyclopentane	0.760271	0.306	187	$C_{18}H_{14}$	1,4-di(phenyl)benzene	1.263979	0.338
92	C_8H_{16}	1,1,3-trimethylcyclopentane	0.727009	0.307	188	$C_{18}H_{36}$	octadec-1-ene	1.148878	0.251
93	C_8H_{16}	*c*,*c*,*t*-1,2,4-trimethyl cyclopentane	0.806784	0.307	189	$C_{18}H_{38}$	octadecane	1.20909	0.269
94	C_8H_{16}	1,2,4-trimethylcyclopentane	0.757857	0.305	190	$C_{19}H_{40}$	nonadecane	1.215852	0.26
95	C_8H_{16}	1-ethyl-1-methylcyclopentane	0.756396	0.306	191	$C_{20}H_{42}$	eicosane	1.3584	0.268
96	C_8H_{16}	propylcyclopentane	0.785313	0.304					

Table 3. F and ζ_c Values for Halogens

no.	molecular formula	IUPAC name	F	ζ_c
1	Cl_2	chlorine	0.581445	0.323
2	$CBrClF_2$	bromochlorodifluoromethane	0.284196	0.215
3	CBr_2F_2	dibromodifluoromethane	0.590995	0.3
4	$CClF_3$	chlorotrifluoromethane	0.689111	0.31
5	CCl_2F_2	dichlorodifluoromethane	0.702242	0.32
6	CCl_2O	carbonyl dichloride	0.742024	0.323
7	CCl_3F	trichlorofluoromethane	0.712392	0.319
8	CF_4	tetrafluoromethane	0.719492	0.325
9	CCl_4	tetrachloromethane	0.7081	0.315
10	$CHClF_2$	chlorodifluoromethane	0.721379	0.31
11	$CHCl_2F$	dichlorofluoromethane	0.701989	0.311
12	$CHCl_3$	trichloromethane	0.736029	0.315
13	CHF_3	trifluoromethane	0.73074	0.299
14	CH_2Br_2	dibromomethane	1.070637	0.335
15	CH_2Cl_2	dichloromethane	0.701056	0.309
16	CH_2F_2	difluoromethane	0.674058	0.283
17	CH_3Br	bromomethane	0.582978	0.302
18	CH_3Cl	chloromethane	0.614656	0.307
19	CH_3F	fluoromethane	0.547697	0.275
20	CH_3I	iodomethane	0.59499	0.305
21	$C_2Br_2ClF_3$	1,2-dibromo-1-chloro-1,2,2-trifluoroethane	0.857701	0.337
22	$C_2Br_2F_4$	1,2-dibromo-1,1,2,2-tetrafluoroethane	0.784229	0.316
23	C_2ClF_3	1-chloro-1,2,2-trifluoroethene	0.787252	0.314
24	C_2ClF_5	1-chloro-1,1,2,2,2-pentafluoroethane	0.847619	0.326
25	$C_2Cl_2F_4$	1,1-dichloro-1,2,2,2-tetrafluoroethane	0.808445	0.32
26	$C_2Cl_2F_4$	1,2-dichloro-1,1,2,2-tetrafluoroethane	0.8084	0.318
27	$C_2Cl_3F_3$	1,1,2-trichloro-1,2,2-trifluoroethane	0.803011	0.317
28	C_2Cl_4	1,1,2,2-tetrachloroethene	0.802765	0.321
29	$C_2Cl_4F_2$	1,1,2,2-tetrachloro-1,2-difluoroethane	1.029828	0.338
30	C_2F_3N	2,2,2-trifluoroacetonitrile	0.848809	0.334
31	C_2F_4	1,1,2,2-tetrafluoroethene	0.742676	0.311
32	C_2F_6	1,1,1,2,2,2-hexafluoroethane	0.836877	0.323
33	C_2HClF_4	chloro-1,1,2,2-tetrafluoroethane	0.831107	0.316
34	C_2HCl_3	1,1,2-trichloroethene	0.775843	0.319
35	C_2HCl_5	1,1,1,2,2-pentachloroethane	0.782502	0.287
36	$C_2H_2Cl_2$	(*Z*)-1,2-dichloroethene	0.732786	0.315
37	$C_2H_2Cl_2$	(*E*)-1,2-dichloroethene	0.607663	0.292
38	$C_2H_2F_2$	1,1-difluoroethene	0.569913	0.305
39	C_2H_3Cl	chloroethene	0.561098	0.298
40	$C_2H_3ClF_2$	1-chloro-1,1-difluoroethane	0.872784	0.325
41	C_2H_3ClO	acetyl chloride	0.903304	0.317
42	$C_2H_3Cl_3$	1,1,1-trichloroethane	0.736148	0.313
43	$C_2H_3Cl_3$	1,1,2-trichloroethane	0.870087	0.325
44	C_2H_3F	fluoroethene	0.638419	0.312
45	$C_2H_3F_3$	1,1,1-trifluoroethane	0.703001	0.294
46	$C_2H_4Br_2$	1,2-dibromoethane	0.71066	0.304
47	$C_2H_4Cl_2$	1,1-dichloroethane	0.781645	0.318
48	$C_2H_4Cl_2$	1,2-dichloroethane	0.749127	0.307
49	$C_2H_4F_2$	1,1-difluoroethane	0.701423	0.292
50	C_2H_5Cl	chloroethane	0.662284	0.305
51	C_2H_5F	fluoroethane	0.648421	0.291
52	C_2H_5I	iodoethane	0.54771	0.286
53	C_3F_8	1,1,1,2,2,3,3,3-octafluoropropane	0.928632	0.323
54	C_4F_{10}	1,1,1,2,2,3,3,4,4,4-decafluorobutane	0.963743	0.317
55	C_4F_8	1,1,2,2,3,3,4,4-octafluorocyclobutane	0.955156	0.318
56	$C_3H_3F_5$	1,1,1,2,2-pentafluoropropane	0.898637	0.321
57	C_3H_5Cl	3-chloroprop-1-ene	0.60834	0.302
58	$C_3H_5Cl_3$	1,2,3-trichloropropane	0.760425	0.288
59	$C_3H_6Cl_2$	1,2-dichloropropane	0.754203	0.31
60	C_3H_7Cl	1-chloropropane	0.770941	0.319
61	C_3H_7Cl	2-chloropropane	0.82114	0.329
62	C_4H_9Cl	1-chlorobutane	0.678683	0.294
63	C_4H_9Cl	2-chlorobutane	0.840291	0.316
64	C_5F_{12}	1,1,1,2,2,3,3,4,4,5,5,5-dodecafluoropentane	1.131806	0.332
65	C_6BrF_5	1-bromo-2,3,4,5,6-pentafluorobenzene	0.794394	0.288
66	C_6ClF_5	1-chloro-2,3,4,5,6-pentafluorobenzene	0.74652	0.263
67	$C_6Cl_3F_3$	1,3,5-trichloro-2,4,6-trifluorobenzene	0.96649	0.304
68	C_6F_6	1,2,3,4,5,6-hexafluorobenzene	0.926248	0.301
69	C_6F_{14}	1,1,1,2,2,3,3,4,4,5,5,6,6,6-tetradecafluorohexane	1.196984	0.327
70	C_6F_{14}	1,1,1,2,2,3,3,4,5,5,5-undecafluoro-4-(trifluoromethyl)pentane	1.044595	0.307
71	C_6F_{14}	1,1,1,2,2,3,4,4,5,5,5-undecafluoro-3-(trifluoromethyl)pentane	1.003516	0.295
72	C_6F_{14}	perfluoro-2,3-dimethyl butane	0.957024	0.302
73	C_6HF_5	1,2,3,4,5-pentafluorobenzene	0.909415	0.306
74	$C_6H_2F_4$	1,2,3,4-tetrafluorobenzene	0.867489	0.305
75	$C_6H_2F_4$	1,2,4,5-tetrafluorobenzene	0.908484	0.311
76	$C_6H_4Cl_2$	1,2-dichlorobenzene	0.491493	0.29
77	C_6H_5Br	bromobenzene	0.74687	0.305
78	C_6H_5Cl	chlorobenzene	0.758261	0.307
79	C_6H_5F	fluorobenzene	0.75884	0.309
80	C_6H_5I	iodobenzene	0.752085	0.306
81	C_7F_8	1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene	1.162642	0.312
82	C_7F_{16}	1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-hexadecafluoroheptane	1.167137	0.308
83	$C_7H_3F_5$	1,2,3,4,5-pentafluoro-6-methylbenzene	0.940686	0.301
84	$C_{10}F_8$	1,2,3,4,5,6,7,8-octafluoronaphtalene	0.810512	0.256

Table 4. F and ζ_c Values for Alcohols and Phenols

no.	molecular formula	IUPAC name	F	ζ_c
1	CH_4O	methanol	0.993221	0.275
2	C_2H_6O	ethanol	1.185526	0.291
3	$C_2H_6O_2$	ethylene glycol	0.990757	0.278
4	C_3H_6O	prop-2-en-1-ol	1.177219	0.289
5	C_3H_8O	propan-1-ol	1.253344	0.303
6	C_3H_8O	propan-2-ol	1.291621	0.299
7	$C_3H_8O_2$	propano-1,2-diol	2.015084	0.312
8	$C_3H_8O_3$	propano-1,2,3-triol	2.683465	0.306
9	$C_4H_{10}O$	butan-1-ol	1.260353	0.306
10	$C_4H_{10}O$	butan-2-ol	1.244349	0.303
11	$C_4H_{10}O$	2-methylpropan-1-ol	1.248311	0.305
12	$C_4H_{10}O$	2-methylpropan-2-ol	1.259177	0.306
13	$C_4H_{10}O_3$	2-(2-hydroxiethoxy)ethanol	2.272613	0.291
14	$C_5H_{12}O$	pentan-1-ol	1.272366	0.308
15	$C_5H_{12}O$	2-methylbutan-1-ol	1.119237	0.281
16	$C_5H_{12}O$	3-methylbutan-1-ol	1.311441	0.315
17	$C_5H_{12}O$	2-methylbutan-2-ol	1.220351	0.323
18	C_6H_6O	phenol	1.113987	0.328
19	$C_6H_{12}O$	cyclohexanol	1.017439	0.284
20	$C_6H_{14}O$	hexan-2-ol	1.224011	0.306
21	$C_6H_{14}O_2$	2-butoxyethanol	1.08944	0.305
22	C_7H_8O	phenylmethanol	0.948783	0.29
23	C_7H_8O	2-methylphenol	1.062203	0.319
24	C_7H_8O	3-methylphenol	0.995234	0.3
25	C_7H_8O	4-methylphenol	1.196632	0.325
26	$C_7H_{16}O$	heptan-1-ol	1.206273	0.302
27	$C_8H_{10}O$	2-ethylphenol	1.130224	0.318
28	$C_8H_{10}O$	3-ethylphenol	1.106714	0.309
29	$C_8H_{10}O$	4-ethylphenol	1.146712	0.309
30	$C_8H_{10}O$	2,3-dimethyllphenol	1.245829	0.337
31	$C_8H_{10}O$	2,4-dimethyllphenol	1.141822	0.316
32	$C_8H_{10}O$	2,5-dimethyllphenol	1.18668	0.319
33	$C_8H_{10}O$	3,4-dimethyllphenol	1.121852	0.309
34	$C_8H_{10}O$	3,5-dimethyllphenol	1.173403	0.312
35	$C_8H_{18}O$	octan-1-ol	1.30112	0.31
36	$C_8H_{18}O$	octan-2-ol	1.22229	0.314
37	$C_8H_{18}O$	4-methylheptan-3-ol	1.265438	0.338
38	$C_8H_{18}O$	5-methylheptan-3-ol	1.370697	0.329
39	$C_8H_{18}O$	2-ethylhexan-1-ol	1.203024	0.307
40	$C_9H_{20}O$	nonan-1-ol	1.244065	0.304
41	$C_{10}H_{22}O$	decan-1-ol	1.163339	0.291
42	$C_{12}H_{26}O$	dodecan-1-ol	1.57994	0.293
43	$C_{17}H_{36}O$	heptadecan-1-ol	1.701115	0.282
44	$C_{18}H_{38}O$	octadecan-1-ol	1.826124	0.293
45	$C_{20}H_{42}O$	eicosan-1-ol	1.70315	0.279

Methodology

F and ζ_c optimal value estimation requires experimental data. However, there are few available data, and the EoS extension to any compound results in difficulties. This paper presents a technique based on "experimental" data generation using the Wagner[10] and the Rackett[11] equations. In Table 1 a comparison between two proposed models with experimental data[12] is made. A 0.6 % average absolute deviation in Wagner's equation, while a 0.45 % average absolute deviation in Rackett's equation were obtained. The proposed methodology has two steps.

PVT Generation Data. Wagner Equation. Fixing a temperature this equation can be used to calculate the vapor pressure. Wagner's equation has the following form:

$$\ln\left(\frac{P^{sat}}{P_c}\right) = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau} \qquad (3)$$

where

$$\tau = 1 - \frac{T}{T_c} \qquad (4)$$

Table 5. F and ζ_c for Other Functional Groups

no.	molecular formula	IUPAC name	F	ζ_c
1	C_3F_6O	1,1,1,3,3,3-hexafluoropropan-2-one	0.919448	0.309
2	C_3ClF_5O	1-chloro-1,1,3,3,3-pentafluoropropan-2-one	1.007992	0.31
3	C_2H_6S	methylsulfanylmethane	0.688105	0.31
4	C_2H_6S	ethanethiol	0.684028	0.311
5	$C_2H_5NO_2$	nitroethane	0.751403	0.277
6	C_2N_2	oxalonitrile	0.798674	0.306
7	CH_4S	methanethiol	0.640790	0.314
8	CH_3NO_2	nitromethane	0.678175	0.265
9	CS_2	methanedithione	0.650998	0.330
10	CO_2	carbon dioxide	0.733560	0.310
11	COS	methylsulfanylmethane	0.570692	0.317
12	CO	carbon monoxide	0.545619	0.329
13	NH_3	azane	0.652782	0.284
14	H_2SO_4	sulfur acid	0.268441	0.2050
15	H_2S	hydrogen sulfide	0.576648	0.320
16	H_2O	water	0.718303	0.275
17	HI	hydrogen iodide	0.520708	0.327
18	HF	hydrogen fluoride	0.248492	0.167
19	HCl	hydrogen chloride	0.571602	0.304
20	HBr	hydrogen bromide	0.554900	0.321
21	Xe	xenon	0.469696	0.321
22	O_3	ozone	0.627113	0.294
23	SO_3	sulfur trioxide	0.924258	0.307
24	SO_2	sulfur dioxide	0.733364	0.308
25	O_2	oxygen	0.495347	0.330
26	N_2O	nitrous oxide	0.595498	0.314
27	N_2	nitrogen	0.523263	0.328
28	NO_2	nitrogen dioxide	1.635188	0.294
29	NO	nitric oxide	1.223946	0.312
30	Kr	krypton	0.457689	0.324
31	F_6S	sulfur hexafluoride	0.982689	0.328
32	F_2	fluor	0.541138	0.329
33	D_2O	deuterium oxide	0.716011	0.269
34	$SiCl_4$	tetrachlorosilane	0.754727	0.314
35	BF_3	trifluoroborane	1.049244	0.311
36	BCl_3	trichloroborane	0.555883	0.286
37	Ar	argon	0.466113	0.328
38	$AsCl_3$	trichloroarsane	0.750221	0.316
39	C_2H_3NO	methylimino(oxo)methane	0.717833	0.280
40	C_3H_8S	methylsulfanylethane	0.680718	0.298
41	C_4H_4S	tiophene	0.703994	0.314
42	$C_4H_8O_2$	1,4-dioxane	0.820666	0.312
43	C_4H_8S	tiolane	0.573372	0.284
44	C_4H_9NO	morpholine	0.959946	0.32
45	$C_4H_{10}S$	ethylsulfanylethane	0.755134	0.307
46	$C_4H_{10}S_2$	ethyldisulfanylethane	0.687944	0.279
47	$C_8H_4O_3$	2-benzofuran-1,3-dione	1.19032	0.31
48	$C_5H_{10}O$	(2*R*)-2-methyloxolane	0.738974	0.294
49	C_7H_6O	benzaldehyde	0.788172	0.296
50	$C_5H_4O_2$	furan-2-carbaldehyde	1.048306	0.317
51	C_4H_8O	2-methylpropanal	0.813122	0.301
52	C_3H_6O	propanal	0.881463	0.337
53	C_3H_4O	prop-2-enal	0.773765	0.281
54	C_2H_4O	acetaldehyde	0.661888	0.274
55	CH_2O	metanal	0.539339	0.253
56	$C_7H_6O_2$	benzoic acid	1.224394	0.299
57	$C_5H_{10}O_2$	pentanoic acid	1.099546	0.281
58	$C_4H_8O_2$	2-methylpropanoic acid	1.184447	0.284
59	$C_4H_8O_2$	butanoic acid	1.450017	0.331
60	$C_4H_6O_4$	butanedioic acid	1.364425	0.252
61	$C_3H_6O_2$	propanoic acid	1.073286	0.295
62	$C_3H_4O_2$	prop-2-enoic acid	1.017851	0.287
63	$C_2H_4O_2$	acetic acid	0.77341	0.259
64	CH_2O_2	methanoic acid	0.687985	0.231
65	C_7H_5N	benzonitrile	0.799997	0.285
66	$C_6H_{11}N$	hexanenitrile	1.087337	0.289
67	C_4H_7N	butanenitrile	0.703604	0.263
68	C_3H_5N	propanenitrile	0.557134	0.245
69	C_3H_3N	prop-2-enenitrile	0.610385	0.254
70	C_2H_3N	acetonitrile	0.494138	0.227
71	$C_{11}H_{14}O_2$	butyl benzoate	1.116851	0.295
72	$C_9H_{10}O_2$	ethyl benzoate	0.839516	0.248
73	$C_8H_{16}O_2$	2-methylpropyl 2-methylpropanoate	1.016658	0.305
74	$C_8H_{16}O_2$	2-methylpropyl butanoate	1.007873	0.298

Table 5. Continued

no.	molecular formula	IUPAC name	*F*	ζ_c
75	$C_8H_{16}O_2$	3-methylbutyl propanoate	0.518355	0.23
76	$C_8H_{14}O_4$	diethyl butanedioate	1.113612	0.275
77	$C_8H_8O_3$	methyl 2-hydroxybenzoate	0.697704	0.243
78	$C_8H_8O_2$	methyl benzoate	0.949654	0.298
79	$C_7H_{14}O_2$	2-methylpropyl propanoate	0.99579	0.301
80	$C_7H_{14}O_2$	propyl-2-methylpropanoate	1.002754	0.307
81	$C_7H_{14}O_2$	propyl butanoate	1.001727	0.298
82	$C_6H_{14}O$	1-propoxypropane	0.952232	0.313
83	$C_6H_{14}O$	1-metoxypentane	0.885947	0.307
84	$C_6H_{12}O_2$	pentyl formate	1.288887	0.329
85	$C_6H_{12}O_2$	propyl propanoate	0.946285	0.299
86	$C_6H_{12}O_2$	ethyl 2-methylpropanoate	0.945852	0.302
87	$C_6H_{12}O_2$	ethyl butanoate	0.929131	0.295
88	$C_6H_{12}O_2$	2-methylpropyl acetate	0.946459	0.301
89	$C_6H_{12}O_2$	butyl acetate	0.976193	0.306
90	$C_5H_{10}O_2$	methyl 2-methylpropanoate	0.919215	0.31
91	$C_5H_{10}O_2$	methylbutanoate	0.899517	0.299
92	$C_5H_{10}O_2$	ethyl propanoate	0.904934	0.298
93	$C_5H_{10}O_2$	propyl acetate	0.888758	0.295
94	$C_5H_{10}O_2$	2-methylpropyl formate	0.946953	0.317
95	$C_6H_8O_4$	dimethyl (*Z*)-but-2-enedioate	1.037685	0.282
96	$C_5H_8O_2$	ethyl prop-2-enoate	0.915171	0.304
97	$C_5H_8O_2$	methyl 2-methylprop-2-enoate	0.843322	0.295
98	$C_4H_8O_2$	propyl formate	0.813729	0.302
99	$C_4H_8O_2$	methyl propanoate	0.85589	0.3
100	$C_4H_8O_2$	ethyl acetate	0.856304	0.296
101	$C_4H_6O_2$	methyl prop-2-enoate	0.84014	0.298
102	$C_4H_6O_3$	acethyl acetate	1.998015	0.329
103	$C_4H_6O_2$	ethenyl acetate	0.888928	0.309
104	$C_3H_6O_2$	methyl acetate	0.810113	0.297
105	$C_3H_6O_2$	ethyl formate	0.768135	0.3
106	$C_2H_4O_2$	methyl formate	0.72919	0.298
107	$C_{12}H_{10}O$	phenoxybenzene	0.999045	0.302
108	$C_8H_{18}O$	2-methyl-2-[(2-methylpropan-2-yl)oxy]propane	0.859843	0.307
109	$C_8H_{18}O$	1-butoxybutane	1.125277	0.309
110	$C_8H_{10}O$	ethoxybenzene	0.950895	0.299
111	C_7H_8O	methoxybenzene	0.89566	0.309
112	$C_6H_{14}O$	2-propan-2-yloxypropane	0.917406	0.315
113	$C_6H_{14}O$	1-ethoxybutane	0.995535	0.315
114	$C_6H_{14}O$	2-methoxy-2-methylbutane	0.844195	0.307
115	$C_5H_{12}O$	2-methoxy-2-methylpropane	0.797988	0.311
116	$C_5H_{12}O$	1-methoxybutane	0.853234	0.309
117	$C_5H_{12}O$	1-ethoxypropane	0.939942	0.318
118	C_5H_6O	2-methylfuran	0.813772	0.319
119	$C_4H_{10}O_2$	1,2-dimethoxyethane	0.918207	0.306
120	$C_4H_{10}O$	2-methoxypropane	0.781607	0.309
121	$C_4H_{10}O$	1-methoxypropane	0.779981	0.307
122	$C_4H_{10}O$	ethoxyethane	0.801315	0.308
123	C_4H_8O	ethoxyethene	0.795326	0.311
124	C_4H_4O	furan	0.717367	0.312
125	$C_3H_8O_2$	dimethoxymethane	0.734817	0.289
126	C_3H_8O	methoxyethane	0.785273	0.313
127	C_3H_6O	methoxyethene	1.031854	0.311
128	C_3H_6O	2-methyloxirane	0.674056	0.286
129	C_2H_6O	methoxymethane	0.686973	0.311
130	C_2H_4O	oxirane	0.637449	0.297
131	$C_{12}H_{27}N$	*N*,*N*-dibutylbutan-1-amine	1.329921	0.306
132	$C_{10}H_{15}N$	*N*-butylaniline	1.068377	0.293
133	C_9H_7N	Isoquinoline	0.956186	0.331
134	$C_8H_{19}N$	2-methyl-*N*-(2-methylpropyl)-propan-1-amine	1.173614	0.334
135	$C_8H_{19}N$	*N*-butylbutan-1-amine	1.126937	0.317
136	$C_8H_{11}N$	*N*-ethylaniline	0.929722	0.292
137	$C_8H_{11}N$	*N*,*N*-dimethylaniline	0.916001	0.299
138	C_7H_9N	4-methylaniline	0.575575	0.207
139	C_7H_9N	3-methylaniline	0.903138	0.292
140	C_7H_9N	1-methylaniline	0.849297	0.274
141	C_7H_9N	*N*-methylaniline	0.927767	0.308
142	$C_6H_{15}N$	*N*,*N*-diethyletanamine	0.95996	0.314
143	$C_6H_{15}N$	*N*-propan-2-ylpropan-2-amine	0.965151	0.321
144	$C_6H_{15}N$	*N*-propylpropan-1-amine	0.922004	0.306
145	C_6H_7N	4-methylpyridine	0.752961	0.296
146	C_6H_7N	3-methylpyridine	0.752375	0.297
147	C_6H_7N	2-methylpyridine	0.835552	0.31
148	C_6H_7N	aniline	0.927155	0.306
149	$C_5H_{11}N$	piperidine	0.827813	0.321
150	C_5H_5N	pyridine	0.750526	0.31
151	$C_4H_{11}N$	*N*-ethylethanamine	0.82656	0.305
152	$C_4H_{11}N$	2-methylpropan-1-amine	0.926849	0.314
153	$C_4H_{11}N$	butan-1-amine	0.879879	0.311
154	C_4H_9N	pyrrolidine	0.868435	0.324
155	C_4H_5N	1H-pyrrole	0.769295	0.297
156	C_3H_9N	*N*,*N*-dimethylmethanamine	0.715215	0.315
157	C_3H_9N	propan-2-amine	0.838326	0.313
158	C_3H_9N	propan-1-amine	0.842004	0.311
159	$C_2H_8N_2$	ethane-1,2-diamine	1.035607	0.303
160	C_2H_7NO	2-aminoethanol	0.997138	0.219
161	C_2H_7N	dimethylamine	0.81977	0.306
162	C_2H_7N	ethanamine	0.821424	0.308
163	CH_5N	methanamine	0.784828	0.3
164	C_8H_8O	1-phenylethanone	0.874993	0.301
165	$C_7H_{14}O$	heptan-2-one	1.239793	0.333
166	$C_6H_{12}O$	4-methylpentan-2-one	0.895106	0.301
167	$C_6H_{12}O$	hexan-2-one	1.124259	0.305
168	$C_6H_{12}O$	hexan-3-one	0.894069	0.299
169	$C_6H_{10}O$	cyclohexanone	0.911008	0.287
170	$C_5H_{10}O$	pentan-3-one	0.845723	0.299
171	$C_5H_{10}O$	3-methylbutan-2-one	0.86589	0.306
172	$C_5H_{10}O$	pentan-2-one	0.838502	0.296
173	C_5H_8O	cyclopentanone	0.765741	0.306
174	C_4H_8O	butan-2-one	0.78905	0.294
175	C_2H_2O	ethenone	0.805777	0.337

Wagner's equation constants *A*, *B*, *C*, and *D* are available in the Reid et al. property data bank.[9] If Wagner's constants are not available for a given substance, they are determined by nonlinear regression using another vapor pressure model.[13]

Rackett Equation. This equation allows saturated liquid volume calculation for a given temperature.

$$V_T^L = \frac{b^{1+(1-\left(\frac{T}{c}\right)^d)}}{a} \tag{5}$$

Rackett's equation constants are available in the Reid et al. property data bank.[9] If Rackett's constants are not available for a given substance, they are determined by nonlinear regression using another saturated liquid volume model.[13]

Objective Function. The ζ_c initial guess is 0.307; this is the resulting value when the critical point criterion is applied to the Peng−Robinson equation.[5] The *F* initial guess is fixed to the average value for 38 reported substances in the Patel and Teja original work.[2] The objective function (OF) is:

$$\mathrm{OF} = \left(\sum_{i=1}^{\mathrm{data}} \frac{|P_{\mathrm{Wagner}}^{\mathrm{sat}} - P_{\mathrm{PT}}^{\mathrm{sat}}|}{P_{\mathrm{Wagner}}^{\mathrm{sat}}} \right)^2 + \sum_{i=1}^{\mathrm{data}} \frac{|v_{\mathrm{Rackett}}^{\mathrm{sat}} - v_{\mathrm{Rackett}}^{\mathrm{sat}}|}{v_{\mathrm{Rackett}}^{\mathrm{sat}}} \tag{6}$$

The first right side term represents the absolute deviation in vapor pressure, and the second one represents the absolute deviation in saturated liquid volume. *F* and ζ_c optimal values are those that minimize the objective function. The optimization procedure was made in Microsoft Excel using the SOLVER add-in.

Results

The new method was applied to 498 pure substances. In Tables 2, 3, 4, and 5, *F* and ζ_c values are reported for

Table 6. Average Absolute Deviations for the Thermodynamical Properties of Some Pure Substances[a]

	P_{sat}(AAD)		V^l(AAD)		V^v(AAD)		ΔH^{vap}(AAD)			
compound	PT	PTNM	PT	PTNM	PT	PTNM	PT	PTNM	T_r min	T_r max
nitrogen	0.63 %	1.71 %	5.03 %	5.04 %	1.57 %	2.88 %	3.95 %	4.23 %	0.5	0.99
oxygen	2.00 %	1.75 %	4.20 %	3.87 %	3.07 %	2.71 %	1.53 %	1.48 %	0.35	0.97
argon	0.77 %	2.24 %	6.87 %	6.82 %	2.46 %	4.52 %	7.64 %	7.92 %	0.56	0.97
carbon dioxide	0.23 %	1.44 %	4.35 %	4.34 %	1.68 %	3.14 %	0.65 %	1.97 %	0.71	0.99
methane	1.19 %	1.49 %	5.49 %	5.43 %	1.66 %	2.09 %	4.29 %	4.43 %	0.48	0.996
ethene	1.64 %	1.28 %	4.52 %	4.09 %	2.49 %	2.28 %	2.37 %	2.33 %	0.37	0.99
ethane	1.18 %	0.74 %	4.49 %	3.98 %	1.59 %	1.35 %	1.61 %	1.70 %	0.39	0.98
acetylene	0.98 %	2.28 %	6.87 %	6.82 %	2.46 %	4.52 %	7.64 %	7.92 %	0.62	0.998
propane	1.66 %	1.36 %	3.47 %	3.34 %	2.44 %	2.20 %	1.50 %	1.46 %	0.38	0.97
propylene	1.25 %	1.81 %	4.15 %	2.82 %	2.07 %	2.82 %	1.00 %	1.22 %	0.36	0.96
butane	1.21 %	1.36 %	4.86 %	4.01 %	1.96 %	2.36 %	1.32 %	1.47 %	0.45	0.99
isobutane	4.16 %	2.89 %	3.80 %	3.90 %	3.87 %	3.18 %	1.57 %	1.69 %	0.34	0.98
heptane	0.88 %	2.24 %	1.81 %	2.37 %	2.46 %	3.43 %	0.58 %	0.78 %	0.54	0.75
octane	5.70 %	4.26 %	4.02 %	3.99 %	5.19 %	4.52 %	3.30 %	3.37 %	0.42	0.98
nonane	1.28 %	1.62 %	3.08 %	3.07 %	2.80 %	2.67 %	6.79 %	7.08 %	0.54	0.91
decane	1.65 %	1.69 %	2.80 %	2.67 %	5.83 %	6.55 %	2.18 %	2.36 %	0.55	0.97
ammonia	2.78 %	1.16 %	3.46 %	3.39 %	4.10 %	3.91 %	2.35 %	2.80 %	0.48	0.99
methanol	0.76 %	0.82 %	4.27 %	3.99 %	6.71 %	7.57 %	5.87 %	6.31 %	0.56	0.97
water	1.03 %	0.31 %	4.77 %	5.86 %	1.88 %	1.61 %	1.50 %	1.66 %	0.42	0.99
average	1.63 %	1.71 %	4.33 %	4.20 %	2.96 %	3.39 %	3.03 %	3.27 %		

[a]

$$Y(\mathrm{AAD}) = \frac{1}{N}\sum_{1}^{N}\frac{|Y_i^{exp} - Y_i^{PT}|}{Y_i^{exp}}$$

where $Y = P^{sat}, V^l, V^v,$ or ΔH^{vap}

hydrocarbons, halogens, alcohols, and phenols and other functional groups.

Thermodynamic Properties Calculations. Pure Substances. New constants were compared with those reported in the Patel and Teja original article[2] by vapor pressure, saturated liquid volume, and saturated vapor volume calculations. The results were compared with experimental data[12] for both groups of constants. In Table 6 the thermodynamical property average absolute deviations for 19 pure compounds are presented. The final row of Table 6 presents the average deviation for each property. Results allow the conclusion that new constants are comparable with those values originally reported by Patel and Teja and validate the method for calculating constants for substances not reported in literature.

Mixtures. New constants can be extended to mixtures using the Panagiotopoulous−Reid[14] mixing rule. Binary interaction coefficients (k_{ij}) are determined using experimental data. New constants were used to predict phase equilibria and excess enthalpies for three binary systems.

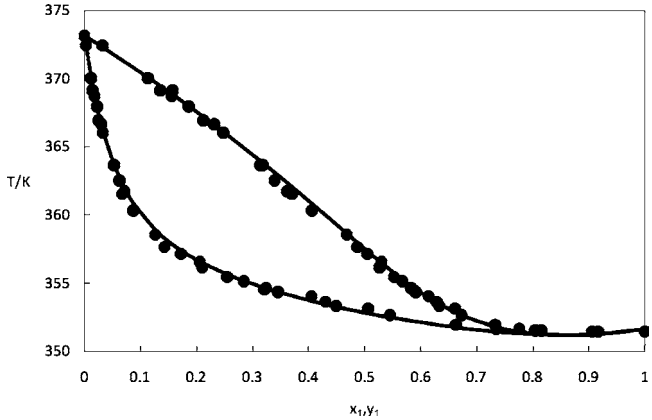

Figure 1. Ethanol−water liquid−vapor equilibria at 101.325 kPa (●, Rieder and Thompson;[18] —, PT EoS using constants from this work and PR mixing rules).

Table 7. Binary Interaction Parameters for the PTPR EoS for Different Systems

N_0	constants	system	k_{12}	k_{21}
1	new	ethanol water	−0.1174451	−0.05754551
2	new	water butanol	−0.01431804	−0.12902278
3	new	ethanol propyl acetate	0.05499081	−0.03821972
4	original	water butanol	−0.01951162	−0.1351486

Liquid−Vapor Equilibria. Liquid−vapor equilibria at 101.325 kPa for the ethanol−water system was evaluated. Binary interaction parameter estimations were made using the Paunović method[15] according to the following objective function:

$$\mathrm{OF} = \sum_{i=1}^{ND}\left(\frac{|x_{1i}\phi_{1i}^{L} - y_{1i}\phi_{1i}^{V}|}{y_{1i}\phi_{1i}^{V}} + \frac{|x_{2i}\phi_{2i}^{L} - y_{2i}\phi_{2i}^{V}|}{y_{2i}\phi_{2i}^{V}}\right) \quad (7)$$

In Figure 1 a comparison between the model and the experimental data[16] was made. The temperature average absolute deviation was 0.06 %. The azeotropic point prediction was 351.2 K and 0.86611 in ethanol molar fraction, and the relative absolute deviation at this point was 0.03 % and 3.3 %, respectively. In Table 7 k_{ij} values are reported.

Vapor−Liquid−Liquid Equilibria. The water−*n*-butanol system at 101.325 kPa was studied. A *Txy* diagram prediction was made using both original and new constants. Binary interaction parameters were estimated minimizing eq 7 and using experimental data reported by Iwakabe and Kosigue.[17] k_{ij} values are reported in Table 7. Figure 2 illustrates the results. Using the new constants, the relative absolute deviation in the vapor−liquid−liquid temperature was 0.01 %. The objective

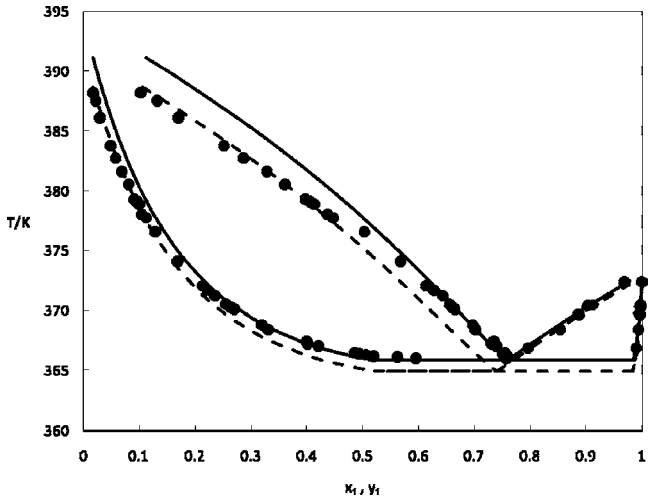

Figure 2. Water−*n*-butanol system vapor−liquid−liquid equilibria at 101.325 kPa (●, Iwakabe and Kosigue;[19] —, PT EoS using constants from this work; ---, PT EoS using original constants and PR mixing rules).

function (eq 7) for the original constants is 3.33; meanwhile, for the new ones it is 2.44.

Excess Enthalpies. Ethanol−propyl acetate at 348.15 K and 101.325 kPa was evaluated. Binary interaction parameters were calculated using the following objective function:

$$\mathrm{OF} = \sum_{i=1}^{\mathrm{ND}} (H_{i\mathrm{exp}}^{\mathrm{E}} - H_{i\mathrm{PTPR}}^{\mathrm{E}})^2 \qquad (8)$$

The proposed objective function corresponds to a nonlinear least-squares regression in excess enthalpies.[18] Experimental data are those reported by Lien, Lee, and Lin.[19] Binary interaction parameters are reported in Table 7. Figure 3 shows that the model adjustment to experimental data is correct.

Conclusions

Estimation of the substance-dependent F and ζ_c PT EoS constants can be done using the Wagner and Rackett equation to generate *PVT* "experimental" data. The new method is equivalent to that presented by Patel and Teja in their original work. New constants confirm the power prediction of the Patel−Teja EoS for polar compounds. The use of the Panagiotopoulous−Reid mixing rule with the Patel−Teja EoS can predict mixture properties correctly. The new 498 constants can be used to extend the Patel−Teja EoS in thermodynamical properties predictions and process design, evaluation, and simulation.

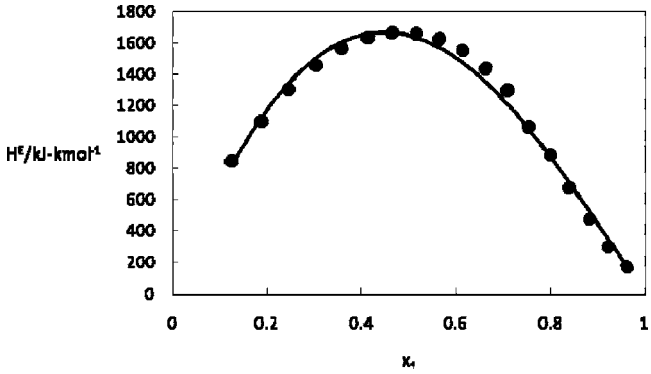

Figure 3. Excess enthalpies for the ethanol−propyl acetate system at 348.15 K and 101.325 kPa (●, Lien et al.[20]; —, PT EoS using constants from this work and PR mixing rules).

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Received for review June 16, 2010. Accepted August 8, 2010. The authors thank to Colciencias "Jóvenes Investigadores" program for economical support during the present research.

JE100656D