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Vapor Pressures from a Corresponding-States Principle for a Wide Range of Polar Molecular Substances

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In this work, the performance of equations that describe vapor-pressure behavior over the entire region from the triple point to the critical point is surveyed and compared. The vapor pressures of highly nonspherical molecules are considered, and the performance of the recently developed general extended corresponding-states principle used with the Xiang–Tan vapor-pressure equation is demonstrated. Comparisons with highly accurate vapor-pressure data and existing models show that the method has an accuracy for a wide range of polar molecules which agrees approximately with the accuracy of highly accurate data over the entire vapor-pressure region.

KEY WORDS: corresponding-states principle; critical parameters; nonspherical molecules; thermodynamic properties; vapor–liquid equilibrium; vapor pressure.

1. INTRODUCTION

The vapor pressure is of great significance in the development of fundamental theories for vapor–liquid phase transitions, and it is also important for obtaining the other thermodynamic properties of a substance. Reliable vapor pressures contribute to efficient process design and operation in engineering applications. For these reasons, it has been the objective of extensive studies to obtain vapor pressure values as a function of temperature along the entire vapor–liquid coexistence curve. Since the experimental determination of all required data is a formidable task, it is useful to have models that can predict vapor pressure, as well as models that allow the extrapolation of vapor-pressure data to wider temperature ranges.

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2. SURVEY OF VAPOR-PRESSURE EQUATIONS

When the vapor phase of a pure fluid is in equilibrium with the liquid phase, the equality of chemical potential, temperature, and pressure in both phases leads to the Clausius–Clapeyron equation, proposed in 1834, which is one of the earliest fundamental contributions to physical chemistry. Most vapor-pressure equations stem from an approximate integration of the Clausius–Clapeyron equation. In addition to giving a reasonably precise fit to vapor-pressure data, an equation should also give suitable values for the heat of vaporization of the substance. The heat of vaporization also depends on the saturated liquid and vapor densities, although the saturated vapor density is usually less well known than the vapor pressure.

Waring [1] proposed a qualitative test for the suitability of various vapor-pressure equations. As a result, a vapor-pressure equation must possess at least three parameters to describe the correct physical behavior. Many models have been proposed for representing experimental data and predicting the behavior in a wide range for vapor pressure [2–40]. A simple form, high accuracy, and good extrapolation are the main requirements in a vapor-pressure equation. An equation is required which can represent vapor pressures over a wide temperature range with a high accuracy using a relatively small number of coefficients. It also should allow for extrapolation to the triple point, interpolation in the range in which data are available, and extrapolation to the critical point. A number of studies have evaluated different equations in terms of their abilities to correlate and/or predict vapor pressures over wide ranges of temperature. The three-parameter Antoine equation proposed in 1888 [2],

$$\ln p = A + B/(T + C) \tag{1}$$

has been used over limited temperature ranges,where p is the pressure and T is temperature. A, B, C are substance-dependent parameters. With $C = 0$, the Antoine equation reverts to the Clapeyron vapor-pressure equation, $\ln p = A + B/T$. The applicable temperature range is not large and, in most instances, corresponds to a pressure interval of about 1 to 200 kPa. The Antoine equation is a useful approximate equation; however, it does not represent vapor pressures to within experimental error, does not reproduce the correct shape of a vapor-pressure curve over the entire temperature range, and should not be used for extrapolation. In 1973, Wagner proposed the equation [12]

$$\ln p_r = (c_1\tau + c_2\tau^{1.5} + c_3\tau^3 + c_4\tau^6)/T_\mathrm{r} \tag{2}$$

where $\tau = 1 - T_\mathrm{r}$ and $T_\mathrm{r} = T/T_\mathrm{c}$ is the reduced temperature, with T_c being the critical temperature. $p_\mathrm{r} = p/p_\mathrm{c}$ is the reduced pressure, with p_c being the critical pressure. This equation generates a reasonable shape for the vapor-pressure curve from a reduced temperature of 0.5 up to the critical point, but it may not extrapolate well to reduced temperatures below 0.5 as pointed out by Reid et al. [30]. As a result, Poling [38], as well as King and Al-Najjar [14], has determined the low vapor pressures from the available heat capacity data by means of the Clausius–Clapeyron equation, neglecting the nonideality of the vapor phase and volume of the liquid phase.

The Xiang-Tan equation [36, 37], which has only three adjustable parameters, represents experimental data over the entire range from the triple point to the critical temperature and represents the vapor-pressure curve based upon known physical behavior. This equation reads

$$\ln p_{\mathrm{r}} = (a_0 + a_1 \tau^{1.89} + a_2 \tau^{5.67}) \ln T_{\mathrm{r}} \tag{3}$$

where the substance-dependent a_0 is the Riedel parameter [4, 7] and a_1 and a_2 are also substance-dependent parameters. The exponent 1.89 in the second term of Eq. (3) was derived from the critical exponent 0.11 of the renormalization-group theory of critical phenomena. The exponent 5.67 in the third term is equal to 3×1.89. The equation reproduces experimental vapor-pressure data over the entire temperature range with an excellent accuracy considering the present experimental uncertainties and agreement with different data sets. The equation with only three parameters represents experimental data with a very high accuracy from the triple point to the critical point. It yields excellent predictions and extrapolations for the range in which data usually are available both to the critical point and to the triple point. The Xiang–Tan equation has a simple functional form comparable to the Antoine equation, and it represents data with an accuracy comparable to the equation of Wagner. The second derivative calculated from the Xiang–Tan equation is only slightly less than that of the critical-power law as the temperature very closely approaches the critical point.

3. THE EXTENDED CORRESPONDING-STATES PRINCIPLE

The two-parameter corresponding-states method holds only for monatomic species such as argon, krypton, and xenon [41]. To apply the corresponding-states principle to molecular fluids, Pitzer et al. [42–44] considered the nonspherical nature of a real molecule through the acentric factor. However, the corresponding-states principle of Pitzer et al. excludes systems containing highly polar species and species exhibiting specific interactions such as hydrogen bonding and association [45, 46]. Generally, an effective fourth parameter can describe polar fluids better than a three-parameter corresponding-states principle. A fourth corresponding-states parameter was recently defined in terms of deviations of the critical compression factor of a real molecule from that of the spherical molecule argon [47–50]. The extended corresponding-states parameter provides a simple convenient means to account for the main effects of highly nonspherical molecular shapes on the physical properties of a real fluid. Consequently, the general extended corresponding-states principle to describe the vapor pressure p is

$$\ln p_{\mathrm{r}} = \ln p_{\mathrm{r}}^{(0)} + \omega \ln p_{\mathrm{r}}^{(1)} + \theta \ln p_{\mathrm{r}}^{(2)} \tag{4}$$

where the acentric factor $\omega = -1 - \log p_{\mathrm{r}}|_{T_{\mathrm{r}}=0.7} = -1 - (a_0 + 0.3^{1.89} a_1 + 0.3^{5.67} a_2) \log 0.7$ according to Eq. (3) and $\theta = (Z_{\mathrm{c}} - 0.29)^2$ are the corresponding-states parameters. Here $Z_{\mathrm{c}} = p_{\mathrm{c}}/R\rho_{\mathrm{c}} T_{\mathrm{c}}$ is the critical compression factor and R is the gas constant. $Z_{\mathrm{c}} = 0.29$ is the corresponding value for argon.

It should be noted that the corresponding-states parameter θ is defined as an independent parameter for a real molecule. Thus, any relation between the defined parameter θ and the acentric factor ω is only approximate for a specified class of fluids and is not, and cannot be, universally correct. In fact, the extended corresponding-states principle corresponds to a quadratic correlation for the acentric factor by means of the approximation $\theta = 0.0064\omega^2$ for nonpolar substances [10, 16, 30, 42] and significantly improves on reflecting the behavior of a polar substance; a detailed explanation and description are given elsewhere [47–50].

To predict the vapor pressure from the corresponding-states principle, it is important to select an equation as a reference equation, which is valid from the triple point to the critical point. For the vapor pressure, the equation proposed by Xiang and Tan fulfills this requirement. It can be used to correlate and extrapolate effectively the vapor-pressure behaviors of simple, nonpolar, polar, hydrogen-bonding, and associating compounds [36, 37]. The corresponding-states method extends the vapor pressure equations, (3) and (4), as

$$\begin{aligned}
\ln p_{\mathrm{r}}^{(0)} &= (a_{00} + a_{10}\tau^{1.89} + a_{20}\tau^{5.67}) \ln T_{\mathrm{r}} \\
\ln p_{\mathrm{r}}^{(1)} &= (a_{01} + a_{11}\tau^{1.89} + a_{21}\tau^{5.67}) \ln T_{\mathrm{r}} \\
\ln p_{\mathrm{r}}^{(2)} &= (a_{02} + a_{12}\tau^{1.89} + a_{22}\tau^{5.67}) \ln T_{\mathrm{r}}
\end{aligned} \tag{5}$$

The coefficients of Eq. (5) are given in Table I from fitting Eqs. (4) and (5) to the vapor-pressure data for argon, the weakly nonspherical molecules

Table I. General Coefficients of Eq. (5) [47–49]

a_{00}	5.790206	a_{10}	6.251894	a_{20}	11.65859
a_{01}	4.888195	a_{11}	15.08591	a_{21}	46.78273
a_{02}	33.91196	a_{12}	-315.0248	a_{22}	-1672.179

ethane, propane, difluoromethane, 1,1,1,2-tetrafluoroethane, and 1,1-difluoroethane, and the highly nonspherical molecule water. The coefficients are independent of the specific substance and are expected to be universal for all classes of molecules. For other comparisons with vapor-pressure data for fluids of other classes, see Refs. 47–49.

4. COMPARISONS OF VARIOUS PREDICTION MODELS

In this section, some representative polar substances tabulated by Wilding et al. [31] have been used to compare and evaluate the existing methods. The critical parameters, acentric factor, and critical compression factor of each substance are listed in Table II. The experimental data result from highly accurate experimental measurements and are regarded as the most reliable and accurate data available. Values of the critical parameters are taken from the recommended values in the literature when available.

The corresponding-states prediction for vapor pressure is calculated from Eqs. (4) and (5). Vapor pressures for 48 polar fluids from Wilding et al. [31] have been calculated from this extended corresponding-states model and have been compared to experimental values and predictions made with three other methods. The Lee–Kesler method [15] was chosen to examine the significance of separating size/shape interactions from polar interactions using a four- rather than a three-parameter corresponding-states principle. The method of Wilding et al. [31] is used as a comparison, because it is also a four-parameter corresponding-states method. The method of Edalat et al. [35] was chosen to test quadratic and higher correlations for the acentric factor.

The extended corresponding-states method can describe the experimental data almost within their experimental uncertainties, as shown in Table III and also in Figs. 1 and 2. The extended corresponding-states principle allows predictions which are almost in agreement with highly accurate data sets in the high-temperature range and which are usually good in the low-temperature range, in contrast to other methods which result in large errors. It can be seen that the extended corresponding-states method is substantially superior to conventional linear and quadratic correlations for the acentric factor. The Lee–Kesler method [15] and the method of Edalat et al. [35], which are correlated only by the acentric factor, cannot follow the

Table II. Molar Masses, Critical Parameters, and Acentric Factors of Polar Substances from Wilding et al. [31]

Formula	Compound	MW ($kg \cdot kmol^{-1}$)	T_c (K)	p_c (kPa)	ρ_c ($kg \cdot m^{-3}$)	ω	Z_c	Ref. No.(s.)
H_2O	Water	18.015	647.1	22045	325	0.344	0.227	51
H_3N	Ammonia	17.043	405.4	11345	234	0.256	0.245	52–54
CCl_4	Carbon tetrachloride	153.823	556.3	4560	558	0.193	0.272	23
$CHCl_3$	Chloroform	119.378	536.0	5480	495	0.218	0.297	23
CHN	Hydrogen cyanide	27.026	456.6	5390	205	0.405	0.187	23
CHF_3	Trifluoromethane	70.014	298.9	4810	540	0.265	0.251	55, 56
CH_2Cl_2	Dichloromethane	84.933	510.2	6080	448	0.199	0.272	23
CH_2O	Formaldehyde	30.026	408.0	6590	260	0.280	0.224	23, 57
CH_3Cl	Methyl chloride	50.488	416.2	6680	363	0.152	0.268	58–60
CH_4O	Methyl alcohol	32.042	512.5	8080	265	0.556	0.229	61–63
CH_4S	Methyl mercaptan	48.109	469.7	7190	330	0.153	0.268	23
CH_5N	Methylamine	31.057	430.0	7430	210	0.292	0.307	65, 66
C_2H_3N	Acetonitrile	41.052	545.3	4830	225	0.338	0.194	67, 68
$C_2H_4Cl_2$	1,1-Dichloroethane	98.959	523.0	5070	440	0.240	0.262	23, 69
$C_2H_4Cl_2$	1,2-Dichloroethane	98.959	561.0	5370	450	0.278	0.253	23
C_2H_4O	Acetaldehyde	44.054	461.0	5570	285	0.303	0.225	23
$C_2H_4O_2$	Acetic acid	60.053	593.0	5780	330	0.450	0.213	70, 71
C_2H_6O	Ethyl alcohol	46.069	513.9	6140	276	0.644	0.240	62, 63, 72
C_2H_6O	Dimethyl ether	46.069	400.0	5330	270	0.197	0.273	23, 73
C_2H_6S	Dimethyl sulfide	62.136	503.0	5530	309	0.191	0.266	23, 74
C_2H_6S	Ethyl mercaptan	62.136	499.0	5490	300	0.190	0.274	23
C_3H_6O	Acetone	58.080	508.1	4696	270	0.308	0.239	75, 76
$C_3H_6O_2$	Ethyl formate	74.079	508.5	4740	320	0.285	0.260	65
$C_3H_6O_2$	Methyl acetate	74.079	506.8	4690	325	0.326	0.254	23, 65

C_3H_8O	Propyl alcohol	60.096	536.5	5200	270	0.630	0.259	63, 77, 78
C_3H_8O	Isopropyl alcohol	60.096	508.0	4780	271	0.665	0.251	63, 79
C_3H_9N	*n*-Propylamine	59.111	496.0	4810	254	0.300	0.271	23, 65
$C_4H_8O_2$	Ethyl acetate	88.106	523.2	3880	300	0.367	0.262	23
C_4H_8O	Methyl ethyl ketone	72.107	536.8	4210	270	0.322	0.252	64
$C_4H_{10}O$	*n*-Butyl alcohol	74.123	563.0	4420	268	0.593	0.261	63, 77
$C_4H_8O_2$	Isobutyric acid	88.107	609.0	4050	315	0.620	0.224	65
$C_4H_8O_2$	Methyl proptonate	88.107	530.6	4000	310	0.350	0.258	23
$C_4H_{10}O$	Ethyl ether	74.123	466.7	3640	258	0.281	0.270	80, 81
$C_4H_{11}N$	Diethylamine	73.138	496.6	3708	242	0.305	0.271	65
$C_5H_{10}O$	Methyl isopropyl ketone	86.134	553.3	3850	282	0.332	0.256	64
$C_5H_{10}O$	2-Pentanone	86.134	561.5	3690	285	0.346	0.239	64
C_6H_5Br	Bromobenzene	157.01	670.0	4520	484	0.251	0.263	23, 65
C_6H_5Cl	Chlorobenzene	112.559	632.3	4520	365	0.250	0.265	23
C_6H_6O	Phenol	94.113	694.3	6100	400	0.438	0.249	23
C_6H_7N	Aniline	93.128	699.0	5350	340	0.384	0.252	23
$C_6H_{12}O$	Methyl isobuyl ketone	100.161	571.0	3300	280	0.385	0.249	23
$C_6H_{14}O$	Diisopropyl ether	102.177	500.0	2850	265	0.335	0.264	23
C_7H_8O	*m*-Cresol	108.14	705.8	4560	342	0.454	0.246	23
C_7H_8O	*o*-Cresol	108.14	697.5	5005	375	0.435	0.249	23
C_7H_8O	*p*-Cresol	108.14	704.6	5150	388	0.505	0.245	23
HBr	Hydrogen bromide	80.912	363.2	8500	800	0.080	0.284	82, 83
HCl	Hydrogen chloride	36.461	324.6	8310	455	0.131	0.247	84
NO_2	Nitrogen dioxide	46.005	431.0	9800	560	0.850	0.225	85
CH_2F_2	Difluoromethane	52.020	351.26	5782	428	0.277	0.241	86–90
$C_2H_2F_4$	1,1,1,2-Tetrafluoroethane	102.030	374.18	4055	511	0.327	0.260	91–94
$C_2H_4F_2$	1,1-Difluoroethane	66.050	386.41	4516	369	0.275	0.252	94–96

Table III. Percentage Deviation of Vapor-Pressure Predictions by Various Methods for Substances Listed in Table II[a]

						LK			EBM			WJR			ECS		
Formula	M	$T_{r,\min}$	$T_{r,\max}$	$p_{r,\min}$	$p_{r,\max}$	AAD	RMS	Max	AAD	RMS	Max	AAD	RMS	Max	AAD	RMS	Max
H_2O	53	0.42	1	0.00003	1	9.69	14.7	36.2	8.47	13.1	34.4	0.27	0.33	1.13	0.03	0.03	0.07
H_3N	137	0.48	1	0.0005	1	3.58	4.46	12.6	1.92	2.45	7.83	1.43	1.68	6.53	0.13	0.17	0.63
CCl_4	25	0.51	0.63	0.00202	0.023	1.73	1.77	2.17	1.16	1.41	2.72	1.21	1.44	2.5	0.43	0.56	1.19
$CHCl_3$	20	0.50	0.62	0.00127	0.018	1.98	2.28	4	0.99	1.14	3.28	1.34	1.69	3.22	0.76	1.02	2.28
CHN	24	0.56	0.69	0.00297	0.035	13.8	16.5	27.6	12.9	15.5	26.2	5.52	6.86	12.7	1.24	1.46	2.41
CHF_3	70	0.39	1	0.00001	1	3.82	5.84	18.9	2.17	3.77	15.3	2.19	2.71	9.68	0.43	0.77	3.27
CH_2Cl_2	16	0.51	0.61	0.00198	0.017	1.42	1.5	1.94	1.71	2.26	4.58	1.01	1.19	2.54	1.11	1.45	3.05
CH_2O	19	0.42	0.62	0.00007	0.013	20.6	22.3	36.7	17.4	19.2	33.3	4.03	4.69	8.62	1.44	1.96	4.53
CH_3Cl	60	0.42	0.99	0.00013	0.95	1.36	2	4.82	0.78	0.88	1.62	1.16	1.81	8.2	0.57	0.74	1.69
CH_4O	95	0.56	0.98	0.00121	0.85	5.39	7.23	16.3	8.2	11.1	25.3	2.92	3.37	6.8	1.79	2.48	6.39
CH_4S	5	0.47	0.59	0.00076	0.014	2.79	2.81	3.27	1.06	1.47	2.92	1.1	1.82	3.91	0.65	0.94	1.97
CH_5N	23	0.41	0.62	0.00002	0.014	1.9	2.11	5.07	2.52	3.51	9.87	9.18	13.1	37.5	0.88	1.09	2.4
C_2H_3N	31	0.59	0.97	0.00701	0.77	4.62	5.21	11.3	4.4	4.96	9.66	5.75	6.11	11.3	1.97	2.43	5.27
$C_2H_4Cl_2$	25	0.40	0.63	0.00003	0.020	6.33	6.77	9.71	2.11	2.42	4.12	3.3	3.66	5.36	1.59	1.88	3.38
$C_2H_4Cl_2$	37	0.46	0.66	0.0002	0.030	4.72	5.81	13.9	2.6	3.32	9.19	2.59	3.08	6.67	1.04	1.39	3.76
C_2H_4O	9	0.59	0.67	0.00795	0.030	5.86	6.59	10.7	4.65	5.3	8.88	2.03	2.63	5.07	0.93	1.21	2.51
$C_2H_4O_2$	27	0.51	0.7	0.0005	0.035	12.5	15.7	29.5	11.9	15.2	29.1	4.77	5.98	12.0	2.12	2.63	4.82
C_2H_6O	55	0.57	1	0.00093	1	1.72	2.69	8.24	0.39	0.51	1.17	2.85	3.48	6.59	1.11	1.37	2.91
C_2H_6O	15	0.44	0.62	0.00021	0.019	2.82	3.44	7.22	1.33	1.37	1.97	1.06	1.17	2.32	0.99	1.72	4.73
d-C_2H_6S	7	0.49	0.58	0.00126	0.010	2.73	2.83	4.19	1.05	1.06	1.27	2.95	3.13	5.02	0.79	0.81	0.97
C_2H_6S	14	0.54	0.68	0.00456	0.049	1.35	1.45	2.1	0.6	0.81	1.71	0.4	0.42	0.53	0.19	0.22	0.39
C_3H_6O	47	0.51	1	0.00091	1	3.92	5.57	12.1	2.61	3.71	8.3	1.74	2.39	4.79	0.24	0.3	0.76
$C_3H_6O_2$	23	0.41	0.64	0.00003	0.021	3.01	3.57	7.2	1.17	1.37	2.47	1.39	2.21	8.72	1.25	1.72	3.83
$C_3H_6O_2$	51	0.42	0.69	0.00003	0.043	3.8	4.19	8.91	1.81	1.95	5.39	1.34	2.08	9.61	0.99	1.26	3.71
C_3H_8O	43	0.62	1	0.00393	0.994	2.54	3.05	4.77	2.79	3.32	7.14	4.7	5.53	8.94	3.09	3.66	5.85
C_3H_8O	34	0.64	0.83	0.00555	0.173	2.07	2.62	6.02	2.29	2.98	7.78	3.71	4.5	9.11	2.71	3.47	8.49

C_3H_9N	12	0.59	0.71	0.00801	0.056	0.91	0.95	1.13	0.79	0.9	1.72	1.7	1.86	2.48	0.73	0.85	1.65
$C_4H_8O_2$	52	0.51	1	0.00074	1	1.42	1.94	3.88	0.44	0.53	0.88	1.11	1.61	4.6	0.27	0.38	0.91
C_4H_8O	17	0.58	0.67	0.00631	0.032	2.02	2.25	4.18	1.08	1.19	2.18	2.45	2.52	3.66	0.12	0.12	0.15
$C_4H_{10}O$	61	0.58	0.99	0.00631	0.917	3.31	3.94	9.22	4.01	5.61	20.9	4.71	5.62	11.7	3.16	4.31	11.7
$C_4H_8O_2$	8	0.53	0.70	0.00033	0.025	8.06	10.4	20.1	0.72	0.83	1.39	4.08	4.64	8.64	1.16	1.77	3.93
$C_4H_8O_2$	15	0.55	0.66	0.0023	0.025	2.9	2.95	3.49	1.24	1.28	1.53	2.01	2.08	2.49	0.68	0.82	1.69
$C_4H_{10}O$	57	0.45	1	0.00014	0.999	1.24	1.62	3.39	0.56	0.86	3.02	0.76	0.86	1.64	0.33	0.4	0.88
$C_4H_{11}N$	26	0.48	0.67	0.00036	0.032	1.52	2.3	6.33	0.84	1.18	3.84	0.83	1.21	4.08	1.04	1.48	3.88
$C_5H_{10}O$	19	0.59	0.68	0.0069	0.034	1.62	1.96	4.08	0.86	1.07	2.27	0.67	0.9	1.96	0.27	0.35	0.78
$C_5H_{10}O$	17	0.59	0.69	0.00719	0.036	2	2.15	3.69	1.31	1.35	2.04	1.56	1.6	2.36	0.52	0.69	1.69
C_6H_5Br	42	0.41	0.64	0.00003	0.022	3.2	3.42	5.91	0.85	1.23	3.68	1.58	1.86	3.87	0.73	1.27	3.93
C_6H_5Cl	39	0.41	0.64	0.00003	0.022	2.56	2.92	5.86	1.1	1.47	4.36	2.03	2.43	5.29	0.96	1.35	4.28
C_6H_6O	24	0.49	0.66	0.00022	0.017	2.87	3.49	9.34	2.42	2.91	8.64	2.13	2.33	3.67	1.81	2.65	6.47
C_6H_7N	12	0.53	0.66	0.00127	0.020	4.2	4.92	8.48	2.88	3.48	6.57	2.68	3	5.83	0.9	1.45	3.65
$C_6H_{12}O$	9	0.51	0.68	0.00067	0.031	5.92	6.5	9.93	4.33	4.76	7.33	3.41	3.64	4.94	1.28	1.5	2.35
$C_6H_{14}O$	31	0.55	0.68	0.0027	0.034	1.85	2.15	4.2	0.74	0.86	1.75	2.42	2.55	3.94	0.31	0.43	1.07
m-C_7H_8O	12	0.59	0.67	0.0045	0.022	1.5	1.59	2.63	1.04	1.23	2.44	1.49	1.67	3.21	1.31	1.73	3.23
o-C_7H_8O	16	0.56	0.67	0.00202	0.021	2.57	2.75	4.64	1.85	1.98	3.4	1.41	1.5	2.17	0.45	0.72	2.28
p-C_7H_8O	18	0.56	0.67	0.00172	0.020	2.74	3.25	5.58	2.82	3.43	6.35	1.82	1.88	2.71	0.34	0.44	0.98
HBr	14	0.52	0.57	0.00406	0.011	2.65	2.72	3.45	1.88	1.91	2.50	31.8	31.9	35.4	0.64	0.74	1.22
HCl	3	0.49	0.60	0.00166	0.018	7.97	8.52	11.9	4.41	4.72	6.67	17.2	17.5	21.6	1.15	1.17	1.45
NO_2	17	0.72	0.98	0.02163	0.815	6.95	8.30	12.2	7.60	9.04	13.1	n.a.	n.a.	n.a.	5.53	6.60	9.71
CH_2F_2	142	0.38	1.00	0.00001	0.998	3.49	6.99	29.8	2.59	5.65	27.2	n.a.	n.a.	n.a.	0.09	0.14	0.74
$C_2H_2F_4$	130	0.46	1.00	0.00016	1.000	0.99	1.68	6.41	0.42	0.61	2.47	n.a.	n.a.	n.a.	0.08	0.24	2.41
$C_2H_4F_2$	127	0.40	1.00	0.00001	0.995	1.99	3.17	16.5	1.03	1.80	12.7	n.a.	n.a.	n.a.	0.11	0.22	1.89
Overall	1452	0.395	1	0.00001	1	3.9	6.3	36	3.0	5.8	34	2.3	3.5	37	1.0	1.8	11

[a] M is the number of data points. $\mathrm{AAD}=100[\sum_1^M |p_{\mathrm{expt}}-p_{\mathrm{calc}}|/p_{\mathrm{expt}}]/M$, where p_{expt} and p_{calc} are the experimental data and the corresponding calculated values. $\mathrm{RMS}=100\{[\sum_1^M |p_{\mathrm{expt}}-p_{\mathrm{calc}}|/p_{\mathrm{expt}}]^2/M\}^{1/2}$, where p_{expt} and p_{calc} are the experimental data and the corresponding calculated values. n.a., not available. Max, the maximum percentage deviation of experimental pressure from the calculated value. LK, Lee and Kesler [15]; EBM, Edalat, Bozar-Jomehri, and Mansoori [35]; WJR, Wilding, Johnson, and Rowley [31]; ECS, the new simple extended corresponding-states principle, Eqs. (3) to (5).

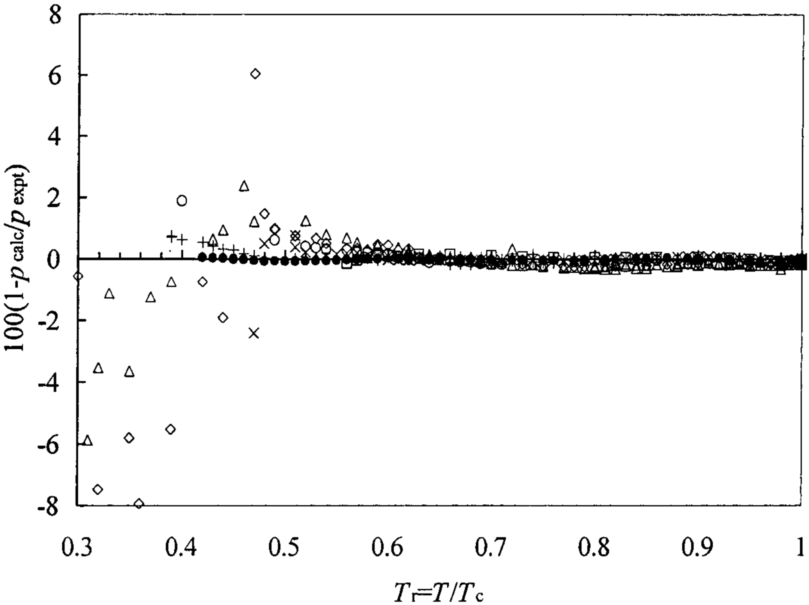

Fig. 1. Comparison of the highly accurate experimental data for substances which were used to determine the general coefficients of Eq. (5) for vapor pressure in the new simple extended corresponding-states principle. (□) Argon; (△) ethane; (◇) propane; (×) 1,1,1,2-tetrafluoroethane (R134a); (○) 1,1-difluoroethane (R152a); (+) difluoromethane (R32); (●) water.

vapor-pressure behavior of highly polar molecules and show very large deviations, up to 36%. Quadratic correlations for the acentric factor are not able to represent the vapor pressure for all classes of fluids.

For polar substances, the present result is much better than that obtainable from any currently available method. Other four-parameter corresponding-states models, for example, by Wu and Stiel [27] and by Wilding et al. [29, 31], require the critical parameters, the radius of gyration or the acentric factor, and a pressure–density–temperature point. As shown in detail in Table III for 1452 vapor-pressure data points, the extended corresponding-states method for vapor pressures, Eq. (5), has an average overall relative deviation of 1.0% (Lee–Kesler method, 3.9%; Edalat et al., 3.0%; Wilding et al., 2.3%), an average overall root-mean-square deviation of 1.8% (Lee–Kesler method, 6.3%; Edalat et al., 5.8%; Wilding et al., 3.5%), and an overall maximum deviation of 11% (Lee–Kesler method, 36%; Edalat et al., 34%; Wilding et al., 37%). Wilding et al. [31] indicated that prediction results for alcohols are not very good for all models, and there are questions about the critical parameters and the

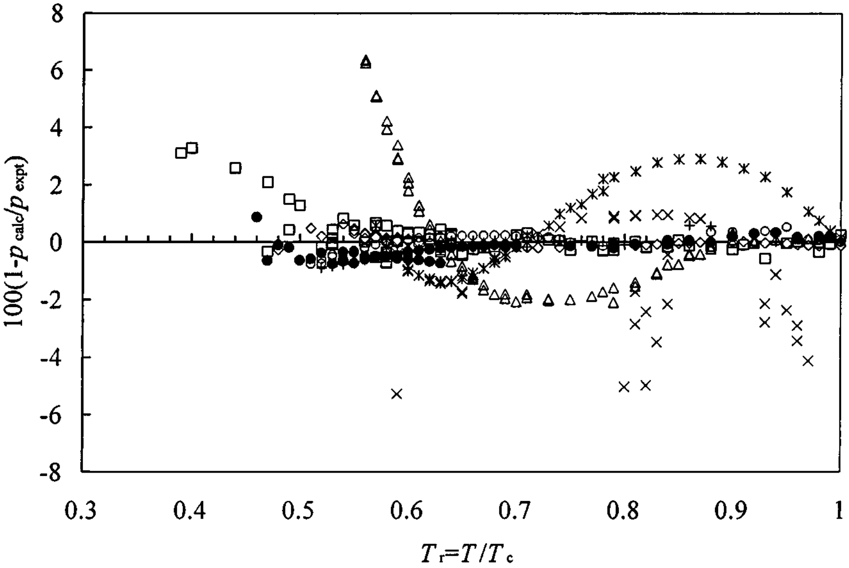

Fig. 2. Comparison of the vapor-pressure data for some highly polar substances with values calculated from the new simple extended corresponding-states principle, Eqs. (3) to (5). (◇) Ammonia; (□) trifluoromethane (R23); (△) methanol; (×) acetonitrile; (∗) ethanol; (○) acetone; (+) ethyl acetate; (●) ethyl ether.

reliability of experimental data because of decomposition. It can be seen that the new method, as a four-parameter corresponding-states principle, provides a good prediction accuracy and that it is superior to commonly used methods.

Using the general corresponding-states principle, one may also determine critical parameters from available experimental data which are usually limited approximately to the range 10 to 150 kPa. That is, if the property of a substance is some function of the reduced temperature, reduced pressure, and/or reduced density, then by knowing the values of the property over a range of temperatures, pressures, and/or densities, it is possible, in principle, to estimate the critical parameters and the acentric factor from this general corresponding-states principle [30]. In principle, only several (not less than three) precise vapor-pressure data points spanning a wide range in the vapor-pressure curve are required to establish the three equations $f(T_c, p_c, \rho_c) = 0$ which have to be solved to obtain the three critical parameters T_c, p_c, and ρ_c. All of the other coefficients or parameters are known in the general corresponding-states principle, Eqs. (4) and (5), if we assume that this extended corresponding-states principle is applicable to the substance, at least in a reasonable degree. For example, a change of 0.1 K in the boiling-point temperature causes a change of about 1% in the critical density for highly nonspherical molecules. Compared to experimental uncertainties of 1 to 3%, sometimes 5%, in the present experimental data, this prediction is considered as very good.

5. CONCLUSIONS

We conclude that the Xiang–Tan vapor-pressure equation is a useful form to represent vapor pressures over the entire temperature range with a very high accuracy using only three parameters, that it can be used for interpolation beyond the range in which data are available, and that it may be extrapolated to both the critical point and the triple point. The simple general extended corresponding-states principle has been successfully used with the Xiang–Tan vapor-pressure equation to include highly nonspherical polar molecules in the corresponding-states framework. The accuracy of predicted vapor pressures approximately agrees with the accuracy of experimental data above a reduced temperature of 0.6 and is also quite good below this temperature. Only the critical parameters and acentric factor are required in the simple extended corresponding-states principle.

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