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A new cubic equation of state and its applications to the modeling of vapor-liquid equilibria and volumetric properties of natural fluids

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Abstract—A cubic equation of state was developed for both pure systems and mixtures in this study. It has only one empirical constant to be evaluated for each component and two constants for each binary. To test its validity, the saturated properties of 22 pure fluids were calculated with the new equation, as compared with the most frequently used or the most recently published cubic equations. The results indicate that the new equation is superior to the previous cubic equations in the overall performance in vapor pressures and saturated volumes. Its overall average deviation of the saturation pressures from experiments is 0.46%, and the maximum deviation is 3.6%. Its average deviation of the liquid volumes from experiments at the reduced temperatures $T_r \leq 0.95$ is 2.80%, and that of vapor volumes is 2.2%. Because of the high accuracy of the new equation for saturation pressures, it can be easily extended to binary mixtures for the prediction of vapor-liquid equilibria (both densities and compositions) with a simple mixing rule, as demonstrated by eight binary systems, including an aqueous mixture. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Equations of state (EOS) formulate the relationship between the pressures (P), temperatures (T), volumes (V) and compositions (x) of components, offering a theoretically strict way to calculate various thermodynamic properties, such as phase equilibrium and *PVTx* properties, which are important in a wide range of geochemical applications. Hundreds of EOS's have been proposed—a few before van der Waals (1887) but mostly later. It would take a long article to classify these equations and to evaluate the strengths, weaknesses and limitations of each. Some equations are better for volumes, others for phase equilibrium, and still others for entropy. Based on the formulation and functionality, the EOS's can be roughly divided into three categories: virial, cubic and complex. The virial type EOS's usually have good representation of volumes, but not of phase equilibria, unless a large number of experimental data are available for parameterization. The cubic EOS's can be formulated to predict phase equilibria, but they are normally poor in yielding correct volumes. The complex EOS's in general have many terms including virial terms and the terms based on certain assumption of molecular shape, size, and electric charges, such as the EOS's of Anderko and Pitzer (1993), Duan et al. (1992b, 1995). These equations can yield both phase equilibria and volumetric properties, but only for those systems with large number of experimental data available. However, experimental data are surprisingly too few, covering too few geochemically important systems in a too small temperature and pressure range, considering that experimentalists have been doing measurements for more than a century.

For the reasons above, researchers sometimes have to use two or more equations to calculate densities and phase equilibria separately to achieve a relatively high accuracy, e.g., Thiery et al. (1994) used a cubic equation (Soave, 1972) to model the phase equilibria and a virial type equation (Lee and Kesler, 1975) to calculate equilibrium volumes. As pointed out by Bakker and Diamond (2000), a disadvantage of this approach is its inconsistency of various fluid parameters. Therefore, it is desirable to develop equations that do not rely on a lot of experimental data, but have a very good predictability in both phase equilibria and volumetric properties for many systems covering a relatively large *T-P* range. We think that the EOS of Duan et al. (1996, 2000) was quite successful for supercritical fluids in this respect, but not in the subcritical range, where phase equilibrium is very important. We are therefore motivated to search for a general EOS to predict saturation pressures, vapor-liquid equilibria and volumes for as many natural systems as possible, including both pure components and mixtures.

As mentioned above, in the calculation of fluid phase equilibria, cubic equations have remarkable advantages over the multi-parameter virial-type equations, because they have only a few empirical parameters to be evaluated from experimental data and thus have better predictability.

In the correlation of the vapor-liquid equilibria of molecular fluids, the first popular cubic equation should be the **RKS** (or **SRK**) equation developed by Soave (1972) from the Redlich and Kwong (1949) (**RK**) equation. It is very successful in the reduced temperature range from $T_r = 0.7$ to 1.0 (where $T_r = T/T_C$, T_C is the critical temperature). For some simple non-polar or weakly polar fluids, it is also reliable at $T_r < 0.7$ (even near the triple point). This progress resulted from Soave's insight that accurate prediction of saturation pressure is an essential base for an EOS to be extended to mixtures for phase equilibrium calculation. Unfortunately, the success of RKS cannot be extended to strongly polar fluids and to the non-polar or weakly polar fluids with small critical compressibility factors (Z_C). The most serious deficiency is its poor prediction of saturated volumetric properties, especially the saturated liquid volumes.

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Table 1. The generalized dimensionless constants in Eqns. (12) and (13).

i	0	1	2	3	4
k_{1i}	−3.5014957E+00	−2.8920174E-01	−2.6894649E-03	−6.6190289E-05	+6.8095677E-07
k_{3i}	4.1988605E+00	−7.1924349E-01	+2.6346420E-03	+6.6733349E-05	−6.8287499E-07

Note: The sources of data used in the parameter regression are given at the end of Section 2.

Since Soave (1972), a great number of cubic equations were proposed for better representation of the phase equilibria and/or the volumetric properties of fluids. Most of them aimed at the improvement in liquid volumes, such as the equations developed by Fuller (1976), Usdin and McAuliffe (1976), Peng and Robinson (1976), Schmidt and Wenzel (1980), Harmens and Knapp (1980), Heyen (1981), Kubic (1982), Aadachi et al. (1983), Lin et al. (1983), Yu and Lu (1987), Trebble and Bishnoi (1987), Iwai et al.(1988), Jan and Tsai (1991), Wang and Guo (1992), Nasrifar and Moshfeghian (2001), Sun (2002), and many others.

Among these equations, the Peng and Robinson (1976) equation (**PR**) is one of the most popular in the improved series. It gives better prediction of saturated liquid volumes than RKS without loss of the good quality of RKS in vapor pressures, but its improvement in liquid volumes remains unsatisfactory for many fluids. Patel and Teja (1982) extended PR into a more general form (**PT**), which is much better than PR in the liquid volumes, but its prediction of saturation pressures is still unsatisfactory.

Aadachi et al. (1983) evaluated and compared sixteen two-term, three-parameter equations of state, which were obtained by combining four different repulsive terms and four different attractive terms. They drew some valuable conclusions: (i) The representation of the liquid compressibility factors is mainly controlled by the repulsive term. (ii) Rigorous or complex repulsive terms provide no real advantage over the van der Waals type repulsive term, which was considered the most suitable one. (iii) The RK type attractive term seemed to be the best one. (iv) Non-convergence was encountered in all the equations containing Harmens-Knapp (**HK**) type attractive terms, and in some of the equations containing PR type attractive terms. Considering these facts, they suggested a new cubic equation (**ALS**) as best one of the sixteen equations in the overall performances.

Trebble and Bishnoi (1986) drew some conclusions from a systematic review of eleven cubic equations. (i) The Fuller (1976) and Heyen (1981) equations showed good precision in liquid volumes, but they may yield enthalpy isotherm crossover and negative heat capacity. These phenomena result from their temperature dependence of the covolume *b*. (ii) The Heyen (1981) and Kubic (1982) equations yield very poor prediction of vapor pressures. (iii) The cubic chain-of-rotators equation, **CCOR**, developed by Lin et al. (1983), has a good accuracy of liquid volumes, but it is less accurate than RKS and PR in saturation pressures and vapor volumes. In terms of the overall average deviations, the PT equation with two component-dependent parameters is the best, and the second is the ALS equation. The general form of the PT (**PTG**) and Schmidt and Wenzel (1980) (**SW**) equations are slightly worse than ALS, but still better than PR and **HK**. The worst are the Kubic and RKS equations.

Jan and Tsai (1991) reported a two-term, four-parameter cubic equation (**JT**). According to their comparisons, this equation is more precise for saturated liquid volumes than the equations of Schmidt and Wenzel (1980), Patel and Teja (1982) (general), Yu and Lu (1987), Trebble and Bishnoi (1987), and Iwai et al. (1988). According to Wang and Guo (1992), the **CSPHC** (Cubic Simplified Perturbed Hard-Chain) equation is also inferior to JT in vapor pressures and saturated liquid volumes.

Recently, Nasrifar and Moshfeghian (2001) put forward a new two-term, cubic equation (**NM**), whose co-volume *b* has a linear dependence on temperature. Compared with RKS and PR in the range from about T_r=0.5 to 0.98, this equation is slightly better in vapor pressures and remarkably better in saturated liquid volumes. Sun (2002) reported a new totally inclusive cubic equation, which has better performance in saturated liquid volumes, but no obvious advantage over RKS or PR in vapor pressures.

Since the 1980s there is a trend to introduce temperature-dependent functions into cubic equations, and most of the functions were determined from trial-and-error experiences, not from strict or sound theories (Yun et al., 1998). Many of these efforts were expected to improve the description of the volumetric properties, but they usually contributed little to the predictability of phase equilibria of either pure or mixed systems.

Table 2. The dimensionless α_2 values of twenty-two pure fluids.

Fluid	α_2	Fluid	α_2	Fluid	α_2	Fluid	α_2
CO	16.254222	H_2S	51.208607	Xe	24.450343	C_4H_{10}	61.308540
CO_2	−61.983246	SO_2	70.025327	CH_4	24.524105	isoC_4H_{10}	61.747360
N_2	19.128920	N_2O	57.070783	C_2H_6	49.640221	C_5H_{12}	67.987248
O_2	21.699171	Ne	27.900811	C_2H_4	49.692745	isoC_5H_{12}	64.958233
NH_3	96.023222	Ar	25.795825	C_3H_6	58.699550		
H_2O	96.240059	Kr	24.352252	C_3H_8	55.585545		

Note: The sources of data used in the parameter regression are given at the end of Section 2.

Table 3. The estimated uncertainties in the saturated properties of pure fluids.

	Uncertainty				
Fluid	Vapor pressure	Liquid density	Vapor density	Critical region[1]	References
CO		no report	no report		McCarty (1989a)
CO_2		0.03%–0.05%	0.03%–0.05%		Span, Wagner (1996)
N_2	0.02%	0.02%	0.02%		Span et al. (2000)
O_2		0.1%	0.1%	except	Schmidt, Wagner (1985)
NH_3	0.2%	0.2%	0.2%	except(d)[2]	Tillner-Roth et al. (1993)
H_2O	0.025%	0.025%	0.1%		Wagner, Pruss (2002)
Ne	0.2%	0.1%	0.1%	except(d)[2]	Katti et al. (1986)
Ar		$<0.02\%$	$<0.02\%$	except	Tegeler et al. (1999)
Kr	0.2%	~0.1%	~0.1%	except	Polt et al. (1992)
Xe	0.2%	~0.2%	~0.2%	except	McCarty (1989b)
CH_4		0.03%	0.03%		Setzmann, Wagner (1991)
C_2H_6		0.2%	0.2%		Friend et al. (1991)
C_2H_4	$<0.05\%(>140K)$	0.02%			Smukala et al. (2000)
C_3H_6		0.1%	0.1%	except	Angus et al. (1980)
C_3H_8	0.02%	0.05%	0.05%		Miyamoto, Watanabe (2000)
C_4H_{10}	0.2%	~0.2%	~0.2%	except	Younglove, Ely (1987)
isoC_4H_{10}	0.2%	~0.2%	~0.2%	except	Younglove, Ely (1987)
C_5H_{12}	0.2%	~0.2%	~0.2%	except	Span (2000)

[1] in this column, "except" denotes that the uncertainties in the three saturated properties (satuartion pressure, liquid density and vapor density) are estimated except for the critical region; [2] "except (d)" denotes that the uncertainties in liquid and vapor density are estimated except in the critical region.

In general, most of the cubic equations using acentric factor as their specific parameter fail to describe the vapor pressures of strongly polar fluids and some non-polar or weakly polar fluids with small Z_C. This, of course, is a big problem, since the exact description of vapor pressures is a prerequisite of the accurate representation of phase equilibria in fluid mixtures (Soave, 1972). However, only much fewer studies focus on the improvement in vapor pressures along the whole vapor-liquid coexistence curve. For instance, Stryjek and Vera (1986) introduced a new component-dependent constant into the alpha function of PR. For many pure fluids (including very polar substances like H_2O), this modified PR equation (**PRSV**) allows one to reproduce vapor pressures much better, especially at $T_r<0.7$. Consequently, this advantage has brought about good improvement in the related phase equilibria in mixtures. Again, Twu et al. (1995a, 1995b) proposed a new general approach to correlate alpha functions and acentric factors, which remarkably improved the accuracy of vapor-pressure predictions, but the approach is not satisfactory at low temperatures for strongly polar fluids and some chain-like alkanes (even with a moderate length). In general, it is still not as accurate as PRSV.

Table 4. The p-T-ρ range in the calculation of saturation properties ($\rho = 1/V$).

Fluid	ρ_{min}/bar	P_{max}/bar	T_{min}/K	T_{max}/K	$\rho_{\text{min}}/(\text{mol.cm}^{-3})$	$\rho_{\text{max}}/(\text{mol.cm}^{-3})$
CO	1.54E-01	34.935	68.127	132.8	2.75E-05	3.03E-02
CO_2	5.18E+00	73.773	216.59	304.128	3.13E-04	2.68E-02
N_2	1.25E-01	33.958	63.151	126.192	2.41E-05	3.10E-02
O_2	1.46E-03	50.430	54.361	154.581	3.24E-07	4.08E-02
NH_3	6.09E-02	113.330	195.50	405.40	3.76E-06	4.30E-02
H_2O	6.12E-03	220.64	273.16	647.096	2.69E-07	5.55E-02
H_2S	3.38E-01	89.3	193.15	373.15	1.02E-02	2.83E-02
SO_2	2.67E-02	78.83	203.15	430.75	8.20E-03	2.50E-02
N_2O	9.24E-01	72.45	183.15	309.55	1.03E-02	2.77E-02
Ne	4.35E-01	26.786	24.562	44.4918	2.20E-04	6.21E-02
Ar	6.89E-01	48.63	83.806	150.687	1.01E-04	3.55E-02
Kr	7.32E-01	55.1	115.77	209.48	7.81E-05	2.92E-02
Xe	8.17E-01	58.4	161.36	289.734	6.25E-05	2.26E-02
CH_4	1.17E-01	45.992	90.694	190.564	1.56E-05	2.81E-02
C_2H_6	3.80E-03	48.718	120.50	305.33	3.80E-07	2.06E-02
C_2H_4	1.22E-03	50.418	103.99	282.35	1.41E-07	2.33E-02
C_3H_6	1.20E-03	46.646	140.00	365.57	1.03E-07	1.68E-02
C_3H_8	4.12E-04	42.4709	135.48	369.825	3.66E-08	1.55E-02
C_4H_{10}	2.02E-03	37.96	174.87	425.125	1.39E-07	1.20E-02
isoC_4H_{10}	1.31E-03	36.40	163.56	407.817	9.63E-08	1.19E-02
C_5H_{12}	3.50E-04	33.665	183.47	469.7	2.30E-08	1.01E-02
isoC_5H_{12}	2.21E-02	33.81	223.15	460.39	3.27E-03	9.52E-03

Table 5. The percentage deviations of the saturated vapor pressures of some pure fluids predicted with different equations of state.

	New		PRSV		NM		JT		ALS		PT	
Fluid	AD	MD	AD	MD	AD	MD	AD	MD	AD	MD	AD	MD
CO	0.65	1.47	0.69	1.16	0.99	7.05	1.53	4.27	0.86	1.40	0.52	1.62
CO_2	0.07	0.13	0.21	0.62	0.17	0.45	0.24	1.15	0.29	0.77	0.39	1.56
N_2	0.29	0.76	0.38	0.75	0.56	5.14	0.89	2.26	0.83	3.13	0.63	1.28
O_2	0.42	2.80	0.47	1.79	1.13	4.70	1.70	11.46	2.52	11.82	1.37	5.21
NH_3	0.26	0.46	0.45	1.99	1.95	18.22	1.14	11.46	1.86	11.59	2.03	12.25
H_2O	0.08	0.53	0.20	0.65	3.12	60.15	1.64	51.80	2.16	33.45	0.91	4.88
H_2S	0.25	0.69	0.84	1.70	1.17	2.17	0.38	0.82	1.50	4.20	1.74	3.23
SO_2	0.20	0.38	1.07	1.98	1.58	7.32	1.39	2.46	0.93	1.70	1.02	5.08
N_2O	0.23	0.40	0.62	1.27	0.64	3.03	0.80	2.80	0.50	1.30		
Ne	0.48	0.81	0.24	0.38	1.54	2.90	1.81	3.07	2.36	5.36		
Ar	0.27	0.79	0.35	0.72	0.34	1.67	0.85	1.97	0.82	2.52	0.65	1.38
Kr	0.18	0.49	0.25	0.54	0.46	1.83	1.00	2.24	0.78	2.55		
Xe	0.23	0.51	0.35	0.68	0.38	1.71	0.97	1.87	0.90	2.64		
CH_4	0.28	0.75	0.31	0.67	0.31	1.28	0.65	2.34	1.28	7.75	0.74	2.85
C_2H_6	0.57	1.09	0.74	1.76	0.78	3.07	1.08	10.85	1.94	8.82	0.95	4.76
C_2H_4	0.69	2.72	0.69	1.39	1.58	8.91	0.81	3.38	0.76	1.56	1.23	11.42
C_3H_6	1.76	3.51	0.57	1.57	0.97	5.22	1.65	9.62	0.97	1.90	0.74	3.76
C_3H_8	0.74	1.99	0.64	4.49	0.76	17.36	1.06	16.03	1.09	4.11	1.05	7.25
C_4H_{10}	1.12	2.20	0.90	1.73	1.44	17.77	1.43	14.01	1.61	6.66	1.06	9.18
isoC_4H_{10}	0.82	2.79	0.69	1.40	0.67	10.07	1.15	7.92	0.83	1.46	1.73	15.01
C_5H_{12}	0.32	0.99	0.70	1.80	2.95	35.31	1.57	18.35	1.33	4.06	2.02	18.16
isoC_5H_{12}	0.11	0.27	0.38	0.76	0.90	6.44	0.56	3.26	1.14	2.98	0.70	3.71
Average	0.46	1.21	0.53	1.35	1.11	10.08	1.10	8.34	1.24	5.53	1.08	6.26

(1) AD, MD are the average and maximum percentage deviations, $(P_{cal}/P_{exp} - 1)\times 100\%$, of the calculated vapor pressures;

(2) All the six cubic equations include the critical properties. Additionally, the differences between the six equations are as follows: New: contains one specific parameter; PRSV: contains an acentric factor and another specific parameter; NM: contains an acentric factor and a temperature function for covolume *b;* JT: contains an acentric factor and two different expressions for alpha function; ALS: contains an acentric factor; PT: contains two specific parameters and a temperature function for pseudo compressibility factor.

(3) For PRSV, the values of the specific parameter k_1 of N_2O, Ne, Kr, Xe, C_2H_4 and isoC_5H_{12} are fitted in this work. They are 0.04, 0.033, 0.005, 0.001, 0.047, and 0.035, respectively.

Table 6. The percentage deviations of the saturated liquid volumes of some pure fluids predicted with different equations of state ($T_r \leq 0.95$).

	New		PRSV		NM		JT		ALS		PT	
Fluid	AD	MD	AD	MD	AD	MD	AD	MD	AD	MD	AD	MD
CO	1.76	3.47	8.71	11.50	1.99	3.20	1.28	4.48	3.01	12.89	2.15	5.48
CO_2	3.62	4.62	3.06	7.60	1.60	6.73	1.01	4.48	4.67	14.93	2.03	3.38
N_2	2.15	3.60	9.03	11.85	1.84	3.03	1.87	2.88	3.00	12.09	2.39	6.83
O_2	2.98	6.30	9.18	11.45	1.87	4.25	1.72	3.73	2.54	14.19	2.50	6.27
NH_3	4.29	11.90	13.58	21.51	14.58	20.92	8.68	13.56	18.12	29.01	1.22	2.83
H_2O	2.72	5.50	22.12	32.61	19.28	32.17	6.01	8.43	21.88	37.52	1.78	4.15
H_2S	2.23	3.89	6.93	9.42	1.31	4.45	1.61	4.44	3.60	14.75	2.68	4.34
SO_2	3.01	5.93	1.64	10.16	1.74	9.30	2.28	6.10	4.75	16.66	1.20	4.39
N_2O	3.99	5.84	4.51	7.29	1.34	6.97	3.89	2.20	5.18	16.43		
Ne	0.91	1.87	14.49	17.04	6.80	7.88	3.09	3.75	4.26	9.80		
Ar	2.25	3.72	8.40	12.12	1.97	2.86	2.26	4.19	4.27	14.72	2.51	6.22
Kr	1.26	2.54	7.97	11.57	1.47	2.95	1.41	5.51	4.75	15.23		
Xe	1.18	2.55	7.03	10.54	1.03	4.66	1.39	6.44	6.09	17.00		
CH_4	2.45	4.15	8.40	11.36	1.17	2.76	2.11	3.19	3.78	14.39	2.96	5.75
C_2H_6	2.53	5.19	6.59	8.13	1.57	6.08	1.47	4.48	3.25	16.65	2.89	4.70
C_2H_4	3.05	6.91	6.35	8.29	1.94	5.65	1.73	4.50	4.01	16.21	2.50	4.87
C_3H_6	4.41	11.34	6.26	7.95	1.24	3.51	3.57	8.06	2.00	12.91	1.37	6.69
C_3H_8	3.14	6.74	5.17	7.17	1.89	6.90	2.16	5.13	4.78	16.56	1.56	4.99
C_4H_{10}	2.97	5.91	4.50	8.20	2.07	7.58	2.06	4.85	4.67	16.33	2.74	4.41
isoC_4H_{10}	2.87	7.18	4.77	7.59	1.37	6.95	1.86	5.70	2.94	15.98	1.97	4.78
C_5H_{12}	3.65	6.41	2.89	10.53	2.43	9.47	2.10	6.12	3.71	17.25	1.80	4.43
isoC_5H_{12}	4.11	7.25	3.92	7.13	2.13	6.52	2.88	2.06	3.10	14.39	1.62	5.03
Average	2.80	5.58	7.52	11.41	3.30	7.49	2.57	5.19	5.38	16.63	2.10	4.97

Note: AD, MD are the average and maximum percentage deviations of calculated volumes.

Table 7. The deviations of the saturated vapor volumes of some pure fluids predicted with different equations of state ($T_r \leq 0.95$).

	New		PRSV		NM		JT		ALS		PT	
Fluid	AD	MD	AD	MD	AD	MD	AD	MD	AD	MD	AD	MD
CO	3.20	9.87	1.82	6.71	2.65	6.78	3.80	7.17	1.22	3.16	1.32	3.62
CO_2	2.17	7.66	0.70	2.22	0.92	1.99	1.16	4.04	0.84	1.20	0.47	0.82
N_2	2.39	7.54	1.12	4.32	1.68	4.81	2.56	5.12	1.30	3.41	0.74	1.73
O_2	1.73	7.54	1.07	4.19	1.95	4.45	3.29	12.96	3.87	13.41	1.97	5.50
NH_3	1.11	3.37	2.99	5.12	5.76	22.67	4.08	13.28	5.36	13.45	3.74	10.68
H_2O	0.91	5.12	1.86	4.70	20.99	150.90	6.05	34.10	11.02	50.33	2.20	4.61
Ne	1.82	5.44	0.68	2.94	2.45	3.80	2.38	4.23	3.12	6.67		
Ar	2.01	7.61	1.35	4.44	1.23	4.82	2.62	5.27	1.09	2.97	0.91	1.81
Kr	1.79	6.82	1.02	3.66	1.09	4.14	2.42	4.40	0.95	3.12		
Xe	2.02	7.44	1.15	4.03	1.19	4.57	2.46	5.02	1.10	3.22		
CH_4	1.69	7.19	1.00	3.81	0.98	4.22	1.95	5.06	2.29	8.63	1.26	3.12
C_2H_6	1.98	8.88	1.24	3.40	1.34	3.55	2.03	12.11	2.71	9.62	0.99	4.59
C_2H_4	2.56	8.53	1.39	3.94	2.94	8.15	1.91	5.00	0.95	1.81	1.76	10.24
C_3H_6	3.08	7.04	0.84	2.28	1.39	5.53	2.35	10.65	1.25	2.08	1.11	3.62
C_3H_8	3.36	9.15	1.38	4.29	2.37	21.06	3.34	19.10	1.77	4.30	1.33	6.74
C_4H_{10}	3.71	9.30	1.59	3.20	3.25	21.65	3.35	16.32	2.29	7.16	1.61	8.39
$IsoC_4H_{10}$	2.34	8.31	1.06	2.93	1.13	11.21	2.01	8.62	0.89	1.62	2.02	13.04
C_5H_{12}	1.77	7.90	0.99	1.77	6.80	54.39	3.58	22.42	1.89	4.28	2.54	15.37
Average	2.20	7.48	1.29	3.78	3.34	18.821	2.85	10.83	2.44	7.80	1.60	6.26

Note: AD, MD are the average and maximum percentage deviations of the calculated volumes.

In summary, most of the existing cubic equations are designed to improve the performance in either the volumetric properties or the vapor pressures at $T_r \geq 0.7$, few improve both aspects over the whole vapor-liquid coexistence region.

The purpose of this work is to develop a cubic equation of state, which is capable of calculating vapor pressures and saturated volumes over the whole coexistence region for both pure systems and binary mixtures. This article is organized as follows: Section 2 introduces the new equation we propose. Section 3 reports the application of the new equation to the prediction of the liquid-vapor equilibrium properties of 22 pure fluids, as compared with the PRSV, PT, ALS, JT and NM EOS reviewed above, which are considered the best among the cubic EOS's. Section 4 presents a mixing rule and the application of the new equation to the calculation of the phase equilibria and saturated volumes of some binaries. In the final section, some conclusions are drawn.

2. THE NEW CUBIC EOS

During our research on various cubic equations of sate, we found that all of the cubic equations (simple or complex, two-term or three-term) have very similar behavior for vapor pressures if the optimization technique of Soave (1972) is employed. However, this is not the case for the reproduction of volumetric properties. We found that the three-term cubic equations are more desirable than the two-term ones in volume prediction. So we propose the following cubic equation:

$$P = \frac{RT}{V - b_1} - \frac{a(T)}{(V - b_1)(V - b_2)} + \frac{c}{(V - b_1)^2(V - b_2)} \quad (1)$$

$$a(T) = a_C \alpha(T), \quad a_C = a(T_C) = \Omega_a \frac{R^2 T_C^2}{P_C},$$

$$c = \Omega_c \frac{R^3 T_C^3}{P_C^2}, \quad b_1 = \Omega_{b_1} \frac{RT_C}{P_C}, \quad b_2 = \Omega_{b_2} \frac{RT_C}{P_C} \quad (2)$$

where P, V, T, R is pressure (in bar), molar volume (in $cm^3 \cdot mol^{-1}$), temperature (in K) and the universal gas constant ($83.14467 bar \cdot cm^3 \cdot K^{-1} \cdot mol^{-1}$), respectively. $a(T)$, b_1, b_2 and b_3 are empirical parameters, subscript "C" denotes the critical condition, $\alpha(T)$ is the temperature coefficient of $a(T)$ (namely alpha function), and Ω_a, Ω_c, Ω_{b_1} and Ω_{b_2} are dimensionless coefficients to be determined. We select Ω_{b_1} as the unique parameter to be optimized, and the remaining three parameters are determined from the constraints of critical conditions:

$$\left[\frac{\partial P}{\partial V}\right]_{T=T_C} = 0, \quad \left[\frac{\partial^2 P}{\partial V^2}\right]_{T=T_C} = 0, \quad V = V_C = \frac{Z_C R T_C}{P_C} \quad (3)$$

where Z_C is the critical compressibility factor. From (3), we have

$$\Omega_{b_2} = (3Z_C - 1 - 2\Omega_{b_1}) \quad (4)$$

$$\Omega_a = 3Z_C^2 - 3(\Omega_{b_1} + \Omega_{b_2}) Z_C + \Omega_{b_1}^2 + \Omega_{b_2}^2 + \Omega_{b_1}\Omega_{b_2} \quad (5)$$

$$\Omega_c = (Z_C - \Omega_{b_1})^3 \quad (6)$$

To optimize Ω_{b_1}, it is necessary to derive the fugacity coefficients of fluids from a given equation. For convenience of the derivation, the new equation is transformed to a new form:

$$P = \frac{RT}{V - b_1} - A\left[\frac{1}{(V - b_2)} - \frac{1}{(V - b_1)}\right] + \frac{C}{(V - b_1)^2} \quad (7)$$

where

$$A = -\left[\frac{a}{(b_1 - b_2)} + \frac{c}{(b_1 - b_2)^2}\right], \quad C = \frac{c}{(b_1 - b_2)} \quad (8)$$

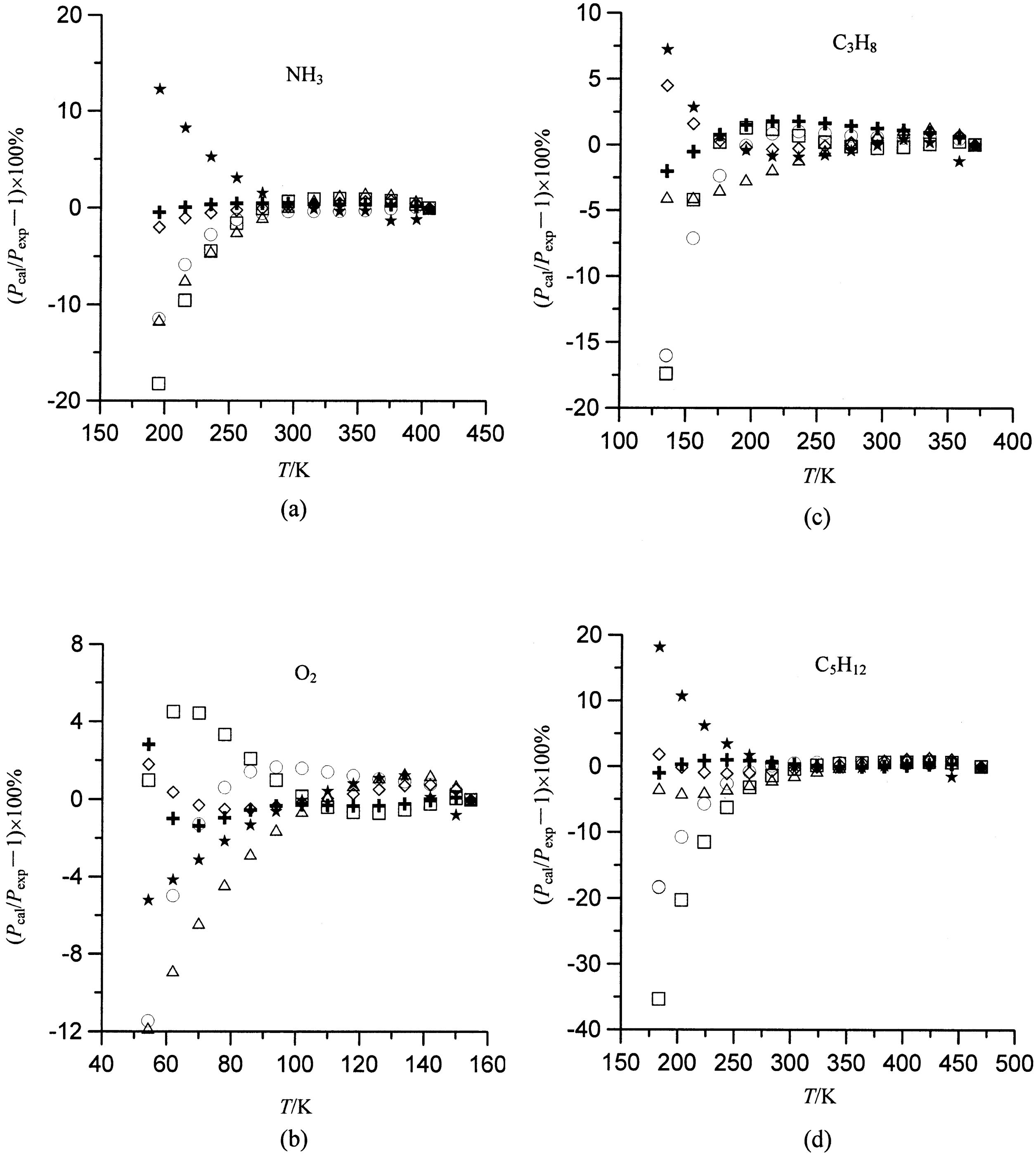


Fig. 1. The deviations of the calculated vapor pressures from experimental data. **cross:** New equation; **diamond:** PRSV equation; **square:** NM equation; **circle:** JT equation; **triangle:** ALS equation; **star:** PT equation.

This can be done by factorizing twice,

$$\frac{1}{(V-b_1)(V-b_2)} = \frac{1}{(b_2-b_1)}\left[\frac{1}{(V-b_2)} - \frac{1}{(V-b_1)}\right], \quad (8a)$$

where the first factorization is applied to the cubic term, and the second is applied to the new quadratic term after resetting the equation. The fugacity coefficient of fluid i, ϕ_i, at a given temperature and pressure is derived:

$$\ln\phi_i = \frac{1}{RT}\int_0^P\left(V-\frac{RT}{P}\right)\mathrm{d}P = Z - 1 - \ln Z - \ln\left(1-\frac{b_{1i}}{V}\right) + \frac{A_i}{RT}\ln\frac{(V-b_{2i})}{(V-b_{1i})} + \frac{C_i}{RT(V-b_{1i})} \quad (9)$$

where $Z = \frac{PV}{RT}$. ϕ_i has a value of 1 at standard state, which is

Table 8. The interaction parameters in the new cubic equation of state for some mixtures.

Mixture	k_{a12}	k_{c112} (k_{c122})	Mixture	k_{a12}	k_{c112} (k_{c122})
CO_2-CH_4	0.095	0.08	CH_4-C_2H_4	0.055	0.11
N_2-CO_2	0.075	0.0	CO_2-C_2H_6	0.107	0.02
CH_4-C_2H_6	0.030	0.13	H_2S-C_2H_6	0.085	0.08
N_2-CH_4	0.07	0.15	N_2-C_3-H_6	0.127	−0.10
N_2-C_2H_6	0.12	0.2	NH_3-H_2O	−0.273	−0.35

Note: all the interaction parameters are dimensionless.

defined as hypothetical ideal gas at 1 bar for a given temperature.

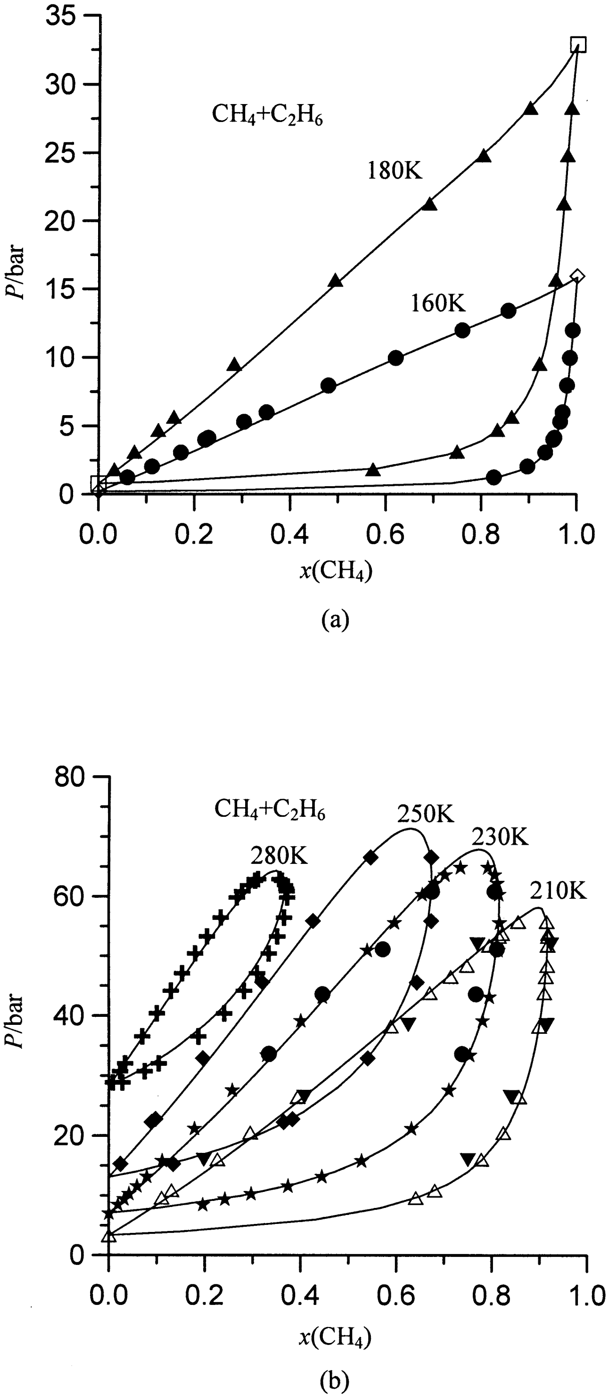
Using the equations above, we optimize Ω_{b_1} as follows: (1) Guess a Ω_{b_1}; (2) For a given *T*, guess an *α(T)* and read the corresponding saturated *p* (experimental), then compute the three volume roots at the *T* and *p*, where the maximum and minimum roots correspond to the vapor and liquid, respectively;. (3) Compute fugacities of vapor and liquid, f^L and f^V; (4) If $|f^L/f^V - 1|$ is small enough (within the range of the allowable deviations), record the *α(T)* and the corresponding volumes of vapor and liquid; otherwise, guess a new *α(T)* and repeat (2) and (3) until $|f^L/f^V - 1|$ is small enough; (5) Calculate the average and standard volume deviations and find the maximum volume deviation; (6) Repeat (1) to (5), and find the best Ω_{b_1}, which minimize the deviation between experiment and the equation; (7) Correlate Ω_{b_1} and Z_C with a generalized polynomial, where the correlation excludes the Ω_{b_1}'s of some fluids in Table 4 (namely CO_2, NH_3, N_2O, C_3H_6, C_5H_{12} and isoC_5H_{12}). In the correlation, the saturated *p-V-T* data of H_2S and SO_2 are taken from Lu (1988), while the data of other fluids, as well as the related uncertainty reports, are from the references in Table 3. The final optimized form of Ω_{b_1} is a simple generalized function of Z_C:

$$\Omega_{b_1} = -0.0128765 + 0.3833530 Z_C - 0.1291949 Z_C^2 \quad (10)$$

To optimize the representation of vapor pressures, it is very important to select a suitable form of the alpha function. We found that a temperature-dependent polynomial with negative exponents permits an excellent extrapolation to the supercritical region. We also noticed that a small difference between the exponents of two terms can enhance the correlation between the coefficients of the two terms. To decrease the sensitivity of vapor pressures to the deviations of the fitted parameters in the alpha function, a small exponent, $\frac{1}{9}$, was assigned to the temperature polynomial. Combining these considerations together, the alpha function takes the following form:

$$\alpha(T_r) = [1 + \alpha_1(T_r^{-2.8} - 1) + \alpha_2(T_r^{-3.0} - 1) + \alpha_3(T_r^{-3.2} - 1)]^{\frac{1}{9}} \quad (11)$$

where α_1, α_2 and α_3 are dimensionless empirical coefficients to be determined. From the performances of many previously published cubic equations, it is found that generalized alpha functions cannot yield precise descriptions of vapor pressures for many different fluids over the whole vapor-liquid coexistence region. We have to retain one specific constant, $\acute{a}_2$, for each pure fluid in the alpha function, while α_1 and α_3 are treated as general functions of α_2:



(a)

(b)

Fig. 2. Liquid-vapor phase equilibria of the CH_4-C_2H_6 system at different temperatures. **solid line:** calculated with the equation of state in this study. (a) **solid triangle, dot:** experimental data of Miller et al. (1977); **square, diamond:** data for pure fluids from Setzmann and Wagner (1991), Friend et al. (1991). (b) **dot, solid triangle:** Monte Carlo simulated data of Zhang and Duan (2002), **open triangle, solid star:** experimental data of Wei and Brown (1995), **solid diamond:** experimental data of Davalos et al. (1976), **cross:** experimental data of Gupta et al. (1980).

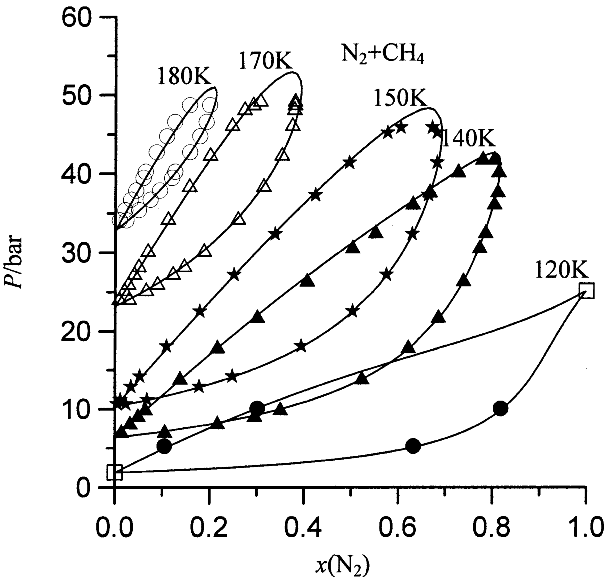


Fig. 3. Liquid-vapor phase equilibria of the N_2-CH_4 system. **square:** experimental data of pure fluids from Span (2000), Setzmann and Wagner (1991); **other symbols:** experimental data of Kidnay et al. (1975); **solid lines:** the equation of state of this study.

$$\alpha_1 = k_{10} + k_{11}\alpha_2 + k_{12}\alpha_2^2 + k_{13}\alpha_2^3 + k_{14}\alpha_2^4, \tag{12}$$

$$\alpha_3 = k_{30} + k_{31}\alpha_2 + k_{32}\alpha_2^2 + k_{33}\alpha_2^3 + k_{34}\alpha_2^4. \tag{13}$$

where α_2 and k_{ij} are dimensionless empirical coefficients, which are regressed from the vapor pressures of pure fluids, see Tables 1 and 2. In the regression, the data of H_2S, SO_2, N_2O and isoC_5H_{12} are taken from Lu (1988), while the others are taken from the references in Table 3. Note that α_2 is the only parameter, besides critical parameters, to be evaluated from data of individual components.

3. PREDICTION OF SATURATED PRESSURES, LIQUID AND VAPOR VOLUMES OF PURE FLUIDS

To test the new equation, the vapor pressures, saturated liquid and vapor volumes of 22 pure fluids of geological interest were calculated with the new equation. The procedure is as follows: (1) Specify a T, and compute $\alpha(T)$; (2) Guess a P, and compute the three volume roots at the T and P, where the maximum and minimum roots correspond to the vapor and liquid, respectively; (3) Compute the fugacities of vapor and liquid, f^{L} and f^{V}; (4) If $|f^{\mathrm{L}}/f^{\mathrm{V}}-1|$ is within a small tolerance, the pressure and its corresponding vapor and liquid volumes are recorded as the saturated properties at the given T, otherwise, guess a new P and repeat (2) and (3) until the tolerance for $|f^{\mathrm{L}}/f^{\mathrm{V}}-1|$ is satisfied; (5) For another T, repeat (1) to (4); (6) Calculate the average and standard deviations and find the maximum deviation.

At the same time, the five most competitive EOS reviewed above were selected to make a comparison under the same conditions. The P-T-ρ range ($\rho=1/V$) and statistical results of the calculation are listed in Tables 4 to 7.

It can be seen from Table 5 that the new EOS and the PRSV equation are the most accurate for vapor pressure calculation, and that the new EOS is slightly better than PRSV. The average deviations of the remaining four equations are close to each other, but the maximum deviations are very different. All the four equations (NM, JT, ALS and PT) show big deviations (from experimental data) for strongly polar fluids at low temperatures. Although the PT equation is valid for H_2O (the maximum deviation is 4.88%), it is not for NH_3. These four equations give disappointing results for some non-polar or weakly polar fluids. Nevertheless, the ALS equation is better than NM, JT, and PT equations for hydrocarbons, but its maximum deviations for CH_4 and C_2H_6 are unusually large. For the six equations, more detailed information on the saturation pressures of some fluids can also be seen from Figure 1.

The results of the comparison of the six EOS (the new EOS, PRSV, NM, JT, ALS, PT) with the available experimental volumetric data of 22 pure fluids covering the T-P ranges of Table 4 are listed in Tables 6 and 7. The overall average deviations of both liquid and vapor from experiments of PT, this new EOS, JT, ALS, NM and PRSV are 1.85%, 2.5%, 2.71%, 2.95%, 3.17% and 4.45%, respectively. Overall, the PT EOS is the best in the volumetric prediction, and our new EOS is the next. We notice that the PT EOS has a better prediction mainly because it uses two component-dependent constants for correlation, where one of the constants is the pseudocritical compressibility factor ζ_{C}, which makes it impossible to reproduce the critical point. To compensate for this shortcoming, an artificial temperature-segment function ($0.9<T_{\mathrm{r}}\leq 1$) is introduced to force the ζ_{C} back to Z_{C}, which leads to the discontinuity of some thermodynamic properties at $T_{\mathrm{r}}=0.9$.

4. PREDICTION OF PHASE EQUILIBRIA AND SATURATED VOLUMES OF MIXTURES

Generally, a relatively simpler mixing rule can be applied to cubic equations of state than to other types of equations. This

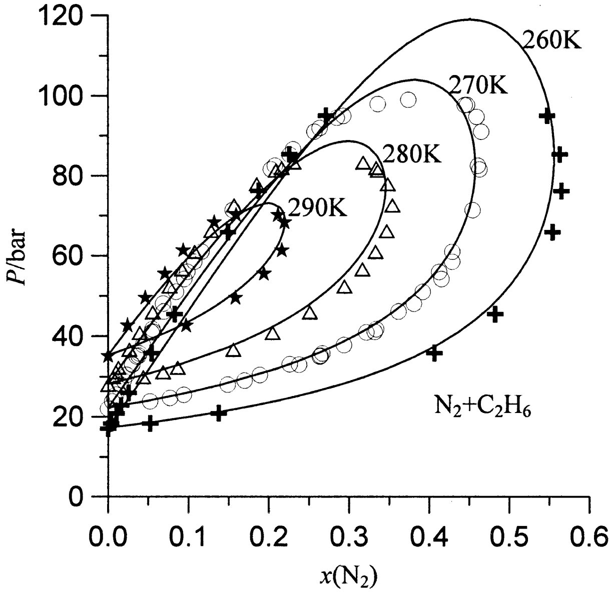


Fig. 4. Liquid-vapor phase equilibria of the N_2-C_2H_6 system. **star:** experimental data of Grausф et al. (1977); **other symbols:** experimental data of Gupta et al. (1980); **solid lines:** the equation of state of this study.

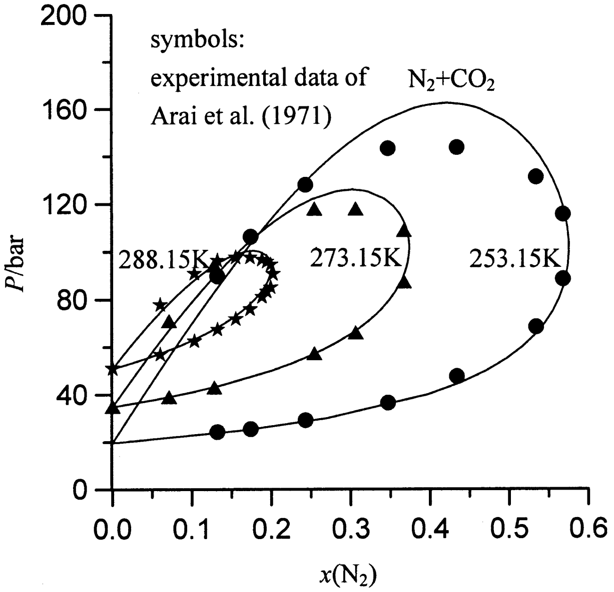


Fig. 5. Liquid-vapor phase equilibrium of the N_2-CO_2 system: experimental data vs. the equation of state of this study.

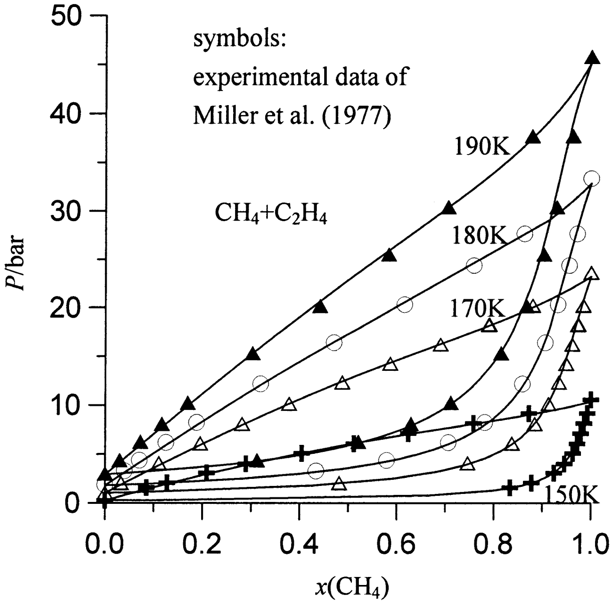


Fig. 7. Liquid-vapor phase equilibrium of the CH_4-C_2H_4 system: experimental data vs. the equation of state of this study.

is one of the advantages of the cubic equations. In most of the cubic equations for mixtures, the co-volume of a mixture is almost always a linear function of composition, e.g., Soave (1972); Peng and Robinson (1976); Patel and Teja (1982), and few equations use the quadratic combination, e.g., Lin et al. (1983). In this study, we tried both of the two forms and found that the quadratic form was essentially impractical because of the frequent overflow in calculations, while the linear form is very reliable. A similar phenomenon was found for b_2 in the new EOS. So the linear mixing rule is used for both b_1 and b_2 in this work. On the other hand, almost every cubic EOS with a cubic term uses a quadratic function of compositions for *a(T)*, e.g., Soave(1972), Peng and Robinson (1976), Patel and Teja (1982), Lin et al. (1983), and uses a cubic one for *c*, which are analogized by the rigorous mixing rule for the second and third virial coefficients, e.g., Benedict et al.(1942), Spycher and Reed (1988), and Duan et al.(1992a,II). The main differences among different mixing rules for *a(T)* and *c* usually lie in the estimation of the interaction terms of different molecules, most of which take the geometrical average of component parame-

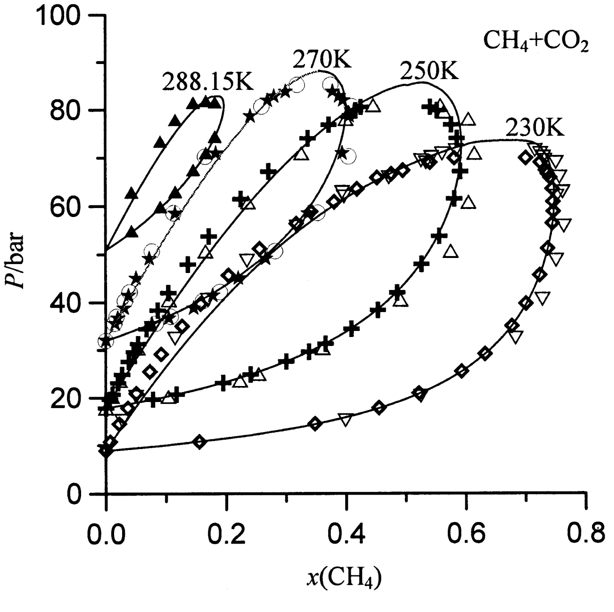


Fig. 6. Liquid-vapor phase equilibria of the CO_2-CH_4 system. **star, cross, diamond:** experimental data of Wei and Brown (1995); **circle, open triangles:** experimental data of Davalos et al. (1976); **solid triangle:** experimental data of Arai et al. (1971).

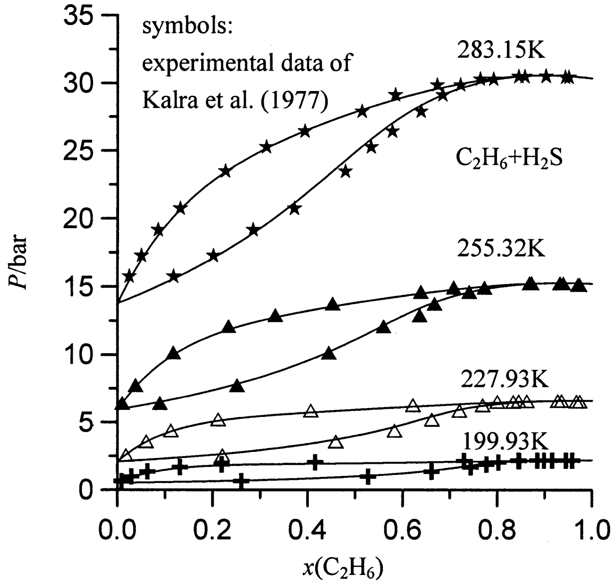


Fig. 8. Liquid-vapor phase equilibrium of the C_2H_6-H_2S system: experimental data vs. the equation of state of this study.

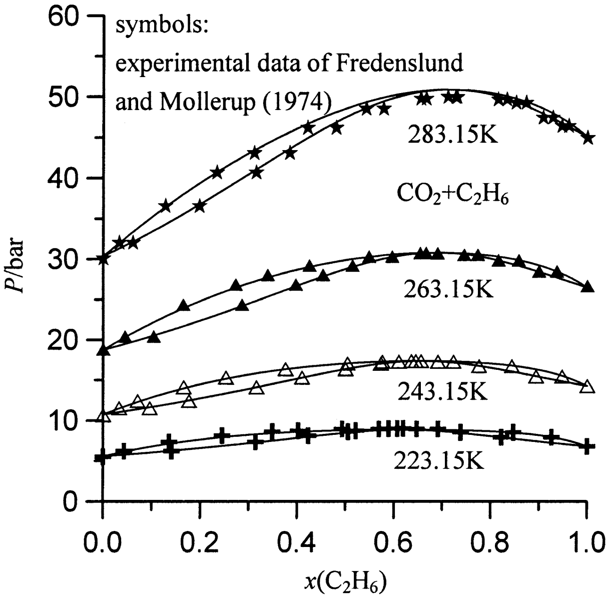


Fig. 9. Liquid-vapor phase equilibrium of the CO_2-C_2H_6 system: experimental data vs. the equation of state of this study.

ters with an adjustable interaction parameter, e.g., Benedict et al. (1942), Spycher and Reed (1988). In this study, we use the usual mixing rule:

$$b_{1\mathrm{m}} = \sum_i x_i b_{1i}, \quad b_{2\mathrm{m}} = \sum_i x_i b_{2i},$$

$$a_{\mathrm{m}} = \sum_i \sum_j x_i x_j a_{ij}, \quad c_{\mathrm{m}} = \sum_i \sum_j \sum_k x_i x_j x_k c_{ijk}, \tag{14}$$

$$a_{ij} = (1 - k_{a_{ij}})(a_{ii}a_{jj})^{\frac{1}{2}}, \quad c_{ijk} = (1 - k_{c_{ijk}})(c_{iii}c_{jjj}c_{kkk})^{\frac{1}{3}}, \tag{15}$$

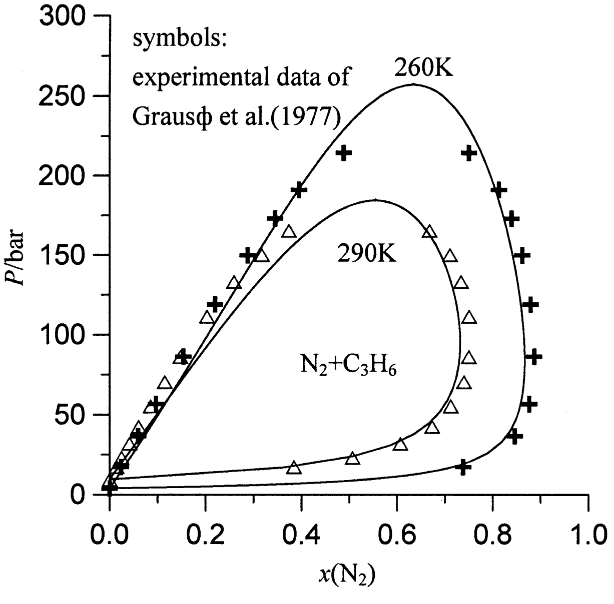


Fig. 10. Liquid-vapor phase equilibrium of the N_2-C_3H_6 system: experimental data vs. the equation of state of this study.

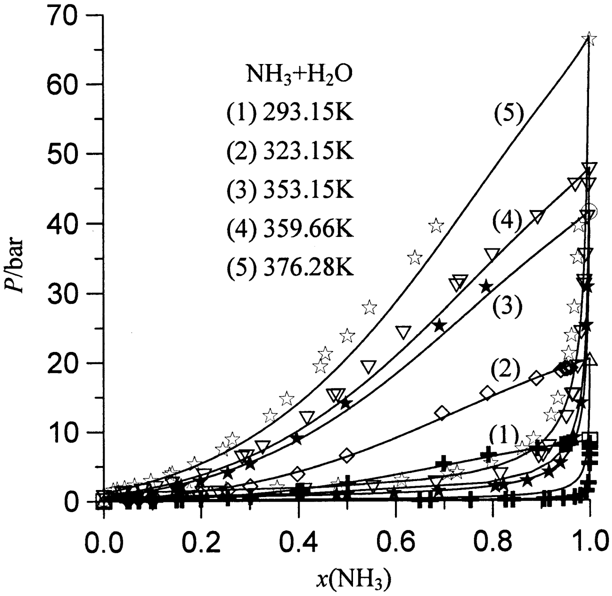


Fig. 11. Liquid-vapor phase equilibria of the NH_3-H_2O system. **cross, diamond, star:** Experimental data of Smolen et al. (1991); **square, triangle, circle:** vapor pressures from Tillner-Roth et al. (1993), Wagner and Pruss (2002), and the solid lines are the equation of state of this study.

$$a_{ij} = a_{ji}, \quad c_{ijk} = c_{ikj} = c_{jik} = c_{jki} = c_{kij} = c_{kji}, \tag{16}$$

$$k_{a_{ii}} = k_{a_{jj}} = k_{c_{iii}} = k_{c_{jjj}} = k_{c_{kkk}} = 0. \tag{17}$$

where the subscript "m" denotes the mixture; the subscripts "i," "j" and "k" stand for components in the mixture; x_i is the mole fraction of component i, a_{ij} and c_{ijk} represents *i-j* binary interaction and *i-j-k* ternary interaction respectively, $k_{a_{ij}}$ and $k_{c_{ijk}}$ are the dimensionless coefficients of i-j and i-j-k interactions, respectively. In Eqn. 17, $k_{a_{ij}} = k_{a_{ji}}$ is widely used in cubic equations, and $k_{c_{iij}} = k_{c_{ijj}}$ is the same as Duan et al.(1992a,II).

The fugacity coefficient of an arbitrary component i in the mixture, Φ_{i}, can be derived as:

$$\ln \phi_i = \frac{1}{RT}\int_{nV}^{\infty}\left(\left[\frac{\partial P}{\partial n_i}\right]_{T,nV,n_j} - \frac{RT}{nV}\right)d(nV) - \ln Z = -\ln Z$$

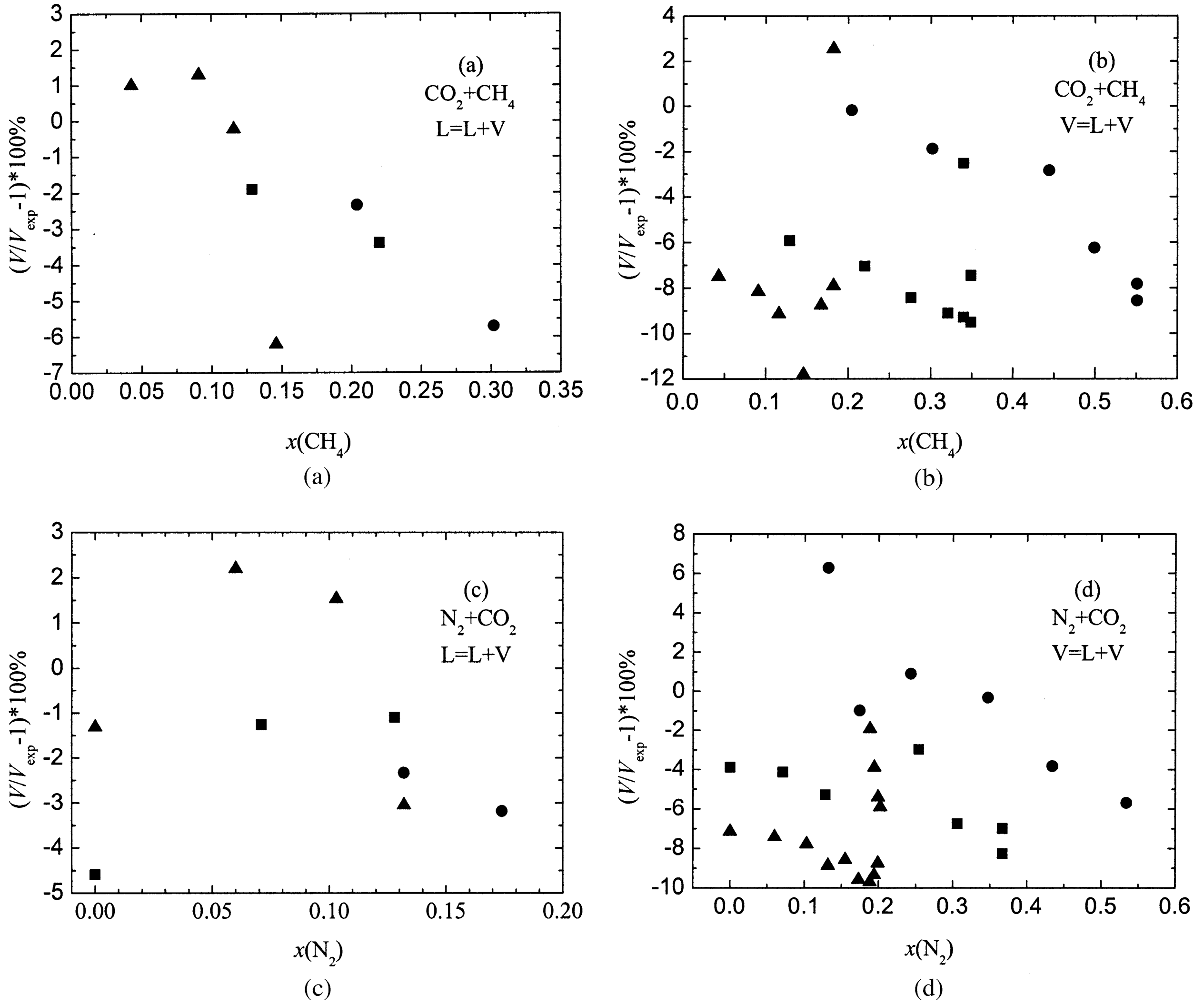
$$-\ln\left(1 - \frac{b_{1\mathrm{m}}}{V}\right) + \frac{b_{1i}}{V - b_{1\mathrm{m}}} - \frac{A_{\mathrm{m}}}{RT}\left[\frac{b_{2i}}{(V - b_{2\mathrm{m}})} - \frac{b_{1i}}{(V - b_{1\mathrm{m}})}\right]$$

$$+\frac{A_i^*}{RT}\ln\frac{(V - b_{2\mathrm{m}})}{(V - b_{1\mathrm{m}})} + \frac{C_{\mathrm{m}}b_{1i}}{RT(V - b_{1\mathrm{m}})^2} + \frac{C_i^*}{RT(V - b_{1\mathrm{m}})} \tag{18}$$

$$A_i^* = \left[\frac{\partial(nA_{\mathrm{m}})}{\partial n_i}\right]_{T,nV,n_j} = -\frac{2\sum_j x_j a_{ij}}{b_{1\mathrm{m}} - b_{2\mathrm{m}}} - \frac{3\sum_j\sum_k x_j x_k c_{ijk}}{(b_{1\mathrm{m}} - b_{2\mathrm{m}})^2}$$

$$+\frac{a_{\mathrm{m}}(b_{1i} - b_{2i})}{(b_{1\mathrm{m}} - b_{2\mathrm{m}})^2} + \frac{2c_{\mathrm{m}}(b_{1i} - b_{2i})}{(b_{1\mathrm{m}} - b_{2\mathrm{m}})^3} \tag{19}$$

$$C_i^* = \left[\frac{\partial(nC_{\mathrm{m}})}{\partial n_i}\right]_{T,nV,n_j} = \frac{3\sum_j\sum_k x_j x_k c_{ijk}}{b_{1\mathrm{m}} - b_{2\mathrm{m}}} - \frac{c_{\mathrm{m}}(b_{1i} - b_{2i})}{(b_{1\mathrm{m}} - b_{2\mathrm{m}})^2} \tag{20}$$



(a) (b) (c) (d)

Fig. 12. The deviation of the equation of state of this study from the experimental volume in the non-critical region of mixtures. **dot:** 253.15K; **solid square:** 273.15K; **solid triangle:** 288.15K. The experimental data used are from Arai (1971).

$$A_m = -\left[\frac{a_m}{(b_{1m} - b_{2m})} + \frac{c_m}{(b_{1m} - b_{2m})^2}\right] \tag{21}$$

$$C_m = \frac{c_m}{(b_{1m} - b_{2m})} \tag{22}$$

where n is the total number of moles of the components in a mixture, nV is the total volume of the mixture, the intermediate variables A_i^*, C_i^*, A_m and C_m are defined for convenience.

Like the studies of many others in the past, this work also finds that the interaction parameters play a very important role in the binary phase equilibria. We evaluated the interaction parameters of some binary systems from experimental liquid-vapor equilibrium data, which are listed in Table 8. It should be mentioned that the interaction parameters in the new equation show little temperature dependence, so we can treat them as temperature-independent, and the parameterization does not need many experimental points.

Figures 2 to 11 are some binary vapor-liquid equilibrium diagrams at constant temperatures. They were calculated as follows: (1) At the given a T and P, compute the $\alpha_i(T)$, $a_i(T)$ and saturated pressure (p_i^S) of every component in the given mixture; (2) Estimate the liquid composition on the assumption that p and p_i^S approximately follows Raoult's law ($p = \sum_i x_i p_i^S$), and then estimate the partial pressures of components and vapor composition; (3) Calculate the total composition of the mixture from the liquid and vapor compositions; (4) Use the known compositions to calculate the parameters in the mixture EOS according to the mixing rule, and to calculate the parameters in Eqn. 18 according to Eqns. (19)–(22); (5) Compute the liquid and vapor volumes at the T and P, then compute the fugacity coefficient and fugacity of every component in vapor and liquid (Φ_i^L and Φ_i^V, f_i^L and f_i^V); (6) If $|f_1^L/f_1^V-1| + |f_2^L/f_2^V-1|$ is within the range of the allowable deviations, the liquid and vapor compositions and volumes are recorded as the equilibrium properties at the given T and P, otherwise, use Eqns. (12) and (13) of Michelsen (1993) to calculate the component equilibrium factors and vapor fraction, respectively, then use Eqn. 11 of Michelsen (1993) to calculate the liquid and vapor compositions; (7) Repeat (4) to (6). Repeat (4) and (6) until the condition in (6) is satisfied. Note that if $T > T_{Ci}$, the p_i^s in step (2) will not exist any longer, and it should be replaced with a properly estimated pressure. Figures 2 to 11 include some typical types of binary vapor-liquid equilibria, where the calculations are in good agreements with experiments. A program (supported by Turbo PASCAL 6.0) for the calculation of the equilibrium properties of these binary mixtures and the 22 pure fluids in Table 4 is available as an electronic annex (EA1) on the website page of Geochimica et Cosmochimica Acta (http://gca.wustl.edu/information/manform.html#3.16).

As mentioned earlier, cubic equations of state are generally considered poor in volumetric calculations, so Thiery et al. (1994) have to use a virial type EOS, Lee-Kesler (1975) EOS or LK, to calculate the volumetric properties for CO_2-N_2 and CO_2-CH_4 systems. As shown by Figure 12, the new EOS of this study has about the same accuracy as LK (See Fig. 5 of Thiery et al., 1994).

5. CONCLUSIONS

There have been numerous cubic equations of state proposed for fluids. However, few of them can give a satisfactory description of both the volumetric properties and the vapor pressures in the whole vapor-liquid coexistence region. For this reason, we proposed a new cubic equation of state with only one empirical constant for each pure fluid in addition to the critical properties. According to the calculation of the liquid-vapor equilibria of 22 fluids, the new equation is superior to the most competitive cubic EOS (including PRSV, PT, ALS, JT and NM equation) in vapor pressures. At the reduced temperatures of $T_r \leq 0.95$, the new equation is also superior to most of them for volumetric predictions, except for PT, which uses two specific parameters and a temperature segment function for pseudocritical compressibility factor in the correlation. With a simple mixing rule, the new EOS can be easily extended to binaries, including aqueous systems. The liquid-vapor phase equilibria of binary mixtures are remarkably predicted with very good accuracy. In the prediction of the volumetric properties of a binary mixture ($T_{C1} < T_{C2}$), the new equation is more accurate at $T < T_{C1}$ than in the range $T_{C1} < T < T_{C2}$.

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