An improved method to evaluate the solubility of several gases in polar and non-polar solvents

by Alessandro Vetere

Some modifications of a previous method of the author which predicts the solubility of several gases in polar and non-polar solvents are proposed. The main assumptions of the method are maintained, as the use of the NRTL equation and the symmetric convention for the activity coefficients of supercritical components, but a better reliabilty and wider generality are obtained by assuming a constant value for the molar volume of the supercritical component in the reference state. Thanks to this choice it is possible to calculate the pseudo-fugacity of a supercritical gas through an Antoine equation and to improve the coherence of the method. The NRTL binary constants are still evaluated through simple generalized correlations which link these parameters to the pure components properties expressed by the Hildebrand solubility parameter and the molar volume. As a rule, the calculation of the solubility of a gas in a whatever solvent requires only two sets of relations for polar and non polar mixtures, respectively. The method is evaluated with respect to the previous on the basis of the prediction of the solubilities of nine gases (H_2, N_2, CH_4, C_2H_4, C_2H_6, C_3H_8, CO, CO_2, H_2S) in both non-polar and polar solvents and in a wide range of experimental conditions. The possibility of evaluating the solubility of different gases with a same set of relations is also examined.

Recent trends in chemical industry are mainly dictated by the need of a strenous optimization of industrial plants which, however, must obey the contraints imposed by more severe rules against pollution. As a result, many processes dealing with this type of problems have a common point: the separation or the recovery of low volatile components from very complex mixtures. Beside the supercritical extraction, enhanced oil recovery, petroleum refining and coal conversion are noticeable examples of the area in which there is a strong demand of phase equilibria calculations involving also supercritical components. The thermodynamics of the last twenty years has given some bright answers to this difficult problem. The introduction of the equations of state (EOS) method in the field of VLE is surely the most rational and successful approach to the phase equilibrium of supercritical mixtures. The EOS route not only avoids the main difficulty posed by the activity coefficient methods, that is the arbitrariness of the pseudo vapour-pressures of uncondensables, but also it offers a unitary treatment of the non-ideality of both phases at equilibrium. This fact becomes very important when the mixture is near to the critical point. Further, the new mixing rules introduced by Vidal [1-2] lead to the so called EOS/G^e models in which the excess Gibbs energy relations, as UNIFAC or NRTL, are incorporated in the fugacity coefficient relations. The work by Vidal is a good example of a synergic effect: the flexibility of EOS in dealing with non-ideal liquid mixture is greatly improved and the principle of the group-contribution method (GCM) can be also applied. It is not surprising that the EOS/G^e models, coupled with the GCM, is now the privileged way of correlating or predicting the fluid phase equilibrium of whatever type of mixture. A review of methods and results obtained by following the above quoted route is reported by Fischer and Gmehling, [3], Apostolu *et al.,* [4] and by Cattè *et al.,* [5]. In spite of the undeniable success

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Table 1 - Empirical constants of the method

Gases	***Solvents***	V_i^{Ref}	***Antoine parameters***			***NRTL constants***
			A	***B***	***C***	
Hydrogen[a]	Non polar	80	6.423	640.567	135.0	$G_{21} = 1.894 - 0.2039\ \Delta\delta_i;\ A + B = 1806 - 1.2 \cdot 10^{-6}\ \Delta\delta_i^{10.0}$
	Polar	80				$A + B = Rv^{0.4}\{-6479 + 4068\ \Delta\delta^{0.4}\}\ G_{21} = 0.754 - 0.0235\ \Delta\delta^{0.97}$
Nitrogen[a]	Non polar	60	6.887	557.357	15.0	$G_{21} = 1.20 - 0.095\ \Delta\delta_i + 0.0025\ Rv^{3.5};\ A + B = Rv^{1.1}\{11.40 + 29.7\ \Delta\delta_i^{3.5}\}$
	Polar	60				$A + B = (1/Rv)^{0.5}\{-1707 + 1891\ \Delta\delta_i^{0.3}\}\ B = A \cdot \{0.86 + 0.0385\ \Delta\delta_i\}$
Oxygen	Non polar	70	6.856	761.076	60.0	$A = 52.5\ \Delta\delta_i\ ;\ A + B = 70 + 153\ \Delta\delta_i$
	Polar	70				$A = 200 \quad A + B = 253.0 + 129.4 \cdot \Delta\delta_i$
Methane[a]	Non polar	70	7.094	832.713	25.0	$G_{21} = 1.332 - 0.0526\ \Delta\delta_i;\ A + B = Rv^{1.4}\{4.0 + 204.94\ \Delta\delta_i^{0.9} - 95.81\ Rv\}$ (paraffins) $G_{21} = 1.232 - 0.0526\ \Delta\delta_i;\ A + B = Rv^{0.5}\{140\ \Delta\delta_i^{1.5} + 7.8\ Rv\}$ (unsaturated hydrocarbons)
	Polar	70				$G_{12} = 0.975 - 0.05\ \Delta\delta_i;\ A + B = -1090 + 1.667\ \Delta\delta_i^3 + 2050\ Rv$
Ethane[a]	Non polar	100	7.129	1043.005	20.0	$G_{21} = 1.0;\ G_{12} = (1/Rv)^{0.1}\{1 - 0.048\ \Delta\delta_i^{1.5} + 0.045\ Rv\}$ $G_{12} = 1.015 - 0.0127\ \Delta\delta_i;\ A + B = Rv^{1.9}\{2355 + 80.91\ \Delta\delta_i^{1.8} - 3352\ Rv\}$ (slightly polar solvents)
	Polar	100				$G_{12} = 0.65;\ G_{21} = Rv\{1.04 - 0.00611\ \Delta\delta_i^{1.6} + 0.021\ Rv\}$ (alcohols)
Ethylene[a]	Non polar	100	6.939	1099.36	20.0	$G_{21} = 1.15;\ G_{12} = 0.85 - 0.0255\ \Delta\delta_i^{1.7} - 0.0323\ Rv$ (for both non polar on slightly polar solvents)
	Polar	100				
Propane[a]	Non polar	140	6.976	1487.456	20.0	$G_{21} = 1.0;\ G_{12} = 0.99 - 0.053\ \Delta\delta_i + 0.02\ Rv$ (for both polar and non polar solvents)
	Polar	140				
Carbon monoxide	Non polar	70	6.871	676.160	40.0	$G_{12} = (1/Rv)^{0.3}\{1.505 - 0.07\ \Delta\delta^{1.5} - 0.1853\ Rv\};$ $G_{21} = 2 - G_{12} - Rv^{0.3}\{0.043 + 0.059\ \Delta\delta_i^{1.5}\}$
	Polar	70				no experimental data
Carbon dioxide	Non polar	80	7.092	1095.280	15.0	$G_{21} = 1.0;\ A + B = Rv^{0.5}\{-243 + 590\ \Delta\delta^{-0.5}\}$ for saturated hydrocarbons $G_{21}=;\ G_{12}=0.965-0.0938\ Dd_i$ for unsaturated hydrocarbons
	Polar	60	7.680	1217.895	5.0	$G_{12} = 0.625 - 0.07\ \Delta\delta^{0.6} + 0.376\ Rv;\ G_{21} = 2.31 - 0.0537\ \Delta\delta^{1.2} - G_{12}$
Hydrogen Sulfide	Non polar	80	7.319	1362.038	20.0	$G_{21} = 1.0;\ G_{12} = 1.018 - 0.0883\ \Delta\delta_i^{0.1}$
	Polar	80				$A + B = Rv\{-76.5 + 70.6\ \Delta\delta_i - 7.45 \cdot 10^{-5}\ \Delta\delta_i^7\}\ B = 1.5\ A$

[a] *d_2 of non polar solvents calculated by using eqn (3)*

of the EOS methods, the work proposed in this paper is not in the mainstream of current researches. Instead, an attempt has been made to improve a previous work [6] that describes the VLE of mixtures containing supercritical components according to the same rules applied to the subcritical systems. The aim is that of increasing the reliability and the field of application of the method by pushing further the analogy between a gas compressed to a liquid-like density and a subcritical component. Accordingly, it is saved not only the formalism of usual VLE calculations based on the activity coefficient method but also the use of the same empirical relations, as the Antoine equation for calculating the pseudo-fugacity of gases and the NRTL equation for calculating the activity coefficients of solutes. The prediction of VLE of mixtures containing supercritical gases is feasible according to the same methodology previously proposed but with a simplified set of empirical relations which cover all the corpus of literature experimental data.

The proposed method

In this work we retain the main assumptions of the previous method [6], namely the symmetric convention for the activity coefficients of uncondensable also, expressed as $g_i=1$, when $x_i=1$, and an arbitrary reference molar volume, V_i^{ref}, for supercritical gases. This latter datum characterises the pseudo-liquid behaviour of fluids compressed above their critical temperature. The choice of V_i^{ref} is of paramount importance, since it rules the values of the pseudo vapour-pressure of a supercritical gas from which the corresponding fugacity, $(f_i^\circ)^{P=0}$, is then calculated according to the Redlich-Kwong equation by fixing the temperature and a zero reference pressure. As a result, all the quantities that appear in the fundamental relation describing the VLE of subcritical mixtures

$$P_t y_i \varphi_i = \gamma_i x_i \left(f_i^\circ\right)^{P=0} \exp\left(P_t \overline{V}_i / RT\right) \tag{1}$$

are also defined for uncondensable, provided that V_i^{ref} substitutes V_i (note that the partial molar volumes are disregarded in the Poynting term, as previously discussed [6]). Previously, the value of V_i^{ref} was assumed to be constant for some gases (as N_2, O_2, C_2H_4, C_2H_6, C_3H_8) and varying with temperature as $V_i^{ref} = a_1 + b_1 T(K)$ for other gases (H_2, CH_4, CO, CO_2 and H_2S). In this work we assume a value of V_i^{ref} independent of temperature for all the ten gases considered. This step is essential in order to represent the fugacity of compressed gases, considered as pseudo-liquids, with the same relations used to calculate the vapour-pressure of subcritical components.

From the results reported in this work it was found that $(f_i^\circ)^{P=0}$ varies with temperature for each gas in the supercritical range according to an Antoine equation, being:

$$(f_i^\circ)^{P=0}=\exp[a-b/(c+T(K))] \tag{2}$$

The values of Antoine constants are reported in Table 1 for ten gases along with the corresponding reference molar volumes. It must be stressed that the relation (2) correlates the $(f_i^\circ)^{P=0}$ data calculated according to the previous more complex two steps procedure with an AAD% of 0.1-0.5. With the use of Equations (1)-(2) the attempt of extending to the supercritical components the same methodology used in the VLE calculations for the subcritical components is fully realised also from a formal point of view.

A second modification proposed in this work touches another important point. The V_i^{ref} datum defines not only the fugacity of the supercritical component but also the solubility parameter, δ_i, being:

$$[\delta_i]_{gas}=[\delta_i]_b V_b / V_i^{ref} \tag{3}$$

while the corresponding δ_i of subcritical components is calculated with the usual methods. It was empirically found that for mixtures of non-polar gases in non-polar solvents appreciably better results are obtained in some cases if Equation (3) is applied for the solvent also, provided that V_i^{ref} is taken equal to molar volume of the liquid compound at the considered temperature. Apart from these modifications, the predictive method proposed in this work follows the same methodology proposed in previous papers [6]-[7], based on the fundamental assumption that the two energetic terms of the NRTL equation:

$$\tau_{ij}=(g_{ij}-g_{jj})/RT=A/RT \tag{4}$$

$$\tau_{ji}=(g_{ij}-g_{ii})/RT=B/RT \tag{5}$$

and the absolute difference between the solubility parameters of solutes and solvents are both significant parameters to evaluate the non-ideality of a mixture, so that they can be linked according to relation of the type:

$$A+B=a+b(\delta_i-\delta_j)_{abs} \tag{6}$$

In some instance, it is more useful to evaluate directly the NRTL binary parameters defined as:

$$G_{ij}=\exp(-\alpha_{ij}\tau_{ij}) \tag{7}$$

$$G_{ji}=\exp(-\alpha_{ji}\tau_{ji}) \tag{8}$$

according to a relation of the above type:

$$G_{ij}+G_{ji}=a+b(\delta_i-\delta_j)_{abs} \tag{9}$$

Relations (6) and (9) are valid to evaluate also the single energetic terms (A or B) or the single NRTL constants (G_{ij} or G_{ji}). However, very often better results are obtained by introducing in Equations (6) or (9) a corrective term which is function of the ratio between the molar volume of the solvent, V_l, and the molar volume of the supercritical component, V_i^{ref}. Conclusively, if we pose $\alpha_{ij}=0.3$, each binary system containing supercritical gases is defined by two simple relations which relate the binary NRTL constants to the Hildebrand solubility parameters and to the molar volume ratio, Rv. In turn, the VLE data of a supercritical gas in any solvent can be predicted by using two or three sets of relations, depending on the polarity degree of the solution. Usually, the experimental data pertaining to a supercritical solute are subdivided in three families, according to the nature of the solvent: saturated hydrocarbons, unsaturated hydrocarbons, polar compounds. Each of these families deserves an *ad hoc* set of generalised relations. The aims of this work are:

i) to improve the standardisation of the predictive method by using always a same, simple, procedure which avoids the cumbersome trial and error calculations required in some instances by the previous method;

ii) to reduce the set of empirical relations by grouping in the same sub-class, when possible, saturated and insaturated hydrocarbons;

iii) to enlarge the fied of applicability of the method to systems containing high molecular weight solvents.

Experimental data processed and relations applied

The proposed method was tested on the basis of the same experimental data of nine gases, studied in the previous work [6]: H_2, N_2, O_2, CH_4, C_2H_4, C_2H_6, C_3H_8, CO, CO_2, H_2S in mixture with both polar and non polar solvents. Only the data of the O_2 /solvent systems are here disregarded, since the previous method fulfils for these mixtures both the requirements invoked in this work: a fixed value for V_i^{ref} and simple relations to calculate the binary NRTL constants. The literature data processed are reported elsewhere [6]. It must be stressed that the experimental conditions investigated covers both the high and low pressure range, this latter being peculiar of the systems constituted by non polar gases dissolved in very polar solvents, as water. Some data pertain to the subcritical range also.

As an example: the equilibrium pressure varies between 0.7-137.9 bar for the system nitrogen/methane and between 100-800 bar for the system carbon dioxide/water (see Table 2). Equally wide is the field of temperatures: the isotherm of the hydrogen/carbon monoxide system is determined at 100 K and that of the carbon dioxide/*n*-decane system at 510.9 K (see Table 3). The calculation of the pure component properties closely follows the procedures reported previously [6]. The critical constants and the vapor pressure data of the pure subcritical components required by the application of the method were taken from Reid *et*

Table 2 - VLE predictions of six non polar gases in several solvents

Solvent	*T (K)*	R_V	$(f_i^{\circ})^{P=0}$	$(\delta_1-\delta_2)_{abs}$	G_{12}	G_{21}	$\Delta P\%$	$100\ \Delta Y$	*Pressure Range (bar)*
Hydrogen									
Ethane	148.2	0.648	64.12	7.26	0.6297	0.4141	3.79	0.50	20.3 - 81.1
Ethane	223.2	0.772	102.97	5.95	0.4536	0.6798	3.57	0.53	20.3 - 81.1
Propylene	297.1	1.001	139.8	5.57	0.5365	0.7576	7.70	2.33	17.3 - 551.2
Propylene	199.9	0.794	90.9	7.24	0.8789	0.4170	20.16	0.11	17.3 - 551.2
n-Butane	377.6	1.573	176.5	4.55	0.5041	0.9653	4.04	2.04	28.3 - 167.4
Carbon Monoxide	100.0	0.506	40.3	4.18	0.6584	0.6544	0.69	1.25	21.7 - 137.9
Carbon Dioxide	259.9	0.549	121.6	6.40	0.6405	0.6061	1.27	2.12	32.7 - 203.1
Water	278.2	0.205	130.7	24.23	0.4243	0.2296	0.61	0.13	1.013
Nitrogen									
Methane	138.5	0.701	25.92	2.72	0.8360	0.9422	1.33	0.26	6.0 - 38.6
Methane	183.2	1.122	58.8	0.868	0.8681	1.1218	2.86	0.88	36.5 - 48.5
Propane	173.2	1.159	50.6	4.64	0.4210	0.7631	2.89	0.33	0.7 - 137.9
Propane	343.2	1.837	206.6	1.68	0.8556	1.0608	4.97	2.85	25.5 - 82.7
n-Decane	310.9	3.179	177.1	3.93	0.2804	0.9699	2.77	0.26	34.5 - 344.7
n-Decane	410.9	3.589	264.7	3.10	0.4639	1.1248	10.99	0.25	172.4 - 344.7
Benzene	348.2	1.582	211.1	5.04	0.5209	0.7339	4.78	0.35	62.1 - 302.6
Benzene	398.2	1.701	254.2	4.45	0.6371	0.7933	6.02	0.74	64.4 - 307.1
Sulfur Dioxide	241.1	0.712	111.1	8.26	0.5284	0.4775	14.35	0.22	18.1 - 35.5
Sulfur Dioxide	301.5	0.793	168.3	6.68	0.6411	0.6214	2.50	0.77	15.5 - 35.5
Ammonia	277.6	0.432	145.8	9.82	0.4709	0.3911	6.88	3.21	5.1 - 413.7
Ammonia	377.6	0.618	236.8	4.14	0.7308	0.7478	6.81	3.78	68.2 - 172.4
Methane									
Propane	213.7	1.063	36.8	3.83	0.5628	1.1303	2.51	0.25	1.87 - 63.9
n-Butane	294.3	1.426	88.7	3.13	0.5914	1.1668	8.49	1.18	2.76 - 68.9
n-Pentane	310.9	1.635	101.0	3.30	0.5605	1.1581	4.06	2.07	1.4 - 137.9
n-Hexane	310.9	1.883	101.0	3.37	0.5190	1.1545	3.16	0.08	43.5 - 17.2
n-Octane	273.2	2.261	73.8	3.77	0.3951	1.1334	6.47	0.03	10.1 - 70.9
n-Decane	444.3	3.233	204.3	2.47	0.6314	1.2015	8.72	0.59	1.4 - 170.1
Cyclohexane	310.9	1.561	101.0	4.23	0.4695	1.0089	1.11	0.53	13.8 - 172.4
Benzene	338.7	1.339	122.1	4.83	0.4725	0.9774	1.58	0.96	6.9 - 103.4
Toluene	422.5	1.764	187.4	3.74	0.5939	1.0351	1.93	1.03	20.2 - 202.7
m-Xylene	460.8	2.125	217.0	3.34	0.6244	1.0558	7.15	1.79	20.7 - 201.9
Methanol	298.2	0.518	91.6	11.66	0.3918	0.6779	0.50	1.35	1.2
Ethanol	298.2	0.773	91.6	9.75	0.4876	0.7302	1.97	0.44	40.0 - 236.4
Ethanol	448.2	1.065	207.3	5.07	0.7215	0.8911	4.48	2.54	67.7 - 115.6
Acetone	298.2	0.945	91.6	6.49	0.6506	0.7947	5.31	4.67	1.3

al., [8]. The molar volumes of solvents were calculated by applying the Rackett equation, while the vaporisation enthalpies required to calculate the Hildebrand solubility parameters are reported at the normal boiling temperatures by Zwolinski and Wilhoit, [9] and by Majer and Svoboda, [10]. These data were extrapolated to the experimental temperature by using the Watson relation.

The deviations from ideality of gas phase, expressed by the fugacity coefficient φi, were calculated by applying the Redlich-Kwong equation to both pure components and mixtures. Looking at the panorama of Table 1, which reports the relations used to calculate the NRTL constants for several classes of mixtures, the standardization program appears to be realized. The main procedure is represented by a couple of relations of the type:

$$G_{21}(\text{or } G_{12})=f(Rv,\Delta\delta) \tag{10}$$

and

$$A+B=f(Rv, \Delta\delta) \tag{11}$$

from which the other NRTL binary constant, G_{12} or G_{21}, can be easily derived. Some alternative methods rely on the following relations:

$$A=f(\Delta\delta) \tag{12}$$

and

$$G_{21}=\text{constant} \tag{13}$$

The reference molar volume, V_i^{ref}, of each gas is always a constant independent of temperature. This value is equal for both polar and non polar systems, with CO_2 the only exception. As a rule, all types of hydrocarbons pertain to the same class of solvents so that the same relations hold for the VLE prediction of a supercritical gas in any non-polar solvents. Only methane requires different rules for saturat-

Table 2 - (2nd part)

Solvent	*T (K)*	*R_V*	*$(f_i^\circ)^{P=0}$*	*$(\delta_1-\delta_2)_{abs}$*	*G_{12}*	*G_{21}*	*$\Delta P\%$*	*$100\ \Delta Y$*	*Pressure Range (bar)*
Ethane									
n-Butane	338.7	1.106	39.0	1.94	0.9110	1.0	3.09	1.24	35.4 - 55.5
n-Butane	394.3	1.364	62.1	0.78	0.9968	1.0	1.66	2.16	32.4 - 50.3
n-Decane	377.6	2.060	54.7	2.55	0.8342	1.0	7.52	0.17	6.9 - 55.2
n-Decane	444.3	2.263	85.8	1.95	0.8952	1.0	2.57	0.48	6.9 - 89.6
Cyclohexane	333.2	1.123	36.9	3.49	0.7287	1.0	6.86	1.07	0.5 - 41.4
Cyclohexane	466.5	1.417	96.9	1.90	0.9062	1.0	3.89	1.94	13.8 - 55.2
Benzene	353.2	0.956	44.6	4.15	0.6405	1.0	0.61	0.32	20.7 - 48.3
Benzene	513.2	1.334	121.2	1.78	0.9192	1.0	2.74	1.79	27.6 - 68.9
Hydrogen Sulfide	357.9	0.587	46.5	0.17	0.9913	0.95	0.38	0.87	68.9 - 82.7
Ethylether	298.2	1.065	25.1	5.10	0.8843	0.95	3.44	0.61	9.6 - 38.6
Methylacetate	298.2	0.818	25.1	7.00	0.4758	0.95	3.57	0.26	4.8 - 38.5
Acetone	298.2*	0.696	25.1	7.59	0.4745	0.95	5.91	0.42	4.8 - 39.4
Methanol	373.2	0.415	8.78	52.8	0.65	0.7796	25.92	2.25	3.5 - 60.0
Methanol	298.2*	0.382	25.1	12.77	0.65	0.6251	2.34	0.04	10.0 - 30.0
Ethanol	298.2*	0.569	25.1	10.85	0.65	0.7322	8.50	0.40	4.8 - 39.0
Ethanol	448.2	0.746	87.7	4.53	0.65	0.9586	7.25	6.26	34.6 - 87.0
Water	298.2*	0.176	25.1	21.95	0.65	0.1578	3.18	0.07	1.013
Ethylene									
Acetylene	252.95*	0.751	19.0	3.17	0.7074	1.15	4.25	0.70	26.7 - 27.2
n-Heptane	333.2	1.541	45.9	3.11	0.6245	1.15	5.62	0.87	6.9 - 68.9
n-Heptane	433.2	1.835	91.2	2.02	0.7068	1.15	6.25	1.31	6.9 - 82.7
n-Decane	353.1	1.999	54.2	3.21	0.6002	1.15	3.48	3.60	20.2 - 40.5
Benzene	348.1	0.949	52.1	4.66	0.4710	1.15	10.54	0.85	15.2 - 91.2
Carbon Dioxide	293.2	0.561	30.8	0.64	0.8200	1.15	4.50	1.11	57.1 - 64.9
Carbon Dioxide	253.0*	0.644	18.4	2.96	0.6675	1.15	4.52	2.12	0.06 - 25.8
Propane									
n-Butane	393.2	0.968	29.2	0.03	1.0076	1.0	3.18	1.73	22.4 - 40.7
n-Butane	413.2	1.126	34.5	0.33	0.9949	1.0	1.52	0.56	31.3 - 37.9
n-Hexane	413.2	1.145	34.5	1.82	0.9164	1.0	3.27	1.22	17.2 - 48.3
n-Decane	410.9	1.538	33.9	2.48	0.8892	1.0	6.17	0.85	3.4 - 60.2
n-Decane	510.9	1.832	65.0	1.45	0.9500	1.0	2.17	0.94	6.9 - 55.2
Benzene	410.9	0.744	33.9	3.67	0.8101	1.0	7.26	1.05	5.5 - 48.3
Benzene	477.6	0.854	53.9	2.69	0.8644	1.0	4.23	2.17	13.3 - 58.6
Ethanol	400.0	0.466	31.0	6.61	0.6492	1.0	3.49	2.75	6.9 - 48.3
Ethanol	450.0	0.536	45.2	4.66	0.7536	1.0	8.17	6.03	20.7 - 55.2
Hydrogen Sulfide	327.6*	0.481	13.87	1.93	0.8975	1.0	1.99	0.13	20.7 - 27.6

** Subcritical temperature*

ed and unsaturated hydrocarbons. In the case of ethylene, the same relations hold for both non-polar and slightly polar solvents. Surprisingly enough, the solubility of propane in both non polar and strongly polar solvents can be evaluated by using a same couple of relations.

Results

The results obtained by applying the proposed predictive method are reported in Tables 2-3 along with the relevant empirical parameters used and experimental range investigated. The reliability of prediction is evaluated through the average absolute % deviation (AAD%) of calculated pressures and vapour phase compositions from the experimental data. An overall comparison with the previous method is given in Table 4.
Here the new method performances are briefly commented for each of the nine examined systems taking as reference the results obtained with the old method.

Systems with hydrogen

The new method appears superior in predicting the solubility of hydrogen in polar solvents, while the only advantage offered by applying it to non-polar systems is the possibility of dealing also with high molecular weight solvents, as *n*-decane, to which the old method cannot be applied. However, it must be stressed that even the correlation of these systems with an EOS is difficult (see, for example, the results reported by Knapp *et al.,* [11] for some well known EOS).

Systems with nitrogen

The gain in reliability is limited to the predictions of non polar systems which is due, perhaps, to the application of relation [3] also for the sub-critical component.
Relevant errors are still found for some polar systems, which can be only partly justified on the basis of the low solubility limits of nitrogen.

Systems with methane

The most relevant improvement given by the new procedures is found for these mixtures, since the trial and error method of calculation for methane in non polar solvents and the complex rules to calculate V_i^{ref} are avoided. However, two correlations are still required to calculate the solubility of methane in saturated and unsaturated hydrocarbons, respectively. The gain in accuracy is also appreciable for both polar and non-polar mixtures.

Mixtures with ethane

Although it is still assumed a same constant value (V_i^{ref}=100) for the reference gas volume, the new method enables the prediction of the ethane solubility in both saturated and unsaturated hydrocarbons with a same couple of relations. In-

Table 3 - VLE predictions of three polar gases in several polar and non-polar solvents

Solvent	*T (K)*	R_V	$(f_i^\circ)^{P=0}$	$(\delta_1\text{-}\delta_2)_{abs}$	G_{12}	G_{21}	*ΔP%*	*100 ΔY*	*Pressure Range (bar)*
Carbon monoxide									
Ethane	248.2	0.961	92.3	2.58	1.0490	0.6664	7.10	7.67	41.4 - 69.0
Propane	148.5	0.958	26.7	5.61	0.4025	0.7811	1.52	0.10	13.8 - 55.2
Propane	273.5	1.207	111.5	3.23	0.8274	0.7653	8.44	2.63	13.8 - 137.9
Propane	323.2	1.420	149.8	1.76	0.9715	0.8283	3.32	1.74	34.5 - 82.7
Carbon dioxide									
Propylene	252.9*	1.664	16.0	0.55	0.8600	1.00	2.88	0.61	3.0 - 17.9
n-Pentane	377.6	1.626	73.8	1.37	0.7955	1.00	4.35	2.76	9.1 - 96.3
Cyclohexane	473.2	1.015	127.4	1.80	0.8602	1.00	1.07	1.82	13.4 - 101.3
Toluene	311.3	1.324	41.9	4.50	0.5695	1.00	5.46	0.15	3.3 - 69.4
Toluene	477.0	1.688	129.7	1.98	0.7856	1.00	6.97	2.33	11.8 - 136.2
Benzene	313.2	1.136	42.7	4.59	0.5917	1.00	7.05	0.30	14.4 - 77.5
Hydrogen sulfide									
Propane	322.0*	2.075	26.2	2.00	0.9234	1.00	7.58	2.60	20.7 - 27.6
n-Pentane	410.9	1.798	64.0	0.07	0.9500	1.00	3.35	2.77	13.8 - 75.8
n-Pentane	444.3	2.104	80.3	1.18	0.9282	1.00	-	-	27.6 - 75.8
n-Decane	344.3*	3.730	36.2	1.73	0.9247	1.00	3.72	0.07	6.9 - 41.4
n-Decane	444.3	2.829	80.3	1.37	0.9268	1.00	5.58	0.62	13.8 - 124.1
Toluene	310.9*	2.314	21.5	1.45	0.9264	1.00	4.96	0.15	2.0 - 21.9
Toluene	477.6	1.690	97.7	1.52	0.9259	1.00	2.11	1.27	13.8 - 101.2
Methanol	298.2*	0.824	16.6	7.39	0.9142	0.8741	6.05	-	1.013
Butanol	298.2*	2.076	16.6	3.33	0.9353	0.8046	12.57	-	1.013
Chlorobenzene	298.2*	2.292	16.6	1.80	0.9767	0.9652	1.10	-	1.013
Ethylenglycol	298.2*	1.267	16.6	8.65	0.8134	0.7336	5.16	-	1.013
Acetic Acid	298.2*	1.034	16.6	6.73	0.9109	0.8694	1.88	-	1.013
Water	443.2	0.249	79.7	15.02	0.6256	0.4948	9.65	2.34	17.2 - 23.4

* *Subcritical temperature*

stead, alcohols still deserve an *ad hoc* correlation. Overall, a relevant improvement in the accuracy is found for both polar and non-polar systems.

Mixtures with ethylene

The new and old method are very similar: a same $V_i^{(ref)}=100$ is adopted and a similar set of relations can be applied to evaluate the solubility of ethylene in both hydrocarbons and CO_2 (the only polar solvent examined due to the scarcity of experimental data). However, the accuracy of the new method is slightly better.

Systems with propane

The new method shares with the old one the capability of predicting the solubility of propane in both non-polar and polar systems with two simple relations for G_{12} and G_{21}, respectively. The results obtained with the new method are, however, appreciably better.

Systems with carbon monoxide

The very few literature data in the supercritical range limits the comparison with the old method to non-polar mixtures. The new method is not superior to the old one for the prediction of solubilities in low molecular hydrocarbons but its range of applicability is wider, since it is reliable also for the CO/C_{10+} paraffins systems for which the previous method gives strongly erroneous results (data is not reported here).

Table 4 - Comparison between two predective methods

	Hydrogen		*Nitrogen*		*Methane*		*Ethane*		*Ethylene*		*Propane*		*Carbon Monoxide*		*Carbon Dioxide*		*Hydrogen Sulfide*	
	ΔP%	*100 ΔY*	*ΔP%*	*100 ΔY*	*ΔP%*	*100 ΔY*	*ΔP%*	*100 ΔY*	*ΔP%*	*100 ΔY*	*ΔP%*	*100 ΔY*	*ΔP%*	*100 ΔY*	*ΔP%*	*100 ΔY*	*ΔP%*	*100 ΔY*
This work	5.26	1.13	5.60	1.16	4.11	1.25	3.71	1.06	5.59	1.51	4.15	1.74	5.10	3.04	4.63	1.33	5.31	1.41
Previous work	7.26	1.69	9.06	1.28	6.86	1.10	6.20	1.02	5.63	1.64	4.59	1.89	5.14	1.51	5.16	1.69	5.29	1.01

Systems with carbon dioxide and hydrogen sulfide

The main advantages offered by the new method are the assumption of a constant value for V_i^{ref} and the calculation of the solubility of CO_2 in both saturated and unsaturated hydrocarbons with the same set of relations. Instead, the CO_2/polar solvent systems must be studied according to the previous rules.

Observations

A striking aspect of the validity of the proposed method is the possibility of predicting the solubility of different gases in hydrocarbons by using a same set of relations to calculate the NRTL binary parameters. As an example, if the equations pertaining to ethane reported in Table 1 to calculate G_{12} and G_{21} are used also for methane and propane, the accuracy of the method is still appreciable. To illustrate, the AAD%, evaluated on the basis of the experimental data of the non polar systems reported in Table 2, increases for calculated pressures as follows: from 4.11% to 10.89% for methane, from 5.59 % to 6.70% for ethylene and from 4.15% to 6.31% for propane. On the contrary, there is no increase of the AAD % for the calculated vapour phase compositions. Of course, polar mixtures represent a more difficult problem, the deviations from the ideal behaviour being greater with respect to mixtures of hydrocarbons.
On the whole, the final goal of an universal method which enables the VLE calculations of systems with supercritical components with only two sets of relations, for polar and non polar systems respectively, is still remote but not impossible. At present, however, we can assume that some modest extrapolations are reasonable. Accordingly, the relations proposed for propane can be confidently used also to predict the VLE of mixtures with propylene, a compound for which very few literature data are reported. In fact, propylene and propane have very similar values for all the thermodynamic properties which characterise their behaviour. Therefore, it is reasonable to assume also the possibility of evaluating the VLE of COS in non polar solvents by using the same relations proposed for CO_2.

Comparison with two methods of literature

A convenient point of reference to evaluate the reliability of the proposed method is a comparison with two well reputed literature predictive methods: the SRK equation equipped with the Kij values reported Reid *et al.,* [8] and the procedure proposed by Skjold-Jørgensen, [12], which is based on a very complex version of the group-contribution method. We report in Table 5 the results obtained for several systems which cover a wide experimental range for both pressure and temperature. The chosen systems represent a severe test, since some isotherms are near to or at the critical temperature of the supercritical compound. Unfortunately, the comparison is limited to the calculated vapour compositions, no data being reported by Skjold-Jorgensen for the calculated pressures. On the whole, the new method appears of comparable accuracy with respect to both literature methods. However, a distinct advantage must be stressed: when the two components have very different molecular weights, as in the case of methane/*n*-heptane system, the molar fraction in vapour phase of the supercritical gas approaches to unity. This value is calculated with a greater accuracy by applying our method (Table 5). The reason appears clear by observing equation (1): when the volatilities are very different, the y_i value is mainly dictated by the ratio of the fugacities, $(f_i^\circ)^{P=0}$, no matter the non-ideality of the system. This constraint is absent in the EOS methods, which evaluate the K values on the basis of the ratio of the fugacity coefficients only.

Nomenclature

a,b and c=constants of equation (2)
A and B=constants of equation (4) and (5), cal mol^{-1}
AAD%=absolute average per cent deviation
$(f_i^\circ)^{P=0}$=fugacity of compound i at zero reference pressure
g^E=molar excess Gibbs energy, cal mol^{-1}
g_{ij}=energy parameter for the i-j interactions, cal mol^{-1}
G_{ij}=binary constant of the NRTL equation
Kij=binary interaction parameter of the SRK equation
K=parameter defined as y/x
p=reference pressure, 10^5 Pa
p_t=equilibrium pressure, 10^5 Pa
ΔP%=absolute percentage error of calculated pressures
R=universal gas constant, cal mol^{-1} K^{-1}
Rv=constant defined as V_2/V_1^{ref}
T=absolute temperature, K
Vi=liquid molar volume of compound i, cm^3 mol^{-1}
$\overline{V}_i$=liquid partial molar volume of compound i, cm^3 mol^{-1}
$V_1^{(ref)}$=reference molar volume of the gaseous component cm^3 mol^{-1}
x_i=molar fraction of compound i in liquid phase
y_i=molar fraction of compound i in vapor phase
Δy=absolute mean deviation of calculated vapor compositions from experimental ones.

Table 5 - Comparison with two literature methods in predicting the K values of the supercritical component[a]

Systems	Experimental range		Expt.	R.S.m. deviation (%)		
	Temperature (K)	Pressure (bar)	Points	SRK[b]	S-J[b]	this work
N_2/CH_4	113-183	1.2-48.5	119	4.5	5.1	3.9
N_2/H_2S	256-344	17-205	57	35.0	11.0	9.9
CH_4/*n*-heptane	200-255	6.9-205	69	17.4	9.4	0.3
CO_2/*n*-pentane	278-378	2.3-95.7	49	7.9	7.6	3.3
CO_2/*n*-heptane	311-477	1.9-132	64	10.3	8.8	4.2
H_2S/*n*-pentane	311-394	1.6-94.9	37	12.2	6.1	3.5

[a] K=y/x [b] Skyold-Jørgensen [12]

Subscripts
1=supercritical gas
2=solvent
b=normal boiling temperature

Greek Letters
α_{ij}=non randomness constant of the NRTL equation
γ_i=activity coefficient of compound i
δ_i=Hildebrand solubility parameter, cal$^{0.5}$ cm$^{-1.5}$
$\Delta\delta_i$=parameter defined as $(\delta_i - \delta_j)_{abs}$, cal$^{0.5}$ cm$^{-1.5}$
τ_{ij}=NRTL energy parameter, defined by equation (3)
τ_{ji}=NRTL energy parameter, defined by equation (4)
φ_i=fugacity coefficient of compounds i in vapor phase

References

[1] J. Vidal, *Chem.Eng.Sci.,* 1978, **33,** 787.
[2] M.J. Huron, J. Vidal, *Fluid Phase Equilibria,* 1979 **3,** 255.
[3] K. Fischer, J. Gmehling, *Fluid Phase Eq.,* 1996, **121,** 185.
[4] D.A. Apostolu, S.N. Kalospiros, D.P. Tassios, *I&EC Res.,* 1995, **34,** 948.
[5] M. Cattè, C. Achard *et al., Ind. Eng. Chem. Res.,* 1993, **32,** 2193.
[6] A. Vetere, *Fluid Phase Eq.,* 1997, **132,** 77.
[7] A. Vetere, *Fluid Phase Eq.,* 1993, **91,** 265.
[8] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids. 4th Ed., McGraw-Hill, New York, 1987.
[9] B.J. Zwolinski, R.C. Wilhoit, Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds, Thermodynamic Research Center,Texas A&M University,College Station, Texas, 1971.
[10] V. Majer, V. Svoboda, Enthalpies of Vaporization of Organic Compounds, Blackwell Scientific Publications, Oxford, 1985.
[11] H. Knapp, R. Doring *et al.,* Dechema data series, vol. VI, Dechema, Frankfurt, 1982.
[12] S. Skjold-Jorgensen, *Fluid Phase Eq.,* 1984,**16,** 317.