

Table V. Effect of the Lennard-Jones Parameters for the Gas on the Description of the Measured Oxygen Solubilities by the Scaled-Particle Theory

$10^{10}\sigma, \text{m}$	$\epsilon/k, \text{K}$	source	mean devn, %
3.460	118.0	ref 9	52.7
3.467	106.7	ref 10	18.8
2.902	73.4	optimization	2.2

advantage of the scaled-particle theory is its applicability to polar solvents.

In the case of hydrogen, the predictions of the scaled-particle theory are very close to the experimental results. It was tried to get a better fit also for oxygen by modification of the gas-specific Lennard-Jones parameters (Table V). If the parameters of Hirschfelder et al. (9) used by Battino and Wilhelm (7) are substituted by those suggested by Reid et al. (10), the mean error of the estimated oxygen solubilities is reduced from 52.7% to 18.8%. Fitting the two parameters to the experimental data but still using the same liquid-specific parameters, the mean error is only 2.2%. This is already close to the experimental error. It is therefore considered to empirically modify the scaled-particle theory by fitting also the gas-specific parameters to a larger set of experimental gas solubilities.

Acknowledgment

We thank Prof. W.-D. Deckwer for helpful discussions.

Glossary

H	Henry's constant, Pa m ³ mol ⁻¹
k	Boltzmann constant, J K ⁻¹
ΔP	pressure change by absorption, Pa
P_0	barometric pressure, Pa
P_L	vapor pressure of liquid, Pa
R	gas constant, J K ⁻¹ mol ⁻¹

T	temperature, K
V_{GL}	gas (liquid) volume, m ³
$x_{1(2)}$	mole fraction of component 1 (2) in binary mixtures

Greek Letters

$\alpha_{1,2}$	expansion factor (eq 2)
ϵ	Lennard-Jones energy, J K ⁻¹
σ	Lennard-Jones distance, m

Registry No. H, 1333-74-0; He, 7440-59-7; N, 7727-37-9; CO, 630-08-0; O, 7782-44-7; CO₂, 124-38-9; acetone, 67-64-1; aniline, 62-53-3; benzene, 71-43-2; 1-butanol, 71-36-3; *n*-butyl acetate, 123-86-4; carbon tetrachloride, 56-23-5; cyclohexane, 110-82-7; decalin, 91-17-8; 1,2-dichloroethane, 107-06-2; 1,4-dioxane, 123-91-1; ethanol, 64-17-5; ethyl acetate, 141-78-6; ethylbenzene, 100-41-4; methanol, 67-56-1; nitrobenzene, 98-95-3; 2-propanol, 67-63-0; 1-tetradecene, 1120-36-1; tetralin, 119-64-2; 1,2,4-trimethylbenzene, 95-63-6; toluene, 108-88-3; *m*-xylene, 108-38-3.

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Representation of Vapor-Liquid Equilibrium Data for Binary Refrigerant Mixtures

Krister Ström, Urban Gren,* and Kjell Ljungkvist

Department of Chemical Engineering Design, Chalmers University of Technology, Göteborg, Sweden

Vapor-liquid measurements were performed on binary refrigerant mixtures by using a Jones circulation unit with circulated vapor phase. Results from the equilibrium measurements on the binary refrigerants CCl₂F₂/C₂Cl₂F₄, CHClF₂/C₂Cl₂F₄, and CHClF₂/CCl₂F₂ in the pressure range 3.50-14.50 bar are presented. Comparisons were made between experimental equilibrium data and theoretically calculated data based on the following equations of state: Soave-Redlich-Kwong, de Santis, and Lee-Kesler-Plöcker. Good agreement was obtained between the modified Redlich-Kwong equation of state by Soave and the Lee-Kesler-Plöcker equation of state. In some cases and within small concentration intervals, the de Santis equation of state was found to give divergences. This may be explained by the uncertainty in the temperature-dependent parameters determined from pressure-volume-temperature data at temperatures near the critical.

Introduction

It is necessary to have relevant experimental data in order to make a comparison possible between different theoretical models that describe vapor-liquid equilibrium properties. An area of increasing interest is that of binary systems of refrigerant mixtures. However, such data have been published only to a very limited extent (1, 2). In the present study isobaric measurements of vapor-liquid equilibrium data were performed for the three systems CCl₂F₂/C₂Cl₂F₄, CHClF₂/C₂Cl₂F₄, and CHClF₂/CCl₂F₂, in the pressure range 3.5-14.5 bar.

Theory

The conditions for equilibrium between the vapor and the liquid phase can be expressed as

$$f_i^V = f_i^L \quad (1)$$

where f_i^V is the fugacity of component i in the vapor phase and f_i^L is the fugacity of component i in the liquid phase.

The fugacity of component i in a mixture is related to the pressure P and the composition z_i by the fugacity coefficient according to

* Author to whom correspondence should be addressed.

$$f_i = \phi_i z_i P \quad (2)$$

The fugacity coefficient is a function of pressure, temperature, and composition. The pressure and volume explicit expressions for the fugacity coefficient are respectively

$$\ln \phi_i = \frac{1}{RT} \int_0^P \left(v_i - \frac{RT}{P} \right) dP \quad (3)$$

$$\ln \phi_i = \frac{1}{RT} \int_v^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{T,v,n_j} - \frac{RT}{v} \right) dv - \ln Z \quad (4)$$

To solve the integrals, an equation of state is required in order to determine v_i and $(\partial P / \partial n_i)_{T,v,n_j}$.

Equations of State. The equation of state proposed by Redlich-Kwong (3) is considered a good equation of state for the calculation of volumetric and thermal properties of pure compounds and mixtures. The Redlich-Kwong equation does not, however, give as good results for the calculations of vapor-liquid equilibria, which is due to the relatively small temperature dependence of the parameters in the equation of state. The original form of the Redlich-Kwong equation of state is

$$P = \frac{RT}{v-b} - \frac{a/T^{0.5}}{v(v+b)} \quad (5)$$

where the constants a and b can be expressed as

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{P_c} \quad (6a)$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad (6b)$$

The parameter $a/T^{0.5}$ in the Redlich-Kwong equation was modified by Soave (4) in order to increase the influence of the temperature. The parameter, $a(T)$, was correlated to vapor pressure data by Soave who found a more appropriate form to be

$$a(T) = a_c (1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - T_r^{0.5})) \quad (7)$$

The constants a_c and b can be calculated in the same way as in the original Redlich-Kwong equation.

These two types of equations of state are composed of two terms. The first term gives the contribution of the repulsion forces, and the second term gives that of the attraction forces. This can be expressed more generally in terms of compressibility, according to

$$Z = Z_r - Z_a \quad (8)$$

As a term for the repulsion forces, de Santis et al. (5) made use of an expression developed by Carnahan and Starling (6) for the repulsion forces of a so-called hard-sphere fluid. Expressed in terms of compressibility, this can be written

$$Z_r = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \quad (9)$$

where $y = b/4v$. As a term for the attraction forces they chose the same as in the original Redlich-Kwong equation. The equation of state can thus be written

$$Z = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(v + b)} \quad (10)$$

The parameters a and b have been determined from published pressure-volume-temperature data (7); see Figure 1. They were calculated for pure components by fitting a and b to the

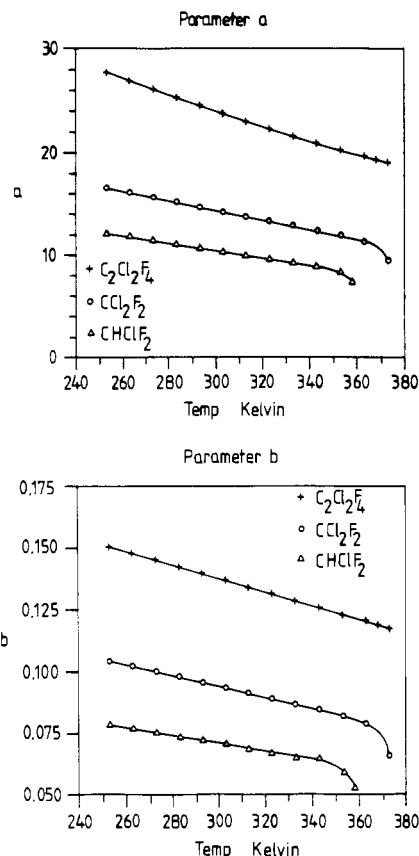


Figure 1. Parameters a and b in the de Santis equation of state.

equation of state (10) at saturated liquid conditions subject to the equilibrium conditions expressed by equating the Gibbs free energy using the equation of state for both the saturated liquid and vapor, setting a tolerance of 0.000 01 maximum.

To use the equations of state mentioned above for mixtures, mixing rules are required for the determination of the parameters involved. The parameters can be calculated from the following expressions.

$$a_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij} \quad (11)$$

$$b_m = \sum_{i=1}^n x_i b_i \quad (12)$$

The cross coefficient, a_{ij} , can be determined from

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{0.5} \quad (13)$$

where k_{ij} is the interaction parameter.

The equation of state according to Lee-Kesler (8) was developed from an equation of state analogous to the three-parameter correlation of Pitzer (9).

$$Z = Z^{(0)} - \frac{\omega}{\omega^{(r)}} (Z^{(r)} - Z^{(0)}) \quad (14)$$

Here the compressibility Z is expressed by using the compressibility $Z^{(0)}$ of a simple fluid and the compressibility $Z^{(r)}$ of a reference fluid. The compressibilities $Z^{(0)}$ and $Z^{(r)}$ can be calculated by a modified Benedict-Webb-Rubin equation (10) according to

$$Z = \left(\frac{P_r v_r}{T_r} \right) = 1 + \frac{B}{v_r} + \frac{C}{v_r^2} + \frac{D}{v_r^5} + \frac{c_4}{T_r^3 v_r^2} \left(\beta + \frac{\gamma}{v_r^2} \right) \exp \left(-\frac{\gamma}{v_r^2} \right) \quad (15)$$

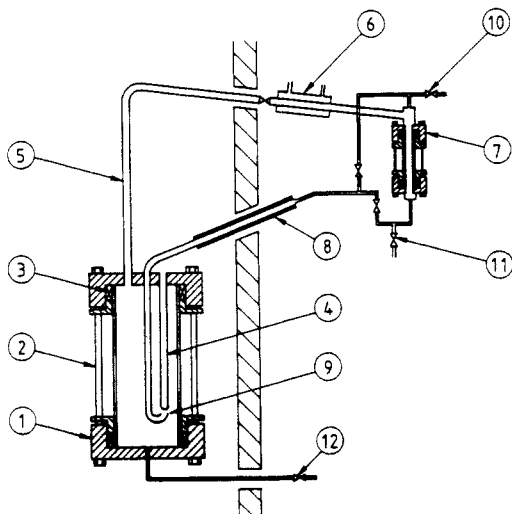


Figure 2. Experimental equipment: Jones circulation unit.

The constants B , C , D , c_4 , β , and γ are universal constants, with one set for the simple fluid and one set for the reference fluid.

The mixing rules that were proposed by Plöcker (11) are

$$T_{cm} = \frac{1}{v_{cm}^n} \sum_i \sum_j x_i x_j v_{cij}^n T_{cij} \quad (16)$$

$$v_{cm} = \sum_i \sum_j x_i x_j v_{cij} \quad (17)$$

where the cross coefficients are determined from

$$T_{cij} = (T_{ci} T_{cj})^{0.5} (1 - k_{ij}) \quad (18)$$

$$v_{cij} = \frac{1}{8} (v_{ci}^{1/3} + v_{cj}^{1/3})^3 \quad (19)$$

By use of an exponent n in the mixing rule, a better adaption to the symmetry in question can be obtained. Plöcker made studies of different mixtures, varying the molecular size of the components, in order to determine the exponent n . He found that n varied depending on the system, but he could conclude that a generally good agreement with experimental data was obtained for a value of 0.25 for n .

Experimental Equipment. The basic principle of the Jones circulation unit (12) is based on the continuous separation of the vapor phase from the liquid phase. The vapor phase is condensed and recirculated to the equilibrium cell.

The equilibrium cell (1) (see Figure 2) consists of two flanges with a glass tube in between secured by three bolts (2). The seal between the flanges and the glass tube is achieved with special glass tube gaskets (3). The equilibrium cell is equipped with a thermometer pocket (4), in which a Pt element is inserted to measure the equilibrium temperature.

The vapor leaves the equilibrium cell by the vapor pipe (5). The vapor is condensed in the condenser (6), and the condensate is brought to the receiver (7). The receiver is designed in the same way as the equilibrium cell but is smaller and is not equipped with a thermometer pocket. The condensate is vaporized in a vaporizer (8), equipped with a heating coil. The vapor is then conducted into the equilibrium cell by the pipe (9). The system can be subjected to a selected high pressure by a pressure controller, a pressure manometer, and a nitrogen gas tube connected via the valve and tube (10). The valves (11) and (12) permit samples to be taken from the vapor phase and liquid phase.

The equilibrium cell is assembled in an air bath that consists of a well-insulated chamber containing thermostated air which circulates over the equilibrium cell by a fan.

A binary mixture of refrigerants is fed through the pipe and valve (12) (see Figure 2). After the introduction of a suitable amount of samples in the equilibrium cell, the pressure of the system is raised by means of nitrogen and heat is supplied to such an extent that the mixture begins to boil. When the circulation of the vapor phase has started and a constant equilibrium temperature has been obtained, the circulation is continued for 2.5–3 h in order to obtain proper equilibrium conditions. Samples are then taken on the vapor phase through valve (11) and on the liquid phase through valve (12) (see Figure 2). The composition of the condensed vapor phase and the liquid phase were determined by a densitometer of the type Anton Paar DM 602. Since departure from ideality was observed when density was correlated with composition, calibration curves were prepared for each mixture. Calibration of the densitometer were performed for each system based on the determination of the oscillation time as a function of the composition at 20 °C and 14.0 bar. The variation in density can be measured with an accuracy of six digits and the composition with an accuracy of four digits.

The temperature in the equilibrium cell is measured with a Pt-100 transmitter. The transmitter was calibrated with a quartz thermometer, which in turn was calibrated against the temperature norm at the Swedish Test Laboratory. The accuracy of the quartz thermometer was estimated to be within ± 0.005 °C in the temperature range -20 to 90 °C, and to be within ± 0.01 °C in the range above 90 °C. The pressure was measured by high-precision pressure transducers, of the NAF type, which were calibrated against a Budenberg dead-weight pressure tester.

Results and Discussion

In order to make a comparison possible between different theoretical models for the description of vapor–liquid equilibrium properties, it is necessary to have relevant experimental data. Such data has been published only to a very limited extent for binary refrigerant mixtures. It was therefore of great interest to obtain experimental data, and isobaric measurements were thus performed for the following three systems: $\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$, $\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$, and $\text{CHClF}_2/\text{CCl}_2\text{F}_2$.

The experimental equipment used in these experiments is described above. The measurements were performed at different pressures within the range 3.5–14.5 bar, which is of primary interest in various technical applications.

That the different, experimentally determined, equilibrium data were thermodynamically consistent was tested by a method proposed by Fredenslund et al. (13). The consistency test consisted of calculating vapor composition from temperature and liquid mole fraction data from the Gibbs–Duhem equation. For thermodynamically consistent data the difference between experimental and calculated vapor mole fraction will be small. The experimentally determined data were found to be within the range of consistency. The deviations of the experimental data calculated from the consistency test proved to be within the range 1–2 mol %, which is comparable with other published results (14). The mixture containing $\text{C}_2\text{Cl}_2\text{F}_4$ of high mole fractions showed some deviation from consistency, probably due to impurities in the technical grade of $\text{C}_2\text{Cl}_2\text{F}_4$ used. The experimental results from the vapor–liquid equilibrium measurements determined are presented in Tables I–III.

The results from the experimental measurements show that the systems $\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$ and $\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$ do not behave azeotropically in the pressure and temperature range studied. These systems can be considered practically ideal. The third system $\text{CHClF}_2/\text{CCl}_2\text{F}_2$ is generally held to be an azeotropic refrigerant mixture.

In the literature authors (15–17) have presented the azeotropic composition of the system $\text{CHClF}_2/\text{CCl}_2\text{F}_2$ as a function

Table I. Experimental VLE Data: $\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$

T, K	mole fraction		T, K	mole fraction	
	x	y		x	y
$P = 3.5 \text{ bar}$					
314.83	0.000	0.000	293.10	0.478	0.714
310.19	0.087	0.209	289.04	0.576	0.798
308.67	0.087	0.202	286.07	0.682	0.864
305.87	0.155	0.305	285.17	0.710	0.874
305.62	0.177	0.350	280.09	0.882	0.925
304.88	0.181	0.354	279.68	0.908	0.961
300.00	0.310	0.551	277.60	1.000	1.000
296.11	0.378	0.652			
$P = 8.85 \text{ bar}$					
351.17	0.000	0.000	321.75	0.666	0.803
342.75	0.133	0.216	320.31	0.710	0.827
335.81	0.278	0.466	319.85	0.723	0.839
334.75	0.357	0.498	316.96	0.794	0.892
333.62	0.357	0.534	315.28	0.812	0.909
331.06	0.402	0.595	313.10	0.867	0.947
324.06	0.600	0.772	310.39	1.000	1.000
$P = 14.5 \text{ bar}$					
372.27	0.000	0.000	336.76	0.796	0.902
365.49	0.133	0.232	335.73	0.834	0.925
365.40	0.134	0.240	335.39	0.835	0.937
353.37	0.378	0.579	333.00	0.945	0.978
350.41	0.436	0.648	330.00	1.000	1.000
347.57	0.505	0.703			

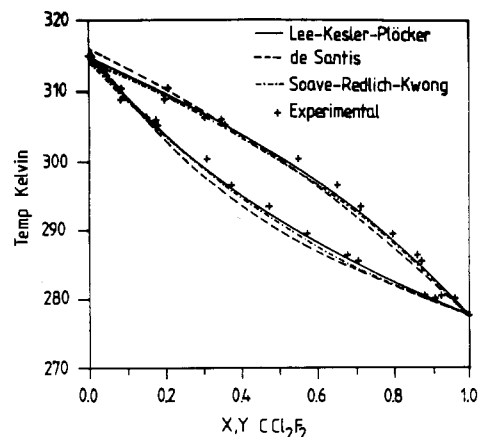
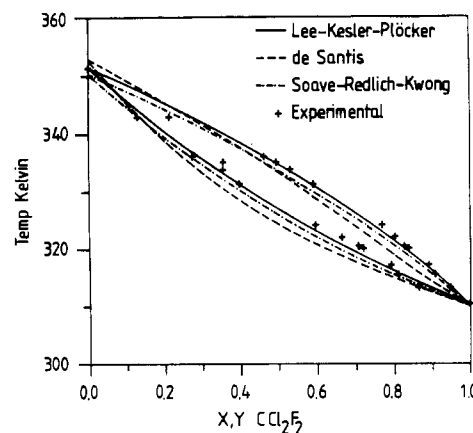
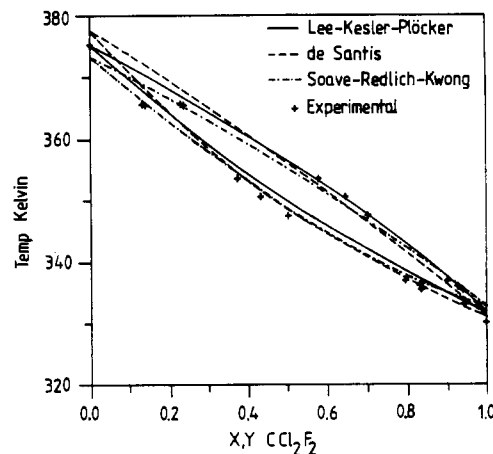
Table II. Experimental VLE Data: $\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$

T, K	mole fraction		T, K	mole fraction	
	x	y		x	y
$P = 9.85 \text{ bar}$					
356.21	0.000	0.000	310.60	0.546	0.819
347.38	0.029	0.148	303.70	0.694	0.884
344.40	0.048	0.249	296.95	0.922	0.975
349.98	0.076	0.103	296.23	1.000	1.000
331.19	0.192	0.546			
$P = 13.5 \text{ bar}$					
371.24	0.000	0.000	319.18	0.646	0.879
334.02	0.335	0.670	317.54	0.729	0.900
322.89	0.559	0.813	316.54	0.813	0.970
321.59	0.584	0.868	308.03	1.000	1.000

Table III. Experimental VLE Data: $\text{CHClF}_2/\text{CCl}_2\text{F}_2$

T, K	mole fraction		T, K	mole fraction	
	x	y		x	y
$P = 9.85 \text{ bar}$					
314.30	0.000	0.000	300.51	0.456	0.598
310.47	0.078	0.132	298.73	0.574	0.687
306.78	0.177	0.300	296.51	0.760	0.830
305.28	0.206	0.377	295.80	0.987	0.983
303.28	0.310	0.414	295.98	1.000	1.000
302.73	0.312	0.484			
$P = 13.95 \text{ bar}$					
329.15	0.000	0.000	309.43	0.740	0.847
322.76	0.059	0.212	308.71	0.985	0.987
317.27	0.345	0.472	308.61	0.993	0.994
312.16	0.526	0.673	308.69	1.000	1.000
310.15	0.669	0.799			

of temperature. The results in literature about the composition of the azeotrope are not in accordance with each other. Kriebel (15) found that the composition moves from 88.4 mol % CHClF_2 at -41.5°C to 100 mol % at -14.5°C . Spauschus (16), on the other hand, shows that the azeotrope varies from 90 mol % CHClF_2 at -20°C to 98.8 mol % at 40°C . Experimental data by Löffler (17) also show a linear relationship between the azeotropic composition and the temperature, but the temperature at a certain composition is lower in comparison to the data of Spauschus. In the present study equilibrium measurements were performed on this system at two pres-

**Figure 3. Bubble and dew point curves for $\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$ at 3.50 bar.****Figure 4. Bubble and dew point curves for $\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$ at 8.85 bar.****Figure 5. Bubble and dew point curves for $\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$ at 14.50 bar.**

ures, 9.85 and 13.95 bar. The measurements show that the azeotrope can be detected at 9.85 bar but not at 13.95 bar. The data in this study are thus in satisfactory agreement with data by Löffler.

A comparative study was done between theoretically calculated vapor-liquid equilibrium data based on the equations of state by Lee-Kesler-Plöcker, Soave-Redlich-Kwong, and de Santis and experimentally determined equilibrium data.

The system $\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$ was examined at three pressures, 3.50, 8.85, and 14.50 bar; see Figures 3, 4, and 5, respectively.

The equations of Lee-Kesler-Plöcker and Soave-Redlich-Kwong show good agreement between calculated and experimental data obtained in the measurements. The equation by

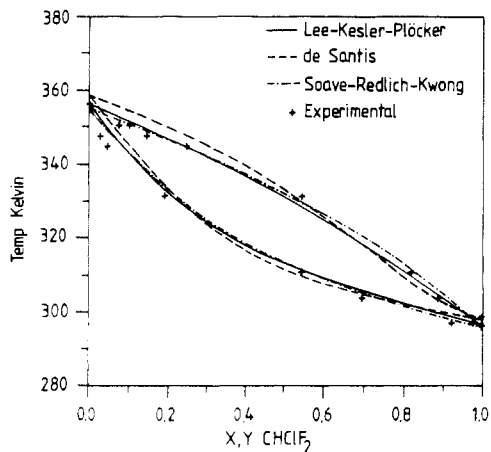


Figure 6. Bubble and dew point curves for $\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$ at 9.85 bar.

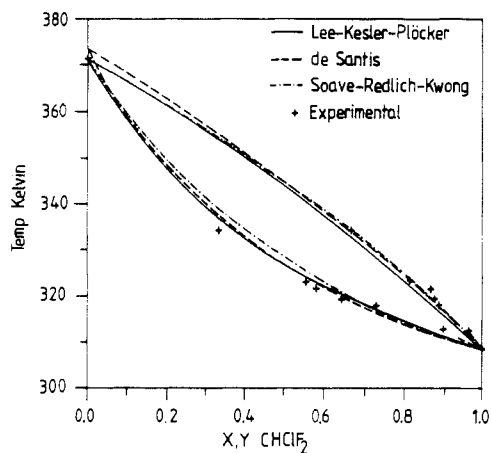


Figure 7. Bubble and dew point curves for $\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$ at 13.50 bar.

de Santis gives slightly lower bubble and dew point temperatures than the other two equations of state. At higher mole fractions of $\text{C}_2\text{Cl}_2\text{F}_4$, the deviation between the three equations will be greater. The equations according to Lee-Kesler-Plöcker and Soave-Redlich-Kwong give a good prediction of the vapor-liquid equilibrium for this system, even at elevated pressures.

For the system $\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$ measurements were done at two pressures, 9.85 and 13.50 bar; see Figures 6 and 7. Of course, the bubble and dew point curves will be more separated as compared with the systems discussed above, due to the greater boiling point interval between the pure components. The same discussion given for the system $\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$ is also valid for $\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$. The system $\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$ is probably more nonideal than $\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$ due to the hydrogen content in CHClF_2 .

A comparison of the system $\text{CHClF}_2/\text{CCl}_2\text{F}_2$ proves a good agreement between the equations of state of Lee-Kesler-Plöcker, Soave-Redlich-Kwong, and the experimental data at the pressures examined; see Figures 8 and 9.

The de Santis equation of state deviates from the other equations. However, a deviation is observed for all the equations of state compared with experimental data at high concentrations of CHClF_2 . This may be due to the difficulties in calculating vapor-liquid equilibria with these equations of state with systems that show an azeotropic behavior. The theoretically calculated equilibrium data presented are calculated with parameters of interaction that were obtained by a fitting procedure giving the least deviation between calculated and experimental data. The method used is a modification of a method presented by Zudkevitch and Joffe (18). The interaction

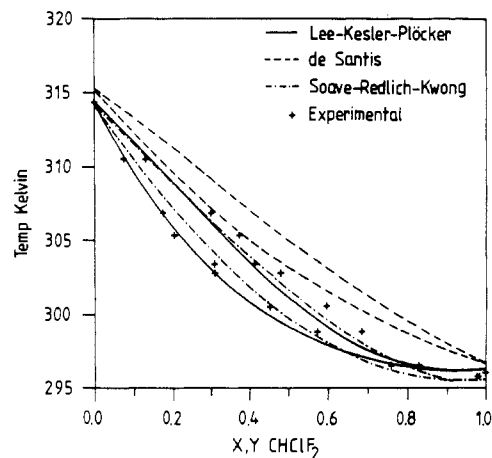


Figure 8. Bubble and dew point curves for $\text{CHClF}_2/\text{CCl}_2\text{F}_2$ at 9.85 bar.

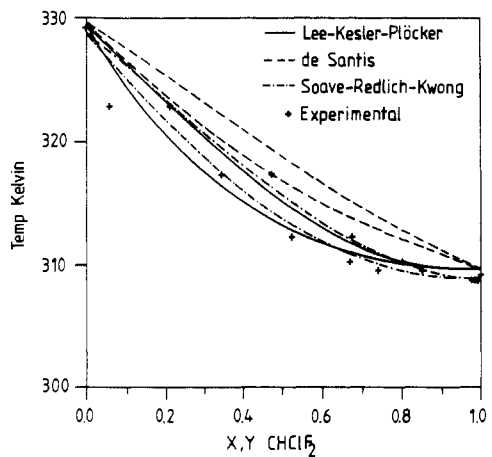


Figure 9. Bubble and dew point curves for $\text{CHClF}_2/\text{CCl}_2\text{F}_2$ at 13.95 bar.

Table IV. Interaction Parameters

	Soave-Redlich-Kwong	Lee-Kesler-Plöcker	de Santis
$\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$	0.01	0.00	0.02
$\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$	0.025	0.03	0.04
$\text{CHClF}_2/\text{CCl}_2\text{F}_2$	0.05	0.04	0.02

parameter is calculated from the least deviation in the equilibrium ratio between the experimental ratio $y_i^{\text{exptl}}/x_i^{\text{exptl}}$ and the ratio $y_i^{\text{calcd}}/x_i^{\text{exptl}}$, where the y_i^{calcd} value is calculated from the pressure and the x_i^{exptl} value by a bubble point calculation. The effect of temperature and pressure on the binary interaction parameters is neglected. These parameters are presented in Table IV.

Conclusions

In order to obtain experimental data to form a basis for the analysis of the applicability of different equations of state to different binary refrigerant systems, vapor-liquid equilibrium data were determined for $\text{CCl}_2\text{F}_2/\text{C}_2\text{Cl}_2\text{F}_4$, $\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$, and $\text{CHClF}_2/\text{CCl}_2\text{F}_2$.

The experimental method used to determine the vapor-liquid equilibrium data, the Jones circulation method, was found to work well in the pressure range, 3.5–14.5 bar, prevailing in these measurements, and the data obtained were found to be thermodynamically consistent.

On the basis of the determination of equilibrium data for the refrigerant systems and the comparisons made with theoretically calculated bubble and dew point curves, it may be concluded that there is a good agreement between experimental results and those calculated from the equations of state ac-

ording to Lee-Kesler-Plöcker and Soave-Redlich-Kwong. The equation of state according to de Santis yields equilibrium compositions that differ from the other equations of state, which may be explained by the uncertainty in the temperature-dependent parameters determined from pressure-volume-temperature data at temperatures near the critical. All the equations of state studied yield results that differ from those obtained experimentally, when the differences in equilibrium composition between the vapor phase and the liquid phase are small.

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Glossary

A, B	constants in the equation of state according to Redlich-Kwong and Soave-Redlich-Kwong
A, B, C, D	constants in the equation of state according to Lee-Kesler-Plöcker
P	pressure, Pa
T	temperature, K
v	mole volume, $\text{m}^3 \text{mol}^{-1}$
z	compressibility
R	gas constant per mole, $\text{J mol}^{-1} \text{K}^{-1}$
n	exponent in the equation of Lee-Kesler-Plöcker
k	interaction parameter
a, b	parameters in the equation of state according to Redlich-Kwong, Soave-Redlich-Kwong, and de Santis
a, b, c, d	constants in the equation of Lee-Kesler-Plöcker
x	mole fraction, liquid phase
y	mole fraction, vapor phase
z	mole fraction
f	fugacity
Greek Letters	
β	constant in the equation according to Lee-Kesler-Plöcker
γ	constant in the equation according to Lee-Kesler-Plöcker
ϕ	fugacity coefficient

Ω_a	constant in the equation according to Redlich-Kwong and Soave-Redlich-Kwong
Ω_b	constant in the equation according to Redlich-Kwong and Soave-Redlich-Kwong
ω	acentric factor

Superscripts and Subscripts

L	liquid phase
V	vapor phase
i, j	components
c	critical state
cm	pseudocritical state of a mixture
m	mixture
r	reduced state
(0)	simple fluid
(1)	function of deviation
(r)	reference fluid

Registry No. CCl_2F_2 , 75-71-8; $\text{C}_2\text{Cl}_2\text{F}_4$, 76-14-2; CHClF_2 , 75-45-6.

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NEW COMPOUNDS

Synthesis and Spectra of Some Phthalimido Derivatives

Mohamed M. El Sadek,* Mohyl M. El Essawi, and Samy A. Abdel Bakly

Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

The reactions of some aroylhydrazines and amino derivatives of heterocyclic compounds with phthalic anhydride were investigated. Dehydration of the prepared carboxybenzoyl derivatives afforded the corresponding phthalimido products. The structures were confirmed by IR, proton NMR, and mass spectra.

The phthaloyl group has an interesting feature in protection of amino sugars (1-3), amino acids (4), and peptides (5). Removal of the phthaloyl group by hydrazinolysis using hydrazine, phenylhydrazine, or methylhydrazine (6) is well-known. However, hydrazine remains the reagent of choice, because the deblocking can be performed under mild conditions.

1-Aroyl-2-(2'-carboxybenzoyl)hydrazines (1-4) were syn-