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Isothermal Vapor−Liquid Equilibrium Data of 1,1,1,2-Tetrafluoroethane (R134a) + Dimethylformamide (DMF) Working Fluids for an Absorption Heat Transformer

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Vapor−liquid equilibrium data of 1,1,1,2-tetrafluoroethane (R134a) + dimethylformamide (DMF) were measured in the temperature range from (303.30 to 353.24) K by the static analytic method. The results are of interest to test the possibility of using R134a as a refrigerant in combination with an organic absorbent, that is, DMF, in an absorption heat transformer. The experimental data are correlated using the Peng−Robinson equation of state in combination with the Mathias−Copeman α function, MHV1 mixing rules, and the non-random two liquid (NRTL) activity coefficient model. We have compared our experimental results to predictions obtained using the predictive Soave−Redlich−Kwong (PSRK) group contribution equation of state.

1. Introduction

Absorption heat transformers (AHTs) are a particular type of absorption heat pumps, through which waste heat can be upgraded without recourse to an external heat source and hence be used economically, since the primary energy consumption is decreased. With the scope of using environmentally friendly working fluid pairs (no ozone depletion and no global warming potentials[1]), it is worthy to study such new systems.

In industry the use of absorption heat pumps and heat transformers depends on the availability of new working pairs, capable of extending the operating range to higher temperatures. To analyze the behavior of an AHT, operating with the considered working pairs, the main temperature of the system was assumed to be known. The AHT mainly consists of a generator (GE), an absorber (AB), an evaporator (EV), a condenser (CO), and a heat exchanger. Generally the temperature ranges considered for the analysis are: $283 \leq T_{CO} \leq 313$ K, $323 \leq T_{GE}(T_{EV}) \leq 343$ K, and $353 \leq T_{AB} \leq 393$ K.[2]

In fact, many research programs are concerned with the development of adequate and efficient working fluid pairs to meet needs with respect to specific applications concerning the production of cold or heat but ultimately with no negative impact toward the environment. Consequently, methods for assessing the performance of a "refrigerant−absorbent" pair to be used in a refrigeration system or a heat pump unit are needed. This requires the knowledge of the pure and mixture data, such as the thermophysical, the equilibrium, and transport properties and the thermal stability of the refrigerant−absorbent pair.

In the literature, a great number of research studies were concerned with the screening of the best refrigerant−absorbent pairs. For instance, one can cite Fatouh and Murthy[3] who made a comparative study of different working fluids, using R22 as refrigerant and six organic absorbents (*N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), *N*-methyl-2-pyrrolidone (NMP), dimethylether diethylene glycol (DMEDEG), dimethylether tetraethylene glycol (DMETEG), and dimethylether triethylene glycol (DMETrEG)) in a vapor AHT, based on $P-T-x-H$ data. Similarly Borde et al.[4] considered the use of the refrigerant 1,1,1,2-tetrafluoroethane (R134a) as a substitute to chlorofluorocarbons in absorption heat pumps and refrigeration units and tested it in combination with different commercial absorbents such as DMETEG, *N*-methyl *ε*-caprolactam (MCL), or dimethylethyleneurea (DMEU), in absorption systems. Interesting results were obtained indicating that the R134a−DMETEG pair was the best performing.[4] This has stimulated and encouraged the test of this refrigerant with further organic absorbent such as the DMF in an AHT. Also, a thorough literature search has shown published vapor−liquid phase equilibrium data concerning the carbon dioxide (CO_2) + DMF pair at (293.95, 313.05, and 338.05) K and pressures up 12 MPa (Duran-Valencia et al.[5]), rather than the R134a + DMF system.

The experimental method used for the vapor−liquid phase equilibrium (P, T, x) measurements and the model used to correlate the obtained results are described below.

Table 1. Suppliers and Purities of the Used Chemicals

chemical	supplier	purity/wt %
R134a	ARKEMA	99.5
DMF	Aldrich	99.9[a]

[a] Chromasolv+ for high-performance liquid chromatography (HPLC).

2. Experimental Section

2.1. Materials. Table 1 shows the sources and the purities of the used chemicals, as certified by the manufacturers. Apart from a careful degassing of DMF, no further purification or pretreatment was performed.

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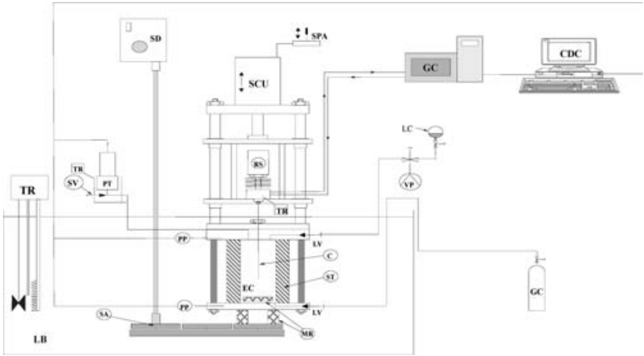

Figure 1. Flow diagram of the static analytic apparatus, where: C, capillary; CDC, central desktop computer; LC, liquid component (DMF); EC, equilibrium cell; GC, gas component (R134a); LB, liquid bath; LV, loading valve; MR, magnetic rod; PP, platinum probe for temperature measurements; PT, pressure transducer; RS, phase sampler; SA, steering assembly; SCU, sampler control unit; SD, steering device; SPA, sampler position adjustment joy stick; ST, sapphire tube; SV, separating valve; TC, temperature controller; TR, thermal regulator; VP, vacuum pump.

Table 2. Critical Parameters[9]

chemical	P_C / MPa	T_C / K
R134a	4.064	374.25
DMF	5.499	650.00

2.2. Apparatus. The measurements of vapor−liquid equilibrium (VLE) of R134a + DMF binary systems were made using a static analytic technique. The general technique was already reported in details by Laugier and Richon.[6] However, a brief description is presently given to show improved equipment. The major part of the experimental setup is the equilibrium cell (Figure 1), which is a sapphire tube fixed between two stainless steel flanges, equipped with valves, for loading and cleaning the cell. At the bottom of the cell, a magnetic stirrer is used to ensure fast equilibrium. The agitation intensity inside the cell is controlled by means of an external motor, and the temperature in the equilibrium cell was maintained constant inside a temperature-regulated liquid bath. The cell is connected to a sampling system (electromagnetic online micro sampler, ROLSI)[7] and connected to a gas chromatograph. The equilibrium temperature was measured using two (Pt-100) platinum probes; one is placed at the top of the cell and the other one at its bottom. Using a 25 Ω reference platinum probe (Tinsley, France) to calibrate both temperature sensors, the uncertainty in the temperature measurements is estimated within ± 0.02 K. The equilibrium pressure is measured using a Druck pressure transducer (up to 4.0 MPa), which is connected to the cell through the upper flange. The pressure transducer is calibrated by means of a dead weight balance (Desgranges and Huot model 5202S, France). The estimated uncertainty on pressure measurements is within ± 0.2 kPa.

Liquid samples were analyzed by means of a gas chromatograph (Varian, CP-3800), using a thermal conductivity detector (TCD). The calibration of the TCD was made by introducing pure components with appropriate syringes. The uncertainty on liquid mole fractions is estimated to be within 3 %. The chromatographic column used is RTX-5-Amine (3 μm, 15 m × 0.53 mm ID).

2.3. Experimental Procedure. The liquid component, DMF, is loaded into the equilibrium cell by gravity and degassed under vacuum. After pure DMF vapor pressure is recorded on the required range of temperature. Temperature is set at its lowest values, and then the lighter component (R134a) is loaded through successive additions that will allow working on the whole concentration range. After each addition of R134a the agitation is initiated, and then the system is left to reach equilibrium. At this moment samples of liquid are withdrawn using a pneumatic sampler (ROLSI) and analyzed by gas chromatography. At each equilibrium condition of temperature and pressure, six samples of the liquid phase are withdrawn to check for repeatability.

Table 3. Experimental and Calculated R134a Vapor Pressures Using the PR EoS with Mathias−Copeman α Function

T / K	P_{exp} / MPa	P_{cal} / MPa
298.44	0.6696	0.6706
303.45	0.7757	0.7761
308.44	0.8922	0.8931
313.30	1.0188	1.0198
318.39	1.1654	1.1660
323.30	1.3190	1.3218
328.26	1.4924	1.4943
333.30	1.6837	1.6866
338.24	1.8896	1.8929
343.23	2.1153	2.1200
348.22	2.3525	2.3678
353.10	2.6059	2.6310

Table 4. Mathias−Copeman Parameters

coefficient	R134a[a]	R134a[b]	DMF[c]
c_1	0.965	1.154	0.8165
c_2	−2.407	−3.062	0.1164
c_3	12.638	14.520	0.0594

[a] Mathias−Copeman parameter adjusted for the PR EoS. [b] Mathias−Copeman parameter adjusted for the Soave−Redlich−Kwong (SRK) EoS. [c] Ref 14.

3. Correlation

The experimental VLE data are correlated by means of homemade software developed in our laboratory. The correlation of the experimental measurements is obtained by the combination of Peng−Robinson[8] equation of state (PR EoS) with the Mathias−Copeman α function, MHV1 mixing rules, and the non-random two liquid (NRTL) model.

The critical properties[9] of the considered components are indicated in Table 2.

The Mathias−Copeman α function[10] for $T < T_C$ is expressed as follow

$$\alpha(T) = \left[1 + c_1\left(1 - \sqrt{\frac{T}{T_C}}\right) + c_2\left(1 - \sqrt{\frac{T}{T_C}}\right)^2 + c_3\left(1 - \sqrt{\frac{T}{T_C}}\right)^3\right]^2 \tag{1}$$

where c_1, c_2, and c_3 are the adjustable parameters.

The MHV1 mixing rule[11] is represented as:

$$a = b\left[\sum_i x_i \frac{a_i}{b_i} - \frac{1}{q_1}\left(\sum_i x_i \ln\left(\frac{b_i}{b}\right) + \frac{g^{E*}}{RT}\right)\right] \tag{2}$$

$$b = \sum_i x_i b_i \tag{3}$$

where a_i and b_i are respectively the attractive parameters and molar covolume and q_1 is equal to −0.53 for the PR EoS.

Table 5. Experimental and Calculated VLE Data of R134a (1) + DMF (2) Mixture at Different Temperatures

T	$P_{i,\mathrm{exp}}$	$P_{i,\mathrm{cal}}$			ΔP
K	MPa	MPa	$x_{i,\mathrm{exp}}$	$y_{i,\mathrm{cal}}$	MPa
303.30	0.1525	0.1471	0.2050	0.9946	0.0054
303.30	0.2339	0.2342	0.3185	0.9970	−0.0003
303.30	0.2806	0.2751	0.3715	0.9976	0.0055
303.30	0.3370	0.3333	0.4437	0.9982	0.0037
303.30	0.3555	0.3678	0.4872	0.9984	−0.0123
303.30	0.4294	0.4436	0.5809	0.9989	−0.0141
303.30	0.4681	0.4748	0.6203	0.9990	−0.0067
303.30	0.4892	0.4916	0.6414	0.9991	−0.0024
303.30	0.5451	0.5661	0.7361	0.9994	−0.0210
303.30	0.5834	0.6013	0.7816	0.9995	−0.0179
303.30	0.5929	0.6082	0.7913	0.9995	−0.0153
303.30	0.6546	0.6540	0.8518	0.9997	0.0006
303.30	0.6705	0.6668	0.8686	0.9997	0.0037
303.30	0.7757	0.7723	1	1	0.0034
313.18	0.2886	0.2805	0.2950	0.9953	0.0081
313.18	0.3158	0.3049	0.3185	0.9958	0.0109
313.18	0.4047	0.4063	0.4173	0.9971	−0.0016
313.18	0.4911	0.5077	0.5132	0.9979	−0.0166
313.18	0.5839	0.6032	0.6025	0.9985	−0.0193
313.18	0.6386	0.6632	0.6597	0.9988	−0.0246
313.18	0.7441	0.7621	0.7557	0.9991	−0.0180
313.18	0.8011	0.8203	0.8141	0.9993	−0.0192
313.18	0.9115	0.9119	0.9064	0.9996	−0.0004
313.18	1.0188	1.0168	1	1	0.0020
323.34	0.3642	0.3484	0.2834	0.9932	0.0158
323.34	0.4851	0.4836	0.3846	0.9955	0.0015
323.34	0.5414	0.5377	0.4254	0.9961	0.0037
323.34	0.6628	0.6814	0.5302	0.9972	−0.0186
323.34	0.7145	0.7350	0.5689	0.9976	−0.0205
323.34	0.8350	0.8618	0.6624	0.9982	−0.0268
323.34	0.9238	0.9460	0.7247	0.9986	−0.0222
323.34	1.0564	1.0735	0.8230	0.9990	−0.0171
323.34	1.0831	1.0979	0.8421	0.9991	−0.0148
323.34	1.1208	1.1300	0.8668	0.9992	−0.0092
323.34	1.1537	1.1572	0.8875	0.9993	−0.0035
323.34	1.3190	1.3216	1	1	−0.0026
338.26	0.6984	0.6833	0.3833	0.9928	0.0151
338.26	0.8154	0.7964	0.4415	0.9941	0.0190
338.26	0.9137	0.9183	0.5051	0.9951	−0.0046
338.26	1.0736	1.1063	0.6015	0.9963	−0.0327
338.26	1.1044	1.1313	0.6149	0.9964	−0.0269
338.26	1.2985	1.3271	0.7182	0.9974	−0.0286
338.26	1.4262	1.4528	0.7864	0.9979	−0.0266
338.26	1.6147	1.6149	0.8747	0.9986	−0.0002
338.26	1.6698	1.6578	0.8982	0.9988	0.0120
338.26	1.8896	1.8856	1	1	0.0040
353.24	0.8513	0.8492	0.3545	0.9879	0.0021
353.24	1.0808	1.0766	0.4421	0.9907	0.0042
353.24	1.2924	1.2959	0.5238	0.9926	−0.0035
353.24	1.4236	1.4253	0.5724	0.9935	−0.0017
353.24	1.5257	1.5252	0.6091	0.9941	0.0005
353.24	1.5939	1.6032	0.6383	0.9945	−0.0093
353.24	1.6652	1.6595	0.6594	0.9948	0.0057
353.24	1.8358	1.8373	0.7263	0.9956	−0.0015
353.24	1.9894	2.0089	0.7922	0.9963	−0.0195
353.24	2.0121	2.0217	0.7968	0.9964	−0.0096
353.24	2.3987	2.3685	0.9289	0.9980	0.0302
353.24	2.6059	2.6258	1	1	−0.0199

The excess Gibbs energy model used is the NRTL,[12] which is expressed as follows:

$$\frac{g^{\mathrm{E}}(T, P, x_i)}{RT} = -q\sum_{i=1}^{n} x_i \ln\left(\sum_{j=1}^{n} G_{ji}x_j\right) + p\sum_{i=1}^{n} x_i\left(\frac{\sum_{j=1}^{n}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{n} G_{ki}\tau_k}\right) \tag{4}$$

where n is the number of components in the system and

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{5}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{6}$$

where $\tau_{ii} = 0$ and $\alpha_{ii} = 0$.

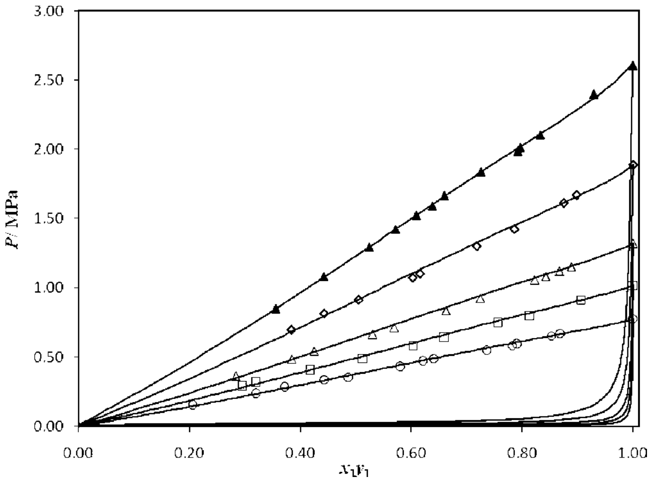

Figure 2. Isothermal VLE data for R134a (1) + DMF (2) at different temperatures; ○, 303.30 K; □, 313.18 K; Δ, 323.34 K; ◇, 338.26 K; ▲, 353.24 K; solid line, calculated results using our model.

$\alpha_{ij} = \alpha_{ji}$, and τ_{ij} and τ_{ji} are adjustable parameters. α_{ij} is the non-randomness parameter, taken equal to 0.3 in this work. The Simplex algorithm[13] was used to minimize the following objective function:

$$F = \frac{100}{N}\left[\sum_{1}^{N}\left(\frac{P_{\mathrm{exp}} - P_{\mathrm{cal}}}{P_{\mathrm{exp}}}\right)^2\right] \tag{7}$$

where N is the number of experimental measurements and P_{exp} and P_{cal} are respectively the experimental and the calculated pressures.

4. Results and Discussion

4.1. Pure Component Vapor Pressure. The vapor pressure of R134a was measured at temperature range between (298 and 353) K, and the results are shown in Table 3. Mathias−Copeman parameters for R134a were fitted using the experimental data (Table 3), and they are listed with the Mathias−Copeman parameters for DMF[14] in Table 4.

The relative deviations, BIASU and MRDU, are defined by:

$$\mathrm{MRDU} = (100/N)\sum |(U_{\mathrm{cal}} - U_{\mathrm{exp}})/U_{\mathrm{exp}}| \tag{8}$$

$$\mathrm{BIASU} = (100/N)\sum ((U_{\mathrm{exp}} - U_{\mathrm{cal}})/U_{\mathrm{exp}}) \tag{9}$$

where N is the number of experimental measurements. The relative deviations on the pressure are BIASP and MRDP ($U = P$). The mean average absolute deviation on the vapor pressure is about 0.25 %.

4.2. VLE for the R134a + DMF Mixture. The experimental and calculated isothermal VLE data for R134a + DMF at (303.30, 313.18, 323.34, 338.26, and 353.24) K are presented in Table 5 and plotted in Figure 2.

The NRTL parameters for MHV1 mixing rules were adjusted at each experimental temperature. The adjusted parameters are negligibly temperature dependent, and for that reason the NRTL parameters were fitted using all experimental data with no temperature dependence, where $\tau_{12} = 2250\ \mathrm{J{\cdot}mol^{-1}}$ and $\tau_{21} = -2650\ \mathrm{J{\cdot}mol^{-1}}$. The deviation in pressure is represented in Figure 3. The relative deviations BIASP and the MRDP are listed in Table 6.

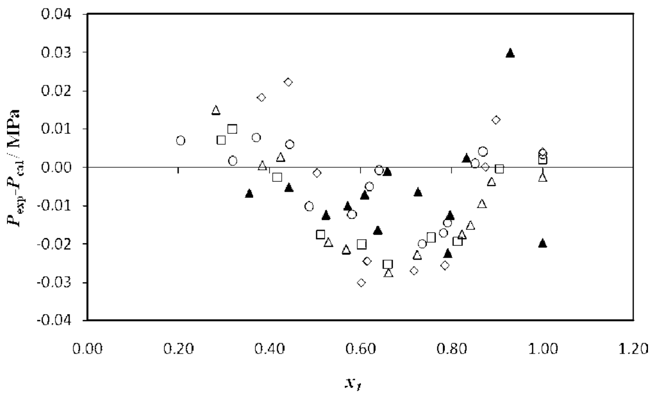

Figure 3. Pressure deviation for R134a (1) + DMF (2) system: ○, 303.30 K; □, 313.18 K; △, 323.34 K; ◇, 338.26 K; ▲, 353.24 K.

Table 6. Relative Deviations BIASP and MRDP Using PR EoS with MHV1 Mixing Rules and NRTL Model

T	BIASP	MRDP
K	%	%
303.30	−0.8	1.9
313.18	−0.9	2.2
323.30	−0.8	1.7
338.26	−0.5	1.5
353.24	−0.1	0.4

Table 7. PSRK Parameters: van der Waals Properties and the Interaction Parameters[14]

				a_{ij}/K	
group	subgroup	r_k	q_k	40	39
40	CF_3	1.4060	1.3800	0.00	55.80
	CF	0.6150	0.4600		
39	DMF	3.0856	2.7360	−5.579	0.00

Table 8. Relative Deviations BIASP and MRDP Using the PSRK Model

T	BIASP	MRDP
K	%	%
303.30	−18	18
313.18	−18	18
323.30	−15	15
338.26	−12	12
353.24	−11	11

4.3. Comparison with the PSRK Model. The PSRK EoS[15] is the combination of the Soave−Redlich−Kwong (SRK) EoS with the UNIFAC group contribution model using PSRK mixing rules. The PSRK EoS is generally used to predict VLE equilibrium data. We have chosen the PSRK EoS with Mathias−Copeman α function to predict the VLE equilibrium data of R134a (CF_3CH_2F) + DMF ($CHON(CH_3)_2$). The Mathias−Copeman parameters were adjusted using experimental vapor pressures of R134a (Table 3) and listed in Table 4. The decomposition of the considered components in subgroups is represented in Table 7.

Because of the important values of the relative deviations BIASP and MRDP as shown in Table 8, we have concluded that the PSRK EoS is not recommended to predict the *P*−*T*−*x*−*y* equilibrium data for the R134a + DMF binary system.

5. Conclusions

Isothermal VLE equilibrium measurements have been performed, using the static analytic method, for the R134a + DMF mixture at (303.30, 313.18, 323.34, 338.26, and 353.24) K up to 2.6 MPa. The experimental data were correlated by means of PR EoS with Mathias−Copeman α function in combination with MHV1 mixing rules and NRTL model. The obtained results are in good agreement with the experimental data. With the PSRK model we have a bad representation of the experimental data.

VLE presented herein will be used in the near future to evalute the performance of an AHT working with the R134a−DMF binary system.

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