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High Pressure Vapor−Liquid Equilibrium Data for the System Carbon Dioxide + Decanal at 288.2, 303.2, and 313.2 K

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Isothermal vapor−liquid equilibrium data for the system carbon dioxide + decanal at 288.2, 303.2, and 313.2 K, and for pressures between 1.6 and 8.3 MPa, are reported. The experimental data are correlated by the Soave−Redlich−Kwong and Peng−Robinson equations of state.

1. Introduction

The production of low-alcohol-content beverages is a challenging problem because of the difficulty in preserving the organoleptic characteristics of the original beverage. To accomplish this, the process must operate at low temperatures, to avoid thermal degradation, and be designed so as to prevent the extraction of the aromatic compounds. Therefore, is important to know the behavior of the aromas during the dealcoholization process.

In our previous work, we reported the solubility of some aromatic compounds of wine in carbon dioxide (CO_2).[1,2] This information is essential for the correct design of the process of dealcoholization of wine by supercritical extraction with CO_2.

In continuation of our research program, we now report experimental vapor−liquid equilibrium data for the system CO_2 + decanal, one of the most abundant aldehydes in wine, at 288.2, 303.2, and 313.2 K. The interaction parameters for the Soave−Redlich−Kwong (SRK) and Peng−Robinson (PR) equations of state (EOS's) that best fit the experimental data were also evaluated.

2. Experimental Section

Chemicals. Decanal and acetone (used as washing solvent) were both supplied by Sigma-Aldrich with massic purities >99% and >99.9%, respectively. The CO_2 and the helium (used as a carrier gas for the GC analysis) were obtained from ArLiquido and had mole fraction purities >0.99998 and >0.99999, respectively. These chemicals were used with no further purification.

Apparatus and Procedure. The vapor−liquid equilibrium data were obtained using the static type equilibrium apparatus described by Vázquez da Silva et al.[2,3] This apparatus consists of a cylindrical sapphire cell, with a volume of 23 cm^3, in a thermostatic air bath, and was designed to operate at pressures below 30 MPa and temperatures between 273.15 and 353.15 K. To cover this temperature range, the air bath has incorporated a heating source (thermoventilator) and a cooling source (refrigeration system).[2]

To obtain the experimental data, we first filled the cell with decanal and tightly closed it. The CO_2, previously compressed in a pressure generator (HIP 68-5.75-15), was then fed, eliminating any air existing in the cell. Depending on the temperature of interest, the thermoventilator or the refrigeration system was switched on. When the desired temperature (controlled by a Omrom/Pt100 probe system with a precision of ±0.1 K) was reached, the cell was depressurized to attain a predetermined pressure, and the mixture in the cell was stirred for about 30 min. The pressure in the cell was measured with a Schaevitz probe, with a precision of ±0.1% of the full scale (for a pressure limit of 35 MPa). After allowing the mixture in the cell to rest for at least 6 h to ensure equilibration as established in preliminary studies, samples of the liquid and vapor phase were collected by depressurization and expansion into glass traps. The amount of CO_2 in each phase was obtained by expansion in glass bottles of calibrated volume. The air in the sampling systems had been previously removed by a vacuum system. To prevent solute losses, the sampling tube was washed with acetone. All parts of the equilibrium apparatus, including the sampling systems, are inside the air bath to maintain a uniform temperature throughout.

To limit the disturbance introduced in the equilibrium by the sampling procedure, it was ensured that only a small amount of sample was collected, by verifying that the pressure drop in the cell was always less than 0.1 MPa during this procedure.

The liquid samples of both phases were weighed and analyzed with a Hewlett-Packard gas chromatograph (model HP5880), with a thermal conductivity detector and a HP20M (Carbowax) column, using helium as the carrier gas.

The reproducibility of the composition results was verified by doing several measurements under the same conditions of pressure and temperature, which allowed an estimate of the precision of ±0.003 mole fraction.

3. Results and Discussion

The experimentally measured phase compositions for the CO_2 + decanal system at 288.2, 303.2, and 313.2 K are summarized in Table 1 and shown in Figure 1. As can be seen, the mole fraction of decanal in the vapor phase is very low (less than 1%) and its solubility is not significantly affected by the change in temperature in the range of temperatures studied. Therefore, we may expect that, during the process of dealcoholization by supercritical extraction with CO_2, the decanal will remain in the liquid

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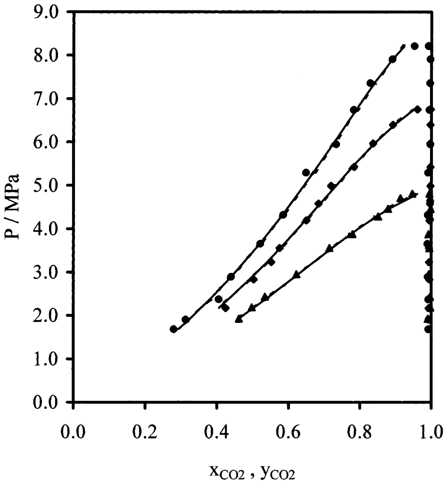

Figure 1. Experimental (▲, 288.2; ◆, 303.2; ●, 313.2 K) and correlated data with the SRK (- - -) and PR (—) EOS's for the system CO_2 + decanal.

Table 1. Experimental Equilibrium Data for the System CO_2 + Decanal at 288.2, 303.2, and 313.2 K

P/MPa	x_{CO_2}	y_{CO_2}	P/MPa	x_{CO_2}	y_{CO_2}	P/MPa	x_{CO_2}	y_{CO_2}
T = 288.2 K			T = 303.2 K			T = 313.2 K		
4.81	0.946	0.995	6.76	0.960	0.998	8.22	0.952	0.992
4.71	0.913	0.996	6.41	0.891	0.997	7.91	0.891	0.997
4.47	0.878	0.998	5.97	0.836	0.996	7.36	0.829	0.996
4.29	0.850	0.996	5.43	0.783	0.997	6.75	0.782	0.995
3.88	0.778	0.992	5.00	0.718	0.997	5.95	0.733	0.997
3.56	0.714	0.995	4.58	0.683	0.996	5.30	0.649	0.991
2.95	0.622	0.993	4.20	0.649	0.995	4.33	0.585	0.990
2.43	0.534	0.996	3.56	0.575	0.994	3.66	0.521	0.989
2.19	0.497	0.997	3.24	0.552	0.994	2.89	0.440	0.990
1.93	0.461	0.990	2.83	0.502	0.995	2.37	0.405	0.992
			2.17	0.424	0.993	1.90	0.313	0.993
						1.68	0.280	0.992

phase, improving the organoleptic characteristics of the final product.

The experimental results were correlated with the Soave−Redlich−Kwong[4] and Peng−Robinson[5] equations of state, using the classic van der Waals mixing rule with two parameters.[6] The critical properties of carbon dioxide and decanal are given in Table 2. The interaction parameters for the SRK-EOS and PR-EOS that best fit the experimental data and the corresponding relative quadratic deviation (RQD), defined as

$$\mathrm{RQD} = \frac{\sum_{k=1}^{n_{\mathrm{res}}}\left(\frac{x_{\mathrm{exp},k} - x_{\mathrm{calc},k}}{x_{\mathrm{exp},k}}\right)^2 + \sum_{k=1}^{n_{\mathrm{res}}}\left(\frac{y_{\mathrm{exp},k} - y_{\mathrm{calc},k}}{y_{\mathrm{exp},k}}\right)^2}{2n_{\mathrm{res}}} \qquad (1)$$

are summarized in Table 3. In eq 1, y and x are the mole fraction of CO_2 in the vapor and liquid phases, respectively, the subscripts exp and calc refer to the experimental values and those calculated by the equation of state, respectively, and n_{res} is the number of experimental results. The interaction parameters and the value of the RQD were obtained by fitting all the data together, because the range of temperatures studied is small (25 K). As shown in Figure 1, both equations of state correlate equally well the experimental data but fail near the critical point, as expected.

Table 2. Critical Properties and Acentric Factors for Pure Components[7]

component	T_c/K	P_c/MPa	ω
carbon dioxide	304.2	7.39	0.239
decanal	652	22.3	0.634

Table 3. SRK and PR EOS Binary Interaction Parameters (k_{ij} and d_{ij}), and Corresponding Values of the RQD, for the System CO_2 + Decanal

EOS	T/K	P/MPa	k_{ij}	d_{ij}	RQD
SRK	288−313	1.6−8.3	0.037 70	0.028 41	2.26×10^{-4}
PR	288−313	1.6−8.3	0.036 52	0.029 73	2.31×10^{-4}

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