

Volumetric Behavior of Decane + Carbon Dioxide at High Pressures. Measurement and Calculation

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The volumetric behavior of carbon dioxide (1) + decane (2) mixtures has been investigated under the high pressures 20, 30, and 40 MPa in the temperature range [308.15 K to 368.15 K]. Densities have been measured for pure decane and for $x_1 = 0.15, 0.30, 0.51, 0.66, 0.78,$ and 0.84 . Density variations show a peculiar behavior: a crossover phenomenon with the composition at a given pressure and temperature is observed. The measured fluid densities have been compared with values predicted by equations of state with various mixing rules. This comparative study has revealed models well adapted to these density estimations.

Introduction

Not only is carbon dioxide naturally present in the reservoir fluids but it is also introduced in great proportion as a mean to improve recovery; therefore, there is great interest in the study of hydrocarbon + carbon dioxide binary mixtures.^{1–4} The thermodynamic characterization of such mixtures involves the experimental knowledge of phase equilibria, transport properties (viscosity), or pure phase properties over extended ranges of pressure and temperature. Density, which is a parameter of great experimental importance among the pure phase properties, was measured for several binary mixtures hydrocarbon + carbon dioxide;² nevertheless, there is less experimental information under high pressures above the bubble pressure, that is, in a one-phase homogeneous liquid. In this context, we have undertaken the present study on the carbon dioxide + decane mixture, already studied, to complement the volumetric behavior of these mixtures. Indeed, we measured the density over the full composition range and over extended ranges of pressure [20 MPa to 40 MPa] and temperature [308.15 K to 368.15 K], that is, close to the storage conditions.

This experimental data were also treated as discriminatory values to test the ability of a number of equations of state combined with various mixing rules commonly applied in chemical engineering to predict the density of these carbon dioxide + decane mixtures.

Experimental Section

Materials. Nitrogen and carbon dioxide were obtained from AgaGaz and have a nominal purity of 99.9 and 99.95%, respectively. Decane was supplied from Sigma-Aldrich with a purity of 99.5 mol %. Water used to calibrate the densimeter was triple-distilled and was degassed prior to use.

Apparatus and Procedure. The experimental arrangement (see Figure 1) and the preparation and transfer methods into the densimeter cell inherent to these mixtures have already been detailed.⁵ Nevertheless, several important points should be noted. The work on mixtures containing dissolved gases (here, the carbon dioxide) required the

separation of the pressurizing system, which is gas (nitrogen) and the sample. Therefore, a separator (3) (cylindrical cell with a floating piston) is placed downstream of the experimental vessels to separate the pressurizing fluid (nitrogen) from the experimental fluid. The mixture is directly prepared in the upper part of this separator. A vacuum is first created, and the liquid component is then introduced by gravity. Thereafter, the quantity of gas injected is checked by a double weighing procedure. A pressure superior to the mixture bubble pressure is communicated. The separator disconnected from the pressurizing system is then stirred during several hours in view of homogenizing the mixture. Transfer toward the measurement cell must be done at constant pressure to avoid problems arising from demixing the liquid and the gas component; such demixing could alter the composition of the mixture. For this purpose, a bypass line (13) was introduced into the pressurization system to fill the densimeter cell and the buffer volume was connected downstream with nitrogen at a pressure slightly below the mixture pressure. The starting up of the pneumatic pump (5) and the simultaneous opening of the upper valve of the separator (8) allow the buffer volume to be filled via the densimeter cell under isobaric conditions. Then, the three-way valve (9) closes off the circuit.

In the design of the experimental device, another important point to be taken into consideration and solved was the reduction of the thermal leaks caused by a convection phenomenon between the heated sample in the cell and the same sample at ambient temperature in the pressurization circuit. For this purpose, the buffer volume (4 cm³) (4) made up by a capillary enclosed in a metallic block, which is regulated at the measurement temperature, enabled us to minimize the thermal leaks, knowing that the connection capillaries between the densimeter cell and the thermostated block are insulated. This configuration is an alternative way to compensate the lack of stirring and enable us to preserve a homogeneous composition.

Density Measurement. The densimeter consists of an Anton/Paar DMA 512 high-pressure cell (2) and a Anton/Paar DMA 60 seven-digit frequency counter (1). In the DMA 512, the measuring cell is made of a U-shaped stainless steel tube with a volume of 1 cm³. The cell was

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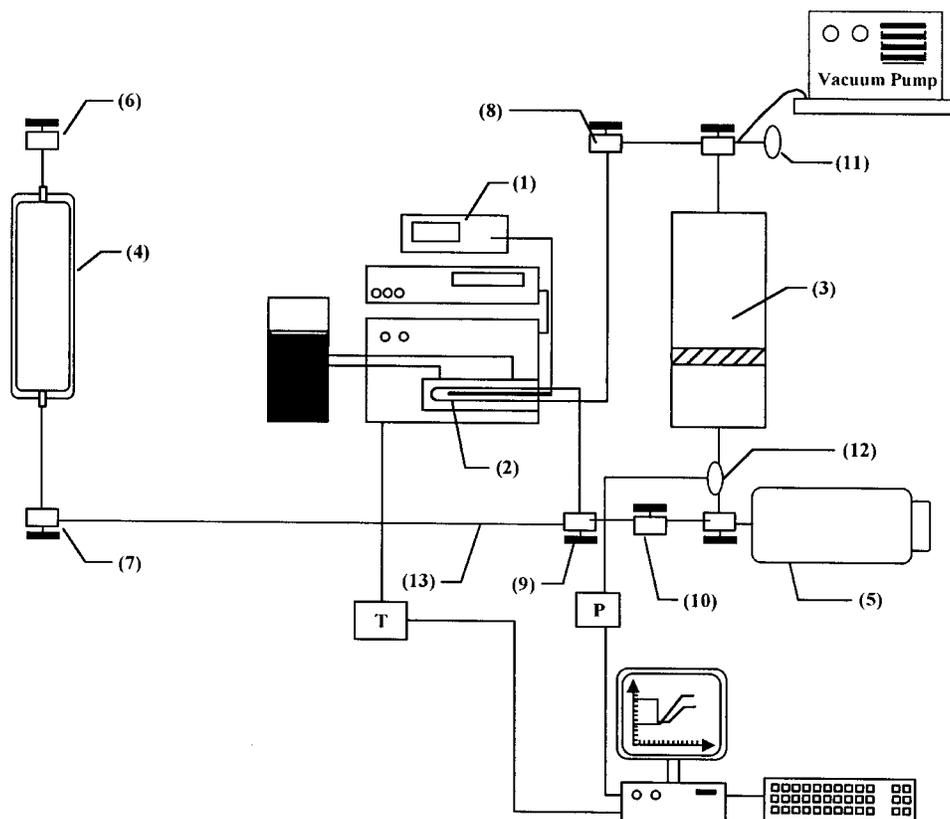


Figure 1. Experimental device: (1) Anton Paar DMA 60; (2) DMA 512 high-pressure cell; (3) separator (Top Industrie); (4) buffer volume; (5) pneumatic pump [0.1–100 MPa] (Top Industrie); (6–10) three-way valve; (11 and 12) HBM manometer [0.1–200 MPa]; (13) bypass line capillary (i.d.: 2.4 mm).

placed inside a double-walled cylinder through which a thermostated fluid of high thermal conductivity can be circulated. The measurement principle, which has already been detailed elsewhere,⁶ consists of determining the period of oscillation of the U-shaped tube. Calibration is compulsory in order to obtain a correlation between the oscillation periods of the tube and the density. The apparatus was calibrated by using water⁷ and the evacuated cell. Measurements were made with water over the entire range of pressure and temperature from 0.1 to 40 MPa and from 298.15 to 368.15 K. The steps adopted were respectively 5 MPa and 10 K. Then, the oscillation periods at all temperatures were measured, with a vacuum (less than 100 Pa).

The temperature was measured within ± 0.1 K by a 100 Ω platinum probe, whereas the static pressure was recorded by two manometers (HBM 0.1–200 MPa, (11), (12)), connected close to the experimental cells which had been calibrated previously by a double weight gauge ("Bunderberg", uncertainty $\pm 0.2\%$ in the entire scale). The estimated uncertainty in the density measurement is about ± 0.2 kg/m³. To test the reliability of the apparatus and its calibration, densities of decane were measured and compared with recommended literature data.⁸ The experimental measurement differed from the literature values by an average absolute deviation of 0.1% (AAD), which does establish the reliability of the system in terms of both its accuracy and reproducibility.

Results and Discussion

Density versus Pressure and Temperature. Table 1 presents the density data for carbon dioxide (1) + decane (2) mixtures for respective concentrations of $x_1 = 0.15, 0.30, 0.51, 0.66, 0.78,$ and 0.84 . All data were obtained above the mixture bubble point pressures. As expected, the

results show a classical behavior for the liquid state: the densities decrease with temperature and increase with pressure. The densities of this binary system have previously been measured¹ for the following compositions $x_1 = 0.15, 0.30,$ and 0.50 . Our results were compared with literature data at similar temperatures and pressures; when not at the same pressures and temperatures, literature data were interpolated to match the pressures and temperatures measured. It is noticeable that the values obtained agree closely with the literature values. For the three compositions, respective absolute average deviations (AADs) of 0.30%, 0.30%, and 0.18% were observed. Comparisons could not be made at higher pressures, since the set of data, available for only four temperatures, is limited to pressures less than 34 MPa. Hence, this study enables us to complement the database on the decane + carbon dioxide binary mixtures.

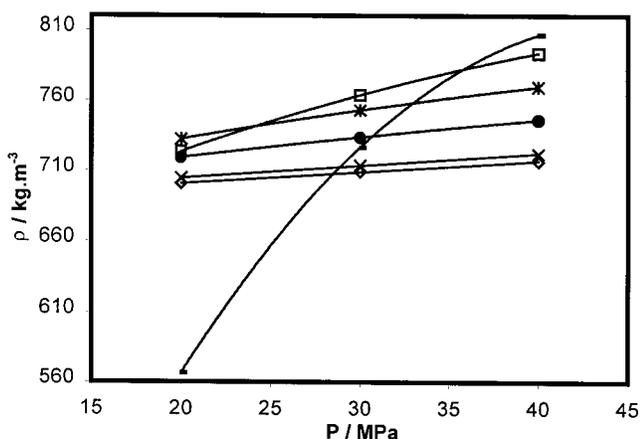
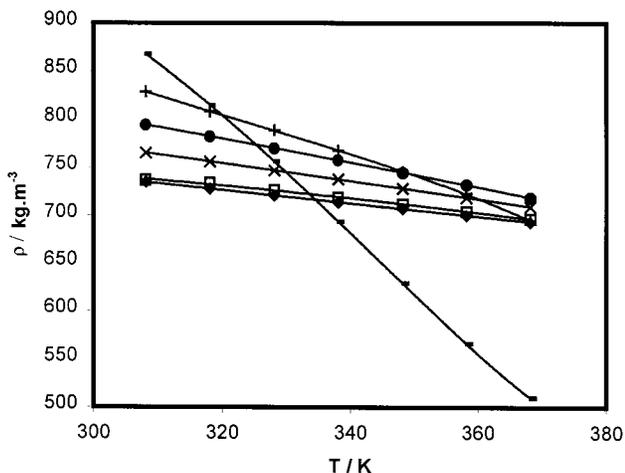
Figure 2 represents the densities of the binary mixtures as a function of pressure whereas in Figure 3 the isobaric curves (density versus temperature) are displayed. The densities of the pure fluids were measured for decane and reported from the literature for carbon dioxide.⁹ At high temperatures and low pressures, the densities of the mixtures show a crossover with composition. It seems that the crossover pressure increases with temperature. This peculiar behavior, already observed in similar studies,³ is clearly explainable by the density variations of pure fluids (see Figures 2 and 3); carbon dioxide has a lower density than decane at low pressures.

"Excess Volumes" (Mixing Excess Values of Volumes). The excess volumes were determined at any given pressure and temperature according to the relation

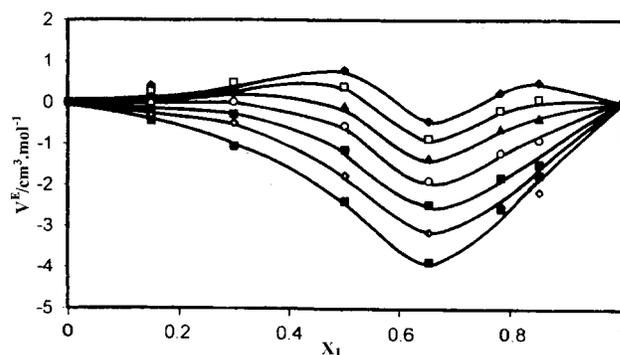
$$V_m^E = V^{\text{mix}} - (x_1 V_1 + x_2 V_2) \quad (1)$$

Table 1. Density ρ for Carbon Dioxide (1) + Decane (2) as a Function of Pressure and Temperature

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$						
		$x_1^a = 0$	$x_1^a = 0.15$	$x_1^a = 0.30$	$x_1^a = 0.51$	$x_1^a = 0.66$	$x_1^a = 0.78$	$x_1^a = 0.84$
308.15	20	734.79	737.18	749.39	765.39	794.35	813.86	828.54
318.15	20	727.82	733.72	741.28	756.20	782.21	797.84	807.83
328.15	20	720.92	726.53	733.32	747.06	770.06	781.59	788.74
338.15	20	714.05	719.05	725.13	737.90	757.89	764.66	767.63
348.15	20	707.19	711.67	717.42	728.42	745.20	747.89	745.84
358.15	20	700.30	704.27	708.94	719.08	732.30	730.40	723.43
368.15	20	693.35	696.95	700.86	709.45	718.88	709.27	694.93
308.15	30	741.46	748.32	757.47	776.16	808.31	832.58	851.82
318.15	30	734.79	741.36	749.79	767.68	797.33	818.35	834.85
328.15	30	728.22	734.42	742.23	759.26	786.56	804.30	817.08
338.15	30	721.72	727.49	734.59	750.84	775.35	790.00	800.08
348.15	30	715.26	720.41	726.96	742.26	764.25	775.43	782.64
358.15	30	708.80	713.59	719.55	733.76	753.09	760.88	763.88
368.15	30	702.31	706.72	711.96	725.13	741.78	737.52	735.17
308.15	40	747.57	754.79	766.92	785.65	820.38	848.04	870.73
318.15	40	741.14	748.16	757.46	777.57	810.25	835.21	855.44
328.15	40	734.84	741.57	750.26	769.81	800.15	822.13	840.02
338.15	40	728.65	735.03	742.94	761.79	790.21	809.60	824.82
348.15	40	722.52	728.46	735.87	754.05	780.03	796.63	809.29
358.15	40	716.42	721.80	728.18	746.21	769.86	783.53	793.70
368.15	40	710.33	715.10	722.00	737.91	759.53	764.10	766.20

^a $x_1 = \text{C}_{10}\text{H}_{22}$ concentration.**Figure 2.** Pressure dependence of the density for the binary mixtures of carbon dioxide (1) and decane (2) at different concentrations x_1 : \diamond , 0; \times , 0.15; \bullet , 0.51; $*$, 0.66; \square , 0.84; $-$, 1.**Figure 3.** Temperature dependence of the density for the binary mixtures of carbon dioxide (1) and decane (2) at different concentrations x_1 : \blacklozenge , 0; \square , 0.15; \times , 0.51; \bullet , 0.66; $+$, 0.84; $-$, 1.

where x_1 and x_2 are the molar fractions of carbon dioxide and decane and $V = M/\rho$ are the molar volumes. The carbon dioxide density data used are those from the literature.⁹

**Figure 4.** Excess volumes for binary mixtures of carbon dioxide (1) with decane (2) at 40 MPa at different temperatures T : \blacklozenge , 308.15 K; \square , 318.15 K; \blacktriangle , 328.15 K; \circ , 338.15 K; \blacksquare , 348.15 K; \diamond , 358.15 K; \blacksquare , 368.15 K.

The uncertainty in the excess volumes, which depends on the uncertainties on densities both of the pure components and of the mixture, is estimated to be about $\pm 2\%$. Moreover, the mixtures are at subcritical conditions (the experimental temperatures are below the critical temperature of the mixtures) in the one-phase homogeneous liquid state whereas, at these conditions, the carbon dioxide is supercritical. Therefore, the value V_m^E is a mixing excess value and not strictly an excess value from a thermodynamic point of view.

As shown in Figures 4 and 5, excess volume data appreciably change with the pressure–temperature conditions. At 40 MPa (Figure 4), the isothermal curves display a negative excess volume increasing with the temperature, whereas (see Figure 5) the excess volumes become less negative with increasing pressure. For these mixtures decane + carbon dioxide excess volumes have not been reported in the literature until this very study was carried out. A similar behavior was already observed for other binary mixtures^{3,4} where one component was supercritical.

Calculation from Equations of State and Mixing Rules. PVT equations of state are used in chemical engineering to estimate thermophysical properties when pressure is to be taken into account. From this perspective, two modified BWR¹⁰ (virial-type) equations of state, the version proposed by Nishiumi et al.¹¹ and the Lee–Kesler¹²

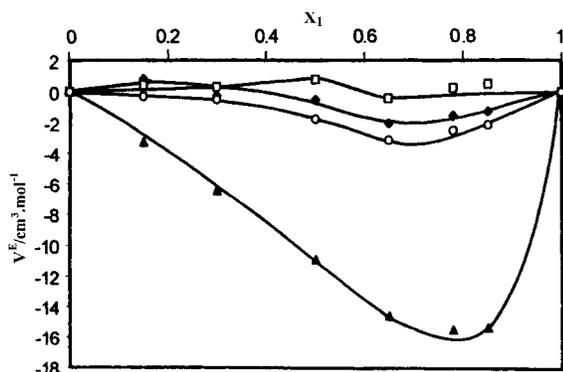


Figure 5. Excess volumes for binary mixtures of carbon dioxide (1) with decane (2) at several (P , T) values: \blacklozenge , (308.15 K, 20 MPa); \square , (308.15 K, 40 MPa); \blacktriangle , (358.15 K, 20 MPa); \circ , (358.15 K, 40 MPa).

Table 2. Absolute Average Deviations (%) of the Density Predicted by the Lee–Kesler Correlation with Various Mixing Rules

x_1	AAD with the following mixing rules					
	Pedersen	Spencer	Teja	Hankinson	Lee–Kesler	Plocker
0.15	3.15	0.23	3.70	3.66	3.98	4.70
0.30	5.50	0.11	6.30	6.08	7.15	8.46
0.51	8.52	0.52	9.00	8.47	10.90	12.65
0.66	10.00	1.71	9.30	8.58	12.46	14.02
0.78	11.87	5.70	9.65	8.69	14.01	14.95
0.84	12.14	8.50	8.85	7.93	13.93	14.35

Table 3. Absolute Average Deviations (%) of the Density Predicted by the Nishiumi Correlation with Various Mixing Rules

x_1	AAD with the following mixing rules						
	Internal	Pedersen	Spencer	Teja	Hankinson	Lee–Kesler	Plocker
0.15	0.30	0.33	2.37	1.56	2.35	0.63	0.60
0.30	0.48	0.28	5.55	2.99	3.00	0.82	1.26
0.51	1.38	0.31	10.68	5.64	4.25	0.92	1.65
0.66	2.51	0.63	15.95	10.50	9.50	1.09	1.15
0.78	2.10	2.70	21.49	14.45	10.5	0.68	2.00
0.84	3.70	4.16	25.38	12.91	12.5	1.89	2.33

correlation, were tested; this final correlation is an application of the corresponding states principle with two references (methane and octane) and three parameters (T_c , P_c , ω). Mixing rules for pseudocritical parameters (which combine the critical properties of the mixture components) were necessary in order to use the two equations of state. Among the great number of mixing rules available in the corresponding literature, those from Pedersen et al.,¹³ Spencer and Danner,¹⁴ Teja,¹⁵ Hankinson and Thomson,¹⁶ Lee and Kesler,¹² and Plocker et al.¹⁷ were tested.

The Nishiumi equation was also applied using an “internal mixing rule”, which combines the equation parameters, taking into account the binary interaction parameters k_{ij} . Thus, the correlation for k_{ij} suggested by Nishiumi and Saito,¹⁸ regarding hydrocarbon + carbon dioxide mixtures, was employed.

The absolute average deviations (AADs) obtained with various equations of state using different mixing rules are reported in Tables 2 and 3. The first observation applicable to all models is that when molar carbon dioxide fraction increases, prediction accuracy decreases. This comparative study also underlines the influence of the mixing rule being used. This is clearly shown by the asymmetry of the mixtures (the critical properties of each component are really different). Indeed, this work has enabled us to draw

models that are well-adapted to a density estimation of these mixtures. As already mentioned in another work,¹⁹ the use of the internal rule with the Nishiumi equation brings no significant improvement to the estimations; however, when the Nishiumi equation is applied using Plocker or Lee and Kesler rules (AAD inferior to 1% for compositions up to 0.78%), satisfactory density predictions are obtained. These associations should be tested in further studies.

Conclusions

This study confirms the peculiar volumetric behavior of the carbon dioxide + decane mixtures for which the densities show a crossover phenomenon with composition. A general trend in the excess values can also be observed. However, the main satisfactory result of this work comes from the density predictions by models whose capability should be confirmed in further studies.

Literature Cited

- (1) Cullick, A. S.; Mathis, M. L. Densities and Viscosities of Mixtures of Carbon Dioxide and *n*-Decane from 310 to 403 K and 7 to 30 MPa. *J. Chem. Eng. Data* **1984**, *29*, 393–396.
- (2) Barrufet, M. A.; El-Sayed Salem S. K.; Tantawy, M.; Iglesias-Silva, G. A. Liquid Viscosities of Carbon Dioxide + Hydrocarbons from 310 K to 403 K. *J. Chem. Eng. Data* **1996**, *41*, 436–439.
- (3) Kiran, E.; Pölher, H.; Xiong, Y. Volumetric properties of Pentane + Carbon Dioxide at High Pressures. *J. Chem. Eng. Data* **1996**, *41*, 158–165.
- (4) Wormald, C. J.; Eyaers, J. M. Excess molar enthalpies and excess molar volumes of $\{x\text{CO}_2 + (1-x)\text{C}_6\text{H}_{14}\}$ at 298.15, 304.10 and 308.15 K from 7.5 to 12.6 MPa. *J. Chem. Thermodyn.* **1987**, *19*, 845–856.
- (5) Bessières, D.; Saint-Guirons, H.; Daridon, J.-L.; Coxam, J.-Y. Apparatus for simultaneous determination of the densities and heat capacities of liquids and of liquids with dissolved gases under an extended range of pressure (0.1–100 MPa). *Meas. Sci. Technol.* **2000**, *11*, N69–N72.
- (6) Lagourette, B.; Boned, C.; Saint-Guirons, H.; Xans, P.; Zhou, H. Densimeter calibration method versus temperature and pressure. *Meas. Sci. Technol.* **1992**, *3*, 699–703.
- (7) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam tables*; Hemisphere: Washington, New York, 1984.
- (8) Cibulka, I.; Hnedkovsky, L. Liquid densities at elevated pressures of *n*-alkanes from C_5 to C_{16} : a critical evaluation of experimental data. *J. Chem. Eng. Data* **1996**, *41*, 657–668.
- (9) *Gas Encyclopaedia*; Elsevier: New York, 1976.
- (10) Benedict, M.; Webb, G. B.; Rubin, L. C. An empirical equation of state for the thermodynamic properties of light hydrocarbons and their mixtures. *J. Chem. Phys.* **1940**, *8*, 334–345.
- (11) Nishiumi, H.; Saito, S. An improved generalized BWR equation of state applicable to low reduced temperatures. *J. Chem. Eng. Jpn.* **1975**, *8*, 356–360.
- (12) Lee, B. I.; Kesler, M. G. A generalized thermodynamic correlation based on three parameter corresponding states. *AIChE J.* **1975**, *21*, 510–527.
- (13) Pedersen, K. S.; Christensen, P. L.; Fredenslund, Aa. Viscosity of crude oils. *Chem. Eng. Sci.* **1984**, *39*, 1011–1016.
- (14) Spencer, C. F.; Danner, R. P. Improved equation for prediction of saturated liquid density. *J. Chem. Eng. Data* **1972**, *17*, 236–241.
- (15) Teja, A. S. A corresponding states equation for saturated liquid densities: I-Applications to LNG. *AIChE J.* **1980**, *26*, 337–341.
- (16) Hankinson, R. N.; Thomson, G. H. A new correlation for saturated densities of liquids and their mixtures. *AIChE J.* **1979**, *25*, 653–663.
- (17) Plöcker, U.; Knapp, H.; Prausnitz, J. Calculation of high-pressure vapor-liquid equilibria from corresponding-states correlation with emphasis on asymmetric mixtures. *Ind. Eng. Chem. Process. Des. Dev.* **1978**, *17*, 324–332.
- (18) Nishiumi, H.; Saito, S. Correlation of the binary interaction parameter of the modified generalized BWR equation of state. *J. Chem. Eng. Jpn.* **1977**, *10*, 176–180.
- (19) Bessières, D.; Saint-Guirons, H.; Daridon, J.-L. Measurement and calculation of heat capacity of heavy distillation cuts under pressure up to 40 MPa. *J. Therm. Anal. Calorim.* **1999**, *58*, 39–49.

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