

PARTIAL MOLAR VOLUMES AT INFINITE DILUTION IN SUPERCRITICAL FLUIDS - PREDICTION WITH CUBIC EQUATIONS OF STATE

Silvio A. B. Vieira de Melo¹, Gloria M. N. Costa² and Fernando L. P. Pessoa³

¹ ITP-UNIT – Institute of Science and Technology, Tiradentes University, Av. Murilo Dantas, 300 - Farolândia, 49032-490, Aracaju-SE, Brazil. Telefax +55-79-2182190. E-mail: sabvm@infonet.com.br

² UNIFACS-University of Salvador, Av. Cardeal da Silva, 132, Federação, 40220-141, Salvador-BA.

³ DEQ - EQ - Federal University of Rio de Janeiro - Centro de Tecnologia, bloco E, S. 209, Ilha do Fundão, 21949-900, Rio de Janeiro-RJ, Brazil.

A comparison among Wong-Sandler, MHV2 and LCVM excess Gibbs free energy mixing rules for Peng-Robinson equation of state is presented for the correlation of partial molar volume at infinite dilution in supercritical fluids. The database employed in this evaluation includes linear, cyclic and aromatic hydrocarbons, alcohols and terpenes. Results show that Wong-Sandler mixing rules are the more accurate in predicting partial molar volume at infinite dilution.

Keywords: cubic equation of state, G^E mixing rules, supercritical fluid, partial molar volume, infinite dilution

INTRODUCTION

The partial molar volume is the key thermodynamic property that describes the pressure effect on supercritical fluid phase behavior. It can be used to determine maxima and minima in the solubility versus pressure isotherms as well as a region of practical interest where the solubility is extremely sensitive to pressure. The partial molar volume exhibits large negative values in the proximity of the critical point of the solvent, being a very stringent test for an equation of state (EOS), and this constraint requires that the differentiated form also be correct. The anomalies that result in predicting the partial molar volume with a cubic EOS are not a consequence of the particular equation used but of the mixing rules employed. Improvement in the correlation can only be realized by utilizing mixing rules more suitable for these types of systems where large differences in size and interactions between the solvent and solute are present [1, 2].

Following the suggested approach of Vidal, several modeling attempts have been proposed by combining a cubic EOS with an excess Gibbs free energy model. These methods have been extensively discussed only for solubilities in supercritical fluids. However, the ability of a EOS to maintain its accuracy under differentiation is better test of its prediction and correlation capacity than the ability to match solubility data.

The aim of this work is to explore the feasibility of excess Gibbs free energy models mixing rules from Wong-Sandler, MHV2 and LCVM, using the Peng-Robinson EOS, to the correlation of partial molar volume at infinite dilution in supercritical fluids. The database employed in this evaluation includes linear, cyclic and aromatic hydrocarbons, alcohols and terpenes [3, 4]. It is important to note that the interaction parameters are obtained by fitting partial molar volume experimental data instead of fitting VLE experimental data because we cannot assure that partial molar volume predictions with Peng-Robinson EOS match the experimental data [2].

MATERIAL AND METHODS

The partial molar volume at infinite dilution of a solute is given by

$$\bar{v}_2^\infty = \beta_1 \cdot v_1 \cdot \lim_{x_2 \rightarrow 0} \left[n \left(\frac{\partial P}{\partial n_2} \right)_{T, V, n_1} \right] \quad (1)$$

where P is the total pressure, v_1 is the molar volume of the pure solvent and β_1 is the isothermal compressibility of the pure solvent given by

$$\beta_1 = -\frac{1}{v_1} \left(\frac{\partial v_1}{\partial P} \right)_T \quad (2)$$

In this work, equation 1 is applied to calculate the partial molar volume at infinite dilution of several solutes in supercritical carbon dioxide using the Peng-Robinson EOS along with Wong-Sandler, MHV2 and LCVM mixing rules incorporating UNIFAC model [5, 6, 7, 8]. To evaluate the performance of these mixing rules, calculation of partial molar volume is done with one adjustable parameter for the solutes listed in Table 1. Correlation results are evaluated using the absolute average relative deviation (AARD) and the root mean square deviation (σ) given, respectively, by

$$AARD = \frac{100}{NDP} \sum_i \left| \frac{(\bar{v}_i^\infty)_{exp} - (\bar{v}_i^\infty)_{cal}}{(\bar{v}_i^\infty)_{exp}} \right| \quad (3)$$

$$\sigma = \sqrt{\frac{\sum_i [(\bar{v}_i^\infty)_{exp} - (\bar{v}_i^\infty)_{cal}]^2}{NDP}} \quad (4)$$

where NDP is the number of data points.

RESULTS AND DISCUSSION

Table 1 presents the dilute solutes in supercritical carbon dioxide investigated in this paper. Experimental data are taken only from the ascendant part of the infinite dilution partial molar volume versus pressure curves given by [3] and [4], that is, in order to make a reasonable comparison among all systems studied (some ones with 13 and others with 8 experimental datapoints), only 8 datapoints are considered for them.

Table 2 shows a comparison among the correlation results obtained by Peng-Robinson EOS using Wong-Sandler, MHV2 and LCVM mixing rules. For each isothermal data set is estimated a parameter for each of the cited mixing rules. It is important to note that even LCVM cannot be used in a fully predictive way and the parameter λ assumes high unusual values. MHV2 mixing rules give parameter values practically constant for all systems. As a rule, for MHV2, increasing molecular weight in an homologue series decreases AARD and increases σ values. Results show that Wong-Sandler mixing rules give the best performance

for all systems, except for CO₂-benzaldehyde. However, no rule is observed between AARD and σ values with molecular weight for each homologue series.

Figures 1 to 4 illustrate the ability of Peng-Robinson-Wong-Sandler-UNIFAC model to describe quite well infinite dilution partial molar volume for the systems CO₂-hexene, CO₂-ethylcyclohexane, CO₂-1-octanol and CO₂-linalool.

Table 1. Systems investigated in this work.

| CO ₂ / | T (°C) | P (bar) | NDP | Reference |
|-------------------|--------|---------|-----|-----------|
| n-Hexane | 40 | 80-280 | 8 | [3] |
| n-Octane | 40 | 80-280 | 8 | [3] |
| n-Nonane | 40 | 100-280 | 8 | [3] |
| n-Decane | 40 | 80-280 | 8 | [3] |
| n-Dodecane | 40 | 80-280 | 8 | [3] |
| Hexene | 40 | 100-280 | 8 | [3] |
| Heptene | 40 | 100-280 | 8 | [3] |
| Cyclohexane | 40 | 100-280 | 8 | [3] |
| Methylcyclohexane | 40 | 100-280 | 8 | [3] |
| Ethylcyclohexane | 40 | 100-280 | 8 | [3] |
| Decalene | 40 | 100-280 | 8 | [3] |
| 1-Propanol | 40 | 100-280 | 8 | [4] |
| 1-Butanol | 40 | 100-280 | 8 | [4] |
| 1-Pentanol | 40 | 100-280 | 8 | [4] |
| 1-Hexanol | 40 | 100-280 | 8 | [4] |
| 1-Heptanol | 40 | 100-280 | 8 | [4] |
| 1-Octanol | 40 | 100-280 | 8 | [4] |
| Geraniol | 40 | 80-280 | 8 | [4] |
| Nerol | 40 | 80-280 | 8 | [4] |
| Linalool | 40 | 80-280 | 8 | [4] |
| Terpineol | 40 | 80-280 | 8 | [4] |
| Citronellol | 40 | 80-280 | 8 | [4] |
| Benzene | 40 | 100-280 | 8 | [3] |
| Toluene | 40 | 100-280 | 8 | [3] |
| Ethylbenzene | 40 | 100-280 | 8 | [3] |
| Octylbenzene | 40 | 100-280 | 8 | [3] |
| Benzaldehyde | 40 | 80-280 | 8 | [3] |

CONCLUSIONS

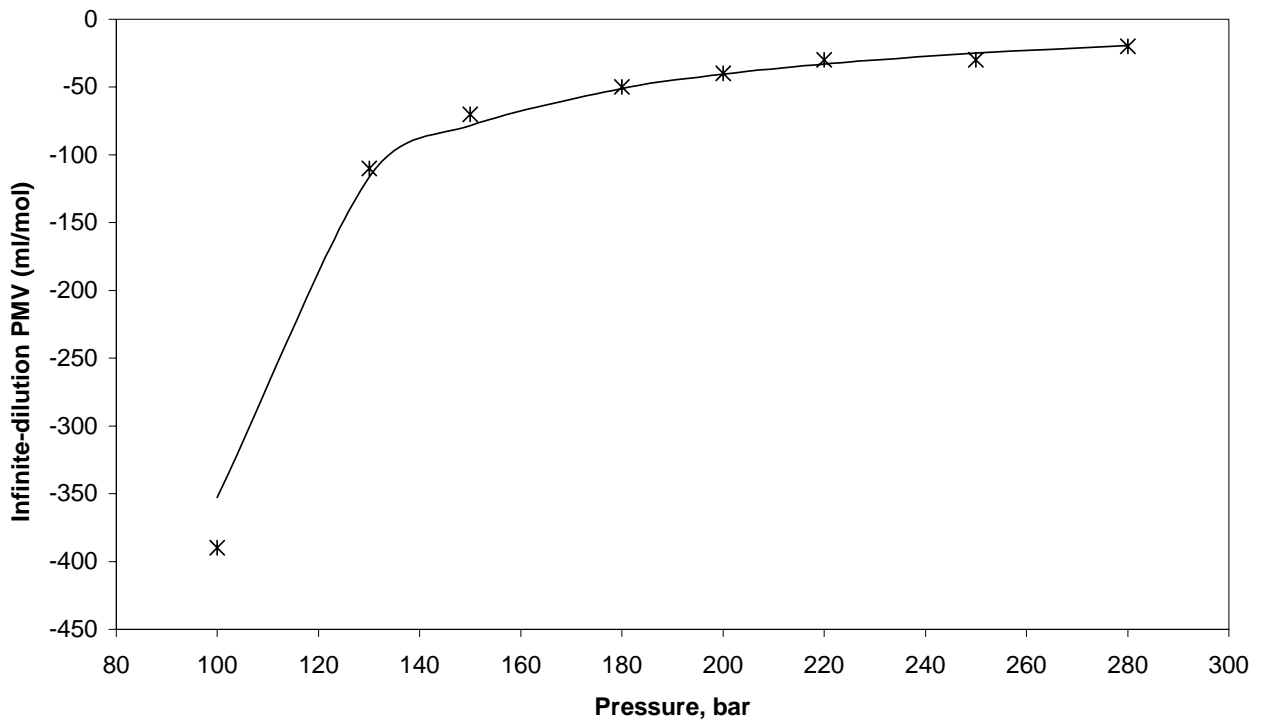
Calculation of partial molar volume is a very stringent test for an equation of state, since this constraint requires that its differentiated form also be correct. In this paper, Peng-Robinson equation of state is used to describe partial molar volume of dilute solute in supercritical carbon dioxide for binary mixtures containing linear, cyclic and aromatic hydrocarbons, alcohols and terpenes. A comparison among Wong-Sandler, MHV2 and LCVM mixing rules (incorporating UNIFAC excess Gibbs free energy) is presented for the correlation of this property. Only one interaction parameter is obtained by fitting the experimental data for each mixing rule. Results show that Wong-Sandler mixing rules are the more accurate and LCVM are the less accurate in predicting partial molar volume at infinite dilution.

Table 2. Comparison among results obtained by Peng-Robinson EOS using Wong-Sandler, MHV2 and LCVm mixing rules (σ unit is ml/mol).

| Systems | Wong-Sandler | | | MHV2 | | | LCVM | | |
|-------------------|--------------|----------|--------|-------|----------|--------|--------|----------|--------|
| | AARD | σ | Param. | AARD | σ | Param. | AARD | σ | Param. |
| CO ₂ / | | | | | | | | | |
| n-Hexane | 23.09 | 188.51 | 0.881 | 26.61 | 189.56 | 1.013 | 68.81 | 329.75 | 5.046 |
| n-Octane | 10.50 | 114.05 | 0.856 | 27.53 | 206.88 | 1.013 | 81.87 | 474.73 | 3.87 |
| n-Nonane | 7.77 | 105.41 | 0.863 | 24.14 | 217.60 | 1.013 | 82.51 | 531.59 | 3.57 |
| n-Decane | 5.55 | 73.71 | 0.864 | 25.23 | 230.83 | 1.013 | 87.96 | 609.80 | 3.34 |
| n-Dodecane | 11.52 | 21.75 | 0.873 | 22.63 | 234.57 | 1.013 | 104.62 | 757.76 | 2.906 |
| Hexene | 7.68 | 13.83 | 0.767 | 46.60 | 145.43 | 1.011 | 133.49 | 340.36 | 4,37 |
| Heptene | 25.08 | 44.52 | 0.770 | 46.90 | 150.05 | 1.011 | 159.55 | 412.37 | 3.62 |
| Cyclohexane | 20.69 | 25.19 | 0.721 | 52.72 | 152.16 | 1.013 | 133.42 | 297.06 | 4.053 |
| Methylcyclohexane | 31.10 | 53.28 | 0.749 | 52.93 | 152.69 | 1.012 | 162.75 | 369.28 | 3.55 |
| Ethylcyclohexane | 7.48 | 10.68 | 0.803 | 35.47 | 176.64 | 1.013 | 112.92 | 448.19 | 3.58 |
| Decalyne | 34.05 | 125.89 | 0.776 | 34.58 | 184.81 | 1.015 | 108.65 | 469.42 | 2.76 |
| 1-Propanol | 11.36 | 19.10 | 0.602 | 28.44 | 175.02 | 1.023 | 48.45 | 185.17 | 4.45 |
| 1-Butanol | 9.36 | 14.05 | 0.659 | 26.61 | 200.82 | 1.023 | 45.75 | 222.56 | 4.14 |
| 1-Pentanol | 8.34 | 24.33 | 0.703 | 23.51 | 217.35 | 1.023 | 44.58 | 260.33 | 3.90 |
| 1-Hexanol | 7.37 | 35.24 | 0.701 | 23.47 | 233.30 | 1.025 | 37.26 | 251.35 | 3.96 |
| 1-Heptanol | 5.98 | 28.05 | 0.768 | 23.79 | 256.09 | 1.021 | 49.96 | 382.29 | 3.45 |
| 1-Octanol | 5.58 | 51.49 | 0.789 | 20.82 | 273.12 | 1.022 | 47.48 | 411.16 | 3.41 |
| Geraniol | 20.65 | 148.43 | 0.773 | 20.22 | 262.68 | 1.023 | 56.61 | 490.32 | 2.51 |
| Nerol | 28.01 | 192.55 | 0.763 | 23.19 | 254.23 | 1.022 | 62.66 | 498.50 | 2.37 |
| Linalool | 18.09 | 107.43 | 0.762 | 24.01 | 258.06 | 1.021 | 59.85 | 469.41 | 2.78 |
| Terpineol | 23.04 | 145.35 | 0.744 | 23.36 | 257.46 | 1.024 | 54.02 | 424.55 | 2.51 |
| Citronellol | 48.74 | 307.88 | 0.757 | - | - | - | 92.07 | 561.16 | 2.05 |
| Benzene | 11.18 | 101.71 | 0.709 | 26.81 | 194.10 | 1.020 | 44.69 | 196.37 | 6.07 |
| Toluene | 6.76 | 63.66 | 0.738 | 26.10 | 189.56 | 1.019 | 53.31 | 264.35 | 4.62 |
| Ethylbenzene | 9.57 | 135.47 | 0.784 | 23.65 | 240.44 | 1.020 | 45.14 | 295.14 | 4.53 |
| Octylbenzene | 20.91 | 138.32 | 0.850 | 21.79 | 256.85 | 1.016 | 93.15 | 763.51 | 2.62 |
| Benzaldehyde | 95.89 | 313.38 | 0.569 | 39.94 | 156.31 | 1.022 | 110.24 | 316.56 | 0.95 |

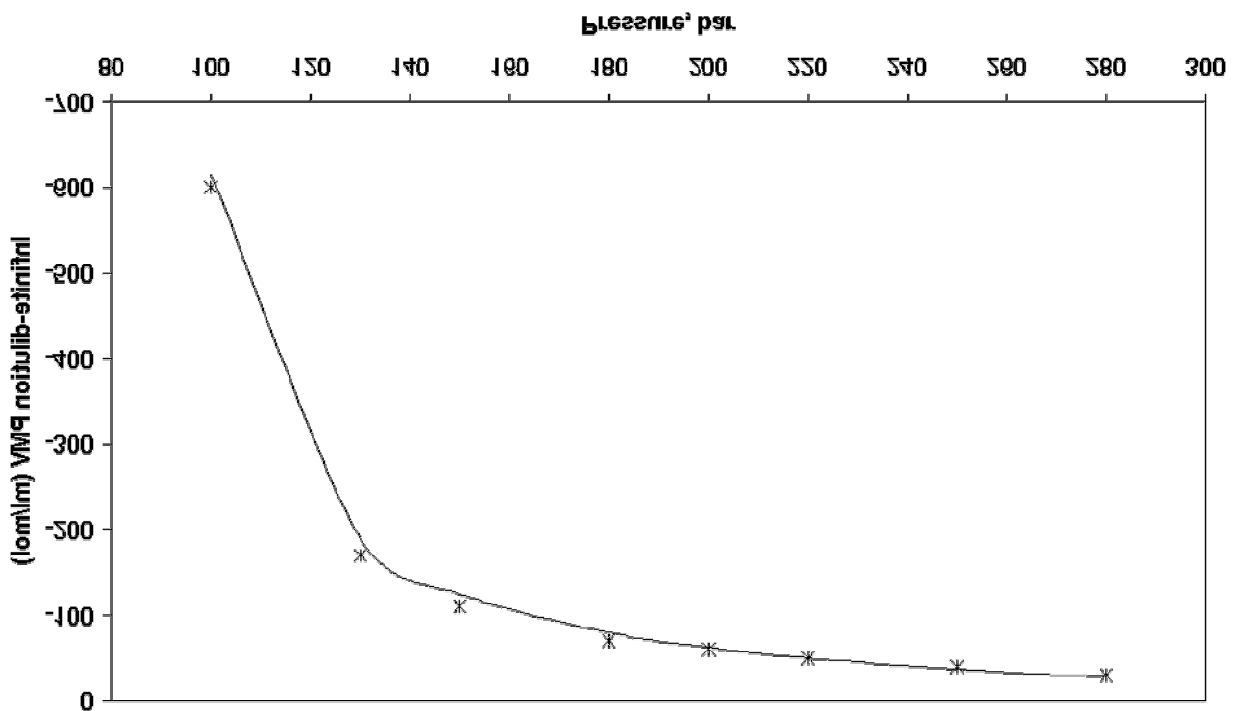
REFERENCES

- [1] ECKERT, C.A., ZIGER, D.H., JOHNSTON, K. P., ELLISON, T.K., Fluid Phase Equilibria, 14, **1983**, 167-175.
- [2] COUTSIKOS, Ph., MAGOULAS, K., TASSIOS, D., CORTESI, A., KIKIC, I., J. Supercritical Fluids, 11, **1997**, 21-35.
- [3] SPICKA, B., CORTESI, A., FERMEGLIA, M., KIKIC, I., J. Supercritical Fluids, 7, **1994**, 171.
- [4] CORTESI, A., KIKIC, I., SPICKA, B., MAGOULAS, K., TASSIOS, D., J. Supercritical Fluids, 9, **1996**, 141.
- [5] PENG, D. Y.; ROBINSON, D. B., Ind. Eng. Chem. Fundam., 15, **1976**, 58-64.
- [6] DAHL, S.; MICHELSEN, M. L., AIChE J., 36 (12), **1990**, 1829-1836.
- [7] WONG, D.S.H., SANDLER, S.I., AIChE J., 38(5), **1992**, 671-680.



[8] BOUKOUVALAS, C.; SPILIOTS, N.; COUTSIKOS, N.; TASSIOS, D., Fluid Phase Equilibria, 92, 1994, 75-106.

Figure 1: Prediction of the infinite-dilution partial molar volume (PMV) of hexene in carbon dioxide at 40°C with Wong-Sandler-UNIFAC-Peng-Robinson EOS (experimental data taken from [3]).



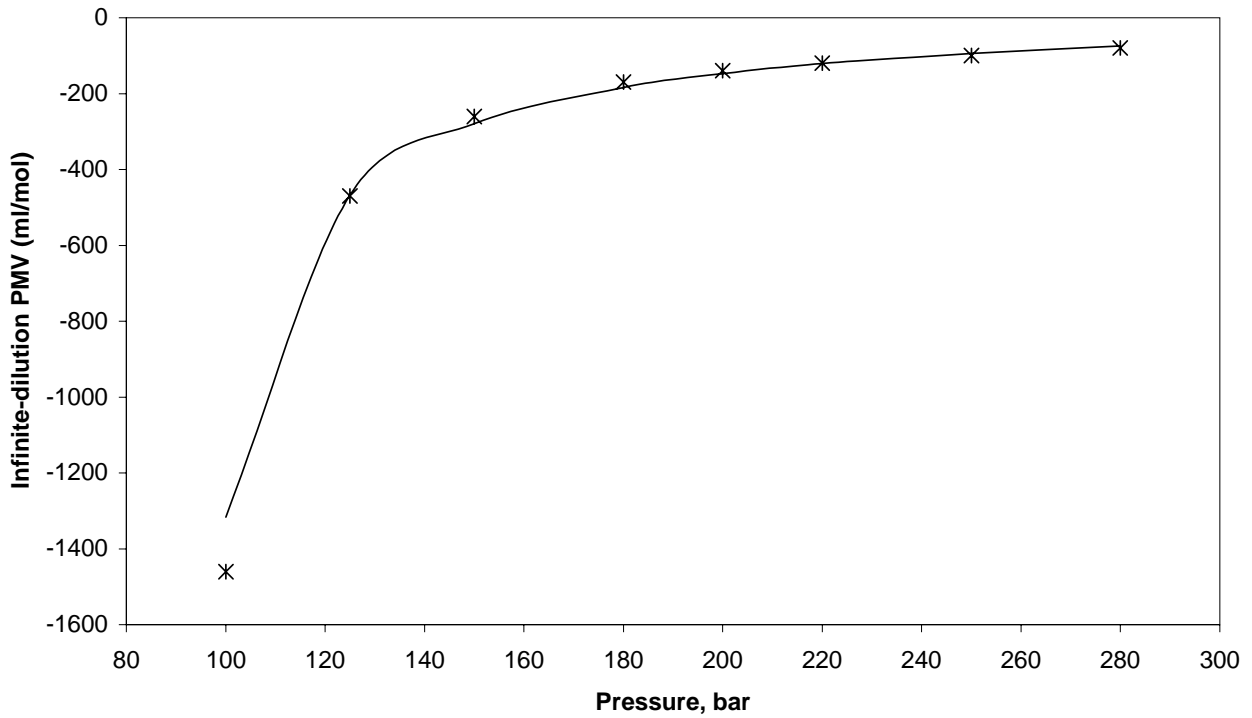


Figure 2: Prediction of the infinite-dilution partial molar volume (PMV) of ethylcyclohexane in carbon dioxide at 40°C with Wong-Sandler-UNIFAC-Peng-Robinson EOS (experimental data taken from [3]).

Figure 3: Prediction of the infinite-dilution partial molar volume (PMV) of 1-octanol in carbon dioxide at 40°C with Wong-Sandler-UNIFAC-Peng-Robinson EOS (experimental data taken from [4]).

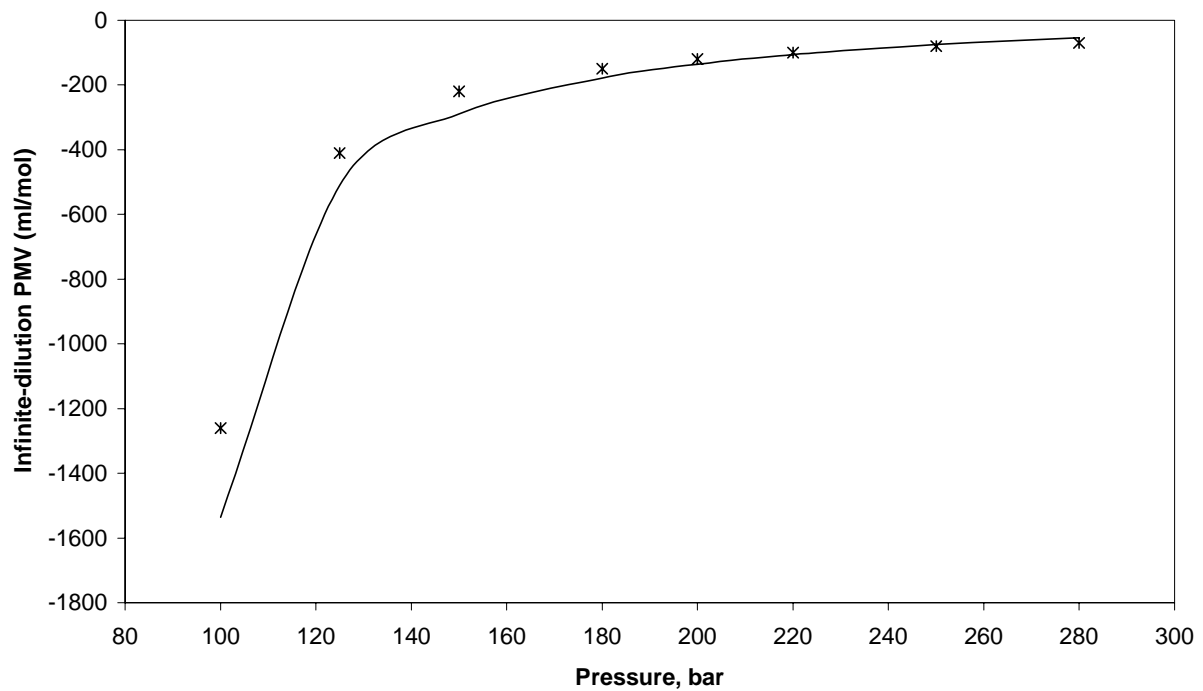


Figure 4: Prediction of the infinite-dilution partial molar volume (PMV) of linalool in carbon dioxide at 40°C with Wong-Sandler-UNIFAC-Peng-Robinson EOS (experimental data taken from [4]).