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Vapor–liquid equilibrium of methane and methane + nitrogen and an equimolar hexane + decane mixture under isothermal conditions

Verónica Uribe-Vargas, Arturo Trejo *

Instituto Mexicano del Petróleo, Programa de Ingeniería Molecular, Área de Investigación en Termofísica,
Eje Lázaro Cárdenas 152, 07730 México, D.F.; México

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Abstract

Experimental vapor–liquid equilibrium data of the ternary system composed of methane and an equimolar hexane + decane mixture are reported. The experimental measurements were carried out under isothermal conditions at 258, 273, and 298 K in the pressure range 1–19 MPa. Also, experimental vapor–liquid measurements were carried out for the quaternary system methane + nitrogen and an equimolar hexane + decane mixture, at 258 K in the range 3.5–12 MPa. The results for the ternary system show that the solubility of methane in the equimolar mixture of alkanes increases when the pressure is increased at constant temperature and it increases as the temperature decreases in the whole pressure range studied. For the quaternary system with a constant amount of nitrogen, the solubility of methane in the liquid phase increases as the pressure increases at the studied temperature. The experimental results for the ternary system were satisfactorily correlated with the Peng–Robinson equation of state in the ranges of pressure and temperature studied. The equation of state was used to predict the behavior of the quaternary system using binary interaction parameters. The applicability of the principle of congruence was corroborated by comparing the vapor–liquid behavior of methane in the equimolar hexane + decane mixture with that in pure octane, at the three temperatures studied in this work.

Keywords: Methane; Nitrogen; Hexane; Decane; Vapor–liquid equilibrium; Bronsted's principle

1. Introduction

The injection of nitrogen as an enhanced oil recovery operation in oilfields promotes that the associated natural gas will have a certain content of nitrogen, which clearly will increase gradually with time along the exploitation of the oil reservoirs. The presence of nitrogen in natural gas beyond the internationally acceptable concentration limits becomes a commercial and a processing drawback. In order to have different options to solve this problem it is necessary to carry out experimental studies on the vapor–liquid equilibrium of selected systems with the aim of obtaining a reliable body of information that will be the basis for the development of separation schemes that will allow the efficient separation of nitrogen from natural gas streams to achieve commercially acceptable concentration standards.

Much of the experimental work reported in the literature on the thermodynamic behavior of mixtures of linear paraffinic hydrocarbons was performed to test the empirical principle of congruence proposed by Bronsted and Koefoed [1]. This principle permits to determine in a simple way thermodynamic properties of a mixture of two or more normal alkanes of known concentration by equating to the properties, at the same pressure and temperature as the mixture, of a congruent pure alkane whose carbon chain length is equal to the average chain length of the mixture of alkanes. Several authors have demonstrated the applicability of this principle with the determination of many thermodynamic properties [2] like vapor pressure [1], excess enthalpy, excess entropy, excess heat capacity, and excess Gibbs energy [3], Henry's constant [4], partial molar quantities at finite concentration and at infinite dilution [4], excess molar volumes [5], and more recently the principle has been applied to dew and bubble points [6].

In this study we present the experimental pressure–temperature–concentration (P, T, x, y) results for the vapor–liquid equilibrium of the ternary system formed by methane and an equimolar (solute-free basis) hexane + decane mixture at 258, 273, and 298 K in the pressure range 1–19 MPa, and also for

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* Corresponding author. Tel.: +52 55 9175 8373; fax: +52 55 9175 6239.
E-mail address: atrejo@imp.mx (A. Trejo).

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the quaternary system of methane + nitrogen and an equimolar (solute-free basis) hexane + decane mixture, at 258 K, in the range 3.5–12 MPa. The experimental P, T, x, y results for the ternary system were correlated using the Peng–Robinson equation of state with the well known van der Waals one-fluid mixing rule. In order to correct the geometric mean of the energy parameters to obtain the corresponding cross parameter we adjusted one binary interaction parameter, k_{ij}, for each pair of components of the studied ternary system. The standard deviation of the fits shows that the data are correlated within the experimental uncertainty, in the whole range of pressure and temperature considered. The adjusted binary interaction parameters were employed to predict the behavior of the quaternary system with satisfactory results. Also, we have tested the validity of Bronsted's principle of congruence by comparing the results of this work for methane and the equimolar hexane + decane solvent mixture with literature data for methane in the congruent pure *n*-octane, at the three isotherms mentioned above.

2. Literature search

We carried out a comprehensive bibliographic search together with the analysis of experimental data from the open literature on the phase equilibria of nitrogen and methane in different liquid solvents with the purpose to find the best prospects as solvents for the efficient separation of nitrogen from natural gas and to establish the most adequate conditions of pressure and temperature for such separation by absorption.

In recent work [7] we reported the results of the bibliographical search on the vapor–liquid and gas–liquid equilibrium for nitrogen in liquid hydrocarbons (paraffins, aromatics and naphthenic hydrocarbons). In the present work we include the results of the same exercise for literature experimental data of methane in the same type of hydrocarbons as above. The review for binary systems is shown in Table 1. It can be observed in this table that the open literature gives extensive results on the phase equilibria for different systems in which methane is one of the components, in large ranges of temper-

Table 1
Previous works reported in the literature on the vapor–liquid (VL), vapor–liquid–solid (VLS) and vapor–liquid–liquid (VLL) equilibria for methane in liquid hydrocarbons

Solvent		Conditions		Uncertainty			Reference
		T (K)	P (MPa)	Mole fraction	T (K)	P (MPa)	
Pentane	VL	311–411	0.1–16	0.015	0.01	0.0001	Reiff et al. [8]
Pentane	VL	173–273	0.1–15	0.005	0.02	0.007	Chu et al. [9]
Pentane	VL	186–282	4–15	–	0.01	0.001	Voronov et al. [10]
Pentane	VL	378	7–14	–	0.3	0.02	Prodany and Williams [11]
Pentane	VL	311–377	3–21	0.002	0.05	0.0007	Sage et al. [12]
Hexane	VL	348–383	2–20	0.003	–	–	Cebola et al. [13]
Hexane	VL	311–423	10	0.002	0.1	0.04	Srivatsan et al. [14]
Hexane	VLS	138–164	0.6–2	–	–	–	Luks et al. [15]
Hexane	VL	190–273	0.1–18	0.0050	0.02	0.0007	Lin et al. [16]
Hexane	VLL	190–273	0.1–18	0.00001	–	–	Chen et al. [17]
Hexane	VL	311–444	2–20	0.002	0.11	0.01	Poston and McKetta [18]
Hexane	VLS	163–423	0.2–16	0.002	0.1	0.02	Shim and Kohn [19]
Hexane	VL	311–378	6–41	–	–	–	Schoch et al. [20]
Hexane	VL	311–377	3–21	0.002	0.05	0.0007	Sage et al. [12]
Heptane	VLL	273–313	0.1–23	0.00001	–	–	Chen et al. [17]
Heptane	VL	278–511	1–68	0.0020	0.02	0.0007	Reamer et al. [21]
Octane	VLS	155–191	1–5	–	0.2	0.01	Kohn et al. [22]
Octane	VLS	163–423	0.1–7	0.0015	0.07	0.01	Kohn and Bradish [23]
Nonane	VLS	223–423	1–32	0.0015	0.07	0.01	Shipman and Kohn [24]
Nonane	VL	323–423	2–28	–	–	0.14	Rousseaux et al. [25]
Decane	VL	311–423	10	0.002	0.1	0.04	Srivatsan et al. [14]
Decane	VL	423–583	3–15	0.01	0.2	–	Lin et al. [26]
Decane	VL	248–423	1–10	0.0014	0.07	0.01	Beaudoin and Kohn [27]
Decane	VL	311–377	3–17	0.003	0.01	0.14	Reamer et al. [28]
Decane	VL	294–394	2–31	0.002	0.04	–	Sage et al. [29]
Decane	VLS	240–315	1–40	1×10^{-8}	0.1	0.002	Rijkers et al. [30]
Dodecane	VL	311–423	10	0.002	0.1	0.04	Srivatsan et al. [14]
Dodecane	VLS	240–315	1–25	1×10^{-8}	0.1	0.02	Rijkers et al. [31]
Tetradecane	VL	320–440	0.2–120	0.001	0.1	0.1	de Leeuw et al. [32]
Hexadecane	VLS	285–360	2–85	0.005	0.01	0.2	Glaser et al. [33]
Hexadecane	VL	463–703	2–25	–	0.01	–	Lin et al. [34]
Eicosane	VL	323–423	1–11	0.002	0.1	0.04	Darwish et al. [35]
Octacosane	VL	323–423	1–7	0.002	0.1	0.04	Darwish et al. [35]
Hexatriacontane	VL	323–423	1–8	0.002	0.1	0.04	Darwish et al. [35]
Hexatriacontane	VL	373–453	3–128	0.001	–	0.4	Marteau et al. [36]
Hexatriacontane	VL	273–373	1–5	0.003	0.1	0.005	Tsal et al. [37]