jection of these immiscibility regions in pressure-temperature space when the solvent pair is that of methane + ethane, the extent of the three-phase behavior starts with the *n*-hexane-containing system and diminishes with the *n*-octane system.

Glossary

K	K point or upper critical end point of an L-L-V region, occurring when the L_2 phase becomes critically identical with the vapor phase
L	liquid phase
L_1	liquid phase rich in solute
L_2	liquid phase lean in solute
LCST	lower critical solution temperature, occurring when the L_1 and L_2 phases become critically identical with each other
Q	quadruple point, the equilibrium coexistence of four phases, for this case the L_1, L_2, V, and S phases
S	solid phase
t	tricritical point
T	temperature
V	vapor phase

Registry No. Methane, 74-82-8; ethane, 74-84-0; hexane, 110-54-3; heptane, 142-82-5.

Literature Cited

(1) Hottovy, J. D.; Kohn, J. P.; Luks, K. D. *J. Chem. Eng. Data*. **1981**, *26*, 135.
(2) Hottovy, J. D.; Kohn, J. P.; Luks, K. D. *J. Chem. Eng. Data*. **1982**, *27*, 298.
(3) Merrill, R. C.; Kohn, J. P.; Luks, K. D. *J. Chem. Eng. Data*. **1983**, *28*, 210.
(4) Merrill, R. C.; Kohn, J. P.; Luks, K. D. *J. Chem. Eng. Data*. **1984**, *29*, 272.
(5) Merrill, R. C.; Kohn, J. P.; Luks, K. D. *Adv. Cryog. Eng*. **1984**, *29*, 949.
(6) Llave, F. M.; Luks, K. D.; Kohn, J. P. *J. Chem. Eng. Data* **1985**, *30*, 435.
(7) Llave, F. M.; Luks, K. D.; Kohn, J. P. *J. Chem. Eng. Data*, submitted for publication.
(8) Lin, Y.-N.; Chen, R. J. J.; Chappelear, P. S.; Kobayashi, R. *J. Chem. Eng. Data* **1977**, *22*, 402.
(9) Kohn, J. P. *AIChE J*. **1961**, *7*, 514.
(10) Luks, K. D.; Kohn, J. P. *Proc. 63rd Annu. GPA Convention* **1984**, 181.
(11) Kohn, J. P. Ph.D. Thesis, University of Kansas, 1956.
(12) Wichterle, I.; Kobayashi, R. *J. Chem. Eng. Data* **1972**, *17*, 13.
(13) Graboski, M. S.; Daubert, T. E. *Ind. Eng. Chem. Process Des. Dev*. **1978**, *17*, 443.
(14) Graboski, M. S.; Daubert, T. E. *Ind. Eng. Chem. Process Des. Dev*. **1978**, *17*, 448.
(15) Chang, H. L.; Hurt, L. J.; Kobayashi, R. *AIChE J*. **1966**, *12*, 1212.

Received for review January 7, 1986. Accepted March 26, 1986. We are grateful for the support of this work provided by the Gas Processors Association (Research Project 795), Tulsa, OK. The apparatus was assembled under research grants from the National Science Foundation.

Solubility of Ethane in *n*-Decane at Pressures to 8.2 MPa and Temperatures from 278 to 411 K

Brian A. Bufkin and Robert L. Robinson, Jr.*

School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma 74078

Susana S. Estrera and Kraemer D. Luks

Department of Chemical Engineering, University of Tulsa, Tulsa, Oklahoma 74104-3189

The solubility of ethane in liquid *n*-decane has been measured as a function of pressure at five temperatures (4.4, 37.8, 71.1, 104.4, and 137.8 °C) by two separate experimental techniques. Liquid-phase molar volumes are also reported at 4.4 and 37.8 °C. The compositional data of the two experiments display minor systematic differences at 37.8 °C; however, both data sets exhibit significant systematic differences at all temperatures from the earlier study of Reamer and Sage.

Introduction

The viability of using rich gases (e.g., mixtures of methane, ethane, and propane) as drive gases for enhancing the recovery of crude oils from reservoirs is being investigated actively by the petroleum production industry. Rich-gas enhanced recovery is an attractive option particularly in remote locations where reinjection of reservoir gases would be an alternative to flaring. The computer simulation of such recovery processes usually requires use of an equation of state (EOS) to describe the local phase equilibria in the reservoir. Parameters for the EOS are generally determined from pure-component thermodynamic data and binary phase equilibria data. Data on the phase equilibria of a binary mixture of ethane + *n*-decane would constitute a prominent contribution to such a data base.

Reamer and Sage (*1*) reported the properties and phase equilibria of mixtures of ethane + *n*-decane at pressures to 69 MPa and temperatures from 40 to 460 °F. The two-phase isotherms were studied up to their critical points, with compositions and molar volumes being measured for both the vapor and liquid phases.

One of us (K.D.L.), while engaged in a study of the liquid-phase diffusion of rich-gas components in well-defined hydrocarbons such as *n*-decane, measured equilibrium solubilities of ethane in *n*-decane at 37.8 °C (100 °F) which were in significant disagreement with the data of Reamer and Sage. Consequently, we decided to undertake a joint study of the solubility of ethane in *n*-decane, using independent experimental apparatuses and procedures, in an attempt to resolve discrepancies with the literature data.

Experimental Section

A detailed description of the experimental apparatus at the University of Tulsa is given in an earlier paper (*2*). The procedures for performing vapor-liquid equilibrium studies are presented in the same reference and will be briefly summarized here. A known amount of *n*-decane is first placed in a 7.5-mL visual (glass) equilibrium cell. During an experimental run, measured amounts of ethane gas are added to the thermostated visual cell from a high-pressure bomb by means of a

0021-9568/86/1731-0421$01.50/0 © 1986 American Chemical Society

manual (Ruska) pump. After each ethane injection, the phase volumes in the calibrated visual cell are determined by a cathetometer to an accuracy of ±0.005 mL. By proper mass balance, the moles of ethane in the liquid phase can be determined. This is done by keeping the amount of vapor phase small and assuming it to be pure ethane, by virtue of the low volatility of *n*-decane at the temperatures of interest (40 and 100 °F).

Temperatures were measured with a Pt-resistant thermometer to an estimated accuracy of ±0.02 K while pressures were measured to ±0.007 MPa (1 psi) with pressure transducers which were calibrated frequently against an accurate deadweight gauge.

The apparatus and procedures used in the measurements at Oklahoma State University have been described previously (*3*, *4*). Briefly, the procedure involves injecting a known amount (about 7 mL) of *n*-decane into a commercial 304 stainless steel high-pressure equilibrium cell. Measured amounts of ethane are then injected into the cell. All injections are made from calibrated manual injection pumps (Temco, Inc.). After each ethane injection, the mixture of known composition is brought to its bubble point pressure as follows. The volume of the mixture is varied by injecting mercury into the cell, and the system pressure is measured after each mercury injection. The bubble point pressure is identified by the break point which occurs in the pressure–volume curve as the system passes from the two-phase to the compressed liquid state.

Temperature measurements were made by using calibrated Pt-resistance thermometers and pressures were measured by using transducers, calibrated periodically against a dead-weight gauge. Estimated uncertainties in the readings from these temperature and pressure sensors are 0.1 K and 0.007 MPa (1.0 psi), respectively.

In the discussion which follows, the TU measurements will be referred to as "solubility data" and the OSU results as "bubble point data".

Materials

The *n*-decane used in this work was supplied by Aldrich Chemical Co. and was listed as GOLD LABEL, 99+ mol %. The ethane was from Matheson, with a reported minimum purity of 99.99 mol %. No further purification of these chemicals was attempted.

The ethane vapor pressure was measured (at TU) to be 607 ± 1 psia at 25 °C, in satisfactory agreement with the literature (*5*). The difference in pressure between the bubble point and dew point was found to be 2 psi at 25 °C.

Results

Solubility measurements were made at 4.4 and 37.8 °C (40 and 100 °F) and bubble points were determined at 37.8, 71.1, 104.4, and 137.8 °C (100, 160, 220, and 280 °F). Temperatures for study were selected to coincide with the previous literature data. Results appear in Table I and Figures 1 and 2. The solubility data are estimated to be good to ±0.003 for the ethane mole fraction in the liquid phase and ±0.8 mL/(g-mol) for the liquid-phase molar volume. These estimates are based on average absolute deviations (AAD) of the raw data from smoothed curves drawn through them. The AAD for the liquid-phase mole fractions is 0.002, while the AAD for the liquid-phase molar volumes is 0.4 mL/(g-mol). The bubble point data are estimated similarly to have uncertainties of 2 psi in bubble point pressure and 0.003 in mole fraction.

Only at 37.8 °C (100 °F) are all three data sets available for comparison; Figure 1 presents these results. The data of Reamer and Sage are shown as a solid curve since they published smoothed data only. The figure reveals a clear systematic difference between the Reamer and Sage results and the

Table I. Solubility of Ethane in *n*-Decane

mole fraction ethane	liq molar vol, mL/mol	pressure	
		MPa	psia
277.6 K (4.4 °C, 40 °F)[a]			
0.173	168.8	0.394	57.1
0.190	167.1	0.444	64.4
0.319	150.7	0.727	105.5
0.324	149.6	0.758	109.9
0.363	144.4	0.871	126.4
0.472	130.6	1.152	167.1
0.498	126.8	1.244	180.4
0.514	124.4	1.251	181.4
0.582	116.5	1.489	216.0
0.609	112.7	1.548	224.5
0.667	105.5	1.700	246.6
0.786	91.8	2.053	297.8
310.9 K (37.8 °C, 100 °F)[a]			
0.102	185.5	0.394	57.2
0.123	182.0	0.476	69.1
0.125	181.2	0.489	70.9
0.147	179.0	0.546	79.2
0.242	165.6	0.956	138.7
0.247	165.1	0.979	142.0
0.265	163.7	1.049	152.2
0.355	150.6	1.463	212.2
0.356	150.6	1.473	213.7
0.446	139.4	1.922	278.8
0.458	138.1	1.975	286.4
0.464	136.5	2.022	293.2
0.493	133.1	2.129	308.8
0.499	132.0	2.155	312.6
0.512	130.4	2.286	331.5
0.530	128.9	2.381	345.4
0.559	124.1	2.499	362.5
0.614	117.4	2.824	409.6
0.645	114.0	2.996	434.6
0.763	99.7	3.724	540.1
0.813	94.3	4.053	587.8
310.9 K (37.8 °C, 100 °F)[b]			
0.108		0.423	61.4
0.127		0.491	71.3
0.211		0.833	120.9
0.226		0.918	133.1
0.271		1.093	158.6
0.300		1.226	177.8
0.308		1.281	185.8
0.361		1.533	222.4
0.413		1.768	256.5
0.466		2.069	300.2
0.471		2.077	301.3
0.501		2.246	325.8
0.601		2.812	408.0
344.3 K (71.1 °C, 160 °F)[b]			
0.105		0.598	86.7
0.203		1.182	171.5
0.305		1.899	275.4
0.422		2.764	401.0
0.510		3.546	514.4
0.579		4.167	604.4
0.631		4.690	680.3
377.6 K (104.4 °C, 220 °F)[b]			
0.106		0.807	117.0
0.202		1.600	232.1
0.328		2.787	404.3
0.408		3.618	524.8
0.505		4.790	694.8
0.600		6.033	875.1
410.9 K (137.8 °C, 280 °F)[b]			
0.105		1.005	145.8
0.215		2.131	309.1
0.323		3.415	495.3
0.404		4.487	650.9
0.500		5.925	859.4
0.582		7.253	1052.1
0.638		8.236	1194.6

[a] Solubility measurements (TU). [b] Bubble point measurements (OSU).

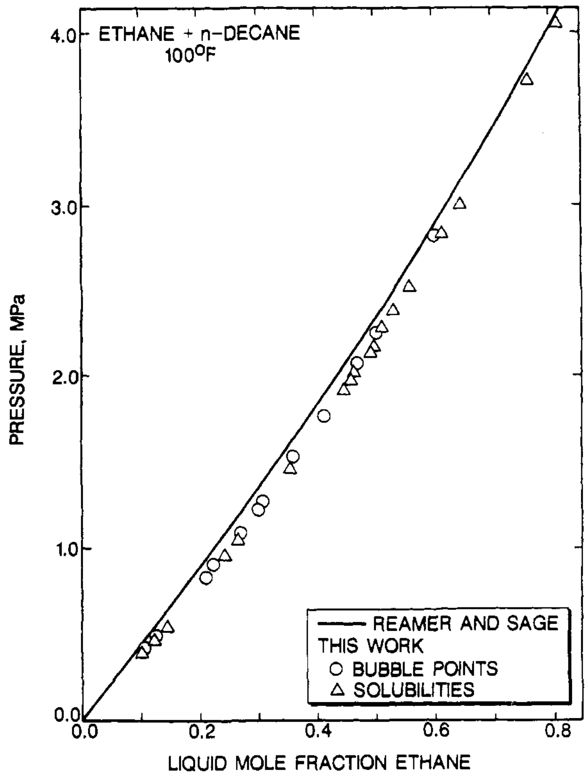

Figure 1. Solubility of ethane in *n*-decane at 37.8 °C (100 °F).

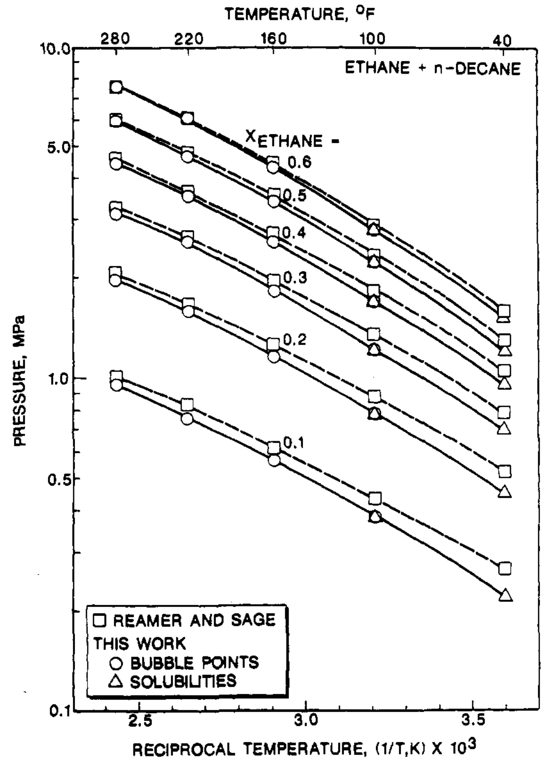

Figure 2. Effect of temperature on saturation pressure of ethane + *n*-decane at constant liquid composition.

two data sets of the present work. More detailed analysis also reveals small systematic differences in the two data sets of the present study. Differences in the measured ethane mole fraction increase with increasing pressure, reaching a maximum of 0.008 at a mole fraction of 0.6. At this composition, the difference in saturation pressures is approximately 6.5 psi. The maximum difference in solubility between the two data sets of the present work is slightly larger than the combined uncertainty estimates of 0.006, with the bubble point data showing systematically lower ethane mole fractions (higher saturation pressures). Such differences between data taken by bubble point and two-phase techniques are not uncommon and are consistent with the presence of a small amount of volatile impurity in the solute gas which must be forced into solution in the solvent in the bubble point measurements, but not in the two-phase measurements.

The Reamer and Sage data display ethane mole fractions as much as 0.027 lower than the combined data of the present study, corresponding to 19 psi higher saturation pressures. These differences may be attributable to differences in the purity of the ethane used in the various studies.

Differences between the data sets persist at all temperatures studied, with the present work showing higher solubilities (lower saturation pressures) than those measured by Reamer and Sage. This behavior is demonstrated in Figure 2, which shows saturation pressures as a function of temperature for several fixed liquid compositions. The figure also reveals the consistency between the two data sets of the present work.

Conclusion

New data are presented for the solubility of ethane in *n*-decane at temperatures from 278 to 411 K and ethane mole fractions to 0.6 or above at each temperature. The data, taken by two separate experimental methods, are believed to be correct to ±0.004 ethane mole fraction and ±3 psi in saturation pressure (as estimated from the mean of the combined data sets at 100 °F). These results suggest that the previous data of Reamer and Sage may contain systematic errors of as much as 0.025 mole fraction (20 psi).

Acknowledgment

Jeff Mapes contributed to the experimental measurements at OSU.

Registry No. *n*-Decane, 124-18-5; ethane, 74-84-0.

Literature Cited

(1) Reamer, H. H.; Sage, B. H. *J. Chem. Eng. Data* **1962**, *7*, 161–168.
(2) Fall, D. J.; Luks, K. D. *J. Chem. Eng. Data* **1984**, *29*, 413–417.
(3) Gasem, K. A. M.; Robinson, Jr., R. L. *J. Chem. Eng. Data* **1985**, *30*, 53–56.
(4) Barrick, M. W.; Anderson, J. M.; Robinson, Jr., R. L. *J. Chem. Eng. Data* **1986**, *31*, 172–175.
(5) Douslin, D. R.; Harrison, R. H. *J. Chem. Thermodyn.* **1973**, *5*, 491–512.

Received for review February 13, 1986. Accepted June 27, 1986. Support for this work was provided by the National Science Foundation, Grant No. CBT-8514599 (S.S.E. and K.D.L.) and by the United States Department of Energy, Grant No. DE-FG22-83OC60039 (B.A.B. and R.L.R.). The apparatus at TU was constructed with funds from several industries, the University of Tulsa, and The National Science Foundation Equipment Grant No. CPE-8014650. The apparatus at OSU was funded by the above-mentioned DOE grant and the Oklahoma State University.