Binary Vapour-Liquid Equilibria of Methanol with Sulfolane, Tetraethylene Glycol Dimethyl Ether and 18-Crown-6

Phasengleichgewichte in binären Systemen von Methanol mit Sulfolan, Tetraethylenglycoldimethylether und 18-Krone-6 Kronenether

M. KUCZYNSKI, W. 't HART and K. R. WESTERTERP

Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, Twente University of Technology, P.O. Box 217, 7500 AE Enschede (The Netherlands)

(Received August 26, 1985)

Abstract

The activity coefficients of methanol in sulfolane, tetraethylene glycol dimethyl ether (TEGDME) and 18-crown-6 under conditions of equilibrium have been determined in the temperature range 423–503 K and in the pressure range 0.28–3.5 MPa. A minimum in the activity coefficient was found for the methanol–TEGDME and methanol–18-crown-6 solutions.

Kurzfassung

Die Aktivitätskoeffizienten von Methanol im Sulfolan, Tetraethylenglycoldimethylether (TEGDME) und 18-Krone-6 Kronenether wurden im Temperaturbereich von 423 bis 503 K und im Druckbereich von 0.28 bis 3.5 MPa gemessen. Erstaunlicherweise wurde ein Minimum in den Aktivitätskoeffizienten im TEGDME und 18-Krone-6 festgestellt.

Synopsis

Angesichts des Mangels an Originaldaten über die Phasengleichgewichte in binären Systemen von flüchtigen und nichtflüchtigen Komponenten muss man sich oft auf eigene Messungen verlassen. Unter den zahlreichen Messmethoden, die man in der Fachliteratur findet, sind nur wenige für Experimente unter erhöhten Temperaturen und Drücken geeignet. In der Regel ist dann auch mit grossem Aufwand an Geld und Arbeit zu rechnen. Im Rahmen dieser Arbeit wurde ein besonders einfaches Messsystem konstruiert, das sich ausschliesslich aus in einem Hochdrucklabor üblichen Apparaturen zusammensetzt. Ein $570 \times 10^{-6} \text{ m}^3$ Hochdruckautoklav aus rostfreiem Stahl (Abb. 1) ist mit einer Absaugleitung mit Ventil V_1 und einem Injektionsventil V_2 sowie mit einem elektronischen temperaturbeständigen Präzisionsmanometer ausgestattet. Zur Kontrolle der Stabilität und der Homogenität der Temperatur sind einige Thermoelemente installiert. Die elektrischen Heizelemente H_1 , H_2 und O werden von elektrischen Temperaturreglern gesteuert. Nach der Injektion des Lösungsmittels wird die Luft aus dem Apparat bei Zimmertemperatur abgesaugt. Eine genau bekannte Menge von Methanol wird dann durch den Injektionsventil in den Autoklav hineingesaugt, die Ventile werden geschlossen und beide mit Verschluss-

pfropfen versehen. Der Totaldruck wird bei fünf verschiedenen Temperaturen zwischen 423 und 503 K gemessen, jeweils nach einer thermischen Stabilisierung des Apparates. Um eine serienmässige Durchführung der Experimenten zu ermöglichen, wurde das Messsystem mit dem Hewlett-Packard Modell 9826 PC und der HP 3497A Interface-Einheit gesteuert. Eine Verzeichnis aller Messungen sowie die Messergebnisse sind in Tab. 3 zu finden. Der Berechnung des Aktivitätskoeffizienten des Methanols γ_i liegt Gl. (1) zugrunde, wobei alle übrigen Parameter entweder gemessen sind (P , T) oder auf theoretischem Wege gefunden werden können. Gleichung (2) stellt den Zusammenhang zwischen x_i und y_i dar, und P_i^0 folgt aus Gl. (3). In einer früheren Arbeit [3] wurde eine hohe Genauigkeit der Peng–Robinson [4] Zustandsgleichung für Methanol (Gl. (4)–(6)) festgestellt.

Zur Berechnung werden Gl. (2) und (4)–(7) simultan mit den die flüssige Phase beschreibenden Gl. (8) und (9) gelöst. Die Fugazitätskoeffizienten ϕ folgen aus den von Peng und Robinson [4] gegebenen (Gl. (10)–(13)). Aus den gemessenen Gleichgewichtskurven (Abb. 2–4) ist es zu sehen, dass auf Gewichtsbasis Sulfolan das beste Lösungsmittel für Methanol ist.

Auf Abb. 5 ist der Aktivitätskoeffizient des Methanols in den drei Lösungsmitteln als Funktion der

Methanolkonzentration in der flüssigen Phase wiedergegeben. In TEGDME und 18-Krone-6 zeigt sich ein Minimum in den γ_i - x_i Kurven. Dieses Phänomen ist ziemlich ungewöhnlich für binäre Systeme; nach unserer Kenntnis waren Gottlieb und Herskowitz [7] die ersten, die diesen Effekt im binären System von Wasser und 18-Krone-6 gefunden haben.

Die beschriebene experimentelle Technik lässt sich überall dort empfehlen, wo die Eigenschaften von beiden Komponenten (Dampfdrücke, Zustandsgleichungen) bekannt sind und wo man z.B. von mehreren Lösungsmitteln das optimale aussuchen will.

Introduction

Literature data on vapour–liquid equilibria of binary systems containing methanol and low-volatility solvents like sulfolane (tetrahydrothiophene-1,1-dioxide, $C_4H_8SO_2$), tetraethylene glycol dimethyl ether (TEGDME) or 18-crown-6 (1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane) are hard to find, especially for elevated pressures and temperatures, so we had to determine them experimentally. Various experimental techniques are described in the literature. Most of them require expensive and sophisticated equipment. In this work we chose to perform the equilibrium pressure measurements in a closed vessel system. The determination of the methanol activity coefficient in the liquid is based on the measurement of the total pressure and on known saturated vapour pressure correlations for both components. Using this method, vapour–liquid equilibria of methanol with three different solvents, sulfolane, TEGDME and 18-crown-6, were measured at temperatures between 423 and 503 K in the pressure range 0.28–3.5 MPa. The method was found to be sufficiently accurate for the comparison at elevated temperatures and pressures of the solution properties of the solvents investigated. A significant advantage of the method is that the experimental system can be kept simple: it consists exclusively of the usual high pressure laboratory equipment.

Experimental technique

Methyl alcohol of analytical purity from Merck was used. The purity of the sulfolane (Merck) was better than 99.5% and that of the TEGDME and the 18-crown-6 (both from Janssen, Brussels) was better than 99%.

The melting ranges of 18-crown-6 and of sulfolane were determined to be 312.5–313 K and 299–300.1 K, respectively. Prior to use the solvents were degassed and dried for 3 h at 513 K under vacuum. No further solvent purification was undertaken. Other properties of the solvents used are specified in Table 1. The experimental system is shown schematically in Fig. 1. The autoclave volume was found to be $570 \times 10^{-6} \text{ m}^3$ by means of volumetric measurements of nitrogen expanding from 1 MPa to atmospheric pressure at 293 K. An accurately weighed solvent sample of about 50 g was placed in the

Fig. 1. The experimental set-up: A, $570 \times 10^{-6} \text{ m}^3$ stainless steel autoclave; V_1 , evacuation valve; V_2 , methanol injection valve; O, autoclave oven; H_1 , H_2 , heating elements; TC, thermocouples; P, electronic pressure transducer; S, sample.

autoclave. Care was taken to avoid long exposures of the solvent to open air. After the autoclave was closed, its gaseous contents were evacuated through valve V_1 for one hour at temperatures of 303–313 K (i.e. above the melting points of the solvents). A possible loss of solvent due to evaporation was checked separately in a glass vacuum apparatus: within the limits of accuracy of our method the solvents do not evaporate. After evacuation, the apparatus was cooled down to room temperature and a liquid methanol sample of known volume, which previously had been degassed by boiling, was sucked into the autoclave using injection valve V_2 . Afterwards plugs were installed on the valves to prevent leaking. Subsequently, the pressure in the autoclave was measured with an electronic pressure transducer at temperatures from 423 to 503 K, each time after thermal stabilization of the system.

TABLE 1. The properties of sulfolane, TEGDME, 18-crown-6 and methanol

	Molar mass (kg kmol^{-1})	Liquid density (kg m^{-3})	$\ln P^0$ (Pa)
Sulfolane [1]	120.17	1260 (298 K)	$70.936 - 10018/T - 6.5633 \ln T$
TEGDME	222.28	1032 (298 K)	$24.747 - 7156.1/T^a$
18-Crown-6	264.32	1250 (313 K)	$14.508 - 1589.4/T^a$
Methanol	32.04	791 (293 K)	Eqn. (3)

^aCorrelations based on own experimental data. Temperature in K.

After each experimental run the transducer was calibrated using a Bourdon-type precision manometer having an accuracy of 2.5×10^{-3} MPa. To prevent thermal shift of the calibration line, the transducer was kept at a constant temperature of 473 ± 0.1 K during the experiments and calibration.

Calibrated chromel–alumel thermocouples were used for temperature measurements; their estimated accuracy was ± 0.1 K. After the completion of an experimental run, the system was cooled again and more methanol was injected into the autoclave. The measurements were repeated for various amounts of methanol ranging from 4.1 to 49×10^{-6} m³. Similar experiments with pure solvent were performed to determine the saturated vapour pressures of TEGDME and 18-crown-6 between 423 and 503 K. The experimental system described was automated by means of a Hewlett-Packard 9826A personal technical computer equipped with an HP 3497A data acquisition/control unit, which allowed accurate temperature regulation with a reproducibility to within 0.1 K.

Evaluation of an experiment

The partial molar thermodynamic potentials of the components at equilibrium are equal in both phases. The following equation relates the activity coefficient of component i in the liquid phase to the composition of both phases at equilibrium:

$$P y_i \phi_i(P, T) = P_i^0 x_i \phi_i(P_i^0, T) \gamma_i \exp \left[\frac{v_{iL}^0 (P - P_i^0)}{RT} \right] \quad (1)$$

P is the total pressure, y_i and x_i are the molar fractions of methanol in the vapour and in the liquid phase respectively, and P_i^0 is the saturated vapour pressure of methanol, γ_i is its activity coefficient in the liquid phase at the actual pressure and temperature, v_{iL}^0 its molar volume in the liquid phase, and $\phi_i(P, T)$ and $\phi_i(P_i^0, T)$ are the fugacity coefficients at the total pressure and at saturated vapour pressure respectively.

Since our aim is to determine the value of γ_i for methanol, all other parameters in eqn. (1) have to be found experimentally or derived from existing correlations. These parameters are evaluated as follows.

P is the total pressure as determined experimentally.

The molar fraction y_i in the vapour phase can be related to x_i according to

$$y_i = [P - P_s^0(1 - x_i)]/P \quad (2)$$

where P_s^0 is the saturated vapour pressure of the solvent. This equation is only valid for values of y_i not too far from unity. In our case, y_i was always greater than 0.96 using sulfolane or TEGDME and greater than 0.9 using 18-crown-6. P_s^0 in eqn. (2) can be calculated using one of the vapour pressure relations given in Table 1. As literature data were not available, we had to determine the vapour pressure relations for TEGDME and 18-crown-6. The experimental set-up was checked by determining the vapour pressures for methanol and sulfolane and comparing results with literature data. The temperature dependence for the 18-crown-6 is surprisingly low.

TABLE 2. Parameters in eqn. (3) [2]

T_c (K)	$\ln P_{ci}$ (Pa)	a_i	b_i	c_i	d_i
512.64	15.90460	-8.48160	0.58803	-2.68463	-0.07940

To find the saturated vapour pressure of methanol in eqn. (1) the correlation given by Ambrose [2] was used:

$$\ln P_i^0 = \ln P_{ci} + (T_c/T)(a_i\tau + b_i\tau^{1.5} + c_i\tau^3 + d_i\tau^6) \quad (3)$$

where $\tau = 1 - T/T_c$. The parameters and units are given in Table 2.

The value of x_i can be calculated if the amounts of methanol, n_{iL} , and of the solvent, n_{sL} , in the liquid phase are known.

n_{iL} equals the difference between the total amount of methanol injected and the amount present in the gas phase. The latter can be calculated from the pressure of the methanol ($P_i = y_i P$) if an appropriate equation of state is available. In a previous experimental study [3] we reported that the two-constant Peng–Robinson equation of state [4] accurately describes the p – v – T behaviour of methanol in the pressure and temperature range of interest.

$$P_i = \frac{RT}{v_i - b} - \frac{a(T)}{v_i(v_i + b) + b(v_i - b)} \quad \text{Pa} \quad (4)$$

where

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} [1 + K(1 - T_r)]^2 \quad \text{Pa m}^6 \text{ mol}^{-2} \quad (5)$$

$$b(T) = b(T_c) = 0.0778 RT_c/P_c \quad \text{m}^3 \text{ mol}^{-1} \quad (6)$$

and

$$K = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (7)$$

whereas ω is Pitzer's acentric factor, which for methanol equals 0.564 [3]. To find the amount of methanol in the vapour phase we divide the volume of the vapour phase V_G by the molar volume of methanol vapour, as calculated from eqns. (3)–(6). This can be done when y_i is not far from unity.

In the calculation of V_G , thermal expansion of the autoclave and that of the liquid-phase volume V_L were taken into account. For V_L we took

$$V_L = n_{iL} v_{iL}^0 + n_{sL} v_{sL}^0 \quad (8)$$

where v_{iL}^0 and v_{sL}^0 are the molar volumes of pure components. In eqn. (8) volume contraction effects due to mixing are neglected: the error caused by this simplification is negligible since the fraction of the autoclave volume occupied by the liquid phase is smaller than 0.1. Owing to some evaporation, n_{sL} is slightly smaller than the amount of solvent n_{s0} placed initially in the autoclave. Since the partial pressure of the solvent is low, n_{sL} is given by

$$n_{sL} = n_{s0} - (1 - x_i)P_s^0 V_G/RT \quad (9)$$

It can be seen that to calculate x_i eqns. (2) and (4)–(9) have to be solved simultaneously.

To calculate v_{s0}^0 in eqn. (8), its values at room temperature (the densities are given in Table 1) were extrapolated to the experimental temperature range using the corresponding-states method [5].

The value of v_{i0}^0 in eqns. (1) and (8) was calculated based on the liquid methanol density taken from the literature [6].

The fugacity coefficients $\phi_i(P, T)$ and $\phi_i(P_i^0, T)$ are the remaining unknown parameters in eqn. (1). A relevant expression has been derived by Peng and Robinson [4]:

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{A}{2B\sqrt{2}} \ln \left(\frac{Z + 2.414 B}{Z - 0.414 B} \right) \quad (10)$$

where

$$A = aP_i/(RT)^2 \quad (11)$$

$$B = bP_i/RT \quad (12)$$

$$Z = P_i v_i / RT \quad (13)$$

The parameters a and b are those of eqns. (5) and (6).

In view of all the assumptions we have made, the estimated maximum error in γ_i amounts to 3%.

Results

The vapour-liquid equilibrium isotherms for the binary systems of methanol with sulfolane, TEGDME and 18-crown-6 as derived from the total pressure measurements are shown in Figs. 2, 3 and 4, respectively. The experimental data and the results are specified in Table 3. The concentration and temperature dependences of the methanol activity coefficient γ_i in the liquid phase are given in Fig. 5. Since the values of the partial molar volumes in the liquid phase are not known exactly, the γ_i values are not reduced to a standard pressure. The results show sulfolane to be the worst methanol solvent, because it has the highest γ_i values in the entire concen-

Fig. 2. The equilibrium isotherms of the sulfolane-methanol system; parameter: temperature in K.

Fig. 3. The equilibrium isotherms of the TEGDME-methanol system; parameter: temperature in K.

Fig. 4. The equilibrium isotherms of the 18-crown-6-methanol system; parameter: temperature in K.

tration range. However, on a mass basis, sulfolane is the best methanol solvent. Regrettably, an accurate estimation of the activity coefficients at infinite dilution, γ_{∞} , is impossible owing to the lack of data for $x_i < 0.1$; in the low x_i region we cannot obtain sufficiently accurate data with the experimental technique described.

It can be seen in Figs. 5(b) and (c) that the activity coefficient as a function of the molar fraction of methanol exhibits a minimum both for TEGDME and 18-crown-6. This is quite uncommon for binary vapour-liquid systems. Gottlieb and Herskowitz [7] to our knowledge were the first to find minima in the activity coefficient, in their case for the system water-18-crown-6 at 298, 313 and 333 K. Our results support their observations. It would be interesting to examine whether other binary systems containing linear and cyclic ethers exhibit a similar behaviour.

Conclusions

The vapour-liquid equilibrium in binary systems of methanol in sulfolane, tetraethylene glycol dimethyl ether and in 18-crown-6 has been determined by means of simple total equilibrium pressure measurements. Based on the data obtained, the methanol activity coef-

TABLE 3. Experimental data and the calculated activity coefficient

Sulfolane					TEGDME					18-Crown-6				
V_{0i} (10 ⁻⁶ m ³)	T (K)	P_T (MPa)	x_i	γ_i	V_{0i} (10 ⁻⁶ m ³)	T (K)	P_T (MPa)	x_i	γ_i	V_{0i} (10 ⁻⁶ m ³)	T (K)	P_T (MPa)	x_i	γ_i
44.94 g solvent injected					51.64 g solvent injected					47.6 g solvent injected				
4.1	423	0.286	0.13	1.75	4.75	423	0.315	0.23	1.08	5.00	423	0.384	0.28	1.10
4.1	443	0.349	0.12	1.61	4.75	443	0.397	0.21	1.02	5.00	443	0.503	0.24	1.15
4.1	463	0.422	0.10	1.61	4.75	463	0.494	0.18	1.04	5.00	463	0.621	0.20	1.24
4.1	483	0.481	0.09	1.52	4.75	483	0.596	0.16	1.10	5.00	483	0.717	0.16	1.29
4.1	503	0.559	0.08	1.64	4.75	503	0.699	0.13	1.19	5.00	503	0.816	0.13	1.46
5.1	423	0.329	0.17	1.59	7.00	423	0.410	0.33	1.01	7.00	423	0.486	0.37	1.06
5.1	443	0.416	0.15	1.53	7.00	443	0.543	0.29	0.99	7.00	443	0.643	0.32	1.08
5.1	463	0.504	0.13	1.51	7.00	463	0.683	0.26	1.00	7.00	463	0.803	0.27	1.15
5.1	483	0.581	0.11	1.46	7.00	483	0.817	0.23	1.02	7.00	483	0.934	0.23	1.18
5.1	503	0.678	0.10	1.59	7.00	503	0.950	0.20	1.06	7.00	503	1.071	0.19	1.32
7.1	423	0.427	0.22	1.52	9.00	423	0.486	0.39	0.98	9.00	423	0.575	0.44	1.04
7.1	443	0.544	0.20	1.45	9.00	443	0.648	0.36	0.96	9.00	443	0.770	0.39	1.06
7.1	463	0.661	0.18	1.41	9.00	463	0.818	0.32	0.95	9.00	463	0.970	0.33	1.10
7.1	483	0.778	0.16	1.42	9.00	483	0.988	0.29	0.96	9.00	483	1.140	0.29	1.13
7.1	503	0.894	0.14	1.47	9.00	503	1.158	0.26	1.00	9.00	503	1.307	0.24	1.23
9.0	423	0.502	0.28	1.44	11.00	423	0.559	0.45	0.98	10.00	423	0.613	0.47	1.03
9.0	443	0.655	0.25	1.40	11.00	443	0.760	0.41	0.97	10.00	443	0.822	0.42	1.03
9.0	463	0.807	0.22	1.38	11.00	463	0.958	0.38	0.95	10.00	463	1.043	0.36	1.07
9.0	483	0.951	0.20	1.37	11.00	483	1.157	0.34	0.95	10.00	483	1.238	0.31	1.11
9.0	503	1.096	0.17	1.41	11.00	503	1.355	0.31	0.97	10.00	503	1.420	0.27	1.19
11.0	423	0.579	0.33	1.40	13.00	423	0.618	0.50	0.98	12.50	423	0.694	0.53	1.01
11.0	443	0.761	0.29	1.36	13.00	443	0.847	0.46	0.96	12.50	443	0.940	0.49	1.00
11.0	463	0.944	0.26	1.34	13.00	463	1.083	0.43	0.94	12.50	463	1.199	0.44	1.01
11.0	483	1.126	0.24	1.34	13.00	483	1.318	0.39	0.94	12.50	483	1.444	0.38	1.04
11.0	503	1.308	0.21	1.40	13.00	503	1.553	0.35	0.97	12.50	503	1.660	0.34	1.08
13.0	423	0.637	0.37	1.34	15.25	423	0.670	0.54	0.96	15.00	423	0.761	0.59	1.00
13.0	443	0.858	0.34	1.33	15.25	443	0.943	0.51	0.96	15.00	443	1.044	0.55	0.98
13.0	463	1.078	0.30	1.32	15.25	463	1.217	0.47	0.95	15.00	463	1.339	0.50	0.98
13.0	483	1.289	0.27	1.32	15.25	483	1.491	0.43	0.94	15.00	483	1.636	0.45	1.00
13.0	503	1.500	0.24	1.36	15.25	503	1.765	0.40	0.96	15.00	503	1.888	0.40	1.02
15.0	423	0.695	0.41	1.32	17.00	423	0.711	0.57	0.96	17.00	423	0.802	0.62	0.99
15.0	443	0.946	0.38	1.30	17.00	443	1.007	0.54	0.96	17.00	443	1.118	0.59	0.98
15.0	463	1.210	0.34	1.31	17.00	463	1.314	0.50	0.95	17.00	463	1.452	0.54	0.97
15.0	483	1.457	0.30	1.31	17.00	483	1.621	0.47	0.95	17.00	483	1.766	0.49	0.97
15.0	503	1.694	0.27	1.35	17.00	503	1.928	0.43	0.97	17.00	503	2.060	0.44	1.00
17.4	423	0.748	0.45	1.27						20.00	423	0.864	0.67	0.99
17.4	443	1.045	0.42	1.28	46.38 g solvent injected					20.00	443	1.214	0.64	0.97
17.4	463	1.342	0.38	1.28						20.00	463	1.581	0.59	0.95
17.4	483	1.625	0.35	1.28	26.50	423	0.914	0.71	0.97	20.00	483	1.984	0.54	0.97
17.4	503	1.892	0.31	1.30	26.50	443	1.347	0.69	0.98	20.00	503	2.328	0.49	0.99
					26.50	463	1.825	0.65	0.98	27.00	423	0.976	0.74	0.99
					26.50	483	2.290	0.61	0.96	27.00	443	1.424	0.72	0.99
					26.50	503	2.727	0.58	0.96	27.00	463	1.886	0.68	0.96
52.29 g solvent injected					34.00	423	0.999	0.77	0.98	27.00	483	2.347	0.64	0.94
33.00	423	0.913	0.61	1.14	34.00	443	1.500	0.75	0.99	27.00	503	2.776	0.61	0.93
33.00	443	1.329	0.59	1.13	34.00	463	2.055	0.72	0.97	32.00	423	1.035	0.78	1.00
33.00	463	1.804	0.56	1.13	34.00	483	2.624	0.69	0.96	32.00	443	1.521	0.76	0.99
33.00	483	2.334	0.52	1.15	34.00	503	3.172	0.66	0.95	32.00	463	2.066	0.73	0.97
33.00	503	2.827	0.49	1.16	40.00	423	1.050	0.80	0.98	32.00	483	2.593	0.69	0.94
40.00	423	0.997	0.66	1.14	40.00	443	1.590	0.78	0.99	32.00	503	3.061	0.67	0.92
40.00	443	1.459	0.64	1.13	40.00	463	2.217	0.76	0.98					
40.00	463	1.984	0.61	1.11	40.00	483	2.865	0.73	0.96					
40.00	483	2.541	0.59	1.09	40.00	503	3.497	0.71	0.95					
40.00	503	3.123	0.56	1.11										
49.00	423	1.051	0.71	1.11										
49.00	443	1.546	0.69	1.09										
49.00	463	2.144	0.67	1.08										
49.00	483	2.762	0.65	1.06										
49.00	503	3.389	0.63	1.04

Fig. 5. Methanol activity coefficient in (a) sulfolane, (b) TEGDME and (c) 18-crown-6.

ficients in the liquid phase have been calculated for temperatures of 423 to 503 K.

Unexpectedly, minima have been found for the methanol activity coefficient in TEGDME and 18-crown-6. Sulfolane, which is not an ether compound, does not exhibit such behaviour. With the procedure outlined, separate chemical analysis of the two phases is not necessary and a disturbance of the equilibrium by sample taking is avoided.

The experimental technique described can be recommended for experiments at moderate pressures, where the simplifying assumptions made do not cause significant errors.

Acknowledgements

The authors wish to thank Twente University of Technology and the Royal Dutch Shell Group for their financial support, and Dr. J. Drexhage of the Royal Dutch Shell Laboratories at Amsterdam for his stimulating and helpful criticism during the work.

Nomenclature

$a(T)$	parameter in Peng–Robinson equation, $\text{Pa mol}^{-2} \text{m}^{-6}$
A	parameter defined by eqn. (11)
$a_i, b_i,$ c_i, d_i	parameters in eqn. (3)
$b(T)$	parameter in Peng–Robinson equation, $\text{m}^3 \text{mol}^{-1}$
B	parameter defined by eqn. (12)
K	characteristic constant in Peng–Robinson equation
n	quantity, mol
P	pressure, Pa
R	gas constant, $8.3144 \text{ J mol}^{-1} \text{K}^{-1}$
T	absolute temperature, K
v	molar volume, $\text{m}^3 \text{mol}^{-1}$
V	volume, m^3

x	molar fraction in liquid phase
y	molar fraction in gas phase
Z	parameter defined by eqn. (13)
γ	activity coefficient in liquid phase
ϕ	fugacity coefficient
τ	parameter in eqn. (3)
ω	acentric factor

Subscripts

c	critical parameter
G	gas phase
i	component i
ℓ	liquid phase
r	reduced parameter
s	solvent
0	amount injected

Superscripts

0	saturated vapour
-----	------------------

References

- 1 J. Martinmaa, Sulfolane, in J. J. Lagowski (ed.), *Solution Phenomena and Aprotic Solvents*, Academic Press, London, 1977.
- 2 D. Ambrose, *J. Chem. Thermodyn.*, **10** (1978) 765–769.
- 3 M. Kuczynski, A. Van Ooteghem and K. R. Westerterp, *Coll. Polymer Sci.*, in preparation.
- 4 D. Yu Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.*, **15** (1976) 59–64.
- 5 R. C. Reid, J. M. Prausnitz and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 3rd edn., 1977.
- 6 C. L. Yaws, *Physical Properties. A Guide to the Physical, Thermodynamic and Transport Property Data of Industrially Important Chemical Compounds*, McGraw-Hill, New York, 1977.
- 7 M. Gottlieb and M. Herskowitz, *Fluid Phase Equilibria*, **17** (1984) 135–138.