MEASUREMENT OF VAPOUR-LIQUID EQUILIBRIUM DATA OF LIQUIDS WITH LOW VAPOUR PRESSURE

Július SUROVÝ, Elena GRACZOVÁ and Ján DOJČANSKÝ

Department of Chemical Engineering,
Slovak Institute of Technology, 812 37 Bratislava

Received October 19th, 1985

A semimicrostill for measuring vapour–liquid equilibrium data suitable especially for the determination at pressures about 100 Pa is described. The still operates isothermally on the principle of differential distillation. The composition of equilibrium phases is determined chromatographically. The error caused by unstationariness of the apparatus was studied. As an example of its use, the vapour–liquid equilibrium data of the N-methylpyrrolidone–ethylene glycol solution at 50°C are reported. The dependence of excess Gibbs energy on composition was expressed by means of the fourth-order Redlich–Kister and NRTL equations. The system exhibits negative deviation from ideal behaviour. Thermodynamic treatment proves a good consistency of the equilibrium data measured.

There exist a number of experimental methods suitable for measuring the vapour–liquid equilibrium data at low and normal pressures. Their survey can be found in the monograph by Hála and coworkers[7], their attention being focussed especially on the stills with circulation of liquid and vapour. In recent years, more emphasis was laid on the development of static methods the survey of which is given by Aim[2]. Advantages of these methods have been discussed (Van Ness and coworkers[13], Abbott and Van Ness[1], Aim[3]).

The use of the respective method depends on the nature of the system investigated. None of those methods is sufficiently accurate or suitable for the systems whose vapour pressure is lower than 200 Pa. Such is, *e.g.*, also the system N-methylpyrrolidone–ethylene glycol (thereinafter NMP–EG) at 50°C, which is used at this temperature as a binary mixed solvent for aromatic hydrocarbons. For the thermodynamic description of the systems hydrocarbon–NMP–EG, it is necessary to know also the values of activity coefficients, source of which are the vapour–liquid equilibrium data.

To determine the L–G equilibrium data in the NMP–EG system, the semimicrostill described in this work was constructed which is suitable for measuring at pressures about 100 Pa. The apparatus operates isothermally on the principle of differential distillation.

EXPERIMENTAL

Semimicrostill for Measuring the L-G Equilibria at Low Pressures

When designing the still for determining the L-G equilibrium data, we stemed from the fact that even the liquids with low vapour pressure distill rapidly into spaces with low temperature if uncondensable gases are exhausted to a sufficient extent from the space of distillation apparatus. So, *e.g.*, if we have an NMP-EG solution at 50°C in a distillation vessel, and the pressure in a receiver is lower than 5 Pa and temperature −70°C, it is possible to obtain a measurable amount of condensate in the receiver in a real time. On using chromatographic analysis, the needed amount of this distillate is several ten microlitres, and the time of distillation several minutes.

Scheme of the semimicrostill for measuring L-G equilibria operating on this principle is given in Fig. 1.

The still is of simple design. It consists of an equilibrium flask **A** whose moderately extended arm is bent and through a three-port vacuum cock connected on one side to a source of vacuum **G** and on the other one to an arm with interchangeable ground vessel **B** for sampling the vapour phase. The flask **A** is provided with a hole serving for inlet or taking the liquid sample. A thorough stirring of the liquid is ensured by a magnetic stirrer **F**.

The isothermal regime in part **I** is maintained by a tempering jacket in which liquid from an ultrathermostat is recirculated. In part **II**, temperature about 30°C higher is maintained by an electric winding to prevent partial condensation of vapours in this part, the temperature being checked by a thermocouple. Pressure is checked by a Pirani gauge inserted into the vacuum part behind the three-port cock. As a rule, the method does not require an accurate determination of pressure. For the analysis, 12—15 cm^3 liquid sample of approximately known composition is used. The volume of caught vapour phase is at most 0·20 cm^3.

Even if the measurement takes place in unstationary state, *i.e.* the compositions of the vapour and liquid phases are changed during all the measurement, the results of measurements can be, in majority of cases, evaluated as results obtained in stationary state. To carry out the evaluation, it is necessary to know for a binary solution: temperature, mole fraction of component 1 in distillate, $x_{1\text{D}}$, mole fraction of component 1 in remainder, $x_{1\text{W}}$, amount of substance in distillate, n_D, amount of substance in remainder, n_W, and mole fraction of component 1 in solution before

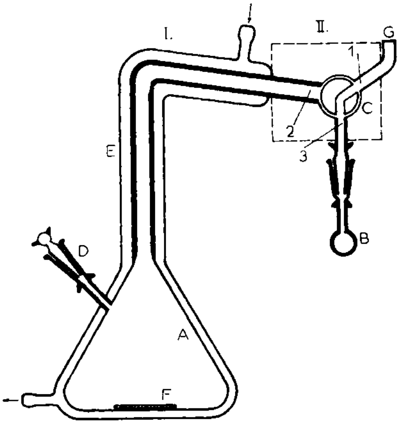

FIG. 1

Semimicrostill for measuring vapour-liquid equilibrium at low pressures. **A** equilibrium flask, **B** interchangeable receiver, **C** three-port vacuum cock, **D** opening with ground glass joint, **E** tempering jacket, **F** magnetic stirrer, **G** connection to vacuum; the other symbols explained in text the distillation, x_{1F}, which is calculated from the material balance

$$x_{1F} = (1 - n_D/n_F)\, x_{1W} + (n_D/n_F)\, x_{1D}\,, \qquad (1)$$

where

$$n_F = n_W + n_D\,. \qquad (2)$$

(A direct determination of n_F and x_{1F} before measurement is not recommended owing to possible losses during exhausting the still.)

The equilibrium mole fraction in the vapour phase, y_1, which corresponds to the arithmetic mean of the liquid mole fractions before and after the measurement,

$$\bar{x}_1 = \tfrac{1}{2}(x_{1W} + x_{1F})\,, \qquad (3)$$

is usually practically identical with the mole fraction of component in distillate, x_{1D}. The error resulting from the replacement of x_{1D} for y_1 is not as a rule, greater than 10^{-4}–10^{-5}. An exception are only some solutions with high relative volatility of components ($\alpha > 10$) and measurements with sampling a great amount of distillate ($n_D/n_F > 0{\cdot}02$). The possibility of replacing the equilibrium y_1 by the value of x_{1D} is illustrated by an example of simulated measurements for $\alpha = 10$, $n_D/n_F = 0{\cdot}02$ and a set of values x_{1F}. The results are given in Table I.

The value of x_{1W} was calculated by means of the Rayleigh equation[9], x_{1D} from material balance (1), and y_1 from the equilibrium relation

$$y_1 = \alpha\bar{x}_1/(\alpha\bar{x}_1 + (1 - \bar{x}_1))\,. \qquad (4)$$

As it follows from the data of the table, the difference $y_1 - x_{1D}$ is, in the whole concentration range, lower than 10^{-3}, *i.e.*, lower than one tenth of the error in chromatographic determination of mole fractions, $\pm 5\,.\,10^{-3}$.

Measurement of L–G Equilibria

The liquid sample of an approximate composition is inserted into the equilibrium flask **A** through the opening **D**. The still is closed with a ground-in stopper and evacuated to a pressure lower

TABLE I

Comparison of the actual and equilibrium composition of distillate in simulated measurement ($\alpha = 10$, $n_D/n_F = 0{\cdot}02$)

x_{1F}	x_{1W}	x_{1D}	y_1	$y_1 - x_{1D}$
0·05000	0·04427	0·33072	0·33096	$24\,.\,10^{-5}$
0·10000	0·09155	0·51426	0·51437	$11\,.\,10^{-5}$
0·30000	0·28965	0·80697	0·80698	$1\,.\,10^{-5}$
0·50000	0·49168	0·90770	0·90771	$1\,.\,10^{-5}$
0·70000	0·69473	0·95841	0·95841	$<10^{-5}$
0·90000	0·89819	0·98890	0·98890	$<10^{-5}$
0·95000	0·94909	0·99472	0·99472	$<10^{-5}$

than 5 Pa. Under continual stirring of the sample, the I and II parts of still are heated to a temperature required. After establishing the temperatures, the sample is deaerated by changing the position of three-way cock in short time intervals from the position connecting the outlets **1—3** to the position **1—2** for several seconds.

Thoroughness of the sample deaeration is checked by the Pirani gauge. After establishing the pressure in the apparatus (about 40 min) the sample may be considered to be deaerated. The system is let become established (three-way cock is in position **1—3**). After establishing, the position of three-way cock is changed to position **2—3**, and the extended part of receiver is intensely cooled with a cooling mixture (mixture of acetone and solid CO_2). In the cooled part, a rapid condensation of the equilibrium vapour phase takes place. After the condensation of 0·1—0·2 cm^3 sample (condensation time 1—5 min), the system is aerated, and the samples of both phases for the chromatographic analysis are taken.

Vapour–liquid equilibrium in the binary system N-methylpyrrolidone(1)–ethylene glycol(2) was determined at the temperature of $50 \pm 0{\cdot}1$°C. The value of pressure in the vacuum part was about 5 Pa, in the system during deaerating the binary system investigated, according to its composition, of the order 10^1 to 10^2 Pa. The pressure measurement served only for checking. The analyses of the liquid and vapour phases were carried out chromatographically after completing the measurement with accuracy higher than $\pm 0{\cdot}5$ mol %. The chemical compounds used for the measurement were of chromatographic purity higher than 99·8%.

RESULTS

The measured y–x equilibrium data for the NMP(1)–EG(2) system at 50°C are given in Table II. (In the table there are the corrected liquid compositions, *i.e.*, the arithmetic mean of fractions before and after measurement.) The y–x diagram of the system measured at 50°C is depicted in Fig. 2. As it can be seen, the system exhibits negative deviations from ideal behaviour.

The dependences of excess Gibbs energy on composition was expressed by the fourth-order Redlich–Kister equation[10] in the form

$$G^E/RT = x_1 x_2 \sum_k A_k (x_1 - x_2)^{k-1} \qquad (5)$$

whose constants were evaluated by the maximum likelihood method by the procedure by Rod and Hančil[12]. The form of the objective function used was

$$F = \sum_{m=1}^{M} [(y_1 - y_1^c)^2 + (x_1 - x_1^c)^2]_m \,. \qquad (6)$$

Here, y_1 and y_1^c (x_1 and x_1^c) are the measured and calculated mole fractions of the more volatile component in the vapour (liquid) phase, respectively. With regard to the low value of total pressure (lower than 100 Pa), the validity of the ideal-gas equation of state was assumed for calculating y_1^c, thus

$$y_1^c = P_1^0 x_1 \gamma_1 / (P_1^0 x_1 \gamma_1 + P_2^0 x_2 \gamma_2) \,. \qquad (7)$$

Objective function (6) was minimized not only with respect to the parameters of G^E equation but also with respect to the incidental parameters – the independent variables x_{1m} and the saturated vapour pressure P_2^0 of EG. In the first cycle, the

TABLE II

Experimental and calculated y–x equilibrium data for the system N-methylpyrrolidone(1)–ethylene glycol(2) at 50°C

y_1	x_1	y_1^c	x_1^c
0·0842	0·0546	0·0863	0·0511
0·2456	0·1550	0·2447	0·1562
0·2475	0·1562	0·2466	0·1575
0·3448	0·2284	0·3463	0·2262
0·3889	0·2534	0·3879	0·2548
0·4843	0·3156	0·4815	0·3196
0·5500	0·3717	0·5518	0·3692
0·5710	0·3861	0·5724	0·3841
0·6864	0·4694	0·6855	0·4705
0·7343	0·5157	0·7362	0·5136
0·7711	0·5602	0·7783	0·5528
0·8314	0·5901	0·8220	0·5985
0·8537	0·6285	0·8500	0·6314
0·9063	0·7210	0·9100	0·7189
0·9556	0·8241	0·9581	0·8232
0·9711	0·8610	0·9705	0·8612
0·9890	0·9324	0·9883	0·9325

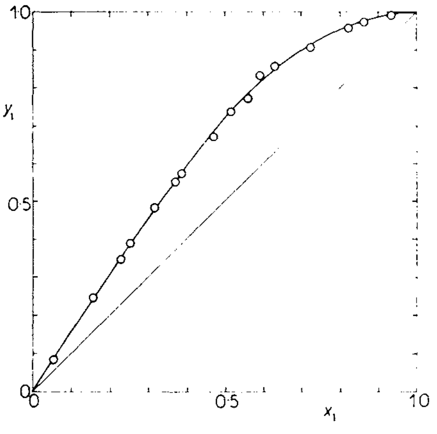

FIG. 2

The y–x diagram of the binary solution N-methylpyrrolidone(1)–ethylene glycol(2) at 50°C. The curve was calculated by means of the Redlich–Kister equation

Redlich–Kister parameters for all the experimental data are optimized simultaneously, at constant value of incidental parameters x_{1m} and P_2^0. In the second cycle, the optimum of objective function (6) is sought with respect to x_{1m}, separately for each measurement. With the set of these data, the optimum parameters of the Redlich–Kister equation are sought again. The alternation of both the iteration cycles is repeated until the minimum of objective function with tolerance required is reached.

The literature data on the value of the EG saturated vapour pressure, P_2^0, at 50°C differ considerably[5,6,8]. Therefore P_2^0 appeared as another parameter, *i.e.*, such a value of P_2^0 was also sought for which objective function (6) is minimum. To calculate P_2^0, the method of passive seeking was used. The saturated vapour pressure of NMP at 50°C, $P_1^0 = 224{\cdot}6$ Pa, was extrapolated from the experimental data by Aim[4].

The following parameters of the fourth-order Redlich–Kister equation were computed: $A_1 = -0{\cdot}77527$, $A_2 = -0{\cdot}20940$, $A_3 = 0{\cdot}10258$, the saturated vapour pressure of EG at 50°C being $P_2^0 = 78{\cdot}4$ Pa. The mole fractions of NMP in the vapour and liquid phases, calculated on the basis of the Redlich–Kister equation, are given in Table II. The mean and standard deviations of measured data from calculated ones are: $d_x = 2{\cdot}55 \,.\, 10^{-3}$, $d_y = 2{\cdot}52 \,.\, 10^{-3}$, $\sigma_x = 3{\cdot}46 \,.\, 10^{-3}$, $\sigma_y = 3{\cdot}54 \,.\, 10^{-3}$. Fig. 2 shows, along with the experimental points, also the curve of the y–x dependence calculated in this way.

The presented evaluation of the experimental data was carried out for comparison also in terms of the NRTL equation[11], the saturated vapour pressure of EG being considered the same as on using the Redlich–Kister equation, *i.e.* $P_2^0 = 78{\cdot}4$ Pa. These parameters of the NRTL equation were calculated: $\alpha_{12} = 0{\cdot}9444$, $\tau_{12} = 1{\cdot}6775$, $\tau_{21} = -0{\cdot}9715$. The mean and standard deviations of the measured y–x data from those calculated on the basis of the NRTL equation are: $d_x = 2{\cdot}66 \,.\, 10^{-3}$, $d_y = 2{\cdot}74 \,.\, 10^{-3}$, $\sigma_x = 3{\cdot}64 \,.\, 10^{-3}$, $\sigma_y = 3{\cdot}85 \,.\, 10^{-3}$, which are deviations practically identical with those on using the Redlich–Kister equation. With regard to the accuracy of the analytical method used (gas chromatography), it is possible to consider the agreement of the measured and calculated data in both the cases as very good.

LIST OF SYMBOLS

A_K	binary parameters of the fourth-order Redlich–Kister equation
d	mean deviation
F	objective function
G^E	molar excess Gibbs energy
M	total number of measurements
n	amount of substance
P	(total) vapour pressure

R	gas constant
t, T	temperature, thermodynamic temperature
x	mole fraction in liquid
y	mole fraction in vapour
α	relative volatility
γ	activity coefficient
σ	standard deviation
α_{12}, τ_{12}, τ_{21}	parameters of NRTL equation

Superscripts

c	calculated value
o	pure substance

Subscripts

D	distillate
F	solution before measurement
W	remainder
i, 1, 2, 3	serial number of substance
k, 1 ,2, 3	serial number of parameters of R–K equation
m	serial number of experimental point

REFERENCES

1. Abbott M., Van Ness H. C.: AIChE J. *21*, 62 (1975).
2. Aim K.: *Static Method of the Measurement of Vapor–Liquid Equilibria at Low and Normal Pressures* (in Czech). *Thesis*, Institute of Chemical Process Fundamentals, Prague 1972.
3. Aim K.: *Vapor–Liquid Equilibrium in Systems with Very Different Volatility of Components* (in Czech). *Thesis*, Institute of Chemical Process Fundamentals, Prague 1977.
4. Aim K.: Fluid Phase Equilib. *2*, 119 (1978).
5. Dykyj J., Repáš M.: *Tlak nasýtenej pary organických zlúčenín.* Published by Veda, vydavatelstvo SAV, Bratislava 1979.
6. Dykyj J., Repáš M., Svoboda J.: *Tlak nasýtenej pary organických zlúčenín.* Published by Veda, vydavatelstvo SAV, Bratislava 1984.
7. Hála E., Pick J., Fried V., Vilím O.: *Vapour–Liquid Equilibrium.* Pergamon Press, London 1967.
8. Joo H., Arlt W.: J. Chem. Eng. Data *26*, 138 (1981).
9. Perry J. H.: *Chemical Engineering Handbook*, 3rd ed. McGraw-Hill, New York 1950.
10. Redlich O., Kister A.: Ind. Eng. Chem. *40*, 345 (1948).
11. Renon H. M., Prausnitz J. M.: AIChE J. *14*, 135 (1968).
12. Rod V., Hančil V.: Comput. Chem. Eng. *4*, 33 (1980).
13. Van Ness H. C., Byer S. M., Gibbs R. E.: AIChE J. *19*, 238 (1973).

Translated by J. Linek.