

A MODIFIED GILLESPIE STILL FOR MEASURING VAPOUR-LIQUID EQUILIBRIA

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A modification of the Gillespie still for measuring vapour-liquid equilibrium data is described. The still was tested at different working pressures within the range of 3.7 to 86.7 kPa by measuring the isothermal L-G equilibrium data for the binary system *p*-xylene-dimethylformamide at the temperatures of 60, 80, 100, 120, and 130°C. The dependence of activity coefficients of components on composition was expressed by means of the Redlich-Kister and Wilson equations. The consistency of the experimental data as well as the agreement of some measured values with the data from literature furnishes an evidence of good functioning of the apparatus.

Most experimental equipments for determining vapour-liquid equilibrium data at low and normal pressures employ the recirculation of liquid and vapour. Their survey is given *e.g.* in the monograph by Hála and coworkers³. The first still of this type, providing comparatively accurate results, was designed by Gillespie². The original Gillespie still was improved by many authors; the description of such stills is given in works^{3,5,6}. The stills differ considerably from one another in construction, however, their principle is identical. In this work we present the description and tests of an apparatus built up of elements of stills described in literature, in such a way for the apparatus not to be demanding constructionally and at the same time to enable one to maintain strict steady-state during measurement.

Still Design and Function

The circulation still described in this work (Fig. 1) is noted for constructional changes in the intake and treatment of the liquid and vapour samples.

The equilibrium liquid and condensate of the equilibrium vapour are directed into the receivers (5) and (6) by means of the swinging funnels (12). The funnels are tipped by magnets before cutting out the still so that the liquid during the unstationary regime may flow directly into the container (9). The samples of liquid and vapour are taken after cutting out the apparatus through the openings (11). The content of the receivers as well as of the container is intensely stirred by the magnetic stirrers (8) so that the formation of concentration gradient in the samples and in back flow to the boiling flask (1) is practically eliminated.

The arrangement and function of the other parts of the still is common. The solution is brought to boiling in flask (1) on which a lower heater Q_1 is wound, operating as the main heater, and an upper heater Q_2 which adjusts the rate of evaporation of liquid. Inner surface of the boiling flask is sintered with crushed glass, which aids a calm boiling of liquid. The vapours formed entrain the liquid through the Cottrell pump (2) to the equilibrium chamber onto thermometer well (3). The adiabatic regime in this part is maintained by heating the insulating jacket. In the drop separator (4), the equilibrium liquid and vapour are separated. The liquid runs down into the receiver (5) and condensed vapour into the receiver (6) through the drop counter (7). The superfluous liquid and condensed vapour flow down through the overflow tubes to the container (9). The still is connected to a vacuum system (V) through reflux condensers, the isothermal regime in the apparatus is ensured by maintaining constant pressure in the system. For measuring, about 200 cm^3 liquid is used. The right height of level in the container (9) and in boiling flask (1) is adjusted by means of the vessel (13) by sucking or discharging the liquid.

Testing the Equilibrium Still

The equilibrium still described in the foregoing part was tested by measuring the L-G equilibrium data of the binary solution *p*-xylene-dimethylformamide (DMFA) at the temperature of 60, 80, 100, 120, and 130°C . The temperature in the still was

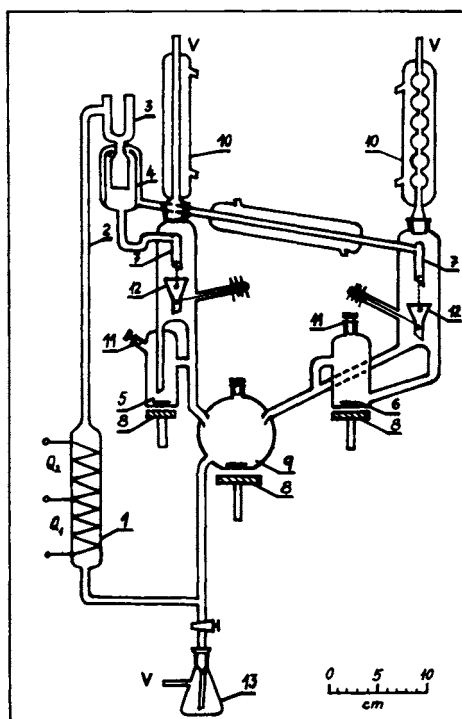


FIG. 1

Scheme of the modified Gillespie still. 1 boiling flask, 2 Cottrell pump, 3 thermometer well, 4 drop separator, 5, 6 receivers for the liquid and vapour phases, 7 drop counter, 8 stirrer, 9 container, 10 condenser, 11 opening with ground joint, 12 swinging funnel, 13 adjusting flask, V vacuum

maintained by adjusting pressure in the range of 3.7 to 86.7 kPa with the accuracy of ± 13 Pa. Temperature was measured by a resistance thermometer with the accuracy of $2-3 \cdot 10^{-2}$ K. The composition of the equilibrium phases was determined by measuring refractive index with the accuracy of ± 0.15 mole %. The chemicals used: *p*-xylene was obtained by twofold crystallization of a pure-grade *p*-xylene (product of Reachim). Its chromatographic purity was higher than 99.8%, refractive index $n_D^{20} = 1.4958$ (ref.⁸, $n_D^{20} = 1.49582$). Dimethylformamide was obtained from a technical product by twofold vacuum rectification in a column equivalent to about 10 theoretical plates. Its refractive index $n_D^{20} = 1.4305$ (ref.⁸, $n_D^{20} = 1.43047$).

The experimental data were correlated by means of the 4th order Redlich-Kister equation⁷

$$G^E/RT = x_1x_2[B + C(x_1 - x_2) + D(x_1 - x_2)^2], \quad (1)$$

and the Wilson equation¹⁰

$$G^E/RT = -x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(A_{21}x_1 + x_2), \quad (2)$$

whose parameters were computed by the maximum likelihood method by the procedure according to Rod and Hančil⁹. The form of the objective function was

$$F = \sum_j [(y_{1j} - \hat{y}_{1j})^2 + (x_{1j} - \hat{x}_{1j})^2]. \quad (3)$$

TABLE I

Parameters of the 4th order Redlich-Kister equation, values of mean deviations and standard deviations of variables for the *p*-xylene-DMFA system at various temperatures

Parameter	<i>t</i> , °C				
	60.04	80.03	100.01	119.99	130.00
<i>B</i>	0.9671	0.9663	0.9325	0.8796	0.8466
<i>C</i>	0.1074	0.1152	0.1032	0.1126	0.0892
<i>D</i>	0.0447	0.0853	0.0660	0.0241	0.0519
<i>d_x</i> · 10 ³	0.57	0.96	0.74	0.86	0.67
<i>d_y</i> · 10 ³	0.58	1.01	0.76	0.60	0.72
<i>d_p</i> /kPa	0.0718	0.0569	0.2095	0.4263	0.5083
<i>s_x</i> · 10 ³	0.70	1.448	1.195	1.301	0.861
<i>s_y</i> · 10 ³	0.72	1.553	1.014	0.895	1.120

It was assumed in calculation that the temperature measurement is accurate. The mole fractions of more volatile component in the vapour phase were calculated from the relation

$$\hat{y}_1 = (\gamma_1 f_1^{\text{OL}} x_1 / \varphi_1^{\text{G}}) / (\gamma_1 f_1^{\text{OL}} x_1 / \varphi_1^{\text{G}} + \gamma_2 f_2^{\text{OL}} x_2 / \varphi_2^{\text{G}}). \quad (4)$$

TABLE II

Parameters of the Wilson equation, values of mean deviations and standard deviations of variables for the *p*-xylene-DMFA system at various temperatures

Parameter	<i>t</i> °C				
	60.04	80.03	100.01	119.99	130.00
A_{12}	0.7289	0.7518	0.7488	0.7936	0.7755
A_{21}	0.4274	0.4126	0.4384	0.4357	0.4763
$d_x \cdot 10^3$	0.66	1.21	0.61	0.81	0.76
$d_y \cdot 10^3$	0.68	1.26	0.83	0.61	0.86
d_p/kPa	0.0722	0.0687	0.2396	0.4603	0.6045
$s_x \cdot 10^3$	0.83	1.69	1.03	1.22	1.16
$s_y \cdot 10^3$	0.87	1.73	1.54	0.81	1.34

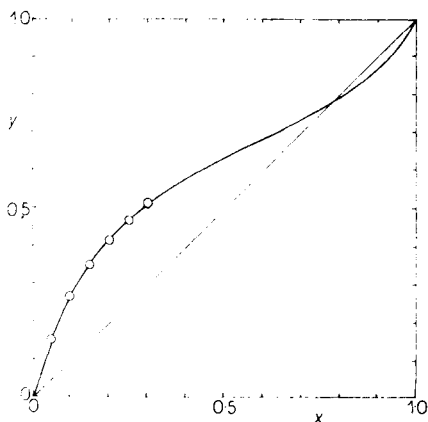


FIG. 2

Equilibrium *x*-*y* diagram for the *p*-xylene-DMFA system at 100°C. Points from ref.⁴, curve this work

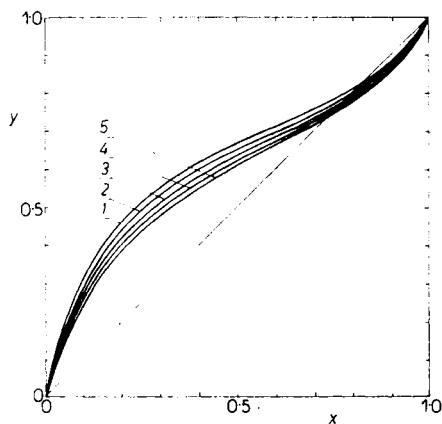


FIG. 3

Equilibrium *x*-*y* diagram for the *p*-xylene-DMFA system at various temperatures. 1 60.04, 2 80.03, 3 100.01, 4 119.99, 5 130.00°C

The computation of parameters of Eqs (1) and (2) consisted in solution of two successive iteration cycles. In the first cycle, the parameters for all the experimental data were optimized simultaneously at a constant value of incidental parameters x_1 . The Gauss–Newton method was used for the solution. In the second iteration cycle, the optimum of objective function (3) was sought with regard to the incidental parameters x_1 , separately for each measurement. Here the method of golden section¹ was used. With the set of these parameters, the first cycle was entered again. Alternating both the cycles was repeated unless the minimum of the objective function was reached within the tolerance required. The values of the Redlich–Kister parameters computed are given in Table I, and of the Wilson parameters, in Table II.

The measured L–G equilibrium data at 100°C were compared with those published in work by Heinrich and Surový⁴, where the latter were given in the form of parameters of the Redlich–Kister equation for the range of *p*-xylene concentrations $x_1 = 0$ to $x_1 = 0.3$. Fig. 2 shows a good agreement between the measured and published data.

The calculated equilibrium *y*–*x* diagrams for the *p*-xylene–DMFA system at various temperatures are illustrated in Fig. 3. The *p*-xylene–DMFA system exhibits an azeotropic point. With increasing pressure, the equilibrium curve approaches diagonal, and a shift of azeotropic point towards decreasing mole fraction of the low-boiling component takes place.

Thermodynamic treatment proves a good consistency of the equilibrium data measured. This is evidenced by the values of statistical indicators given in Tables I and II. The mean deviation of measured mole fractions from calculated ones lies within $5 \cdot 10^{-4}$ to $1.2 \cdot 10^{-3}$, the standard deviation within $7 \cdot 10^{-4}$ to $1.7 \cdot 10^{-3}$, independently of pressure. In the given range of pressures, the apparatus is able to work reliably and to provide sufficiently accurate results. Higher values of mean deviations have occurred in case of pressures. The fluctuation of pressures is connected with difficulties when accurately adjusting the temperature which was made with tolerance of $\pm 0.2^\circ\text{C}$. The change of temperature by 0.05°C results in the pressure change of 130 Pa so that the change of temperature of 0.2°C entails the pressure change of 520 Pa (at atmospheric pressure). The pressure deviations are just in this range.

LIST OF SYMBOLS

<i>B, C, D</i>	binary parameters of the 4th order Redlich–Kister equation
<i>d</i>	mean deviation
<i>f</i>	fugacity
<i>F</i>	objective function
G^E	molar excess Gibbs energy
<i>P</i>	system pressure
<i>R</i>	gas constant

s	standard deviation
t	temperature
T	thermodynamic temperature
x_1, y_1	mole fraction of component 1 in the liquid and vapour phases
γ	activity coefficient
φ	fugacity coefficient
A_{12}, A_{21}	parameters of the Wilson equation

Superscripts

G	vapour phase
oL	pure liquid component
\wedge	calculated value

Subscripts

j	j -th measurement
1, 2	denotation of components
x, y, P	variables

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