

## LIQUID-VAPOUR EQUILIBRIUM. LX.\*

## THE SYSTEM ACETIC ACID-ACRYLIC ACID AT 200 TORR

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Vapour-liquid equilibrium has been measured in the system acetic acid-acrylic acid at 200 Torr. A specially modified circulation still of the Gillespie type was used to this purpose. The data measured have been correlated by the third and fourth order Margules equations and by the second order expansion of relative volatility.

As part of a systematic study of thermodynamic properties of binary mixtures whose components belong to various groups of Ewell's classification of liquids, isobaric vapour-liquid equilibrium was measured for the acetic acid-acrylic acid system.

## EXPERIMENTAL

*Preparation of pure substances.* Acrylic acid (pure, product of BASF) was distilled on an 80 cm long column packed with copper helices under reduced pressure about 40 Torr. The collected main fraction was stabilized by adding 500 p.p.m. of hydroquinone. The acid was prepared, as far as possible, immediately before the measurements because it polymerizes spontaneously very easily on longer storage<sup>1</sup>.  $d_4^{20}$  1.0490 g/cm<sup>3</sup> (ref.<sup>1</sup> 1.0497),  $n_D^{20}$  1.4204 (ref.<sup>2</sup> 1.4210). Acetic acid (for semiconductors, Lachema Brno) was refluxed with 4 per cent of potassium permanganate (to remove aldehydes and alcohols) and 3 per cent of acetic anhydride for six hours. Then it was distilled on a forty plate bubble-cup column<sup>3</sup>.  $d_4^{20}$  1.0494 g/cm<sup>3</sup> (ref.<sup>4</sup> 1.0492),  $n_D^{20}$  1.3718 (ref.<sup>4</sup> 1.3716, ref.<sup>3</sup> 1.3717).

*Analytical method.* The equilibrium samples containing acetic acid and acrylic acid were analyzed by gas chromatography. The conditions were as follows: temperature 135°C, 50 cm long column packed with Porapak P, detection by heat conductivity cell, carrier gas hydrogen. The concentrations of both components were evaluated from the peak heights using an empirical relation calculated on the basis of measured calibration samples. The accuracy of the analysis was better than 1 per cent.

*Apparatus and procedure.* Preliminary measurements showed that all-glass stills<sup>5</sup> could not be used for measurements of the systems containing acrylic acid even under reduced pressure. Acrylic acid began to polymerize in the apparatus already during a short boiling period in those places, where it was not stabilized, *i.e.* in the condensation part, where the vapour separated from the liquid. The placement of copper helices or sheet into the separation space was not

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successful, as the polymerization was only retarded, but not prevented. These difficulties were increased by nearly unfeasible removing the polymers and led to the modification of all the condensation part of the still. The main aim of the modification was: *a*) to ensure cooling the separated vapour phase as quick as possible; *b*) to enable to disassemble the separation part for more thorough lining of glass parts with cooper sheets and for possible cleaning. The definitive variant of the head of equilibrium still, corresponding to the requirements given, is represented in Fig. 1. The head differs from the standard arrangement as follows: the upper 2 and the lower 11 parts are not firmly fused-on and, besides, the lower part can be cooled. The connection is made up by means of two duralumin flanges 6 (each consists of two semicircle parts) which tighten both glass parts packed by 1 mm thick silicone rubber circular ring 7. A soft bearing of the flanges on the glass is ensured by the O-rings 5. After thorough lining the separation space 9 with the copper sheets 10, the flanges are assembled by the screws 8 and the Cottrell pump is fused-on. The disassembling of the upper part of the head can be carried out only after cutting the Cottrell pump but this operation was not necessary to do during the measurements of equilibria with acrylic acid of five systems because in the given arrangement the polymerization practically did not take place. The connection of both parts of the head was vacuum-tight and the silicone rubber packing resisted both chemically and thermally. The description and function of the modified Gillespie circulation still including the vacuum system can be found in the literature<sup>5,6</sup>. The pressure in the system was measured indirectly, *i.e.* by measuring the boiling point of water in an ebulliometer connected in parallel. Temperature was measured by mercury standards calibrated by means of a Mueller bridge with platinum resistance thermometer Leeds and Northrup. The accuracy of the temperature measurements was  $\pm 0.02^{\circ}\text{C}$ . The equilibrium samples were taken for analysis only if the boiling point in the still did not change for 20 minutes (about 1 hour from the beginning of the measurement). After that, with regard to a slow dissolution of cooper in acrylic acid, the bulk of the solution in the still was replaced by the mixture of pure substances. Nevertheless, in the limits of experimental errors, it was not found a difference between the samples taken on using a new mixture and those taken from the mixture which was not replaced during three determinations (*i.e.* about 5 hours). It is evident from it that the presence of the cupric and cuprous salts of acrylic acid does not influence essentially the results of the vapour-liquid equilibrium measurements.

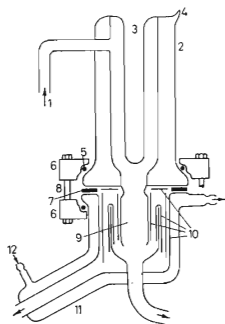


FIG. 1

Modification of the Head of Gillespie Circulation Still for Measuring Vapour-Liquid Equilibria in Systems with Polymerizing Component

1 Cottrell pump, 2 upper part of the head, 3 thermometer well, 4 evacuated jacket, 5 O-rings, 6 flange, 7 silicone rubber packing, 8 screws, 9 separation space, 10 copper sheets, 11 lower part of the head, 12 cooling water.

TABLE I  
Vapour Pressure of Acrylic Acid  
Constants of Eq. (4): *A* 7-80806, *B* 1827-90, *C* 230.

<i>t</i> , °C	68.0	83.65	101.65	109.1	141.0 <sup>a</sup>
<i>P</i> <sub>exp</sub> <sup>0</sup> , Torr	47.2	95.4	200.0	259.8	760.0
$\Delta P^0$ , <sup>b</sup> Torr	0.0	0.1	-2.1	1.8	0.5

<sup>a</sup> Normal boiling point from the literature<sup>1</sup>. <sup>b</sup>  $\Delta P^0 = P_{\text{calc}} - P_{\text{exp}}$ .

TABLE II  
Vapour-Liquid Equilibrium in the Acetic Acid (1)-Acrylic Acid (2) System at 200 Torr

<i>x</i> <sub>1</sub>	<i>y</i> <sub>1</sub>	<i>t</i> , °C	<i>y</i> <sub>calc</sub> - <i>y</i> <sub>exp</sub>		
			Marg. 3	Marg. 4	Alpha
0.030	0.048	100.85	0.069	0.025	0.005
0.086	0.154	98.95	0.089	0.036	-0.011
0.192	0.295	96.10	0.070	0.054	0.000
0.268	0.388	94.20	0.036	0.040	0.002
0.288	0.423	93.80	0.016	0.022	-0.010
0.345	0.480	92.30	0.002	0.011	-0.004
0.408	0.540	91.00	-0.005	0.001	0.003
0.411	0.543	90.65	-0.006	-0.001	0.001
0.464	0.596	89.40	-0.010	-0.010	-0.000
0.514	0.631	88.40	0.004	-0.001	0.011
0.563	0.676	87.25	0.011	0.001	0.008
0.604	0.722	86.25	0.008	-0.003	-0.004
0.677	0.775	85.05	0.033	0.024	0.002
0.717	0.813	84.25	0.034	0.030	-0.006
0.790	0.861	82.80	0.048	0.051	-0.002
0.889	0.934	81.10	0.034	0.041	-0.007
<i>Mean</i>			0.030	0.022	0.005

Constants of the correlation equation

Equation	Order	<i>A</i> <sub>12</sub>	<i>A</i> <sub>21</sub>	<i>D</i> <sub>12</sub>
Margules	3	0.3261	-0.3842	-
Margules	4	0.0401	-0.6998	-0.8105
Alpha	2	0.7892	-0.3554	-

## RESULTS AND DISCUSSION

The measured vapour-liquid equilibrium data were correlated using the following equations for the concentration dependence of activity coefficients: the Margules third order equation<sup>5</sup>

$$\log(\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 (A_{12} - A_{21}), \quad (1)$$

the Margules fourth order equation<sup>5</sup>

$$\log(\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 [A_{12} - A_{21} + (x_2 - x_1) D_{12}], \quad (2)$$

and the empirical expansion of relative volatility<sup>5</sup>

$$\alpha_{12} = (1 + A_{12}x_2)/(1 + A_{21}x_1), \quad (3)$$

where  $x_1, x_2$  are mole fractions of the components 1, 2 in the liquid phase and  $y_1, y_2$  mole fractions in the vapour phase, resp.,  $\gamma_1, \gamma_2$  activity coefficients,  $\alpha_{12}$  is relative volatility, and  $A_{12}, A_{21}, D_{12}$  are constants, characteristic for the given equation and binary mixture. The constants were evaluated by means of the least square method using the statistical weight<sup>7</sup>.

The temperature dependence of the vapour pressures of pure substances which is needed for the computations was expressed in the form of the Antoine equation:

$$\log P^0 = A - B/(t + C), \quad (4)$$

where  $P^0$  is vapour pressure (Torr),  $t$  is temperature ( $^{\circ}\text{C}$ ) and  $A, B, C$  are constants. The constants for acetic acid ( $A = 7.18807, B = 1416.70, C = 211.00$ ) were taken over from the literature<sup>8</sup>. However, the available vapour pressure data for acrylic acid<sup>1,9</sup> are not in good mutual agreement. The data listed in the manufacturer's prospectus<sup>1</sup> when represented in the  $\log P$  vs  $1/T$  diagram show the boiling point  $5^{\circ}\text{C}$  lower than the value accepted. A better course was found with the data smoothed graphically by Stull<sup>9</sup>. Because of this uncertainty as for the reliability of the data, the vapor pressure of acrylic acid was remeasured in the pressure interval 45–260 Torr (Table I). The measurements were carried out in the equilibrium still in order that the consistency of temperature measurements might be ensured. The data obtained were correlated by the Calingaert–Davis equation (Eq. (4) with  $C = 230$ ) taking into account the literary normal boiling point. Our data are in good agreement with the Stull ones.

The measured data on the vapour-liquid equilibrium in the acetic acid (1)–acrylic acid (2) system at 200 Torr and their comparison with calculated ones are given

in Table II. It is evident that for the given system which is a typical system with strong associations in the vapour phase, the Margules-type equations do not give very good result, whereas the correlation by the empirical expansion of the relative volatility is much better.

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