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Liquid−Liquid and Vapor−Liquid Phase Equilibria for Ethyl Acrylate + Water

Elsa Jolimaître, Muriel Triomphe, and Joseph Lieto*

Laboratoire d'Automatique et de Génie des Procédés, LAGEP, Université Claude Bernard, Lyon I et CPE-Lyon,
UPRES-A CNRS Q 5007, bâtiment 308 G, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France

Aleth Boudehen

Centre Technique ELF-ATOCHEM, Chemin de la Lône, BP 22, 69310, Pierre-Bénite, France

The liquid−liquid and the vapor−liquid phase equilibria of the binary system ethyl acrylate + water has been measured at different temperatures. All the data were obtained in a single autoclave, able to work under two different hydrodynamic regimes. With moderate stirring, a turbidimetric technique gave the liquid−liquid data, whereas with a strong agitation inducing the vapor recirculation into the liquid, the vapor−liquid data, with a saw-tooth temperature profile corresponding to a large pressure range (6.2 kPa to 94.5 kPa), were obtained. Our data are in good accordance with the data found in the literature.

Introduction

The liquid−liquid and vapor−liquid phase equilibria of ethyl acrylate + water were obtained for a system design of a distillation column to purify ethyl acrylate. In the literature, one can find several data for this binary (Gmehling et al., 1994; Kirk-Othmer Encyclopedia; The Merck Index), but none of them give a sufficiently wide range of operating conditions to have a safe and optimal distillation column design. However, our data are consistent with the literature data.

Experimental Section

Materials. Ethyl acrylate was supplied by Elf-Atochem at ≥99.5 mass % p.a. purity. The water was distilled twice.

Apparatus and Procedure. The autoclave used to obtain the data was described in Sever et al. (1998) [see also Verneau et al. (1994)]. The principle of the ebulliometric cell is the following: the autoclave is equipped with a turbidimeter in which a beam passes through two vertical windows made of optical glass. The cell is equipped with a special stirrer that is able, at high speed, to induce the vapor recirculation in the liquid and therefore to induce a very efficient heat and mass transfer between the two phases. When this stirrer is used at moderate speed, the turbidimeter cell can be run.

The temperature of the liquid phase was measured with a PT100 sensor with an accuracy of 0.1 K.

The pressure was measured with a MSK Baratron (model 121A) thermostated at 353 K, with an accuracy of 24 Pa (range of measurement: 0 to 100 kPa).

The vapor-phase water composition at the heteroazeotropic point was determined by a Karl-Fischer analysis of the samples, with a maximum absolute error of 0.35%.

Table 1. Temperature (*T*), Pressure (*P*), and Difference between Experimental and Literature Data (Δ*P*)

T/K	lit. data *P*/kPa	this work *P*/kPa	difference |Δ*P*|/kPa
303.2	6.73[a]	6.23	0.5
313.2	10.9[a]	9.95	0.95
323.2	16.8[a]	16.54	0.26
333.2	25.3[a]	25.65	0.35
343.2	37.3[a]	37.6	0.3
353.2	53.5[a]	53.54	0.04
363.2	74.7[a]	74.4	0.3
316.2	13.7[b]	11.53	2.17
323.2	16.8[c]	16.54	0.26
348.2	44.8[c]	44.95	0.15

[a] Kirk-Othmer Encyclopedia, Vol. 1, p 334. [b] Kirk-Othmer Encyclopedia, Vol. 1, p 332. [c] CRC Handbook, p 6-87.

For a given composition, the temperature of the liquid−liquid equilibrium boundary was determined by a turbidimetry technique (MONITECH model 210 turbidimeter coupled to a model 130 transmeter), with an accuracy of 0.1 K. The liquid−liquid equilibrium is assumed to be independent of pressure over the selected temperature range.

Finally, the total liquid-phase composition is determined by mass, with a maximum relative error of 0.1%.

To check the precision of our measures, the vapor−liquid equilibrium of pure ethyl acrylate was measured and compared with literature (Table 1). From Table 1, one can see that the difference between our measures and literature values is higher than that associated to the precision of our apparatus. Several reasons can explain this observation:

1. Before the products are introduced into the autoclave, they are degassed, to eliminate the volatiles that they contain. However, it is impossible to eliminate completely the volatiles, and part of them is injected with the products into the autoclave. Therefore, their partial pressure is taken into account for the total pressure measure, inducing high relative errors at low pressures.

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* To whom correspondence should be addressed: lieto@lagep.univ-lyon1.fr.

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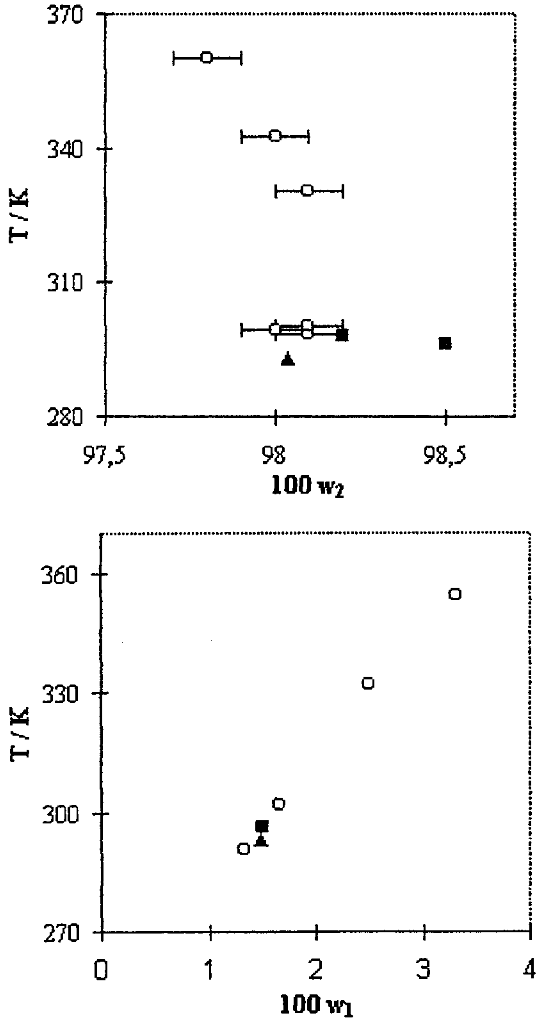

Figure 1. Liquid−liquid equilibrium on the water-rich side (a, top) and on the water-poor side (b, bottom) (○, experimental data; ▲, literature data from the Merck Index; ■, literature data from the Kirk-Othmer Encyclopedia).

2. When the temperature increases, the dependence of pressure on temperature increases. In consequence, a small imprecision in temperature can induce a high imprecision in pressure. The following measures of the vapor−liquid equilibria of pure ethyl acrylate obtained with our apparatus exemplify this:

$T = 353.2$ K $P = 53.54$ kPa
$T = 353.1$ K $P = 53.30$ kPa
$T = 353.3$ K $P = 53.77$ kPa

Hence, at the experiment temperature (with a 0.1 K precision), it is not possible to measure the pressure at a higher precision than ±0.23 kPa. This could also be a concern in the literature results (see point 3.).

3. In the cited literature, nothing is indicated on the precision of the measures. Furthermore, one of the references gives two different sets of values that are not in accordance with each other (Kirk-Othmer Encyclopedia, Vol. 1, p 332; Vol. 14, p 83).

In conclusion, the maximum absolute error on our pressure measures is 1 kPa. This error is due partly to our apparatus (degassing problems) and to the strong dependence of pressure on temperature. However, the existing values are quoted in the literature without error ranges, and we cannot compare their experimental precision with ours.

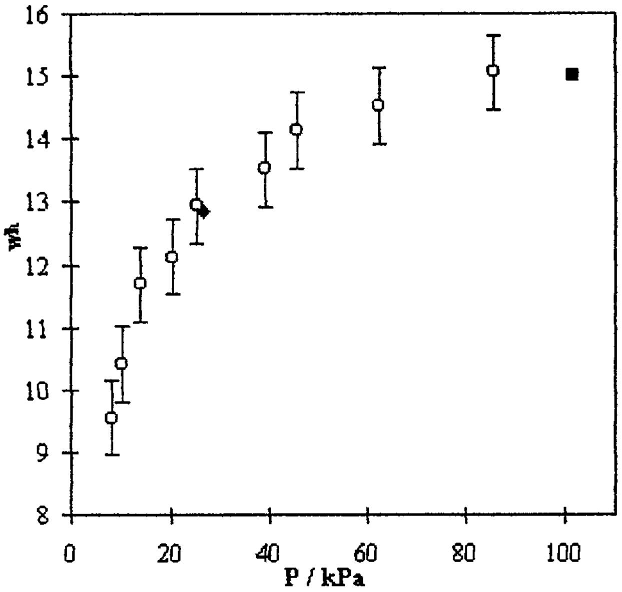

Figure 2. Heteroazeotropic vapor-phase mass fraction of vapor (Y_h) and pressure (P) (○, experimental data; ◆, literature data from Gmehling et al. (1994); ■: literature data from the Kirk-Othmer Encyclopedia.)

Table 2. Temperature (T) and Mass Fractions of Water in the Water-Poor Phase (w_1) and in the Water-Rich Phase (w_2), Experimental and Literature Data

ref	T/K	w_1	w_2
this work	290.5	1.33	
	298.6		98.05 → 98.1
	299.3		97.94 → 98.0
	300.2		98.12 → 98.1
	301.9	1.66	
	332.3	2.49	
	330.6		98.12 → 98.1
	342.5		97.99 → 98.0
	342.7		97.94 → 98.0
	354.2	3.32	
	360.2		97.82 → 97.8
lit. data	296.2[a]	1.5	98.5
	298.2[b]		98.2
	293.2[b]	1.48	98.04

[a] Kirk-Othmer Encyclopedia, Vol. 1, p 332. [b] The Merck Index, p 3806.

Results and Discussion

Liquid−Liquid Equilibrium. The liquid−liquid equilibrium data from 290.5 to 360.2 K are reported in Table 2, along with the literature data.

For the water-rich side, mass fractions are written in a higher precision than normally possible, this in order to explain why we obtained three different dew points for the same composition (for example, at w_2 = 98.0%); each experiment was different, with different masses of each constituent, but the composition difference is smaller than the absolute error.

This was necessary because ethyl acrylate solubility in water is barely dependent on temperature in the experimental temperature range. Therefore the two-phase boundary on the water-rich side is nearly vertical. In Figure 1a, one can see that our experimental results do not permit one to conclude on the general shape of the liquid−liquid equilibrium, even though the experimental error lies within ±0.1% of the measure. Literature data is in good agreement with our results: the points lie inside our experimental error. Only one point from the Kirk-Othmer

Table 3. Temperature (*T*), Pressure (*P*), and Mass Fraction of Water in the Heteroazeotropic Vapor (w_h), Experimental and Literature Data

ref	*T*/K	*P*/kPa	w_h
this work	296.9	8.20	9.55
	302.1	10.32	10.41
	308	13.93	11.68
	316.2	20.50	12.12
	320.9	25.41	12.94
	330.6	38.00	13.52
	334.3	45.72	14.14
	342	62.43	14.52
	350.2	85.70	15.06
lit. data	322.7[a]	26.6	12.84
	354.2[b]	101.3	15

[a] Gmehling et al. (1994). [b] Kirk-Othmer Encyclopedia, Vol. 1, p 332.

Encyclopedia does not corroborate our measures (Vol. 1, p 332, Table 2). This point being also in contradiction with another point found in the same reference (Vol. 14, p 83, Table 1), it seems reasonable to consider it erroneous.

For the water-poor side, our experimental points are precise enough to allow a good representation of the liquid−liquid equilibrium (Figure 1b). In Figure 1b, the experimental error is so small that it cannot be distinguished from the points. Besides, our points are in good agreement with literature.

Heteroazeotropic Vapor-Phase Composition. The variation with temperature of the heteroazeotropic vapor-phase water concentration is given in Table 3. Our experimental results are in good agreement with the literature data listed in Table 3, as shown in Figure 2.

Vapor−Liquid Equilibrium. With the experimental device used to obtain these data, it is possible to reach very rapidly (a few seconds) liquid−vapor equilibrium. Hence, for a given liquid-phase composition, the equilibrium pressure was measured every 0.1 K over the whole temperature range (303−353 K). However, the liquid−vapor equilibrium data presented in Table 4 are given at 10 K temperature intervals.

Table 4. Total Mass Fraction of Water in Liquid Phase (*w*), Temperature (*T*), and Pressure (*P*)

100 × *w*	*T*/K	*P*/kPa	100 × *w*	*T*/K	*P*/kPa
1.33	303.2	11.45	2.49	333.2	45.10
	313.2	17.49		343.2	64.74
	323.2	26.23		353.2	91.26
	333.2	38.54	98.5	303.2	10.91
	343.2	55.48		313.2	17.33
	353.2	78.14		323.2	26.83
1.66	303.2	12.18		333.2	40.44
	313.2	18.63		343.2	57.18
	323.2	27.82		353.2	79.70
	333.2	41.08	98.98	313.2	14.85
	343.2	59.22		323.2	22.98
	353.2	83.17		333.2	34.50
				343.2	50.31
				353.2	71.65

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