Vapor−Liquid Equilibria for Mixtures Containing *cis*-But-2-ene, 1,3-Butadiene, and *N*-Formylmorpholine Measured with the Vangeli Equilibrium Still

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The main features of the Vangeli equilibrium still are discussed with respect to the literature apparatuses based on the use of the Cottrell pump. The Vangeli still is applied to study the binary and ternary systems formed by (a) *cis*-but-2-ene, (b) 1,3-butadiene and (c) *N*-formylmorpholine (CASRN 4394-85-0, supplied by author) at 40 °C, 60 °C, and 80 °C, respectively, in a range of pressure of 2 bar to 9 bar. The experimental data are correlated by using the NRTL equation.

Introduction

More than a decade ago Vangeli coauthored a paper in which a new still was proposed for the experimental determination of fluid phase equilibria (Scaramucci and Vangeli, 1984). Published under the unappealing title “Isobaric Vapor−Liquid Equilibria of the 6-Methyl-5-hepten-2-one/Ethyl 3-Oxobutanoate and Methanol/1,6-Hexanediol Systems”, it is not surpising that the paper passed by without arousing any interest. In the opinion of the writer there are some good reasons to reexamine the merits of the Vangeli still. First, the Vangeli still deserves a careful examination in itself, since it represents an important improvement in the technique for measurement of vapor−liquid equilibria. Second, it is a flow apparatus that enables the determination of VLE of systems constituted by components having strongly different volatilities (see, for example, Figure 7 of the Scaramucci and Vangeli paper). This latter property is especially important in evaluating the selectivity of high-boiling polar solvents used to extract 1,3-butadiene from the C_4 cut of a steam-cracking mixture. One of the literature solvents proposed for this type of separations is *N*-formylmorpholine, an etherocyclic compound that showed good properties also for the extraction of aromatics.

cis-But-2-ene is the key component to evaluate the solvent selectivity to extract 1,3 butadiene from the other C_4 hydrocarbons. Therefore, in this paper the VLE of the binary and ternary systems formed by *cis*-but-2-ene, 1,3-butadiene, and *N*-formylmorpholine are studied in a range of temperature from 40 °C to 80 °C, which covers the experimental conditions found in a distex column feed with this mixture.

Experimental Section

Materials. *cis*-2-But-2-ene and 1,3-butadiene were purchased from Phillips at the highest purity degree (99+%). *N*-formylmorpholine was prepared in our laboratories by reacting morpholine with formic acid and purified after several crystallizations and vacuum distillations (purity 99.5+%).

Apparatus and Procedure. The Vangeli still is designed to enable a fast and reliable determination of both temperature and composition of phases at equilibrium. It consists of two parts: the first one is the feed system to the equilibrium vessel and represents the new feature of the still; the second part is an apparatus described by Vilim et al. (1953). The original part of the Vangeli still, which replaces the Cottrell pump, is depicted in Figure 1, which closely follows Figure 1 of the Scaramucci and Vangeli (1984) paper. In the author's words “The liquid mixture is charged to a reservoir thermostated with a jacket and pressurized with an inert gas (e.g., elium). By careful opening of a valve equipped with an indicator, a fixed amount of the mixture is sent under pressure through a heating coil and then into the equilibrium cell. By means of this simple device, the liquid flow rate can be easily modulated acting on two independent factors: the imposed inert gas pressure and the valve opening, both of which can be separately set at their optimum operating conditions. Furthermore, also the heating flow is split in two stages: a rough temperature regulation of all the mixture in the reservoir and a fine regulation of a small liquid amount in the heating coil submerged in a constant temperature bath. The temperature gradient, ΔT, between the bath and the equilibrium cell is controlled as a function of the component boiling points and the charge composition. Typical values are within a range of about 10 °C−30 °C. The ΔT value is not critical for a correct operation of the instrument and can be regulated, if necessary, on the basis of the collected amount of vapor”. Since the pressures investigated in this work are in the range 2−9 bar, the whole apparatus was built in stainless steel.

The equilibrium temperature was measured with a Lauda thermometer, model R42/2, provided with a 4 mm diameter Pt-100 temperature sensor, with an accuracy of ±0.01 K. The pressure trasducer was from Data Instrument and calibrated against the vapor pressure of pure 1,3-butadiene. The overall uncertainty was estimated to be less than ±0.2 kPa.

The components were charged in the reservoir following the order of increasing volatilities. The extra pressure in the reservoir was generated by the hydrocarbons, so avoiding the need of pressurizing with an inert gas.

The apparatus used differs from the still described by Scaramucci and Vangeli (1984) also for the vapor-phase line. Since the vapor phase consists primarily of the hydrocarbons (*N*-formylmorpholine has a boiling point of

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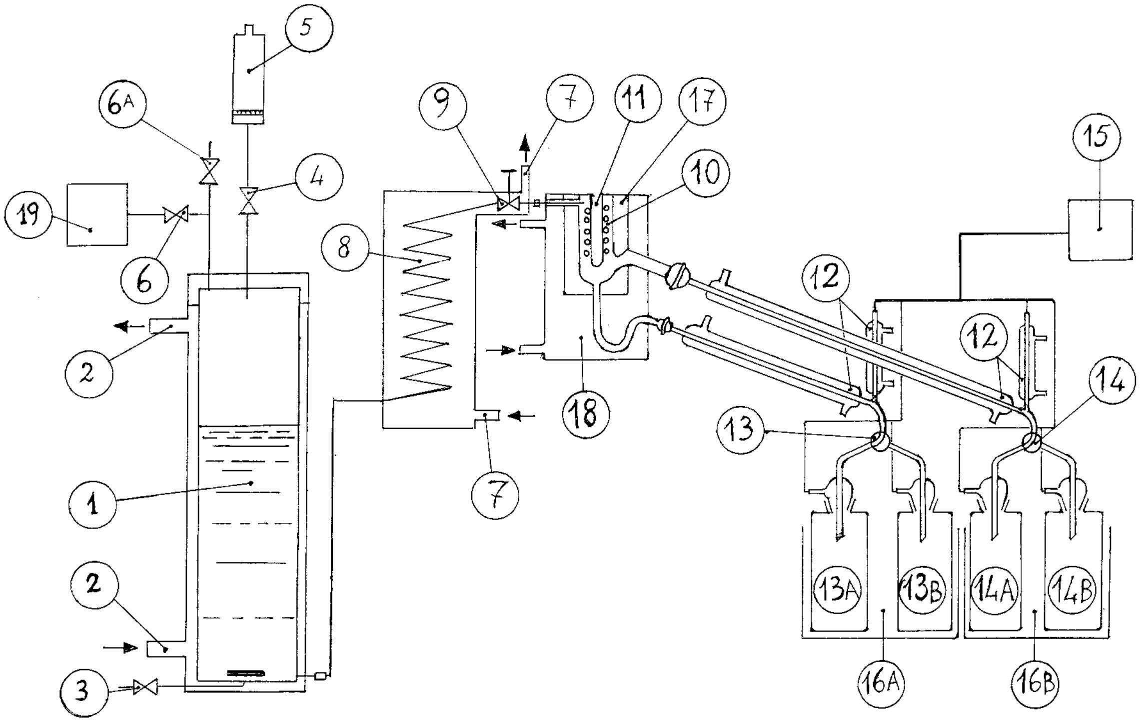

Figure 1. The Vangeli apparatus: (1) reservoir with a thermostating jacket, (2, 7) thermostated lines, (3, 4, 6, 6A, 9) valves, (5) charge vessel equipped with a filter, (8) overheating coil, (10) equilibrium cell, (11) thermowell, (12) vapor and liquid coolers, (13,14) three-way cocks, (13A, 13B) liquid-phase samplers, (14A, 14B) vapor-phase samplers, (15, 19) groove valves and transducers (16A, 16B) cooling baths, (17) insulating jacket under high vacuum, (18) thermostated jacket.

Table 1. VLE Data for Two Binary Systems

cis-but-2-ene (1) + *N*-formylmorpholine (2)				1,3 butadiene (1) + *N*-formylmorpholine (2)			
t/°C	P/bar	x_1	y_1	t/°C	P/bar	x_2	y_2
40	1.99	0.1053	>0.99	40	1.99	0.1738	>0.99
	2.48	0.1500			1.99	0.1740	
	2.97	0.2086			2.48	0.2262	
					2.97	0.2964	
					3.47	0.4000	
60	1.99	0.0639	>0.99	60	2.00	0.0984	>0.99
	2.97	0.0984			2.00	0.0991	
	2.97	0.0989			2.97	0.1558	
	3.96	0.1453			2.97	0.1565	
	4.94	0.2131			3.96	0.2282	
					3.98	0.2227	
					4.94	0.3099	
					4.94	0.3135	
					5.88	0.4624	
					5.92	0.4633	
80	3.96	0.0910	>0.99	80	3.96	0.0910	>0.99
	4.94	0.1265			4.94	0.1225	
	5.92	0.1556			5.92	0.1556	
	6.90	0.2029			6.90	0.2029	
	6.90	0.2045			6.90	0.2045	
	7.88	0.2546			7.88	0.2546	

Table 2. VLE Data for the Ternary System *cis*-But-2-ene (1) + 1,3-Butadiene (2) + *N*-Formylmorpholine (3)

t/°C	P/bar	x_1	x_2	y_1	y_2
40	1.99	0.0226	0.1420	0.1852	0.8148
	2.48	0.0302	0.1813	0.1853	0.8147
	2.99	0.0440	0.2452	0.1827	0.8173
	1.99	0.0895	0.0341	0.7915	0.2085
	2.48	0.1172	0.0441	0.7906	0.2094
	2.97	0.1671	0.0597	0.7895	0.2105
	2.97	0.1645	0.0582	0.7905	0.2095
60	1.99	0.0121	0.0801	0.1837	0.8163
	2.97	0.0202	0.1275	0.1819	0.8181
	3.96	0.0292	0.1790	0.1822	0.8178
	4.94	0.0553	0.2977	0.1817	0.8183
	2.02	0.0512	0.0199	0.7915	0.2085
	2.97	0.0839	0.0326	0.7896	0.2104
	3.96	0.1199	0.0421	0.7949	0.2051
	4.93	0.1797	0.0618	0.7922	0.2078
80	3.96	0.0191	0.1097	0.1861	0.8139
	5.92	0.0340	0.1819	0.1868	0.8132
	6.90	0.0437	0.2174	0.1856	0.8144
	7.88	0.0567	0.2752	0.1891	0.8109
	3.96	0.0739	0.0266	0.7890	0.2110
	5.92	0.1216	0.0432	0.7899	0.2101
	6.90	0.1570	0.0540	0.7925	0.2075
	7.88	0.1984	0.0689	0.7887	0.2113

513 K), it can be sent directly to the chromatograph for analysis or discharged. A more complex procedure is required for the analysis of the liquid phase. The sampler can be connected by means of a hypodermic needle to a flask sealed with a rubber septum. A known mass of the liquid phase is absorbed in a known quantity of a diluter (isobutyl alcohol). *N*-Formylmorpholine is then hydrolyzed to formic acid by reacting with H_2SO_4. Formic acid, in turn, is determined by potentiometric analysis. When a binary system is involved, the concentration of the second component is given by difference. Otherwise, the ratio between the two hydrocarbons involved in a ternary system can be determined by gas chromatography.

Results

Tables 1 and 2 report the VLE data for two binary systems and one ternary system formed by (a) *cis*-but-2-ene, (b) 1,3-butadiene, and (c) *N*-formylmorpholine. The experimental range investigated covers three temperatures at which the equilibrium pressures vary from 2 bar to 9 bar. The reliability of experimental data was evaluated according to

$$P_t y_i \varphi_i = \gamma_i x_i (f_i^0)^{P=0} \exp\left(\frac{P_t V_i}{RT}\right) \qquad (1)$$

in which the various types of nonideality are taken into

Table 3. Pure Component Properties

	V/cm^3·mol^{-1a}			P/bar^b		
t/°C	*cis*-but-2-ene	1,3 buta-diene	N-formyl-morpholine	*cis*-but-2-ene	1,3 buta-diene	*N*-formyl-morpholine^a
40	93.6	90.8	101.4	3.29	4.23	3.26×10^{-6}
60	98.1	95.2	103.0	5.64	7.08	11.03×10^{-6}
80	103.6	100.5	104.6	9.00	11.10	35.06×10^{-6}

[a] Rossini (1953). [b] Ohe (1979).

Table 4. Binary NRTL Constants Used to Correlate and Predict the VLE Data

t/°C	G_{12}	G_{21}	α_{ij}	G_{13}	G_{31}	α_{ij}	G_{23}	G_{32}	α_{ij}
40	1.0	1.0	0.3	0.463 71	0.758 15	0.3	0.467 49	0.981 17	0.3
60	1.0	1.0	0.3	0.430 10	0.789 08	0.3	0.506 73	0.961 60	0.3
80	1.0	1.0	0.3	0.497 01	0.795 81	0.3	0.610 71	0.802 15	0.3

Table 5. Average Absolute % Deviations (AAD%) from the Experimental Data of the Equilibrium Values Calculated by Using the NRTL Equation for *cis*-But-2-ene (1) + 1,3-Butadiene (2) + *N*-Formylmorpholine (3)

	binary Systems P/AAD%		ternary Systems 1 + 2 + 3		
t/°C	1 + 3	2 + 3	P/AAD%	Δy_1	Δy_2
40	0.32	0.58	1.58	0.0162	0.0165
60	1.09	0.54	2.49	0.0100	0.0101
80	0.65	0.61	10.66	0.0377	0.0376

account: the fugacity coefficient, φ_i, for the nonideality of vapor phase and the activity coefficient, γ_i, for the nonideality of liquid phase. Further, the Poynting factor (represented by the exponential term) is introduced in order to refer all the activity coefficients to the same pressure, as recommended by Prausnitz et al. (1967).

In this work φ_i and γ_i were calculated by using the Redlich−Kwong equation and the NRTL equation, respectively. The critical constants involved in the φ_i calculations were taken from Reid et al. (1987) for hydrocarbons and evaluated according to the group contribution method for *N*-formylmorpholine. Other pure component properties required to apply relation 1 are reported in Table 3 along with the literature sources. Tables 4 and 5 report the values of the NRTL constants for the binary systems studied at three temperatures and the results obtained by applying this equation. The binary system *cis*-but-2-ene + 1,3-butadiene is assumed to be ideal, being a mixture of two hydrocarbons with nearly the same degree of unsaturation. The correlating capability of the NRTL equation is evaluated from two values: the absolute average % deviation (AAD%) for calculated pressures and the mean absolute deviations for calculated mole fractions in vapor phase (Δy_i). They are both satisfactory (see Table 5). The set of the NRTL binary constants obtained by correlating the VLE data of the three binary systems investigated can be used to predict the VLE of the ternary systems *cis*-but-2-ene + 1,3 butadiene + *N*-formylmorpholine. The prediction agrees with the experimental data for the isotherms at 40 °C and 60 °C (AAD% varies in the range 1.5−2.5 for pressure), while for the isotherm at 80 °C there are some relevant deviations from the experimental values (AAD% equal to 10.66 for pressure).

Conclusions

The Vangeli equilibrium still has been used in the Snamprogetti laboratories since 1977 for VLE determination of binary and multicomponent mixtures. For people who are experienced with usual stills embodying the Cottrell pump, it is always astonishing to see that the equilibrium is attained in a few minutes even when the components have very different boiling points. This property is especially important in dealing with thermally unstable compounds. As an example of the performances of the Vangeli still at extreme experimental conditions, it was possible to measure the vapor pressures of some alkylurethanes in the range 200 °C−220 °C and 0.0065−0.026 bar by reducing to nearly 60 s the warming time of compounds in the reservoir.

In essence, the Vangeli still is a flow apparatus that does not share the shortcomings of this type of devices, such as complexity and “the need of more material than other methods” (Null, 1970). Therefore, it is reasonable to hope that the scientific community becomes aware of the advantages of the Vangeli still.

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