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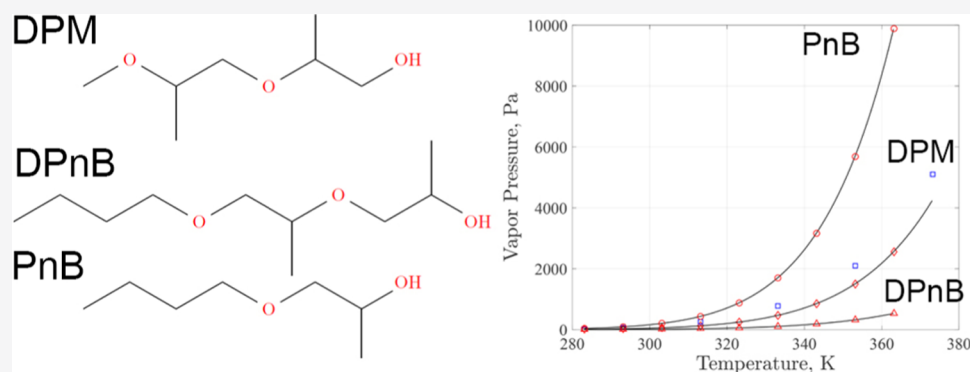
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Vapor–Liquid Equilibria of the Aqueous and Organic Mixtures Composed of Dipropylene Glycol Methyl Ether, Dipropylene Glycol *n*-Butyl Ether, and Propylene Glycol *n*-Butyl Ether. Part I: Experimental Study

Oleksandr Dimitrov, Pierrette Guichardon,* Ilham Mokbel, Fatiha Dergal, and Jacques Jose



ABSTRACT: An experimental and theoretical study was undertaken for three ether glycols (mixtures of isomers). The present paper, being the first part of a complex study, reports the experimental part of the study using a static apparatus, namely, the vapor–liquid equilibria of dipropylene glycol methyl ether (DPM), dipropylene glycol *n*-butyl ether (DPnB), and propylene glycol *n*-butyl ether (PnB), and the vapor–liquid equilibria of their pseudo-binary mixtures composed of (PnB + DPM), (DPM + DPnB), (PnB + DPnB), and the aqueous solutions of each ether. The explored temperature range is between 283.15 and 363.15 K. The experimental points were fitted using the Antoine equation. No literature data was found for comparison. The aim of this paper is not only to provide the obtained experimental data but also to highlight the eventual challenges when working with very low vapor pressure compounds and mixtures. The second part is related to a theoretical study with the development of a thermodynamic model for the representation of the experimental data.

1. INTRODUCTION

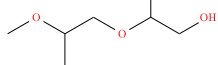
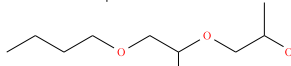
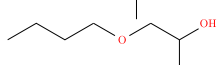
Solvent choice is essential in the industry. Many criteria should be considered in order to respect all the international rules and regulations. Therefore, not only the solvent power and volatility criteria but also the effect on human body, carcinogenicity, and environment and atmosphere impact make a significant influence on solvent choice. The glycol ethers can be a good example of prominent organic solvents that, along with their high performance, match the above-mentioned criteria.

The glycol ethers are used in paint and ink industries, wood, textile processes, and as cleaning compounds. These compounds, having a great degreasing and dissolving power, respect the modern international regulations in terms of toxicity, biodegradability, and ozone layer protection.

Among the glycol ethers widely used in the industry are dipropylene glycol methyl ether (DPM), dipropylene glycol *n*-butyl ether (DPnB), and propylene glycol *n*-butyl ether (PnB).

They are being considered as green solvents and are replacing classically used toxic and hazardous substances in paint and ink preparation, textile treatment, oil processing, and so forth. Such processes usually use closed cycles and therefore require the regeneration of solvents by means of distillation, adsorption, and membrane processes. Consequently, accurate vapor–liquid equilibria (VLE) involving the solvents are essential for the process design. Relevant VLE data can be found for aqueous solutions of ethylene glycol butyl ether,¹ propylene glycol methyl ether,² propylene glycol *n*-propyl ether,³ and different

Table 1. CAS Number and Chemical Structure of the Measured Compounds

Compound	CAS No	Structure
Dipropylene Glycol Methyl Ether (DPM)	34590-94-8	
Dipropylene Glycol n-Butyl Ether (DPnB)	29911-28-2	
Propylene Glycol n-Butyl Ether (PnB)	5131-66-8	

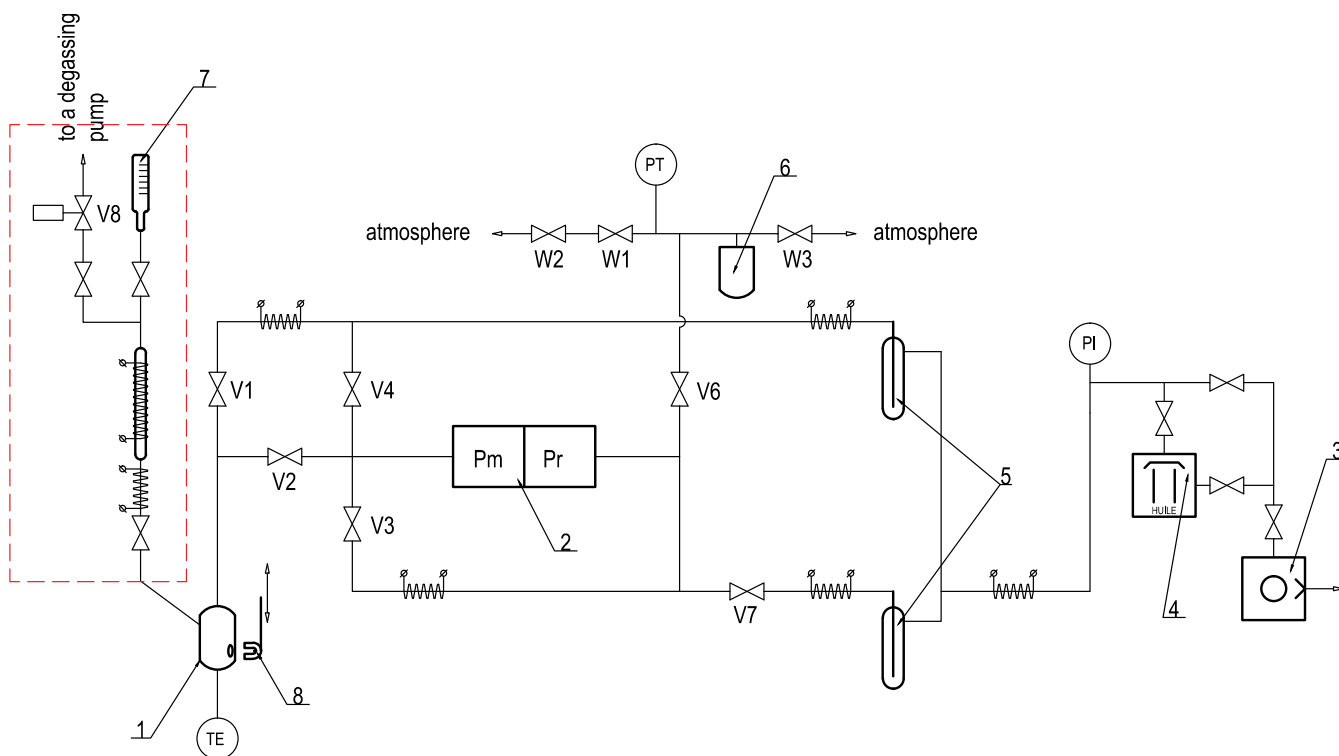


Figure 1. Diagram of the static apparatus. 1—static cell; 2—differential pressure sensor MKS; 3—primary vacuum pump; 4—secondary vacuum pump; 5—cold traps; 6—expansion tank; 7—graduated funnel; and 8—magnetic mixer.

ether mixtures.⁴ Chiavone-Filho et al.⁵ have published the VLE data for aqueous binary mixtures of some glycol ethers. For the best of our knowledge, no VLE data for comparison was found in the literature involving DPM, DPnB, and PnB.

This work represents a first path toward the construction of the VLE database for the DPM, DPnB, PnB, and their aqueous and organic mixtures. We have determined the compounds' (mixture of isomers) vapor pressures and the isothermal VLE for six respective pseudo-binary systems for temperatures ranging from 283.15 to 363.15 K. The data were fitted using the Antoine's equation. The paper ends with an illustration of the obtained points and their representation using the NRTL-PR model (the thermodynamic modeling is the main subject of Part II of this paper).

2. MATERIALS AND METHODS

2.1. Chemical Compounds. The three glycol ethers (DPM, DPnB, and PnB) were provided by Arcane Industries, France. Each of them is a mixture of isomers. The CAS number and the chemical structure of the compounds are presented in Table 1. No particular impurities of the compounds were detected by gas chromatography. The water, used to prepare the aqueous

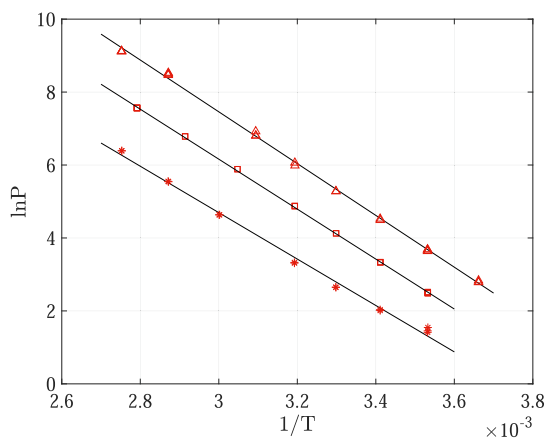


Figure 2. Measured raw experimental points and the Clapeyron regression: (red, \square)—DPM with $R^2 = 0.9998$; (red, $*$)—DPnB with $R^2 = 0.9963$; (red, \triangle)—PnB with $R^2 = 0.9987$; and (—)—the Clapeyron correlation.

Table 2. Experimental Vapor Pressure Data and Pressures Calculated with Antoine's Equation for DPM, DPnB, and PnB at 283.15 ÷ 363.15 K^a

T_{exp} (K)	P_{exp} (Pa)	P_{calc} (Pa)	$\delta P/P$, %	T_{exp} (K)	P_{exp} (Pa)	P_{calc} (Pa)	$\delta P/P$, %
DPM				DPnB			
283.10	12.420	12.0834	2.71	313.15	27.925	29.6571	-6.20
283.08	12.237	12.0618	1.43	333.15	103.077	102.8614	0.21
283.09	12.206	12.0726	1.09	333.15	102.901	102.8614	0.04
283.08	12.028	12.0618	-0.28	348.15	258.056	247.8863	3.94
283.09	11.994	12.0726	-0.65	348.15	255.087	247.8863	2.82
283.09	12.110	12.0726	0.30	363.15	595.081	572.8371	3.74
283.09	12.130	12.0726	0.47	363.15	596.571	572.8371	3.98
293.13	28.000	28.5836	-2.08	PnB			
293.13	27.879	28.5836	-2.52	273.10	17.022	15.7712	7.35
293.12	28.201	28.5600	-1.27	273.10	16.276	15.7712	3.10
303.13	61.883	62.9783	-1.76	273.10	16.182	15.7712	2.54
303.15	62.066	63.0739	-1.62	283.13	37.99	39.6072	-4.26
313.13	130.310	130.6143	-0.23	283.14	38.124	39.6423	-3.98
313.13	130.942	130.6143	0.25	283.14	39.856	39.6423	0.54
313.11	131.472	130.4311	0.79	283.15	39.657	39.6774	-0.05
328.14	359.980	353.5423	1.78	293.16	88.978	93.3303	-4.89
328.11	359.746	352.8775	1.90	293.17	92.513	93.4073	-0.97
343.14	885.957	863.0970	2.58	303.17	195.925	207.3541	-5.83
343.15	880.964	863.5843	1.97	303.18	196.572	207.5130	-5.57
358.23	1925.9228	1939.8116	-0.72	313.09	397.241	434.7345	-9.44
358.20	1924.4972	1937.4208	-0.67	313.11	429.427	435.4975	-1.41
358.25	1928.2767	1942.2051	-0.72	323.18	904.802	880.5127	2.68
358.20	1931.1113	1937.4208	-0.32	323.18	899.677	880.5127	2.13
358.20	1929.2215	1937.4208	-0.42	323.20	1014.644	881.7065	13.10
358.18	1931.1113	1935.0326	-0.20	348.28	4742.1143	4262.8489	10.11
358.20	1923.1321	1937.4208	-0.74	348.28	4847.9484	4262.8489	12.07
358.20	1926.9118	1937.4208	-0.54	348.26	4958.9494	4256.8642	14.16
DPnB				348.26	5044.7130	4256.8642	15.62
283.15	4.690	3.873	17.40	363.33	9059.0008	9875.8483	-9.02
283.15	4.279	3.873	9.47	363.33	9121.6678	9875.8483	-8.27
283.15	4.108	3.873	5.70	363.33	9153.8623	9875.8483	-7.89
293.15	7.651	7.822	-2.24	363.33	9185.6304	9875.8483	-7.51
293.15	7.466	7.822	-4.78	^a $u(T) = \pm 0.1$ K; $u(P/\text{Pa}) = 1$ Pa + $0.3 \cdot P$ for $P < 200$ Pa; $u(P/\text{Pa}) = 1 + 0.1 \cdot P$ for $200 < P/\text{Pa} < 600$ Pa; $0.03 \cdot P$ for $P > 600$.			
303.15	14.076	15.4108	-9.48				
303.15	14.193	15.4108	-8.58				
313.15	27.398	29.6571	-8.25				

samples, was purified in the ion exchange unit. All the compounds were used without further purification and were degassed under the vacuum prior to measurement.

In addition, the high-purity acetone and methanol ($\geq 99\%$) were used as solvents to prepare the samples for gas chromatography analysis.

2.2. Apparatus and Procedure. The vapor pressure measurements were carried out using a static apparatus presented in Figure 1. Its working principle is as follows.

The liquid sample is placed in the graduated funnel (7) installed on top of the degassing system (surrounded by a red dashed line). The latter is heated and held under the vacuum for several hours in order to eliminate air. The sample liquid is then transferred to the degassing flask by opening the valve on the bottom of the funnel and stopping the vacuum. Once the valve is closed, the degassing procedure is started: the liquid is boiled and intermittently subjected to vacuum by an electric valve (V8) programmed to a certain number of triggering cycles. The refrigerant located above the flask and traversed by water mixed with ice minimizes the loss of the sample. The aim of degassing is to remove all possible volatile compounds as well as the air

which can be dissolved in a sample. The degassed sample is then transferred to the static cell (1). The cell itself as well as the whole apparatus is maintained under the vacuum. During the transfer, valves V1 and V2 are kept closed. Then, the valve between the degassing system and the cell closes. The cell is immersed into a thermostatic bath (not presented on the diagram) and the magnetic mixer (8) is turned on.

Once the VLE is achieved, measurements start by closing valves V1, V3, and V4 and by opening valve V2. Valves V6 and V7 are kept opened. The vapor is passed to measurement part of the differential manometer MKS, type 670, model 616A (2). The reference part of the manometer is maintained under continuous pumping, and the residual pressure is 10^{-4} Pa. Once the pressure and temperature reaches stability, one can obtain one P , T experimental point. Then, valve V2 is closed and valves V4 and V3 are opened in order to evacuate the vapor from the measurement part of the manometer. The measurement is then repeated several times to check the reproducibility of results.

The MKS manometer capacity is limited to about 1300 Pa. If the measured vapor pressure is higher than this limit, valves W1 and W2 are opened and the reference part of the manometer is

Table 3. Antoine Coefficients (P in Pa, T in K) and Overall Mean Relative Deviation in Pressure of Eq 2

compound	temperature (K)	A	B	C	100 $\delta P/P$, %
DPM	283.15 \div 363.15	10.072	2077.694	-51.987	0.018
DPnB	283.15 \div 363.15	17.647	9364.4	265.789	0.517
PnB	283.15 \div 363.15	12.361	3013.331	-3.158	0.596

$${}^a\delta P/P, \% = 100 \frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}}$$

filled with air in order to compensate the excess pressure. The pressure in the reference part is measured by a sensor-type Keller (PT). The cell temperature is controlled by a chromel/alumel thermocouple (TE).

The experiment is finished by complete cleaning of the apparatus. The degassing part and the cell are thoroughly rinsed with acetone and dried. Then, the system is again pumped to the vacuum. One should emphasize the importance of the vacuum to be very deep. If it is not the case, the system should be verified and every non-sealing should be fixed.

The calibration of the system was previously checked by measuring water and *n*-decane vapor pressures and compared to the values from different literature sources.^{6,7}

2.3. Pure Compounds. DPM, DPnB, and PnB are very rarely mentioned in the literature. Some of their main physical properties, such as the normal boiling temperature, the molar mass, and so forth, can be found in the respective technical datasheets of different manufacturers.⁸⁻¹⁰ However, in chemical engineering, not only the phase equilibria of mixtures but also the vapor pressure data of the compounds themselves are always needed. To the best of our knowledge, these data concerning the above compounds have not been reported in the literature yet. The only data can be found for DPM;⁸ however, as stated in this document, these data were measured (or estimated) by the company to give their customers a rough idea of the DPM properties, so they provide no guarantee of properties in the legal sense. For that reason, these data will only be used by us for the sake of comparison. As for DPnB and PnB, their vapor pressures were measured for the first time.

2.4. Preparation of Pseudo-binary Mixtures and Degassing. The measurement of VLE was performed for six pseudo-binary mixtures. Three of them were aqueous solutions of DPM, DPnB, and PnB, and the other three mixtures were combinations of the glycol ethers: DPM + PnB, DPM + DPnB, and PnB + DPnB. The pseudo-binary mixtures, water + DPnB and water + PnB, are partially miscible, whereas the water + DPM mixture was completely miscible in the whole range of compositions.

The degassing of these aqueous systems is particular because of the difference of volatility of water and the glycol ether. The components (glycol ether and water) are separately degassed. Each of them is boiled and vacuumed prior to their mixing and their transfer into the measurement cell. At the end of the experiment, the sample is withdrawn from the static cell (1) and its exact composition was checked by gas chromatography.

3. RESULTS AND DISCUSSION

3.1. Raw Data Treatment. The raw experimental points were measured over the temperature range from 283.15 to 363.15 K and plotted as $\ln P_{\text{vap}}$ versus $1/T$. The reason for that is the possibility to check the applicability of the Clapeyron eq 1. The results are then presented in Figure 2 for all the three pure compounds.

Table 4. Mean Enthalpy of Vaporization ΔH_{vap} (in kJ/mol) Calculated Using Eq 1^a

compound	T , K	ΔH_{vap} (calculated), kJ/mol	ΔH_{vap} (literature), kJ/mol
DPM	283–358	57	52
DPnB	303–363	57	
PnB	273–363	58	46

^aComparison with the literature data.

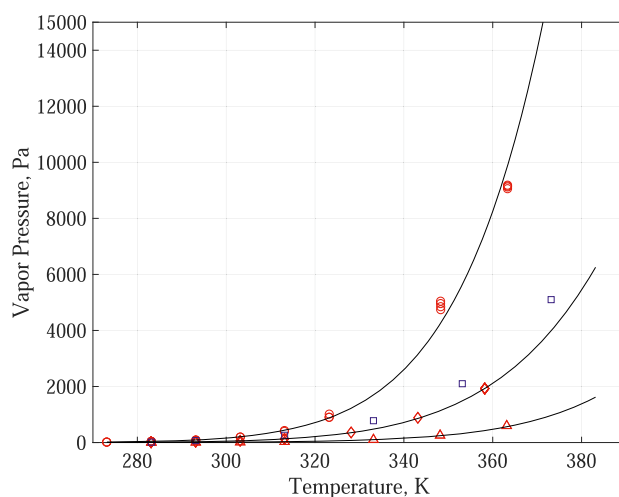


Figure 3. Experimental vapor pressures for pure compounds and their correlation with Antoine's equation: DPM (red, \diamond); DPnB (red, \triangle); PnB (red, \circ); DPM Technical Leaflet⁸ (blue, \square)—for comparison; and Antoine's equation (—).

$$\ln P_{\text{vap}}(T) = -\frac{\Delta H_{\text{vap}}}{R} \frac{1}{T} + C \quad (1)$$

with P_{vap} the vapor pressure in Pa, ΔH_{vap} the enthalpy of vaporization in J/g, T the temperature in K, and R the perfect gas constant in J/(mol·K).

As can be seen, the Clapeyron correlation results in a straight line with a slope $\Delta H_{\text{vap}}/R$, showing the consistency of the measurements.

3.2. Vapor Pressures of the Ether Glycols (Mixture of Isomers). The vapor pressures for the glycol ethers are reported in Table 2. The obtained experimental data were fitted to the widely used Antoine's equation

$$\log_{10} P_{\text{vap}} (\text{Pa}) = A - \frac{B}{T + C} \quad (2)$$

where A , B , and C are the Antoine parameters.

The minimized objective function, F_{obj} is as follows, eq 3.

$$F_{\text{obj}} = \sum_n \left(\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right)^2 \quad (3)$$

The obtained Antoine parameters can be found in Table 3.

Table 5. Measured Isothermal VLE and VLLE Data of the H₂O + DPM, H₂O + DPnB, and H₂O + PnB at 283.15 ÷ 363.15 K^a

temperature (K)	H ₂ O(1) + DPM(2)		H ₂ O(1) + DPnB(2)		H ₂ O(1) + PnB(2)	
	x_1	P_{tot} (Pa)	x_1	P_{tot} (Pa)	x_1	P_{tot} (Pa)
283.15	0.000	12.366	0.000	3.520	0.000	39.447
	0.110	296.703	0.210	840.097	0.217	1149.584
	0.276	570.718	0.461	1224.566	0.427	1246.134
	0.468	821.697	0.720	1213.124	0.693	1214.888
	0.654	969.110	0.851	1229.809	0.841	1283.570
	0.841	1064.926	0.997	1276.743	0.997	1243.413
293.15	1.000	1255.406	1.000	1255.406	1.000	1255.406
	0.000	28.218	0.000	7.661	0.000	92.788
	0.110	575.418	0.210	1586.443	0.217	2126.634
	0.276	1104.041	0.461	2307.919	0.427	2370.585
	0.468	1559.771	0.720	2283.733	0.693	2323.426
	0.654	1867.732	0.851	2308.389	0.841	2417.798
303.15	0.841	2034.668	0.997	2379.262	0.997	2344.697
	1.000	2344.041	1.000	2344.041	1.000	2344.041
	0.000	60.979	0.000	15.840	0.000	206.283
	0.110	1068.236	0.210	2872.792	0.217	3777.634
	0.276	2044.762	0.461	4171.577	0.427	4322.354
	0.468	2838.219	0.720	4123.443	0.693	4257.395
313.15	0.654	3447.126	0.851	4156.601	0.841	4367.947
	0.841	3724.926	0.997	4255.450	0.997	4240.177
	1.000	4200.057	1.000	4200.057	1.000	4200.057
	0.000	125.447	0.000	31.268	0.000	435.790
	0.110	1906.300	0.210	5008.573	0.217	6468.600
	0.276	3640.875	0.461	7260.407	0.427	7584.455
323.15	0.468	4970.802	0.720	7169.441	0.693	7505.176
	0.654	6117.890	0.851	7208.652	0.841	7598.539
	0.841	6560.980	0.997	7333.683	0.997	7383.264
	1.000	7250.505	1.000	7250.505	1.000	7250.505
	0.000	246.800	0.000	59.178	0.000	878.995
	0.110	3282.070	0.210	8436.896	0.217	10,713.804
333.15	0.276	6255.489	0.461	12,210.319	0.427	12,853.294
	0.468	8408.994	0.720	12,046.001	0.693	12,774.365
	0.654	10,479.176	0.851	12,082.887	0.841	12,773.239
	0.841	11,158.447	0.997	12,219.945	0.997	12,422.401
	1.000	12,100.582	1.000	12,100.582	1.000	12,100.582
	0.000	466.237	0.000	107.793	0.000	1699.822
343.15	0.110	5469.400	0.210	13,773.866	0.217	17,215.587
	0.276	10,404.129	0.461	19,903.967	0.427	21,103.358
	0.468	13783.358	0.720	19618.762	0.693	21059.664
	0.654	17378.800	0.851	19634.551	0.841	20812.787
	0.841	18382.015	0.997	19747.139	0.997	20258.059
	1.000	19583.514	1.000	19583.514	1.000	19583.514
353.15	0.000	848.706	0.000	189.599	0.000	3163.202
	0.110	8847.600	0.210	21853.549	0.217	26908.832
	0.276	16798.600	0.461	31534.341	0.427	33661.857
	0.468	21951.200	0.720	31056.619	0.693	33721.700
	0.654	27984.000	0.851	31015.738	0.841	32961.095
	0.841	29413.500	0.997	31030.646	0.997	32107.843
363.15	1.000	30816.900	1.000	30816.889	1.000	30816.889
	0.000	1493.390	0.000	322.994	0.000	5682.967
	0.110	13926.400	0.210	33778.089	0.217	41009.318
	0.276	26397.100	0.461	48675.463	0.427	52292.589
	0.468	34049.800	0.720	47900.432	0.693	52576.104
	0.654	43861.400	0.851	47741.728	0.841	50858.670
363.15	0.841	45828.900	0.997	47529.267	0.997	49578.917
	1.000	47264.600	1.000	47264.602	1.000	47264.602
	0.000	2547.273	0.000	534.332	0.000	9885.757
363.15	0.110	21380.800	0.210	72137.424	0.217	61065.012
	0.276	40460.357	0.461	73359.030	0.427	79287.826

Table 5. continued

temperature (K)	H ₂ O(1) + DPM(2)		H ₂ O(1) + DPnB(2)		H ₂ O(1) + PnB(2)	
	x_1	P_{tot} (Pa)	x_1	P_{tot} (Pa)	x_1	P_{tot} (Pa)
	0.468	51555.087	0.720	72137.424	0.693	79991.673
	0.654	67066.645	0.851	71762.567	0.841	76,622.181
	0.841	69,682.695	0.997	71,110.447	0.997	74,746.580
	1.000	70,803.290	1.000	70,803.290	1.000	70,803.290

^a $u(T) = \pm 0.1$ K; $u(P/\text{Pa}) = 1$ Pa + $0.3 \cdot P$ for $P < 200$ Pa; $u(P/\text{Pa}) = 1 + 0.1 \cdot P$ for $200 < P/\text{Pa} < 600$ Pa; $0.03 \cdot P$ for $P > 600$.

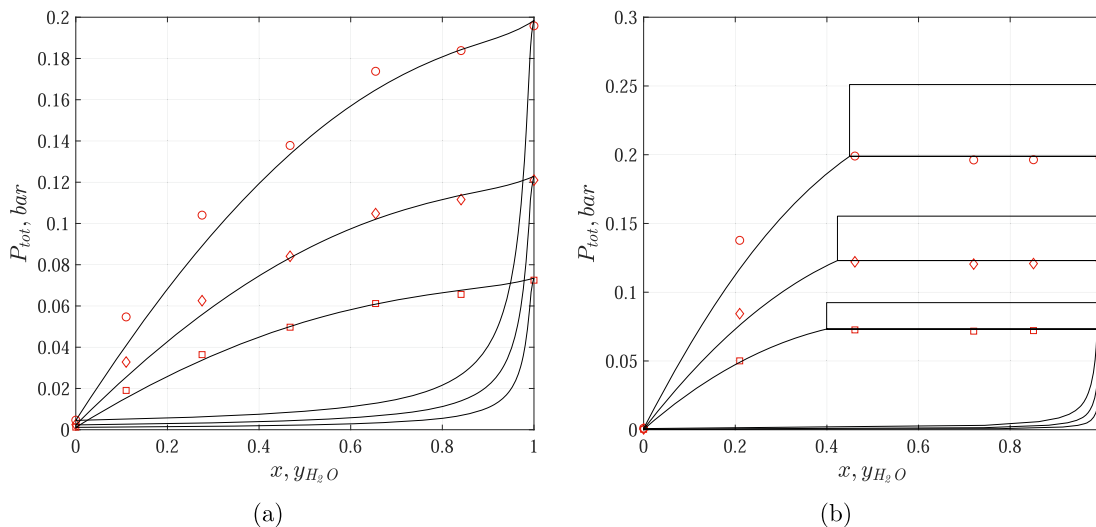


Figure 4. (a) VLE of water + DPM mixture and (b) VLLE of water + DPnB mixture: (red, \square)—313.15 K; (red, \diamond)—323.15 K; (red, \circ)—333.15 K; and (—)—NRTL-PR model.

The overall mean deviation in pressure is written as

$$100\delta P/P (\%) = \left| \frac{100}{N} \sum \left(\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right) \right| \quad (4)$$

where N is the number of experimental points.

From the slope $\Delta H_{\text{vap}}/R$, the mean enthalpy of vaporization was determined and compared with the literature data, Table 4. ΔH_{vap} of DPM is in good agreement with the value reported in Thermophysical Properties of Chemicals and Hydrocarbons,¹¹ and the relative deviation is less than 10%, whereas for PnB, a relative deviation of 20% is observed. No enthalpy of vaporization for comparison was found for DPnB.

Figure 3 demonstrates a very good agreement between experimental results and Antoine's equation for all the three pure compounds. Along with our results, we have also plotted the experimental points for DPM found in the DPM Technical Leaflet.⁸ The origin of these points remains unclear for us as no information about how they were obtained was published in the Leaflet.⁸ Therefore, these points are given exclusively for the sake of comparison.

The Antoine coefficients A , B , and C together with the overall mean deviation in pressure are reported in Table 3.

3.3. Vapor–Liquid and Vapor–Liquid–Liquid Equilibria of Aqueous Binary Mixtures. First of all, the VLE were measured for the water + DPM system at different temperatures ranging from 283.15 to 363.15 K. As expected, this mixture was completely miscible in the whole range of compositions. On the contrary, the mixtures water + DPnB and water + PnB exhibit partial non-miscibility when the water molar fraction is between

0.4 and 0.985, resulting in the determination of the total pressure of the vapor–liquid–liquid equilibria (VLLE).

The vapor pressures of the mixtures were measured at temperatures between 283.15 and 363.15 K and the results are reported in Table 5. In order to analyze the spread of the measured points, we determined the standard deviation and the standard error of the mean for each point. These data can be found in the Appendix.

In order to illustrate the form of the equilibrium curves of fully and partially miscible systems, the mixtures water + DPM and water + DPnB at 313.15, 323.15, and 333.15 K were plotted and presented in Figure 4 together with modeling results using the NRTL-PR model. It can be seen from Figure 4a that the water + DPM mixture has no azeotrope. Figure 4b shows that the partial miscibility zone of the water + DPnB mixture is correctly represented by the model. Concerning the water + PnB mixture, its equilibrium curves have a form analogical to those of the water + DPnB mixture.

3.4. VLE of Organic Binary Mixtures. The VLE for organic mixtures containing DPM, DPnB, and PnB were measured for the same temperature range, between 283 and 363 K. All the mixtures (PnB + DPM, DPM + DPnB, and PnB + DPnB) were completely miscible. The distinctive feature of these systems is their low vapor pressure (below 3 Pa). This fact requires particular attention and thoroughness while performing measurements. The degassing time has a key role in the quality of the result as the slightest amount of dissolved air in the sample can easily perturb the measurements.

Table 6 presents the results of the VLE measurements for PnB + DPM, DPM + DPnB, and PnB + DPnB systems. The equilibrium curves of all the studied organic mixtures do not present any azeotrope. The experimental points for the DPM +

Table 6. Measured Isothermal VLE Data of the PnB + DPM, DPM + DPnB, and PnB + DPnB at 283.15 ÷ 363.15 K^a

temperature (K)	PnB(1) + DPM(2)		DPM(1) + DPnB(2)		PnB(1) + DPnB(2)	
	x_1	P_{tot} (Pa)	x_1	P_{tot} (Pa)	x_1	P_{tot} (Pa)
283.15	0.000	12.366	0.000	3.520	0.000	3.520
	0.160	16.799	0.160	5.758	0.160	11.394
	0.334	26.831	0.336	7.033	0.330	20.711
	0.489	29.831	0.496	7.780	0.493	33.044
	0.667	53.117	0.666	8.558	0.665	44.098
	0.837	47.149	0.836	10.435	0.838	65.180
	0.985	63.822	1.000	12.366	1.000	39.447
	1.000	39.447				
293.15	0.000	28.218	0.000	7.661	0.000	7.661
	0.160	37.691	0.160	12.541	0.160	24.222
	0.334	57.999	0.336	15.791	0.330	43.212
	0.489	65.324	0.496	17.635	0.493	67.981
	0.667	107.422	0.666	19.748	0.665	89.604
	0.837	99.717	0.836	24.012	0.838	135.998
	0.985	133.498	1.000	28.218	1.000	92.788
	1.000	92.788				
303.15	0.000	60.979	0.000	15.840	0.000	15.840
	0.160	80.172	0.160	25.948	0.160	48.994
	0.334	119.158	0.336	33.612	0.330	85.886
	0.489	135.841	0.496	37.871	0.493	133.411
	0.667	207.383	0.666	43.126	0.665	173.750
	0.837	200.725	0.836	52.299	0.838	270.320
	0.985	265.972	1.000	60.979	1.000	206.283
	1.000	206.283				
313.15	0.000	125.447	0.000	31.268	0.000	31.268
	0.160	162.509	0.160	51.252	0.160	94.739
	0.334	233.805	0.336	68.176	0.330	163.379
	0.489	269.574	0.496	77.454	0.493	250.784
	0.667	383.889	0.666	89.594	0.665	322.963
	0.837	386.393	0.836	108.384	0.838	514.244
	0.985	507.080	1.000	125.447	1.000	435.790
	1.000	435.790				
323.15	0.000	246.806	0.000	59.178	0.000	59.178
	0.160	315.311	0.160	97.056	0.160	175.872
	0.334	440.016	0.336	132.361	0.330	298.664
	0.489	512.748	0.496	151.545	0.493	453.358
	0.667	684.050	0.666	177.897	0.665	577.723
	0.837	714.254	0.836	214.712	0.838	940.102
	0.985	928.909	1.000	246.806	1.000	878.995
	1.000	878.995				
333.15	0.000	466.237	0.000	107.793	0.000	107.793
	0.160	587.922	0.160	176.881	0.160	314.581
	0.334	797.255	0.336	246.939	0.330	526.552
	0.489	938.354	0.496	284.801	0.493	790.944
	0.667	1177.359	0.666	338.979	0.665	997.983
	0.837	1272.502	0.836	408.248	0.838	1657.491
	0.985	1640.921	1.000	466.237	1.000	1699.822
	1.000	1699.822				
343.15	0.000	848.706	0.000	189.599	0.000	189.599
	0.160	1057.135	0.160	311.279	0.160	543.940
	0.334	1395.343	0.336	444.256	0.330	898.147
	0.489	1657.803	0.496	515.908	0.493	1335.867
	0.667	1963.294	0.666	622.098	0.665	1669.900
	0.837	2192.030	0.836	747.698	0.838	2827.311
	0.985	2804.137	1.000	848.706	1.000	3163.202
	1.000	3163.202				
353.15	0.000	1493.394	0.000	322.994	0.000	322.994
	0.160	1838.698	0.160	530.537	0.160	911.801
	0.334	2365.909	0.336	773.097	0.330	1486.346

Table 6. continued

temperature (K)	PnB(1) + DPM(2)		DPM(1) + DPnB(2)		PnB(1) + DPnB(2)	
	x_1	P_{tot} (Pa)	x_1	P_{tot} (Pa)	x_1	P_{tot} (Pa)
363.15	0.489	2835.965	0.496	903.627	0.493	2190.230
	0.667	3180.424	0.666	1103.091	0.665	2713.916
	0.837	3661.493	0.836	1323.258	0.838	4679.092
	0.985	4648.701	1.000	1493.394	1.000	5682.967
	1.000	5682.967				
	0.000	2547.273	0.000	534.332	0.000	534.322
	0.160	3102.071	0.160	878.070	0.160	1485.573
	0.334	3896.600	0.336	1304.918	0.330	2392.456
	0.489	4710.073	0.496	1534.620	0.493	3494.544
	0.667	5017.029	0.666	1895.239	0.665	4294.246
	0.837	5945.644	0.836	2269.392	0.838	7531.824
	0.985	7495.032	1.000	2547.273	1.000	9885.757
	1.000	9885.757				

$^a u(T) = \pm 0.1$ K; $u(P/\text{Pa}) = 1$ Pa + $0.3 \cdot P$ for $P < 200$ Pa; $u(P/\text{Pa}) = 1 + 0.1 \cdot P$ for $200 < P/\text{Pa} < 600$ Pa; $0.03 \cdot P$ for $P > 600$.

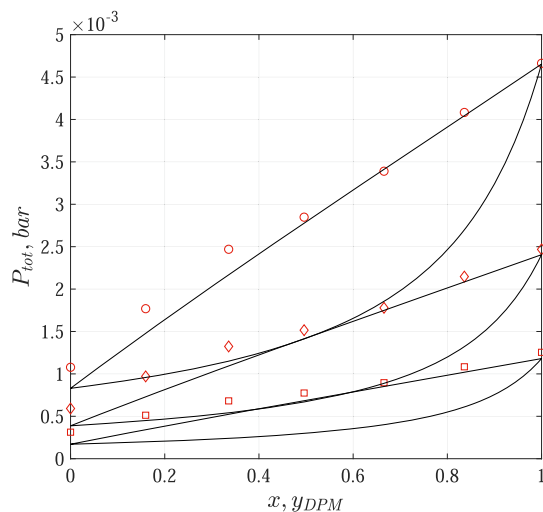


Figure 5. VLE of DPM + DPnB mixture: (red, \square)—313.15 K; (red, \diamond)—323.15 K; (red, \circ)—333.15 K; and (—)—NRTL-PR model.

DPnB mixture are presented in Figure 5 for 313.15, 323.15, and 333.15 K. Here again, the NRTL-PR model was used for calculations, allowing to obtain in general a good representation of this system. One can, however, observe slight negative deviations of the calculated pressures for pure DPnB. These deviations are related to the representation of the DPnB as a pure compound at very low vapor pressures (lower than 1×10^{-3} bar) using the cubic equation of state. The following issues are discussed and detailed in the second part of this paper, entirely devoted to the thermodynamic modeling of all studied mixtures.

For the measured points of organic binary mixtures, the standard deviation as well as the standard error of mean were calculated as well. Tables presented in the Appendix section contain these results for each binary mixture as a function of temperature and molar fraction.

3.5. Challenges Related to the Measurement of Very Low Pressure Systems. The main experimental challenges were the stability of samples during measurements and very low system vapor pressures. Fortunately, the first problem depends mainly on sample degassing as this allows us to evacuate any impurity or non-condensable gas that can strongly influence the measurement results. By performing the degassing more

thoroughly, we were able to improve the majority of experimental points. However, in the case of PnB, much more effort was made in order to obtain satisfactory experimental points as this particular compound had demonstrated the worst stability compared to the others, regardless of degassing. Its vapor pressure was progressively increasing during measurements and was never stable, showing pressure fluctuations in a very large range. Again, any experimental uncertainty or instability is even more visible when measuring very low vapor pressures. If, in the case of high vapor pressures, the measurements are not very sensible to small instabilities, they can easily be perturbed when the pressures are low. Moreover, the precision of measurements was very high (the MKS sensor is capable of detecting a pressure difference of 10^{-2} Pa). This problem was partially solved by paying particular attention to experimental unit maintenance and cleaning, sample preparation, and degassing, increasing the number of measurements for problematic points. In spite of these facts, we were, however, unable to improve the results for certain points.

4. CONCLUSIONS

The VLE of the aqueous and organic mixtures composed of DPM, DPnB, and PnB have been measured by the static method at the temperature ranging from 283.15 to 363.15 K. All the reported results were carried out for the first time, so no comparison with the literature data was possible.

The NRTL-PR model was used to represent the equilibria occurred in binary mixtures. A good agreement between experimental and modeling results was obtained. As stated before, all the details related to the modeling will be presented and discussed in Part II of this paper.

■ APPENDIX

Measurement errors and deviations

The spread of experimental points is represented by means of the following statistical measures:

- Standard deviation
- Standard error of the mean

The standard deviation (in Pa) is calculated using the following expression

Table 7. Standard Deviations and Standard Errors of the Mean for H₂O + DPM and H₂O + DPnB at 283.15–363.15 K

temperature (K)	H ₂ O(1) + DPM(2)			H ₂ O(1) + DPnB(2)		
	x_1	σ (Pa)	$\sigma_{\bar{x}}$ (Pa)	x_1	σ (Pa)	$\sigma_{\bar{x}}$ (Pa)
283.15	0.110	39.60	28.00	0.210	43.06	17.58
	0.276	42.64	24.62	0.461	50.91	20.79
	0.468	36.53	25.83	0.720	86.50	35.31
	0.654	25.23	11.28	0.851	61.61	27.55
	0.841	15.54	5.18	0.997	49.15	21.98
293.15	0.110	61.56	43.53	0.210	9.08	4.54
	0.276	33.98	16.99	0.461	34.29	15.33
	0.468	51.17	17.06	0.720	14.86	7.43
	0.654	12.13	5.42	0.851	5.02	2.90
	0.841	45.08	18.40	0.997	42.41	24.49
303.15	0.110	47.64	19.45	0.210	76.58	38.29
	0.276	38.50	14.55	0.461	123.96	1.18
	0.468	22.57	6.52	0.720	106.60	61.55
	0.654	51.87	29.95	0.851	78.62	45.39
	0.841	57.86	23.62	0.997	30.02	15.01
313.15	0.110	113.76	56.88	0.210	346.12	173.06
	0.276	97.52	39.81	0.461	308.23	177.96
	0.468	157.82	64.43	0.720	219.10	126.50
	0.654	313.73	156.87	0.851	165.27	95.42
	0.841	226.20	85.49	0.997	92.54	53.43
323.15	0.110	156.49	59.15	0.210	449.49	224.74
	0.276	517.12	211.11	0.461	559.34	322.94
	0.468	404.03	164.94	0.720	321.09	185.38
	0.654	454.92	262.65	0.851	291.30	168.18
	0.841	137.60	56.17	0.997	191.60	110.62
333.15	0.110	219.01	82.78	0.210	296.01	148.01
	0.276	769.58	314.18	0.461	106.47	53.24
	0.468	618.84	233.90	0.720	388.17	224.11
	0.654	182.79	105.53	0.851	367.32	212.07
	0.841	129.60	48.98	0.997	256.83	148.28
343.15	0.110	155.71	63.57	0.210	57.10	28.55
	0.276	384.44	156.95	0.461	45.78	26.43
	0.468	116.12	38.71	0.720	243.59	140.64
	0.654	143.78	71.89	0.851	316.39	182.67
	0.841	148.80	56.24	0.997	251.56	145.24
353.15	0.110	285.21	116.44	0.210	1045.45	603.59
	0.276	701.61	286.43	0.461	378.28	189.14
	0.468	3000.21	1133.97	0.720	511.24	295.16
	0.654	1571.51	641.57	0.851	331.94	191.64
	0.841	732.97	299.23	0.997	147.16	73.58
363.15	0.110	1269.37	567.68	0.210	2816.66	1626.20
	0.276	2808.09	1255.82	0.461	2302.97	1151.49
	0.468	8392.98	3172.25	0.720	2243.95	1121.98
	0.654	4312.64	1760.63	0.851	1919.06	1107.97
	0.841	2697.14	1101.10	0.997	1223.94	611.97

$$\sigma = \left(\frac{\sum (x_i - \bar{x})^2}{N} \right)^{0.5} \quad (5)$$

where x_i and \bar{x} are the i th and "true" (or mean) measurement value, respectively. N is the number of measurements. In our case, the \bar{x} value was obtained by fitting the experimental points to the Clapeyron equation.

The standard error of the mean (in Pa) is represented as follows

$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{N}} \quad (6)$$

This standard error of mean is taken as an uncertainty in the best estimate of the "true" value. We have calculated the standard deviation and the standard error of the mean for each measured point for all six binary mixtures.

The obtained values are listed below:

- in Table 7 (H₂O + DPM and H₂O + DPnB);
- in Table 8 (H₂O + PnB and DPM + DPnB);
- in Table 9 (PnB + DPM and PnB + DPnB).

As a general tendency, the errors and deviations decreased with the increase of the molar fraction of the most volatile component even if some points represent the exceptions.

Table 8. Standard Deviations and Standard Errors of the Mean for H₂O + PnB and DPM + DPnB at 283.15–363.15 K

temperature (K)	H ₂ O(1) + PnB(2)			DPM(1) + DPnB(2)		
	x_1	σ (Pa)	$\sigma_{\bar{x}}$ (Pa)	x_1	σ (Pa)	$\sigma_{\bar{x}}$ (Pa)
283.15	0.217	238.03	106.45	0.160	0.93	0.66
	0.427	92.52	53.42	0.336	0.49	0.35
	0.693	53.35	18.86	0.496	0.47	0.33
	0.841	51.94	21.20	0.666	0.23	0.17
	0.997	45.68	20.43	0.836	0.05	0.04
293.15	0.217	108.38	54.19	0.160	0.63	0.45
	0.427	21.66	10.83	0.336	0.47	0.33
	0.693	91.81	53.01	0.496	0.71	0.50
	0.841	47.30	23.65	0.666	0.50	0.36
	0.997	16.02	8.01	0.836	0.45	0.32
303.15	0.217	1122.03	561.02	0.160	3.09	2.19
	0.427	70.49	35.24	0.336	23.79	16.82
	0.693	292.18	146.09	0.496	2.06	1.45
	0.841	56.13	25.10	0.666	0.34	0.24
	0.997	131.30	75.81	0.836	0.61	0.43
313.15	0.217	1170.05	585.03	0.160	1.19	0.84
	0.427	237.99	118.99	0.336	54.48	38.52
	0.693	156.81	90.53	0.496	2.50	1.77
	0.841	339.30	169.65	0.666	0.71	0.50
	0.997	285.35	164.75	0.836	0.42	0.30
323.15	0.217	1413.44	706.72	0.160	6.61	4.67
	0.427	763.52	381.76	0.336	93.61	66.19
	0.693	781.49	390.74	0.496	0.97	0.69
	0.841	475.13	237.57	0.666	4.93	3.49
	0.997	412.84	238.35	0.836	4.36	3.09
333.15	0.217	856.04	382.83	0.160	1.94	1.37
	0.427	1759.80	879.90	0.336	193.37	136.73
	0.693	356.85	206.03	0.496	4.74	3.35
	0.841	347.94	173.97	0.666	1.08	0.76
	0.997	491.15	283.57	0.836	1.13	0.80
343.15	0.217	1516.35	758.17	0.160	4.33	3.06
	0.427	123.09	61.54	0.336	1.66	1.17
	0.693	211.19	105.60	0.496	12.66	8.95
	0.841	95.50	47.75	0.666	17.93	12.68
	0.997	474.82	274.14	0.836	5.61	2.51
353.15	0.217	3010.38	1346.28	0.160	3.01	2.13
	0.427	1728.41	864.21	0.336	8.23	3.68
	0.693	292.02	168.60	0.496	11.58	5.79
	0.841	636.94	318.47	0.666	17.50	8.75
	0.997	48.01	24.00	0.836	4.75	2.74
363.15	0.217	3865.11	1577.92	0.160	63.11	44.63
	0.427	3361.94	1680.97	0.336	36.13	20.86
	0.693	2524.88	1262.44	0.496	14.69	7.34
	0.841	1633.95	816.98	0.666	14.25	7.13
	0.997	1335.52	771.06	0.836	19.50	1.47

Moreover, organic solutions had smaller errors compared to the aqueous ones.

Table 9. Standard Deviations and Standard Errors of the Mean for PnB + DPM and PnB + DPnB at 283.15–363.15 K

temperature (K)	PnB(1) + DPM(2)			PnB(1) + DPnB(2)		
	x_1	σ (Pa)	σ_x (Pa)	x_1	σ (Pa)	σ_x (Pa)
283.15	0.160	0.30	0.21	0.160	0.80	0.57
	0.334	1.10	0.78	0.330	2.19	1.55
	0.489	0.95	0.67	0.493	6.03	3.48
	0.667	4.41	3.12	0.665	3.18	2.25
	0.837	0.81	0.57	0.838	6.18	4.37
	0.985	1.56	0.78			
293.15	0.160	0.99	0.70	0.160	0.65	0.46
	0.334	3.68	2.60	0.330	1.68	1.19
	0.489	1.09	0.77	0.493	5.10	3.60
	0.667	4.38	3.09	0.665	3.20	2.26
	0.837	10.95	7.74	0.838	11.00	7.78
	0.985	4.71	2.72			
303.15	0.160	0.40	0.28	0.160	3.05	2.16
	0.334	6.87	4.86	0.330	7.44	5.26
	0.489	2.90	2.05	0.493	1.67	1.18
	0.667	11.21	7.92	0.665	5.37	3.79
	0.837	2.81	1.98	0.838	10.96	7.75
	0.985	7.52	5.32			
313.15	0.160	2.18	1.54	0.160	0.91	0.64
	0.334	8.39	4.84	0.330	0.47	0.33
	0.489	8.54	6.04	0.493	16.45	11.63
	0.667	4.19	2.96	0.665	7.00	4.95
	0.837	3.98	2.81	0.838	7.34	5.19
	0.985	3.40	2.41			
323.15	0.160	8.11	5.73	0.160	8.70	6.16
	0.334	20.10	14.21	0.330	13.58	9.60
	0.489	23.49	16.61	0.493	6.04	4.27
	0.667	3.30	1.90	0.665	194.73	137.69
	0.837	6.90	3.99	0.838	10.16	7.18
	0.985	8.03	4.63			
333.15	0.160	17.67	12.50	0.160	1.56	1.11
	0.334	9.76	4.37	0.330	1.52	1.08
	0.489	30.18	21.34	0.493	6.15	2.51
	0.667	87.60	61.94	0.665	3.95	2.79
	0.837	55.12	31.82	0.838	5.97	4.22
	0.985	5.02	3.55			
343.15	0.160	26.49	13.25	0.160	11.75	8.31
	0.334	4.59	2.65	0.330	23.28	11.64
	0.489	39.02	27.59	0.493	12.08	6.98
	0.667	66.95	47.34	0.665	14.49	10.24
	0.837	13.95	6.98	0.838	70.90	50.13
	0.985	22.66	13.08			
353.15	0.160	93.65	54.07	0.160	11.36	5.68
	0.334	53.43	30.85	0.330	6.74	3.89
	0.489	73.34	51.86	0.493	19.64	11.34
	0.667	90.70	64.14	0.665	5.76	4.07
	0.837	85.68	42.84	0.838	4.60	3.25
	0.985	6.36	3.67			
363.15	0.160	83.78	48.37	0.160	61.93	35.76
	0.334	105.16	60.71	0.330	46.10	23.05
	0.489	172.69	122.11	0.493	6.14	3.54
	0.667	186.82	132.10	0.665	6.34	4.48
	0.837	50.83	22.73	0.838	4.95	3.50
	0.985	5.89	4.17			

Notes

The authors declare no competing financial interest.

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