JOURNAL OF CHEMICAL & ENGINEERING DATA

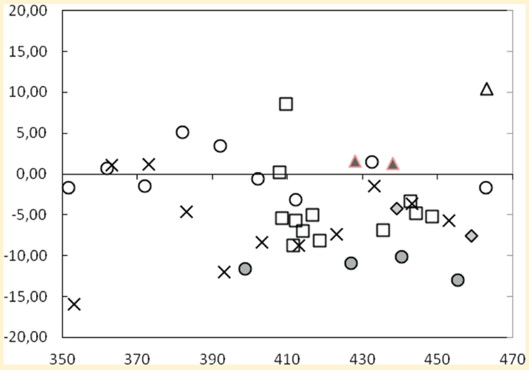
Vapor−Liquid Equilibria of Glycerol, 1,3-Propanediol, Glycerol + Water, and Glycerol + 1,3-Propanediol

Ilham Mokbel,*,† Terufat Sawaya,† Marie-Line Zanota,‡ Ramy Abou Naccoul,† Jacques Jose,† and Claude de Bellefon‡

†Laboratoire des Sciences Analytiques, UMR 5280, Equipe Thermodynamique Analyse et Procédés, Université Claude Bernard Lyon 1, 43 bd du 11 Novembre 1918, 69622 Villeurbanne, France

‡Laboratoire de Génie des Procédés Catalytiques, Centre National de la Recherche Scientifique (CNRS/CPE), UMR 5285 43, bd du 11 novembre 1918 B.P. 82077, 69616 Villeurbanne Cedex, France

ABSTRACT: Vapor−liquid equilibria of two compounds, glycerol (or 1,2,3-propanetriol) and 1,3-propanediol, and two mixtures, glycerol + water and glycerol + 1,3-propanediol, were determined using a static apparatus. The obtained pressure values range from 6 Pa to 45 kPa for the compounds and from (32 to 163) kPa for the mixtures. From the temperature dependence of the vapor pressures, the molar enthalpies of vaporization at the mean temperature of the experimental range were derived from the Clausius−Clapeyron equation. From these results the standard enthalpies of vaporization at T = 298.15 K were calculated. The experimental data of the mixtures were correlated using the nonrandom two-liquid (NRTL) model.



INTRODUCTION

Petroleum reserves reduction and the increase of environmentally friendly comportment promote the development of new green energy research. Fatty acid methyl ester, commonly known as biodiesel, is derived from the triglyceride transesterification. The reaction generates glycerol as a byproduct in high quantities (1 mole of glycerol for every 3 moles of methyl esters synthesized, about 10 wt % of the total product). Glycerol valorization is crucial for the viability of biodiesel plant. One way for glycerol valorization could be its transformation in 1,3-propanediol which is a valuable chemical used in polyethylene and polyurethane production.[1−4] The development of the chemical processes (design and optimization) requires knowledge of physicochemical properties such as vapor pressures, the boiling point, and the vaporization enthalpy for all of the compounds and mixtures involved in the process. These data are often scarce or not available. So, predictive models such as the universal functional activity coefficient (UNIFAC) are largely used.[5,6] But when the systems present a weak nonideality the obtained results are not reliable. In this work, we were interested in the vapor pressures of two compounds and two mixtures, respectively: glycerol, 1,3-propanediol, water + glycerol, and 1,3-propanediol + glycerol. Experimental results were fitted by the Antoine and Clapeyron equations and compared with the available literature data. The two mixtures were correlated using the nonrandom two-liquid (NRTL) equation.

EXPERIMENTAL SECTION

Materials. Glycerol (or 1,2,3-propanetriol) and 1,3-propanediol were purchased from Aldrich. Their purity was 99 %. Ultrapure water with a resistivity of 18 MΩ·cm, obtained with a Milli-Q system, was used.

Apparatus and Procedure. Vapor pressure measurements were carried out using two static apparatuses: "low pressure" and "middle pressure" measurement apparatuses. The low pressure apparatus has been described in several articles, and the details of the experimental procedure can be found elsewhere.[7,8] Shortly, the apparatus is equipped with a differential manometer from MKS, type 670 model 616A, and a Rosemount pressure sensor (model 1151 DPE 22S2). The measurement range of the apparatus is comprised between 0.5 Pa and 200 kPa for the pressure and between 233 K and 463 K for the temperature.

The uncertainty of the measurements is estimated to be: $\sigma(T)$ = 0.02 K for the temperature range 203 ≤ T/ K ≤ 463; $\sigma(P)$ = 0.1 Pa + 0.03 P/Pa for pressures lower than 600 Pa; $\sigma(P)$ = 0.01 P/Pa for the pressure range 600 < P/Pa < 1300; and $\sigma(P)$ = 0.003 P/Pa for pressures over 1300 Pa.

To extend the measurement range, a "middle pressure" apparatus was used. It is identical to the previous one except for the pressure gauge. In the latter case an absolute pressure sensor from Keller is used. The pressure range is from (0.1

Received: July 22, 2011
Accepted: December 14, 2011
Published: January 13, 2012

to 1000) kPa, whereas the temperature range is from (303 to 653) K. The temperature range is much higher because of the use of an air bath, whereas in the low pressure apparatus, an oil bath is used. The uncertainty of the measurements with the "middle" pressure apparatus is estimated to be 2 % for pressure and ± 0.2 K for temperature. Mixtures were prepared by mass and thoroughly degassed by distillation as described by Mokbel et al.[9] The estimated uncertainty in composition is $\sigma(x_i) = 0.0005$.

■ RESULTS AND DISCUSSION

The experimental temperature and pressure values of the pure compounds: glycerol, 1,3-propanediol, and the mixtures (glycerol + water and glycerol + 1,3-propanediol) are reported in Tables 1 and 2. The data were fitted to the Antoine equation:

Table 1. Experimental Vapor Pressures of Pure Compounds: Glycerol and 1,3-Propanediol

1,3-propanediol		glycerol	
T/K	P/Pa	T/K	P/Pa
313.20	11.1	351.80	5.83
323.26	26.0	362.02	12.9
333.23	57.4	372.06	25.8
343.16	120	382.08	54.4
351.33	221	392.18	102
361.61	430	402.16	180
362.97	462	412.24	315
371.65	785	422.28	534
381.70	1395	432.45	981
391.70	2376	452.64	2747
391.73	2374	462.86	4099
401.64	3883		
411.71	6212		
421.69	9628		
431.74	14621		
441.73	21629		
451.78	31436		
461.85	44811		

$$\ln P/\mathrm{Pa} = A - \frac{B}{C + T/\mathrm{K}} \tag{1}$$

where P is the vapor pressure; T is the absolute temperature.

The constants A, B, and C determined from least-squares fitting and the mean relative deviations d (n, number of experimental points) are listed in Table 3:

$$d = \frac{1}{n} \sum \frac{|P_{\mathrm{exp}} - P_{\mathrm{cal}}|}{P_{\mathrm{exp}}} \tag{2}$$

The consistency of the experimental data is good, as the mean relative deviation d is comprised between 0.1 % and 2.4 %. For pure glycerol, the standard deviation is higher than parameter C of the Antoine equation. This is due to the low vapor pressures of glycerol which induces a higher uncertainty on the measurements. In this particular case, it is more suitable to fit the vapor pressures of glycerol by the Clapeyron equation:

$$\ln P/\mathrm{Pa} = A - \frac{B}{T/\mathrm{K}} \tag{3}$$

The fitting parameters of glycerol with the standard deviation are as follows: $A = 29.10$ ($\sigma_A = 0.13$) and $B = 9610$ ($\sigma_B = 53$).

Pure Compounds: Comparison with Literature Data. From the fits of the vapor pressures by the Clausius−Clapeyron equation, the enthalpy of vaporization $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (T_{m}) of the pure compounds at the mean temperature of the experiments, T_{m}, was determined. Vaporization enthalpies at the temperature 298.15 K were then calculated using the Chickos et al.[10] equation, as in Table 4:

$$\begin{aligned} \Delta_{\mathrm{vap}}H_{\mathrm{m}}(298.15\ \mathrm{K})/\mathrm{J{\cdot}mol^{-1}} &= \Delta_{\mathrm{vap}}H_{\mathrm{m}}(T_{\mathrm{m}}) + [10.58 + 0.26C_{p1}(298.15\ \mathrm{K})] \\ &\quad \cdot(T_{\mathrm{m}} - 298.15) \end{aligned} \tag{4}$$

Several authors studied glycerol, as seen in Figure 1. Except for Stedman,[11] the pressure range explored is above 100 Pa. In the present study, the measured pressures range between 6 Pa and 4 kPa. In the whole pressure range our data are in good agreement with Stedman's values[11] particularly in the low pressure range, below 100 Pa. The mean relative deviation is 5 % except at 353 K where the relative deviation reaches 15 %. In the temperature range between (400 and 450) K, the different authors from the literature used ebulliometry. The values obtained in the present study are in good agreement with Richardson's data[12] (mean relative deviation 4 %), Sokolov et al.[13] values (mean relative deviation 5 %), and Chittenden[14] measurements (mean relative deviation less than 2 %). A mean relative deviation of 12 % and 10 % is observed, respectively, with Stull's values[15] and with the sole point of Yan and Suppes.[16]

Regarding the vaporization enthalpy at 298.15 K, the value deduced from our results is in a very good agreement with Cammenga et al.[17] value and with Ross and Heideger[18] $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K). The relative deviation is respectively 2 % and 3 %. On the other hand, the enthalpy of vaporization obtained in the present study deviates from the value reported by Bastos et al.[19] obtained by calorimetry (relative deviation 4 %), as in Table 4.

Many authors reported data of 1,3-propanediol at different temperatures, as seen in Figure 2. At the lower temperature range (between (312 and 330) K), our experimental data are in very good agreement with Verevkin[20] values obtained using the transpiration method but in disagreement with Stull[15] values and Daubert and Danner data.[21] On the other hand, our data are in a good agreement with the latter authors at higher temperatures; over 380 K up to 460 K (mean average deviation less than 3 %). Above 400 K, the vapor pressures of 1,3-propanediol obtained in this work are in quite good agreement with Thomas and Meatyard[22] values and in excellent agreement with Olson's data.[23] In addition, the enthalpy of vaporization deduced from the experimental results is in a very good agreement with Knauth and Sabbah[24] value determined using a calorimeter (within 1.2 kJ·mol^{-1}), as in Table 4.

Binary Mixtures: NRTL Correlation. The studied mixtures were correlated using the NRTL model for liquid-phase activity coefficients. This model was proposed by Renon and Prausnitz.[25] It expresses the mixing energy as a function of

Table 2. Experimental Vapor Pressures of Binary Systems

Glycerol (1) + Water (2)											
x_1 = 0.1634		x_1 = 0.3189		x_1 = 0.3374		x_1 = 0.4997		x_1 = 0.6464		x_1 = 0.8317	
T/K	P/Pa	T/K	P/Pa	T/K	P/Pa	T/K	P/Pa	T/K	P/Pa	T/K	P/Pa
352.74	38415	353.23	30622	353.25	29488	363.1	30622	353.38	13841	353.36	6219
363.12	58274	363.06	45280	362.97	43430	372.85	44276	363.04	20160	382.67	18255
372.59	82447	372.94	65762	372.85	63189	382.63	63089	382.61	41324	397.13	29187
382.59	117251	382.65	92577	387.5	104412	397.36	101704	397.4	67201	412.18	45837
397.44	189667	397.38	148544	402.22	165395	412.3	158173	412.16	104212	427.07	68505
412.28	295885	412.30	232094	422.07	289967	432.19	268102	427.25	157973	442.44	100902
422.31	391571	432.31	396185	442.63	488963	452.77	436205	442.38	228383	452.73	128886
432.31	507719	452.85	646434	452.87	621860	473.19	671709	452.77	292375	462.95	163389
448.10	746232										
453.00	836301										

1,3-Propanediol (1) + Glycerol (2)							
x_1 = 0.1502		x_1 = 0.3059		x_1 = 0.497		x_1 = 0.7037	
T/K	P/Pa	T/K	P/Pa	T/K	P/Pa	T/K	P/Pa
361.96	121	361.99	232	361.80	278	362.03	385
381.98	355	371.99	402	362.95	279	372.02	687
392.04	596	382.03	671	371.76	502	382.05	1181
401.97	975	392.06	1103	381.84	871	392.06	1955
411.97	1560	402.07	1765	391.87	1492	402.01	3151
421.91	2410	412.07	2747	391.88	1477	412.02	4974
432.02	3682	422.03	4188	401.80	2420	421.97	7609
441.99	5465	432.15	6331	411.79	3799	432.07	11457
452.03	7990	442.13	9230	421.72	5826	442.03	16813
462.09	11488	452.18	13323	431.81	8801	452.07	24248
		462.28	18877	441.74	12915	462.14	34470
				451.8	18757		
				451.8	19131		
				461.86	26615		

Table 3. Antoine Equation Parameters, Standard Deviation σ, and Mean Relative Deviation d^a

X_1	temperature range T/K	A (σ_A)	B (σ_B)	C (σ_C)	100d
Glycerol (1) + Water (2)					
0	313−450	23.11 (0.03)	3760 (22)	−48.60 (0.92)	0.10
0.1634	352−453	22.69 (0.09)	3574 (64)	−58.16 (3.07)	0.16
0.3189	353−453	21.98 (0.09)	3270 (58)	−72.55 (2.82)	0.14
0.3374	353−453	22.03 (0.12)	3339 (76)	−68.87 (3.71)	0.18
0.4997	363−473	21.00 (0.08)	2885 (51)	−92.68 (2.77)	0.14
0.6464	353−453	21.25 (0.22)	3300 (145)	−71.71 (7.08)	0.36
0.8317	353−463	21.27 (0.14)	3901 (1011)	−42.16 (4.66)	0.23
1	351−463	28.66 (1.71)	9208 (1348)	−9.43 (28.7)	2.90
1,3-Propanediol (1) + Glycerol (2)					
0	351−463	28.66 (1.71)	9208 (1348)	−9.43 (28.7)	2.90
0.1502	332−462	27.02 (0.47)	8600 (387)	24.92 (9.31)	1.04
0.3059	322−462	28.22 (0.56)	9505 (500)	55.83 (11.52)	1.43
0.4970	313−462	24.59 (0.43)	5936 (286)	−48.98 (7.85)	2.40
0.7037	322−462	26.80 (0.45)	7582 (352)	2.13 (8.90)	1.46
1	313−462	23.92 (0.15)	5077 (91.0)	−77.48 (2.64)	0.81

[a] $d = (1/n)\sum((|P_{\text{exp}} - P_{\text{cal}}|)/P_{\text{exp}})$.

local composition:

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ij} G_{ij} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{k=1}^{n} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{n} G_{kj} x_k} \right) \tag{5}$$

with

$$\tau_{ij} = \frac{C_{ij}^{0} + C_{ij}^{T}(T - 273.15)}{RT} \qquad \tau_{ii} = 0 \tag{6}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$

$$\alpha_{ij} = \alpha_{ij}^{0} + \alpha_{ij}^{T}(T - 273.15) \tag{7}$$

Table 4. Enthalpies of Vaporization $\Delta_{vap}H_m$ (298.15) of Glycerol and 1,3-Propanediol

compound	T range K	$\Delta_{vap}H_m$ (298.15) kJ·mol^{-1}	ref
glycerol	352 to 463	88.2 ± 0.9	this work
		86.8 ± 0.3	17
		85.8	18
		91.7 ± 0.9	19
1,3-propanediol	313 to 462	73.6 ± 0.9	this work
		72.4 ± 0.3	24

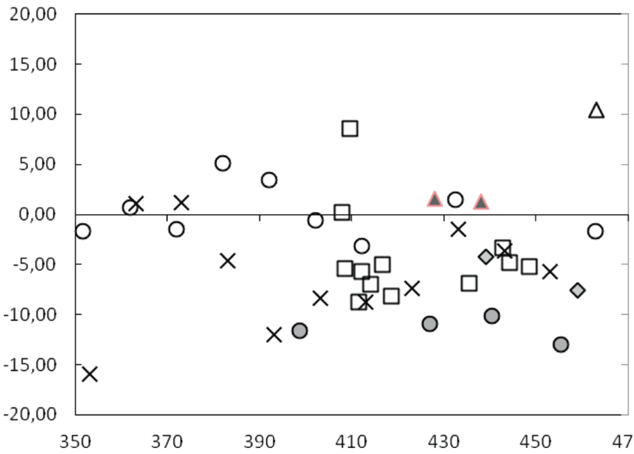


Figure 1. Relative deviation of the experimental vapor pressures of glycerol from values obtained with the Antoine equation as a function of temperature T/K: ○, this work; ×, ref 11; □, ref 12; ♦, ref 13; ▲, ref 14; ●, ref 15; △, ref 16.

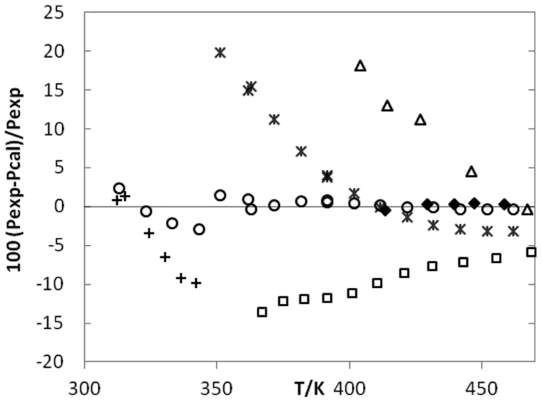


Figure 2. Relative deviation of the experimental vapor pressures of 1,3-propanediol from values obtained with the Antoine equation as a function of temperature T/K: ○, this work; △, ref 15; +, ref 20; ∗, ref 21; □, ref 22; ♦, ref 23.

The parameter α_{ij} is related to the nonrandomness in the mixture. Six parameters are associated to each binary mixture, as in Table 5. They were estimated by minimizing the objective function $\Phi = \sum((P_{exp} - P_{cal})/P_{exp})^2$. In the present study the temperature influence for the α parameter was set to $(\alpha_{ij}^T = 0)$. The vapor phase was considered as perfect due to the low vapor pressures explored in the present study.

Soujanya et al.,[26] Coelho et al.,[27] and Carr et al.[28] studied water–glycerol mixtures by ebulliometry. The measurements of the authors are presented in the forms of isotherm and isobar. To compare our measurements with those of the authors as well as the author's data between them, we fitted our measurements and those of the authors by the Barker method using the Redlich–Kister polynomial equation which restores the data in the form of isotherms. As an example, in Figure 3 the relative deviation between the calculated pressures versus the molar fraction of glycerol at 353.15 K is reported. Our data are in quite good agreement with Coelho et al.[27] and Carr et al.[28] values for the mole fraction of glycerol less than 0.4 (relative deviation of the vapor pressure ranges between 1 and 10 %). The deviations become more significant at a mole fraction of glycerol of 0.5 and 0.6. On the other hand, the present work is in good agreement with Soujanya et al.[26] data (relative deviation of the vapor pressure is less than 5 %). None of the quoted authors have measured the vapor pressures of solutions rich in glycerol (above 0.6 in mole fraction of glycerol) at 353.15 K nor the vapor pressures of pure glycerol, which are probably too low to be measured by ebulliometry. At 413.15 K, Coelho et al.[27] and Carr et al.[28] studied solutions at 0.7 and 0.8 mole fractions of glycerol. The relative deviations of the vapor pressure with Coelho et al.[27] and the present work are 40 % (for glycerol at $x = 0.7$) and 60 % (for glycerol at $x = 0.8$), whereas with Carr et al.[28] the deviation is respectively 33 % and 12 %. We observe that the two authors' data are scattered and present a systematic deviation with our data. We

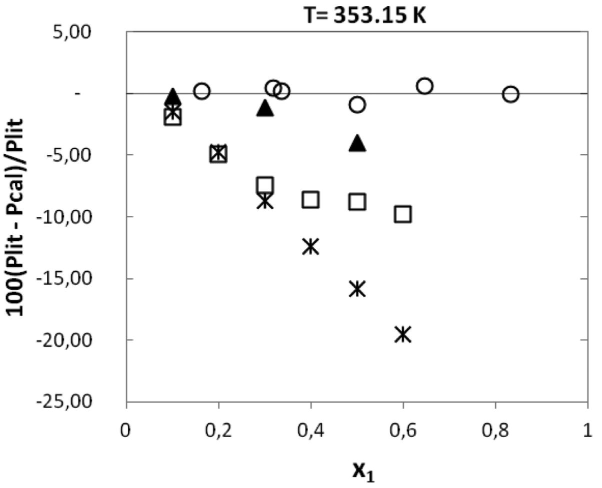


Figure 3. Relative deviation of the calculated vapor pressures at 353.15 K of glycerol (1) + water (2): ○, this work; ▲, ref 26; ∗, ref 27; □, ref 28. The experimental pressures of the literature were fitted by the Barker method using the Redlich–Kister equation.

Table 5. NRTL Binary Parameters in J·mol^{-1a}

binary	C°_{12}	C°_{21}	α_{12}°	C^T_{12}	C^T_{21}	rmsd (P/kPa)
water/glycerol	113883	−1053.78	0.3	−46	−1.3	3.5
glycerol/1,3-propanediol	683.4	1937.43	0.2	4.6	−21.7	0.3

[a] rmsd(P) = $[\sum_{i=0}^{n}(P_i^{exp} - P_i^{cal})^2/n]^{1/2}$, where n is the number of data.

explain the systematically higher values of the present work, comparing to the literature data, by the used measurement methods. The different authors have used ebulliometry, whereas we used a static method. It is well-known that the ebulliometric method is not adapted to mixtures with very different boiling points as is the case of glycerol—water mixtures. When the ebulliometric method is used for these mixtures, vapor hold-up has been identified as a major concern mainly for the volatile compound.[29,30]

Vapor pressures were calculated using the NRTL coefficients obtained from the present study and compared with the literature data. As shown in Figure 4, the NRTL model represents quite satisfactorily the experimental data which was not the case with the UNIQUAC model (not included in this work due to a bad restitution of the experimental data). The Soujanya et al.[26] and Coelho et al.[27] values are in good agreement with the experimental results at temperatures below 393 K and for mixtures below 0.5 mole fraction of glycerol, as in Figure 5. A deviation of 17 % is observed for higher temperatures (423.15 K) and for mixtures rich in glycerol (above 0.5 in mole fraction). On the other hand, the activity coefficient of water at infinite dilution obtained with NRTL parameters were compared with Mierio and Stein[32] values and with Bestani and Shing[31] data determined by both authors using gas—liquid chromatography, as in Figure 6. Bestani and Shing[31] activity coefficients vary strongly with temperature, whereas the variation of our calculated data and those of Mierio and Stein[32] change slightly with temperature. The determination of activity coefficients using gas—liquid chromatography is a fast and convenient method; however one has to pay careful attention to the retention mechanism of the solute. The retention must be based exclusively on the partition of the solute in the stationary phase, namely, glycerol. In their article, only Mieiro and Stein[31] described how they controlled and avoided the adsorption phenomenon.

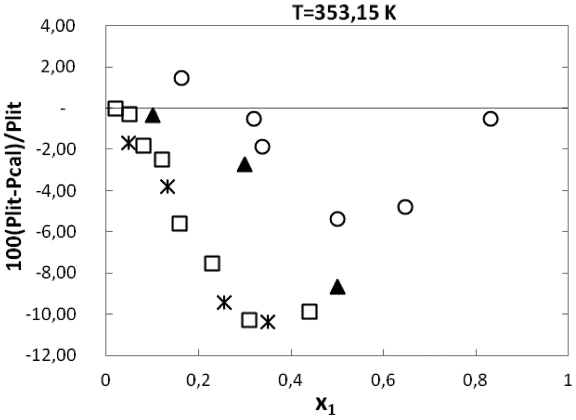


Figure 4. Relative deviation of the calculated glycerol (1) + water (2) vapor pressures at T = 353.15 K using NRTL coefficients obtained from the present study: ○, this work; ▲, ref 26; ∗, ref 27; □, ref 28.

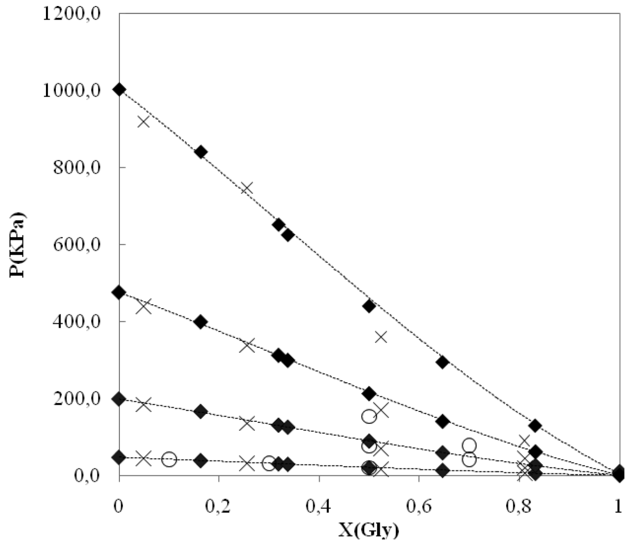


Figure 5. Glycerol (1) + water (2) vapor pressures at four temperatures: 353.15 K, 393,15 K, 423.15 K, and 453.15 K for different glycerol mole fractions. NRTL model: dashed line; ♦, this work; ○, ref 26; ×, ref 27.

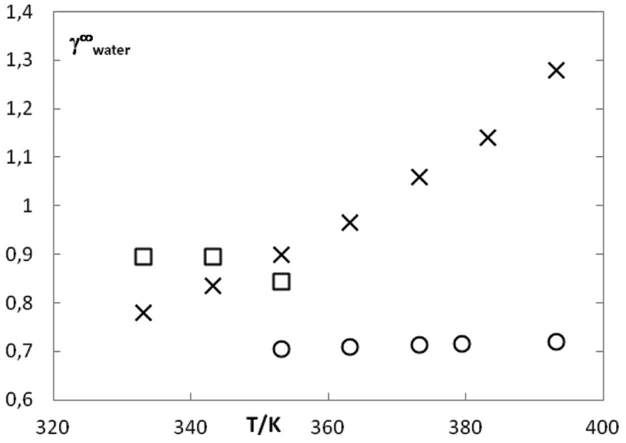


Figure 6. Activity coefficient at infinite dilution of water: ○, this work; ×, ref 31; □, ref 32.

From the Antoine coefficients, as in Table 3, the boiling points of the mixtures studied in the present work were calculated and compared with Oliveira et al.[33] and Chen and Thompson[34] data who determined these values by ebulliometry. The agreement with both authors' values is excellent, as seen in Figure 7.

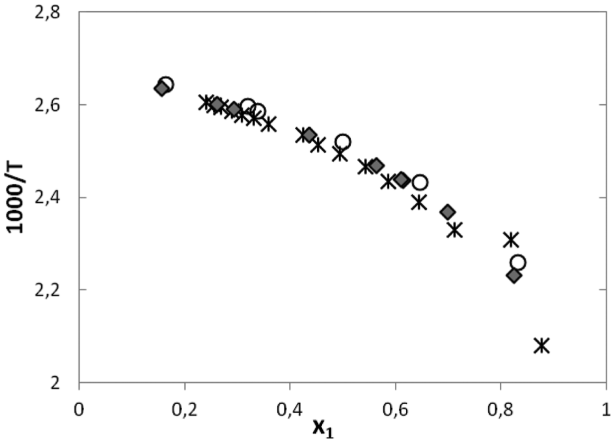


Figure 7. Boiling temperatures of the mixtures glycerol (1) + water (2): ○, this work calculated using the Antoine equation; ∗, ref 33; ♦, ref 34.

In the same way, a set of interaction parameters was obtained when the vapor pressures of glycerol + 1,3-propanediol mixtures were correlated using the NRTL equation, as in

Table 5. The model fits the experimental vapor pressures very well, and the relative mean standard deviation rmsd (P) is about 0.3 kPa for the entire pressure range (n, number of experimental points):

$$\mathrm{rmsd}(P) = \sqrt{\sum_{i=0}^{n} (P_i^{\mathrm{exp}} - P_i^{\mathrm{cal}})^2/n} \tag{8}$$

As for glycerol-1,3-propanediol mixtures, no literature data were found to be compared with the present study.

■ CONCLUSION

In the present study, vapor pressures of pure compounds (glycerol and 1,3-propanediol) and binary mixtures (glycerol + water and glycerol + 1,3-propanediol) were measured using a static apparatus. The experimental data of pure 1,3-propanediol and glycerol are in very good agreement with the literature data. In the same way, the vaporization enthalpy obtained in this work is in excellent agreement with those of the literature. The data of the binary mixtures were correlated quite satisfactorily using the NRTL equation. The experimental vapor pressures of glycerol + water mixtures are in good agreement with the literature data. Additionally, the data obtained for the glycerol + 1,3-propanediol mixtures are original, as no literature data were found to be compared.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mokbel@univ-lyon1.fr.

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