

# Isothermal Vapor-liquid Equilibria in the 2-Propanol + Water and 2-Methylpropan-2-ol + Water Systems



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*This paper is dedicated to the memory of Paolo Alessi.*

Vapor-liquid equilibria were measured isothermally in the two title systems at 333.15, 343.15, and 353.15 K. A dynamic equilibrium still, allowing for the recirculation of both liquid and vapor phases was used. The data were correlated by means of the standard NRTL equation while considering the real behavior of the vapor phase, and with the use of the maximum likelihood procedure. Both the systems exhibited azeotropic behavior.

*Keywords*

alcohol-water system, vapor-liquid equilibrium, azeotropy

## Introduction

Vapor-liquid equilibria in the two water + alcohol systems were measured for further investigation of the effect of ionic liquids as azeotrope breakers. Both the systems are azeotropic, and are miscible over the entire concentration range.

## Experimental

### Materials

2-Propanol (CAS RN 67-63-0), with declared purity >99.8 %, was purchased from Sigma-Aldrich and in addition, kept over a 5 Å molecular sieve. 2-Methylpropan-2-ol [*tert*-butanol], p. a. (CAS RN 75-65-0) was supplied by Lach-Ner, Czech Republic, with a purity of 99.85 %. Water (CAS RN 7732-18-5) was redistilled.

### Experimental setup and measurement

The all-glass circulation still, with a total liquid mixture volume of 160 cm<sup>3</sup>, was used for the measurement in the standard setup, as described earlier, e.g., in<sup>1,2</sup>. The data were determined at three isotherms, namely, 333.15, 343.15, and 353.15 K, with the uncertainty of variables estimated as  $u(x) = u(y) = 0.0005$ ,  $u(P) = 0.005$  kPa,  $u(T) = 0.005$  K for the mole fraction in liquid phase, mole fraction in vapor phase, pressure and temperature, respectively. The data obtained are listed in Tables 1 and 2, and presented in Figs. 1 and 2.

## Data processing

The data were processed by means of a software published earlier<sup>3</sup>, and the NRTL equation was selected for the description of dependence of activity coefficient  $\gamma$  on composition

$$\ln \gamma_1 = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_1 + x_2 G_{12})^2} \right]$$

where  $G_{12} = \exp [-\alpha_{12} \tau_{12}]$ ,  $G_{21} = \exp [-\alpha_{21} \tau_{21}]$ ,  $\tau_{12} = (g_{12} - g_{22})/RT$ , and  $\tau_{21} = (g_{21} - g_{11})/RT$ . The equation contains three adjustable parameters, namely,  $(g_{12} - g_{22})$ ,  $(g_{21} - g_{11})$ , and  $\alpha_{12} = \alpha_{21}$ . The expression for  $\gamma_2$  can be obtained by a simple interchange of indices 1 and 2.

The correction for non-ideal behavior of the vapor phase was considered and calculated by means of virial equation

$$y_i P = x_i \gamma_i P_i^o \exp \left\{ \left[ \frac{(B_{ii} - V_i^o)(P_i^o - P) -}{(2B_{ij} - B_{ii} - B_{jj}) y_j^2 P} \right] / RT \right\},$$

where the virial coefficients  $B$  are determined by the Hayden and O'Connell method<sup>4</sup>. The optimizing procedure is based on the maximum likelihood method with the objective function containing estimated standard deviations  $\sigma^2$  in all variables:  $x$  – mole fraction in liquid phase,  $y$  – mole fraction in vapor phase,  $T$  – temperature, and  $P$  – pressure, thus

$$\text{OF} = \sum_{n=1}^N \left[ \frac{(x_n^e - x_n)^2}{\sigma_{x_n}^2} + \frac{(y_n^e - y_n)^2}{\sigma_{y_n}^2} + \frac{(T_n^e - T_n)^2}{\sigma_{T_n}^2} + \frac{(P_n^e - P_n)^2}{\sigma_{P_n}^2} \right]$$

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where  $n$  denotes  $n$ -th experimental point, and  $N$  is total number of experimental points. Standard deviations used in correlations are as follows:  $\sigma_x^2 = 0.002$ ,  $\sigma_y^2 = 0.002$ ,  $\sigma_P^2 = 0.1\%$  of  $P$ ,  $\sigma_T^2 = 0.02$  K. The three optimized parameters ( $g_{12} - g_{22}$ ), ( $g_{21} - g_{11}$ ), and  $\alpha$ , are summarized in Tables 3 and 4.

## Discussion and conclusions

Both the systems exhibited rather unusual behavior. A relatively large portion of the  $x$ - $P$  curve (within the interval  $0.1 < x < 0.6$ ) is practically linear, which could be expected to result in difficulties

during correlation of the data using just three adjustable parameters. The NRTL equation dealt with that problem successfully, and it was able to describe the double inflex on this curve. Comparison with literature values is very restricted, even in the case of published data, which are still determined mostly at isobaric (atmospheric) conditions. The complete  $x$ - $y$ - $P$  data were found for the 2-propanol + water system measured by Wu, Hagewiesche and Sandler<sup>5</sup> at 353.15 K, which are plotted in Fig. 1; the agreement with our data is excellent. Other isothermal data were published by Sada and Morisue<sup>6</sup> at temperatures 338.1 K and 348.1 K. Even though those data were determined in the Othmer still,

Table 1 – Vapor-liquid equilibrium in the 2-propanol + water (2) system

$x_1$	$y_1$	$P$ (kPa)	$x_1$	$y_1$	$P$ (kPa)	$x_1$	$y_1$	$P$ (kPa)
$T = 333.15$ K			$T = 343.15$ K			$T = 353.15$ K		
0.0056	0.1108	22.000	0.0047	0.1203	35.176	0.0058	0.1076	53.191
0.0245	0.3512	29.904	0.0222	0.3535	46.595	0.0231	0.3498	70.141
0.0719	0.4845	36.439	0.0634	0.4899	56.658	0.0648	0.4823	85.227
0.2156	0.5272	39.551	0.1890	0.5279	61.355	0.2030	0.5291	92.427
0.3566	0.5534	40.944	0.3501	0.5551	63.534	0.3563	0.5571	95.888
0.4720	0.5900	41.731	0.4706	0.5917	64.778	0.4740	0.5913	97.721
0.6320	0.6559	42.472	0.6334	0.6564	66.003	0.6316	0.6575	99.891
0.6791	0.6558	42.529	0.6827	0.6860	66.122	0.6803	0.6805	99.998
0.8313	0.7892	41.911	0.8314	0.7933	65.245	0.8303	0.7987	98.654
0.8851	0.8401	41.339	0.8710	0.8436	64.395	0.8828	0.8460	97.232
0.9445	0.9171	40.267	0.9444	0.9189	62.855	0.9443	0.9213	95.192

Table 2 – Vapor-liquid equilibrium in the 2-methylpropan-2-ol + water (2) system

$x_1$	$y_1$	$P$ (kPa)	$x_1$	$y_1$	$P$ (kPa)	$x_1$	$y_1$	$P$ (kPa)
$T = 333.15$ K			$T = 343.15$ K			$T = 353.15$ K		
0.0306	0.4099	32.822	0.0292	0.4099	51.550	0.0255	0.4171	77.964
0.0710	0.5355	39.381	0.0753	0.5375	61.863	0.0739	0.5329	93.897
0.2064	0.5523	40.973	0.2136	0.5522	63.824	0.2192	0.5483	96.339
0.2805	0.5559	41.282	0.2836	0.5600	64.312	0.2839	0.5591	97.232
0.3870	0.5741	41.808	0.3841	0.5721	65.122	0.3860	0.5707	98.464
0.4786	0.5946	42.361	0.4778	0.6017	65.998	0.4855	0.6017	99.934
0.6069	0.6350	42.820	0.6003	0.6340	66.770	0.5981	0.6323	101.183
0.6395	0.6516	42.830	0.6474	0.6586	66.818	0.6473	0.6572	101.284
0.6731	0.6759	42.856	0.6686	0.6694	66.899	0.6787	0.6750	101.327
0.7158	0.7041	42.821	0.7163	0.7035	66.821	0.7198	0.7028	101.435
0.8161	0.7888	42.248	0.8197	0.7845	65.943	0.8192	0.7735	99.806
0.9103	0.8877	41.074	0.9109	0.8712	64.095	0.9048	0.8670	97.010

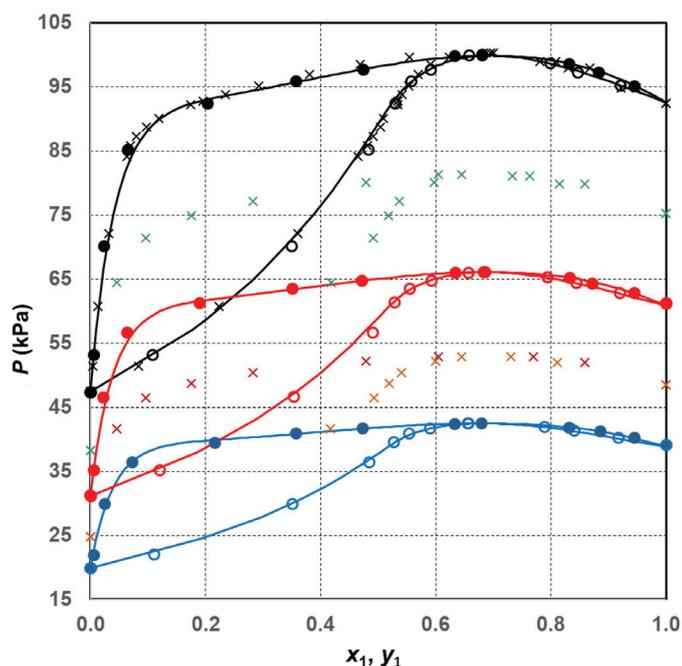


Fig. 1 – Vapor-liquid equilibrium in the 2-propanol + water (2) system. Experimental points: (●, ○) 333.15 K, (●, ○) 343.15 K, (●, ○) 353.15 K, × 353.15 K (ref<sup>6</sup>), × 348.1 K (ref<sup>6</sup>), × 338.1 K (ref<sup>6</sup>). Lines represent NRTL correlation.

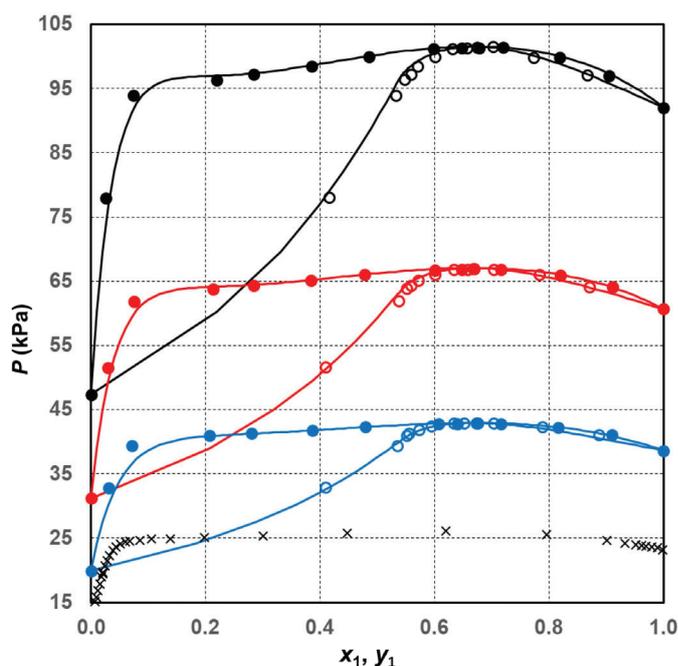


Fig. 2 – Vapor-liquid equilibrium in the 2-methylpropan-2-ol + water (2) system. Experimental points: (●, ○) 333.15 K, (●, ○) 343.15 K, (●, ○) 353.15 K, × 323.15 K (ref<sup>7</sup>). Lines represent NRTL correlation.

which in principle cannot measure accurately boiling points, the qualitative agreement with our data is obviously very good. For the 2-methylpropan-2-ol + water system there are  $x$ - $P$  data by Fischer and Gmehling<sup>7</sup> determined at 323.15 K, therefore the comparison can be made only qualitatively. These data are plotted in Fig. 2, and it is clear that the shape of dependence formed by  $x$ - $P$  data points agrees well with all other isotherms.

The NRTL parameters given in Tables 3 and 4 also show the expectable trend of their dependence on temperature. Average mean deviations provide proof that correlations were carried out properly.

There are greater deviations between correlations and experiments at ranges of very high concentrations of water, but perfect results cannot be expected from the three-parameter equation applied to very irregular systems. Nevertheless, this range is unimportant with regard to its distance from the azeotropic region, since the scheduled future measurements will be targeted at an investigation of the influence of ionic liquids on azeotropic behavior. The main reason for the present work was to prove that the experimental setup is suitable for the determination of good vapor-liquid equilibrium data, and the result was convincing.

Table 3 – NRTL parameters and average absolute deviations  $\Delta$  for the 2-propanol + water (2) system

$T$ (K)	$(g_{12}-g_{22})$ (J mol <sup>-1</sup> )	$(g_{21}-g_{11})$ (J mol <sup>-1</sup> )	$\alpha$	$\Delta x$	$\Delta y$	$\Delta P$ (kPa)	$\Delta T$ (K)
333.15	2289.45	796.425	-1.2694	0.0019	0.0044	0.041	0.04
343.15	2360.81	767.388	-1.2572	0.0028	0.0026	0.061	0.04
353.15	2460.08	723.514	-1.2052	0.0026	0.0026	0.126	0.04

Table 4 – NRTL parameters and average absolute deviations  $\Delta$  for the 2-methylpropan-2-ol + water (2) system

$T$ (K)	$(g_{12}-g_{22})$ (J mol <sup>-1</sup> )	$(g_{21}-g_{11})$ (J mol <sup>-1</sup> )	$\alpha$	$\Delta x$	$\Delta y$	$\Delta P$ (kPa)	$\Delta T$ (K)
333.15	2614.36	744.863	-0.9473	0.0069	0.0044	0.038	0.05
343.15	2607.38	752.833	-1.1022	0.0061	0.0040	0.062	0.04
353.15	2597.42	801.253	-1.2103	0.0026	0.0056	0.066	0.05

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