Bubble Temperature Data for Phenol-Alcohol Systems 1. Phenol-*I*-propanol System

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Isobaric bubble temperature data were collected for the system phenol-*i*-propanol over the entire composition range by indirect method using a standard Swietoslawski type ebulliometer. The measurements were made at 209, 412 and 711 mm Hg. The experimental *t-x* data were correlated with both Gamma–Phi method and equation of state method. In the former approach, Wilson, NRTL and UNIQUAC equations are used whereas in the latter case Soave equation of state is used.

KEY WORDS: Equation of state, boiling point.

INTRODUCTION

Separation of mixtures into useful components or fractions forms one of the most important activities of any chemical process industry. Among the separation processes, distillation is perhaps the most important and energy consuming operation. Hence accurate knowledge of vapor-liquid equilibrium (VLE) of the system is of utmost importance for the optimum design and efficient operation of a distillation column. Phenol is a very useful physical solvent. A literature search reveals that there is very little information on vapor-liquid equilibria (VLE) of phenol-alcohol systems. The only literature information[1] is not easily available. Hence it is attempted to measure experimental bubble-point data for phenol-alcohol systems. Such measurements for phenol-*i*-propanol system are presented here.

Generally VLE data are collected under two fixed conditions, namely, constant pressure and constant temperature. Since most distillation operations are carried out at constant pressure, the temperature-composition curves are of more practical use in making engineering calculations, even though for theoretical considerations pressure-composition curves are preferable. Hence, the experiments were conducted at three constant pressures: 209, 412 and 711 mm Hg.

EXPERIMENTAL SECTION

The vapor-liquid equilibrium measurements were conducted in a Swietoslawski ebulliometer.[2] The ebulliometer was connected to a vacuum system. The pressures

were measured by a mercury manometer with an accuracy of ± 1 mm Hg. The temperature was measured with a PT100 thermometer with an accuracy of 0.1°C.

The boiling points of the system phenol-*i*-propanol were determined over the entire composition range at 209, 412 and 711 mm Hg. Mixtures of different compositions were prepared by taking the pure components by weight. The boiling point was first determined at 209 mm Hg. The temperature was recorded when it remained constant for about half an hour. Then the pressure is raised to 412 mm Hg, and 711 mm Hg and the procedure is repeated.

PURITY OF MATERIALS

Purified *i*-propanol, which has minimum guaranteed purity of 99.7 % (assay GC), was obtained from Merck (India) Ltd. Pure phenol with a minimum guaranteed purity of 99.5 % (assay GC) was supplied by Loba Chemie Ltd. These chemicals were used without any further purification. However, the purity of these materials is checked by measuring the physical properties of these materials. The comparison of measured physical properties with literature values is shown in Table 1. The measured values are in good agreement with the literature values.[3]

Table 1 Comparison of physical properties of pure components with literature values.

	i-Propanol		Phenol	
	Present	*Lit*[3]	*Present*	*Lit*[3]
Refractive index	1.3768	1.3776 @ 25°C	1.538	1.54 @ 45°C
Boiling point, °C	82.3	82.4	181.6	181.8
Melting point, °C			40.9	40.9

RESULTS AND DISCUSSION

The experimental *t-x* measurements at the three different pressures are presented in Tables 2–4. Here the experimental data are correlated by two different approaches: (i) Equation of State (EOS) approach with the Soave modification of Redlich–Kwong equation and (ii) Gamma-Phi method with Wilson, NRTL and UNIQUAC equations.

Equation of State Approach

In the EOS approach, the modification of Soave EOS by Graboski *et al.*[4] is adopted here. The equations involved are:

$$P = RT /(v- b) - a(T)/[v(v+ b)]\tag{1}$$

Table 2 VLE data for phenol-*i*-propanol system at 209 mm Hg.

x_1, mol. fr.	t_{exp} $°C$	Soave equation		Wilson equation		NRTL equation		UNIQUAC equation	
		t_{cal}, $°C$	$y_{1,cal}$	t_{cal}, $°C$	$y_{1,cal}$	t_{cal}, $°C$	$y_{1,cal}$	t_{cal}, $°C$	$y_{1,cal}$
0.0609	54.1	53.8	0.0003	54.5	0.0003	54.5	0.0003	54.3	0.0003
0.1578	55.9	56.7	0.0012	57.4	0.0013	57.3	0.0013	57.2	0.0012
0.2202	58.2	59.0	0.0023	59.8	0.0024	59.7	0.0024	59.6	0.0023
0.2841	61.6	61.6	0.0040	62.4	0.0042	62.3	0.0042	62.2	0.0041
0.3794	66.7	66.5	0.0085	67.1	0.0088	67.0	0.0087	67.0	0.0087
0.4714	73.1	72.1	0.0166	72.5	0.0170	72.5	0.0170	72.5	0.0169
0.5562	79.2	78.4	0.0310	78.3	0.0304	78.3	0.0305	78.4	0.0306
0.6848	89.8	89.6	0.0746	89.4	0.0737	89.5	0.0743	89.7	0.0750
0.7763	99.4	99.7	0.1434	99.4	0.1423	99.5	0.1430	99.6	0.1447
0.8422	108.5	108.8	0.2366	108.5	0.2368	108.4	0.2366	108.6	0.2392
0.9385	125.0	125.7	0.5341	125.6	0.5425	125.4	0.5376	125.3	0.5407

Table 3 VLE data for phenol-*i*-propanol system at 412 mm Hg.

x_1, mol. fr.	t_{exp} $°C$	Soave equation		Wilson equation		NRTL equation		UNIQUAC equation	
		t_{cal}, $°C$	$y_{1,cal}$	t_{cal}, $°C$	$y_{1,cal}$	t_{cal}, $°C$	$y_{1,cal}$	t_{cal}, $°C$	$y_{1,cal}$
0.0609	68.8	68.8	0.0005	69.2	0.0004	69.2	0.0004	69.0	0.0004
0.1578	71.6	71.9	0.0017	72.4	0.0017	72.4	0.0017	72.2	0.0016
0.2202	73.6	74.4	0.0031	74.9	0.0031	74.9	0.0031	74.8	0.0031
0.2841	77.4	77.3	0.0053	77.8	0.0054	77.8	0.0053	77.7	0.0053
0.3794	82.4	82.5	0.0109	82.9	0.0110	82.9	0.0110	82.9	0.0109
0.4714	89.4	88.5	0.0207	88.8	0.0208	88.9	0.0209	88.8	0.0209
0.5562	96.1	95.3	0.0376	95.1	0.0366	95.2	0.0370	95.2	0.0371
0.6848	107.9	107.3	0.0866	107.1	0.0859	107.3	0.0870	107.3	0.0875
0.7763	117.9	118.1	0.1617	118.0	0.1616	118.0	0.1627	118.0	0.1638
0.8422	127.5	127.6	0.2597	127.6	0.2623	127.6	0.2621	127.5	0.2635
0.9385	145.0	145.6	0.5594	145.6	0.5695	145.4	0.5652	145.2	0.5662

Table 4 VLE data for phenol-*i*-propanol system at 711 mm Hg.

x_1, mol. fr.	t_{exp} $°C$	Soave equation		Wilson equation		NRTL equation		UNIQUAC equation	
		t_{cal}, $°C$	$y_{1,cal}$	t_{cal}, $°C$	$y_{1,cal}$	t_{cal}, $°C$	$y_{1,cal}$	t_{cal}, $°C$	$y_{1,cal}$
0.0609	81.8	82.2	0.0006	82.3	0.0005	82.3	0.0005	82.1	0.0005
0.1578	84.3	85.6	0.0023	85.7	0.0021	85.7	0.0021	85.5	0.0020
0.2202	87.1	88.2	0.0041	88.4	0.0038	88.4	0.0038	88.2	0.0037
0.2841	91.2	91.4	0.0068	91.5	0.0065	91.5	0.0065	91.4	0.0064
0.3794	95.3	96.9	0.0135	96.9	0.0130	97.0	0.0131	96.9	0.0130
0.4714	103.9	103.3	0.0250	103.2	0.0242	103.4	0.0245	103.3	0.0245
0.5562	111.4	110.6	0.0444	110.1	0.0420	110.3	0.0426	110.3	0.0427
0.6848	123.7	123.1	0.0985	122.9	0.0962	123.1	0.0976	123.0	0.0979
0.7763	134.2	134.6	0.1792	134.5	0.1773	134.5	0.1784	134.4	0.1789
0.8422	143.6	143.6	0.2818	144.7	0.2819	144.6	0.2818	144.5	0.2822
0.9385	162.0	162.0	0.5827	163.6	0.5885	163.4	0.5850	163.2	0.5845

where

$$a(T) = a_c \alpha \tag{2}$$

$$a_c = 0.42747 R^2 T_c^2/P_c \tag{3}$$

$$b = 0.08664\, R T_c/P_c \tag{4}$$

$$\alpha = [1 + S(1 - T_r^{1/2})]^2 \tag{5}$$

$$S = 0.48508 + 1.55171\omega - 0.15613\omega^2 \tag{6}$$

$$a_m = \sum \sum z_i z_j a_{ij} \tag{7}$$

$$a_{ij} = [a_j(T)a_j(T)]^{1/2}(1 - k_{ij}) \tag{8}$$

$$b_m = \sum z_i b_i \tag{9}$$

$$\ln(f_i/z_i P) = (b_i/b_m)(Z - 1) - \ln(Z - B) \\ \qquad - (A/B)[2 \sum z_j a_{ij}/a_m - b_i/b_m] \ln(1 + B/Z) \tag{10}$$

$$A = a_m P'(R^2 T^2) \tag{11}$$

$$B = b_m P/RT \tag{12}$$

$$R = 82.057 \text{ cc. atm/g mol K}$$

The pressure P is in atmospheres, temperature T in Kelvin and volume v in cc/g mol.

The bubble-point calculations were carried out by using the algorithm proposed by Veeranna and Rihani.[5] The optimum binary interaction parameter k_{ij} of -0.091 obtained by minimising absolute deviation of experimental and calculated temperaturtes gave an average absolute deviation of 0.6°C. The observed and calculated temperatures and vapor compositions are also given in Tables 2–4.

Gamma-Phi Approach

i) Wilson Equation[6]

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1}\right) \tag{12}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) + x_1\left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2}\right)$$

Where

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left[\frac{-(\lambda_{12} - \lambda_{11})}{RT}\right] \tag{13}$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left[\frac{-(\lambda_{12} - \lambda_{22})}{RT}\right]$$

V_1 and V_2 are the liquid molar volumes which are calculated through Rackett Equation.[7] λ's are the energies of interaction between the molecules designated in the subscripts.

ii) NRTL equation[8]

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \tag{14}$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

where

$$\ln G_{12} = -\alpha_{12} \tau_{12} \tag{15}$$

$$\ln G_{21} = \alpha_{12} \tau_{21} \tag{16}$$

$$\tau_{12} = \Delta g_{12}/RT$$

$$\tau_{21} = \Delta g_{21}/RT$$

$$\Delta g_{12} = g_{12} - g_{22} \tag{17}$$

$$\Delta g_{21} = g_{21} - g_{11}$$

$$\alpha_{12} = 0.12$$

Here g's are the energies of interaction between different molecular species designated by the subscripts.

iii) UNIQUAC equation[9]

$$\ln \gamma_1 = \ln(\phi_1/x_1) + (z/2)q_1 \ln(\theta_1/\phi_1) + \phi_2[l_1 - l_2(r_1/r_2)]$$
$$- q_1 \ln(\theta_1 + \theta_2 \tau_{21}) + \theta_2 q_1 [\tau_{21}/(\theta_1 + \theta_2 \tau_{21})$$
$$- \tau_{12}/(\theta_2 + \theta_1 \tau_{12})] \tag{18}$$

$$\ln \gamma_2 = \ln(\phi_2/x_2) + (z/2)q_2 \ln(\theta_2/\phi_2) + \phi_1[l_2 - l_1(r_2/r_1)]$$
$$- q_2 \ln(\theta_2 + \theta_1 \tau_{12}) + \theta_1 q_2 [\tau_{12}/(\theta_2 + \theta_1 \tau_{12})$$
$$- \tau_{21}/(\theta_1 + \theta_2 \tau_{21})]$$

Where

$$l_1 = (z/2)(r_1 - q_1) - (r_1 - 1) \tag{19}$$

$$l_2 = (z/2)(r_2 - q_2) - (r_2 - 1)$$

$$\phi_1 = x_1 r_1/(x_1 r_1 + x_2 r_2) \tag{20}$$

$$\phi_2 = x_2 r_2/(x_1 r_1 + x_2 r_2)$$

$$\theta_1 = x_1 q_1/(x_1 q_1 + x_2 q_2) \tag{21}$$

$$\theta_2 = x_2 q_2/(x_1 q_1 + x_2 q_2)$$

$$\ln \tau_{12} = -(U_{12} - U_{22})/RT \tag{22}$$

$$\ln \tau_{21} = -(U_{21} - U_{11})/RT \tag{22}$$

U's are the energies of interaction between different molecular species designated by the subscripts.

In the above equation, R is 1.987 cal/g mol K and temperature T in Kelvin. In all the three cases gas phase is assumed to be ideal and hence fugacity coefficient is taken

Table 5 Model parameters for Wilson, NRTL and UNIQUAC equations.

Model	Parameters	RMS error in temperature
Wilson	$\Delta\lambda_{12} = -60.42$ K	
	$\Delta\lambda_{21} = -274.8$ K	0.9 K
NRTL	$\Delta g_{12} = -442.1$ K	
($\alpha_{12} = 0.12$)	$\Delta g_{21} = 98.31$ K	0.8 K
UNIQUAC	$\Delta U_{12} = -117.8$ K	
	$\Delta U_{21} = -43.94$ K	0.8 K

as 1.0. The optimum model parameters in each case were obtained by minimizing sum of the squares of the deviation in bubble pressure, using Nelder–Mead optimization technique. The model parameters along with root mean square error in temperature are presented in Table 5.

Among the Gamma–Phi methods, UNIQUAC equation correlated the data with least possible deviation. Surprisingly, the Soave equation also correlated the data very well with deviation comparable to that of UNIQUAC method. The calculated temperatures and vapor compositions for all the models are presented in Tables 2–4. As can be seen from these tables, the predictions from the four models are almost identical.

CONCLUSIONS

The system is well correlated by all the models studied here. The UNIQUAC model correlated the data a little better than the other two Gamma–Phi models. The assumption of ideal vapor phase behaviour is justified because the pressures treated here are low. The Soave equation correlated the data remarkably well even with temperature independent binary interaction parameter. It may be expected that Soave equation would correlate well other phenol-alcohol systems also.

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