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LIQUID-LIQUID PHASE EQUILIBRIA FOR THE TERNARY (NEOPENTYL GLYCOL + SODIUM FORMATE + WATER) SYSTEM

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ABSTRACT. Liquid–liquid equilibrium data and the phase diagrams were measured for the ternary (neopentyl glycol + sodium formate + water) system at various temperatures of 303.15, 313.15 and 323.15 K. The effect of temperature on the conjugate phase and the tie-line length of the investigated system have been studied. The results showed that the length of the tie-line increases and the two-phase area was slightly increased by decreasing temperature. The fitting parameters of the Pirdashti and Merchuk equations were obtained with the temperature dependence expressed in the linear form, respectively. Compared with the Pirdashti equation, the binodal curves were satisfactorily described using the Merchuk equation at T = (303.15, 313.15 and 323.15) K, and the critical points at different temperatures were estimated by extrapolation. Furthermore, the Hand, Othmer-Tobias and Bachman models were used for the correlation of the phase behavior of the studied system. According to the reported correlation coefficients values, it was found that the measured tie-line data have acceptable consistency and the better fitness was with Othmer-Tobias equation.

KEY WORDS: Liquid–liquid equilibrium, Neopentyl glycol, Phase diagram, Merchuk

INTRODUCTION

Neopentyl glycol is an important chemical raw material, which is widely used in textile, chemical, automobile, pharmaceutical, petroleum, plastic and other industries. It is often used in the synthetic process of chemical fibers, coatings and lubricating oil additives, unsaturated resin, plasticizer, polyurethane foam, polymer inhibitor, printing ink and so on. Because of the presence of neopentyl structure in neopentyl glycol molecule, the synthetic products with it have excellent hydrolysis resistance, chemical thermal stability, acid and alkali resistance, thermal stability and aging resistance. So, it is mainly used to produce resins, polyester powder coating, surfactant, insulating material, oil-free alkyd resin and so on. Neopentyl glycol is a kind of diol and an excellent solvent, which is easily soluble in water, ketones, ethers, lower alcohols, and aromatic compounds, and can be used for selective separation of naphthenic and aromatic hydrocarbons [1-5].

At present, there are two main methods in producing neopentyl glycol, which are disproportionation process and hydrogenation process. The hydrogenation process has large investment, high requirements for the external environment, and the product price is high. The disproportionation process, also called sodium formate method, can overcome the disadvantages of the above description, and the product price is low. The sodium formate method (disproportionation process) is as follows: (under the certain temperature and pH value, isobutylaldehyde and formaldehyde are condensed to form hydroxy-tert-butylaldehyde in the presence of alkali catalyst. Hydroxy-tert-butylaldehyde is reduced to neopentyl glycol with excess formaldehyde in strong alkali condition, while formaldehyde is oxidized and reacts with alkali to form sodium formate. The reaction solution is neutralized with formic acid, and dehydrated by distillation under reduced pressure, then the concentrated solution is extracted by layers, and after sodium formate is removed, the solution is cooled, crystallized and separated to obtain the finished

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product). The reaction will produce a large amount of sodium formate, which is the main by-product in the neopentyl glycol product. The content of sodium formate directly affects the quality of neopentyl glycol product. Contrasted by the hydrogenation process, the disadvantage of the disproportionation process is that the purity of neopentyl glycol is limited in the process [6-8]. In this production process, the removal and separation of the by-product (sodium formate) determines the purity and quality of neopentyl glycol products. Therefore, it is very important to study the solubility relationship of neopentyl glycol and sodium formate in aqueous solution, but there is no report on the liquid-liquid equilibrium of the ternary system.

In this paper, the dissolution process and liquid-liquid equilibrium relationship of NPG+ HCOONa+H_2O system were studied, and the phase equilibrium data were measured [9-12]. The correlation and rule between the equilibrium data were found out, which provided a theoretical basis for the separation of neopentyl glycol and sodium formate in the disproportionation process.

EXPERIMENTAL

Materials

Neopentyl glycol (NPG) with a purity of 99% by mass was supplied from Guangdong Wengjiang Chemical Reagent Co., Ltd, China. Sodium formate (HCOONa) (analytical reagent, 99.5%) was obtained from Nanjing Chemical Reagent Co., Ltd. China. The NPG and HCOONa were used without additional purification, and deionized water was used. The ultrapure water was prepared for application of liquid chromatography.

Methods

A glass balance vessel was used to carry out the phase equilibrium determinations. The certain amount of the ternary mixture including NPG, HCOONa and water was prepared in the balance vessel. The mixture was placed in a thermostatic bath, and the temperature was controlled constant within ±0.01 °C. At this temperature, the mixture was mixed and dissolved for 1 h. For proper phase separation, the solution was settled for 8 h. After the equilibrium system was divided into two layers, the samples of the upper and lower phase were taken out respectively with syringes.

The samples were weighed and diluted, and then the mass concentration of each component in the processed samples was quantitatively analyzed by liquid chromatography (Dionex, U-3000). The analytical conditions using liquid chromatography were as follows: column temperature: 50 °C; mobile phase: ultrapure water; flow rate: 1mL/min; injection volume: 50 μL; inspection temperature: 50 °C; detector: differential refractive detector.

RESULTS AND DISCUSSION

Phase diagrams

The liquid-liquid equilibrium compositions of the ternary NPG (1) + HCOONa (2) + H_2O (3) system at 303.15, 313.15, 323.15 K were obtained and listed in Table 1. All compositions were expressed by mass fraction, $W_{(i)}$.

It can be seen from the data in Table 1 that the upper phase is the NPG-rich phase and the bottom phase is the salt (HCOONa)-rich phase. The phase diagram of this system (as an example, at 303.15 K) is presented in Figure 1. The binodal curves and tie-line of the two-conjugate phase (through the top and bottom phase points) can be seen from the diagrams. It can be seen from Table 1 and Figure 1 that the addition of sodium formate can cause the stratification of the mixed solution of neopentyl glycol and water, which may be caused by the electrostatic effect of the weak electrolyte sodium formate ions, and the competition result between sodium formate and neopentyl glycol for water molecular. Under the action of the electrostatic field of sodium formate ions, the water molecules with higher dielectric constants gather around them, and the alcohol molecules with lower dielectric constants are driven away. As the ions undergo selective solvation, the free energy of the system and the activity coefficient of each component are changed, which can cause the liquid-liquid equilibrium and phase separation.

Table 1. Experimental phase equilibrium data for the NPG (1) + HCOONa (2) +H_2O (3) at different temperatures.[a]

Temperature (K)	Top phase			Bottom phase			TLL
	$W_{(1)}$	$W_{(2)}$	$W_{(3)}$	$W_{(1)}$	$W_{(2)}$	$W_{(3)}$	
303.15	0.7980	0.0627	0.1393	0.0136	0.4876	0.4988	0.8921
	0.7666	0.0677	0.1657	0.0227	0.4523	0.5250	0.8314
	0.6766	0.0851	0.2383	0.0619	0.3696	0.5685	0.6773
	0.6136	0.1039	0.2825	0.0978	0.3223	0.5799	0.5601
	0.5175	0.1321	0.3304	0.1744	0.2765	0.5491	0.3722
313.15	0.7848	0.0646	0.1507	0.0155	0.4946	0.4899	0.8813
	0.7598	0.0708	0.1694	0.0243	0.4535	0.5223	0.8291
	0.6690	0.0900	0.2410	0.0620	0.3630	0.5750	0.6656
	0.6110	0.1089	0.2800	0.1049	0.3246	0.5705	0.5501
	0.5071	0.1399	0.3530	0.1822	0.2625	0.5553	0.3473
323.15	0.7800	0.0672	0.1528	0.0187	0.4930	0.4882	0.8723
	0.7514	0.0733	0.1753	0.0289	0.4519	0.5192	0.8157
	0.6608	0.0929	0.2462	0.0685	0.3705	0.5610	0.6541
	0.5999	0.1124	0.2877	0.1084	0.3215	0.5701	0.5341
	0.5036	0.1466	0.3498	0.2081	0.2597	0.5322	0.3164

[a]Uncertainties for mass fraction and temperature are 0.0002 and 0.01 K, respectively.

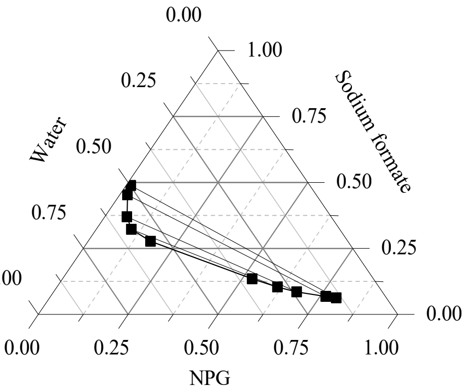

Figure 1. Equilibrium phase diagram of NPG + HCOONa + H_2O at 303.15 K.

Effect of temperature

The effect of temperature on the phase diagram studied is also illustrated in Figure 2. It can be seen from Figures 1, 2 that the overall change trend of the liquid-liquid equilibrium for the ternary mixtures of (NPG+HCOONa+H_2O) is consistent and it is slightly affected by temperature. The binodal curves are seen to be close to each other. Just, when the temperature increased from

303.15 K to 323.15 K, the binodal region is little changed. The locus for the experimental conjugate data shown in Figures 1 and 2 demonstrate that the two-phase area is slightly expanded with a decrease in temperature.

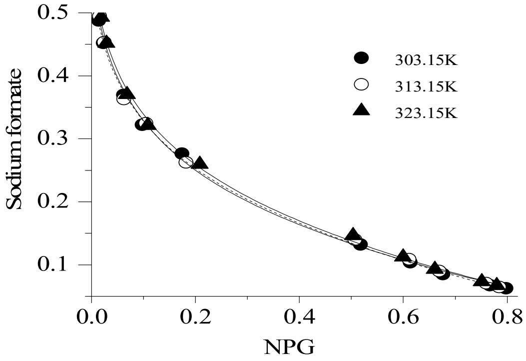

Figure 2. Effect of temperature on the phase diagram and experimental fitting curves for NPG +HCOONa+H_2O system at different temperatures.

For further investigation of the temperature influence on the equilibrium phase compositions for the studied systems, the tie-line length, TLL, at different compositions and temperatures were calculated as follows and collected in the Table 1 [13-16].

$$\mathrm{TLL} = \left[\left(w_{(1)}^{top} - w_{(1)}^{bot}\right)^2 + \left(w_{(2)}^{top} - w_{(2)}^{bot}\right)^2\right]^{0.5} \quad (1)$$

The experimental tie-line obtained by connecting the experimental equilibrium phase composition data are compared in Figure 3, for the temperatures 303.15 K and 323.15 K, as an example. As can be seen from Table 1 and Figure 3, the tie-line length decreases with an increase in temperature. This may be because the concentration of sodium formate in the rich phase increases gradually, and the concentration in the poor phase decreases gradually, while neopentyl glycol is just the opposite. And the concentration change of sodium formate is greater than that of neopentyl glycol.

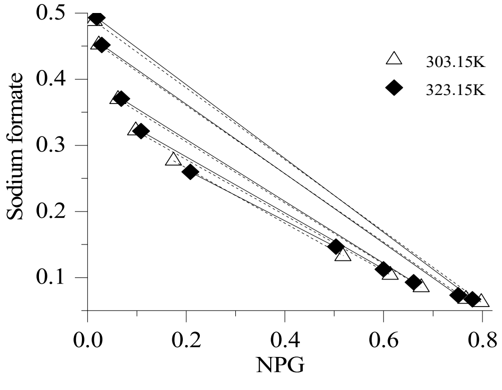

Figure 3. Effect of temperature on the phase diagram and experimental tie-lines at T =303.15 K, 323.15 K.

Estimation of critical point

When the tie-line length becomes shorter and shorter, it finally becomes zero, it is a critical point (plait point), which is somewhere in the binodal curve. At this point, the two liquid phases become identical. The location of plait points for this system at different temperatures was estimated by extrapolation from the auxiliary curves. The form of auxiliary curve is as follows:

$$w_{(2)} = d + ew_{(1)} \tag{2}$$

where d and e represent the fitting parameters, $w_{(1)}$, $w_{(2)}$ represent the mass concentrations of NPG and HCOONa, in the conjugate phase, respectively. The obtained fitting parameters and estimated values for the plait points are listed in Table 2. According to the correlation coefficients, R^2, it can be seen that the studied system was satisfactorily fitted with the linear Eq. (2).

Table 2. Values of parameters of the auxiliary curves and the plait points, for the NPG + HCOONa +H_2O system at different temperatures.

T(K)	d	e	R^2	Plait point ($w_{(1)}$, $w_{(2)}$)
303.15	-0.1322	0.7618	0.9697	(0.3941, 0.1681)
313.15	-0.1693	0.8238	0.9644	(0.4030, 0.1627)
323.15	-0.1712	0.8353	0.9829	(0.4059, 0.1678)

As an example, the locus of estimated critical point for this system along with the used steps is illustrated in Figure 4 at T = 303.15 K.

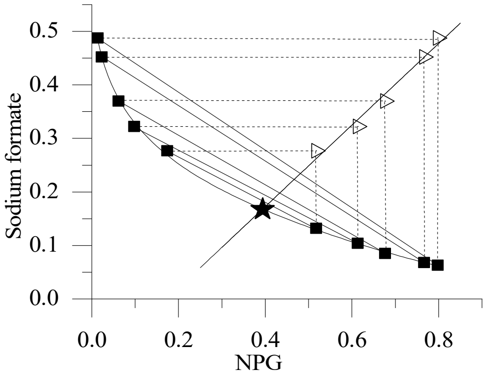

Figure 4. Binodal curve, tie-line and plait point for the NPG + HCOONa + H_2O system at T = 303.15 K, [(★) plait point].

Correlation

In order to study the liquid-liquid equilibrium process of the system, firstly, the experimental data were fitted by least-squares regression method to the expression developed by Merchuk equation (3) and Pirdashti equation (4) [17-19]. These empirical nonlinear equations are expressed as follows:

$$w_{(2)} = a\exp\left(bw_{(1)}{}^{0.5} - cw_{(1)}{}^{3}\right) \tag{3}$$

$$w_{(2)} = \left(a_1 + b_1 w_{(1)}\right)^{\frac{-1}{c_1}} \tag{4}$$

where a, b, c, a_1, b_1 and c_1 are fit parameters, and $w_{(1)}$, $w_{(2)}$ represent the mass concentrations of NPG and HCOONa, respectively. The parameters a, b, c, a_1, b_1, c_1 and correlation coefficient R^2 obtained from the correlation of experimental conjugate data are given in Table 3.

Table 3. Values of the parameters for Eq. (3, 4) for NPG + HCOONa +H_2O system at different temperatures.

Temperature (K)	a	b	c	R^2	Deviation (%)
303.15	0.6059	-1.9371	1.0843	0.9992	0.02
313.15	0.6252	-2.0325	0.8572	0.9984	0.03
323.15	0.6365	-1.9919	0.9585	0.9986	0.03
	a_1	b_1	c_1	R^2	Deviation (%)
303.15	1.5823	5.2268	0.6749	0.9940	0.21
313.15	1.6760	7.2238	0.7903	0.9927	0.25
323.15	1.5904	5.6217	0.7158	0.9924	0.25

On the basis of obtained regression coefficient R^2, compared with equation (4), we conclude the equation (3) can be better satisfactorily used to describe the binodal curves of the NPG + HCOONa + H_2O system. The fitting curves by the equation (3) at different temperatures are shown in Figure 2. It can be seen the equation (3) has been successfully used for the correlation of the equilibrium data.

Then, the correlation equations given by Hand (Eq. 5), Othmer-Tobias (Eq. 6) and Bachman (Eq. 7) have been used to correlate the tie-line compositions [20-23].

$$\log\left(\frac{w_{(3)}^{\mathrm{top}}}{w_{(1)}^{\mathrm{top}}}\right) = f + g\log\left(\frac{w_{(3)}^{\mathrm{bot}}}{w_{(2)}^{\mathrm{bot}}}\right) \tag{5}$$

$$\log\left(\frac{1-w_{(1)}}{w_{(1)}}\right)^{\mathrm{top}} = s + n\log\left(\frac{1-w_{(2)}}{w_{(2)}}\right)^{\mathrm{bot}} \tag{6}$$

$$w_{(1)}{}^{top} = m + k\left(\frac{w_{(1)}{}^{top}}{w_{(3)}{}^{bot}}\right) \tag{7}$$

where f, g, s, n, m and k represent the fitting parameters. Superscripts “top” and “bot” stand for neopentyl glycol rich phase and sodium formate rich phase, respectively. The fitting parameters of the Hand, Othmer-Tobias and Bachman models along with the corresponding correlation coefficient values, R^2, are given in Table 4.

Table 4. Values of the parameters for Eq. (5, 6, 7) for NPG + HCOONa + H_2O system at different temperatures.

Temperature (K)	f	g	R^2	Deviation (%)
303.15	-0.7868	1.8730	0.9856	0.23
313.15	-0.7396	1.6801	0.9741	0.41
323.15	-0.7222	1.7130	0.9848	0.23
	s	n	R^2	Deviation (%)
303.15	-0.6347	1.4005	0.9945	0.08
313.15	-0.5925	1.2588	0.9926	0.11
323.15	-0.5743	1.2392	0.9985	0.02
	m	k	R^2	Deviation (%)
303.15	0.1670	0.4059	0.9538	0.24
313.15	0.1825	0.3899	0.9455	0.28
323.15	0.1589	0.4019	0.9416	0.30

On the basis of the obtained correlation coefficient values, we conclude that it is feasible to describe the liquid–liquid equilibrium of the investigated aqueous two-phase systems with these equations. And, it is satisfactory to assess the reliability of the data with these models. Also based on correlation coefficient values, R, reported in table 4, we conclude that the reported tie-line data have acceptable consistency. Compared with the Hand and Bachman models, the quality of fitting is better with Othmer-Tobias model.

CONCLUSION

Liquid-liquid equilibrium data for the NPG + HCOONa + H_2O system were obtained at T = (303.15, 313.15, and 323.15) K. The phase diagrams of this ternary dissolution system at different temperatures were presented. The effect of temperature on the phase diagram was also studied, and it was observed that the two-phase area is slightly expanded with a decrease in temperature. The location of plait points for this system at different temperatures was estimated by extrapolation from the auxiliary curves. The experimental equilibrium data were satisfactorily fitted with the Merchuk equation, and the fitting curves were in good agreement with the experimental data. Additionally, the Hand, Othmer–Tobias and Bachman models were used for the correlation of the phase behavior of this investigated system. The correlation coefficients showed that the measured tie-line data have good consistency. On the basis of the results obtained, it was found that Othmer–Tobias equation has a good performance in the correlation of the tie-line compositions.

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