Phase Diagrams for Liquid-Liquid Equilibrium of Neopentyl Glycol + Sodium Formate + Water

Yanli, Zhang*[*+]; *Dongguang, Li

Chemistry and Chemical School, Henan University of Technology, Zhengzhou, P.R. CHINA

ABSTRACT: *Phase diagrams for the ternary (neopentyl glycol + sodium formate + water) system were measured. Phase equilibrium data were obtained at different temperatures of 333.15, 343.15, and 353.15 K. The effect of temperature on the liquid–liquid phase equilibrium was studied and the length, and slope of the tie-line at different temperatures for the conjugate phase were investigated. It was found that the tie-line length decreases and the two-phase area is slightly reduced by increasing temperature. The three fitting parameters of the Merchuk and Pirdashti equations were obtained with the temperature dependence expressed in the linear form, respectively. Compared with the Pirdashti equation, the binodal curves were described satisfactorily with the Merchuk equation, further, the plait points at various temperatures were estimated by extrapolation. The Othmer-Tobias and Hand models were used for the correlation of the phase equilibrium behavior. The correlation coefficients of the models were obtained for the corresponding temperatures. The results showed that it was well fitted with the Othmer-Tobias model by contrast with the Hand model.*

KEYWORDS: *Liquid-liquid equilibrium; Liquid Chromatography (LC); Merchuk; Othmer-Tobias.*

INTRODUCTION

Neopentyl glycol is a kind of diol with neopentyl structure, which is easily soluble in water, lower alcohols, ketones, ethers, and aromatic compounds. Neopentyl glycol is an important chemical raw material, which is widely used in the chemical, pharmaceutical, textile, automobile, plastic, and petroleum industries. Due to the presence of neopentyl structure and side group in neopentyl glycol molecule, the synthetic polyester resins with it and other products have excellent chemical thermal stability, acid and alkali resistance, hydrolysis resistance, aging resistance, and thermal stability. So, it is mainly used to produce unsaturated resin, polyester powder coating, polyurethane foam, oil-free alkyd resin, plasticizers, surfactants, insulating material, printing ink, polymer inhibitor, lubricating oil additives and so on. At the same time, neopentyl glycol is an excellent solvent and can be used for selective separation of aromatic and naphthenic hydrocarbons [1-6].

At present, there are two main production methods of neopentyl glycol: hydrogenation process and disproportionation process. The hydrogenation process has high investment, high requirements on external environment and high product price. The disproportionation process (sodium formate (HCOONa) method) overcomes the disadvantages of large investment, and the product price is low. However, compared with the hydrogenation process, the disadvantage is that the purity of neopentyl glycol is limited in the process [7,8].

* *To whom correspondence should be addressed.*
\+ *E-mail: yanli95@126.com*
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The sodium formate method of producing neopentyl glycol refers to the disproportionation reaction of formaldehyde and isobutyraldehyde under alkaline conditions. There are going to be a lot of by-products (sodium formate) in the sodium formate method. So, the purity of neopentyl glycol is limited in the process. The separation and removal of the by-product (sodium formate) from the mixture of neopentyl glycol and sodium formate determine the quality and purity of neopentyl glycol products. Therefore, it is very useful to study the solubility relationship of sodium formate and neopentyl glycol in an aqueous solution, but there is no report on the phase diagram and liquid-liquid equilibrium relation of the ternary system.

In this paper, we have studied the phase diagram, dissolution process and equilibrium relationship of neopentyl glycol + sodium formate + water system [9-13]. The phase equilibrium data were measured, and the correlation and rule of the investigated system were found out [14-16]. These results are not only useful for providing a theoretical basis for the separation of sodium formate and neopentyl glycol in the disproportionation process, but also can be used to develop thermodynamic models of aqueous two-phase systems containing neopentyl glycol and sodium formate.

EXPERIMENTAL SECTION

Materials

The neopentyl glycol (NPG, analytical reagent, 99%) was supplied from Wengjiang Chemical Reagent Co., Ltd, Guangdong, China. The sodium formate (HCOONa) (analytical reagent, 99.5%) was obtained from Nanjing Chemical Reagent Co., Ltd., Nanjing, China. All chemicals were used without further purification. The stock solutions were made by deionized water and their concentrations were ascertained by liquid chromatography.

Apparatus and Procedure

A glass balance vessel (100cm^3) was used to carry out the phase equilibrium determinations. It was placed in a thermostatic bath (DCW-1006, Shunma Instrument Co., Ltd, Nanjing, China), and the temperature was controlled constant within ±0.05°C. A certain amount of the ternary mixtures including neopentyl glycol, sodium formate, and water were prepared in the balance vessel. At a certain temperature, the mixtures were mixed and dissolved for 1 h. For proper phase separation, the solutions were settled for 8 h. When the equilibrium systems were divided into two layers, the samples of the upper and lower phases were taken out respectively with syringes.

Analytical method

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

RESULTS AND DISCUSSION

Phase diagrams

The liquid-liquid equilibrium compositions of the ternary neopentyl glycol (1) + sodium formate (2) + water (3) system at 333.15^{0}K, 343.15^{0}K, 353.15^{0}K were obtained and given in Table 1. All compositions were expressed by mass fraction.

The data in Table 1 show that the upper phase is the neopentyl glycol rich phase and the bottom phase is the salt (sodium formate) rich phase. The phase diagrams of this studied system at various temperatures are presented in Figures 1-3. The binodal curves for neopentyl glycol + sodium formate + water system and tie-lines of the two-conjugate phases (through the top and bottom phase points) can also be seen from the diagrams.

The effect of temperature on the phase diagram is presented in Figure 1-4. It can be seen that the overall change trend of phase equilibrium for the ternary mixtures of neopentyl glycol + sodium formate + water is consistent and it is slightly affected by temperature. These figures show that when the temperature increased from 333.15 ^{0}K to 353.15^{0}K, the binodal curves are seen to be close to each other. On the other hand, when temperature increases up to 353.15 ^{0}K, the region of the binodal is changed. The locus for the experimental conjugate data presented in Figs 1-4 demonstrates that the two-phase area is decreased with an increase in temperature.

For further investigation of the temperature influence, the tie-line length, TLL, and the tie-line slope, S, at different temperatures and compositions, were calculated as follows and listed in Table 1 [17-19].

Table 1: Phase equilibrium binodal data for the neopentyl glycol (1) + sodium formate (2) + water (3) at different temperatures

Temperature(^{0}K)	Top phase			Bottom phase			*TLL*	*S*
	$W_{(1)}$	$W_{(2)}$	$W_{(3)}$	$W_{(1)}$	$W_{(2)}$	$W_{(3)}$		
333.15	0.7943	0.0719	0.1338	0.0186	0.5163	0.4651	0.8940	-0.5729
	0.7475	0.0733	0.1792	0.0380	0.4480	0.5140	0.8024	-0.5281
	0.6618	0.0972	0.2410	0.0757	0.3645	0.5598	0.6442	-0.4561
	0.5902	0.1174	0.2924	0.1195	0.3170	0.5635	0.5113	-0.4240
	0.5432	0.1338	0.3230	0.1579	0.2870	0.5551	0.4146	-0.3976
343.15	0.7854	0.0725	0.1421	0.0188	0.5105	0.4707	0.8829	-0.5714
	0.7310	0.0796	0.1894	0.0562	0.4360	0.5078	0.7631	-0.5282
	0.6403	0.1197	0.2400	0.0821	0.3602	0.5577	0.6078	-0.4308
	0.5466	0.1391	0.3143	0.1303	0.3104	0.5593	0.4502	-0.4115
	0.4835	0.1654	0.3511	0.1698	0.2628	0.5674	0.3285	-0.3105
353.15	0.7525	0.0882	0.1593	0.0324	0.5002	0.4674	0.8296	-0.5721
	0.6899	0.1047	0.2054	0.0588	0.4343	0.5069	0.7120	-0.5223
	0.5727	0.1351	0.2922	0.1115	0.3501	0.5384	0.5089	-0.4662
	0.5061	0.1568	0.3371	0.1550	0.3148	0.5302	0.3850	-0.4500
	0.4555	0.1802	0.3643	0.2359	0.2701	0.4940	0.2373	-0.4094

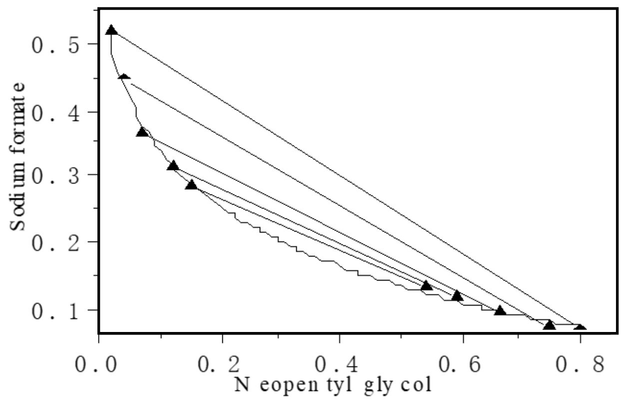

Fig. 1: Phase diagram of neopentyl glycol + sodium formate + water at 333.15K

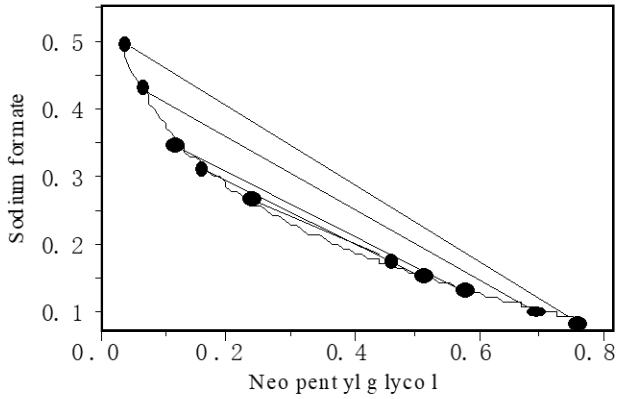

Fig. 3: Phase diagram of neopentyl glycol + sodium formate + water at 353.15K

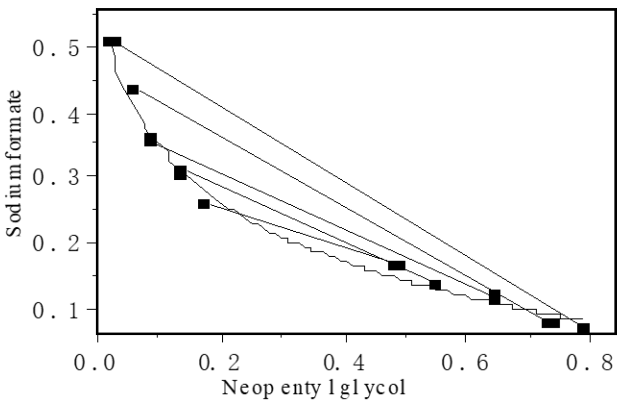

Fig. 2: Phase diagram of neopentyl glycol + sodium formate + water at 343.15K

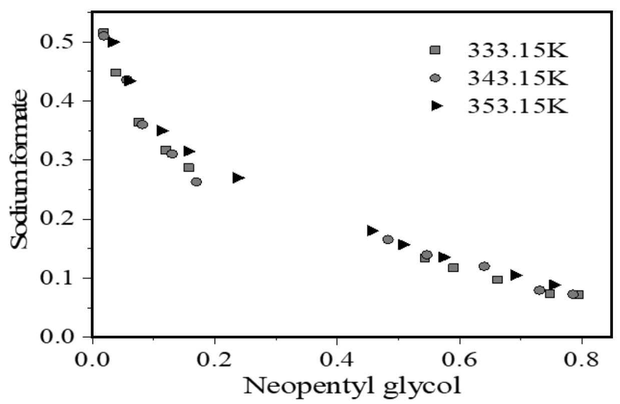

Fig. 4: Effect of temperature on the phase diagram of neopentyl glycol + sodium formate + water

Table 2: Estimated values of the plait point and parameters of the auxiliary curves for the neopentyl glycol + sodium formate +water system

T (K)	a	b	R^2	Plait point ($w_{(1)}$, $w_{(2)}$)
333.15	0.8932	-0.2096	0.9706	(0.4131, 0.1594)
343.15	0.7804	-0.1214	0.9682	(0.3829, 0.1774)
353.15	0.7441	-0.0691	0.9888	(0.3658, 0.2031)

Table 3: Values of the parameters of equation (4, 5) for neopentyl glycol + sodium formate +water system

Temperature (K)	c	d	e	R^2	f	g	h	R^2
333.15	0.6911	-2.2243	0.5222	0.9982	1.6669	9.7122	0.9029	0.9941
343.15	0.6874	-2.1465	0.4717	0.9888	1.7406	11.4429	1.0029	0.9850
353.15	0.7078	-2.0072	0.7077	0.9976	1.5616	5.5642	0.7762	0.9872

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

$$S = (w_{(2)}^{top} - w_{(2)}^{bot})/(w_{(1)}^{top} - w_{(1)}^{bot}) \quad (2)$$

These two parameters are often used to reflect the concentration difference between the top and bottom phase components in liquid-liquid equilibrium. Table 1 shows that an increase in temperature decreased the tie-line length and increased the tie-line slope. This may be because the concentration of neopentyl glycol in the rich phase decreases gradually, and the concentration in the poor phase increases gradually, while sodium formate is just the opposite. And the concentration change of sodium formate is greater than that of neopentyl glycol.

Estimation of plait point

As the length of tie-line becomes shorter and shorter, it finally becomes zero, it is a plait point (critical point), which is somewhere in the binodal curve. At this point, the two liquid phases merge into one phase. The locations of plait points for the studied system at various temperatures were estimated by extrapolation of the auxiliary curves, which are satisfactorily fitted with the following linear form:

$$w_{(2)} = b + aw_{(1)} \quad (3)$$

where a and b represent the fitting parameters, $w_{(1)}$, $w_{(2)}$ represent the mass concentrations of neopentyl glycol and sodium formate, in the conjugate phase, respectively. The estimated values of the plait point at different temperatures along with the obtained fitting parameters for equation (3), and the correlation coefficients (R^2) are listed in Table 2. From the correlation coefficients (R^2), the studied system was satisfactorily fitted by the linear equation (3).

As an example, the locus of estimated plait point for this studied system along with the used steps is illustrated in Figure 5 at T = 353.15 K.

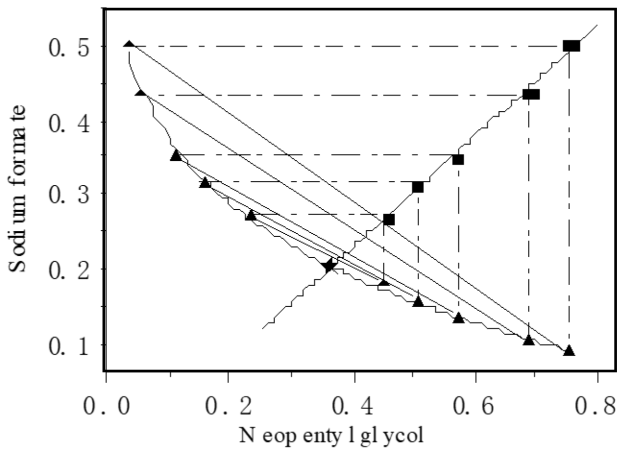

Fig. 5: Binodal curve, tie-lines and plait point of neopentyl glycol + sodium formate + water at T = 353.15^{0}K, {(★) plait point}

Correlation

In order to research the phase equilibrium process of the neopentyl glycol + sodium formate + water system, firstly, the binodal data were fitted with the Merchuk Equation (4), Pirdashti Equation (5) developed by the least-squares regression method [20-23]. These empirical nonlinear equations have the following forms, respectively:

$$w_{(2)} = c\exp\left(dw_{(1)}{}^{0.5} - ew_{(1)}{}^3\right) \quad (4)$$

$$w_{(2)} = (f + gw_{(1)})^{\frac{-1}{h}} \quad (5)$$

where c, d, e, f, g and h are fit parameters, and $w_{(1)}$, $w_{(2)}$ represent the mass concentrations of neopentyl glycol and sodium formate, respectively. The parameters c, d, e, f, g, h and correlation coefficient R^2 obtained from the experimental conjugate data are listed in Table 3. Compared with Equation (5), the correlation coefficients (R^2) indicate that Equation (4) can be better successfully used to correlate the binodal curves of the neopentyl glycol + sodium formate + water system.

Table 4: Values of the parameters for equation (6,7) for (neopentyl glycol + sodium formate +water) system at different temperatures

Temperature(⁰K)	a_1	b_1	R^2	a_2	b_2	R^2
333.15	1.6243	-0.7121	0.9902	1.2170	-0.5679	0.9934
343.15	1.6566	-0.6955	0.9826	1.3124	-0.5587	0.9903
353.15	1.9875	-0.6367	0.9877	1.3425	-0.4876	0.9940

Then, for the correlation of LLE data of (neopentyl glycol + sodium formate + water) system, the Hand (equation 6) and Othmer-Tobias (equation 7) models have been developed [24-27].

$$\log\left(\frac{w_{(3)}^{top}}{w_{(1)}^{top}}\right) = b_1 + a_1\log\left(\frac{w_{(3)}^{bot}}{w_{(2)}^{bot}}\right) \quad (6)$$

$$\log\left(\frac{1-w_{(1)}}{w_{(1)}}\right)^{top} = b_2 + a_2\log\left(\frac{1-w_{(2)}}{w_{(2)}}\right)^{bot} \quad (7)$$

where a_1, b_1, a_2 and b_2 represent the fitting parameters. Superscripts "top" and "bot" stand for neopentyl glycol rich phase and sodium formate rich phase, respectively. The corresponding correlation coefficient values, R^2, and the fitting parameters are given in Table 4. On the basis of the obtained correlation coefficient values, we conclude that the equation (6) and (7) can be satisfactorily used to correlate the liquid–liquid equilibrium of the investigated system. And, it is feasible to assess the reliability of the tie-line data with these models. Compared with the Hand model, the Othmer-Tobias model has a better performance in the correlation.

CONCLUSIONS

Liquid-liquid equilibrium data for the neopentyl glycol + sodium formate + water system were obtained at T= (333.15, 343.15, and 353.15) ⁰K. The phase diagrams and binodal curves of this ternary dissolve system at various temperatures were presented. It was found that the tie-line length decreases and the two-phase area is slightly reduced by increasing temperature. The locations of plait points for the investigated system were estimated by extrapolation with the auxiliary curves. It was observed that the fitting curves are in good agreement with the experimental equilibrium data with the Merchuk equation. Additionally, the Hand and Othmer–Tobias models were used to correlate the equilibrium data. According to the results obtained, it was found that the fitting quality is better with the Othmer–Tobias model.

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