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LIQUID-LIQUID EQUILIBRIUM IN BINARY GLYCOLS-TOLUENE AND GLYCOLS-XYLENE SYSTEMS

Lumír MANDÍK and František LEŠEK

Research Institute of Synthetic Resins and Lacquers, 532 07 Pardubice

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Liquid-liquid equilibria were determined in the following binary systems: 1,2-ethandiol/toluene, 1,2-bthandiol/xylene, 1,2-propandiol/xylene, 1,4-butandiol/yylene, 1,3-butandiol/toluene, 1,3-butandiol/yene, 1,3-butandiol/yene, 2,2'-dioxydiethanol/toluene, 2,2'-dioxydiethanol/xylene. The solubility of 2,2-dimethyl-1,3-propandiol in benzene, toluene and xylene was also measured. Critical solubility temperatures at atmospheric pressure were determined for systems containing 1,2-propandiol and 1,3-butandiol.

Existing studies on mutual solubilities in binary glycols/aromatic hydrocarbon systems are limited almost exclusively to systems containing glycols and benzene. Staveley and Milward¹ have measured 1,2-ethandiol/benzene, 1,2-propandiol/benzene, 1,4-butandiol/benzene, 1,5-prentandiol/benzene and 1,6-hexandiol/benzene systems. It follows from their data on mutual solubilities of the same glycols and cyclohexane, resp. heptane, that the mutual solubility in glycols//paraffin, resp. glycols/cycloparaffin systems is substantially lower than in glycols/aromate systems. It 1,2-ethandiol/benzene and 2,2'-dioxydiethanol/benzene systems have been measured by Koennecke and coworkers², the 1,2-propandiol/benzene systems by Palit and McBain³. The 2,2'-dioxydiethanol/benzene systems together with the corresponding ternary systems were investigated by Johnson and Francis⁴. Critical solubility temperatures for some of the above systems are reported in the monograph by Timmermans⁵. The possibility to use glycols as the third component for separating aliphatic from aromatic hydrocarbons by extractive distillation has been proposed, *e.g.*, by Wichterle and Mertl⁶. The knowledge of liquid-liquid, resp. vapour-liquid equilibria of the above mentioned systems is desirable for the preparation of both saturated and unsaturated polyesters by azeotropic polyesterification⁷.

Our study was aimed at finding the mutual solubility in glycol/aromate systems for those glycols, which are being preferably employed as main alcohol components during the preparation of unsaturated polyesters. Our solubility measurements were performed between approximately 30°C and temperatures close to the boiling point of the aromatic component at atmospheric pressure.

EXPERIMENTAL

Properties of Glycols

1,2-Ethandiol (ethylene glycol, EG): a pure grade product of Lachema, Brno, was dried with pure CaO and then rectified in vacuum over fresh sodium; $n_D^{55} = 1.43063$, density at 25°C, $\rho^{25} = 1.43063$

= 1·1099 gcm⁻³; 1,2-propandiol (1,2-propylene glycol, 1,2-PG): a pure grade product of Lachema, Brno, was dried by pure Na₂SO₄ and, after decantation, rectified in vacuum; $n_D^{2.5} = 1 \cdot 133242$, $e^{2.5} = 1 \cdot 0323$ gcm⁻³; 1,4-butandiol (1,4-butylene glycol, 1,4-BD): a product of Merck FRG, was rectified in vacuum; $e^{2.5} = 1 \cdot 0127$ gcm⁻³; 1,3-butandiol (1,3-butylene glycol, 1,3-BD); a product of BASF, FRG, was not purified at all, its hydroxyl number was 1 238 mg KOH/g); $e^{2.5} = 1 \cdot 0042$ gcm⁻³; 2,2'-dioxydiethanol (diethylene glycol, DEG): a technical grade product of Slovnaft, Bratislava, was rectified in vacuum; $e^{2.5} = 1 \cdot 1122$ gcm⁻³; 2,2-dioxydiethanol (diethylene glycol, DEG): a technical grade product of Slovnaft, Bratislava, was rectified in vacuum; $e^{2.5} = 1 \cdot 1122$ gcm⁻³; 2,2-dioxydiethanol (diethylene glycol, DEG): a technical grade product of Slovnaft, Bratislava, was rectified in vacuum; $e^{2.5} = 1 \cdot 1122$ gcm⁻³; 2,2-dioxydiethanol (diethylene glycol, DEG): a technical grade product of Slovnaft, Bratislava, was rectified in vacuum; $e^{2.5} = 1 \cdot 1122$ gcm⁻³; 2,2-dioxydiethanol (diethylene glycol, DEG): a technical grade product of BASF, FRG, was not purified; it contained 0.87 wt.% H₂O as determined by the Fischer method.

The content of water in all the glycols except neopentyl glycol, as determined by the Fischer method, did not exceed 0.1 wt.%.

Properties of Aromates

Benzene: an A.R. grade product (ČSN 68-6051) of Lachema, Brno, was not purified.

Toluene: an A.R. grade product (ČSN 68-6724) of Lachema, Brno, was dried with metallic sodium before use and then rectified over sodium; $e^{25} = 0.8622 \text{ gcm}^{-3}$.

Xylene: a product of Lachema, Brno, was not purified before use. The gas chromatographic analysis indicated *o*-xylene 15, *m*- and *p*-xylene 55, and ethylbenzene 30 wt.%; $e^{25} = 0.8584$ gcm⁻³.

p-Xylene: a product of Slovnaft, Bratislava, was not purified further. The gas chromatographic analysis indicated 99.7 wt.% of p-xylene; $a^{20} = 0.8611$ gcm⁻³.

To enable an easy comparison, the properties of glycols and aromates found in the literature⁸ are given in Table I. It is obvious that our experimental data agree well with those reported in the literature.

Measurements

Solubilities were determined in a 500 ml triple-neck round flask connected to a cooler with a glass agitator passing through its center. The temperature was determined by a thermometer working

Glycol, resp. aromate	ϱ , g cm ⁻³	n _D
1.2-Ethandiol	1·1133 (25/25°C)	1·4306 (20°C)
1.2-Propandiol	1.0381 (20/20°C)	1·4326 (20°C)
1.4-Butandiol	1.012-1.016 (25°C)	1·4435-1·4445 (25°C
1.3-Butandiol	1.0062 (20/20°C)	1·4401 (20°C)
2,2'-Dioxydiethanol	1·1161 (20°C)	1·4475 (20°C)
Toluene	0·867 (20/4°C)	1·497 (20°C)
<i>p</i> -xylene	0.861 (20/4°C)	1·496 (20°C)

TABLE I

Densities and refractive indexes of glycols and aromated investigated

in the range $0-150^{\circ}$ C, which was preliminarily calibrated against accurate standards. The flasks with their contents were heated by an electric jacket heating.

The flask was filled with 200-300 g of one component (a glycol or an aromate) and then the second component was being added during an intensive agitation. After the initial addition of the solvent, the mixture was heated up to $80-100^{\circ}$ C until the solution became clear and then it was allowed to cool down slowly and agitated. The temperature was recorded as soon as first signs of turbidity appeared. Then it was raised again just to remove the turbidity and the cooling process and recording of the turbidity temperature were repeated. After the correction according to the calibration curve, this temperature was taken to be the turbidity temperature. In this manner, the dependence of mutual solubilities of the components was investigated along one branch of the binodal curve.

In the next step, the same flask was filled with 200-300 g of the second solvent and that solvent was subsequently being added in corresponding amounts, which was during the first measurement placed initially into the flask. In this manner, the second branch of the binodal curve was obtained.

In some cases, transparent drops of glycols appeared during the addition of glycols to aromate³ and they did not merge with the solution until the temperature was raised to approximately 100°C, even though the amount of the glycol added was small or the turbidity temperature was rather low (below 60°C). This phenomenon points to high cohesive forces inside the glycol phase. The accuracy of the determination of the turbidity temperature was $\pm 0.3^{\circ}$ C. The difference in the determination of the turbidity temperature between two persons was $0.5 - 1.0^{\circ}$ C, however, it was a systematic deviation, which could be eliminated by using identical standard samples.

RESULTS AND CONCLUSIONS

The relation between the turbidity temperature, t (°C), and the system composition; w_1 , resp. w_2 (wt.% of the component added to the system), is given in Table II. For 2,2'-dioxydiethanol, its common commercial name diethylene glycol is being used.

Systems investigated in our study belong to those types, where significant interactions appear between molecules of the same component, *i.e.*, glycols. Hydrogen atoms in glycol hydroxyl groups create strong cohesive bonds and this manifests itself already in the difficult mechanical dispersibility of glycols in the aromatic component. Another interaction, which decreases the effect of the cohesive bonds between the individual glycol molecules, is the possibility of the formation of hydrogen bonds between the proton of the glycol OH-group and π -electrons in the double bond of the aromatic nucleus. This phenomenon accounts for the increase of solubilities of the individual aromates in glycols in the series xylene < toluene < benzene. Due to this reason, a thermodynamic description of binary glycols/aromate systems is almost impossible and therefore we must work with experimentally determined phase diagrams, which (for measurements at atmospheric pressure) form only in some cases the complete binodal curve with the critical solution temperature.

This curve could be determined by the experimental procedure outlined only for the following systems: 1,2-propandiol/toluene, 1,2-propandiol/xylene, 1,3-butandiol/toluene, 1,3-butandiol/xylene, and 1,3-butandiol/p-xylene. Both glycols are

TABLE II

Relation between the turbidity temperature, l (°C), and the system composition, w. The symbol w_1 , resp. w_2 , denotes wt.% of the component added to the solution

Value					S	ystem								
		1,2-ethandiol(1)-toluene(2)												
w ₂ t	3·20 42·5	3·47 52·4	3·74 61·3	4·01 69·5	4·27 77·1	4·53 83·8	4·80 90·5	5·32 100·0	5·83 106·8					
$\frac{w_1}{t}$	0·30 53·0	0∙60 70∙4	0-83 77-9	1·10 86·4	1·37 92·1	1∙64 96∙4	1∙90 99∙8	2·17 103·4	2·44 106·2	2·70 108·5				
				1,2-6	ethandiol(1)-xylen	e(2)							
w ₂ t	1∙69 51∙4	1∙86 58∙5	2·02 67·2	2·19 74·3	2·35 81·5	2·53 87·2	2·84 96·4	3·16 106·8	3·48 110·9	3·80 117·6				
w ₂ t	4·12 125·4	4·44 130·6	4·75 133·8											
$\frac{w_1}{t}$	0∙05 33∙6	0·17 45·7	0·28 52·4	0·55 70·2	0·83 83·7	1·10 95·4	1·37 105·2	1.64 113.2	1.64 117.6					
$\frac{w_1}{t}$	2·17 121·2	2-44 123-8	2·96 127·3	4·00 131·6	5·01 133·2									
				1,2-p	ropandiol	(1)-tolue	ne(2)							
w2 t	11·9 32·1	12·4 36·1	12·9 40·2	13·4 43·7	14·5 49·8	15·2 54·5	16·0 57·5	17·2 63·6	18·2 69·2					
w ₂ t	19·5 71·8	21·7 77·9	23·7 84·5	26∙6 90∙3	29-3 93-3	32·6 95·5	35-6 98-8	38·3 100·6	40·9 102·1					
w ₁ t	0·52 35·1	1·03 47·3	1·53 56·9	2·02 61·0	2·52 65·6	3·01 69·7	3·97 75·9	4·91 80·5	7·19 87·7					
w ₁ 1	8·51 90·8	10∙60 94∙5	12·60 96·9	14∙6 98∙0	18·2 101·1	21·5 103·1	24·6 104·7	28·7 105·7	32·5 106·6					
w ₁ t	36·2 107·0	40-2 107-1	45·3 106·5	50·8 150·4	56·4 103·8		•							

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(Continued)

Value					Sy	stem							
		1,2-propandiol(1)-xylene(2)											
w ₂	7·62	8·20	8·78	9·35	9·91	10∙50	11∙5	12·6	14·2				
t	37·1	44·7	50·8	56·9	60·5	64∙6	70∙7	76·9	85·0				
w ₂	15·4	16∙6	17·8	18∙9	21·1	23·2	25·2	27·1	28·9				
t	89·7	94∙0	96·9	99∙5	105·3	108·8	111·7	114·0	116·1				
w ₂ t	30∙6 117∙6	32·2 118·7	35·5 121·3	38·2 122·5									
t^{w_1}	0·51	1·02	1·27	2·27	2·76	4·20	5∙60	6∙96	8·29				
	37·6	52·9	56·4	71·2	76·4	87·1	93∙8	99∙5	107·1				
w ₁	9·36	11·0	13·0	15·3	18·8	21·2	26·5	31·7	36·2				
t	107·2 -	110·6	114·0	115·5	118·6	120·3	122·3	123·6	124·4				
t^{w_1}	41·2 124·9	45·2 125·1	50·8 125·0	56·3 124·2	58·2 123·7								
	1,4-butandiol(1)-toluene(2)												
w ₂	10·2	11·9	12·4	13·2	13·9	14·7	15·9	17·1					
t	33·0	61·3	66·5	75·6	83·0	89·4	99·5	107·2					
$\frac{w_1}{t}$	0·25	0·50	0·75	1·00	1·23	1·74	2·23	2·71	3·42				
	31·0	45·2	53·4	62·0	66·5	76·8	83·9	90·1	97·4				
v_1	4·35 105·5	5·27 111·4	6·17 116·1										
				1,4-1	outandiol	(1)-xylen	e(2)						
w ₂	7∙90	8·63	9·34	10∙0	10∙7	11·4	12·1	12·7	13·4				
t	60∙0	73·2	83·9	91∙6	98∙4	104·5	109·9	115·0	119·2				
w ₂ t	14·2 124·4	15∙0 128∙5	15·9 132·7										
w_1	0·25	0·50	0·75	1·00	1·25	1·49	1∙98	2·47	2∙95				
	36·6	52·2	62·0	70·2	76·8	81·5	90∙6	97·4	103∙6				
w_1	3·42	3·89	4·35	4·81	5·27	5·72	6·61	7∙49					
t	107·7	111·9	115·0	118·1	120·8	123·3	127·8	131∙6					

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TABLE II
(Continued)

Value					Sys	stem					
		1,3-butandiol(1)-toluene(2)									
w ₂ t	12·2 34·1	12·9 38·6	13·9 44·5	15·1 50·6	16∙6 57∙1	18·4 64·6	20·1 67·8	22·0 73·2	24-0 77-4		
w ₂ t	26·2 81·5	28·5 84·8	31-1 88-4	34∙0 90∙9	37∙6 93∙5	42·3 95·5	48∙7 97∙0	56·9 98·0			
w ₁ t	1·00 42·3	1·09 45·0	1·29 47·8	2·11 56·2	2·59 60·5	3·30 65·8	4·23 71·3	5∙59 77∙0	7·35 82·2		
w _i t	9∙45 86∙5	11∙9 90∙2	14·9 83·1	18∙8 95∙0	20∙9 96∙8	28·1 98·0	39·1 98·5	53·3 97·8			
				1,3-8	outandiol	(1)-xylene	(2)				
w ₂ t	9·09 35·3	9·81 42·2	10∙5 48∙0	11·6 54·5	12·9 62·4	14·5 69·6	16·1 75·3	17·9 81·5	19·9 87·0	22·1 91·8	
w2 t	24·1 95·5	26∙6 98∙4	29·9 103·6	33·0 107·5	43-0 110-8	54∙3 113∙0					
w ₁ t	0∙65 40∙5	0∙86 48∙6	1·29 56·4	1·71 64·2	2·13 70·3	2.76 75.5	3·57 81·5	4·77 87·8	6∙51 94∙0	9·1 100·2	
w ₁ t	12·5 105·0	18·2 109·5	26·1 112·3	39·6 113·2	52·2 112·3						
				1,3-b	utandiol(1)-p-xylen	ie(2)				
w ₂ t	9·01 36·8	9·72 43·5	10·8 51·4	11·8 58·2	13·1 65·5	14·7 72·6	16·5 79·4	19∙0 86∙0	20·7 91·3		
w ₂ t	23·4 96·6	27·0 102·0	32·3 107·4	40·9 112·6	52·9 114·5						
w1 1	0·75 42·4	0·99 52·1	1·24 55·0	1·72 60·4	2·45 72·6	3·16 78·1	4·09 84·2	5∙47 89∙5	7∙44 95∙8		
w ₁ t	10·35 101·8	14·2 106·8	19∙4 110∙5	26·8 113·4	38·2 114·5	52·8 114·3					

TA (Cont	BLE II inued)									
Value					System	n				
				diethy	lene glyco	ol(1)-tolue	ene(2)			
w2	16.4	16.9	17.4	17.8	18.3	19.0	19.4	20.1	21.2	22.3
t	33.5	43.2	54.4	60.2	67.1	72.8	78.9	83-9	90.1	94.4
Wa	22.9	23.7	24.3	24.9						
t	97.9	100.7	103-2	105-2						
Ws	1.64	2.18	2.70	3.23	3.75	4.26	5.02	5.76	6.98	8.17
ť	35.5	48.8	57-4	66-6	72-2	76.4	81-9	86-2	92.7	97 ∙5
w ₁	9.56	10.9	12.2	14.3						
t	102.4	106.7	109.8	113.0						
				diethy	lene glyce	ol(1)-xyle	ne(2)			
Wo	9.3	10.2	11.0	11.8	12.4	12.9	13.7	14.4	15.2	15.7
ı Î	54-4	64.6	78-9	87.6	95.4	100.5	106.8	111.9	116-1	121.2
Wa	16.1	16.6	17.1	17.6	18.0					
1 [°]	123.8	126.9	129.6	131.6	133.8					
<i>W</i> ,	0.55	1.10	1.64	2.18	2.71	3.23	3.75	4.26	4.77	5.77
t	32.0	51.3	63-5	74.3	81.5	87.7	92.2	97.7	102-1	108.8
w.	6.26	6.75	7.23	7.71	8.18	8.64	9.11	9.56	10.02	
1	112.4	114.5	117-3	119.7	121.2	124.4	125.9	128.0	130.6	

compounds, which possess one primary and one secondary alcohol group. The solubility of aromates in these systems is higher than that of their isomers with both primary alcohol groups.

It follows from the data on neopentyl glycol/aromate systems reported in Table III that the neopentyl glycol/toluene and neopentyl glycol/xylene systems exhibit analogous dependences of the mutual solubility reaching the critical solution temperature on the binodal curves (Table IV). Since the melting point of neopentyl glycol (128° C) (ref.⁸) lies above the boiling point of toluene and only $7-16^{\circ}$ C below the boiling point of xylene isomers, the high-temperature branch of the binodal curve was not investigated.

It also follows from the solubility measurements of *p*-xylene and the mixture of xylene isomers (so called xylene), that differences between their solubilities, *e.g.*, in 1,3-butandiol, are insignificant, resp. they are within the range of experimental error. This is obvious from the following interpolation of our data in the temperature range $40-100^{\circ}$ C:

TABLE III

Solubilities of neopentyl glycol in benzene, toluene and xylene

Benzene		Tolu	iene	Xylene		
NPG % mass	t turb. °C	NPG % mass	NPG t turb. NP % mass °C % m		t turb. °C	
3.21	33.5	1.77	35-1	1.20	32.0	
6.16	39.5	3.09	41.2	1.47	35-1	
9.75	43.1	5.92	49.3	2.65	46.3	
13.03	44-6	9.71	54.44	4.25	5 2 ·9	
16-17	45-4	12-45	56-8	6-06	59-0	
20.97	46.5	18.44	58-8	7.42	61-4	
25.42	47.0	23.33	59.5	10.23	65-2	
30.11	47.3	28.86	59.5	12.67	67-5	
33.60	47.5	33.70	58-2	16.97	69-8	
37.72	48-0	_	_	21.90	70.3	
40.35	48.6	_	-	25.64	69-5	
43.01	48.9	-	_		_	

TABLE IV

Critical solution temperatures (°C)

Glycol	benzene	ref.	toluene	ref.	xylene	ref.	p-xylene
1.2-Ethandiol	_	_	210	5	_	_	
1.2-Propandiol	79.8	3	107.2		125-1	_	_
1,3-Butandiol	_		98-5	_	133-3		114.5
Diethylene glycol		_	134.0	5	162·0 ^a	5	_
Triethylene glycol	_	_	90.0	5	120·0 ^a	5	-
Neopentyl glycol	49∙0	-	59.5	-	70.3		_

a m-Xylene.

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Turbidity temperature °C	40	50	60	70	80	90	100
xylene, wt.% in the solution	9.7	11.0	12.3	14.4	17.3	21.3	27.2
p-xylene, wt.% in the solution	9.5	10.7	12.0	13.7	16.5	20.2	25.7

No satisfactory correlation between the turbidity temperature and the system composition could be found along the binodal curves, resp. along their separate branches.

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