

LIQUID-LIQUID EQUILIBRIUM OF TERNARY SYSTEMS WATER-GLYCOL-AROMATIC HYDROCARBON

František LEŠEK, Josef EICHLER and Miroslav BALCAR

*Research Institute of Synthetic Resins and Lacquers,
532 07 Pardubice*

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By using the method of determining cloud point, the liquid-liquid equilibria of the systems water-1,2-propanediol-toluene, water-1,2-propanediol-xylene, water-1,3-butanediol-toluene and water-1,3-butanediol-xylene were measured within the range of 40°C up to azeotropic points at atmospheric pressure. The solubility of the hydrocarbons w_3 in the glycols has increased with temperature t according to the relation $w_3 = (A - Bt)^{-1}$, where A and B have been functions of water content in the glycols. The solubility of the water(1)-glycol(2) binary system in the hydrocarbons has increased with temperature according to the relation $(w_1 + w_2) = C \exp(Dt)$. The decrease of mutual solubilities of toluene or xylene in aqueous 1,2-propanediol or 1,3-butanediol was found experimentally to be proportional to the increasing content of water in glycols.

The studies published hitherto on mutual solubilities in ternary systems water-glycol-aromatic hydrocarbon are limited to two references¹: Johnson and Francis² have dealt with mutual solubility of components in the system water-2,2'-dioxidiethanol (diethylene glycol)-benzene and Francis³ has reported a triangle diagram for the system water-1,2-ethanediol-benzene. From practical insolubility of aromatic hydrocarbons in water it is possible to assume an expressive reduction of solubility of aromatic hydrocarbons in glycols if the glycols contain an amount of water. This factor comes forward *e.g.* in preparing saturated and unsaturated polyesters by azeotropic polyesterification⁴ when either aqueous or hydrocarbon phase of distillate is returned into the reactor or column above reactor, when it turns out that even the temperature of reflux and consequently its composition have an effect on the separation efficiency of dephlegmation devices above reactor⁵.

Our work has aimed at mutual solubility of the systems water-glycol-aromatic hydrocarbon for those basic types of glycols reaching their critical solution temperature⁶ under atmospheric pressure in the binary systems glycol-aromatic hydrocarbon. The measurement of solubilities was carried out by determining cloud point from about 40°C to the the temperature close to the temperatures of azeotropic points of the water-aromatic hydrocarbon binary systems or the water-glycol-aromatic hydrocarbon ternary systems, respectively, under atmospheric pressure.

EXPERIMENTAL

Chemicals Used

1,2-Propanediol (1,2-propylene glycol, 1,2-PG): a product supplied by Lachema Brno as pure was not further purified. Its hydroxyl number was 1 452 mg KOH/g (theoretical value 1 472 mg KOH/g), it contained 0.21 mass % water as determined by the Fischer method, the 1,2-PG content as determined by gas chromatography was 99%, $\rho^{25} = 1.0320 \text{ g cm}^{-3}$.

1,3-Butanediol (1,3-butylene glycol, 1,3-BD): a product supplied by BASF (West Germany) was not further purified. Its hydroxyl number amounted to 1 238 mg KOH/g (theoretical value 1 245.5 mg KOH/g), and it contained 0.07 mass % water as determined by the Fischer method, $\rho^{25} = 1.0042 \text{ g cm}^{-3}$.

Toluene: a product supplied by Lachema, Brno, corresponded to ČSN 68-6724, A.R. grade, was not further purified, $\rho^{25} = 0.8622 \text{ g cm}^{-3}$.

Xylene: a product supplied by Lachema, Brno, A.R. grade, contained according to a gas-chromatographic analysis approximately 15 mass % *o*-xylene, 55 mass % *m*- and *p*-xylene and about 30 mass% ethylbenzene. It was not further purified, $\rho^{25} = 0.8584 \text{ g cm}^{-3}$.

Procedure

The determination of solubilities was carried out similarly to that in foregoing study⁶, *i.e.* by determining the temperature of cloud point t (°C). As a starting charge served either 200 g glycol which contained water, to which toluene or xylene was added or 200 g toluene or xylene to which a glycol with different content of water was added. So, *e.g.*, with water content g_1 3.21 mass % in 1,2-propanediol, 6 g (± 0.05 g) water was added to the starting amount of 194 g (± 0.1 g) glycol. The water content in initial glycol is subject to an error of the method of determination ($\pm 0.05 \div 0.10$ mass %), whereas for the water addition we considered an error of ± 0.05 g. In this way it is possible to separate the two sources of errors which may manifest themselves more expressively when expressing the water content in the binary system water-glycol in terms of mol% especially at low water contents.

RESULTS AND CONCLUSIONS

When determining the mutual solubilities, the method⁷ was employed which is recommended for multicomponent systems when one pair of components is replaced by a one-component reference medium or a quantity, and in this way, *e.g.*, a four-component system is transferred to a three-component one. In our study, the solution of water in a glycol is considered as one component; the advantage of this way arises above all when estimating graphically the effect of water on the solubility of toluene or xylene in glycol as it is evident from Fig. 1 for the system water-1,3-butanediol-toluene. From the dependence of solubilities of single components on temperature as it is given, *e.g.*, in Table I for the system of 1,3-butanediol with 2.07 mass % water-toluene, the solubilities were interpolated at the reference temperatures of 40, 50, ... °C by a graphical way; the result of these interpolations is presented in Tables II–V. In this way, a great number of experimental data was reduced

to an acceptable extent. The graphical comparison of results led to the conclusion that, from the point of view of the dependence of solubilities of individual components on temperature, there exist two different functional regions, viz. 1) the region of hyper-

TABLE I

The relation between the cloud point temperature t ($^{\circ}\text{C}$) and composition of system w^a (mass %) in the system water(1)–1,3-butanediol(2)–toluene(3)

w_3	12.17	12.83	13.81	15.08	16.61	18.38	
t	45	49	54.5	60	66.5	72.5	
w_3	20.35	22.49	24.76	27.13	29.79	33.43	38.74
t	78.5	83.5	87.5	91.5	95	98	101.5
$w_1 + w_2$	0.65	0.84	1.19	1.72	2.91	3.85	4.76
t	34	39	47.5	56.5	68	74.5	79.5
$w_1 + w_2$	7.98	9.90	13.04	16.67			
t	87	93	99	101.5			

^a The symbol w_3 or $(w_1 + w_2)$ denotes mass % of the component which was added to the system.

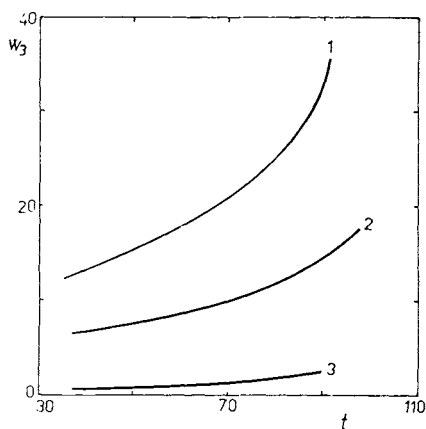


FIG. 1

The solubility w_3 (mass %) of toluene in the system water(1)–1,3-butanediol(2) as a function of temperature t ($^{\circ}\text{C}$). Curves 1 0.07, 2 10.06, 3 50.035 mass % water in 1,3-butanediol

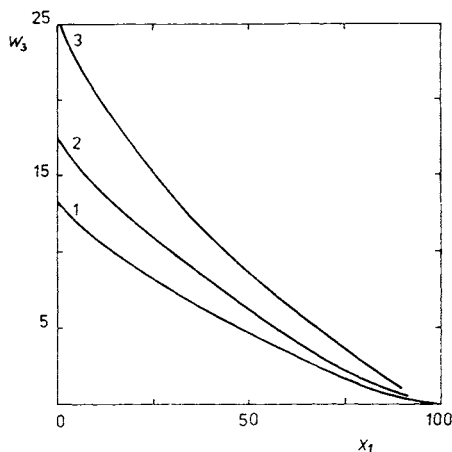


FIG. 2

The solubility w_3 (mass %) of toluene in the system water(1)–1,3-butanediol(2) as a function of x_1 (mol %) of water in 1,3-butanediol. Curves 1 40, 2 60, 3 80 $^{\circ}\text{C}$

bolic dependence of solubility of toluene or xylene in aqueous glycol on temperature,
 2) the region of exponential dependence of solubility of aqueous glycol in toluene or xylene on temperature.

TABLE II

The relation between the interpolated cloud point temperatures t (°C) and interpolated composition w (mass %) of the ternary system water(1)–1,2-propanediol(2)–toluene(3)

t	Toluene added to 1,2-PG; w_1/w_3 given, water content (mass %) in 1,2-PG:			
	0·21	1·21	2·21	3·21
40	0·18/14·0	1·06/12·7	1·95/11·6	2·86/10·6
50	0·18/15·8	1·03/14·5	1·92/13·2	2·82/11·9
60	0·17/18·0	1·01/16·6	1·87/15·2	2·76/13·7
70	0·16/21·0	0·98/19·2	1·82/17·6	2·69/16·0
80	0·16/24·9	0·94/22·4	1·75/20·8	2·60/18·7
90	0·14/31·8	0·88/27·6	1·66/25·3	2·47/22·8
100	0·11/46·6	0·78/36·3	1·50/32·0	2·28/28·8
t	1,2-PG added to toluene; w_1/w_2 given, water content (mass %) in 1,2-PG:			
	0·21	2·21	5·20	10·19
40	0·01/0·69	0·01/0·65	0·03/0·50	0·04/0·41
50	0·01/1·20	0·01/0·97	0·05/0·83	0·075/0·68
60	0·01/1·92	0·01/1·60	0·07/1·31	0·11/1·03
70	0·01/2·99	0·01/2·49	0·10/1·90	0·17/1·53
80	0·01/4·59	0·01/4·02	0·15/2·83	0·25/2·25
90	0·02/8·08	0·01/6·46	0·24/4·45	0·39/3·49
100	0·02/14·47	0·02/11·00	—	—

TABLE III

The relation between the interpolated cloud point temperatures t ($^{\circ}\text{C}$) and interpolated composition w (mass %) of the ternary system water(1)-1,2-propanediol(2)-xylene(3)

t	Xylene added to 1,2-PG; w_1/w_3 given, water content (mass %) in 1,2-PG:			
	0.21	1.21	2.21	3.21
40	0.19/9.6	1.11/8.5	2.04/7.7	2.98/7.0
50	0.19/10.8	1.09/9.6	2.02/8.4	2.94/8.0
60	0.18/12.2	1.08/10.8	1.99/9.8	2.91/9.15
70	0.18/14.1	1.06/12.4	1.96/11.4	2.86/10.5
80	0.17/16.6	1.04/14.4	1.91/13.4	2.81/12.2
90	0.17/19.8	1.00/17.1	1.85/16.0	2.74/14.3
100	0.16/24.7	0.96/21.0	1.78/19.4	2.66/17.0
110	0.14/32.4	0.89/26.5	1.67/24.3	2.52/21.1
120	—	0.76/27.0	1.49/32.5	2.30/28.2

	5.20	10.19	25.16	50.10
40	4.89/5.9	9.86/3.3	24.9/1.2	49.9/0.35
50	4.85/6.7	9.82/3.7	24.85/1.4	49.9/0.4
60	4.80/7.6	9.77/4.25	24.8/1.6	49.85/0.5
70	4.74/8.8	9.69/4.95	24.75/1.8	49.8/0.57
80	4.66/10.3	9.61/5.8	24.7/2.1	49.7/0.75
90	4.57/12.2	9.51/6.8	24.55/2.55	49.6/1.0
100	4.43/14.8	9.38/8.0	—	—
110	4.26/18.0	—	—	—

1,2-PG added to xylene; w_1/w_2 given, water content (mass %) in 1,2-PG:					
	0.21	2.21	5.20	10.19	20.17
40	0.01/0.53	0.01/0.48	—	—	0.08/0.33
50	0.01/0.85	0.02/0.77	0.03/0.68	—	0.12/0.51
60	0.01/1.40	0.02/1.22	0.05/1.04	0.09/0.90	0.18/0.72
70	0.01/2.05	0.03/1.84	0.07/1.50	0.14/1.30	0.24/1.01
80	0.01/2.04	0.04/2.65	0.12/2.33	0.20/1.90	0.34/1.34
90	0.01/4.42	0.08/3.90	0.17/3.30	0.28/2.57	0.47/1.92
100	0.01/6.88	0.12/5.80	0.24/4.72	0.40/4.72	—
110	0.02/10.95	0.17/8.81	0.34/6.40	—	—
120	0.04/21.75	0.29/14.65	—	—	—

Solubility of Toluene or Xylene in Aqueous Glycols

In addition to the relation $Y = w_3 = (A - BX)^{-1} = (A - Bt)^{-1}$, the dependence of w_3 on temperature t (and in a derived way also on w_1) was checked by means of five further models for it was not possible to assume that the only functional

TABLE IV

The relation between the interpolated cloud point temperatures t (°C) and interpolated composition w (mass %) of the ternary system water(1)–1,3-butanediol(2)–toluene(3)

t	Toluene added to 1,3-BD; w_1/w_3 given, water content (mass %) in 1,3-BD:				
	0.07	1.07	2.07	3.07	
40	0.07/13.1	0.94/12.2	1.83/11.4	2.76/10.2	
50	0.06/15.0	0.92/13.8	1.80/13.0	2.71/11.7	
60	0.06/17.5	0.90/16.1	1.76/15.0	2.65/13.6	
70	0.06/20.7	0.87/18.9	1.71/17.5	2.58/16.1	
80	0.05/25.3	0.83/22.7	1.63/21.0	2.48/19.2	
90	0.05/33.0	0.76/28.5	1.53/26.2	2.34/23.8	
100	—	0.62/41.6	1.34/35.5	2.10/31.5	
	5.07	10.06	25.05	50.035	
40	4.62/8.8	9.39/6.7	24.35/2.8	49.63/0.8	
50	4.55/10.2	9.30/7.6	24.25/3.2	49.58/0.9	
60	4.46/12.0	9.18/8.7	24.10/3.8	49.48/1.1	
70	4.26/14.0	9.04/10.1	23.95/4.4	49.33/1.4	
80	4.22/16.6	8.88/11.8	23.75/5.2	49.08/1.9	
90	4.06/19.9	8.61/14.4	—	—	
	1,3-BD added to toluene; w_1/w_2 given, water content (mass %) in 1,3-BD:				
	0.07	2.07	5.07	10.06	20.05
40	0.01/0.88	0.02/0.77	0.04/0.70	0.05/0.46	0.05/0.22
50	0.01/1.60	0.02/1.19	0.05/1.03	0.09/0.79	0.08/0.35
60	0.01/2.48	0.04/1.94	0.08/1.56	0.14/1.22	0.19/0.75
70	0.01/4.10	0.06/3.12	0.13/2.42	0.21/1.93	0.34/1.35
80	0.01/6.68	0.10/4.85	0.22/4.11	0.35/3.10	0.53/2.09
90	—	0.17/8.57	0.35/6.70	0.52/4.66	—

model⁸ would comply with the entire region studied. The following models were considered:

$$1) Y = A + BX \quad (1)$$

$$2) Y = A \exp(BX) \quad (2)$$

$$3) Y = AX^B \quad (3)$$

$$4) Y = A + B/X \quad (4)$$

$$5) Y = (A - BX)^{-1} \quad (5)$$

$$6) Y = X/(A + BX). \quad (6)$$

In Eqs (1)–(6), Y denotes the value of w_3 , mass % hydrocarbon in the water–glycol–hydrocarbon ternary system or the value of $(w_1 + w_2)$ mass % water and glycol, respectively, in the same ternary system when dissolving a glycol in an aromatic hydrocarbon. Considering the dependence of solubility on temperature, X denotes the temperature of the cloud point t ($^{\circ}\text{C}$), considering the dependence of solubility of either an aromate in an aqueous glycol or an aqueous glycol in an aromate on the water content, X corresponds either to g_1 , mass % water in the corresponding binary water–glycol or x_1 , mol % water in the same binary system.

Model (5) appeared to be optimum for the solubility of both toluene and xylene in glycols with water content 0–25 mass %, at higher water content, model (2) was equivalent to model (5). The values of the coefficients A and B for the toluene content in 1,3-butanediol and model (5) are given in Table VI. It is evident here that $A = f(g_1)$ or $A = f(x_1)$ and analogously also $B = f(g_1)$ or $B = f(x_1)$ apply, respectively. The numerical evaluation of the dependence of coefficients A and B on g_1 and x_1 showed that a more accurate correlation, measured by the value of correlation coefficient r , was reached in terms of the functions $A = f(g_1)$ and $B = f(g_1)$, respectively, these functions having been described best by model (2). The values of coefficients C, D, E, F in terms of Eqs (7) and (8)

$$A = C \exp(Dg_1), \quad (7)$$

$$B = E \exp(Fg_1), \quad (8)$$

including the correlation coefficients r and standard deviations s are given in Table VII. It follows from the graphical comparison of solubilities of toluene in 1,3-butanediol with mol content of water x_1 and mass content of water g_1 at the reference temperatures of 40, 60, and 80 $^{\circ}\text{C}$ (Fig. 2) that the solubility of toluene and xylene

in both the glycols decreases extremely with the water content in glycol. By extrapolating the experimental data to 100 mol % water in the binary system water-glycol,

TABLE V

The relation between the interpolated cloud point temperatures t (°C) and interpolated composition w (mass %) of the ternary system water(1)–1,3-butanediol(2)–xylene(3)

t	Xylene added to 1,3-BD; w_1/w_3 given, water content (mass %) in 1,3-BD:				
	0.07	1.07	2.07	3.07	
40	0.06/9.6	0.98/8.8	1.91/7.9	2.84/7.4	
50	0.06/10.8	0.97/9.8	1.88/9.0	2.81/8.4	
60	0.06/12.5	0.95/11.4	1.85/10.4	2.77/9.7	
70	0.06/14.6	0.93/13.2	1.82/12.3	2.72/11.4	
80	0.05/17.4	0.90/15.8	1.76/14.9	2.65/13.6	
90	0.05/21.2	0.86/19.2	1.70/18.0	2.57/16.4	
100	0.05/26.8	0.81/23.9	1.60/22.8	2.44/20.6	
110	0.04/40.0	0.72/32.8	1.46/29.3	2.27/26.0	
	5.07	10.06	25.05	50.035	
40	4.75/6.4	9.67/3.9	24.71/1.35	49.83/0.40	
50	4.69/7.4	9.61/3.5	24.65/1.6	49.78/0.50	
60	4.64/8.5	9.55/5.1	24.56/1.95	49.71/0.65	
70	4.57/9.9	9.46/6.0	24.49/2.25	49.61/0.85	
80	4.47/11.8	9.34/7.2	24.39/2.65	39.51/1.05	
90	4.35/14.2	9.17/8.8	24.24/3.25	49.33/1.40	
100	4.20/17.1	9.05/10.0	—	—	
110	4.00/21.2	—	—	—	
1,3-BD added to xylene; w_1/w_2 given, water content (mass %) in 1,3-BD:					
	0.07	2.07	5.07	10.06	20.05
40	0.01/0.74	0.01/0.60	0.02/0.48	0.04/0.40	0.07/0.28
50	0.01/1.10	0.02/0.92	0.04/0.76	0.07/0.68	0.13/0.51
60	0.01/1.66	0.03/1.42	0.05/1.05	0.10/0.99	0.20/0.86
70	0.01/2.45	0.04/2.10	0.10/1.88	0.18/1.68	0.34/1.35
80	0.01/3.72	0.07/3.30	0.15/3.02	0.28/2.50	0.47/1.88
90	0.01/5.75	0.10/5.10	0.23/4.37	0.36/3.28	0.62/2.52
100	0.02/9.45	0.16/8.10	0.34/6.42	0.49/4.46	0.82/3.30

we obtain the solubilities of toluene and xylene in water which are identical with the published data⁹.

TABLE VI

The values^a of coefficients A and B in the equation $w_3 = (A - Bt)^{-1}$ for the solubility of toluene in 1,3-butanediol, the corresponding values of correlation coefficients r and standard deviations s

g_1	x_1	A	$B \cdot 10^4$	r	s
0.07	0.35	0.1135	9.276	0.9996	0.6619
1.07	5.14	0.1193	9.393	0.9998	0.4122
2.07	8.90	0.1255	9.747	0.9997	0.4145
3.07	13.68	0.1350	10.339	0.9998	0.2338
5.07	21.09	0.1531	11.477	0.9987	0.2731
10.06	35.89	0.2139	16.224	0.9984	0.2398
25.05	66.15	0.5386	43.576	0.9963	0.1370
50.035	83.37	2.0914	195.674	0.9981	0.0375

^a The units of A and B correspond to w_3 in mass % and t in °C.

TABLE VII

The values of coefficients in correlations for the solubility of toluene and xylene, respectively, in 1,2-propanediol and 1,3-butanediol, respectively, in dependence on the water content g_1 (mass %) in glycol and the values of corresponding correlation coefficients r and standard deviations s

$A = C \exp(Dg_1)$	C	D	r	s
Toluene-1,2-PG	0.10990	0.05276	0.9967	0.0939
Xylene-1,2-PG	0.16011	0.06753	0.9904	0.3120
Toluene-1,3-BD	0.11397	0.05900	0.9993	0.0403
Xylene-1,3-BD	0.15742	0.06553	0.9952	0.1895

$B = E \exp(Fg_1)$	E	F	r	s
Toluene-1,2-PG	0.00081	0.06618	0.9986	0.0005
Xylene-1,2-PG	0.00111	0.07075	0.9925	0.0023
Toluene-1,3-BD	0.00087	0.06243	0.9995	0.0001
Xylene-1,3-BD	0.00115	0.06969	0.9968	0.0012

The data in Tables II–V have made it possible to employ multiple regression for direct correlation of solubilities of toluene and xylene with temperature and the water content in glycol. As a result we obtained relations (9)–(12): Toluene in 1,2-PG

$$w_3 = 7.0620x_1^{0.106} \exp(0.0158t - 0.0407x_1). \quad (9)$$

Xylene in 1,2-PG

$$w_3 = 28.9306t^{-0.567}x_1^{0.097} \exp(0.0243t - 0.0436x_1). \quad (10)$$

Toluene in 1,3-BD

$$w_3 = 6.9776x_1^{0.0945} \exp(0.0163t - 0.0347x_1). \quad (11)$$

Xylene in 1,3-BD

$$w_3 = 4.7358x_1^{0.0971} \exp(0.0173t - 0.0386x_1). \quad (12)$$

The statistical characteristics of these relations are given in Table VIII. The possibility of sufficiently accurate correlation of solubilities is evident from them even in terms of the interpolated data from Tables II–V. In addition to models (1)–(6), the polynomial model in the form

$$w_3 = G + Ht + Jt^2 + Kt^3 + Lt^4 \quad (13a)$$

TABLE VIII

Statistical characteristics of Eqs (9)–(12) and (13)–(16)

Relation	N^a	r^b	F -test	s^c
(9)	40	0.995	1 311.6	0.100
(10)	48	0.998	2 295.4	0.079
(11)	40	0.981	309.7	0.187
(12)	48	0.992	853.6	0.139
(13)	24	0.998	1 402.9	0.060
(14)	28	0.997	1 199.4	0.058
(15)	25	0.993	739.2	0.102
(16)	35	0.996	1 051.6	0.079

^a Number of experimental points; ^b multiple correlation coefficient; ^c standard deviation for $\ln w_3$ (Eqs (9)–(12)), or for $\ln(w_1 + w_2)$ (Eqs (13)–(16)), respectively.

was also checked. This model has yielded relations correlating the solubility of toluene and xylene in glycols with temperature better than *e.g.* model (5) or (2) but the values of the coefficients $G - L$ have not made it possible to correlate the solubilities of aromates with the water content, which has been the decisive priority of model (5).

Solubility of Aqueous Glycols in Toluene or Xylene

Unlike the determination of solubilities of toluene or xylene in aqueous 1,2-propanediol or 1,3-butanediol, the cloud point method enabled to obtain consistent data of solubilities only to the maximum content of 25 mass % water in glycol. On cooling the solutions, heated to their boiling points, the separation of drops on the walls of flask took place without disappearing the turbidity in glycol, and the disappearance of turbidity at the water content exceeding 20 mass % took place at temperatures below 40°C within 8–24 hours if the solubility of aqueous glycol in aromatic hydrocarbon was measured.

The change of the water and glycol content ($w_1 + w_2$) in an aromate with temperature could be described best in the entire range (0–25 mass %) of water by model (2),

$$(w_1 + w_2) = M \exp(Nt).$$

The values of the coefficients M , N , r and s are presented in Table IX for the ternary system water–1,3-butanediol–toluene. It is evident from the table that a correlation between the parameter ($w_1 + w_2$) and the water content in glycol cannot be derived

TABLE IX

The values of coefficients M and N in the equation $(w_1 + w_2) = M \exp(Nt)$ for the solubility of aqueous 1,3-butanediol in toluene and the values of corresponding correlation coefficients r and standard deviations s

g_1	x_1	$M \cdot 10^2$ mass %	$N \cdot 10^2$	r	s
0.07	0.35	8.418	5.553	0.9895	3.800
1.07	5.14	11.531	4.894	0.9922	1.832
2.07	8.90	13.552	4.561	0.9986	1.262
5.07	21.09	10.343	4.654	0.9996	0.137
10.06	35.89	8.542	4.628	0.9961	0.122
15.06	46.90	12.437	3.987	0.9902	0.291
20.05	55.67	2.200	6.011	0.9889	0.216
25.05	66.15	5.480	5.408	0.9870	0.160

from the values M and N . This conclusion has held for the other three ternary systems, too. It follows from the graphical correlation for the reference temperatures of 40, 60 and 80°C in the ternary system water–1,3-butanediol–toluene (Fig. 3) that unlike Fig. 2 we do not attain, by extrapolating to 100 mol % content of water in glycol, the solubilities of water in aromates which would agree with the published data⁹.

From the data in Tables II–V it was possible to derive equations analogous to Eqs (9)–(12). The validity of these equations extends, however, only within the concentrations w_1 given in Tables II–V:

1,2-PG in toluene:

$$(w_1 + w_2) = 0.1299x_1^{-0.0337} \exp(0.0448t - 0.0142x_1). \quad (13b)$$

1,2-PG in xylene:

$$(w_1 + w_2) = 0.1428x_1^{-0.0361} \exp(0.0381t - 0.0074x_1). \quad (14)$$

1,3-BD in toluene:

$$(w_1 + w_2) = 0.1277 \exp(0.0493t - 0.0182x_1). \quad (15)$$

1,3-BD in xylene:

$$(w_1 + w_2) = 0.0080t^{0.885}x_1^{-0.0289} \exp(0.0283t - 0.00746x_1). \quad (16)$$

The statistical characteristics of Eqs (13)–(16) are given in Table VIII. It is possible to state that Eqs (13)–(16) are as to their value, comparable to Eqs (9)–(12).

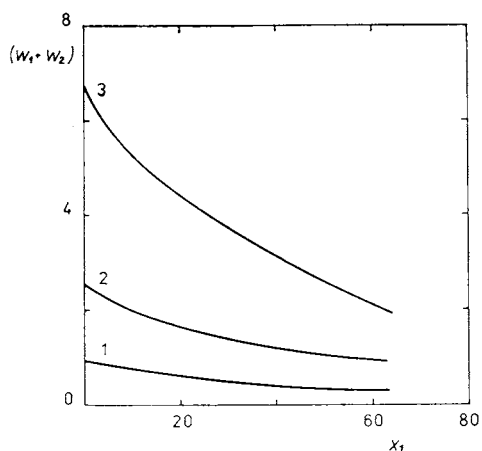


FIG. 3

The solubility $w_1 + w_2$ (mass %) of aqueous 1,3-butanediol in toluene as a function of x_1 (mol %) of water in 1,3-butanediol. Curves 1 40, 2 60, 3 80°C

*Critical Solution Temperature of the Ternary Systems
Water–Glycol–Aromatic Hydrocarbon*

It was determined graphically that the presence of 1 mass % water in glycol increases the critical solution temperature t_c of systems 1,2-propanediol–toluene or xylene and 1,3-butanediol–toluene or xylene approximately by 5°C. At higher water content, the increase in the critical temperature under atmospheric conditions (101.1 kPa) is limited by the azeotropic temperature of the systems which is 84.5°C for the binary system water–toluene and approximately 93°C for the binary system water–xylene. To attain complete solubility of both phases at higher contents of water, it would be necessary to use a pressure apparatus. The hypothetical critical solution temperature t_c of the systems under higher mass % water could be determined from the condition $dw_3/dt = d(w_1 + w_2)/dt = 0$ at t_c or $w_3(t_c) = (100 - w_1 - w_2) t_c$ but the determination of the cloud point temperature t in the vicinity of azeotropic temperature of system was subject to the highest error, which also reflected in a number of cases on the highest deviation of the theoretical values t from those measured experimentally regardless of the fact whether the model $w_3 = (A - Bt)^{-1}$ or $(w_1 + w_2) = M \exp(Nt)$ was used.

Despite that water and glycols pertain to the same group of Ewell's classification of liquids¹⁰ (1st group, i.e. the liquids with pronounced formation of three-dimensional structures through hydrogen bonds), the decrease in solubility of aromatic hydrocarbons with increasing water content in glycol is still more conspicuous than that corresponding to the molar ratio of water in the binary system water–1,2-propanediol or water–1,3-butanediol. The data obtained from the measurements of solubilities can be employed even for estimating the activity coefficients needed for calculating vapour–liquid equilibria^{11,12} in ternary systems with limited mutual solubilities of single binary systems.

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