

# VAPOUR-LIQUID EQUILIBRIUM IN BINARY WATER-1,2-PROPYLENE GLYCOL, WATER-DIETHYLENE GLYCOL AND WATER-1,4-BUTANDIOL SYSTEMS

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Vapour-liquid equilibrium in binary water-1,2-propylene glycol, water-diethylene glycol and water-1,4-butandiol systems was determined in Othmer's apparatus at atmospheric pressure and at a pressure of  $13.3 \pm 0.3 \cdot 10^3$  Pa. Constants  $A_{1-2}$  and  $A_{2-1}$  in Margules equations were found by extrapolation. Deviations from the ideal behaviour were established.

Glycols are chemical substances with extensive industrial use. They belong to main reaction components during preparation of both saturated and unsaturated polyesters and the knowledge of the vapour-liquid equilibrium in glycol-water systems is the starting point for an effective design of separation of both components, representing simultaneously an important moment in design of drying of the gases by removing their moisture in absorbers containing diethylene glycol as the drying medium. So far, only vapour-liquid equilibrium data of the binary water-ethylene glycol system have been published<sup>1</sup>, for other binaries the ideal behaviour of systems according to Raoult's law was being assumed as suggested by apparent physical affinity of glycols and water<sup>2,3</sup>.

## EXPERIMENTAL

*Materials used.* Demineralized water from the demineralizing VÚSPL unit was being employed. Commercial glycols were distilled before use at a pressure of  $13.3 \pm 0.3 \cdot 10^3$  Pa; first fractions as well as tails in the distillation flask in the amount of 5 and 20 wt. %, respectively, were dismissed. Physical constants of employed middle fractions are given in Table I.

*Apparatus.* Experimental determinations of the equilibria were being performed on a modified Othmer's still<sup>4</sup>, concentrations of glycols in the feed, distillates and tails were being determined refractometrically on a Zeiss refractometer at 20°C. Dependences of refractive indexes on concentrations of glycols are given in Table II.

*Methods.* The apparatus was filled with approximately 170 ml of the sample and the liquid was heated to its boiling point with the help of a glass spiral containing a resistance heating. The intensity of boiling was maintained by a variable voltage transformer at approximately 45-60 drops of the condensate/min. The phase equilibrium was established in a usual manner,

which was followed by determination of the liquid composition in the condensate receiver ( $y$ ) and in the distilling flask ( $x$ ). Measurements at the pressure of  $13.3 \pm 0.3 \cdot 10^3$  Pa differed from those at atmospheric pressure only by connection of the condenser to a vacuumeter, manostat, and oil vacuum pump. Experimental determinations of the equilibrium in solutions with low amounts of glycols did not present any difficulties, however, experiments at  $x_{\text{H}_2\text{O}} \rightarrow 0$  were extremely difficult and loaded with large errors, because even with boiling chips in the boiling flask of the apparatus, irregular boiling and bumping occurred and the condensed vapour phase became contaminated with the liquid phase both at atmospheric pressure and at vacuum. Results of all measurements are given in Table III.

TABLE I  
Physical Constants of Pure Glycols (middle fractions)

Property	1,2-Propylene glycol	Diethylene glycol	1,4-Butandiol
Molecular weight	76.09	106.12	90.12
Density, kg/l (25°C)	1.0383	0.9905	1.0106
Boiling point, °C (760 Torr)	187.5	202.4	226.5
Refractive index, $n_D^{20}$	1.4327	1.4470	1.4420
Content of water	traces	traces	traces

TABLE II  
Dependence of Refractive Indexes  $n_D^{20}$  on the Concentration of Glycol (wt. %) in the Glycol-Water Mixture

Propylene glycol	$n_D^{20}$	Diethylene glycol	$n_D^{20}$	1,4-Butandiol	$n_D^{20}$
0.00	1.3329	0.00	1.3331	0.00	1.3329
4.57	1.3388	11.16	1.3461	10.29	1.3406
10.04	1.3441	20.75	1.3570	19.85	1.3520
19.92	1.3554	32.19	1.3710	26.72	1.3604
37.87	1.3766	42.96	1.3845	39.88	1.3767
40.67	1.3790	52.24	1.3958	48.93	1.3878
48.51	1.3880	62.20	1.4080	60.19	1.4010
58.12	1.3987	71.91	1.4192	71.06	1.4136
69.30	1.4084	81.25	1.4290	79.42	1.4228
80.04	1.4177	90.75	1.4385	89.94	1.4330
90.58	1.4256	100.00	1.4470	100.00	1.4420
00.00	1.4327				

TABLE III

Vapour-Liquid Equilibria in Water-Glycol Binary Systems (in mole fractions)

Feed		Liquid phase		Vapour phase		Mixture B.p., °C
glycol	water	glycol	water	glycol	water	
Propylene glycol, 98.6 kPa						
0.810	0.190	0.875	0.125	0.190	0.810	141.0
0.772	0.228	0.865	0.135	0.107	0.893	138.0
0.720	0.280	0.770	0.230	0.063	0.937	130.6
0.690	0.310	0.720	0.280	0.055	0.945	125.5
0.631	0.369	0.653	0.347	0.042	0.958	120.0
0.570	0.430	0.618	0.382	0.035	0.965	117.5
0.492	0.508	0.549	0.451	0.023	0.977	111.4
0.427	0.573	0.460	0.540	0.020	0.980	109.2
0.350	0.650	0.380	0.620	0.016	0.984	106.5
0.277	0.723	0.304	0.696	0.010	0.990	104.4
0.210	0.790	0.227	0.773	0.008	0.992	102.5
0.090	0.910	0.105	0.895	0.006	0.994	100.2
Propylene glycol, 13.3 ± 0.3 kPa						
0.770	0.230	0.750	0.250	0.342	0.658	92.5
0.750	0.250	0.720	0.280	0.156	0.844	82.0
0.670	0.330	0.573	0.427	0.046	0.954	72.3
0.573	0.427	0.595	0.405	0.026	0.974	66.0
0.490	0.510	0.485	0.515	0.015	0.985	60.9
0.405	0.595	0.410	0.590	0.012	0.988	58.1
0.355	0.645	0.340	0.660	0.010	0.990	55.9
0.203	0.797	0.250	0.750	0.009	0.991	51.0
0.101	0.899	0.161	0.839	0.007	0.993	50.0
Diethylene glycol, 99.3 kPa						
0.604	0.316	0.830	0.170	0.0043	0.9957	116.0
0.615	0.385	0.756	0.244	0.0042	0.9958	114.5
0.506	0.494	0.669	0.331	0.0032	0.9968	110.0
0.424	0.576	0.572	0.428	0.0026	0.9974	107.5
0.303	0.697	0.331	0.669	0.0011	0.9989	103.1
0.216	0.784	0.254	0.746	0.0010	0.9990	102.2
0.155	0.845	0.185	0.815	0.0006	0.9994	101.0
0.145	0.855	0.181	0.819	0.0005	0.9995	100.5
0.109	0.891	0.127	0.873	0.0004	0.9996	100.3
0.074	0.926	0.082	0.918	0.0003	0.9997	100.2
0.045	0.955	0.048	0.952	0.0002	0.9998	100.1

TABLE III  
(continued)

Feed		Liquid phase		Vapour phase		Mixture B.p., °C
glycol	water	glycol	water	glycol	water	
Diethylene glycol, 13.3 ± 0.3 kPa						
0.803	0.197	0.885	0.115	0.0072	0.9928	76.2
0.718	0.282	0.803	0.197	0.0048	0.9952	71.5
0.604	0.396	0.693	0.307	0.0017	0.9983	64.0
0.423	0.577	0.483	0.517	0.0010	0.9990	56.7
0.296	0.704	0.323	0.677	0.0008	0.9992	53.0
0.215	0.785	0.246	0.754	0.0006	0.9994	51.3
0.157	0.843	0.164	0.836	0.0005	0.9995	49.0
0.113	0.887	0.119	0.881	0.0004	0.9996	48.7
0.076	0.924	0.077	0.923	0.0003	0.9997	48.3
0.045	0.955	0.048	0.952	0.0002	0.9998	47.7
1,4-Butandiol, 99.3 kPa						
0.643	0.357	0.758	0.242	0.0024	0.9976	106.0
0.475	0.525	0.583	0.417	0.0018	0.9982	104.1
0.468	0.532	0.494	0.506	0.0016	0.9984	103.0
0.334	0.666	0.408	0.592	0.0011	0.9989	102.1
0.232	0.768	0.234	0.726	0.0009	0.9991	101.5
0.182	0.818	0.202	0.798	0.0006	0.9994	101.1
0.125	0.875	0.138	0.862	0.0004	0.9996	100.8
0.081	0.919	0.090	0.910	0.0004	0.9996	100.5
0.048	0.952	0.0505	0.9495	0.0003	0.9997	100.3
0.024	0.976	0.025	0.975	0.0002	0.9998	100.1
1,4-Butandiol, 13.3 ± 0.3 kPa						
0.643	0.357	0.758	0.242	0.0083	0.9917	58.0
0.451	0.549	0.618	0.382	0.0019	0.9981	55.1
0.334	0.666	0.430	0.570	0.0009	0.9991	51.0
0.244	0.756	0.280	0.720	0.0009	0.9991	47.5
0.177	0.823	0.216	0.784	0.0006	0.9994	47.2
0.124	0.876	0.156	0.844	0.0004	0.9996	47.0
0.0825	0.9175	0.114	0.886	0.0004	0.9996	46.5
0.048	0.952	0.0495	0.9505	0.0003	0.9997	46.0
0.023	0.977	0.026	0.974	0.0002	0.9998	45.7

## RESULTS AND DISCUSSION

As stated above, an ideal behaviour in accordance with Raoult's law could be expected for the studied systems. In that case, values of the activity coefficients in the relations

$$Py_1 = \gamma_1 P_1 x_1 \quad \text{resp.} \quad (1)$$

$$Py_2 = \gamma_2 P_2 x_2 \quad (2)$$

should be equal or close to unity. Necessary calculations were performed by using values from the measured vapour-liquid equilibria or, in the case of ethylene glycol and water, from tabulated data<sup>1</sup>. The Calingaert-Davis equation

$$\ln P_1, \text{ resp. } \ln P_2 = A - B/(230 + t) \quad (3)$$

was employed for interpolation resp. extrapolation of tabulated saturated vapour pressures<sup>2</sup> of pure components. The values of constants  $A$  and  $B$  are given in Table IV, their substitution into Eq. (3) leads to values of saturated vapour pressures in Torr, which is in agreement with original data<sup>2</sup>. According to the following equations

$$x_1 \rightarrow 0 \quad \log \gamma_1 = A_{1-2}, \quad (4)$$

$$x_2 \rightarrow 0 \quad \log \gamma_2 = A_{2-1}, \quad (5)$$

values of the activity coefficients  $\gamma_1$ , resp.  $\gamma_2$  yield constants  $A_{1-2}$  and  $A_{2-1}$  in the Margules equations. A calculation of constants  $A_{1-2}$  and  $A_{2-1}$  in the Margules equations from

$$A_{1-2} = \log \gamma_1/x_2^2 + 2x_1[\log \gamma_2/x_1^2 - (\log \gamma_1/x_2^2)] \quad (6)$$

$$A_{2-1} = \log \gamma_2/x_1^2 + 2x_2[\log \gamma_1/x_2^2 - (\log \gamma_2/x_1^2)] \quad (7)$$

led only in a limited number of cases to constant values of  $A_{1-2}$  resp.  $A_{2-1}$ ; therefore, Table IV contains only those values of  $A_{1-2}$  and  $A_{2-1}$  which were obtained by graphical extrapolation according to Eqs (4, 5). It is obvious from Table IV that the assumption of ideal behaviour is satisfied only in the water-ethylene glycol binary system at the decreased pressure of 228 Torr, whereas already at atmospheric pressure deviations from the ideal behaviour appear. The relatively highest value of the activity coefficient  $\gamma_2$  in the binary water-diethylene glycol system is most probably due to the fact that values of the saturated vapour pressure of pure diethylene

TABLE IV

Activity Coefficients  $\gamma_1$  and  $\gamma_2$  for  $x_1 \leftarrow 0$  and  $x_2 \leftarrow 0$ , Margules  $A_{1-2}$  and  $A_{2-1}$  and Calingaert-Davis  $A$ ,  $B$  Constants for Binary Water-Glycol Systems

Glycol	Pressure kPa	$\gamma_1$	$A_{1-2}$	$\gamma_2$	$A_{2-1}$	$A$	$B$
Ethylene glycol	30.4	0.935	-0.029	1.001	0.00043	19.435	5604.990
	101.3	2.68	0.428	0.84	-0.076		
Propylene glycol	13.3	0.05	-1.30	4.45	0.667	19.462	5380.747
	98.6	2.00	0.301	1.16	0.064		
Diethylene glycol	13.3	3.50	0.544	12.3	1.09	20.572	6677.087
	99.3	3.74	0.573	2.30	0.362		
1,4-Butandiol	13.3	4.9	0.69	4.9	0.69	20.337	6257.857
	99.3	3.7	0.568	1.27	0.104		

glycol were extrapolated in the whole range of temperatures 47.7–76.2°C and that the reliability of this extrapolation is relatively low. Values of the saturated vapour pressure of 1,4-butandiol at 45.7–58.0°C were also extrapolated, which probably resulted in the relatively high value of  $\gamma_2$  resp.  $A_{2-1}$  in Table IV.

The values thus obtained constitute a starting point for interpolation and extrapolation calculations as well as for calculations in ternary systems consisting *e.g.* of water and two different glycols.

## LIST OF SYMBOLS

$x$	mole fraction of the more volatile component (water) in the liquid phase
$y$	mole fraction of the more volatile component (water) in the vapour phase
$t$	temperature (°C)
$x_1, x_2$	mole fraction of water resp. glycol in the liquid phase
$y_1, y_2$	mole fraction of water resp. glycol in the vapour phase
$A, B$	constants in the Calingaert-Davis equation (3)
$P$	total pressure of vapours in the system (Pa)
$P_1, P_2$	pressure of vapours of water resp. glycol at the given temperature (Pa, resp. Torr)
$A_{1-2}, A_{2-1}$	constants in the Margules equation (6)
$\gamma_1, \gamma_2$	activity coefficient of water resp. glycol

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