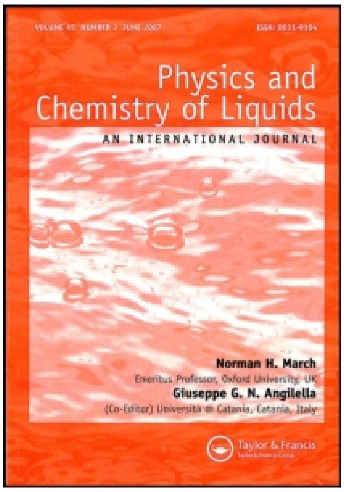

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The Excess Gibbs Free Energies of Chloroethanes with sec-Butanol

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Isobaric boiling point data for systems of 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and sec-butanol have been measured over the whole composition range at 300, 500 and 700 mmHg. The experimental t–x data have been used to predict Wilson parameters and equilibrium vapor compositions. The parameters are in turn used to predict activity coefficients and excess Gibbs free energies for these systems over the entire composition range. The values of G^E are positive in the systems at all pressures studied.

KEY WORDS: Activity coefficients, vapour–liquid equilibrium.

INTRODUCTION

Evaporation has been used as an effective means of separation in chemical processing. An accurate, reliable and complete knowledge of vapor–liquid equilibrium (VLE) data on the system under consideration is essential for the design and fabrication of the distillation equipment. VLE data could be obtained under two fixed conditions, namely isothermal and isobaric. Most separation processes are carried

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out at constant pressure rather than at constant temperature. In view of this isobaric vapor–liquid equilibrium data for the systems of sec-butanol with 1,2-dichloroethane, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane at 300, 500 and 700 mmHg are predicted and reported in this paper. The data are used to calculate vapour compositions, activity coefficients and excess Gibbs free energies over the entire composition range for these systems at 300, 500 and 700 mmHg.

EXPERIMENTAL

A Swietoslawski ebulliometer[1] was used for the measurement of the boiling points of the mixtures. The condenser of the ebulliometer was connected through a surge tank to a vacuum system to ensure the required pressure. The pressure is regulated by a valve at the required constant value which is then measured with an accuracy of ± 1 mmHg. The temperatures of the boiling mixtures were measured with a precalibrated platinum resistance thermometer, connected to a digital display with 0.01°C resolution. Mixtures of known composition were prepared gravimetrically and introduced into the ebulliometer. When steady state was reached, the temperature was read.

All the chemicals were purified by the methods described by Riddick and Bunger.[2] 1,2-Dichloroethane (BDH) was washed with concentrated hydrochloric acid, followed by 10% potassium hydroxide solution and water, dried over anhydrous calcium chloride and fractionally distilled. 1,1,1-trichloroethane (Koch–Light) was washed with concentrated hydrochloric acid, followed by 10% potassium carbonate solution then with 10% sodium chloride solution. It is dried over calcium chloride and distilled twice and the middle fraction was collected. During the distillation about 0.5 grams of phenol was added as a stabilizer. 1,1,2,2-tetrachloroethane (Riedel) was shaken with concentrated sulphuric acid for 10 minutes. The operation was repeated until the acid developed no more colour. The chloroalkane was then washed with water, steam distilled, dried with potassium carbonate and finally fractionated. sec-Butanol (BDH) were dried by refluxing with fused calcium oxide and fractionally distilled. The purity of the samples was checked by comparing the measured densities and boiling points with those reported in the literature.[3] The data are presented in Table 1 along with the Antoine constants.

Table 1 Densities, boiling points and Antoine constants of pure components.

Compound	Density gms/cc		Boiling point, °K		Antoine constants		
	Present work	Literature	Present work	Literature	*A*	*B*	*C*
1,2-Dichloroethane	1.23836	1.23831	356.6	356.6	6.66301	1073.99	200.406
1,1,1-Trichloroethane	1.32092	1.32096	347.2	347.3	6.51385	988.54	197.936
1,1,2,2-Tetrachloroethane	1.57800	1.57860	419.2	419.4	6.81569	1361.62	199.858
sec-Butanol	0.79898	0.79896	372.6	372.7	7.47428	1314.19	186.500

RESULTS AND DISCUSSION

For the three binary systems the boiling point curves were determined at 300, 500 and 700 mmHg. The vapor phase composition and excess Gibbs energies can be calculated if a model is assumed for the activity coefficients in the liquid phase. The empirical constants of the model can then be calculated from the experimental data by minimising the following objected function

$$\delta = \sum_{i=1}^{N} \left(\frac{P_{\mathrm{exp}} - P_{\mathrm{cal}}}{P_{\mathrm{exp}}} \right)^2 \tag{1}$$

where P_{exp} and P_{cal} are the experimental and calculated values of the total boiling pressures at the ith run for a mixture at composition x and temperature t, and N is the number of experimental data.

The calculation of the boiling pressure at each point was made by solving the following equation.

$$P_{\mathrm{cal}} = \frac{\gamma_1(x, t) x f^0_{1,L}(t, P)}{\hat{\phi}_1(y, P, t)} + \frac{\gamma_2(x, t)(1 - x) f^0_{2,L}(t, P)}{\hat{\phi}_2(y, P, t)} \tag{2}$$

In Eq. (2), γ_1 and γ_2 are the activity coefficients given by the liquid phase model chosen, $f^0_{i,L}$ is the standard state fugacity of component i in the liquid phase at temperature t and pressure P and $\hat{\phi}_i$ is the fugacity coefficient of component i in the vapor phase. For normal liquids, the standard state fugacity $f^0_{i,L}$ at temperature t and pressure P is given by

$$f^0_{i,L} = P_{s,i}(t)\hat{\phi}_{s,i}(t) \exp \frac{V_{i,L}(P - P_{s,i})}{RT} \tag{3}$$

Here $P_{s,i}$ is the vapor pressure of component i at temperature t, $\hat{\phi}_{s,i}$ is the fugacity coefficient of pure component i at saturation and $V_{i,L}$ is the liquid molal volume of component i which is estimated by the modified Rackett[4] equation. The vapor pressures of pure components can be calculated by means of Antoine equation.

Table 2 Wilson constants $(\lambda_{12} - \lambda_{11})/R$ and $(\lambda_{21} - \lambda_{22})/R$ for three systems along with standard deviation.

System	$(\lambda_{12} - \lambda_{11})/R$ °K	$(\lambda_{21} - \lambda_{22})/R$ °K	σt, °K
1,2-Dichloroethane-sec-Butanol	117.95	403.49	0.4
1,1,1-Trichloroethane-sec-Butanol	−11.454	713.65	0.4
1,1,2,2-Tetrachloroethane-sec-Butanol	−52.855	453.06	0.3

The fugacity coefficients $\hat{\phi}_i$ and $\hat{\phi}_{s,i}$ were calculated through the virial equation of state,

$$\ln \hat{\phi}_{s,i} = \frac{B_i P_{s,i}}{RT} \tag{4}$$

and

$$\ln \hat{\phi}_i = \frac{P}{RT}\left[B_i + (1 - Y_i)^2 \delta_{12}\right] \tag{5}$$

Table 3 1,2-Dichloroethane-sec-Butanol t-x data at 300, 500 and 700 mmHg.

x	$t_{(\text{exptl})}$ °C	$t_{(\text{calcd})}$ °C	Δt °C
	300 mmHg		
0.0975	68.7	69.2	−0.5
0.2068	63.7	64.1	−0.4
0.2811	61.2	61.7	−0.5
0.3641	59.1	59.7	−0.6
0.4269	58.5	58.6	−0.1
0.5408	56.9	57.1	−0.2
0.6263	56.1	56.3	−0.2
0.7137	55.4	55.8	−0.4
0.7908	54.6	55.4	−0.8
0.9103	55.0	55.3	−0.3
	500 mmHg		
0.0975	81.7	82.1	−0.4
0.2068	77.3	77.2	0.1
0.2811	74.9	74.9	0.0
0.3641	73.1	73.0	0.1
0.4269	72.1	71.9	0.2
0.5408	70.4	70.5	−0.1
0.6263	70.0	69.7	0.3
0.7137	69.4	69.2	0.2
0.7908	68.9	69.0	−0.1
0.9103	68.9	69.1	−0.2
	700 mmHg		
0.0975	91.2	91.2	0.0
0.2068	87.0	86.5	0.5
0.2811	85.0	84.2	0.8
0.3641	83.2	82.4	0.8
0.4269	81.6	81.3	0.3
0.5408	80.1	80.0	0.1
0.6263	79.5	79.3	0.2
0.7137	79.5	78.8	0.7
0.7908	78.8	78.7	0.1
0.9103	79.0	79.0	0.0

Table 4 1,1,1-Trichloroethane-sec-Butanol $t - x$ data at 300, 500 and 700 mmHg.

x	$t_{(\text{exptl})}$ °C	$t_{(\text{calcd})}$ °C	Δt °C
	300 mmHg		
0.0847	66.7	67.4	−0.7
0.1651	61.2	61.4	−0.2
0.2841	55.5	55.5	0.0
0.3867	52.4	52.2	0.2
0.4783	50.0	50.2	−0.2
0.5460	48.7	49.1	−0.4
0.6198	47.2	48.1	−0.9
0.7664	46.7	47.0	−0.3
0.8693	46.3	46.5	−0.2
0.9301	46.4	46.4	0.0
	500 mmHg		
0.0847	80.2	80.4	−0.2
0.1651	74.7	74.8	−0.1
0.2841	69.0	69.0	0.0
0.3867	66.3	65.8	0.5
0.4783	63.8	63.7	0.1
0.5460	63.0	62.6	0.4
0.6198	61.1	61.7	−0.6
0.7664	60.4	60.5	−0.1
0.8693	60.0	60.1	−0.1
0.9301	60.1	60.1	0.0
	700 mmHg		
0.0847	89.5	89.6	−0.1
0.1651	84.5	84.2	0.3
0.2841	78.7	78.6	0.1
0.3867	76.2	75.4	0.8
0.4783	73.8	73.4	0.4
0.5460	73.1	72.3	0.8
0.6198	71.4	71.4	0.0
0.7664	70.1	70.2	−0.1
0.8693	69.8	69.9	−0.1
0.9301	70.0	70.0	0.0

Table 5 1,1,2,2-Tetrachloroethane-sec-Butanol t-x data at 300, 500 and 700 mmHg.

x	$t_{(\text{exptl})}$ °C	$t_{(\text{calcd})}$ °C	Δt °C
	300 mmHg		
0.0614	76.6	76.9	−0.3
0.1381	77.0	77.5	−0.5
0.2016	78.0	78.1	−0.1
0.2905	79.2	79.2	0.0
0.3955	80.5	80.7	−0.2
0.4640	82.0	82.0	0.0
0.5586	84.0	84.2	−0.2
0.6507	86.4	87.0	−0.6
0.7524	91.2	91.2	0.0
0.8756	98.6	99.1	−0.5
	500 mmHg		
0.0614	89.1	89.2	−0.1
0.1381	89.3	89.9	−0.6
0.2016	90.5	90.6	−0.1
0.2905	92.0	91.8	0.2
0.3955	93.5	93.5	0.0
0.4640	95.2	95.0	0.2
0.5586	97.5	97.4	−0.1
0.6507	100.6	100.6	0.0
0.7524	105.3	105.3	0.0
0.8756	114.1	114.1	0.0
	700 mmHg		
0.0614	97.8	97.9	−0.1
0.1381	98.2	98.8	−0.6
0.2016	99.5	99.5	0.0
0.2905	101.0	100.8	0.2
0.3955	102.9	102.7	0.2
0.4640	104.7	104.2	0.5
0.5586	107.5	106.9	0.6
0.6507	110.6	110.3	0.3
0.7524	115.2	115.4	−0.2
0.8756	125.4	124.9	0.5

with

$$\delta_{12} = 2B_{12} - B_1 - B_2$$

where B_1 and B_2 are the second virial coefficients of components 1 and 2 respectively and B_{12} is the cross virial coefficient. The second virial coefficients were calculated by Tsonopoulos correlation.[5]

Table 6 Vapor compositions, activity coefficients and excess Gibbs free energies for the system 1,2-dichloroethane-sec-butanol.

x	y	γ_1	γ_2	G^E
		300 mmHg		
0.0975	0.3405	2.2168	1.0066	238.0
0.2068	0.5333	1.9495	1.0320	456.6
0.2811	0.6120	1.7889	1.0625	575.6
0.3641	0.6736	1.6294	1.1126	678.5
0.4269	0.7087	1.5219	1.1647	735.3
0.5408	0.7574	1.3536	1.3030	782.8
0.6263	0.7867	1.2481	1.4622	768.6
0.7137	0.8146	1.1575	1.7070	703.3
0.7908	0.8409	1.0921	2.0408	596.5
0.9103	0.8995	1.0205	3.0314	321.8
		500 mmHg		
0.0975	0.3027	2.1690	1.0064	239.7
0.2068	0.4883	1.9132	1.0311	461.7
0.2811	0.5680	1.7594	1.0607	582.1
0.3641	0.6324	1.6063	1.1093	686.6
0.4269	0.6700	1.5029	1.1599	785.3
0.5408	0.7232	1.3407	1.2938	790.7
0.6263	0.7560	1.2388	1.4474	776.9
0.7137	0.7877	1.1513	1.6822	710.5
0.7908	0.8178	1.0882	1.9996	602.3
0.9103	0.8853	1.0195	2.9228	323.6
		700 mmHg		
0.0975	0.2796	2.1369	1.0063	241.4
0.2068	0.4594	1.8889	1.0304	464.3
0.2811	0.5392	1.7396	1.0594	586.9
0.3641	0.6049	1.5907	1.1071	692.4
0.4269	0.6438	1.4901	1.1566	748.1
0.5408	0.6998	1.3320	1.2875	796.1
0.6263	0.7349	1.2326	1.4373	781.5
0.7137	0.7690	1.1472	1.6654	715.5
0.7908	0.8018	1.0856	1.9717	605.6
0.9103	0.8755	1.0188	2.8509	324.8

The model chosen to describe the activity coefficients in the liquid phase is the Wilson model.[6]

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1\left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right) \qquad (6)$$

Table 7 Vapor compositions, activity coefficients and excess Gibbs free energies for the system 1,1,1-trichloroethane-sec-butanol.

x	y	γ_1	γ_2	G^E
		300 mmHg		
0.0847	0.3856	2.2719	1.0041	207.0
0.1651	0.5730	2.0970	1.0164	377.6
0.2841	0.7174	1.8602	1.0540	584.7
0.3867	0.7848	1.6779	1.1121	718.1
0.4783	0.8237	1.5314	1.1941	796.3
0.5460	0.8448	1.4325	1.2821	827.0
0.6198	0.8632	1.3335	1.4188	829.3
0.7664	0.8919	1.1637	1.9473	723.0
0.8693	0.9125	1.0681	2.8924	520.8
0.9301	0.9321	1.0248	4.2267	328.2
		500 mmHg		
0.0847	0.3404	2.2476	1.0040	212.3
0.1651	0.5211	2.0749	1.0163	387.6
0.2841	0.6703	1.8416	1.0538	586.9
0.3867	0.7439	1.6620	1.1115	737.4
0.4783	0.7877	1.5179	1.1929	817.0
0.5460	0.8120	1.4207	1.2800	849.1
0.6198	0.8335	1.3235	1.4151	849.6
0.7664	0.8680	1.1573	1.9327	737.3
0.8693	0.8936	1.0645	2.8402	528.4
0.9301	0.9183	1.0231	4.0821	331.3
		700 mmHg		
0.0847	0.3125	2.2304	1.0040	215.9
0.1651	0.4873	2.0593	1.0163	394.8
0.2841	0.6380	1.8285	1.0535	610.7
0.3867	0.7149	1.6509	1.1110	750.6
0.4783	0.7618	1.5084	1.1919	831.3
0.5460	0.7882	1.4124	1.2784	863.7
0.6198	0.8118	1.3165	1.4122	864.1
0.7664	0.8503	1.1529	1.9219	746.7
0.8693	0.8797	1.0622	2.8027	533.6
0.9301	0.9082	1.0221	3.9823	333.6

where

$$\Lambda_{12} = \frac{V_{2,L}}{V_{1,L}} \exp\left(- \frac{\lambda_{12} - \lambda_{11}}{RT} \right)$$

and

$$\Lambda_{21} = \frac{V_{1,L}}{V_{2,L}} \exp\left(- \frac{\lambda_{21} - \lambda_{22}}{RT} \right)$$

Table 8 Vapor compositions, activity coefficients and excess Gibbs free energies for the system 1,1,2,2-tetrachloroethane-sec-butanol.

x	$1-y$	γ_1	γ_2	G^E
		300 mmHg		
0.0614	0.9626	2.2749	1.0085	169.8
0.1381	0.9325	1.7821	1.0355	319.8
0.2016	0.9124	1.5441	1.0658	404.2
0.2905	0.8861	1.3380	1.1159	475.7
0.3955	0.8528	1.1952	1.1823	505.0
0.4640	0.8276	1.1353	1.2284	499.4
0.5586	0.7853	1.0788	1.2945	464.1
0.6507	0.7308	1.0434	1.3608	404.3
0.7524	0.6441	1.0193	1.4358	314.9
0.8756	0.4606	1.0043	1.5287	174.8
		500 mmHg		
0.0614	0.9640	2.2318	1.0081	171.3
0.1381	0.9342	1.7666	1.0338	323.2
0.2016	0.9142	1.5376	1.0632	410.2
0.2905	0.8878	1.3366	1.1120	484.5
0.3955	0.8546	1.1953	1.1773	515.9
0.4640	0.8295	1.1361	1.2228	511.5
0.5586	0.7874	1.0796	1.2885	476.6
0.6507	0.7331	1.0440	1.3549	416.7
0.7524	0.6466	1.0197	1.4303	325.0
0.8756	0.4627	1.0044	1.5246	181.3
		700 mmHg		
0.0614	0.9648	2.2030	1.0078	172.1
0.1381	0.9350	1.7560	1.0327	325.7
0.2016	0.9150	1.5330	1.0614	414.2
0.2905	0.8886	1.3356	1.1093	490.4
0.3955	0.8553	1.1961	1.1738	324.3
0.4640	0.8302	1.1367	1.2190	520.2
0.5586	0.7881	1.0802	1.2844	486.6
0.6507	0.7338	1.0445	1.3508	425.5
0.7524	0.6472	1.0999	1.4266	331.9
0.8756	0.4630	1.0045	1.5222	186.2

Here $V_{1,L}$ and $V_{2,L}$ are the liquid molal volumes and $\Delta\lambda_{12}$ and $\Delta\lambda_{22}$ are model constants. The optimum Wilson constants for the four binary systems are reported in Table 2. All the three sets of data were used in data reduction.

The measured boiling points, calculated boiling points from the Wilson's equation and $\Delta t(t_{\text{exptl}} - t_{\text{calcd}})$ are presented in Tables 3–5.

The excess Gibbs energies for the systems were also calculated using the equation

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (7)$$

The vapor composition (y), activity coefficients and excess Gibbs free energy are included in Tables 6-8.

The values of G^E are positive over the entire composition range in all the systems at 300, 500 and 700 mmHg. The G^E values fall in the order

1,1,2,2-Tetrachloroethane < 1,2-dichloroethane
< 1,1,1-trichloroethane.

The values are increasing with increase in pressure.

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