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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Ramanjaneyulu, K. , Krishnaiah, A. and Ramakrishna, M.(1988) 'The Excess Gibbs Free Energies of Chloromethane with Iso-butanol', *Physics and Chemistry of Liquids*, 18: 3, 241 — 251

To link to this Article: DOI: 10.1080/00319108808078598

URL: <http://dx.doi.org/10.1080/00319108808078598>

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Phys. Chem. Liq., 1988, Vol. 18, pp. 241-251
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Printed in the United Kingdom

The Excess Gibbs Free Energies of Chloroethanes with Iso-butanol

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(Received 3 March 1988)

Isobaric boiling point data for the systems of 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane with iso-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 vapour compositions. The parameters are in turn used to predict activity co-efficients 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 the pressures studied.

Key Words: Activities, binary non-electrolyte solutions.

INTRODUCTION

The present work forms part of a programme of measurement of excess thermodynamic properties of binary non-electrolyte solutions. In continuation of our earlier studies on excess Gibbs free energies of Chloroethanes with Sec-butanol,¹ we have now extended the work to chloroethanes with iso-butanol. New experimental data on isobaric vapour-liquid equilibria (VLE) for the systems of 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane with iso-butanol at 300, 500 and 700 mm Hg have been reported in this paper. The VLE data are used to

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calculate vapour compositions, activity co-efficients and excess Gibbs free energies over the entire composition range for these systems at 300, 500 and 700 mm Hg.

EXPERIMENTAL SECTION

A Swietoslowski ebulliometer² was used for the measurement of the boiling points of the mixtures. The condenser of the ebulliometer was connected through a ballast to a vacuum system to ensure the required pressure. The pressure is regulated by a valve at the required constant value which is then determined with an accuracy of ± 1 mm Hg. The temperatures of the boiling mixtures were measured with a precalibrated platinum resistance thermometer, connected to a digital display with a 0.1°C resolution.

Mixtures of known compositions were prepared gravimetrically and introduced into the ebulliometer. When the steady state was reached, the temperature was read.

All the chemicals were purified by the methods described by Riddick and Bunger.³ 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 was 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. Iso-butanol (BDH) was 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.⁴ The data are presented in Table 1.

RESULTS AND DISCUSSION

For the two binary systems the boiling point curves were determined at 300, 500 and 700 mm Hg. The vapour phase composition and excess Gibbs free energies can be calculated if a model is assumed for the activity co-efficients in the liquid phase. The empirical parameters of the

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

Component	Density gms/cc		Boiling point, °K		Antoine constants		
	Present work	Literature	Present work	Literature	A	B	C
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
Iso-butanol	0.79435	0.79437	380.9	381.1	7.32705	1248.48	172.850

model can then be calculated from the experimental data by minimising the following objective function.

$$\delta = \sum_{i=1}^N \left[\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right]^2 \quad (1)$$

Where P_{exp} and P_{cal} are the experimental and calculated values of the total boiling pressures at the i th 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.

$$P_{\text{cal}} = \frac{r_1(x, t) x f_{1,L}^0(t, P)}{\hat{\phi}_1(y, P, t)} + \frac{r_2(x, t) (1-x) f_{2,L}^0(t, P)}{\hat{\phi}_2(y, P, t)} \quad (2)$$

In the Eq. (2), r_1 and r_2 are the activity co-efficients given by the liquid phase model chosen, $f_{i,L}^0$ 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 co-efficient of component i in the vapour phase. For normal liquids, the standard state fugacity $f_{i,L}^0$ at temperature t and pressure P is given by

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

Here $P_{s,i}$ is the vapour pressure of component i at temperature t , $\hat{\phi}_{s,i}$ is the fugacity of pure component i at saturation condition and $V_{i,L}$ is the liquid molar volume of component i which is estimated by the modified Rackett⁵ equation. The vapour pressures of pure components can be calculated by means of Antoine equation. The Antoine constants are taken from the literature⁶ and are given in Table 1.

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

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

and

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

with

$$\delta_{12} = 2B_{12} - B_1 - B_2 \quad (6)$$

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

System	$(\lambda_{12} - \lambda_{11})/R$ °K	$(\lambda_{21} - \lambda_{22})/R$ °K	$\sigma(t)$ °K
1,1,1-trichloroethane-Iso-butanol	-17.147	769.670	0.4
1,1,2,2-tetrachloroethane-Iso-butanol	-155.678	187.883	0.5

Table 3 1,1,1-trichloroethane-Iso-butanol, t - x data at 300, 500 and 700 mm Hg.

x_1	$t_{(\text{exp})}$ °C	$t_{(\text{cal})}$ °C	Δt °C
300 mm Hg			
0.0893	72.0	72.4	-0.4
0.1643	65.2	65.4	-0.2
0.2808	57.7	58.2	-0.5
0.3954	53.9	53.8	0.1
0.4770	51.2	51.7	-0.5
0.5642	49.9	50.0	-0.1
0.6187	48.7	49.2	-0.5
0.7739	47.2	47.7	-0.5
0.8811	46.8	47.1	-0.3
0.9454	46.6	46.8	-0.2
500 mm Hg			
0.0893	85.7	85.8	-0.1
0.1643	79.0	79.2	-0.2
0.2808	72.3	72.2	0.1
0.3954	67.7	67.8	-0.1
0.4770	65.9	65.6	0.3
0.5642	64.4	63.9	0.5
0.6187	62.8	63.1	-0.3
0.7739	61.2	61.5	-0.3
0.8811	60.8	60.9	-0.1
0.9454	60.5	60.7	-0.2
700 mm Hg			
0.0893	95.6	95.3	0.3
0.1643	89.0	88.9	0.1
0.2808	82.7	82.1	0.6
0.3954	77.9	77.6	0.3
0.4770	76.2	75.5	0.7
0.5642	74.6	73.8	0.8
0.6187	73.0	72.9	0.1
0.7739	71.6	71.4	0.2
0.8811	70.8	70.8	0.0
0.9454	70.7	70.7	0.0

Table 4 1,1,2,2-tetrachloroethane, Iso-butanol, $t-x$ data at 300, 500 and 700 mm Hg.

x_1	$t_{(exp)}$ °C	$t_{(cal)}$ °C	Δt °C
300 mm Hg			
0.0611	84.9	84.8	-0.1
0.1109	85.2	85.0	-0.2
0.1795	85.6	85.5	-0.1
0.2576	86.0	86.1	0.1
0.3153	86.4	86.6	0.2
0.3661	86.8	87.1	0.3
0.4052	87.3	87.6	0.3
0.4610	87.9	88.2	0.3
0.5101	88.6	88.9	0.3
0.5600	89.4	89.7	0.3
0.6406	91.1	91.3	0.2
0.7479	93.5	94.4	0.9
0.8682	98.8	100.1	1.3
500 mm Hg			
0.0611	97.4	97.2	-0.2
0.1109	97.8	97.6	-0.2
0.1795	98.3	98.1	-0.2
0.2576	98.8	98.9	0.1
0.3153	99.4	99.5	0.1
0.3661	100.0	100.1	0.1
0.4052	100.5	100.6	0.1
0.4610	101.2	101.4	0.2
0.5101	102.1	102.2	0.1
0.5600	103.1	103.2	0.1
0.6406	104.8	105.1	0.3
0.7479	108.8	108.6	-0.2
0.8682	114.9	115.1	0.2
700 mm Hg			
0.0611	105.8	106.1	0.3
0.1109	106.2	106.5	0.3
0.1795	106.9	107.2	0.3
0.2576	107.8	108.0	0.2
0.3153	108.6	108.7	0.1
0.3661	109.3	109.4	0.1
0.4052	110.2	110.0	-0.2
0.4610	111.4	110.9	-0.5
0.5101	112.6	111.8	-0.8
0.5600	113.5	112.8	-0.7
0.6406	115.8	114.9	-0.9
0.7479	120.1	118.7	-1.4
0.8682	127.0	125.9	-1.1

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 Tsionopoulos⁷ correlation.

The model chosen to describe the activity coefficients in the liquid phase is the Wilson model.⁸

$$\ln r_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right) \quad (7)$$

$$\ln r_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1 \left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} \right) \quad (8)$$

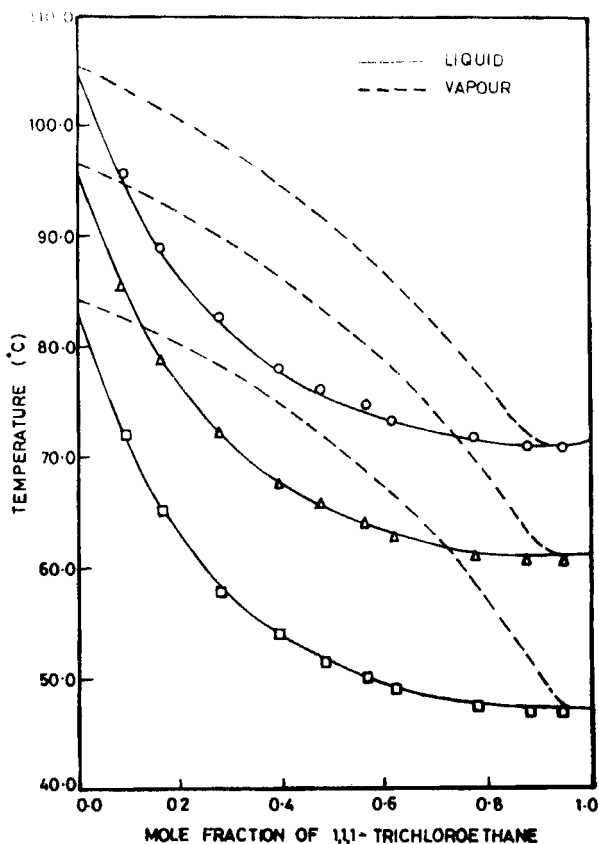


Figure 1 1,1,1-trichloroethane + iso-butanol at 700 mm Hg(O), 500 mm Hg(Δ), 300 mm Hg(□).

Where

$$\Lambda_{12} = \frac{V_{2,L}}{V_{1,L}} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \quad (9)$$

$$\Lambda_{21} = \frac{V_{1,L}}{V_{2,L}} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) \quad (10)$$

Here $V_{1,L}$ and $V_{2,L}$ are the liquid molar volumes and $(\Delta\lambda_{12})$ and $(\Delta\lambda_{22})$ are the model parameters with $\lambda_{12} = \lambda_{21}$. The optimum Wilson constants for the two binary systems are reported in Table 2. All the three sets of data were used in data reduction.

The measured boiling points (t_{exp}), calculated boiling points (t_{cal}) using Wilson equation and $\Delta t(t_{\text{exp}} - t_{\text{cal}})$ are presented in Tables 3 and

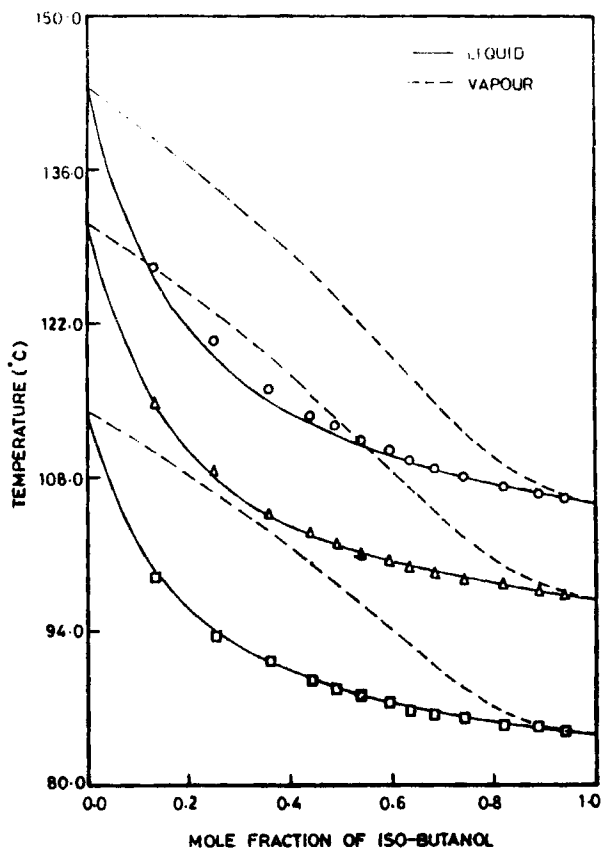


Figure 2 Iso-butanol + 1,1,2,2-tetrachloroethane at 700 mm Hg(O), 500 mm Hg(Δ), 300 mm Hg(\square).

4, each at 300, 500 and 700 mm Hg. Temperatures (t) versus liquid mole fraction (x) and vapour composition (y) are graphically represented in Figures 1 and 2 at the three pressures.

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

$$G^E = RT(x_1 \ln r_1 + x_2 \ln r_2) \quad (11)$$

The vapour composition (y_1), activity co-efficients r_1 and r_2 and excess Gibbs free energy (G^E) are included in Tables 5 and 6.

Table 5 Vapour compositions, activity co-efficients and excess Gibbs free energies for the system 1,1,1-trichloroethane-iso-butanol.

x_1	y_1	r_1	r_2	G^E
300 mm Hg				
0.0893	0.4706	2.2613	1.0044	220.6
0.1643	0.6499	2.1035	1.0157	463.5
0.2808	0.7846	1.8768	1.0511	584.9
0.3954	0.8488	1.6767	1.1155	735.3
0.4770	0.8764	1.5476	1.1883	808.3
0.5642	0.8971	1.4215	1.3052	844.7
0.6187	0.9071	1.3487	1.4097	845.6
0.7739	0.9288	1.1663	1.9896	731.4
0.8811	0.9432	1.0646	3.1296	502.6
0.9454	0.9585	1.0186	5.0613	281.7
500 mm Hg				
0.0893	0.4148	2.2409	1.0044	226.9
0.1643	0.5918	2.0844	1.0157	391.4
0.2808	0.7363	1.8602	1.0510	603.7
0.3954	0.8099	1.6625	1.1152	756.4
0.4770	0.8427	1.5351	1.1877	837.7
0.5642	0.8679	1.4107	1.3039	869.4
0.6187	0.8803	1.3390	1.4075	868.5
0.7739	0.9078	1.1600	1.9779	748.0
0.8811	0.9269	1.0612	3.0757	547.4
0.9454	0.9475	1.0172	4.8657	284.4
700 mm Hg				
0.0893	0.3801	2.2265	1.0044	231.4
0.1643	0.5534	2.0710	1.0157	399.4
0.2808	0.7022	1.8484	1.0509	616.0
0.3954	0.7814	1.6524	1.1150	769.6
0.4770	0.8176	1.5262	1.1872	849.9
0.5642	0.8459	1.4031	1.3029	885.8
0.6187	0.8599	1.3322	1.4057	884.4
0.7739	0.8917	1.1556	1.9689	759.8
0.8811	0.9145	1.0588	3.0365	521.6
0.9454	0.9392	1.0164	4.7311	286.6

Table 6 Vapour compositions, activity coefficients and excess Gibbs free energies for the system 1,1,2,2-tetrachloroethane-iso-butanol.

x_1	y_1	r_1	r_2	G^E
300 mm Hg				
0.0611	0.0488	2.1871	1.0041	153.8
0.1109	0.0812	1.9883	1.0130	261.3
0.1795	0.1190	1.7685	1.0332	305.2
0.2576	0.1556	1.5753	1.0668	492.9
0.3153	0.1803	1.4619	1.0989	550.9
0.3661	0.2012	1.3783	1.1324	587.4
0.4052	0.2171	1.3226	1.1617	606.7
0.4610	0.2404	1.2542	1.2091	620.6
0.5101	0.2618	1.2033	1.2564	620.2
0.5600	0.2853	1.1592	1.3105	608.0
0.6406	0.3291	1.1020	1.4114	563.5
0.7479	0.4076	1.0480	1.5755	456.2
0.8682	0.5583	1.0126	1.8056	274.5
500 mm Hg				
0.0611	0.0457	2.1344	1.0039	154.0
0.1109	0.0766	1.9472	1.0125	262.0
0.1795	0.1128	1.7390	1.0319	386.3
0.2576	0.1486	1.5549	1.0643	494.7
0.3153	0.1728	1.4463	1.0953	553.4
0.3661	0.1935	1.3660	1.1276	590.4
0.4052	0.2094	1.3124	1.1559	609.4
0.4610	0.2325	1.2464	1.2015	624.0
0.5101	0.2540	1.1972	1.2471	623.9
0.5600	0.2776	1.1546	1.2991	612.0
0.6404	0.3216	1.0991	1.3961	567.0
0.7479	0.4009	1.0467	1.5532	460.9
0.8682	0.5534	1.0123	1.7722	277.6
700 mm Hg				
0.0611	0.0439	2.0993	1.0038	142.8
0.1109	0.0739	1.9198	1.0122	262.1
0.1795	0.1094	1.7193	1.0311	386.8
0.2576	0.1446	1.5412	1.0626	495.7
0.3153	0.1687	1.4359	1.0928	554.9
0.3661	0.1893	1.3578	1.1244	592.4
0.4052	0.2051	1.3056	1.1519	612.5
0.4610	0.2283	1.2413	1.1964	627.6
0.5101	0.2499	1.1932	1.2409	628.1
0.5600	0.2736	1.1515	1.2915	615.8
0.6406	0.3179	1.0971	1.3858	571.2
0.7479	0.3978	1.0458	1.5383	464.5
0.8682	0.5517	1.0121	1.7501	280.1

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

1,1,1-trichloroethane > 1,1,2,2-tetrachloroethane.

This order is similar to that observed in mixtures containing Sec-butanol.¹ This suggests that same type of molecular interactions occur in both the sets of systems. Further, this order suggests that decrease in polarity of chloroethane results in lowering of excess Gibbs free energy. Positive excess Gibbs free energies for mixtures of chloroethane with alcohols were reported earlier.^{9,10}

Acknowledgement

This work is supported by the financial assistance from UGC, New Delhi.

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