

ACTIVITY COEFFICIENTS AND EXCESS GIBBS FREE ENERGIES OF 1,1,1-TRICHLOROETHANE WITH 1-BUTANOL AND 1-PENTANOL

K. DAYANANDA REDDY and M.V. PRABHAKARA RAO

Chemical Laboratories, Sri Venkateswara University, Tirupati 517 502 (A.P.) (India)

M. RAMAKRISHNA

Regional Research Laboratory, Hyderabad 500 009 (India)

(Received 8 December 1983)

ABSTRACT

Vapour–liquid equilibrium data for the systems 1,1,1-trichloroethane(1)–1-butanol(2) and 1,1,1-trichloroethane(1)–1-pentanol(2) have been measured by an indirect method from composition vs. boiling point ($x-t$) measurements made in a Swietoslowski type ebulliometer. The measurements were made at 200 and 700 mm Hg. The experimental $t-x$ data were used to estimate Wilson parameters, these, in turn, are used to calculate vapour compositions, boiling points and activity coefficients; from the activity coefficients G^E is calculated.

INTRODUCTION

Evaporation operation has been conducted as an effective means of separation in chemical processing. An accurate and complete knowledge of vapour–liquid equilibrium (VLE) data on the mixtures under consideration is necessary for the design of distillation equipment. Generally, VLE data are obtainable under two fixed conditions; namely, isothermal and isobaric. Most distillation processes are carried out at constant pressure rather than constant temperature. Therefore, isobaric vapour–liquid equilibrium data for the binary systems 1,1,1-trichloroethane(1)–1-butanol(2) and 1,1,1-trichloroethane(1)–1-pentanol(2) at 200 and 700 mm Hg are presented in this communication. The data have been interpreted in terms of dissociation of alcohol aggregates, interstitial accommodation of chloroethane in alcohol aggregates, and possible interaction of the type $\text{Cl} \cdots \text{H}-\text{O}$ between unlike molecules.

EXPERIMENTAL

1,1,1-Trichloroethane (Koch-Light Laboratories), 1-butanol (BDH) and 1-pentanol (Merck) were purified as described previously [1,2]. The purity of

the samples was checked by measuring densities, refractive indices and boiling points. The densities were measured using a standard bi-capillary pycnometer which gave an accuracy of 5 parts in 10^5 . Refractive indices were determined using an Abbe's refractometer which gave an accuracy of ± 0.0002 . The boiling points were measured using a Swietoslowski type ebulliometer, which gave an accuracy of $\pm 0.2^\circ\text{C}$. The measured values are in good agreement with the literature values [3,4].

The vapour-liquid equilibrium measurements were studied in a Swietoslowski type ebulliometer [5]. The ebulliometer was connected to a vacuum system. The pressures were measured using a mercury manometer which gave an accuracy of ± 1 mm Hg. The temperatures were measured using a PT100 thermometer with an accuracy of $\pm 0.1^\circ\text{C}$. The detailed experimental procedure has been described previously [5].

Isobaric binary systems

The boiling points of the systems 1,1,1-trichloroethane(1)-1-butanol(2) and 1,1,1-trichloroethane(1)-1-pentanol(2) were determined over the entire range of composition. Mixtures of different compositions were prepared by taking quantities (by weight) of the pure compounds. The boiling points for the known binary compositions were measured at 200 and 700 mm Hg. The boiling temperature of a specified composition was first measured at 200 mm Hg. The pressure was raised to 700 mm Hg and the boiling point was determined. The system was brought back to 200 mm Hg, where the boiling point measurement was repeated and, finally, the measurement was repeated at 700 mm Hg, thereby obtaining duplicate sets of the boiling points at each pressure of interest. This procedure also helps in detecting any possible dissociation and loss of materials under study.

RESULTS

In the present work, isobaric $t-x$ measurements are used for the data reduction. The model chosen for expressing the composition and temperature dependence is the Wilson equation [6]

$$\ln v_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right) \quad (1)$$

$$\ln v_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1 \left(\frac{\Lambda_{21}}{x_1 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} \right) \quad (2)$$

where

$$\Lambda_{12} = \frac{V_2^L}{V_1^L} \exp\left(\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \quad (3)$$

TABLE 1

Wilson parameters with standard deviation

System	Λ_{12}	Λ_{21}	Standard deviation (σ)
1,1,1-Trichloroethane(1)– 1-butanol(2) at 200 mm Hg	103.340	383.791	0.13
1,1,1-Trichloroethane(1)– 1-butanol(2) at 700 mm Hg	267.606	5.789	0.25
1,1,1-Trichloroethane(1)– 1-pentanol(2) at 200 mm Hg	–226.559	1780.720	0.23
1,1,1-Trichloroethane(1)– 1-pentanol(2) at 700 mm Hg	–274.116	288.749	0.49

$$\Lambda_{21} = \frac{V_1^L}{V_2^L} \exp\left(\frac{\lambda_{12} - \lambda_{22}}{RT}\right) \quad (4)$$

Where V_1^L and V_2^L are liquid molal volumes ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{12} - \lambda_{22}$) are temperature independent (to some extent) Wilson parameters; λ is the energy of interaction between the molecules designated in the subscripts. The optimum Wilson parameters Λ_{12} and Λ_{21} are obtained by minimising the objective function ϕ

$$\phi = \sum \left(\frac{P_{\text{cal}}}{P_{\text{exp}}} - 1.0 \right)^2 \quad (5)$$

The optimum Wilson parameters are obtained by minimising the above objective function using Nelder–Mead optimization techniques. The Wilson parameters thus obtained are presented in Table 1 along with the standard deviation of the fit.

DISCUSSION

Since the prediction of vapour–liquid equilibrium data involves the vapour pressure measurements of the pure compounds, the same has been measured for 1,1,1-trichloroethane, 1-butanol and 1-pentanol. The Antoine constants for the pure components were obtained by non-linear regression analyses of the experimental data, and are presented in Table 2 along with the standard deviation. The measured boiling points, calculated boiling points from the Wilson equation and ideal boiling points are presented in Tables 3–6. The excess Gibbs free energies were calculated using the following equation

$$\frac{G^E}{RT} = x_1 \ln v_1 + x_2 \ln v_2 \quad (6)$$

TABLE 2

Antoine constants for the pure compounds with standard deviation

Compound	<i>A</i>	<i>B</i>	<i>C</i>	σ_p (%)
1,1,1-Trichloroethane	15.0010	2276.62	197.94	0.35
1-Butanol	18.1868	3722.47	204.58	0.3
1-Pentanol	17.8107	3786.78	21.29	0.4

TABLE 3

1,1,1-Trichloroethane(1)-1-butanol(2) *t*-*x* data at 200 mm Hg

<i>x</i>	<i>t</i> _{exp} (°C)	<i>t</i> _{cal} using Wilson equation (°C)	<i>t</i> _{ideal} (°C)	<i>t</i> _{exp} - <i>t</i> _{cal} (°C)
0.1251	61.0	61.0	73.6	0.0
0.1251	61.0	61.0	73.6	0.0
0.4068	45.5	45.5	56.1	0.0
0.4068	45.5	45.5	56.1	0.0
0.5852	42.0	42.1	48.6	0.1
0.5852	42.0	42.1	48.6	0.1
0.6764	41.0	40.9	45.4	0.1
0.6764	41.0	40.9	45.4	0.1
0.7454	40.1	40.0	43.3	0.1
0.7454	40.0	40.0	43.3	0.0
0.8076	39.4	39.3	41.5	0.1
0.8076	39.5	39.3	41.5	0.2
0.9668	37.0	37.2	37.5	-0.2
0.9668	37.0	37.2	37.5	-0.2

TABLE 4

1,1,1-Trichloroethane(1)-1-butanol(2) *t*-*x* data at 700 mm Hg

<i>x</i>	<i>t</i> _{exp} (°C)	<i>t</i> _{cal} using Wilson equation (°C)	<i>t</i> _{ideal} (°C)	<i>t</i> _{exp} - <i>t</i> _{cal} (°C)
0.1251	101.5	101.5	107.8	0.0
0.1251	101.5	101.5	107.8	0.0
0.3161	91.0	90.8	97.2	0.2
0.3161	91.0	90.8	97.2	0.2
0.4068	87.2	87.4	92.8	-0.2
0.4068	87.4	87.4	92.8	0.0
0.5852	81.7	81.9	85.1	-0.2
0.5852	81.6	81.9	85.1	-0.3
0.6764	79.5	79.5	81.6	0.0
0.6764	79.5	79.5	81.6	0.0
0.7454	78.1	77.7	79.2	0.4
0.7454	78.1	77.7	79.2	0.4
0.8076	77.0	76.1	77.2	0.9
0.8076	77.1	76.1	77.2	1.0

TABLE 5

1,1,1-Trichloroethane(1)-1-pentanol(2) $t-x$ data at 200 mm Hg

x	t_{exp} (°C)	t_{cal} using Wilson equation (°C)	t_{ideal} (°C)	$t_{\text{exp}} - t_{\text{cal}}$ (°C)
0.1043	81.2	80.8	85.4	0.4
0.1043	81.2	80.8	85.4	0.4
0.1924	69.5	69.4	75.1	0.1
0.1924	69.5	69.4	75.1	0.1
0.2928	60.0	60.1	66.2	-0.1
0.2928	60.1	60.1	66.2	0.0
0.3818	54.1	54.1	59.9	0.0
0.3818	54.3	54.1	59.9	0.2
0.4515	50.0	50.2	55.9	-0.2
0.4515	50.0	50.2	55.9	-0.2
0.5233	46.8	46.9	52.3	-0.1
0.5233	47.0	46.9	52.3	0.1
0.5989	43.5	44.0	49.0	-0.5
0.5989	43.6	44.0	49.0	-0.4
0.6488	42.0	42.4	47.1	-0.4
0.6488	42.2	42.4	47.1	-0.2
0.7471	39.6	39.8	43.6	-0.2
0.7471	39.6	39.8	43.6	-0.1
0.8485	38.0	37.8	40.6	0.2
0.8485	38.1	37.8	40.6	0.3
0.9602	36.8	36.8	37.7	0.0
0.9602	36.9	36.8	37.7	0.1

TABLE 6

1,1,1-Trichloroethane(1)-1-pentanol(2) $t-x$ data at 700 mm Hg

x	t_{exp} (°C)	t_{cal} using Wilson equation (°C)	t_{ideal} (°C)	$t_{\text{exp}} - t_{\text{cal}}$ (°C)
0.1043	120.1	119.8	123.2	0.3
0.1043	120.2	119.8	123.2	0.4
0.1924	109.5	109.4	114.4	0.1
0.1924	109.6	109.4	114.4	0.2
0.2928	99.2	100.0	105.7	-0.8
0.2928	99.4	100.0	105.7	-0.6
0.3818	93.0	93.1	99.2	-0.1
0.3818	93.0	93.1	99.2	-0.1
0.4515	88.5	88.6	94.7	-0.1
0.4515	88.6	88.6	94.7	0.0
0.5233	84.5	84.6	90.6	-0.1
0.5233	84.7	84.6	90.6	0.1
0.5989	81.7	80.9	86.7	0.8
0.5989	81.8	80.9	86.7	0.9
0.8485	72.0	72.8	76.4	-0.8
0.8485	72.2	72.8	76.4	-0.6
0.9602	71.6	71.4	72.7	0.2
0.9602	71.7	71.4	72.7	0.3

TABLE 7

Vapour compositions, activity coefficients and excess Gibbs free energies for the system 1,1,1-trichloroethane(1)-1-butanol(2) at 200 mm Hg

x	y_{cal}	t_{cal} (°C)	ν_1	ν_2	G^E (J mol ⁻¹)
0.05	0.4567	72.2	2.5536	1.0023	136
0.10	0.6555	64.1	2.3818	1.0093	257
0.15	0.7555	58.4	2.2166	1.0213	364
0.20	0.8126	54.3	2.0628	1.0387	459
0.25	0.8484	51.3	1.9222	1.0619	541
0.30	0.8727	49.0	1.7950	1.0915	610
0.35	0.8901	47.2	1.6803	1.1284	667
0.40	0.9032	45.7	1.5774	1.1737	710
0.45	0.9135	45.5	1.4852	1.2287	740
0.50	0.9220	43.5	1.4028	1.2956	757
0.55	0.9292	42.7	1.3293	1.3768	759
0.60	0.9355	41.9	1.2640	1.4758	747
0.65	0.9414	41.2	1.2062	1.5976	719
0.70	0.9472	40.6	1.1555	1.7490	675
0.75	0.9529	40.0	1.1117	1.9400	614
0.80	0.9591	39.4	1.0745	2.1852	535
0.85	0.9662	38.8	1.0440	2.5075	436
0.90	0.9746	38.2	1.0208	2.9436	315
0.95	0.9853	37.5	1.0056	3.5560	171

TABLE 8

Vapour compositions, activity coefficients and excess Gibbs free energies for the system 1,1,1-trichloroethane(1)-1-butanol(2) at 200 mm Hg

x	y_{cal}	t_{cal} (°C)	ν_1	ν_2	G^E (J mol ⁻¹)
0.05	0.2563	108.7	1.8399	1.0026	101
0.10	0.4160	103.6	1.6915	1.0101	186
0.15	0.5231	99.7	1.5680	1.0219	256
0.20	0.5999	96.5	1.4655	1.0376	313
0.25	0.6580	93.8	1.3804	1.0568	342
0.30	0.7042	91.5	1.3095	1.0791	392
0.35	0.7422	89.5	1.2505	1.1044	414
0.40	0.7745	87.7	1.2011	1.1324	427
0.45	0.8027	86.0	1.1599	1.1631	431
0.50	0.8279	84.4	1.1255	1.1964	426
0.55	0.8507	82.9	1.0968	1.2322	412
0.60	0.8716	81.5	1.0731	1.2704	392
0.65	0.8910	80.2	1.0536	1.3111	364
0.70	0.9092	78.9	1.0378	1.3541	329
0.75	0.9263	77.6	1.0253	1.3996	288
0.80	0.9425	76.3	1.0156	1.4475	241
0.85	0.9579	75.1	1.0085	1.4979	189
0.90	0.9726	73.9	1.6037	1.5508	131
0.95	0.9866	72.7	1.009	1.6062	68

TABLE 9

Vapour compositions, activity coefficients and excess Gibbs free energies for the system 1,1,1-trichloroethane(1)-1-pentanol(2) at 200 mm Hg

x	y_{cal}	t_{cal} (°C)	ν_1	ν_2	G^E (J mol ⁻¹)
0.05	0.4074	90.4	1.3403	1.0000	43
0.10	0.6258	81.5	1.3214	1.0000	79
0.15	0.7500	74.4	1.3064	0.9999	111
0.20	0.8251	68.6	1.2944	0.9998	141
0.25	0.8733	63.7	1.2842	0.9997	168
0.30	0.9056	59.6	1.2753	0.9997	194
0.35	0.9281	56.1	1.2669	1.0001	218
0.40	0.9444	53.0	1.2587	1.0010	242
0.45	0.9565	50.3	1.2502	1.0030	264
0.50	0.9656	47.9	1.2409	1.0065	286
0.55	0.9726	45.8	1.2304	1.0127	306
0.60	0.9781	44.0	1.2184	1.0229	324
0.65	0.9824	42.3	1.2042	1.0396	339
0.70	0.9859	40.9	1.1875	1.0668	351
0.75	0.9889	39.7	1.1676	1.1121	357
0.80	0.9909	38.7	1.1440	1.1904	356
0.85	0.9928	37.8	1.1159	1.3369	340
0.90	0.9943	37.2	1.0826	1.6571	303
0.95	0.9955	36.8	1.0434	1.6761	222

TABLE 10

Vapour compositions, activity coefficients and excess Gibbs free energies for the system 1,1,1-trichloroethane(1)-1-pentanol(2) at 700 mm Hg

x	y_{cal}	t_{cal} (°C)	ν_1	ν_2	G^E (J mol ⁻¹)
0.05	0.1875	130.4	0.8239	0.9997	-32
0.10	0.3436	125.9	0.8816	0.9986	-63
0.15	0.4721	121.5	0.8397	0.9966	-92
0.20	0.5771	117.2	0.8483	0.9936	-119
0.25	0.6623	113.0	0.8573	0.9895	-143
0.30	0.7312	109.1	0.8669	0.9840	-168
0.35	0.7868	105.3	0.8768	0.9770	-185
0.40	0.8315	101.7	0.8872	0.9683	-202
0.45	0.8675	98.3	0.8980	0.9477	-215
0.50	0.8965	95.1	0.9092	0.9448	-224
0.55	0.9198	92.0	0.9205	0.9294	-229
0.60	0.9386	89.1	0.9321	0.9112	-230
0.65	0.9536	86.4	0.9436	0.8898	-226
0.70	0.9657	83.8	0.9550	0.8649	-216
0.75	0.9754	81.3	0.9659	0.8361	-201
0.80	0.9830	79.1	0.9762	0.8029	-178
0.85	0.9891	76.9	0.9853	0.7650	-148
0.90	0.9938	74.9	0.9928	0.7219	-109
0.95	0.9973	73.1	0.9980	0.6735	-60

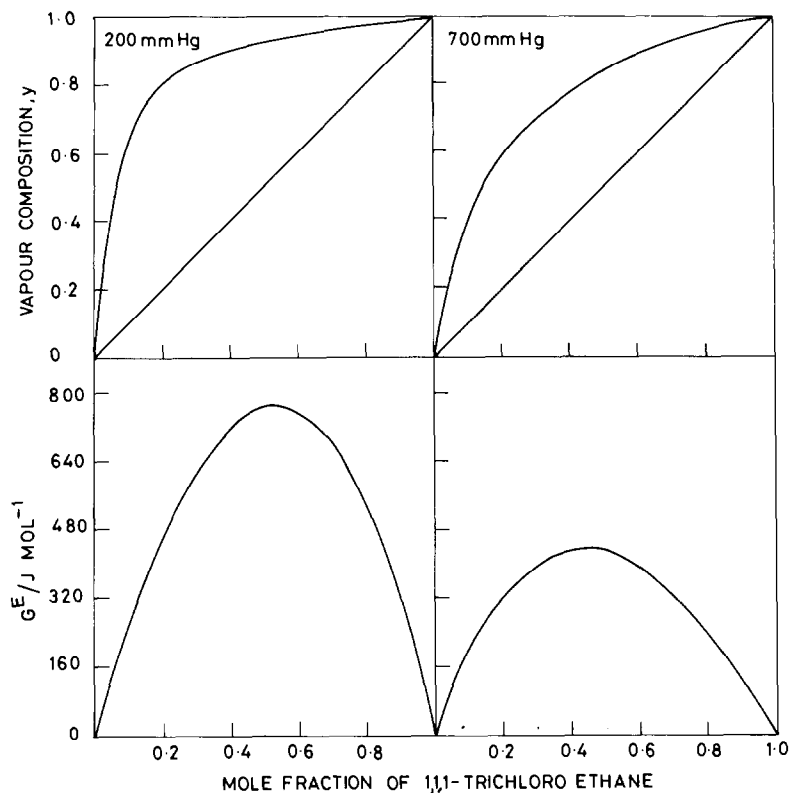


Fig. 1. Vapour compositions and excess Gibbs free energies for the system 1,1,1-trichloroethane(1)-1-butanol(2) at 200 and 700 mm Hg.

The vapour compositions, activity coefficients and excess Gibbs free energies are presented in Tables 7-10. The mole fraction vs. vapour composition and excess Gibbs free energies are represented in Figs. 1 and 2. The calculated G^E values are positive over the entire range of composition, except in the system 1,1,1-trichloroethane(1)-1-pentanol(2) at 700 mm Hg. The G^E values decrease from 1,1,1-trichloroethane(1)-1-butanol(2) to 1,1,1-trichloroethane(1)-1-pentanol(2) at 200 mm Hg.

The same trend has been observed at 700 mm Hg. The decrease in G^E values from 1-butanol to 1-pentanol can be attributed to the interstitial accommodation of chloroalkane in the aggregates of alcohols and to weak hydrogen bond interactions of the type $\text{Cl} \cdots \text{H}-\text{O}$ between unlike molecules. From the plot of vapour composition (y) vs. mole fraction (x), it can be concluded that both systems are non-ideal.

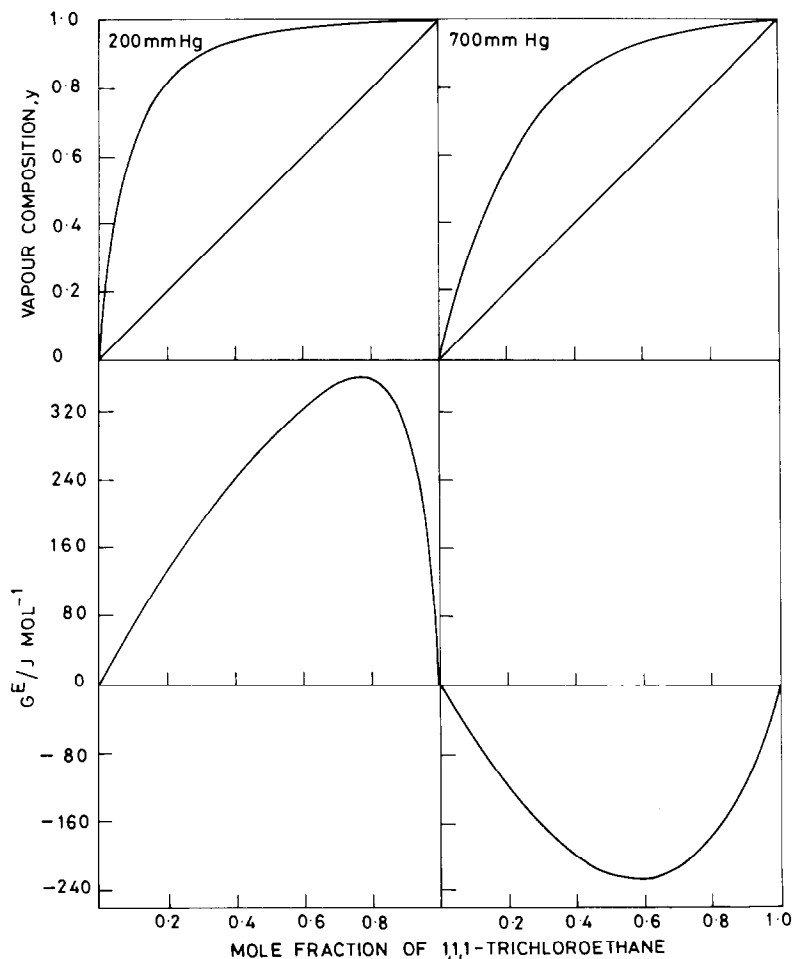


Fig. 2. Vapour compositions and excess Gibbs free energies for the system 1,1,1-trichloroethane(1)-1-pentanol(2) at 200 and 700 mm Hg.

ACKNOWLEDGEMENTS

One of the authors (K.D.R.) is grateful to the Council of Scientific and Industrial Research for the award of a senior Research Fellowship, and to the Director and Head, Chemical Engineering Division, Regional Research Laboratory, Hyderabad, for providing the necessary facilities.

REFERENCES

- 1 J.A. Reddick and W.B. Bunger, *Organic Solvents*, Wiley-Interscience, New York, 1970.
- 2 M.V.P. Rao and P.R. Naidu, *Can. J. Chem.*, 52 (1974) 788.

- 3 J. Timmermans, *Physico Chemical Constants of Pure Organic Compounds*, Elsevier, Amsterdam, 1950.
- 4 J.A. Dean, *Langes Handbook of Chemistry*, 11th edn., McGraw-Hill, New York, 1973.
- 5 E. Hala, J. Pick, V. Fried and O. Vilim, *Vapour-Liquid Equilibrium*, Pergamon Press, Oxford, 1967.
- 6 G.M. Wilson, *J. Am. Chem. Soc.*, 86 (1964) 127.