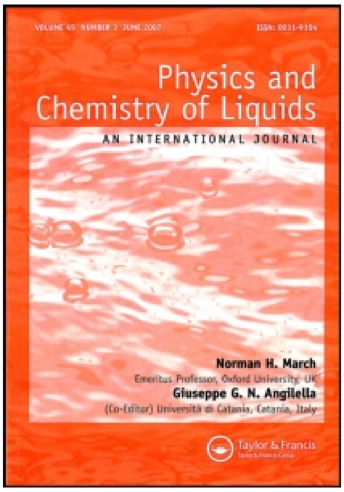

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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K. Rambabu[a]; G. K. Raman[a]; Y. V. L. Ravikumar[b]
[a] Thermochemical Laboratories, College of Engineering, S.V. University, Tirupati, India [b] Indian Institute of Chemical Technology, Hyderabad, India

To cite this Article Rambabu, K. , Raman, G. K. and Ravikumar, Y. V. L.(1993) 'Vapour Liquid Equilibrium of the Systems of 1-Bromobutane with *n-Hexane* and *n*-Heptane', Physics and Chemistry of Liquids, 26: 1, 39 — 45
To link to this Article: DOI: 10.1080/00319109308030371
URL: http://dx.doi.org/10.1080/00319109308030371

Phys. Chem. Liq., 1993, Vol. 26, pp. 39–45
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VAPOUR LIQUID EQUILIBRIUM OF THE SYSTEMS OF 1-BROMOBUTANE WITH *n*-HEXANE AND *n*-HEPTANE

K. RAMBABU, G. K. RAMAN

Thermochemical Laboratories, College of Engineering, S. V. University, Tirupati-517502, India.

and

Y. V. L. RAVIKUMAR

Indian Institute of Chemical Technology, Hyderabad-7, India.

(Received 6 August 1992)

Vapour liquid equilibrium data for the systems 1-Bromobutane (1)-*n*-Hexane (2) and 1-Bromobutane (1)-*n*-Heptane (2) were measured by the indirect method from the composition Vs. boiling point ($x - t$) measurements made at 715 mm Hg. The experimental $t - x$ data were used to estimate Wilson parameters; these in turn are useful to calculate vapour compositions, boiling points and activity coefficients. These activity coefficients are useful to calculate excess Gibbs free energy G^E.

KEY WORDS: Activities, binary non-electrolyte solutions.

INTRODUCTION

Distillation has been used as an effective means of separation in chemical processing. Evidently an accurate and complete knowledge of vapour–liquid equilibrium data on the mixture under consideration is necessary for the design of separation equipment. Generally vapour–liquid equilibrium data are obtained under two fixed conditions, namely, isothermal and isobaric. Most distillation processes are carried out at constant pressure rather than at constant temperature, so that the temperature–composition curves are more practical in making calculations such as the number of plates, although for theoretical consideration the pressure–composition curves are preferable. Hence, an attempt is made to determine the isobaric boiling points and to calculate vapour compositions, activity coefficients, and excess Gibbs free energies for the systems of 1-Bromobutane with *n*-Hexane and *n*-Heptane at 715 mm Hg.

EXPERIMENTAL SECTION

The isobaric vapour–liquid equilibrium measurements are made in a Swietoslawski ebulliometer[1]. The ebulliometer is connected to a pressure controlling system. The pressure is measured with a mercury-filled U-tube manometer with an accuracy of

±1 mm Hg. The equilibrium temperatures are measured by a standard mercury-in glass thermometer having an accuracy of ±0.1°C. In order to obtain a more reliable equilibrium temperature, stem connection is made for the mercury thermometer readings. The detailed procedure is described elsewhere[1].

The boiling points for the systems of 1-Bromobutane with *n*-Hexane and *n*-Heptane are determined over the entire range of composition. Mixtures of different compositions are made by taking suitable quantities (by weight) of the pure materials. The equilibrium compositions are not determined experimentally. The liquid compositions are assumed from the gravimetric composition of the mixture. Vapour compositions are estimated by using the Wilson model. The boiling points for the known binary composition are measured at 715 mm Hg.

All the chemicals were purified by the methods described by Riddick and Bunger[2]. The purity of the samples was checked by measuring densities, refractive indices, and boiling points. The densities were measured with a standard bicapillary pycnometer which gave an accuracy of 5 parts in 10^5. Refractive indices were determined with an Abbe's refractometer which gave an accuracy of ±0.002. The measured values are in good agreement with the literature values[3,4].

RESULTS AND DISCUSSION

For the two binary systems the boiling point curves were determined at 715 mm Hg. The vapour phase composition and excess Gibbs free energies can be calculated if a model is assumed for the activity coefficient in the liquid phase. The empirical parameters of the model can then be calculated from the experimental data by minimising the following objective function.

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

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

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

In the 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 $\hat{\phi}_1$ is the fugacity coefficient of component i in the vapour phase. For normal liquids, the standard state fugacity $f^0_{i,L}$ at tempera-

Table 1 Antoine constants of pure components.

Component	*Antoine constants*		
	A	*B*	*C*
1-Bromobutane	6.92254	1298.61	219.720
n-Hexane	6.87770	1171.53	224.376
n-Heptane	6.89390	1264.37	216.640

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-Bromobutane + *n*-Hexane	249.09	−93.23	0.8
1-Bromobutane + *n*-Heptane	136.38	10.61	0.4

Table 3 T-X_1-Y_1-γ_1-γ_2-Data for 1-Bromobutane with *n*-alkanes at 715 mm Hg.

T, °*C*	X_1	Y_1	γ_1	γ_2
		1-Bromobutane + *n*-Hexane		
68.8	0.1079	0.0552	1.4011	1.0048
70.8	0.2042	0.1033	1.3086	1.0172
73.7	0.3004	0.1520	1.2320	1.0374
73.9	0.4012	0.2061	1.1662	1.0676
75.0	0.5062	0.2689	1.1112	1.1098
78.8	0.6012	0.3357	1.0718	1.1586
82.6	0.7077	0.4296	1.0385	1.2270
86.1	0.8002	0.5393	1.0180	1.3000
92.7	0.9012	0.7145	1.0045	1.3969
		1-Bromobutane + *n*-Heptane		
96.1	0.1235	0.1329	1.1962	1.0021
95.9	0.2091	0.2188	1.1703	1.0066
95.8	0.3019	0.3073	1.1426	1.0149
95.7	0.4077	0.4036	1.1119	1.0304
94.8	0.5003	0.4854	1.0862	1.0506
96.0	0.6014	0.5739	1.0601	1.0823
96.5	0.6999	0.6619	1.0375	1.1265
97.3	0.7987	0.7559	1.0187	1.1894
98.4	0.9014	0.8671	1.0051	1.2838

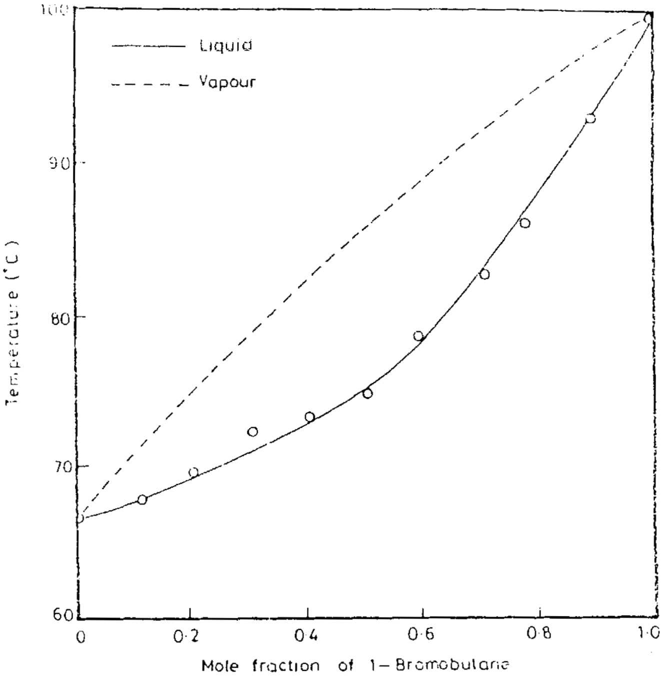

Figure 1 1-Bromobutane + *n*-Hexane (○) at 715 mm Hg.

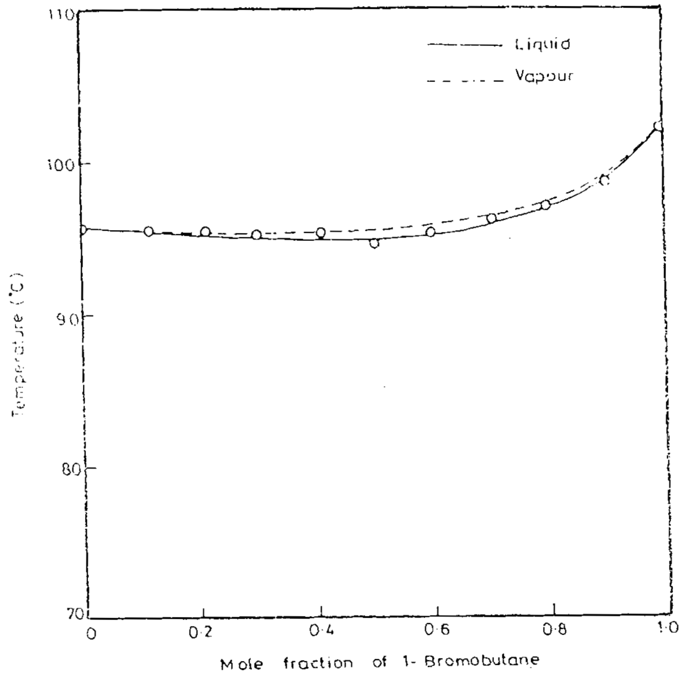

Figure 2 1-Bromobutane + *n*-Heptane (○) at 715 mm Hg.

ture t and pressure P is given by

$$f^0_{1,L} = P_{s,i}(t)\hat{\phi}_{s,i}(t)\exp\frac{V_{i,L}(P - P_{s,i})}{RT} \tag{3}$$

Here $P_{s,i}$ is the 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 Rackett[5] equation. The vapour pressures of pure components can be calculated by means of Antoine equation. The Antoine Constants are taken from the literature[6] and are given in Table 1.

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

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

and

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

with

$$\delta_{12} = 2B_{12} - B_1 - B_2 \tag{6}$$

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 are calculated by Tsonopoulos[7] correlation.

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

$$\ln\gamma_1 = -\ln(X_1 + \Lambda_{12}X_2) + X_2\left(\frac{\Lambda_{12}}{X_1 + \Lambda_{12}X_2} - \frac{\Lambda_{21}}{X_2 + \Lambda_{21}X_1}\right) \tag{7}$$

$$\ln\gamma_2 = -\ln(X_2 + \Lambda_{21}X_1) + X_1\left(\frac{\Lambda_{21}}{X_2 + \Lambda_{21}X_1} - \frac{\Lambda_{12}}{X_1 + \Lambda_{12}X_1}\right) \tag{8}$$

Where

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

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

Table 4 Excess Gibbs Energy Data at 25°C for the systems 1-Bromobutane with *n*-Hexane and *n*-Heptane.

X_1	G^E, J/mol	X_1	G^E, J/mol
1-Bromobutane + *n*-Hexane		1-Bromobutane + *n*-Heptane	
0.05	57.63	0.05	36.92
0.10	108.83	0.10	71.16
0.15	153.67	0.15	102.56
0.20	192.23	0.20	130.99
0.25	224.59	0.25	156.29
0.30	250.81	0.30	178.28
0.35	270.96	0.35	196.80
0.40	285.09	0.40	211.63
0.45	293.26	0.45	222.56
0.50	295.51	0.50	229.37
0.55	291.88	0.55	231.80
0.60	282.42	0.60	229.57
0.65	267.15	0.65	222.38
0.70	246.12	0.70	209.89
0.75	219.34	0.75	191.73
0.80	186.84	0.80	167.50
0.85	148.65	0.85	136.75
0.90	104.77	0.90	98.98
0.95	55.21	0.95	53.60

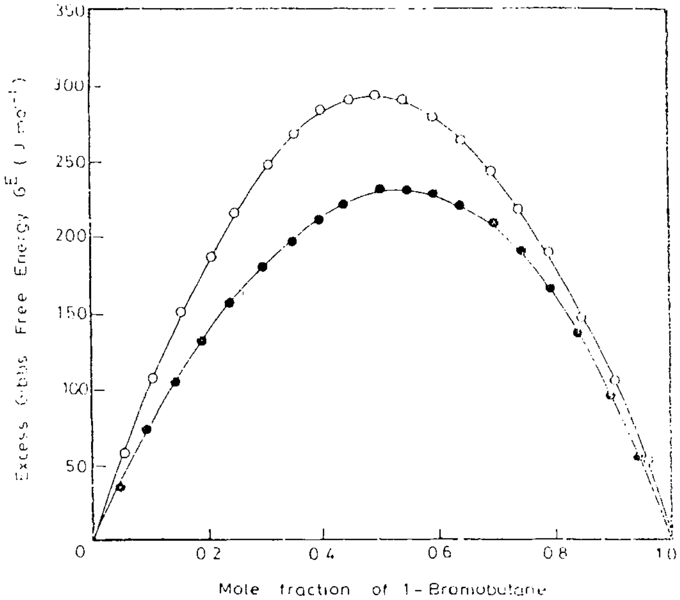

Figure 3 1-Bromobutane + *n*-Hexane (○) and + *n*-Heptane (●) at 298·15 K.

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. The two systems were used in data reduction.

The boiling points (t_{exp}) liquid composition and vapour composition along with the activity coefficients using Wilson equation are presented in Table 3 each at 715 mm Hg. Temperature (t_1 versus liquid mole fraction (x) and vapour composition (y) are graphically represented in Figures 1 and 2 at 715 mm Hg.

The excess Gibbs free energies at 25°C for the two systems were also calculated with these model parameters by using the equation

$$G^E = RT(X_1 \ln \gamma_1 + X_2 \ln \gamma_2) \tag{11}$$

and are presented in Tables 4 and represented in Figure 3.

The values of G^E are positive over the entire composition range in both the systems at 715 mm Hg.

The G^E values fall in the order

$$n\text{-Hexane} > n\text{-Heptane}$$

This suggests that the same type of molecular interactions occur in both the sets of systems. Further this order suggest that decrease in polarity 1-Bromobutane results in lowering of excess Gibbs free energy. The positive G^E values over the entire range of composition indicated that there is a strong attraction between unlike molecules through hydrogen bonding.

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