VAPOUR–LIQUID EQUILIBRIUM IN THE ISOBUTYL ALCOHOL–ISOBUTYL ACETATE BINARY SYSTEM*

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Isobaric vapour–liquid equilibrium in the isobutyl alcohol–isobutyl acetate binary system was measured at atmospheric pressure. A modified circulation still of the Gillespie type was used for the measurement. The system is characterized by an azeotropic point at 107·61°C and 87·5 mol% isobutyl alcohol.

The knowledge of vapour–liquid equilibrium data in the isobutyl alcohol–isobutyl acetate system is required for the separation of isobutyl acetate produced by esterification of isobutyl alcohol with acetic acid. As the equilibrium data were not found in the literature and, in addition, azeotropic data on the system are ambiguous we decided to carry out the experimental determination.

EXPERIMENTAL

Substances used. Isobutyl alcohol, analytical reagent grade, was dried with anhydrous K_2CO_3, filtered and rectified on a fifty-plate bubble-cup column[1]. Its determined values of physical constants are: n.b.p. 107·885°C (ref.[2–4] 107·89—108·10), d_4^{20} 0·80193 g/cm^3 (ref.[2–4] 0·80196 to 0·8021), n_D^{20} 1·3959 (ref.[2–4] 1·3959). Isobutyl acetate was a technical reagent which contained approximately 10% free alcohols (isobutyl alcohol and small amounts of n-butyl alcohol). Since these alcohols form azeotropes with the ester the product was refluxed with acetic anhydride (100 ml/1 l ester), then washed with saturated K_2CO_3 solution and several times with water. Afterwards it was dried with anhydrous $MgSO_4$ and $CaCl_2$ (ref.[1]). Finally it was distilled on a twenty-plate packed column. The purity of isobutyl acetate obtained was checked by chromatography. The product did not contain free acetic acid nor alcohols and the n-butyl acetate content was approximately 1%. The found values of physical constants of isobutyl acetate used were as follows: n.b.p. 117·5°C (ref.[2] 118·0, ref.[5] 117·2—118·0), d_4^{20} 0·8715 (ref.[2] 0·8745), n_D^{20} 1·3902 (ref.[2] 1·39018).

Analytical method. The analysis of the equilibrium phase samples was made by means of a Paar digital densitometer DMA 02C. The dependence of sample compositions on the measured values of period was expressed by the relation

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$$(x_1M_1 + x_2M_2)/T = x_1M_1/T_1 + x_2M_2/T_2 + \\ + x_1x_2(x_1A_1 + x_2A_2 - x_1x_2A_3)\,, \tag{1}$$

where T is measured value of oscillation period with sample (mixture), M_1 and M_2 are molecular masses of pure component 1 and 2, T_1 and T_2 periods with pure components, x_1 and x_2 sample mole fractions, and A_1, A_2, A_3 are constants evaluated from experimental data by the least-square method. Calibration interpolation tables were then computed for direct reading sample compositions.

Apparatus and procedure. The equilibrium measurements were carried out in a modified Gillespie still. The description of the apparatus and measuring procedure can be found in the literature[6]. The pressure in the system was maintained at 101·3 kPa (760 Torr) and checked by measuring boiling point of water in an ebulliometer connected parallel to the equilibrium still. Temperature was measured by mercury standards calibrated by means of a Mueller bridge with platinum resistance thermometer Leeds and Northrup. The equilibrium samples were taken for analysis only if the boiling point in the still did not change for 20 minutes.

RESULTS AND DISCUSSION

The mutual dependence of equilibrium compositions of the liquid and vapour phases in a binary system is given by

$$y_1 = \alpha_{12}(x_1/x_2)/[1 + \alpha_{12}(x_1/x_2)]\,, \tag{2a}$$

$$y_2 = 1/[1 + \alpha_{12}(x_1/x_2)]\,, \tag{2b}$$

where x_1, x_2 are mole fractions of the component 1 and 2 in the liquid phase and y_1, y_2 those in the vapour phase. The relative volatility α_{12} is defined by

$$\alpha_{12} = (y_1/y_2)/(x_1/x_2)\,, \tag{3}$$

and for a low pressure region holds

$$\alpha_{12} = (\gamma_1/\gamma_2)\,(P_1^0/P_2^0)\,, \tag{4}$$

where P_1^0 and P_2^0 denote the vapour pressure of pure components at a given temperature and γ_1, γ_2 their activity coefficients. The temperature dependence of the vapour pressures of pure components P^0 (kPa) in the form of the Antoine equation

$$\log P^0 = A - B/(t + C)\,, \tag{5}$$

t is temperature (°C) and A, B, C are constants, was taken over from the literature (isobutyl alcohol: $A_1 = 6·41982$, $B_1 = 1230·810$, $C_1 = 170·947$ (ref.[7]); isobutyl acetate: $A_2 = 6·66967$, $B_2 = 1709·030$, $C_2 = 248·371$ (ref.[8])).

TABLE I

Vapour–Liquid Equilibrium in the Isobutyl Alcohol(1)–Isobutyl Acetate(2) System at 101·3 kPa

x_1	y_1	t, °C	$y_{1,\text{calc}}{}^{a} - y_{1,\text{exp}}$	
			Marg. 3	Marg. 4
0·003	0·007	117·17	−0·0013	−0·0012
0·009	0·017	116·74	0·0000	0·0002
0·017	0·030	116·53	0·0018	0·0020
0·031	0·054	116·17	0·0027	0·0029
0·041	0·070	115·87	0·0038	0·0040
0·053	0·091	115·52	0·0028	0·0028
0·073	0·121	115·07	0·0046	0·0042
0·100	0·160	114·51	0·0059	0·0049
0·133	0·203	113·82	0·0087	0·0069
0·171	0·253	112·97	0·0072	0·0047
0·217	0·307	112·15	0·0071	0·0043
0·268	0·362	111·39	0·0070	0·0043
0·325	0·418	110·65	0·0075	0·0057
0·388	0·476	109·96	0·0074	0·0070
0·455	0·532	109·34	0·0091	0·0106
0·539	0·597	108·73	0·0129	0·0164
0·642	0·681	108·16	0·0107	0·0151
0·759	0·774	107·74	0·0111	0·0139
0·846	0·848	107·62	0·0096	0·0099
0·923	0·920	107·65	0·0060	0·0045
Mean			0·0063	0·0063

[a] Constants of correlation equations: Marg. 3: A_{12} = 0·1298, A_{21} = 0·1357; Marg. 4: A_{12} = = 0·1355, A_{21} = 0·1604, D = 0·0751.

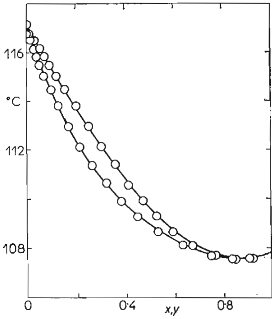

FIG. 1

t-x-y Diagram of the Isobutyl Alcohol(1)–Isobutyl Acetate(2) System at 101·3 kPa, t in °C

The concentration dependence of the activity coefficients was expressed by the Margules 3rd and 4th order equations:

$$\log(\gamma_1/\gamma_2) = x_2^2A_{12} - x_1^2A_{21} - 2x_1x_2(A_{12} - A_{21}) \tag{6}$$

and

$$\log(\gamma_1/\gamma_2) = x_2^2A_{12} - x_1^2A_{21} - 2x_1x_2[A_{12} - A_{21} + (x_2 - x_1)\,D]\,, \tag{7}$$

where A_{12}, A_{21}, D are constants characteristic for the given binary mixture and evaluated by means of the least-square method. The experimental vapour-liquid equilibrium data together with deviations between calculated and experimental values and with constants of correlation equations are given in Table I. The Margules equations do not provide the best fit of external data, probably because of neglecting the real behaviour of the vapour phase. Therefore an attempt was made to recalculate the data by using the correction factor in terms of virial coefficients. However, for isobutyl acetate neither virial coefficient nor critical constants were found in the literature. On using estimated values both for the critical constants and for the virial coefficient of isobutyl acetate and for the cross virial coefficient, no substantial improvement of the fit was reached.

As it is evident from Fig. 1, the system forms an azeotrope (107·61°C, 87·5 mol% isobutyl alcohol). The literature data on azeotropic behaviour in this system are unsatisfactory. In Horsley's Azeotropic Data[5] we find that the system is either azeotropic (Hannotte[9], 107·4°C, 55 mass% isobutyl alcohol) or nonazeotropic (Holley and Weaver[10], Lecat[11]). Nevertheless in the original Lecat work[11] the system is characterized as azeotropic one (107·6°C, ≈95 mass% isobutyl alcohol) as well as in his further work[12] (107·6°C, ~92 mass% isobutyl alcohol).

REFERENCES

1. Perrin D. D., Armarego W. L. F., Perrin D. R.: *Purification of Laboratory Chemicals.* Pergamon Press, London 1966.
2. *Technique of Organic Chemistry*, Vol. VIII, *Organic Solvents* (A. Weissberger, Ed.). Interscience, New York 1955.
3. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*, Vol. I. Elsevier, New York 1950.
4. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*, Vol. II. Elsevier, New York 1965.
5. Horsley L. H.: *Azeotropic Data III.* Adv. Chem. Ser. 116, Amer. Chem. Soc., Washinton 1973.
6. Hála E., Pick J., Fried V., Vilím O.: *Vapour–Liquid Equilibrium*, 2nd Ed. Pergamon Press, London 1967.
7. Boublík T., Fried V., Hála E.: *The Vapour Pressures of Pure Substances.* Elsevier, Amsterdam 1973.

8. Wichterle I., Linek J.: *Antoine Vapor Pressure Constants of Pure Compounds.* Academia, Prague 1971.
9. Hannotte T.: Bull. Soc. Chim. Belg. *35*, 85 (1926).
10. Holley C. D., Weaver J. T.: J. Amer. Chem. Soc. *27*, 1049 (1905).
11. Lecat M.: Rec. Trav. Chim. *45*, 620 (1926).
12. Lecat M.: Ann. Soc. Sci. (Bruxelles) *48B II*, 1 (1928).

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