Vapor-Liquid Equilibrium of System Methyl Isobutylketone–*n*-Butanol

Ebulliometric Method

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Vapor-liquid equilibrium data for the system methyl–isobutyl ketone–*n*-butanol were determined at 80°, 90°, and 100°C and 760 mm Hg total pressure from ebulliometric measurements obtained using a Swietolawski-type ebulliometer. Vapor compositions were obtained by numerical integration, and the vapor-liquid equilibrium data were then analyzed in terms of the three constant Redlich-Kister equations.

The importance of vapor-liquid equilibrium data cannot be overemphasized. Direct determinations of the vapor-liquid equilibria of the system methyl isobutylketone–*n*-butanol were limited by analytical difficulties. But in such cases like this, it is possible to calculate equilibrium compositions from indirect data such as ebulliometric measurements which are more precisely determined. In recent years, a number of methods have been described in literature (*1–6*) for interpreting isothermal and isobaric ebulliometric data. In the present investigation the vapor-liquid equilibrium data of the system methyl isobutylketone–*n*-butanol were determined from ebulliometric measurements at 80°, 90°, and 100°C and at a total pressure of 760 mm Hg.

MATERIALS AND APPARATUS

Purified methyl isobutylketone (n^{31}_{D} 1.3910, n_{d}^{30} 0.7909) and *n*-butanol (n^{31}_{D} 1.3960, n_{d}^{30} 0.8026) were used in the experiment. The ebulliometer used in the present work is similar to Swietolawski's (*5*) type with a minor modification. The accuracy of the temperature measurement was ±0.1°C; that of pressure ±1 mm Hg. Solutions prepared on weight basis were used in the experiment. To standardize the ebulliometer, a few pressure composition data on the system benzene–cyclohexane were taken at 45° and 55°C. From this, by the method of Scatchard et al. (*10*), the vapor compositions were calculated, and they were in good agreement. Thus it was demonstrated that the ebulliometer was giving consistent and accurate results.

Erdös (*3*) has proposed a method to obtain equilibrium vapor compositions from P-x measurements adopting the Runge-Kutta method of numerical integration. For the present system, the Erdös (*3*) method has been applied to obtain the equilibrium vapor compositions from the experimental P-x measurements at 80°, 90°, and 100°C. In the case of T-x data at 760 mm Hg total pressure, the vapor compositions are obtained by following the method of Hala et al. (*4*) adopting Milne's (*8*) method of numerical integration. After obtaining the calculated vapor compositions for isothermal and isobaric data, the data have been correlated by means of three constant Redlich-Kister (*9*) equations; the constants obtained in each case are reported in Table I. The vapor compositions and total pressures in the case of isothermal data and vapor compositions and temperatures of boiling in the case of isobaric data are calculated through the three constant Redlich-Kister equations. Sample data for each case have been presented in Table I. The calculated total pressure data showed an average deviation of 3.0, 3.2, and 4.2 mm Hg, respectively, for the data at 80°, 90°, and 100°C; the calculated temperatures of boiling showed an average deviation of 0.3°C for the data at 760 mm Hg total pressure. For each condition, about 29 readings were taken.

This system forms an azeotrope at 760 mm Hg total pressure. The azeotrope has a composition of 63.41 mol % methyl isobutylketone with a boiling point of 111.2°C; whereas Lecat (*7*) has reported it to be 63.36 mol % of methyl isobutylketone with a boiling point of 114.35°C. Though there is fair agreement between the two regarding the composition of azeotrope, the boiling points differ. Considering the accuracy of ebulliometric measurement of the present system, the authors' observed temperature of the azeotrope appears to be more reliable.

An expanded version of this paper, with the calculations and experimental results, has been deposited with the American Chemical Society Microfilm Depository Service.

Table I. Sample of Experimental Data on Ebulliometric Isothermal Data for System Methylisobutyl Ketone–*n*-Butanol

Sample no.	x_1	y_1 Calcd	P_T	Log γ_1	Log γ_2	ΔG_x^E
at 80°C, B = 0.3401, C = 0.1950, D = −0.1733						
5	0.1368	0.2465	194	0.1708	−0.0124	21
9	0.3001	0.4985	224	0.2129	−0.0209	80
16	0.5360	0.6418	249	0.1153	0.0562	143
22	0.7682	0.7352	255	0.0220	0.2305	114
26	0.9064	0.8608	244	0.0020	0.3289	53
at 90°C, B = 0.3394, C = 0.1800, D = −0.1156						
5	0.1368	0.2352	296	0.1810	−0.0085	29
9	0.3001	0.4683	331	0.2021	−0.0119	88
16	0.5360	0.6192	367	0.1134	0.0575	146
22	0.7682	0.7261	317	0.0263	0.2223	120
26	0.9064	0.8492	352	0.0035	0.3376	58
at 100°C, B = 0.3252, C = 0.1382, D = −0.047						
4	0.1368	0.2249	442	0.1912	−0.0039	39
8	0.3019	0.4325	484	0.1798	0.0016	95
13	0.5360	0.5973	521	0.1024	0.0612	143
19	0.7682	0.7211	520	0.0280	0.2037	118
22	0.9064	0.8441	493	0.0045	0.3245	59

at 760 Mm Hg Total Pressure

Sample no.	x_1	y_1	Temp, °C	Log γ_1	Log γ_2	ΔG_x^E
B = 0.3097, C = 0.1600, D = −0.0774						
4	0.1498	0.2202	115.0	0.1735	−0.0067	37
7	0.3019	0.4159	113.1	0.1793	−0.0069	88
12	0.5360	0.5856	111.3	0.1034	0.0525	141
18	0.7682	0.7075	111.7	0.0264	0.1992	118
22	0.9064	0.8356	113.5	0.0039	0.3140	59

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NOMENCLATURE

B, C, D = constants in Redlich-Kister equation
ΔG_x^E = excess free energy of mixing, cal/mole of the mixture
P_T = total pressure, mm Hg
x_i = mole fraction of component i in liquid
y_i = mole fraction of component i in vapor

GREEK LETTERS

γ_i = activity coefficient of component i

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Adsorption Isotherms at High Pressures

Comment on Data of Stacy et al.

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The adsorption isotherms of methane on carbon and on silica gel at 38–121°C up to 650 atm pressure, reported by Stacy et al., have an abnormal shape and give too high adsorption values. High-pressure adsorption isotherms theoretically should, and experimentally always do, exhibit a maximum at 100–200 atm pressure. The solitary exception in the case of Stacy et al. is apparently due to an error in their dead-space determination; the gas simply compressed into the unaccounted part of the dead space has completely masked the true adsorption.

In two recent papers in this Journal, Stacy et al. (*6*, *7*) have reported the adsorption isotherms of methane on carbon and on silica at 38–121°C and pressures up to 650 atm. These isotherms continuously increase with pressure. All hitherto published high-pressure adsorption isotherms (for reviews see *2*, *3*), however, show a distinct maximum in the isotherm at 100–300 atm pressure, provided the measurements have been carried out to at least 200 atm pressure. Examples are (*2*): the adsorption of CH_4 and H_2 on charcoal; CO_2, N_2O, and SiF_4 on charcoal; CH_4 on coal; Ar and N_2 on active carbon; N_2 and CO on alumina; and CH_4 on silica gel. It is possible even to predict (*4*) the pressure $P_{\max}$ at which adsorption isotherms should exhibit a maximum: $P_{\max} = (T/T_c)^2 P_c$, where T is the temperature of adsorption and T_c and P_c are the critical temperature and critical pressure of the adsorbate gas. This relationship holds good for ordinary adsorbents with not too fine pores. For microporous adsorbents with pores of molecular dimensions (e.g., activated charcoal or molecular sieves), the maximum in adsorption isotherm is reached even earlier: $P_{\max}$ = 60–80% of $(T/T_c)^2 P_c$. In the light of such results the data of Stacy et al. are examined and indications are given of the source of error which may have masked the true adsorption.

Stacy et al. (*6*) report [see correction (*6a*)] that the accuracy in the determination of the dead-space volume in their apparatus is only 1%. This is 0.66 cc for the dead-space volume of 66.4 cc. The quantity of gas which can be simply compressed into this 0.66 cc at high gas densities, attained at pressures of 300–600 atm, can be too large compared to the physical adsorption of methane at the same pressure on only 14.6 grams of carbon or 12.9 grams of silica used as the adsorbent at 38–121°C. This may perhaps have masked the true adsorption.

At pressures of 200–650 atm, the dimensional changes (compressibility as also the swelling on adsorption) of carbon and the penetration of methane into the interlamellar space in the graphitic planes in carbon will be appreciable (*5*), and what one measures can no longer be called adsorption in the ordinary sense of the term. Since Stacy et al. find continuously increasing isotherms for silica gel (*7*) as well, the inaccuracy in the dead-space determination seems to be the major source of error in their high-pressure adsorption isotherms.

It is also instructive here to compare the adsorption of methane on silica gel reported by Stacy et al. with the data for the same adsorbent-adsorbate system obtained by Gilmer and Kobayashi (*1*) in 1964 at temperatures of −40°, −20°, 0°, 20°, and 40°C and pressures up to 137 atm. Such comparisons of physical adsorption are permissible even if the chemical nature of the two silica surfaces may not be very similar. The BET surface areas for the two silicas are 145 and 532 m²/g, respectively. The nitrogen monolayer values (v_m) corresponding to these two surface areas are 1.48 and 5.4 mmol/g. These values may be taken as a rough indication for the maximum at-

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