Activity coefficients for the binary mixtures of methyl-ethylketone with some chlorohydrocarbons at 94.8 kPa

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ACTIVITY COEFFICIENTS FOR THE BINARY MIXTURES OF METHYL-ETHYLKETONE WITH SOME CHLOROHYDROCARBONS AT 94.8 kPa

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Activity coefficient at 94.8 kPa are evaluated over the entire composition range for the binary mixtures of methylethylketone with 1,2 dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane and tetrachloroethylene, through bubble point temperature measurements. A Swietoslawski-type ebulliometer is used for the measurements and the composition versus bubble point temperature measurements are well represented by the Wilson model.

Keywords: Activity coefficients; Bubble point temperatures; Methylethylketone; Chlorohydrocarbons

INTRODUCTION

The investigation on the activity coefficients of the binary mixtures noted in the abstract is in continuation of our recent studies on the phase equilibria of the binary mixtures containing chlorohydrocarbons [1,2]. The measurements have been carried out at 94.8 kPa. We could not locate any published phase equilibrium data on the mixtures chosen for this study.

EXPERIMENTAL SECTION

Method

A Swietoslawski type ebulliometer, very similar to the one described by Hala *et al.* [3] is used for this experimental investigation. Connection of the ebulliometer to a good vacuum system, through a mercury manometer in line, facilitated the creation and maintainance of the chosen pressure within ± 0.1 kPa. Equilibrium temperatures are measured to an accuracy of ± 0.1 K by means of a platinum resistance thermometer (carefully calibrated by point-to-point comparison with a Standard Platinum

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Resistance Thermometer certified by the National Institute of Standards and Technology, Boulder, USA). The liquid mixtures for the studies are prepared gravimetrically, making use of electronic balance precise to $+0.0001\,g$ and are stirred well before being placed in the ebulliometer. The heating rate is adjusted to yield the desired condensate drop rate of 30 drops per minute, in accordance with the suggestion of Hala *et al.* [3]. The equilibrium temperatures, measured after the steady condensate drop rate and constancy of temperature are maintained for at least thirty minutes, are reported.

Materials

Extrapure AR grade ethylmethylketone (SISCO Research Laboratories, Mumbai, India) is fractionally distilled twice, after prior drying over silica gel for two days. The middle fraction of the second distillation is stored in amber-colored bottles for use in the experiments. AR grade 1,2-dichloroethane (BDH Chemicals, Mumbai, India) is further purified by washing with dilute potassium hydroxide solution and water, dried over phosphorous pentoxide and fractional distillation twice. The middle fraction of the second distillation is stored in amber colored bottles for use in the experiments.

AR grade 1,1,1-trichloroethane (SD's Fine Chemicals, Boisar, India) is washed with concentrated hydrochloric acid followed by washing with 10% sodium chloride solution and drying over calcium chloride. A $0.5\,g$ phenol is added as stabilizer before subjecting the sample to fractional distillations. The middle fraction of the second distillation is stored in amber-colored bottles for use in the experiments.

AR grade 1,1,2,2-tetrachloroethane (SD's Fine Chemicals, Boisar, India) is shaken with concentrated sulfuric acid for ten minutes at 355 K. The discolored acid is removed and the acid washing is repeated several times until the acid discoloration stops. The product is then washed with water, dried over potassium carbonate and fractionally distilled twice. The middle fraction of the second distillation is stored in amber-colored bottles for use in the experiments.

AR grade tetrachloroethylene (SD's Fine Chemicals, Boisar, India) is dried over anhydrous sodium sulfate fractionally twice. The middle fraction of the second distillation is stored in amber-colored bottles for use in the experiments.

The fractional distillations are carried out using a packed column of length equivalent to thirty theoretical plates. The middle fractions of the second distillations are collected in amber-colored bottles for use in the experiments. The final distillations of the substances are carried out only a few hours before the commencement of the phase equilibrium experiments and enough care is taken to prevent absorption of moisture, oxidation, etc., during the intervening period. The purity of the chemicals is ascertained by measuring their density and refractive-index, which compare favourably with the literature values of Riddick *et al.* [4] as shown in Table I.

RESULTS AND DISCUSSION

The experimental liquid phase composition (x_1) versus temperature (T) data, summarized in Table II, are fitted to the Wilson [5] model.

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2[\{\Lambda_{12}/(x_1 + \Lambda_{12}x_2)\} - \{\Lambda_{21}/(x_2 + \Lambda_{21}x_1)\}] \qquad (1)$$

ACTIVITY COEFFICIENTS FOR MIXTURES

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TABLE I. Comparison of the density (D) and refractive-index (n) of the pure liquids used in this study with literature data of Riddick et al. [4] at 298.15 K

Substance	$D/(kg/m^{-3})$		n	
	This work	Literature	This work	Literature
Methylethylketone	800.0	799.70	1.3769	1.37685
1,2-Dichloroethane	1246.4	1246.37	1.4442	1.44210
1,1,1-Trichloroethane	1330.0	1329.90	1.4360	1.43590
1,1,2,2-Tetrachloroethane	1586.7	1586.66	1.4914	1.49140
Tetrachloroethylene	1614.3	1614.32	1.5030	1.50320

TABLE II. Bubble temperatures and activity coefficients of selected binary Methylethylketone + Chlorohydrocarbon mixtures at 94.8 k Pa

x_1	T/K	γ_1	γ_2	x_1	T/K	γ_1	γ_2
Methylethylketone (1) + 1,2-Dichloroethane (2)				1,1,1-Trichloroethane (1) + Methylethylketone (2)			
0.0000	354.95	0.9284	1.0000	0.0000	350.85	1.0199	1.0000
0.1283	354.65	0.9475	0.9986	0.1270	349.65	1.0810	1.0018
0.2690	354.25	0.9668	0.9935	0.3050	348.35	1.0491	1.0101
0.4490	353.55	0.9874	0.9815	0.4680	347.35	1.0277	1.0234
0.6020	353.75	0.9995	0.9681	0.6402	346.55	1.0122	1.0430
0.7790	351.85	1.0046	0.9576	0.7850	345.95	1.0042	1.0637
0.9130	351.15	1.0019	0.9743	0.9231	345.55	1.0005	1.0870
1.0000	350.85	1.0000	1.0237	1.0000	345.35	1.0000	1.1014
Methylethylketone (1) + 1,1,2,2-Tetrachloroethane				Methylethylketone (1) + Tetrachloroethylene (2)			
0.0000	426.95	0.5562	1.0000	0.0000	391.45	1.7588	1.0000
0.1638	402.95	0.6524	0.9790	0.1565	373.65	1.6154	1.0085
0.3290	388.15	0.7694	0.9210	0.3169	363.95	1.4665	1.0417
0.4690	376.95	0.8546	0.8516	0.4551	358.75	1.3427	1.1040
0.6100	367.55	0.9224	0.7713	0.6253	354.85	1.2013	1.2652
0.7010	362.55	0.9551	0.7174	0.7694	352.65	1.0969	1.5713
0.9340	352.85	0.9979	0.5829	0.9031	351.25	1.0232	2.2794
1.0000	350.85	1.0000	0.5472	1.0000	350.85	1.0000	3.7335

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1[\{\Lambda_{21}/(x_2 + \Lambda_{21}x_1)\} - \{\Lambda_{12}/(x_1 + \Lambda_{12}x_2)\}] \quad (2)$$

where

$$\Lambda_{12} = (V_1^L/V_2^L)\exp - [(\lambda_{12}-\lambda_{11})/RT] \quad (3)$$

and

$$\Lambda_{21} = (V_2^L/V_1^L)\exp - [(\lambda_{12}-\lambda_{22})/RT] \quad (4)$$

V_1^L and V_2^L are the liquid molar volumes and $(\lambda_{12} - \lambda_{11})/R$ and $(\lambda_{12} - \lambda_{22})/R$ are the Wilson parameters. Λ's are the energies of interaction between the molecules denoted by the subscripts. The optimum Wilson parameters are obtained by minimizing the objective function defined as

$$\varphi = \sum [(P_{cal}/P_{expt}) - 1]^2 \quad (5)$$

where P_{cal} and P_{expt} for the calculated and experimental total pressures. The Nelder-Mead optimization technique described by the Kuester and Mize [6] is used.

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TABLE III.   Antoine Constants for the Equation in $(P/kPa) = A - B/[(T/K) + C]$

Substance	A	B	C
Methylethylketone	14.5813	3150.41	−36.65
1,2-Dichloroethane	14.1590	2927.16	−50.22
1,1,1-Trichloroethane	13.9897	2802.75	−48.15
1,1,2,2-Tetrachloroethane	14.0633	3341.88	−62.15
Tetrachloroethylene	14.1690	3259.29	−52.20

TABLE IV.   Representation of the Measurements by the Wilson Model

System	$[(\lambda_{12} - \lambda_{11})/R]/K$	$[(\lambda_{12} - \lambda_{22})/R]/K$	Std. Dev. in T/K
Methylethylketone(1) + 1,2-Dichloroethanene(2)	−234.97	382.24	0.02
1,1,1-Trichloroethane(1) + Methylethylketone(2)	865.44	−497.37	0.02
Methylethylketone(1) + 1,1,2,2-Tetrachloroethane (2)	319.22	−243.43	0.04
Methylethylketone(1) + Tetrachloroethylene(2)	−308.25	500.00	0.05

Vapor pressures required in the computations are calculated from the Antoine constants, noted in Table III. The Antoine equation, with the constants noted in Table III, represents the literature vapor pressure data as well the present measurements on pure liquids with an average absolute deviation of 0.5%. The molar volumes of the pure liquids, calculated from the density measurements of this study (recorded in Table I) are used as the input in obtaining the optimum Wilson parameter. The result of the representation of the phase equilibrium data by the Wilson [5] model, summarized in Table IV, indicate that the data and the representation are quite good. Table II also presents the evaluated values of the activity coefficients for the binary mixtures investigated. The data and the representation presented in the paper are expected for engineering design purposes.

References

[1] P. Gnana Kumari, M.V. Prabhakara Rao, D.H.L Prasad and Y.V.L Ravikumar (2003). *Journal of Chemical Engineering Data*, **48**, 535–540.
[2] T.E. Vittal Prasad, B. Sarkar, R. Pavan Kumar and D.H.L Prasad (1998). *Fluid Phase Equilibria*, **213**, 147–152.
[3] E. Hala, J. Pick, V. Fried, and O. Villim (1958). *Vapor Liquid Euilibrium*. Pergamon, Oxford.
[4] J.A. Riddick, W. S. Bunger and T.K. Sakano (1986). *Organic Solvents: Physical Properties and Methods of Purification*, 4th Edn. Vol. 2. John Wiley, New York.
[5] G.M. Wilson (1964). *Journal of American Chemical Society*, **86**, 127–130.
[6] R.T. Kuester and J.H. Mize (1973). *Optimization Techniques with Fortran*. McGraw-Hill, New York.