Bubble Temperatures of the Binary Mixtures of Dimethylcarbonate with Some Alcohols at 95.8 kPa

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Boiling temperatures at 95.8 kPa over the entire composition range are measured for the binary systems formed by dimethylcarbonate with ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, *sec*-butanol, and *tert*-butanol. A Swietoslawski-type ebulliometer was used for the measurements. The composition vs temperature measurements are well represented by the Wilson model.

Introduction

This investigation on the boiling-temperature measurements 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 or alcohols.[1,2] The measurements have been carried out at 95.8 kPa. We could not locate any experimental data in the literature on the systems chosen for the present study for comparison purposes.

Experimental Section

Method. A Swietoslawski-type ebulliometer, very similar to the one described by Hala et al.[3] and briefly presented in our publication,[1] was used for this experimental investigation. Connection of the ebulliometer to a good vacuum system, through a mercury manometer in line, facilitated the creation and the maintenance of the chosen pressure within ±0.1 kPa. The equilibrium temperatures were measured to an accuracy of ±0.1 K by using a platinum-resistance thermometer, carefully calibrated by means of a point-to-point comparison with a Standard Platinum-Resistance Thermometer. The liquid mixtures for the studies were prepared gravimetrically, making use of an electronic balance precise to ±0.0001 g and stirred well before being placed in the ebulliometer. The estimated accuracies of the observed variables are ±0.1 kPa (pressure), ±0.1 K (temperature) and ±0.0005 (liquid-phase mole fraction). The heating rate was 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 were measured after a steady drop rate and constancy of temperature were maintained for at least 30 min.

Table 1. Comparison of the Density (*D*) and Refractive Index (*n*) of the Pure Substances Used in This Study with Literature Data at 298.15 K

	$D/(\mathrm{kg.m^{-3}})$		n	
substance	this work	lit[4,5]	this work	lit[4,5]
dimethylcarbonate[a]	1071.0	1070.00	1.3537	1.36870
ethanol	783.7	784.93	1.3600	1.35941
n-propanol	800.0	799.60	1.3807	1.38370
iso*p*ropanol	780.8	781.26	1.3800	1.37520
n-butanol	804.9	805.73	1.3980	1.39741
isobutanol	796.8	797.80	1.3839	1.39389
sec-butanol	802.0	802.41	1.3983	1.39530
tert-butanol	780.8	781.20	1.3887	1.38770

[a] At 293.15 K.

Materials. AR-grade chemicals used in this study are further purified according to the easiest possible method described in Riddick et al.[4] The purity of the chemicals is ascertained by measuring their density by means of a carefully calibrated pycnometer accurate to ±0.05% and refractive index for the sodium D-line using an Abbe-type refractometer accurate to ±0.05%, which compares favorably with the literature values[4,5] as shown in Table 1.

Results and Discussion

The experimental liquid-phase composition (x_1) vs temperature (T) data, summarized in Table 2, were fitted to the Wilson[6] model. The optimum Wilson parameters were obtained by minimizing the objective function defined as

$$\varphi = \sum[(P_{\mathrm{cal}}/P_{\mathrm{exp}}) - 1]^2 \tag{1}$$

where P_{cal} and P_{exp} stand for the calculated and experimental total pressures. The Nelder−Mead optimization technique described by Kuester and Mize[7] was used. Vapor pressures needed in the computations were calculated by using the Antoine equation with the constants noted in Table 3. Prior to use, the Antoine equation, with the constants noted in Table 3, was compared to all the

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Table 2. Boiling-Point Temperatures of Select Binary Dimethylcarbonate + Alcohol Mixtures at 95.8 kPa

ethanol (1) + dimethyl-carbonate (2)		dimethyl-carbonate (1) + *n*-propanol (2)		isopropanol (1) + dimethyl-carbonate (2)		dimethyl-carbonate (1) + *n*-butanol (2)		dimethyl-carbonate (1) + isobutanol (2)		dimethyl-carbonate (1) + *sec*-butanol (2)		*tert*-butanol (1) + dimethyl-carbonate (2)	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.0000	361.25	0.0000	369.95	0.0000	361.25	0.0000	389.45	0.0000	379.65	0.0000	371.35	0.0000	361.25
0.1980	348.45	0.0750	364.05	0.1805	354.25	0.0910	375.95	0.0910	370.95	0.0910	365.75	0.1510	355.95
0.3310	347.35	0.1540	362.35	0.3050	352.35	0.1651	372.35	0.1670	367.95	0.1660	363.95	0.2630	353.95
0.4264	347.05	0.2450	361.15	0.3970	351.55	0.2842	369.05	0.2870	365.25	0.2650	362.55	0.3430	353.05
0.4978	346.85	0.3540	360.55	0.4670	351.25	0.3721	367.65	0.3750	364.05	0.3741	361.45	0.4162	352.35
0.5534	346.65	0.4710	360.35	0.5220	350.95	0.4422	366.65	0.4400	363.45	0.4432	360.95	0.5510	351.95
0.6942	346.85	0.5260	359.95	0.6680	350.85	0.5760	364.95	0.5780	362.35	0.5781	360.45	0.6200	351.85
0.7730	347.05	0.5970	359.75	0.7511	351.05	0.6450	364.05	0.6470	361.85	0.6460	360.25	0.7101	351.95
0.8739	347.95	0.6910	359.65	0.8580	351.75	0.7311	363.15	0.7330	361.45	0.7331	360.35	0.8302	352.35
0.9316	348.55	0.8170	360.35	0.9240	352.45	0.8450	362.05	0.8460	361.05	0.8470	360.45	0.9072	352.95
1.0000	339.45	1.0000	361.25	1.0000	354.05	1.0000	361.25	1.0000	361.25	1.0000	361.25	1.0000	353.15

Table 3. Antoine Constants for the Equation $\ln(P/\text{kPa}) = A - B/[(T/\text{K}) + C]$

substance	A	B	C
dimethylcarbonate	13.4072	2365.21	−70.15
ethanol	16.8945	3803.98	−41.08
n-propanol	15.5289	3166.37	−80.20
isopropanol	16.6755	3640.20	−53.54
n-butanol	15.1986	3137.02	−94.43
isobutanol	14.8538	2874.72	−100.30
sec-butanol	15.1928	3026.03	−86.65
tert-butanol	14.8374	2658.29	−95.50

Table 4. 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
ethanol (1) + dimethylcarbonate (2)	781.46	−15.00	0.07
dimethylcarbonate (1) + *n*- propanol (2)	729.20	−70.48	0.10
dimethylcarbonate (1) + isopropanol (2)	130.66	220.69	0.06
dimethylcarbonate (1) + *n*-butanol(2)	625.23	34.81	0.03
dimethylcarbonate (1) + isobutanol (2)	496.36	43.57	0.07
dimethylcarbonate (1) + *sec*-butanol (2)	565.56	−64.35	0.06
tert-butanol (1) + dimethylcarbonate (2)	129.47	152.58	0.06

available literature vapor pressure data. It represented the literature vapor pressure data as well as 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 1) were used as the input in obtaining the optimum Wilson parameters. The results of the representation of the phase equilibrium data by the Wilson[6] model, summarized in Table 4, indicate that the data and the representation are quite good. The data and the representation presented in the paper are expected to be useful for engineering design purposes.

Literature Cited

(1) Vittal Prasad, T. E.; Sravan Kumar, S.; Prasad, D. H. L. Boiling Temperature Measurements on the Binary Mixtures Formed by Acetonitrile with Some Chloroethanes and Chloroethylenes. *Fluid Phase Equilib.* **2002**, *201*, 47−55.

(2) Vittal Prasad, T. E.; Satya Kishore, P.; Ramserish, G. V.; Prasad, D. H. L. Boiling Temperature Measurements on the Binary Mixtures of *n*-Heptane with Some Aliphatic Alcohols. *J. Chem. Eng. Data* **2001**, *46*, 1266−1268.

(3) Hala, E.; Pick, J.; Fried, V.; Villim, O. *Vapor Liquid Equilibrium*; Pergamon: Oxford, 1958.

(4) Riddick, J. A.; Bunger, W. S.; Sakno, T. K. *Organic Solvents−Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986; Vol. 2.

(5) *Dictionary of Organic Compounds*, 6th ed.; Chapman & Hall: London, 1996; Vol. 3.

(6) Wilson, G. M. Vapor Liquid Equilibrium XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−137.

(7) Kuester, R. T.; Mize, J. H. *Optimization Techniques with Fortran*; McGraw-Hill: New York, 1973.

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