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for the system of ethylene and ethane because the adsorption sites with higher energies were predominantly occupied by the propylene molecules.

Registry No. Carbon, 7440-44-0; ethylene, 74-85-1; ethane, 74-84-0; propylene, 115-07-1.

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Liquid Density as a Function of Temperature of Five Organic Solvents

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The liquid densities of pure samples of monoethanolamine, diethanolamine, sulfolane, *N*-methylpyrrolidone, and propylene carbonate were measured at several temperatures ranging from 10 to 60 °C. The experimental data as a function of temperature were fitted to a polynomial equation of the following form: $d/(g\ cm^{-3}) = a + b(t/^\circ C) + c(t/^\circ C)^2$. Values of the constant Z_{RA} of the modified Rackett equation were evaluated from the experimental data.

Introduction

There has always been a continuing need for reliable values of liquid densities of organic solvents particularly of those involved in industrial processes. During an investigation of the solubility of acid gases in aqueous solutions of alkanolamines and in mixtures of physical solvents with chemical solvents (1) we measured the density of monoethanolamine (MEA) at 8 temperatures from 25 to 60 °C, diethanolamine (DEA) at 8 temperatures from 25 to 60 °C, tetramethylene sulfone or sulfolane (TMSO₂) at 7 temperatures from 30 to 60 °C, *N*-methylpyrrolidone (NMP) at 11 temperatures from 10 to 60 °C, and propylene carbonate (PC) at 11 temperatures from 10 to 60 °C.

Experimental Section

Materials. The samples of MEA and DEA were obtained from J. T. Baker with a reported purity of 99.56 and 98.5 mol %, respectively. The TMSO₂ was obtained from Eastman Organic Chemicals. The NMP was from Matheson Coleman and Bell with a quoted purity of 98 mol %. The PC was obtained from Merck with a reported purity of 99 mol %. Each of the five solvents was further purified by repeated fractionation in a stream of nitrogen under reduced atmosphere in a 70-cm packed glass column and then stored over molecular sieve to remove any traces of water. Analysis of the purified samples by gas-liquid chromatography using an OV-101 packed column showed no impurities with a lower limit of detection of impurities of 0.05 mol %.

Table I presents a comparison of the refractive indices measured in this work with values from the literature for each of the five solvents studied.

Apparatus and Procedure. Measurements of liquid densities were carried out with a Sodev 03D vibrating densimeter thermostated by a Heto circulating bath which controlled the temperature within ± 0.003 K as measured with a H-P quartz thermometer. The densimeter used here applies the principle of the vibrating tube first developed by Kratky et al. (8) which determines the density from the period of oscillation of a tube

containing the liquid investigated. The instrument and procedure have been described in the literature (8).

Results

In order to test the precision of the method we measured the density of aqueous NaCl solutions at 25 °C in the concentration range 0–2 *m*. Our results were compared with those of Picker et al. (9) and showed a mean percent deviation of 0.02. Figure 1 shows this comparison. We believe the precision and accuracy of our density measurements to be $\pm 0.03\%$ in the whole range of density values and in the temperature range considered.

All the experimental results for MEA, DEA, TMSO₂, NMP, and PC are summarized in Table II along with data from other studies. The two values for MEA quoted by Maddox (3) are in better agreement with our results than the values reported by Matthews et al. (10), which are systematically lower. It is probable that the sample of MEA used in the latter work was not pure enough. The literature values for DEA (3) at 30 and 60 °C are in reasonable agreement with our values. There exist differences for TMSO₂ between our values and those reported in the literature (5, 11) which fall outside the precision of our measurements. The same purification procedure was used in these studies. We have uncovered no previous reports of measurements for NMP so that comparison was not possible. Only three values were found in the literature for PC (7) at three different temperatures and the agreement is poor.

The set of values for each solvent was fitted by a least-squares method to the following polynomial equation:

$$d/(g\ cm^{-3}) = a + b(t/^\circ C) + c(t/^\circ C)^2 \quad (1)$$

The calculated values for the coefficients *a*, *b*, and *c* are compiled in Table III, which also contains the mean percent deviation.

A rather complete study (12, 13) on correlations for predicting liquid densities as a function of temperature showed that a modified form of the Rackett equation (14) is quite suitable for reproduction of experimental data. The modified Rackett equation is

$$1/d = (RT^c/p^c)Z_{RA}^{[1+(1-T_c/T)^{2/7}]} \quad (2)$$

where Z_{RA} is a constant which is to be determined from experimental data.

We have determined values of Z_{RA} for each of the five solvents studied by using calculated values of the critical temperature T^c and pressure P^c through Lydersen's method (15). There exist in the literature values of T^c and P^c for MEA (3, 16) and DEA (3); however, in order to keep consistency throughout we chose to use the calculated values. When the

Table I. Refractive Indices of the Solvents Studied

solvent	refractive index					
	this work			lit.		
	20 °C	25 °C	30 °C	20 °C	25 °C	30 °C
MEA	1.4545	1.4525		1.4540 ^a	1.4525, ^b 1.4068 ^c	
DEA	1.4750	1.4735	1.4721			1.4750 ^b
TMSO ₂		1.4833	1.4816		1.4840, ^c 1.4830 ^d	1.4817 ^d
NMP	1.4700	1.4675		1.4700 ^e	1.4684 ^c	
PC	1.4215	1.4199		1.4209 ^f	1.4193, ^f 1.4189 ^c	

^a Reference 2. ^b Reference 3. ^c Reference 4. ^d Reference 5. ^e Reference 6. ^f Reference 7.

Table II. Experimental Data at Different Temperatures *t*

d/(g cm ⁻³)			d/(g cm ⁻³)		
t/°C	this work	lit.	t/°C	this work	lit.
MEA			NMP		
25	1.0127	0.9837, ^a 1.0113 ^b	10	1.0389	
30	1.0089	0.9798 ^a	15	1.0347	
35	1.0033	0.9759 ^a	20	1.0304	
40	1.0002	0.9719 ^a	25	1.0259	
45	0.9967		30	1.0217	
50	0.9918		35	1.0159	
55	0.9876		40	1.0120	
60	0.9833	0.9844 ^b	45	1.0082	
DEA			50	1.0030	
25	1.0936		55	0.9979	
30	1.0909	1.0881 ^b	60	0.9934	
35	1.0860		PC		
40	1.0838		10	1.2105	
45	1.0811		15	1.2054	
50	1.0771		20	1.2006	1.203 ^e
55	1.0736		25	1.1951	1.198 ^e
60	1.0700	1.0693 ^b	30	1.1901	
TMSO ₂			35	1.1832	
30	1.2604	1.2614, ^c 1.2619 ^d	40	1.1786	1.183 ^e
35	1.2541	1.2568 ^c	45	1.1738	
40	1.2506	1.2525, ^c 1.2534 ^d	50	1.1677	
45	1.2467	1.2494 ^c	55	1.1619	
50	1.2412	1.2447, ^c 1.2447 ^d	60	1.1565	
55	1.2376	1.2403 ^d			
60	1.2319	1.2360, ^c 1.2360 ^d			

^a Reference 10. ^b Reference 3. ^c Reference 5. ^d Reference 11. ^e Reference 7.

Table III. Coefficients of Eq 1

solvent	<i>a</i>	10 ⁴ (- <i>b</i>)	10 ⁷ (- <i>c</i>)	10 ³ . (mean deviation), ^a %
MEA	1.03297	8.0498	3.595	30
DEA	1.10897	5.9374	8.905	26
TMSO ₂	1.28635	8.7470	4.400	45
NMP	1.04753	8.437	10.000	27
PC	1.22084	10.0700	11.000	25

^a Mean % deviation = $(100/N) \sum_{i=1}^N |d_{\text{exptl}} - d_{\text{calcd}}| / d_{\text{exptl}}$

Table IV. *Z*_{RA} Values for Modified Rackett Equation, Critical Constants,^a and Mean Percent Deviation

solvent	NP	<i>T_r</i> range	<i>Z</i> _{RA}	<i>T^c</i> /K	<i>P^c</i> /atm	mean deviation, %
MEA	8	0.468-0.523	0.2491	636.73	67.84	0.20
DEA	8	0.422-0.471	0.2507	706.63	46.52	0.25
TMSO ₂	7	0.357-0.392	0.2396	849.54	49.63	0.06
NMP	11	0.391-0.460	0.2516	724.09	47.20	0.13
PC	11	0.365-0.429	0.2446	775.43	53.38	0.24
TMSO ₂ ^b	20	0.357-0.469	0.2393	849.54	49.63	0.04

^a Calculated with Lydersen's method (15). ^b Data from ref 11.

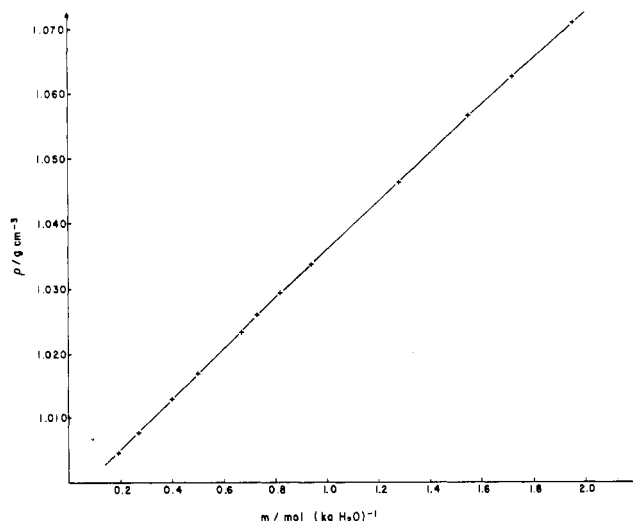


Figure 1. Comparison of density values for aqueous solutions of NaCl: (+) experimental points obtained in this work; (-) experimental results of ref 8.

literature values of *T^c* and *P^c* are used for the calculation of *Z*_{RA}, the mean percent deviation obtained is 0.43 and 0.35 for MEA and DEA, respectively, whereas a lower deviation was obtained for the same solvents when using the calculated *T^c* and *P^c*. Table IV contains values of *Z*_{RA}, *T^c*, and *P^c* for the five solvents together with the mean percent deviation. It is worthwhile to note that for TMSO₂ the value of *Z*_{RA} obtained from our experimental data is very similar to the value obtained when using data of ref 11 in a larger range of *T_r*. This means that extrapolation with the modified Rackett equation is possible without losing too much precision in relatively large intervals of *T_r*.

Glossary

<i>m</i>	molality, mol (kg of H ₂ O) ⁻¹
<i>d</i>	density, g cm ⁻³
<i>t</i>	temperature, °C
<i>T^c</i>	critical temperature, K
<i>P^c</i>	critical pressure, atm
<i>R</i>	molar gas constant, (atm cm ³)/(mol K)
<i>T_r</i>	reduced temperature, <i>T</i> / <i>T^c</i>
NP	number of data points
<i>a</i> , <i>b</i> , <i>c</i>	constants in eq 1

Z_{RA} constant of the modified Rackett equation (eq 2)

Registry No. MEA, 141-43-5; DEA, 111-42-2; TMSO₂, 126-33-0; NMP, 872-50-4; PC, 108-32-7.

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Excess Gibbs Energies and Excess Volumes of 1-Butanol-*n*-Heptane and 2-Methyl-1-propanol-*n*-Heptane Binary Systems

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Isothermal P - x - y and excess volume data for 1-butanol and 2-methyl-1-propanol in *n*-heptane are measured. The vapor-liquid equilibrium data were reduced according to the maximum likelihood principle. The parameters of NRTL, Wilson, and UNIQUAC equations were calculated and reported.

Introduction

In a previous paper (1) of this series we presented the vapor-liquid equilibrium and excess volume data of 1-butanol and 2-methyl-1-propanol in *n*-hexane. Here we carry on the study of aliphatic alcohol-alkane systems.

This article reports the results of measurements on vapor-liquid equilibria for the 1-butanol-*n*-heptane system at 333.15 and 363.15 K and for the 2-methyl-1-propanol-*n*-heptane system at 333.15 K. The experimental excess volumes at 298.15 K for both systems are reported too.

Experimental Section

Materials. The 1-butanol and 2-methyl-1-propanol used in this work were Merck "pro analysis" products, with a stated minimum purity of 99.5% and 99.0%, respectively.

The *n*-heptane was "Lichrosolv" reagent from Merck with a 99.7% grade.

These materials were purified by fractional distillations under 80-kPa pressure, with an Oldershaw type, 60 real plates, column.

The measured densities and vapor pressures of purified samples are shown in Table I compared with the literature values.

Apparatus and Procedure. The vapor-liquid equilibrium data were determined by using the still and the technique described

previously (2). The temperature inside the equilibrium cell was measured by means of a Lauda digital R 42 thermometer, with a platinum resistance thermometer calibrated in the apparatus by consecutive measurements of boiling points for several pure components in the pressure range of 5-100 kPa and at 298.15-373.15 K. In this case, the temperature uncertainty is $\sigma_e(T) = 0.01$ K. Pressure was measured by means of a Texas Instruments precision pressure gauge, with a fused-quartz Bourdon tube, calibrated against a mercury manometer for the range 0-101 kPa. The inaccuracy of the pressure measurements was determined as $\sigma_e(P) = 0.009$ kPa. Temperature was maintained constant by using the method described previously (3).

Liquid and vapor compositions were determined by densimetric analysis with an Anton Paar DMA 60 densimeter and two DMA 601 M cells. Measuring cells were thermoregulated better than 0.01 K.

The sampling of vapor and liquid phases from the ebulliometer was carried out by a recently published (2) technique. Compositions of both phases were analyzed continuously in the flow system.

Experimental Results and Treatments

Excess Volume Data. The excess volumes were calculated for the measured densities from mixtures of known composition prepared by weighing into syringes equipped with three-way valves. The best attention was given to reduce the vapor volume and to dry the internal parts of the valve. This technique is used for preventing the partial evaporation of samples. The experimental data are given in Table II.

Equation 1, proposed by Neau (4) for alcohol-alkane binary systems, correlated the excess volumes calculated from density:

$$v^E/x_1x_2 = \sum_{j=1}^m A_j Y_j \quad (1)$$