Table III. Entropy of Solution (cal deg^{-1}) and Solubility of Mercury(II) Octadecanoate at 298.15 K

solvent	ΔS^a	$-R \ln X_{2,satd}$
formamide	−14.85	19.51
N,N-dimethylformamide	34.97	25.04
cyclohexanone	8.52	16.91
water	29.58	35.19

$^a = -R[\partial \ln X_2/\partial \ln T]_{satd,P}$.

corded in Table III along with $-R \ln X_{2,satd}$ values at 298.15 K.

The entropy of solution can alternatively be obtained by dividing the process of transfer of solute from solid to saturated solution at constant temperature into three steps, viz., (i) fusion of solid solute, (ii) expansion of $(1 - X_{2,satd})/X_{2,satd}$ mol of solvent by a volume equivalent to $\bar{V}_2 - V_2°$, i.e., the difference in the partial molar volume of solute in the solvent $\bar{V}_2$ and the molar volume of pure liquid solute $V_2°$, and (iii) mixing the liquid solute and liquid solvent at constant volume, so that

$$\Delta S = \Delta S_{fusion} + \Delta S_{expan} + (\Delta S_{mix})_V$$

$$= \Delta S_{fusion} + (\bar{V}_2 - V_2°)(\partial P/\partial T)_V - R[\ln \phi_2 + \phi_1(1 - v_2°/v_1°)] \quad (2)$$

where ϕ_1 and ϕ_2 are the volume fractions of the solvent and the solute, respectively. When $X_{2,satd}$ is small, eq 2 can be rewritten as

$$\Delta S = \Delta S_{fusion} + (\bar{V}_2 - V_2°)(\partial P/\partial T)_V - R \ln X_{2,satd} - R[1 - v_2°/v_1° + \ln(v_2°/v_1°)] \quad (3)$$

For the systems under investigation, very low values for the term $\Delta S + R \ln X_2$ are obtained (Table III). The numerical value of the last term of eq 3 is expected to be between 2 and 6 cal deg^{-1} and therefore does not contribute significantly to this. Apparently ΔS_{expan} offers large negative contribution to the entropy of dissolution revealing that $\bar{V}_2 \ll V_2°$.

The data clearly indicate the existence of specific solute–solvent interactions resulting in either complexation or intermolecular bonding of MOD with the polar solvents. In highly polar solvents, namely, formamide, N,N-dimethylformamide, and cyclohexanone, the association effect of soap dipoles is expected to be considerably reduced and, as a result of this, solutions of unimolecular solute are obtained. The increased solubilities of MOD in these solvents may be a consequence of increased unimolecular solute–solvent interactions (*8–10*).

The results reported here shall be used along with other solution and surfactant properties of MOD to assess its applied utility.

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Registry No. Mercury(II) octadecanoate, 645-99-8; dimethylformamide, 68-12-2; cyclohexanone, 108-94-1; water, 7732-18-5; formamide, 75-12-7.

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Adsorption of Binary Gaseous Mixtures of Ethylene–Ethane and Ethylene–Propylene on a Carbon Molecular Sieve

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The adsorption of two binary gaseous mixtures on a carbon molecular sieve (MSC·5A) was measured. The adsorption equilibrium data for the system of ethylene–ethane–MSC·5A were obtained at 30 °C and at pressures of 20, 50, and 100 mmHg. The adsorption for the system of ethylene–propylene–MSC·5A was measured at 1.4 (at 5, 10, and 30 mmHg), 30 (20 and 50 mmHg), and 50 (30 and 70 mmHg) °C. The selectivity for the heavy component from the mixture was observed in both systems. The heterogeneity of the surface of the adsorbent was quite evident at low pressures for the system of ethylene and propylene, but was not evident at any pressure for the system of ethylene and ethane.

In the adsorption of binary gaseous mixtures on a heterogeneous and microporous adsorbent the adsorbed amount of the heavier component of the two was always greater than the value predicted from the isotherms of the pure components (*1*, *2*). There is a need for systematic experimental data for the adsorption of mixtures on a microporous adsorbent in order to develop prediction and correlation methods. In this paper the adsorption equilibrium were measured at 30 °C and at 20, 50, and 100 mmHg for the system of ethylene–ethane–carbon molecular sieve (MSC·5A), and at 1.4 (at 5, 10, and 30 mmHg), 30 (20 and 50 mmHg), and 50 (30 and 70 mmHg) °C for the system of ethylene–propylene–MSC·5A.

Experimental Section

The experimental apparatus and the procedure were the same as those previously reported (*1*) except that an integrator

Table I. Coefficients of Eq 1

i	C_i	i	C_i
0	-1.7075151	5	2.2905741×10^{-7}
1	2.1405734×10^{-1}	6	$-2.2507213 \times 10^{-9}$
2	$-1.4298913 \times 10^{-2}$	7	$1.3443779 \times 10^{-11}$
3	5.8357688×10^{-4}	8	$-4.4570719 \times 10^{-14}$
4	$-1.4612735 \times 10^{-5}$	9	$6.2848773 \times 10^{-17}$

Table II. Adsorption Equilibrium Data for the System of Ethylene (1)-Ethane (2)-MSC·5A at 30 °C

press., mmHg	adsorbed amount, mmol/(g of adsorbent)		Y_1 [a]
	ethylene	ethane	
19.63	0.0834	0.7226	0.1449
19.53	0.1209	0.6578	0.2319
19.43	0.1879	0.5826	0.3404
19.98	0.2592	0.5208	0.4486
20.06	0.3198	0.4500	0.5562
20.12	0.4000	0.3585	0.6521
19.97	0.4478	0.2760	0.7373
19.81	0.5480	0.1896	0.8452
20.28	0.6079	0.0874	0.9258
50.00	0.1148	1.0642	0.1398
49.62	0.1743	0.9737	0.2204
50.07	0.2765	0.8886	0.3250
50.45	0.3832	0.7662	0.4283
50.29	0.4807	0.6617	0.5302
50.03	0.6004	0.5271	0.6290
50.43	0.6866	0.4124	0.7193
49.79	0.8428	0.2740	0.8235
50.12	0.9319	0.1263	0.9149
100.00	0.1405	1.3353	0.1335
100.85	0.2133	1.2434	0.2142
100.88	0.3575	1.0884	0.3152
98.85	0.4979	0.9653	0.4165
100.28	0.6217	0.8307	0.5166
99.56	0.7816	0.6505	0.6156
100.03	0.9087	0.5014	0.7075
100.58	1.1119	0.3346	0.8123
99.95	1.2143	0.1639	0.9112

[a] Gas-phase mole fraction.

was used for the gas-chromatographic analysis and that the volume of the sampling cell for the analysis was reduced to 0.69 mL. The carbon molecular sieve (MSC·5A) had the same physical properties as that used previously (*2*). The purities of ethylene, ethane, and propylene were 99.9, 99.7, and 99.7 mol %, respectively. The adsorption isotherms of ethane were measured by using an electric balance (Cahn RG-HV) with a mercury manometer and an electric pressure gage (Baratron 221A-1000).

Results

The adsorption isotherms for pure ethylene and propylene at 30 and 50 °C, which were necessary to the study of their mixtures, were reported elsewhere (*2*). Instead of the required isotherms of ethylene and propylene at 1.4 °C in this work, the isotherms at 1.7 °C (*2*) were applied because the difference in the amounts adsorbed at 1.4 and 1.7 °C was so small that it could be neglected. The isotherm for pure ethane at 30 °C was measured in this study up to a pressure of 150 mmHg. The 29 data points of three runs could be well correlated by the following equation with a standard deviation of 0.010 mmol/(g of adsorbent):

$$\ln a = \sum_{i=0}^{9} C_i P^i \qquad (1)$$

where a is the amount adsorbed in mmol/(g of adsorbent) and P is the pressure in mmHg. The values of the coefficients are listed in Table I. Table II shows the adsorption equilibrium data for the system of ethylene–ethane–MSC·5A at 30 °C.

Table III. Adsorption Equilibrium Data for the System of Ethylene (1)-Propylene (2)-MSC·5A

press., mmHg	adsorbed amount, mmol/(g of adsorbent)		Y_1 [a]
	ethylene	propylene	
	Temperature = 1.4 °C		
4.61	0.0323	1.6069	0.4112
5.12	0.0877	1.3859	0.7483
4.87	0.1846	1.0255	0.8959
5.26	0.2498	0.8344	0.9435
5.35	0.2888	0.5632	0.9795
4.64	0.3939	0.3733	0.9913
9.94	0.0367	1.8312	0.2755
9.31	0.1763	1.4035	0.8148
9.96	0.2624	1.0939	0.9168
10.46	0.3850	0.8213	0.9620
9.25	0.4959	0.6109	0.9837
31.47	0.0279	2.1564	0.1749
30.11	0.0385	2.0663	0.3722
29.98	0.1133	1.9222	0.5890
31.16	0.1626	1.6704	0.7642
29.02	0.2789	1.4505	0.8914
29.43	0.3971	1.2814	0.9468
	Temperature = 30.0 °C		
19.89	0.0045	1.5730	0.1849
19.56	0.0099	1.4745	0.3949
19.76	0.0310	1.3463	0.5748
19.84	0.0700	1.2946	0.6657
20.32	0.0891	1.2005	0.7564
20.07	0.1764	0.9701	0.8779
20.70	0.2246	0.7545	0.9403
21.92	0.3222	0.5787	0.9680
21.67	0.5858	0.2396	0.9898
51.80	0.0047	1.8757	0.1349
50.59	0.0057	1.7959	0.3004
49.79	0.0333	1.7095	0.4580
49.77	0.0634	1.6679	0.5366
49.83	0.0687	1.6101	0.6251
49.64	0.1315	1.4150	0.7778
48.93	0.2067	1.2040	0.8729
51.27	0.3190	0.9759	0.9282
52.53	0.7152	0.4683	0.9818
	Temperature = 50.0 °C		
30.04	0.0005	1.3723	0.1627
29.82	0.0197	1.2896	0.4536
29.87	0.0481	1.1732	0.5663
30.02	0.0660	1.0449	0.7111
30.83	0.1248	0.8904	0.8087
30.91	0.2083	0.6609	0.9143
29.88	0.3069	0.3393	0.9767
69.15	0.0071	1.7098	0.1353
69.44	0.0271	1.6065	0.2807
69.95	0.0585	1.4732	0.4861
70.12	0.1777	1.1989	0.7365
68.99	0.2278	0.9764	0.8597
69.85	0.3777	0.5950	0.9537
69.31	0.6272	0.2783	0.9865

[a] Gas-phase mole fraction.

Table III shows the adsorption equilibria for the system of ethylene–propylene–MSC·5A at 1.4, 30, and 50 °C.

By plotting the amount adsorbed of component 1 on the *X* axis and that of component 2 on the *Y* axis at a constant temperature and pressure, one can get information on the heterogeneity of the surface of the adsorbent, since the plotted curve for the adsorption on a homogeneous surface without interactions among the adsorbed molecules is a linear line. The plotted curves for the mixtures of ethylene and ethane at three different pressures and at 30 °C were almost linear and the surface in this case could be considered homogeneous. The plotted curves for the adsorption of the mixture of ethylene and propylene were considerably concave. This suggested that the surface heterogeneity was more evident for this system than 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: $d/(\mathrm{g\ cm^{-3}}) = a + b(t/°\mathrm{C}) + c(t/°\mathrm{C})^2$. 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 ($TMSO_2$) 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 $TMSO_2$ 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 ±0.03% in the whole range of density values and in the temperature range considered.

All the experimental results for MEA, DEA, $TMSO_2$, 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 $TMSO_2$ 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:

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

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

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

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

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