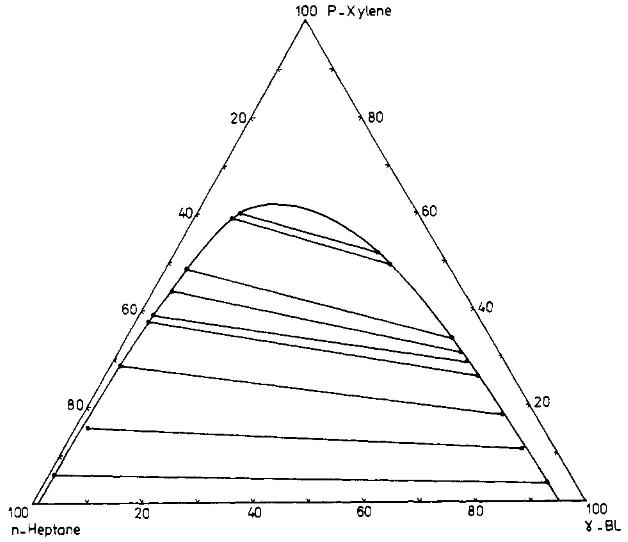

Figure 3. Phase equilibrium for the γ-butyrolactone–*n*-heptane–*p*-xylene system at 298.15 K.

Figures 1, 2, and 3 show that the slopes of the tie lines are steeper in the benzene system than that in the corresponding toluene and *p*-xylene systems; i.e., the plait point is located in the region of mixtures containing more γ-butyrolactone in the case of benzene. So the separation of benzene from *n*-heptane by extraction with γ-butyrolactone can be achieved in fewer stages than the separation of toluene and *p*-xylene from *n*-heptane. On the other hand, comparison of the solubility gaps in Figures 1, 2, and 3 shows that the capacity of γ-butyrolactone is a little greater for *p*-xylene than for benzene and toluene.

A comparison of the selectivities of γ-butyrolactone, *N*-formylmorpholine, dimethyl sulfoxide, glycols, sulfolane, and *N*-methylpyrrolidone was based on the liquid–liquid equilibria data available in the literature for the system solvent–benzene–*n*-heptane. The selectivity of γ-butyrolactone is higher than that of glycols, dimethyl sulfoxide, and *N*-methylpyrrolidone (*4*). γ-Butyrolactone has low selectivity for aromatic hydrocarbons compared to that of sulfolane (*13*). The selectivities of γ-butyrolactone and *N*-formylmorpholine are not comparable because the hydrocarbon models in the two cases are different.

Glossary

K_i	distribution coefficient of component *i*
n_D	refractive index
ρ	density, g cm^{-3}
S	selectivity (K_1/K_2)
γ-BL	γ-butyrolactone

Registry No. γ-Butyrolactone, 96-48-0; *n*-heptane, 142-82-5; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3.

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Excess Molar Volumes of Mixtures Containing Morpholine at 298.15 K

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Excess molar volumes were determined from precise density measurements at 298.15 K for morpholine + methanol, + acetone, + benzene, + chloroform, + dimethyl sulfoxide, and + dimethylformamide. The results are interpreted qualitatively in terms of various specific interactions.

Introduction

In a previous paper (*1*) the excess molar volumes morpholine + 2-ethoxyethanol were reported. Our interest in the morpholine derivatives arose from their high efficiency for the extraction of monocyclic aromatic hydrocarbons from petroleum products. We have initiated a program on studying the thermodynamic properties of these solvents. This paper reports the excess molar volumes of binary mixtures of morpholine + methanol, + benzene, + chloroform, + acetone, + dimethyl sulfoxide, and + dimethylformamide at 298.15 K.

Table I. Densities of the Pure Component Liquids at 298.15 K

liquid	ρ/g cm^{-3} obsd	ρ/g cm^{-3} lit.
methanol	0.786 65	0.786 64[b]
acetone	0.785 16	0.784 40[b]
chloroform	1.478 99	1.479 88[b]
benzene	0.873 61	0.873 72[a]
M	0.905 71	0.995 47[b]
DMSO	1.095 68	1.095 80[b]
DMF	0.943 93	0.943 97[b]

[a] Reference *3*. [b] Reference *4*.

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Table II. Experimental Excess Molar Volumes at 298.15 K

x	V^E/cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}
	xMethanol + $(1 - x)$Morpholine		
0.0449	-0.2600	0.7080	-1.2292
0.1059	-0.4503	0.8134	-0.9482
0.2013	-0.7260	0.8661	-0.7603
0.3260	-1.0277	0.8918	-0.6426
0.4267	-1.2112	0.9157	-0.5207
0.5266	-1.3122	0.9666	-0.2258
0.5990	-1.3613	0.9859	-0.0897
	xChloroform + $(1 - x)$Morpholine		
0.0369	-0.0793	0.5435	-0.6318
0.0586	-0.0773	0.6258	-0.6388
0.1041	-0.1411	0.7917	-0.5194
0.2147	-0.2906	0.8359	-0.4435
0.2607	-0.3403	0.9109	-0.2898
0.3683	-0.4882	0.9621	-0.1339
0.4175	-0.5244		
	xDMSO + $(1 - x)$Morpholine		
0.0526	0.0084	0.7908	-0.0013
0.1116	-0.0092	0.8181	-0.0040
0.2176	-0.0066	0.8532	-0.0050
0.3893	-0.0928	0.9319	-0.0015
0.5713	-0.0010	0.9598	-0.0058
0.7377	-0.0077		
	xAcetone + $(1 - x)$Morpholine		
0.0468	-0.2302	0.6835	-1.1617
0.2097	-0.8509	0.7814	-0.8212
0.3108	-1.1399	0.9244	-0.2737
0.4391	-1.3933		
	xBenzene + $(1 - x)$Morpholine		
0.0210	-0.0103	0.5067	-0.2319
0.0427	-0.0258	0.6448	-0.2148
0.1858	-0.1392	0.7488	-0.1740
0.2412	-0.1836	0.8276	-0.1249
0.3444	-0.2074	0.9060	-0.0786
0.3950	-0.2213	0.9605	-0.0322
	xDMF + $(1 - x)$Morpholine		
0.1014	0.0337	0.6935	0.0974
0.1981	0.0720	0.7974	0.0837
0.2732	0.0804	0.8113	0.0812
0.3812	0.1019	0.8503	0.0591
0.4311	0.1060	0.9237	0.0356
0.5615	0.1123	0.9563	0.0231

Experimental Section

Acetone, chloroform, and methanol (Fluka AG, pure grade) were used without further purification. Morpholine (M), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and benzene (Fluka AG, pure grade) were purified as previously described (*1*, *2*). The pure liquids were kept over freshly activated molecular sieve of type 4A (Union Carbide) and filtered before use. The densities of the pure liquids are listed in Table I along with values from the literature.

Densities, ρ, of the pure liquids and binary mixtures were measured with a Anton Paar digital densimeter (Model DMA 60/601) with a resolution of 2×10^{-6} g cm^{-3} achieved by determining the period of oscillation T of the sample in a U-tube. For each experimental determination the apparatus constant, K, was determined by calibrating the apparatus with doubly distilled and degassed water (ρ at 298.15 K = 997.047/kg m^{-3}) and dehumidified air at atmospheric pressure (ρ at 298.15 K = 1.185/kg m^{-3}).

The temperature of the water bath containing the oscillator tube was kept constant to within ±0.002 K with a Schott-Gerate CT 1150 thermostat. The overall precision of the density measurement is estimated to be better than 4×10^{-6} g cm^{-3}.

Binary mixtures were prepared on a weight basis and the mole fraction error is estimated to be less than 2×10^{-4}.

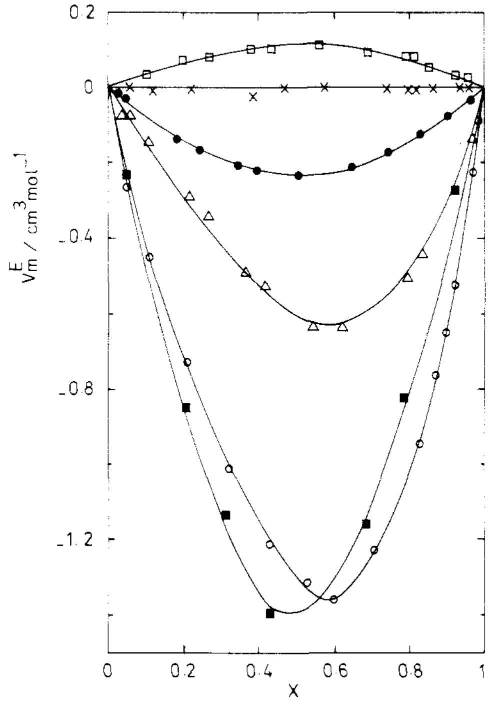

Figure 1. Excess molar volumes at 298.15 K for (○) CH_3OH + C_4H_9NO; (■) $(CH_3)_2CO$ + C_4H_9NO; (△) $CHCl_3$ + C_4H_9NO; (●) C_6H_6 + C_4H_9NO; (×) C_2H_6SO + C_4H_9NO; (□) C_3H_7NO + C_4H_9NO.

Table III. Coefficients a_j and Standard Deviations s of Eq 1

system	a_1	a_2	a_3	a_4	a_5	s
methanol + M	-5.2359	-1.9213	0.2007	1.3586	-1.7426	0.0015
chloroform + M	-2.4206	-1.3170	0.2851	0.2015	-0.7154	0.0019
acetone + M	-5.7098	-0.1446	2.8219	1.2272	-1.5937	0.0027
benzene + M	-0.9260	0.0123	0.0359	-0.1031	0.2709	0.0024
DMF + M	0.4386	0.0582	0.1177	0.0249	-0.1400	0.0043

Results and Discussion

The experimental V^E obtained from the precise density measurements are presented in Table II and plotted in Figure 1. The smoothing function

$$V^E/\mathrm{cm}^3\ \mathrm{mol}^{-1} = x(1 - x) \sum_{j=1}^{K} a_j(1 - 2x)^{j-1} \qquad (1)$$

was fitted to the results for each mixture by the method of least squares with all points weighed equally. The values of the coefficients a_j are given in Table III, along with standard deviations s.

The negative V^E values of morpholine + acetone, + methanol, and + chloroform suggest a strong hydrogen bonding. Morpholine acts as a proton donor and the other solvents act as a proton acceptor ($\ddot{\mathrm{N}}$-H···OH, $\ddot{\mathrm{N}}$-H···O═C, $\ddot{\mathrm{N}}$-H···Cl-C). This is substantiated by the largest negative V^E, Figure 1. In the case of the benzene system, a weak charge-transfer complex is formed due to the electron donor ability of benzene and the weak acceptor ability of morpholine.

The mixture of morpholine and dimethyl sulfoxide behaves as an ideal solution. V^E is approximately zero within the experimental error. In the case of the morpholine and dimethylformamdide system, V^E is small and positive. This behavior is probably due to a weak interaction between M and DMF and the steric effect of methyl groups of DMF. Spectroscopic investigations are being carried out to confirm the above suggestions.

Glossary

a_j	coefficients in representation of excess molar volume by eq 1
k	number of coefficients in eq 1

s	standard deviation
T	thermodynamic temperature, K
V^E	excess volume, cm^3 mol^{-1}
x	mole fraction
M	morpholine
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide

Registry No. DMF, 68-12-2; morpholine, 110-91-8; methanol, 67-56-1; acetone, 67-64-1; benzene, 71-43-2; chloroform, 67-66-3; dimethyl sulfoxide, 67-68-5.

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Gas Viscosities of Azeotropic Mixtures of the Halogenated Hydrocarbons R500, R502, and R503

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Gas viscosities of azeotropic mixtures R500 (dichlorodifluoromethane (R12)–1,1-difluoroethane (R152a)), R502 (chlorodifluoromethane (R22)–chloropentafluoroethane (R115)), and R503 (chlorotrifluoromethane (R13)–trifluoromethane (R23)) were measured with an oscillating disk viscometer of the Maxwell type at 273.15–423.15 K up to 7.5 MPa. Two empirical equations for the viscosities were obtained; one is for the atmospheric viscosities as a function of temperature, and the other is for the viscosities in the whole range of the present measurement as a function of temperature and density.

The measurements of gas viscosities of halogenated hydrocarbons under pressure are being continued by the present authors, and the viscosity data for dichloromethane (R12), chlorotrifluoromethane (R13), bromotrifluoromethane (R13B1), chlorodifluoromethane (R22), 1,2,2-trichloro-1,1,2-trifluoroethane (R113), 1,2-dichloro-1,1,2,2-tetrafluoroethane (R114), chloropentafluoroethane (R115), 1-chloro-1,1-difluoroethane (R142b), and 1,1-difluoroethane (R152a) were reported previously (*1–5*). Gas viscosities of azeotropic mixtures of halogenated hydrocarbons R500, R502, and R503 are described in the present paper.

Table I shows the composition and the physical properties of azeotropic mixtures (*6*), and Table II shows the physical properties of the components of azeotropic mixtures (*6*).

The gas viscosity of R500 was measured by Latto et al. (*7*) in the temperature range from 244 to 360 K at atmospheric pressure but has not been measured under pressure. The gas viscosities of R502 and R503 have not been measured in any pressure range.

The atmospheric viscosity vs temperature equations were obtained for R500 (*7*, *8*) on the basis of the experimental viscosity values (*7*), and the equation of the same type was obtained for R502 (*8*) on the basis of predicted values (*9*). Description for the viscosity of R503 was not found in the literature.

Experimental Section

***Viscosity Measurement* (*10*, *11*).** The viscosity was measured with an oscillating disk viscometer of the Maxwell type shown in Figure 1. The main part is the suspension system shown in Figure 2, which is composed of an oscillating stainless steel disk (A), a fine suspension quartz wire (C), two fixed stainless steel disks (K), and a stainless steel stem (B) with a nickel-plated glass mirror and with a Permalloy piece (F). In this system the distance between the oscillating disk and the upper fixed disk should be equal to the distance between the oscillating disk and the lower fixed disk at any ambient temperatures. In order to satisfy this requirement, three quartz tubes (M) were inserted between the upper fixed disk and a fixing disk (I), and three stainless steel spacers (L) were inserted between the two fixed disks, and the length of the stem was adjusted. The three quartz tubes and the three spacers were fixed by using three stainless steel rods (N), nuts (O, Q), and springs (P). The characteristics of the suspension system are shown in Table III.

Newell's theory (*12*) was used for analysis in a manner similar to that used by Iwasaki and Kestin (*13*). The apparatus constant, C_N, was determined experimentally with nitrogen as standard at 298.15, 323.15, 348.15, 373.15, and 398.15 K in the pressure range from 0.1 to 6 MPa. The viscosity values of nitrogen recommended by Hanley et al. (*14*, *15*) were used and the density of nitrogen was calculated from a BWR equation of state (*15*). The obtained C_N values were nearly constant, independent of temperature and pressure. The mean value was 1.1338 and the probable error was 0.03% for 39 experimental points. The error in the viscosity determination was estimated to be less than 0.3% considering the error of logarithmic decrement (0.25%) and the error of the period of oscillation (0.01%).

***Density Measurement* (*16*).** In this study the density was measured at the temperature and pressures at which the viscosity was measured. A schematic diagram of the apparatus is shown in Figure 3. A high-pressure pipet (B), the detail of which is shown in Figure 4, was designed for the measurement in the critical region and was located at the same level as the oscillating disk. Sample gas was introduced into the high-pressure pipet at the same temperature and pressure at which the viscosity was measured, and then introduced into an expansion system composed of a mercury manometer (H), a connecting capillary (D), and four glass cylinders (K). The expansion system was thermostated at 298.15 K, and evacuated before introducing the gas. Residual gas in the pipet was

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