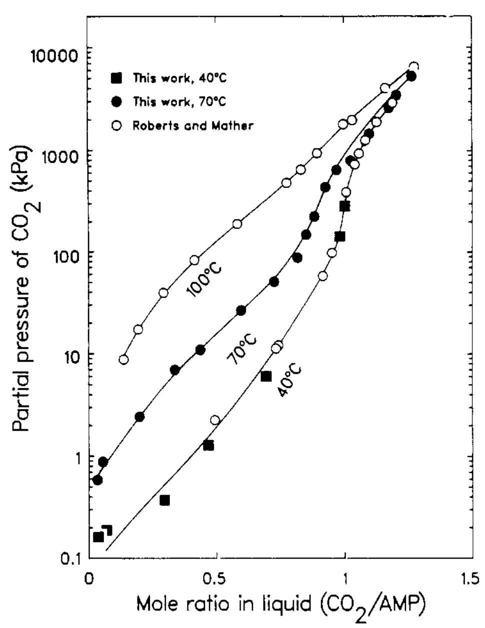

Figure 1. Solubility of CO_2 in a 2.0 mol/L AMP solution.

to reach equilibrium. At vapor-liquid equilibrium, the vapor phase was analyzed by means of a H-P gas chromatograph Model 5710A with a 3-m length, 6.35-mm o.d. column packed with Chromosorb 104. The response factors for the gases were as follows: N_2, 1.17; CO_2, 1.00. The partial pressure of the water over the aqueous AMP solution was calculated from Raoult's law:

$$p_w = x_w P_w^s \qquad (1)$$

The partial pressure of water calculated in this way varied from 6.8 to 7.1 kPa at 40 °C and from 28.3 to 29.8 kPa at 70 °C.

A known amount of the loaded solution was withdrawn from the cell through the liquid sample line into a 1 N NaOH solution for analysis. The CO_2 content of the loaded solution was determined by mixing an aliquot of the sample solution with an excess of 0.1 N $BaCl_2$ solution to form $BaCO_3$ precipitate. The precipitate was then filtered, washed with distilled water, and titrated with standardized 0.1 N HCl solution by using methyl orange-xylene cyanol indicator.

A 40-cm^3 high-pressure metal sampling bomb containing the 1 N NaOH solution was used for sampling at CO_2 loadings where the reaction rate was not fast enough to prevent pressure buildup over the basic solution. A 50-cm^3 Erlenmeyer flask fitted with a rubber septum was used to collect liquid samples for partial pressures lower than 1000 kPa. The experimental error in the solution loading (moles of CO_2/mole of AMP) is estimated to be ±2-3%.

Results and Discussion

To test the analytical procedures and experimental technique, data were obtained at 40 °C for comparison with those of Roberts and Mather (*7*), who obtained data for a similar solution at 40 and 100 °C. Figure 1 shows that the new results are in good agreement with the previous work. Data were also obtained at 70 °C over the pressure range 0.6-5279 kPa. The experimental data are presented in Table I, and all the data for a 2.0 mol/L AMP solution are shown in Figure 1. The solubility of CO_2 in the AMP solution is indeed higher than that in comparable DEA or TEA solutions; at 70 °C and a partial pressure of 100 kPa, the corresponding α would be 0.52 and 0.22, respectively, compared with 0.81 for the AMP solution. At CO_2 loadings greater than unity, there is little effect of temperature on the solubility. This behavior is similar to that noted in MDEA solutions by Jou et al. (*5*).

Registry No. AMP, 124-68-5; CO_2, 124-38-9.

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Excess Molar Volumes, Excess Logarithmic Viscosities, and Excess Activation Energies of Viscous Flow for 2-Ethoxyethanol + γ-Butyrolactone and + Sulfolane at 303.15 K

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Densities, excess volumes, excess logarithmic viscosities, and excess activation energies of viscous flow are reported for binary mixtures of 2-ethoxyethanol + γ-butyrolactone and + sulfolane over the whole mole fraction range at 303.15 K. The excess volumes, excess logarithmic viscosities, and excess activation energies of viscous flow are all negative over the whole mole fraction range. The sulfolane system shows a larger negative deviation from ideality than that of the γ-butyrolactone system.

Introduction

In previous papers (*1*, *2*), the excess molar volumes of 2-ethoxyethanol + a glycol and + morpholine derivatives were reported. Our interest in these solvents and their binary mixtures arose from their high efficiency for the extraction of monocyclic aromatic hydrocarbons from petroleum products. Although an extensive search in the literature was made, we could not trace any thermodynamic and spectroscopic data for these systems. In the present paper, we report the densities, excess volume viscosities, excess logarithmic viscosities, and

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Table I. Densities, ρ, and Viscosities, η, for the Pure-Component Liquids at 303.15 K

liquid	ρ/(g cm^{-3}) obsd	ρ/(g cm^{-3}) lit.	η/cP obsd	η/cP lit.
sulfolane	1.261 84	1.261 4[a]	10.356	10.29[c] 10.286[a]
γ-Butyrolactone	1.117 92	1.119 22[b]	1.765	
2-Ethoxyethanol	0.922 06		1.629	

[a] Reference 5. [b] Reference 6. [c] Reference 7.

excess activation energies of viscous flow for binary mixtures of 2-ethoxyethanol + γ-butyrolactone and + sulfolane over the whole mole fraction range at 303.15 K.

Experimental Section

Materials. 2-Ethoxyethanol (stated purity of 99.5 mol %), γ-butyrolactone (stated purity of 99 mol %), and sulfolane (stated purity of 99.5 mol %) were obtained from Fluka AG and purified, as previously described (*3*). All liquids were kept over freshly activated molecular sieves of Type 3A (Union Carbide) and filtered before use. The purity of all liquids was confirmed by gas–liquid chromatographic analysis.

Densities, ρ, of the pure liquids and binary mixtures were measured with an Anton Paar digital densimeter (Model DMA 60/602) 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(303.15 K) = 995.6454/(kg m^{-3})] and dehumidified air at atmospheric pressure [ρ(303.15 K) = 1.165/(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 densities were then obtained for pure benzene (ρ = 0.868 48), toluene (ρ = 0.857 68), and 1,2-ethanediol (ρ = 1.106 47) and were found to be in good agreement with values published in the literature. The overall precision of the densities measured is found to be better than $\pm 3 \times 10^{-5}$ g cm^{-3}. The determined V^E values from the density measurements are accurate within $\pm 1.5 \times 10^{-3}$ cm^3 mol^{-1}.

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

Kinematic viscosities of the pure liquids and their binary mixtures at different concentrations were determined at 303.15 K with a Schott-Gerate measuring system, consisting of a basic control unit, a measuring stand, a constant-temperature bath, and a calibrated Ubbelohde suspended level viscometer. Viscometer constants were controlled by using high-purity cyclohexane and toluene as standard fluids. Temperature fluctuations were limited to ±0.002 K. The temperature was measured by a Hewlett-Packard A quartz thermometer. The flow-time measurements were made automatically by using two light barriers across the viscometer and an electronic timer (Schott-Gerade AVS 300) with a precision of ±0.01 s. The kinetic energy correction was considered not necessary on account of a long flow time obtained by a proper selection of the capillary. The reproducibility in viscosity measurements was within ±0.003 cP.

Results and Discussion

The experimental excess molar volumes, V^E, derived from precise density measurements for mixtures of $xC_4H_{10}O_2$ + $(1 - x)C_4H_6O_2$ and + $(1 - x)C_4H_8O_2S$ are summarized in Table II, where x represents the mole fraction of 2-ethoxyethanol. Each set of V^E results was fitted to an empirical equation of the form

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

Table II. Densities, ρ, Excess Molar Volumes, V^E, Viscosities, η, Excess Logarithmic Viscosities, ln η^E, and Excess Activation Energies of Viscous Flow, ΔG^{*E} for $xC_4H_{10}O_2$ + $(1 - x)C_4H_6O_2$ and $(1 - x)C_4H_8O_2S$ at 303.15 K

x	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	η/cP	ln η^E	ΔG^{*E}/(J mol^{-1})
		$xC_4H_{10}O_2 + (1 - x)C_4H_6O_2$			
0.0345	1.109 96	-0.0358	1.722	-0.020	-51
0.0509	1.106 20	-0.0518	1.708	-0.026	-61
0.0767	1.000 33	-0.0759	1.687	-0.035	-81
0.1125	1.092 21	-0.1023	1.658	-0.047	-115
0.2033	1.072 22	-0.1661	1.603	-0.068	-164
0.3137	1.048 65	-0.2086	1.561	-0.079	-190
0.4404	1.022 90	-0.2360	1.544	-0.074	-182
0.5421	1.003 03	-0.2371	1.538	-0.065	-163
0.6504	0.982 77	-0.2238	1.535	-0.053	-133
0.7638	0.939 09	-0.1741	1.501	-0.038	-101
0.8807	0.942 08	-0.1142	1.541	-0.022	-52
0.9372	0.932 50	-0.0637	1.538	-0.018	-27
0.9693	0.927 10	-0.0283	1.553	-0.004	-14
		$xC_4H_{10}O_2 + (1 - x)C_4H_8O_2S$			
0.0420	1.248 33	-0.0855	8.909	-0.073	-186
0.0712	1.238 59	-0.1260	7.997	-0.126	-322
0.1090	1.226 49	-0.1986	7.117	-0.175	-445
0.1849	1.201 51	-0.3055	5.742	-0.248	-632
0.2899	1.156 54	-0.4126	4.443	-0.300	-475
0.3942	1.131 59	-0.4934	3.612	-0.320	-820
0.5561	1.076 79	-0.5451	2.759	-0.284	-730
0.6236	1.053 78	-0.5409	2.472	-0.265	-683
0.6586	1.041 43	-0.4971	2.349	-0.249	-640
0.7385	1.013 82	-0.4405	2.108	-0.204	-527
0.7622	1.002 78	-0.4251	2.027	-0.195	-496
0.8406	0.978 28	-0.3124	1.843	-0.141	-365
0.9162	0.951 84	-0.2025	1.688	-0.082	-212
0.9539	0.938 54	-0.1248	1.619	-0.050	-128

Table III. Coefficients A_j and Standard Deviation, s, for Least-Squares Representations of Excess Molar Volumes by Equation 1

system	A_1	A_2	A_3	A_4	s
$xC_4H_{10}O_2$ +					
$(1 - x)C_4H_6O_2$	-0.9651	0.0396	-0.1072	-0.0821	0.0041
$(1 - x)C_4H_8O_2S$	-2.0892	0.2235	-0.3666	0.2310	0.0097

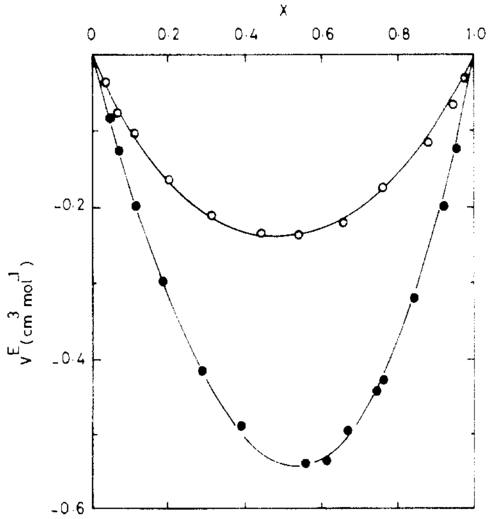

Figure 1. Excess molar volumes of (○) 2-ethoxyethanol + γ-butyrolactone and (●) + sulfolane at 303.15 K.

The values of the coefficients A_j and the standard deviation s are given in Table III. The deviation of our results from their representation by eq 1 are for the most part less than 1%. The V^E results are plotted against x, the mole fraction of 2-ethoxyethanol, in Figure 1.

Experimental viscosities, η, for the binary mixtures are listed in Table II and plotted against x, in Figure 2. Excess loga-

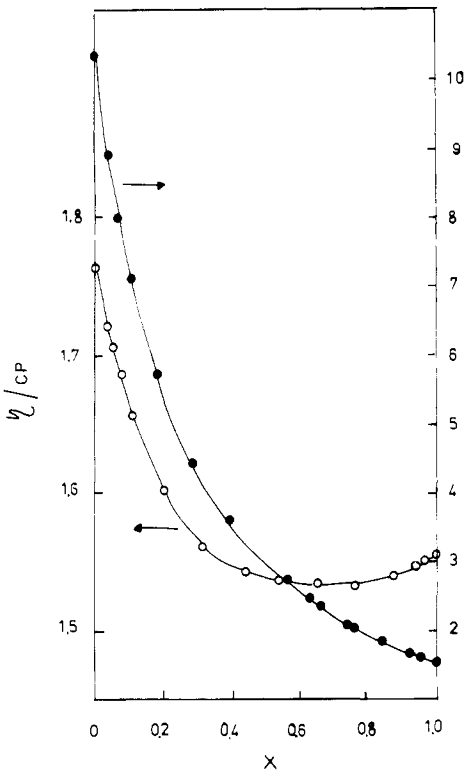

Figure 2. Viscosities of (○) 2-ethoxyethanol + γ-butyrolactone and (●) + sulfolane at 303.15 K.

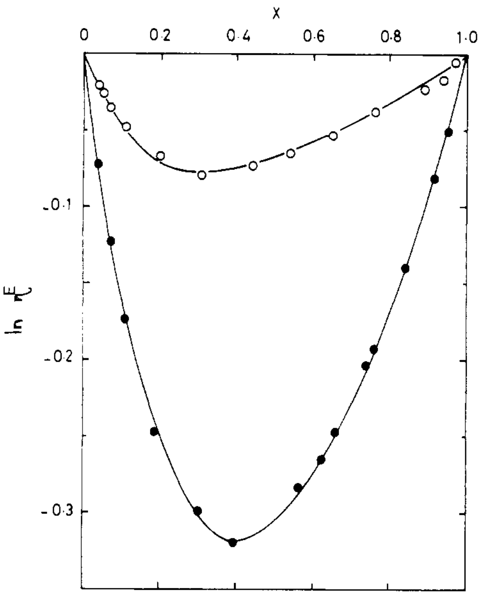

Figure 3. Excess logarithmic viscosities of (○) 2-ethoxyethanol + γ-butyrolactone and (●) + sulfolane at 303.15 K.

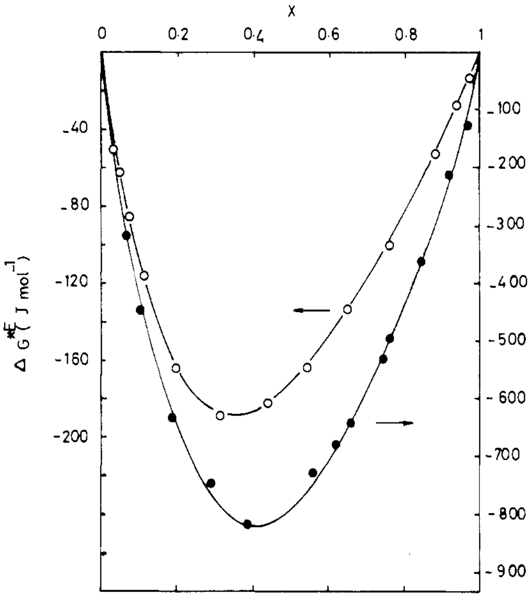

Figure 4. Excess activation energies of viscous flow of (○) 2-ethoxyethanol + γ-butyrolactone and (●) + sulfolane at 303.15 K.

rithmic viscosities, ln η^E, at 303.15 K were calculated from experimental viscosities by using the following relation

$$\ln \eta^E = \ln \eta - x \ln \eta_1 - (1 - x) \ln \eta_2 \qquad (2)$$

where η and η_i are the viscosities of the binary mixture and the pure component i, respectively.

Excess activation energies of the binary mixtures, ΔG^{*E}, were calculated from the following relation

$$\Delta G^{*E} = RT(\ln \eta V - x \ln \eta_1 V_1 - (1 - x) \ln \eta_2 V_2) \qquad (3)$$

where η and V are respectively the viscosity and the molar volume, $(xM_1 + (1 - x)M_2)/\rho$, of the binary mixture. η_i and V_i represent the viscosity and the molar volume of the pure component i. R and T have their usual meaning. The obtained results of ln η^E and ΔG^{*E} are listed in Table II and illustrated in Figures 3 and 4 over the whole mole fraction range.

The excess volumes, V^E, excess logarithmic viscosities, η^E, and excess activation energies of viscous flow for binary mixtures of 2-ethoxyethanol + γ-butyrolactone and + sulfolane are all negative over the whole mole fraction range at 303.15 K. Such volumetric and viscometric behavior of these systems may be explained qualitatively by the molecular interaction between unlike molecules through hydrogen bonding and the disruption of the molecular order existing in the pure 2-ethoxyethanol (*4*) by nonassociated globular molecules of sulfolane and γ-butyrolactone. Since sulfolane and γ-butyrolactone are relatively weak proton acceptors and 2-ethoxyethanol is a relatively weak proton donor, a weak hydrogen bond is formed. This leads to the observed negative behavior of V^E. Such behavior might also arise from interstitial accommodation of the globular molecules of γ-butyrolactone and sulfolane molecules within the branched multimer structure (*4*) of 2-ethoxyethanol. The viscometric behavior obtained here may be due to the disruption of molecular order of the pure components, which gives a decrease in the viscosity data (negative values for ln η^E and ΔG^{*E}). The largest negative V^E, ln η^E, and ΔG^{*E} found for the 2-ethoxyethanol + sulfolane system, in comparison with the values obtained for 2-ethoxyethanol + γ-butyrolactone, may be due to the stronger hydrogen bonding between 2-ethoxyethanol and sulfolane and more disruption of the molecular order of the pure components than that of 2-ethoxyethanol and γ-butyrolactone.

Glossary

A_1, A_2, ..., A_j	coefficients in eq 1
ΔG^{*E}	excess activation energy of viscous flow, J mol^{-1}
k	number of coefficients in eq 1
s	standard deviation
V^E	excess molar volume, cm^3 mol^{-1}
V	molar volume of mixture
V_i	molar volume of pure component i
x	mole fraction of 2-ethoxyethanol

Greek Letters

η	viscosity of mixture
η_i	viscosity of pure component i
ρ	density of mixture

ρ_i	density of pure component *i*
ln η^E	excess logarithmic viscosity

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Bubble Point Pressures for Binary Mixtures of Bromotrifluoromethane (R13B1) and Chloropentafluoroethane (R115) with Chlorodifluoromethane (R22)

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The bubble point pressures for two binary mixtures of bromotrifluoromethane (R13B1) and chloropentafluoroethane (R115) with chlorodifluoromethane (R22) were measured by a new apparatus based on a static method employing a pressure vessel of 46-cm^3 volume. The results for various compositions covering the range of temperatures from 298.15 K to near their critical values were obtained. The uncertainty of the present data was estimated to be no greater than ±0.3%. The bubble point pressures for pure substances and an azeotropic mixture (R502) were correlated by the Wagner equation, and those for refrigerant mixtures were also correlated by the Wagner equation, based on the corresponding states principle.

Introduction

The binary mixtures of fluorocarbon refrigerants have been noted as new working fluids of heat pump and air conditioning units for the purpose of the effective application of thermal energy. For refrigerant mixtures, the direct measurement of the thermophysical properties, especially those of the equilibrium properties near the critical region, is difficult and has therefore seldom been investigated systematically.

In this work, we constructed a new apparatus based on a static method, which is able to measure the bubble point pressure of binary mixtures of fluorocarbon refrigerants over a wide range of temperature, and we present new experimental data for two binary systems: bromotrifluoromethane (R13B1) and chloropentafluoroethane (R115) with chlorodifluoromethane (R22), covering from 298.15 K to the neighborhood of the critical temperature.

The experimental results for three pure substances and an azeotropic mixture (R502) were successfully correlated by the Wagner equation, and those of two binary mixtures were also correlated by the Wagner equation using the corresponding states principle.

Table I. Melting Points T_f (*1*), Boiling Points T_b (*1*), Dipole Moments μ (*8*), Critical Temperatures T_c (*2*), Critical Pressures P_c (*2*), and Critical Densities ρ_c (*2*) of Refrigerants

refrigerant	T_f/K	T_b/K	$\mu/10^{30}$ Cm	T_c/K	P_c/ MPa	ρ_c/ (kg·m^{-3})
R22 ($CHClF_2$)	113	232.4	4.74	369.2	4.98	525
R13B1 ($CBrF_3$)	105	215.4	2.17	340.2	3.96	745
R115 ($CClF_2CF_3$)	167	235.2	1.73	353.2	3.12	596
R502 (48.8 wt % R22 + 51.2 wt % R115)	113	227.6		355.4	4.07	559

Experimental Section

Materials. Three refrigerants, chlorodifluoromethane, $CHClF_2$ (R22), bromotrifluoromethane, $CBrF_3$ (R13B1), and chloropentafluoroethane, C_2ClF_5 (R115), were supplied from the Daikin Kogyo Co., Ltd., as special research grade materials, and their purities were reported as being more than 99.9 wt %. The physical properties of pure refrigerants are listed in Table I, along with those of R502, which is an azeotropic mixture of R115 and R22 (*1*, *2*, *8*).

Apparatus. There are basically two types of bubble point pressure measurements, that is, the dynamic method at constant pressure and the static one at constant temperature. In this work, a new apparatus of the static method was constructed, and the schematic diagram is shown in Figure 1. The apparatus consists primarily of a sample cell (1), a thermostated oil bath (2), a thermostated air bath (3), a U-tube-type detector containing mercury (4), an oil-operated dead-weight gage (5), an oil pump (6), a pressure gage (7), a vacuum pump (8), and pipe lines.

Bubble Point Pressure Measurements. The sample cell was made of a low-density aluminum alloy (Cu, 3.5–4.5%; Si, less than 0.8%; Fe, less than 1.0%; Mn, 0.4–1.0%; Mg, 0.2–0.8%; Al, the rest) (*9*), and its volume was about 46 cm^3. Each component of the desired binary system was individually introduced into the sample cell, which was previously evacuated, by slow distillation until it was almost full and a small amount of vapor phase remained. The composition of the refrigerant mixtures was determined by measuring the weight of each component of the mixtures by use of a precision direct-reading

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