Table VI. Minimum Weight Percent Cosolvent Necessary to Produce Miscibility in 1:1 Weight Percent Mixtures of Toluene and 2.0 m Aqueous Solutions of Sodium Salicylate, Sodium Benzoate, or Sodium Benzenesulfonate

aqueous solution	cosolvent	wt % cosolvent
sodium salicylate (2.0 m)	*n*-butylcarbitol	31.8
sodium benzoate (2.0 m)	*n*-butylcarbitol	35.1
sodium benzenesulfonate (2.0 m)	*n*-butylcarbitol	36.0
sodium salicylate (2.0 m)	1-butanol	37.5
sodium benzoate (2.0 m)	1-butanol	43.0
sodium benzenesulfonate (2.0 m)	1-butanol	53.7

2.0 m aqueous solutions of sodium salicylate, sodium benzoate, or sodium benzenesulfonate. These values were either determined in the present study or are taken from ref 2 and 3.

Thus it is apparent that with either *n*-butylcarbitol or 1-butanol a smaller weight percent of cosolvent is required to produce miscibility of toluene and the aqueous solution when sodium salicylate is the protosurfactant than when either sodium benzoate or sodium benzenesulfonate is used. Moreover, with any of the three protosurfactants *n*-butylcarbitol is a more efficient cosolvent in promoting miscibility in 1:1 weight percent mixtures of toluene and aqueous solution.

Hence, the cosolvent plays an important role in determining miscibility relationships in systems containing an aqueous solution of a protosurfactant and a hydrocarbon. Not only is the minimum amount of cosolvent necessary for miscibility affected but so are the relative miscibilities of alkanes and the corresponding alkylbenzenes.

The role of the cosolvent in interfacial tension studies involving hyrocarbon–cosolvent–aqueous surfactant systems has been examined by many (see, e.g., ref 5). In such systems sharp minima in interfacial tension occur as a function of the number of alkyl carbon atoms (ACN) in the hydrocarbon. Cosolvents of low molecular weight, such as 2-propanol, may shift the value of the ACN of lowest interfacial tension, $n_{\min}$, downward to lower values (compared to $n_{\min}$ with no cosolvent present), while cosolvents of higher molecular weight, such as 3-methyl-1-butanol, may have a large upward effect on $n_{\min}$. In the interfacial tension studies the presence of a benzene ring in the hydrocarbon does not affect the value of $n_{\min}$. Only the alkyl carbon atoms are involved. Thus a system exhibiting a minimum interfacial tension with decane also shows a minimum with phenyldecane.[6] Nearly analogous behavior was observed in our studies of miscibility in aqueous–hydrocarbon systems containing 1-butanol as the cosolvent and a sodium benzenesulfonate as the protosurfactant. In those systems almost the same amount of 1-butanol was required to produce miscibility of the aqueous benzenesulfonate solution and either hexane or phenylhexane. Such behavior is, however, not observed in the miscibility studies reported here. Comparison of the plots in Figures 3 and 4 reveals that in all cases considerably more *n*-butylcarbitol is required to produce miscibility in 1:1 weight percent mixtures of aqueous sodium salicylate solution and the series of alkanes than with the corresponding series of alkylbenzenes. Hence, whereas the presence of a benzene ring does not contribute to the effective carbon number for minima in interfacial tension, its presence has an influence on miscibility in the systems studied here, the extent depending on the cosolvent used.

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Solubility of Carbon Dioxide in Molten Salts

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The solubilities of carbon dioxide in molten $ZnCl_2$, $ZnBr_2$, $SnCl_2$, and $NaNO_3$ were determined at 1 atm and temperatures from 270 to 475 °C. By the simplified elution method used in this work, solubilities of carbon dioxide were able to be measured with the use of small amounts of molten salts. The solubilities of carbon dioxide slightly decreased with increasing temperature in this temperature range.

Molten salts have recently been used as solvents, catalysts, and/or reactants in organic and inorganic reactions such as the chlorination of hydrocarbons and the desulfurization of waste gas. For the investigation of the kinetics of these reactions, physical properties of gases in molten salts, such as the solubility and the diffusivity, are essential. However, there have been few data of gas solubilities in molten salts (*2*, *3*, *6*, *7*). Especially, the solubility data of triatomic gases, such as CO_2 and SO_2, are very scarce.

In the present work, solubilities of carbon dioxide in molten salts were determined with a simplified elution method at 1 atm and temperatures from 270 to 475 °C. In this temperature range there is no reaction between carbon dioxide and molten halides and nitrates. The molten salts used were the halides which showed some degree of association above the melting point, such as $ZnCl_2$, $ZnBr_2$, and $SnCl_2$, and the ionic nitrate, i.e., $NaNO_3$.

Experimental Section

The experimental apparatus is shown in Figure 1. A stainless steel crucible, used as an absorption and elution chamber, was

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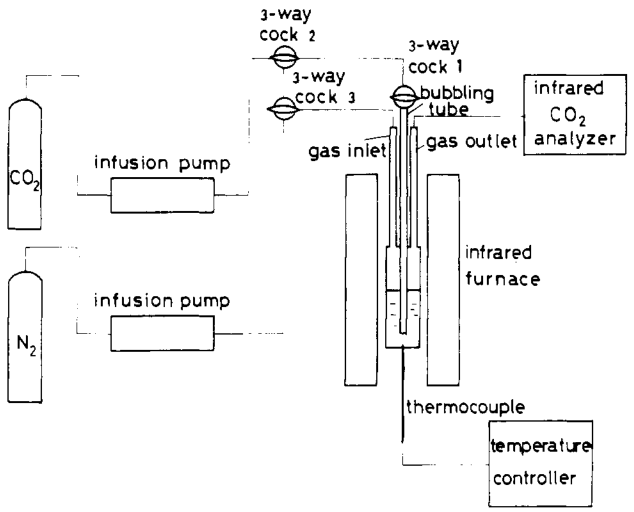

Figure 1. Experimental apparatus.

lined with a platinum cylinder, 13 mm in inside diameter and 48 mm in height. A gas inlet, a gas outlet, and a bubbling tube, made of stainless steel, were welded to the cap of the crucible. Inside the crucible the bubbling tube was made of platinum to prevent contamination of the salts. The crucible was heated in an infrared furnace (Shinku Riko, Japan). The temperature of the furnace was measured with a platinum-platinum-rhodium thermocouple fitted to the bottom of the crucible and kept constant within ±1 °C.

The salts used were of reagent grade. Since the amounts of oxide and carbonate contained in the salts were very little, the effect of impurities on the solubility data was neglected (*4*). The salts were dried in a desiccator for a few days and in a vacuum oven at 150-200 °C for several hours. A weighed quantity of the salt was transferred to the crucible, molten at a desired temperature, and dried again by bubbling anhydrous nitrogen through the bubbling tube for 1 h. All gas supply and outlet lines were of Pyrex glass and stainless steel construction.

Carbon dioxide was bubbled into the molten salt with a flow rate of 9.3 cm^3/min. Carbon dioxide used was superpure grade, 99.96%, and free from water. Saturation was carried out for 50 min. In some experiments to determine the effect of carbon dioxide fraction on the solubility, mixtures of carbon dioxide and nitrogen at 1 atm were bubbled. After saturation of the system, the gas supply line leading to cock 1 was swept with nitrogen until all carbon dioxide had been displaced. The gas bubbling tube was also washed with nitrogen for 7 s with a flow rate of 44 cm^3/min. Then, nitrogen was introduced from the gas inlet to sweep the upper space of the crucible for 2 min. Losses of dissolved carbon dioxide during these procedures were estimated to be less than 0.005 cm^3 and amounts of carbon dioxide remaining in the lines and in the upper space of the crucible were negligibly small.

Carbon dioxide dissolved in the salt was eluted by bubbling nitrogen through the bubbling tube with a flow rate of 44 cm^3/min. The concentration of carbon dioxide in eluted gas was measured with an infrared carbon dioxide analyzer (Shimadzu, Type URA-2s) and was recorded continuously. Within 30 min all carbon dioxide dissolved in the salt was eluted. The amount of carbon dioxide dissolved in the salt was obtained by graphical integration of the concentration of carbon dioxide multiplied by the flow rate of eluted gas.

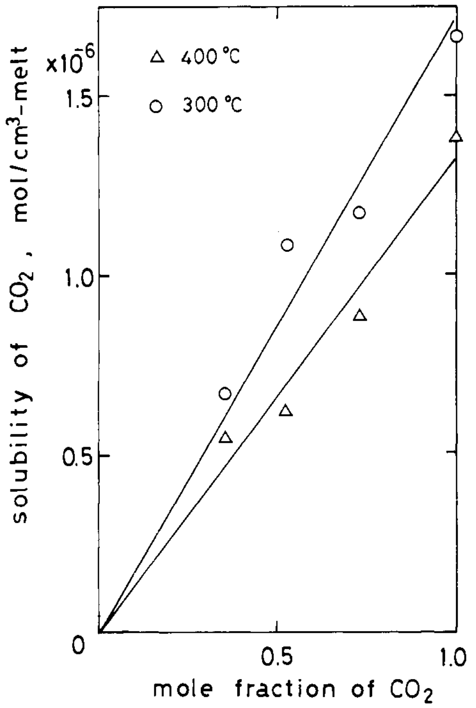

Figure 2. Variation of solubility with carbon dioxide fraction.

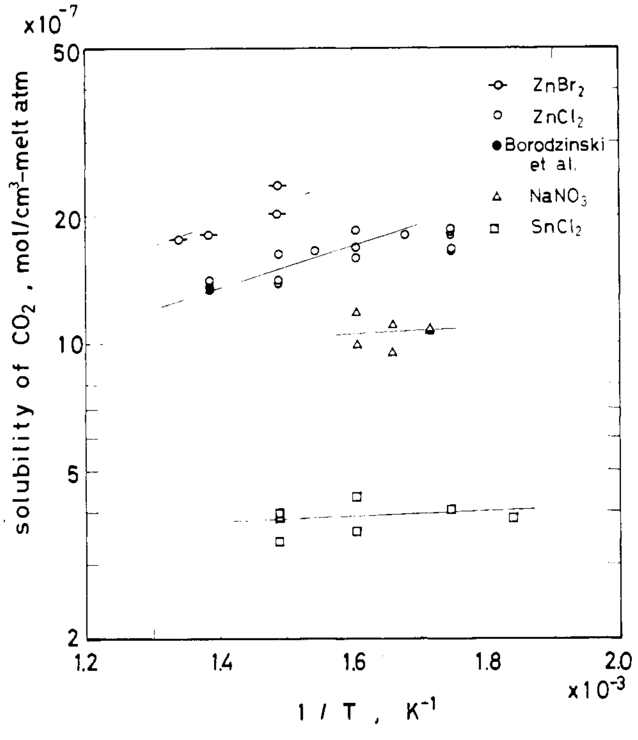

Figure 3. Solubility of carbon dioxide in molten salts.

Results and Discussion

The solubilities of carbon dioxide in molten salts were expressed as moles of carbon dioxide per cubic centimeter of salt at the observed temperature. The data of density and vapor pressure for the molten salts were taken from literature (*1*, *5*, *8*). Since the vapor pressures of these salts were lower than 1.5% of the total pressure, the effect of the vapor pressure on the solubility data was neglected in the temperature range.

To determine the reliability of the equipment and procedure, we measured the solubility of carbon dioxide in pure water at room temperature. The value agreed well with the value in the literature (*10*).

Figure 2 shows the solubilities of carbon dioxide in molten $ZnCl_2$ at varying carbon dioxide fractions in nitrogen. The solubilities obey Henry's law.

Table I shows the solubilities of carbon dioxide in molten $ZnCl_2$, $ZnBr_2$, $SnCl_2$, and $NaNO_3$ at 1 atm. The standard error of the solubility data was less than ±10%. In Figure 3 solubility data

Table I. Experimental Data for the Solubility of Carbon Dioxide in Molten Salts

salt	temp, °C	density, g/cm^3	solubility,[a] mol/cm^3	std dev
$ZnCl_2$	300	2.534	1.76×10^{-6}	0.08×10^{-6}
	325	2.521	1.80×10^{-6}	
	350	2.504	1.71×10^{-6}	0.11×10^{-6}
	375	2.494	1.65×10^{-6}	
	400	2.481	1.47×10^{-6}	0.10×10^{-6}
	450	2.459	1.38×10^{-6}	0.02×10^{-6}
$ZnBr_2$	400	3.467	2.19×10^{-6}	0.17×10^{-6}
	450	3.420	1.80×10^{-6}	
	475	3.396	1.78×10^{-6}	
$SnCl_2$	270	3.336	3.86×10^{-7}	
	300	3.328	4.01×10^{-7}	
	350	3.268	3.96×10^{-7}	0.37×10^{-7}
	400	3.208	3.75×10^{-7}	0.25×10^{-7}
$NaNO_3$	310	1.916	1.07×10^{-6}	0.01×10^{-6}
	330	1.902	1.03×10^{-6}	0.08×10^{-6}
	350	1.888	1.08×10^{-6}	0.10×10^{-6}

[a] mol/cm^3 of CO_2 in molten salt at 1 atm.

are plotted against $1/T$ on semilogarithmic coordinates. The solubilities slightly decrease with increasing temperature in this temperature range. The slopes are steeper in $ZnCl_2$ and $ZnBr_2$ than in the others. It is said that these two salts are to some extent associated liquids at temperatures above the melting point and that the degree of association diminishes with temperature (*9*). This might be responsible for the steep slopes and the relatively high solubilities in these salts. The value of the solubility of carbon dioxide in molten $ZnCl_2$ measured by Borodzinski et al. (*2*) is shown in Figure 3. The result obtained in this work agrees well with their result.

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Heat Capacities of Binary C_8 Alkylbenzene Mixtures

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A Picker flow microcalorimeter was used to determine volumetric heat capacities at 298.15 K for the six binary systems formed from the C_8 alkylbenzenes: ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene. Excess heat capacities obtained from the results are compared with the meager information available in the literature for the temperature variation of the excess enthalpies of these mixtures.

Previously we described determinations of excess heat capacities of binary systems formed by mixing the C_8 alkylbenzenes (ethylbenzene and the three isomeric xylenes) with benzene and with toluene (*3*). As an extension of that investigation we have carried out similar measurements for binary mixtures comprised of the C_8 aromatics alone.

We are not aware of previous measurements of the excess heat capacities of binary C_8 alkylbenzene mixtures. However, excess enthalpies at two different temperatures have been reported for some of them (*5*).

Experimental Section

The samples of the component liquids were the same as used in our earlier work (*3*) where characteristic densities and refractive indices are reported. The use of the Picker flow microcalorimeter for measuring differences of volumetric heat capacity following a stepwise procedure has been described previously (*1*, *3*, *4*). The initial reference liquids adopted in order of precedence were ethylbenzene, *o*-xylene, and *m*-xylene; values of their heat capacities determined relative to benzene were taken from ref 3. A temperature interval of about 1.4 K centered on 298.15 K was used for all measurements. The precision of the excess heat capacities is believed to be about ±0.02 J K^{-1} mol^{-1}.

Results and Discussion

A summary of the experimental measurements is given in Table I. At any mole fraction, $\Delta(C_p/V)$ is the amount by which the volumetric heat capacity of the mixture exceeds that of the preceding mixture. Each entry for $\Delta(C_p/V)$ is an average of two measurements in which the roles of the two mixtures, as test and reference, were reversed (*1*). Molar heat capacities were obtained from the volumetric heat capacities using molar volumes calculated from the densities of the component liquids (*3*) and the excess volumes of the mixtures (*6*, *10*).

In all cases the heat capacities of the pure xylenes obtained from measurements with respect to different reference liquids agree within less than 0.1%. Close agreement is also evident between these results and the values obtained in our previous studies in which the xylenes were measured against toluene (*1*) and tetrachloromethane (*2*).

The values of the excess heat capacity in Table I were calculated from the equation

$$C_p{}^E = C_p - x_1C_{p1} - x_2C_{p2} \qquad (1)$$

where C_p and C_{pi} are the molar heat capacities of the mixture and of pure component i, respectively. In each case the value of C_{p2} measured for the particular system was used to ensure

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