thod (modification of Lydersen's method) (*15*).

The H^E values at 298.15 K and G^E values at 348.15 K are collected in Tables II and III. Smoothing equations of the type

$$H^E_{calc}/x_1(1 - x_1) = \sum A_j(2x_1 - 1)^{j-1} \quad (1)$$

and

$$G^E_{calc}/x_1(1 - x_1)RT = \sum A_j(2x_1 - 1)^{j-1} \quad (2)$$

were fitted by the method of least-squares.

The A_j parameters are given in Tables II and III together with the standard deviations $\sigma(Q)$ calculated as

$$\sigma(Q) = [\sum(Q - Q_{calc})^2/N]^{1/2} \quad (3)$$

where N is the number of experimental values and $Q = H^E$, P, or y_1.

For 1,3-dibromopropane + n-nonane (Figure 2), formation of a maximum-boiling azeotrope was observed ($x_{1,Az} = 0.2926$, $P_{Az} = 8603$ Pa).

The H^E values are all positive (Figure 3) and decrease with increasing separation of the bromine atoms in the molecule. At the same time, the maxima of the H^E–x curves shift gradually toward the α,ω-dibromo-rich side. A general discussion of these results is deferred until other mixtures containing polybromoalkanes are investigated.

Glossary

A_j	parameters in eq 1 or 2
B_{ij}	molar second virial coefficients, cm^3 mol^{-1}
G	molar Gibbs energy, J mol^{-1}
H	molar enthalpy, J mol^{-1}
N	total number of measurements
P	total vapor pressure, Pa
Q	any property
R	molar gas constant (8.31451 J K^{-1} mol^{-1})
T	temperature, K
V	liquid molar volume, cm^3 mol^{-1}
x	liquid mole fraction
y	vapor mole fraction

Greek Letters

$\sigma(Q)$	standard deviation of property Q, eq 3
σ_e	experimental uncertainty

Superscripts

E	excess property
o	pure component

Subscripts

Az	azeotropic property
calc	calculated property
i	type of component

Registry No. n-Hexane, 110-54-3; 1,4-dibromobutane, 110-52-1; 1,5-dibromopentane, 111-24-0; 1,6-dibromohexane, 629-03-8; 1,8-dibromooctane, 4549-32-0; 1,3-dibromopropane, 109-64-8; nonane, 111-84-2.

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Solubilities of Myristic Acid, Palmitic Acid, and Cetyl Alcohol in Supercritical Carbon Dioxide at 35 °C

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A flow-type apparatus was constructed to measure the solubilities of myristic acid (tetradecanoic acid), palmitic acid (hexadecanoic acid), and cetyl alcohol (hexadecanol) in supercritical carbon dioxide at 35 °C from 8.1 to 22.8, 9.9 to 20.6, and 8.9 to 21.8 MPa, respectively. The logorithm of the enhancement factor was plotted against the density of carbon dioxide, and a good linear relationship was observed for each system.

Introduction

It is very useful if natural products can be separated and purified with high selectivity. The supercritical gas extraction has been given much attention recently as one of the new separation technologies in the chemical industry. The solubility data of natural products in supercritical gas are essentially important in the process design of the supercritical gas extraction. In this work, a flow-type apparatus was constructed to measure the solubilities of myristic acid, palmitic acid, and

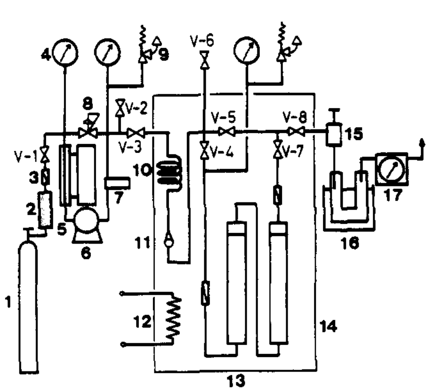

Figure 1. Flow-type apparatus to measure solubilities of solid components in supercritical carbon dioxide: (1) gas cylinder; (2) dryer; (3) filter; (4) pressure gage; (5) cooling unit; (6) feed pump; (7) damper; (8) back-pressure regulator; (9) safety valve; (10) preheating coil; (11) check valve; (12) heater; (13) equilibrium cell; (14) water bath; (15) expansion valve; (16) trap; (17) flow meter; (V-1–V-8) stop valve.

cetyl alcohol in supercritical carbon dioxide at 35 °C. Their solubilities in supercritical CO_2 have been measured previously (*1–4*), but all of the data were reported at temperatures higher than 40 °C. A relatively small pressure change in the region 5–7 MPa at 35 °C causes a large change in the solubility of the solid component. At higher temperature, the change is not so dramatic. The solubilities of naphthalene in supercritical CO_2 were measured to check the reliability of the apparatus.

Experimental Section

Equipment and Procedures. A flow-type apparatus was constructed to measure the solubilities of solid components in supercritical carbon dioxide. The apparatus is shown schematically in Figure 1. Carbon dioxide, supplied from a gas cylinder and liquefied through a cooling unit, was directed to a compressor. A back-pressure regulator was used to maintain a constant pressure within the system. The equilibrium pressure was measured by a Bourdon gauge. Two equilibrium cells were used, the inner diameter, height, and volume of each cell being 30 mm, 45 cm, and 315 mL. The solid component and glass beads were packed in the second equilibrium cell, while the first cell was used as a buffer tank. These cells were attached to a preheating coil and submerged in a water bath controlled to within ±0.1 °C. Valve V-5 was closed, and valves V-4 and V-7 were opened to introduce supercritical CO_2 into the equilibrium cells. Supercritical CO_2 saturated with solid component was depressurized through an expansion valve and introduced into a U-shaped glass tube cooled in an ice bath. In the tube, gaseous CO_2 and solid component were separated. The amount of solid component trapped was determined by mass. The volume of CO_2 was measured by a wet-gas meter. Usually, 0.1–0.5 g of solute was trapped and the flow rate of carbon dioxide was adjusted to be 3.3–16.7 $cm^3\ s^{-1}$. A small amount of solid remaining in the tubing and the expansion valve was removed and trapped by using CO_2 through valves V-5 and V-8 after closing valves V-4 and V-7.

Materials. Reagent-grade myristic acid (supplied by Nacalai Tesque, Inc.), palmitic acid and cetyl alcohol (Sigma Chemical Co.), and naphthalene (Nakarai Chemicals, Ltd.) were used without further purification. The purities of myristic acid, palmitic acid, cetyl alcohol, and naphthalene are more than 99, 99, 99, and 99.9%, respectively. High-purity CO_2 (more than 99.9%, Seitetsu Kagaku Co., Ltd.) was used as received.

Results and Discussion

To check the reliability of the apparatus, the solubilities of naphthalene in supercritical CO_2 at 35 °C were measured. The measurements were carried out for several flow rates of CO_2 at known pressures. The solubilities obtained were independent of the flow rate of CO_2. The reproducibility of the solubilities was within ±3%. The experimental data are shown in Table I. The values listed in Table I are obtained from an arithmetic average of several measurements at each pressure. The values are in good agreement with those of Tsekhanskaya et al. (*5*)

Table I. Solubilities (y_2) of Naphthalene, Myristic Acid, Palmitic Acid, and Cetyl Alcohol in Supercritical CO_2 at 35 °C

naphthalene		myristic acid		palmitic acid		cetyl alcohol	
p/MPa	10^2y_2	p/MPa	10^3y_2	p/MPa	10^4y_2	p/MPa	10^3y_2
8.5	0.834	8.1	0.343	9.9	1.53	8.9	1.01
13.3	1.41	9.9	1.16	12.7	3.26	10.9	1.64
17.0	1.65	12.8	2.31	15.7	3.98	12.8	2.09
20.7	1.76	14.8	3.33	18.6	4.41	15.8	2.49
23.8	1.76	19.7	4.03	20.6	4.82	18.7	2.70
		22.8	4.34	23.0	4.94	21.8	2.87

Table II. Coefficients of Equation 1

	A	B/($m^3\ kg^{-1}$)
myristic acid	0.4716	0.01254
palmitic acid	−0.2229	0.01081
cetyl alcohol	3.178	0.008953

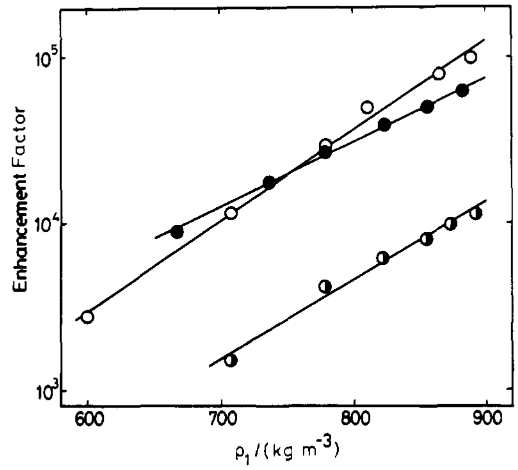

Figure 2. Relationship between enhancement factor E and density of carbon dioxide ρ_1: (○) myristic acid; (◑) palmitic acid; (●) cetyl alcohol; (—) results calculated from eq 1.

Table I also gives the solubility results for myristic acid, palmitic acid, and cetyl alcohol in supercritical CO_2 at 35 °C.

The enhancement factor $E = py_2/p_2°$ was plotted against the density of pure CO_2, ρ_1. Usually the saturated vapor pressure of the solute is used as $p_2°$ to calculate E. However, the saturated vapor pressures of myristic acid, palmitic acid, and cetyl alcohol at 35 °C are not available. So, the value $p_2°$ is fixed to be 1 Pa. The density of CO_2 was calculated by a five-parameter van der Waals type cubic equation of state proposed by Adachi et al. (*6*) with the optimized parameters. Figure 2 shows a good linear relationship between ln E and ρ_1 for each system. The relationship can be represented by using the following equation

$$\ln E = A + B(\rho_1/(\mathrm{kg\ m^{-3}})) \tag{1}$$

where coefficients A and B are given in Table II.

Glossary

E	enhancement factor ($=py_2/p_2°$)
p	pressure, Pa
y	solubility (mole fraction)
ρ	density, kg m^{-3}

Subscripts

1	carbon dioxide
2	solute (solid component)

Registry No. $H_3C(CH_2)_{12}CO_2H$, 544-63-8; $H_3C(CH_2)_{14}CO_2H$, 57-10-3; $H_3C(CH_2)_{15}OH$, 36653-82-4; CO_2, 124-38-9.

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Activity and Osmotic Coefficients of Dilute Sodium Chloride Solutions at 273 K

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The cryoscopic data reported in the literature for aqueous NaCl solutions were systematically recalculated. In these calculations, it was found that most of the measured freezing points up to the molality of 0.45 mol·kg^{-1} can be predicted within experimental error by a two-parameter equation of the Hückel type. The two parameters of this Hückel equation were determined from the results of the most accurate freezing point measurements found for NaCl solutions in the literature. With these parameter values, accurate estimates of the activity and osmotic coefficients of NaCl solutions at 273 K can be obtained. These values, in addition to the recommended freezing point depressions, have been tabulated at rounded molalities. The standard deviations for the estimated values have been presented graphically and were computed by using the recently developed nonparametric jackknife method.

Introduction

It is well-known that the most reliable activity coefficients of dilute aqueous solutions of alkali-metal halides at different temperatures are obtained from measurements on appropriate concentration cells with transference. In our previous studies (*1*), it has been shown that the existing measured results of the cells of this kind at 298 K can be successfully predicted by a two-parameter equation of the Hückel type for the activity coefficients. In most cases, this concentration cell method has been used only in such solutions where the molality is less than about 0.1 mol·kg^{-1}. When activities of less dilute alkali-metal-salt solutions are determined, the isopiestic method is most often used. The difficulty in applying this method is that the method needs a reference electrolyte and the activities of the interesting electrolyte alone cannot thus be studied. Another potentially accurate method to study the thermodynamics of less dilute salt solutions is the cryoscopic method. This method was very popular at the beginning of this century, and a number of precise cryoscopic data of different salt solutions have been, therefore, reported in the literature.

In the wide recalculation work carried out by Hamer and Wu (*2*) and by Pitzer and Mayorga (*3*), the activities of uni-univalent electrolytes were determined for aqueous solutions at 298 K. Because of the choice of this temperature, the freezing point data had to be omitted from the calculations. No recent study, as far as we know, has been reported in literature where the existing freezing point results of uni-univalent electrolytes have been collected and critically analyzed. In the present paper, an analysis of this kind is performed for NaCl solutions.

According to our understanding, the generally accepted activities for NaCl solutions at 273 K have not been reported in the literature. The most reliable values so far have been presented by Scatchard and Prentiss (*4*), on the basis of their freezing point determinations, and by Platford (*5*), on the basis of his isopiestic studies. The values of these two origins do not, unfortunately, agree with each other as well as desired. At the molality of 0.1 mol·kg^{-1}, for example, Scatchard and Prentiss presented the value of 0.9337 for the osmotic coefficient and the Platford value is 0.931.

Silvester and Pitzer (*6*) have developed for the activities of NaCl solutions a very general multiparameter equation which covers wide ranges of molalities and temperatures. We tested the validity of this equation at 273 K and used it to predict the measured freezing points of this electrolyte at different molalities (see below). According to our calculations, however, the predictions of this equation are systematically too high above the molality of 0.15 mol·kg^{-1}. At 0.8 mol·kg^{-1}, e.g., the error is about −0.02 K, and this is a value which by far exceeds the experimental precision of the best freezing point determinations presented in the literature (this precision has been probably well below ±0.0005 K).

In the present article, we apply the above-mentioned Hückel equation to the existing freezing point data measured in NaCl solutions and show that even the most accurate experimental cryoscopic results of NaCl solutions can be predicted almost completely up to the molality of 0.45 mol·kg^{-1} by the Hückel equation. In addition, our preliminary calculations with the cryoscopic data reported by Scatchard and his co-workers (*4*, *7–10*) show that the activities of all 21 electrolytes considered in those studies can also be correlated to the molalities by a simple equation of the Hückel type. Usually these activities can be predicted within experimental error at least up to the molality of 0.3 mol·kg^{-1}, but in the best cases this equation applies satisfactorily near the molality of 1.5 mol·kg^{-1}. In the previous literature, such simple equations as the Hückel equation are seldom used above the molality of about 0.1 mol·kg^{-1}.

Equations and Estimation of the Hückel Parameters

The Hückel equation for the activity coefficient ($\gamma_\pm$) of a uni-univalent electrolyte can be written in the form presented by Pan (*11*):

0021-9568/91/1736-0432$02.50/0