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## Cryoscopic Constant, Molar Volumes, Compressibility, and Viscosity in the Systems $\text{CH}_3(\text{CH}_2)_7\text{COOH}-\text{CH}_3(\text{CH}_2)_7\text{COOM}$ ( $M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) at $30^\circ\text{C}$

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The cryoscopic constant of nonanoic acid is measured and the enthalpy of fusion deduced is compared with the value extrapolated from previous measurements on higher homologues. Density, compressibility, and viscosity of solutions of alkali metal nonanoates in nonanoic acid are reported.

## Introduction

As a part of our research on fused aliphatic acids, we report the experimental values of some measurements carried out on mixtures of nonanoic acid (pelargonic acid) and alkali metal nonanoates.

## Experimental Section

Pycnometric, viscosimetric, ultrasonic, and cryoscopic experimental methods are described in previous papers (3-6). In the pycnometric measurements care was taken to minimize the error due to the adhesion of solutions on the capillaries; e.g., the capillaries were cleaned with a very thin tube of plastic and with cleaning paper rolled around a very thin metallic wire. Notwithstanding, the density and  $\varphi_v$  values are obtained at a reliability of  $0.7 \times 10^{-4}$  g/mL and 1 mL/mol, respectively. The compressibility data, obtained via ultrasonic velocity ( $\beta_s = 1/u^2d$ ) (9), and viscosimetric data are given with a reliability of  $0.1 \times 10^{-6}$  bar $^{-1}$  and 0.1 cP, respectively. The cryoscopic measurements were performed as previously described (4), but in this procedure the furnace was substituted by a glass double vessel with circulation of methyl alcohol thermostated in a Lauda ultracryostat. Fluka Puriss nonanoic acid was used without further purification; the melting temperature and some physical properties measured at  $30^\circ\text{C}$  are given in Table I. The alkali metal nonanoates were prepared by complete reaction between stoichiometric amounts of the corresponding carbonates and of a warm alcoholic solution of nonanoic acid. The soap precipitated at room temperature was recrystallized twice from ethyl alcohol and dried under dynamic vacuum at increasing temperature ( $90^\circ\text{C}$  maximum). C. Erba RP carbonates were used. Owing to the high cost of  $\text{Cs}_2\text{CO}_3$ , the cesium soap prepared was sufficient only for three measurements. The lithium nonanoate is practically insoluble in nonanoic acid and the corresponding system was not studied.

Table I. Some Physical Properties of Nonanoic Acid

$d^\circ$ , g/mL	0.8968 <sub>4</sub>
$\eta^\circ$ , cP	6.0
$\beta_s^\circ$ , bar $^{-1}$	$65.7 \times 10^{-6}$
$T_{\text{fus}}$ , K	285.0

Table II. Experimental Values of Density, Compressibility, and Viscosity for the Solutions of Alkali Metal Nonanoates in Nonanoic Acid

nonanoate salt	$C$ , mol/L	$d$ , g/mL	$10^6\beta_s$ , bar $^{-1}$	$\eta$ , cP
Na	0.0400	0.8979 <sub>7</sub>	65.7	6.3
	0.0612	0.8986 <sub>1</sub>	65.6	6.5
	0.1166	0.9001 <sub>8</sub>	65.4	7.1
	0.1767	0.9018 <sub>8</sub>	65.0	7.5
	0.2277	0.9033 <sub>5</sub>	65.2	7.9
K	0.0410	0.8986 <sub>1</sub>	65.4	6.4
	0.0869	0.9005 <sub>6</sub>	65.2	6.9
	0.1229	0.9021 <sub>1</sub>	64.9	7.4
	0.1374	0.9027 <sub>3</sub>	65.0	7.5
	0.1749	0.9043 <sub>3</sub>	64.9	8.1
Rb	0.2298	0.9066 <sub>0</sub>	64.6	8.8
	0.0761	0.9031 <sub>0</sub>	65.3	6.8
	0.1093	0.9057 <sub>5</sub>	65.0	7.2
	0.1474	0.9088 <sub>7</sub>	64.9	7.7
Cs	0.2156	0.9143 <sub>0</sub>	64.4	8.6
	0.0992	0.9093 <sub>4</sub>	65.0	7.2
	0.1225	0.9122 <sub>8</sub>	65.0	7.5
	0.1768	0.9190 <sub>5</sub>	64.6	8.3

## Results

**Cryoscopy.** On the basis of previous experiences (6), diphenyl is a good cryoscopic solute in aliphatic acids because the corresponding crystallization curves approach the ideal one and formation of mixed crystals is not evident. For this reason diphenyl has been employed in order to determine the cryoscopic constant ( $\Delta T/m$ ) $^\circ$ . The ( $\Delta T/m$ ) $^\circ$  value is, on the contrary, very low when K or Na soaps are employed as solutes: diphenyl 8.0 K  $m^{-1}$ ; potassium nonanoate 4.6 K  $m^{-1}$ ; sodium nonanoate 5.1 K  $m^{-1}$ . A value of 8.0 is assumed for the cryoscopic constant and the enthalpy of fusion is calculated following the formula

$$H_f = (RT_0^2 M / 1000k)$$

where  $k$  is the cryoscopic constant. The values  $H_f = 3.19$  kcal/mol, and  $S_f = 11.2$  eu are obtained with a precision of  $\pm 2\%$ . These values agree satisfactorily with the equation

Table III. Parameters of Equations 1, 2, and 3 and Standard Deviations

	nonanoate			
	Na	K	Rb	Cs
$\varphi_v^0$ , mL/mol	168	170	180	(182)
$S_v$ , ( $10^{3/2}$ mL <sup>3/2</sup> mol <sup>-3/2</sup> )	2.53	3.76	0.94	(3.46)
$\sigma$	0.2	0.4	0.6	(0.2)
$10^6\gamma$ , bar <sup>-1</sup>	65.8	65.5	65.8	(65.6)
$10^6\delta$ , (bar M) <sup>-1</sup>	3.24	3.75	6.45	(5.55)
$\sigma$	0.1	0.08	0.08	(0.07)
$\lambda$ , cP M <sup>-1</sup>	8.61	11.80	11.83	(12.84)
$\sigma$	0.06	0.10	0.09	(0.07)

previously proposed for the higher homologues (2),  $S_{f(\text{odd})} = 2.56n - 9.64$ ; from this equation in fact a value of  $S_f = 13.4$  eu may be calculated.

**Density, Compressibility, and Viscosity.** The density values and the apparent molar volumes derived from the equation  $\varphi_v = 10^3(d^0 - d)/mdd^0 + M_2/d(9)$ , the compressibility, and the viscosity data are given in Table II, whereas in Table III are given the parameters of the following equations

$$\varphi_v = \varphi_v^0 + S_v\sqrt{C} \quad (1)$$

$$\beta_s = \gamma - \delta C \quad (2)$$

$$\eta = \eta^0 + \lambda C \quad (3)$$

that fit the experimental data;  $\eta^0$  is given in Table I. Parameter  $A$  of the Jones–Dole equation (8),  $\eta/\eta^0 = 1 + AC^{1/2} + BC$ , is  $\approx 0$  in the limits of experimental error. From Table III it is evident that the dependence of  $\eta/C$  or  $\beta_s/C$  is more important in solutions with higher cation soaps, generally. Under the assumption that the salts are completely dissociated, the Glueckauf method (7), slightly modified as previously reported (1), may be employed in order to obtain  $\varphi_v^+$  and  $\varphi_v^-$ . The  $\varphi_v^0$  values concerning Na, K, and Rb soaps (more reliable owing to the high number of experimental measurements) expressed in the form

$$\varphi_v^0 = (4/3)\pi r^3 N + Kr^2 - A'z^2/r + \varphi_v^- \quad (4)$$

give the following values:  $A' = 40 (\pm 5)$  (mL/mol) Å;  $K = 11$

( $\pm 2$ ) mL/(mol Å<sup>2</sup>);  $\varphi_v^- = 174 (\pm 2)$  mL/mol. The low values of  $\varphi_v^+$  obtained from the additivity rule ( $-6$ , Na<sup>+</sup>;  $-4$ , K<sup>+</sup>;  $6$ , Rb<sup>+</sup>;  $8$ , Cs<sup>+</sup>) may be ascribed to the high value of the electrostriction constant. It is noteworthy that  $\varphi_v^- \approx V_{\text{nonanoic acid}}$ .

### Glossary

$\varphi_v$	apparent molar volume of the solute, the symbols 0, +, - have the following meaning, respectively: at infinite dilution, of the cation, of the anion, mL/mol
$\beta_s$	adiabatic compressibility, $\beta^0$ is of the pure solvent, bar <sup>-1</sup>
$u$	ultrasonic velocity
$d$	density, $d^0$ is density of pure solvent, g/mL
$\eta$	viscosity, cP
$m$	molality
$C$	molarity
$M$	molecular weight of the solvent
$M_2$	molecular weight of the solute
$N$	Avogadro's number
$n$	number of carbon atoms in the molecule
$k$	cryoscopic constant
$\Delta T$	cryoscopic lowering
$H_f$	fusion enthalpy
$S_f$	fusion entropy
$T_0, T_{\text{fus}}$	fusion temperature of nonanoic acid
$S_v$	slope of the Masson equation
$\sigma$	standard deviation

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## Low-Temperature Heat Capacities of Potassium Disilicate

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Low-temperature heat capacities of crystalline potassium disilicate,  $K_2Si_2O_5(c)$ , were measured over the range 5–308 K by adiabatic calorimetry. The entropy,  $S^0$  at 298.15 K, was calculated to be  $45.55 \pm 0.05$  cal K<sup>-1</sup> mol<sup>-1</sup>. The heat capacity,  $C_p^0$ , entropy,  $S^0$ , and Gibbs energy function,  $(G^0 - H_0^0)/T$ , are tabulated over the temperature range investigated. The heat capacity curve showed a normal sigmoid shape.

One of the Bureau of Mines overall goals is to maintain an adequate supply of minerals to meet national economic and strategic needs. Part of this effort involves supplying ther-

modynamic data on compounds of mineral and metallurgical interest, such as potassium disilicate. The heat capacities of potassium disilicate,  $K_2Si_2O_5(c)$ , were measured over the range of 5–308 K by adiabatic calorimetry. Related thermodynamic functions are tabulated over the range 5–300 K.

### Materials and Apparatus

Crystalline potassium disilicate was prepared by reacting a mixture of reagent-grade potassium carbonate,  $K_2CO_3$ , and silicic acid,  $SiO_2 \cdot xH_2O$ , in stoichiometric quantities of  $K_2O$  and  $SiO_2$ . The reaction was initiated by heating the mixture in a platinum dish at 813 K for several hours, followed by a 5-day heating