J. Chem. Eng. Data 1982, 27, 133-135

Binary Mixtures of Sodium and Potassium Dodecanoates in Dodecanoic Acid

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Liquid–solid equilibrium temperatures, viscosity, density, and ultrasonic velocity at 10 MHz are measured in the binary systems composed of sodium or potassium dodecanoate in dodecanoic acid.

Introduction

As a part of wider research (*1–3*) on the properties of nonaqueous mixtures, experimental results are reported here concerning cryoscopic, volumetric, viscosimetric, and ultrasonic measurements in binary mixtures of two soaps (sodium and potassium dodecanoates) in dodecanoic acid.

Experimental Section

The experimental methods are extensively reported in previous notes (*4–7*). The lauric (dodecanoic) acid employed is an Ega product (purity > 99%). The sodium and potassium soaps are prepared by reaction of stoichiometric quantities of the acid and of the respective carbonates. The soap obtained is recrystallized from C_2H_5OH. The products were dried under dynamic vacuum at increasing temperature. In this note, 1 stands for dodecanoic acid and 2 for K or Na soap.

Results

Cryoscopy. The liquid–solid equilibria were measured by a potentiometric method, whose details are given elsewhere (*6*). Each measurement is always repeated 2 or 3 times, and the agreement is better than 0.9 μV ~ 0.02 K. $T^0 - T$ values are calculated with two-decimal figures, but in Table I T values are given with one-decimal figures. In fact, in differential values $T^0 - T$, some causes of error arising from the calibration of the thermocouple are less important than in the absolute values T. As an example, we report the experimental data of a run of measurements: $W_1 = 11.241$ g; $W_2 = 0.2284$ g; $T^0 = 316.02$ K; $T = 315.45$ K; $(T^0 - T)/m = 4.7$ K/m. In Table I the fusion temperatures of 316.0 K ($x_1 = 1.0$) and 315.5 K ($x_1 = 0.9820$) are reported.

The phase diagram, shown in Figure 1, exhibits a eutectic and an inflection point in the two systems; the coordinates are as follows: for the system with sodium soap $x_{1E} = 0.945$, $T_E = 314.7$ K, $x_{1P} = 0.700$, $T_P = 328.7$ K; for the system with potassium soap $x_{1E} = 0.880$, $T_E = 314.7$ K, $x_{1P} = 0.800$, $T_P = 324.2$ K. The values $(T^0 - T)/m$ extrapolate (when $m \rightarrow 0$) to 3.4 and 4.7 K/m for the solutions of K soap and Na soap, respectively, in dodecanoic acid. Previously, the value of the enthalpy of fusion of the dodecanoic acid was reported as 8.2 kcal/mol, which gives a cryoscopic constant $RT^{0\,2}M_1/(1000\Delta H_{f1})$ of 4.8 K/m (*8*). The two phenomena that affect the $\Delta T/m$ value (dissociation of the solute and solubility of the solute in the solid solvent) cannot be ascertained by means of a comparison between the experimental and thermodynamic cryoscopic constant in this case.

Density. The experimental values of density are given in Tables II and III, with the parameters of the interpolating equation ($d = a - bT$) and the correlation coefficient r. The mean volume V_m, obtained from d data, allow us to calculate the partial molar volume $\bar{V}_j$ following the usual thermodynamic relation:

$$\bar{V}_j = V_m - x_i(\partial V_m/\partial x_i) \qquad (1)$$

Table I. Liquid-Solid Equilibrium Temperatures

x_1	T, K	x_1	T, K
Dodecanoic Acid + Sodium Dodecanoate			
1.0000	316.0	0.8603	321.1
0.9820	315.5	0.8581	321.1
0.9702	315.3	0.8518	322.3
0.9652	315.2	0.8418	323.2
0.9399	315.6	0.7472	327.0
0.9372	314.7	0.6978	329.1
0.9259	318.0	0.6757	335.3
0.9221	317.6	0.6196	348.8
0.8918	319.5	0.5934	354.4
Dodecanoic Acid + Potassium Dodecanoate			
1.0000	316.0	0.8791	315.0
0.9783	315.6	0.8650	317.6
0.9635	315.4	0.8523	318.8
0.9604	315.4	0.8262	322.4
0.9466	315.1	0.7980	325.4
0.9260	314.7	0.7482	334.1
0.9037	314.8	0.7094	339.5

Table II. Density of the Mixtures of Sodium Dodecanoate in Dodecanoic Acid

T, K	d, g/mL	T, K	d, g/mL
$x_1 = 1.0000$			
378.7	0.8258	347.7	0.8500
386.1	0.8199	340.5	0.8556
386.5	0.8196	328.5	0.8645
370.0	0.8333	319.6	0.8713
366.6	0.8357	318.9	0.8717
348.1	0.8496		
$a = 1.1174$ g/mL, $b = 7.69 \times 10^{-4}$ g/(mL K), $r = 0.9999$			
$x_1 = 0.9743$			
389.4	0.8229	344.6	0.8569
372.6	0.8360	333.0	0.8661
372.0	0.8363	324.1	0.8728
356.5	0.8480		
$a = 1.1198$ g/mL, $b = 7.62 \times 10^{-4}$ g/(mL K), $r = -0.9999$			
$x_1 = 0.8518$			
375.9	0.8423	345.2	0.8684
364.6	0.8522	340.4	0.8725
354.7	0.8603	336.6	0.8752
346.3	0.8680	335.7	0.8763
$a = 1.1594$ g/mL, $b = 8.43 \times 10^{-4}$ g/(mL K), $r = -0.9998$			
$x_1 = 0.7460$			
383.1	0.8568	359.6	0.8744
371.6	0.8655	348.8	0.8825
371.2	0.8658	339.6	0.8894
365.0	0.8699	335.9	0.8920
$a = 1.1432$ g/mL, $b = 7.48 \times 10^{-4}$ g/(mL K), $r = -0.9999$			
$x_1 = 0.6522$			
387.8	0.8643	355.1	0.8879
376.1	0.8734	344.1	0.8972
366.9	0.8802		
$a = 1.1517$ g/mL, $b = 7.41 \times 10^{-4}$ g/(mL K), $r = -0.9993$			

$\bar{V}_j$, at the precision of the method employed, is a constant in the concentration range investigated. At 70 °C, as an example, $\bar{V}_j$ is as follows: Na soap, $225._9$ mL/mol; K soap, $245._5$ mL/mol; lauric acid, $235._1$ mL/mol. The mean volume as a function of

0021-9568/82/1727-0133$01.25/0

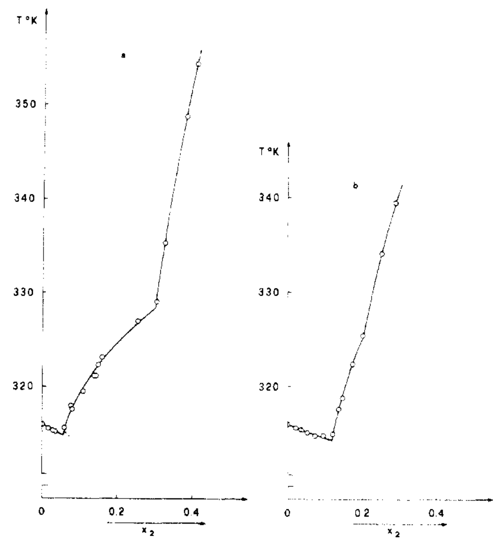

Figure 1. (a) Liquid-solid equilibria in the binary system dodecanoic acid + sodium dodecanoate. (b) Liquid-solid equilibria in the binary system dodecanoic acid + potassium dodecanoate.

Table III. Density of the Mixtures of Potassium Dodecanoate in Dodecanoic Acid

T, K	d, g/mL	T, K	d, g/mL
$x_1 = 0.9474$			
387.8	0.8163	352.0	0.8501
384.4	0.8222	343.1	0.8577
371.9	0.8291	333.4	0.8663
370.4	0.8313	326.6	0.8716
365.3	0.8390		
$a = 1.1667$ g/mL, $b = 9.02 \times 10^{-4}$ g/(mL K), $r = 0.9974$			
$x_1 = 0.8983$			
390.4	0.8220	362.0	0.8477
389.6	0.8237	342.4	0.8638
376.1	0.8347	325.8	0.8771
374.5	0.8364	323.9	0.8783
$a = 1.1509$ g/mL, $b = 8.40 \times 10^{-4}$ g/(mL K), $r = 0.9997$			
$x_1 = 0.7997$			
390.1	0.8353	353.1	0.8669
389.9	0.8357	334.5	0.8822
372.2	0.8507	328.0	0.8876
$a = 1.1631$ g/mL, $b = 8.39 \times 10^{-4}$ g/(mL K), $r = 1.0$			
$x_1 = 0.7019$			
390.9	0.8496	347.2	0.8844
379.5	0.8587	334.9	0.8938
359.9	0.8745	334.1	0.8944
$a = 1.1582$ g/mL, $b = 7.89 \times 10^{-4}$ g/(mL K), $r = -0.9999$			

the temperature and of the composition may be expressed by the equation $V_m = \alpha + \beta T - \gamma(1 - \delta T)x_1$, where $\alpha = 167.7$ and 199.9 mL/mol, $\beta = 0.1695$ and 0.1331 mL/(K mol), $\gamma = 8.511$ and 52.746 mL/mol, and $\delta = 0.00592$ and 0.00236 K^{-1} for the Na and K soaps, respectively. The standard deviation is 0.5 (Na soap) and 0.4 (K soap). A rough estimate of the disorder volume in the solutions may be performed by comparing the experimental $\bar{V}$ values and the intrinsic molar volumes (estimated from the van der Waals volumes ($\mathcal{V}$) for the anion and as $^4/_3\pi r_+{}^3N$ for the cation). In these systems $\bar{V}_2 \gg \bar{V}_{\mathrm{intr}}$.

Viscosity. The viscosity values are given in Tables IV and V and are expressed following the Arrhenius equation: $\ln \eta = \bar{m} + n/T$; the parameters are given in Table VI. The dependence of the viscosity on the mole fraction is more important for the Na soap. The activation energy rises with an irregular trend from 5.5 kcal/mol (dodecanoic acid) to 6.1 kcal/mol in the investigated concentration range.

Table IV. Viscosity of the Mixtures of Sodium Dodecanoate in Dodecanoic Acid

T, K	η, cP	T, K	η, cP
$x_1 = 1.0000$			
329.9	6.2	359.2	3.4
336.7	5.5	363.5	2.9
343.4	4.5	381.2	2.1
351.8	4.0	393.0	1.6
$x_1 = 0.9739$			
326.2	9.1	362.4	3.8
330.2	7.9	383.2	2.5
336.2	6.7	395.4	2.0
347.2	5.4		
$x_1 = 0.8986$			
328.8	11.9	361.3	5.8
335.2	10.9	381.6	3.9
345.2	7.9	389.2	3.3
355.0	6.9		
$x_1 = 0.8045$			
334.7	18.8	364.2	9.0
338.7	17.2	386.2	5.6
345.9	13.9	391.4	5.0
355.9	11.3		
$x_1 = 0.7458$			
335.7	28.5	370.7	11.9
349.6	20.0	380.2	9.7
360.2	15.9	397.8	7.0

Table V. Viscosity of the Mixtures of Potassium Dodecanoate in Dodecanoic Acid

T, K	η, cP	T, K	η, cP
$x_1 = 0.8992$			
323.7	13.3	348.3	7.4
327.2	12.3	353.2	6.5
338.4	9.1	358.1	6.0
343.3	8.0		
$x_1 = 0.8286$			
323.3	19.6	341.3	11.5
328.2	16.7	348.4	9.7
333.2	14.3	358.3	7.7
$x_1 = 0.7753$			
323.2	24.4	346.5	12.2
330.2	17.0	353.5	10.6
338.3	14.6		
$x_1 = 0.7299$			
340.2	20.2	354.4	14.2
344.2	18.2	358.3	12.6
349.4	15.7		

Table VI. Parameters of the Arrhenius Equation

$\bar{m}$	n(K)	r	x_1
K Soap			
−5.86	2733.9	0.9987	0.8992
−6.56	3075.8	0.9993	0.8286
−6.08	2972.2	0.9810	0.7753
−6.19	3127.9	0.9985	0.7299
Na Soap			
−6.57	2781.1	0.9970	1.0000
−6.33	2777.6	0.9995	0.9739
−5.83	2739.5	0.9977	0.8986
−6.22	3067.8	0.9997	0.8045
−5.76	3058.6	0.9993	0.7458

Ultrasonic Velocity. The ultrasonic velocity measured at 10 MHz is given in Table VII for the different concentrations investigated of sodium dodecanoate in dodecanoic acid. A chemical attack performed by these solutions on the transducers prevents us from performing the measurements on the solutions of K soap. The adiabatic compressibility obtained by

Table VII. Ultrasonic Velocity at 10 MHz in Mixtures of Sodium Dodecanoate in Dodecanoic Acid

T, K	*u*, m/s	$10^6\beta_S$, bar^{-1}	*T*, K	*u*, m/s	$10^6\beta_S$, bar^{-1}
		$x_1 = 0.9490$			
318.4	$1280._5$	69.3	328.2	$1248._9$	73.5
321.5	$1272._4$	70.4	332.2	$1237._8$	75.1
324.4	$1262._2$	71.7	335.7	$1222._9$	77.2
		$x_1 = 0.8600$			
327.2	$1258._8$	71.4	337.7	$1224._4$	76.2
330.2	$1249._9$	72.6	341.4	$1214._3$	77.7
333.7	$1235._4$	74.5			
		$x_1 = 0.7030$			
333.2	$1250._8$	71.1	340.2	$1230._9$	73.8
336.7	$1240._6$	72.5	344.2	$1215._0$	76.1

the formula $\beta_s = (u^2d)^{-1}$ is fitted by the equation $10^6\beta_s = -87.7 + 0.4351T + 13.368(1 + 0.00139T)x_1$, where β_s is expressed in bar^{-1}, with a standard deviation of 0.2.

Acknowledgment

Thanks are due to L. Amici for technical assistance.

Glossary

d	density
η	coefficient of viscosity
β_s	coefficient of adiabatic compressibility
m	molality
M	molar weight
n	number of moles
r	correlation coefficient
r_+	cation radius
N	Avogadro's number
x_{1E}	mole fraction of component 1 in the eutectic mixture
x_{1P}	mole fraction of component 1 in the peritectic mixture
T^0	melting temperature of the pure compound
T_E	eutectic temperature
T_P	peritectic temperature
u	ultrasonic velocity
$\bar{V}_j$	molar volume = $(\partial V/\partial n_j)_{T,P,n_i}$
V_m	mean volume = $V/(n_1 + n_2)$
V_{intr}	intrinsic volume

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Received for review April 7, 1981. Revised manuscript received October 20, 1981. Accepted November 19, 1981. CNR (Rome) provided finanical support for this work.

Relative Volatilities of the Ethane–Ethylene System from Total Pressure Measurements

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A new apparatus has been developed for making vapor pressure measurements on high-pressure systems. Using this equipment, we have made a large number of new total pressure measurements on the ethane–ethylene binary from 198.15 to 278.15 K. By integration of the general coexistence equation, relative volatilities have been calculated for ethane–ethylene over the entire temperature range.

The viability of using the total pressure method for determining relative volatilities in systems at high pressure has been shown by Manley (*1*) and Manley and Swift (*2*). Walker (*3*) and Steele (*4*, *5*) have developed an apparatus capable of producing rapid and accurate *P–T–X* measurements for moderate-pressure systems at near ambient temperatures. Barclay (*6*) incorporated the desirable features of that equipment into an apparatus useful at higher pressures and lower temperatures and provides new data on a system of economic significance.

No recent study of the ethane–ethylene system has been made which covers the entire region of industrial interest. Fredenslund et al. (*7*) produced high-quality VLE measurements for two isotherms, 263.15 and 293.15 K, the second being above the critical point of ethylene. Earlier measurements by Hanson et al. (*8*) at 273.15, 233.17, and 199.85 K are not of comparable accuracy. The results of this study should improve the consistency and the accuracy of the relative volatility information on the ethane–ethylene system and aid in the design of distillation columns for processing these two chemicals.

Experimental Equipment

The equipment developed to measure vapor pressures is very similar to that described by Walker and Steele. It was designed to operate at pressures up to 4.5 MPa with the capability of being easily modified to work almost to 7.0 MPa.

A major equipment modification was the redesign of the sample cell–transducer combination. Figure 1 is a proportional drawing of these.

The cell is constructed of 316 stainless steel with a 0.002-in. type 302 stainless diaphragm and is assembled by silver solder brazing. The cavity is machined from 2-in. disks approximately $^1/_8$ in. thick. The diameter of the cavity is 1.50 in., and it is cut at a lathe setting of 1.5° for the entire radius to give a maximum span at the center of about 0.031 in. The sample chamber is made from 1-in. o.d. tubing and has an approximate

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