(5) Brown, L. R.; Reid, A. J. U.S. Patent 3361647, 1968.
(6) Anthony, P.; Berkowitz, L. *U.S. Natl. Acad. Sci. Publ.* **1958**, *568*, 80–90.
(7) Parisod, C. Ph.D. Thesis, No. 380, Federal Institute of Technology, Lausanne, Switzerland, 1980.
(8) Haas, J. L. *Geol. Surv. Bull.* (*U.S.*) **1976**, *1421-A*.
(9) Haas, J. L. *Geol. Surv. Bull.* (*U.S.*) **1976**, *1421-B*.
(10) Keevil, N. B. *J. Am. Chem. Soc.* **1942**, *64*, 841–50.
(11) Khaibullin, I. Kh.; Borisov, N. M. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1965**, *39*, 361–4.
(12) Khaibullin, I. Kh.; Borisov, N. M. *High Temp.* (*Engl. Transl.*) **1966**, *4*, 489–94.
(13) Urosova, M. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1974**, *19*, 450–4.
(14) Copeland, C. S.; Silverman, J.; Benson, S. W. *J. Chem. Phys.* **1953**, *21*, 12–6.
(15) Styrikovich, M. A.; Khaibullin, I. Kh. *Dokl. Akad. Nauk. SSSR*, **1953**, *109*, 962–5.
(16) "Gmelins Handbuch der Anorganisch Chemie"; 1973; Vol. 21, pp 1–183.

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Density and Viscosity in the Binary System Octadecanoic Acid–Hexanedioic Acid

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The experimental values of density and viscosity and the calculated values of molar volume, volume coefficient of thermal expansion, and activation energy are given for the binary system octadecanoic acid–hexanedioic acid.

Introduction

As a part of broader research program on physicochemical properties of pure and mixed organic melts (*4–6, 8*), the results of measurements of density and viscosity on the binary mixture octadecanoic (stearic) acid–hexanedioic (adipic) acid, in a temperature range above the melting curve (*1*), are presented herein.

Experimental Section

Density. The density measurements were performed by means of the Archimedean method described in the literature (*7*). A Mettler H 20 T analytical balance mounted above the thermoregulated furnace was used. The level of the furnace was changed by means of a laboratory elevator. From the pan of the balance a gold chain, joined to a steel double cone bob by means of a steel wire (0.05-mm diameter; 1-cm length), allowed the measurements to be performed. The melt was placed in a Pyrex container positioned in the central zone of the furnace, and the furnace was raised until the bob and half of the steel wire were submerged. This condition was observed by means of a set of mirrors. The temperature of the furnace was controlled by means of a chromel–alumel thermocouple connected to a Leeds and Northrup CAT system, and the temperature of the melt was read with a second thermocouple immersed in the fused substance. The thermocouple was checked against a Pt-resistance thermometer certified by NBS and connected to a Leeds and Northrup K-3 potentiometer. The system was calibrated by using H_2O, KCNS, $LiNO_3$, and $NaNO_3$ (*7*) for which the densities are known. The following equation was obtained for the volume of the bob up to 350 °C: $V(\mathrm{cm}^3) = 1.172_0 + 8.71 \times 10^{-5}t$. In Table I the process of calibration in molten $NaNO_3$ is reported. In run I the level of the furnace is settled in order to submerge the bob and half of the steel wire. In run II the balance is locked and then released after some minutes. In run III the level of the furnace is changed and then brought again to the same level as in run I. A precision on the density of $\pm 2 \times 10^{-4}$ g/cm^3 is obtained. The molar volume of lauric acid (*2*) measured with this system agrees with that measured by a conventional pycnometric method (*3*): 234.5 and 234.0 cm^3/mol, respectively, at 345.1 K.

Table I. Measures of Calibration of the Bob in $NaNO_3$

run	t, °C	$W_{\mathrm{air}}^{\mathrm{bob}} - W_{\mathrm{melt}}^{\mathrm{bob}}$, g	V_{bob}, cm^3
I	329.8	2.266_0	1.199_7
II	329.9	2.266_0	1.199_7
III	329.9	2.265_2	1.199_4

Table II. Density as Function of the Temperature at Different Compositions[a]

T, K	$10^{-3}d$, kg/m^3	T, K	$10^{-3}d$, kg/m^3
	$x_1 = 0.0$		
351.8	0.8404	393.9	0.8102
352.7	0.8397	406.1	0.8011
368.7	0.8286	433.2	0.7826
380.9	0.8202	461.1	0.7609
383.4	0.8184		
	$x_1 = 0.2024$		
424.0	0.8145	453.4	0.7930
431.7	0.8083	476.0	0.7754
442.5	0.8007	477.2	0.7744
	$x_1 = 0.4002$		
435.1	0.8321	460.2	0.8135
437.9	0.8308	481.2	0.7960
448.4	0.8229	483.1	0.7945
	$x_1 = 0.6606$		
431.7	0.8888	456.7	0.8692
436.7	0.8866	465.7	0.8263
448.1	0.8751		
	$x_1 = 0.8064$		
434.1	0.9684	464.9	0.9447
448.7	0.9602	473.8	0.9298
458.4	0.9472	473.3	0.9294
	$x_1 = 1.0$		
434.5	1.0916	461.1	1.0700
436.8	1.0893	476.2	1.0582
459.8	1.0710		

[a] x_1 = molar fraction of the adipic acid in the mixture.

Viscosity. The viscosity was measured by means of a commercial VEB MLW, DDR Freital, rotating viscometer. The substance was placed in the annular space between two coaxial cylinders. The stationary outer cylinder of radius R was the sample container and was surrounded by a circulating thermostat liquid. The internal cylinder of radius r and length l rotated at a selected constant angular speed ω (24 different

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Table III. Viscosity Values as Function of the Temperature at Different Composition[a]

T, K	η, cP	T, K	η, cP
$x_1 = 0.0503$			
353.4	10.2	370.2	6.9
358.6	8.8	382.2	5.7
362.9	7.9		
$x_1 = 0.2004$			
404.9	4.4	429.1	3.0
415.7	3.7	439.5	2.5
422.0	3.3	451.7	2.3
$x_1 = 0.3998$			
413.2	5.1	441.5	2.9
420.7	3.9	452.6	2.6
431.7	3.3		
$x_1 = 0.6335$			
430.8	3.4	445.0	2.9
434.7	3.6	450.0	2.8
441.7	3.4	453.7	2.7
$x_1 = 0.7999$			
444.5	3.9	458.6	3.1
449.0	3.4	463.3	3.1
453.7	3.2		
$x_1 = 1.0$			
449.7	4.8	469.9	3.4
457.0	4.0	475.6	3.1
464.2	3.7		

[a] x_1 = molar fraction of the adipic acid in the mixture.

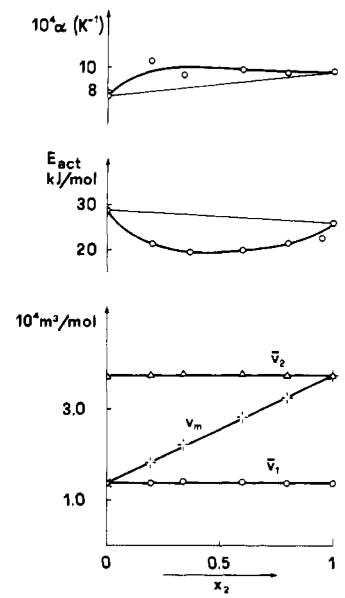

Figure 1. Trend of the coefficient of thermal expansion (reported as $10^4\alpha$), of the activation energy, and of the mean and partial volumes (reported as $10^4 \bar{V}_i$ and $10^4 V_m$) vs. the molar fraction of stearic acid. α and V_m (consequently $\bar{V}_i$) are calculated at 450 K.

speeds could be chosen) and was connected to a helical spring whose deviation was a measure of the torque M on the inside cylinder. The torque M, converted to an electric signal, was read as a deviation of an index on a metric scale (α_η). The viscosity was then obtained by following eq 1, in which z is a

$$\eta = z\alpha_\eta/D_r \qquad (1)$$

constant which involves the torsion constant of the helical spring in the viscometer and D_r is a viscometer constant which depends upon the dimensions of the cylinder and the angular frequency of rotation. The values z and D_r were certified by the manufacturer of the viscometer. The certified value D_r, valid as long as the line frequency is 50 Hz, was corrected for a frequency ν as follows:

$$D_r = D_{r,50}\nu/50 \qquad (2)$$

The frequency was read on a meter connected to the equipment. This viscometer was calibrated by measuring the viscosity of doubly distilled H_2O and of some oils certified and furnished by the same manufacturing firm. The difference between the values obtained and those given in the literature (*7*) for H_2O or in the certificate for the oils was less than ±1%. The values reported in the Tables I and II are the averages of replicates. Merck chemicals (purity 99%) were employed after a recrystallization from ethanol. They were dried at ~60 °C under vacuum. The mixtures showed thermal stability for 3 h as indicated by the repeatability of the measurement, both viscosimetric and densimetric. The temperature was controlled within ±0.2 K. In this paper component 1 is adipic acid and component 2 is stearic acid. The molecular weights employed are 146.14 amu for 1 and 284.50 amu for 2.

Results and Discussion

The experimental values of density are given in Table II, and those of viscosity in Table III for the different mixtures. In Tables IV and V the parameters of eq 3-5 and the corre-

$$V_m = a + bT + cT^2 \qquad (3)$$

$$\alpha = d + eT \qquad (4)$$

$$\ln \eta = \ln (f) + E/RT \qquad (5)$$

sponding standard deviations are given. Equation 3 for stearic acid agrees satisfactorily with the values previously published (*3*) obtained by pycnometric methods in a slightly lower temperature range, as shown by the following values: T = 341.2 K, $V_{exptl} = 3.351 \times 10^{-4}$ m^3/mol (*3*), $V_{calcd} = 3.356 \times 10^{-4}$ m^3/mol; T = 348.2 K, $V_{exptl} = 3.371 \times 10^{-4}$ m^3/mol (*3*), $V_{calcd} = 3.375 \times 10^{-4}$ m^3/mol. The mean molar volume $V_m = V/(n_1 + n_2)$ shows a linear dependence on the composition within the experimental error (Figure 1) and consequently $\Delta V = 0$ on mixing. $\bar{V}_1$ and $\bar{V}_2$ were calculated by following eq 6, where

$$\bar{V}_j = V_m - x_i(\partial V_m/\partial x_i) \qquad (6)$$

i and j represent the two components. The trend of the partial

Table IV. Parameters of Eq 3-5

x_1	10^6a, m^3/mol	10^6b, m^3/(mol K^2)	$10^{10}c$, m^3/(mol K^2)	10^4d, K^{-1}	10^7e, K^{-2}	f, cP	E/R, K
0.0	292.6	−0.0160	4.17	5.73	8.2		
0.0503						0.0047	2703
0.2024	299.4	−0.1998	5.59	5.47	8.8		
0.2004						0.0073	2587
0.4002	153.7	0.2786		5.34	9.7		
0.3998						0.0127	2401
0.6606	130.2	0.2014		5.40	8.5		
0.6335						0.0156	2347
0.8064	94.2	0.1928		5.47	11.0		
0.7999						0.0114	2575
1.0	90.2	0.1007		4.89	5.6	0.0022	3448

Table V. Standard Deviation of Eq 3 (σ_V), 4 (σ_α), and 5 (σ_η), Concerning the Different Mixtures

x_1	$10^6\sigma_V$	$10^4\sigma_\alpha$	σ_η
0.0	0.2	0.01	
0.0503			0.02
0.2024	0.2	0.005	
0.2004			0.03
0.4002	0.3	0.01	
0.3998			0.09
0.6606	0.3	0.01	
0.6335			0.05
0.8064	0.7	0.03	
0.7999			0.04
1.0	0.03	0.002	0.04

molar volumes vs. x_1 (Figure 1) points out the constancy of the molar volumes in the complete concentration range. The volume coefficient of expansion, α, shows a positive deviation from simple additivity and is roughly constant in the composition range $0.2 < x_2 < 1$ and is decreasing in the range $x_2 < 0.2$ (Figure 1). The activation energy $E = R\,\partial \ln \eta/\partial(1/T)$ of viscous flow for the mixtures agrees satisfactorily with the corresponding value for octadecanoic acid previously reported (*3*) (Figure 1). The plot E vs. x_2 shows a negative deviation from additivity.

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Glossary

α	volume coefficient of thermal expansion
d	density
E	activation energy
η	viscosity
ν	line frequency
T	absolute temperature
t	Celsius temperature
V	volume
V_m	mean volume per mixture mole
V_{exptl}	experimental volume
V_{calcd}	calculated volume
$\bar{V}_i$	partial molar volume of the *i*th component
x_i	molar fraction of the *i*th component
ω	angular speed of rotation of the internal cylinder
$W^{\text{bob}}_{\text{air,melt}}$	weight fo the bob in the air or in the melt, respectively

Literature Cited

(1) G. Berchiesi, A. Cingolani, and D. Leonesi, *J. Thermal Anal.*, **6**, 91 (1974).

(2) G. Berchiesi, G. Gioia-Lobbia, and M. A. Berchiesi, *J. Chem. Eng. Data*, **25**, 9 (1980).

(3) G. Berchiesi, D. Leonesi, and A. Cingolani, *J. Thermal Anal.*, **9**, 171 (1976).

(4) G. Berchiesi, G. Vitali, M. A. Berchiesi, and V. Valenti, *Gazz. Chim. Ital.*, **108**, 483 (1978).

(5) A. Cingolani, G. Berchiesi, and D. Leonesi, *J. Chem. Thermodyn.*, **6**, 1191 (1974).

(6) G. Gioia-Lobbia, G. Berchiesi, M. A. Berchiesi, and G. Vitali, *Ann. Chim.* (*Rome*), **67**, 407 (1977).

(7) G. J. Janz, "Molten Salts Handbook", Academic Press, London, 1967, p 510; R. C. Weast, Ed., "Handbook of Chemistry and Physics", The Chemical Rubber Co., Cleveland, OH, 1971-1972.

(8) G. Vitali, G. Berchiesi, and M. A. Berchiesi, *J. Chem. Eng. Data*, **24**, 169 (1979).

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Isothermal Compressibility of Cyclohexane–*n*-Decane, Cyclohexane–*n*-Dodecane, and Cyclohexane–*n*-Tetradecane

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Isothermal compressibilities for the binary mixtures of cyclohexane–*n*-decane, cyclohexane–*n*-dodecane, and cyclohexane–*n*-tetradecane have been measured at 298.15, 308.15, 318.15, and 333.15 K. The calculated "excess" function $\kappa_T{}^E$ is positive for the three mixtures, having its maximum at or around $x_1 = 0.5$.

Introduction

In a previous paper (*1*) we published our experimental results on the isothermal compressibility of binary systems consisting of cyclohexane–*n*-hexane, –*n*-heptane, –*n*-octane, and –*n*-nonane. Here we present similar measurements on another set of binary mixtures of cyclohexane with *n*-alkanes, namely, *n*-decane, *n*-dodecane, and *n*-tetradecane. The purpose is to round out this type of experimental result on a set of systems for which we already have data on excess enthalpy (*2*) and excess volume (*3*).

Experimental Section

The liquid isothermal compressibility, defined as

$$\kappa_T = -V^{-1}(\partial V/\partial p)_T \tag{1}$$

has been determined by using a direct-measurement piezometric method. The details of this technique were described in depth in previous papers (*4–6*). It allows individual measurements with errors below 0.5%.

The liquid volume involved in compressibility determination is calculated from its weight and density. Therefore we measured this for the pure substances at the four temperatures at which this work was carried out. In Table I we report the chemical source, the research grade claimed by the manufacturer, and the experimental density values obtained by us. For comparison sake, literature (*7*) values at 298.15 K are shown in the last column.

The mercury purification procedure has been described in a previous paper (*6*).

As usual the volume of a mixture is expressed by eq 2,

$$V = x_1V_1 + x_2V_2 + V^E \tag{2}$$

where the excess volume V^E has to be systematically measured. The cyclohexane–*n*-dodecane system at 288.15, 298.15, and 308.15 K was done by Gómez and Liu (*8*), who found no change with temperature; but their values at 298.15 K were slightly lower than those reported by Sánchez and Núñez (*3*). These authors measured V^E for the whole set of

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