

Figure 4. Modified mole fraction plot for water.

be used to correlate the three sets of data in the 0.1–1.0 mole fraction range.

Acknowledgment

The authors are indebted to Dr. D. Jaques of the Royal Melbourne Institute of Technology, Australia, for revising the manuscript.

Glossary

A_i, B_i	arbitrary constants in eq 2 for liquid component i
p°	saturation vapor pressure of pure liquid component, mmHg
p	partial vapor pressure of liquid component in mixture
t	temperature, °C
x	mole fraction of ethanol in the liquid phase, calculated on a salt-free basis
x'	modified mole fraction (θ) defined for ethanol: $= x / [x(p_E^{\circ}/p_E) + (1-x)(p_W^{\circ}/p_W)]$
y	mole fraction of ethanol in the vapor phase
Δt	temperature correction, °C
π	atmospheric pressure, mmHg

Subscripts

E	ethanol
i	either liquid component
W	water

Literature Cited

- (1) Alvarez, J. R., Ph.D. Thesis, University of Madrid, 1956.
- (2) Alvarez, J. R., Vega, M., *An. R. Soc. Esp. Fis. Quim., Ser. B*, **64**, 89 (1968).
- (3) Galan, M. A., Labrador, M. D., Alvarez, J. R., *Adv. Chem. Ser.*, No. **155**, 85 (1975).
- (4) Jaques, D., *Ind. Eng. Chem. Process Des. Develop.*, **16**, 129 (1977).
- (5) Jaques, D., Furter, W. F., *AIChE J.*, **18**, 343 (1972).
- (6) Lu, B. C.-Y., *Ind. Eng. Chem.*, **52**, 871 (1960).
- (7) Rius, A., Alvarez, J. R., Uriarte, A., *An. Real Soc. Esp. Fis. Quim., Ser. B*, **56**, 629 (1960).
- (8) Weissberger, A., Proskauer, E. S., "Organic Solvents", 2nd ed., Interscience, New York, 1955.

Received for review June 30, 1977. Resubmitted May 7, 1979. Accepted July 24, 1979.

Partial Molar Volumes and Expansibility in the Binary System Dodecanoic Acid–Hexanedioic Acid

Gianfrancesco Berchiesi,* Giancarlo Gioia-Lobbia, and Maria A. Berchiesi

Istituto Chimico dell'Università, 62032 Camerino, Italy

The experimental values of density and the calculated values of molar volumes and expansibility are given for the binary system dodecanoic (lauric) acid–hexanedioic (adipic) acid.

Introduction

As a part of a wider research on the physicochemical properties of pure and mixed organic melts (2–4, 6), the results of measurements of density in the binary system dodecanoic (lauric) acid–hexanedioic (adipic) acid are reported in this paper for temperature ranging from 326.8 to 479.2 K. As used herein, components 1 and 2 are hexanedioic acid and dodecanoic acid, respectively.

Experimental Section

The density measurements were performed by means of the Archimedian method described in the literature (5). A Mettler

balance H20T, placed upon the thermoregulated furnace, was used. The height of the furnace was changed by means of an 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 and 1 cm length) allows the measurements to be performed. The melt was placed in a Pyrex container dipped in the central zone of the furnace, that was raised as long as the bob and the half of the steel wire was dipped. This condition was observed by means of a set of mirrors. The furnace was thermoregulated by means of a chromel–alumel thermocouple connected to a Leeds & Northrup CAT system and the temperature of the melt was read by means of a second thermocouple, dipped in the melt, checked against a Pt-resistance thermometer certified by NBS and connected to a Leeds & Northrup K-3 potentiometer. The system was calibrated by means of H₂O, KCNS, LiNO₃, and NaNO₃ (5, 7) and the following equation was obtained for the volume (cm³) of the bob until 350 °C: $V = 1.172_0 + (8.71 \times 10^{-5})t$. In order to minimize the

Table I. Density of Different Mixtures at Various Temperatures

$x_1 = 0$		$x_1 = 0.1022$		$x_1 = 0.2990$		$x_1 = 0.4957$		$x_1 = 0.6685$		$x_1 = 0.7999$		$x_1 = 1$	
T, K	$\rho, g/mL$	T, K	$\rho, g/mL$	T, K	$\rho, g/mL$	T, K	$\rho, g/mL$	T, K	$\rho, g/mL$	T, K	$\rho, g/mL$	T, K	$\rho, g/mL$
326.8	0.8692	410.0	0.8180	425.1	0.8448	424.7	0.8932	421.3	0.9217	434.6	0.9905	434.5	1.0916
332.2	0.8642	417.3	0.8122	428.4	0.8396	436.8	0.8824	427.4	0.9113	436.4	0.9889	436.8	1.0893
338.1	0.8598	426.0	0.8055	435.1	0.8329	444.9	0.8728	435.5	0.9001	437.3	0.9874	459.8	1.0710
346.4	0.8541	433.6	0.7982	443.3	0.8242	456.5	0.8605	444.5	0.8868	444.0	0.9782	461.1	1.0700
362.9	0.8414	450.1	0.7824	450.6	0.8178	456.8	0.8599	456.0	0.8763	445.0	0.9761	476.2	1.0582
384.5	0.8256	463.8	0.7701	457.4	0.8119	466.5	0.8481	463.9	0.8694	453.5	0.9637		
408.6	0.8081			466.4	0.8041	479.0	0.8307	464.9	0.8688	469.6	0.9453		
408.8	0.8081					479.2	0.8309	464.9	0.8686				
433.6	0.7879					479.2	0.8307						
434.1	0.7866												

error due to the differences of the level of the furnace in the different measurements, we used a very thin wire (joining the bob to the gold chain); the following precision is obtained: on $W \pm 10^{-4}$ g, on $V_{bob} \pm 3 \times 10^{-4}$ cm³.

Merck chemicals (purity 99%, tested by gas chromatography) were employed after a recrystallization from ethanol. These were dried at ~ 60 °C under dynamic vacuum. The mixtures showed thermal stability for a time of 2–3 h as pointed out by the constancy of the weight of the bob. The temperature was constant within 0.2 K.

Results and Discussion

The experimental values of density are given in Table I for the different mixtures investigated as a function of the temperature. The values of density concerning lauric acid are in agreement with pycnometric data (measured in the temperature range 323–345 K) previously published (1). In fact the equation $V = 243.7 - 0.2290T + 0.000586T^2$ ($\sigma = 0.4$) (that fits the molar volume of lauric acid) gives the values 230.9 and 234.5 cm³/mol at 323.2 and 345.1 K, respectively. These values agree satisfactorily with the experimental values previously published (1), 229.9 and 234.0 cm³/mol. No other measurements concerning this binary system are reported in the literature.

The mean volume $V_m = V/(n_1 + n_2)$ as function of composition and also the partial molar volumes \bar{V}_1 and \bar{V}_2 obtained by following the thermodynamic relation

$$\bar{V}_1 = V_m - x_2(\partial V_m / \partial x_2) \quad (1)$$

are calculated at 434 K. The trend of V_m , \bar{V}_1 , and \bar{V}_2 vs. the composition, shown in Figure 1, points out a $\Delta V_{mix} = 0$.

The expansibility $\alpha = -(1/\rho)(\partial \rho / \partial T)_P$, shown in Figure 1 (at the temperature of 434 K), exhibits a positive deviation from the additivity, probably due to the breaking of the hydrogen bonds in the structure of hexanedioic acid.

Glossary

α	expansibility
P	pressure
ρ	density
T	absolute temperature

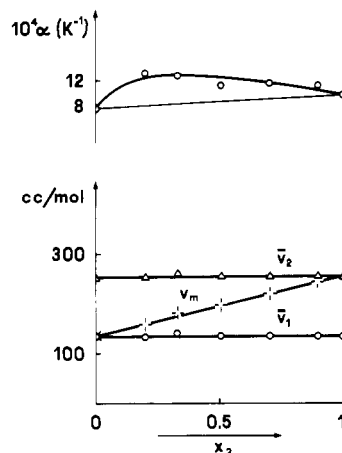


Figure 1. Expansibility α vs. x_2 (top) and mean volume and partial molar volumes vs. x_2 (bottom).

t	centigrade temperature
V	volume
V_m	mean volume
\bar{V}_1	partial molar volume of component 1
x_1	molar fraction of component 1
W	weight
σ	standard deviation

Literature Cited

- (1) Berchiesi, G., Leonesi, D., Cingolani, A., *J. Therm. Anal.*, **9**, 171 (1976).
- (2) Berchiesi, G., Vitalli, G., Berchiesi, M. A., Valenti, V., *Gazz. Chim. Ital.*, **108**, 487 (1978).
- (3) Gioia-Lobbia, G., Berchiesi, G., Berchiesi, M. A., *J. Therm. Anal.*, **10**, 133 (1976).
- (4) Gioia-Lobbia, G., Berchiesi, G., Berchiesi, M. A., Vitalli, G., *Ann. Chim. (Rome)*, **87**, 407 (1977).
- (5) Janz, G. J., "Molten Salts Handbook", Academic Press, London, 1967, p 510.
- (6) Vitalli, G., Berchiesi, G., Berchiesi, M. A., *J. Chem. Eng. Data*, **24**, 169 (1979).
- (7) Weast, R. C., "Handbook of Chemistry and Physics", The Chemical Rubber Co., Cleveland, Ohio, 1971, F-5.

Received for review March 23, 1979. Accepted July 23, 1979. Thanks are due to CNR (Rome) for financial support.