Molar Volumes of the Molten $NaNO_3$–KNO_3–$NaNO_2$ System

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The molar volumes of the molten ternary $NaNO_3$–KNO_3–$NaNO_2$ system have been measured dilatometrically under atmospheric pressure. The molar volumes are represented by empirical formulas as functions of temperature and mole fraction. The smoothed equation for molten $NaNO_3$ (7 m/o)–KNO_3 (44 m/o)–$NaNO_2$ (49 m/o) mixture, called HTS, is expressed as $V_m = 34.63 + 1.885 \times 10^{-2}T$.

Introduction

Knowledge of molar volumes is often necessary for experimental and theoretical considerations on transport properties and structural information. A number of molar volume data have been reported by many authors (*1*). In recent years, interest has been focused on various alkali–nitrate mixtures in the molten state as good heat storage materials (*2*) because of their low melting points and chemical stability over intermediate temperature range ca. 400–700 K.

As the molar volumes of these molten mixtures do not always hold the additivity, the molar volume measurements of the molten alkali–nitrate and alkali–nitrite mixtures are needed to be carried out, the data being represented by the empirical polynomial formulas. If the densities are necessary, they can be obtained from dividing the averaged molecular weight by the corresponding molar volume.

The dilatometer technique is most suitable for the molar volume measurement of molten mixture because the composition change of the molten mixture due to vaporization of the component is very small.

Experimental Section

Chemicals. The salts $NaNO_3$, KNO_3, and $NaNO_2$ used were of reagent grade. These salts were dried at a temperature lower than the melting point of each by 50 K in vacuo for about 10 h. Prior to the measurement it was confirmed by ultraviolet spectrophotometry (*3*) that there were virtually neither NO_3^- in $NaNO_2$ nor NO_2^- in $NaNO_3$ and KNO_3. The composition of the melt was determined by accurately weighing out the component salts, which remained unchanged during the experimental run.

Molar Volume Measurements. A transparent dilatometer made of quartz was employed. The schematic diagram of the apparatus is shown in Figure 1. The so-called "gold furnace" was used to heat the samples. This was made of concentric dual tubes of transparent quartz, and the external diameters of inner and outer tubes were 61 and 110 mm, respectively. The thickness of both tubes was about 2 mm, and the lengths of inner and outer tubes were 610 and 508 mm, respectively. As illustrated in Figure 1, a Kanthal wire heater has been wound noninductively on the outside surface of inner tube, and on both edge parts of this tube the heater has been wound closely to ensure uniform temperature distribution in this furnace. On the inside surface of outer tube a thin gold film has been adhibited to reflect the radiant heat. The meniscus of molten mixture in a dilatometer can be read through this gold film with a cathetometer. Since the thermal expansion coefficient of quartz is quite small, viz., 5.5×10^{-7} K^{-1} (*4*), calibration runs were performed using distilled water. The error caused by thermal expansion was estimated to be 0.05% at most.

Table I. Molar Volume Equations of Molten Binary Mixtures

system	*$NaNO_3$*–KNO_3[a]	*$NaNO_3$*–$NaNO_2$[a]	*KNO_3*–$NaNO_2$[a]
a_0	0.38345E+02	0.29326E+02	0.29326E+02
a_1	−0.18240E+01	0.66655E+01	0.16391E+02
a_2	−0.30068E+01	−0.33867E+01	−0.11112E+02
a_3	0.28385E+00	0.11933E+01	0.37400E+01
b_0	0.25853E−01	0.15765E−01	0.15765E−01
b_1	−0.10999E−01	−0.92872E−03	0.21244E−02
b_2	0.34157E−02	0.56747E−02	0.63716E−02
b_3	0.13252E−03	−0.21083E−02	0.15922E−02
σ	0.6097E−01	0.5583E−01	0.1305E+00
min temp, K	523.2	503.2	413.2
exptl point	129	143	178

[a] The italicized species refers to the key component corresponding to the mole fraction in the empirical formula. The maximum temperature in the measurements (723.2 K) is common for every system. The notation E represents an exponential function with a base 10, i.e., E−01 = 10^{-1}. See also Tables II and III.

Results and Discussion

Estimation of Uncertainty. In order to indicate the uncertainty in the present work, comparisons were made among the recommended values and the measured ones for three pure melts. Here, the uncertainty is defined as a percent departure (pd) in the form

$$\text{pd} = 100 \times (\text{experimental value} - \text{recommended value})/\text{recommended value}$$

At 673 K, the uncertainty for $NaNO_3$ (*5*), KNO_3 (*6*), and $NaNO_2$ (*5*) was found to be +0.16%, −0.22%, and +0.29%, respectively. Similar trends in pd were observed over the measured temperature ranges. This means that the dilatometry is reliable enough to evaluate the molar volume of molten salt, although the Archimedean method has been utilized presently.

Binary Systems. When x, y, and z represent the mole fractions of $NaNO_3$, KNO_3, and $NaNO_2$ in the binary mixtures, the molar volumes of the molten mixtures are given in the following forms: for $NaNO_3$–KNO_3 and $NaNO_3$–$NaNO_2$ systems

$$V_m = \sum_{n=0}^{3} a_n x^n + \left(\sum_{n=0}^{3} b_n x^n\right) T$$

for KNO_3–$NaNO_2$ system

$$V_m = \sum_{n=0}^{3} a_n y^n + \left(\sum_{n=0}^{3} b_n y^n\right) T$$

where V_m is the molar volume of molten binary mixture in cm^3 mol^{-1}, a_n and b_n the smoothed parameters, and T the absolute temperature. At first, the parameters a_0 and b_0 were determined at $x = 0$, and the sums $a_0 + a_1 + a_2 + a_3$ and $b_0 + b_1 + b_2 + b_3$ were obtained at $x = 1$. Next, the other individual parameters were calculated by the method of least squares. The results for molten binary $NaNO_3$–KNO_3, $NaNO_3$–$NaNO_2$, and KNO_3–$NaNO_2$ systems are listed in Table I, in which the key components as variables in the molten mixtures are specified.

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Table II. Molar Volume Equations of Molten Ternary Mixtures along the Lines AA_n

system	$NaNO_3$–(KNO_3(0.85)-*$NaNO_2$(0.15))	$NaNO_3$–(KNO_3(0.70)-*$NaNO_2$(0.30))	$NaNO_3$–(KNO_3(0.57)-*$NaNO_2$(0.43))	$NaNO_3$–(KNO_3(0.475)-*$NaNO_2$(0.525))	$NaNO_3$–(KNO_3(0.455)-*$NaNO_2$(0.545))	$NaNO_3$–(KNO_3(0.30)-*$NaNO_2$(0.70))	$NaNO_3$–(KNO_3(0.15)-*$NaNO_2$(0.85))
line	AA_1	AA_2	AA_3	AA_4	AA_5	AA_6	AA_7
a_0	0.37894E+02	0.36592E+02	0.35534E+02	0.35010E+02	0.34526E+02	0.32800E+02	0.31244E+02
a_1	−0.15338E+01	0.29112E+01	−0.18285E+01	−0.45604E+01	−0.10850E+01	0.27388E+01	0.32692E+01
a_2	−0.52758E+01	−0.18505E+02	0.16749E+01	0.99268E+01	0.50209E+00	−0.40573E+01	−0.15005E+01
a_3	0.27141E+01	0.12799E+02	−0.15825E+01	−0.65779E+01	−0.16264E+00	0.23161E+01	0.78513E+00
b_0	0.22698E−01	0.20710E−01	0.19643E−01	0.18751E−01	0.18769E−01	0.17731E−01	0.16570E−01
b_1	−0.47020E−02	−0.40263E−02	−0.28393E−03	0.41481E−02	−0.28599E−03	−0.16610E−02	0.11635E−03
b_2	−0.97518E−03	0.77712E−02	−0.39994E−02	−0.14551E−01	0.33249E−03	0.59768E−02	0.32830E−02
b_3	0.13824E−02	−0.60523E−02	0.30435E−02	0.10056E−01	−0.38638E−03	−0.36436E−02	−0.15667E−02
σ	0.1025E+00	0.2018E+00	0.1023E+00	0.9480E−01	0.1003E+00	0.5441E−01	0.5947E−01
min temp, K	483.2	463.2	443.2	413.2	463.2	453.2	483.2
exptl point	179	184	190	178	177	162	154

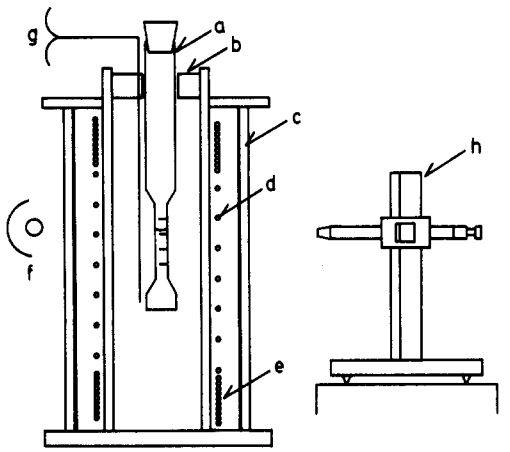

Figure 1. Dilatometer and support assembly: (a) quartz dilatometer, (b) silica fiber shield, (c) gold-adhibited tube, (d) central heater element, (e) guard coil, (f) light source, (g) thermocouple, (h) cathetometer.

Ternary Systems. When X, Y, and Z are the mole fractions of $NaNO_3$, KNO_3, and $NaNO_2$ in the molten ternary mixture, the molar volumes of the mixtures shown by lines AA_n and BB_n in Figure 2 are given by the same forms as those for binary systems: for lines AA_n

$$V_m = \sum_{n=0}^{3} a_n X^n + (\sum_{n=0}^{3} b_n X^n)T$$

for lines BB_n

$$V_m = \sum_{n=0}^{3} a_n Y^n + (\sum_{n=0}^{3} b_n Y^n)T$$

The following relations hold good among these variables:

$$x + y = y + z = z + x = 1$$

$$X + Y + Z = 1$$

for lines AA_n

$$X = x \quad Y = (1 - X)y \quad Z = (1 - X)z$$

for lines BB_n

$$X = (1 - Y)x \quad Y = y \quad Z = (1 - Y)z$$

The parameters a_n and b_n were determined by a similar procedure in the case of molten binary mixtures. The numerical results are tabulated in Tables II and III. According to the empirical formulas the molar volumes could be reproduced with ease and accuracy, as demonstrated in Tables I, II, and III. Especially for ternary systems, the data were smoothed along the lines AA_n or BB_n. A similar procedure has been employed for the molar volumes of molten NaCl–CsCl–$MnCl_2$ by Carmichael and Flengas (*7*). Owing to this treatment, the same type of expression as utilized in binary systems could be applied to ternary systems, in which the molar volume deviation from the additivity was assumed to be very small for binary systems. This assumption is almost valid as can be seen from Table I. No attempt was made to express the molar volume of ternary system by a unique formula since complexity is sure to occur in the formula due to a lot of parameters and cross terms. The molar volume isotherms are shown in Figure 3.

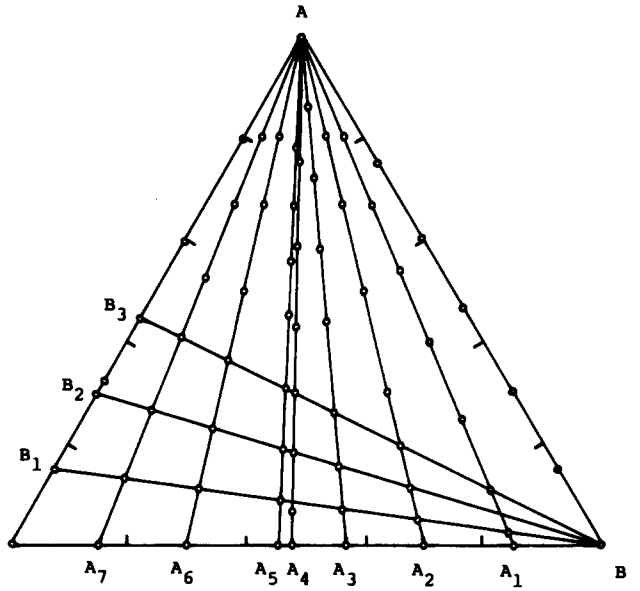

Figure 2. Measured points in ternary format: (A) $NaNO_3$, (B) KNO_3, (C) $NaNO_2$.

Table III. Molar Volume Equations of Molten Ternary Mixtures along the Lines BB_n

system	KNO_3–($NaNO_3$(0.15)-*$NaNO_2$(0.85))	KNO_3–($NaNO_3$(0.30)-*$NaNO_2$(0.70))	KNO_3–($NaNO_3$(0.45)-*$NaNO_2$(0.55))
line	BB_1	BB_2	BB_3
a_0	0.30184E+02	0.30915E+02	0.31758E+02
a_1	0.11908E+02	0.89492E+01	0.66965E+01
a_2	−0.28357E+01	0.20008E+01	0.67579E+01
a_3	−0.91337E+00	−0.35195E+01	−0.68676E+01
b_0	0.15757E−01	0.16069E−01	0.16321E−01
b_1	0.60553E−02	0.90088E−02	0.97988E−02
b_2	0.22529E−03	−0.65162E−02	−0.10663E−01
b_3	0.38205E−02	0.72922E−02	0.10397E−01
σ	0.8359E−01	0.1910E+00	0.7263E−01
min temp, K	443.2	443.2	463.2
exptl point	154	189	186

In the present ternary system, the $NaNO_3$(7 m/o)–KNO_3(44 m/o)–$NaNO_2$(49 m/o) mixture called "heat transfer salt" (*8*) is the most useful in industrial aspects; it is stable over the wide temperature range 415–727 K. The final expression of the molar volume is in the form $V_m = 34.63 + 1.885 \times 10^{-2}T$.

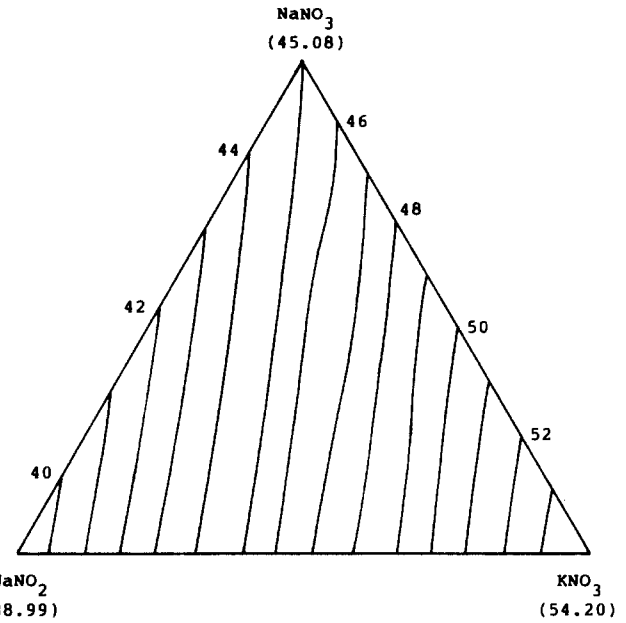

Figure 3. Molar volume isotherms at 613 K; unit: cm^3 mol^{-1}. The numerical data on pure melts are designated in parentheses.

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We express our sincere gratitude to Mr. M. Misawa for assistance in measuring the molar volumes.

Glossary

V_m	molar volume, cm^3 mol^{-1}
a_n, b_n	smoothed parameters in the empirical equations
x, y, z	mole fractions of components in binary systems
X, Y, Z	mole fractions of components in ternary systems
T	absolute temperature, K

Greek Letters

σ	standard errors of the molar volume equations, cm^3 mol^{-1}

Registry No. $NaNO_3$, 7631-99-4; KNO_3, 7757-79-1; $NaNO_2$, 7632-00-0.

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Supplementary Material Available: All of the original data on the molar volume of molten $NaNO_3$-KNO_3-$NaNO_2$ mixtures listed in computer-output format (43 pages). In this data file, the molar volumes are expressed as polynomial functions of composition and temperature by a least-squares method. Four significant figures are given for molar volume and temperature. The units used in the file are cm^3 mol^{-1} for molar volume and K for temperature. Ordering information is given on any current masthead page.

Liquid–Liquid–Vapor Phase Equilibria of the Binary System Carbon Dioxide + *n*-Tridecane

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The binary mixture carbon dioxide + *n*-tridecane is studied as a system exhibiting liquid–liquid–vapor equilibria. Pressure, temperature, and molar volumes and compositions of the two liquid phases are reported for a heretofore undetected *second* liquid–liquid–vapor locus, making this binary mixture a type IV system in the classification of van Konynenburg and Scott. This second locus extends from a lower critical end point (L = L–V) at 310.6 K and 81.1 bar to an upper critical end point (L–L = V) at 313.9 K and 87.2 bar. A discussion on the evolution of the liquid–liquid–vapor equilibria in the homologous series of carbon dioxide + *n*-paraffin binary mixtures is presented.

Introduction

We have undertaken a detailed study of the multiphase equilibria behavior of CO_2 + hydrocarbon mixtures. Specific attention has recently been directed by us to the liquid–liquid–vapor (LLV) phase equilibria behavior of the homologous series of binary CO_2 + *n*-paraffin mixtures. These binary mixtures are important constituent pairs in CO_2 + crude oil systems as encountered in CO_2-enhanced recovery processes. These "natural" multicomponent systems (*1*, *2*) have been known to exhibit LLV immiscibility, and it has become apparent that hydrocarbon species of size *n*-heptane and larger are responsible for generating that immiscibility.

LLV immiscibility has been observed in a number of CO_2 + *n*-paraffin binary mixtures: *n*-heptane (*3*), *n*-octane (*4–7*), *n*-decane (*8*), *n*-undecane (*5–7*), *n*-dodecane (*9*), *n*-tridecane (*5–7*, *9*), *n*-tetradecane (*9*), *n*-pentadecane (*9*), *n*-hexadecane (*5–7*), *n*-nonadecane (*10*), *n*-eicosane (*10*, *11*), and *n*-heneicosane (*10*). Reference 3 demonstrated that *n*-heptane is the first of the *n*-paraffin homologous series to exhibit LLV immiscibility with CO_2, while ref 10 identified *n*-heneicosane as the highest member of the series to do so.

It has been generally held that the LLV loci in this series of binary mixtures has been of two types, topographically speaking. For the hydrocarbons *n*-heptane to *n*-tridecane, the LLV locus has evolved from the solid–liquid–vapor (SLV) locus bounding the low-pressure end of the LV region, with its lower end point being a quadruple point (Q point, or four-phase point, SLLV) and its upper end point being a critical end point with liquid–liquid criticality (L = L–V). Hottovy et al. (*9*) reported that a change occurs in the nature of that LLV locus between *n*-

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