Table III. Comparison of Results

ref	A	B	ΔH_s, kcal/mol	A	B	ΔH_v, kcal/mol
5	4400	11.76	20.14 ± 0.02	3330	9.53	15.16 ± 0.05
7			21.70 ± 1			11.0 ± 1
4	4000	10.83	18.3	3684	10.18	16.84
6			18.3 ± 0.5			16.5 ± 0.5
this work	4380	11.67	20.0 ± 0.4	3449	9.74	15.8 ± 0.7

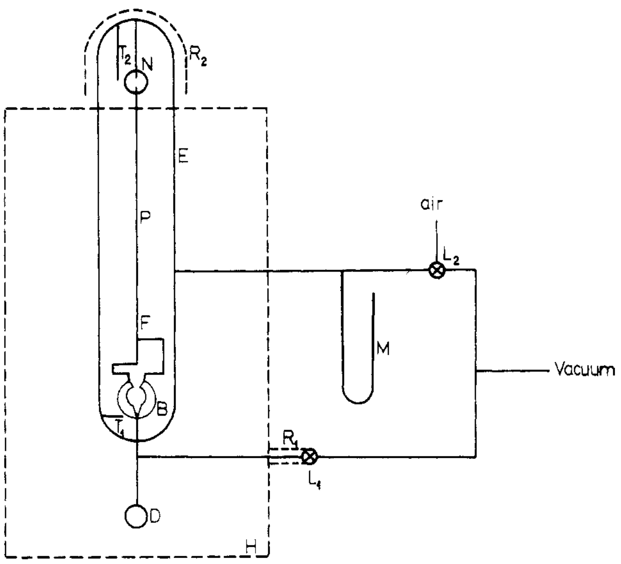

Figure 1. Schematic diagram of equipment: (D) vaporization chamber, (B) double-spoon gauge, (E) jacket, (F) fulcrum, (H) oven, (L_1, L_2) valves, (M) Hg manometer, (N) fixed pointer, (P) pointer, (R_1, R_2) heating wire, (T_1, T_2) thermometers.

Measurements proceeded during cooling cycles at each run; thus, delay in reaching equilibrium could be detected, showing at the same time formation of decomposition products. The zero reading remained unaltered up to 523 K during blank test. Within the pressure range used in this work the gauge was found to give a linear response with pressure and to be free of hysteresis.

For a purity test of the sample the following criterion was applied along with the ones previously mentioned: a sample was submitted to successive vapor pressure measurements and subsequent vacuum, all at the same temperature, until the solid sample was almost exhausted. The value obtained was used as a reference for all samples under test.

For testing the accurate performance of the whole device vapor pressure of benzoic acid was measured.

Results and Discussion

Data on vapor pressure vs. temperature are shown on Table II for processes of sublimation and vaporization of $WOCl_4$.

The results mentioned above were adjusted through a computer program using the expression $\log p(\text{mmHg}) = -A/T(\text{K}) + B$.

1. Sublimation pressure was given by

$$\log p(\text{mmHg}) = (-4380/T + 11.67) \pm 0.03$$

from which

$$\Delta H_s = 20.0 \pm 0.4 \text{ kcal/mol}$$

could be calculated.

2. Vaporization pressure may be expressed by

$$\log p(\text{mmHg}) = (-3449/T + 9.74) \pm 0.006$$

from which

$$\Delta H_v = 15.8 \pm 0.7 \text{ kcal/mol}$$

could be calculated.

In Table III these results are compared with those given by other authors. This shows that the sublimation heat obtained here, ΔH_s, differs from Funaki's (*5*) by 0.24%. The difference with the results of Reinders (*4*) and Shchukarev (*6*) is 9.4%.

With regard to vaporization heat our values are reasonably close to Funaki's (*5*), the greatest difference being with the results obtained by Suvorov (*7*).

Registry No. $WOCl_4$, 13520-78-0.

Literature Cited

(1) Castro Luna, A. E.; Rivarola, J. B. *Lat. Am. J. Chem. Eng. Appl. Chem.* **1971**, *1*, 77-82.
(2) Papa, J.; Calderón, J. B.; Marchese, J.; Rivarola, J. B. *AIChE J.* **1977**, *23*, 938-40.
(3) Calderón, J. B.; Papa, J.; Rivarola, J. B. *Ind. Quím.* **1969**, *27*, 27-31.
(4) Reinders, W.; Van Liempf, J. A. M. *Recl. Trav. Chim. Pays-Bas* **1931**, *50*, 997-1003.
(5) Funaki, K.; Uchimura, K. *Denki Kagaku* **1962**, *30*, 35.
(6) Shchukarev, S. A.; Novikov, G. I.; Vasil'kova, I. V.; Suvorov, A. V.; Andreeva, N. V.; Scharupin, B. N.; Baev, A. K. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1960**, *5*, 802-4.
(7) Suvorov, A. V.; Novikov, G. I.; Dobrotin, R. B.; Tarasov, A. V. *Khim. Redk. Elem.* **1964**, 26-32.
(8) Adams, D. M.; Churchill, R. G. *J. Chem. Soc. A* **1968**, 2310.
(9) Swanwick, J. D. *J. Chem. Soc.* **1956**, 3214-5.

Received for review March 30, 1982. Revised manuscript received March 14, 1983. Accepted April 25, 1983. We thank the Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina for financial support granted.

Sound Velocity in Simple Carboxylic Acids

M. A. Goodman and Scott L. Whittenburg*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

The speed of sound and isentropic compressibility of formic, acetic, and propionic acid were measured by Brillouin spectroscopy in the temperature range from 293 to 353 K.

Introduction

The sound velocity and isentropic compressibility of the simple carboxylic acids were measured from 293 to 353 K by using Brillouin light scattering. The measurements were made as part

0021-9568/83/1728-0350$01.50/0 © 1983 American Chemical Society

352 J. Chem. Eng. Data 1983, 28, 352-354

Magnetic Behavior of Binary Liquid Mixtures of Methyl Isobutyl Ketone with Butyl Alcohols

Roque Riggio,[*] Juan F. Ramos, Hector E. Martinez, José A. Espíndola, and Horacio N. Sólimo

Departamento de Ciencias Exactas, Universidad Nacional de Salta, 4400 Salta, República Argentina

Densities, refractive indexes, and magnetic susceptibilities of methyl isobutyl ketone with *n*-butyl, *sec*-butyl, and isobutyl alcohols have been measured at 25 °C. For all systems, the excess molar susceptibility ($\chi_M{}^E$) shows positive deviation over the whole concentration range, which is indicative of solute–solvent interaction. From the analysis of the refractive indexes of these systems, we can conclude that no intermolecular complexes are formed. The Kirkwood correlation, modified by Boyer-Donzelot (KBD correlation) and extended to mixtures by us, was used to predict the diamagnetic molar susceptibilities for the three systems.

In mixtures of polar–polar molecules (e.g., A and B), the interactions could be described in terms of strong AB or BB ones (*1*), which is our case.

The purpose of the investigation reported here was to obtain information, through the study of the magnetic behavior of the mixtures, on how the molar magnetic susceptibility is affected by these interactions.

In order to bring out a clear comparison, we have chosen the following systems: methyl isobutyl ketone (MIK) with *n*-butyl (B_1), *sec*-butyl (B_2), and isobutyl (B_3) alcohols, all polar liquids; and the butyl alcohols show O–H···O type association in the pure state.

Excess molar susceptibility, $\chi_M{}^E$, defined as

$$\chi_M{}^E = \chi_M - (x_1\chi_1 + x_2\chi_2)$$

was computed and represented as a function of molar fraction of the MIK.

Based on the analysis of this property, we have obtained conclusions that are in agreement with previous ones obtained from other excess properties for the same systems (*2*).

An extension of the Kirkwood correlation (*3*), modified by Boyer-Donzelot, was used for the calculation of χ_M (*4*). Boyer-Donzelot's modification is based on her experimental results about the variation of optical dispersion in pure organic compounds (*5*, *6*) due to valence electrons. The calculated values of χ_M were in moderate agreement with the experimental data (see Table II).

The refractive indexes, previously measured (*2*), were analyzed in order to obtain information about the type and degree of interaction among molecules of different kinds.

Experimental Section

Material and Solutions. The butyl alcohols and MIK (A.R. Merck) were dried with anhydrous K_2CO_3 and fractionally distilled under nitrogen atmosphere. The middle fraction was collected and kept out of humidity with 3-Å molecular sieves for the butyl alcohols and 4-Å for the MIK.

All samples were maintained over molecular sieves to prevent water absorption. The mixtures were prepared by mixing accurately weighed quantities of pure liquids. Caution was taken to prevent evaporation.

Density. Densities were determined with a Robertson specific gravity bottle (*7*). We estimate the reported densities to be accurate to within ±0.0001 g cm^{-3}. A thermostatically controlled bath, constant to ±0.01 °C, was used.

Magnetic Susceptibility. The magnetic susceptibility was determined by a Gouy method using a Mettler H20T balance. Measurements have been made in a 9-kG magnetic field. The Gouy force ranged from 10 to 15 mg, and the reliability of weighing was estimated to be ±0.01 mg. Water twice distilled from alkaline permanganate ($\chi = -0.720 \times 10^{-6}$ cgs g^{-1}) and $HgCo(SCN)_4$ ($\chi = 16.49 \times 10^{-6}$ cgs g^{-1}) (*8*) were used as reference substances.

The balance and specimen tube were enclosed in a draft-proof case and air-drying agents employed.

Results

The experimental results for pure liquids are reported in Table I along with the values from the literature for comparison.

The molar magnetic susceptibilities of binary systems were measured over the whole concentration range. The experimental values are reported in Table II along with the calculated values (eq 2) from the KBD correlation for comparison.

The diamagnetic susceptibility was related to the molecular polarizability by the KBD equation (*5*), for organic pure compounds:

$$\chi_i = f(n_i'\alpha_i)^{1/2} \qquad (1)$$

For mixtures, we can assume that the additivity law for molar diamagnetic susceptibility is correct (*4*); then

$$\chi_M = f\sum x_i(n_i'\alpha_i)^{1/2} \qquad (2)$$

where, n_i' is calculated (*6*) as

$$n_i' = n_i - n_{i0} \qquad (3)$$

where n_{i0} is a characteristic constant for each family of substances (ketones = 4.3 and aliphatic alcohols = 2.6).

A reasonable agreement between the calculated and experimental values is observed, which is indicative of the validity of the additivity law for these systems.

Each set of results was fitted to a smoothing equation:

$$\chi_M{}^E = a_0 + \sum_{j=1}^{n} a_j x^j \qquad (4)$$

A least-squares method was used to determine the a_j. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard error of the estimate (σ_x) with n:

$$\sigma_x = [\sum(\chi^E{}_{calcd} - \chi^E{}_{exptl})/(n_{obsd} - n)]^{1/2} \qquad (5)$$

The values adopted for the coefficients a_j and the standard error of the estimate associated with the use of eq 4 are summarized in Table III.

Discussion

The general behavior of $\chi_M{}^E$ is plotted vs. x_{MIK} in Figure 1, where the continuous curves were calculated from eq 4 using the coefficients reported in Table III.

0021-9568/83/1728-0352$01.50/0 © 1983 American Chemical Society