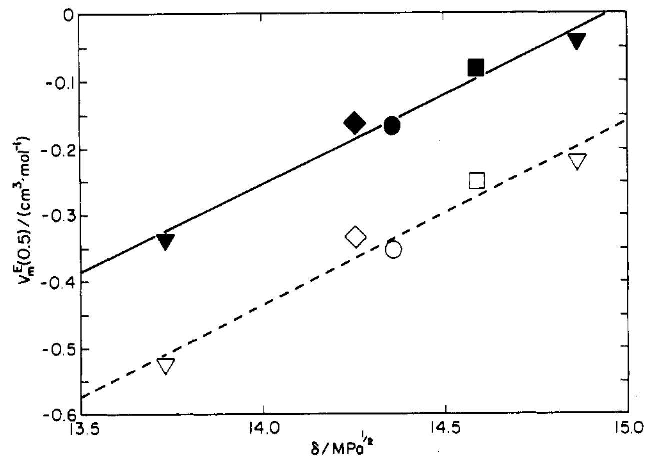

Figure 3. Plot of $V_m^E(0.5)$, the exces molar volume of an equimolar C_6-alcohol–hexane isomer mixture against δ, the solubility parameter of the isomer. Present results for 2-methyl-1-pentanol mixtures: (▼) n-C6, (●) 2-MP, (■) 3-MP, (▲) 2,2-DMB, (◆) 2,3-DMB; (—) least-squares line ($r = 0.99$). Results for 1-hexanol mixtures (taken from ref *4*) are represented by the corresponding open symbols and the broken line ($r = 0.98$).

$V_m^E(0.5)$ for equimolar mixtures of 1-hexanol with hexane isomers varied nearly linearly with the solubility parameter δ of the isomer. Figure 3 shows that this is also true for the 2-methyl-1-pentanol mixtures. The least-squares line, which corresponds to a coefficient of correlation $r = 0.99$, provides further evidence of the behavioral similarity of the two sets of systems.

Acknowledgment

We are indebted to Dr. M. K. Kumaran for helpful discussions and to Mr. P. J. D'Arcy and Mr. C. J. Halpin for technical assistance.

Glossary

n	number of coefficients in eq 1 or 2
n_D	refractive index for sodium light
r	coefficient of correlation
s	standard deviation
$v_1, v_2, ..., v_j$	coefficients in representation of excess molar volume by eq 1 or 2
V_m^E	excess molar volume, $cm^3 \cdot mol^{-1}$
x	mole fraction of 2-methyl-1-pentanol

Greek Letters

δ	solubility parameter, $MPa^{-1/2}$

Registry No. 2-Methyl-1-pentanol hexane, 110-54-3; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0; 2,2-dimethylbutane, 75-83-2; 2,3-dimethylbutane, 79-29-8.

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Molar Volume Contraction for Alcohols in Acetic Acid

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The densities of binary mixtures containing acetic acid and a series of alcohols (methyl, ethyl, propyl, and butyl alcohols) are measured at 25 °C. The molar volume contraction and the degree of association of alcohols are calculated. It is found that the molar volume contraction exhibits a maximum value at $m \simeq 0.5$ mole fraction of acetic acid; this indicates that complex formation occurs at a molar ratio of 1:1 of the acid and the alcohol. Furthermore, it is found that the degree of association decreases in the sequence MeOH > EtOH > PrOH > *n*-BuOH. The effect of various factors such as the hydrocarbon length, the solubility, and the degree of association are discussed.

The change in molar volume for binary mixtures is considered as an important tool for studying solute–solvent interactions. I (*1*) previously studied the molar volume change for binary mixtures containing glycerol with a series of carboxylic acids. It was found that there is a maximum molar volume contraction at 0.34 mole fraction of glycerol. This behavior was attributed to complex formation between glycerol and each of the carboxylic acids at a molar ratio of 1:2, respectively.

The present investigation aims to study the effect of the chain length and the structure of alcohols and acetic acid in their binary mixtures.

Experimental Section

The methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and isobutyl alcohols and acetic acid used were of AnalaR grade. The materials were further purified according to the recommended methods (*2*). The purity of each substance was checked by measuring the density, *d*, the refractive index, *n*, the dielectric constant, ϵ, and the difference between the boiling and condensation points, Δt. The density was measured by the usual Sprengel-Ostwald pycnometer to an accuracy of ±0.0001 $g \cdot mL^{-1}$ (*3*). The refractive index was measured for the sodium D line with an Abbe refractometer. The refractive index could be directly read to 0.0001 unit. The dielectric constant was measured by a multi-Dekameter type DK06 which has a frequency band from 0.2 to 10 MHz. The measurements were based on the superheterodyne principle; the beat frequencies were indicated on a cathode ray tube. The tuning condenser, which had 4500 uniform divisions, permitted fine adjustments and allowed a sensitivity of order 10^{-5}. The difference between

Table I. Some Physical Properties of Alcohols and Acetic Acid at 25 °C

substance	d, g·mL^{-1}	ϵ	ϵ_∞[a]	Δt, °C
methyl alcohol	0.7896	32.63	1.7641	0.02
ethyl alochol	0.7871	24.30	1.8479	0.02
n-propyl alcohol	0.8012	20.10	1.9132	0.03
isopropyl alcohol	0.7823	18.30	1.8917	0.03
n-butyl alcohol	0.8074	17.10	1.9435	0.03
isobutyl alcohol	0.8094	16.10	1.9432	0.03
acetic acid	1.0446	6.13	1.3718	0.02

[a] $\epsilon_\infty = n^2$.

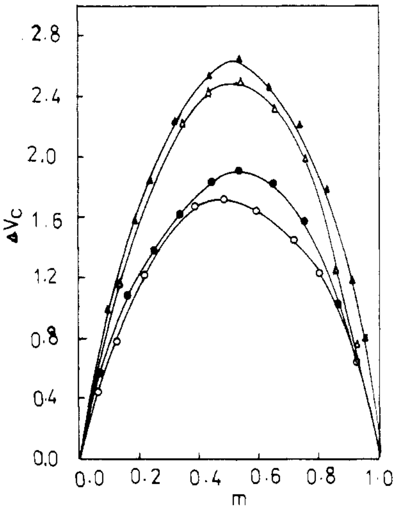

Figure 1. Variation of molar volume contractions, ΔV_c, with mole fraction, m, of acetic acid with normal alcohols at 25 °C: MeOH (△), EtOH (▲), n-PrOH (●), and n-BuOH (○).

Table II. Molar Volume Contractions for Acetic Acid in Alcohols at 25 °C

m_2	d_{12}	ΔV_c, mL·mol^{-1}	m_2	d_{12}	ΔV_c, mL·mol^{-1}
		Acetic Acid–Methyl Alcohol Mixture			
0.0000	1.0426	0.0000	0.6335	0.9549	0.4631
0.0993	1.0421	0.7839	0.7308	0.9240	2.2203
0.1993	1.0354	1.5863	0.8305	0.8840	1.7844
0.3212	1.0224	2.2347	0.9068	0.8497	1.1925
0.4352	1.0042	2.5397	0.9687	0.8097	0.8066
0.5372	0.9837	2.6280	1.0000	0.7896	0.0000
		Acetic Acid–Ethyl Alcohol Mixture			
0.0000	1.0446	0.0000	0.5452	0.9402	2.4965
0.0633	1.0395	0.7234	0.6528	0.9104	2.3034
0.1475	1.0274	1.1647	0.7681	0.8762	1.9807
0.2464	1.0098	1.8558	0.8606	0.8439	1.2502
0.3456	0.9917	2.2206	0.9450	0.8122	0.7723
0.4452	0.9674	2.4277	1.0000	0.7871	0.0000
		Acetic Acid–Propyl Alcohol Mixture			
0.0000	1.0446	0.0000	0.5349	0.9213	1.8975
0.0784	1.0279	0.5790	0.6514	0.8947	1.8347
0.1608	1.0119	1.0795	0.7541	0.8626	1.5882
0.2473	0.9951	1.3883	0.8735	0.8304	1.0333
0.3382	0.9696	1.6470	0.9450	0.8168	0.6552
0.4339	0.9450	1.8211	1.0000	0.8012	0.0000
		Acetic Acid–Isopropyl Alcohol Mixture			
0.0000	1.0446	0.0000	0.5290	0.9129	1.8234
0.0767	1.0250	0.5343	0.6360	0.8867	1.7672
0.1577	1.0063	0.9279	0.7498	0.8559	1.5021
0.2408	0.9841	1.2788	0.8710	0.8208	0.9824
0.3329	0.9632	0.4780	0.9307	0.8042	0.5247
0.4261	0.9371	1.7072	1.0000	0.7825	0.0000
		Acetic Acid–n-Butyl Alcohol Mixture			
0.0000	1.0466	0.0000	0.4843	0.9212	1.7157
0.0650	1.0273	0.4576	0.5938	0.9064	1.6598
0.1353	1.0099	0.7886	0.7148	0.8716	1.4397
0.2116	0.9903	1.2313	0.8026	0.8515	1.2476
0.2996	0.9684	1.5042	0.8493	0.8338	1.1548
0.3851	0.9457	1.6672	1.0000	0.8074	0.0000
		Acetic Acid–Isobutyl Alcohol Mixture			
0.0000	1.0446	0.0000	0.4838	0.9224	1.6980
0.0649	1.0297	0.4527	0.5940	0.8943	1.6120
0.1254	1.0118	0.7057	0.7144	0.8692	1.3866
0.2109	0.9903	1.1935	0.8444	0.8394	1.0536
0.2941	0.9688	1.4080	0.9226	0.8277	0.7046
0.3884	0.9437	1.6114	1.0000	0.8094	0.0000

Table III. Values of the Association Factor, S, the Maximum Molar Volume Contraction, ΔV_c(mix), and the Dipole Moment in the Vapor State

substance	S	ΔV_c-(mix)	μ_g, D
methyl alcohol	2.2503	2.64	1.69
ethyl alcohol	2.2178	2.51	1.69
n-propyl alcohol	2.0610	1.89	1.65
isopropyl alcohol	2.1722	1.81	1.63
n-butyl alcohol	2.0600	1.71	1.65
isobutyl alcohol	2.0700	1.68	1.60
acetic acid	0.6832		1.73

the boiling and condensation points was measured by using the ebulliometric method (*4*). The temperature was always measured by using a Beckmann thermometer and was subject to an error not larger than 0.05 °C (*4*). The obtained values were found to agree very well with the corresponding values given in the literature (*5*).

The densities of the binary mixtures, d_{12}, were measured immediately after mixing at 25 °C. The changes in the molar volumes for the mixtures were calculated by using the intercept method (*6*).

Results

The density, the refractive index, the dielectric constant (at 2 MHz at 25 °C), and the difference between the boiling and condensation points for the pure substances are given in Table I. Table II represents the variation of densities, d_{12}, and molar volume contraction, ΔV_c, with mole fraction, m, for acetic acid–alcohol mixtures at 25 °C.

The calculated values of the association factor, S, and the maximum molar volume contraction ΔV_c(mix) are given in Table III as well as the values of the dipole moment of pure alcohols and acetic acid in the vapor state, μ_g (*7*).

Discussion

From Table II, it is found that there is a contraction in the molar volume for all acetic acid–alcohol systems. This molar volume contraction exhibits a maximum value at ~0.5 mole fraction for each of the acid–alcohol systems (Figure 1). This may be due to complex formation between acetic acid and alcohols. Also, it is noticed that the value of the maximum molar volume contraction decreases from 2.64 for acetic acid–methyl alcohol to 1.71 for acetic acid–n-butyl alcohol mixtures. This decrease may be due to the association of the pure-state components as well as the complex formation between the acid and the alcohol.

For carboxylic acids, the experimental studies of density (*8*), electron diffraction (*9*), and infrared (*10*, *11*) indicated that the acids even in the vapor state were almost completely associated into dimer units via the hydrogen bridge between the carboxylic groups. Also, Ritter and Simons (*12*) showed that acetic acid tends to form stable polymeric forms rather than dimers.

For alcohols, Smyth (*13*, *14*) attributed the deviation of the linear relation between polarization and concentration to the association of the alcohol through the hydrogen bond of the hydroxyl groups.

For such highly associated liquids as alcohols and acetic acid, it is found that the dipole moment, μ, calculated with the Onsager equation (*15*), is not in agreement with that calculated in the vapor state, μ_g

$$\frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\frac{M}{d} = \frac{3\epsilon(\epsilon_\infty + 2)}{(2\epsilon + \epsilon_\infty)(\epsilon + 2)}\frac{4\pi N}{9kT}\mu \quad (1)$$

where ϵ is the dielectric constant ($\epsilon = n^2$), M the molecular weight, d the density, N Avogadro's number, k the Boltzmann constant, T the temperature, and μ the dipole moment of the molecule in the liquid state. This disagreement was attributed to the association which occurs between the molecules in the liquid state. Kirkwood (*16*) devised a very elegant theoretical treatment which takes into consideration the effect of association formally. He derived an equation of the same form as eq 1 but μ is replaced by $\mu\bar{\mu}$

$$\frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\frac{M}{d} = \frac{3\epsilon(\epsilon_\infty + 2)}{(2\epsilon + \epsilon_\infty)(\epsilon + 2)}\frac{4\pi N}{9kT}\mu\bar{\mu} \quad (2)$$

where $\bar{\mu}$ is the dipole moment of the molecule and the moment induced as the result of hindered rotation in the spherical region surrounding the molecule. The value of $\mu\bar{\mu}$ may be higher or lower than μ^2 depending on the nature of the association (*17*).

Considering the dipole moment in the vapor state as the dipole moment of the molecule without any interaction with the surrounding molecules and the dipole moment in the liquid state as the dipole moment of the molecule in interaction with the surrounding molecules, one can calculate the association error (*17*) or the association factor (*18*), S. Taking the departure of the association factor from unity as a measure for the degree of association in the liquid state, we find that the association factor of acetic acid is lower than unity (coassociation type). The association factor of alcohols is higher than unity (contraassociation type) (*17*), and its value decreases in sequence from methyl alcohol (S = 2.503) to *n*-butyl alcohol (S = 2.0600). This decrease indicates that the association decreases from methyl alcohol to *n*-butyl alcohol and the association of normal alcohols is smaller than that of iso alcohols.

Accordingly, the complex formation between acetic acid and alcohols may involve two consequent steps. The first step is the dissociation of the associated units to give monomer molecules and hence the number of OH and COOH groups will increase (*19*). The second step is the formation of a complex molecule (ester) between 1 mol of acetic acid and 1 mol of alcohol. The first step, the dissociation step, is more pronounced in methyl alcohol than in *n*-butyl alcohol; consequently, the second step is larger in the former alcohol than in the latter. On the other hand, the complex formation, the second step, depends on the solubility of alcohols in acetic acid. The solubility decreases from methyl alcohol, having lower molecular weight, to *n*-butyl alcohol, having higher molecular weight. Hence, the complex formation decreases from methyl alcohol–acetic acid to *n*-butyl alcohol–acetic acid mixtures, which may contribute to the decrease in the molar volume contraction in the same sequence.

When one compares the association factor, S, for iso alcohols and normal alcohols, it is clear that the iso alcohols are more associated than the normal alcohols. Thus, it is expected that the complex formation in the iso alcohol–acetic acid mixture is higher than in the normal alcohol–acetic acid mixture, which is not the case. The molar volume contraction–mole fraction curves (Figures 2 and 3) exhibit results which contradict this expectation. This may be attributed to the higher values of the dipole moment and the dielectric constant for normal alcohols than for iso alcohols. The high values of the dipole moment for normal alcohols enhance dipole–dipole interaction between the normal alcohols and acetic acid compared to the dipole–dipole interaction between the iso alcohols and acetic acid. The dipole–dipole interaction forms an aggregate unit which increases the number of complexes; hence, the molar volume contraction in the case of normal alcohols is higher than it is with iso alcohols.

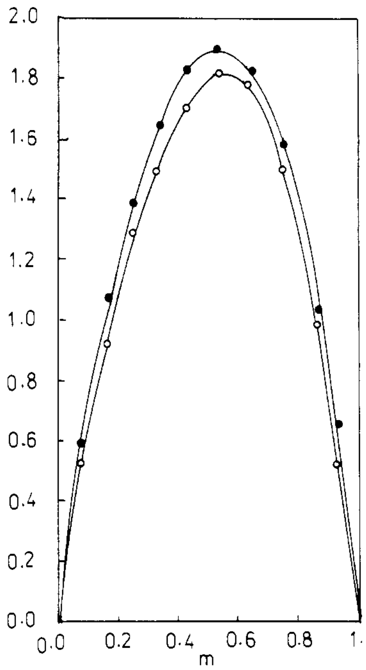

Figure 2. Variation of molar volume contraction, ΔV_c, with mole fraction, m, of acetic acid with propyl alcohols at 25 °C: *n*-propyl (▲) and isopropyl (○) alcohols.

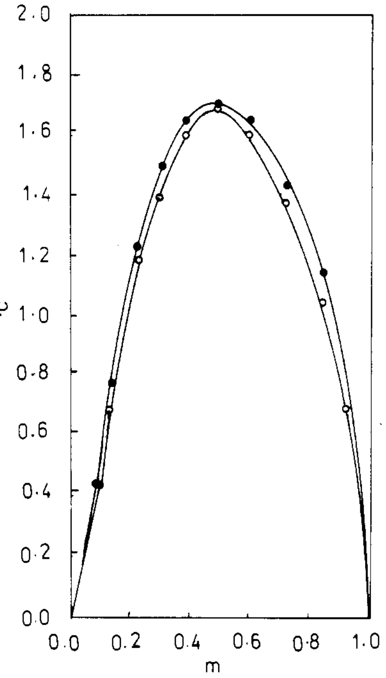

Figure 3. Variation of molar volume contraction, ΔV_c, with mole fraction, m, of acetic acid with butyl alcohols at 25 °C: *n*-butyl (●) and isobutyl (○) alcohols.

Glossary

d	density
n	refractive index
ϵ	dielectric constant
Δt	difference between the boiling and condensation points
d_{12}	density of binary mixture

J. Chem. Eng. Data 1984, 29, 78-80

ΔV_c	molar volume contraction
m	mole fraction
S	association factor
ΔV(mix)	maximum molar volume contraction
μ_g	dipole moment of pure substance in vapor state
μ	dipole moment of pure substance in liquid state
$\bar{\mu}$	dipole moment of the molecule and the induced moment
M	molecular weight
N	Avogadro's number
k	Boltzmann constant
T	temperature, K

Registry No. Acetic acid, 64-19-7; methyl alcohol, 67-56-1; ethyl alcohol, 64-17-5; propyl alcohol, 71-23-8; butyl alcohol, 71-36-3; isopropyl alcohol, 67-63-0; isobutyl alcohol, 78-83-1.

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Vaporization Study of Solid Bi_2Se_3

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The vaporization behavior of Bi_2Se_3(s) and the vapor pressure over this compound were measured by torsion-effusion, thermogravimetric, and high-temperature Knudsen-effusion techniques in the temperature range 800-900 K. The gas phase in equilibrium with the solid Bi_2Se_3 in the first steps of its vaporization is practically composed of only Se_2(g) and consequently, in the condensed phase Bi_4Se_5, a solid solution of BiSe-Se is formed. The practically null value of the heat of solution obtained for the process 4BiSe(s) + Se(s) → Bi_4Se_5(s) shows the nearly ideal behavior of the solid solution Bi_4Se_5.

Introduction

The vaporization behavior of Bi_2Se_3 and its vapor pressure are not well-known. By employing static methods some authors (*1*, *2*) measured pressure data larger by about 2 orders of magnitude than those derived by using effusion techniques (*3*, *4*). The mass-spectrometric analysis of the vapor over Bi_2Se_3 at 1050 K carried out by Porter and Spencer (*5*) has shown that it is initially constituted of Se_2(g) and of a small amount of BiSe(g) and Bi(g). After prolonged heating of the sample, with the consequent evaporation of selenium at constant temperature, these authors observed that the amount of Bi_2(g) and BiSe(g) became larger than that of Se_2(g). As part of a research program for investigation of the vaporization of bismuth compounds (*6*, *7*), also in view of the observed discrepancies between pressure values obtained with static and effusion methods and also within effusion experiments made by different authors (*3*, *4*), we were prompted to perform new, extensive, and more accurate pressure determinations for Bi_2Se_3(s). The measurements were made with the effusion method using two different techniques and the results are reported below.

Experimental Section and Results

The Bi_2Se_3, 99.8 mol % pure, with impurities mostly due to selenium, was supplied by CERAC. Before the determination of the vapor pressures the samples of the compound were purified by heating at about 550 K, so that the selenium impurities were lost by vaporization. After this treatment the sample did not change weight up to about 750 K. The vaporization of Bi_2Se_3 was investigated by torsion- and Knudsen-effusion techniques, employing vitreous graphite crucibles. No interaction of the samples with the used crucibles was observed.

Torsion Effusion. The vapor pressure over Bi_2Se_3(s) was measured by the torsion-effusion method. The technique and the assembly have been describe previously (*8*, *9*). From the torsion angle α of the effusion cell, at each experimental temperature the poressure value was derived by the relation $P = K\alpha$, where in K are included the torsion constant of the suspension tungsten wire, the geometrical constants of the used cell, and the correction factors (*10*) for the effusion orifice geometry. In this study the value $K = (1.72 \pm 0.25) \times 10^{-6}$ atm deg^{-1} was employed. In order to test the reliability of the assembly and of the temperature measurements, the vapor pressure of pure Zn, used as a standard, was measured. Vapor pressure values measured in the temperature range 685-751 K were treated by the second- and third-law methods. The second-law $\Delta H_v°(298.15\ K) = 133.8 \pm 0.8$ kJ mol^{-1} and the third-law $\Delta H_v°(298.15\ K) = 129.2 \pm 4.6$ kJ mol^{-1} values, where the associated errors are standard deviations, are in good agreement with the value selected by Hultgren (*11*), $\Delta H_v°(298.15\ K) = 130.3 \pm 4.2$ kJ mol^{-1}. The vaporization of

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