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Apparent Molar Volume and Viscosity of Compounds with Asymmetric Carbon Atoms

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Apparent molar volumes and viscosities of *l*- and *meso*-tartaric acid in water and of (1*R*,2*S*,5*R*)- and (1*S*,2*R*,5*S*)-menthyl *p*-toluenesulfinate in 1-butanol at 25 °C are reported. The differences observed between *l*- and *meso*-forms of tartaric acid and between (1*R*,2*S*,5*R*)- and (1*S*,2*R*,5*S*)-forms of menthyl *p*-toluenesulfinates are interpreted in terms of structural differences arising from different configurations of isomeric compounds. The results support the conclusion that different forms of compounds with more than one asymmetric center show differences in solution behavior.

Introduction

The determination of thermodynamic properties such as apparent molar volume, apparent molar compressibility, and viscosity of different forms of compounds having asymmetric centers is of interest in relation to their behavior in solution. Recent works from our laboratories (Ayranci and Conway, 1983; Conway and Ayranci, 1988; Ayranci and Conway, 1990; Belibağli and Ayranci, 1990; Ayranci, 1994; Ayranci and Kaya, 1990) have been concerned with the interpretation of measured viscosities, apparent molar volumes, and compressibilities in terms of various types of solute−solvent interactions involving some inorganic and organic molecules of related structures. Mathieson and Conway (1975) reported the volume and adiabatic compressibility behavior of very closely related isomeric compounds differing only in configuration, namely optically active and inactive tartaric acids and tartrates. Later, we extended this type of work to optically active *l*-forms and inactive *dl*-mixtures of other compounds such as alanine, threonine, ∝-methylbenzylamine, and mandelic acid (Ayranci, 1985). Here, we report further studies on volume and viscosity behavior of (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (*RSR*-MTS) and (1*S*,2*R*,5*S*)-(+)-menthyl (*R*)-*p*-toluenesulfinate (*SRS*-MTS), as well as *l*-tartaric (*l*-TA) and *meso*-tartaric acid (*meso*-TA).

Experimental Section

Materials. *RSR*-MTS, *SRS*-MTS, and 1-butanol were obtained from Aldrich. *l*-TA and *meso*-TA were obtained from Sigma. Water used in all experiments was doubly distilled.

Density Determination. The buoyancy balance method (Conway et al., 1966; Desnoyers and Arel, 1967) was used for density determinations. The apparatus used for this purpose was a Kern model balance having an accuracy of ±0.1 mg. It was modified for underbalance weighings. It was mounted on top of a large thermostat in which the temperature was controlled to an accuracy of better than ±0.01 °C. A float of known volume that was suspended from the front pan of the balance was weighed accurately once in pure solvent and then in solutions of increasing molality which were placed in the thermostat inside a large test tube. Details of the apparatus were given previously (Ayranci and Kaya, 1990). The differences between weighings in pure solvent (in water or in 1-butanol) and in solution of any molality were used in calculating densities of solutions by eq 1 (Conway et al., 1966; Desnoyers and Arel, 1967)

$$\Delta d = (w_0 - w)/V \tag{1}$$

where w_0 and w are readings from the balance when the test tube contains pure solvent and solution of known molality, respectively. V is the volume of float, and Δd is the density difference between solvent and solution. The density of water was taken as 0.997 047 g·cm^{-3} (Kell, 1967), and the density of 1-butanol was determined as 0.803 234 g·cm^{-3} at 25 °C. The measured densities were used to calculate apparent molar volumes by eq 2 (Millero, 1972)

$$V_{\varnothing} = [1000(d_0 - d)]/(m d d_0) + M/d \tag{2}$$

where $V_{\varnothing}$ is the apparent molar volume, m is the molality, M is the molecular weight of solute, and d_0 and d are densities of solvent and solution, respectively. $V_{\varnothing}$ was found to vary linearly with molality for the systems studied except at very low concentrations, where deviation from linearity may result from experimental uncertainty and from hydrolysis of solutes. Thus, $V_{\varnothing}$ results were fitted to

$$V_{\varnothing} = V_{\varnothing}^{\circ} + b_{\mathrm{v}} m \tag{3}$$

where $V_{\varnothing}^{\circ}$ is the apparent molar volume at infinite dilution and b_{v} is an experimentally determined parameter. It was found that the reproducibility of density measurement to $\pm 3 \times 10^{-6}$ g·cm^{-3} gave an uncertainty of ±0.3 cm^3·mol^{-1} in $V_{\varnothing}$ at a molality of 0.01 mol·kg^{-1}. This uncertainty decreases to ±0.03 cm^3·mol^{-1} at molality of 0.1 mol·kg^{-1}.

Viscosity Measurement. The viscosity measurements were made with Cannon-Fenske glass capillary viscometers obtained from Herzog-Lauda Co. as certified. The provided calibration constants were checked with a few liquids of known viscosity. Viscometers were placed in a thermostat that is equipped with a stirrer, heater, and lamp. The temperature was kept at (25.00 ± 0.01) °C in the thermostat. The method described in ASTM-D 2515 was followed to measure the flow time in seconds. Then the absolute viscosities of solutions, η, in centipoise (mPa·s) were calculated from

$$\eta = (\text{viscometer constant})dt \tag{4}$$

where t is the flow time and d is the density of the solution,

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Table 1. Densities and Apparent Molar Volumes of *meso*-TA Solutions in Water at 25 °C

m/mol·kg^{-1}	ρ/g·cm^{-3}	$V_\varnothing$/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	$V_\varnothing$/cm^3·mol^{-1}
0.0121	0.997 790	88.53	0.3835	1.019 528	89.55
0.0469	0.999 899	89.12	0.4190	1.021 496	89.64
0.0725	1.001 440	89.23	0.4570	1.023 616	89.66
0.1101	1.003 683	89.32	0.4915	1.025 537	89.67
0.1605	1.006 658	89.43	0.5204	1.027 124	89.69
0.1968	1.008 776	89.52	0.5604	1.029 315	89.71
0.2271	1.010 564	89.45	0.5991	1.031 411	89.75
0.2641	1.012 698	89.51	0.6321	1.033 193	89.76
0.2964	1.014 562	89.53	0.6633	1.034 871	89.77
0.3402	1.017 065	89.55			

Table 2. Densities and Apparent Molar Volumes of *l*-TA Solutions in Water at 25 °C

m/mol·kg^{-1}	ρ/g·cm^{-3}	$V_\varnothing$/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	$V_\varnothing$/cm^3·mol^{-1}
0.0161	0.998 095	84.81	0.3155	1.017 662	83.10
0.0338	0.999 291	83.52	0.3494	1.019 797	83.14
0.0543	1.000 667	83.19	0.3890	1.022 267	83.21
0.0799	1.002 368	83.11	0.4270	1.024 754	82.95
0.1064	1.004 184	82.46	0.4632	1.026 882	83.25
0.1399	1.006 329	83.02	0.4894	1.028 487	83.29
0.1716	1.008 431	82.87	0.5267	1.030 783	83.29
0.2037	1.010 496	83.00	0.5743	1.033 650	83.36
0.2354	1.012 541	83.02	0.6136	1.036 011	83.40
0.2740	1.015 025	83.03	0.6584	1.038 689	83.43

Table 3. Viscosities of *meso*-TA Solutions in Water at 25 °C

m/mol·kg^{-1}	η/mPa·s	m/mol·kg^{-1}	η/mPa·s
0.0457	0.9012	0.3850	0.9900
0.0920	0.9144	0.4883	1.0185
0.1987	0.9399	0.5628	1.0342
0.3044	0.9656	0.6633	1.0665

Table 4. Viscosities of *l*-TA Solutions in Water at 25 °C

m/mol·kg^{-1}	η/mPa·s	m/mol·kg^{-1}	η/mPa·s
0.0693	0.9157	0.4846	1.0428
0.1531	0.9420	0.5819	1.0464
0.2526	0.9725	0.6584	1.0884
0.3643	0.9964		

Table 5. Densities and Apparent Molar Volumes of *RSR*-MTS Solutions in 1-Butanol at 25 °C

m/mol·kg^{-1}	ρ/g·cm^{-3}	$V_\varnothing$/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	$V_\varnothing$/cm^3·mol^{-1}
0.0	0.803 234		0.0880	0.808 344	274.85
0.0147	0.804 096	275.33	0.1018	0.809 139	274.70
0.0315	0.805 055	276.48	0.1152	0.809 893	274.73
0.0461	0.805 906	275.76	0.1295	0.810 697	274.73
0.0608	0.806 765	275.40	0.1427	0.811 445	274.61
0.0742	0.807 553	274.92	0.1587	0.812 346	274.46

which is determined by interpolation from experimental density vs molality data obtained as described in the subsection above. It was found that the reproducibility of ±0.5 s in flow time measurements allowed an uncertainty of $\pm 5 \times 10^{-5}$ mPa·s in η. A linear relation was observed between η and the molality of solutions.

Results

The measured densities in aqueous solutions at varying molalities and corresponding apparent molar volumes calculated from eq 2 using measured densities are given in Table 1 for *meso*-TA and in Table 2 for *l*-TA. The results are also given in graphical form according to eq 3 in Figure 1. Viscosities of aqueous solutions of *meso*-TA and *l*-TA are given in Tables 3 and 4, respectively. Viscosity data as a function of molality are also presented in graphical form in Figure 2.

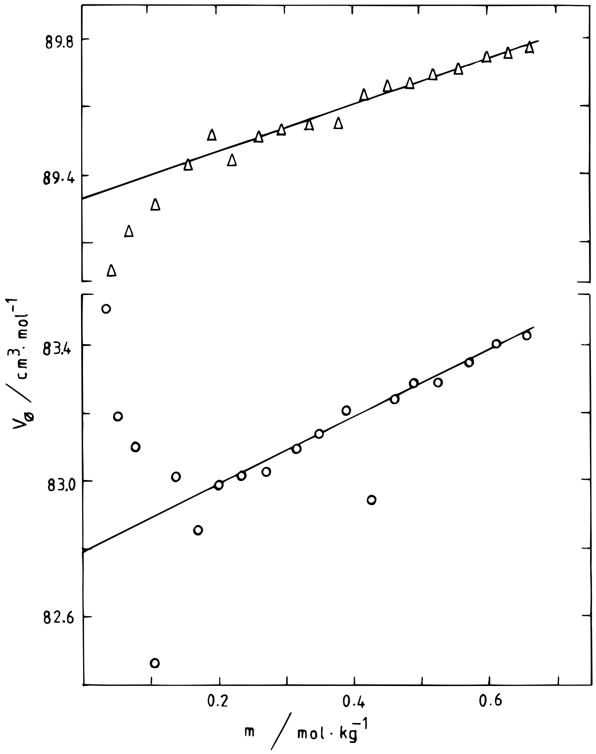


Figure 1. Apparent molar volume as a function of molality for *meso*-TA (△) and *l*-TA (○) in water at 25 °C.

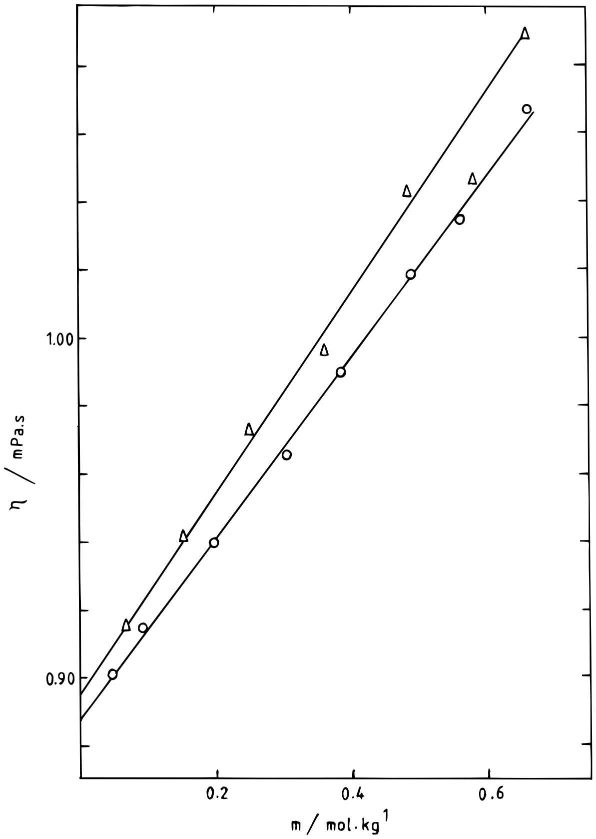


Figure 2. Viscosity as a function of molality for *meso*-TA (○) and *l*-TA (△) in water at 25 °C.

Due to the low solubility of menthyl *p*-toluenesulfinates in water, these compounds were studied in 1-butanol. Density and apparent molar volume data are given in Table 5 for *RSR*-MTS and in Table 6 for *SRS*-MTS. $V_\varnothing$ data as a function of molality for these two compounds are also presented in graphical form in Figure 3. Viscosities in

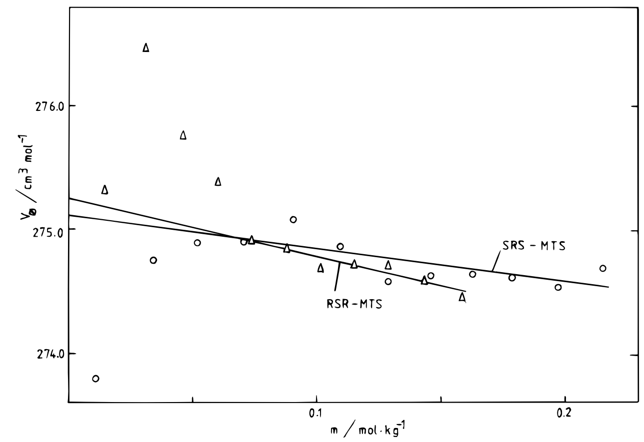


Figure 3. Apparent molar volume as a function of molality for *RSR*-MTS (△) and *SRS*-MTS (○) in 1-butanol at 25 °C.

Table 6. Densities and Apparent Molar Volumes of *SRS*-MTS Solutions in 1-Butanol at 25 °C

m/mol·kg^{-1}	ρ/g·cm^{-3}	$V_\varnothing$/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	$V_\varnothing$/cm^3·mol^{-1}
0.0	0.803 234		0.1291	0.810 687	274.60
0.0115	0.803 922	273.80	0.1458	0.811 617	274.63
0.0347	0.805 276	274.75	0.1629	0.812 561	274.66
0.0523	0.806 294	274.90	0.1784	0.813 417	274.63
0.0717	0.807 411	274.90	0.1968	0.814 432	274.56
0.0907	0.808 486	275.08	0.2148	0.815 396	274.70
0.1095	0.809 563	274.87			

Table 7. Viscosities of *RSR*-MTS Solutions in 1-Butanol at 25 °C

m/mol·kg^{-1}	η/mPa·s	m/mol·kg^{-1}	η/mPa·s
0.0	2.5068	0.0879	2.5728
0.0301	2.5300	0.1184	2.5862
0.0582	2.5484	0.1587	2.6281

Table 8. Viscosities of *SRS*-MTS Solutions in 1-Butanol at 25 °C

m/mol·kg^{-1}	η/mPa·s	m/mol·kg^{-1}	η/mPa·s
0.0	2.5068	0.1370	2.6229
0.0385	2.5298	0.1780	2.6527
0.0699	2.5382	0.2148	2.6833
0.1043	2.5947		

1-butanol are given in Table 7 for *RSR*-MTS and in Table 8 for *SRS*-MTS. Graphical presentation of the same data is shown in Figure 4.

The parameters $V_\varnothing^\circ$ and b_v of eq 3 were determined by linear regression analysis of the data, and the results are given in Table 9. In this analysis, the data at very low concentrations where deviation from linearity is obviously large were excluded.

Discussion

Tartaric Acid. The volume behavior of *l*-TA and *meso*-TA show a large difference (Figure 1). This difference is observed not only in infinite dilution values but also in concentration dependence as shown from $V_\varnothing^\circ$ and b_v values given in Table 9. When these values are compared with those reported by Mathieson and Conway (1975), a good agreement is observed for the results of *l*-TA. However, $V_\varnothing$ values obtained for *meso*-TA in the present work are much higher than theirs. For example their $V_\varnothing^\circ$ value for *meso*-TA is 82.90 cm^3·mol^{-1}. It should be noted that Mathieson and Conway studied both acids in 0.02 M $HClO_4$ instead of water in order to suppress acidic dissociation of tartaric acids. These acidic dissociations may be important at very low concentrations, but, at molalities higher than 0.1 mol·kg^{-1}, ionization is calculated to be less than 10%. Besides, both forms of tartaric acid will ionize. Since one of the main aims of the present study is to determine the differences in solution behavior of the two forms of tartaric acid, pure water was used as the solvent without taking ionization effects into account. Furthermore, it is also recognized that ionization effects (<10%) are probably insufficient to explain the disagreement in $V_\varnothing$ of only *meso*-TA obtained in the two works.

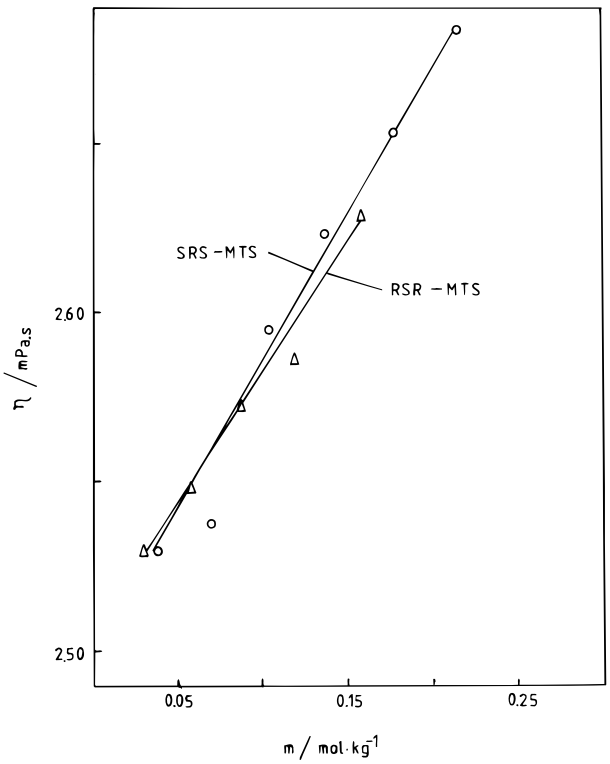


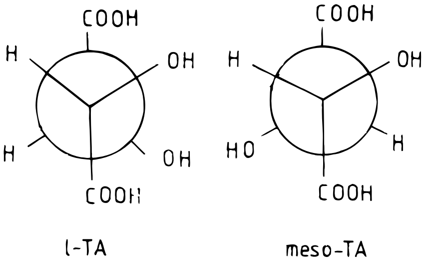
Figure 4. Viscosity as a function of molality for *RSR*-MTS (△) and *SRS*-MTS (○) in 1-butanol at 25 °C.

Table 9. $V_\varnothing^\circ$ and b_v Parameters of Eq 3 Obtained by Linear Regression Analysis of the Data for the Systems Studied

compound	solvent	$V_\varnothing^\circ \pm 0.05$ cm^3·mol^{-1}	$b_v \pm 0.10$ cm^3·mol^{-2}·kg
meso-TA	H_2O	89.33	0.67
l-TA	H_2O	82.79	0.99
RSR-MTS	1-butanol	275.26	−4.70
SRS-MTS	1-butanol	275.12	−2.65

The clearly observed difference between $V_\varnothing$ of *l*-TA and *meso*-TA is not so striking in viscosity results (Figure 2). It might be considered that viscosity is not as sensitive as apparent molar volume to reflect differences in solute—solvent interactions arising from structural effects such as those configurational in origin.

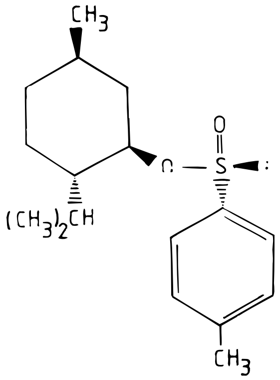
The overall difference in solution behavior of *l*-TA and *meso*-TA can be explained by examining Newman projections of the two isomers:



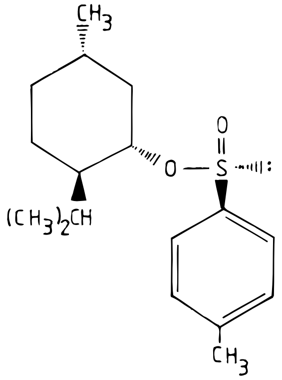
When an −OH group is taken as a reference, the closest neighboring groups in the next carbon that are in *trans*-position to the reference are seen to be different in the two forms.

***p*-Menthyl Toluenesulfinate.** *p*-Menthyl toluenesulfinates were studied in 1-butanol due to its low solubility in water. The volume data are scattered at molalities lower than 0.07 mol·kg^{-1} due to experimental uncertainties (Figure 3). However, the data above this concentration are sufficient to show the trends in concentration dependence of $V_\varnothing$ and to reflect the differences in solution behavior of the two isomeric compounds. This can also be seen in $V_\varnothing°$ and b_v values given in Table 9. Although $V_\varnothing°$ values of the two forms are very close to each other, there is a significant difference in b_v values.

Here, the structural differences between *RSR*-MTS and *SRS*-MTS are arising from different configurations in three asymmetric centers:



RSR-MTS



SRS-MTS

Simple projection formulas may not easily be drawn for these isomers. Thus, it is difficult to explain the difference in $V_\varnothing$ behavior of the isomers in terms of specific group interactions.

Viscosity results for *RSR*-MTS and *SRS*-MTS (Figure 4) do not reflect the differences in solution behavior of them as striking as in the case of volume results.

Correlation with Previous Results. Mathieson and Conway (1975) had reported the differences in volume and adiabatic compressibility behavior of optically active and inactive tartaric acids and tartrates. In order to examine the effect of optical activity on solution behavior of other systems, we had studied the optically active *l*-form and inactive *dl*-mixture of compounds such as alanine, ∝-methylbenzylamine, and mandelic acid (Ayranci, 1985). It was interesting that the differences observed in apparent molar volume and compressibility in aqueous solution between the *l*-form and *dl*-mixture of these compounds were within the range of experimental uncertainty throughout the wide concentration range studied. It is to be noted that there is only one asymmetric center in all these compounds while there are two asymmetric centers in tartaric acid. Thus, it was concluded that when optical activity results from more than one asymmetric center, different forms of the compound may show differences in solution behavior. Present work further supports this conclusion. Different forms of tartaric acid with two asymmetric centers and *p*-menthyl toluenesulfinates with three asymmetric centers show differences in volume behavior and to a lesser extend in viscosity behavior.

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