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Isothermal Compressibility and Isobaric Thermal Expansivity of Linear and Branched Hexanols at 298.15 K

Gloria Tardajos, Elena Junquera, and Emilio Aicart*

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid, Spain

The isothermal compressibility, κ_T, and the isobaric thermal expansivity, α_P, have been measured at 298.15 K for hexan-2-ol, 2-methylpentan-1-ol, 2-methylpentan-2-ol, 3-methylpentan-2-ol, 4-methylpentan-2-ol, and 3-methylpentan-2-ol and also for 1-chlorohexane. The results are discussed in terms of two factors: (1) the substitution of the –H atom by –OH or –Cl groups and (2) the position of the hydroxyl or methyl groups on the linear or branched alcohol molecule.

Introduction

The isothermal compressibility κ_T and the isobaric thermal expansivity α_P, together with the molar volume V, are thermodynamic properties used in the Flory theory of liquids (*1–3*) to calculate the characteristic parameters P^*, V^*, and T^* of the pure components. This theory has been considered valid only for apolar liquids, pure and in mixtures, consisting of molecules with different sizes and shapes.

Heintz (*4*) has recently reported the extended real association solution model (ERAS model), which combines the association model proposed by Renon and Prausnitz (*5*), valid for associated liquids, and the previous Flory theory. This model, which generalizes the Flory equation of state, can be applied not only to nonassociated molecules such as hydrocarbons but also to other molecules where association is present. The validity of this model has been successfully checked for hydrocarbon + alcohol (*4*) or hydrocarbon + amine (*6*) mixtures.

The use of the model for hydrocarbon + alcohol mixtures requires κ_T and α_P values for the pure alcohols, and in an effort to rectify the lack of values in the literature, we report in this paper results of κ_T, α_P, and V for several polar fluids, mostly alcohols, containing six carbon atoms. The influence on κ_T and α_P of both the substitution of the –H by the –OH or –Cl groups and the position of –OH or –CH_3 groups on the linear or branched alcohol molecule will be discussed.

Experimental Section

All the solvents were Fluka with purities greater than 99 mass % for 1-chlorohexane or 2-methylpentan-1-ol and greater than 98 mass % for the other alcohols. They were used without further purification.

Experimental densities at 298.15 K were determined with an Anton-Paar densimeter with an accuracy of 0.01 kg·m^{-3}. These values are in agreement with literature data, both reported in Table 1.

The isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial P)_T$ and the isobaric thermal expansivity $\alpha_P = V^{-1}(\partial V/\partial T)_P$ were measured using a piezometric technique, the details of which have been fully described previously (*7–9*). The experimental procedure evaluates κ_T and α_P by measuring changes in volume with pressure at constant T and with temperature at constant P, respectively. We have made a minimum of 12 measurements of changes in volume between 0 and 2 MPa for κ_T and in an interval of ±1.5 K centered at 298.15 K for α_P. The bath temperature, controlled by a Tronac, was constant to ±1 mK and was measured by a Hewlett-Packard quartz thermometer. The accuracies of κ_T and α_P are estimated at 0.3%.

Results and Discussion

Measurements on all the fluids were run twice. Table 1 reports the average value of the changes in molar volume with pressure at constant temperature $(\partial V/\partial P)_T$ or with temperature at constant pressure $(\partial V/\partial T)_P$ for 1-chlorohexane, hexan-2-ol, 2-methylpentan-1-ol, 2-methylpentan-2-ol, 3-methylpentan-2-ol, 4-methylpentan-2-ol, and 3-methylpentan-3-ol at 298.15 K. From these values and the molar volume V, calculated from the measured densities and molecular weight, the isothermal compressibility κ_T and the isobaric thermal expansivity α_P were calculated and are reported in Table 1. Literature values (*8*, *10–17*) of these properties for the studied substances and for similar fluids containing six carbon atoms are shown in Table 1. The α_P values in the literature are mostly obtained from measurements of density vs T ($\alpha_P = -(\partial \ln \rho/\partial T)_P$). When it is done in a wide range of temperature, which is the case for data from ref 10, the resulting α_P values are affected by a higher uncertainty (from 1% to 4%) than our data. However, the agreement of our results with recent and precise data of Kumaran et al. (*17*) is very good. Values of the thermal pressure coefficient $\gamma = \alpha_P/\kappa_T$ can be easily obtained for the values of Table 1.

The behavior of κ_T and α_P with density, temperature, or chain length of the molecule is not always similar to the behavior of $(\partial V/\partial P)_T$ and $(\partial V/\partial T)_P$, respectively, because the latter quantities are sometimes affected by the trends in the molar volume. This aspect has been considered previously (*11*). In the present paper we comment only on the κ_T and α_P results. In general, these quantities decrease as the density increases. This behavior can be explained considering that when the density increases, the intermolecular free space decreases and consequently the liquid's ability to compress or expand also decreases. This behavior is true for a

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* To whom correspondence should be addressed.

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Table 1. Experimental Values of Pure Liquids at 298.15 K

substance	$\rho/(\mathrm{kg\cdot m^{-3}})$		$(\partial V/\partial P)_T/$ $(\mathrm{m^3\cdot mol\cdot TPa^{-1}})$	$(\partial V/\partial T)_P/$ $(10^{-6}\ \mathrm{m^3\cdot mol^{-1}\cdot K^{-1}})$	$\kappa_T/\mathrm{TPa^{-1}}$	$\alpha_P\ (10^{-3}\ \mathrm{K^{-1}})$	
	this work	lit.				this work	lit.
hexane		665.04[a]	−0.2196[a]	0.1817[a]	1669[a]		1.381[g]
1-chlorohexane	873.40	873.9[b]	−0.1390	0.1476	1007	1.069	1.017[b]
hexan-1-ol		815.65[c]	−0.1047[c]	0.1090[h]	836[c]		0.870[g]
hexan-2-ol	809.61	809.95[d]	−0.1161	0.1255	920	0.994	0.975[b]
2-methylpentan-1-ol	817.99	817.92[e]	−0.1083	0.1102	867	0.882	0.882[i]
2-methylpentan-2-ol	814.79	809.5[b]	−0.1183	0.1321	943	1.053	1.032[b]
3-methylpentan-2-ol	831.08	830.30[e]	−0.1077	0.1247	876	1.014	1.036[b]
4-methylpentan-2-ol	802.98	802.72[e]	−0.1252	0.1293	984	1.016	1.062[b]
3-methylpentan-3-ol	823.63	823.00[e]	−0.1157	0.1339	933	1.079	1.039[b]
2-methylpentane		648.55[f]	−0.2443[f]	0.1895[f]	1839[f]		1.426[f]
3-methylpentane		659.81[f]	−0.2245[f]	0.1823[f]	1719[f]		1.396[f]

[a] Reference 8. [b] Reference 10. [c] Reference 11. [d] Reference 12. [e] Reference 13. [f] Reference 14. [g] Reference 15. [h] Reference 16. [i] Reference 17.

homologous series, but may not be true for molecules withdifferent functional groups. Nevertheless, this general behavior is corroborated by the results of Table 1. Alcohol molecules associate in solution, being more closely packed than their corresponding hydrocarbon. This corresponds to lower κ_T and α_P values, corroborating the similar behavior for linear 1-alcohols and *n*-alkanes reported previously (*8, 11*).

Several features can be deduced from the results. The substitution of a terminal hydrogen by a chlorine or hydroxyl group (hexane, 1-chlorohexane, hexan-1-ol or 2-methylpentane, 2-methylpentan-1-ol) decreases κ_T and α_P, following the order –H > –Cl > –OH. Further, it is concluded that a hydroxyl group in the terminal position of the molecule leads to stronger association between the alcohol molecules, thus increasing the density ρ and therefore decreasing α_P and κ_T. This conclusion is supported by the results for linear hexanols (hexan-1-ol, hexan-2-ol) but also for branched hexanols (2-methylpentan-1-ol, 2-methylpentan-2-ol or 3-methylpentan-2-ol, 3-methylpentan-3-ol). Finally, the position of the methyl group has the same effect on κ_T and ρ (2-methylpentan-2-ol, 3-methylpentan-2-ol, 4-methylpentan-2-ol). Nevertheless, as Benson et al. (*14*) has shown also for branched hexanes, the values of α_P and ρ do not show a regular behavior with respect to the methyl group position.

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