

A general relationship for the compressibility of organic solvents

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Applying an additional hydrostatic pressure, which is determined by the difference ($B_i - B_j$) in Tait's equation coefficients, to liquids (S_j) with a higher compressibility coefficient equalizes the compressibility of all the liquids studied (S_i). The correlation obtained makes it possible to predict the compression curve of any liquid over a wide pressure range based on the value of β_T determined at ambient pressure.

The activation volumes (ΔV^\ddagger) and reaction volumes ($\Delta_{r-n}V$) provide important information on a process mechanism and allow one to predict the effect of pressure on the reaction rate and equilibrium.^{1–3} For isopolar processes, such as the Diels–Alder reaction, the changes in the solvent properties induced by pressure do not affect the rate and equilibrium constants and hence do not alter the (ΔV^\ddagger) and ($\Delta_{r-n}V$) values determined. Reliable and consistent data on the effect of pressure on both forward and reverse processes have been obtained for this reaction.⁴ The effect of solvent electrostriction can be very strong for polar and ionic processes, which often results in negative partial molar volumes of ions in solution.^{5–8}

The compressibility of liquids ($\partial V/\partial P$) is the main reason of electrostriction.^{1,2,6,8} Organic solvents differ greatly in physical and chemical properties and hence in solvation energy, which explains the large effect of the environment on the rate and equilibrium of polar and ionic processes.^{9,10} The compressibility of a liquid depends on the balance of intermolecular attraction and repulsion forces. The liquid state involves intermolecular cavities, which provides the translational and rotational motion of molecules.^{1,10} The volume decrease of a liquid ($\Delta V/V_0$) upon a moderate increase in pressure (up to ~3 kbar) results from the compression of these intermolecular cavities^{1,10,11} and is reliably described by Tait's equation

$$\Delta V/V_0 = C \ln[(B + P)/B]. \quad (1)$$

Recent analysis of a large set of compressibility data ($N = 272$) revealed that the 'non-crossing rule' is observed for V – P curves.¹² It means that a distinct linear dependence (2) between the tangent modulus [$K_0 = 1/\beta_0 = -V_0(\partial P/\partial V)_T$] at atmospheric pressure and the secant modulus at 1000 bar ($-1000V_0/\Delta V_{1 \text{ kbar}}$) is observed for compounds with quite diverse properties. This dependence is observed for compounds of various classes and over a wide temperature range.¹²

$$1/\beta_0 = (-4559 \pm 22.9) + (0.9865 \pm 0.0010)(1000V_0/\Delta V_{1 \text{ kbar}}); \quad (2)$$

$$R = 0.9999; N = 272$$

A few unsuccessful attempts^{6,12,13} to predict the compressibility of liquids have been undertaken based on other known molecular properties, such as molecular refraction, density, boiling point, viscosity, surface tension, packing factor, enthalpy of evaporation and vapour pressure. The compressibility is an independent parameter of a liquid, which is valuable for attaining a deeper understanding of the liquid behaviour.

Another interesting property of P – V curves is considered in this work. The compressibility of even a very thin liquid can

be used as a basis for predicting the compressibility of very dissimilar liquids.

Gibson and Loeffler noted¹³ that the compressibility of substituted benzenes can be predicted based on the compressibility of benzene, taking into account the difference in coefficients B . The values of C were considered as a measure of the intermolecular repulsion forces that are the same for benzene derivatives, while the values of B were correlated¹³ with the difference in the intermolecular attraction forces. Gibson and Loeffler¹³ interpreted the coefficient B as the resulting internal pressure equal to the difference between the Hildebrand cohesive pressure¹⁴ determined by intermolecular attractive forces, on the one hand, and the expansive pressure resulting from the thermal motion energy, on the other hand. By now, ample data on the compressibility of liquids in a broad range of temperatures and pressures have been accumulated.^{1,6,12} Analysis of these data shows that, given a proportional variation of the value of B , coefficient C in Tait's equation (1) for all the liquids studied previously¹² can be considered as a constant of 0.094. This results in compressibility curves that differ by no more than 2% from the experimental curves. As an example, Table 1 lists a few liquids from the database¹² that represent various classes of nonpolar, polar aprotic and protogenic solvents, whose compressibility coefficients differ more than fivefold.

Let us consider the compressibility curves of low-boiling liquids, namely, diethyl ether and n -hexane (Figure 1). The values of coefficient C for these liquids, like those for the rest of the solvents in Table 1, can be considered to be the same within $\pm 2\%$. It follows from equation (1) that the compressibility curve of diethyl ether will almost coincide with that of n -hexane (a) at pressures above 98 bar ($B_2 - B_1$, Table 1). Similarly, it can be

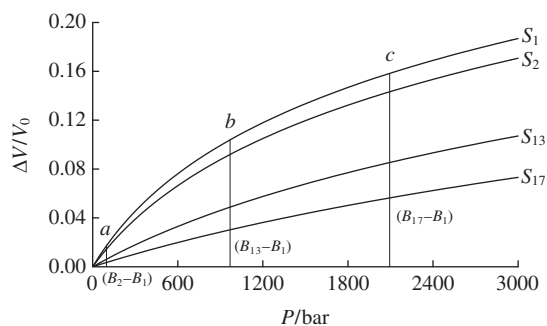


Figure 1 Compressibility curves of n -hexane (S_2), anisole (S_{13}), and ethane-1,2-diol (S_{17}) with new origins of coordinates a , b and c , respectively, coincide with the compressibility curve of diethyl ether (S_1).

Table 1 Permittivity (ϵ), dipole moment (μ), specific density ($d/\text{g cm}^{-3}$), compressibility coefficient (β_T/bar), and coefficients (C) and (B/bar) of Tait's equation (1) for some liquids at 25 °C.

Entry	Solvent	ϵ^a	μ^a	d^a	$10^6 \times \beta_T^b$	C_i^b	B_i^b
1	Diethyl ether	4.20	1.15	0.7078	195	0.0951	489
2	<i>n</i> -Hexane	1.88	0.085	0.6548	161	0.0943	587
3	Bromoethane	9.39	1.90	1.4505	134	0.0943	702
4	<i>n</i> -Octane	1.95	0.00	0.6986	120	0.0943	787
5	1-Chlorobutane	7.39	1.90	0.8809	119	0.0964	811
6	Butan-2-one	18.5	2.76	0.7997	116	0.0950	818
7	Ethanol	24.5	1.66	0.7849	112	0.0950	849
8	Tetrahydrofuran	7.58	1.75	0.8811	101	0.0930	921
9	Acetic acid	6.17	1.68	1.0439	91.9	0.0924	1005
10	Toluene	2.38	0.31	0.8622	89.9	0.0937	1042
11	Chlorobenzene	5.62	1.62	1.1009	73.4	0.0938	1278
12	Nitromethane	35.9	3.56	1.1313	72.5	0.0943	1300
13	Anisole	4.33	1.24	0.9893	65.7	0.0959	1460
14	<i>N,N</i> -Dimethylformamide	36.7	3.24	0.9439	64.0	0.0982	1535
15	Nitrobenzene	34.8	4.00	1.1983	50.3	0.0932	1852
16	Aniline	6.71	1.51	1.0175	46.7	0.0937	2007
17	Ethane-1,2-diol	37.7	2.31	1.1100	36.8	0.0950	2585

^aFrom ref. 15. ^bFrom ref. 12.**Table 2** Comparison of the reduced compressibility of diethyl ether (Y_1^*) with that of other liquids (Y_i^*) at 25 °C.^a

Solvent ($B_i - B_1$)	P/bar	Y_i^*	Y_1^*	Error (%) ^b	Solvent ($B_i - B_1$)	P/bar	Y_i^*	Y_1^*	Error (%) ^b	
<i>n</i> -Hexane (98)	0	0.01737	0.01737	0	Acetic acid (516)	1000	0.13232	0.13418	-1.38	
	1000	0.11115	0.11195	-0.71		2000	0.16971	0.17267	-1.71	
	2000	0.15723	0.15842	-0.74		Toluene (553)	0	0.07195	0.07195	0
	3000	0.18805	0.18950	-0.76			1000	0.13499	0.13592	-0.69
Bromoethane (213)	0	0.03438	0.03438	0	2000	0.17233	0.17383	-0.86		
	1000	0.11789	0.11860	-0.60	Chlorobenzene (789)	0	0.09136	0.09136	0	
	2000	0.16147	0.16256	-0.66		1000	0.14557	0.14632	-0.51	
	3000	0.19117	0.19250	-0.69	2000	0.17971	0.18093	-0.67		
<i>n</i> -Octane (298)	0	0.04525	0.04525	0	Nitromethane (811)	0	0.09298	0.09298	0	
	1000	0.12258	0.12324	-0.53		1000	0.14678	0.14724	-0.31	
	2000	0.16449	0.16550	-0.61	2000	0.18082	0.18157	-0.41		
	3000	0.19340	0.19466	-0.64	Anisole (971)	0	0.10400	0.10400	0	
1-Chlorobutane (322)	0	0.04811	0.04811	0		1000	0.15403	0.15363	0.25	
	1000	0.12555	0.12451	0.83	2000	0.18674	0.18607	0.35		
	2000	0.16793	0.16632	0.97	2500	0.19968	0.19891	0.38		
	3000	0.19727	0.19526	1.02	0	0.10880	0.10880	0		
Butan-2-one (329)	0	0.04893	0.04893	0	<i>N,N</i> -Dimethylformamide (1046)	1000	0.15806	0.15649	1.00	
	1000	0.12479	0.12487	-0.06		2000	0.19071	0.18811	1.38	
	2000	0.16643	0.16656	-0.07	2500	0.20370	0.20069	1.49		
	3000	0.19528	0.19544	-0.07	Nitrobenzene (1363)	0	0.12668	0.12668	0	
Ethanol (360)	0	0.05246	0.05246	0		1000	0.16691	0.16766	-0.44	
	1000	0.12640	0.12648	-0.06	2000	0.19493	0.19628	-0.68		
	2000	0.16747	0.16760	-0.07	2500	0.20630	0.20789	-0.76		
	3000	0.19605	0.19621	-0.08	Aniline (1518)	0	0.13430	0.13430	0	
Tetrahydrofuran (432)	0	0.06021	0.06020	0		1000	0.17218	0.17273	-0.31	
	1000	0.12857	0.13011	-1.18	2000	0.19908	0.20003	-0.47		
	2000	0.16755	0.16997	-1.42	Ethane-1,2-diol (2096)	0	0.15830	0.15830	0	
	3000	0.19493	0.19797	-1.53		1000	0.18936	0.18945	-0.04	
Acetic acid (516)	0	0.06850	0.06850	0	2000	0.20177	0.20187	-0.04		

^aSome liquids can actually solidify at these pressures. ^bDeviations were calculated as $100 \times (Y_i - Y_1)/Y_1$ (%).

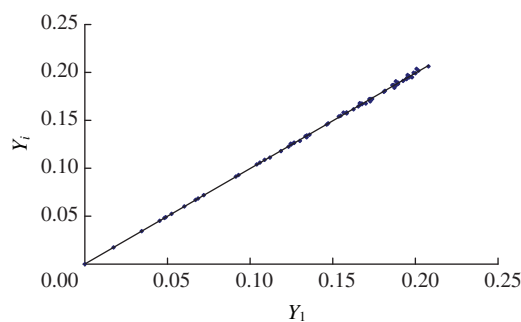
expected that point (b) on the compressibility curve of diethyl ether will be the point of origin for the compressibility curve of anisole ($B_{13} - B_1 = 971$ bar), while point (c) will be the point of origin for the compressibility curve of ethylene glycol ($B_{17} - B_1 = 2096$ bar), etc.

In other words, the reduced compressibility functions for each liquid $Y_i^* = C_i \ln[(B_i + P)/B_i] + C_1 \ln(B_i/B_1)$ should closely match the data for diethyl ether $Y_1^* = C_1 \ln[(B_1 + P^*)/B_1]$, where $P_i^* = (B_i - B_1) + P$ (Table 2). As follows from equation (1), these functions only differ in the factors C_i and C_1 . To assess the deviations, it is more convenient to compare the values of Y_1^* for diethyl ether with the values Y_i^* for all the liquids considered (Table 2). It is rather unexpected that diethyl ether compressed to a pressure of ($B_i - B_1$) or *n*-hexane compressed to ($B_i - B_2$) have the same compressibility curve as liquids with quite dissimilar properties (Figure 2).

$$Y_i^* = (1.6 \pm 3.9) \times 10^{-4} + (0.9962 \pm 0.0026) Y_1^* \quad (3)$$

$R = 0.9998$; $SD = 0.001117$; $N = 58$

All these results [Table 2, Figure 2, equation (3)] are consistent with the assumption that an applied additional hydrostatic pressure equal to the difference ($B_i - B_j$) equalizes the balance of intermolecular attraction and repulsion pressures, which was

**Figure 2** Correlation of the reduced compressibility of diethyl ether, $Y_1^* = C_1 \ln[(B_1 + P^*)/B_1]$, with that of other liquids, $Y_i^* = C_i \ln[(B_i + P)/B_i] + C_1 \ln(B_i/B_1)$ from Table 2.

called ‘the net internal pressure of the liquid’,¹³ in all the liquids considered here. It follows that the compressibility curve of a liquid can be predicted for a comparatively broad range of pressure (usually up to 3 kbar), based on just the value of β_T determined at normal pressure. Given the compressibility coefficient $\beta_T = (\partial V/\partial P)/V_0 = C/B_i$, the coefficient B_i can be calculated from the relationship $C_i = C/\beta_T$, where $C = 0.094 \pm 0.002$.

It is usually considered that the compression of a liquid under pressure results from the compression of such intermolecular spaces for which the minimum energies of dispersion (intermolecular) interaction are implemented.^{1,6,11} Intermolecular spaces with strong dispersion (intermolecular) interactions and with H-bonds are more difficult to compress.¹¹ This is confirmed by the fact that considerable differences are observed between the overall cohesion pressure¹⁴ in liquids $[(\Delta_{\text{vap}}H_S - RT)/V_S]$ and the internal pressure $(T \times \gamma_S)$.¹¹ These values are rather close only for nonpolar isotropic liquids with an equal energy of intermolecular interaction along all directions, and strongly differ for polar and protogenic solvents.¹¹

Two facts can be noted in conclusion:

1. Additional hydrostatic pressure equal to the difference $(B_i - B_j)$ results in a close match of the compressibility curves. The results obtained allow us to make the conclusion that the compressibility curve of a liquid can be predicted for a wide range of pressures, based just on the β_T value determined at ordinary pressure.

2. The compressibility coefficient β_T is primarily determined by the decrease in the volume of the space within the liquid, where the intermolecular interaction energy is the smallest. Therefore, its value cannot be predicted with high accuracy based on data on other available molecular properties of a liquid.

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