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Note

Isotope effects on solution properties

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The gas–liquid chromatographic (GLC) method of obtaining ΔG^0, ΔH^0 and ΔS^0 for the transfer of vapors into infinitely dilute solution has been shown to be quite reliable when dealing with alkane systems for which interfacial effects are negligible[1]. Thus an extension of the studies of Jakli *et al.*[2] on the vaporization properties of pure deuterium-substituted molecules becomes possible using this method, and we provide herein the necessary data for comparison of the solution properties of three pairs of "light" and "heavy" hydrocarbons in *n*-hexadecane (C_{16}) and in *n*-tetracosane (C_{24}).

EXPERIMENTAL

The apparatus and data handling have been described[3]. C_{16} and C_{24} were used as received from the Chemical Samples Co. The "heavy" hydrocarbons were obtained from Merck, Sharp and Dohme of Canada. The C_5 and C_6 compounds had a stated deuterium content of 98; the C_7, 99 atom %, corresponding to ^1H contents of 0.24, 0.28 and 0.16 atom per "heavy" molecule, respectively. A run involved measurement of the retention times of both members individually at each temperature. In no case was solvent bleeding as great as 0.1 mass %, and no corrections were required. Lack of certainty in the exact mass of solvent in the column may affect the accuracy of the equilibrium pressures, ΔG^0 and ΔS^0 values, but the ratio of pressures for each pair, as well as ΔH^0 values, are independent of this variable. Comparison of the present data for *n*-hexane in the C_{16} solvent with earlier results from this laboratory[1] indicate, in fact, that 3.2 % of the original mass of solvent had bled from the column before it was used for this work. A similar comparison for the C_{24} solvent indicates that 1.5 % had been lost. The values reported in Table I have been adjusted to take this into account. The ΔH^0 values for *n*-hexane in C_{16} and C_{24} in the present work are 0.13 % lower, and 0.23 % higher, respectively, than those observed with the original columns[1]. The thermodynamic properties of solution were derived from quadratic correlations of the logarithm of the specific retention volume *versus* inverse temperature, except in the case of the *n*-pentane pair in C_{16}, for which a linear correlation was used.

TABLE I

VAPOR PRESSURES OF HYPOTHETICAL PURE LIQUID SOLUTES IN n-$C_{16}H_{34}$ AND n-$C_{24}H_{50}$

T = Temperature; P = pressure.

Solvent	T (°K)	$P_{C_5H_{12}}$ (kPa)	$P_{C_5{}^2H_{12}}$ (kPa)	T (°K)	$P_{C_6H_{14}}$ (kPa)	$P_{C_6{}^2H_{14}}$ (kPa)	T (°K)	$P_{C_7H_{16}}$ (kPa)	$P_{C_7{}^2H_{16}}$ (kPa)
n-$C_{16}H_{34}$	291.85	47.56	52.93	292.44	14.17	15.81	293.63	4.441	5.036
	292.47	48.86	54.00	293.66	14.94	16.69	298.52	5.674	6.398
	297.30	58.56	64.56	297.28	17.50	19.49	303.35	7.201	8.111
	302.16	69.47	76.68	303.35	22.54	25.06	308.26	9.023	10.14
				308.23	27.46	30.40	313.10	11.23	12.59
n-$C_{24}H_{50}$	329.01	133.2	145.4	325.87	44.99	49.66	329.64	19.24	21.40
	333.91	151.8	165.9	335.07	60.76	66.87	339.35	27.43	30.51
	338.78	173.3	188.6	344.80	81.69	89.64	349.10	38.43	42.57
	343.69	196.1	213.0	349.68	94.22	103.0	358.79	52.52	57.85
	348.52	220.7	239.9	354.60	107.8	117.6	368.50	69.92	76.98
				364.23	138.9	150.8			

RESULTS

The relationship between the specific retention volume, V_g^0, and the equilibrium vapor pressure of the hypothetical pure liquid solute (*i.e.*, the Henry's law constant, k) is

$$k = \frac{273.15\ R}{M_l V_g^0}$$

where R is the gas constant and M_l is the relative molar mass of the solvent in the column. If V_g^0 has units of $cm^3\ g^{-1}$, this equation may be written

$$k\ (kPa) = \frac{2.271 \cdot 10^6}{M_l V_g^0}$$

Table I presents these pressures for both pairs of solutes at each temperature measured for both solvents. Table II presents the standard thermodynamic property changes for transfer of the ideal vapor at 101.325 kPa to the hypothetical pure solute liquid with intermolecular interactions characteristic of infinite dilution in solvent.

TABLE II

STANDARD THERMODYNAMIC PROPERTY CHANGES FROM VAPOR TO INFINITELY DILUTE SOLUTION IN n-$C_{16}H_{34}$ AND IN n-$C_{24}H_{50}$

Solute	In n-$C_{16}H_{34}$ at 298.15°K		In n-$C_{24}H_{50}$ at 333.15°K	
	$-\Delta H^\circ$ (kJ mol^{-1})	$-\Delta S^\circ$ (J mol^{-1} °K^{-1})	$-\Delta H^\circ$ (kJ mol^{-1})	$-\Delta S^\circ$ (J mol^{-1} °K^{-1})
n-C_5H_{12}	26.90	85.63	24.94	78.03
n-$C_5{}^2H_{12}$	26.44	85.00	24.64	77.90
n-C_6H_{14}	31.42	90.86	29.57	84.01
n-$C_6{}^2H_{14}$	31.09	90.65	29.27	83.89
n-C_7H_{16}	36.74	98.77	34.40	90.52
n-$C_7{}^2H_{16}$	36.23	98.10	34.14	90.65

DISCUSSION

The deuterium content of the solutes studied is such that if the ^{1}H were present as one atom per solute molecule. the purity of the "heavy" compounds is quite low: 76. 72 and 84 mole%. in fact. for C_5, C_6 and C_7, respectively. The vapor pressure isotope effect (VPIE) is approximately 0.7% per ^{2}H atom[2]; for n-C_6^{2}H$_{14}$ at 300°K. a true vapor pressure of 20 kPa would be lowered to 19.96 kPa by the presence of 30 mole% of n-C_6^{2}H$_{13}$H. The effect of isotopic impurity on measured enthalpy of solution would be still smaller. Consequently. no corrections to take into account the presence of protium in the "heavy" compounds were made.

As is true for the VPIE of the pure n-heptanes[2], equilibrium pressures of all solutes herein above both C_{16} and C_{24} are greater for the "heavy" member of each pair. Likewise. the enthalpy of vaporization from these solvents is smaller in every case for the "heavy" solute. in accord with analogous values for the pure n-heptanes. Entropies of vaporization appear to be less positive for the "heavy" than for the "light" alkanes. but the magnitude of the differences is close to experimental error ($ca.$ 0.15 J mol^{-1} K^{-1}). We can state that the isotope effect on entropy of vaporization is considerably smaller than that on enthalpy of vaporization for these compounds. and that the VPIE is the result of energetic rather than entropic factors. This is in spite of the expected role of greater mass and moment of inertia in providing an entropic advantage for the "heavy" alkane in the vapor phase.

In principle. we should be able to produce values for the change in heat capacity upon solution, $\Delta C_p'$. from these data. but reliable values of this quantity require more data than were collected here[1]. Qualitatively. it appears that $\Delta C_p'$ for the solution process is more positive by roughly 10 J mol^{-1} K^{-1} for the "heavy" member of each pair. for the C_{24} solvent at 333°K.

The purpose of this note is not the interpretation of the isotope effects observed; others are better qualified. It is to give further evidence for the value of the GLC approach to the study of thermodynamics. In particular. we should note two significant advantages offered by the present approach as applied to the study of VPIE: (1) The environment of the vaporizing molecule can be varied (by using different solvents) allowing an attempt at separating out external from internal contributions to the VPIE. (2) Since the vapor phase solute is at a very low partial pressure in helium. it is behaving essentially ideally, and second virial coefficient data for the "heavy" molecule are not required in order to carry out statistical thermodynamic analysis of the results. This is particularly important because such data are generally not available. and the calculation of reduced partition function ratios has been a fruitful approach to the study of VPIE[4,5].

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