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STUDIES ON THE THERMODYNAMICS OF SOLUTION BY GAS CHROMATOGRAPHY

SOLUBILITY MEASUREMENTS OF HYDROCARBONS IN β -ALKOXY-PROPIONITRILES

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SUMMARY

Gas chromatography was used to obtain activity coefficients at infinite dilution for twelve hydrocarbon solutes in five alkoxypropionitrile solvents at three temperatures, 30, 40 and 50°C. A comparative study of elution characteristics and thermodynamic parameters for the alkoxypropionitriles was made. The activity coefficient data were analysed in the light of the molecular structure of the solutes.

INTRODUCTION

Gas chromatography (GC) is an effective technique for studying the thermodynamics of non-electrolyte solutions¹⁻⁷. The objective of this work was to obtain retention volumes for five β -alkoxypropionitriles (some of which are selective for C₄ isomer separation) and thus provide information bearing on theories of solution which might lead to a more quantitative approach to liquid phase selection and design. Propionitriles have long been known for their outstanding solvent characteristics for aromatics^{8,9} and 1,3-butadiene¹⁰⁻¹⁵. Among the β -alkoxypropionitriles, the first member of the series, β -methoxypropionitrile, has already been established as superior to furfural for 1,3-butadiene extraction. Preliminary experimental data indicated¹⁵ that β -ethoxypropionitrile may also be used as an extractant. In earlier detailed studies¹⁶⁻¹⁸, we reported that β -alkoxypropionitriles could be used as stationary phases for the analysis of lighter hydrocarbons, particularly for the resolution of difficult C₄ isomer pairs under appropriate conditions. So far, to our knowledge, no studies on the thermodynamics of solution have been reported for these β -alkoxypropionitriles. In this work, the thermodynamics of dilute solutions were investigated by determining activity coefficients.

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EXPERIMENTAL

The solvents β -methoxy- (MOPN), β -ethoxy- (EOPN), β -propoxy- (PrOPN), β -butoxy- (BOPN) and β -pentoxy- (POPEN) propionitrile were synthesized by reaction of acrylonitrile with methyl, ethyl, *n*-propyl-, *n*-butyl and *n*-pentyl alcohol, respectively, according to Bruson and Riener¹⁹, the details of which have been described elsewhere²⁰. The purity of the synthesized compounds was checked by gas chromatographic analysis and carbon and hydrogen determinations. The purity of each compound was found to be not less than 99.8%. The physical properties of the β -alkoxy-propionitriles are reported in Table I.

TABLE I
PHYSICAL PROPERTIES OF SOLVENTS

<i>Solvent</i>	<i>Mol. wt.</i>	<i>Boiling point (°C)</i>	<i>Density (d_4^{30})</i>	<i>Refractive index (20°C)</i>
β -Methoxypropionitrile	85.1	166	0.9328	1.4032
β -Ethoxypropionitrile	99.1	58/10 mmHg	0.8940	1.4075
β -Propoxypropionitrile	113.2	73.5/10 mmHg	0.8891	1.4131
β -Butoxypropionitrile	127.2	98/20 mmHg	0.8810	1.4182
β -Pentoxypropionitrile	141.2	117/18 mmHg	0.8794	1.4245

The solutes used were of analytical reagent grade from Philips Petroleum or BDH. In order to obtain a better comparison, the experimental conditions for all five solvents were kept almost identical. These solvents, used as typical GC stationary phases, were impregnated on a solid support, Chromosorb P (50–60 mesh). The stationary phase loading was maintained as high as 29% in order to prevent any significant solute adsorption at the gas–liquid interface. The coated support materials were packed in 2-m copper tubes (3 mm I.D.).

A Chrome-Alyzer-100 gas chromatograph equipped with a thermal conductivity detector was used. Hydrogen was used as the carrier gas. The size of the samples injected into the column ranged from 0.1 to 1.0 μ l for liquids and from 20 to 50 μ l for gaseous hydrocarbons.

Because of the low boiling points of the solvents, the columns were operated at low temperatures. MOPN and EOPN were studied at 30°C, PrOPN at 30 and 40°C and BOPN and POPN at 30, 40 and 50°C (all $\pm 0.1^\circ\text{C}$). In order to minimize the depletion of solvents, a presaturator was used before the analytical column so that the carrier gas was saturated with the solvent, thus reducing the possibility of depletion of the stationary phase. While working with various volatile solvents in studies on the thermodynamics of solution during the last few years, we have found that the presaturator column helps to obtain consistent and accurate thermodynamic data²⁰⁻²³. The presaturator column (30 cm \times 3 mm I.D.), packed with about 35% (w/w) of the desired solvent-coated support material, was located prior to the point of sample injection and manometer. Satisfactory functioning of the presaturator columns was reflected in the stability of the baseline, as no discernible changes were observed

throughout the brief experimental work. Moreover, the solvent loss, if any, was monitored by weighing the analytical column before and after each experimental run and making corrections accordingly.

The retention time (t'_R) for each solute was measured from the air peak to solute peak maxima and the values used in calculations were averages of at least triplicate runs. The pressure difference was monitored with the help of a mercury manometer and was taken as the inlet pressure of the column. The outlet pressure was atmospheric at all times. The vapour pressures for hydrocarbon solutes were calculated from Antoine's equation constants^{24,25}.

RESULTS

Specific retention volumes (V'_g) were determined for twelve hydrocarbons using the well known expression described by Littlewood *et al.*²⁶. The V'_g data are reported in Table II.

Solute activity coefficients at infinite dilution in the liquid phase ($\gamma_{2,p}^\infty$) were determined from the equation²⁷⁻²⁹

$$\gamma_{2,p}^\infty = \frac{1.704 \cdot 10^7}{M P_2^\infty V'_g} \quad (1)$$

where M is the solvent molecular weight and P_2^∞ Torr is the vapour pressure of the pure saturated solute vapour. This equation has been discussed in detail elsewhere^{20,21}.

Activity coefficients corrected for vapour phase imperfections, $\gamma_{2,f}^\infty$, are given by^{6,7}

$$\ln \gamma_{2,f}^\infty = \ln \gamma_{2,p}^\infty - \frac{(\beta_{22} - v_2^\infty) p_2^\infty}{R T} + \frac{(2\beta_{12} - v_2^\infty) \bar{p}}{R T} \quad (2)$$

where v_2^∞ is the molar volume and β_{22} is the second virial coefficient for the pure solute at temperature T . In the last term, β_{12} , v_2^∞ and \bar{p} are the cross second virial coefficient, the partial molar volume of the solute at infinite dilution and the mean column pressure, respectively. The β_{22} data for the solutes studied lie between -500 and -1800 cm³/mole in the temperature range 30–50°C, and the mixed virial coefficient (β_{12}) data for the hydrogen–hydrocarbon system may be of either sign (values are of the order of -40 to 30 cm³/mole³⁰). More specifically, the β_{12} values with hydrogen as the carrier gas are towards the negative end and some cancellation occurs between the two gas-phase imperfection terms in eqn. 2. Hence, the activity coefficient at infinite dilution values were determined employing eqn. 1.

Table III gives the activity coefficient data for twelve hydrocarbons at infinite dilution. The values are the means of at least three experimental runs. No values are available in the literature for these solvents for comparison. The reliability of the method for the determination of $\gamma_{2,p}^\infty$ has been demonstrated in earlier papers²⁰⁻²³, where comparisons were made of GC-derived $\gamma_{2,p}^\infty$ values with those obtained either from the static method, vapour–liquid equilibria or from earlier reported GC data for a number of binary systems. In this study the reproducibility of $\gamma_{2,p}^\infty$ was 2–3%.

TABLE II
SPECIFIC RETENTION VOLUME IN β -ALKOXYPROPIONITRILES

Solute	MOPN, 30°C		EOPN, 30°C		PiOPN		BOPN		POPn		
	30°C	40°C	30°C	40°C	30°C	40°C	30°C	40°C	30°C	40°C	50°C
Isobutane	4.28	8.65	7.24	10.69	10.69	8.65	11.69	9.26	13.42	10.30	8.34
<i>n</i> -Butane	6.22	13.03	10.57	15.52	15.52	13.03	17.40	13.25	19.89	15.10	12.07
<i>n</i> -Pentane	15.24	32.03	28.03	43.00	43.00	32.03	49.88	37.12	57.50	41.32	31.93
<i>n</i> -Hexane	36.81	86.78	77.27	116.50	116.50	86.78	138.7	96.65	167.0	111.1	82.60
Isobutene	12.94	17.00	16.74	21.72	21.72	17.00	23.35	17.64	25.34	19.54	15.02
1-Butene	11.40	16.50	15.66	21.23	21.23	16.50	22.93	17.36	24.75	19.08	15.39
<i>trans</i> -2-Butene	14.14	20.25	19.88	25.58	25.58	20.25	28.67	21.42	30.38	23.67	17.80
<i>cis</i> -2-Butene	16.65	23.37	23.67	30.87	30.87	23.37	33.78	24.91	36.24	27.46	20.65
<i>trans</i> -2-Pentene	28.01	49.15	51.44	68.48	68.48	49.15	75.43	54.55	83.41	59.36	45.27
<i>cis</i> -2-Pentene	31.61	53.98	57.48	75.65	75.65	53.98	82.39	59.40	93.44	64.54	48.87
<i>trans</i> -2-Hexene	74.99	—	126.1	—	—	—	196.9	133.0	224.1	157.2	106.9
<i>cis</i> -2-Hexene	87.30	—	144.6	199.5	199.5	—	222.9	150.2	252.2	171.4	119.6

DISCUSSION

With all the five stationary phases, it was possible to resolve saturated and unsaturated lower hydrocarbons in a relatively short time. The chromatograms of all of the compounds showed symmetrical peaks useful for analytical studies. The first member of the series, MOPN, separated a pair that is difficult to resolve, isobutene and butene-1.

Table II reveals that the $\log V_g^s$ values are linearly related to the carbon number of the solutes at a particular temperature, and V_g^s increases systematically with increase in the carbon number of the alkyl chain attached to the β -alkoxypropionitrile solvents. Interestingly, this observation is in conformity with that of Langer *et al.*³¹.

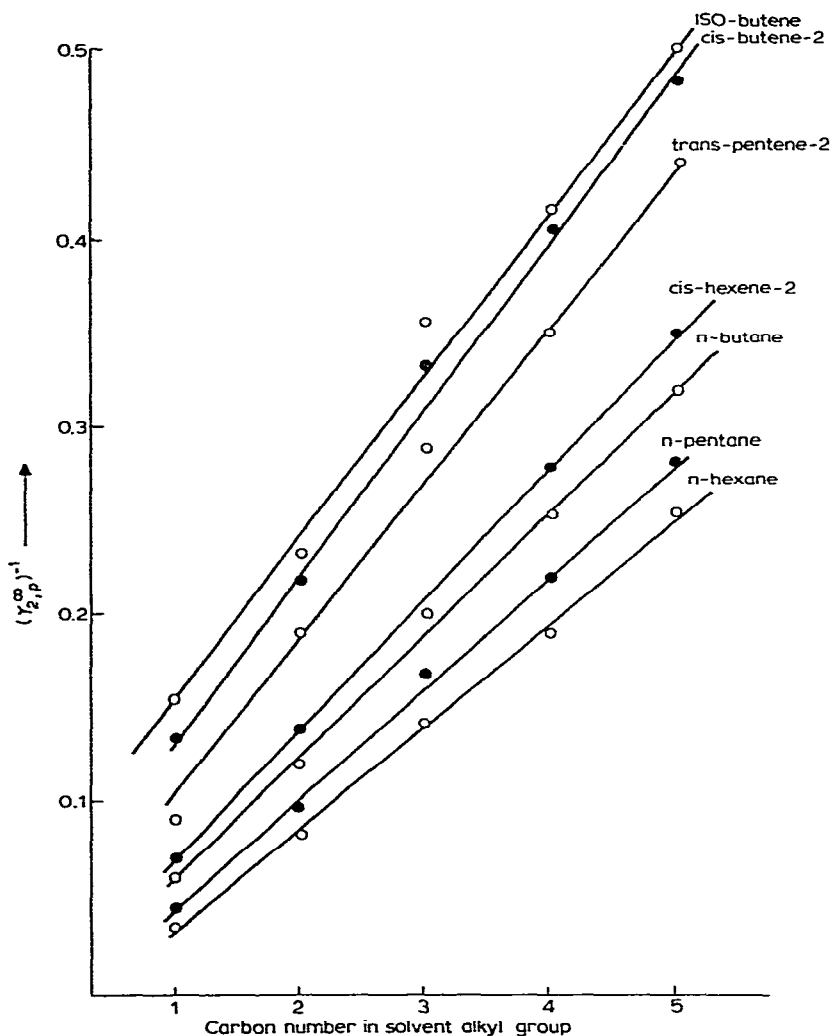


Fig. 1. Incremental relationship between solute activity coefficient and alkyl chain length of β -alkoxypropionitrile solvents.

TABLE III

LIMITED ACTIVITY COEFFICIENT DATA FOR HYDROCARBONS IN *n*-ALKOXYPROPIONITRILES

Solute	MOPN, 30°C		EOPN, 30°C		i-PropN		nOPN		POPn		
	30°C	40°C	30°C	40°C	30°C	40°C	30°C	40°C	30°C	40°C	50°C
Isobutane	15.53	4.68	7.89	4.43	3.81	3.68	3.53	2.99	2.98	2.87	
<i>n</i> -Butane	15.18	4.58	7.67	4.09	3.63	3.58	3.37	2.86	2.83	2.71	
<i>n</i> -Pentane	21.33	5.69	9.96	5.43	4.34	4.17	4.06	3.41	3.37	3.17	
<i>n</i> -Hexane	29.04	6.90	11.88	6.22	5.16	4.97	4.74	3.86	3.79	3.61	
Isobutene	5.84	2.53	3.89	2.52	2.17	2.17	2.12	1.80	1.76	1.73	
1-Butene	6.79	4.25	4.25	2.66	2.26	2.25	2.20	1.89	1.84	1.80	
<i>trans</i> -2-Butene	6.42	2.60	3.87	2.54	2.12	2.13	2.04	1.78	1.74	1.75	
<i>cis</i> -2-Butene	6.93	2.88	4.23	2.72	2.29	2.28	2.21	1.92	1.86	1.88	
<i>trans</i> -2-Pentene	10.66	3.35	5.03	3.15	2.74	2.68	2.65	2.17	2.20	2.12	
<i>cis</i> -2-Pentene	11.76	3.62	5.51	3.59	2.93	2.86	2.80	2.38	2.37	2.23	
<i>trans</i> -2-Hexene	12.27	—	6.36	—	3.22	3.22	3.09	2.56	2.54	2.49	
<i>cis</i> -2-Hexene	13.87	4.04	7.08	—	3.53	3.51	3.39	2.80	2.78	2.72	

TABLE IV

RELATIONSHIP BETWEEN SOLUTION PROPERTIES AND PHYSICAL PROPERTIES OF SOLUTES

Solute pair	Vapour pressure	Molar volume	Critical temperature	Electron polarizability (α_e^*)	Activity coefficient ($\gamma_{2,n}^*$)	Chromatographic elution
<i>n</i> -Alkane to <i>n</i> -alkane (e.g., <i>n</i> -butane to <i>n</i> -pentane)	$n-C_3 < n-C_4$	$n-C_3 > n-C_4$	$n-C_3 > n-C_4$	$n-C_3 > n-C_4$	$n-C_3 > n-C_4$	$n-C_3 > n-C_4$
<i>n</i> -Alkane to branched-chain alkane (e.g., <i>n</i> -butane to isobutane)	$n-C_4 < i-C_4$	$n-C_4 < i-C_4$	$n-C_4 > i-C_4$	$n-C_4 > i-C_4$	$n-C_4 < i-C_4$	$n-C_4 > i-C_4$
<i>n</i> -Alkane to <i>n</i> -olefin (e.g., <i>n</i> -butane to 1-butene)	$n-C_4 < C_4^{-1}$	$n-C_4 > C_4^{-1}$	$n-C_4 > C_4^{-1}$	$n-C_4 < C_4^{-1}$	$n-C_4 > C_4^{-1}$	$n-C_4 < C_4^{-1}$
<i>n</i> -Olefin to branched-chain olefin (1-butene to isobutene)	$C_4^{-1} < i-C_4$	$C_4^{-1} < i-C_4$	$C_4^{-1} > i-C_4$	$C_4^{-1} < i-C_4$	$C_4^{-1} > i-C_4$	$C_4^{-1} < i-C_4$
<i>cis</i> -2-Alkene to <i>trans</i> -2-alkene (e.g., pentene-2)	$trans > cis$	$trans > cis$	$trans < cis$	$trans < cis$	$trans < cis$	$trans < cis$

The V_g^* values of ethylbenzene increase with increase in the alkyl chain length of di-*n*-alkylhalophthalate esters. The $\gamma_{2,p}^\infty$ values for the solutes decrease from MOPN to POPN. A linear relationship exists between the inverse of the solute activity coefficient at infinite dilution and the carbon number of the alkyl group in the β -alkoxypropionitrile solvents, as indicated in Fig. 1. However, the logarithmic activity coefficients, as shown in Fig. 2, are directly related to the carbon number of the solutes. Both of these results indicate that the group contribution model of Pierotti and co-workers³²⁻³⁴ can perhaps be employed.

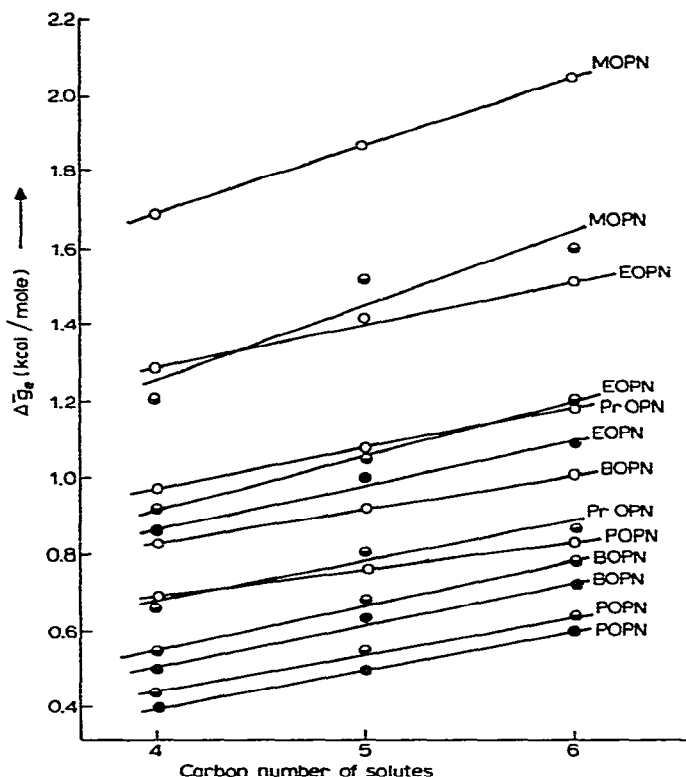


Fig. 2. Incremental relationship between excess free energy and molecular structure for solutes in β -alkoxypropionitrile solvents. O, *n*-Alkane; \ominus , *cis*-2-alkene; \bullet , *trans*-2-alkene.

Newman and Prausnitz³⁵ discussed the energetic effects in solution and classified them according to the chemical and physical forces operative in it. In the present system, it would be safer to assume that chemical forces are not very strong and the physical forces (dispersion and orientational) predominate. The physical interactions are best represented by electron polarizability. The electron polarizability per unit volume (α_c^v) can be obtained from the Clausius-Mosotti equation:

$$\alpha_c^v = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{3}{4 \pi N} \cdot \frac{M}{\rho} \quad (3)$$

α_c^v was calculated from this equation for all solutes. Fig. 3 shows an interesting linear

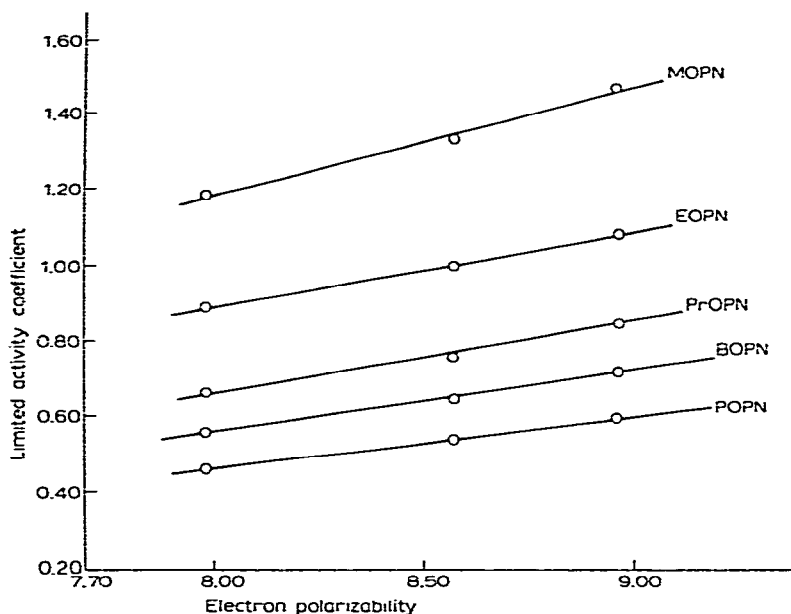


Fig. 3. Relationship between limited activity coefficient and electron polarizability of *n*-alkanes at 30°C.

relationship between $\gamma_{2,p}^x$ and α_c^x for *n*-alkane solutes at 30°C for all five solvents studied.

A comparison of the $\gamma_{2,p}^x$ data for each *n*-alkane with those for the corresponding alkene indicates that the latter are strongly solvated in all five solvents owing to enhanced solute-solvent interactions (a dipole-induced dipole interaction between a strongly polar $-\text{C}\equiv\text{N}^+$ group and a polarizable delocalized π -electron. Examination of the $\gamma_{2,p}^x$ values for C_4 olefins reveals that isobutene and *trans*-2-butene have preferential spatial arrangements compared with 1-butene and *cis*-2-butene, the interchange energy being minimized. In order to rationalize the solution properties of various isomers, it is worth considering solution properties in relation to some of the fundamental properties (additive as well as constitutive) of the solute. Table IV shows that $\gamma_{2,p}^x$ values in general increase with the increase in molar volume and critical temperature and decrease with increase in the vapour pressure of the solutes. The data also indicate that the behaviour of two homologues (*n*-alkanes) is in accordance with their fundamental properties. For the pair *n*-butane-isobutane, it appears the molar volume predominates, isobutane has higher values of $\gamma_{2,p}^x$ although the vapour pressure of isobutane is higher than that of *n*-butane. In a physical sense it seems that the higher molecular volume of isobutane molecules require a higher free energy to create a cavity in the solvent. Similarly, with two geometrical isomers *e.g.*, *cis*- and *trans*-2-alkenes, the *trans*-isomers have lower $\gamma_{2,p}^x$ values, which reflects the fact that the *trans*-isomers have a favourable configuration for entering into solution. However, excluding vapour pressure, the electron polarizability and molar volume data of these olefins do not support this behaviour, because the $\gamma_{2,p}^x$ values for *cis*-isomers should be lower than those of the *trans*-isomers, as the former have higher α_c^x values and molar volumes. Interestingly, *cis*-2-alkenes are eluted later than the *trans*-isomers at all

temperatures in all five alkoxypropionitrile columns. In the absence of detailed data, it is difficult to explain this effect; however, perhaps when the alkyl groups are attached to the *syn*-position of an ethylenic double bond these bulky alkyl groups can hinder the approach of polar solvent molecules or *vice versa*, and thus reduce the interaction with polarizable π -bonds.

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