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## CHROMATOGRAPHIC STUDY OF SOLUTIONS OF HYDROCARBONS IN ACETONITRILE

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## SUMMARY

LLC appears to offer reliable infinite dilution activity coefficient data where solute retention can be attributed solely to liquid-liquid partitioning. A refined experimental system is required for precise measurements. Further elucidation of the role of interfacial solute adsorption phenomena in LLC systems is warranted. The technique is less suited to the determination of the related excess partial molar thermodynamic quantities, since differentiation of the primary data is required. GLC should serve as an important source of information about one of the LLC liquid phases. The acetonitrile/squalane system has good potential as a general purpose solvent pair for hydrocarbon analysis.

## INTRODUCTION

Knowledge of liquid phase activity coefficients is of theoretical and practical importance in chemical engineering and physical chemistry. Rapid new techniques for the accurate determination of these quantities at infinite dilution are consequently welcome. In many cases, chromatographic methods offer reliable activity coefficient data, are rapid, technically simple, and have other advantages. Static techniques are accurate but often tedious and time-consuming; gas-liquid chromatography (GLC) has been shown by comparison to be capable of 1-2% accuracy<sup>1</sup>. The most important solvents in practical engineering systems, however, are of low molecular weight, and GLC is not readily amenable to their study. In contrast, liquid-liquid chromatography (LLC) is suited for volatile solvents, and the theory of solute retention in LLC<sup>2</sup> indicates its potential value for solution thermodynamic measurements.

Nonetheless, since two immiscible solvents are required in LLC, in order to obtain data for the solvent of interest, say the mobile phase, the corresponding information is required about the second phase. Effectively, this latter phase is usually a compound of higher molecular weight or even a polymer. If this compound is used as the stationary phase for both GLC and LLC measurements, at the same temperature, then from the

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GLC retention volumes are calculated the required activity coefficients in that phase. Solute activity coefficients in the mobile phase, the solvent under study in this case, are obtained by combination of the GLC values and the LLC retention data.

Notably simple though this procedure may appear in principle, there exist in practice severe limitations on its general application. Each LLC solvent pair must not only be immiscible, but one must be independently characterized, and as will be seen, for meaningful thermodynamic measurements, the solutes under study must exhibit substantial solubility in both phases.

Application of LLC to the study of solutions of hydrocarbons in acetonitrile was tested here. The mobile phase, acetonitrile, is a solvent with good properties for use as an entrainer in the extractive distillation separation of hydrocarbons. In this study, squalane, which has been extensively examined by GLC, served as the stationary phase. Naphthenes, paraffins, olefins, and aromatic hydrocarbons in the  $C_4$  to  $C_{14}$  range were the solutes used, and represent a broad variety of hydrocarbon-acetonitrile solution types. Data were obtained at four temperatures over the range  $15^\circ$  to  $35^\circ$ . Excess partial molar free energies, enthalpies, and entropies of mixing with acetonitrile were calculated from the data, and comparison made with static measurements wherever possible. Except for the compounds of small solubility in acetonitrile (activity coefficients exceeding about 15), reasonable agreement was obtained between the LLC values and the reported static measurements. Definite evidence exists for the operation of a retention mechanism in addition to liquid-liquid partitioning, probably interfacial solute adsorption, for the hydrocarbons of lower solubility in acetonitrile.

## THEORY

The ratio of solute activity coefficients at infinite dilution in the mobile phase,  $\gamma_2^{m,\infty}$ , and the stationary phase,  $\gamma_2^{s,\infty}$ , is related to the solute specific retention volume,  $V_g$ , according to<sup>2</sup>

$$V_g = \frac{\gamma_2^{m,\infty} M_m}{\gamma_2^{s,\infty} M_s \rho_m} \quad (1)$$

where  $M_m$  and  $M_s$  are respectively the molecular weights of the mobile and stationary phases, and  $\rho_m$  is the eluent density at the column temperature,  $T$ . From the temperature dependence of the solute activity coefficient, *e.g.*,

$$R \left( \frac{\partial \ln \gamma_2^{m,\infty}}{\partial (1/T)} \right)_P = \bar{h}_2^{e,m} \quad (2)$$

where  $\bar{h}_2^{e,m}$  is the excess partial molar enthalpy of mixing at infinite dilution of solute with mobile phase, the variation of  $V_g$  with temperature becomes

$$R \frac{\partial \ln V_g}{\partial (1/T)} = \Delta \bar{h}_2^e + RT^2 \alpha_m \quad (3)$$

where  $\Delta \bar{h}_2^e = (\bar{h}_2^{e,m} - \bar{h}_2^{e,s})$  and  $\alpha_m$  is the coefficient of thermal expansion of the eluent. The solute excess partial molar Gibbs free energy,  $\mu_2^{e,m}$ , is determined from the activity coefficient, since

$$RT \ln \gamma_2^{m,\infty} = \mu_2^{e,m} \quad (4)$$

and the excess partial molar entropy,  $\bar{s}_2^{e,m}$ , from the familiar equation

$$\mu_2^{e,m} = \bar{h}_2^{e,m} - T\bar{s}_2^{e,m} \quad (5)$$

The excess partial molar quantities all refer to infinite dilution, if the activity coefficient is measured at effectively infinite dilution.

#### EXPERIMENTAL

The apparatus was essentially the same as that described previously<sup>3</sup>. The principal procedural modifications involved the Waters R-4 Differential Refractometer Detector. Better baseline stability was achieved by dead-ending the reference side of the detector and by operation of the cell under ambient conditions. Once or twice a day the reference line through the detector was flushed out with eluent and the flow then shut off with a valve on the inlet side. Although the detector is supplied with its own Haake constant temperature water circulator, less baseline drift was observed with the bath turned off, at least in an airconditioned room.

The separation column was 3 m  $\times$   $\frac{1}{4}$  in. O.D. stainless steel in each case, coiled to fit into the water bath, and was preceded in the eluent flow line by a 1 m precolumn packed in the same manner with the same material. Column packings were in all cases nominally 25 wt. % squalane coated on carefully silanized 100/120 mesh Chromosorb P. The constancy of the amount of stationary phase present in the column was readily checked after a series of measurements by removing the column from the apparatus, blowing out the eluent overnight in a stream of N<sub>2</sub>, and weighing the dry column on a high capacity Mettler balance to 0.001 g. No systematic variation in retention volume was observed to be caused by this procedure, which allowed correction for the small loss (less than 0.2% of the stationary phase present) of squalane resulting from a temperature increase of 5° or 10°.

The Leeds and Northrup Model N recorder had a chart speed of 1.015 cm/min, checked periodically by the same stop watch that was used to measure the flow rate. Retention measurements were made on the recorded chromatogram. The interstitial plus dead volume in the column and apparatus were measured by frequent injection of small samples of acetone, which was not retained by the column.

The eluent was Matheson Chromatoquality acetonitrile, continuously refluxed in a 5 l flask to exclude air before passing into the pump. Its density was measured at several temperatures with a double stem Robertson-type pycnometer. The densities are presented in Table I along with the values of the coefficient of thermal expansion of acetonitrile calculated from these data.

Hydrocarbon solutes were of the best grade available (many were API standards) and were used without further purification. Sample sizes were the smallest detectable, which in acetonitrile ranged from about 0.01  $\mu$ l for the aromatic hydrocarbons to about 1.0  $\mu$ l for the paraffins. Butane was liquified in dry ice before injection. The silicone rubber septum in the injection tee was wrapped with Teflon tape to increase its lifetime.

#### RESULTS

The  $V_g$  values determined at the four temperatures studied are listed in Table II.

TABLE I

DENSITY OF ACETONITRILE AND COEFFICIENT OF THERMAL EXPANSION

Temp. (°K)	$\rho_{ACN}$ (g/c.c.)	$\alpha_m \times 10^3$ (deg <sup>-1</sup> )	$RT^2\alpha_m$ (kcal/mole)
288.16	0.7848	1.125	0.199
293.16	0.7805	1.119	0.198
298.16	0.7762	1.113	0.197
303.16	0.7719	1.107	0.196
308.16	0.7675	1.100	0.194

Each value was calculated from the average of at least three measured retention volumes. Since the specific retention volume is determined from the difference in the solute retention volume and that of non-retained acetone, the reproducibility of the  $V_g$  values of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  was to within about 10%; for benzene and toluene, about 3%; and increasing with increasing retention volume to about 1%. Plots of  $\log V_g$  vs.  $1/T$  were linear over the temperature range studied for all solutes except  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . Included in Table II are the enthalpies of transfer of solute from squalane to acetonitrile at 25° calculated by regression analysis from eqn 3.

In order to calculate values of  $\gamma_2^{m,\infty}$ , the limiting activity coefficients of the hydrocarbon solutes in acetonitrile, the corresponding values in squalane are required.

TABLE II

SPECIFIC RETENTION VOLUMES<sup>a</sup> AND ENTHALPIES OF TRANSFER<sup>b</sup> AT 25°C IN THE SYSTEM SQUALANE/ACETONITRILE

Compound	15.05° C	20.00° C	25.00° C	35.10° C	$\Delta\bar{h}_2^e$
<i>n</i> -Butane	3.33	3.24	3.16	3.01	1.08
2-Methylbutane	4.62	4.38	4.12	3.70	2.17
<i>n</i> -Pentane	4.90	4.60	4.32	3.84	2.35
2,2-Dimethylbutane	5.24	4.84	4.48	3.86	2.90
2,3-Dimethylbutane	5.89	5.50	5.15	4.58	2.42
3-Methylpentane	6.12	5.79	5.44	4.88	2.21
2-Methylpentane	6.23	5.89	5.54	4.99	2.17
<i>n</i> -Hexane	6.87	6.36	5.90	5.11	2.81
2,2-Dimethylpentane	7.30	6.70	6.18	5.29	3.04
2,3-Dimethylpentane	—	—	6.82	—	—
2,4-Dimethylpentane	7.40	6.83	6.32	5.48	2.85
3-Ethylpentane	8.49	7.73	7.08	5.99	3.27
2-Methylhexane	8.76	7.95	7.21	6.00	3.54
<i>n</i> -Heptane	9.50	8.61	7.82	6.51	3.54
2,2,4-Trimethylpentane	8.65	8.11	7.62	6.75	2.39
2,4-Dimethylhexane	10.15	9.24	8.43	7.09	3.37
<i>n</i> -Octane	13.20	11.80	10.65	8.75	3.82
<i>n</i> -Nonane	17.75	15.90	14.35	11.65	3.91
2-Methylbutene-1	—	—	2.41	—	—
3-Methylpentene-1	2.98	2.82	2.67	2.40	2.11
2-Methylpentene-1	—	—	2.78	—	—
2,3-Dimethylbutene-1	—	—	2.74	—	—
Pentene-1	2.10	2.00	1.91	1.75	1.81
Hexene-1	3.10	2.94	2.79	2.53	1.99
1,5-Hexadiene	1.47	1.38	1.31	1.17	2.20

(continued on p. 28)

TABLE II (continued)

Compound	15.05° C	20.00° C	25.00° C	35.10° C	$\Delta\bar{h}_2^e$
Heptene-1	4.23	3.98	3.73	3.32	2.35
Octene-1	5.78	5.45	5.13	4.61	2.20
2,4,4-Trimethylpentene-1	4.83	4.58	4.35	3.94	2.00
Cyclopentane	4.55	4.31	4.09	3.70	2.02
Methylcyclopentane	5.82	5.50	5.19	4.66	2.16
Cyclohexane	6.60	6.11	5.68	4.93	2.77
Methylcyclohexane	8.16	7.71	7.29	6.52	2.18
Ethylcyclohexane	11.30	10.49	9.78	8.50	2.71
Cyclopentene	2.45	2.36	2.28	2.14	1.39
Cyclohexene	3.26	3.08	2.92	2.64	2.06
Benzene	0.554	0.550	0.548	0.539	0.435
Toluene	0.804	0.786	0.770	0.738	0.952
Ethylbenzene	1.04	1.01	0.989	0.935	1.16
<i>o</i> -Xylene	1.06	1.03	1.00	0.950	1.17
<i>m</i> -Xylene	1.16	1.12	1.08	1.02	1.32
<i>p</i> -Xylene	1.17	1.14	1.10	1.03	1.37
<i>n</i> -Propylbenzene	1.38	1.33	1.26	1.13	1.99
<i>n</i> -Butylbenzene	1.98	1.90	1.84	1.71	1.48
<i>n</i> -Pentylbenzene	2.53	2.48	2.38	2.12	1.80
<i>n</i> -Hexylbenzene	3.89	3.58	3.30	2.83	3.01
<i>n</i> -Octylbenzene	6.84	6.37	5.92	5.18	2.66
<i>n</i> -Nonylbenzene	9.41	8.56	7.80	6.52	3.44
Isopropylbenzene	—	—	1.26	—	—
1,2,4-Trimethylbenzene	—	—	1.54	—	—
1,3,5-Trimethylbenzene	—	—	1.57	—	—
<i>tert.</i> -Butylbenzene	—	—	1.45	—	—
<i>sec.</i> -Butylbenzene	—	—	1.63	—	—
<i>o</i> -Diethylbenzene	—	—	1.71	—	—
<i>m</i> -Diethylbenzene	—	—	1.81	—	—
<i>p</i> -Diethylbenzene	—	—	1.78	—	—
1,3,5-Triethylbenzene	—	—	2.88	—	—
1-Methyl-4-isopropylbenzene	—	—	1.84	—	—
Tetralin	—	—	1.83	—	—
Naphthalene	0.643	0.620	0.593	0.550	1.59
CH <sub>2</sub> Cl <sub>2</sub>	—	—	0.107	—	—
CHCl <sub>3</sub>	—	—	0.232	—	—
CCl <sub>4</sub>	1.52	1.49	1.45	1.39	1.00

<sup>a</sup> Units of  $V_g$  are c.c./g of squalane.

<sup>b</sup> Units of  $\Delta\bar{h}_2^e$  are kcal/mole.

Squalane has been extensively studied by GLC and by static techniques, and considerable activity coefficient data are available<sup>4-13</sup>. However, because most of these data were obtained at temperatures exceeding those studied here, and because of some systematic as well as random variation in the values reported by different groups, all of the available data for a particular solute were plotted *vs.*  $1/T$ . The required values were obtained from this semi-log plot. An attempt was made when required to compensate for systematic variations in some of the available GLC data, occasioned, for example, by the use of initial retention volumes rather than the peak maximum values. The resulting values at 25° are listed in Table III, together with the calculated  $\bar{h}_2^{e,s}$ . This procedure, while somewhat arbitrary and potentially subject to a variety of errors, is a necessary compromise in view of the lack of data at the temperatures studied here. Recent GLC measurements<sup>28</sup> have confirmed the extrapolated values for the

TABLE III

LIMITING ACTIVITY COEFFICIENTS OF HYDROCARBONS IN SQUALANE AT 25° C<sup>a</sup> AND PARTIAL MOLAR ENTHALPIES OF MIXING<sup>b</sup>

Compound	$\gamma_2^{s,\infty}$	$\bar{h}_2^{e,s}$	References
<i>n</i> -Butane	0.59	0	4
2-Methylbutane	0.63	0	4, 9, 10
<i>n</i> -Pentane	0.62	0	4, 5, 7-10
2,2-Dimethylbutane	0.69	0	4, 7-10
2,3-Dimethylbutane	0.64	0	4, 9
3-Methylpentane	0.64	0	4
2-Methylpentane	0.67	0	4, 9
<i>n</i> -Hexane	0.65	0	4, 5, 7-12
2,2-Dimethylpentane	0.71	0	4, 9
2,4-Dimethylpentane	0.72	0	4, 9
3-Ethylpentane	0.65	0	4
2-Methylhexane	0.70	0	4
<i>n</i> -Heptane	0.68	0	4, 5, 7-10
2,2,4-Trimethylpentane	0.72	0	4, 9
<i>n</i> -Octane	0.72	0	4, 5, 10
<i>n</i> -Nonane	0.75	0	4, 5
2-Methylpentene-1	0.62	0	4, 9
Pentene-1	0.62	0	9
Hexene-1	0.64	0	4, 9
Heptene-1	0.67	0	4, 9
Octene-1	0.71	0	4
Cyclopentane	0.48	0	4, 9, 10
Methylcyclopentane	0.55	0	4, 9, 10
Cyclohexane	0.54	0	4, 7-10, 13
Methylcyclohexane	0.55	0	4, 10
Ethylcyclohexane	0.56	0	4
Cyclohexene	0.52	0	9
Benzene	0.70	0.46	4, 7-10
Toluene	0.73	0.45	4, 9, 10
Ethylbenzene	0.78	0.42	4, 10
<i>p</i> -Xylene	0.75	0.43	4, 10
<i>m</i> -Xylene	0.76	0.43	4
<i>o</i> -Xylene	0.76	0.43	4
CH <sub>2</sub> Cl <sub>2</sub>	1.12	—	7, 9
CHCl <sub>3</sub>	0.65	—	7, 9
CCl <sub>4</sub>	0.55	0	7, 9

<sup>a</sup> Values at 25° obtained from plots of literature values<sup>4-13</sup>.<sup>b</sup>  $\bar{h}_2^{e,s}$  (kcal/mole) calculated over temperature range 15-35°C.

aromatic hydrocarbons. Nonetheless, the reader can evaluate for himself the values in Table III and make appropriate alterations as desired.

From these  $\gamma_2^{s,\infty}$  and  $V_\theta$  values, the phase molecular weights, and the eluent densities obtained from a plot of the data in Table I, the apparent solute limiting activity coefficients in acetonitrile were calculated at the four temperatures. Over the temperature range 15°-35°, the plots of  $\log \gamma_2^{m,\infty}$  vs.  $1/T$  were linear, and values of the excess partial molar enthalpy of mixing,  $\bar{h}_2^{e,m}$ , were determined by least squares analysis. The related excess partial molar thermodynamic quantities at infinite dilution were calculated from equations 4 and 5. The values at 25° are all given in Tables IV and V. Table IV lists the solutes with apparent activity coefficients less

TABLE IV

APPARENT LIMITING ACTIVITY COEFFICIENTS OF HYDROCARBONS IN ACETONITRILE LESS THAN 16 AND RELATED EXCESS PARTIAL MOLAR THERMODYNAMIC QUANTITIES, AT 25° C

No	Compound	$\gamma_2^{m,\infty}$	$\mu_2^{e,m}$ <sup>a</sup>	$\bar{h}_2^{e,m}$ <sup>a</sup>	$\bar{s}_2^{e,m}$ <sup>b</sup>	Electron polarizability per unit volume $\times 10^{20}$ <sup>c</sup>
1	Benzene	3.08	0.67	0.90	0.78	11.68
2	Toluene	4.51	0.89	1.40	1.70	11.59
3	Ethylbenzene	6.17	1.08	1.58	1.68	11.58
4	<i>o</i> -Xylene	6.12	1.07	1.59	1.75	11.78
5	<i>m</i> -Xylene	6.64	1.12	1.75	2.12	11.62
6	<i>p</i> -Xylene	6.64	1.12	1.80	2.28	11.58
7	Pentene-1	9.47	1.33	1.80	1.57	8.99
8	3-Methylpentene-1	13.8	1.55	—	—	9.26
9	Hexene-1	14.3	1.58	2.00	1.41	9.23
10	Cyclohexene	12.1	1.48	2.06	1.95	10.58
11	<i>n</i> -Butane	14.8	1.60	1.09	-1.70	8.63
12	Cyclopentane	15.7	1.63	2.02	1.31	9.75
13	CH <sub>2</sub> Cl <sub>2</sub>	0.96	-0.02	—	—	8.20
14	CHCl <sub>3</sub>	1.21	0.11	—	—	10.52
15	CCl <sub>4</sub>	6.38	1.10	0.91	-0.63	10.99

<sup>a</sup> Units of  $\mu_2^{e,m}$  and  $\bar{h}_2^{e,m}$  are kcal/mole.

<sup>b</sup> Units of  $\bar{s}_2^{e,m}$  are cal/mole °K (e.u.).

<sup>c</sup> Calculated from the Clausius-Mosotti equation. The electron polarizability per unit volume of acetonitrile is  $8.40 \times 10^{-20}$ .

TABLE V

APPARENT LIMITING ACTIVITY COEFFICIENTS OF HYDROCARBONS IN ACETONITRILE EXCEEDING 16 AND RELATED EXCESS PARTIAL MOLAR THERMODYNAMIC QUANTITIES, AT 25° C

No.	Compound	$\gamma_2^{m,\infty}$	$\mu_2^{e,m}$ <sup>a</sup>	$\bar{h}_2^{e,m}$ <sup>a</sup>	$\bar{s}_2^{e,m}$ <sup>b</sup>
16	2-Methylbutane	20.7	1.80	2.18	1.27
17	<i>n</i> -Pentane	21.4	1.81	2.36	1.84
18	2,2-Dimethylbutane	24.7	1.90	2.90	3.41
19	2,3-Dimethylbutane	26.3	1.94	2.42	1.64
20	3-Methylpentane	27.8	1.97	2.21	0.82
21	2-Methylpentane	29.1	2.00	2.39	1.34
22	<i>n</i> -Hexane	30.7	2.03	2.82	2.69
23	2,2-Dimethylpentane	35.1	2.11	3.04	3.18
24	2,4-Dimethylpentane	36.4	2.13	2.85	2.46
25	3-Ethylpentane	36.8	2.14	3.28	3.89
26	2-Methylhexane	40.3	2.19	3.55	4.63
27	<i>n</i> -Heptane	42.5	2.22	3.53	4.48
28	2,2,4-Trimethylpentane	43.9	2.24	2.39	0.51
29	<i>n</i> -Octane	61.3	2.44	3.82	4.71
30	<i>n</i> -Nonane	86.0	2.64	3.91	4.34
31	Heptene-1	20.0	1.77	2.35	1.96
32	Octene-1	29.1	2.00	2.20	0.69
33	Methylcyclopentane	22.8	1.85	2.17	1.07
34	Cyclohexane	24.5	1.90	2.77	3.00
35	Methylcyclohexane	32.1	2.05	2.18	0.45
36	Ethylcyclohexane	43.8	2.24	2.71	1.61

<sup>a</sup> Units of  $\mu_2^{e,m}$  and  $\bar{h}_2^{e,m}$  are kcal/mole.

<sup>b</sup> Units  $\bar{s}_2^{e,m}$  are cal/mole-°K (e.u.).

TABLE VI

COMPARISON OF LIMITING ACTIVITY COEFFICIENTS IN ACETONITRILE BY LLC AND STATIC TECHNIQUES

Compound	Temp. (°C)	$\gamma_2^{m,\infty}$ (Lit.) <sup>a</sup>	$\gamma_2^{m,\infty}$ (LLC) <sup>b</sup>	References
Benzene	25	2.7	3.08	17
	45	3.08	2.83	18
	60	2.6	2.66	17
Toluene	45	3.93	3.90	19
Pentene-1	25	9.45	9.47	15
	35	8.68	8.58	15
<i>n</i> -Butane	65	12.3	12.4	14
<i>n</i> -Pentane	25	20.40	21.4	15
	35	17.29	18.8	15
	45	15.42	16.6	15
	50	15.5	15.8	16
<i>n</i> -Hexane	25	25.5	30.7	17
	60	15.8	18.9	17
<i>n</i> -Heptane	50	19.5	27.5	16
CCl <sub>4</sub>	45	7.54	5.90	20

<sup>a</sup> Literature values, from references in column 5.<sup>b</sup> LLC values from Table IV or extrapolated from plots of  $\ln \gamma_2^{m,\infty}$  vs.  $1/T$ .

than 16 and Table V, those greater than 16. The reasons for this division are discussed in the next section.

The absolute accuracy of these values cannot be predicted because of the unknown errors in  $\gamma_2^{s,\infty}$ . However, that part of the uncertainty due to variations in the specific retention volume can be estimated. A variation of 3% in  $V_g$  leads to a corresponding uncertainty of 3% in  $\gamma_2^{m,\infty}$ , or about  $\pm 0.01$  kcal/mole in the calculated  $\mu_2^{e,m}$ . The consequent effect upon the derived  $\bar{h}_2^{e,m}$ , however, can produce a variation as large as  $\pm 0.3$  kcal/mole, and thus as much as  $\pm 0.8$  e.u. in  $\bar{s}_2^{e,m}$ . A smaller variation in  $V_g$ , of course, results in reduced uncertainties, and errors in  $\gamma_2^{s,\infty}$  will compound the uncertainties.

## DISCUSSION

*Apparent activity coefficients at infinite dilution in acetonitrile*

A further estimate of the accuracy of the values determined from the LLC retention data is given by comparison with independent measurements obtained using different techniques. Table VI presents the literature values<sup>14-20</sup> at several different temperatures and those obtained from LLC. The LLC values at temperatures greater than 35° were extrapolated from the  $\log \gamma_2^{m,\infty}$  vs.  $1/T$  plots. The agreement between the two sets of measurements for *n*-butane, pentene-1, benzene, and toluene, and pentane at the higher temperatures, is quite satisfactory. The literature data for benzene from the two different sources<sup>17,18</sup> are not in good agreement, but the value calculated from the data of BROWN AND SMITH<sup>18</sup> is probably the more accurate. The reason for the poor agreement for CCl<sub>4</sub> is not clear.

The coincidence of the two sets of  $\gamma_2^{m,\infty}$  deteriorates increasingly for pentane, hexane and heptane. The apparent activity coefficients are larger than those measured



statically, meaning that the  $V_g$  values are in excess of that attributable solely to liquid-liquid partition. The apparent values are consequently not true liquid phase solute activity coefficients, but rather parameters reflecting both solution effects and interactions of some other type. Eqn. 1 does not necessarily validly describe the retention behavior of these solutes.

The additional retention mechanism operative in this case cannot be ascribed to solute adsorption on the deactivated solid support, nor simply to errors in  $\gamma_2^{s,\infty}$ . It is more probable that these solutes are adsorbed on the liquid-liquid interface. The occurrence of this phenomenon is likely where the system temperature is near ambient, the solute solubility in one phase is small, and one of the phases has a large dipole moment<sup>21,22</sup>. All these conditions exist in this system, and it is therefore reasonable to attribute the additional retention mechanism to interfacial solute adsorption. This effect, the magnitude of which increases with molecular weight, can often be identified and corrected for experimentally<sup>21</sup>. No attempt was made here to perform this correction procedure, because the purpose of the present study was to evaluate LLC as a simple method for obtaining solution thermodynamic information. An extensive project will be required (and should be undertaken) to investigate fully the interfacial adsorption effect in LLC. Where necessary, the correction procedure clearly diminishes the simplicity and even the applicability of chromatographic techniques.

It would seem justified, consequently, to regard with suspicion apparent solute activity coefficients derived from LLC retention data that exceed about 15. In the absence of more information, this limit may advisably be reduced to 10 or lower; a limit of 5 has been recommended for GLC<sup>23</sup> for the same reason: the complication of interfacial adsorption. In view of the unknown character of the values in Table V, there is little point to further discussion of them. Quantitative interpretation of these data may be made only after a thorough study of the occurrence of interfacial phenomena in this system.

However, for the solutes with greater solubility in acetonitrile, the LLC activity coefficient values are apparently reliable. The anticipated trends among the hydrocarbon types are displayed, aromatics interacting with acetonitrile more strongly than olefins, and saturated hydrocarbons being effectively excluded from or squeezed out of the solution.  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  have activity coefficients close to unity, reflecting strong dipolar interactions between these solutes and the nitrile group of the acetonitrile. For the olefins and aromatics, the magnitude of the activity coefficients relative to those of the paraffins indicates the existence of moderately strong interactions with acetonitrile, perhaps (see below) of the charge-transfer type in the case of the aromatic hydrocarbons. The expected correlation between  $\gamma_2^{m,\infty}$ , and the electron polarizability of the solute molecule is generally observed (Table IV). Their absolute magnitude, however, suggests substantial positive deviations from ideal (Raoult's Law) solution behavior, a result of the high cohesive energy density of acetonitrile.

#### *Excess enthalpies and entropies*

Because of the unknown character of the apparent activity coefficients in Table V, the nature of any derived quantities is equally uncertain. These enthalpies and entropies presumably refer to some complex combination of partition and adsorption, and consequently have little quantitative significance. Nonetheless, it is curious that the apparent  $\bar{h}_2^{e,m}$  value for *n*-pentane, 2.36 kcal/mole, is quite close to

the value given by GERSTER *et al.*<sup>15</sup>, 2.27 kcal/mole. It is further notable that plots of  $\log \gamma_2^{m,\infty}$  or  $\log V_g$  vs. carbon number are linear for the olefins and paraffins, the linearity extending from the compounds listed in Table IV to those in the same homologous series in Table V.

Limited comparison is possible for the  $\bar{h}_2^{e,m}$  values in Table IV with literature quantities obtained calorimetrically. The enthalpy of mixing,  $HM$ , data at 45° of BROWN AND FOCK<sup>24</sup> for benzene in acetonitrile and  $\text{CCl}_4$  in acetonitrile, and that of ORYE AND PRAUSNITZ<sup>19</sup> for toluene in acetonitrile at 45°, can be represented by the equations

$$HM = x_1x_2 [461.5 + 88.0(x_1 - x_2) + 130.6(x_1 - x_2)^2] \text{ (benzene + acetonitrile)}$$

$$HM = x_1x_2 [475.8 - 164.9(x_1 - x_2) + 16.1(x_1 - x_2)^2] \text{ (toluene + acetonitrile)}$$

$$HM = x_1x_2 [859.5 - 262.2(x_1 - x_2) + 418.6(x_1 - x_2)^2] \text{ (CCl}_4 \text{ + acetonitrile)}$$

where  $x_1$  and  $x_2$  are the mole fractions of solvent and solute, respectively, in the solution. From these representations, the  $\bar{h}_2^{e,m}$  values at infinite dilution are found to be 0.680 kcal/mole for benzene, 0.657 kcal/mole for toluene, and 1.016 kcal/mole for  $\text{CCl}_4$ . The corresponding values derived from the variation of the LLC activity coefficients with temperature are 0.90 kcal/mole for benzene, 1.40 kcal/mole for toluene, and 0.91 kcal/mole for  $\text{CCl}_4$ . The values for toluene seem abnormally high by LLC and low by calorimetry. GERSTER *et al.*<sup>15</sup> give  $\bar{h}_2^{e,m} = 1.63$  kcal/mole for pentene-1 in acetonitrile, and by LLC we obtain 1.80 kcal/mole. Except for toluene, the agreement is as good as can be expected.

All these  $\bar{h}_2^{e,m}$  are positive, and the reduced endothermicity of mixing of the unsaturated compounds relative to the saturates again indicates the existence of specific interactions between these compounds and acetonitrile, the magnitude of which increase with increasing electron polarizability (Table IV). The partial molar enthalpies are apparently constant over the limited temperature range studied; imprecision in the measurements may have obscured a slight curvature in the  $\log \gamma_2^{m,\infty}$  vs.  $1/T$  plots for the aromatic hydrocarbons. GERSTER *et al.*<sup>15</sup>, however, found  $\bar{h}_2^{e,m}$  for pentane and pentene-1 in acetonitrile to be constant over the range from 0° to 45°. The retention volume data for  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  were unfortunately too scattered to allow reliable estimation of the relevant enthalpies for these compounds.

Excess partial molar entropies were also derived from the literature data cited above, for comparison with the values in Table IV. The literature values and those from LLC are, respectively, for benzene, 0.05 e.u. and 0.78 e.u.; toluene, -0.51 and 1.70 e.u.;  $\text{CCl}_4$ , -0.60 and -0.63 e.u.; *n*-pentane, 1.61 and 1.84 e.u.; and pentene-1, 1.01 and 1.57 e.u. Again, except for toluene, the agreement is satisfactory.

A reasonably linear relationship exists between the entropy and enthalpy values in Table IV, as shown in Fig. 1. This is not surprising, since entropy requirements accompanying energetic interactions are found in a variety of interacting or reacting systems. The data for the saturated hydrocarbons fall along one line, and that for the aromatics along another. The displacement of the aromatic line to higher excess entropy values relative to that for the saturates reflects the requirement of a particular orientation of the aromatic hydrocarbon with respect to the acetonitrile molecule before the presumed interaction of the aromatic ring electrons with the dipole of the nitrile group can occur. Because of the participation of interfacial effects in the case of the paraffins and naphthenes, the significance of the near-linearity is not clear.

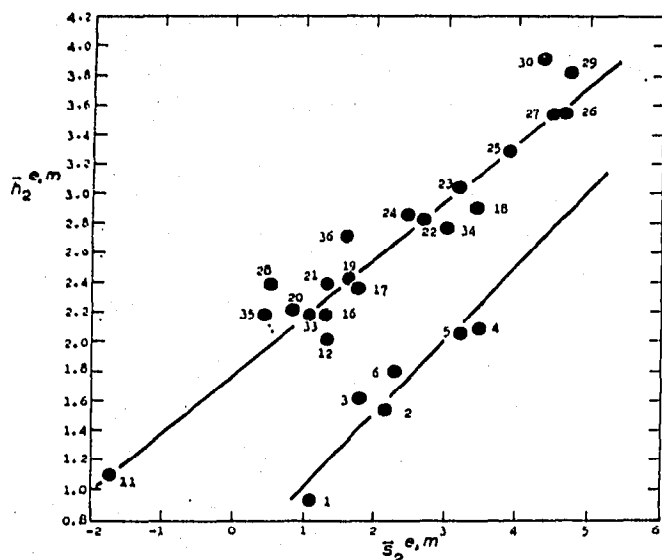


Fig. 1. Entropy-enthalpy relationship for hydrocarbons in acetonitrile. Numbers on the figure refer to numbered compounds in Tables IV and V. Units of  $\bar{h}_2^{e,m}$  are kcal mole<sup>-1</sup>; units of  $\bar{s}_2^{e,m}$  are cal mole<sup>-1</sup> deg<sup>-1</sup>.

#### Charge-transfer complexation

The formation of charge-transfer complexes has often been invoked (and often uncritically<sup>25</sup>) as an explanation for the greater solubility of aromatic organic compounds compared with saturated compounds in solvents with electron-acceptor groups. For example, COOPER *et al.*<sup>26</sup> have recently studied a variety of electron-donor-acceptor systems by GLC, correlating the chromatographic retention of aromatic compounds with spectroscopic measurements of complex stability constants. The traditionally difficult separation of *m*- and *p*-xylene and other *m*- and *p*-substituted aromatics has inspired most of these investigations. It is always found that with chromatographic solvents considered to enter into charge-transfer complexation with aromatic compounds, the usual GLC elution order according to vapor pressure (*p*- before *m*-xylene) is reversed; in other words, the solute activity coefficients in these solvents are in the order *o*- < *p*- < *m*-xylene (*e.g.*, 27).

In the case of acetonitrile, ORYE AND PRAUSNITZ<sup>10</sup> have tentatively suggested the existence of a charge-transfer-type interaction in solutions of aromatic hydrocarbons in acetonitrile on the basis of the excess entropy and excess volume of mixing. Direct spectral evidence, however, could not be obtained because of experimental difficulties. While there are certainly specific interactions in aromatic hydrocarbon/acetonitrile solutions, there is no firm evidence for charge-transfer complex formation. The LLC results for the xylenes are in accord with this; there is no remarkable difference in the activity coefficients of *m*- and *p*-xylene.

#### Analytical utility of the acetonitrile/squalane system

Although all of the solutes used in this investigation can and would be analyzed by GLC, some conclusions can be drawn by extrapolation to solute molecular weights more properly in the domain of LLC. The system should serve as a general purpose solvent pair for hydrocarbon analysis, if efficient columns are constructed. No attempt was made in this work to optimize column parameters with regard to column efficiency;

so the discussion here must be restricted to consideration of relative retentions, which are, of course, independent of column efficiency.

The elution order is aromatics < olefins < paraffins and naphthenes, opposite to that found with polar stationary phases or common adsorbents. For the compounds listed in Table II, introduction of one double bond reduces retention relative to a paraffin by the equivalent of about two carbon atoms; two double bonds by about five carbon atoms; and *n*-alkyl benzenes have retention volumes equivalent to paraffins with eight fewer carbon atoms. If the linear plots of  $\log V_g$  vs. carbon number are extrapolated into the  $C_{20}$  range, the lines for the paraffins, olefins, and *n*-alkyl aromatics remain parallel, indicating the same hydrocarbon group separation ability at higher molecular weights. However, the absolute retention volumes become quite large; the  $V_g$  values for *n*-eicosane, eicosene-1, and *n*-tetradecyl benzene are about 380, 205, and 35 c.c./g, respectively, which for a column containing 5 g ( $\sim 17$  wt.%) of squalane and a flow rate of acetonitrile of 5 c.c./min, would correspond to retention times of about 6.3, 3.4, and 0.6 h, respectively. Elution time could be decreased, of course, by reducing the liquid loading.

An indication of the ability of the system to separate isomers is given by comparison of the retentions of 2-methyl paraffins relative to their normal isomers. The relative retentions,  $\alpha$ , increase slightly for 2-methyl butane/*n*-pentane ( $\alpha = 1.048$ ), 2-methyl pentane/*n*-hexane ( $\alpha = 1.065$ ), and 2-methyl hexane/*n*-heptane ( $\alpha = 1.085$ ). If the trend continues to higher carbon numbers, good separations will be attainable within a given carbon number. A value of  $\alpha = 1.05$  corresponds to a required number of theoretical plates roughly equal to 7000, or for a 10 ft. column, an HETP of about 0.5 mm. This degree of efficiency should be achievable if the operating conditions are optimized.

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