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A STUDY ON THE RELIABILITY OF THE EXCESS ENTHALPIES CALCULATED FROM GAS-LIQUID CHROMATOGRAPHIC RETENTION DATA

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A statistical analysis was performed on the activity coefficients and partial molar excess enthalpies determined from gas chromatographic retention data measured on a high-precision gas chromatograph. Systems displaying slight, medium and high dependences on temperature were studied. The excess enthalpy data obtained from gas chromatographic measurements were of a precision comparable with that of the corresponding data measured calorimetrically for values in excess of 500 cal/mole. With the slightly temperature-dependent systems (athermal solutions), the non-ideal effects that occur in the condensed phase appear to be obscured by gas-phase imperfection effects.

INTRODUCTION

The results given in several papers¹⁻⁶ have shown that the typical error in the partial molar excess enthalpy (of mixing) determined by calorimetry in systems with finite solute concentrations amounts to about 2-3%. Gas chromatography (GC) offers the potentiality of determining the excess thermodynamic properties at extreme dilutions of the solute.

Despite the doubts that have been expressed^{7,8} as to the precision of GC measurements necessary to obtain reliable excess thermodynamic data, several attempts have been made to determine excess enthalpies from GC retention data. CLARK AND SCHMIDT⁹ determined the excess enthalpy (ΔH^E) for benzene in diphenyl and in the isomers of terphenyl. They claimed that there was good agreement between these ΔH^E values and those measured calorimetrically, but the error of the chromatographic measurement was not quoted. GAINES AND YOUNG¹⁰ calculated ΔH^E for benzene in aliphatic hydrocarbons with a precision of 7-11%, the ΔH^E values measured being in the range 640-790 cal/mole. One of the values measured was compared with the corresponding one obtained calorimetrically; agreement was found within the limits of experimental error. CRUICKSHANK *et al.*¹¹ measured ΔH^E for fluorinated benzenes in octadecane; the ΔH^E values and their errors were in the ranges 840-970 cal/mole and 4-6%, respectively.

The aim of the present paper was to establish the conditions under which the reliability of ΔH^E values calculated from GC retention data might approach that of calorimetric measurements. The study was based on statistical analysis. The theoretical predictions are compared with the results obtained experimentally by using a gas chromatograph designed especially for high-precision measurements¹².

THEORETICAL

For the physico-chemical interpretation of GC retention data, a most convenient retention parameter to use is the specific retention volume¹³, V_g , which is related to the sorption-equilibrium characteristics by the equation^{14,15}:

$$V_g = \frac{273.16 R}{M_L p^\circ \gamma^\infty(o)} \exp \left[\frac{(2B_{12} - B_{22} - \bar{v}_1^\infty) \bar{p}}{RT} \right] \exp \left[- \frac{(B_{11} - v_1^\circ) p^\circ}{RT} \right] \quad (1)$$

where R is the gas constant, M_L is the molecular weight of the stationary phase, p° is the saturated vapour pressure of pure solute at the temperature of the column, $\gamma^\infty(o)$ is the Raoult-law activity coefficient of the solute at infinite dilution in the stationary phase and at the temperature of the column (T) and zero carrier gas pressure, \bar{p} is the mean absolute column pressure, \bar{v}_1^∞ and v_1° are the partial molar volume of the solute at infinite dilution in the stationary phase and the molar volume of pure solute, respectively, at the temperature of the column, and B_{11} , B_{22} and B_{12} are the second virial coefficients of pure solute vapour, carrier gas and the mixture, respectively, at the temperature of the column.

Since the specific retention volume is always reduced to 0° , it is very suitable for describing the temperature dependence of retention. The temperature dependence of retention is not modified by that of the carrier gas when expressed as the specific retention volume, which is not the case with, e.g., the net retention volume or the conventionally defined partition coefficient.

Eqn. 1 may be rearranged to read:

$$\begin{aligned} \ln \gamma^\infty(o) &= \ln \left(\frac{273.16 R}{M_L p^\circ V_g} \right) + \frac{(2B_{12} - B_{22} - \bar{v}_1^\infty) \bar{p}}{RT} - \frac{(B_{11} - v_1^\circ) p^\circ}{RT} \\ &= \ln \gamma' + z \end{aligned} \quad (2)$$

Within narrow temperature limits, $\ln \gamma^\infty(o)$ is a linear function of $1/T$, and the slope of the line is related to the excess enthalpy by the equation¹⁴:

$$\frac{d(\ln \gamma^\infty(o))}{d(1/T)} = \frac{\Delta H^E}{R} \quad (3)$$

Provided the measurements contain only random errors, the use of the conventional rules of statistics permits the estimation of the precision of ΔH^E from that of the individual variables. The respective relations are as follows:

$$S_{\Delta H} = \left[\left(\frac{\partial \Delta H^E}{\partial \gamma} \right)^2 S_{\gamma^2} + \left(\frac{\partial \Delta H^E}{\partial T} \right)^2 S_{T^2} \right]^{\frac{1}{2}} \quad (4)$$

$$S_{\gamma'} = \left[\left(\frac{\partial \gamma'}{\partial p^\circ} \right)^2 S_{p^\circ}^2 + \left(\frac{\partial \gamma'}{\partial V_g} \right)^2 S_{V_g}^2 \right]^{\frac{1}{2}} \quad (5)$$

$$S_{\gamma} = \left(e^{2z} S_{\gamma'}^2 + \gamma'^2 e^{2z} S_z^2 \right)^{\frac{1}{2}} \quad (6)$$

where each S denotes an estimation of standard deviation and γ represents $\gamma^{\infty}(0)$.

The above relations were used to calculate the errors in ΔH^E and γ for a system that showed a slight temperature dependence (hexane-squalane) and for a strongly

TABLE I

THEORETICALLY ESTIMATED VALUES OF THE STANDARD DEVIATIONS AND COEFFICIENTS OF VARIATION (V) FOR THE HEXANE-SQUALANE SYSTEM

Variable	Dimension	Value	S	V (%)
T	°K	303-338	0.06	0.02 ^a
p°	torr	189.9-675.4	0.025	0.006 ^a
γ		0.6531 ^{b,c}	0.00115	0.18
ΔH^E	cal/mole	-96.5 ^c	15	15

^a Mean value.

^b Measured at 30°C.

^c Determined experimentally in this work.

TABLE II

THEORETICALLY ESTIMATED VALUES OF THE STANDARD DEVIATIONS AND COEFFICIENTS OF VARIATION (V) FOR THE NONANE- α -NAPHTHYLAMINE SYSTEM

Variable	Dimension	Value	S	V (%)
T	°K	338.7-354.2	0.015 ^d	0.004 ^a
p°	torr	38.594-77.21	0.02	0.03 ^a
γ		20.91 ^{b,c}	0.051	0.24
ΔH^E	cal/mole	1450 ^c	57.8	3.9

^a Mean value.

^b Measured at 65.5°C.

^c D. H. DESTY AND W. T. SWANTON, *J. Phys. Chem.*, 65 (1961) 766.

^d Measured with a Beckman thermometer.

temperature-dependent system (nonane - α -naphthylamine). If values of 0.284 ml/g and 0.06°K (or 0.015°K) for S_{V_g} and S_T , respectively, are used, as ascertained in a previous work¹², taking $S_{p^{\circ}}$ to be equal to about 0.025 torr¹⁰, and having chosen a value of 0.0015 for S_z , the data summarized in Tables I and II are obtained. For the variable z a value of -0.003 was used, derived from the data given by EVERETT AND STODDART¹⁵ for hexane in nitrogen.

EXPERIMENTAL

The data necessary for determining ΔH^E were measured on a home-made gas chromatograph designed for the high-precision measurement of specific retention volumes. The construction and performance of the apparatus have been described in a previous paper¹².

The following systems were studied: hexane-hexadecane, benzene-hexadecane,

pentane-squalane, hexane-squalane, benzene-squalane and nonane- α -naphthylamine. The hexane and squalane were obtained from Carlo Erba, Italy, and BDH Ltd., Great Britain, respectively, and the α -naphthylamine was obtained from Lachema, N.E., Czechoslovakia. The solutes were of analytical-reagent grade, obtained from Lachema. In all cases, packings with 25% w/w of the stationary phase on Chromosorb W, 60-80 mesh (Carlo Erba) were used. The measurements were carried out with stainless-steel columns of length 190 cm and I.D. 4 mm.

The hexadecane column was filled with 10.8373 g of the packing (2.707 g of hexadecane) and operated at a constant column inlet excess pressure of 380 torr. The hexane samples were chromatographed at three temperatures and those of benzene at seven temperatures in the range 30-60°. The carrier gas flow-rate was varied within the range 0.41-0.42 ml/sec, depending on the column temperature, as measured at 30° and at the column inlet pressure.

The squalane column contained 13.5509 g of the packing (3.4817 g of squalane) and was operated at a column inlet excess pressure of 650 torr. The solutes were chromatographed at seven temperatures in the range 30-65°, and the carrier gas flow-rate was varied within the range 0.33-0.41 ml/sec.

The α -naphthylamine column contained 10.8760 g of the packing (2.7229 g of α -naphthylamine) and was operated at an inlet excess pressure of 500 torr. The nonane samples were chromatographed at nine temperatures in the range 50-60°, and the carrier gas flow-rate was about 0.42 ml/sec.

In order to determine the true amount of the stationary liquid in the column, samples of the column packings were extracted and the extracts weighed after the extractant was evaporated.

In the case of systems containing hexadecane and squalane, the temperature was measured with a mercury thermometer graduated with 0.1° divisions. For the nonane- α -naphthylamine system, a Beckman thermometer (graduated with 0.01° divisions) was used.

RESULTS

In all the above cases, 15-20 measurements were carried out at each temperature, and then the γ and ΔH^E values were calculated and the results were processed statistically. The vapour pressure data were calculated by the Antoine equation,

TABLE III

COMPARISON OF THE THEORETICALLY PREDICTED AND ACTUAL ERRORS OF THE γ AND ΔH^E (CAL/MOLE) VALUES FOR THE SYSTEMS STUDIED

Property	System	Value determined chromatographically	V (%)	
			Theoretical	Experimental
γ	Hydrocarbon-squalane	0.6291-0.7017	0.18	0.21
γ	Nonane- α -naphthylamine	20.94-22.43	0.24	0.23
ΔH^E	Pentane-squalane	-139	15	4.3
ΔH^E	Hexane-squalane	-96	15	4.3
ΔH^E	Benzene-squalane	515.7	—	1.0
ΔH^E	Nonane- α -naphthylamine	1580	3.9	1.6

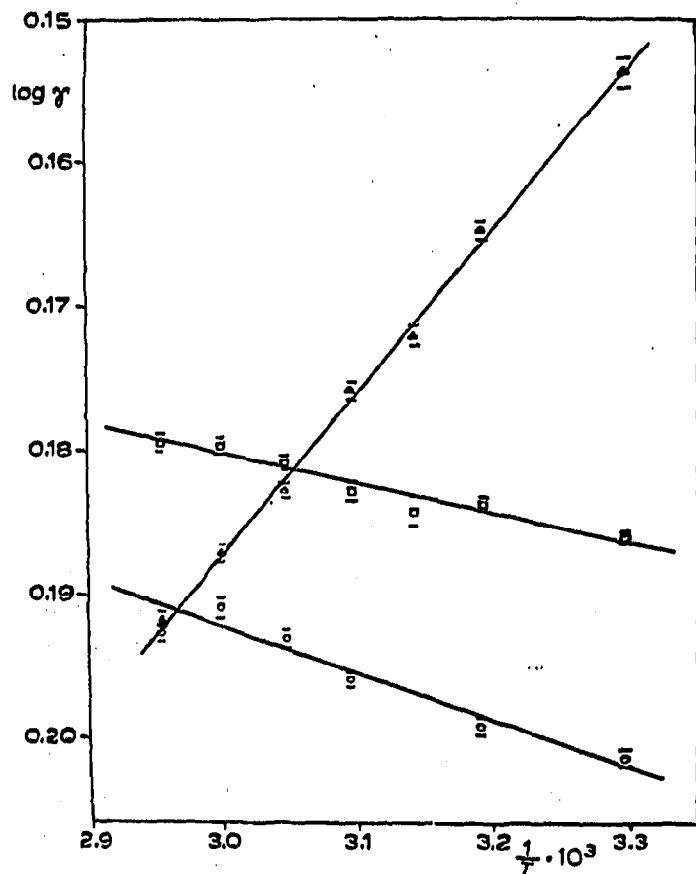


Fig. 1. Plot of the logarithms of the activity coefficients of *n*-pentane, *n*-hexane and benzene in squalane versus the inverse of the absolute temperature. ○, *n*-pentane; □, *n*-hexane; △, benzene.

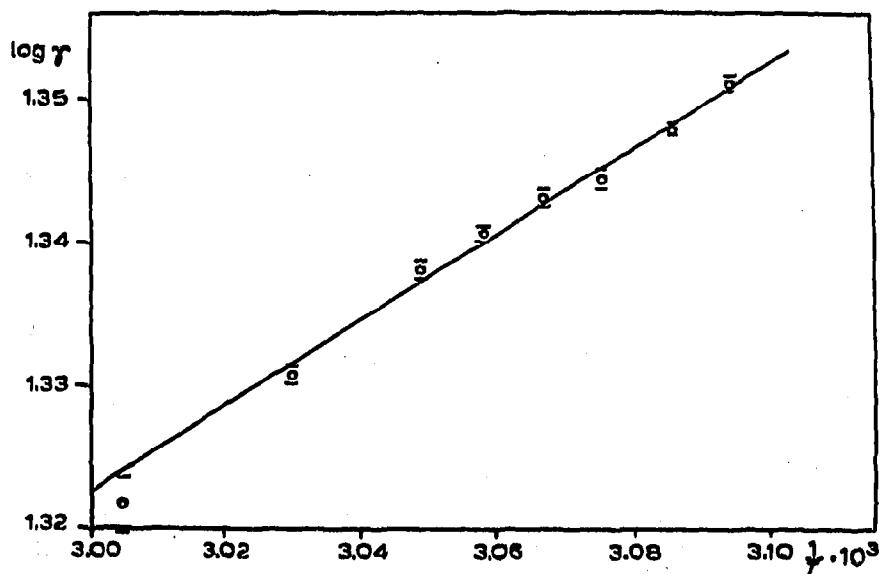


Fig. 2. Plot of the logarithm of the activity coefficients of *n*-nonane in α -naphthylamine versus the inverse of the absolute temperature.

TABLE IV

COMPARISON OF THE CHROMATOGRAPHICALLY DETERMINED γ VALUES FOR THE HEXANE-HEXADECANE AND BENZENE-HEXADECANE SYSTEMS WITH THE γ VALUES OBTAINED BY STATIC MEASUREMENTS

Solute	T (°K)	γ	
		Chromatographic	Static
Hexane	313.16	0.9100	0.8995
	323.16	0.9016	0.8974
	333.16	0.9099	0.8974
Benzene	303.16	1.007	1.006
	323.16	0.9886	0.9954

$\log p^\circ = A - B/(C + t)$, the constants A , B and C being taken from the paper by WILLINGHAM *et al.*¹⁰. The second virial coefficients for the hydrocarbons and for the carrier gas were calculated by the Berthelot relation¹⁷ and the BEATTIE-BRIDGEMAN equation¹⁸, respectively. The second cross-term virial coefficients were obtained from the relations derived from the theorem of corresponding states¹⁷. The molar volumes of the pure solutes were estimated by use of the temperature dependences of density¹⁹, and the approximation $\bar{v}^\infty \simeq v^\circ$ was used in the calculation.

In Table III, the errors in the γ and ΔH^E values obtained experimentally are compared with those predicted theoretically. The actual errors in the ΔH^E values for all the systems were evaluated by processing about 120 measurements by the least-squares method in each case. Figs. 1 and 2 show the temperature dependences of the activity coefficients in systems having different dependences on temperature. Each point in the figures represents an average value from 15–20 determinations, the bars designating the confidence intervals for the 95% level. The standard deviation of $\log \gamma$, relative to the regression line, was about 0.001.

A comparison of the γ values for hexane and benzene in hexadecane obtained chromatographically and by a static method^{20,21} is presented in Table IV, while Table V gives similar data for pentane, hexane and benzene in squalane.

DISCUSSION AND CONCLUSIONS

The data in Table III indicate that there is no significant difference between the predicted and the actual precision of the activity coefficients, while for the ΔH^E

TABLE V

COMPARISON OF THE ACTIVITY COEFFICIENTS CALCULATED FROM GC DATA WITH THOSE MEASURED BY A STATIC METHOD FOR PENTANE, HEXANE AND BENZENE IN SQUALANE

Hydrocarbon	T (°K)	γ	
		Chromatographic	Static ^a
Pentane	303.14	0.6575	0.6398
Hexane	303.14	0.6813	0.6487
Benzene	303.14	0.7334	0.6967

^a A. J. ASHWORTH AND D. H. EVERETT, *Trans. Faraday Soc.*, 56 (1960) 1609.

values the actual error is appreciably lower than the predicted error. It may be inferred from the ΔH^E values that the precision of the GC determination of the excess enthalpy is comparable with that of the calorimetric measurement if the ΔH^E value measured exceeds 500 cal/mole.

A more difficult question is the accuracy of the γ and ΔH^E values, which is closely associated with the problems of the purity of the stationary phase and gas-phase imperfection effects. Thus, it was ascertained by GC analysis (Hewlett-Packard 402 gas chromatograph; 150-cm long glass column packed with 3.8% w/w of UCCW 95-HP on Chromosorb G, AW, DMCS; flame-ionization detector) of the stationary phases used in this work that the squalane (chromatographed at 200°) contained about 6% w/w of other hydrocarbons (C_{17} – C_{31}), whereas the content of impurities in the hexadecane (chromatographed at 150°) was only about 1% w/w. This probably explains why poorer agreement has been found between the activity coefficients calculated from GC data and those obtained by static measurements for the hydrocarbon–squalane system compared with the analogous situation with the hydrocarbon–hexadecane systems (*cf.* the data in Tables IV and V, respectively).

Owing to the insignificant extent of the solute–sorbent interactions in the condensed phase with hydrocarbon–hydrocarbon systems, it can be expected that the ΔH^E values will not be affected appreciably by hydrocarbon impurities in a hydrocarbon stationary phase. This assumption obviously cannot be applied to the nonane– α -naphthylamine system.

In the case of the gas-phase imperfection effects, the differences between the activity coefficients calculated by using the whole of eqn. 2 and those obtained by using only the first term of the right-hand side of eqn. 2 are about 0.5% for the hydrocarbon–hydrocarbon systems and 3.9% for the nonane– α -naphthylamine system, expressed relative to the non-corrected γ values under the conditions used. However, the ΔH^E values for the systems with low temperature dependence are affected so greatly by the corrections for the gas-phase imperfections that positive ΔH^E values are obtained from non-corrected retention data while negative values of about the same magnitude are obtained from the corrected data; ΔH^E values of +97.7 cal/mole and –96.5 cal/mole, respectively, were obtained for the hexane–squalane system. As all the existing methods for gas-phase imperfection corrections are more or less approximate, the reliability of low ΔH^E values determined from GC data is questionable. A substantial part of the ΔH^E value obtained may actually be due to the error of the corrections for the gas-phase imperfection in these cases. Theoretically, the ΔH^E value associated with hydrocarbon–hydrocarbon systems (athermal solutions) should be close to zero.

With the nonane– α -naphthylamine system, this situation is much more favourable. The pronounced condensed-phase non-ideal effects manifest themselves in a rather high ΔH^E value. In this case, the corrections for the gas-phase imperfection amount to about 4% of the non-corrected ΔH^E value, so that the error of the correction is relatively unimportant.

The accuracy of the ΔH^E values calculated from GC data for moderately temperature-dependent systems may be appreciated by comparing ΔH^E obtained chromatographically for the benzene–hexadecane system in this work with ΔH^E measured calorimetrically for the same system by LUNDBERG²² and extrapolated to an infinite dilution by GAINEY AND YOUNG¹⁰; ΔH^E values of 754 ± 37 cal/mole at

40–60° and 560 ± 95 cal/mole at 50° were found in the above two cases, respectively. It is difficult to decide which of these two values is the more accurate or to define the cause of the difference between them. In the GC method, the most questionable factor is the correction for gas-phase imperfection. The effects on retention of the surface activity of the support and of the deviations from sorption equilibrium owing to the non-stationary character of the GC process were believed to have been eliminated by having used the packings with high loadings of the stationary liquids and by chromatographing the solutes at relatively low carrier-gas flow-rates. With the calorimetric ΔH^E values, on the other hand, the result may be modified by the errors incidental to the extrapolation.

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