

CHROM. 15,176

EVALUATION OF THE EFFECT OF LIQUID-SURFACE ADSORPTION ON ENTHALPIES OF SOLUTION DETERMINED USING GAS-LIQUID CHROMATOGRAPHY

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(First received May 17th, 1982; revised manuscript received July 7th, 1982)

SUMMARY

Enthalpies of solution of *n*-hexane, carbon tetrachloride, benzene, and acetone in benzylacetone at 298.15°K were obtained using gas-liquid chromatography. Results for the first three solutes were compared with values based on calorimetric heats of mixing at infinite dilution, and discrepancies were observed whose magnitudes correlate qualitatively with the infinite dilution Raoult's law activity coefficients of the solutes in question. The discrepancies are believed to be the result of significant contributions from liquid-surface adsorption to the observed retention volumes. In the worst case (hexane), the error in the derived enthalpy is 0.3 kcal/mol.

INTRODUCTION

A recent study in this laboratory¹ showed that infinite dilution enthalpies of solution for representative alkane systems can be obtained using gas-liquid chromatography (GLC) with an accuracy that approaches that of calorimetry. For a total of fourteen comparisons, the average value of the absolute difference between the two methods was 15 cal/mol; the greatest difference was 31 cal/mol.

When polar systems are studied using GLC, two factors are expected to affect the accuracy of thermodynamic results: (a) the longer range of polar interactions lowers the upper concentration limit for Henry's law behavior by the solute, and (b) solute adsorption at the gas-liquid interface² is likely to contribute to the retention of solute in the column. The latter effect is in general small relative to the bulk solution contribution to retention, and its influence decreases as the sample size of the injected solute increases³. However, in order to attain the Henry's law concentration range for polar solutes, small sample sizes are necessary, and the likelihood of interference from the interfacial effect becomes a matter of concern.

When the Henry's law region for solution is exceeded, non-linearity in the solute partial pressure isotherm results in either slower or faster travel of the central portion of the solute peak (relative to the front and rear edges) as it traverses the column, depending on the sign of its curvature. Thus, retention times measured to the peak maximum may increase or decrease as larger sample sizes are used. Interfacial

effects, when significant, most commonly lead to longer retention times than in their absence.

Methods have been developed to evaluate and eliminate the contribution of interfacial effects to retention⁴, and to obtain fully corrected bulk solution thermodynamic data. They generally involve using several columns of different weight loadings (*i.e.*, different surface to volume ratios for the solvent) and are rather time consuming. Our goal in the present study was to use a single GLC column for each system, and estimate the magnitude of the error introduced into the derived enthalpy of solution by the above-mentioned characteristics of polar systems.

Calorimetric enthalpies of mixing for *n*-hexane (C_6), carbon tetrachloride (CCl_4), and benzene (Bz) with benzylacetone (BA) have been published by Grolier *et al.*⁵ Their results allow calculation of enthalpies of mixing at infinite dilution of the former three components, which, combined with corresponding vaporization enthalpies, provide the values that should be observed in the GLC experiment when the latter component is used as the liquid phase. (Because of the low partial pressures of solute in helium carrier gas in these experiments, we have used the enthalpy of vaporization to the ideal gas state, ΔH^0 , in adjusting the GLC enthalpies to the calorimetric mixing values, as in ref. 1) Acetone (Ac) was included in the study even though no calorimetric data are available for comparison, in order to examine the behavior of an even more polar system.

Because the calorimetric results are not used directly in our comparison, but are extrapolated to infinite dilution, we should attempt a quantitative estimate of the reliability of what we refer to as the calorimetric enthalpy of mixing at infinite dilution, ΔH_m^∞ . Grolier *et al.*⁵ provide analytical expressions for the excess enthalpy as a function of composition for the systems they studied, from which it can be shown¹ that

$$\Delta H_m^\infty = \sum_j (\pm 1)^{j-1} C_j$$

where the + sign refers to the C_6 results, and the - sign, to those for CCl_4 and Bz, and the constants C_j are presented in their Table 3. The standard deviation in ΔH_m^∞ , δ_m , can thus be expressed in terms of the standard deviations in the C_j :

$$\delta_m = (\sum_j \delta_{c_j}^2)^{\frac{1}{2}}$$

We have refitted the data of Grolier *et al.*⁵ to their equations using the rigorous method described by Wentworth⁶, in order to be able to evaluate the $\delta_{c_j}^2$ by propagation of error analysis. The standard deviation in mole fraction was taken as 0.00005, and that in excess enthalpy was taken from their Table 3: C_6 , 5.5; CCl_4 , 3.5; and Bz, 1.5 J/mol. The values of the C_j we obtained do not differ significantly from those in the original work, and the resulting estimated standard deviations in ΔH_m^∞ are included below in our Table II.

EXPERIMENTAL AND RESULTS

A general discussion of the experimental approach is contained in ref. 1 and

references therein. The only new aspect in the present study is the dependence of retention time (and calculated specific retention volumes, V_g^0) on sample size. BA was used as received from Aldrich Chemical Co., and the solutes were used as received from well-established chemical suppliers.

All columns used in this study contained nominally 14% (w/w) liquid phase. Retention times were measured at four temperatures between 287 and 298°K after which the first (lowest temperature) run was repeated to check for solvent bleeding. Typical percentage losses of BA during a run are: C₆, 0.2%; CCl₄, 2%; Bz, 4%; and Ac, 1%. The percentage loss is of course inversely related to the length of the column for a given time interval; hence the correlation of extent of bleeding with V_g^0 (shorter columns were used for solutes with longer retention times). Corrections were applied as in ref. 1.

The same batch of packing was used to prepare all columns used in the present study. After standing in the laboratory for some weeks, the flask in which the packing was stored developed a fine film of liquid BA on its walls. In order to ensure accurate values of V_g^0 , three samples of packing were taken simultaneously from the flask, two of which were subjected to ignition, and the third was used to make a column in the usual way. Retention times were measured for each solute at the lowest temperature used in the study, in duplicate cycles to check for bleeding during this "calibration" experiment. The latter amounted to 0.16% per cycle, and appropriate adjustment was made to each retention time. A blank was included in the procedure for ignition of the packing, to account for the loss of silanizing agent, and the two trials agreed to within 0.01%. Calculation of specific retention volumes from measured retention times consequently used a weight loading of BA which produced accord with the "calibration" values at the lowest temperature of a given experiment. (Differences in V_g^0 values at 25°C in Table I for duplicate experiments are the result of slightly different derived enthalpies of solution for the two runs.) The actual weight loading of BA never fell below 11% in any of the experiments.

Before measuring enthalpies of solution, an examination of the dependence of retention time on sample size was made for each solute. All four displayed increasing retention times when sufficiently large samples were used, indicating downward curvature in their $p(x)$ solution isotherms when the Henry's law region is exceeded (anti-Langmuir behavior). As sample size was decreased, both Bz and Ac retention times went through minima and abrupt rises below about 2 μ mol, presumably due to interfacial adsorption contributions to retention. For Bz, the rise amounted to about 0.5% of the minimum value; for Ac, about 2%. For CCl₄ and C₆, no clear minima were observed. The retention times for the former seemed to be decreasing slightly ($\approx 0.1\%$ per micromole injected) for the smallest sample sizes used (0.05 μ mol), and the limited sensitivity of the thermal conductivity detector prevented finding a region below which Henry's law behavior could be definitely established. In the case of C₆, sample sizes below 1 μ mol produced apparently constant retention times, but considerable scatter of the data again disallows an unequivocal statement that the sample obeyed Henry's law under the conditions of the experiment.

As a practical approach to taking into account the variability of retention time with sample size for Bz and Ac, it was decided to use values characteristic of the minima discussed above when evaluating their enthalpies of solution. It happens that the asymmetries of the elution peaks go through zero and change sign in the region of the minima for these two solutes (the Henry's law region for interfacial adsorption is

much more narrow than that for solution, and the adsorption isotherms are curved oppositely (Langmuir behavior) from the solution isotherms), making identification of this condition possible during each individual run.

The observation of Henry's law behavior for C_6 and CCl_4 would not rule out the possibility of an adsorption contribution to retention for these solutes in any case. It would imply that the adsorption contribution is either (a) negligible, or (b) occurring in its own Henry's law region. In the latter case, if bulk solubility is low, a significant surface effect should be anticipated. For both CCl_4 and C_6 , sample sizes of $\approx 1 \mu\text{mol}$ were used, allowing as close an approach to the Henry's law region(s) as is consistent with good reproducibility using the present equipment.

Averaged results of two experiments for each solute are presented in Table I. No corrections have been made for surface adsorption. Enthalpies of mixing at infinite dilution for comparison with calorimetrically determined values are evaluated by adding the GLC-determined enthalpy to the enthalpy of vaporization of solute to the ideal gas state. The comparison appears in Table II. It is to be emphasized that evaluation of the infinite dilution enthalpy of mixing is *not* a goal of the GLC approach to studying the thermodynamics of solution; it is used simply as a more stringent basis for comparison than would result from conversion of the calorimetric enthalpies of mixing to enthalpies of solution from the gas phase¹.

DISCUSSION

The agreement between the GLC and calorimetrically determined enthalpies for these polar systems is definitely poorer than for the alkane systems studied pre-

TABLE I
SUMMARY OF GLC RESULTS AT 25°C

Enthalpy changes (in kcal/mol) were adjusted from midpoint of temperature range to 25°C by reducing their magnitude by 0.055 kcal/mol.

Solute	V_0^0	$-\Delta H^0$	$10^2 \Delta V_0^0/V_0^0$
C_6	128.1	6.14	0.08
	127.8	6.18	0.04
CCl_4	652.7	7.56	0.08
	652.8	7.56	0.07
Bz	1141	8.07	0.12
	1125	8.13	0.04
Ac	455.1	7.48	0.13
	454.7	7.50	0.03

TABLE II
COMPARISON OF ENTHALPIES OF MIXING FROM GLC AND FROM CALORIMETRY

Solute	$\Delta H_{1,2}^0$	$-\Delta H^0$	$\Delta H_{\text{mix, GLC}}$	$\Delta H_{\text{mix, cal}}$	Diff.	\bar{V}_{298}^0
C_6	7.58*	6.16	1.42 ± 0.02	1.16 ± 0.18	0.26	6.0
CCl_4	7.79**	7.56	0.23	0.05 ± 0.02	0.18	1.6
Bz	8.10***	8.10	0.00 ± 0.03	0.00 ± 0.01	—	1.1
Ac	7.48 [†]	7.49	-0.01 ± 0.01	—	—	1.1

* Ref. 1.

** Ref. 7.

*** Ref. 8. Second virial coefficient taken from ref. 9.

[†] Ref. 10.

viously¹. Bleeding of the solvent was a more serious problem in the present study, and it is likely that this factor is responsible for its lower precision. The differences in Table II for C₆ and CCl₄, however, are greater than can be accounted for by this imprecision, and must stem from another cause.

The most likely explanation for a discrepancy between the methods, in light of the good agreement demonstrated for alkane systems, is a contribution from interfacial adsorption in the GLC-determined enthalpies. Martire¹¹ has suggested that the contribution to retention due to adsorption at the carrier gas-liquid interface increases with the solute activity coefficient (relative to Raoult's law behavior). When the latter are estimated (see last column in Table II) from the data in Table I, it is apparent that the discrepancies in enthalpies correlate qualitatively with the non-ideality of the solutions formed, in support of this explanation.

If in fact the results for C₆ are characteristic of Henry's law for both solution and adsorption, the discrepancy between the GLC-derived and the "true" enthalpy of mixing should be at its maximum. The rôle of the interfacial effect increases relative to bulk solution with decreasing sample size only until the adsorption achieves its Henry's law region; smaller samples reflect a constant contribution from both mechanisms.

The results of Martire *et al.*¹² are relevant in this connection. They examined, under static conditions, the relative importance of solution and liquid surface adsorption for the solutes cyclohexane (c-C₆) and benzene in thiodipropionitrile (TDPN). While the latter is more polar than BA, their results might be expected to provide qualitative information concerning the systems C₆ and Bz in BA.

Using their partition coefficients for solution and adsorption, and the information in their plots of surface mole fraction vs. bulk mole fraction, it is possible to correlate partial pressure of solute in the GLC column with surface adsorption. It turns out that the Henry's law region for adsorption of c-C₆ extends to partial pressures of *ca.* 10 Torr, while that for adsorption of Bz extends to only *ca.* 2 Torr. Furthermore, at partial pressures of *ca.* 40 Torr, Bz adsorption deviates from Henry's Law by 100% c-C₆ by only 10%.

Thus the likelihood that C₆ obeys Henry's law for both solution and adsorption under the conditions of our experiment, while Bz exceeds it for the latter, is made quite plausible. As explained above, this would imply that the discrepancy for hexane is at its maximum, and that the error in the GLC-determined enthalpy of solution for a non-polar solute in a polar solvent should in general not exceed 0.3 kcal/mol, as long as γ^{∞} does not exceed 6, and a solvent weight loading greater than about 10% is used.

The good agreement for Bz in Table II may be fortuitous. However, its much greater solubility in BA relative to that of C₆ (by a factor of 9 at 25°C) relegates the adsorption contribution to a much smaller fraction of the total retention mechanism for this solute. Thus, even though the Henry's law region is exceeded, it is not unreasonable to conclude that the influence of the adsorption effect on the GLC-derived enthalpy change is negligible.

The results for CCl₄ indicate that the activity coefficient need not be extremely different from unity in order to cause a measurable effect on the GLC-derived enthalpy change. Because of the very slight dependence of retention time on sample size for this solute, it is likely that the observed discrepancy is near the maximum that could be observed due to the adsorption effect for this system, as in the case of C₆.

Unfortunately, we have no calorimetric results for Ac in BA, precluding an evaluation of the adsorption effect on its GLC-derived enthalpy of solution. For the

other three solutes, however, we can make the following observations. (1) Use of sample sizes at the minimum in the retention time-sample size plots for Bz eliminates, within the accuracy limits of this study, the influence of adsorption on its derived enthalpy of solution. (2) Use of sample sizes in the horizontal regions of those plots for C_6 and CCl_2 includes the rôle of adsorption in the GLC calculations, and it is not negligible. Plotting $\ln V_g^0$ vs. $1/T$ in order to estimate the enthalpy change when such data are used is questionable at best. The fact that the "enthalpy changes" so derived (Table II) are reasonably close to those predicted using the calorimetric results implies that the adsorption contribution to V_g^0 has only a minor effect on its temperature dependence.

It is worth noting that the sense of the discrepancy between the two sets of results is in the direction to be expected if the enthalpy change for the adsorption process is less negative than that for the solution process, as is surely the case.

In order to examine the surface effects in more detail, retention times for the solutes in question would have to be determined for several columns of various weight loadings of BA, according to the method of Conder.⁴ Because of the extent of solvent bleeding in the present study we believe that such effects would be more profitably studied by using systems involving a much less volatile liquid phase.

In conclusion, it should be emphasized that in the worst case studied (*n*-hexane, with $\gamma^\infty = 6$), the error introduced by surface effects is but 0.3 kcal/mol, or 4% of the enthalpy of solution. Thus when only rough values are required, the surface effects may be considered negligible. However, if one is interested in the highest accuracy, as is required in thermodynamic studies of liquid phase interactions, explicit consideration must be given to the influence of surface effects on derived quantities whenever the Raoult's law activity coefficient is significantly different from unity.

CONCLUSIONS

Enthalpies of solution based on the temperature dependence of V_g^0 have been compared with appropriate calorimetric values for *n*-hexane, carbon tetrachloride, and benzene in benzylacetone solvent at 25°C. Discrepancies were observed which correlate with the solute Raoult's law activity coefficients. It is suggested that for solutes expected to deviate positively from Raoult's law, neglect of the liquid-surface adsorption contribution to retention can lead to significant, though small, positive errors in the derived enthalpy of solution. For benzene ($\gamma^\infty \approx 1$) the observed discrepancy was <0.03 kcal/mol; for hexane ($\gamma^\infty \approx 6$), it was 0.3 kcal/mol.

ACKNOWLEDGEMENT

Thanks are due to Research Corporation for a summer stipend for J.E.

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