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Note

Linear relationship in the thermodynamics of gas–liquid chromatography

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Gas–liquid chromatography (GLC) is an effective method for the study of the thermodynamic functions of a volatile vapour in a non-volatile solvent. The activity coefficient at infinite dilution is obtained from the expression[1]:

$$\gamma_2^\infty = \frac{RT}{M_1 V_g^0 P_2^0} \tag{1}$$

where M_1 is the molecular weight of the solvent and P_2^0 is the vapour pressure of solute at the column temperature.

From the activity coefficient, three excess partial molar functions can be derived:

$$\bar{G}_e^\infty = RT \ln\gamma_2^\infty \tag{2}$$

$$\bar{H}_e^\infty = \frac{\partial \ln\gamma_2^\infty}{\partial(1/T)} \tag{3}$$

and

$$\bar{G}_e^\infty = \bar{H}_e^\infty - T\,\bar{S}_e^\infty \tag{4}$$

where $\bar{G}_e^\infty$ is the partial molar excess free energy of mixing, $\bar{H}_e^\infty$ is the partial molar excess enthalpy of mixing, and $\bar{S}_e^\infty$ is the partial molar excess entropy of mixing. From the definition, $\bar{H}_e^\infty$ and $\bar{S}_e^\infty$ have no relationship and should be treated as two independent components of $\bar{G}_e^\infty$; however, a significant amount of evidence in the literature indicates the existence of the enthalpy–entropy relationship. Historically, the enthalpy–entropy relationship was first discussed in the study of chemical kinetics, and sometimes it was called an extra-thermodynamic relation because it originated from molecular properties rather than from thermodynamic laws. The discussion using enthalpy–entropy relation is popular in chromatographic studies.

In two recent articles, Krug *et al.*[2,3] made a statistical study of the use of temperature differentiation methods to calculate $\bar{H}_e^\infty$ and $\bar{G}_e^\infty$, and drew two conclusions:

(1) Because of experimental errors, $\bar{H}_e^\infty$ and $\bar{S}_e^\infty$ tend to have a high artificial

correlation with a slope to the harmonic average of the experimental temperatures[2];

(2) The relation between $\bar{G}_e^\infty$ (instead of any other linear combination of $\bar{H}_e^\infty$ and $\bar{S}_e^\infty$ and $\bar{S}_e^\infty$) and $\bar{H}_e^\infty$ gives the minimum likelihood of experimental errors and should be used for extra-thermodynamic study[3].

It should be pointed out immediately that the conclusion of Krug et al. is valid only when the enthalpy is calculated from eqn. 3. If the enthalpy is measured independently, the H–S and G–H plots are equally good. Mathematically speaking, the experimental errors in $\bar{H}_e^\infty$ and TS_e^∞ tend to compensate each other and cannot be observed because their signs are opposite to each other. The errors, however, cancel out when $\bar{G}_e^\infty$ is used. Therefore, G vs. H is a more critical test than H vs. S because errors involved in the calculation of H can be detected in the G–H plot. Since differentiation of experimental results usually is applied to calculate the excess enthalpy, it is worthwhile discussing the linear free energy relationship using the approach of Krug et al.

RESULTS AND DISCUSSION

Kopečni et al.[4] measured the retention volumes of chlorinated alkanes in several tri-n-alkyamine solvents at temperatures between 25°C and 50°C. Their results were reported in terms of excess thermodynamic functions. They also studied an inert solvent, n-tetradecane. From the comparison between the inert solvent and the tri-n-alkylamine solvents, it is possible to obtain the association equilibrium constant through the equation suggested by Martire and Riedl[5]:

$$K' + 1 = KC_A\gamma_A + 1 = \frac{(\bar{V}_g^0)_R \, (V_g^0)_A}{(V_g^0)_R \, (\bar{V}_g^0)_A} \tag{5}$$

where $(\bar{V}_g^0)_R$ and $(\bar{V}_g^0)_A$ are the specific retention volumes of the alkane solute, and $(V_g^0)_R$ and $(V_g^0)_A$ are the specific retention volumes of the donor solute on the reference and proton-acceptor solvents, respectively.

From the excess free energy of solution, the corresponding excess enthalpy and excess entropy can be calculated. Table I lists the correlation coefficients of the H–S and G–H plots, and the slope of the H–S plot, which has the unit of temperature, for eight solutes and five solvents used by Kopečni et al.[4]. From the association constant,

TABLE I

CORRELATION COEFFICIENTS FOR BOTH H–S AND G–H PLOTS AND THE SLOPE OF THE H–S PLOT USING EXCESS THERMODYNAMIC FUNCTIONS OF SOLUTION

Solvent	Correlation coefficients		Slope of H–S plot (°K)
	H–S	G–H	
Tri-n-butylamine	0.9842	0.8960	409
Tri-n-pentylamine	0.9106	0.7913	408
Tri-n-hexylamine	0.9862	0.8033	404
Tri-n-octylamine	0.9655	0.4740	331
n-Tetradecane	0.9558	0.9200	488

TABLE II

CORRELATION COEFFICIENTS FOR BOTH *H–S* AND *G–H* PLOTS AND THE SLOPE OF THE
H–S PLOT USING THE THERMODYNAMIC FUNCTION OF THE ASSOCIATION EQUILI-
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Solvent	Correlation coefficients		Slope of H–S plot (°K)
	H–S	G–H	
Tri-*n*-butylamine	0.7892	0.0820	214
Tri-*n*-pentylamine	0.7536	0.2397	186
Tri-*n*-hexylamine	0.7953	0.7602	371
Tri-*n*-octylamine	0.9108	0.5184	288

K, the free energy of association is also calculated. Table II shows the results of
similar calculations for association reactions. Only five chlorinated hydrocarbons
were considered here for molecular association.

The correlation coefficients of the *H–S* plots for excess thermodynamic func-
tions were all higher than 0.9, an indication of good linear relationships. However,
when *G–H* was used, tri-*n*-octylamine turned out to be a poor relation.

In no instance did *G–H* give better correlation than *H–S*. As pointed out, *G–
H* is a stronger criterion than *H–S* and should have a smaller correlation coefficient
than *H–S*. *n*-Tetradecane is a hydrocarbon and does not participate in association,
but its *G–H* plot had the highest correlation. In a previous article[6], it was pointed
out that when hydrocarbons are used as a stationary phase, excess thermodynamic
properties of the solution process reflect the interaction in the pure solute. Examina-
tion at the results of Kopečni *et al.* for the excess entropy of chlorinated hydrocarbons
in *n*-tetradecane showed that all except non-polar carbon tetrachloride had a positive
entropy. This demonstrates that pure solute phases are more ordered than solutions.
Since *n*-tetradecane does not have a specific interaction with solutes, the correlation
of the *H–S* or the *G–H* plot becomes the correlation of properties of pure solutes.
This certainly involves fewer variables than a solution process in tri-*n*-alkylamine
solvents, which will be affected by both solvents and solutes. Therefore, one can
expect that *n*-tetradecane will give the highest correlation for the excess thermody-
namic function, which is demonstrated in the *G–H* plot.

Although there are three phases with a higher correlation coefficient for the
H–S plot than *n*-tetradecane, none of them is better when the *G–H* plot is used.
Tri-*n*-octylamine is the phase with the lowest correlation for the *G–H* plot. This can
also be seen in the slope of the *H–S* plot. According to the argument of Krug *et al.*[2],
when substantial experimental errors exist, a false correlation with a slope equal to
the experimental temperature is obtained. For tri-*n*-octylamine the slope was 331 °K,
which is very close to the average temperature, 310 °K. The reverse statement is not
necessarily true. For example, Table II shows the similar results from association
equilibrium constants. For tri-*n*-octylamine the slope of the *H–S* plot was closer to
310 °K than for tri-*n*-butylamine and tri-*n*-pentylamine but the correlation coefficient
was higher. Again, the correlation coefficients of the *G–H* plots were lower than those
of the *H–S* plots, and the solvent with the highest correlation for the *H–S* plot did
not have the highest correlation for the *G–H* plot.

The success or failure of a linear correlation does not reflect the accuracy of the experimental work. Sometimes a higher-order relation exists. This is most likely to happen when polar solutes dissolve in polar solvents, so that several variables are required to describe the solution process. One such example is the decomposition of the solubility parameter into several components to represent non-polar, polar, and hydrogen bonding[7]. Another example that can explain the poor correlation in excess thermodynamic properties is the combinatory entropy, which has no counterpart in enthalpy. Langer et al.[6] have demonstrated that a correction for the combinatory entropy based on the Flory–Huggins equation[8] gives a better correlation for H–S plot of squalane solvent for a variety of solutes. In a recent note[9], Huang and Madey also demonstrated that when the free volume effect is separated from the free energy, a more meaningful contact energy is obtained from the activity coefficient. If the purpose is to compare donor–acceptor reactions, one may wish to remove the free volume effect because it may superimpose another relation on the true relation between free energy and enthalpy.

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