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Note

Free volume effect in the thermodynamics of gas-liquid chromatography

JAN-CHAN HUANG* and RICHARD MADEY*

Department of Physics, Kent State University, Kent, OH 44242 (U.S.A.)

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Gas-liquid chromatography (GLC) is an effective tool for measuring the thermodynamic properties of a solution in the infinite dilution state¹⁻⁴. By the nature of GLC, the solvent used is usually a low-vapor-pressure liquid or even a high-molecular-weight polymer; the solutes, which are free to vary, are volatile and have a low molecular weight. Since low-molecular-weight compounds usually have more free volume between molecules than polymeric compounds, the thermodynamic properties of GLC shall contain quantities which represent the dissimilarity in the free volume of solutes and solvents.

It is not surprising that in the literature the thermodynamic treatments of GLC data usually do not include the discussion of free volume effects because the solvents used in most in most GLC studies have specific interactions such as hydrogen bonding or charge-transfer complexing, which are strong enough to outweigh the free volume effect. The free volume effect is demonstrated most significantly in the *n*-alkane-polyethylene system⁵, which consists of chemically-similar structure units. An upper critical solution temperature is observed near the critical temperature of the more volatile component. An approach to include the free volume effect in thermodynamic functions of liquids and liquid mixtures was suggested by Flory *et al.*^{6,7}. In their derivation, they consider the external motion of molecules or molecular segments and consider free volume as the volume of liquid minus the core volume of molecules. From their partition function, it is possible to derive an equation-of-state for pure liquids and to extract the parameters of this equation from *PVT* data of pure liquids. A complete representation of excess thermodynamic functions can be derived also from the partition function and only a few adjustable parameters are needed.

Not all GLC solvents have specific interactions. When one wants to conduct a "distillation" type elution, a solvent without a specific interaction is used. When di-nonyl phthalate (DNP) is used as the solvent, it gives a size-corrected activity coefficient between one and two for a variety of solutes because of its dual nature⁸. This property makes DNP an effective solvent for separating solutes based on their boiling points. In this paper we discuss literature results of excess free energy with DNP as the solvent. The small value of the specific interaction with DNP helps to distinguish the free volume effect.

* Present address: General Electric Company, P.O. Box 8, Schenectady, NY 12308, U.S.A.

THEORY

The equation-of-state obtained by Flory *et al.*⁶ is:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{(\tilde{V}^{1/3} - 1)} - \frac{1}{\tilde{V}\tilde{T}} \quad (1)$$

\tilde{P} , \tilde{V} and \tilde{T} are reduced properties defined as:

$$\tilde{V} = V/V^* \quad (2)$$

$$\tilde{P} = P/P^* \quad (3)$$

$$\tilde{T} = T/T^* \quad (4)$$

where P , T and V denote the pressure and temperature of the system and the molar volume of liquid, respectively. The three characteristic parameters P^* , T^* and V^* can be determined from more accessible fluid properties at low pressure as follows⁶:

$$\tilde{V}^{1/3} = 1 + \alpha T/3(1 + \alpha T) \quad (5)$$

$$T^* = T\tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1) \quad (6)$$

$$P^* = \gamma T \tilde{V}^2 \quad (7)$$

Here α is the thermal expansion coefficient and γ is the thermal pressure coefficient of the liquids. The three characteristic parameters depend slightly on temperature; however, this weak temperature dependence can be neglected over a moderate temperature range.

The chemical potential of a binary mixture at finite concentration is a complicated expression; however, in the finite dilution state for component 1 in a solvent 2, the expression is⁹:

$$\begin{aligned} \mu_1 - \mu_1^0 = RT \left[\ln \frac{V_1^*}{V_2^*} + \left(1 - \frac{V_1^*}{V_2^*} \right) \right] + P_1^* V_1^* \left(3\tilde{T}_1 \ln \frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_2^{1/3} - 1} + \right. \\ \left. \frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_2} \right) + V_1^* X_{12}/\tilde{V}_2 \end{aligned} \quad (8)$$

Eqn. 8 requires the core volume V_2^* and the reduced volume \tilde{V}_2 of solvent; these quantities can be determined conveniently from a density measurement. The parameter X_{12} in the last term represents the contact-energy difference between solvents and solutes. Note that the first term on the right-hand side represents the combinational entropy, and the third term represents the contact-energy difference. These two terms are similar to the Flory-Huggin treatment¹⁰. The second term represents a P - V work which originated from a density change to bring a molecule from a liquid

with reduced volume \bar{V}_1 into a liquid with reduced volume V_2 . Conceptually, this is the free volume effect of excess free energy. It should be noted that there is no unique expression for the free volume effect. The expression one obtains depends on the partition function used. Adlard *et al.*¹¹ derived the expression of excess enthalpy and excess entropy from a different partition function. Although the free volume term existed in both expressions, the excess free energy term does not. The partition function of Flory *et al.* is more convenient because most parameters are determined from pure component properties.

TREATMENT OF DATA

Adlard *et al.*^{11,12} measured the retention volumes of benzene, ethanol and carbon tetrachloride in DNP both with capillary columns and packed columns. For benzene and carbon tetrachloride, the results agree very well; while for ethanol, the packed column results are poor because of the surface adsorption on the Celite solid support. They used the capillary column results in their discussion¹¹. Even with a capillary, the results should be viewed with caution because adsorption on a liquid surface can also occur¹³. The excess free energies of benzene in DNP, which were not reported by Adlard *et al.*^{11,12}, were calculated based on the procedure described in their paper. Results of the benzene-DNP system at much higher temperatures⁸ were included for comparison. Both sources use the same method to correct vapor-phase non-ideality.

Table I lists the characteristic parameters of each of the compounds. Note that the characteristic pressure P^* of DNP is not calculated because the thermal pressure coefficient is not available. The excess free energy and the three components of the excess free energy are listed in Tables II-IV for the three solutes carbon tetrachloride, ethanol, and benzene, respectively. The excess free energy is negative for both benzene and carbon tetrachloride, and is positive for ethanol. The combinatorial part of the excess free energy is negative for each of these three solutes. Ethanol, which is the smallest in size, shows the largest value. It is interesting to point out that the combinatorial part of the excess free energy is a negative number also when the solute size is larger than the solvent, which can be seen from the expression in eqn. 8 for the combinatorial part of the excess free energy.

The free volume contribution is small for ethanol and large for carbon tetrachloride and benzene. This results reflects the fact than ethanol, although small in

TABLE I
CHARACTERISTIC VOLUME, TEMPERATURE AND PRESSURE OF FOUR COMPOUNDS

Compound	V^* (ml/mole)	T^* ($^{\circ}K$)	P^* (cal/ml)
DNP*	343.2	5340	
Benzene**	69.5	4770	147
Ethanol***	45.3	4980	110
Carbon tetrachloride**	75.4	4750	133

* Density and thermal expansion coefficient are taken from ref. 11.

** Numbers are taken from ref. 9 for an assumed $T = 40^{\circ}C$.

*** Density and thermal expansion coefficient are taken from ref. 11. Thermal pressure coefficient is taken from ref. 14.

TABLE II

THE TOTAL EXCESS FREE ENERGY AND ITS COMPONENT PARTS FOR CARBON TETRACHLORIDE IN DNP

Temperature, <i>T</i> (°K)	Total excess free energy, $RT \ln \gamma_1^\infty$ (cal/mole)	Combinatorial part of excess free energy (cal/mole)	Free volume contribution to excess free energy (cal/mole)	Contact energy difference (cal/mole)	Contact energy parameter X_{12} (cal/ml)
293.20	-340	-428	17.1	70.9	1.16
298.18	-331	-435	17.6	86.4	1.42
303.18	-334	-443	18.1	90.0	1.50
308.17	-337	-450	18.5	94.5	1.57
313.16	-347	-457	19.0	91.0	1.52
318.15	-339	-465	19.5	106.5	1.79

TABLE III

THE TOTAL EXCESS FREE ENERGY AND ITS COMPONENT PARTS FOR ETHANOL IN DNP

Temperature, <i>T</i> (°K)	Total excess free energy, $RT \ln \gamma_1^\infty$ (cal/mole)	Combinatorial part of excess free energy (cal/mole)	Free volume contribution to excess free energy (cal/mole)	Contact energy difference (cal/mole)	Contact energy parameter, X_{12} (cal/ml)
293.19	650	-674	2.9	1321	36.0
298.17	638	-686	3.0	1321	36.2
303.21	623	-697	3.1	1317	36.3
308.18	611	-709	3.1	1316	36.4
313.16	581	-720	3.2	1298	36.1
318.16	590	-731	3.3	1318	36.8

TABLE IV

THE TOTAL EXCESS FREE ENERGY AND ITS COMPONENT PARTS FOR BENZENE IN DNP

Temperature, <i>T</i> (°K)	Total excess free energy, $RN \ln \gamma_1^\infty$ (cal/mole)	Combinatorial part of excess free energy (cal/mole)	Free volume contribution to excess free energy (cal/mole)	Contact energy difference (cal/mole)	Contact energy parameter, X_{12} (cal/ml)
321.95	-393.8	-511	18.8	98.9	1.8
329.75	-402.2	-524	19.5	102.1	1.9
353.15*	-430.3	-561	22.0	108.7	2.1
373.15*	-461.8	-593	24.5	106.5	2.1
398.15*	-492.0	-633	28.1	112.4	2.2

* The activity coefficients γ_1^∞ are taken from ref. 8.

size, is more condensed compared to carbon tetrachloride or benzene. This argument is supported also by the fact that ethanol has a higher heat of vaporization and a higher normal boiling point. One can also predict this result from the sequence of characteristic temperatures T^* . The characteristic temperature T^* of ethanol lies between that of DNP and those of benzene and carbon tetrachloride; accordingly, the reduced volume of ethanol will be near that of DNP. For none of these three solutes is the free-volume contribution important; however, for the case of polymeric solvent, which has a characteristic temperature of around 8000°K^{15} , the free-volume effect can be around 100 cal/mole which is of the same order of magnitude as the contact energy term.

The values of the contact energy parameters were calculated to be small for benzene and carbon tetrachloride. Results calculated from three sources^{8,11,12} give close values for benzene. Despite the possibility of surface adsorption, ethanol has consistently large values for the contact energy parameter X_{12} ; even if surface adsorption exists, it may have the same temperature dependence as bulk adsorption for ethanol in DNP. Apparently there are no unusual trends in the contact energy parameters. A large positive contact energy is not surprising; it represents the unfavorable process for breaking hydrogen bonds in the pure ethanol phase when the solution process takes place.

CONCLUSION

We separated the excess free energy of three solutes in DNP based on the theory of Flory. The free volume effect appears to be small relative to other contributions to the excess free energy. The relative importance of the free volume effect should be even smaller for other GLC solvents with specific interactions.

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