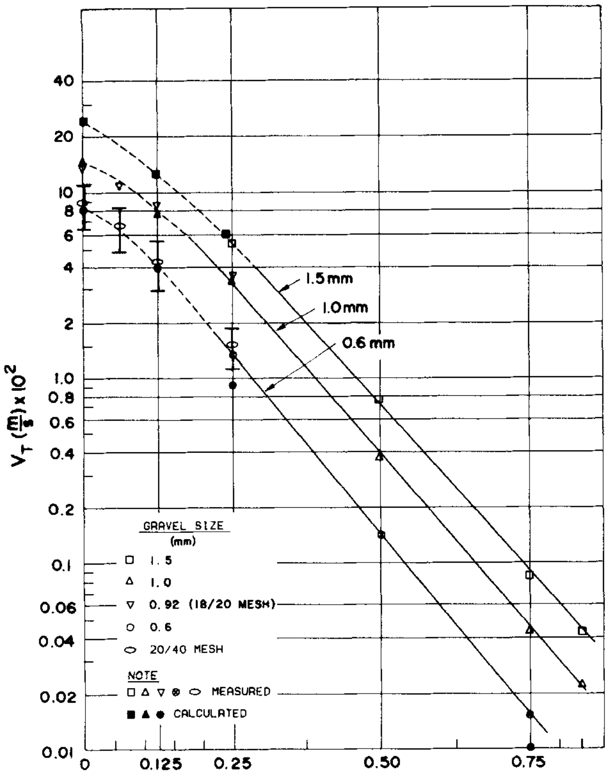

Figure 4. Influence of polymer concentration on settling velocity for several particle sizes.

concentration, at least above 0.25%w. At lower concentrations, the apparent viscosity is low so that Stokes' Law with η_a chosen for the actual shear rate doesn't provide a good estimate. Instead an estimate is made using an empirical relationship for the drag coefficient (Bird et al., 1963) valid for $2 < Re_p < 500$. Then, with V_T calculated using an estimate of η_a, the shear rate is checked to see if it is high enough to require a reduction of η_a. An iteration or two gives satisfactory agreement with experimental values with the straight lines at higher concentrations curving down as the solutions become more dilute until they are water without polymer. Note that the average velocity of 20–40 gravel is essentially the same as that for 0.6 mm gravel (as extrapolated from measurements). Vertical lines through the data points show approximate extremes of the velocities.

The large variation in settling velocity for gravel particles with variation in polymer concentration could be used as a convenient test of fluid quality in field applications. For example, V_T varies by about 2 orders of magnitude between 0.5%w HEC and water. Hence, measurement of the settling velocity of particles of known size would give a reasonable estimate of polymer concentration and viscosity. Using a pinch of 20–40 mesh gravel the average settling velocity is increased by about 100-fold from that for 0.75%w to 0.25%w for which V_T = 15 mm/s although the apparent viscosity is still about 0.025 to 0.04 Pa·s at 0.25%w.

NOTATION

D_p = particle diameter
n = power law exponent
V_T = particle settling velocity
Re_p = particle Reynolds number
η_a = apparent viscosity, Pa·s
η_s = Stokes viscosity, Pa·s
ρ = liquid density
ρ_s = solid density
$\dot{\gamma}$ = shear rate, s^{-1}

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Effects of Association on Enthalpy of Coal-Derived Liquids: Cryoscopic Molecular Weight As a Function of Concentration

RAJ SHARMA,
V. F. YESAVAGE
and A. J. KIDNAY

Colorado School of Mines
Golden, CO 80401

INTRODUCTION

A major difficulty in estimating physical and thermophysical properties of petroleum fractions and coal-derived liquids is the fact that such mixtures represent an essentially infinite continua of components and as such they cannot be defined by component mole or mass fraction. In the petroleum industry, this problem has been overcome by the use of easy to measure characterization variables such as density (or API gravity) and the Watson Characterization Factor, K, defined as

$$K = \frac{\sqrt[3]{T_b(^0R)}}{d}$$

Present address of R. Sharma: Tosco Corp., Golden, CO.

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where T_b is the mean boiling point of the mixture and d is the specific gravity. Thus, the properties of an oil are defined based on two relatively simple laboratory analyses—specific gravity and distillation. Furthermore, different oils with the same gravity and boiling point are assumed to have identical properties. This approach has been somewhat successful for the essentially nonpolar petroleum oils and is the basis for many of the correlations of the *A.P.I. Technical Data Book* (1970).

The authors have had an ongoing program for measuring the enthalpy of coal-derived liquids and model compounds representative of coal liquids. The enthalpy data were initially used to test correlations developed for petroleum oils. The Johnson, Grayson (1961) and the Kesler, Lee (1976) correlations, developed for estimating enthalpy of undefined mixtures, which were both evaluated were based on the API gravity and the Watson K parameter. Typical comparisons as reported elsewhere (Sharma, 1980; Sharma et al., 1981) indicated that for almost all of the coal liquids, and for both the correlations considered, the predicted values were biased low relative to the experimental values.

However, in some cases, the comparisons were excellent, while in others the deviations were too large for the petroleum correlations to be used as predictive techniques for enthalpies of coal liquids. Comparisons also showed that the correlations do an excellent job of predicting enthalpies of petroleum fractions. Of particular note is a comparison between two coal-derived liquids, a Western Kentucky distillate and a Utah distillate (arbitrary identification used for laboratory convenience). These two oils have virtually identical characterization properties (^{0}API and K), and yet the correlation works well for the Western Kentucky distillate but is poor for the Utah distillate. Based on comparisons of errors in the correlations vs. heteroatomic content and the large errors in the correlations when they were used to estimate enthalpies for polar alcohol and phenolic compounds, it became apparent that the large errors in the correlations were primarily the result of high levels of heteroatomic compounds capable of hydrogen bonding and association.

Since the experimental enthalpy data for the coal liquids are higher than the calculated enthalpies, this would be consistent with an association effect and an energy of association. Thus, to develop an accurate method of conveniently calculating the enthalpy of coal-derived liquids, some method of easily characterizing this degree of association is required. It was found that molecular weight determinations as a function of concentration in benzene solvent seem to offer a reliable means of characterizing the effects of association in coal-derived liquids. Furthermore, such measurements can be obtained in a short (several days) time span by routine measurement, while measurement of enthalpies as a function of pressure and temperature requires specialized equipment, experienced staff and even then is difficult particularly with relatively unstable fluids such as coal-derived liquids.

MOLECULAR WEIGHT MEASUREMENTS

Colligative property measurements such as the freezing-point depression, vapor-pressure lowering, boiling-point elevation, and osmotic pressure are the most common methods employed for molecular weight determinations. These techniques are discussed extensively in the literature (Shoemaker et al., 1974; Billmeyer, 1971). In the present study, it was found that for coal-derived liquids the freezing point depression was the most appropriate colligative property to measure in determining molecular weights. Cryoscopy, or the measurement of freezing-point lowering by a solute, to determine molecular weights has been applied extensively to study the effect of association due to hydrogen bonding. A mass of literature (Beckmann, 1888; Lassettre, 1937; Chaplin and Hunter, 1937, 1938a, 1938b, 1939; Peddle and Turner, 1911; Auwers, 1895; Beckmann, 1895), to name a few, exists on this subject and thus the methods need not be discussed further.

The cryoscopic determinations of molecular weights as a function of concentration were undertaken using a Beckman molecular weight apparatus shown in Figure 1. Benzene and nitrobenzene were both used as solvents to observe the effect of the solvent on the molecular weight (Sharma, 1980), but only the benzene results are discussed here.

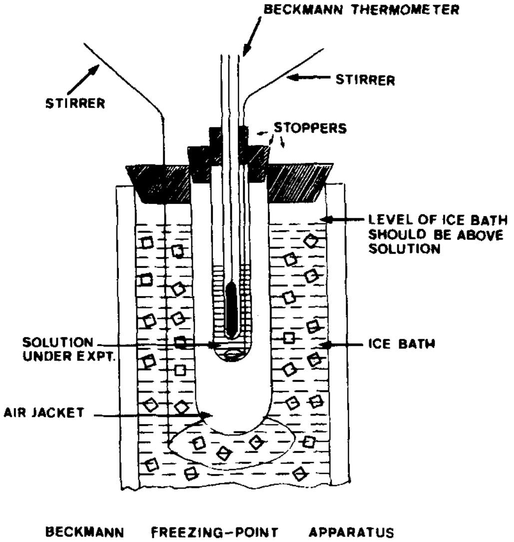

Figure 1. Beckmann freezing point apparatus for cryoscopic determination of molecular weight.

Freezing points, of both the pure solvent and the solution, were determined in the following manner. By means of a pipette, 20 mL of the solvent were measured into the inner tube (Figure 1). The tube (without the jacket) was placed in the freezing mixture (ice + salt + water) and cooled until the solvent just started to freeze. This point was usually signaled by a sudden rise in temperature. The stirrer was operated constantly throughout the freezing operation. The tube, containing the solvent, was then set into the jacket in the freezing mixture. As soon as the temperature stopped rising rapidly, the temperature was recorded as the freezing point. The tube was removed from the jacket, warmed to melt the frozen solvent, and the measurement repeated. Two determinations of the freezing point (of both the solvent and the solution) were usually made.

The concentration of the solute was varied by successive addition of measured volumes of the solute using a 1 × 100 mL pipette. The freezing-point measurement at each concentration was done in the above manner.

Having determined the freezing point depression at a particular concentration, the molecular weight of the solute, at that concentration, was calculated using the following equation (Billmeyer, 1971):

$$M = \frac{1{,}000 k_f g}{G \Delta T_f} \qquad (1)$$

The freezing-point constants, k_f, were estimated for the solvents used by the following relationship:

$$k_f = \frac{R T_f^2}{1{,}000 l_f} \qquad (2)$$

As a test of the reliability of the equipment and the procedure, molecular weights of pure compounds were determined. The results are presented in detail elsewhere (Sharma, 1980) for ethanol, n-butanol, m-xylene in benzene and nitrobenzene solvents and m-cresol in benzene. Typical results are presented in Figure 2.

As is evident from the figure, the molecular weight of associating compounds such as ethanol increased with an increase in concentration, while for nonassociating compounds such as m-xylene the molecular weight was independent of concentration and remained constant.

The experimental data were fit by linear regression and the intercept gave the extrapolated value of the molecular weight at infinite dilution. These values were then compared with the known

TABLE 1. RESULTS OF CRYOSCOPIC MOLECULAR WEIGHT EXPERIMENTS AND ENTHALPY PREDICTION CALCULATIONS BY KESLER-LEE (1976) METHOD

Compound	Formula Wt.	α, M.W. @ ∞ Dilution	β, M.W./(cc/20cc C_6H_6)	Average Error (kJ/kg)	No. of Points Predicted	⁰API	K
W. Kent. Whole Oil	—	175.0	1.2	3.7	13	21.8	10.9
W. Kent. Distillate	—	150.2	3.1	8.4	42	28.5	10.7
SRC-I Naphtha	—	101.7	4.8	9.5	51	49.7	11.2
Utah Distillate	—	137.8	11.9	28.1	33	29.4	10.8
SRC-II Naphtha	—	105.1	11.6	25.8	29	41.0	10.9
SRC-II Middle Dist.	—	136.2	19.3	62.1	36	13.5	9.9
Synthoil Distillate	—	140.4	24.1	83.0	19	13.2	10.0
Ethanol	46.07	45.0	76.7	*	—	—	—
Butanol	74.20	78.2	63.2	*	—	—	—
m-Xylene	106.17	100.6	2.6	10.5	60	—	—
m-Cresol	108.14	100.2	34.9	166.5	52	—	—

* Data not available.

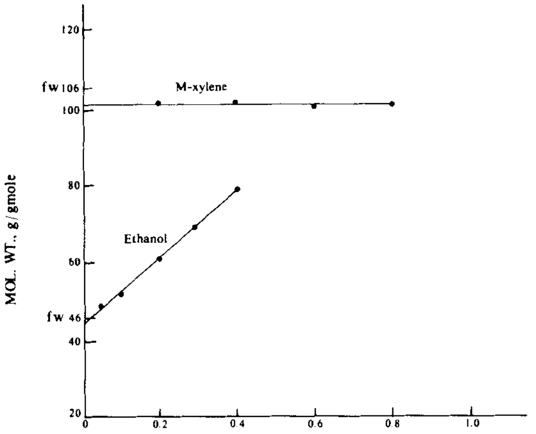

Figure 2. Molecular weight as a function of concentration for ethanol and m-xylene.

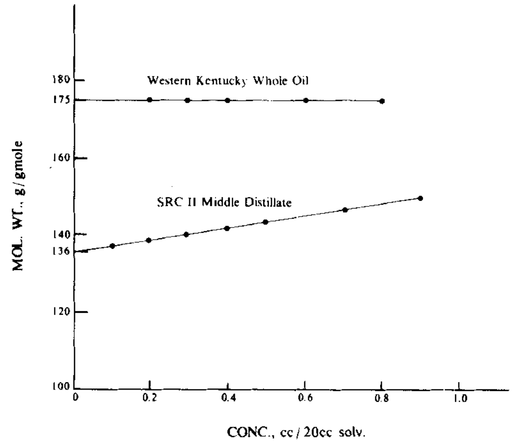

Figure 3. Molecular weight as a function of concentration for two coal-derived liquids.

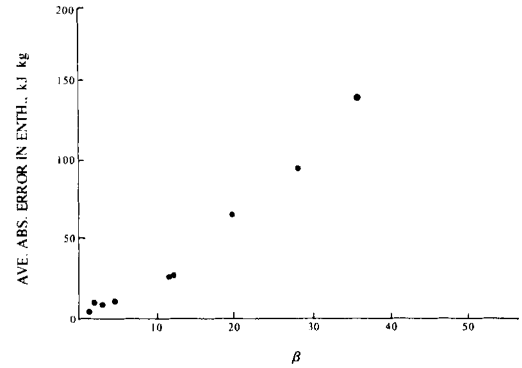

Figure 4. Average absolute error in enthalpy as a function of the slope of the molecular weight vs. concentration curve.

formula weights and the results for benzene as the solvent are presented in Table 1. As can be seen from the table, the extrapolated value of the molecular weight at infinite dilution is a very good approximation of the formula weight or the "true" weight of the "test" compound. Also shown is the slope, β, which decreases from ethanol to butanol, m-cresol and m-xylene. Thus, this slope of molecular weight determination as a function of concentration in benzene solvent appears to be a means of characterizing association. For this reason, such determinations were made on seven samples of coal liquids.

Figure 3 presents typical data on molecular weight determinations for two coal-derived liquids.

Least squares regression was also performed on these data and the results are also presented in Table 1. The intercept gives the values of the molecular weight at infinite dilution while the slope, β, should be related to the degree of association within the fluid. If such is the case and if differences between calculated and experimental enthalpies are related to the degree of association, then the differences in the enthalpy values should be related to β. Table 2 and Figure 4 present the average differences between experimental enthalpies and enthalpies calculated using the Kesler-Lee correlation as a function of β, the slope of the molecular weight versus concentration curve, for all of the systems studied. These systems include both coal-derived liquids and pure compounds.

It is apparent that there is a direct correlation between the absolute error in the enthalpy prediction and the slope of the molecular weight versus concentration curve. It seems reasonable to conclude that as the slope increases, the degree of association increases, and hence the absolute error in the enthalpy values increases. It is important, however, to note that the values of the "actual" average errors are somewhat arbitrary and can be changed by neglecting or adding data points. Thus, Figure 4 cannot be used as a correction factor to the enthalpies calculated with the Lee and Kesler correlation. Yet in any event, the slope of the molecular weight vs concentration curve is an excellent indication of the association effect in any pure compound or coal-derived liquid and could eventually serve as a parameter in an enthalpy correlation.

CONCLUSIONS

It appears that a correlation applicable to the enthalpy of coal-derived liquids must take into account the extent of association in the fluid. It seems likely that other properties of coal-derived liquids might also require an understanding of the effects of association.

Furthermore, for undefined mixtures, such as coal liquids, a method of determining the extent of association is required. The slope of the molecular weight versus concentration curve appears to be a parameter which can be used to characterize this association, although at present the results cannot be used to quantitatively correct for errors in enthalpy correlations.

ACKNOWLEDGMENTS

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NOTATION

g = grams of solute
G = grams of solvent
k_f = constant defined in Eq. 2 (K g/gmol)
l_f = latent heat of fusion of the solvent (J/g)
M = apparent molecular weight of the solute (g/gmol)
R = gas constant (J/gmol·K)
T_f = freezing-point of the solvent (°R or K)
ΔT_f = observed depression of the freezing point (K)
α = molecular weight at infinite dilution (g/gmol)
β = slope of molecular weight versus solute concentration in benzene [g/gmol/(cc/20cc benzene)]
X = composition of solute in benzene (cc/20cc solvent)

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Rise in Free Surface Caused by Submerged Jet Directed Upward

UICHIRO NARUSAWA,
SHINGO TAKAO,
and YUTAKA SUZUKAWA

Technical Research Center,
Nippon Kokan, K.K., Kawasaki, Japan

Because of their importance in many industrial and environmental studies, the areas of research on fluid jets are numerous and diverse. (See Rose, 1956; Martin, 1977; Turner, 1979, for example.) However, we have failed to find any literature concerning the effect of fluid jets on a free surface, resulting in the experimental invesetigation reported here. The ability to predict the surface rise in a fluid due to an impinging jet would certainly contribute to our present understanding of the degree to which the presence of free surface affects a fluid jet, and vice versa.

Figure 1 is a sketch of the present problem, in which d_S and u_S are respectively the average value of effective jet diameter and vertical velocity at the distance H from the jet nozzle in the absence of a free surface. They are related to jet nozzle characteristics, u_o and d_o, by:

$$u_s = u_o(d_o/d_s), \tag{1}$$

$$d_s = d_o + \beta H, \tag{2}$$

where $\beta = 4\,\alpha = 2\tan(\theta/2)$. The entrainment coefficient, α, indicates the ratio of a mean flow velocity across the jet boundary to the mean jet upward velocity. The value of β obtained by previous investigators ranges from ~0.32 to ~0.45 (Folsom and Ferguson, 1949; Donald and Singer, 1959; Ricou and Spalding, 1961; Turner, 1979), and in the discussion to follow, the two values of β = 0.32 and 0.45 will be employed. It should also be noted that Eq. 2 is valid only when Re_N is greater than ~3,000 (Folsom and Furguson, 1949), a condition which is satisfied for all practical purposes. Then, based on dimensional analysis, the present problem can be expressed in terms of three nondimensional parameters of h/d_o, d_o/d_s and $u_o/\sqrt{gd_o}$ ($\equiv Fr_N$).

The experimental apparatus consisted of an acrylic tank (1.2 m dia. × 1.0 m height), a vertically-directed nozzle and a recirculation lines fitted with a valve, a flowmeter and a pump. The nozzle, made of glass, was placed at the center of the tank bottom. A scale, which could be moved perpendicular to the free surface, was installed above the jet nozzle. At the tip of the scale was attached a

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Correspondence concerning this paper should be addressed to: S. Takao, Department No. 5, Technical Research Center, Nippon Kokan, K.K., 1-1 Minamiwatarida, Kawasaki-ku, Kawasaki, Japan 210.

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