J. Chem. Eng. Data **1993,** *38,* 516–519

Lower Critical Solution Coexistence Curve and Physical Properties (Density, Viscosity, Surface Tension, and Interfacial Tension) of 2,6-Lutidine + Water

Carlos A. Grattoni, Richard A. Dawe,* C. Yen Seah, and Jane D. Gray

Mineral Resources Engineering, Imperial College, London SW7 2AZ, U.K.

The coexistence curve and physical property data (densities, viscosities, surface tensions, and interfacial tensions of the equilibrated coexisting phases) for 2,6-lutidine + water have been determined over the range 34–60 °C, and the density and viscosity differences calculated. The compositions were determined through the refractive index at 22 °C, densities by a commercial electronic oscillating U-tube, viscosities by a U-tube viscometer, surface tensions by a du Noüy ring method, and interfacial tensions by a spinning drop interfacial tensiometer.

Introduction

In recent work of examining pore scale mechanisms of flow in porous media at low interfacial tensions (below 0.1 mN m^{-1}) use was made of the system 2,6-lutidine (2,6-dimethylpyridine) in water (denoted as L + W throughout this paper) (*1, 2*).

The L + W fluid system has a lower critical solution temperature (LCST) of 34.1 °C for a critical mixture of 28 mass % L (i.e., 28% L, 72% W) (*3–5*). Thus, at temperatures below 34.1 °C any proportion of lutidine and water is completely miscible and the mixture is a single phase. On heating to a temperature, t, above 34.1 °C, the phase rule (*6*) dictates that an initial single-phase mixture, composition C_1 (within the range ~5 mass % L to ~70 mass % L), will separate into two immiscible phases, A and B, with compositions C_A and C_B, respectively (Figure 1). Phase A will be rich in water (termed the W-rich phase); phase B will be rich in lutidine (termed the L-rich phase). These compositions will be fixed for any given temperature, regardless of the initial fluid composition, C_1. The relative amount of each of the phases A and B (the phase fraction) is controlled by the tie-line (lever) rule and the choice of the initial composition (*6*). Thus, at any given temperature within the two-phase region, by changing the initial fluid composition C_1, the complete phase fraction range (from 100% phase A to 100% phase B) can be covered. The equilibrated L + W liquid system above the LCST has uniquely defined physical properties (density, viscosity, and interfacial tension) which can be readily varied in a systematic manner by changing the temperature including controllable very low interfacial tensions. For instance at 46 °C the interfacial tension between the two phases is 0.4 mN·m^{-1}, and at 34.6 °C it is 0.02 mN·m^{-1} (that of water + air at 22 °C is around 72 mN·m^{-1}). This is especially useful for studying phenomena at low interfacial tension where the values need to be known and varied in a controlled manner.

This paper presents results of the density, viscosity, surface tension, and interfacial tension of the equilibrated phases of the L + W system through the temperature range 34–60 °C, and the calculated density and viscosity differences. The compositions were determined through the refractive index at 22 °C.

Materials

2,6-Lutidine (2,6-dimethylpyridine, Aldrich Chemicals Ltd., minimum assay 99%) was used without further preparation, with singly distilled water. The purities of the fluids were sufficient for the precision of this work since it is the system's phase separation and physical property behavior as a function of temperature that were required. Care must be exercised when using 2,6-lutidine since it is flammable and harmful if swallowed and can disintegrate into toxic gas when heated (*7*).

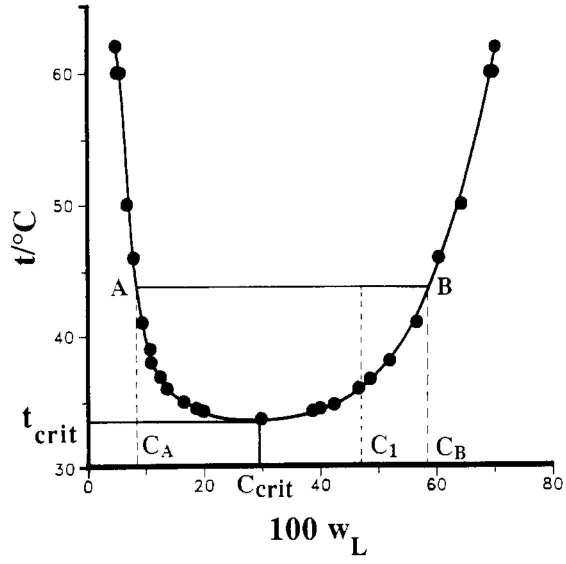

Figure 1. Lutidine + water coexistence curve.

Previous Data

The coexistence curve of the L + W system was published by Cox and Herington (*3*) in 1956, who provided data up to 64 °C, i.e., 30 K above the critical temperature. They determined the critical temperature to be 34.06 °C. In this work the LCST was determined to be 34.1 °C. The tie-line data of Cox and Herington compare favorably with those presented here. Discrepancies between the two sets of data can be attributed to the difference in specimen purities and to experimental error. Following Cox and Herington, Loven and Rice (*8*) carried out a study of the shape of the coexistence curve of the L + W system in a temperature range within 0.13 K of the critical point (i.e., near-critical). More recently, Handschy et al. (*5*) published refractive index data for the L + W system up to 15 K from the critical temperature (34.106 °C in their work). Their refractive index values are lower

---

* To whom correspondence should be addressed.

0021-9568/93/1738-0516$04.00/0

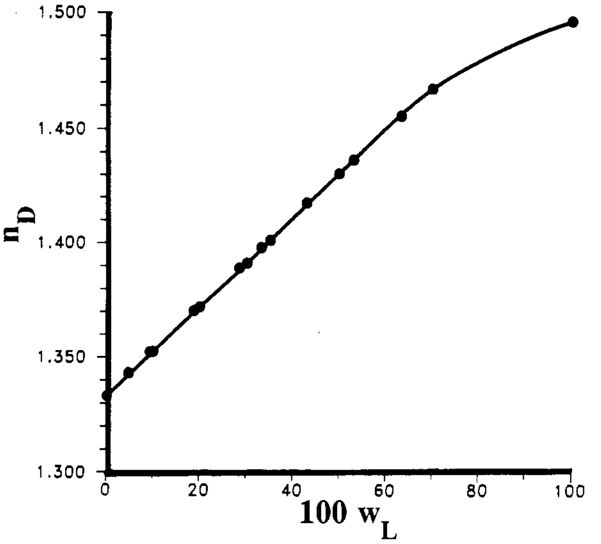

Figure 2. Refractive index as a function of $100w_L$ at 22 °C.

than those presented in this work, probably due to different impurities in the lutidine samples.

Coexistence Curve

Different compositions of L + W mixtures were prepared by weighing; the compositions are presented as $100w_L$ (w_L is the mass fraction of lutidine, and $1 - w_L$ is the mass fraction of water). For convenience in this work mass fractions are presented but the mole fraction x_L can be readily calculated when desired since $x_L = \{[100w_L/107.16]/[(100w_L/107.16) + (100(1 - w_L)/18)]\}$. The samples were heated in test tubes to temperatures between 34 and 60 °C. When the phases had equilibrated (which was taken to be when both the top and bottom phases in the tube had cleared), a sample of each phase was removed by syringe for compositional analysis by refractive index. The two equilibrated phase compositions were plotted as a function of temperature, and the phase curve was drawn. Care was required as the more dense phase, the W-rich phase, appeared to completely shield the top phase from both the walls of the container and the air (i.e., it was the wetting phase). Before drawing a sample of the top phase into the syringe, a small bubble of air was ejected from the syringe into the top phase in order to ensure the sample was not contaminated with the more dense phase.

The critical temperature (34.1 °C for a composition of 28 mass % L) was determined by noting the lowest temperature at which phase separation occurred and confirming this by extrapolation of the phase diagram (Figure 1).

Refractive Index

The compositions were analyzed in this work by refractive index since lutidine has a refractive index, n_D, of 1.4998 and water 1.3338 (measured at 22 °C). An equilibrated phase was taken at a temperature t and cooled to 22 °C; since the L + W system has a LSCT, there is no phase separation on cooling; thus, accurate compositions can be obtained. The refractive index measurements were made using a Bellingham and Stanley Abbé 60 instrument (sodium D_1 line), precise to 0.000 02 and thermostated at 22 ± 0.1 °C. A 1 mass % concentration corresponds to a refractive index of approximately 0.0019, and so a L + W sample can be measured easily to 0.1 mass % precision. The refractive index of 16 samples covering the composition range was measured at 22 °C. The results are presented in Table Ia. A calibration graph of composition $100w_L$ against refractive index at 22 °C was determined (Figure 2). Over the composition range 0–60 mass % L, the refractive index is approximately linear, but around 70 mass % L, there is a change in slope, and as will be seen later, the viscosity and volume of mixing per unit mass have a maximum around 70 mass % L. These effects are probably due to hydrogen bonding breakdown in the water structure.

Table I. Refractive Indices n_D (Sodium D Line) of the Single-Phase Lutidine + Water at 22 ± 0.1 °C and the Coexisting Compositions Separated at Temperature t and Cooled to 22 °C

a. Single-Phase Lutidine + Water

$100w_L$	n_D	$100w_L$	n_D
0.0	1.3338	33.2	1.3995
4.7	1.3433	35.1	1.4011
9.3	1.3526	43.0	1.4186
10.0	1.3523	50.0	1.4305
18.7	1.3710	53.1	1.4380
20.0	1.3720	63.3	1.4569
28.4	1.3901	70.0	1.4672
30.1	1.3911	100.0	1.4998

b. Coexisting Compositions

	L-rich phase		W-rich phase	
t/°C	n_D	$100w_L$	n_D	$100w_L$
34.2	1.408 61	39.1	1.373 98	21.1
34.5	1.413 01	41.4	1.371 83	20.0
35.0	1.417 78	43.9	1.367 31	17.7
36.0	1.424 33	47.3	1.362 30	15.0
37.0	1.426 70	48.5	1.357 77	12.7
38.0	1.433 83	52.2	1.354 51	11.0
41.0	1.442 72	56.9	1.351 90	9.6
46.0	1.453 30	62.4	1.350 80	9.1
50.0	1.457 71	64.7	1.346 95	7.1
60.0	1.466 77	69.4	1.343 63	5.3

Table Ib presents the measured data for the conjugate equilibrated phases, and the resulting phase equilibrium curve is shown in Figure 1.

Density

The densities ρ of the single-phase samples were measured using Anton Paar DMA46 and DMA602WM density meters to ±0.1 kg·m^{-3} calibrated with water and air according to the manufacturer's instructions (the DMA602WM density meter can be used at temperatures other than room temperature by means of circulating water) at temperatures up to 60 °C.

The principle of measurement is the variation in frequency of a fluid-filled vibrating U-tube caused by changes in density. At 22 °C, the density of lutidine, ρ_L, was 921.3 kg·m^{-3}, and that of water, ρ_w, was 997.8 kg·m^{-3}. The densities of 10 mixtures were determined, Table II, and the excess volume (or volume of mixing) V^E_m was calculated by $V^E_m = V^\circ_m - x_L V^\circ_L - x_W V^\circ_W$ where V°_m, V°_L, and V°_W are the molar volumes of the mixture, lutidine, and water, and x_L ($=1 - x_W$) is the mole fraction of lutidine. The excess volumes are presented in Table II along with the excess volume per unit mass (V^E_m/M, where M is the molecular weight of the mixture). There is a maximum in V^E_m/M around 70 mass % L (Figure 3).

The densities of the coexisting phases over the temperature range 34–60 °C were obtained by preparing density–composition–temperature plots, extrapolating the single-phase density values measured over the range of temperatures to the composition and temperature of the two-phase boundary, and reading from the graph. Table III and Figure 4 show the density data obtained with the corresponding L + W compositions obtained from the coexistence curve. The density difference at each equilibrium temperature was then calculated. The density difference as a function of Δt, the temperature difference from the critical temperature ($\Delta t = t - t_c$ where t_c = 34.1 °C), can be calculated by $\Delta\rho/(\text{kg·m}^{-3}) = 7.3(\Delta t/°\text{C})^{0.47}$ from 34.1 to 60 °C (Figure 5). Figure 5 shows the quality of fit.

Viscosity

Viscosities η of the single-phase compositions were measured by a U-tube (Ubbelöhde) viscometer (type A) at

Table II. Density, Excess Volume, and Volume of Mixing per Unit Mass and Viscosity of L + W at 22 °C

$100w_L$	x_L	$10^3M/(\mathrm{kg\cdot mol^{-1}})$	$\rho/(\mathrm{kg\cdot m^{-3}})$	$-10^6V^E_m/(\mathrm{m^3\cdot mol^{-1}})$	$(-10^6V^E_m/M)/(\mathrm{m^3\cdot kg^{-1}})$	$\eta/(\mathrm{mPa\cdot s})$
0.0	0.0000	18.00	997.8	0.00	0.0	0.955
10.0	0.0183	19.63	997.5	0.16	8.0	1.357
20.0	0.0403	21.59	997.1	0.34	15.9	1.932
30.1	0.0675	24.01	996.7	0.57	23.9	2.915
35.1	0.0833	25.42	996.0	0.70	27.7	3.275
50.0	0.1438	30.82	993.0	1.13	36.7	4.298
70.0	0.2816	43.09	982.0	1.82	42.1	5.153
80.0	0.4019	53.80	971.9	2.14	39.9	4.278
90.0	0.6019	71.60	956.2	2.24	31.3	2.687
100.0	1.0000	107.16	921.3	0.0	0.0	0.929

Table III. Physical Properties (Composition, Density, Viscosity, Surface Tension, Density Difference, Viscosity Difference, and Interfacial Tension) of the Equilibrated Phases between 34.2 and 60 °C

	lutidine-rich phase				water-rich phase				between phases		
$t/°\mathrm{C}$	$100w_L$	$\rho/(\mathrm{kg\cdot m^{-3}})$	$\eta/(\mathrm{mPa\cdot s})$	$\gamma/(\mathrm{mN\cdot m^{-1}})$	$100w_L$	$\rho/(\mathrm{kg\cdot m^{-3}})$	$\eta/(\mathrm{mPa\cdot s})$	$\gamma/(\mathrm{mN\cdot m^{-1}})$	$\Delta\rho/(\mathrm{kg\cdot m^{-3}})$	$\Delta\eta/(\mathrm{mPa\cdot s})$	$\gamma/(\mathrm{mN\cdot m^{-1}})$
34.2	39.1	985.6	1.80		21.1	988.5	1.50		2.9	0.30	0.007
34.5	41.1	984.2	1.95	36.6	20.0	989.0	1.35	36.4	4.8	0.60	0.017
35.0	43.9	983.2	2.20	36.4	17.7	989.4	1.20	35.9	6.2	1.00	0.043
36.0	47.3	983.3	2.57	36.1	15.0	990.2	1.10	35.8	6.9	1.47	0.077
38.0	52.2	979.2	2.47	36.0	11.0	990.3	0.96	35.7	11.1	1.51	0.11
40.0	55.3	974.8	2.38	35.3	10.1	990.4	0.88	34.2	15.6	1.50	0.22
46.0	62.4	967.5	1.81	34.5	9.1	989.1	0.73	31.5	21.6	1.08	0.4
50.0	64.7	960.1	1.70	32.9	7.1	988.9	0.63	28.6	28.8	1.07	0.5
60.0	69.4	949.0	1.22	31.9	5.3	985.0	0.46	25.6	36.0	0.76	0.8

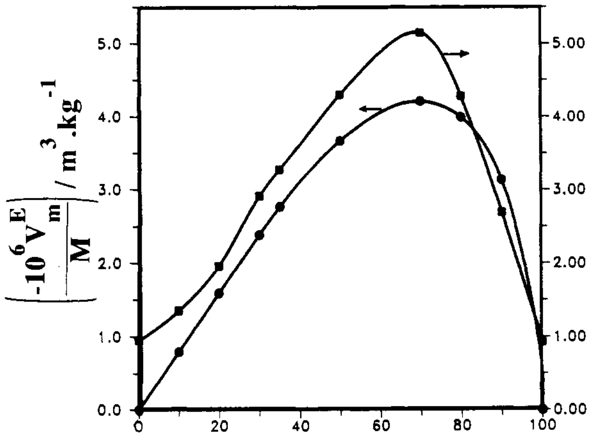

Figure 3. Viscosity and volume of mixing per unit mass for L + W at 22 °C.

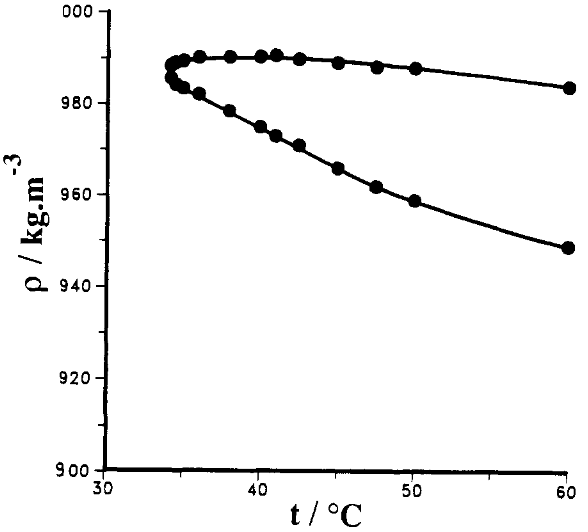

Figure 4. Densities of L + W along the two-phase boundary.

temperatures over the range 22–60 °C (Tables II and III and Figures 3 and 6). The standard fluid viscosity was water, with values taken from standard tables and the densities determined by a densitometer as described earlier. At 22 °C the accuracy is estimated to be ±0.01 mPa·s and there is a maximum at around 70 mass % L (Figure 3). The viscosities of the coexisting phases were obtained by measuring the single-phase mixtures over the temperature range, extrapolating the values to the two-phase boundary, and reading from the graph in a manner similar to that used for the densities. These viscosities are presented in Table III and Figure 6. The viscosity difference between the two phases was then calculated and is also given in Table III and Figure 7. Figure 7 shows how the viscosity difference changes with temperature; there is a maximum around 36 °C, again probably due to hydrogen bonding breakdown.

Surface Tension

The surface tensions γ of the separated equilibrated phases were measured using the du Noüy ring method on a Krüss K10 (Hamburg) automatic tensiometer to ±0.2 mN·m^{-1} over the range 35–60 °C. The values are given in Table III.

Interfacial Tension

The interfacial tensions γ between coexisting phases were measured over the temperature range 34–60 °C using a spinning drop interfacial tensiometer (University of Texas Model 300) (*9*). The temperature, the period of rotation, and the diameter of the drop were measured, the density difference was calculated as described earlier, a correction factor taking into account the refractive indices of the glass tube and the outer phase was determined (*9*), and the interfacial tension was obtained through $\gamma = (\pi^2\Delta\rho d^3)/8P^2$ where $\Delta\rho$ is the density difference between the two phases, P is the period of rotation of the tube, and d is the equatorial drop diameter. This equation is applicable provided the length of the drop is more than 4 times its diameter. The maximum period of rotation of the tube in the equipment used was about 18.40 ms/cycle (≃50 Hz), and the minimum was about 5.70 ms/cycle.

The measured values of the interfacial tension for the L + W system are presented in Table III and as a function of $\Delta t = t - t_c$ in Figure 8, and can be interpolated by $\gamma/(\mathrm{mN\cdot m^{-1}}) = 0.043(\Delta t/°\mathrm{C})^{0.88}$. There are no standard values with which to compare these data; the values fully rely on the equation of the spinning drop. It is therefore possible that the values

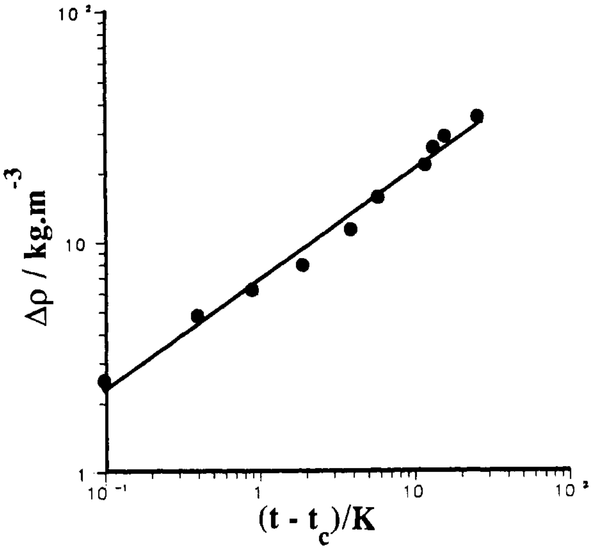

Figure 5. Density difference between the equilibrated upper and lower phases of L + W as a function of the temperature difference ($t - t_c$, where t_c = 34.1 °C).

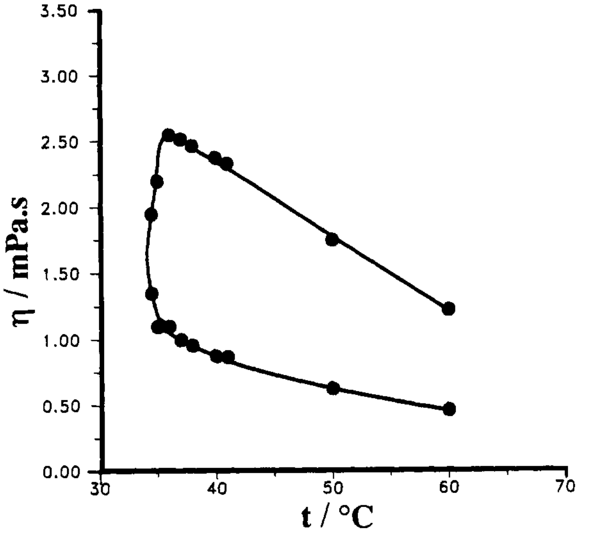

Figure 6. Viscosities of the equilibrated phases of L + W as a function of temperature.

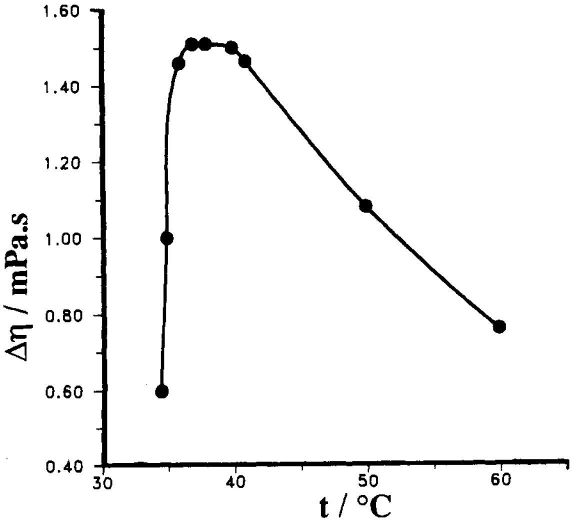

Figure 7. Viscosity difference between the equilibrated upper and lower phases of L + W as a function of temperature.

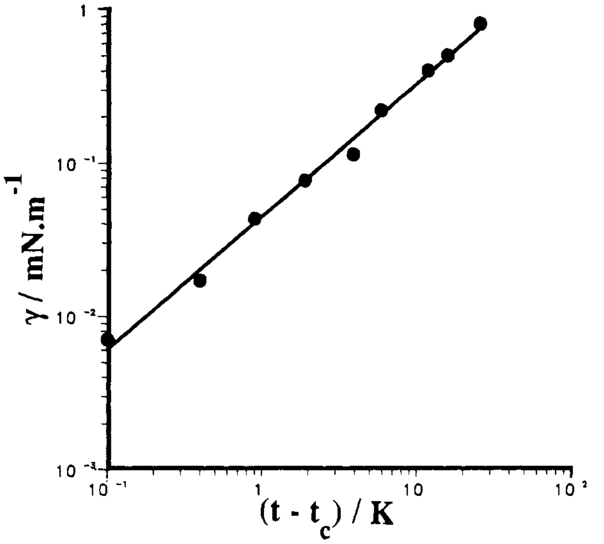

Figure 8. Interfacial tension between the equilibrated phases of L + W as a function of the temperature difference ($t - t_c$, where t_c = 34.1 °C).

here are not accurate and could have perhaps 100% (or greater) error; however, for this work the trends in the data are the important point and not the absolute values. Huygens (*10, 11*), using a pendant drop method, obtained values within 10% using the density difference values of Table III. If the L + W mixtures have added dye, e.g., as used in refs 1 and 2, the values can decrease, by perhaps a factor of 100%.

Summary

Table III summarizes values of the composition of the two equilibrated phases and their density and density differences, viscosity and viscosity differences, surface tension, and interfacial tension between 34 and 60 °C. Tables Ia and II present the data for the refractive index, viscosity, and excess volume for different mixtures of L + W at 22 °C.

Acknowledgment

We thank British Gas plc for use of their spinning drop equipment and Dr. R. J. M. Huygens (Delft University) for interest in the study.

Literature Cited

(1) Gray, J. D.; Dawe, R. A. SPE Reservoir Eng. **1991**, *6*, 353–9.
(2) Gray, J. D. Low Interfacial (<1 mN/m) Studies of Multiphase Fluid Behaviour in Porous Media. Ph.D. Thesis, Imperial College, University of London, August 1990.
(3) Cox, J. D.; Herington, E. F. G. *Trans. Faraday Soc.* **1956**, *52*, 926–30.
(4) Francis, A. W. *Critical Solution Temperatures*; Advances in Chemistry Series 31; American Chemical Society: Washington DC, 1961.
(5) Handschy, M. A.; Mockler, R. C.; O'Sullivan, W. J. *J. Chem. Phys.* **1980**, *76*, 172–74.
(6) Glasstone, S. *Textbook of Physical Chemistry*, 2nd ed.; Macmillan and Co.: London, 1946; pp 724–730.
(7) Transport Emergency Card TEC(R)-61G04.
(8) Loven, A. W.; Rice, O. K. *Trans. Faraday Soc.* **1963**, *59*, 2723–7.
(9) Coucoulas, L. M.; Dawe, R. A.; Mahers, E. G. *J. Colloid Interface Sci.* **1983**, *93*, 281–4.
(10) Huygens, R. J. M. (Delft University). Personal communication, 1992.
(11) Huygens, R. J. M.; Boersma, D. M.; Ronde, H.; Hagoort, J. SPE/DOE 8th Symposium on Enhanced Oil Recovery, Tulsa, OK, 1992; Paper No. SPE 24169.

Received for review November 3, 1992. Revised May 24, 1993. Accepted June 7, 1993.* C.A.G. thanks Deminex for support. J.D.G. thanks British Gas plc for support.

---

* Abstract published in *Advance ACS Abstracts*, August 15, 1993.