could take place through these liquid filled capillaries, yielding an over-all flux of propane far in excess of that which might be anticipated on a basis of its average concentration in the plug as a whole. Furthermore, capillaries filled with liquid propane would not be readily accessible to carbon dioxide, so that the transport rate of carbon dioxide would be correspondingly reduced.

Data of Kammermeyer and Wyrick showed that the apparent surface diffusivities for propane increased rapidly with average pressure at −5° and 12° C., which could be explained by capillary transport. However, even such a seemingly plausible explanation must be treated with caution, as permeability data for ammonia on porous glass (*7*) showed that the permeabilities decreased from peak values when condensation conditions were approached.

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Extraction of Benzene with Di- and Triethylene Glycols

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THE UDEX SYSTEM (*2, 3*) for recovery of aromatics from mixtures of aromatics and saturates by solvent extraction normally requires a mixture of diethylene glycol and water as the solvent. The extraction column and stripper for recovery of solvent from the extract stream are usually operated between 250° and 300° F. The only equilibrium data available for this aqueous system were taken at temperatures of 257° F. and below (*1*). The present work presents equilibrium data at 250° and 300° F. for both diethylene and triethylene glycol with two different water concentrations.

MATERIALS

The equilibrium curves were determined from tie line data and cloud point measurements. In each case the phases were contacted in a high pressure bomb previously designed and built for this purpose. The bombs were built of stainless steel with sight glasses fitted on opposite sides so that it was possible to observe the contents at all times. A stirrer was built into the bomb and was actuated with a solenoid coil. The bomb was equipped with three 0.125-inch stainless steel sampling or charging tubes. One went to the bottom, one went to approximately the middle, and one went to the top of the mixing chamber.

The desired temperatures were obtained by immersion in a constant temperature oil bath of Dow Corning 550 fluid. A thermowell was built into the bomb to facilitate temperature measurement of the fluids being contacted. The temperature was determined with a portable precision potentiometer, using an iron-constantan thermocouple.

EXPERIMENTAL PROCEDURES

The components were all charged to the bomb through the tube that went to the bottom of the chamber. The bomb was washed with distilled water and then acetone, dried with air, and then evacuated. The glycol phase was charged first, the saturate phase second, and the benzene last, in an effort to minimize any liquid holdup on the tube walls. In every case a sample bottle was tared, the liquid was introduced into the bottle, and it was weighed again. The liquid was then charged to the bomb and the sample bottle weighed so that the amount of liquid charged could be determined by the difference in weights before and after charging. The balance weighed to the nearest 0.1 gram, and it was possible to estimate the next place past the decimal. A sample weight of approximately 165 grams was used each time.

The bomb was placed in the constant temperature bath. The liquids were blanketed with nitrogen at 100 p.s.i. gage to keep them from boiling. The vapor space was small with respect to the capacity of the mixing chamber. The phases were mixed periodically as the temperature approached the desired point. The phases were stirred vigorously when the desired temperature was attained in order to bring them to complete equilibrium.

The samples were removed from the bomb through a 0.188-inch stainless steel tube which acted as an air-cooled condenser. A hypodermic needle was attached to this condenser by a small piece of surgical rubber tubing. This made it possible to introduce the samples into glass sample tubes. (The tubes were 5-mm. O.D., standard wall, borosilicate glass.) These tubes were immediately placed in beakers containing dry ice. As soon as the samples were frozen, the tip of each sample tube was heat-sealed to prevent any possibility of sample loss. These samples were analyzed by nuclear magnetic resonance (NMR). Duplicate samples were taken each time to check the precision of the analysis. The accuracy could be checked by material balance when the phases had been analyzed.

Cloud point measurements were made to determine the location of the equilibrium curve for those portions of the curve that were very hard to obtain by tie line data. The phases were charged to the bomb as before, but a constant visual check was maintained on the contents of the bomb as the temperature was raised. A temperature reading was taken when the cloud disappeared. The temperature was then lowered, and a visual check maintained on the contents of the bomb. A temperature reading was taken when the cloud appeared. The temperatures were never more than 1° F. apart and usually no more than 0.330° F. apart. An average of these two temperature readings was taken as the cloud point.

These data were taken in such a manner as to permit interpolation of cloud point data between the extreme temperatures. Data were also taken using mixtures that did not contain saturates. This defines the upper temperature at which the ternary diagram will be of Type II, since this temperature and the critical solution temperature of the solvent and benzene are precisely the same.

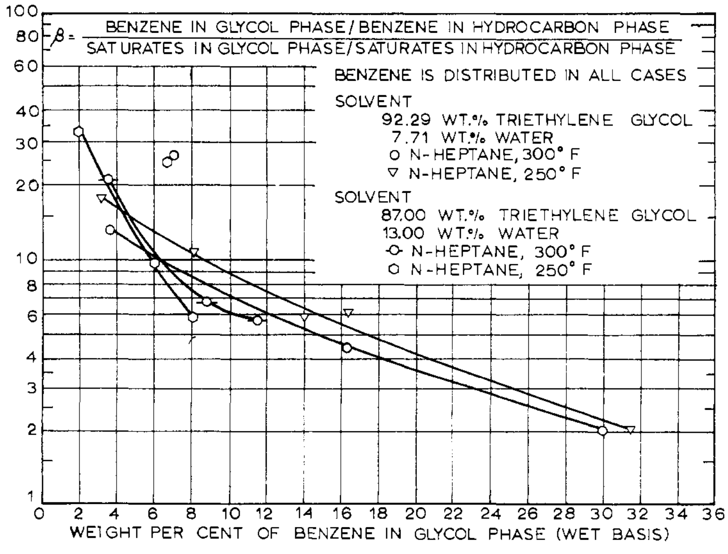

Figure 1. Plot of selectivity for triethylene glycol

ANALYTICAL TECHNIQUES

All equilibrium samples from the single-stage extractions in the laboratory were analyzed by nuclear magnetic resonance. NMR is normally used for structural identifications and for functional group analyses. In this case, however, NMR separated the samples into a ternary system of saturates, aromatics, and glycol solvent. Because of a fortuitous set of circumstances the glycol and water come out in the same place on the spectral curve. They could be separated, if desired, by ratioing the height of the OH peak of the spectral curve with the main peak of the glycol water curve and then backing the water out of the calculation. To the author's knowledge, this is the first time that NMR has been used as a routine analytical tool for this type of analysis.

All analyses were reported by NMR as mole per cent hydrogen. This necessitates knowing the weight per cent hydrogen in each component (saturates, solvent, benzene), if data are to be reported in weight per cent. It is a fairly easy matter when pure components are used.

Refractive indices of pure components were as follows:

Component	n_D^{20}
Diethylene glycol	1.4474
Triethylene glycol	1.4560
n-Heptane	1.3878
Benzene	1.5010

Since all samples were taken at temperatures of 250° and 300° F., they separated into two phases when they were cooled to room temperature. Each phase was measured for volume, analyzed, and then recombined with the assumption of additive volumes. The material balances on the tie line samples showed this assumption to be a reasonable one.

DISCUSSION OF RESULTS

Figure 1 is a plot of selectivity, β, *vs.* the weight per cent of benzene in the glycol phase on a wet basis. Selectivity is defined as follows:

$$\beta = \frac{\text{benzene in glycol phase/benzene in hydrocarbon phase}}{\text{saturates in glycol phase/saturates in hydrocarbon phase}}$$

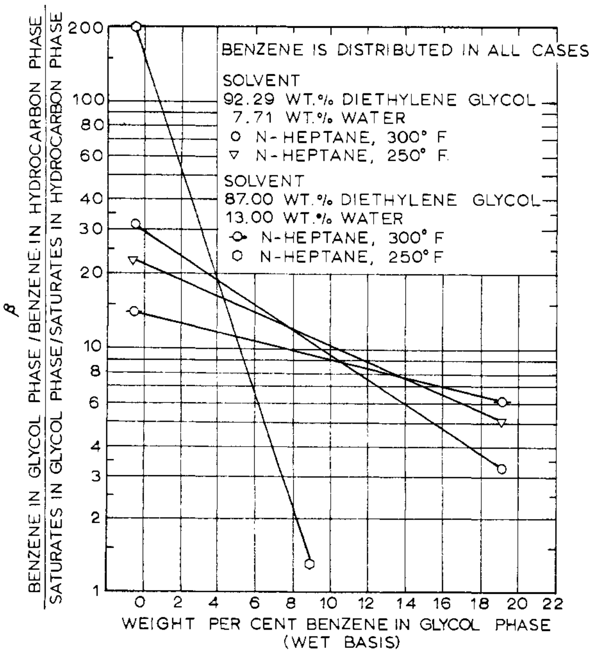

Figure 2. Plot of selectivity for diethylene glycol

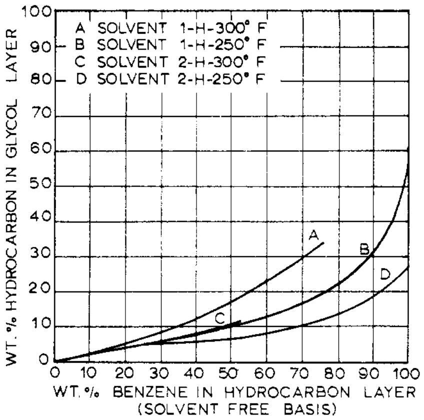

Figure 3. Comparison of solvents 1 and 2

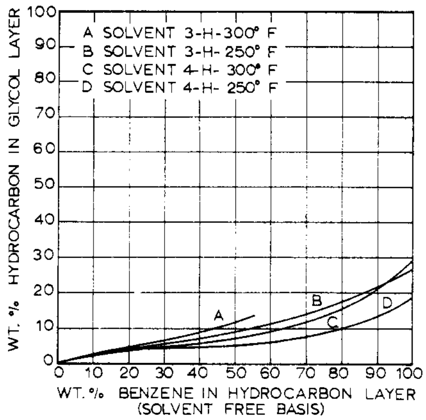

Figure 4. Comparison of solvents 3 and 4

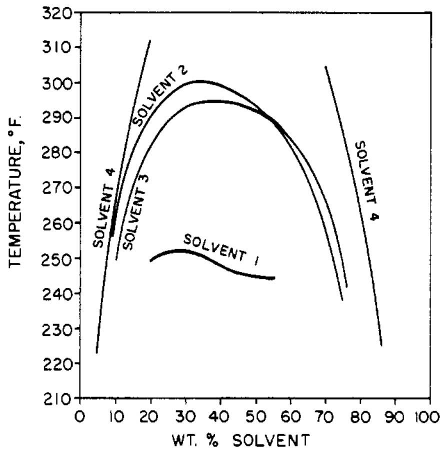

Figure 5. Benzene–mixed solvent system

This plot deals with triethylene glycol. Some rather unexpected results were observed. When the solvent was 7.71 weight % water and 92.29 weight % triethylene glycol, the selectivity decreased gradually with an increase in the amount of benzene in the glycol phase. The selectivity also decreases with increasing temperature. When the solvent was 13.00 weight % water and 87.00 weight % triethylene glycol, the selectivity decreased rapidly with increasing concentration of benzene in the glycol phase. In this case, selectivity increased with increasing temperature. At high concentration of benzene, the selectivity was greater when using the solvent with the least amount of water.

Figure 2 should give the same information for the diethylene glycol–water solvent that the previous figure did for the triethylene glycol–water solvent. The concentration of the saturates in the glycol phase was so low with this solvent that an absolute variation of even a small fraction of 1% would have a tremendous effect on the value of the selectivity. Since there was so much scatter in the data, no attempt was made to draw curves through the data points. Instead, all the data were fitted to straight lines by the method of least squares and these are the lines presented in Figure 2. These data are still so poor that only a general statement may be made about them. The same general trend as in Figure 1 was evident in Figure 2. There seems to be very little difference in the absolute value of the selectivity of the two systems. Perhaps there is a slight selectivity advantage for the diethylene glycol systems, if any trust can be placed in the curves of Figure 2.

Figure 3 deals with the comparison of solvent power among the various combinations of triethylene glycol, water, *n*-heptane, benzene, and temperature. In every case the solvent power increased with increasing temperature. Increasing the water concentration in the solvent always decreased the solvent power. The solvent power is greater at 300° F. when the solvent is 13.00 weight % water, than at 250° F., when the solvent is 7.71 weight % water.

Figure 4 presents the same comparison for the diethylene glycol. The same observations may be made for this plot as for the previous one. The same comparisons may be made with the triangular plots, although many times the results are not so apparent.

Equilibrium curves are presented with the mixtures treated as ternary systems in Figures 5 to 7. These figures include plots of tie line data and cloud point data. The data for all these figures are tabulated in Tables I and II. The solvents used in the determination of these data were mixtures of diethylene glycol and water and mixtures of triethylene glycol and water. These mixtures were treated as single components on the equilibrium plots.

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Figure 6. Equilibrium curve
A. *n*-Heptane
B. Solvent 1
C. Benzene
Temperature. 300° F.

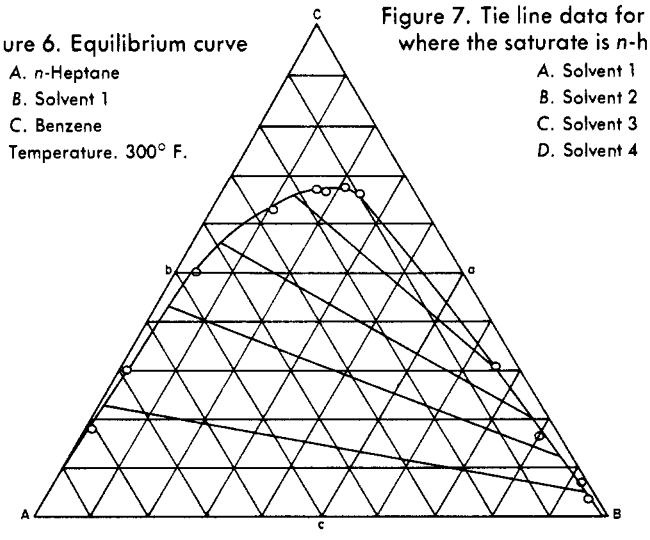

Figure 7. Tie line data for benzene where the saturate is *n*-heptane
A. Solvent 1
B. Solvent 2
C. Solvent 3
D. Solvent 4

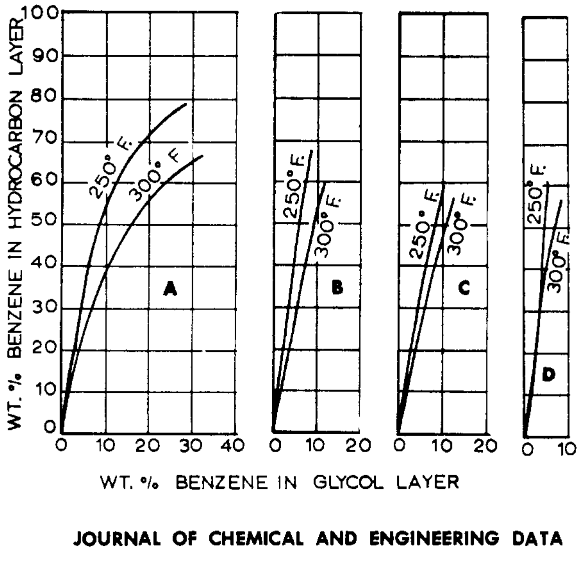

Table I. Single Stage Extraction Data

Solvent, Wt. %	*n*-Heptane, Wt. %	Benzene, Wt. %	Temp., ° F.
Solvent 1. 92.29 Wt. % Triethylene Glycol, 7.71 Wt. % Water			
95.01	1.27	3.72	300
1.59	80.42	17.99	300
92.33	0.62	7.05	300
1.41	68.58	30.03	300
80.12	3.47	16.42	300
3.95	46.25	49.80	300
65.69	3.76	30.56	300
16.68	16.41	66.91	300
99.44	0.56	0.00	250
0.00	100.00	0.00	250
95.96	0.86	3.18	250
0.00	82.57	17.43	250
92.76	1.19	6.06	250
0.00	65.34	34.66	250
90.99	0.79	8.23	250
0.45	50.87	48.70	250
84.62	1.33	14.10	250
4.00	33.79	62.20	250
82.48	1.08	16.45	250
4.83	27.08	68.00	250
67.19	1.35	31.46	250
14.56	6.89	78.56	250
Solvent 2. 87.00 Wt. % Triethylene Glycol, 13.00 Wt. % Water			
97.68	0.32	2.01	250
0.00	83.88	16.13	250
92.91	0.37	6.73	250
0.00	57.30	42.71	250
91.23	0.67	8.10	250
0.00	32.66	67.35	250
95.54	0.82	3.65	300
0.00	82.50	17.50	300
89.67	1.42	8.91	300
0.00	51.48	48.52	300
87.08	1.37	11.55	300
0.67	39.96	59.37	300
Solvent 3. 92.29 Wt. % Diethylene Glycol, 7.71 Wt. % Water			
96.24	0.85	2.91	300
0.39	84.95	14.67	300
92.11	0.37	7.17	300
0.00	64.46	35.54	300
86.53	1.42	12.05	300
0.00	44.29	55.71	300
97.20	0.55	2.25	250
0.00	83.87	16.13	250
91.89	1.06	7.06	250
0.00	59.60	40.40	250
89.10	0.60	10.30	250
0.00	41.46	58.54	250
Solvent 4. 87.00 Wt. % Diethylene Glycol, 13.00 Wt. % Water			
96.80	0.83	2.38	300
0.00	84.86	15.14	300
94.37	0.92	4.72	300
0.00	60.19	39.81	300
90.42	0.65	8.94	300
0.00	44.19	55.81	300
97.81	0.15	2.04	250
0.00	84.66	15.34	250
95.24	0.50	4.26	250
0.00	57.81	42.19	250
94.14	0.31	5.55	250
0.00	39.82	60.18	250

Table II. Cloud Point Data

Benzene, Wt. %	*n*-Heptane, Wt. %	Solvent, Wt. %	Temp., ° F.
Solvent 1. 92.29 Wt. % Triethylene Glycol, 7.71 Wt. % Water			
68.05	11.94	20.01	296.9
72.93	12.84	14.23	277.3
75.91	13.37	10.72	259.0
78.96	13.92	7.12	205.0
73.85	17.03	9.12	259.3
68.04	15.68	16.28	294.7
75.27	17.32	7.41	235.0
63.08	26.96	9.96	279.0
62.16	26.46	11.40	304.3
45.12	5.10	49.77	298.0
45.04	0.00	54.96	244.3
65.21	0.00	34.79	250.3
55.07	0.00	44.93	247.0
79.93	0.00	20.07	248.7
77.48	0.00	22.52	250.7
64.97	11.02	24.01	304.5
70.94	2.88	26.18	267.0
72.29	1.06	26.65	257.8
Solvent 2. 87.00 Wt. % Triethylene Glycol, 13.00 Wt. % Water			
77.44	0.00	22.56	293.7
70.01	0.00	29.99	299.3
65.02	0.00	34.98	300.5
60.02	0.00	39.98	298.7
49.98	0.00	50.02	293.3
30.00	0.00	70.00	259.3
24.98	0.00	75.02	239.5
89.94	0.00	10.06	258.4
Solvent 3. 92.29 Wt. % Diethylene Glycol, 7.71 Wt. % Water			
79.98	0.00	20.02	282.0
90.00	0.00	10.00	249.7
74.98	0.00	25.02	290.3
70.00	0.00	30.00	294.2
55.00	0.00	45.00	293.0
60.00	0.00	40.00	293.5
40.01	0.00	59.99	285.6
25.00	0.00	75.00	242.4
32.00	0.00	68.00	268.6
66.41	5.14	28.44	314.5
66.99	16.54	16.47	329.6
74.93	12.55	12.52	298.6
86.88	6.56	6.56	231.7
Solvent 4. 87.00 Wt. % Diethylene Glycol, 13.00 Wt. % Water			
79.99	0.00	20.01	312.2
94.85	0.00	5.15	222.5
90.00	0.00	10.00	268.3
20.02	0.00	79.98	258.8
30.02	0.00	69.98	304.7
15.05	0.00	84.95	225.8

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