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Density, Viscosity, and Refractivity Data of Solutions of Potassium Iodide in *N*-Formylmorpholine–Water at 25, 35, and 45 °C

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The densities, viscosities, and refractive indexes of a wide range of potassium iodide concentrations in *N*-formylmorpholine–water mixtures have been determined at 25, 35, and 45 °C. From these experimental data, the apparent molar volumes, apparent molar refractivities, and Jones–Dole *B* coefficients have been calculated. It was found that in the investigated range of concentrations the values of the apparent molar volumes and apparent molar refractivities are practically independent of temperature but concentration-dependent. Jones–Dole *B* coefficients show a negative deviation from ideality. The values of *B* are negative for the very low concentrations and positive for the higher concentrations.

Introduction

N-Formylmorpholine (NFM) is a highly polar and dense solvent, showing a good suitability for the recovery of monocyclic aromatic hydrocarbons from petroleum products such as gasoline and reformate (*1*, *2*). Recently the aqueous solutions of NFM have been used on an industrial scale for extraction processes (*3*). The addition of small quantities of water increases the efficiency of NFM for the extraction. The thermodynamic properties of NFM and the aqueous solutions have been studied extensively, and we could not trace in the literature the effect of electrolytes on NFM and NFM–water properties; therefore we have initiated a program to study these effects. In a previous work, we have studied the viscosity behavior of potassium iodide (KI) in NFM solutions at several temperatures (*4*). As a continuation of these studies, we measured here the densities, viscosities, and refractive indexes at 25, 35, and 45 °C of KI solutions in NFM–water mixtures. The obtained results of dilute electrolyte solutions were analyzed in terms of the Jones–Dole equation and the apparent molar volumes and molar refractivities.

Experimental Section

Materials. *N*-Formylmorpholine (NFM), puriss grade (Fluka AG), was used without further purification and kept over an activated molecular sieve of type 4A (Union Carbide) for 2 days before use. The purity was confirmed by GLC analysis and was found to be >99.5 mol %. Potassium iodide (KI), Chemically Pure (Riedel-de Haen AG), was dried for 24 h at 110 °C prior to use and stored over P_2O_5 in a glass desicator.

Density Measurements. Densities were determined with an Anton Paar digital densimeter (DMA 60/602), thermostated to ±0.01 °C. The overall precision of the densities is found to be better than $\pm 2 \times 10^{-5}$ g cm^{-3}.

Viscosity Measurements. Viscosities were determined with a suspended-level Ubbelhode viscometer. The flow times were determined electronically with an electronic timer (Schott-Gerate AVS 400) of precision ±0.01 s, and the temperature of the bath was controlled better than ±0.01 °C. The viscosities of the samples were measured with a reproducibility of ±0.002.

Refractive Index Measurements. Refractive indexes were measured with an Abbe refractometer with a temperature-controlled bath to ±0.01 °C. Reproducibility of the refractive index data was within 1×10^{-4}.

Preparation of Aqueous Solutions of NFM and Salt Solutions. Binary mixtures of NFM and deionized distilled water were prepared by mass. The weight percentage error is estimated to be less than 0.1%. Salt solutions were made by weight with use of a four-place digital balance. Stock solutions of KI in each concentration of NFM–water binary mixtures were prepared by direct weighing, and these were diluted accurately by using previously calibrated glassware to obtain different required concentrations.

Results and Discussion

The obtained densities, viscosities, and refractive indexes of the aqueous solution of NFM and the solutions of KI in NFM–water mixtures at 25, 35, and 45 °C are listed in Tables I and II. The viscosity behavior of aqueous solutions of NFM shows a negative deviation from ideality (Figure 1). The viscosity of the solution of KI in NFM–water shows an ideality for mixtures containing from 0 to 50 wt % NFM, and when the concentration of NFM increases, the viscosity behaves negatively toward ideality (Figure 2).

The Jones–Dole *B* coefficients were calculated from the slope of the linear regression of the following equation (*5*).

$$(\eta/\eta_0 - 1)/C^{1/2} = A + BC^{1/2}$$

where η is the viscosity of the solution of KI in the NMF–water mixture and η_0 is the viscosity of the mixture of NFM–water only. *A* and *B* are the characteristic parameters for the salt and solvent depending on ion–ion and ion–solvent interactions, respectively, and *C* is the molar concentration of KI in NMF–water mixtures. The Jones–Dole *B* coefficients are listed in Table II and plotted versus the weight percent of NFM in Figure

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Table I. Densities ρ, Viscosities η, and Refractive Indexes n_D of Binary Mixtures of *N*-Formylmorpholine–Water at 25, 35, and 45 °C

	25 °C			35 °C			45 °C		
wt % NFM	ρ, g cm^{-3}	η, cP	n_D	ρ, g cm^{-3}	η, cP	n_D	ρ, g cm^{-3}	η, cP	n_D
0 (H_2O)[a]	0.997 05	0.8903	1.3325	0.994 03	0.7190	1.3313	0.990 22	0.5972	1.3298
10	1.015 86	1.1129	1.3499	1.012 21	0.8912	1.3483	1.007 58	0.7391	1.3468
25	1.043 72	1.6345	1.3747	1.039 58	1.2713	1.3678	1.033 41	1.0249	1.3661
50	1.084 68	3.0567	1.4316	1.077 70	2.3322	1.4018	1.070 58	1.8327	1.4066
75	1.121 99	5.3744	1.4550	1.114 71	3.9974	1.4522	1.108 36	3.0908	1.4490
90	1.138 52	6.9623	1.4715	1.130 12	5.1256	1.4689	1.121 29	3.8879	1.4649
100 (NFM)[b]	1.146 3	7.827	1.4847	1.137 1	5.9170	1.4811	1.128 7	4.513	1.4767

[a] Reference 6. [b] Reference 4.

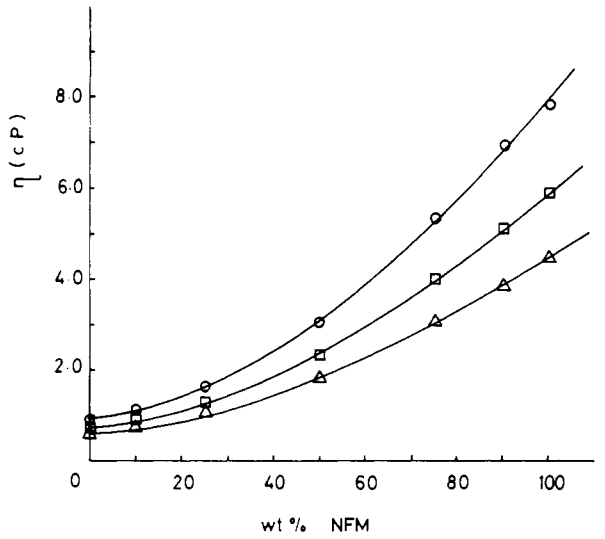

Figure 1. Viscosities of NFM–water mixtures at 25 °C (O), 35 °C (□), and 45 °C (△).

3. Figure 4 shows that the Jones–Dole plots are linear for KI concentrations below 1 M for 10% NFM, below 0.2 M ($C^{1/2}$ = 0.4472) for the 25 and 50 wt % NFM, below 0.9 M ($C^{1/2}$ = 0.9487) for 75 wt % NFM, and below 0.2 M ($C^{1/2}$ = 0.4472) for 90 wt % NFM.

The apparent molar volumes V_ϕ and the apparent molar refractivities R_D were calculated from the following relations

$$V_\phi = (1000/C\rho\rho_0)(\rho_0 - \rho) + M/\rho$$

and

$$R_D = (1000/C)(n_D^2 - 1)/(n_D^2 + 2) - (\rho - CM/1000)(1/\rho_0)(n_{D0}^2 - 1)/(n_{D0}^2 + 2)$$

where ρ_0 and n_{D0} are respectively the density and the refractive index of the binary mixture of NFM–water, M and C are the molecular weight of KI and its molality in the binary mixture of NFM–water, and ρ and n_D are the density and the refractive

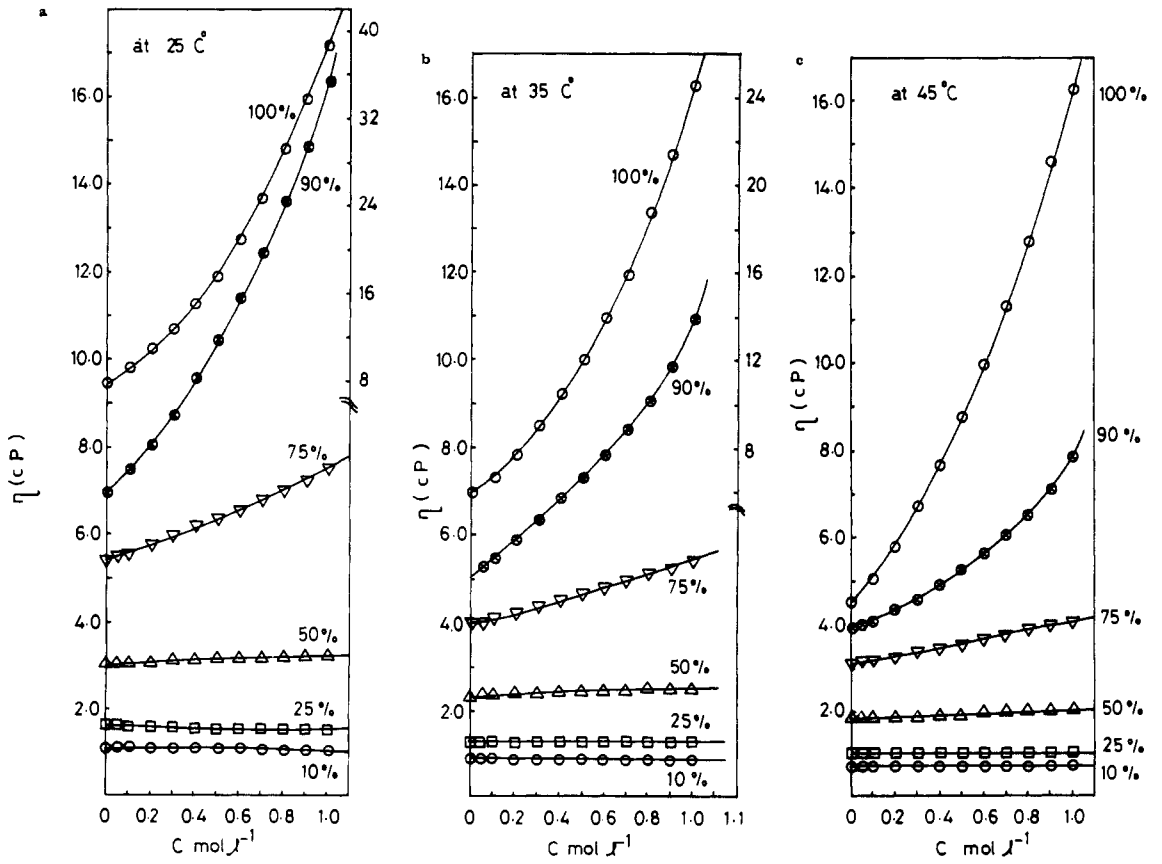

Figure 2. Viscosities of solutions of KI in NFM–water mixtures at (a) 25 °C, (b) 35 °C, and (c) 45 °C.

Table II. Densities ρ, Viscosities η, and Refractive Indexes n_D of Solutions of KI in *N*-Formylmorpholine–Water Mixtures at 25, 35, and 45 °C

C, mol L^{-1}	25 °C			35 °C			45 °C		
	ρ, g cm^{-3}	η, cP	n_D	ρ, g cm^{-3}	η, cP	n_D	ρ, g cm^{-3}	η, cP	n_D
				10 wt % NFM + 90 wt % Water					
0.02	1.018 42	1.1122	1.3503	1.014 51	0.8909	1.3486	1.010 07	0.7387	1.3472
0.04	1.020 45	1.1109	1.3507	1.016 18	0.8904	1.3489	1.011 68	0.7383	1.3476
0.05	1.021 66	1.1103	1.3509	1.017 68	0.8901	1.3492	1.012 75	0.7380	1.3479
0.06	1.022 76	1.1095	1.3512	1.019 61	0.8898	1.3496	1.014 33	0.7378	1.3482
0.08	1.025 35	1.1082	1.3516	1.021 58	0.8893	1.3500	1.017 20	0.7374	1.3486
0.10	1.027 50	1.1068	1.3519	1.023 72	0.8887	1.3504	1.018 37	0.7370	1.3490
0.20	1.039 23	1.0997	1.3537	1.035 30	0.8859	1.3534	1.031 04	0.7350	1.3514
0.30	1.051 64	1.0924	1.3555	1.046 54	0.8833	1.3546	1.042 15	0.7731	1.3533
0.40	1.062 25	1.0850	1.3574	1.058 47	0.8809	1.3563	1.053 21	0.7312	1.3554
0.50	1.073 83	1.0778	1.3603	1.070 13	0.8784	1.3587	1.065 84	0.7295	1.3575
0.60	1.085 62	1.0701	1.3617	1.081 82	0.8767	1.3602	1.077 23	0.7279	1.3598
0.70	1.096 88	1.0625	1.3640	1.093 68	0.8749	1.3627	1.088 92	0.7262	1.3621
0.80	1.108 76	1.0551	1.3655	1.105 44	0.8734	1.3650	1.100 51	0.7245	1.3642
0.90	1.120 62	1.0582	1.3676	1.117 21	0.8717	1.3672	1.112 35	0.7230	1.3662
1.00	1.132 14	1.0400	1.3702	1.128 95	0.8701	1.3689	1.122 68	0.7215	1.3683
				25 wt % NFM + 75 wt % Water					
0.02	1.046 00	1.6290	1.3750	1.041 69	1.2715	1.3686	1.035 95	1.0253	1.3665
0.04	1.048 82	1.6232	1.3756	1.044 20	1.2717	1.3692	1.037 91	1.0255	1.3669
0.05	1.050 63	1.6201	1.3758	1.045 31	1.2718	1.3697	1.039 52	1.0256	1.3672
0.06	1.051 22	1.6171	1.3760	1.046 58	1.2719	1.3702	1.040 67	1.0257	1.3676
0.08	1.053 54	1.6110	1.3764	1.049 27	1.2721	1.3708	1.043 00	1.0259	1.3679
0.10	1.054 73	1.6048	1.3768	1.051 11	1.2723	1.3713	1.045 30	1.0261	1.3683
0.20	1.066 88	1.5832	1.3787	1.063 51	1.2732	1.3738	1.058 19	1.0271	1.3710
0.30	1.078 24	1.5664	1.3806	1.075 82	1.2742	1.3765	1.070 34	1.0281	1.3758
0.40	1.090 15	1.5560	1.3830	1.087 89	1.2753	1.3794	1.081 99	1.0291	1.3762
0.50	1.103 40	1.5512	1.3843	1.099 78	1.2765	1.3822	1.094 24	1.0301	1.3789
0.60	1.113 23	1.5501	1.3870	1.111 92	1.2777	1.3848	1.105 83	1.0313	1.3817
0.70	1.125 13	1.5473	1.3879	1.124 21	1.2790	1.3873	1.117 55	1.0322	1.3843
0.80	1.135 48	1.5474	1.3902	1.136 44	1.2800	1.3900	1.129 88	1.0332	1.3870
0.90	1.148 23	1.5459	1.3930	1.148 52	1.2813	1.3937	1.142 22	1.0343	1.3898
1.00	1.158 73	1.5451	1.3933	1.160 73	1.2826	1.3960	1.154 85	1.0355	1.3929
				50 wt % NFM + 50 wt % Water					
0.02	1.087 31	3.0622	1.4118	1.080 01	2.3380	1.4110	1.072 96	1.8383	1.4070
0.04	1.089 54	3.0685	1.4120	1.082 22	2.3422	1.4112	1.074 75	1.8427	1.4072
0.05	1.090 35	3.0722	1.4122	1.083 75	2.3446	1.4115	1.076 27	1.8447	1.4074
0.06	1.091 85	3.0750	1.4124	1.084 67	2.3466	1.4118	1.077 22	1.8467	1.4077
0.08	1.093 99	3.0821	1.4126	1.086 86	2.3503	1.4121	1.079 34	1.8507	1.4080
0.10	1.095 62	3.0881	1.4128	1.088 85	2.3542	1.4127	1.081 65	1.8544	1.4083
0.20	1.107 08	3.1129	1.4157	1.100 10	2.3736	1.4143	1.092 92	1.8751	1.4108
0.30	1.118 91	3.1350	1.4174	1.111 76	2.3921	1.4156	1.104 02	1.8935	1.4120
0.40	1.130 31	3.1553	1.4192	1.122 88	2.4117	1.4177	1.115 36	1.9138	1.4140
0.50	1.141 72	3.1743	1.4223	1.134 59	2.4300	1.4199	1.126 57	1.9345	1.4160
0.60	1.152 63	3.1925	1.4236	1.145 37	2.4514	1.4220	1.137 66	1.9534	1.4179
0.70	1.163 57	3.2106	1.4254	1.156 45	2.4698	1.4241	1.149 22	1.9732	1.4199
0.80	1.175 32	3.2278	1.4278	1.167 64	2.4887	1.4257	1.160 00	1.9953	1.4214
0.90	1.186 68	3.2442	1.4299	1.178 81	2.5076	1.4275	1.171 47	2.0166	1.4235
1.00	1.197 35	3.2603	1.4320	1.189 87	2.5262	1.4289	1.182 35	2.0398	1.4259
				75 wt % NFM + 25 wt % Water					
0.02	1.124 11	5.4169	1.4552	1.116 79	4.0287	11.4525	1.110 10	3.1189	1.4492
0.04	1.126 32	5.4579	1.4554	1.119 33	4.0545	1.4527	1.112 40	3.1392	1.4495
0.05	1.127 50	5.4788	1.4556	1.120 32	4.0671	1.4529	1.113 56	3.1505	1.4497
0.06	1.128 63	5.5013	1.4558	1.121 25	4.0832	1.4531	1.114 63	3.1604	1.4499
0.08	1.130 78	5.5421	1.4560	1.123 44	4.1098	1.4533	1.116 76	3.1789	1.4501
0.10	1.132 74	5.5800	1.4565	1.125 43	4.1315	1.4538	1.118 35	3.2000	1.4503
0.20	1.143 91	5.7789	1.4577	1.136 81	4.2614	1.4549	1.130 62	3.2964	1.4514
0.30	1.164 63	5.9875	1.4588	1.147 54	4.3980	1.4560	1.140 89	3.3955	1.4523
0.40	1.165 59	6.1918	1.4600	1.158 64	4.5333	1.4573	1.152 22	3.4913	1.4538
0.50	1.176 68	6.3937	1.4617	1.169 79	4.6854	1.4583	1.163 00	3.5889	1.4549
0.60	1.187 02	6.5955	1.4622	1.181 11	4.8354	1.4596	1.173 31	3.6875	1.4560
0.70	1.197 80	6.7976	1.4639	1.192 02	5.0001	1.4615	1.184 78	3.7922	1.4576
0.80	1.209 54	7.0267	1.4643	1.203 11	5.1428	1.4621	1.195 47	3.8843	1.4588
0.90	1.220 21	7.2837	1.4660	1.214 73	5.3031	1.4634	1.206 51	3.9878	1.4603
1.00	1.231 23	7.5474	1.4672	1.225 80	5.4512	1.4645	1.217 23	4.0855	1.4618
				90 wt % NFM + 10 wt % Water					
0.02	1.141 00	7.0820	1.4718	1.132 62	5.1937	1.4693	1.123 54	3.9254	1.4652
0.04	1.143 24	7.1722	1.4720	1.134 89	5.2673	1.4696	1.125 85	3.9681	1.4654
0.05	1.144 51	7.2290	1.4722	1.135 72	5.3058	1.4698	1.126 86	3.9913	1.4656
0.06	1.145 33	7.2726	1.4724	1.136 84	5.3488	1.4700	1.128 02	4.0141	1.4658
0.08	1.147 61	7.3759	1.4727	1.139 11	5.4255	1.4704	1.130 34	4.0583	1.4660
0.10	1.149 90	7.4687	1.4733	1.141 61	5.5032	1.4708	1.132 72	4.0997	1.4662
0.20	1.160 64	8.0617	1.4748	1.152 52	5.9211	1.4722	1.143 88	4.3445	1.4681

Table II (Continued)

C, mol L^{-1}	25 °C			35 °C			45 °C		
	ρ, g cm^{-3}	η, cP	n_D	ρ, g cm^{-3}	η, cP	n_D	ρ, g cm^{-3}	η, cP	n_D
				90 wt % NFM + 10 wt % Water					
0.30	1.17245	8.7621	1.4763	1.16415	6.3527	1.4739	1.15543	4.5957	1.4695
0.40	1.18382	9.5548	1.4780	1.17563	6.8498	1.4758	1.16721	4.9000	1.4712
0.50	1.19524	10.4190	1.4802	1.18682	7.3326	1.4774	1.17876	5.2316	1.4733
0.60	1.20675	11.4046	1.4818	1.19789	7.8685	1.4790	1.18935	5.6199	1.4745
0.70	1.21813	12.4378	1.4835	1.20944	8.4500	1.4813	1.20090	6.0244	1.4768
0.80	1.22951	13.5894	1.4850	1.22068	9.1112	1.4825	1.21232	6.5145	1.4781
0.90	1.24044	14.8775	1.4870	1.23201	9.8711	1.4844	1.22368	7.0889	1.4804
1.00	1.25202	16.3544	1.4889	1.24357	10.9760	1.4863	1.23493	7.8555	1.4820

Table III. Jones–Dole *B* Coefficients for KI Solutions in NFM–Water Mixtures at 25, 35, and 45 °C

wt % NFM	*B* coefficients		
	25 °C	35 °C	45 °C
10	−0.0705	−0.0357	−0.0279
25	−0.1930	0.0079	0.0075
50	0.1146	0.0739	0.0975
75	0.3771	0.3133	0.2774
90	0.6341	0.8301	0.6024
100[a]	1.778	1.700	1.384

[a] Reference 4.

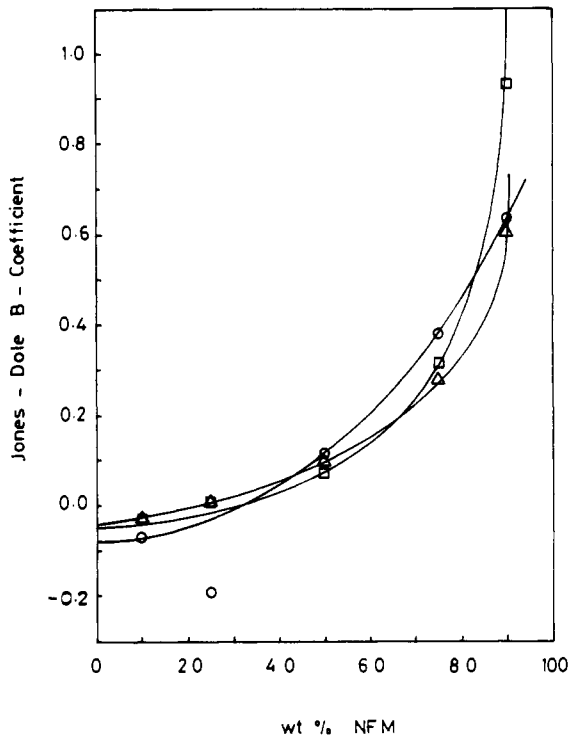

Figure 3. Jones–Dole *B* coefficients for KI in the binary solvent system NFM–water at 25 °C (○), 35 °C (□), and 45 °C (△).

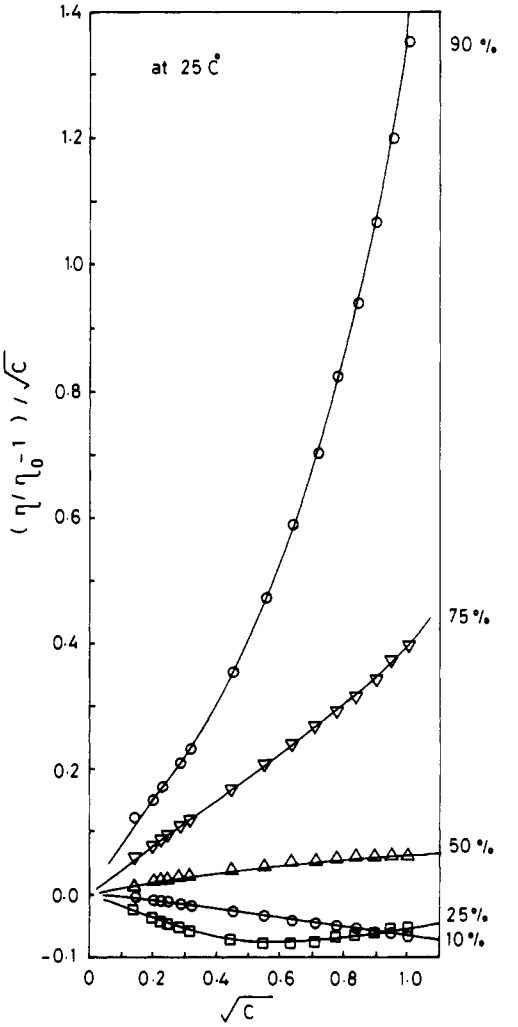

Figure 4. Jones–Dole plots of the variables $(\eta/\eta_0 - 1)/C^{1/2}$ versus $C^{1/2}$ for the data at 25 °C.

index of KI in the NFM–water mixture. The values of V_ϕ and R_D can, in principle, depend on the solent and on the concentration C of the solution. Infinite dilution values, V_ϕ^∞ and R_D^∞, are obtained by extrapolation.

The structural changes in the NFM–water system studied previously (*7*) suggested that when NFM is added to water, it first introduces hydrogen bonding and ordering of water molecules not bound into an extended Ice I tetrahedral structure; then at higher concentrations it disrupts this structure to a less open, but no less compressible, hydrogen-bonded structure. Addition of KI to this system increases the viscosity and the Jones–Dole *B* coefficients show a negative deviation at all three temperatures studied. As the temperature increases, the *B* coefficient becomes less negative from ideality. The values of the Jones–Dole *B* coefficient obtained here for this system reflects the change in solution structure brought about by the addition of KI. The negative values of the *B* coefficient for the low concentrations of NFM suggest that KI enhances the hydrogen-bonded structure of the NFM–water mixture so that the solute enhances the structure and close packing in the disordered region. For higher concentrations of NFM in the NFM–water mixture, the *B* coefficient values become positive, indicating that KI is a structure breaker for the NFM–water system. This suggests that potassium iodide shows a greater preference for water than NFM molecules and permits the exchange of water molecules between the ordered and disordered regions. The above has been observed in the appearance of maxima of V_ϕ^∞ and R_D^∞, which reflects the specific interactions in solute–solvent interaction. This behavior has been observed for the simple 1–1-type chlorides and bromides in water–methanol, water–ethanol, and water–acetamide systems (*8–10*).

Glossary

A	characteristic parameter for the salt in the Jones-Dole equation
B	characteristic parameter for the solvent in the Jones-Dole equation
C	the concentration of KI in the NFM-water mixture, $cm^3\ mol^{-1}$
M	molecular weight of KI
n_{D0}	refractive index of the solvent (NFM-water mixture)
n_D	refractive index of the solution of KI in the NFM-water mixture
V_ϕ	apparent molar volume, $cm^3\ mol^{-1}$
V_ϕ^∞	apparent molar volume at infinite dilution
R_D	apparent molar refractivity
R_D^∞	apparent molar refractivity at infinite dilution
ρ_0	density of the NFM-water mixture, $g\ cm^{-3}$
ρ	density of the solution of KI in the NFM-water mixture, $g\ cm^{-3}$
η_0	viscosity of the NFM-water mixture, cP
η	viscosity of solutions of KI in the NFM-water mixture, cP
NFM	N-formylmorpholine

Registry No. NFM, 4394-85-8; KI, 7681-11-0; water, 7732-18-5.

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Vapor-Liquid Equilibria for the Systems Hexane-Aniline and Hexane-Benzene-Aniline at Atmospheric Pressure

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Isobaric vapor-liquid equilibria at 101.325 kPa have been measured for the systems hexane-aniline and hexane-benzene-aniline. The measured data for the binary system hexane-aniline, along with published data for hexane-benzene and benzene-aniline, were correlated using Wilson, nonrandom two-liquid (NRTL), and UNIQUAC equations. The binary parameters, thus determined, were used to predict the ternary vapor-liquid equilibria (VLE) for the system hexane-benzene-aniline in good agreement with the measured data. The use of the UNIFAC group contribution method is also seen to provide a good estimation of both binary and ternary VLE data. For the partially miscible hexane-aniline system the mutual solubility data are also presented.

Introduction

The knowledge of vapor-liquid equilibria (VLE) is essential for the design of various separation processes like distillation, evaporation, and adsorption. The separation of benzene from a typical hexane-benzene mixture representing light naphtha poses a problem in the petroleum industry. The present study was taken up to examine the suitability of aniline as a solvent for the separation of this model mixture. Isothermal VLE data for ternary hexane-benzene-aniline at 20 °C (*1*) and isobaric data for hexane-benzene (*2*) and benzene-aniline (*3*) systems are reported at 101.325 kPa. Isothermal VLE data for the partially miscible hexane-aniline binary from 0 to 67.5 °C (*4*, *5*) and isobaric from 74.13 to 97.46 kPa (*6*) are also available in the literature. All three binaries are nonazeotropic (*7*). The mutual solubility data for the binary hexane-aniline are reported from 16.5 to 59.6 °C and from 41.17 to 65.85 °C by Keyes and Hildebrand (*8*) and by Drucker (*9*), respectively.

In the present study the VLE data for the binary hexane-aniline and the ternary hexane-benzene-aniline were determined at 101.325 ± 0.07 kPa of pressure and correlated by using Wilson (*10*), nonrandom two-liquid (NRTL) (*11*), and UNIQUAC (*12*) equations. The results have also been compared with those calculated from the UNIFAC group contribution method (*13-15*).

Experimental Section

Materials. The sources of the chemicals are given in Table I. The purity of hexane and benzene was checked by gas chromatography. Aniline was vacuum distilled, and the heart cut collected was used in the study. The properties of these chemicals compared to those reported in the literature (*16*) indicate a minimum purity of 99% (Table I).

Apparatus and Procedure. The VLE studies for the binary and ternary systems were carried out in a modified Smith and Bonner type still (*17*) equipped with a magnetic stirrer. The equilibrium vapor temperatures t were measured by a mercury-in-glass thermometer having an accuracy of ±0.05 °C and subsequently corrected (*18*) for the exposed stem.

The pressure in the system was maintained at 101.325 ± 0.07 kPa with the help of a regulated air supply through a water column connected to a water manometer. The phases were equilibrated for 4 h before about 2 cm^3 of vapor sample was withdrawn in an iodine flask for analysis.

Since there is a wide difference in the boiling points of hydrocarbons and aniline, the amount of aniline in the vapor phase was expected to be small. A titration method (*19*) was, therefore, used for its determination. A known amount of the condensed vapor sample was titrated against standard perchloric acid using crystal violet as indicator. During titration the sample was vigorously stirred with the help of a magnetic stirrer. For the ternary system the samples were divided into two parts. The first part as well as vapor samples in the case of the binary were analyzed for aniline by the titration method,

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