Several Properties of the 2-Pyrrolidone–Water System as Functions of Composition and Temperature

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Dielectric constants, viscosities, densities, and refractive indices for the binary system of 2-pyrrolidone and water have been determined at five temperatures within the range of 31° to 50°C. The dielectric constant and viscosity data have been fitted to appropriate equations by least squares procedures. Although a binary system with compound formation is involved, no maximum occurs in any of the viscosity-composition isotherms. The activation energy of viscous flow shows less than 2% variation over a broad middle composition range and does not exhibit a well-defined maximum at the composition corresponding to 2-pyrrolidone monohydrate.

THE freezing point–composition curve for the binary system of 2-pyrrolidone and water was investigated in 1958 by Lohr (8). His results reveal that 2-pyrrolidone and water react to form a single compound—a monohydrate that melts congruently at 30.4° C. which is higher than the melting point of either of the constituents. The 2-pyrrolidone–water system, therefore, provides an excellent example for studying the possible effects of compound formation upon the variation of physical properties as a function of composition. In other recent studies (2, 7, 12), maxima in viscosity-composition curves for the N,N-dimethylacetamide–water and the dimethyl sulfoxide–water systems have been discussed in terms of association complexes or possible compound formation. In these two systems, however, specific evidence for compound formation is lacking.

EXPERIMENTAL

2-Pyrrolidone was purified by successive fractional freezings until its freezing point became constant at 25.67°. This compares favorably with the value of 25.57° reported by Lohr (8). Distilled water was further treated by passing it through an Illco-Way Research Model ion-exchange column. Solutions in glass-stoppered flasks were prepared on a weight basis using calibrated weights. The mixing of 2-pyrrolidone and water is slightly exothermic and is accompanied by some diminution of volume. Since crystals of 2-pyrrolidone and monohydrate separated from the 40, 50, and 60 mole % solutions upon standing at room temperature, all experimental measurements on the mixtures were made at 31° C. or above.

The Twin-T impedance bridge assembly, capacitance cells, temperature control, and principal aspects of the procedures for calibrating the cells and calculating the dielectric constants have been described previously in detail (1, 3, 6). The standard media which were used in the determination of cell constants were air and water which have dielectric constants of unity and 78.30 (9), respectively, at 25° C. All capacitance measurements were made at 10 Mc. after it was confirmed that capacitance changes were independent of frequency in the 1 to 10 Mc. range.

A size 50 or 100 Cannon-Fenske viscometer was used as the case demanded in order to have an efflux time of 200 seconds or more and thereby eliminate the necessity for making kinetic energy corrections. Calibrations for the viscometers were provided by the Cannon Instrument Co. Densities were determined using 25-ml. Reischauer pycnometers which had been calibrated using freshly distilled water. Appropriate buoyancy corrections were applied prior to the calculation of densities or concentrations. Refractive indices were measured with a Spencer-Abbe Model 2214 refractometer. Further details concerning the procedures for determining viscosities, densities, and refractive indices have been discussed in previous articles (13, 15).

All measurements were made in duplicate and corresponding values agreed consistently within the expected limits of 0.2% for dielectric constants and viscosities and 0.02% for densities and refractive indices. Mean values are reported in the tables of experimental data. Values for the physical properties of water which were obtained in this study compare excellently with corresponding data in the literature.

A digital computer was used for the fitting of data by the method of least squares to various polynomial equations.

RESULTS AND DISCUSSION

The experimental dielectric constant data are summarized in Table I. At each temperature the dielectric constant as a function of composition may be calculated within 1% using a polynomial equation of the type:

$$\epsilon = A + BX_{\scriptscriptstyle w} + DX_{\scriptscriptstyle w}^2 \tag{1}$$

The least squares values for the constants in Equation 1 and for the deviations between experimental and calculated dielectric constants are compiled in Table II.

For any given composition in the 2-pyrrolidone–water system, the dielectric constant is a linear function of the reciprocal of the absolute temperature. Similar variation of dielectric constant data with temperature for the 1-propanol-methanol system has been reported by Denny and Cole (4).

Table I. Experimental Dielectric Constant Data

Water		Dielectric Constants				
Wt. %	Mole %	31° C.	35° C.	40° C.	45° C.	50° C.
0.000	0.000	27.37	27.07	26.64	26.25	25.87
2.706	11.616	30.19	29.86	29.43	28.99	28.48
4.686	18.852	32.24	31.79	31.34	30.82	30.27
8.182	29.624	35.73	35.25	34.64	34.01	33.44
12.685	40.697	40.06	39.40	38.71	37.98	37.27
17.824	50.607	44.58	43.89	43.04	42.17	41.33
23.912	59.751	49.38	48.56	47.65	46.57	45.61
31.411	68.309	54.55	53.61	52.44	51.23	50.09
46.883	80.656	62.60	61.43	60.05	58.64	57.32
66.062	90.193	69.27	67.94	66.32	64.78	63.31
100.000	100.000	76.20	74.80	73.12	71.43	69.78

Table II. Results for Dielectric Constant Data Fitted to Equation 1

Temp., °C.	A	B	D	Deviations Std.	Max.
31	27.41	19.37	29.61	0.20	0.31
35	27.12	18.78	29.05	0.18	0.26
40	26.72	18.38	28.12	0.15	0.22
45	26.36	17.60	27.55	0.14	0.17
50	25.96	17.06	26.82	0.13	0.15

Table III. Experimental Viscosity Data

Water, Mole %	Viscosities, Cp. 31° C.	35° C.	40° C.	45° C.	50° C.
0.000	10.50	9.102	7.687	6.593	5.666
11.616	10.05	8.702	7.300	6.211	5.336
18.852	9.771	8.419	7.066	5.985	5.140
29.624	9.280	7.958	6.647	5.641	4.823
40.697	8.553	7.333	6.111	5.164	4.414
50.607	7.697	6.591	5.506	4.656	3.987
59.751	6.611	5.665	4.740	4.004	3.433
68.309	5.353	4.612	3.873	3.308	2.845
80.656	3.322	2.917	2.495	2.165	1.901
90.193	1.885	1.690	1.483	1.313	1.173
100.000	0.778	0.717	0.650	0.594	0.546

Table IV. Results for Viscosity Data Fitted to Equation 2

Water, Mole %	α	−β	γ	E_{vis} at 31° C., (Cal.)	Std. Dev. in E_{vis} (Cal.)
0.000	0.70391	1270.159	415,664	6695	170
11.616	0.80482	1389.789	441,006	6910	118
18.852	1.30890	1734.943	498,200	7052	74
29.624	2.27711	2381.840	603,297	7254	99
40.697	1.98250	2238.710	583,762	7321	41
50.607	2.50219	2583.464	636,290	7324	27
59.751	2.22126	2443.482	613,594	7281	77
68.309	2.51662	2628.546	634,073	7051	115
80.656	2.50734	2580.793	601,278	6282	110
90.193	0.51468	1283.968	368,402	5210	55
100.000	0.27154	1084.862	294,777	3905	47

Table V. Experimental Density Data

Water, Mole %	Densities, Grams per Ml. 31° C.	35° C.	40° C.	45° C.	50° C.
0.000	1.1027	1.0995	1.0953	1.0916	1.0875
11.616	1.1020	1.0987	1.0944	1.0904	1.0862
18.852	1.1012	1.0979	1.0937	1.0894	1.0858
29.624	1.0997	1.0963	1.0921	1.0878	1.0838
40.697	1.0974	1.0940	1.0897	1.0854	1.0812
50.607	1.0941	1.0906	1.0865	1.0821	1.0789
59.751	1.0888	1.0854	1.0811	1.0769	1.0727
68.309	1.0817	1.0786	1.0744	1.0712	1.0659
80.656	1.0631	1.0601	1.0562	1.0526	1.0489
90.193	1.0372	1.0350	1.0319	1.0286	1.0255
100.000	0.9958	0.9941	0.9923	0.9903	0.9882

Table VI. Experimental Refractive Index Data

Water, Mole %	Refractive Indices 31° C.	35° C.	40° C.	45° C.	50° C.
0.000	1.4835	1.4822	1.4805	1.4790	1.4775
11.616	1.4804	1.4791	1.4771	1.4758	1.4739
18.852	1.4778	1.4760	1.4745	1.4729	1.4710
29.624	1.4730	1.4720	1.4699	1.4682	1.4665
40.697	1.4650	1.4639	1.4622	1.4605	1.4580
50.607	1.4589	1.4579	1.4560	1.4549	1.4530
59.751	1.4500	1.4482	1.4470	1.4451	1.4440
68.309	1.4381	1.4369	1.4350	1.4331	1.4320
80.656	1.4131	1.4120	1.4102	1.4090	1.4080
90.193	1.3821	1.3811	1.3801	1.3789	1.3780
100.000	1.3319	1.3314	1.3308	1.3299	1.3290

The experimental viscosity data for the pure liquids and the mixtures are summarized in Table III. The magnitude of the viscosity of 2-pyrrolidone reflects extensive association through hydrogen bonding. At each temperature, the results reveal that the viscosity decreases continuously as the water content increases; however, the variation of viscosity with composition apparently cannot be described accurately by any relatively simple relationship. Although the congruent melting point of the 1-to-1 compound of 2-pyrrolidone and water (8) indicates that the compound is stable also in the liquid state, the presence of such a species does not produce a maximum or other significantly unusual characteristic in any of the viscosity-composition isotherms. Nevertheless, if one compares the experimental values of the viscosities for the mixtures with values calculated from the viscosities of the pure constituents using a linear mole fraction relationship, experimental values exceed calculated values, and a maximum deviation of 2.2 cp. occurs for the 2-pyrrolidone monohydrate composition.

The viscosity-temperature relationship for each of the pure liquids and mixtures is described excellently by the Girifalco equation (5, 10, 14):

$$\log \eta = \alpha + \frac{\beta}{T} + \frac{\gamma}{T^2} \qquad (2)$$

Upon differentiation, this equation also makes possible the calculation of the activation energy of viscous flow (5, 11):

$$\frac{E_{vis}}{2.303\,R} = \frac{d(\log \eta)}{d(1/T)} = \beta + \frac{2\gamma}{T} \qquad (3)$$

Values for α, β, γ, and E_{vis} (31° C.) are listed in Table IV. The calculated activation energy shows very little variation over a broad middle composition range; consequently, a well-defined maximum in the activation energy cannot be clearly correlated with the 1-to-1 compound composition.

Experimental data for the densities and refractive indices are compiled in Tables V and VI. The density data show that a 5% maximum diminution of volume on mixing occurs at about 70 rather than 50 mole % of water. Also, a potentially useful relationship for analytical work is that the refractive index is a linear function of the weight fraction of water at each temperature:

$$n_D = a - bW_w \qquad (4)$$

The least squares values for the constants in Equation 4 and for the deviations between experimental and calculated refractive indices are summarized in Table VII.

Table VIII contains additional useful data for 2-pyrrolidone which could not be conveniently incorporated in the other tables.

Table VII. Results for Refractive Index Data Fitted to Equation 4

Temp., °C.	a	$b \times 10^3$	Deviations × 10⁴ Std.	Max.
31	1.4850	1.5342	11	16
35	1.4836	1.5266	11	17
40	1.4818	1.5149	10	16
45	1.4801	1.5087	10	16
50	1.4783	1.4966	10	15

Table VIII. Additional Data for 2-Pyrrolidone

Temp., °C.	ε	η, Cp.	d, Grams/Ml.	n_D
26	27.75	12.75	1.1068	1.4848
30	27.46	10.90	1.1035	1.4837

NOMENCLATURE

A, B, D = constants in Equation 1
α, β, γ = constants in Equation 2
a, b = constants in Equation 4
d = density, grams/ml. or grams/cc.
E_{vis} = activation energy of viscous flow, cal./mole
η = viscosity, cp.
ϵ = dielectric constant
n_D = refractive index (sodium D line)
R = molar gas constant, cal./(mole deg.)
T = temperature, °K.
W_w = weight fraction of water
X_w = mole fraction of water

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Flow Calorimeter Measurements of Binary Heats of Mixing for Liquid Normal, Primary Alcohols in Normal Alkanes

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A steady-flow calorimeter assembled to measure the heats of mixing of binary mixtures is described. Its performance is compared to the batch and semibatch procedures conventionally used. The data in the 0.1- to 0.9-volume fraction range were determined and compared to literature values. An accuracy of ±5% is obtained and the data reported are satisfactory for most engineering calculations. Heats of mixing data for 1-hexanol–n-heptane, 1-decanol–n-heptane, 1-butanol–n-undecane, and 1-hexanol–n-undecane binaries at 35° and 45° C. are reported.

Heats of mixing data for nonideal liquid systems are useful for design calculations and for the information they provide concerning the structure of the liquid phase. Since the theory of the liquid phase is comparatively incomplete, a common basis for reliable predictive procedures for estimating heats of mixing has not been developed. It appears that empirical methods to extend available data should be based on a systematic study of similar compounds.

To obtain systematic data to develop an empirical procedure, the heats of mixing of several binary mixtures of primary, normal alcohols in normal alkanes were measured in a flow calorimeter (7), at 35° and 45°C. and atmospheric pressure. Recent measurements reported by Savini, Winterhalter, and Van Ness (9) on 1-propanol, 1-butanol, and 1-butanol and 1-hexanol in n-hexane were duplicated in this work and provide a comparison for the data obtained with the flow calorimeter. The heats of mixing data on the 1-hexanol and 1-decanol in n-heptane systems and the 1-butanol and 1-hexanol in n-undecane systems are reported.

APPARATUS

The problems associated with the design of a calorimeter to measure heats of mixing have been discussed by White (13), Weissberger (12), Rossini (8), and Skinner (11). Although both nonisothermal and isothermal calorimetry have been extensively used, the latter offers the advantage of direct measurement of the heats of mixing. If the systems under study are endothermic, energy can be added to the mixture. Constant temperature can be maintained by adjusting either the energy input or the rate of addition of pure components.

Mrazek and Van Ness (4) have developed an isothermal calorimeter that allows rapid determination of the heats of mixing. The mixing chamber contains an initial charge of one component. The second component is added at a variable rate just to compensate the constant rate of electrical energy input. Simultaneous readings of the energy input and the amount of component added yield the heats of mixing data. Evaporation and condensation effects were eliminated by using an expandable mixing chamber to eliminate the vapor space. The data obtained were of excellent quality and compared favorably with the best literature values.

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